## Contents

### Editorial
1. 100-Year anniversary of X-ray crystallography

### Technical Articles
4. A current perspective of the state-of-the-art in stress analysis
13. Elemental analysis of PM2.5 with energy dispersive X-ray fluorescence spectrometer NEX CG
18. Introduction to single crystal X-ray analysis
23. Sample preparation for X-ray fluorescence analysis
   VI. About CIFs—Alerts and how to handle them—

### New Products
28. Highly versatile multipurpose X-ray diffractometer
   SmartLab 3
31. Single crystal diffraction systems based on hybrid pixel array technology
   XtaLAB PRO series
35. Thermo plus EVO2
   Thermodilatometer TDL 8411
38. High-resolution/high-speed 2D photon counting X-ray detector
   HyPix-3000

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**English version**
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100-Year anniversary of X-ray crystallography

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1. International Year of Crystallography 2014

Solid materials in the crystalline state are characterized by a periodic structure, which acts as a diffraction grating at an atomic scale for incident X-rays. The famous experiment of X-ray diffraction, using a zinc-blende crystal, was suggested by Max von Laue at the University of Munich, Germany and was conducted by W. Friedrich and P. Knipping in 1912. The Nobel Prize in Physics was awarded to Max von Laue in 1914 for his discovery of the X-ray diffraction phenomena, which verified the wave nature of X-rays. Discovery of X-ray diffraction changed the field of mathematical crystallography in the 19th century to an experimental science.

X-ray crystal structure analysis is a reverse process of X-ray diffraction. Intensities at individual diffraction spots recorded on the surface of a detector in reciprocal space are converted into their frequencies, and then inversely Fourier transformed into the crystal structure in real space. The X-ray diffraction method provides us the information about the spatial arrangement of atoms in the crystal lattice together with precise data concerning interatomic distances and bond angles. The three-dimensional information and the highly quantitative nature of the data distinguish X-ray crystallography from other analytical sciences such as microscopy or spectroscopy.

A proposal for celebrating the 100-year anniversary of X-ray crystallography since the discovery of X-ray diffraction was approved at General Assembly of the United Nations, and the year 2014 was assigned as International Year of Crystallography 2014 (IYCr2014). It is our great pleasure that X-ray crystallography has been used as one of the most important tools for materials characterization for more than 100 years.

2. Crystal structure analysis toward more complex structures

A year after the discovery of X-ray diffraction, the crystal structure of NaCl was analyzed by W. L. Bragg(1). It turned out to have a quite simple structure, having a face-centered cubic lattice. Fourier methods, first suggested by W. L. Bragg in 1929(2), were demonstrated to be efficient for determining more complex structures. Fourier series, used for calculating the electron density distribution function, is a sum of a number of sine and cosine terms. Hand calculation with patience for calculating Fourier series was relieved by the use of Beevers-Lipson strips in the 1930s~1950s(3).

M. F. Perutz had chosen Haemoglobin as a research subject for his doctoral thesis in 1937 when the modern electronic computer was not available. It was 1960 that he reported a final result of the three-dimensional structure analysis of Haemoglobin(4). Nowadays, structure analysis of small molecules can be achieved in minutes. Even for the crystal structure analysis of proteins, it can take roughly ten minutes for a moderate sized structure using a notebook PC and one week or more for more complex structures if the quality of diffraction data is of good quality. The improvement of computing performance contributes to shorten the time required for the data analysis, and it has been a rate-determining factor in the development of X-ray crystallography as well as in other fields of the science. Nowadays, the standard procedure of single crystal structure analysis is considered as an established technique, and it is used almost routinely as a tool at every laboratory. People, who are interested in the investigation of materials themselves, can easily learn the technique due to today’s easy to use software and intuitive graphical interfaces.

3. The advent of modern powder diffraction method

Some people are more interested in the development of tools rather than materials investigation. In the early days of the modern powder diffraction method, a common was problem that single crystals with adequate volume size for the diffraction experiment were difficult to obtain, in particular, for neutron powder diffraction. The powder diffraction method was the only means for the structure analysis of crystals with micro-meter size, although it was considered to be much less reliable compared to the single crystal diffraction method. However, many crystallographers as well as mathematicians and physicists were enthusiastic about solving and refining crystal structures under difficult conditions, that is to use one-dimensionally collapsed diffraction data from the powder specimen. Evolution of the modern powder diffraction method had been started by “a small step”, which changed from using integrated intensities as the observed data and instead to use the profile intensities as described by H. M. Rietveld in his retrospect(5).

In the late 1960s, the Rietveld method was first proposed as a technique of crystal structure refinement using neutron powder diffraction data(6). In the late 1970s, it became more widely known by people after it was applied to structure refinement using X-ray powder diffraction data(7),(8). The proposal by G. S. Pawley(9)

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in 1981 would also be a key step, which enabled the decomposition of a powder diffraction pattern into individual Bragg reflection components by least-squares fitting of the whole-powder-diffraction pattern. Once the integrated intensity dataset could be obtained with the Pawley method, it would be quite natural to use it for the crystal structure determination by direct methods in the manner similar to the single crystal technique. In the whole-powder-pattern decomposition, however, severely or intrinsically overlapping reflections remain undecomposed, and the degree of overlapping is generally higher for the powder diffraction patterns of organic materials. Global optimization techniques such as the Monte Carlo method, simulated annealing, genetic algorithms (10) were introduced in 1990s, and these techniques once again enabled researchers to solve crystal structures without decomposing the diffraction pattern. These methods are called “direct-space methods” in opposition to direct methods in “reciprocal-space approach”. Charge flipping (11) proposed in the 2000s is the method, which travels between reciprocal and direct spaces.

4. Promotion of scientific activities

Setting the table is also an important issue for the promotion of science. The IUCr Commission on Powder Diffraction (CPD) was established when the Congress and General Assembly of IUCr were held in Perth, Australia in 1987. It first organized a Workshop on the Rietveld method at Reactor Centrum Nederland in Petten, Netherlands in 1989. Then the European powder Diffraction Conference was organized, the first meeting of which was held in Munich in 1991. Many schools and workshops, co-sponsored by local committees and CPD were successively held all over the world for learning these new techniques. Knowledge and computer software of Rietveld refinement and related methods were gradually spreading from university professors and students to materials researchers in private companies. Today, the powder diffraction methods, derived from the Rietveld method, are widely used not only for scientific research but also for industrial purposes such as quality control on production lines.

Hardware and software developments are another factor supporting the promotion of scientific activities. Powder diffraction using synchrotron radiation produces higher resolution and thus less overlapping peaks. High quality synchrotron radiation data also stimulated the improvements of laboratory systems: one example is the use of high flux and brilliant X-ray sources, coupled with graded multi-layer optics for beam-tailoring and the other is the development of fast one- and two-dimensional detectors. Developments of mathematical tools for data analysis could not be achieved without the improved performance of computers, and wide spread use of these techniques with low cost/high performance PCs. From the 1960s to 1980s, researchers used mainframe computers, and they could only have the chance of crystallographic computation a few times a day when punched cards were used as storage media. Nowadays, people can incessantly manipulate the PC for the data analysis at his/her own desk.

5. Accumulated knowledge and experiences in crystallography

Now X-ray crystallography looks like a complex of tall buildings. The single crystal building is consolidated, consisting of two main parts of small and macro molecules. The powder diffraction building has a long tradition. But in the neighborhood, the building of modern powder diffraction has been constructed for more than 40 years. A nano material building is under construction, one of the columns of which is the classical pair distribution function based on the Debye equation (12) proposed 100 years ago. Some buildings are renewed by introducing new techniques as in the case of the whole-pattern-fitting technique for microstructural analysis. Someone can go up to the top of the building with an elevator, but he/she will lose the chance to see and grasp a whole view of the building. Of course, it is practically impossible for him/her to visit every room. Knowledge of basic theories, used for the analysis, is, however, very important and required for understanding and properly evaluating results of analysis. It will also be necessary to create new tools and to participate in new building construction. It may be unfortunate for X-ray crystallography if the chance of studying X-ray crystallography is decreased at universities.

6. Mission of Rigaku Corporation

Rigaku Corporation (RC), established with the name Rigaku-Denki Corporation in 1951, celebrated its 60-year anniversary three years ago. Yoshihiro Shimura, a founder of RC, had been engaged in X-ray analysis since the time of World War II when he was studying at the university. After the war when he had to determine his career, it was natural for him to be deeply interested...
with the fabrication of X-ray analytical instruments. It was his experience at that time that X-ray analysis techniques were used for very important subjects of studies. X-ray analytical instruments were, however, not easy to use, and moreover, their performance was not high enough to obtain the best observed data. These concerns in his mind bore fruit in the form of his first commercialized XRD instrument with an automatic-recording function.

Hikaru Shimura, a successor to the former president Y. Shimura, followed his father’s philosophy. He also focused on the development of basic technologies in order to meet the requirements of a higher intensity X-ray beam, more sensitive detection of X-ray, faster data acquisition and data analysis for advanced studies of materials. Some basic technological elements of RC are the rotating anode X-ray generator, graded multi-layer optics for parallel and convergent X-ray beams, imaging plate, CCD, one-dimensional strip detector, two-dimensional hybrid pixel detector, high-precision goniometers etc. Rigaku continues to develop higher performance hardware and software by incorporating advanced scientific research results in X-ray crystallography into the products. It is our mission to produce X-ray analytical instruments, which are more useful and easier to handle to help advance X-ray crystallography.

References

A current perspective of the state-of-the-art in stress analysis

Akimitsu Nezu*, Hitomi Matsuzaka* and Ryouichi Yokoyama**

1. Introduction
This paper discusses recent methods in X-ray stress analysis. The authors have selected three examples thought to be the most practical from among the many X-ray stress measurement and analysis methods other than the conventional \( \sin^2 \phi \) method. The examples of analyses presented here are: (1) residual stress measurement using the multiple-hkl method, (2) residual stress measurement of samples with shear stress in the depth direction, and (3) residual stress measurement and line-broadening of diffraction in samples with fibre texture using the crystallite strain analysis method.

2. X-ray residual stress measurement using the multiple-hkl method
2.1. Thin-film X-ray diffraction measurement using the grazing-angle incidence method
In surface treatment using hard ceramic films, the materials used have outstanding properties such as low friction, and wear, heat, and corrosion resistance, and thus such films are widely used in cutting tools, machinery parts, dies, decorations, magnetic recording media and other applications. Typical examples of ceramic films include nitrides such as TiN, TiAlN, TiC, AlN and CrN. Among these, TiN films can be used at high temperatures while maintaining high hardness and good adhesion with steel and cemented carbide. As a result TiN is used in a wide range of fields as a protective coating material. The PVD (Physical Vapor Deposition) and CVD (Chemical Vapor Deposition) methods are used to form TiN films. The PVD method, in particular, has a treatment temperature of 500°C or less. This allows TiN coatings to be applied to high-speed steel or die steel at or below the tempering temperature. In addition, since these hard films are made of chemical compounds they can be embed with previously unattainable characteristics such as the ability to form a very high-hardness film by shifting chemical composition ratios. Therefore, much R&D is being carried out with the aim of achieving new functional materials for coating using the PVD method. However, residual stress and strain during film formation and in use shorten the material life through film peeling and cracking. Thus it is extremely important to understand the film stress conditions.

The most effective means of measuring residual stress is X-ray diffractometry, which enables non-destructive, non-contact evaluation of crystalline materials. However, X-ray penetration depth for metals and ceramics is just a few \( \mu m \), and with general-purpose measurement (\( \theta/2\theta \) scanning) there are limits on selective evaluation of information only from thin films or extreme surface layers of thickness 1 \( \mu m \) or less. If the grazing-angle incidence method, in which X-rays are radiated only onto the sample surface, is used in this case, it is possible to control the X-ray penetration depth, and this makes it possible to evaluate residual stress in regions which can not be evaluated with a general-purpose measurement. This section presents an example of measuring residual stress in a TiN film coated on a steel material.

2.2. Multiple-hkl method
The most widely known X-ray stress measurement method, the \( \sin^2 \phi \) method, is a technique that uses a specific lattice plane \((h k l)\) in a polycrystalline material and observes each of the lattice spacings \((d)\) by tilting the angle \( \phi \). Here \( \phi \) indicates the angle between the sample surface normal and the lattice plane normal. The advantages of the \( \sin^2 \phi \) method are that the stress can be analyzed even if the lattice spacing \((d_0)\) in the unstrained state is not exactly known. The stress value is easily obtained by the slope of a regression line on a graph called a \( \sin^2 \phi \cdot 2 \theta \) graph, in which \( \sin^2 \phi \) is taken as the horizontal axis and \( 2 \theta \) as the vertical axis. At this time, the residual stress \((\sigma)\) in the tilt of the direction of \( \phi \) angle is given as the product \((\sigma=M \cdot K)\) of the regression line slope \((M)\) and the stress constant \((K)\) determined by the elastic constants of the material under examination.

However, a problem arises here when considering stress measurement of a thin film with the \( \sin^2 \phi \) method. More specifically, if the X-ray incident angle increases in order to measure the variation in lattice spacings in a single lattice plane \((h k l)\), then the volume of the thin film which contributes to diffraction gets smaller. This makes it impossible to obtain sufficient diffraction intensity, and the S/N ratio from the diffraction coming from the substrate crystal worsens. To resolve this problem, a method has been proposed in which, as indicated in Fig. 1, the incident X-ray beam is introduced into the film by fixing the direction at a specific grazing-angle, and then measuring the diffraction of multiple lattice planes through \( 2 \theta \) scanning.

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Since stress is analyzed using multiple lattice planes \((h_i, k_i, l_i; i=1\text{ to } n)\), this method was later called the “multiple-hkl” method. The \(\psi_i\) angles of lattice planes observed through \(2\theta\) scanning are different from each other, and as a result, it is possible to observe the variation in the lattice spacings accompanying changes in the \(\psi_i\) angle. Therefore, this measurement method has the advantages that, for a thin film, the volume contributing to X-ray diffraction can be increased and the X-ray penetration depth can be controlled at nano nanometer scale even with thick films. The hard films presented in this section are films with fibre texture. The multiple-hkl method was applied to crystal grains with random orientation present in the film.

Equation (1) below indicates the relationship between strain and stress \((\varepsilon, \sigma)\) which holds for general materials including crystalline and amorphous materials

\[
\varepsilon_{\phi\psi} = \frac{1}{2} S_1 \sin^2 \psi (\sigma_{11} \cos^2 \phi + \sigma_{12} \sin(2\phi) + \sigma_{22} \sin^2 \phi)
+ \frac{1}{2} S_2 \left[ \sigma_{13} \cos \phi \sin(2\phi) + \sigma_{23} \sin \phi \sin(2\phi) \right]
+ S_3 [\sigma_{11} + \sigma_{22} + \sigma_{33}]
\]  

(1)

The strain \(\varepsilon_{\phi\psi}\) given here indicates strain of the diffraction plane, whose surface normal is the orientation inclined by \(\psi\) in the direction rotated by \(\phi\) in the counterclockwise direction about the surface normal of the sample. \(\sigma_{ij}\) \((i, j = 1, 2, 3)\) indicates the components of the stress tensor, and \(S_1\) and \(S_2\) are the X-ray elastic constants, represented by the Young’s modulus \((E)\) and Poisson’s ratio \((\nu)\), as shown in Equation (2).

\[
S_1 = -\frac{\nu}{E}, \quad \frac{1}{2} S_2 = \frac{1 + \nu}{E}
\]  

(2)

With the multiple-hkl method, it is possible to analyze the stress \(\sigma_{ij}\) by observing the rate of change in the lattice spacing \((d_i)\) of multiple lattice planes, i.e., the strain \(\varepsilon_{\phi\psi} = (d_i - d_{0i})/d_{0i}\). At this time, \(d_{0i}\) indicates the lattice spacing in the unstrained state of the \(i\)th lattice plane.

The following equation, (3), can be derived for the equi-biaxial stress state by setting the conditions \(\sigma_{33} = 0, \sigma_{23} = \sigma_{31} = \sigma_{12} = 0, \sigma_{11} = \sigma_{22} = \sigma\) in Equation (1).

\[
\varepsilon_{\phi\psi}^{\text{total}} = f(\phi, \psi, S_1^{\phi\psi}, S_2^{\phi\psi})\sigma,
\]

\[
f(\phi, \psi, S_1^{\phi\psi}, S_2^{\phi\psi}) = 2S_1^{\phi\psi} + \frac{1}{2} S_2^{\phi\psi} \sin^2 \psi
\]  

(3)

A steel material coated with a TiN film, using an ion plating method classified as a PVD technique, was used for the measurement. The film thickness was approximately 5 \(\mu\)m, and the film surface had a silver luster. Incidentally, it is generally known that the color of a Ti\(_x\)N\(_{1-x}\) film varies depending on the nitrogen content, exhibiting a gold color with \(x=0.5\) and a silver color with \(x=0.5\). That is, it was assumed that the TiN film had a low reaction amount of nitrogen since the sample used was silver.

Figure 3 shows the diffraction profile observed through \(2\theta\) scanning with the incident X-ray angle fixed at approximately 0.4\(^{\circ}\). By comparing the intensity ratio of each reflection in the actual measured profile with the intensity ratio of each reflection in the diffraction profile for a randomly oriented sample, it was determined...
that the sample has a weak preferred orientation in the [111] axis direction. When the incident X-ray beam was introduced at a grazing-angle, the penetration depth of X-rays into the TiN film was a few tens of nm, and thus, the stress state of the extreme surface layer is evaluated relative to the film thickness.

Here, Table 1 shows the diffraction peak information for the TiN film, obtained from profile fitting.

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<th>I (counts)</th>
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2.5. Discussion

The main cause of residual stress in thin films is thought to be thermal stress, which arises due to differences in the linear expansion coefficients of the substrate and film. The linear expansion coefficients of Fe and TiN near room temperature are, respectively, 11.8×10⁻⁶/K and 9.2×10⁻⁶/K, and after film formation, it is thought that compressive stress remains due to thermal contraction of the substrate. However, in the stress measurement, the residual stress of the extreme surface layer is evaluated relative to the film thickness, and it is certainly possible that the way in which strain develops is different from that near the boundary between the film and substrate. That is, while the substrate is strongly restrained near the boundary, there is a possibility that stress relaxation occurs at the film surface. In addition, a linear relationship is obviously shown in the function $f(\phi, \psi, S_1^{hkl}, S_2^{hkl})$ vs. strain $\varepsilon_{\phi}^{hkl}$ graph, and thus it can be seen that the conditions used to derive Equation (3) reflect the stress state of the film, and that tensile stress remains in the film surface in an isotropic state. If an anisotropic stress state needs to be taken into account, the stress can be analyzed by setting $\sigma_1 \neq \sigma_2$ and $\sigma_1 \neq 0$ in Equation (1).

In addition, the linearity of the observed graph shows that the stress gradient has no effect within the X-ray penetration depth.

2.6. Review of the multiple-hkl method

Another advantage of the multiple-hkl method is that it can be applied to stress measurements in narrow areas. At measurement points with fixing the X-ray angle of incidence, such as those in the narrow bottoms between gear teeth or in the inside of wheels, the stress is facilitated to be measured by taking into account only the X-ray angle of diffraction.

For the above reason, the multiple-hkl method is effective for evaluating residual stress in thin films and narrow areas, and it is an analysis technique indispensable for complementing general-purpose methods of X-ray measurement.

3. Evaluation of residual stress in a sample with shear stress in the depth direction

3.1. Comparison with the conventional method of residual stress measurement

If the sin²Ψ method, which is a uniaxial stress measurement method, is used with a polycrystalline sample, the sample must satisfy the following four conditions.

1. Sufficient crystal grains are present in the area irradiated by X-ray.
2. No strong texture is present in a sample.
Stress induced in a sample is bi-axial ($\sigma_{13} = \sigma_{23} = \sigma_{13} = 0$).

No stress gradient is present within the X-ray penetration depth.

Since the above four preconditions exist with the sin$^2 \phi$ method, depending on the sample’s crystal state, the sin$^2 \psi - 2\theta$ graph may display large deviations or may bend and become non-linear. The cause of this is thought to be the following four crystal states given by ① to ④ below, which correspond to the above ① to ④, respectively.

① Coarse crystal grains have been formed, thus a sufficient number of crystal grains are not present within the X-ray irradiated area.
② Texture is present.
③ Shear stress component ($\sigma_{13}$ or $\sigma_{23}$) is present within the X-ray penetration depth.
④ Steep stress gradient is present within the X-ray penetration depth.

In addition, it is known, by taking into account the triaxial stress state for the above crystal states, that the four features indicated in the following ①” to ④” appear in the sin$^2 \psi - 2\theta$ graph, corresponding to the above ①’ to ④’, respectively.

①” A continuous profile is not observed, and thus there is a large error in the slope of the sin$^2 \psi - 2\theta$ graph.
②” Peak intensities of the profiles observed with $\psi$ in specific directions are remarkably low.
③” $\psi$ split is produced(4)(5).
④” Waving appears in the sin$^2 \psi - 2\theta$ graph.

Various residual stress measurement and analysis techniques have previously been proposed for samples with crystal states outside the scope of application of the sin$^2 \phi$ method. However, even if phenomena like those indicated here appear in the sin$^2 \psi - 2\theta$ graph, it is a well-known fact that the sin$^2 \phi$ method can still be used if the confidence limit (an indicator of the match to the ① to ④ split method. However, a laboratory X-ray source was used here, and thus the stress in the depth direction was set to 0 ($\sigma_{13} = 0$).

3.2. Theory and technique evaluating residual stress with $\psi$ split

When evaluating residual stress for a certain material, typical samples which might contain a shear stress component ($\sigma_{12}$ or $\sigma_{23}$) are those in which a directionally processing layer is formed using techniques such as cutting or grinding. This section discusses the method of evaluating residual stress when a $\psi$ split occurs, using as an example a sample with a directionally processed layer formed through shot peening treated from one direction only.

When residual stress parallel to the in-plane component of the force (red arrow mark) is evaluated using the sin$^2 \psi$ method in the directionally processing layer (on the B line) as shown in Fig. 5, it is known that the sin$^2 \psi - 2\theta$ graphs in the two directions observed for the $+\psi$ and $-\psi$ directions are divided into the top and bottom of an ellipse. Hereafter, the $+\psi$ direction will be indicated as $\psi_+$ and the $-\psi$ direction as $\psi_-$. The X-ray residual stress was evaluated for a sample for which a $\psi$ split was intentionally produced by treating shot peening from one direction on a round iron rod.

The close-up view in Fig. 5 shows the stress component added to the round rod by the shot, viewing from the rod’s cross section. Relative to the positions A and B in the circumferential direction where the shot contacts the round rod, the shot strikes the sample surface perpendicularly at A. At B, on the other hand, the shot strikes in a “shearing” fashion from an inclined direction, and thus at B a stress (strain) component parallel to the sample surface, i.e., a shear stress component, is produced, and a directionally processing layer is formed.

Figure 6 shows the triaxial stress state in the directionally processing layer B. If the direction of incidence of the shot is taken to be parallel to the $\sigma_{13}$ plane, then there is a shear stress component $\sigma_{13}$ in the depth direction, and thus the $\sigma_{13}$ axis will tilt from the surface normal of the sample ($\sigma_{13}$ axis direction) due to rotation of the principal stress axes (red arrow; the three normal stress components when the shear stress components in all directions become zero are called the principal stress) around the $\sigma_2$ axis.
A current perspective of the state-of-the-art in stress analysis

In addition, the relationship between strain and stress in the sample coordinate system is given by the following Equation (4) due to the assumption here that $\sigma_{33}$ is set equal to zero in the general Equation (1) which indicates the state of triaxial stress.

$$\varepsilon_{\phi} = \frac{1}{2} S_2 (\sigma_{11} \cos^2 \phi + \sigma_{22} \sin 2\phi + \sigma_{22} \sin^2 \phi) \sin^2 \psi + S_3 (\sigma_{11} + \sigma_{22}) + \frac{1}{2} S_2 (\sigma_{11} \cos \phi + \sigma_{22} \sin \phi) \sin 2\psi \quad (4)$$

For Equation (4), the strain $\varepsilon_{\phi}$ and $\varepsilon_{\phi}$ in the $\phi$ direction and $\psi$ direction with respect to $\phi$ correspond, respectively, to the strain $\varepsilon_{\phi}$ and $\varepsilon_{\phi}$ in the $\psi$ direction with respect to $\phi$ and $\phi+180^\circ$. Therefore, the following Equation (5) is obtained if the average of these strains is set equal to zero in the general Equation (1) (setting $\psi=0^\circ$) is calculated using Equation (4).

$$\frac{1}{2} (\varepsilon_{\phi} + \varepsilon_{\phi+180^\circ}) = \frac{1}{2} S_2 \sigma_{11} \sin^2 \phi + S_3 (\sigma_{11} + \sigma_{22}) \quad (5)$$

In addition, strain at the crystal plane in the X-ray diffraction method is expressed as $\varepsilon_{\phi} = (d-d_0)/d_0$, and thus $\varepsilon_{\phi} = (\sin \theta_0/\sin \theta - 1$ is obtained using Bragg’s equation $2d \sin \theta = n \lambda \quad (n=1)$. Therefore, if the diffraction angle $2\theta$ in the $\psi$ direction is indicated as $2\theta_0$, and the diffraction angle $2\theta$ in the $\phi$ direction as $2\theta_1$, and if $2\theta$ is partially differentiated by $\sin^2 \psi$ in Equation (5), and the result is rewritten using $S_2/2(1+n)$, the following Equation (6) is obtained:

$$-(\partial \partial \theta + \partial \theta) \cot \theta_0/2 = \frac{2(1+n)}{E} \sigma \partial \sin^2 \phi \quad (6)$$

where $\sigma = \sigma_{11}$. If $M_\psi$ and $M_\phi$ are taken to be, respectively, the slopes of the sin$^2 \psi - 2\theta$ graphs obtained when the sample is treated using the sin$^2 \psi$ method for the $\phi$ and $\psi$ directions, and if the stress constant is assumed to be $K$, then the stress $\sigma$ can be given finally by the following equation.

$$\sigma = -\frac{E}{2(1+n)} \cot \theta_0 \cdot \frac{\pi}{180} \left( \frac{\partial \partial \theta_0}{\partial \sin^2 \phi} + \frac{\partial \partial \theta_1}{\partial \sin^2 \phi} \right)/2$$

$$\sigma = K \cdot (M_\phi + M_\psi)/2 \quad (7)$$

$$K = -\frac{E \cot \theta_0 \cdot \pi}{2(1+n)}$$

$$M_\phi = \frac{\partial \partial \theta_0}{\partial \sin^2 \phi}$$

$$M_\psi = \frac{\partial \partial \theta_1}{\partial \sin^2 \phi} \quad (10)$$

In other words, this indicates that the stress given by Equation (7) is equal to the average, $\sigma_{\text{ave}}$, of the residual stress values for $\sigma_{\phi}$ and $\sigma_{180\phi}$ when the $\psi$ and $\psi$ directions are respectively treated using the sin$^2 \psi$ method.

If it is assumed here that the confidence limits, $\Delta \sigma_{\phi}$ and $\Delta \sigma_{180\phi}$, corresponding to the stress values, $\sigma_{\phi}$ and $\sigma_{180\phi}$, are evaluated for the $\psi$ and $\psi$ directions, respectively, then the stress values evaluated using the sin$^2 \psi$ method are given as follows:

$$\sigma_{\phi} \pm \Delta \sigma_{\phi} = K(M_\phi \pm \Delta M_\phi)$$

$$\sigma_{180\phi} \pm \Delta \sigma_{180\phi} = K(M_{180\phi} \pm \Delta M_{180\phi}) \quad (11)$$

where $M_\phi$ and $M_{180\phi}$ indicate the errors of the respective slopes $M_\phi$ and $M_{180\phi}$ of the sin$^2 \psi - 2\theta$ graphs for the $\phi$ and $\psi$ directions.

Therefore, the stress, $\sigma_{\text{ave}}$, obtained using the $\psi$ split method and its error $\Delta \sigma_{\text{ave}}$ are given by the following Equation (12) by taking the respective averages using $\sigma_{\phi}$, $\sigma_{180\phi}$, $\Delta \sigma_{\phi}$, and $\Delta \sigma_{180\phi}$, evaluated with the sin$^2 \psi$ method.

$$\sigma_{\text{ave}} = \frac{\sigma_{180\phi} + \sigma_{\phi}}{2}$$

$$\Delta \sigma_{\text{ave}} = \sqrt{\frac{\Delta \sigma_{180\phi}^2 + \Delta \sigma_{\phi}^2}{2}} \quad (12)$$

Accordingly, residual stress can be easily evaluated, with samples when $\psi$ split occurs, by evaluating the average of the stress values in the $\phi$ and $\psi$ directions using the sin$^2 \psi$ method.

3.3. Introduction of a sample measurement

The SmartLab, fully-automatic $\theta$-$\theta$ rotating anode X-ray diffractometer (Fig. 2), was utilized to measure X-ray residual stress, and the residual stress was evaluated using the iso-inclination method in a parallel beam method optical system. Table 2 shows the measurement conditions, and Table 3 the parameters used for the analysis.

For the stress measurement, the residual stress was measured at a point on B in the two directions as shown in Fig. 5: the shot direction $\psi_\phi$ ($\phi=0^\circ$) and the opposite direction $\psi_\phi$ ($\phi=180^\circ$). Figure 7 shows these two directions of stress measurements with the sample placed on the sample stage of the SmartLab.

Figure 8 shows the sin$^2 \psi - 2\theta$ graph observed with the sin$^2 \psi$ method for the $\psi_\phi$ ($\phi=0^\circ$) and the $\psi_\phi$ ($\phi=180^\circ$) directions.

At one measurement point on B, compressive stress was observed at both $\phi=0^\circ$ and $\phi=180^\circ$, but a typical $\psi$ split was observed in which the sin$^2 \psi - 2\theta$ graphs are curved and the respective stress values are
different from each other. The residual stress value in the $\phi=0^\circ$ direction at a measurement point on B was $-286.74\pm34.44$ MPa, and the residual stress value in the $\phi=180^\circ$ direction was $-29.03\pm34.49$ MPa. Thus, the residual stress value at the measurement point where the $\psi$ split occurred was calculated to be $-157.89\pm24.37$ MPa by taking the average value based on the $\psi$ split method.

**Table 2.** Measurement conditions.

<table>
<thead>
<tr>
<th>Characteristic X-rays</th>
<th>CuK$\alpha$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diffraction surface</td>
<td>$\alpha$-Fe (3 1 0)</td>
</tr>
<tr>
<td>Strain-free diffraction angle</td>
<td>$2\theta_r=116.38^\circ$</td>
</tr>
<tr>
<td>Measurement method</td>
<td>Constant $\psi$ method (iso-inclination method)</td>
</tr>
</tbody>
</table>

**Table 3.** Analysis conditions.

<table>
<thead>
<tr>
<th>Analysis technique</th>
<th>$\sin^2 \psi$ method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Young’s modulus</td>
<td>223300 MPa</td>
</tr>
<tr>
<td>Poisson’s ratio</td>
<td>0.28</td>
</tr>
<tr>
<td>Stress constant</td>
<td>$-941.53$ MPa$^\circ$</td>
</tr>
</tbody>
</table>

**Fig. 7.** Stress measurement directions at a measurement point on B viewing from the cross-section side of the round rod.

**Fig. 8.** $\sin^2\psi$–$2\theta$ graph in working directions ($\phi=0^\circ$, $\phi=180^\circ$) of shot peening at a measurement point on B. (Sample provided by: Professor Shinichi Oya, Tokyo City University)

**Fig. 9.** A polycrystalline material consisting of numerous crystallites (crystal grains). Each crystallite has its own coordinate system.

4 Residual stress measurement and line-broadening of diffraction in a sample with fibre texture using the crystallite strain analysis method

4.1 Residual stress measurement using the crystallite strain analysis method

This is a technique for analyzing residual stress from crystallites comprising a polycrystalline material. In Europe, this technique is generally known as the crystallite group method (CGM)$^6$. Since this analysis method determines the strain of the entire crystal from a point of view of the orientation and strain of the crystallites comprising the polycrystalline material, we call this technique the “crystallite strain analysis method.” This section discusses a technique for applying the crystallite strain analysis method to polycrystalline materials with fibre texture. Developments of this measurement method for films with fibre texture was proposed by Hanabusa$^7$ for the hexagonal system, and since then analysis techniques for biaxial and triaxial stress states have been proposed by Sasaki$^8$, Ejiri$^8$, Tanaka$^9$ and others. Recently, Yokoyama et al.$^1$ have developed formulae indicating the relationships between strain and stress, obtained by taking account of the symmetries of a single crystal to which the constituent crystallites belong. In addition, when crystallite strain in samples with fibre texture is taken into account, it has also turned out that line-broadening is observed from the crystallite symmetries$^10$. This line-broadening will also be discussed.

In Fig. 9, focusing on one crystallite in a polycrystalline material, the sample coordinate system $P$, for the stress measurement is taken into account. When the crystallite under measurement is shown by the crystal coordinate system $X_i$ in the sample, the laboratory coordinate system, in which strain of lattice planes is measured, is taken to be $L_0$, as shown in Fig. 10.

The direction in which strain of a lattice plane is
A current perspective of the state-of-the-art in stress analysis

Figure 10. The four coordinate systems, $X'$, $P$, $L$, and $X$, in a polycrystalline material. $K_{i\alpha l}$ indicates a scattering vector in the $L_\alpha$ direction.

Figure 11. The four coordinate systems transformable from one to another using the matrices ($\alpha$, $\beta$, $\pi$, $\omega$, $\gamma$). $X'$ indicates a coordinate system added for convenience.

In the Reuss model, since the stress is equal to the average stress (macro stress) of the sample, the stress $\sigma_{i\alpha l}$ can be expressed on the outside of the angular parentheses $\langle \rangle$ in Equation (17).

Figure 12 shows a stereographic projection in the $\langle 111 \rangle$ axis direction when the constituent crystallites of a sample, having the $\langle 111 \rangle$ axis as the fibre texture, belong to the cubic system with $m$-$3m$ for the Laue symmetry. Based on the symmetries in a single crystal of the crystallite, each crystallite has three mirror planes containing the $\langle 111 \rangle$ axis and the reciprocal lattice axes $a^*$, $b^*$ and $c^*$, respectively, so that there are six equivalent reflections around the $\langle 111 \rangle$ axis. When taking these six equivalent reflections to be (a), (a)'', (b), (b)', (c) and (c)', both groups of the three reflections (a), (b), (c) and the three reflection (a)'', (b)', (c)' have a relationship of $120^\circ$ rotational symmetry, and the corresponding reflections such as (a) and (a)'' have a mirror plane between them.

Since the sample has the $\langle 111 \rangle$ axis as the fibre texture, it is likely that numerous crystallites are arranged at random around the $\langle 111 \rangle$ axis. That is, the position (a) of a certain crystallite is overlapped by equivalent reflections (a)', (b)', ..., (c)' of other crystallites. However, generally there is no way to distinguish the overlapping reflections of multiple crystallites such as (a), (b), (c) and (a)', (b)', (c)'

Next, let us consider the relationships between the symmetries in a single crystal and its residual stress. As shown in Fig. 12, when strain is observed at $\phi=0^\circ$, the positions (a), (b), (c) and (a)', (b)', (c)', which have the $120^\circ$ rotational symmetry and are equivalent, cannot be distinguished, so that it is enough if one point from each group is taken as a representative point that the residual stress should be taken into account only for (a) and (a)'.

These two representatives are shown as type I and type II in Fig. 12. If $\varepsilon^I_{33}$ and $\varepsilon^II_{33}$ indicate, respectively, two strains observed when the diffraction conditions are satisfied in type I and type II, and the biaxial stress state is assumed, then $\varepsilon^I_{33}$ and $\varepsilon^II_{33}$ are calculated as follows from Equation (16):

$$\varepsilon^I_{33} = \langle \omega_{3j} \omega_{3j} S^p_{ijkl} \sigma_{kl} \rangle = \langle \omega_{3j} \omega_{3j} S^p_{ijkl} \rangle \sigma_{kl}$$  

In the Reuss model, since the stress is equal to the average stress (macro stress) of the sample, the stress $\sigma_{i\alpha l}$ can be expressed on the outside of the angular parentheses $\langle \rangle$ in Equation (17).

In other words, $\varepsilon^I_{33}$ is the strain derived from the relationship between the strain and stress in the single crystal of a constituent crystallite in a polycrystalline material.

In this stress analysis, it is treated that the stress of each crystallite in a polycrystalline material with fibre texture is equal to the macro stress based on the Reuss model. The average stress in the polycrystalline material $\langle \varepsilon^I_{33} \rangle$ is given by the following equation.
\[ e_{33}^{I} = \frac{1}{12} ((3s_{44} + 3s_{44} \cos 2\phi + 2s_{0} \cos 2\phi) \sin^{2}\psi - 2\sqrt{2}s_{0} \cos(3\beta - 2\phi) \sin 2\psi + 12s_{12} + 4s_{0})\sigma_{11} \]
\[ + \frac{1}{12} ((3s_{44} - 3s_{44} \cos 2\phi - 2s_{0} \cos 2\phi) \sin^{2}\psi + 2\sqrt{2}s_{0} \cos(3\beta - 2\phi) \sin 2\psi + 12s_{12} + 4s_{0})\sigma_{22} \]
\[ + \frac{1}{6} ((3s_{44} + 2s_{0}) \sin 2\phi \sin^{2}\psi + 2\sqrt{2}s_{0} \sin(3\beta - 2\phi) \sin 2\psi)\sigma_{12} \] (18)

\[ e_{33}^{II} = \frac{1}{12} ((3s_{44} + 3s_{44} \cos 2\phi + 2s_{0} \cos 2\phi) \sin^{2}\psi - 2\sqrt{2}s_{0} \cos(3\beta - 2\phi) \sin 2\psi + 12s_{12} + 4s_{0})\sigma_{11} \]
\[ + \frac{1}{12} ((3s_{44} - 3s_{44} \cos 2\phi - 2s_{0} \cos 2\phi) \sin^{2}\psi + 2\sqrt{2}s_{0} \cos(3\beta - 2\phi) \sin 2\psi + 12s_{12} + 4s_{0})\sigma_{22} \]
\[ + \frac{1}{6} ((3s_{44} + 2s_{0}) \sin 2\phi \sin^{2}\psi + 2\sqrt{2}s_{0} \sin(3\beta - 2\phi) \sin 2\psi)\sigma_{12} \] (19)

where \( \sigma_{11}, \sigma_{22} \) and \( \sigma_{12} \) are the stress components in the sample coordinate system, \( \phi \) and \( \psi \) observed orientations of \( e_{33}^{I} \) shown in Fig. 10, and \( \beta \) the angle from the mirror plane to (a) or (a)', as indicated in Fig. 12. In addition, when \( s_{11}, s_{12} \), and \( s_{44} \) indicate the elastic compliance constants of a single crystal in cubic system, then \( s_{11}, s_{12}, s_{44} \) indicate the elastic compliance constants of a single crystal in cubic system, then \( s_{11}, s_{12}, s_{44} \). Here, the following equations show the relationships \( \psi \) and \( \beta \) have to the scattering vector \( H_{44} \) and the vectors \( H_{1} \) and \( H_{3} \) shown in Fig. 10.

\[ \psi = \cos^{-1} \left( \frac{H_{44} \cdot K_{44}}{|K_{44}|} \right) \] (20)
\[ \beta = \cos^{-1} \left( \frac{(K_{44} \times H_{1}) \cdot (H_{1} \times H_{3})}{|K_{44} \times H_{1}| |H_{1} |} \right) \] (21)

It is predicted that the two types of strains, which differ from each other in a stress state of the sample, will be observed simultaneously at the same point (\( \phi=0^\circ \)). This is attributable to the fact that the crystallinity of the sample with fibre texture displays a rocking curve \( \leq 0.1^\circ \), and that the X-ray source for measurement has some angular divergence and some wavelength dispersion. Therefore, the strains of the respective crystallographic planes in the type I and type II differ from each other. However in the observed diffractions, it is expected that the respective diffraction lines observed will overlap each other and form a single peak.

In the Reuss model, the observed strain, i.e., the average strain of the sample \( e_{33}^{I} \) is calculated as follows as the average of the strains \( e_{33}^{I} \) and \( e_{33}^{II} \) for type I and type II.

\[ \langle e_{33}^{I} \rangle = \frac{1}{12} ((3s_{44} + 3s_{44} \cos 2\phi + 2s_{0} \cos 2\phi) \sin^{2}\psi - 2\sqrt{2}s_{0} \cos(3\beta - 2\phi) \sin 2\psi + 12s_{12} + 4s_{0})\sigma_{11} \]
\[ + \frac{1}{12} ((3s_{44} - 3s_{44} \cos 2\phi - 2s_{0} \cos 2\phi) \sin^{2}\psi + 2\sqrt{2}s_{0} \cos(3\beta - 2\phi) \sin 2\psi + 12s_{12} + 4s_{0})\sigma_{22} \]
\[ + \frac{1}{6} ((3s_{44} + 2s_{0}) \sin 2\phi \sin^{2}\psi + 2\sqrt{2}s_{0} \sin(3\beta - 2\phi) \sin 2\psi)\sigma_{12} \] (22)

In general, stress is obtained from data consisting of strain observed at several points by applying the method of least squares refinement to Equation (22). In this paper, the relationship between strain and stress in the constituent crystallites was evaluated by assuming a biaxial stress state, however relationship for a triaxial stress state can also be estimated in the same way from Equation (16).

### 4.2. Line-broadening of diffraction in the crystallite strain analysis method

If two strains observed at the type I and type II orientations, respectively, of the constituent crystallites in a sample with fibre texture are different from each other, as expected in the previous section, it is predicted that line-broadening \( \Delta \theta \) of the diffraction will be observed.

Thus, the line-broadening of the diffraction, \( \Delta 2\theta(\beta, \phi, \psi) \), is estimated as follows, where the difference of strains in Equations (18) and (19) is indicated as \( \Delta 2\theta^{I} = \Delta 2\theta^{I} \).

\[ \Delta 2\theta(\beta, \phi, \psi) = 2\tan(\theta_{0}) \Delta 2\theta^{I} \] (23)

The following equation shows the results of calculating the strain difference \( \Delta 2\theta^{I} \) which is the cause of the line- broadening of diffraction of a sample with \( \{111 \} \) fibre texture in a cubic system.

\[ \Delta 2\theta^{I} = \Delta 2\theta^{I} = \Delta 2\theta^{I} = \Delta 2\theta^{I} \] (24)

Equation (24) shows that, when the difference of the normal stress components (difference of \( \sigma_{11} \) and \( \sigma_{22} \) is large, i.e., in an anisotropic stress state, there is a tendency for a large amount of line-broadening in diffraction to appear in the \( \phi=45^\circ \) direction. On the other hand, there is tendency for a large amount of the shear stress components \( \sigma_{12} \) and \( \sigma_{23} \) to appear in the \( \phi=0^\circ \) direction.

### 5. Conclusion

The three examples of X-ray stress analysis methods presented here are not frequently discussed as ordinary.
A current perspective of the state-of-the-art in stress analysis methods, but they are practical and effective stress analysis methods. Quantification of residual stress can serve as an indicator of material and structure strength, and thus it is an important issue for evaluating materials. Some of the techniques shown here have been commercialized by Rigaku in Japan.

References

Elemental analysis of PM2.5 with energy dispersive X-ray fluorescence spectrometer NEX CG

Atsushi Morikawa*

1. Introduction

1.1. Elemental analysis of PM2.5

Concerns about the effect of atmospheric aerosol particles have been increasing in recent years and its impact on global climate, air pollution and human health have been studied extensively. Recent reports of extremely high concentration levels of PM2.5 in China have drawn worldwide attention to this issue as well. PM2.5 are small particles suspended in the atmosphere with diameter less than 2.5 μm. The size is sufficiently small such that breathing can cause the particles to enter deep regions in the lungs where the air and blood are in intimate contact. This has raised concern not only about its effect on the respiratory but also on the cardiovascular system(1).

Elemental analysis of atmospheric aerosols including PM2.5 is an important means that can provide information about its source and environmental impact. In Japan, for the analysis of inorganic elements of PM2.5, acid decomposition of the collected sample followed by inductively coupled plasma-mass spectrometry (ICP-MS) method has been recommended. However, the sample preparation of this analysis method is complicated and analysis error can vary depending on the operator. Furthermore, the sample cannot be recovered after measurement since ICP-MS requires that the sample be dissolved in an acid solution.

To overcome these issues, the Japanese ministry of environment established a “Guideline for Component Analysis of PM2.5” in 2007 which is a simple and non-destructive analysis method of inorganic elements by X-ray fluorescence (XRF) analysis. The guideline was partially revised in 2013 which describes the analysis process of PM2.5 by XRF more concretely(2).

1.2. Elemental analysis of PM2.5 with XRF

Inorganic components in atmospheric aerosols such as PM2.5 collected on filter can be analyzed easily and non-destructively by XRF. It is also effective when many samples have to be analyzed rapidly. In addition, it has the advantage of being able to easily measure the major component of soil silicon (Si), which is difficult to analyze by the acid decomposition and ICP-MS method.

There are two types of X-ray fluorescence spectrometry methods—energy dispersive and wavelength dispersive XRF (EDXRF and WDXRF). Both types have been demonstrated to be suitable for aerosol analysis(3),(4), but EDXRF systems are often times preferred over WDXRF due to fewer installation requirements(5).

Especially when using the Rigaku EDXRF instrument NEX CG which is equipped with secondary targets for polarized irradiation, superior measurement results can be obtained due to lower background levels and LLD. The characteristics of polarized EDXRF, quantitative calculation process with thin film FP method and analysis results of real samples are introduced.

2. Experimental setup

2.1. System

The Rigaku EDXRF spectrometer NEX CG is shown in Fig.1 and its specifications are shown in Table 1. It does not require any special utilities such as liquid nitrogen or cooling water since it is equipped with a thermoelectrically cooled semiconductor detector and air cooled X-ray tube.

Secondary targets and polarized optics are illustrated in the left panel of Fig. 2. The right panel compares the spectrum of an oil sample for direct excitation to the spectrum obtained with NEX CG. It can be seen that NEX CG has superior peak to background (P/B) ratio resulting in higher sensitivity. The PM2.5 component analysis guideline mentions the use of secondary targets and polarized optics as well(2). Since the aerosol filter sample is not irradiated directly, damage to the sample due to X-ray irradiation is reduced.

NEX CG has a wide measurement range from sodium (Na) to uranium (U) with high sensitivity. The monochromatic excitation by the Pd-Lα line allows ppm level analysis of the halogen chlorine (Cl) which is difficult to analyze with ICP. The measurement diameter is 20 mm and the measurements are performed under vacuum environment. It is also possible to measure in helium (He) atmosphere to prevent evaporation of volatile components such as Cl. The instrument can be equipped with up to five secondary targets which allows for measurements with high P/B ratio over a wide element range(6).

2.2. Quantitative analysis method

For quantification, two methods are described in the established XRF guideline—empirical and fundamental parameter (FP) methods, both of which can be performed with NEX CG.

In case of the empirical method which uses standard samples for calibration, it is possible to obtain results with high precision. However, this requires the need to...
prepare many standard samples especially when there are many elements of interest\(^{(2)}\). In addition, when peaks of elements of interest are overlapped by peaks from other elements, or if the amount of collected sample varies in weight, additional corrections need to be applied and reliability of analysis result decreases. Actual aerosol samples consist of many components resulting in complex spectra with many overlapping peaks.

On the other hand, if FP method is used to perform semi-quantitative analysis, there is no need for standard samples since quantification is carried out based on the sensitivities that are pre-registered in the instrument. FP method is therefore also referred to as “standardless analysis.” When performing quantitative analysis with FP method, absorption and excitation effects due to co-existing elements are taken into account when calculating concentrations (or amount deposited on filter). Therefore, accurate analysis results can be obtained without the need to apply complex corrections even for samples which contain many elements. NEX CG is equipped with a FP calculation program that allows accurate quantitative calculation for thin film samples as described below\(^{(7)}\).

2.3. Outline for semi-quantitative analysis software "RPF-SQX"

The RPF-SQX (Rigaku Profile Fitting-Spectra Quant X) software\(^{(8)}\) for standardless analysis combines FP method with full profile fitting. The sensitivities are pre-calibrated using pure materials to cover the analysis of elements Na to U.

The computational scheme of RPF-SQX is summarized in Fig. 3. First (1), a sample is measured to obtain its spectrum. Next (2), the initial values of the thickness and contents of the sample is set. Then (3), a profile is constructed for each individual set element using the intensity obtained by the FP method and response function. The total spectrum is then calculated by summing up each individual profile. (4) The calculated total spectrum is then compared with the actual measured spectrum. The sample content and thickness are adjusted until both calculated and measured spectra match. The final result is obtained by fitting the entire spectrum, not just the peak intensity. The profile of each individual element is calculated using the FP method and the response function of the detector to match the measured spectrum.

Since this method utilizes the theoretically calculated

<table>
<thead>
<tr>
<th>Table 1. NEX CG specification.</th>
</tr>
</thead>
<tbody>
<tr>
<td>X-ray tube</td>
</tr>
<tr>
<td>Tube Power</td>
</tr>
<tr>
<td>Secondary targets</td>
</tr>
<tr>
<td>Detector</td>
</tr>
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</table>

Fig. 1. Rigaku EDXRF spectrometer NEX CG.

Fig. 2. Polarized optics and comparison to direct excitation optics of an oil sample (Spectra are normalized at Mo-Kα Compton scattered X-ray intensity).

Fig. 3. Computational scheme of RPF-SQX\(^{(8)}\).
peak profile for each element in the fitting process, accurate quantitative results can be obtained even when complex overlaps exist. Analysis results can be further improved by calibrating the sensitivities using the matching library function\(^5\).

2.4. RPF-SQX analysis for thin film sample

For filter samples, it is necessary to use the thin film FP analysis method. RPF-SQX is also applicable to thin film samples by calculating theoretical XRF intensities with an additional term for sample thickness\(^9\).

The XRF intensity ratio of different line types varies with sample thickness. Figure 4 shows the Pb-L\(\beta\) and Pb-L\(\alpha\) intensity ratio for varying sample thickness. Due to self-absorption of Pb the intensity ratio of L\(\beta\) to L\(\alpha\) decreases as the sample becomes thinner. Therefore, in order to obtain accurate full profile fitting, it is necessary to perform profile fitting using the thin film FP method to reflect the effect of self-absorption.

Figure 5 shows the measured and fitted spectra by the RPF-SQX method for polyethylene standard samples with different thicknesses. This sample contains not only Pb but also As, which Pb-L\(\alpha\) and As-K\(\alpha\) lines overlap with each other.

It can be seen in Fig. 5(b) that the profiles of both analytical lines are constructed separately. Since the combined profiles to form the spectrum matches the measured spectrum, accurate quantification results can be obtained even if sample thickness varies. This result demonstrates that RPF-SQX is able to calculate accurate results even when complicated overlaps exist or sample thickness varies\(^7\).

3. Aerosol filter sample analysis

3.1. Analytical procedure for aerosol filter sample

The analysis procedure of an actual aerosol filter sample is shown in Fig. 6. The aerosol filter is placed in a sample cup with the collected sample side facing down and an aluminum cup is placed on top to hold the filter. The sample cup is then placed in the turret.

Information regarding the sample is set in the software. If “EZ analysis” mode is selected, measurement can be carried out with only a minimum amount of settings such as sample position or application type. Measurement time is typically several minutes to 1 hour. After measurement, the software automatically carries out spectral identification and RPF-SQX calculation to display the standardless analysis result. By using XRF method, analysis result can be obtained easily without any tedious sample preparation.

3.2. Analysis result for aerosol filter samples

The spectra of an aerosol filter standard sample (NIST SRM2783) measured with NEX CG are shown in Fig. 7. The energy ranges where the sensitivity is optimum for each secondary target are shown. Spectra with good P/B ratio are obtained over a wide energy range from light to heavy elements. The Na-K\(\alpha\) line can be clearly seen although the Zn-L\(\alpha\) and Zn-L\(\beta\) lines overlap. This shows that it is important to correct for line overlaps in order to obtain accurate analysis results.

Table 2 shows the RPF-SQX result based on the spectra shown in Fig. 7. The result demonstrates that accurate analysis values can be obtained even without the use of standard samples. Since the effect of the immeasurable elements is not taken into consideration,
Elemental analysis of PM2.5 with energy dispersive X-ray fluorescence spectrometer NEX CG

1. Sample Setting
   - Place sample into the cup
   - Hold sample with Al cup
   - Place sample cup in the turret

2. Software setting
   “EZ analysis” interface

3. Measurement
   Identification and RPF-SQX analysis (automated)

4. Output of analysis result

Fig. 6. Flow chart of aerosol filter sample analysis with NEX CG.

the results for light elements are low. Reliability of analysis results of inorganic elements such as Al, K, Ca, V, Fe, Zn by the FP method has previously been confirmed by finding that the results correlate with ICP-MS analysis results\(^{(3)}\).

3.3. Lower Limit of Detection

Figure 8 shows the LLDs for various elements for NEX CG. These values were determined by measuring MICROMATTER™ thin film standard samples. Measurement time is 300 sec for each secondary target. The LLDs are lower than 10 ng/cm\(^2\), which corresponds to 5.2 ng/m\(^3\) when converted to concentration in air assuming that the aerosol particles are collected on the surface.

Table 2. Analysis results of aerosol filter standard sample (NIST SRM 2783) using RPF-SQX analysis.

<table>
<thead>
<tr>
<th></th>
<th>Na</th>
<th>Mg</th>
<th>Al</th>
<th>Si</th>
<th>P</th>
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<tr>
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<td>865</td>
<td>2330</td>
<td>(5880)</td>
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<td>(105)</td>
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<td>Analysis result</td>
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<td>610</td>
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<td>8.3</td>
<td>48.4</td>
<td>208</td>
<td>38.9</td>
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( ): not certified

Fig. 7. Spectra of aerosol filter standard sample (NIST SRM 2783).

Fig. 8. LLDs for each element.
Elemental analysis of PM2.5 with energy dispersive X-ray fluorescence spectrometer NEX CG

filter paper (diameter 47 mm, effective diameter 40 mm) at a flow rate of 16.7 L/min for 24 hours.

4. Summary
Using NEX CG, analysis of atmospheric aerosol such as PM2.5 collected on filters can be easily and non-destructively carried out for a wide element range. RPF-SQX allows accurate analysis even if complicated line overlaps exist. In addition, analysis can be performed without the need to prepare standard samples since FP method assures sufficiently accurate results. NEX CG is therefore an effective tool for the analysis of PM2.5 and is expected to contribute to the advancement in this field.

References
Introduction to single crystal X-ray analysis
VI. About CIFs—Alerts and how to handle them—

Akihito Yamano*

1. Introduction
CIF is an abbreviation for Crystallographic Information File, and these files record all of the information pertaining to crystal structure analysis. A CIF is written as a text file, and thus its content can be checked and edited using ordinary text editing software. CIFs are written with a special-purpose syntax, but they have spread rapidly due to their adoption by the IUCr (International Union of Crystallography), and are indispensable in X-ray structure analysis and related fields. In particular, when submitting papers whose focus is reporting the structure of a molecule, authors are frequently asked to submit a CIF, and there are likely many researchers who have struggled to understand and handle the alerts which appear during checking with checkCIF/PLATON on the IUCr website.

This paper discusses the purpose of and background behind the adoption of CIFs, alerts which frequently appear when checking using checkCIF/PLATON and how to handle them, details on judgment criteria, and vrf's (validation reply/response forms). To deal with these alerts, one must first be familiar with checkCIF/PLATON, and the author will be thrilled if this paper serves as an opportunity for readers to improve their understanding.

2. CIF significance and background
CIFs were originally devised as a way to transfer crystal structure information in the form of an electronic file. Before CIFs appeared, structure data was described in formats specific to various software packages. In some cases data had to be exchanged in a free format when no common format could be found between different types of software. This method was extremely inconvenient because information such as lattice constants and space groups had to be input separately by hand.

In the late 70s, IUCr began to encourage transfer of data in a fixed format to facilitate tasks such as processing of submitted papers. In the beginning, they encouraged use of a format called SCFS (Standard Crystallographic File Structure). General-purpose files need to be easy to use with various types of software, and, more specifically, it must be easy to program the reading/writing part. However, SCFS did not have general versatility sufficient for responding to these sort of needs.

In 1987, at the 14th Congress of the IUCr held in Perth, Australia, electronic paper submissions were encouraged by the crystallographic journal Acta Crystallographica. At the European Crystallographic Meeting held later that same year, it was decided to describe structure information in the STAR format (Self-defining Text Archive and Retrieval) developed for CIF by Mr. Syd Hall. In 1990, CIF was announced at the 15th Congress of the IUCr held in Bordeaux, France. Later, Syd Hall et al. published a paper on CIF in Acta Crystallographica Section A in 1991, and CIF subsequently came into use for transferring crystal structure information. At present, the original purpose of enabling transfer of structure information has been fully achieved, and there are journals such as Acta Crystallographica Section C and E to which papers are submitted in CIF itself. In addition, software for structure analysis, and almost all software using crystal structure as basic information, can now import CIF data. It can also be imported by modeling software for analysis of protein structure, and is used for analysis of the cocrystal structure of proteins and small molecule compounds.

3. checkCIF/PLATON
When a CIF is created, its content must be checked before submission. Checking is done using checkCIF/PLATON, available at the IUCr website. checkCIF/PLATON combines both checkCIF produced by IUCr, and the CIF check function of the PLATON crystallographic software. Some items are duplicated by checkCIF and PLATON, but basically they each have their own validation criteria. A deeper understanding of checkCIF/PLATON can be achieved by understanding the nature of these validation criteria.

When CIF check is executed, the first step is checking of the CIF syntax. When syntax checking is finished, the page changes and crystallographic data are displayed. Alerts are displayed under that (Fig. 1).

On the left side of an alert line, the name of the test involved in the alert is indicated. Here the test name is PLAT230. Next is the type of alert. There are four types of alert: 1–4. In this example, the type is 2. Type 2 is an alert relating to a mistake or defect in the molecule model. To the right of the type, the alert level is indicated. There are four alert levels, and in this line the level is B. This is the second most severe alert level. Finally, there is the alert message. In this example, the content of the message is that there is variation

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Introduction to single crystal X-ray analysis VI

4. Frequently occurring alerts and how to handle them

With the CrystalStructure structure analysis program package, if the Check Acta option is designated, major items are checked at the end of refinement. The following description covers alerts which often appear with checkCIF/PLATON even when all of the Check Acta items of CrystalStructure are satisfied.

Alerts which frequently occur include those relating to: (1) Residual electron density, (2) General temperature factors, (3) Magnitude of temperature factors, (4) Extension direction of anisotropic temperature factors, and (5) Shape of anisotropic temperature factors.

4.1. Alerts relating to residual electron density

The maximum difference density is > 0.1ZMAX*1.00_refine_diff_density_max given=1.020 Test value=0.800

Large Reported Max. (Positive) Residual Density 1.02 eA⁻³

Here, ZMAX is the atomic number of the heaviest atom. Possible causes of this alert include improper absorption correction and overlooking twins. It also sometimes occurs when crystallinity is poor and data precision is low. The simplest cause may be mistaken atom assignment. In particular, large residual electron density may appear due to an excess or insufficiency of electrons around heavy atoms. In cases where there is a large residual electron density in the solvent region, and this cannot be addressed with a feasible solvent molecule model, the issue can be addressed by smoothing the electron density in the solvent region using SQUEEZE (one of the functions of PLATON).

4.2. Alerts relating to general temperature factors

Large Non-Solvent C Ueq(max)/Ueq(min) ... 6.03 Ratio

In structures at non-solvent parts, this alert indicates that there is a large range of sizes of temperature factors for the same atomic species, in this case carbon. The cause may be mistaken atom assignment. To address the issue, first check that there are no mistakes in assignment of atoms. If there are no mistakes, try to avoid the alert using the DELU instruction of SHELXL.

4.3. Alerts relating to the size of temperature factors

Check High (Low) Ueq as Compared to Neighbors for O13

This alert indicates that, comparing the temperature factors of the bonded atoms, the temperature factor of the parent atom (in this case O13) is too large or too small (Fig. 2). The cause may be mistaken atom assignment. This alert tends to occur with tert-butyl groups and similar structures. If there is thought to be no problem with the structures, try to avoid the alert using such as the SIMU instruction of SHELXL.
4.4. Alerts relating to the extension direction of anisotropic temperature factors
Hirshfeld Test Diff for O20 -- C79 ... 8.57 su
Large Hirshfeld Difference O50 -- C174 ...
0.24 Ang.

This alert originated from the Hirshfeld test. Hirshfeld is a person’s name. He was active in the field of precision structure analysis, took notice of temperature factors, and proposed a criterion for determining the validity of temperature factors. The alert given here indicates a difference in displacement in the bonding axis direction of two bonded atoms. This is because the two atoms with the covalent bond can be viewed as approximately rigid. Possible causes of this alert include: occurrence of site disorder where different atomic species are present at the same site, non-crystallographic symmetry in the molecule itself, and overlapping of the entire molecule with a rotated or inverted structure. It is also necessary to check for mistaken atom placement. Temperature factors are sensitive to effects such as measurement error and correction, and thus one should check whether proper absorption correction has been employed. This alert occurs frequently even in structures based on fairly high precision data, and thus some questioned whether the Hirshfeld test is too sensitive, but the basic approach is to first examine the structure while taking into account the above points. If the cause cannot be specified, the alert can be avoided by using DELU instruction of SHELXL.

4.5. Alerts relating to the form of anisotropic temperature factors
Atom C95 has ADP max/min Ratio ... 3.40 prola

This alert indicates unusual elongation of the anisotropic temperature factor in a specific direction. In this example, the temperature factor of C95 in the end methyl group is elongated (Fig. 3). This is a classic sign of an disordered structure. It is handled by introducing a disorder model. The modeling method for disordered structure in SHELXL is given here as an example. C94 to C95 are the atoms in the original structure. C294 to C295 are newly introduced atoms. They are linked with FVAR so that the sum of the occupancies becomes 1.0. In addition, the temperature factors are restrained by inserting DELU and SIMU instructions.

5. Method of writing in vrf
When it is difficult to eliminate an Alert level A, and if there is a legitimate reason, the alert can be avoided by writing reasons into the CIF as a vrf. There are two ways of inserting a vrf.

With the first method, the vrf is directly written in after a line including data in the CIF. When checkCIF/PLATON is executed, a vrf template for Alert level A is displayed at the end. This can be copied, and inserted after the data_line. The reason should be described in the RESPONSE section.

In the second method, the vrf is written in two stages. Just like the above method, the vrf template shown in checkCIF/PLATON is inserted after the data_line. Next, in this case, “see publ_section_exptl_refinement” is written in the RESPONSE section, and the reason is written in ‘publ_section_exptl_refinement’.

Various examples of CIFs in which vrf’s have been written are available on the IUCr website.

6. Let’s get familiar with checkCIF/PLATON

Thus far, this article has introduced frequently occurring alerts and how to handle them. Since the number of possible alerts is about 400 for check.def and about 50 for data validation procedure, the total is about 450. It is impossible to memorize methods of handling each of these alerts. Thus the aim of the remaining portion of this article is to improve familiarity with the criteria and mechanisms by which CIF alerts occur, and thereby enable readers to handle a broader range of alerts themselves.

All the check items and thresholds of checkCIF/PLATON can be examined in the ‘Details of checkCIF/PLATON tests’ located at the bottom of the checkCIF/PLATON page(2). If you click on ‘Details of checkCIF/PLATON tests’, a table listing full check items will appear (Fig. 4). If you look closely at the test names, you can see that they are divided into two types: those that start with PLAT, and those that do not. Threshold values of tests which start with PLAT are given in a PLATON file called check.def. Threshold values for test names other than PLAT are given in the data validation procedure. checkCIF/PLATON combines the content of these two types of checks.

These two tests are generally complementary, but there are some items included in both. One example is the Flack parameter used to determine the absolute structure (Table 1). From this table it is evident that, depending on the situation, there may be cases where two or more messages are issued simultaneously in connection with the Flack parameter alone.

Here we will ascertain these by actually changing...
the value of the CIF Flack parameter. First, we edit the value of refine_abs_structure_Flack of CIF, and try entering the value 0.40.

STRVA01 is a test stipulated in the data validation procedure. The alert level is C, and the alert type is 4 (Fig. 5). The message indicates that the absolute structure is not determined by the Flack parameter.

In addition, PLAT033 is a test name stipulated in check.def, and the alert indicates that the Flack parameter deviates significantly from zero. The alert level is C, and the alert type is 4. In this way, multiple alerts are sometimes issued by two tests for one parameter.

Here will try to make the checking system issue more warnings by entering 10.1 for the Flack parameter, and 0.6 for the reliability ‘su’. An alert level A should occur. This is an actual alert (Fig. 6).

Just as before, STRVA01 is a test item stipulated in the data validation procedure. PLAT033 is a test result stipulated in check.def. What is different from before is that the alert level has changed to A. PLAT024 indicates that there is no anomalous dispersion signal. In addition, PLAT032 is an alert indicating that the standard deviation ‘su’ is large. PLAT024 and PLAT032 are also stipulated in check.def.

Alerts from checkCIF/PLATON are stipulated in the data validation procedure and check.def, and thus if you keep these two files on hand, it will likely be extremely useful for dealing with alerts.

In the data validation procedure, if you click on a test name other than PLAT at the page on the details of the checkCIF/PLATON test, the window for the corresponding test will open. At the bottom of this window is an item “Full list of validation algorithms.” If you click here, all of the test items can be seen at once.

check.def can be obtained at the PLATON website (5). check.def is frequently revised.

7. Conclusion

Today, CIFs are indispensable for transferring crystal structure information. Crystallographic journals now receive submissions in CIF form, and checking using checkCIF/PLATON is mandatory at a level appropriate to the journal being submitted to. Even in cases where CIF checking is unnecessary, it is extremely useful as a tool for checking whether there are any errors in analysis results.

Checking with checkCIF/PLATON is done using the items and threshold values listed in check.def and the data validation procedure. If you print out each of those files and keep them on hand, it will deepen your...
understanding and make it easier to respond to alerts. Numerous hints for responding to alerts are given on the checkCIF/PLATON\(^{(2)}\) page and the check results page.

**References**

(1) http://www.iucr.org/
(2) http://journals.iucr.org/services/cif/checking/checkfull.html
(5) http://www.cryst.chem.uu.nl/spek/platon/
Sample preparation for X-ray fluorescence analysis
II. Pulverizing methods of powder samples

Atsushi Morikawa*

1. Introduction
In the X-ray Fluorescence analysis (XRF) field, it may fairly be said that sample preparation can be the largest factor that cause analysis error\(^1\), \(^2\). Especially for the analysis of powder samples, as mentioned in the previous edition [Sample preparation for X-ray Fluorescence Analysis I.], heterogeneity effects such as grain size effect, mineralogical effect and segregation can result in analysis error because of its effect on the X-ray fluorescence intensity. When more precise analysis is required, it is recommended to analyze the sample after pulverization to eliminate the grain size effect and segregation as much as possible. For the fusion bead method which can remove the influences of grain size and mineralogical effects, the pulverization of the sample beforehand may be a key point in successfully preparing a homogeneous fusion bead sample with high reproducibility.

This issue describes the important points for pulverization to make powder samples with particle size less than 50\(\mu\)m.

2. Pulverizers and vessels
Commonly used pulverization tools are described below.

2.1. Pulverizers
As a pulverizer, vibration type pulverizers such as disk, rod and ball mills, or automatic mortars are used. In this section, commonly used vibration type pulverizer is explained. Figure 1 shows typical pulverizers. Disk mill shown in Fig. 1(a) can pulverize samples of about 100g at a time. Using this disk mill, when small pulverizing vessels are used, three vessels can be mounted at a time, although sample amount which can be pulverized is 10–20g for each. On the other hand, rod mill of the Fig. 1(b) can mount two small vessels at a time.

On the other hand, a small amount of sample (less than several grams) can be pulverized manually with an agate mortar, since the preparation with a pulverizer can be quite difficult.

2.2. Vessels
2.2.1. Materials
Grain size of sample after pulverization varies depending on weight of the vessel and its material. Typical vessel materials are alumina, tungsten carbide, chrome steel, zirconia, etc. For example, since the tungsten carbide is heavy and hard, it has a high grinding capability. Figures 2 show commonly used pulverizing vessels.

Regardless of vessel type, small amounts of the vessel material can be contaminated into the sample. Therefore, it is important to be aware of the elements of interest and its concentrations. Details about the contamination are discussed in section 5.2.

2.2.2. Rods
Available pulverizing rods with different shape are shown in Fig. 3. The cutting rod is used for coarse crushing of fibrous samples such as a plant leaves or resin sample. To obtain highly fine powders, pulverizing balls can be used. The standard round rod can be said to be the most practical rod in terms of pulverization efficiency and ease in cleaning.

However, pulverization capability will decline with long term use due to wearing of the rod. Such a case, X-ray intensity obtained from the sample measurement may change because of insufficient pulverization efficiency.

3. Pulverizing methods
3.1. Pulverizing time
Common pulverizing times are several tens of seconds up to 5min. It is necessary to increase pulverizing time in case of hard samples such like ores. In case of quantitative analyses, it is necessary to keep the pulverizing condition consistent for both standard samples and unknown samples by using the same sample amount and pulverizing time (Refer to section 5.1.).

Grain size after pulverization of less than 50\(\mu\)m is

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Sample preparation for X-ray fluorescence analysis II. Pulverizing methods of powder samples

3.1. Desirable grain size

A general rule of desirable grain size is that the powder does not feel rough or that it can thumb for fit between a fingertip grooves\(^2\). If possible, it is recommended to measure the actual sample to find the relationship between X-ray intensity and pulverizing time, and choose the pulverizing time where X-ray intensity saturates\(^1\). Figure 4 shows the relationship between X-ray intensity and pulverizing time for silicon dioxide (SiO\(_2\)) reagent pulverized by a tungsten carbide vessel. If speed of sample preparation is more important than analysis precision, pulverizing time can be set at 2 min where change in X-ray intensity of Si-K\(_\alpha\) is small. On the other hand, if high analysis precision is required and speed is not critical, pulverizing time of 5 min can be chosen.

3.2. Effects of pulverization aid

Some samples can show agglomeration when pulverized, which results in reduced impact force on the sample by the rod\(^3\). To counter this effect, pulverization aids are used which can prevent build up of agglomeration.

There are liquid and solid pulverization aids.
Liquid aid has the advantage that it does not remain in the sample by drying and volatilizing whereas after pulverization. Pulverization with liquid aid is called wet pulverization, without liquid is called dry pulverization. Figures 5 show the inside of the vessel after pulverization with and without n-hexane as pulverization aid. As clearly shown in Fig. 5, it is possible to improve pulverization capability and reduce powder adhesion to the vessel wall by using the pulverization aid. Additive amount is roughly 0.6–0.8 mL of n-hexane for 1 g of sample, but it is recommended to adjust the amount of aid so that the sample is reasonably wet when collected from the vessel after pulverization.

When using n-hexane as pulverization aid, the sample should be dried at 80°C for 30 min prior to forming the powder into a pressed pellet. Since the generated heat due to friction during pulverization turns into vaporized heat when using n-hexane, it has also the effect of reducing the likelihood of igniting easily ignitable samples.

On the other hand, when solid pulverization aids such as carbon is used, it is possible to get high pulverization capability by dry pulverization. However, it is important to keep the weight ratio of sample vs. aid constant since solid aids remain in the sample after pulverization.

3.3. Pulverization with binder

When a powder sample is formed into pressed pellet, a binding aid such as boric acid or Spectro Blend® can be mixed with the sample at a certain ratio to improve the forming capability. Mixing of binder with sample can also be performed in the vessel during the pulverization process.

4. Pulverization procedures

When pulverizing samples, it is also necessary to pay attention to the possible contamination from the previously pulverized sample. When same type of samples are pulverized in sequence, clean the vessel with an air blower or vacuum cleaner, then pulverize the next sample. Cleaning the vessel with water followed by drying decreases contamination from the previous sample. To pulverize different type of samples in sequence, pulverize a small amount of the new sample before pulverizing the new sample to “pre-wash” the vessel with the actual sample. Figure 6 is an example of pulverization procedures.

5. Other important considerations

5.1. Influence of pulverization on analysis results

Quantification error of powder samples such as minerals is mostly due to grain size effect. However, as mentioned already, the heterogeneity effect such as grain size effect can be reduced by pulverization. Grain size effect has a larger influence on light than heavy elements. Moreover, it is recommended that the grain size for a set of samples is the same. If pulverization condition differs, the analysis result can be different even for the same sample. This is because the X-ray intensity can vary depending on grain size distribution after pulverization. Figures 7 show calibration curves for Al₂O₃ in clay with different grain sizes. It can be seen that the analysis with finer grain size sample gives better accuracy, and confirms that pulverization reduces quantitative error.

5.2. Contamination of sample

There are two sources of sample contaminations, namely from the pulverization vessel material and the remained sample from the previous pulverization.
Sample preparation for X-ray fluorescence analysis II. Pulverizing methods of powder samples

5.2.1. Contamination from pulverization vessel

During pulverization, the vessel and rod are worn down and small amount of its material enters the sample. For example, several 100 ppm–several 1000 ppm of tungsten may be mixed into the sample when hard materials such as silicate rock, are pulverized in the tungsten vessel for a long time. Therefore, in case of trace element analysis, use of the vessel containing the analyte element should be avoided. Table 1 shows the material of common vessels which are the elements that can be mixed into the sample when pulverized.

Furthermore, it is necessary to consider overlap on the analyte spectrum from the vessel material. For example, trace analysis of mercury (Hg), selenium (Se), and arsenic (As) which are important elements for environmental monitoring analysis become difficult if tungsten (W) is mixed into the sample\(^4\). Tungsten carbide vessel is therefore not an appropriate choice since Hg-\(\text{L}_\alpha\) line is overlapped by W-\(\text{L}_\beta\)\(_2\) (Refer to Fig. 8.). Although the overlap correction of W-\(\text{L}_\beta\)\(_2\) is performed, it is preferred to choose Hg-\(\text{L}_\beta\) as the analysis line which does not have any overlap, or choose a different pulverization vessel such as zirconia. Compared to wavelength dispersive instruments, contamination from the vessel can be especially problematic for energy dispersive instruments. The poorer resolution results in many overlaps from the tungsten contamination.

<table>
<thead>
<tr>
<th>Material of vessel</th>
<th>Impurity mixed into sample</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alumina</td>
<td>Al</td>
</tr>
<tr>
<td>Tungsten carbide</td>
<td>W, Co, C</td>
</tr>
<tr>
<td>Special steel</td>
<td>Cr, Fe</td>
</tr>
<tr>
<td>Chrome steel</td>
<td>Cr, Fe</td>
</tr>
<tr>
<td>Zirconia</td>
<td>Zr, Hf</td>
</tr>
</tbody>
</table>

5.2.2. Contamination from the previously pulverized sample

Contamination can occur from the previously pulverized sample if the vessel is not sufficiently cleaned. Refer to section 4 “Pulverization procedure” for details.

5.3. Drying of sample

Powder samples can easily absorb the moisture contained in the air. Sample after pulverization increases moisture absorption capability since the surface area to volume ratio of the particles is increased due to smaller grain size. Care should be taken especially for hygroscopic materials. Absorption of moisture by the sample not only decreases X-ray intensity for light element range but also may lead to preventing the inside of the instrument not properly being evacuated for measurement. Considering these points, it is therefore recommended to dry the sample at 105–115°C for about two hours after pulverization and store it in a desiccator.

5.4. Samples having possibility of ignition

Ferroalloys or powders composed mostly of rare earth elements can potentially ignite due to increase of surface area by pulverization. Spontaneous ignition can occur even at ambient temperatures by reacting with oxygen in the air. Use of liquid nitrogen as a pulverization aid can be effective in such cases\(^5\). Liquid nitrogen itself is an effective pulverization aid, and also eliminates the possibility of ignition due to its low temperature and causing an absence of oxygen. Furthermore, if a gas replacement type vessel as shown in Fig. 9 is used, pressure build-up due to liquid nitrogen evaporation can be prevented by slowly leaking gas out of the valve. In addition, wearing for example leather gloves is essential when liquid nitrogen is used since the vessel itself becomes extremely-low in temperature.

5.5. Samples difficult to pulverize

When layered sheet like objects such as mica are contained in the sample, it has a tendency to remain unpulverized or only coarsely ground, while the rest of the sample is finely pulverized (mica effect). When such
Sample preparation for X-ray fluorescence analysis II. Pulverizing methods of powder samples

Inconsistently pulverized are formed into pressed pellets, the X-ray intensities can vary greatly. In such cases, fusion bead method is preferred preparation technique (1).

6. Summary
This issue describes appropriate pulverization procedures to obtain analysis results with improved accuracy for powder samples. In practice, the accuracy and precision required by the application are needed to be weighed against the time and effort that can be allotted to sample preparation. The actual sample preparation method is chosen by balancing these considerations.

References
Highly versatile multipurpose X-ray diffractometer
SmartLab 3

1. Introduction

SmartLab 3 offers continued refinement of the original ease of use features awarded the R&D 100 Award in 2006: automatic alignment, component recognition, cross beam optics and a five axis goniometer. Award winning guidance software recognizes installed components and seamlessly integrates them into data collection and data analysis methods. The Cross beam optics module offers permanently mounted, permanently aligned and user selectable optical geometries for various diffraction experiments. As an example, one can choose a Bragg–Brentano and parallel beam combination for measurements of both powders and thin films without the need for instrument reconfiguration. One could also choose a Bragg–Brentano and focusing transmission combination to measure organic materials in both transmission and reflection modes. The fifth axis or in-plane axis of the SmartLab allows the measurement of structures that are in the surface plane of the sample. This allows the measurement of extremely thin films and depth profiling in coatings. The SmartLab 3 system further extends application capability with the HyPix-400, a next generation 2-D detector. This hybrid pixel array detector offers the highest resolution and count rates available today. It is fully manufactured and integrated into the SmartLab 3 system by Rigaku and, as such, offers the superior ease of use pioneered by Rigaku in the original SmartLab system model. The SmartLab 3 configured with a HyPix-400 detector operates in 0-, 1-, and 2-D models without the need to exchange a detector.

2. Unique features

2.1. A true multipurpose X-ray diffractometer

Modern X-ray diffractometers are expected to support multiple applications; e.g., powder diffraction, thin film analysis, small angle X-ray scattering, residual stress and texture, to name a few. However, with the increase in complexity and sophistication that accompanies a multipurpose instrument comes the risk of a decrease in usability. How do you know for certain that you or your fellow researcher is selecting the best optics for each application? When switching between complex configurations, how can you be absolutely certain that your instrument remains aligned and that the data that you measure is of the utmost quality? The SmartLab 3 answers these questions in two ways. First, the instrument recognizes the specific optic components that are currently mounted on the diffractometer and checks the configuration against the type of measurement that you have selected. If the current configuration is not the best one for your intended measurement, the software suggests how you should change the hardware configuration for the type of application selected. Second, after the proper hardware components have been added to the instrument, the instrument performs an automatic alignment—a unique feature of Rigaku and the only true way to know that your instrument is ready to collect the high quality data that your research demands.

2.2. HyPix-400: Next generation 2-D detector

In recent years, two-dimensional detectors have become popular for powder and thin film X-ray
Highly versatile multipurpose X-ray diffractometer SmartLab 3

2.3. 5-axis goniometer gives additional information on thin film samples

Thin film diffraction measurements have grown steadily over the last two decades. In some large shared X-ray facilities, thin film work now constitutes 50% of the work being done. Because of this, it is now very important to have a diffractometer that has the most flexibility in measuring the unique properties of thin film materials. Rigaku’s unique solution to this problem is to include a fifth axis of rotation for the goniometer. This design enables the thin-film researcher to perform an “in-plane” scan, where the detector rotates in a plane parallel to the sample surface. This experimental configuration provides unique information for thin film materials; e.g., in-plane lattice constants and in-plane preferred orientation as a function of depth from the sample surface. If you are interested in thin film diffraction, this is a feature that will give you information that cannot be obtained on competitive diffractometers.

2.4. Maximize your uptime

Changing hardware configurations or consumables on some diffractometers is so daunting that people often invite their service engineer to perform the task. This can be costly and time consuming. Research stops when you are waiting for your service engineer to...
realign or configure your instrument. Rigaku addressed this issue years ago by designing and incorporating an automatic alignment system into a diffractometer, and this useful and safety oriented design is included in the SmartLab 3. The optics configuration on the SmartLab 3 is self-aligned. From the tube height to the monochromator alignment, all of the optics alignment is done automatically under computer control. This feature drastically reduces down time and cost of ownership of the instrument, and it allows you to be confident that your instrument will always be in aligned condition.
Single crystal diffraction systems based on hybrid pixel array technology

XtaLAB PRO series

1. Introduction

Rigaku has developed a new series of single crystal diffractometers that address a wide range of sample types, from small molecules to MOFs, to biological macromolecules. The key component that is common for this series of diffractometers is the use of an HPAD (hybrid pixel array detector), a technology that produces an almost perfect detector and greatly expands the capabilities of a single crystal diffractometer in terms of speed of data acquisition and more accurate measurement of weak data. The standard detector in the XtaLAB PRO series is the PILATUS 200K (Fig. 1), a detector that is well proven in the field and based on the same technology adopted by synchrotron beamlines around the world. The outstanding characteristics of these detectors ensure that every XtaLAB PRO diffractometer will perform to produce the best data possible for the X-ray source selected.

2. Why the HPAD outperforms other detectors

There are basically four types of detectors currently being used with single crystal diffractometers. The newest, the HPAD detector (Fig. 2), is a photon counting detector. Here’s how it works:

1. X-ray photon absorbed in the Si wafer.
2. Electron hole pairs are generated and funneled towards Indium bump.
3. Si wafer is connected to CMOS circuit by Indium bump for effective charge transfer.
4. Pixel signal processing unit, shapes and amplifies then compares vs reference value, if above, it is counted, if below not counted.

The outstanding characteristics of these detectors ensure that every XtaLAB PRO diffractometer will perform to produce the best data possible for the X-ray source selected.

Fig. 1. The PILATUS 200K HPAD detector.

Fig. 2. How the HPAD detector works.
detector that differs from the other three detectors in that it directly detects X-ray photons without the intermediate step of converting the photons to light with a phosphor. Without a phosphor and associated substrates, the point spread function of the HPAD detector is defined by the actual pixel size and there is none of the blooming that occurs from the phosphor and substrate.

Imaging plate (IP) based diffractometers have been in production for over 25 years but still are in use because very large apertures can be created, they can be exposed for long periods of time due to the lack of electronic dark current and they are comparatively inexpensive. CCD based detectors are more sensitive than IP based systems but suffer from a reduced dynamic range and errors introduced from the phosphor and glass stub/taper assembly. CMOS based detectors have been introduced more recently and offer a larger aperture than a CCD detector but are intrinsically noisy and still require a phosphor and glass stub assembly for converting X-ray photons to visible light.

Integrating detectors such as CCDs and standard CMOS detectors, have some additional disadvantages. As they use a fiber optic stub (CMOS) or taper (CCD) light loss occurs at the interfaces between the phosphor-stub and stub-sensor as well as in the glass material itself. Diffusion of light in the phosphor and loss of light through the fiber optic stub means CCDs and standard CMOS detectors have a point spread function with longer tails than a Gaussian such that data is spread across many pixels.

As a result of no light diffusion within the detector, HPAD spots have a ‘top-hat’ point spread function of one pixel rather than the long tail PSF seen with CMOS and CCD detectors.

There are three characteristics of the HPAD detector that make it especially good for the measurement of single crystal diffraction data. First, the readout speed of the detector is so fast that the diffractometer can be run in true shutterless mode. The shutter is opened at the beginning of a scan and the scan axis moves continuously until the scan is finished. Images are constantly being readout during the scan and since the readout time is insignificant they can be treated the same way that single images are normally handled. Shutterless data collection mode leads to huge time savings in data acquisition.

The second characteristic of the HPAD detector that makes shutterless data collection a routine technique is the high dynamic range which means that rescans due to intense reflections are not necessary. With a CCD detector, the shutter is opened and closed with each image and you have to wait as the image is read out. If there is an overload (due to the restricted dynamic range) then a rescan has to occur. In addition to the speed improvement, shutterless data collection eliminates errors that are associated with the opening and closing of shutters as well as the ramping up and ramping down of scan axes.

The third important characteristic of the HPAD detector is the fact that the noise level is essentially zero (no detector is perfect and so it is not correct to call it a noiseless detector, but the HPAD is the closest thing to a noiseless detector available today). A detector with extremely low noise is important because it means that you can measure weak reflections more accurately since backgrounds are as low as possible. Any crystal will have a combination of relatively weak and strong reflections but crystals that most benefit from the accurate measurement of weak reflections are crystals that scatter poorly. With an HPAD detector, the low noise characteristic means that you can expose a crystal for significantly longer periods of time than either a CCD or a CMOS based detector. There is no significant build up of noise with the HPAD detector and you can measure diffraction from poorly diffracting crystals that would be swamped with electronic noise in other types of detectors.

3. X-ray Source Configurations

While the HPAD detector is the common element of the XtaLAB PRO series, the selection of X-ray sources is quite diverse and allows one to select an X-ray source configuration based on the radiation type or types as well as the level of flux desired.

The standard configuration for the XtaLAB PRO (Fig. 3) includes a Cu MicroMax-003 microfocus sealed tube source and a 3 kW Mo standard sealed tube source with a SHINE (curved graphite monochromator) optic. The selection of a microfocus Cu source and a standard focus Mo source is based on the difference in efficiency between Cu and Mo radiations when coupling micro focal spots with multilayer optics. Figure 4 shows the relative flux through a 100 μm aperture at the crystal position for both a standard sealed tube Cu source with graphite monochromator and a microfocus Cu X-ray source with a multilayer optic. The approximately 12-fold improvement in flux at the sample makes the use of the Cu microfocus X-ray source an easy decision.

Figure 5 shows the relative flux through a 100 μm aperture at the crystal position for a standard sealed tube Mo source with graphite monochromator, a standard sealed tube Mo source with a curved graphite...
monochromator (SHINE optic) and a microfocus Mo X-ray source with a multilayer optic. It is easy to see that the standard Mo source with the SHINE optic produces equivalent X-ray flux at the sample as the microfocus Mo source. The decision to include a standard Mo X-ray source with the XtaLAB PRO standard model is based on the wide availability and ease of replacement of standard Mo X-ray tubes. While the XtaLAB PRO can be equipped with a Cu and Mo microfocus source, the performance will not be improved and, in fact, for larger crystals, the microfocus Mo source produces less flux at the sample than the standard Mo sealed tube source with a SHINE optic.

Beyond the standard configuration of the XtaLAB PRO, it is possible to increase the flux at the sample significantly by utilizing a rotating anode based X-ray source and Rigaku offers a number of models and configurations to choose from.

The MicroMax-007HF is a microfocus rotating anode generator and the most popular rotating anode source utilized for single crystal analysis around the world. It is available in both a single wavelength configuration as well as a unique double wavelength configuration. In the double wavelength configurations (Mo/Cu or Cu/Cr), the wavelength to be used can be selected automatically.

For even more flux at the sample, the FR-X microfocus rotating anode generator is available and is the most powerful rotating anode X-ray source for single crystal analysis available today.

These two rotating anode sources are well proven in the field and offer a low-maintenance regimen compared to rotating anodes of the past. While the ongoing maintenance of a rotating anode generator is more than that of a sealed tube generator, the increase in flux at the sample is significantly higher and allows the researcher to measure samples that could only previously be measured at a synchrotron.

Figures 7 and 8 show the relative flux through a 100μm aperture at the crystal position for a standard sealed tube source, a microfocus sealed tube source, the MicroMax-007HF, and the FR-X for Cu and Mo radiation respectively.

For Cu radiation, the 7 and 19 fold increases in
flux for the MicroMax-007HF and FR-X respectively compared to the MicroMax-003 (microfocus sealed tube) is a clear indication of the performance improvements that are possible when using rotating anode based X-ray sources. It is even more significant for Mo radiation where 12 and 30 fold improvements can be gained from the MicroMax-007HF and FR-X respectively compared to a Mo sealed tube source with a SHINE optic or a Mo microfocus sealed tube source.

4. A Work Environment Designed for Research

The XtaLAB PRO series is housed in a newly developed enclosure (Fig. 9) that was designed to improve the workflow of mounting air-sensitive and temperature sensitive samples. There is space inside the XtaLAB PRO enclosure for a microscope and a dewar (Fig. 10). No matter what type of samples you are working with, the ability to identify and mount crystals in the proximity of the diffractometer can be a true time saver. In the case of air-sensitive and temperature-sensitive crystals, having close proximity of the mounting station to the goniometer can mean the difference between a crystal that diffracts and a crystal that dies.
1. Introduction

Thermodilatometry is a thermal analysis technique in which a constant load is applied to a sample, and the amount of expansion and/or shrinkage of the sample is measured during heating. TDL 8411 was recently added to the lineup of the Thermo plus EVO2 series as a high-performance thermodilatometer using the horizontal differential expansion system. It is equipped with various new functions, including space-saving design, ECO mode for reducing standby power and an auto sample changer holding 24 samples.

Two types of instruments are available: a standard type with a maximum use temperature of 1100°C (the support tube and detection rod are made of SiO₂), and a high temperature type ranging up to 1500°C (the support tube and detection rod are made of Al₂O₃).

2. Features

2.1. High-sensitivity and high-accuracy measurement through differential expansion system

TDL8411 adopts the Rigaku’s established reputation on differential expansion principle where the thermal expansion or shrinkage generated from the detection mechanism itself can be cancelled. It offers high accuracy and excellent reproducibility in expansion and shrinkage measurements, even with low expansion materials and samples with low-thickness.

2.2. Load setting

The load applied to a sample is set by the software. Changing the sample is easy because of the on/off in sample loading which can be done by the operating switch on the main unit.

2.3. Automatic length determination function

The sample length is automatically measured and can be recorded. It is easy to operate at continuous measurement.

2.4. Cooling after the measurement

Cooling fan unit can be automatically operated after measurement. With a cooling time within 15 minutes from 1000°C to 50°C, the system is capable of high throughput.
2.5. **ECO mode, reducing standby power**
Setting to ECO mode to reduce standby power during standby state or after the completion of measurement.
In the ECO mode, the recovery time is short because the electric power for warming up is ON at minimum.

2.6. **Fusion prevention function**
When measuring a glass or ceramic sample in detecting shrinkage with fusion, the measurement can be stopped during heating at a temperature where specified amount of shrinkage has been attained. Thus, this makes it possible to prevent the damage of the support tube and the detection rod.

2.7. **Auto sample changer**
This unit can set a maximum of 24 measurement samples and 2 reference samples. The measurement can be done with a single window and, the system can perform continuous, individual and interruption measurements.
It is suitable for quality control and routine analysis flexibly.

2.8. **Literature calibration software**
It enables to create and register a calibration file calculated from differences in the amount of expansion at each temperature. Comparing a standard sample with a known expansion coefficient or sample measurement results will serve as a standard against literature values (reference values). Using this calibration file, it is possible to calibrate the amount of expansion in measurement results of an unknown sample, and thereby obtain more accurate measurement results.
In addition, it is possible to evaluate the accuracy and to manage the data obtained between multiple instruments.

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**Table 1.** Specification.

<table>
<thead>
<tr>
<th></th>
<th>Standard model</th>
<th>High temperature model</th>
</tr>
</thead>
<tbody>
<tr>
<td>Measurement temperature range</td>
<td>Ambient ~ 1100°C</td>
<td>Ambient ~ 1500°C</td>
</tr>
<tr>
<td>Measurement method</td>
<td>Compression loading method</td>
<td></td>
</tr>
<tr>
<td>Detection system</td>
<td>Differential expansion method</td>
<td></td>
</tr>
<tr>
<td>Standard sample size</td>
<td>( \phi 5 \times 10 \text{ mm} \rightarrow 20 \text{ mm} )</td>
<td></td>
</tr>
<tr>
<td>Maximum load</td>
<td>50 mN ~ 300 mN</td>
<td></td>
</tr>
<tr>
<td>Measurement atmosphere</td>
<td>Air, inert gas or gas flow</td>
<td></td>
</tr>
<tr>
<td>Auto sample changer</td>
<td>Measurement sample 24 pieces. Standard sample 2 pieces.</td>
<td></td>
</tr>
</tbody>
</table>
2.9. Excel and Word output
The measurement file can be directly exported to Microsoft Word or Excel. In the case of exported in Excel, numerical data is automatically created at the same time (see Fig. 3.), it is useful for data analysis and graph preparation using other application software.

2.10. Instrument usage history listing function
Various information such as data, user name, temperature program and measurement file name are saved as Excel data when a measurement is complete. This clearly indicates the usage history and operating time of instruments, and is effective for maintenance and management.

2.11. Email function
By connecting with a LAN, it is possible to transmit information by email such as end of measurement, measurement data and occurrence of an error to PC station.
The user can confirm the status of the instrument and the on-going measurement from remote locations.

3. Conclusion
TDL 8411 is newly added to the lineup of the Thermo plus EVO2 series with compact and high-performance thermal analysis.
Together with DSC, TG-DTA and TMA, TDL can be used to evaluate the thermal property of samples in a whole range of fields such as research development and quality control.
High-resolution/high-speed
2D photon counting X-ray detector

HyPix-3000

1. Introduction
Rigaku’s HyPix-3000 is a next-generation two-dimensional semiconductor detector designed specifically to meet the needs of the home lab diffractionist. One of the HyPix-3000’s unique features is its large active area of approximately 3000 mm² with a small pixel size of 100 μm square, resulting in a detector with high spatial resolution. In addition, the HyPix-3000 is a single photon counting X-ray detector with a high count rate of greater than 10^6 cps/pixel, a fast readout speed and essentially no noise.

HyPix-3000 has the following features:
- Ultra-high dynamic range and high sensitivity
- Seamless switching from 2D-TDI (Time Delay and Integration) mode to 2D snapshot mode to 1D-TDI mode to 0D mode with a single detector
- XRF suppression by high and low energy discrimination
- High spatial resolution, direct-detection pixel array detector

2. State of the art detector technology
Featuring a double-threshold (window) discriminator, the HyPix-3000 has three readout modes that can be selected based on the purpose of a measurement. “Differential” mode can be used to suppress fluorescence from elements in a sample or background derived from cosmic rays. “31-bit” mode is used for experiments in which a very wide dynamic range is needed. “Zero dead time” mode makes it possible to perform extremely fast data collection.

The HyPix-3000 was designed for optimal flexibility and minimal maintenance. For example, the compact angular enclosure was designed to allow excellent high angle accessibility. Compared to the design of other types of detectors, the HyPix-3000 is essentially maintenance free. Unlike other types of detectors, it does not require an external cooling device as required on CCD detectors, or gas exchange and anode wire washing as required on multi-wire detectors.

3. How do you most effectively suppress background noise?
Each pixel on the HyPix-3000 detector has dual energy discriminators, which makes it possible to adjust the energy window width by setting the energy threshold to “high” and “low”, respectively. The low-energy

![Fig. 1](image-url) X-ray diffraction patterns of iron oxide powder, measured in standard mode and XRF reduction mode.
 discriminator can eliminate electrical noise and reduce fluorescence background, and the high-energy discriminator can eliminate cosmic rays and white radiation. As a result, you can measure data with an optimized signal-to-noise ratio. Figure 1 shows the X-ray diffraction pattern of a powder sample containing iron measured in standard mode (upper) and XRF reduction mode (lower). By using differential XRF reduction, it is possible to obtain an X-ray diffraction pattern with low background, and thereby improve the ability to detect trace components, even when measuring Fe-based compounds with a Cu source.

4. What is the best way to measure very strong reflections?
A big advantage of a hybrid pixel array detector is that each pixel is independent and the overall dynamic range of a detector is a sum of the dynamic range of each individual pixel. Each pixel of the HyPix-3000 has two 16-bit counters, and these can be combined to work as a single 31-bit counter achieving very wide dynamic range. This means that, wide dynamic range measurements can be performed without an attenuator, thus removing the error associated with the attenuator factor, as well as optimizing data measurement time. Figure 2 shows the high-resolution rocking curve profiles of InGaN/GaN multiple quantum wells (MQW) with the HyPix-3000 (wide dynamic range 31-bit mode) and scintillation counter. The profile obtained in 31-bit mode clearly indicates separated peaks without saturation.

5. How do you obtain data with excellent spatial resolution?
The HyPix-3000 detector’s small pixel size provides outstanding spatial resolution. Figure 3 shows a typical qualitative analysis, which, in this example, was done in 2 minutes. In this case, the detector was run in a one dimensional Time Delay and Integration mode (1D-TDI mode), which allows continuous movement of the detector during measurement. If you want resolution less than 0.03 degrees at full width at half maximum (FWHM), as shown in Fig. 4, you can run the detector in 0D mode which requires placing a mechanical slit on the face of the detector.

6. How can you effectively investigate phenomena that are constantly changing over time?
The HyPix-3000 detector is equipped with high-speed readout circuit. This means that dead time during readout is actually zero. Due to true shutterless operation, in situ and time resolved measurement can be easily performed. As shown in Fig. 5, the phase transition process in the synthesis of gehlenite from the mixture of corundum, quarts, and calcite under conditions of continuous temperature rise was visually recorded at each stage by utilizing the detector features.
High-resolution/high-speed 2D photon counting X-ray detector HyPix-3000

of fast readout and large active area.

7. How can you measure a wide angle range rapidly?

The HyPix-3000 supports two-dimensional Time Delay and Integration mode measurement, so a 2D detector can be used for simultaneous scanning like a 0D or 1D detector is used.

The ability to operate a fast 2D detector in TDI mode is best illustrated for the measurement of a reciprocal space map. Figure 6 shows a wide range reciprocal space map of a (Pb, La)TiO₃ (PLT) orinetated film on a Pt base layer and a Si substrate. Data collection for the calculation of this reciprocal space map was completed within 10 minutes. This fast data measurement speed was accomplished due to the size of the detector, the TDI data measurement mode and the high readout speed, which allows shutterless data collection.

Table 1. Specifications.

<p>| | |</p>
<table>
<thead>
<tr>
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<tbody>
<tr>
<td>Sensors</td>
<td>Semiconductor pixel sensor</td>
</tr>
<tr>
<td>Active area</td>
<td>2,984 mm² (77.5 x 38.5 mm)</td>
</tr>
<tr>
<td>Pixel size</td>
<td>100 x 100 μm</td>
</tr>
<tr>
<td>Number of pixels</td>
<td>775 x 385 = 298,375 pixels</td>
</tr>
<tr>
<td>Counter mode</td>
<td>Differential/31-bit/zero dead time</td>
</tr>
<tr>
<td>Count rate</td>
<td>Global: &gt; 2.9 x 10¹¹ cps</td>
</tr>
<tr>
<td></td>
<td>Local: &gt; 1 x 10⁹ cps/pixel</td>
</tr>
<tr>
<td>Efficiencies</td>
<td>Cr, Fe, Co, Cu: 99%</td>
</tr>
<tr>
<td></td>
<td>Mo: 38%</td>
</tr>
<tr>
<td>Readout time</td>
<td>3.7 ms (0 ms for zero dead time mode)</td>
</tr>
<tr>
<td>Energy resolution</td>
<td>Better than 25% at Cu Kα</td>
</tr>
<tr>
<td>Dimensions</td>
<td>147(W) x 93(H) x 180(D) mm</td>
</tr>
<tr>
<td>Weight</td>
<td>Approximately 2 kg</td>
</tr>
</tbody>
</table>