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Cover images: The picture on the cover illustrates a structural model of flufenamic acid/nicotinamide 1:1 cocrystal determined with powder diffraction data collected using the SmartLab high-resolution diffraction system shown in the lower-right. The 9 kW rotating-anode X-ray source and Johannson monochromator make it possible to obtain the focused, brilliant, monochromatised X-rays used to collect the powder diffraction data.
X-ray thin-film measurement techniques

V. X-ray reflectivity measurement

1. Introduction

This is the fifth article in the series of X-ray thin-film measurement techniques. The second, third and forth articles of this series, previously published in the Rigaku Journal, describe out-of-plane, high-resolution and in-plane XRD measurements to obtain crystallographic information on crystal size, lattice strain and orientation relationship of a thin-film material. These measurements have been based on the premise of a crystalline thin film. On the other hand, the X-ray reflectivity (XRR) measurement is not a technique to evaluate diffraction phenomenon. The XRR measurement technique described in this article is used to analyze X-ray reflection intensity curves from grazing incident X-ray beam to determine thin-film parameters including thickness, density, and surface or interface roughness. This article will provide an overview of the principles of X-ray reflectivity, measurement procedures, and analysis methods. It also discusses the procedural flow from measurement to analysis, as well as precautions.

2. X-ray reflectivity measurement

The X-ray reflectivity method has the following characteristics:
A) It can be used to study a single-crystalline, polycrystalline or amorphous material.
B) It can be used to evaluate surface roughness and interface width (arising from roughness and interdiffusion) nondestructively.
C) It can be used to study an opaque film under visible light.
D) It can be used to determine the layer structure of a multilayer or single-layer film.
E) It can be used to measure film thickness from several to 1000 nm.

2.1. The phenomenon of sample surfaces at grazing-angle incidence

When electromagnetic waves including visible wavelength are incident onto a sample surface, these electromagnetic waves are reflected off it. The incident electromagnetic waves generate a specularly reflected wave, a refracted wave a diffused reflections, as shown in Fig. 1.

In the case of X-rays, which are incident electromagnetic waves, the refractive index of a material is slightly less than 1. Therefore, the X-rays undergo total reflection when incident on a flat surface of a material at a grazing angle is smaller than the critical angle for total reflection (θc). Thus X-ray reflectivity is related to the values of refractive index and X-ray wavelength. It should be noted that Cu-Kα X-rays is used throughout this article.

Figure 2 shows a calculated X-ray reflectivity curve for bulk Si and Figure 3 shows the X-ray optics for the cases of the incident angles smaller, equal to, and greater than the critical angle for total reflection, θc. As shown in Fig. 2, when an X-ray beam is impinged at a grazing angle on to an ideal flat surface of a material, total reflection occurs at below the incident angle θc, and the incident X-rays do not penetrate into the material. X-ray reflectivity decreases rapidly with increasing incident angle, θ above θc. The ratio of specularly reflected X-rays decreases proportionally to θ4.
2.2. Information provided by an X-ray reflectivity measurement

The X-ray optics for an X-ray beam onto a flat surface of material at grazing angles has been described in the previous section. In this section, the analysis of the resulting X-ray reflectivity curve to obtain information on the structural parameters of a thin film is described.

2.2.1. Film thickness

Changes in reflected intensity when a substrate made of an ideal material is laminated uniformly with a substance having a different electron density are described below. The observed scattering X-rays are the sum of individual electron scatterings. The intensity of X-ray reflectivity is calculated from each layer which is constructed from elemental species and filling rate of space. Section 5 will describe total reflection and refraction in more detail. Figure 4 shows the X-ray reflectivity curve of an Au film deposited on a Si substrate. Generally, the Y-axis of X-ray reflectivity curve is shown in a logarithmic scale of the normalized intensity of $I/I_0$. A logarithmic scale is used because of the wide dynamic range of X-ray reflectivity intensity.

Interference occurs between the X-rays reflected from the surface of the Au film and the interface between the Au film and the Si substrate. As shown in Fig. 4, the reflectivity profile shows oscillations caused by this X-ray interference. These oscillations were first observed in 1931 by Kiessing and is called Kiessing fringes\(^1\). The oscillation depends on the film thickness, and the thicker film, the shorter period of the oscillations.

2.2.2. Density

The effects of thin-film density on an X-ray reflectivity curve are described below. Figure 5 shows the reflectivity curves of three 20 nm thick films with different densities deposited on Si substrates. The Au, Cu and SiO\(_2\) films in Fig. 5 are used as examples for the cases of heavy, medium and light density materials, respectively.

The results indicated that the amplitude of the oscillation and the critical angle for total reflection provide information on the density of films. The amplitude of the oscillation depends on the difference between the densities of the film and its substrate, the larger the difference in the film density, the higher the amplitude of the oscillation.

2.2.3. Surface or interface roughness

Figure 6 shows the reflectivity curves for a Si substrate with two different values of surface roughness. The results shown in Fig. 6 indicate that reflected X-rays decrease more rapidly with a larger surface roughness. In other words, the larger the roughness of a film, the faster the decay rate of X-ray reflectivity.

On the other hand, Figure 7 shows the results of measurement for two types of substrates with different values of interface roughness. The results indicate that amplitude of the oscillation decreases with increasing
interface roughness. The term “interface roughness” includes that physical uneven interface and transitional boundary layer which continually changes in density. In both cases, interface roughness is recognized to a continuous variation of electric density along the thickness direction.

Figure 8 shows the summaries of the effect of film thickness, density, roughness of surface and interface on the X-ray reflectivity curve of a thin film deposited on a Si substrate.

Therefore, the X-ray reflectivity technique is a method for determining the layer structure of a thin film. The principles of X-ray reflectivity method will be described in section 5 in greater detail.

3. Useful methods and practices in X-ray reflectivity measurement

An accurate X-ray reflectivity curve is defined by clear appearances of the total reflection critical angle, the period and the amplitudes of the oscillation. It is necessary to obtain precise information so that appropriate X-ray optics depending on the film thickness and sample size are used. In addition, when an X-ray beam is incident on the sample at a grazing angle, a strict having adjustment is necessary.

3.1. Selecting incident optics

The X-ray reflectivity measurements must accurately measure a wide range of intensities measured at grazing X-ray incident angles. For grazing X-ray incidence, the use of a well-collimated incident X-ray beam is important. Conventional X-ray optics use narrow slits to collimate the incident X-ray beam. The intensity of the incident X-ray beam is thus very weak, and X-ray reflected curve with a wide dynamic range of intensity is difficult to obtain. Recently, an X-ray optical system equipped with a parabolic multilayer mirror and an incident-beam monochromator has been used to produce a high-brightness and parallel incident X-ray beam.

The angular divergence of an incident X-ray beam can be controlled by incident X-ray optical systems. Therefore, X-ray optics must be selected on the basis of film thickness. Nowadays, to obtain a high-resolution and parallel incident X-ray beam, a parabolic multilayer mirror and an incident monochromator are commonly used. Two X-ray reflectivity curves are compared using the X-ray optics system with a multilayer mirror, which gives the highest intensity among all incident X-ray optics. The multilayer mirror produces a parallel incident beam with a vertical divergence of around 0.04°. Figure 9 shows the X-ray reflectivity curves for two Au films with different thicknesses deposited on Si substrates.
For the 300 nm thick film, oscillations of X-ray reflectivity cannot be observed using the optics system with a multilayer mirror. This is because the period of the oscillation changes depending on film thickness. With a larger film thickness, the period of the oscillation is smaller, and the resolution of the X-ray optics used for measuring X-ray reflectivity must be increased. Table 1 provides an overview of the optics used in reflectivity measurement and guidelines for film thickness measurement.

### Table 1. Overview of optics used in a reflectivity measurement and guide for film thickness measurement.

<table>
<thead>
<tr>
<th>Monochromator</th>
<th>Multilayer mirror</th>
<th>Ge(220) 2-bounce</th>
<th>Ge(220) 4-bounce</th>
</tr>
</thead>
<tbody>
<tr>
<td>Relative intensity (Reference estimation)</td>
<td>200</td>
<td>10</td>
<td>1</td>
</tr>
<tr>
<td>Resolution (Angular divergence)</td>
<td>up to 0.04°</td>
<td>up to 0.02°</td>
<td>up to 0.003°</td>
</tr>
<tr>
<td>Wavelength monochromacity</td>
<td>(k_\theta + k_\theta (1 + k^2))</td>
<td>(k_\theta)</td>
<td>Part of (k_\theta)</td>
</tr>
<tr>
<td>Applicable film thickness</td>
<td>0.5 to 100 nm</td>
<td>50 to 200 nm</td>
<td>200 nm or greater</td>
</tr>
</tbody>
</table>

### 3.2. Relationship between incident angle and irradiated width

For a reflectivity measurement at a low-angle range \(2\theta = 0°\), the incident X-ray beam impinges onto a large area of the sample surface, even when a narrow incident slit is used. The length of the incident X-ray beam \(x\) projected onto the sample surface can be calculated as follows:

\[
x = \frac{W}{\sin \alpha}
\]

(1)

where \(\alpha\) is the angle of the incident X-ray beam \(W\) is the width of the incident beam slit. For example, in the case of an angle of incident X-ray of 0.2° and the width of the incident beam slit of 0.05 mm, the length of the incident X-ray beam projected onto the sample surface is calculated to be 15 mm. The spread of the incident beam is large when the incident angle is at and below the critical angle, the incident beam can spill over the sample surface. In this case, the critical angle, surface and internal roughness cannot be determined with a high degree of accuracy.

In addition, the irradiated X-ray beam also spreads along the horizontal direction. The irradiated width in the vertical direction is dependent on the height-limiting slit. However, the irradiated width should be approximately one-and-a-half times the height of the height limiting slit.

### 3.3. Sample alignment

In the sample alignment process, the first step is to align the sample surface to be parallel to the incident X-ray beam (i.e., the direct beam), and an adjustment of the sample lengthwise axis (i.e., the Z axis) so that beam widths are divided into halves.

1. Set the \(2\theta\) axis to 0° to detect the incident X-ray beam directly.
2. Set the sample and retract the Z axis to the rear to avoid blocking the incident X-ray beam. Check intensity in this geometry.
3. Scan and set the Z axis at which intensity is half the intensity measured in step 2.
4. Scan the sample rotation axis (the \(\omega\) axis) and adjust the alignment incident X-ray beam to obtain a maximum intensity.
5. Repeat the scans of both the Z and the \(\omega\) axes for two or three times to make sure these axes and the sample surface are properly aligned.

After the alignment, the sample surface and incident X-ray beam are essentially parallel.

In the next step for a sample alignment, the incident X-ray beam is adjusted strictly in the total reflection range. The total reflection phenomenon occurs when the incident X-ray beam and the reflected X-ray beam have the same angle with respect to the sample surface. The total reflection phenomenon is highly sensitive to a change in intensity, which is accompanied by the incident X-ray angle, as shown in Fig. 2. Therefore, the angular position of the \(2\theta\) axis is set in the total reflection range (approximately 0.45° for Si), and multiple axes are aligned as follows:

1. Match the zero position of the \(2\theta\) axis and the zero position of the \(\omega\) axis obtained in the previous halving adjustment, and perform the reflectivity measurement by a \(2\theta/\omega\) scan.
2. In this case, the total reflection occurs in the range near 0.2° to 0.45° on the \(2\theta/\omega\) axis as shown in Fig. 10. Here, the halving adjustment with total reflection performs at 0.4° slightly lower than the critical angle.
3. Set \(2\theta/\omega\) to 0.3° and scan the \(\omega\) axis. The total reflection is observed when the incident X-ray beam and the reflected X-ray beam have the same angle with respect to the sample surface. At the peak angle position, the \(\omega\) axis is approximately half of the position on the \(2\theta\) axis.

\[\text{Fig. 10. X-ray reflectivity measurement after halving adjustment.}\]
4. Set the w axis at the peak position on 3.
5. Scan a sample swing axis (c, Rx or Ry axes).
6. Set the swing axis at the peak position on 5.
7. Repeat steps 3 to 6 until the peak positions on the w and the swing axes agree with those in the previous scan.

The two types of halving adjustments described above can be done using an appropriate X-ray reflectivity curve.

To ensure a precise X-ray incidence angle also requires various procedures for an accurate sample alignment. To facilitate these complex procedures, the software enabling easy acquisition of an appropriate reflectivity curve has been developed, recently. This software is equipped with an innovative function which makes the measurements under the conditions determined based on the sample width and height, film thickness, optics, etc.

### 3.4. Precaution attributable to sample

The preceding paragraph indicated that the incident optics and the height limiting slit size are dependent on the film thickness and the sample width. The precautions attributable to a sample are described below.

Rough sample surfaces may keep reflectivity profiles from exhibiting oscillations clearly because of diffused reflections. The reason is that diffused reflections are observed through the receiving slit. Diffused reflections should be removed so that high angular resolution capability can be achieved. In this case, depending on the extent of the roughness, using a narrow receiving slit and an analyzer crystal in the receiving optics may help to observe clearer oscillations.

If the sample is bent or corrugated, total reflection intensity may be stronger or weaker than that of the incident X-ray beam, as shown in Fig. 11(a), (b).

**Fig. 11(a).** Effects when sample is bent convexly.

**Fig. 11(b).** Effects when sample is bent concavely.

If the sample is bent convexly, X-ray beams reflected from the sample will diverge. Some of the divergent intensities are shielded by the receiving slit resulting in a lower measured intensity. When the sample is concavely bent, the X-ray beam reflected from the sample converges, including the original divergent component in the incident X-ray beam, potentially resulting in a higher measured intensity. If the sample is not bent uniformly but is corrugated, both of the effects above occur simultaneously. If the sample is bent as above, a slightly larger receiving slit is recommended to detect all total reflection X-rays. A slightly larger high-limit slit is also recommended to obtain a more intense X-ray reflectivity curve for thin film analysis.

### 4. X-ray reflectivity measurement

Following selective optics and sample alignment perform reflectivity measurement, X-ray reflectivity measurement is based on the angles of ω and 2θ, which were obtained from the sample alignment, and each movement is scanned in the speed of 2:1 (i.e., the 2θ/ω scan).

The scanning range is measured from below the critical angle to the angle where the measured reflection intensity reaches the level of the background. Generally, the scanning range is from 2θ=0.1°~0.2° to 4°~12°.

The sampling width is applied to width in which profile shape near the critical angle or the oscillation in the reflection intensity is clearly observed without being squashed (0.001° to 0.01°). It is suitable to approximately 1/5 to 1/7 of the minimum period of the oscillation.

Scanning speed is set at the speed that statistical fluctuations can be suppressed to levels permitting a clear observation of the oscillation in the reflection intensities, clear of noise (e.g., 0.01° to 2°/min.).

### 5. Reflectivity Analysis Method

The principles of the X-ray reflectivity method for determining film density, film thickness, and surface and interface roughness of a thin-film sample from the measured X-ray reflectivity curve are described below.

#### 5.1. Total reflection and refractive index for X-Rays

The X-ray refractive index of a substance is slightly less than 1. If an X-ray beam strikes a substance with a flat surface at an incident angle equal to or less than the critical angle for total reflection, θ<sub>c</sub>, and total reflection will occur as described in Section 2.1. The refractive index n of a material for X-rays can be calculated using the following equations:

\[
n = 1 - \frac{\delta}{\beta} \tag{2}
\]

\[
\delta = \left(\frac{r_e \lambda^2}{2\pi}\right) N_0 \rho \sum_i x_i (Z_i + f_i') \left/ \sum_i x_i M_i \right. \tag{3}
\]

\[
\beta = \left(\frac{r_e \lambda^2}{2\pi}\right) N_0 \rho \sum_i x_i (Z_i + f_i'') \left/ \sum_i x_i M_i \right. \tag{4}
\]

- r<sub>e</sub>: Classical radius of an electron (2.818×10<sup>-9</sup> m)
- N<sub>0</sub>: Avogadro number
- λ: X-ray wavelength
- ρ: Density (g/cm<sup>3</sup>)
As shown in Eq. (2), the refractive index is expressed as a complex number. The value of the parameter $\delta$ in the formula is ranging from $10^{-5}$ to $10^{-6}$ for X-rays with wavelength approximately 1 Å. As shown in Eq. (3), the critical angle $q_c$ for total reflection is given by the formula:

$$q_c = \sqrt{\frac{2\delta}{\lambda}}$$

(6)

Thus, the density of the surface film can be obtained from the critical angle for total reflection, $\theta_c$. As shown in Eq. (2), the refractive index depends on the X-ray wavelength and the density and composition of the material. When the X-ray wavelength is longer or the density of the material is greater the value of $\theta_c$ is larger. The $\theta_c$ is usually 0.2 deg to 0.5 deg.

5.2. Determining the thickness of a single-layer film

A periodic oscillation in intensity related to the thickness of a thin layer normally appears in an X-ray reflectivity curve. The thickness of a thin layer can be obtained by Fourier transformation of the extracted oscillation curve (see the right-hand curve in Fig. 12).

The extracted oscillation curve is a function of the thickness $d$ and refractive index $\delta$ of the layer. The oscillation is related to the following an equation:

$$\cos\left(\frac{4\pi d}{\sqrt{\sin^2 \theta - 2\delta}}\right)$$

(7)

The thickness can be estimated from the peak position of the profile of Fourier transformation plotted with a horizontal axis in the scale of $\lambda\sqrt{\sin^2 \theta - 2\delta}$ as shown in Fig. 13.

However, this method cannot be used to obtain the density, surface nor interface roughness of a multilayer film. Values of thickness, density, surface and interface roughness of a multilayer film can be obtained by a non-linear least-squares fitting as described below.

5.3. Theoretical calculation of X-ray reflectivity from multilayer films

X-ray reflection occurs at all interfaces in a multilayer film. The X-ray reflectivity of a multilayer film as a function of $\theta$ can be theoretically calculated using the recurrence Eq. (8)(2),(3).

In Eq. (8), the vacuum or gas phase on top of a film with $n$ layers is regarded as the $j=1$st layer. Each layer in the multilayer film is numbered in sequence starting with $j=2$, and a substrate is considered as the $j=n+1$ layer. When the reflection coefficient at the interface between the $j$th and $(j+1)$th layers is defined as $R_{j+1}$, the value of $R_{j+1}$ can be calculated using the following recurrence formula:

$$R_{j+1} = \frac{R_{j+1}}{R_{j+1} + 1}$$

$$a_j = \exp\left(-i\pi g_j \sqrt{\sin^2 \theta - 2\delta}\right)$$

(10)

$$g_j = \sqrt{n_j^2 - \cos^2 \theta}$$

(11)

The recurrence Eq. (8) together with Eqs. (9) to (11), can be used to calculate the values of $R_{j+1}$ first starting at the interface on top of the substrate, and then the next upper interface in sequence up to the surface layer. The X-ray reflectivity $I/I_0 = R_{j+1}$ is last calculated. Please note that the substance is assumed to be sufficiently thick that no reflectivity will occur from the bottom of the...
substrate.

5.4. Reflectivity analysis method of a multilayer film

Generally, an X-ray experimental reflectivity curve is compared to the theoretical curve calculated based on a layer structure model. The solution with optimal parameter values of thickness, density, and roughness of the interface in the multilayer film is obtained when the residual between the measured and calculated reflectivity data reaches a minimum. Figure 14 shows an example of using the GlobalFit software in the Integrated Thin Film Analysis Software package for an X-ray reflectivity analysis. The GlobalFit software can simulate a reflectivity curve based on the created layer structure even without the need of measured data. In addition, this software can analyze a periodic multilayer film or layers with a density-depth distribution. Most of the common data analysis technique used to obtain values of layer parameters is the least-squares method. If the measured profile and the simulation result do not agree, it is not easy to obtain the optimum layer structure parameters, because the least-squares refinement can be trapped in a local minimum. To avoid the local minimum problem, two other optimization methods along with the conventional least-square methods are included in the Rigaku reflectivity analysis software package for the determination of optimum layer structure parameters. One of the methods is called “extended Fourier analysis”, and the other is called “global optimization”. These two optimization methods make it possible to perform an X-ray reflectivity analysis of a complex multilayer film efficiently.

6. Examples of X-ray Reflectivity Analysis

This section discusses the analysis of measured data for a multilayer film with a complex layer structure. The sample used in this example is a magnetic Ta/NiFe film on a glass substrate. The nominal thickness for the Ta and the NiFe layers are 20 nm and 15 nm, respectively.

Figure 15 shows the experimental data (the red curve) and the calculated simulation data (the blue curve) for the sample. As shown in Fig. 15, the oscillations in the measured and simulated data do not match. Therefore, the thickness values for Ta and/or NiFe layers are probably slightly different from the true values. The “extended Fourier analysis” software was then used to optimize the initial value of the layer structure parameters specified initially to the actual sample structure. Figure 16 reveals that there is an additional exceedingly thin layer presented in the multilayer film.

As shown in Fig. 16, from the result of the Fourier transform analysis, a thin layer approximately 2~3 nm thick should be presented in the film. However, the results of the Fourier analysis do not give information on the sequence of the layers among the depth direction. Therefore, the thin layer which is approximately 2~3 nm thick can be presented with one of the following three possibilities:
1. The thin layer is presented on the surface of the Ta layer.
2. The thin layer is presented at the interface between the Ta and the NiFe layers.
3. The thin layer is presented at the interface between the NiFe layer and the glass substrate.

The thickness was first optimized based on the results of the Fourier analysis and X-ray reflectivity profile was then refined using the GlobalFit and the least-squares methods based on the layer structure of the above three possibilities: No. 1, 2 and 3. Figure 17 shows the analysis results for No. 1, 2 and 3.

Among the three figures in Fig. 17, possibility No. 1 gives the best match between the experimental and the calculated curves, suggesting that this thin layer, probably a tantalum oxide layer, is presented on the surface on the Ta layer. It should be noted that an XRD analysis of thin-film diffraction peaks obtained by out-of-plane and in-plane diffraction may be able to provide more structural information on this film including the thin tantalum oxide layer.

7. Concluding remarks

The principles of the X-ray reflectivity method, measurement procedures, and data-analysis methods have been described. The X-ray reflectivity method is nondestructive and can be used for evaluating the layer structure, thickness, density, and surface or interface roughness of a multilayer film.

In recent years, a working group has been set up to share information and problem consciousness because of diversification of target samples and highly-developed and complicated analysis techniques. Recently many articles on the applications of the X-ray reflectivity method have been published in the literature. For examples:

1. Articles of accurate thin-film analysis using the X-ray reflectivity method.
2. An article on a study of the coefficients of thermal expansion of thin films prepared under high temperatures.
3. Articles on the study of the flatness of “buried interface” and detections of reaction phases at interfaces.
5. Articles on the analysis of organic layers of a film with density-depth distributions.

In addition, the average density of a porous material obtained by the X-ray reflectivity method was used to evaluate the proportion of pore and the evaluation of layer structure.

The next review article of this series will be X-ray thin-film measurements using the small angle X-ray scattering (SAXS) method.
References

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(9) H. Ohta, T. Mizoguchi and Y. Ikuhara: *Material Integration* (Japanese), 22 (2009), No. 9–10, 38–42.
1. Introduction

Physical and chemical properties of a crystalline solid depend strongly on the molecular arrangement, that is, on both the crystal structure and the composition of the molecule comprising the solid. In order to understand the mechanisms and developing properties of a crystalline solid, it is essential to know the crystal structure. Typically, crystal structure analysis has been performed using hundreds or thousands of X-ray intensity data collected from a single crystal. The data is collected with a four-circle diffractometer or a diffractometer equipped with an image plate or other 2D detector. Just 10 years ago, single crystals several hundred microns in diameter were needed. Recent improvements in X-ray sources and detectors enable the collection of intensity data which can be used in the analysis of crystal structures from crystal specimens measuring only a few microns across.

There are many substances which cannot be grown to a single crystal of quality and size sufficient for single crystal diffraction measurements. Inorganic compounds have often had their crystal structures analyzed using the Rietveld method(1) devised in 1969. Fundamentally, the Rietveld method is used to refine crystal structure parameters such as lattice constants, atomic coordinates, occupancies, temperature factors, etc. based on powder diffraction data. There are many groups of inorganic compounds which have almost identical composition and crystal structure. In these cases, the crystal structure can usually be solved using the Rietveld method using the structure parameters of an analogous compound as the initial structural model.

On the contrary, since organic compounds are formed molecular crystals, their crystal structures are affected by even very small changes in composition. This makes it exceptionally difficult to perform ab initio crystal structure analysis of organic compounds using only the Rietveld method.

Then, how can we determine the ab initio crystal structure of organic compounds from powder diffraction data? As shown in Fig. 1, there are several steps in the analysis procedure. While intensity data of independent diffraction spots are collected from single crystal diffraction measurements, with powder diffraction measurements, the diffraction spots, 3-dimensionally arranged in the reciprocal space, are compressed to 1-dimensional diffraction patterns. As a result, the number of intensity readings from independent diffraction spots decreases. For this reason, crystal structure analysis based on powder diffraction data collected with the methods used for single crystal diffraction data is often unsuccessful.

This paper describes the analytical process used for the ab initio crystal structure determination of, in particular, organic compounds based on powder diffraction data. It also introduces PDXL(2), the integrated X-ray powder diffraction software package in which all these features are implemented.

2. Individual steps

2.1. Indexing

"Indexing" refers to the process of assigning Miller indices to each diffraction peak as well as the determination of lattice constants. ITO, DICVOL, TREOR are very popular indexing programs, and recent versions of each of these programs are integrated into the PDXL package (ITO13(3), DICVOL06(A), and N-TREOR(5)). Each of these programs searches for the unit cell based on about 10 to 30 peak positions picked up from the low angles of the powder diffraction data. As described above, the 3-dimensional diffraction spots are compressed into a 1-dimensional diffraction pattern, which makes it very hard to obtain a correct and unique set of lattice constants. Regardless of which program is used, several candidates for lattice constants will be listed along with the degree of reliability for each. From among the candidates, you have to select a set of lattice constants.
constants which can generate all the peak positions in higher angles. Needless to say, the more accurately the peak positions used for indexing, the higher the probability correct lattice constants can be found. On this basis it is strongly recommended that powder diffraction data are collected using optics which provide the highest-possible resolution. It is also recommended to use a very high flux X-ray source to detect all low-angle peaks even if the peak intensities are low. If indexing fails and correct lattice constants cannot be found, the correct crystal structure cannot be obtained. Scrupulous attention should be given to the correct determination of lattice constants.

2.2. Space group determination

Space group is determined based on the systematic absences obtained from Miller indices vs. diffraction intensity data. Since only Miller indices are assigned to each peak at the indexing step, the intensity of overlapping diffraction peaks need to be decomposed and distributed to each diffraction line. PDXL performs intensity decomposition using Pawley’s method\(^\text{(6)}\). After decomposition, which distributes diffraction intensity to each diffraction line, PDXL determines space groups. Like indexing, space groups typically cannot be determined uniquely, that is, several space group candidates are listed with the degree of reliability for each. PDXL expresses the reliability of a space group candidate in terms of \(N\) and \(R\). \(N\) is the number of diffraction lines calculated from the space group and the \(R\) value is the degree of coincidence between the calculated \(N\) and observed diffraction lines in measurement data. The smaller the \(N\) and \(R\) values are, the higher the probability that the space group is correct. Figure 2 shows the space group candidates calculated from the powder diffraction data of \(\text{Al}_2\text{O}_3\). A candidate whose \(N\) and \(R\) values are both small should be selected from among these as described above. In some cases, taking the small \(N\) candidate rather than the small \(R\) candidate will result in a higher probability of obtaining the correct space group. In the case of Fig. 2, the correct space group is \(R-3c\) belonging to \(R^{**}c\) with \(R=0\%\) and \(N=53\). In this way, the user selects one space group thought to be correct from among candidates and goes on to the next step.

2.3. Initial structure determination

Information on diffraction spots is compressed in powder diffraction data as described above, therefore, some innovation has been introduced to the initial structure determination process. Three methods implemented in PDXL for determining initial structures are introduced below. Since either method requires as precise diffraction intensity for each set of Miller indices as possible, pattern decomposition has to be performed after the space group determination and before the initial structure determination.

2.3.1. Direct method

In the direct method, phases are predicted based on the tangent formula\(^{(7)}\) and the initial structure is determined using sets of Miller indices vs. diffraction intensity data. Although the data obtained from powder diffraction is limited, there are some cases in which the initial structure can successfully be determined by the direct method. PDXL allows the user to make use of the direct method with EXPO2009\(^{(8)}\) developed by Giacovazzo et al. part of the group that developed SIR\(^{(9)}\), the direct method program for single crystal structure analysis. Their direct method programs have become a tried and trusted part of the analysis process for many users. Many sets of Miller indices vs. diffraction intensity data are necessary to achieve the initial structure determination using the direct method. Therefore, powder diffraction data at high angles and with as high intensity as possible are required.

2.3.2. Charge flipping

Electron density distribution is calculated by the Fourier synthesis of Miller indices vs. diffraction intensity data. Since electron density peaks in an electron density distribution map indicate atomic positions, an initial structure can be determined from the electron density distribution map. However, the Fourier synthesis cannot be performed without phases because information on phases is missing in diffraction data.

Recently, Oszlányi et al. have developed a new method called “charge flipping\(^{(10)}\) (CF)”. In this method,

(1) Diffraction lines are assigned randomly determined phases. (2) Fourier synthesis is performed on measurement data to obtain an electron density distribution map. (3) The signs of charges below a certain threshold are flipped. (4) A Fourier transform is performed on the modified charge density map to obtain new sets of intensity data. (5) Phases of measured intensity data are updated based on the phases of the calculated intensity data. (6) Steps (2) through (5) are repeated. Advantages of the CF method include the relatively short amount of time needed to calculate and improve the electron density distribution map and the ability to start without any knowledge on the structure at all (Fig. 3).

---

**Fig. 2.** Space group candidates.
2.3.3. Direct space method

When molecular crystals of organic compounds are the main targets of structure analysis, there is a method in which crystal structure can be obtained by constructing a structural model and searching for the position and orientation of the molecular model in the unit cell. This is called the “direct space method” or “real space method”. In the case of organic molecules, a molecular orbital calculation program such as MOPAC\(^{(12)}\) can calculate the stable conformation of a molecule. The obtained molecular structural model is set as an initial state for the direct space method, and the position and possible orientations of the molecule within the unit cell are searched for. At the same time, rotation (torsion) angles around free rotation bonds are optimized to determine the molecular conformation while the other rigid parts of the molecule are fixed. The method is called “global optimization method”. When the initial structural model is somewhat different from the real structure, the global optimization methods can give the real solution (almost global minimum), whereas the Rietveld method may give a false solution (local minimum). While the genetic algorithm\(^{(11)}\) and simulated annealing\(^{(13)}\) are popular as a global optimization methods, PDXL adapts the parallel tempering algorithm\(^{(14)}\).

The direct space method is effective when the structural formula of a molecule is given and the molecular conformation is known to some extent. In the case of organic compounds, the structural formula can be given by spectroscopic methods such as NMR, IR, etc. The theoretically-stable conformation of a molecule can be calculated using molecular orbital or dynamics calculation. Therefore, the direct space method is very powerful for determining the initial crystal structure of organic compounds.

2.4. Structure refinement

After determining the initial structure, the structure is refined using the Rietveld method. In the \textit{ab initio} crystal structure analysis, while lattice constants and the preferred orientation function are normally fixed, structure parameters such as atomic coordinates, temperature factors, etc. are generally refined. In the case of organic compounds, the molecular structure may break apart, which means that, if atomic coordinates are refined individually, bond lengths and angles will deviate from their theoretical values. To avoid this, PDXL has a feature to express atomic coordinates in Z-matrix so that crystal structure can be refined in a manner such that the structure is retained to some degree. Since atomic coordinates expressed in Z-matrix are constrained by bond lengths and angles, the structure of an organic molecule comprised of light atoms can be refined without disassembling. In addition, using PDXL the refinement process can be followed by the crystal structure transitions as well as the numerical values, that is, the degree of coincidence between measured and calculated data.

2.5. Searching missing atoms

In both powder and single crystal structure analysis, it is often the case that some atoms will be missing from the initial structure determination. In these cases, the remaining atoms may be found using an electron density distribution analysis method such as MEM\(^{(15,16)}\), difference Fourier synthesis etc. The electron density distribution map will include the atoms whose positions have already been determined. If there are electron density peaks in the distribution map which have not been assigned atoms, it can be determined that the peaks are the atoms which were not found at the initial structure determination step. Using difference Fourier synthesis, which performs a Fourier synthesis on the measured data from which the structure factors based on the known atoms have been subtracted, an electron density distribution map can be created that shows only the unassigned areas. The peak positions in the resulting map show the residual atom positions. Whenever either method is applied, it is strongly recommended that pattern decomposition be performed again before electron density distribution analysis.

It is often the case that very light atoms like hydrogen cannot be found. In the case of organic compounds, the positions of hydrogen atoms, in particular, will be determined through calculation. When all the atoms have been found, including hydrogen, the crystal structure will be refined using the Rietveld method before it is considered complete.

2.6. Validation of the crystal structure

The obtained crystal structure has to been evaluated to determine whether it is appropriate as an actual representation of the crystal structure. There are several indicative points of validation, as follows:

1. \(R\)-factor is small, \(\delta\) nearly equals one.

   Needless to say, these are very important. But please note that these only give an indication that the assumed model (crystal structure) explains the measured data. In general, use \(R_{wp}<10\%\) and \(\delta<2\) as measuring sticks for successful analysis.

2. Obtained molecular structures are reasonable.

   Confirm the obtained molecular structures are reasonable based on the bond lengths and angles.

3. Density calculated from the crystal structure equals observed density.

   This is extremely important. If the calculated density differs from the observed, it is a strong indication that...
elements or the number of atoms in the unit cell is wrong.

(4) Interatomic distances are not too short.

Confirm that any non-bonded interatomic distance is not much shorter than the sum of Van der Waals radius of each atom.

(5) There is no big void.

Draw the crystal structure as a space-filling model, in which atom sizes are expressed by the Van der Waals radius, and confirm there are not any big voids between molecules. If there are, confirm whether it is possible that another molecule such as a solvent molecule may exist in the void using a thermal analysis method.

(6) Intermolecular forces are appropriate.

If in the comprising molecules there exist any groups like the O–H, N–H, C=O groups which will form hydrogen bonds, confirm that intermolecular hydrogen bonds are formed properly, also taking angles and distances into consideration. And if there exist any other functional groups with large polarization, confirm that the molecules are arranged such that the dipole moment is cancelled.

PDXL includes various drawing tools to create graphical representations of obtained molecular structures (the position and orientation of the molecule(s) in the asymmetric unit of unit cell). You can select the display style of a molecule, display molecular packing, expand/collapse the molecular/crystal structure, display interatomic distances, bond angles, torsion angles, change the perspective, and so forth. Making use of these functionalities, you can confirm the above points one by one, then you can easily validate whether the obtained crystal structure is correct. As a result of validation, if there are some uncertainties remaining, trace back through the structure analysis steps. The analysis can be re-performed from the indexing step if necessary.

3. Structure analysis examples

Figure 4 summarizes the ab initio structure analysis flow based on powder diffraction data using PDXL.

3.1. Cimetidine

Cimetidine is well known as a medicine for the treatment of gastric ulcers. A cimetidine molecule is comprised of 17 non-hydrogen atoms, and indicative of very high crystallinity. Here, ab initio structure analysis was attempted using the direct method with EXPO2009. To make the direct method successful, pattern decomposition needs to be performed with high accuracy. Owing to the 2-bounce Ge(220) crystals in the incident optics and CALSA(17) in the receiving optics, it was possible to collect high-intensity and high-resolution data (Fig. 5), which was then used for the structure analysis.

3.2. Nicotinamide

Nicotinamide is also known as vitamin B3. The molecular structure is shown in Fig. 7. The molecular structure optimized by MOPAC was used as the initial structural model for the direct space method. The initial crystal structure was obtained giving freedom of rotation to the carbon-carbon bond between the benzene ring and the amide group. In the crystalline environment, four types of structure are possible, depending on the orientations of the amide group and the pyridine ring.
The structure shown in Fig. 7(b) was determined by the direct space method of PDXL. However, based on the schematic presentation of molecular packing, for the structures shown in Fig. 7(b), (c), and (d) it was determined that there existed steric hindrance between the hydrogen atoms and/or there were not any intermolecular hydrogen bonds supposed to exist. As a result, we concluded that the most probable structure was (a) (Fig. 8).

![Fig. 7. Possible molecular structure of nicotinamide.](image)

4. Summary

Recent years have seen a rapid increase in the number of people who utilize ab initio crystal structure analysis based on powder diffraction data. However, unlike for single crystal structure analysis, there is no standard procedure for powder structure analysis. The user has to perform the analysis through a process of trial and error. Therefore, an easy-to-use tool for the powder structure analysis has been eagerly anticipated. PDXL provides for this need by offering multiple algorithms for indexing and the initial structure determination, simplifying the normally complex ab initio crystal structure analysis steps. Preparing multiple analysis paths, as described above, is strongly associated with a high probability of the success in crystal structure analysis.

We hope that the application of this structure analysis process will lead to the crystal structures of various powder materials being solved, resulting in significant advances in structural and properties sciences.

References


![Fig. 8. Crystal structure of nicotinamide.](image)
X-ray fluorescence analysis by fusion bead method for ores and rocks

Yasujiro Yamada*

1. Introduction
The fusion bead method is an effective sample preparation technique for accurate XRF analysis results of ores, rocks and refractory materials since the technique eliminates heterogeneity due to grain size and mineralogical effect.

This report describes various data processing methods to obtain more accurate analysis results showing practical examples of analysis obtained by using a wavelength dispersive X-ray fluorescence spectrometer (WDXRF), ZSX Primus II, and its data processing system.

2. What is fusion beads method?
Table 1 shows the application fields of XRF analysis and of fusion beads method (underlined). Wide application range for oxide powder can be seen.

The fusion bead method is an advanced analysis method having advantages shown below and registered as an international standard analysis method for refractory and iron ore.

- ISO12677: Chemical analysis of refractory products by XRF—fused cast bead method
- ISO9516: Iron ores—Determination of various elements by X-ray fluorescence spectrometry

- Features
  - Eliminate the mineralogical effect and grain size effect
  - Reduce coexisting component effect by dilution effect
  - Possible to make standard samples from synthetic oxides.

3. Error in fusion bead method
Dominant causes of various analytical errors in fusion bead method(1),(2) are shown below, and also in the image shown in Fig. 1.

- Weighing error (Dilution factor error)
Sample powder and flux must be weighed accurately down to 0.1 mg unit for designated amount, but it is time consuming so that magnitude of the error depends on the operators skill.

- Loss on ignition (LOI), Gain on ignition (GOI)
If there is water of crystallization or a carbonate present in the sample, volatilization of these compounds leads to an analytical error due to the loss of these compounds in the high temperature of the fusion melt.

For example, in case of iron ore, the oxidization reaction of Fe$^{2+}$ to Fe$^{3+}$ when the melt occurs causes weight gain (GOI), and it becomes a source of error.

- Flux evaporation (Dilution factor error)
Using low melting point flux or fusions that take place over a long period of time makes flux evaporate; this becomes a source of dilution error.

<table>
<thead>
<tr>
<th>Iron and Steel</th>
<th>Non-ferrous</th>
<th>Environment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Special steel</td>
<td>Aluminum can</td>
<td>Drain, River water</td>
</tr>
<tr>
<td>Coated steel sheet</td>
<td>Shaped-memory alloy</td>
<td>Soil pollution</td>
</tr>
<tr>
<td>Ferralloy</td>
<td>Copper alloy</td>
<td>Air pollution</td>
</tr>
<tr>
<td>Cast iron</td>
<td>Precious metal</td>
<td>Industrial waste</td>
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<tr>
<td>Iron ore</td>
<td>Nickel alloy</td>
<td>Mud polluted</td>
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<tr>
<td>Plating solution</td>
<td>Soldering paste</td>
<td>Coal ashes</td>
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<td>Lubricant oil</td>
<td>Kerowere, Heavy oil</td>
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<td>Cutting oil</td>
<td>Coal</td>
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</table>

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<td>Opt: magnetic disk</td>
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<td>Medicine</td>
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<tr>
<td>Magnetic head</td>
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<td></td>
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</tr>
<tr>
<td>Magnetic materials</td>
<td></td>
<td></td>
<td>Paints</td>
</tr>
</tbody>
</table>

* SBU WDX, X-ray Analysis Division, Rigaku Corporation.

Fig. 1. Image of analytical errors of fused bead method.

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4. Study of correction against Dilution factor, Loss on ignition (LOI) and Gain on ignition (GOI)

Image of 4 models of Dilution factor, LOI and GOI are shown in Fig. 2.

In the above figures, the left side is the sample model including LOI and GOI, and the right side expresses the effect these factors have on the weight of the sample-flux mixture.

Figure 2 (a) is the case of no LOI and no GOI; the dilution factor can be calculated with the weights of sample and flux.

Figure 2 (b) is the case that an LOI component is included. As the LOI does not exist in the glass beads any more due to evaporation, concentration of components in a sample becomes higher from the viewpoint of concentration in the fused bead.

Figure 2 (c) is the case that GOI takes place. Concentration of component in a fused bead sample becomes lower.

Figure 2 (d) is the case that both LOI and GOI take place. Concentration of component in a sample may be higher or lower depending on the respective amount of LOI and GOI.

As mentioned above, concentration of components in the fused bead sample can vary due to the LOI or GOI, and it has an effect on the analysis result.

This phenomenon is treated by assuming total concentration in a sample is 100%, the LOI is considered as a positive concentration, and GOI as LOI having a negative concentration.

Since the LOI and GOI make concentration in a fused bead sample vary, matrix correction using the net effect of the concentration of LOI or concentration of the negative GOI can be made.

5. General calibration equation and dilution correction

General calibration equation incorporating correction for LOI, GOI and dilution factor including a term of co-existing component correction is shown in the equation (1) below.

\[ W_i = (a_i^2 + b_i + c)(1 + \sum a_j w_j + \alpha_{LOI} W_{LOI} + \alpha_{GOI} R_F + K_F) \]  \hspace{1cm} (1)

Where

- \( \alpha_j \): Inter element correction factor
- \( \alpha_{LOI} \): LOI (GOI) correction factor
- \( \alpha_{GOI} \): Correction coefficient for dilution factor
- \( R_F \): Dilution factor (flux weight/sample weight)
- \( K_F \): Constant

Term of \( \alpha_{GOI} R_F + K_F \) is a correction term of flux dilution factor. All co-existing component correction coefficients \( \alpha_j, \alpha_{LOI}, \alpha_{GOI} \) can be calculated using the fundamental parameter method (FP method). And, when co-existing component correction factors are calculated by FP method, in case that the LOI (GOI) is considered as a base component (except for correction component) in a correction model, the term of \( \alpha_{LOI} W_{LOI} \) is not used and the LOI (GOI) correction can be made without concentration information of the LOI (GOI).

The equation (2) below removes the term \( \alpha_{LOI} W_{LOI} \) from the equation (1).

\[ W_i = (b_i + c)(1 + \sum a_j w_j + \alpha_{GOI} R_F + K_F) \]  \hspace{1cm} (2)

In above (2), \( \alpha_{GOI} R_F + K_F \) is the term of dilution factor correction and it can be neglected when dilution factor is constant. This term of dilution factor is explained hereunder.

The equation (3) below is a calibration equation including dilution factor correction.

\[ W_i = (b_i + c)(1 + \sum a_j w_j + \alpha_{GOI} \Delta R_F) \]  \hspace{1cm} (3)

Regarding \( \overline{R_F} \) as a standard dilution factor and as the difference from standard dilution factor, the equation (4) can be shown.

\[ \Delta R_F = R_F - \overline{R_F} \]  \hspace{1cm} (4)

Substitution (4) for (3) makes equation (5) below.

\[ W_i = (b_i + c)(1 + \sum a_j w_j + \alpha_{GOI} R_F - \alpha_{GOI} \overline{R_F}) \]  \hspace{1cm} (5)

By defining equation (6) below, the equation (2) is obtained.

\[ W_i = (b_i + c)(1 + \sum a_j w_j + \alpha_{GOI} R_F - \alpha_{GOI} \overline{R_F}) \]  \hspace{1cm} (6)
It is understood that, even for fused beads with different dilution factors, the correction of difference of dilution factor can be made by using the equation (2).

5. Inter element correction model (Matrix correction model)

As an inter element correction model for iron and steel analysis, JIS method is popular in Japan. But there are 3 inter element influence coefficient correction models as shown below including JIS method.

- Lachance-Traill model
  This is a model considering all other components except for analysis component as correction components. Calibration equation is linear model. This model can not be used when the concentration of the LOI (including GOI) is unknown. If it is known, it can be applied as it is treated as one of the concentrations.

- de Jongh model
  This is a model handling all components including analysis component except for base component (as balance) as correction components. LOI (including GOI) correction can be made even if LOI (including GOI) is not known. Calibration equation is a linear model.

- JIS model
  This is a model designating all components except for analysis component and base component as correction components. When LOI (including GOI) is set as the except analysis component (base component), LOI (including GOI) correction can be made even if LOI (including GOI) is not known. Calibration equation used is a quadratic or linear model. When the concentration of LOI (including GOI) is not known, de Jongh model or JIS model can be applied.

6. Comparison between JIS and de Jongh models

When LOI (including GOI) is not known, both de Jongh and JIS model can be used. So, coexisting components correction factors (matrix correction coefficients) are calculated by FP method and compared. Analysis object is rock, and fusion beads are made with Li$_2$B$_4$O$_7$ flux at a dilution factor of 5 : 1 (flux : sample). Si-K$_\alpha$ and Ca-K$_\alpha$ as representatives are used and calculated. Results are shown in Table 2 and Table 3.

It can be said that the factors for JIS and de Jongh model compare very closely to one another. The only difference is that the de Jongh model has a self absorption factor, by including the analysis component, in the correction term. In JIS model the combination of analysis component and base component is a snap-shot sample of the basic calibration line, therefore, the equation is linear in the case of a narrow concentration range, but quadratic if employed over a wide range. On the other hand, as the de Jongh model regresses nearly linearly due to self absorption correction including the analysis component in the correction term, the equation can be approximated linear over a wide range of concentrations.

Calibration lines of SiO$_2$ and CaO with the correction factors in Table 2 and 3 are shown in Fig. 3 and 4. There is no big difference between both models. The calibration lines were approximated with quadratic curve for JIS model and linear for de Jongh model.

7. Comparison of coexisting component correction factors (Matrix correction coefficients) for the analysis of various refractory by fusion beads method

Basically, matrix correction factors are calculated for each kind of materials and calibration lines are made for the same. JIS R 2216 (XRF analysis of refractory)
designates coexisting component correction factors for each kind of materials.

Meanwhile, making calibration lines for each kind of materials requires lots of preparation of calibration lines and analysis operation is troublesome, while making a universal calibration line covering many kinds of different materials makes a wide range of analyses with less calibration lines possible.

It is possible to apply a universal calibration line to the analyses of various kinds of materials if the differences of coexisting components correction factors among them are small. Table 4 is a list of concentration ranges of major components of various refractory and dilution factors.

Table 4. List of concentration ranges of major components of various refractory and dilution factors.

<table>
<thead>
<tr>
<th>Material</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>MgO</th>
<th>Cr₂O₃</th>
<th>ZrO₂</th>
<th>Dilution Factor (Flux/Sample)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clay</td>
<td>37~86</td>
<td>6~49</td>
<td>~5</td>
<td>~1</td>
<td>~1</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>Silica Stone</td>
<td>84~97</td>
<td>~10</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>10</td>
</tr>
<tr>
<td>High Alumina</td>
<td>~44</td>
<td>47~94</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Magnesia</td>
<td></td>
<td></td>
<td><del>81</del>99</td>
<td>10</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chrome-Magnesia</td>
<td></td>
<td></td>
<td><del>27</del>52</td>
<td>2~53</td>
<td>22.16</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zircon-Zirconia</td>
<td>~45</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>48~92</td>
</tr>
<tr>
<td>Alumina-Zirconia-Silica</td>
<td>~42</td>
<td>10~82</td>
<td></td>
<td></td>
<td>12~48</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>Alumina-Magnesia</td>
<td>10~93</td>
<td>3~79</td>
<td></td>
<td>10</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>All Materials</td>
<td>~97</td>
<td>~94</td>
<td><del>27</del>99</td>
<td>~53</td>
<td>~92</td>
<td>10~22.16</td>
<td></td>
</tr>
</tbody>
</table>

Flux: Li₃B₄O₇ (Oxidizing agent LiNO₃ was used for Chrome-Magnesia.)

For the table, major component in each material is different and the concentration range of each component is very wide. And dilution factor of chrome-magnesia is different from others. (Dilution factor correction is discussed later in section 8.). Then, as an example, comparison of coexisting component correction factors among clay (SiO₂–Al₂O₃ group), high alumina (Al₂O₃ group) and alumina-zircon-silica (SiO₂–ZrO₂–Al₂O₃ group) was calculated. Coexisting component correction factors for Si–K α and Fe–K α are shown in Table 5 and 6, respectively. Calculations of correction factors are made using the Lachance–Traill model.

It is obvious that the correction factors for both analysis lines are approximately the same for these different materials. This is due to the sample dilution by flux resulting that the sample matrices in fusion beads are similar in each material. It means that making calibration lines for each material is not necessary and analysis with single calibration line covering a wide range of materials. Then, the universal calibration lines of SiO₂ and Fe₂O₃ for various materials are shown in Fig. 5 and Fig. 6. Satisfactory calibration lines for various materials are obtained. Standard samples used for the study are shown in Table 7.

8. Application of dilution factor correction and coexisting component correction

Usually, sample is made at fixed dilution factor in fusion beads method. But the accurate weighing of sample and flux requires skill and time, and it is one of the sources of error at sample preparation stage. To overcome these problems, there is a method to make dilution factor correction using correction term of equation (1) in Section 5, which corrects a difference between dilution factor of each sample and standard factor using actual weights after designation of weighing allowance.

These dilution factor correction coefficients can be calculated along with the coexisting components
correction coefficients by the software. Example of application of the dilution factor correction is shown below.

Contents of samples used for this study are as follows.

- **Sample:** Rock
- **Conditions for making fusion beads:**
  - Flux: Li$_2$B$_4$O$_7$
  - Dilution factor (Flux: Sample): 10 : 1 and 5 : 1
- **Analysis component:** SiO$_2$
- **Spectrum:** Si-K$_α$
- **Standard samples used:**
  - CCRMP: SY -2, SY -3
  - GSJ: JA1, JA2, JA3, JB2, JB3, JG1A, JG2, JG3, JGb1, JR1, JR2, JLs1, JCp1

Figure 7 shows SiO$_2$ calibration line without correction. Big error due to difference of dilution factor is observed. Figure 8 is the line with dilution factor correction only. Dilution factor correction improves the error due to difference of dilution factor significantly. But error due to coexisting component matrix effect is still there. Figure 9 shows the calibration line after correction.
applying the coexisting component correction as well. It can be said that application of both corrections makes correlation better and improves accuracy by one order of magnitude.

The above study was made with the case of a big difference of the dilution factor to show the effect of the dilution factor correction. From this result, it can be seen that an accurate analysis by means of making the dilution factor correction using actual weights of sample and flux when fusion beads are made is possible. Moreover, the correction can be made for the fusion beads with different dilution factors by group of the materials.

9. Application of LOI (including GOI) correction

When natural minerals containing crystal water and carbonate, etc. are used for fusion beads, they are volatile. (Corresponds to the model (b) of Fig. 2) In case of iron ore, FeO and Fe3O4 is oxidized to Fe2O3, the resulting GOI, and hydroxide (OH) volatiles (corresponds to the model (c)(d) of Fig. 2), then become sources of analysis error.

To verify the LOI correction, the fusion beads with dilution factor 10:1 made in the section 8, are set at a dilution ratio of 5:1 and the imaginary LOI at 50 mass%. The effect of LOI correction was verified with this imaginary model of SiO2.

Table 8 shows the coexisting component correction factors of analysis component SiO2 for the cases of with and without LOI correction. The effect of LOI correction was discussed with these correction factors.

Figure 10 is the uncorrected calibration line, Figure 11 is the calibration line with coexisting component correction but without LOI correction, and Figure 12 is with both of them. In the case of with coexisting component correction but without LOI correction, accuracy of SiO2 calibration line is 3.5 mass%, but it is improved up to 0.26 mass% using LOI correction. Thus it can be said that the accurate analysis is realized by employing coexisting component correction incorporated with the LOI correction.

Next, a study of fusion beads samples of which both LOI and GOI take place at a same time using iron ore. Contents of sample used for the study are shown below.

- Sample: Iron ore
- Dilution factor: 10:1
- Flux: Li2B4O7: 4 g, Sample: 0.4 g
- Oxidizing agent: NaNO3: 0.24 g
- Analysis component: Fe2O3
- Standard sample used:
  - JSS: 801, 803, 804, 805, 810, 812, 814, 820, 850, 851, 009
  - NBS: 692, 693
  - BS: 104
  - BCS: 301, 302, 175
  - BAS: 676, 683
  - NBS: 27e

Table 9 shows the coexisting component correction factors without LOI correction and with it (Correction model: de Jongh).
This correction for iron ore is an application example in case of practical appearance of LOI and GOI, and we learn that this method is the effective method for making LOI (including GOI) correction.

10. Application of flux volatilization correction

There is a type of error made by dilution factor change due to flux volatilization during fusion at high temperature making difference of flux weights before and after fusion.

Correction of flux volatilization effect can be made by using weight of fusion beads instead of flux weight for dilution factor calculation.

Equation for dilution factor $R_F$ calculation without LOI (including GOI) is as below.

$$R_F = \frac{F}{S} = \frac{B - S}{S} = \frac{B}{S} - 1$$  \hspace{1cm} (7)

where

- $F$: Weight of flux
- $S$: Weight of sample
- $B$: Weight of fusion beads

As shown in the equation (7) above, dilution factor correction can be applied by using dilution factor calculated from fusion beads weight ($B$) and sample weight ($S$).

Next, let’s study the case of sample including LOI. The relation among sample, LOI and weight of flux in this case is explained by an image of Fig. 16.

As shown in the image above, it is understood that the LOI is replaced with a part of flux. Therefore, the LOI (including GOI) correction can be made by designating base component (balance) for calculation of coexisting component correction factor as a component of flux.

Table 9. Coexisting component correction factors without LOI correction and with it (Correction model: de Jongh).

<table>
<thead>
<tr>
<th>Analysis Component</th>
<th>FeO_x</th>
<th>SiO_2</th>
<th>LOI</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeO_x</td>
<td>0.00188</td>
<td>0.00687</td>
<td></td>
</tr>
<tr>
<td>SiO_2</td>
<td>-</td>
<td>0.00419</td>
<td></td>
</tr>
<tr>
<td>MnO</td>
<td>0.00165</td>
<td>0.00655</td>
<td></td>
</tr>
<tr>
<td>P_2O_5</td>
<td>0.000262</td>
<td>0.00457</td>
<td></td>
</tr>
<tr>
<td>SO_3</td>
<td>0.000560</td>
<td>0.00499</td>
<td></td>
</tr>
<tr>
<td>TiO_2</td>
<td>0.00681</td>
<td>0.0139</td>
<td></td>
</tr>
<tr>
<td>CaO</td>
<td>0.00692</td>
<td>0.0140</td>
<td></td>
</tr>
<tr>
<td>MgO</td>
<td>-0.000577</td>
<td>0.00338</td>
<td></td>
</tr>
<tr>
<td>AlO_3</td>
<td>-0.000368</td>
<td>0.00367</td>
<td></td>
</tr>
</tbody>
</table>
Flux volatilization correction was discussed with Fe$_2$O$_3$ in the glass beads used in the Section 9 and one of two kinds of iron ore of which volatilization amounts are quite different each other.

Following is the comparison between the method without flux volatilization correction and with the said correction.

Coexisting component correction factors for each method are shown in Table 10. Calculation of the correction factor was made as follow.

- **Without volatilization correction**: Coexisting component correction factors were calculated with dilution factor (Flux/Sample) correction and incorporation of the LOI correction designating LOI as a base component.
- **With volatilization correction**: The factors were calculated with flux volatilization correction using the dilution factor using fusion beads and sample weights, and adding LOI correction of which base component is the flux component which is the LOI amount.

Besides, as the flux used are Li$_2$B$_4$O$_7$ 4g and oxidizing agent NaNO$_3$ 0.24 g (corresponding to Na$_2$O 0.0875 g which is a residual in the fusion beads), compound composition of the flux is set as Li: 1.518, B: 3.036, O: 5.375, Na: 0.089.

Moreover, standard dilution factor ($R_f$) was set to 10.2188 (4.0875 g/0.4 g). De Jongh model was used for the coexisting component correction.

Calibration line of Fe$_2$O$_3$ without volatilization correction is shown in Fig. 17. Calibration line accuracy for all samples is 0.38 mass% which is rather big. Data of the fusion beads of which volatilization is big are shown by yellow markers. They obviously do not fall on the line. The difference between standard value and quantification value for the sample of which volatilization amount is as big as 1.43 mass%, and the difference for the sample of which volatilization amount is intermediate is 0.24 mass%. It can be said that the flux volatilization effect is quite big.

On the other hand, the calibration line for Fe$_2$O$_3$ with flux volatilization correction is shown in Fig. 18. It is understood that the accuracy of the calibration line is improved greatly to 0.11 mass%. For the samples of which volatilization amount is rather big, as errors are as much as 0.07 mass% or 0.04 mass%, it is said that the flux volatilization correction is effective.

### 11. Precautions for glass beads method

Described above that the fusion beads method makes accuracy of the analysis improved by employing the above correction. The following are precautions for the
• Sensitivity of trace elements is decreased due to dilution by flux.

12. Conclusion

In conclusion, the above explanation of correction methods, a list of various dominant causes of error and their correction methods in fusion beads is shown in Table 11.

Accurate analysis can be made with corrections for LOI, GOI and the effect of flux volatilization by using appropriate coexisting component correction models. And the dilution factor correction is also possible even in case that dilution factors are varied. Moreover, use of actual weights of sample and flux, or sample and fusion beads, makes accurate weighing unnecessary, and operator is released from troublesome weighing. Accurate analysis covering wide concentration range from low to high can be made by employing coexisting component correction in this report to fusion beads method.

References


<table>
<thead>
<tr>
<th>Table 11. Various dominant causes of error and its correction method in fusion beads method.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Cause of error</strong></td>
</tr>
<tr>
<td><strong>Correction method</strong></td>
</tr>
<tr>
<td>Dilution factor correction</td>
</tr>
<tr>
<td>Sample weight : S</td>
</tr>
<tr>
<td>Flux weight : F</td>
</tr>
<tr>
<td>Beads weight : B</td>
</tr>
<tr>
<td><strong>Application</strong></td>
</tr>
<tr>
<td>Sample not affected by LOI</td>
</tr>
<tr>
<td><strong>Application example</strong></td>
</tr>
<tr>
<td>Firebrick, etc.</td>
</tr>
</tbody>
</table>

fusion bead method.

- Analysis of elements with low boiling point (F, Cl, etc.) are difficult due to volatilization of sample during fusion.
- Metallic components [Not oxide; C (Organic matter) and sulfide (CuS₂)] reacts with platinum so that the platinum crucible is damaged. Oxidization process of sample in advance is required for this kind of sample.
1. Introduction

In thermal analysis, the measurement condition influences the measurement results. Therefore, it is important to select the most desirable measurement condition in response to the objective of the measurement.

Conditions such as sample amount, heating rate as well as the measurement atmosphere are selected freely in thermal analysis measurement. Especially the measurement atmosphere, where it directly affects the sample's reaction, for example, measuring under atmospheric air may cause combustion or oxidation reaction and the suppression of these reactions can be confirmed by measuring under inert atmosphere. Therefore, it is essential to select the appropriate atmospheric gas suitable to the objective of the measurement.

But the difference among atmospheric gases is not only the presence or absence of oxygen (O₂), such as when using an air pump for an air atmospheric measurement also includes the room humidity (water vapor partial pressure) while using a gas cylinder for an inert gas atmospheric measurement creates a dry atmosphere(1).

The dehydration behavior of the sample is most affected by the effects of humidity and in some cases degradation reaction may also be affected. Hence, it is important to measure under a predetermined humidity to perform simulation on the sample's thermal behavior. Also, evaluating the material's hygroscopic behavior (percentage of water absorption) as a property is the most important factor. On the other hand, since dehydration behavior is determined from the heating process, accurately estimating the coefficient of water absorption is extremely difficult in the conventional thermal analysis.

In recent years, various fields of specialization have applied thermal measurements where humidity in the atmosphere is controlled because of its ease and simplicity. Although the effects of humidity on the measurement results were thoroughly discussed in 2009(1), this paper discusses the basic terminologies related to humidity, thermal analysis under water vapor atmosphere and its measurement methods. It also includes applications such as effects of water vapor on the thermal degradation of polymers and organic metal compounds; and measurement of adsorption and desorption of moisture levels in relation to change in humidity. Finally, this paper ends with a general conclusion.

2. Definition of humidity

Humidity is defined as the amount of water vapor (H₂O gas) in gas (atmosphere), where values are expressed in several units. Most familiar and deeper terminology is the relative humidity, expressed in percentage, which refers to the ratio of the amount of water vapor at a particular temperature to the amount of saturated water vapor (also used in weather forecasts). Shown below are related terminologies of humidity and their units of expression.

- Water vapor partial pressure (vapor pressure), Pa, is the partial pressure of water vapor in gas
- Relative Humidity, % RH, is the ratio of the partial pressure of water vapor at a particular temperature to the saturated water vapor pressure expressed in percentage.
- Absolute humidity, kg/m³ is the mass of water vapor per unit volume (1 m³).
- Dew point temperature, °C, is the temperature at which the water vapor pressure is equivalent to the saturated water vapor.

3. Thermal analysis under water vapor atmosphere

3.1. Modular structure

When performing a thermal analysis measurement under a water vapor atmosphere, the modular structure consists of (1) a humidity generator allowing the generation of an arbitrary water vapor concentration (humidity generator, HUM-1 by Rigaku), (2) an isothermal-type thermal analysis module without the occurrence of condensation even under high humidity concentration; and (3) a circulator for an isothermal-type thermal analysis module. Also, when conducting a measurement under a humid atmosphere (25°C, 90%RH) without condensation, measurement can be done using a standard thermal analyzer attached with a water vapor generator.

3.2. Measurement range

Generally, the thermal analysis module equipped with

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isothermal furnace used for water vapor atmosphere has a similar specification with the standard thermal analysis module where it can be heated up to a maximum of 1500°C, to avoid water condensation. Also, it can be humidified up to a maximum water vapor concentration of 80°C, 90% RH.

4. Thermal analysis measurement technique under humidity controlled atmosphere

Humidity controlled thermal analysis is categorized into 2 major types namely, a measurement where the water vapor concentration is held constant at a changing temperature; and a measurement where changes in water vapor concentration is performed at an isothermal condition.

4.1. Measurement at a constant humidity

The conventional thermal analysis technique pays less attention on the humidity condition. Therefore, performing a thermal analysis measurement under an arbitrary humidity as a measurement atmosphere condition enables to compare the material’s thermal behaviors in response to different humidity conditions. Fig. 1 illustrates a thermal analysis measurement condition showing a constant water vapor partial pressure at a constantly changing temperature.

4.2. Constant temperature measurement at a changing humidity

Changing the humidity at an arbitrary isothermal temperature condition is a technique where the amount of water absorbed or desorbed from the sample is measured. Figure 2 illustrates a thermal analysis measurement condition showing a constant temperature at a stepwise change in water vapor partial pressure. Plotting humidity against the amount of change will represent the adsorption isotherm.

5. Effect of water vapor on the thermal degradation reaction

5.1. Thermal degradation of resin

Figure 3 shows the TG result of PET in N\textsubscript{2} atmosphere with different water vapor partial pressure. Although mass losses due to degradation is seen from 350°C to 450°C, the reaction occurred at low temperature for measurements with high water vapor partial pressure and the mass loss ratio tends to be large. Figure 4 shows the plotted result of the residual amounts at 500°C with regards to the respective water vapor partial pressure.

It is understood that increasing the water vapor partial pressure is associated with a decrease in residual amount. Although carbon still remains after thermal degradation of PET (polyethylene terephthalate) under inert dry atmosphere, it suggests that as water vapor partial pressure increases, the thermal degradation reaction controlling the carbonization phenomena occurs. Usually, it is known that PET is degraded into ethylene glycol and terephthalic acid during hydrolysis. A similar measurement was performed using water
vapor TG-MS (thermogravimetry coupled with mass spectrometry) and the generation of ethylene glycol and terephthalic acid were confirmed. Under humidity controlled atmosphere, the degradation of PET as well as hydrolysis simultaneously occurred, thus the higher the water vapor partial pressure, the lesser the carbon residue.

5.2. Thermal behavior of organic metal compounds

Figures 5 and 6 show the respective TG curve and DTA curve of zinc acetylacetonate monohydrate \((\text{C}_{10}\text{H}_{14}\text{Zn}\cdot\text{H}_{2}\text{O})\) measured under different levels of water vapor partial pressure. Under dry atmosphere, the TG curve showed more than 90% mass losses while the DTA curve showed 4 endothermic peaks. Associated with an increase in water vapor in the TG curve are mass losses in the TG shifting to low temperature with a tendency of a smaller mass loss ratio. While the first and fourth peaks in the DTA curve tend to shift towards the high temperature and low temperature, respectively.

Furthermore, the water vapor partial pressure at 9.3 kPa condition showed that the residual amount agrees to the theoretical generation of zinc oxide, the DTA curve is reduced to 2 endothermic peaks. On the other hand, the results of TG-MS and XRD-DSC (simultaneous measurement of XRD and DSC) indicated that the thermal behaviors of zinc acetylacetonate monohydrate are in the following order: dehydration, transition, melting and evaporation. All these associated endothermic reactions are confirmed in the DTA curve. The increase in water vapor partial pressure associated with dehydration inhibited the reaction resulting to a shift towards high temperature. This result indicated that the degradation of the hydrate state progressed.

As a result, only dehydration of the hydrate occurred when measured under high water vapor atmosphere condition and that the reaction progressed into 2 stages. In addition, although the DTA curve showed that the increase in water vapor partial pressure to \(P_{\text{H}_{2}\text{O}}=6\text{kPa}\) did not affect the transition and melting as shown in the DTA curve, but as the vapor pressure increased to \(P_{\text{H}_{2}\text{O}}=9.3\text{kPa}\), the degradation caused chemical changes in the sample and peaks due to transition and melting disappeared. Also, accelerating the degradation reaction associated with an increase in water vapor partial pressure allowed the evaporation reaction to complete in the low temperature shifting the peak due to evaporation towards the low temperature.

In the humidity controlled atmosphere of Dynamic TG (sample controlled thermogravimetry: SCTG), the degradation progressed below 100°C and that \(\text{ZnO}\) was confirmed as a residue. From this measurement result, performing thermal treatment under humidity controlled atmosphere below 100°C enabled the direct generation of \(\text{ZnO}\) from zinc acetylacetonate monohydrate.

6. Measurement of adsorption and desorption of moisture levels due to change in humidity

The sample is held at isothermal and stepwisely changing the humidity enables to measure the amount of moisture absorbed and desorbed with regards to humidity. Figure 7 shows the TG result of perflourosulfonic acid.
sulfonic acid membrane isothermally held at 25°C while humidity was changed stepwisely from dry→30%RH→60→90→60→30→dry. In the TG results, an increase in mass was seen due to an increase in humidity associated with absorbed moisture and a decrease in mass was confirmed due to a decrease in humidity accompanied with dehydration.

Similarly, a measurement with more detailed changes in humidity was performed and the absorbed water ratio in relation to relative humidity is plotted in Fig. 8.

In less than 10%RH, the water adsorption ratio of persulfonic acid membrane is high in the low humidity condition and then at 60%RH, the water adsorption increased almost linearly. The water adsorption ratio in relation to change in humidity further increased at a high relative humidity condition of 60%RH. This indicates that the water adsorption property of the sample in response to various humidity levels is different. The graph showing the gaseous concentration (partial pressure) plotted against amount absorbed is called an adsorption isotherm, where the adsorption mechanism of the curve depends on the surface profile and pore size of the sample.

Figure 9 shows the TG result of the inclusion organic compound in cyclodextrin measured under controlled humidity which was carried out at room temperature (25°C) from dry→90%RH→dry condition and then heated at dry condition. Due to change in humidity at room temperature, a 6.5% adsorption-desorption reaction was confirmed. On the other hand, 5.5% dehydration was confirmed in the heating process indicating that the difference in dehydration behavior was due to difference in water binding energy. Identifying adhesive water (free water) as well as bound water (crystal water) in materials such as organic compounds and pharmaceuticals is extremely important; it is usually differentiated thru their dehydration temperature using the constant heating method in the TG. However if the dehydration temperature of the bound water is near the room temperature, identification will be complicated. As shown earlier, water is differentiated as adhesive water and free water where the former is the type of water which reacts to change in humidity while the latter is the type of water which does not react to change in humidity. As shown earlier, loosely bound water or free water may or may not react on change humidity.

7. Change in dimension due to change in humidity

We have discussed the evaluation of adsorbed water ratio (adsorption-desorption associated with mass change) using TG in Section 6. The amount of swelling with regards to change in humidity can be measured using TMA. Figure 10 shows the moisture adsorption property measurement results of a photocopy paper and a coat paper at room temperature using TMA. The sample’s expansion was measured at room temperature (25°C) while the atmosphere’s humidity was changed from dry→25°C30%RH→60%RH→90%RH. Although expansion associated with increase in humidity were observed in both paper samples but differed in the amount of expansion. Comparing the 90% RH and the dry atmosphere, the respective expansions were 1.1% in photocopy paper and 0.4% in coat paper indicating that the effect of humidity in the change in dimension of the coat paper was small.

8. Conclusion

This article has introduced the use of humidity or a
humidity generator to perform thermal analysis under controlled humidity. When compared to the conventional thermal analysis where it neglects the humidity, the application of humidity as a measurement condition broadens the measurement condition which may lead to obtaining new information of the material.

Humidity related thermo-physical properties such as dehydration reaction, hydrolysis, glass transition, sintering are affected by humidity, also hydrates such as the zinc acetylacetonate monohydrate where the reaction is likely to change. In addition, it is possible to evaluate properties such as amount adsorbed or swelling amount to obtain a clear and detailed knowledge in relation to moisture adsorption property which cannot be accomplished in the conventional thermal analysis. Also, when performing material evaluation, it is usually summarized as “evaluating at nearly the same atmosphere of the usage environment.”

Although thermal analysis is considered as one of the simple measurement techniques that can be performed in such evaluation, “humidity” always exists in atmospheric environments and cannot be neglected. In addition “humidity” varies according to place, time and season.

Performing thermal analysis under a controlled humidity atmosphere is a promising tool where the humidity can be arbitrarily changed because it enables evaluation at the same atmosphere as the usage environment, hoping to solve problems or screen materials effectively.

References

1. Introduction

Rigaku SmartLab is a multipurpose, fully-automated horizontal X-ray diffractometer that allows many types of measurements and evaluations of materials ranging from powders to thin films. Rigaku’s expansion system and Cross Beam Optics (CBO) system enable configuration of a wide range of optics, while the SmartLab Guidance control software permits easy switching between optics for added versatility.

The many optics systems offered by Rigaku for SmartLab include CBO system incorporating a parabolic multilayer mirror, CBO-E system incorporating an elliptical multilayer mirror, and optics configured with the Kα₁ unit with a Johansson Ge crystal for monochromatization of incident X-rays to the Kα₁, designed to measure powder samples. These systems allow the user to configure the ideal optics for specific measurement or evaluation purposes. The new and unique Kα₁ system enables various types of measurement while maintaining samples in a horizontal position.

2. CBO system

The optics of the CBO system permits easy switching of incident X-rays by simply changing the selection slit. Two systems are available: The CBO (Fig. 1) lets the user select the Bragg-Brentano focusing method or parallel beam method using a parabolic multilayer mirror, while the CBO-E (Fig. 2) lets the user select the Bragg-Brentano focusing method or convergent beam method using an elliptical multilayer mirror.

2.1 Bragg-Brentano optics

The Bragg-Brentano optics enables easy acquisition of high resolution and high intensity data by the reflection method (Fig. 3). It is generally used for qualitative and quantitative analysis of powder samples.

2.2 Parallel beam optics

The parallel beam optics allows accurate measurement of diffracted X-ray positions unaffected by sample shape (Fig. 4). It is generally used to analyze powder sample profiles and measure the degree of preferred orientation, as well as to measure thin-film samples.

2.3 Convergent beam optics

The convergent beam optics enables high resolution measurements by the transmission method (Fig. 5). It is used to measure samples with low absorption...
coefficients and preferred orientation, such as pharmaceuticals. Diffracted X-rays are focused on the detector surface for efficient measurement when combined with the D/teX Ultra 1D high-speed detector.

3. Kα1 system

Rigaku’s expansion system also enables to install the Kα1 unit (Fig. 6). The user can easily switch between the conventional Kα and new Kα1 optics by installing/removing the Kα1 unit. Either of the optics can be selected depending on the purpose of measurements using your SmartLab.

Since incident X-rays are monochromatized to Kα1, even overlapped diffraction peaks can easily be decomposed. The peak positions, widths, and intensities will be determined more precisely in the diffraction patterns obtained using the Kα1 optics than using the conventional Kα optics. The Kα1 unit is recommended to be used for indexing or ab initio structure analysis, which requires high-resolution data.

4. Kα1 system+CBO system

The Kα1 system incorporates a Johansson Ge crystal for monochromatization. To allow use of the CBO system without modification, the focus position of the Kα1 system is designed to align with the conventional focus position. Simply by changing the selection slit, the user can direct X-rays monochromatized to Kα1 (Fig. 7) to Bragg-Brentano optics (Fig. 8), parallel beam optics (Fig. 9), or convergent beam optics (Fig. 10).

X-rays monochromatized to Kα1 can be used with the Bragg-Brentano focusing method and convergent beam method whereby diffracted X-rays are focused on the detector surface for efficient measurement when combined with the D/teX Ultra 1D high-speed detector. Compared to conventional monochromatization methods, this achieves faster high intensity measurements. Pairing the Kα1 unit with the CBO system lets users configure the ideal optics for the specific purpose of a measurement or analysis.
1. Introduction

X-ray fluorescence (XRF) analysis is widely used in a number of fields, including quality control and research & development, due to its high degree of accuracy and extremely simple sample preparation. Quantitative analysis with XRF spectrometry requires reference materials in order to generate calibration curves. The rapidly improving performance of personal computers has opened the door to sophisticated data processing techniques like SQX Scatter FP (Fundamental Parameter) method, improving the accuracy of semi-quantitative analysis, where reference material is not used for quantitative calculation by the FP method. The even more accurate quantitative analysis method, however, requires the user to generate calibration curves using calibration standards made of the same material as the samples to be analyzed.

While quantitative analysis provides an unparalleled level of accuracy, correctly setting up the sample measurement conditions and creating the calibration curves requires expertise in XRF spectrometry and can be a time-consuming process. Rigaku has seen a growing need among XRF spectrometry users to be able to start up quantitative analyses quickly and easily.

The Application Package for XRF analysis introduced here is a product which is designed to enable even novices in XRF to start up quantitative analyses easily. The package provides the user with reference materials for calibration, drift correction samples for daily analysis and analysis parameters such as measurement conditions and correction coefficients for calibration.

2. The Application Package

The Application Package includes the following items:

- Calibration standards (reference material)
- Drift correction samples
- Installation CD, instruction manual

The user prepares the calibration samples as the same preparation method needs to be applied to both the calibration samples and analysis samples. Since the standard values for the calibration standards are stored in the software, the user does not need to type in the standard values.

By measuring the included drift correction samples prior to sample analyses, the user can correct for the sensitivity drift that can occur with long-term use of a spectrometer. Using the drift correction samples prior to sample analysis enables the user to employ a given set of calibration curves for an extended period of time without re-calibrating.

Parameters such as measurement conditions and correction coefficients for calibration are installed automatically from the installation CD. After installation, the instruction manual provides simple, step-by-step instructions on how to set up quantitative analyses. The inclusion of matrix correction coefficients and/or spectrum overlap correction coefficients for calibration makes it possible for less-experienced users to generate accurate calibration curves.

3. Product line-up

The series of the Application Package currently
available are listed in Table 1. The packages are available for the ZSX Primus series (ZSX Primus and ZSX Primus II) and ZSX 100e (N/A for Polymer).

(1) Alloy series
The alloy package series use commercially available alloy standards for calibration.

The “Special steel, Nickel alloy” package makes use of an FP method—sensitivity calibration curves created using this FP method are linear throughout a wide range of concentrations. In addition, a secondary calibration method is applied, where calibration curves have been established with plenty of the reference materials Rigaku owns and several reference materials commercially available are used for re-establishing the calibration curves. Thus, this package is suitable for use with a wide concentration range of Fe- and Ni-based alloys.

(2) Refractories series
These series are designed to conform to JIS R 2216, “Methods for X-ray fluorescence spectrometric analysis of refractory products.” The certified reference material series by The Technical Association of Refractories, Japan are used as calibration standards.

These package series employ a fusion bead sample preparation method, in which a powder sample is mixed with flux and the mixture is fused into a glass disk. This eliminates the impact of differences in particle size or mineral composition, improving the accuracy of the quantitative analysis.

(3) Polymer (Polyethylene)
This series is designed for application with polymer plates. The samples are polished with sand paper prior to measurement.

With this package series, pellet samples are reshaped into plates before being analyzed.

(4) Petro-Pak (Application Package for fuel oil)
This package series is used for the analysis of sulfur in fuel oil (ASTM D2622, ISO 20884 and JIS K 2541-7).

Petro-Pak consists of a “Low Sulfur” series and “High Sulfur” series. All required parameters for the materials contained in each series are provided. The user does not have to purchase calibration standards for all of the materials contained in each series. The user can buy the requisite standards for the material that the user intends to analyze. Table 2 shows a list of the materials in Petro-Pak.

Liquid samples such as fuel oil are poured into a liquid cell with analysis film and then measured. As an option, the Petro-Pak includes a starter kit containing liquid cells and analysis film, along with a number of disposable pipettes. The process is simple. After assembling the liquid cell and film, the user dispenses a fuel oil sample into the cell with a disposable pipette. Then, the sample is measured in a helium atmosphere. The catalog numbers of the liquid cell and the film from the starter kit are shown in the instruction manual, so the user can order the replacement cells and films as needed.

Currently, Petro-Pak is only available for the ZSX Primus (not available for ZSX Primus II). Petro-Pak for Supermini and Mini-Z Sulfur Analyzer will be released soon.

4. Summary
The Application Package makes it easier for users of all experience levels to add quantitative analysis to their process. Rigaku will continue to expand the Application Package library in order to meet the analytical needs of our users.

<table>
<thead>
<tr>
<th>Table 1. List of Application Package series</th>
</tr>
</thead>
<tbody>
<tr>
<td>Series (material)</td>
</tr>
<tr>
<td>-------------------</td>
</tr>
<tr>
<td>Low alloy, stainless steel</td>
</tr>
<tr>
<td>Special steel, Nickel alloy</td>
</tr>
<tr>
<td>Brass, Lead brass</td>
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<tr>
<td>Refractory: Magnesia</td>
</tr>
<tr>
<td>Refractory: Chrome-Magnesia</td>
</tr>
<tr>
<td>Polymer (Polyethylene)</td>
</tr>
<tr>
<td>Petro-Pak (Fuel oil)</td>
</tr>
</tbody>
</table>

* Empirical calibration