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Rigaku Group manufactures and supplies state-of-art analytical and scientific instruments in the fields of X-ray diffraction, X-ray spectrometry, thermal analysis, and non-destructive inspection worldwide. As a service to our customers and friends, Rigaku also publishes The Rigaku Journal, a semiannual journal on the advances of Rigaku technology. It features Rigaku articles on leading-edge technology, analytical know-how, application notes, scientific reviews, and the latest information on Rigaku products. Rigaku welcomes any comments and suggestions.

Cover images: The main image exhibits a wide range reciprocal space map (RSM) for an epitaxial \((\text{La,Sr})\text{MnO}_3\) film on ZnO/Sapphire substrates. Indices for diffraction spots analyzed with the reciprocal space simulation software were also shown. This map was measured with a high speed 2-dimensional detector PILATUS 100K/R on SmartLab system (shown in the lower-right).
Lithium ion battery (LIB) has been successfully applied to portable electronics for the last decade. Recently, application of LIB in the field of energy vehicles and stationary storage systems has attracted considerable attention, in order to efficiently utilize renewable energies such as solar and wind energies. As higher energy capacity and power, long-term stability, safety, and lower costs are required, further development and studies are accelerated around the globe. To attain this goal, extensive research about the materials and the configurations of the battery is being carried out. In addition, characterization techniques are strongly required because it is essential to understand the fundamental behavior of the material in the electrochemical reaction, the mechanism of cell deterioration, the interphase phenomena of the electrode and electrolyte, and many indeterminate ideas not yet well understood. The schematic illustration of a lithium ion cell is shown in Fig. 1. It is composed of a positive electrode, a negative electrode, organic liquid electrolyte with lithium-ion conductivity, and an electrically insulating polymer separator. Lithium insertion compounds such as LiCoO$_2$, LiMn$_2$O$_4$, and LiFePO$_4$ are typically employed for the positive electrode. Graphite is typical for a negative electrode, and more recently Si or Sn alloy having higher energy capacities and Li$_4$Ti$_5$O$_12$ with an advantage in safety are also used. The lithium ion migrates from the positive electrode material to the negative electrode material through the electrolyte and the electron flows through the external circuit from the positive electrode to the negative electrode during the charge process. An inverse reaction occurs during the discharge process. It follows that the number of lithium ions migrating between the electrodes determines the energy capacity of the cell, and the mobility and the repeatability on the migration of lithium ion affect the power and lifespan of the cell, respectively. At the interface between the electrolyte and the electrode during the charge-discharge process, passivation film called a solid electrolyte interphase (SEI) is precipitated. In the electrode, accompanied with de-intercalation/intercalation of the lithium ion, oxidation/reduction of the electrode material is taken place and the crystalline structural is converted. Additionally numerous side-reactions represented by decomposition of electrolyte and gas evolution could occur in the lithium ion cell, and all of which could affect the cell performance. Studying and controlling the phenomena therefore, are critical for the development of LIB.

At the 220th ECS fall meeting in Boston in October 2011(1), many reports on advanced characterization were presented. In addition to conventional and basic uses of laboratory analysis tools, spatial-resolved or time-resolved functions approaches are carried out for the investigation of interfacial reaction, reaction distribution and reaction process of LIB. In situ analysis technique allows the analysis condition to more closely resemble the actual operating condition. Synchrotron radiation enables us to obtain higher sensitivity and resolution. In situ TEM observation with the atomic scale spatial resolution reveals how the electrode interface phase forms during lithium intercalation and de-intercalation(2). The combination of time-resolved X-ray diffraction (XRD) and mass spectroscopy identifies the structural change and gas evolution during thermal decomposition of the electrode(3). Various advanced techniques including NMR, X-ray absorption spectroscopy (XAS), X-ray tomography, neutron, FT-IR, AFM, ellipsometry, and glow discharge–optical emission spectroscopy (GD-OES) show their characterization capabilities to enhance the research and

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development of LIB. The 52nd battery symposium was held in Tokyo in October 2011 (4). There were approximately 600 oral presentations and more than 2800 participants from Japan, China, Korea, and others. The sessions were conducted on an all-solid-state LIB which was expected to solve the safety problem of the flammable organic solvent and on a Li-O2 battery which was expected to supplant the LIB due to the benefit of its energy density being much higher. There also came to increase reports on polymer binders and current collectors, which had received little attention, although they are important components supporting LIB engineering. The RISING project supported by NEDO (New Energy and Industrial Technology Development Organization) in Japan has focused on the development of advanced characterization techniques to comprehensively illustrate the reaction mechanism of LIB. Several studies with advanced XAS techniques were also shown during the conference. Reaction distribution and its relaxation process in the positive electrodes were studied using micro- and depth-resolved XAS techniques having the microscopically capability (5). The results show that lithium ionic diffusion is fast in LiCoO2 electrode but is not in LiFePO4, and the ionic migration is affected by the slope in voltage profile of the charge-discharge reactions. The interface reaction between electrode and organic electrolyte is monitored by using total reflection-XAS with surface sensitivity (6). It reveals only the top surface of LiCoO2 electrode is reduced without any electronic load and it may be suppressed with ZnO2 coating.

Among such various characterization techniques for LIB, X-ray is one of the most powerful probes. Figure 2 summarizes the laboratory analysis tools which are available from Rigaku. The structural analysis by XRD and the structural refinement with Rietveld method are utilized to characterize the electrode materials. The sample holder attachments enable us to obtain in-situ XRD analysis during the charge/discharge process and during the interaction with reactive gas. The next article introduces the application of XRD for LIB research and development in detail. SAXS (small angle X-ray scattering) is useful for the evaluation of the particle size and its distribution of nano-particles. LiFePO4 is usually coated with carbon to improve its electronic conductivity (7). Figure 3 shows small angle scattering patterns obtained by X-ray diffractometer, SmartLab and the core/shell model calculation analysis are applied to LiFePO4/C composite. The calculation result of 1.6 to 1.9 nm in thickness of the carbon coat layer is in good agreement with TEM observation as shown in Fig. 4 (8). X-ray fluorescence (XRF) spectrometry is useful for qualitative and quantitative analysis of the electrode
materials. It is well established in the LIB industry for quality control of the components and detection of contamination of electrodes. It is also applied to evaluate the thickness of the coating layer on the electrode film, for example thickness of Al₂O₃ layer coated on electrode film. Figure 5 shows XRF spectra with wavelength dispersive (WD) XRF spectrometer, ZSX PrimusII for LiFePO₄/C composite materials, which were synthesized with high frequency induction heating method. The C peak intensity varies with the sintering condition and its amount corresponds well with the discharge capacity and the rate characteristics. X-ray radiography (2D) and X-ray computed tomography (CT) reveal the inner structures of cylindrical battery and packaged battery. The stacking structure of electrodes, space inside, and defects can be observed without interference. Figure 6 shows a typical example of X-ray radiography image by a Rigaku digital X-ray radiography system for a commercially available battery pack for an energy vehicle. These characterization capabilities available with X-ray analysis tools strongly support the research and development in the LIB field as well as other advanced industrial fields.

Acknowledgements
Author would like to thank Prof. Masaki Yamagata of Kansai University, Dr. Hironori Kobayashi of AIST (National Institute of Advanced Industrial Science and Technology), and Prof. Tatsuya Nakamura of University of Hyogo for their technical comments. Author would also like to thank Mr. Hisashi Yashiro and Mr. Akira Kishi of Rigaku Corporation for helpful discussions.

References
(1) http://www.electrochem.org/meetings/biannual/220/220.htm
Characterization in lithium ion battery

The latest X-ray diffraction techniques for advanced research and development in lithium-ion battery materials

Akira Kishi*

1. Introduction
The materials used in the manufacture of lithium-ion batteries include positive electrode materials, negative electrode materials, electrolytes, separators, binders (for positive and negative electrodes), and cladding materials (for battery housings). Research and development on these materials is active and ongoing.

This paper describes recent expectations for X-ray diffractometers in research and development activities that seek to improve the performance of such materials. It also introduces measurement methods that respond to those expectations.

2. Use of in situ cells to analyze changes in crystal structure during charging and discharging
It is recognized that controlling charging and discharging conditions extends the service life of lithium-ion batteries. This control requires more than observations of electrode structures in the fully charged/discharged state; it requires real-time measurements of the relationship between the states of charge/discharge and the electrode structures using in situ cells. The 2011 Spring issue of Rigaku Journal introduced the results of in situ X-ray diffraction measurements of changes in the crystal structure of olivine-type positive electrode LiFePO4 (provided by Tatsuya Nakamura, Professor, Graduate School of Engineering, University of Hyogo) using lithium-battery cells[1]. In this experiment, when the state of charge (SOC) was 0%, the material was LiFePO4. However, as SOC increased, X-ray diffraction peaks generated by FePO4 began to appear. At 100% SOC, X-ray diffraction patterns indicated a near-complete FePO4 phase after a coexistence state of two phases. Professor Nakamura and Yasiro (of Rigaku Corporation) et al. recently showed that a slight peak shift occurs at 20% SOC relative to 0% SOC, and that lattice constants decrease by around 0.05%. However, virtually no change in lattice constants occurs from that state to 60% SOC. These findings were presented in the conference held by the Electrochemical Society (U.S.A.) in October 2011[2]. As this example suggests, we believe detailed analyses of changes in crystal structure during charging and discharging will become increasingly important in controlling charge/discharge states.

3. Observations of trace quantities of coexisting compounds
Research and development efforts currently target various compounds for use as positive and negative electrode materials. Since positive electrode materials are multi-element metal oxides, compounds differing slightly in composition or crystal structure may be mixed in during synthesis, or slight changes may occur in the crystal structure or composition of the material during repeated charges/discharges. In addition, trace amounts of compound may be deliberately added to improve the material performance. Conventionally, X-ray diffractometry has been used for qualitative and quantitative analysis of trace amounts of coexisting compounds and for analysis of polymorphic compounds having identical chemical composition but different crystal structure. This method is widely used for both inorganic and organic materials. We expect similar demand to grow in the field of lithium-ion battery materials.

3.1. Measurements using D/teX Ultra, high-speed one-dimensional detector
The features and characteristics of the D/teX Ultra high-speed one-dimensional detector have been described in Rigaku Journal[3]. This detector offers roughly 100 times the detection sensitivity of scintillation counters. It is ideally suited to measurements of materials for lithium-ion batteries, because this detector offers high energy resolution that reduces the effects of fluorescent X-rays from Co, Fe, or other materials found in the positive electrode material of the lithium-ion battery. Figure 1 compares measuring results of CoLiO2, removed from a coin cell battery charged and discharged 100 times, using a scintillation counter and the D/teX Ultra.

3.2. Measurements using Kα1 optics and D/teX Ultra
When a Cu target is used as an X-ray source, the following three K-series X-rays with neighboring wavelengths are included: Kβ1 1.392 Å, Kα1 1.541 Å, and Kα2 1.544 Å. With the most common X-ray diffraction measurement method, a nickel filter is used to remove peaks by Kβ X-rays. However, this also reduces the intensity of the sample’s other diffraction peaks.

To offset this drawback, the Kα1 optic system is used to extract only Kα1 X-rays. Top level researchers in the field of lithium-ion battery who visit the Rigaku
laboratory often show great interest in the following two newest Rigaku systems. These systems allow to measure infinitesimal impurities in positive electrode materials:

1. The combination of Rigaku’s SmartLab Automated Multipurpose X-ray Diffractometer, the Kα1 optics, and the D/teX Ultra,
2. The combination of the Kα optics (Kα1 and Kα2 with intensity ratio of 2:1), monochromator, and the D/teX Ultra.

Figure 2 shows a schematic of the SmartLab combined with the Kα1 optics and D/teX Ultra.

To date, measurements of infinitesimal compounds have been very hard to perform without a synchrotron radiation facility like SPring-8. However, the capacity to
measure minute peaks against background noise in ordinary laboratory settings is expected to advance studies of the positive and negative effects of trace coexisting compounds.

4. Structure analysis of the positive electrode materials of lithium-ion battery based on powder X-ray diffraction data

In the field of lithium-ion battery materials, researchers have expressed more interest in analyzing crystal structures based on powder X-ray diffraction data. Introduced below is an example of a structure analysis of LiFe$_{0.8}$Mn$_{0.2}$PO$_4$, an FeMn olivine-type positive electrode material offering excellent thermal stability and safety (sample courtesy of Nobuya Machida, Professor of Department of Chemistry of Functional Molecules, Konan University).

A baked at 550°C sample was measured using the Ultima IV Protectus general-purpose X-ray diffractometer. The results obtained are given in Fig. 3, Fig. 4, Table 1, and Table 2.

Using this method, the relationship between fine structure of various battery materials and their performance will be easily verified in ordinary laboratories.

**References**


**Table 1.** Crystallographic data.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical formula</td>
<td>LiFe$<em>{0.8}$Mn$</em>{0.2}$PO$_4$</td>
</tr>
<tr>
<td>Space group</td>
<td>Pnma</td>
</tr>
<tr>
<td>a(A)</td>
<td>10.3463(5)</td>
</tr>
<tr>
<td>b(A)</td>
<td>6.0219(3)</td>
</tr>
<tr>
<td>c(A)</td>
<td>4.7046(2)</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
</tr>
<tr>
<td>D$_0$(g/cm$^3$)</td>
<td>3.57</td>
</tr>
</tbody>
</table>

**Table 2.** Structural parameters.

<table>
<thead>
<tr>
<th>Label</th>
<th>Occupancy</th>
<th>Fractional coordinates</th>
<th>Temperature factor</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>x</td>
<td>y</td>
</tr>
<tr>
<td>Fe/Mn</td>
<td>0.8/0.2*</td>
<td>0.28189(5)</td>
<td>1/4</td>
</tr>
<tr>
<td>P</td>
<td>1</td>
<td>0.0947(1)</td>
<td>1/4</td>
</tr>
<tr>
<td>O1</td>
<td>1</td>
<td>0.0962(3)</td>
<td>1/4</td>
</tr>
<tr>
<td>O2</td>
<td>1</td>
<td>0.455(8)</td>
<td>1/4</td>
</tr>
<tr>
<td>O3</td>
<td>1</td>
<td>0.3348(2)</td>
<td>0.549(3)</td>
</tr>
<tr>
<td>Li</td>
<td>1**</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

*The ratio of Fe to Mn was fixed (due to the nearby atomic scattering factor.)

**We attempted to obtain the precise occupancy of Li, but since the value was 1.00(1), we set the ratio to 1.
1. Introduction
The various XRD techniques as the characterization tools for thin film samples have been presented in this series of “X-ray thin-film measurement technique” lecture course. There has heretofore been remarkable progress with detectors equipped with XRD apparatus. In this lecture, some explanation of the features and functions of 1-dimensional (1D)/2-dimensional (2D) detectors should be presented before summarizing this technical lecture course.

2. Detectors for XRD system
As has been shown in first lecture of the series(1), an X-ray diffractometer system for thin film characterization is composed of 5 parts:

1. X-ray source
2. Incident optical system
3. Goniometer
4. Receiving optical system
5. Detection section

Scintillation counters and proportional counters are the most popular detectors for XRD systems and they are regarded as 0-dimensional (0D) detectors (or point detectors) because they do not have position information on the surface of the detecting components. Recently, however, detectors equipped with many detector-elements on its detection area have also come into general use in laboratory equipment. They are referred to as 1D or 2D detectors used for the high speed measurement. The functions and features of these detectors can be seen in references (2)–(5).

The variation of typical detectors available with the SmartLab system is shown in Fig. 1.

2.1. 0D Detector
The scintillation counter (SC) is mainly used for the SmartLab system because of its good sensitivity, low noise level and easy handling, etc. This detector can measure the count-rate from 0.1 to several 100,000 counts/second after the counting-loss correction. Using SC, diffracted signals from a sample are
detected with wide detection area of a diameter around 1 inch. This type of detector, known as a 0D detector, does not have positional sensitivity, thus the signals for a given range of 2θ angles are summed up. In order to attain the angle resolution for 2θ, suitable receiving optics should be installed in front of the 0D detector, such as single or double receiving slits or a parallel slit analyzer (PSA), etc.

The wide detection area of SC is utilized by a PSA as a receiving element. By using PSA, it becomes possible to collect the signals spread and scattered on a sample surface without losing the angular resolution. In this lecture series, this situation was explained in the lectures on “Thin-film XRD method” in the 2nd lecture (6) and “In-plane XRD method” in the 4th lecture (7).

2.2. 1D Detector

It is getting easier to obtain solid-state semiconductor devices for X-ray detectors. By using this semiconductor device, detecting elements in a shape of strips are arranged in a one-dimensional array with narrow intervals. In recent years, this kind of solid-state semiconductor device has come to be utilized for the X-ray detector in a conventional X-ray diffractometer, and is usually referred to as a “high-speed 1D detector”. This detector is imbued with characteristics of high response and high energy discrimination, but the high speed measurement with this detector is actually enabled by the arranged strips on the detection area.

2.2.1. Principle of performing “high-speed measurement”

Figure 2 shows a measuring geometry for the Bragg-Brentano (BB) para-focusing method. Figure 2(a) shows a typical geometry for the measurement with a 0D detector (SC). The angle resolution is controlled by the combination of incident and receiving slits. Usually, narrow slits around 0.1 mm to 0.5 mm are employed for receiving slits, and this means, only a few parts of detection area of SC are utilized for this measurement. On the other hand, Figure 2(b) shows geometry of the BB method using a 1D detector (D/teX Ultra). In this geometry, narrow receiving slits which are employed in measurements with a 0D detector will be no longer used, but diffracted signals for different 2θ angles can be detected by strips on the detection area simultaneously. In the case of 2θ/ω scan, the intensity is integrated by a number of strips. This mode is referred to as “Time Delay Integration (TDI)” mode measurement. This is how “high-speed measurement” is enabled (8), (9).

This technique is effective for measurements by the para-focusing method for samples with textures of random orientation. For a sample with a texture of strong preferred orientation measured with a Parallel Beam (PB) geometry, this advantage of signal integration will be greatly reduced.

Signal integration cannot be restricted to the diffracted signals, but also is adapted inevitably to the signals of X-ray fluorescence from samples, which causes high background noises. For the solution of this problem, Rigaku’s 1D detector, “D/teX Ultra”, is equipped with a function called fluorescence-reduction mode. In this mode of measurement, the range of energy levels for signal integration can be controlled utilizing the energy discrimination of the semiconductor detector (21) (9).

2.2.2. 1D detector for thin film samples

Some notes and features using a 1D detector for a thin film sample are listed below.

• Conventional 2θ/ω measurement

As explained in the previous section, the advantage of signal integration (thus high-speed measurements) will be greatly reduced for samples with a texture of strong preferred orientation measured with a Parallel Beam (PB) geometry. If the divergence of the incident X-ray is larger, the integration effect increases. Angular resolution nevertheless, will be decreased.

By using this detector however, weak signals can be detected in a short time, which is advantageous for samples of small amount or minor phase detection (9), and also for the analysis of phase transitions in samples in a short time (8).

• Reciprocal space map measurement

A 1D detector has an advantage in Reciprocal Space Map (RSM) measurement in the field of high resolution thin film sample measurement. RSMs using conventional scintillation counters, are measured by the iterative motion of ω-step motions and 2θ/ω scans by changing scattering vector direction (10). This measuring sequence cannot be directly applied to 1D detection. This is because a 1D detector in the TDI mode will integrate the scattering vector of different directions in the course of 2θ/ω scan. Instead, this problem will be cleared by iterative motion of ω-step and 2θ scans in TDI mode (not with 2θ/ω scan), and then, 2-dimensional RSM data can be obtained (Fig. 3). This measuring sequence with TDI mode is useful for RSM where data of a wide range of 2θ will be measured. Since the strip arrangement of detecting elements can cover a certain range of 2θ without scanning of 2θ (i.e., the detector is standing still), signals for a certain range of 2θ can be simultaneously collected by exposing an incident X-ray (with a fixed ω) for a short time. This mode of signal collection is called “Still mode” measurement (Fig. 4), and then, a high-speed...
measurement is attained, due to the multiplication of the number of strips of detecting elements. In the SmartLab system, the two measurement modes above are installed.

Figure 3 shows \(\omega\)-step 2\(\theta\)-scan measurement for reciprocal space mapping using 1D detector. An \(\omega\) angle is fixed for every step while 2\(\theta\) scan. This method has an advantage for wide angle measurement.

Figure 4 shows 2\(\theta\)-step \(\omega\)-scan measurement for reciprocal space mapping using 1D detector. By this method, 2\(\theta\) angle will be fixed while \(\omega\) axis scanning. This method has advantage for small angle measurement.

For the RSM measurement, the geometry of incident/diffracted X-ray is also important. Figures 5 (a) and (b) show 2 different geometries for asymmetric RSM measurements. In general, low incident angle geometry (also called as Grazing-Incident geometry) is convenient for detecting weak signals from thin films. Thus, the geometry shown in Fig. 5(a) is generally employed for measurements for thin film samples, but the incident beam is spread over the sample surface due to the low incident angle, and consequently, the width of diffracted beam is wide.

Another geometry, i.e., low exit angle geometry (also called as Grazing-Exit geometry) is possible to be employed for measuring thin film samples (Fig. 5(b)), where a width of diffracted X-ray beam will be narrower than the one for the incident beam. For the RSM measurements using a 1D detector, the width of diffracted beam should be the same size as a strip of the detecting elements. The geometry shown in Fig. 5(b) should therefore be used for RSM measurements using 1D detector. Even if it is the symmetric-geometry, the width of incident beam should be controlled to be the same width as that of a detecting strip. A wider incident beam causes the reduction of resolution, and it often causes a streak in RSM data running along the trace of \(2\theta\) motion (thus, along the Ewald’s circle).

- 0-dimensional mode

A 1D detector has many strips on the detection area, but by canceling out the 2\(\theta\) information (positional sensitivity), this detector can be used as a 0D detector. This mode is called “0D mode” measurement. By using this mode, optical alignment and sample alignment can be carried out like using a scintillation counter. Also, with any kind of receiving optics, various measurements, such as high resolution Rocking Curve measurement (3rd lecture)\(^{10}\) and X-ray reflectivity (5th lecture)\(^{11}\), will be available. Selection of measuring modes can be performed in a manual control window or in measurement dialog boxes.

2.3. 2D Detector

There have been already equipped 2D detectors such as CCDs, Imaging Plates, X-ray films in a conventional...
XRD system, but these detectors or recording media have some disadvantages like sensitivity, reading time, etc.

Recently, solid-state semiconductor devices such as X-ray detectors where detection pixels are arranged in 2 dimensional arrays on a detection area, have come to be commercially available. The SmartLab system can be equipped with “PILATUS 100K/R” as a high speed and quick read-time, single-photon counting 2D detector, which also has high dynamic range and high sensitivity. The details and features of this detector are described in articles (3)–(5), (12).

In comparison with a 2D gaseous detector, 2D solid-state semiconductor detectors have various advantages, including not only the high energy discrimination, but also the applicability of TDI mode like a 1D detector utilizing its potentiality of short readout time. In addition, due to the difference in finite thickness in the active sensing regions, solid-state semiconductor detectors have advantages (thin sensing region) over the gaseous detectors in the aspect of oblique incidence of X-ray to detectors.

### 2.3.1. Principle of performing “high-speed measurement”

Figure 6 shows a SmartLab system equipped with PILATUS 100K/R. The incident X-ray and diffracted X-rays are drawn as red lines. 2-dimensionally arranged detecting pixels can record data which can be obtained by data acquisition with the goniometric motion of 2θ scan and with that of almost equivalent to χ scan. An example of a data image measured by 2D detector is shown in Fig. 6(b). With this figure, it can be easily recognized that information of 2θ (i.e. information of d-spacing, thus those of lattice constants) and distribution of crystallite orientation (mosaic spreading) is recorded in a single shot of 2D image data, then, high speed measurement is attained.

### 2.3.2. 2D detector for thin film sample measurement

In a previous paragraph, it is explained as “data acquisition with that of almost equivalent to χ scan”. It should be noted that it is, expressly, not equivalent to the data acquisition with χ scan. As shown in Fig. 6(a), the diffracted beam which is detected at the position close to the edge of 2-dimensional detector enters the detector in a condition far away from the normal incidence to the detector surface; i.e., the shape of the diffraction spots would be distorted due to the effect of oblique projection to the detecting plane.

Another factor which should be taken into account for the analysis of data detected close to the edge of 2D detectors is the interpretation of azimuthal directions, which is crucial for the analysis of epitaxial films. If the detection area is large enough, one might surmise that all of the diffraction signals both for θ/2θ scans and In-plane scans can be obtained simultaneously, yet this is not correct. The diffraction condition should be satisfied with the sample rotation. This indicates that the diffraction condition should be satisfied with the sample rotation with φ axis for the diffraction signals observed with In-plane scans. Thus, a 2D data image with a single snapshot (or Still mode measurement) will collect signals with different azimuth information for the points of center and edge (right and left edge in figure) in the detection area. For the RSM measurements for single crystalline epitaxial films or substrates, RSM measurements of wide χ angle range covered with a big detection area detector are not appropriate. Instead, measurements with small χ steps, followed by the compilation data processing of these data in the data analysis software are effective. One may wonder whether the ω rotation will not be required as for the φ rotation of a sample. The answer is that it is required but it can be attained with the TDI mode scan. The PILATUS 100K/R can be covered the wide range of 2θ/ω angles by using TDI measurement mode like the 1D detector(5),(13),(14).

Cautions mentioned above are very important in measurements of epitaxial films or single crystalline samples, but almost negligible in those for thin film samples with textures of weak or no preferred orientations.

For the general measurement with 2D detector, nothing can be placed between sample and detector (Fig. 6(a)), so it is difficult to avoid scattering signals except...
from a sample itself, such as scattering from sample stages, or from dome covers or window materials of high temperature stages, etc.

The 2D detector will also work as a powerful tool of analysis via wide angle RSM measurements for epitaxial films with lattice distortions or tilting. High angular resolution will not be required for RSM measurements for these films, rather, data for the wide area in reciprocal space will be preferable. These requirements for measurements are complementary with the features of 2D detectors with TDI mode.

The geometries of RSM measurements are schematically shown in Fig. 7. The area marked with red lines is that for RSM measured by 2θ/ω scans combined with χ axis step-tilting (RSM with skew geometry for asymmetric lattice planes), which can be measured with 2D detector. The relative χ angle range will be ±5 to 10 degrees at one 2θ/ω scan. Iterative motions of a goniometer as repeating χ steps and 2θ/ω scans, will lead to obtaining data for a wide area RSM.

As explained in the 6th lecture “Small angle X-ray scattering measurement”\(^{(15)}\) and 7th lecture “Pole figure measurement”\(^{(16)}\), 2D detectors have great advantages in these measurements, especially for GI-SAXS measurements\(^{(15)-(17)-(19)}\).

For the measurement using a 2D detector, it is generally required to set the incident X-ray beam as small as possible to be a point shape. However, this does not necessarily mean that a line-focused X-ray source should be changed to a point-focus source. For example, a combined set of narrow limit slits and PSCs (Parallel Slit Collimator) or collimators can be adopted for this purpose. Additionally, the SmartLab system can be equipped with a unique functional tool “CBO-f” as a converter from a line-shaped beam to a point-shaped beam in the incident optics.

Moreover, a line-shaped incident beam itself can be adopted for RSM measurements where higher signal intensities are preferred over the resolution. The data image with this optics configuration will be suffer from defocusing due to the umbrella effect, but the center of the image will not be affected as much, as shown in Fig. 8.

3. Summary of this lecture course

With this, the eight lectures for basic measurement techniques of X-ray characterization of thin-film samples have been published. Titles for all lectures are listed as below.

I. “Overview” 2008, Vol. 24, No. 1
II. “Out-of-plane diffraction measurement” 2008, Vol. 25, No. 1
III. “High resolution X-ray diffractometry” 2009, Vol. 25, No. 2
IV. “In-plane XRD measurement” 2010, Vol. 26, No. 1
V. “X-ray reflectivity measurement” 2010, Vol. 26, No. 2
VI. “Small angle X-ray scattering” 2011, Vol. 27, No. 1
VII. “Pole figure measurement” 2011, Vol. 27, No. 2
VIII. “Detectors and Series Summary” this lecture

Recently, thin film materials are exhibiting remarkable evolution and progress. It may be required soon to make the updating revision for the list of measurement examples (1st lecture, Table 2)\(^{(1)}\).

We have been asked many questions about measurement and analytical techniques from many users in the various fields. For the answers to each question, we have come to plan and edit this “X-ray Thin-film Measurement Techniques” lecture course. We hope these lectures will be helpful for many users, and may assist the thin film material research activity in the world.

References

\(^{(6)}\) T. Mitsunaga: *The Rigaku Journal (English version)*, 25 (2009),
No. 1, 7–12.


Introduction to single crystal X-ray analysis

1. What is X-ray crystallography?

1. Introduction

All substances around us consist of atoms. The types of atoms and their three-dimensional arrangement define the structure of materials, therefore the nature of materials. Since the properties and functions of materials relate directly to its structure, there exist extensive researches for various materials such as semiconductor, electronic, food, pharmaceutical, or life science related materials.

However, we can’t recognize the structure of materials at the atomic level because of the limited resolution mainly due to the wavelength, as long as we see objects with our eyes by using visible light. For example, we neither can distinguish a grain of table salt from that of sugar by their atomic level structures, nor can have a clear view of the turtle shell-shaped 6-membered rings (benzene rings) by just staring at the medicine for colds.

Recently, elucidation of molecular structures is becoming more common owing to the developments of various measurement techniques (See Table 1). Nuclear magnetic resonance (NMR), mass spectrometry (MS), and infrared spectroscopy (IR) are the typical examples. However, these spectroscopic techniques derive just a list of partial structures, and it is sometimes difficult to deduce the three-dimensional structure of a whole molecule. On the other hand, it is the molecular structure itself that is derived from the single crystal X-ray analysis (SCXRD). The single crystal analysis provides a unanimous conclusion that sometimes puts an end to arguments over molecular or crystal structures.

However, it is the fact that X-ray crystallography tends to be averted despite its efficiencies because it gives an impression to be difficult method requiring special knowledge. Through this series of articles, we would like to deliver an introductory course to the single crystal X-ray analysis to those who are not familiar with this technique. The course includes what X-ray crystallography is, what X-ray crystallography reveals, and how to solve the problems you will encounter in the future.

2. History of X-ray crystallography

The history of crystallography starts with the discovery of X-rays in 1895 by Wilhelm Conrad Röntgen whose name is used as a synonym of the X-ray photography in the medical field. In 1912, Max von Laue observed the first X-ray diffraction pattern from the copper sulfate crystal. Next year, William Lawrence Bragg and his father William Henry Bragg discovered the Bragg’s law that makes it possible to calculate the positions of the atoms. In the 1910s, the structures of inorganic materials including sodium chloride, mineral and diamond were determined by the X-ray crystallography. The single crystal analysis was first applied to physics and chemistry.

In the 1920s, organic materials including hexamethylenetetramine were subjected to the study of X-ray crystallography. In the 1940s, biological materials, such as cholesterol, vitamin B12, and penicillin, were studied. The structure of insulin, a biological molecule, was finally solved by Dorothy Hodgkin in 1969 after 35 years of elaborating work.

In 1950, John C. Kendrew and Max F. Perutz solved the structure of heme-containing proteins, myoglobin and hemoglobin, respectively. In 1953, James D. Watson and Francis Crick published the double helical structure of nucleic acids based on the X-ray diffraction patterns of DNA.

In the early 1980s, Ada Yonath started working on ribosome. It is still fresh in our memory that the Nobel Prize in Chemistry in 2009 was awarded to Dr. Yonath for her contribution to the elucidation of the underlying mechanisms of protein synthesis along with Dr. Venkatraman Ramakrishnan and Dr. Thomas Steitz.

3. Why single crystal? Why X-ray?

By the way, why is a single crystal necessary and why are X-rays used for X-ray crystallography? For viewing the three-dimensional structure of molecules quantitatively, it is required to satisfy the following three
conditions.

1) Types of atoms are distinguishable.
2) The position of the individual atom which is buried inside of the molecule can be determined even if the molecule is large like proteins.
3) The view of molecules from as many different directions as possible can be obtained. In addition, the relative positions among the molecules from different view can be determined precisely.

It is the X-ray crystallography that satisfies these conditions and currently it is the most popular analytical method to solve the three-dimensional structure of the molecule. The third condition is certainly satisfied by the nature of crystals.

Now, let's proceed to how to determine the molecular structure using X-rays. Talking of X-ray crystallography, you may have seen an image with black dots as shown in Fig. 1. These dots contain information to construct the molecular model of material you'd like to clarify its structure at the atomic level. The first step of X-ray crystallography is to collect several thousands to several tens of thousands of these dots. From the positions and intensities of these black dots, an atomic model can be determined.

The fundamentals of viewing the object using X-rays are similar to those of using a microscope for viewing the color and shape of the object. Let's think about using an optical microscope first. When parallel rays of light hit an object, only a shadow is projected to the screen. So you can’t look the details of the object. At the same time as the shadow image is projected, most of the light is reflected. When we look at an object using an optical microscope, the objective lens gather and focus scattered light from the object. As a result, we can get the magnified and real image of the object.

By the way, visible light is an electromagnetic radiation with wavelength ranging from 400 to 700 nm. These wavelengths are visible to human eyes. However, submicroscopic objects requires shorter wavelength. Most molecules usually have dimensions in the range of a few to several dozens of Ås, and are far too small to be seen with the visible light. A typical wavelength used for crystallography is roughly 1 Å (0.1 nm). This is in the order of the covalent bonds and the radius of an atom. This is the reason why X-rays must be used for crystal structure determination.

Neutron radiation which is a kind of ionizing radiation can be used for viewing the object at the atomic level as well as X-rays. Although X-rays are scattered by the electrons of the atom, neutrons are scattered by the nuclei. For the determination of the positions of light atoms, chemical composition, or magnetic structure, neutron diffraction is superior to X-ray diffraction. However, there are limitations to use the neutron diffraction because of the weak diffraction intensities due to the extremely small scattering cross section. For example, it demands a considerably larger crystal than that of X-ray diffraction and it takes a long time for measurement. On the other hand, the ability of scattering X-rays is proportional to the atomic number (number of electrons), and thus X-ray diffraction is more suited to the structure determination of various materials from inorganic to organic compounds including proteins.

Let's get back to X-rays. There are no lenses to focus X-rays. However, one can substitute the calculation for the objective lens to reproduce a magnified image. (Strictly speaking, there is an optical element, Fresnel zone plate, which can focus X-rays and is widely used in the X-ray microscope.)

When parallel X-rays irradiate an object, only shadow image is projected on the screen. At the same time, most of the X-rays are reflected similar to visible light. It is called scattered X-rays. Scattered X-rays induce the phenomenon of coherent interference because X-rays can be thought as waves, and result in X-ray diffraction. If the object is a crystal, X-ray diffraction forms diffraction spots to the specific directions on the screen (black dots shown in Fig. 1). Each diffraction spot carries contribution from all atoms in the original object, and it is necessary to collect all diffraction spots to recreate the real image.

The information about the positions and the intensities of diffraction spots is recorded on the screen, so-called a “detector”. Previously, the scintillation counter was used to measure the X-ray diffraction, and it could collect only one diffraction at a time. Recently, thanks to the development of two-dimensional detector, a large number of diffraction spots can be collected at a time, allowing it to reduce the measurement time substantially.

As shown in Fig. 2, based on the positions and the intensities of collected diffraction pattern, electron density distributions in crystals can be obtained after the calculation corresponding to the lenses in the microscope. X-ray crystallography assumes that atoms are present at the electron density maxima. Determination of positions of atoms, or atomic coordinates, results in a molecular model. The step of mathematical calculation might sounds difficult, but there is nothing to worry about performing this calculation because of the recent development of

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**Fig. 1.** X-ray diffraction pattern of single crystal.
4. Methods

Three fundamental facts to understand the principles of X-ray crystallography are:

a) The X-ray scattering of materials is caused by the electron density $\rho$, and the scattering amplitude is the summation of scattering wave from an each electron. The scattering intensity is proportional to the square of the amplitude.

b) Electron density $\rho$ within the crystal has a periodicity, which is virtually an infinite repetition in three independent directions.

c) Materials consist of atoms and the electron density of atoms stays similar even in different materials.

Among the equations derived from the facts listed above, the three most basic equations are the next three equations;

$$|F(K)|^2 = I(K) \quad (1)$$

$$F(K) = \int_V \rho(r) \exp\{2\pi i (K \cdot r)\} dv \quad (2)$$

$$\rho(r) = \frac{1}{V} \int_K F(K) \exp\{-2\pi i (K \cdot r)\} dv_K \quad (3)$$

It is a natural feeling that you don’t want to deal with difficult mathematical evaluation if possible. All you have to do is to keep the three equations above in your mind at least at the beginning of understanding X-ray crystallography.

The right-hand side of Eq. (1) can be obtained directly from the diffraction measurements. The $F(K)$ on the left-hand side is called structure factor, which is involved in the atomic positions directly. Eq. (2) shows that the structure factor can be calculated from the electron density $\rho$. On the other hand, Eq. (3) shows that the electron density within the crystal can be obtained from structure factors. It is important to know that the atomic positions are derived from this electron density.

However, Eq. (1) gives only the absolute value of $F(K)$ ($|F(K)|$), but the $F(K)$ is generally defined as a complex number; $F(K) = |F(K)| \exp\{i\phi(K)\}$, where $\phi(K)$ is phase, as represented in Eq (2). Electron density cannot be determined from Eq. (3) readily because of the loss of phase information in the diffraction experiment. This is so-called the “phase problem”, and a large part of X-ray crystallography is devoted to finding correct phases.

Therefore, it is needed to determine the phases in some way. The direct method is almost uniquely employed to solve the phase problem for small molecule crystals. This methods estimate phases statistically from the amplitudes of the normalized structure factor. There are other methods for solving the phase problem in addition to the direct methods. One is the Patterson function which uses the square of the structure factors, that are intensities, as Fourier coefficients to eliminate phases, because the phase problem arises from using structure factors in the first place. This method is utilized in the heavy-atom methods which is applied to solving a structure containing heavy atoms and the Patterson search methods by rotating and then translating the Patterson function calculated from a known structure to match that from an observed intensities. Additionally, the heavy atom isomorphous replacement method is used for protein crystals. With any one of these method, the key to the successful phasing is to collect accurate diffraction data to higher resolution (at higher diffraction angle).

5. Procedure

Now that you understand the principle, let’s take a look at the flow diagram of single crystal X-ray analysis briefly (summarized in Fig. 3). Further details and technical descriptions in each step will be discussed in the successive articles.

5.1. Crystallization

The first and often most difficult step is to obtain an adequate crystal. In the crystallization, you have no choice but to proceed by taking the trial and error approach. It is independent from the development of the hardware and software. The truth is that obtaining only one well diffracting crystal assures good results.

Previously, a relatively large crystal was required for the diffraction measurement. However, small crystals with dimensions of 0.05 mm cube or smaller are becoming measurable by an in-house system. In addition, although it is said that a cube shaped crystal is preferable, yet a needle-like or a plate-like crystals can be used. The shape of the crystals is not critical in these days due to the development of robust absorption correction software.

5.2. Data collection

In the second step, diffraction data need to be collected on an X-ray diffractometer. The crystal is placed in the X-ray beam and the intensity of every
diffraction spots is recorded by rotating the crystal. For the techniques of mounting crystals, please see the reference\(^{(11)}\).

Once the crystal-like objects are acquired, try out a diffraction experiment. As is often the case with real experiments, diffractions are fuzzy or a crystal is twinned, even though the appearances of crystals are good. In contrast, it sometimes happens that excellent diffraction patterns can be observed from bad-looking crystals.

In the case of twinned crystals, it is possible to perform the data processing using advanced software\(^{(12)}\). However, crystals low in quality often leads to the struggle in the next step, solving the structure. If possible, such a problematic crystal should not be used for the data collection. You should take the trouble to change the crystal or may have to explore the crystallization conditions in some cases. 80% of the X-ray structure analysis may be considered to be finished if good crystals are obtained.

### 5.3. Solving a structure

After the data collection, the third step is to solve the structure. The information from the data collection is passed to the structural analysis program and the atomic level structure will be obtained finally. It is the most exciting moment that molecular structure appears on the computer screen.

People may think that the only intensity data is required for structure analysis. However, at least the chemical composition of your sample is necessary. In the cases where the constituent of the molecule is unknown, it is basically hard to conclude the crystal structure. So, the X-ray crystallography is the technique better at solving the crystal structure than at identifying the types of atoms.

As described in chapter 4, the elaborate and difficult calculations are performed in this step. Fortunately, however, software development provides the “black box” method, allowing us to perform the structure solution just like solving a puzzle.

The data are combined computationally with complementary chemical information to produce an electron density map. Then, atoms are fitted to the electron density map. After repetition of phase refinement and model fitting, the final refined atomic model can be obtained—now called a crystal structure. Nowadays there is a piece of software which automatically executes every step, and it takes only minutes or less before showing the molecular structure on the computer screen.

### 5.4. Creating a report

The information provided by the final model is atomic coordinates and temperature factors for each atom. With this information, one can easily calculate the bond distances and angles, and draw the molecular model and the Ortep diagram. Temperature factors, otherwise known as the thermal vibration parameters, describe the anisotropic vibrations of atoms.

International Union of Crystallography (IUCr) defines a file format called CIF for easy exchange of crystallographic information. Most program packages have a capability to output the final model in the CIF format.

Finally, the model may be submitted to a public database prior to publication—such as ICSD (Inorganic Crystal Structure Database), CSD (Cambridge Structural Database), or PDB (Protein Data Bank). The PDB is open to the public.

### 6. What reveals?

What does the single crystal X-ray analysis reveal? As well as determining the molecular structure, single crystal X-ray analysis reveals the chirality of a molecule.

The primary information is the molecular structure. Diamond, graphite and fullerene are the molecules which equally consist of carbon atoms alone, but their molecular structures are completely different. Having the same constituent atoms doesn’t always mean to carry out the same function. And thus, investigating how the differences in the molecular structure effect on the materials with specific functionality helps us to design the new materials with desired functions. Furthermore, in the drug discovery, elucidating the three-dimensional structure can greatly contribute to the molecular design and refinement of the leads.

Next is the chirality. There are molecules which can’t be superposed on its mirror image. It is called chirality. Human hands are the most familiar example of chirality. The molecule having a chirality is called a chiral molecule. The physical and chemical properties of two molecules in different handedness are almost the same, but the biological effects are sometimes quite different. Thalidomide is one the most famous cases caused by the chiral molecule. One of the two chiral molecules has teratogenicity. You will find the importance distinguishing the chirality.

Third is the molecular arrangement. A crystal is a solid material formed by the arrangement of constituent atoms or molecules in a periodic repetition extending in all directions. Even if the constituent molecule is the same, it sometimes happens that the molecular arrangements of resulting crystal vary depending on...
the crystallization conditions. It is called packing polymorphism. Interestingly, the solid state properties such as melting point and the solubility alter because of the difference in the molecular arrangement. For example, the differences in the molecular packing of drugs results in differences in solubility, and leading to different medicinal effects. It is crucial to know the molecular arrangement in material design. In fact, there are many researches—such as modulated structure by altering the arrangement of anthracene molecules within the crystal\(^{(13)}\), absorption mechanisms of gases going into the void space in the crystal arising from the specific combination of molecules\(^{(14)}\), and nonlinear optical materials which modulate incident wavelength\(^{(15)}\).

7. Concluding remarks
Single crystal X-ray analysis uses the phenomena of interference and diffraction of X-rays which arise from scattering by the electrons in the atoms. Furthermore, the electron density \(\rho\) is calculated from the diffraction intensity \(I\), and the average three-dimensional arrangement of molecules or atoms in the crystal is revealed.

In the old days, you might have needed to have much knowledge and techniques on the crystallization, data collection and solving the structure including the fundamentals in crystallography for carrying out the X-ray crystallography by yourself. However, times have changed. The X-ray crystallography has become a freely usable technique for anyone with a little knowledge, because of the astonishing progress in both hardware and software.

The atomic world is beautiful. Once you could look into such a wonderful world by your own efforts, you will definitely become fascinated with this world. We wish we could invite you all into our world through this series of articles.

References

Simultaneous measurement system of thermogravimetry-differential thermal analysis and photoionization mass spectroscopy equipped with a skimmer-type interface
—TG-DTA-PIMS—

Tadashi Arii*

1. Introduction
Although thermal analysis has wide range of applications, to understand thermophysical and chemical changes at a macro-molecular level, it is necessary to perform complex measurements, such as hyphenated methodology combined with other spectroscopic methods to obtain specific micro-molecular information on reaction products(1)–(4). An example of a complex measurement is the thermogravimetry-differential thermal analysis-mass spectrometry (TG-DTA-MS), which is a simultaneous measurement technique composed of thermogravimetry-differential thermal analysis (TG-DTA) combined with mass spectrometry (MS) through an interface system. This process has garnered attention as a major thermoanalytical technique(5)–(7). It is suitable for the qualitative analysis of the different gases evolved in response to heating a sample in the TG-DTA process.

This article aims to propose a novel thermoanalytical method that integrates a “skimmer-type interface” and a “photoionization method” in order to overcome the serious disadvantages of the conventional TG-DTA-MS. A simultaneous thermogravimetry-differential thermal analysis and photoionization mass spectrometry (TG-DTA-PIMS) system equipped with a unique skimmer-type interface has been thus successfully developed.

The principles and the instrumental composition of the TG-DTA-PIMS are described in detail and compared with those of the conventional TG-DTA-MS. To demonstrate the effectiveness of the technique, the results of its application to the evolved gas analysis of typical polymeric materials are presented.

2. Principle
2.1. From Capillary-type interface to Skimmer-type interface
A photograph and the structural diagram of the skimmer-type TG-DTA-PIMS are illustrated in Fig. 1. An interface is necessary for gaseous transport to accurately inject the gaseous compounds evolved from the TG-DTA sample chamber into the mass spectrometer. Various devices are necessary in this interface to prevent condensation, side reactions, and delay in evolution of gases. This complex composition of the interface results in limitations of the analysis, which governs the sensitivity and analytical accuracy.

In general mass spectrometry, the interface is a structure that creates a difference in pressure between the TG-DTA sample chamber at atmospheric pressure and the MS vacuum chamber in order to operate in a vacuum. The conventional TG-DTA-MS employs a capillary-type interface. The capillary-type interface is a relatively long narrow tube connecting both modules, and it adopts the principle that the injection tube is
injected into the MS chamber by the effect of the jet toward the skimmer-type interface and efficiently sample together with the carrier gas are transmitted line. Through heating, the evolved gases from the as well as the MS ion source are arranged in a straight position and two orifices of the skimmer-type interface by the vacuum pump. As shown in Fig. 1, the sample vacuum MS chamber, and the space between the two vacuum. The inner tube is directly connected to the high pressure under 10⁻³ Pa. In the capillary-type interface, transformation of the gas in the inner injection tube becomes uncertain if the interface path length is too long. Furthermore, shortening the capillary decreases the tube diameter resulting in easy occurrence of gas selectivity. Therefore, these factors must be optimized. Considering ease of use and maintenance of a general-purpose instrument, the interface is often constructed with a length of 1–2 m. The holding temperature of the interface is determined by considering re-condensation and transformation of the injected gas as well as the user's safety; therefore, the upper limit is usually set below 300°C. However, if the boiling point of the gasification products exceeds this interface temperature, the gases re- condense within the interface and are trapped internally. On the other hand, increasing the interface temperature to more than 300°C will lead to problems such as gas transformation due to secondary reactions. This may be due to surface activation caused by the degradation of the inner wall of the interface tube and the acceleration of secondary reactions between the activated pyrolyses. In case of unknown samples where the prediction of the boiling points of the gases is impossible, the evolved gases may condense and/or be transformed within the interface, which often interferes with the measurement results.

Consequently, because of the limitations of the capillary-type interface, the conventional TG-DTA-MS was mainly used initially for inorganic materials and ceramics. However, in recent years, TG-DTA-MS analysis has been applied to organic compounds such as polymer resins, highly functional polymers, and pharmaceuticals. In particular, polymer characterization is often performed by a traditional method called pyrolysis gas chromatography which may be influenced by the restrictions of the capillary-type interface. For this reason, the skimmer-type interface was introduced. This interface solves the potential problems and limitations of the capillary-type interface as described below in detail.

As shown in Fig. 2, the skimmer-type interface consists of two concentric ceramic tubes with orifices in which the orifice diameter of the outer tube is smaller than that of the inner tube. The interface connects the two devices, one at atmospheric pressure and the other at vacuum. The inner tube is directly connected to the high vacuum MS chamber, and the space between the two tubes exists as a differential vacuum structure evacuated by the vacuum pump. As shown in Fig. 1, the sample position and two orifices of the skimmer-type interface as well as the MS ion source are arranged in a straight line. Through heating, the evolved gases from the sample together with the carrier gas are transmitted toward the skimmer-type interface and efficiently injected into the MS chamber by the effect of the jet separator principle. In this way, high-precision gas analysis becomes fundamentally possible because the interface length connecting the sample chamber under atmospheric gas flow and the MS high vacuum chamber is minimized and, therefore, negligible.

Because the differential vacuum source of the skimmer-type interface is located in the furnace in close proximity to the sample, the temperature of the gas injection chamber and the sample temperature are thermally programmed under the same environment. Consequently, problems such as re-condensation and transformation of evolved gases or gas leaks in the interface path can be avoided.

As a result, because the skimmer-type interface and the sample can be heated to the maximum operating temperature of the module, components with boiling points higher than the interface maintenance temperature can be measured; lack of this feature inevitably restricts the high-temperature utility of the capillary-type interface. These are the advantages offered by the skimmer-type interface compared with the conventional capillary-type interface.

With the abovementioned advantages, use of the skimmer-type interface for the analysis of evolved gases greatly enhances instrument adaptability to broader classes of organic compounds, including polymer resins. However, because many organic compound gases will be simultaneously measured, the gas detection mass spectra may be more complicated, and therefore, data interpretation becomes more difficult.

2.2. From Electro impact ionization method to Photoionization (soft ionization) method

Traditionally, the gaseous species introduced into the MS by evolved gas analysis-mass spectrometry (EGA-MS) have been elucidated by the electron ionization (EI) method of 70 eV. Although a gaseous molecule is ionized by colliding with an accelerated electron by the EI method, a part of the generated molecular ion further decomposes, and consequently, the molecular ion is observed simultaneously with the fragment ions. When multiple gases are ionized simultaneously, and the resulting fragment ions mutually overlap, although the fragment ions give significant information about the structure of the molecule, the apparent mass spectrum may be too complicated.

As mentioned above, qualitative analyses of complex organic species formed by the pyrolysis of polymeric

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materials using conventional EGA-MS with EI become substantially more difficult because many kinds of pyrolysates may evolve simultaneously or continuously by heating. This means that the fragment ions generated as a result of the higher ionization potential of EI often obstruct the identification of the gaseous species formed by heating.

In order to differentiate the mixed multiple evolution gases, use of separation and quantitative techniques such as gas chromatography-mass spectrometry (GC-MS) can be effective\(^{(14)}\). However, this prevents real-time monitoring and measurement of the amount of evolved gases as a function of temperature. In addition, because the thermal hysteresis of the evolved gases may change, it is difficult to confidently state that the gaseous components evolved from the sample are traced directly and accurately without modification.

The essential problem of differentiation of multiple organic gaseous species evolved simultaneously from the sample by conventional EGA-MS using EI still remains. In order to solve this issue, one feasible approach is the use of MS with a selective and soft (fragment-free) ionization method, such as chemical ionization, laser desorption ionization, ion attachment\(^{(15)}\), and photoionization (PI), all of which control fragmentation during the ionization process.

Single-photon ionization with a vacuum ultraviolet (VUV) light source is a particularly soft and selective ionization method\(^{(16)}-^{(18)}\), suited well for the detection of both aromatic and aliphatic species. The PI process that is used to distinguish mixed gases evolved simultaneously in real-time, is described in the following paragraphs.

The PI process is the simplest electron transfer reaction induced by photoabsorption. In this process, ionization occurs when a photon of sufficient energy is absorbed by a molecule, resulting in the formation of a positively charged ion and an electron. The associated energy is described by the equation

\[
E = hv
\]

where \(h\) is Planck’s constant and \(v\) is the frequency of the incident photon.

It is a process whereby a molecule at the ground state (\(M\)) is irradiated with a photon of sufficient energy resulting in molecular excitation to an ion level. Therefore, ionization occurs as follows:

\[
M + hv \rightarrow M^+ + e
\]

where \(M\) is an ionizable species and \(hv\) is a photon with sufficient energy to ionize \(M\).

In general, although a gaseous molecule is ionizable when the energy of the supplied photon is at the same level as the ionization energy of the molecule, the molecular ion thus formed dissociates if the energy of the photon is relatively higher than that, and ionization cannot occur if it is too low. The ionization potentials of typical components are listed in Table 1\(^{(19)}\). The ionization potentials of many organic compounds are generally 8–11 eV and are lower than those of inorganic compounds such as water vapor, nitrogen, oxygen, carbon monoxide, and carbon dioxide. When the energy of the irradiated photon is larger than the ionization energy and smaller than the dissociation energy, ionization of almost all organic compounds becomes possible by the VUV lamp source of approximately 10 eV. Thus, because only the parent ions of the gas molecules are observed in the resulting fragment-free mass spectrum, it is possible to directly differentiate multiple gases evolved by using the discrete information on their molecular ions. Furthermore, this fragment-free ionization information is also useful when observing individual organic species in the presence of ionizing components such as oxygen, nitrogen, and water vapor in the atmosphere being measured. This is especially valuable for TG-DTA-MS conducted in various heated atmospheres, including oxidative and experimental humidity conditions\(^{(20)}^{(21)}\).

### Table 1. Ionization potentials of typical organic

<table>
<thead>
<tr>
<th>Compound</th>
<th>E(eV)</th>
<th>Compound</th>
<th>E(eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Argon</td>
<td>15.76</td>
<td>Benzene</td>
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<td>Oxygen</td>
<td>12.07</td>
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<td>Nitrogen</td>
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<td>Naphthalene</td>
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<td>Anthracene</td>
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<td>Water</td>
<td>12.61</td>
<td>Phenanthrene</td>
<td>7.86</td>
</tr>
<tr>
<td>Methane</td>
<td>12.60</td>
<td>Biphenyl</td>
<td>8.27</td>
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<tr>
<td>Ethane</td>
<td>11.52</td>
<td>Biphenyle</td>
<td>7.53</td>
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<td>Propane</td>
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<td>Butane</td>
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<td>7.95</td>
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<td>9.71</td>
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<td>8.50</td>
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<td>Tetrachloromethane</td>
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<td>n-Butylamine</td>
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<tr>
<td>Tetrabromomethane</td>
<td>10.31</td>
<td>Aniline</td>
<td>7.72</td>
</tr>
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</table>

3. Construction Details

Figure 3 shows the schematic diagram of a quadrupole mass spectrometer equipped with a 30 W VUV photoionization source for PIMS. The VUV lamp...
directly irradiates through the MgF₂ window toward the MS ionization chamber, where the emission line is λ = 112.6 nm, and the maximum photoionization energy is 10.2 eV(22). Moreover, the EI source is also attached in the MS ion source chamber making it possible to arbitrarily select EI or PI ionization mode. Nevertheless, because the PI source is installed within the MS vacuum chamber, regardless of the interface type, it can be used for TG-DTA-PIMS.

The following different types of commercially available reagent grade polymers were used without further purification: polymethylacrylate (PMMA) (Kanto Chemical Co., Inc.), polystyrene (PS), high-density polyethylene (HDPE) and Nylons (Scientific Polymer Products, Inc.), including polycaproamide (Nylon6), polyhexamethyleneadipamide (Nylon6/6), polydodecamethyleneadipamide (Nylon6/12), polyundecanoamide (Nylon11), polylauroamide (Nylon12), and poly(m-xylene adipamide) (NylonMXD6). Commercially available Nylon resins, including cable ties (INSULOK), tubes, and edge guards, were used to characterize the original materials of the polymers.

The samples were weighed into a platinum crucible, and then heated in high-purity helium gas (99.999%) at a flow rate of 200 mL · min⁻¹.

4. Results and Discussion

4.1. Thermal degradation of polymer resins

The thermal degradation of polymers is a typical example where several complex organic gases simultaneously evolve upon heating. The application of thermal degradation to commercially available reagents is described below.

When degraded alone in the pure state, PMMA breaks down in a very simple manner. It has been established that homolysis occurs at some points in the polymer backbone and is followed by depolymerization to monomers. Figure 4 shows the TG-DTA-PIMS results for PMMA at 20°C · min⁻¹ in a helium atmosphere. PMMA breaks down in a very simple manner in which homolysis occurs at some points in the polymer backbone followed by depolymerization to the corresponding monomers. Through the soft-ionization effect of PI, the molecular ion of the monomer (m/z = 100) can be clearly seen. In addition, the existence of molecular ions from some minor impurities, such as undecene (m/z = 154) and phenyl benzoate (m/z = 198), are directly detected at high sensitivity near 200°C.

On the other hand, PS, when degraded alone at temperatures exceeding 300°C, it undergoes chain scission, depolymerization and both intra- and intermolecular transfer. A styrene unit, when present in copolymers, does not become involved in inter-unit reactions. When pyrolysis was carried out using PMMA in the presence of an equal weight of PS, no evidence of any interactions were found.

Figure 5 shows conventional TG-DTA-EIMS data for a mixture of PMMA and PS, at a heating rate of 20°C · min⁻¹ in a flow of dry helium. The pyrolysis of the sample proceeds via a single step with the appearance of an inflection point in the course of the reaction. A
The comparison of the mass spectra obtained at 400°C and 412°C in the total ion current (TIC) chromatogram are shown in Fig. 5(b). The apparent mass spectra are completely different from each other, and suggest that different gaseous species were evolved in each temperature region. However, both of the mass spectra consisted of molecular ions along with numerous fragment ions formed by the high ionization energy of the EI. Since the detected fragmentation and molecular ions were mutually mixed, the identification of the evolved gas species was complicated and difficult.

Figure 6(a) illustrates the TG-DTA-PIMS of a PMMA and PS mixture, measured at a heating rate of 20°C min\(^{-1}\) in a flow of dry helium, while Figure 6(b) shows the mass spectra obtained for the TIC chromatogram at 385°C and 405°C.

![Figure 6. Typical TG-DTA-PIMS results at 20°C·min\(^{-1}\) for blended sample of PMMA and PS in a helium atmosphere and mass spectra obtained at TIC curves at 385°C and 405°C.](image)

The thermal behavior of both ions differed and was not synchronized to each other. The pyrolysis of the blended sample proceeded via PMMA followed by PS without any interaction. Based on these results, it can be concluded that the pyrolysis of the blended sample of PMMA and PS progressed via two independent reactions which were respectively controlled by depolymerization to form a monomer.

By the introduction of the PI fragment-free ionization method to TG-DTA, the elucidation of the pyrolysis mechanism of blend of polymers became very clear because only molecular ions of the pyrolyzates, produced by degradation of the sample were observed.

Thermal degradation of PE progresses through intramolecular radical transfer and/or transfer hydrogenation, and the thermal degradation products consist of \(n\)-paraffins, which are saturated hydrocarbons, and the principal components, \(n\)-1-olefins, which are derived from unsaturated hydrocarbons with a large carbon number distribution. The thermal degradation analyses of HDPE measured by TG-DTA-PIMS are shown in Fig. 8. By the skimmer-type interface effect, the apparent mass spectra clearly illustrate the detection of ion clusters of \(m/z > 200\), indicating the presence of high boiling point compounds. In the EI spectra, it is difficult to directly distinguish the evolved gas components because of overlapping signals resulting from fragmentation during ionization. On the other hand, by controlling fragmentation using the PI method, the presumption that each component is associated with an unfragmented molecular ion becomes possible in real-time because the high boiling point components, having more than 20 carbons, can be directly detected in the molecular ion state.

### 4.2. Characterizing thermal degradation of polymers

Nylon is a polyamide consisting of several amide-linked aliphatic monomers. A comparison between the results from EIMS and PIMS for pyrolysates of Nylon6 obtained by TG-DTA-EI/PIMS is shown in Figs. 9 and 10. It is difficult to individually characterize each...
pyrolysate in the spectrum acquired with the EI method because of mutually overlapping fragment ions in the lower m/z region, as shown in Fig. 9. On the other hand, because the PI method controls the fragmentation of the molecules during ionization, the resulting pyrolysates are detected as the molecular ions that originate directly from the structure of Nylon6, as shown in Fig. 10. Therefore, the identification of pyrolysates can be made directly from the apparent mass spectrum. As a result, caprolactam, a monomer generated using the PI method (m/z = 113), is definitively characterized in the mass spectrum.
Subsequently, related experiments with five different types of Nylons (Nylon6/6, Nylon6/12, NylonMXD6, Nylon11, and Nylon12) that have similar structures were carried out using TG-DTA-EI/PIMS. The spectral differences between EIMS and PIMS are compared as shown in Fig. 11. Because the observed EI mass spectra seem similar to each other, it is difficult to directly characterize them and to differentiate the individual Nylons. On the other hand, because the PI spectra are composed of only the molecular ions from the degradation products that originate from the polymer backbone structure, which are unique to each sample, the individual Nylons can be definitively identified. Nylons are easily assigned by their characteristic molecular ions in the mass spectrum [(Nylon6/6, cyclopentanone (m/z = 84) and hexanenitrile (m/z = 97); Nylon 6/12, caprolactam (m/z = 113) and hexanenitrile (m/z = 97); Nylon 6MXD, xylene (m/z = 106); Nylon11, undecanlactam (m/z = 183); and Nylon12, lauryllactam (m/z = 197)]. In this way, the fragment-free feature of PIMS enables simplified characterization of the degradation products of polymers because of its sensitivity for the minute structural changes between the samples. Consequently, it is useful for fingerprint analyses owing to its unique PI features.

The following is an illustration of a fingerprint analysis of the components of a commercially available resin. Figure 12 shows a photograph of the three different types of commercially available Nylon resins; namely, cable tie (INSULOK tie), edge guard, and tube. On the other hand, Figure 13 illustrates a comparison of the TG-DTA-PIMS results for their respective evolved gases. The spectral differences are obvious from the PIMS results, although these differences are few in spectra from EIMS, making sample identification difficult with the latter. Comparing the PIMS spectra obtained from the reagent Nylons mentioned above, the cable tie, edge guard, and tube can be easily assigned as Nylon 6/6, Nylon 6, and Nylon 12, respectively.

Thus, as shown in this fingerprint analysis, the unique features of PIMS allows easy differentiation of resins, and its advantages are demonstrated in the rapid identification of organic compounds such as polymers.

7. Conclusions

It is confirmed that the new TG-DTA-MS instrument equipped with a skimmer-type interface and PIMS using a VUV lamp as the photon source has been successfully developed. The application limit of conventional thermoanalytical methods is decreased remarkably and the analytical needs have been greatly increased to mainly polymer resins and organic compounds. Features such as the quality of the evolved gases and the reproducibility of the data are also very important. Furthermore, the prevention of gas condensation throughout the gas injection pathway is remarkably improved by the skimmer-type interface. Significantly, the spectra produced using this system are generally unaffected by interfering ions, such as fragment ions because only the molecular ions of a mixed gas are ionized selectively. Because the fragment-free spectra from PIMS enable direct characterization of polymer degradation products by focusing on the minute structural differences between the samples, the new instrument will be very useful for fingerprint analyses.

In EGA-MS, the combined methodology of the skimmer-type interface and soft-photoionization technique will greatly contribute to quantitative analyses in near future.
Simultaneous measurement system of TG-DTA-PIMS equipped with a skimmer type interface

References

( 4 ) M. Mittleman: Thermochimica Acta, 166 (1990), 301–308.
1. Introduction
Total reflection X-ray fluorescence (TXRF) spectrometry is widely used in semiconductor manufacturing processes for nondestructive analyses of metallic contamination on wafer surfaces. Sensitivity requirements for such devices have increased in recent years. Currently, metallic contamination in advanced device manufacturing processes is controlled to $10^8$ atoms/cm$^2$. In a conflicting trend, the growing diversification of semiconductor devices has generated demand for low-cost equipment with advanced functionality rather than sensitivity. The TXRF 3800e is a low-cost, total reflection X-ray fluorescence spectrometer with advanced functions that meets these demands.

2. Low cost

2.1. Sealed X-ray tube
The TXRF 3800e incorporates a sealed X-ray tube to reduce the frequency of filament changes and X-ray source maintenance compared to conventional equipment, thereby improving uptime.

2.2. SDD (Silicon Drift Detector)
The TXRF 3800e is equipped with an SDD (Silicon Drift Detector) that requires no liquid nitrogen cooling. This detector eliminates labor charges associated with liquid nitrogen replenishment as well as the initial investment for peripheral equipment, such as a liquid nitrogen generator. Operating costs are therefore lower.

2.3. Single-target, dual-beam system
Two types of excitation X-rays are software-selectable: W-L$\beta$ (9.67 keV) and H.E. (High Energy excitation X-rays obtained by monochromatizing the 24 keV portion of the continuous spectrum). Switching excitation X-rays allows optimized measurement of various elements with a single X-ray tube, ranging from transition elements to heavy elements. This reduces operating costs compared to conventional systems based on multiple X-ray tubes. Figures 1 and 2 show typical measurement examples.

2.4. Reduced space requirements
The TXRF 3800e has a footprint of 1 m x 1 m (main unit) for the most effective use of valuable clean room space.

3. Multifunction

3.1. Sweeping-TXRF
Sweeping-TXRF capability, optional with the TXRF 3800e, enables high-speed, full-surface mapping. Figure 3 shows a measurement example. Full-surface measurements with this function make it possible to detect contamination on wafer surfaces that might otherwise be missed by conventional five-point or nine-point measurements.

3.2. ZEE-TXRF
ZEE-TXRF capability, standard with the TXRF 3800e, enables zero edge exclusion measurements, right up to the wafer edge. As shown in Figure 3, ZEE-TXRF
is capable of detecting contamination at the wafer edge that is overlooked by conventional equipment.

4. Performance

4.1. Detection limits

Table 1 shows the detection limits of the TXRF 3800e for representative elements. For most of the elements, the TXRF 3800e offers a detection limit of the order of $10^9$ atoms/cm$^2$.

<table>
<thead>
<tr>
<th>Element</th>
<th>Fe</th>
<th>Ni</th>
<th>Cu</th>
<th>Hg</th>
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<tbody>
<tr>
<td>TXRF 3800e</td>
<td>$1.6 \times 10^9$</td>
<td>$1.6 \times 10^9$</td>
<td>$3.2 \times 10^8$</td>
<td>$2.0 \times 10^8$</td>
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</table>

4.2. Repeatability

Table 2 shows the results of repeatability measurements (ten repeats including incident angle adjustments) for a sample with contamination levels of the order of $10^{10}$ atoms/cm$^2$, contamination levels typically encountered in real-world processes.

<table>
<thead>
<tr>
<th>n</th>
<th>Fe</th>
<th>Ni</th>
<th>Cu</th>
<th>Cu</th>
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</table>
1. Introduction

PDXL is a one-stop powder diffraction analysis software suite\textsuperscript{(1)}\textsuperscript{(2)}. The advanced engine and user-friendly GUI have been satisfying both experienced and novice users since PDXL was released in 2007.

PDXL provides various analysis tools such as automatic phase identification, quantitative analysis, crystallite-size analysis, lattice constants refinement, Rietveld analysis, \textit{ab initio} structure determination, etc.

In May 2011, Rigaku released a new version “PDXL 2” with several excellent new features, which are introduced in the following sections.

2. New features

2.1. Fundamental parameter method

The peak shape in a powder diffraction pattern would appear to be a delta function if measured under ideal conditions. In reality, the peak shape changes depending on a number of measurement conditions: wavelength distribution of the source, optical systems, slit conditions, crystallite size and strain, and so on. The peak shapes obtained from measurements made under real-world conditions are described using an empirical function such as a split pseudo-Voigt function, or a split Pearson VII function which has a good agreement with the obtained peak shapes.

The fundamental parameter method (FP method) is a method to calculate peak shape by convolution of the shapes caused by all the instrumental and sample conditions as shown in Fig. 1.

The advantages of the FP method are as follow:

![Image of PDXL 2 software]

Fig. 1. Some examples of broadening caused by instrument and sample conditions. a: spectroscopic profile of X-ray radiation; b: effect of focus size of X-ray generator; c: axial divergence effect; d: flat-specimen effect; e: sample transparency effect; f: effect of receiving slit size; g: crystallite size and size distribution; h: a resultant profile convoluted the effects a–g.
1. Correct peak positions can be obtained from a profile where many peaks overlap;
2. In quantitative analysis, more correct quantities can be obtained from a sample consisting of many phases;
3. Sample information, such as crystallite size, size distribution and strain, can be obtained precisely without using any standard reference materials in the measurement as shown in Fig. 2.

2.2. Phase identification using COD

The Crystallography Open Database (COD)\(^3\) is a free, public-domain database of the crystal structures published in International Union of Crystallography, Mineralogical Society of America and so on.

Earlier versions of PDXL could only use paid databases such as ICDD’s PDF-2 to perform automatic phase identification. PDXL 2 can incorporate both ICDD/PDF-2 and COD\(^4\), adding the COD library of over 150,000 crystal structures to PDXL 2’s already substantial capabilities.

2.3. Wizard for ab initio crystal structure analysis

Recently, there have been many published examples of \textit{ab initio} crystal structure analysis performed on powder diffraction data. This development is attributed primarily to significant improvements in PC processing speed and in the efficiency of the algorithms used for structure determination.

PDXL has so far provided all of the functions required for \textit{ab initio} crystal structure analysis, such as indexing (ITO, DICVOL and N-TREOR programs), structure determination (direct methods of EXPO2009, direct-space methods of EXPO2009 or PDXL, and charge flipping method) and structure refinement by the Rietveld method.

Now the “Structure Analysis Wizard” is available in PDXL 2 to provide support and guidance for users undertaking the complicated procedure of structure analysis, particularly of organic compounds. This wizard system will make it possible for even the beginner to achieve analytical success (Fig. 3).

2.4. Clustering function

The PDXL clustering feature can group multiple scan data based on the similarity of powder diffraction patterns and peak positions, and displays the grouped data in an easy-to-read tree. This is particularly effective when it comes to classifying and screening the data from a large number of scans.

References

\(1\) Rigaku Journal (Japanese version), \textbf{40} (2009), No.1, 36–40.
\(2\) The Rigaku Journal (English version), \textbf{26} (2010), No. 1, 23–27.
\(4\) The database for PDXL can be downloaded from the COD homepage (http://www.crystallography.net/).