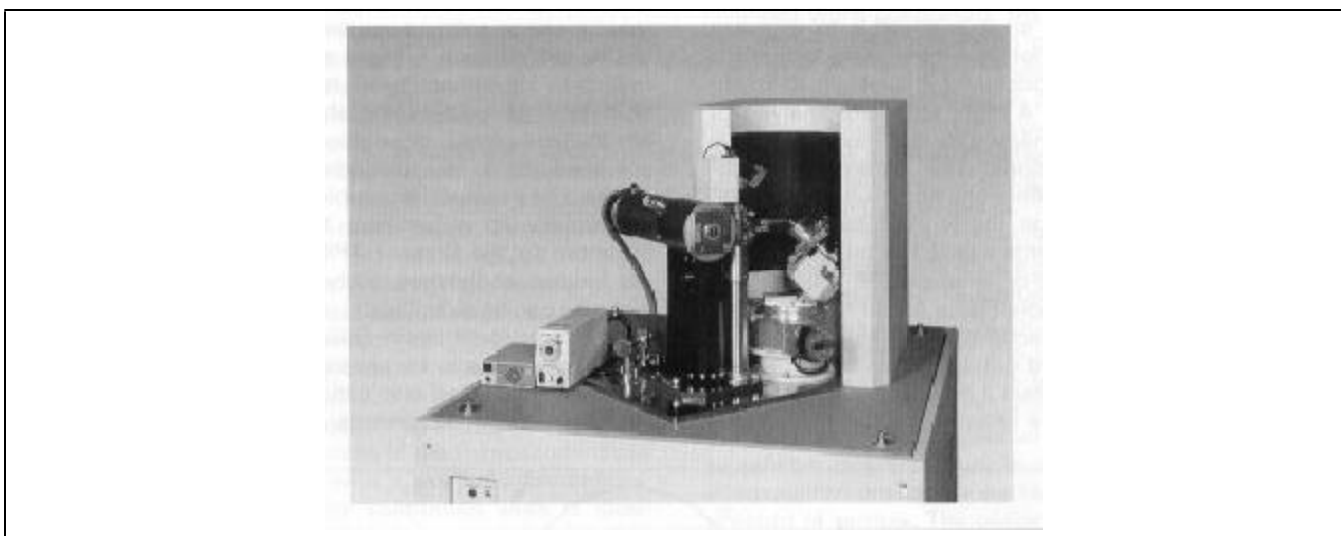

Product Information

D/max-RAPID:

Fast X-ray Diffractometer with Area Detector



1. Introduction

X-ray microdiffraction describes the analysis of microscopic quantities of materials and the examination of selected microscopic areas on larger specimens. Microdiffraction finds wide application in materials research and development. Material properties such as chemical phase, degree of crystallinity, crystallite size, texture, and residual stress can be characterized with microdiffraction that also offers the possibility to examine the spatial variation of material properties,

Rigaku developed the D/max-RAPID, a fast X-ray diffractometer with area detector, to meet demanding materials analysis requirements. In this system, a cylindrical imaging plate (IP) is set at 12.74cm from a sample and covers 204E in 2θ and from 88E in P (at $2\theta=90E$) to 360E in P (at $2\theta<45E$). An T axis carries either a fixed-angle P goniometer fixed at 45E or a $3-P$ circle.

The fixed axis goniometer can be configured with several sample stages to extend P to 90E for stress work or add automatic X-Y mapping capabilities. These configurations enable rapid measurement of a two-dimensional X-ray diffraction image over a broad

range. The IP offers several advantages over linear position-sensitive detectors (PSD's), curved PSD'S, and multiwire detectors. Advantages include a large area to view oriented diffraction patterns and a large dynamic range for thin film/substrate studies. The D/max-RAPID permits the analysis of microareas and microquantities as well as bulk samples.

2. Features

(1) The D/max-RAPID can measure a 2-D X-ray diffraction image over a broad range, covering 204E 2θ horizontally and $\pm 45E$ 2θ vertically from the direct beam position. In transmission, the complete area is recorded simultaneously, 360E in P (the complete Debye ring) with $2\theta<45E$. In reflection, only the forward scatter of the plate is used. One can observe Laue spots (multiple wavelength data) and Debye ring images from powders not obtainable from ordinary powder diffractometers. The 2-D image can show partial Debye rings, indicating texture in systems as diverse as polymers and thin films on silicon wafers. Integrating out the P dimension of the 2-D image produces an intensity versus 2θ plot, the conventional powder pattern, which can be analyzed by standard and specialized powder diffraction analysis software

for phase identification, quantitative analysis, crystallite size determination, percent crystallinity, etc.

(2) Debye rings contain information on crystallite orientation, so it is possible to evaluate preferred orientation by integrating around a Debye ring (at a constant 2θ) to obtain an intensity versus ϕ plot. A more complete analysis of texture requires many different incident angles and many reflections. The D/max-RAPID observes multiple reflections and multiple orientations on each image, thereby reducing the number of measurements needed to produce multiple pole figures. For example, 36 images will give a complete pole figure for all transmission pole figures of reflections at $2\theta < 45^\circ$.

(3) With standard diffraction instruments, it is not possible to obtain a powder pattern of a microarea by in-plane (N-axis) rotation alone since the number of grains illuminated may be small in relation to the size of the X-ray beam. The low grain-size-to-beam-diameter ratio makes it necessary to oscillate the sample along two axes with either scintillation or 1-D position-sensitive detectors. With the D/max-RAPID, the 2-D detection plane (IP) plays the role of one axis so that a powder pattern can be obtained by sample inplane rotation alone. This system is therefore effective for qualitative analysis of tiny crystals (transmission method) and microareas (reflection method). Two-axis oscillation, N and T, can also be

selected. This data collection method is useful for qualitative measurements of highly oriented grains. The sample mount and the measurement method are selectable according to the sample type. Various sample mounts for reflection or transmission methods are available. Mounts are also available for films, fibers, blocks, and plates. In addition, different stages are available to accommodate various experiments. For example, if sample mapping is to be performed, an automated X-Y stage can be mounted to the D/max-RAPID. Between different holders and stages, all types and shapes of samples can be examined.

(4) The incident beam collimators enable different spot sizes to be projected onto the sample. The illuminated area can be from 0.5 mm to 10 : m in fixed increments (see specification section). To aid in selecting the area for examination, a color CCD camera is used to view the specimen. The video image can be viewed in a window on the control computer and saved to disk. An optional black-and-white monitor can be installed on the instrument to position the sample if the computer console is inconvenient.

3. Optical System

Fig. 1 shows the optical system of the D/maxRAPID. The incident optical system consists of a CCD camera and high intensity light. Exchanging

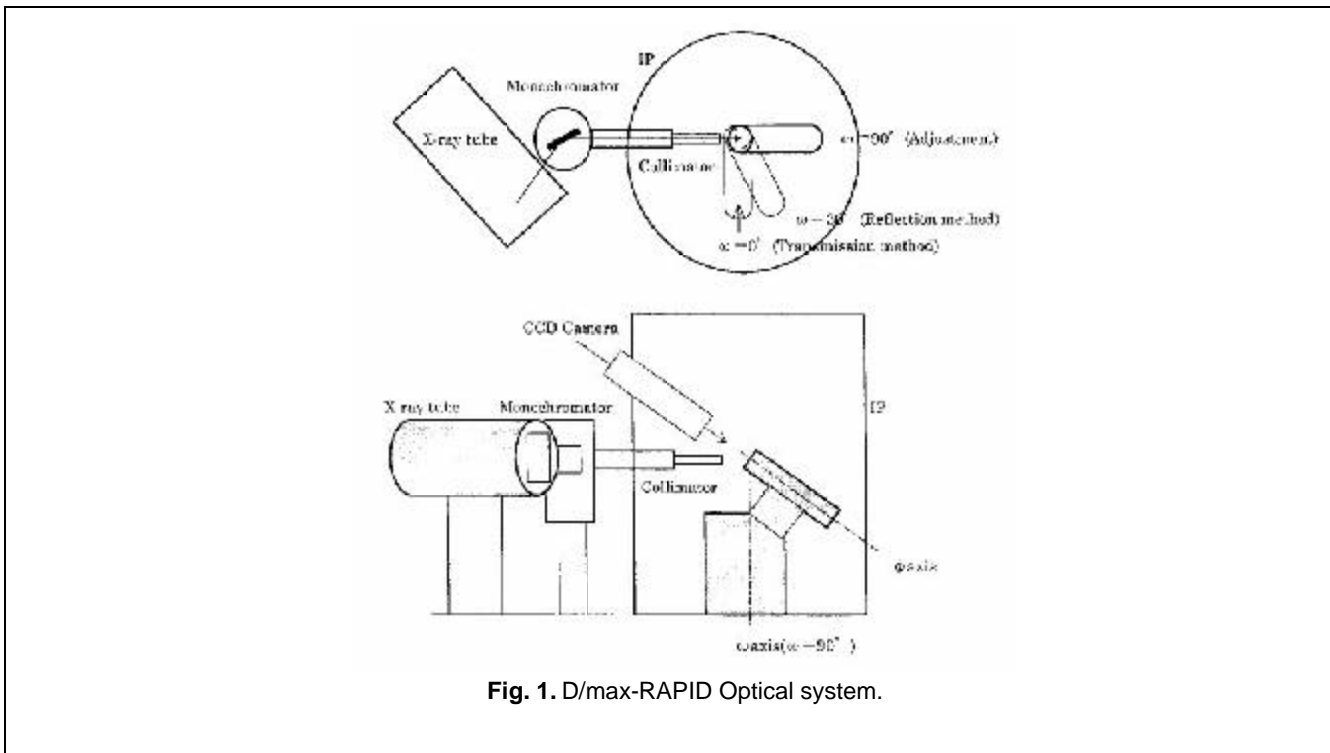


Fig. 1. D/max-RAPID Optical system.

collimators can vary the analysis area. As illustrated, the goniometer is a 2-axis system comprising the T axis, which coincides with the central axis of the cylindrical IP, and the N axis, which is inclined 45E to the T axis. The N axis serves as the sample in-plane rotation axis. The 45E inclination of this axis enables the IP surface to detect all diffracted rays over the whole 2 θ range and a large segment of ϕ . Moreover, a powder (reflection method) sample can be held at a 45E inclination much easier than a sample at 90E.

In order to visually identify the region to be measured, the optical axis must be adjusted to the point of intersection of the T axis, the N axis, and the X-ray beam. If the sample is not positioned at this point, there will be a Δ offset of the diffraction pattern as a function of the T angle. Field adjustment of the microscope cross hairs is performed with a small (50 : m) calibration slide. Once the calibration slide is positioned so that the object's center is invariant to rotation, the cross hairs on the CCD camera are adjusted to the object's center.

4. Measurement Examples

4.1 Polymer materials and Debye ring measurement by the transmission method

From the Debye ring, one can directly observe not only the grain size but also the preferred orientation. Fig. 2 shows Debye ring measurement images by the vertical transmission method along with ϕ -I data from three kinds of polymer materials. In the 2 θ -I data, peaks detected by integration along the Debye ring appear in a regular manner. With a conventional X-ray diffractometer (XRD), the intensity at the equatorial position is detected, so none of the diffraction lines can be detected in (c) POM. Historically, it has been difficult for conventional XRD to accurately measure crystallinity from polymeric materials having preferred orientation. Today, the D/max-RAPID enables measurement tantamount to 3-axis oscillation, thus improving the quantitative precision of such difficult measurements.

4.2 Diffraction pattern of a tiny single crystal (transmission/reflection method)

Fig. 3 shows differences in diffraction patterns of a tiny MoO₃ single crystal depending on the oscillation condition. Measurement of this sample in a stationary state without the monochromator resulted in a Laue pattern in (a). It shows diffraction due to continuous X-rays. In (b) and (c), the monochromator was used and 1-axis oscillation (N-axis rotation) and

2-axis oscillation (N-axis rotation and T-axis oscillation) were conducted, respectively. The resemblance of pattern (b) to pattern (c) shows, from the 2 θ -I integrated data, that the points (single crystal reflections) in pattern (a) can be integrated into a standard powder pattern. This indicates that a powder pattern of a tiny single crystal is obtainable by one-axis oscillation (rotation). The transmission method measurement can be used for identification of polymorphs, which in some processes are susceptible to preferred orientation. Quantitative analyses of these samples are difficult for conventional XRD instruments because of the intensity variation from sample to sample due to preferred orientation. The D/max-RAPID can obtain random patterns for these samples which will then lead to reliable quantification. In addition, this type of measurement can be performed with a small amount of sample. The optional automated X-Y stage can be used as a sample changer, enabling large numbers of samples to be examined for quality control.

4.3 Analysis example of micro areas

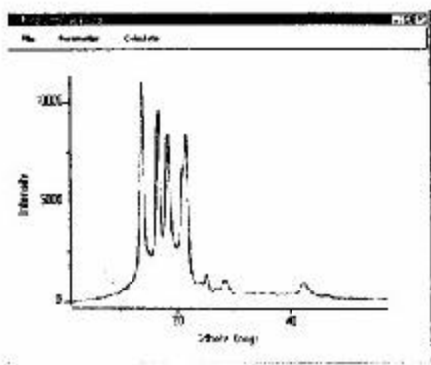
Fig. 4(a) is the observed image of a measurement section with a CCD camera. The cross point is the center of measurement. Fig. 4(b) shows the initial screen of D/max-RAPID measurement software. After a sample is mounted and measuring conditions are entered, the user will begin the measurement. Upon completion of the measurement, the IP data will be automatically read and stored. Automatic processing of the IP image to obtain a 2 θ -I diffraction pattern is also selectable. Fig. 4(c) shows multiple images of the measurement from points (A) and (B), identifying (A) as CuFeS₂ and (B) as Fe₇S₈.

5. Major Specifications

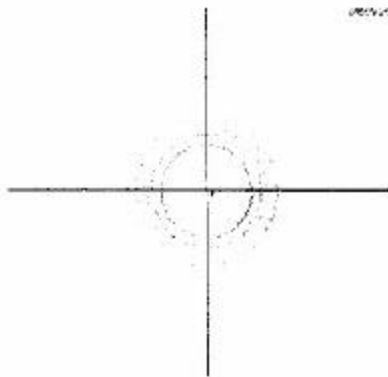
Table 1 shows the major specifications of the D/max-RAPID. Available as optional sample stages are an automatic X-Y stage and a vertical sample stage designed to allow X-Y motion with a sample held vertically. Moreover, a variety of sample mounts are available according to the measurement purpose, such as a sample mount for fiber and film and a low-background sample mount for extremely small quantities of sample.

6. Software

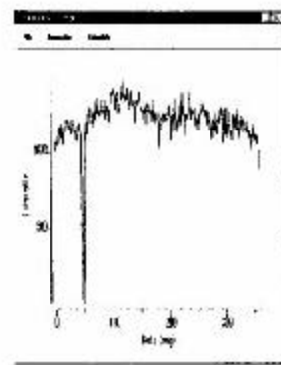
Newly developed Rapid/XRD software is a comprehensive package controlling the video image of the sample, data collection, and X-ray image processing. Processing tools enable the 2-D



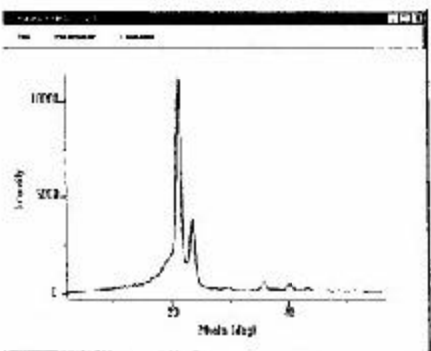
(a) PP (2θ-I data)



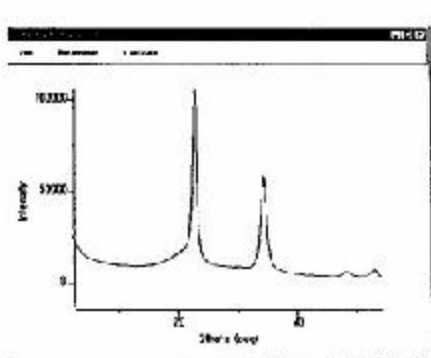
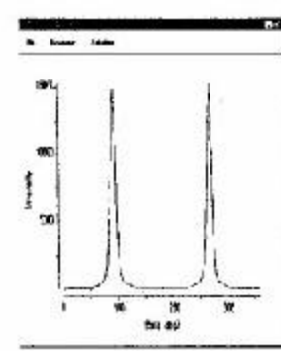
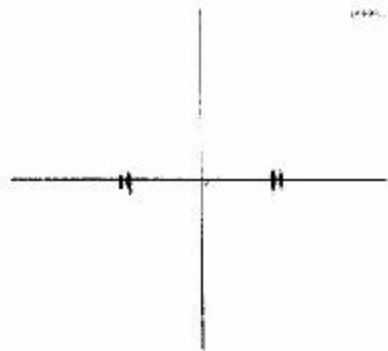
(Debye ring)



(β-I data)



(b) PE



(c) POM

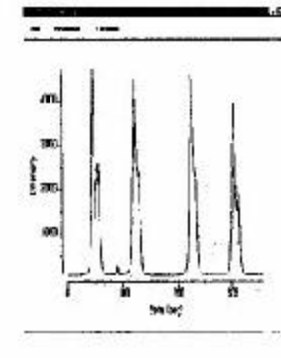
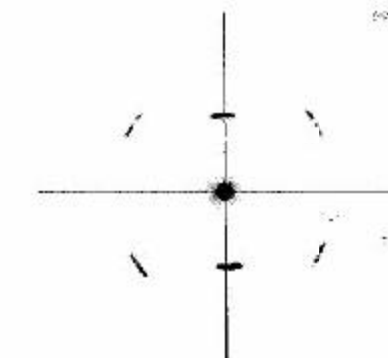
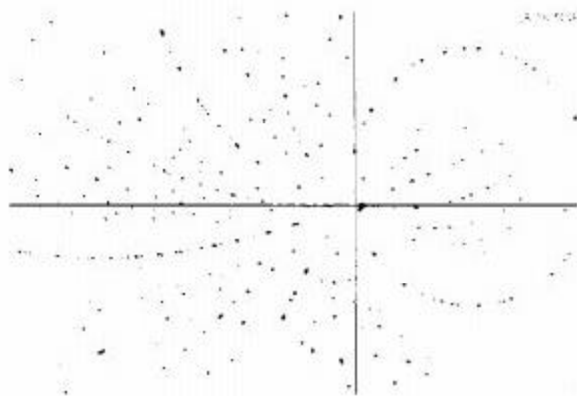


Fig. 2. Debye Ring Measurement Example of Molecular Materials by the Transmission Method.

Measuring conditions: X-rays (Cu, 40kV-50 mA), with monochromator 100 : m dia. Collimator (single), 500 sec exposure, N fixed, T=0E (transmission method)

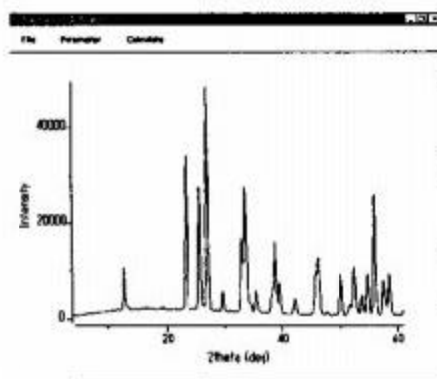
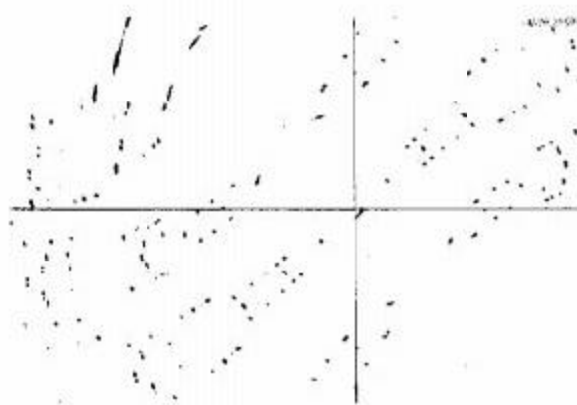
* A drop in intensity in β-I data of (a) is due to a beam stop.

diffraction image(s) to be reduced to 2θ-I, β-I, pole figures, or rocking curves for analysis with optional powder diffraction packages.

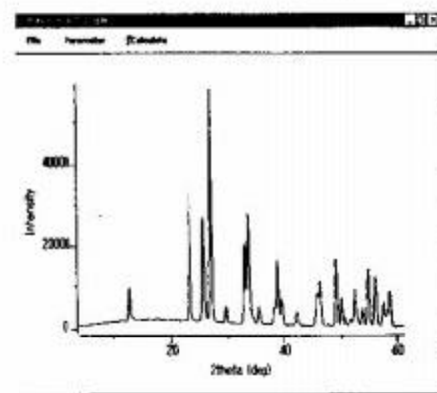
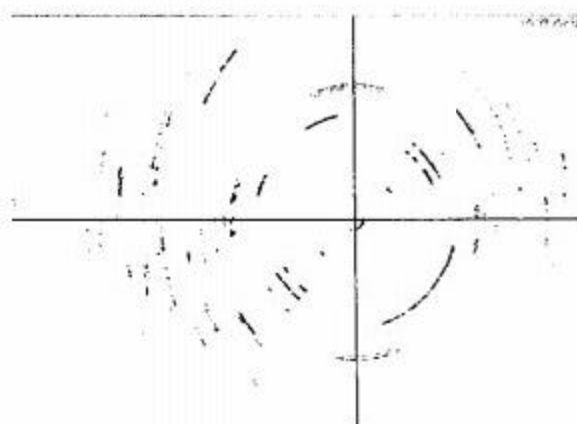


←Laue spots due to continuous X-rays

(a) No oscillation (without monochromator)

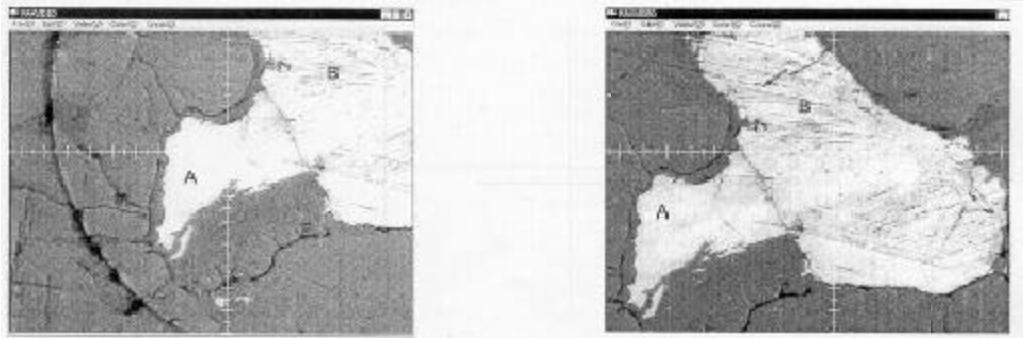


(b) One-axis oscillation (N: continuous rotation, T: fixed) with monochromator



(c) 2-axis oscillation (N: continuous rotation, T: 45E oscillation) with monochromator

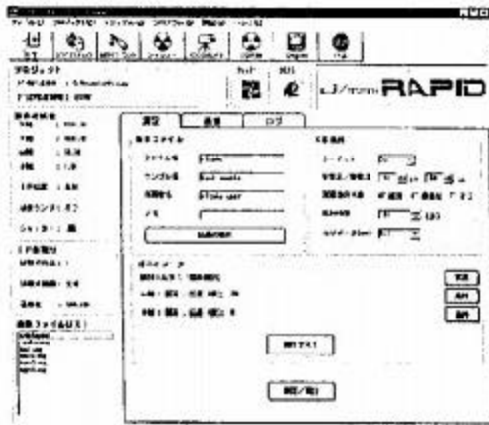
Fig. 3 Diffraction Image of a Tiny Single Crystal: Sample MoO_3 single crystal. Measuring conditions: X-rays (Cu, 40kV-50 mA), with monochromator 100 : m dia. Collimator (single), 500 sec exposure



(One graduation \varnothing 30 : μ m)

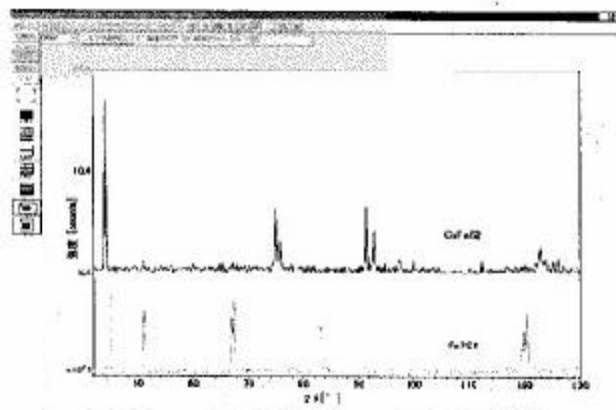
(a) image of measurement section: Measurement A

Measurement B



(b) Initial screen:
Measuring condition input

Measuring condition:
X-rays (Cu, 40kV-50 mA, V filter)
100 : μ m dia. collimator (single)
500 sec exposure
N: continuous rotation
T=25E (reflection method)

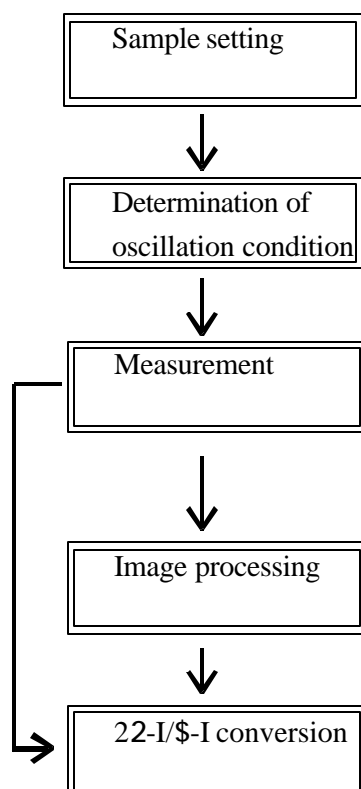


(c) Analysis result display by multiple recording: A (top): CuFeS_2 , B (bottom): Fe_7S_8 . Software: JADE

Fig. 4. Example of Microarea Qualitative Analysis

Table. 1. D/max-RAPID Specifications.

Model name	D-max/RAPID-S	D-max/RAPID-R
X-ray generator	Sealed X-ray tube 2kW	Rotating anode type 18 kW
Target	Select from Cu, Co, Cr and Mo.	
X-ray optics (monochromator)	Flat graphite monochromator	
Collimator	300, 100, 50, 30 : diameter (optional: 500 : m, 10 : m diameters)	
Goniometer driving range	N axis: 360E, T axis: -15E~+150E	
Sample adjusting range	X, Y-axes: " 5 mm, Z-axis: 10 mm (can accomodate 40 mm sample thickness)	
Sample alignment	With CCD camera (~200 magnification on CRT) zooming: optional	
Camera length	127.4 mm	
Measuring angle range	-60E ~ +144E (optional: -44E ~ +160E)	
IP size	466 x 256 mm	
Picture element size	100 x 100 : m	
Read-out time	80 sec	
Erase time	20 sec	
Read-out sensitivity	1 photon/pixel	
Computer	PC (Windows NT)	



Rapid/XRD

Input a sample holder to be used. Conduct sample centering while watching CCD camera.

Determine the oscillation condition of T, N axes suitable for sample

Input the sample name, filename, etc. And execute measurement. Exposure time: A few minutes with 300 : m collimator, about an hour with 30 : m collimator.

Display

Data is obtained as a 2-dimensional image. 3-D stereographic display and a conversion to general imaging

Data is converted to a 1-D profile. The 22-I data is for qualitative analysis, etc. And \$-I data is for calculation of preferred orientation.

Fig. 5. Flowchart of Measurement.