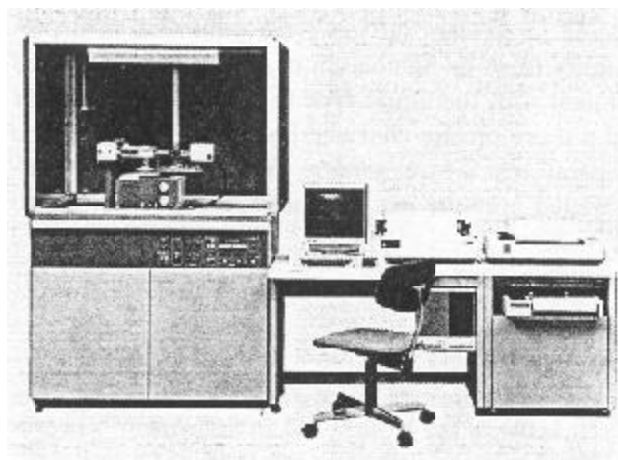


Product Information

NEW X-RAY DIFFRACTOMETER SYSTEM D/MAX-B SERIES

1. Introduction



The X-ray diffraction technique offers a tool for direct observation of the interatomic bonding state in matter, a characteristic which cannot be found in any other analytical means.

Table 1 shows the application fields of X-ray diffraction techniques that are classified according to the sample forms and are accompanied by the corresponding measuring devices. Powder X-ray diffractometers (PD) can be utilized most widely except for single crystal samples and as such are frequently used. The pole figure diffractometer, the high and low temperature diffractometers, etc. listed in the table respectively indicate the case that the related attachment is added to the PD system, which in this way shows a rare example that just one type of analyzer is capable of meeting diversified analytical purposes. Introduced here is the outline of Rigaku new D/max-B powder X-ray diffractometer system.

The D/max-B is composed of an X-ray generator, X-ray optics and goniometer, X-ray detector and counting system, and recorder for data recording or storing.

The X-ray generator in general use is either one of 3 kW output in the case of the sealed-off tube type or, 12 kW output in the case of the demountable tube type using the rotating anode. Regarding the rotating

anode X-ray generator, the procedures for filament replacement and maintenance of the vacuum system were considered troublesome in the past. The current model is so designed that it employs a cassette type filament, a magnetic fluid seal for vacuum sealing and a turbomolecular pump to supersede the oil diffusion pump resulting in substantial improvement in operational productivity, stability and service life. Its operating procedures are now as easy as those for the sealed-off tube type X-ray generator.

The X-ray source stability is less than 0.03% with the sealed-off tube type (3kW) and less than 0.05% with the demountable tube type (1.2 kW) for both kV and mA. The variations of this extent are negligible in the present-day X-ray measurement.

The goniometer operation is digitized by stepping-motor driving and is finely controllable up to $1/1000^\circ$ (θ axis) in the minimum feed of one pulse.

In the X-ray counting system the current role occupied by the scintillation counter as the detector is unlikely to be taken over by any other type of counter for the foreseeable future in view of its advantages in timewise resolution and counting efficiency. Indeed the SSD (Solid-state Detector) and the PSPC (Position Sensitive Proportional Counter) have excellent characteristics and are displaying high performance in specific applications, but their capabilities as a whole are still not so much as to substitute for the features of the angle dispersion method.

Regarding the improvement of the counting circuit a remarkable progress has been made for the past several years so that the linearity in counting efficiency is now obtainable to the extent of 10^5 cps.

Powder X-ray diffractometers are most often utilized for identification of compounds, confirmation of the crystal state, comparative examination of diffraction patterns, etc. in the initial research stage. In such instances the measurement of the diffraction patterns of large amounts of samples is often necessitated. Also, quick data collection is called for in case of measurement under high temperatures or when dealing with a sample which

Sample Form	Application Field	Measuring Device *	
Polycrystalline sample (Powder X-ray diffraction techniques) 1. Powder sample	Identification of compounds	PD, G, P, L, etc.	
	Quantitation of compounds	PD	
	Crystal structure of inorganic compounds	PD	
	Measurement of crystal grain size and crystal distortions	PD	
	Measurement of crystallinity	PD	
	Determination or measurement of lattice constant	PD, G	
	Measurement of component ratio of solid solution	PD, G	
	2. Polycrystal block sample	Measurement of texture	PF
		Determination of phase diagram	HT, LT, H
		Measurement of thermal expansion	HT, H
		Measurement of residual stress	MSF
Measurement of thickness of thin film		PD, G	
	Measurement of long-period structure	SAX	
Single crystal	Crystal structure analysis	AFC, W, PR, etc.	
1. Small single crystal	Precision measurement of lattice constant ($10^{-5} \sim 10^7$)	BG	
2. Large single crystal	Measurement of crystal distortions	LC, C	
	Observation of lattice defects (point defect, dislocation, stacking fault, etc.)	LC	
	Observation of crystal grain structure	LC, BB	
Others			
1. Non crystalline sample	Radial distribution analysis of noncrystalline materials	PD	
2. Liquid sample	Grain size measurement of solid phase,	SAX	
3. Colloidal and other grain-structure samples	liquid phase, colloid, etc.		
	Analysis of grain structure of polymers	SAX	
	PD Powder X-ray diffractometer	MSF X-ray stress analyzer	
	G Guinier camera	AFC Four-circle X-ray diffractometer	
	P Debye-Scherrer camera	W Weissenberg camera	
	L Laue camera	PR Buerger-precession camera	
	PF Pole figure diffractometer	LC Lang camera	
	HT High temperature X-ray diffractometer	C Kossel camera	
	LT Low temperature X-ray diffractometer	BG Bond goniometer	
	H High temperature X-ray diffraction camera	BB Berg-Barrette camera	
	SAX Small angle scattering X-ray goniometer		

Table 1. Application Fields of X-ray Diffraction Techniques and Measuring Devices

tends to change with the lapse of time. The different kinds of measurements shown in Table 1 will not produce the ultimate result unless some processing is made following data collection. Further, as mentioned above, since the same single unit is applied to multi-purpose measurement, it is unavoidable that inputting of the measurement conditions is diversified and troublesome. The new diffractometer system should cope with these problems properly. To resolve them it should be able to perform high-degree data processing and high-speed data collection. Also, its counting system should be highly productive in terms of operation.

2. Control System of the New D/max-B

Normally, the X-ray generator is provided with two or more X-ray windows. When a powerful X-ray generator like the Rigaku "Rotaflex" rotating anode X-ray generator is used, there are not a few cases that two different diffractometers each having a different measurement purpose are arranged to use each of the two X-ray windows located at right and left aiming at the effective use of the X-ray source. The control system shown in Fig. 1 is designed to control such two diffractometers concurrently. On this occasion either one of the two diffractometers can be the small

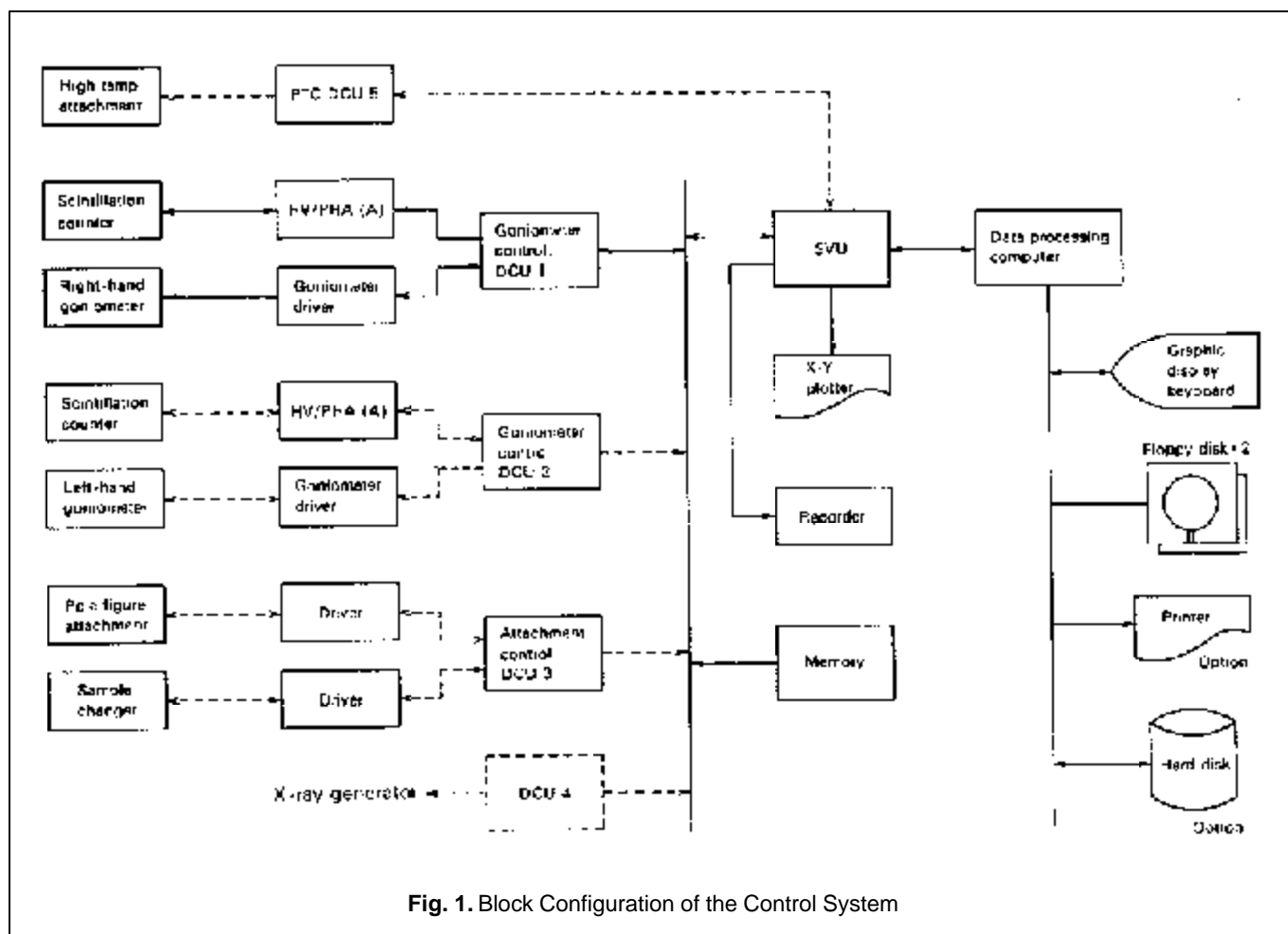


Fig. 1. Block Configuration of the Control System

angle scattering goniometer or the microdiffractometer. On the other hand, when two routine type wide angle goniometers are mounted instead, either one of them can be equipped with the pole figure attachment, high temperature attachment, or the like.

With the two diffractometers arranged at right and left, high-speed driving and high-speed data collection (max. 90°/min) can be carried out by means of the dedicated CPU and the control system DCUs (Device Control Units) self-containing 16 KB ROM and 16 KB RAM memories. These DCUs are organically combined with the supervising SVU (Supervisor Unit) so as to enable the associated operations. The instructions for measurement are given by a higher-graded host data processing computer.

The SVU possesses 32 KB ROM and 32 KB RAM and is capable of storing 50 sets, 10 sets, 20 sets, etc. of programs depending on each DCU. Through a command from the processing computer the associated operations for temperature control and diffraction data collection, for example, can be optionally con-

ducted with the indications of measurement parameters and combined information.

Regarding the real-time display of data coming from the two diffractometers, the data from either one of them can be optionally designated.

The data processing computer is made up of a 16-bit CPU playing the central part with 256KB main memory, two 1.2MB floppy disks (FPD), a printer, a color graphic display and a keyboard. A 10MB hard disk is available additionally when necessary. This data processing computer can execute a data processing program to be described in the next section even when the two diffractometers are operating. The measuring system is run by the background mode in this instance.

3. Software System of the New D/max-B

Figure 2 shows the program package of the new D/max-B system. The 'setting program' is designed for adjustment of the optics (zero alignment) and that of the high tension (HT) and the PHA of the counting system. These adjustment are made automatically ac-

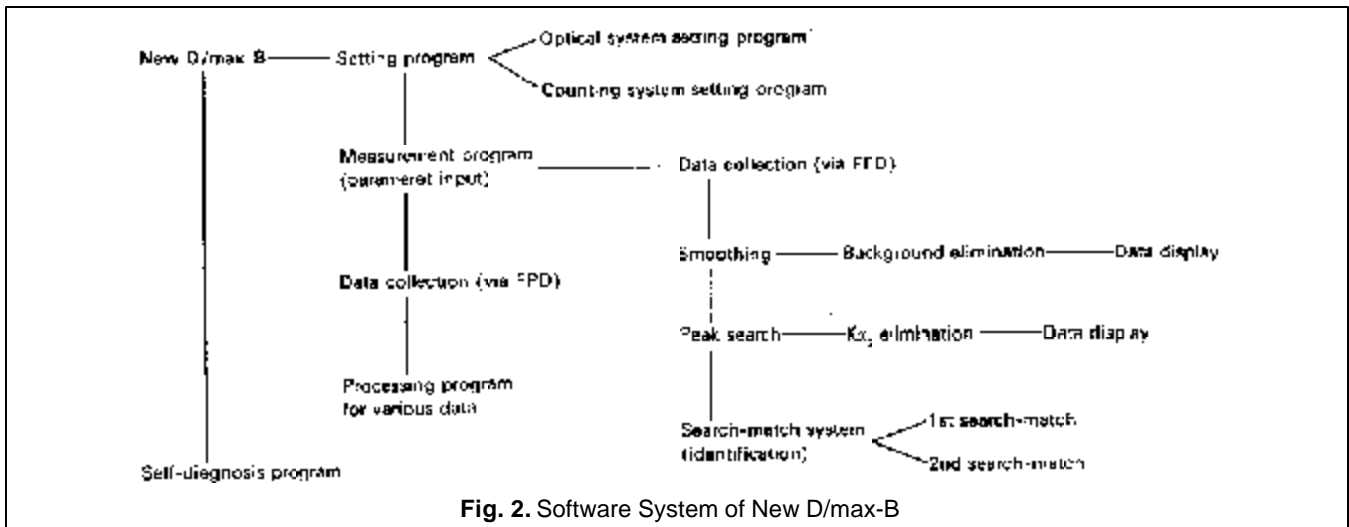


Fig. 2. Software System of New D/max-B

According to instructions from the host data processing computer excepting part of the optical alignment which requires auxiliary manual operation and should therefore be conducted by the operator according to

instructions from the computer. It is possible, however, to fully automate this operation by adding one more driving motor. The instructions from the computer are given via colored graphs on the graphic display, as illustrated in Fig. 3. Further, automatic adjustment of the PHA can be made using a reference diffraction peak upon completion of the optical alignment. The result appears on the display as in Fig. 4. The entries of all parameters for the measurement

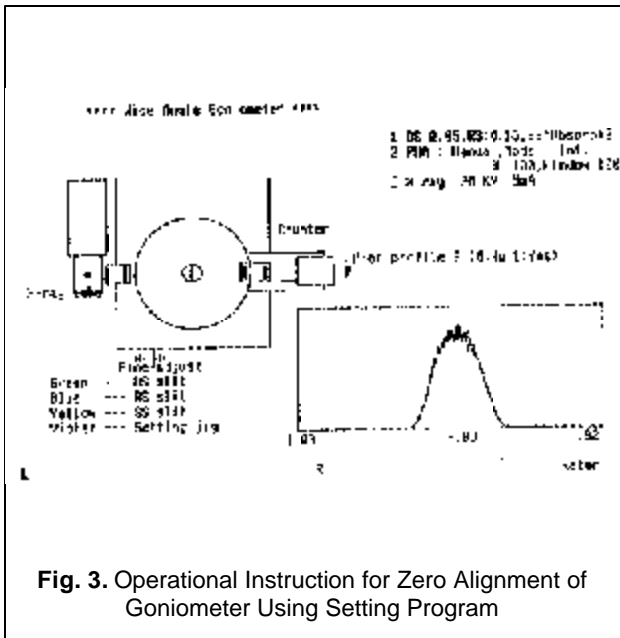


Fig. 3. Operational Instruction for Zero Alignment of Goniometer Using Setting Program

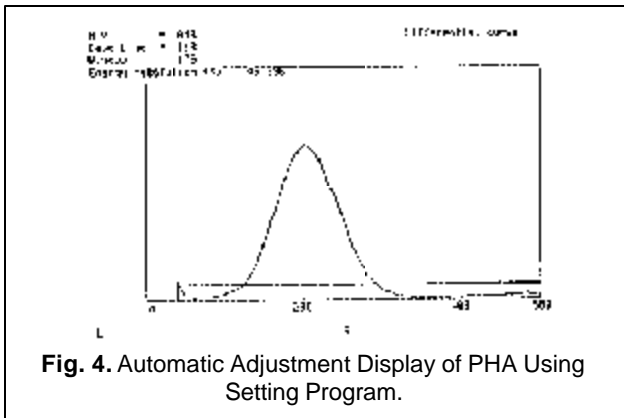


Fig. 4. Automatic Adjustment Display of PHA Using Setting Program.

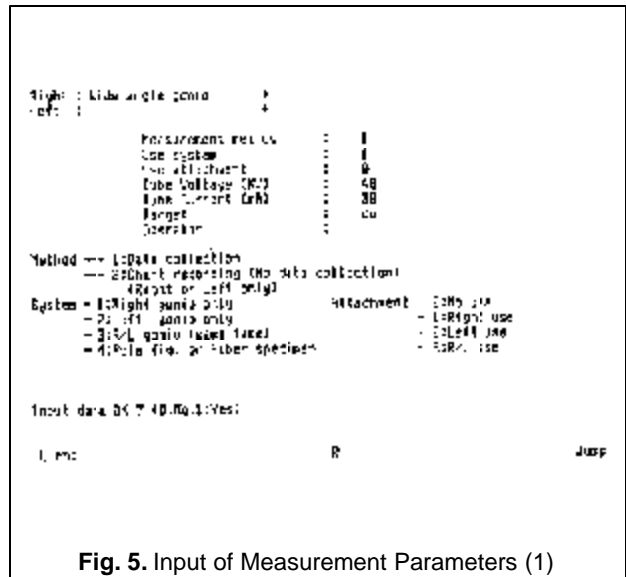


Fig. 5. Input of Measurement Parameters (1)

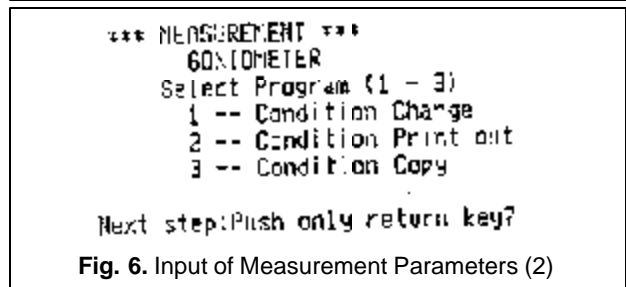


Fig. 6. Input of Measurement Parameters (2)

behind will oversmooth Y_j^* deteriorating the data quality. One way that permits the best use of many pieces of data around Y_j without impairing the data quality is to apply the least squares method to a tertiary polynomial and to make it hit the $2m+1$ data located around Y_j , and thereby to denote the calculated value of this polynomial as Y_j^* . This operation requires just the calculation of equation (1) by, for example, using the value of a quadratic curve for the weight function C_i , as in Fig. 9.

$$f_m \quad (1)$$

The new D/max-B system employs quadratic differentiation for the peak detection. Incidentally, to accurately determine the peak position when there exists an overlap of peaks, it is necessary to go through further procedures for peak separation by the iterative least square refinement of the peak position with the initial values of the peak position and peak number determined by quadratic differentiation.

Figures 10 and 11 respectively show an example of specifying the substance of data processing and that of the input of peak search condition. Further, Fig. 12 illustrates an example of the graphic display of raw

data and smoothed data. It is also possible to determine the smoothing condition while observing this display. In this case the time required for changing the smoothing condition for subsequent re-display is about two seconds. Table 2 shows an example of a

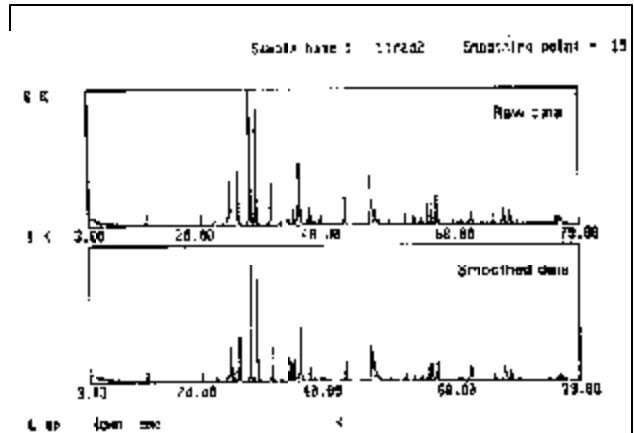


Fig. 12. Graphic Display of Raw Data and Smoothed Data

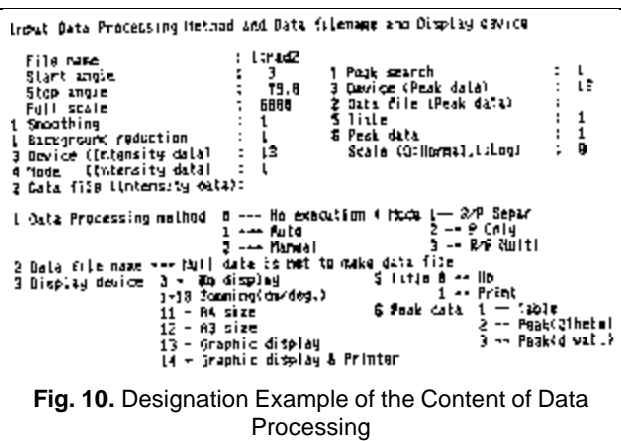


Fig. 10. Designation Example of the Content of Data Processing

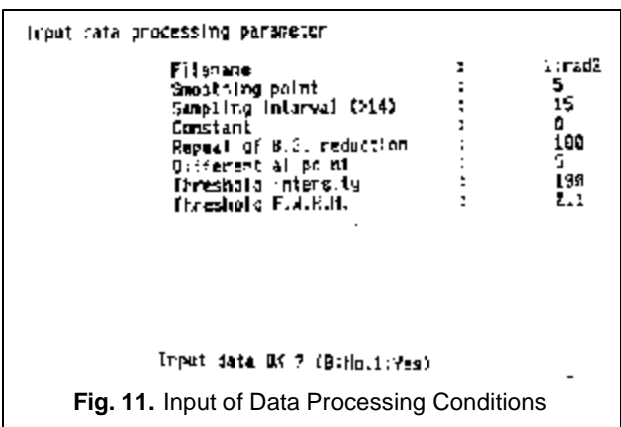


Fig. 11. Input of Data Processing Conditions

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**** Peak Search conditions ****
SAMPLE & FILE NAME = 1:rad2
THRESHOLD LEVEL = 100
THRESHOLD FWHM = 1.1

```

No.	THETA	INT.	FWHM	D	I/I0
1	12.380	234	0.265	7.149	3
2	20.880	315	0.135	4.254	4
3	22.100	150	0.135	3.050	7
4	25.220	1016	0.270	5.517	25
5	25.280	621	0.105	3.485	8
6	26.640	2322	0.165	3.245	32
7	28.440	7385	0.150	3.138	100
8	29.420	5521	0.120	3.026	73
9	31.740	1758	0.145	2.816	26
10	34.420	1177	0.120	2.605	16
11	35.150	1194	0.150	2.582	16
12	35.260	1377	0.150	2.477	14
13	37.740	640	0.135	2.359	9
14	39.540	172	0.135	2.275	3
15	47.560	1185	0.120	2.097	15
16	47.590	2162	0.120	1.922	23
17	48.040	459	0.150	1.884	6
18	48.660	160	0.105	1.878	2
19	48.540	215	0.155	1.876	3
20	48.840	125	0.125	1.870	2
21	50.140	154	0.120	1.819	2
22	52.850	413	0.120	1.751	4
23	52.700	185	0.120	1.737	3
24	53.900	240	0.120	1.701	3
25	55.100	208	0.140	1.667	7
26	56.130	780	0.130	1.626	11
27	56.500	177	0.120	1.624	3
28	56.800	422	0.120	1.624	11
29	56.750	484	0.120	1.622	7
30	57.520	1253	0.120	1.602	17
31	57.650	600	0.120	1.599	8
32	58.580	255	0.120	1.492	3
33	58.860	873	0.120	1.478	13
34	55.540	459	0.120	1.405	6
35	61.750	147	0.120	1.402	3
36	67.960	770	0.120	1.378	10
37	68.200	892	0.120	1.375	12
38	68.400	204	0.120	1.372	3
39	69.100	472	0.120	1.359	9
40	69.500	328	0.120	1.356	9
41	70.280	167	0.125	1.353	2
42	75.040	173	0.120	1.266	2
43	75.400	209	0.120	1.267	7
44	75.500	225	0.120	1.264	3
45	75.880	177	0.120	1.260	5
46	77.260	248	0.125	1.225	3

Table 2. Output of the Result of Peak Search by Quadratic Differentiation

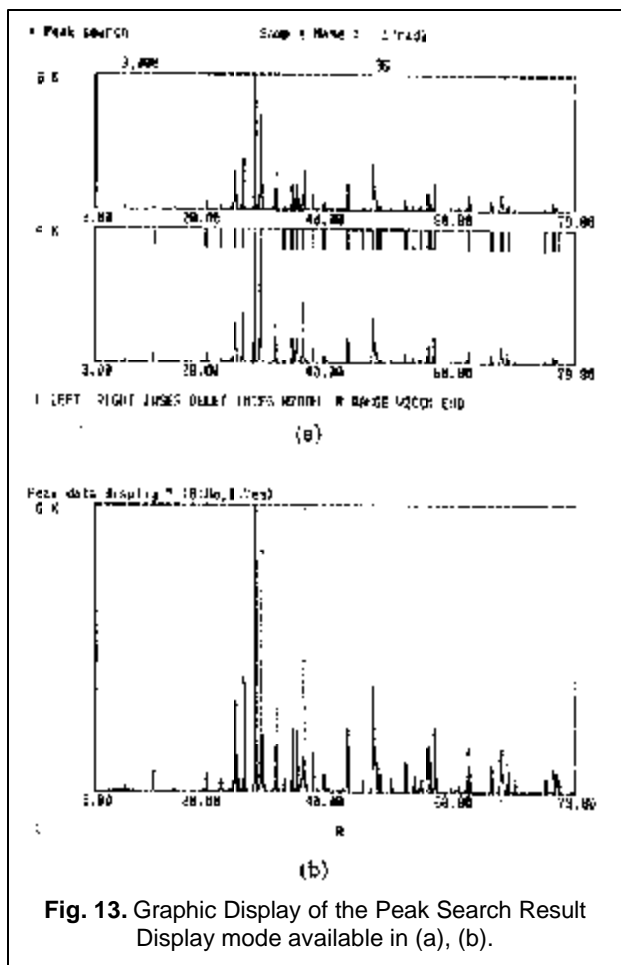


Fig. 13. Graphic Display of the Peak Search Result Display mode available in (a), (b).

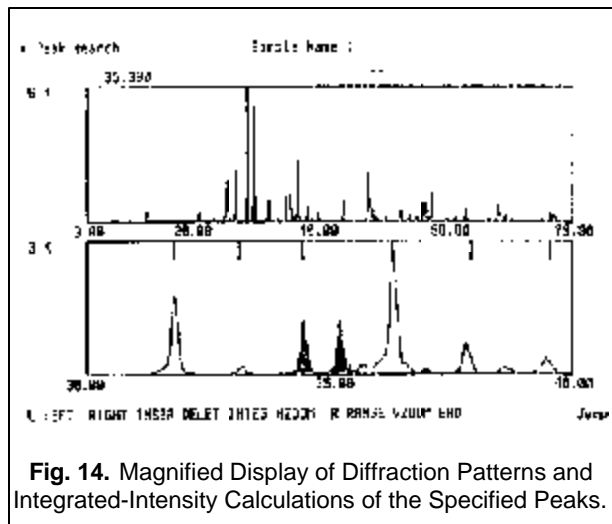


Fig. 14. Magnified Display of Diffraction Patterns and Integrated-Intensity Calculations of the Specified Peaks.

printout of the peak search result obtained by quadratic differentiation. This peak result also appears, at the same time, in a bar graph format at the upper part of the display along with the smoothed data, as shown in Fig. 13(a). A magnified display can be made, moreover, for minute observation of diffrac-

tion patterns (Fig. 14). Figure 15 gives an example of background elimination.

5. Search-Match System

The method of locating compounds present in a sample through powder X-ray diffraction patterns was announced by Hanawalt *et al.* in 1983. This technique played an epoch-making role at the time as a means of determining compounds by powder X-ray diffraction, although the standard reference data available for comparison was no more than 1000

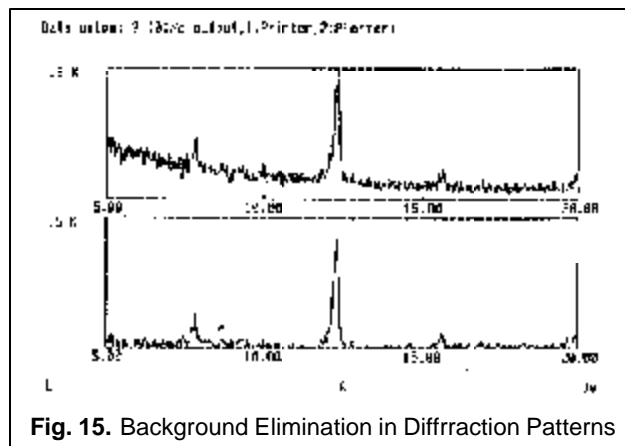


Fig. 15. Background Elimination in Diffraction Patterns

kinds or so in number. Even today this method studied by them remains as the central means among manual search-match techniques, being retained in the JCPDS search manual.

It was around 1965 that a search-match program by means of a computer was first announced (Frelve). Since then a number of search-match programs have been in use up to now. At present the Johnson-Vand program put on sale by JCPDS together with the standard data appears to be most prevalent, but unfortunately this program is designed for IBM large computers and not utilizable for minicomputers and microcomputers used in laboratories in general.

Personal Computers have been notably spreading of late, infiltrating into the data processing part of a variety of analytical equipment. Since, however, the operation speed of such computers is none too fast, some good idea is needed to reduce the time required for search-match.

Just recently, the development group at Rigaku has created a program package which enables rapid search-match with the data processing computer (personal computer) of the new D/max-B. This system employs an algorithm such that a decision can be made far more quickly on the qualified candidates

among possible substances by direct approach to the very position in the measured peak search data that corresponds to the strongest line of the taken-up reference material. This has realized a few times faster speed than the search-match speed of the existing minicomputers.

The search-match files prepared at Rigaku are 947 phases of the NBS file, 2719 phases of the JCPDS FEP file (Common Phase File), 3549 phases of the JCPDS mineral file, 6000 phases of the JCPDS metal and alloy file, 31799 phases of the JCPDS inorganic full file and 11378 phases of the JCPDS organic file, totaling six files. The inorganic full file is contained in 4 sheets of 1.2 MB FPD, so the exchange of these FPDS. is required during serach-match operation.

The actual search-match time is approximately 8 seconds for the NBS file. The search-match time for the other files is proportional to the number of the standard data. The search-match time for the inorganic full file is approximately five minutes including the time required for exchanging the FPDS. It is possible to reduce this time to within one minute by adding a 10 MB hard disk.

Frevel *et al.*³⁾ mentioned in their report to the effect that among 3457 phases of the file kept at Dow Chemical during the time span of about 2.5 years from April 1 949 to October 1951, the number of the standard data never used throughout that period was as many as 3000 phases, the number of those used once was 336 phases, that of those used twice was 68 phases, and so on. The second similar survey conducted by them also revealed that among approximately 14800 phases of the file during five years from 1965 to 1969, the standard data never used, those used once, and those used twice were respectively 13800 phases, 336 phases, and 137 phaese in numbers. They concluded as a result that even a small file could be satisfactory if it consists of a collection of carefully selected standard data. Under the current circumstances, however, where the identification work for artificial materials produced from laboratories and others is rapidly increasing, there are more and more cases that such small files can no longer meet the requirement properly.

The fundamental of search-match by X-ray diffraction is to examine the correspondence between *d*-value and *I*. But the fact is that good matching with the JCPDS data is not necessarily obtainable in terms of not only *I* but also *d*-value. The reasons are that there are overlapping peaks in measurement data causing a

shift in the detected value, and that, above all, the JCPDS data files themselves contain such shifted data as they are. Moreover, some of the old data retained are those obtained by the film technique. It is therefore needed to broaden the window width of *d*-value to 0.2°-0.3° by 2θ conversion.

Under such situations the element information is important as a means of limiting the possible substances to be chosen by search-match. In the search-match system of the new D/max-B the element information is specified being classified into three ranks: major elements, minor elements, and undetermined elements. Among them, when it is desired to detect any compound of a certain element which is given particular attention in the sample in addition to other co-existing elements in large quantities as major elements, this element is specified as a major element regardless of its quantity contained. On the other hand, elements of no particular importance and in small quantities are designated as minor elements; further, those anions such as C, H, O, N, F, S, Cl, P, etc. and those elements which always need partners are specified as undetermined elements in operation. Figure 16 shows an example of inputting of the search-match conditions in the D/max-B system. Twenty elements can be specified for each rank. In the illustrated example, since there is no element information on the major and minor elements, the element information will be disregarded in this case.

Compounds chosen based on the above information are no more than possible ones that can exist, and as such this search-match is referred to as the 1st search-match. An example of the resulting output is given in Fig. 17. Regarding those possible compounds which have passed several selection standards with AND logic, the R-value (called the reliability factor and calculated based on roughly the same

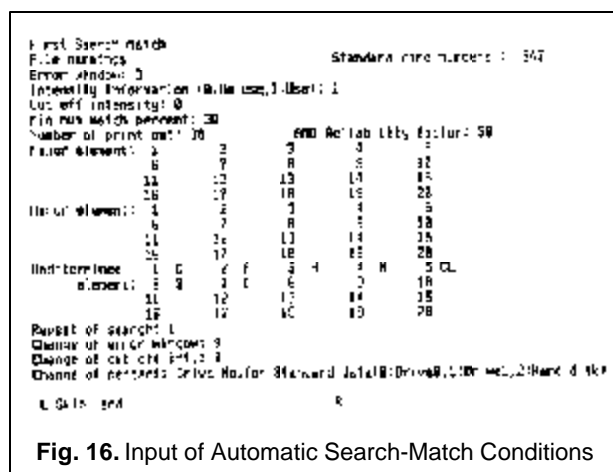


Fig. 16. Input of Automatic Search-Match Conditions

NO	CLASS No.	J	Q	CHOP	CHARACTER FORMULA	R.F.
1	500177	10	10		AL ₂ O ₃	612
2	50025	20	20		CaO	207
3	50040	30	30		CaF ₂	244
4	50041	30	30		CaF ₂	244
5	500722	40	40		Fe ₂ O ₃	176
6	50086	50	50		Fe ₂ O ₃	176
7	501272	10	10		Fe ₂ O ₃	176
8	50087	50	50		Fe ₂ O ₃	176
9	50087	50	50		Fe ₂ O ₃	176
10	50088	50	50		Fe ₂ O ₃	176
11	50092	50	50		Fe ₂ O ₃	176
12	500103	5	10		Fe ₂ O ₃	176
13	50021	20	20		Fe ₂ O ₃	176
14	50088	50	50		Fe ₂ O ₃	176
15	50088	50	50		Fe ₂ O ₃	176
16	50088	50	50		Fe ₂ O ₃	176
17	50088	50	50		Fe ₂ O ₃	176
18	50088	50	50		Fe ₂ O ₃	176
19	50088	50	50		Fe ₂ O ₃	176
20	50088	50	50		Fe ₂ O ₃	176
21	50088	50	50		Fe ₂ O ₃	176
22	50088	50	50		Fe ₂ O ₃	176
23	50088	50	50		Fe ₂ O ₃	176
24	50088	50	50		Fe ₂ O ₃	176
25	50088	50	50		Fe ₂ O ₃	176
26	50088	50	50		Fe ₂ O ₃	176
27	50088	50	50		Fe ₂ O ₃	176

Fig. 17. Output Example of 1st Search-Match

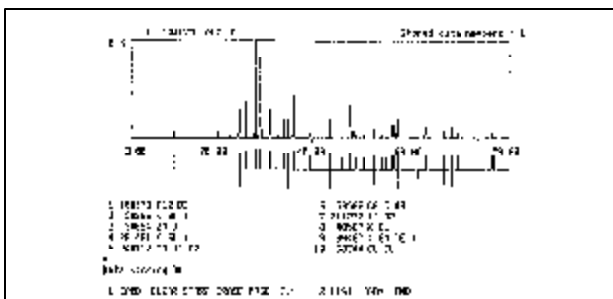


Fig. 18. Display for Decision by 2nd Search-Match. Matched peaks are displayed in color to facilitate the decision. Also, standard data is superposed on raw data with a red line.

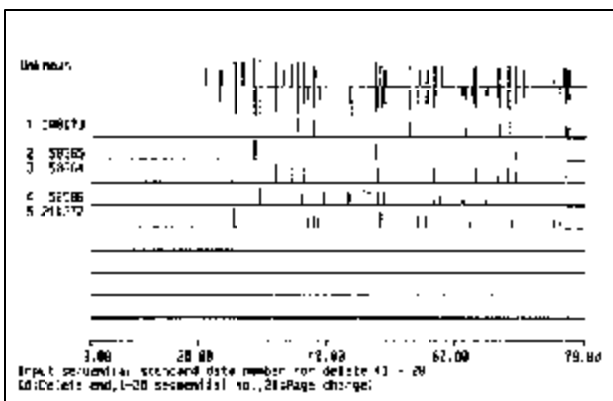


Fig. 19. Accumulated Display of Searched-out Standard Data

definition as of Johnson-Vand) is obtained from them, and as many candidates as specified are finally employed in order of the R-Value (50 kinds in max.). The next step is to decide the actually existing substances from among the candidates selected by the computer. For the procedure the diffraction patterns and the possible data are directly superposed on the graphic display for a visual decision by the operator. This operation is referred to as the 2nd search-match.

Figures 18 and 19 respectively show a display for decision by the 2nd search-match and an accumulated display of the compounds which have been picked up.

The need for such secondary search-match operation seems to be unavoidable for the long time ahead. The first step toward enhancement of the search-match accuracy to the extent that can save the above secondary procedure should be an increase in the reliability of the standard data. Also, regarding the measurement data the separation of overlapping peaks should be made and, moreover, the problems related to the crystal grain size, preferred orientation and the like should be resolved about this data. The balance between such efforts and the labor spent on the 2nd search-match is likely to determine the future course for the solution of the problem.

6. Multiple Recording

The multiple recording mode which permits simultaneous observation of plural measurement data obtained by changing the environmental conditions of the sample may be said to be a convenient way of presentation.

Figure 20 shows an example of inputting of the multiple recording conditions, while Figs. 21 and 22 respectively show examples of multiple recording of the variations of diffraction patterns due to temperatures. The sample is MnOFe₂O₃.

7. Concluding Remarks

The above descriptions are a part of the functions of the new X-ray diffractometer system D/max-B. Further preparations of various data processing programs are being made in sequence at Rigaku covering the application fields of the powder diffraction techniques listed in Table 1. We are confident that a library of these applied programs may not a

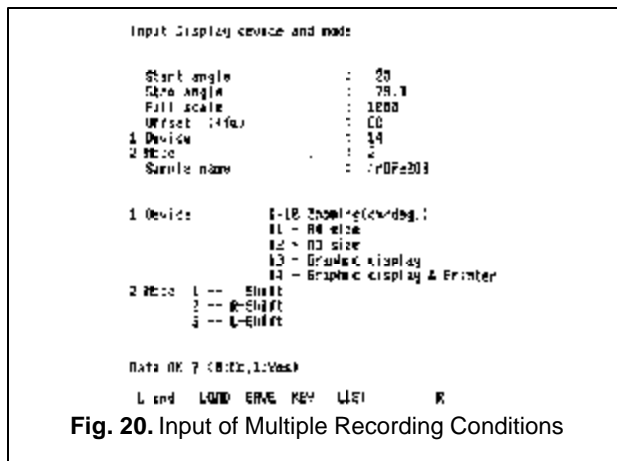
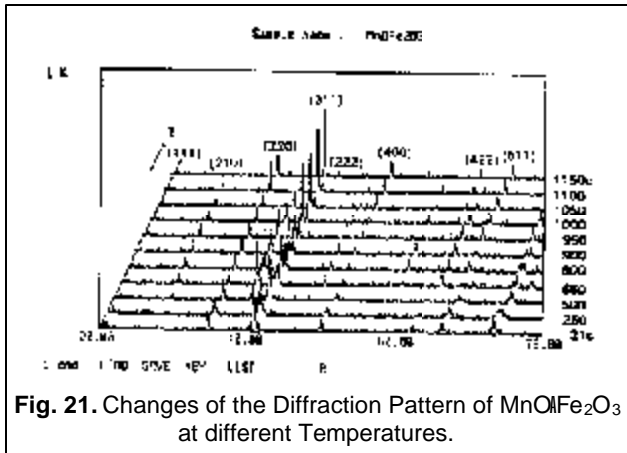


Fig. 20. Input of Multiple Recording Conditions

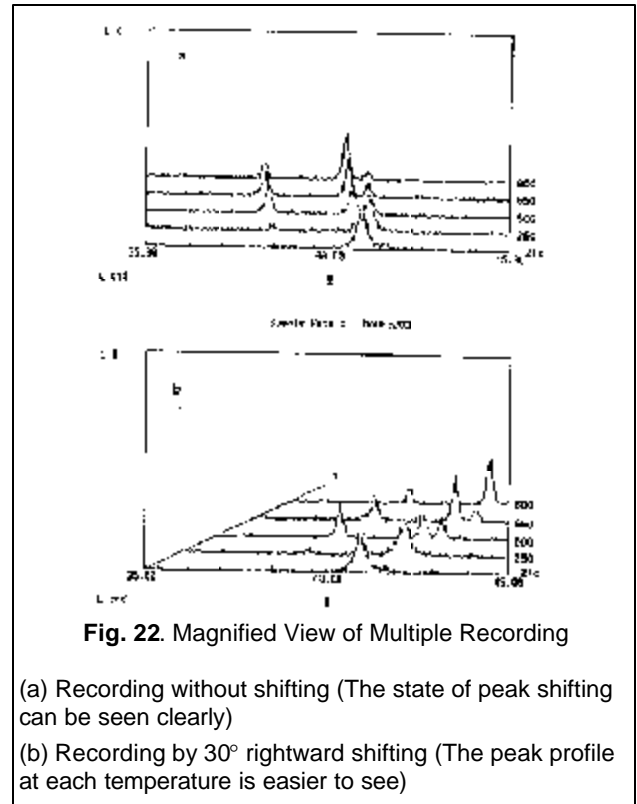


little contribute to the future enlargement of the application range of X-ray diffraction by those not particularly specializing in X-rays.

Another model (RAX-12) which employs a minicomputer as the data processing computer is also available from Rigaku. While this system offers a very convenient tool to handle such processing as requires a long time for calculations, one disadvantage is that its cost has to be higher than the model introduced here, thus keeping it from coming into wide use.

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(1) A. Savitzky and M. J. E. Goley: *Anal. Chem.* **36** (1964), 1627.



(2) S. V. N. Naidu and C. R. Houska: *J. Appl. Cryst.* **16** (1982), 190.

(3) L. K. Frevel, C. E. Adams and L. R. Ruhberg: *J. Appl. Cryst.* **9** (1976), 199.