

Technical Note

RIGAKU D/MAX-B AND MICRO-PROCESSOR

1. Introduction

In 1978, Rigaku pronounced D/max-A and took the lead in developing an automatic X-ray diffractometer controlled by microprocessor. This system based on Motrola 6800 to carry out all measurement and controles softwarewise. The system also was capable for the real time data processing under execution of data acquisition. Included in this data processing were smoothing, peak search, d-value conversion and output of the result to the plotter. Besides, in off-line operation, the system allowed search-match using a cassette magnetic tape with about 1000 phases or so equivalent to NBS file available from JCPDS (Joint Committee on Powder Diffraction Standard). Because of low-speed run of the cassette, however, it took about 10 minutes for operation.

For more complex data processing beyond the above function, a host computer was to be utilized. In this case it was also possible to control the D/max-A from the host computer. Anyway the D/max-A found a wide range of users when put on the market.

Then, in 1983, based on the experience about the D/max-A and making most of state-of-the-art technologies, Rigaku developed an improved version announcing the current D/max-B series. Its characteristic aspects are described below.

2. D/max-B and Microprocessor

The progress in the manufacturing technique of semiconductor devices has reduced the cost of IC's so that it has become possible to realize good system in term of the total cost-to-performance ratio without assigning many functions to a single processor. Thus the D/max-B employs many CPU chips as shown in Table 1.

3. Main Controller

The main controller controls the equipment and measuring instrument according to instructions from the personal computer. In measurement this controller conducts goniometer movement and X-ray photon counting devices. Data acquisition with the D/max-B

Table 1. D/max-B and Micro processor

Component Designation	Microprocessor and Major Function Assigned	
X-ray generator	6809 (2MHz)	Digital PID control
Goniometer/driver	6802 (1 MHz)	Stepping motor control
Sample changer	6802 (1 MHz)	Control of run
Main controller	6802 (1 MHz)	Control of run and that of measuring circuit
	Am 9511	Numerical processing
Personal computer	8088 (8 MHz)	Run of personal computer
	Operating system: MS-DOS	
	8087 (option)	Floating point co-processor

is such that the counted value by sampling is not used as is, but a conversion to a 2-byte integer is made applying the scaling factor to the square root of the counted value. Its purpose is to facilitate the assessment, at the time of data processing, about statistical fluctuations contained in measurement data.

Now, let's denote the counted value by sampling as N and the standard deviation due to statistical fluctuation as δN . Since N follows the Poisson's distribution, δN equals \sqrt{N} . Thus

$$\begin{aligned} \sqrt{N + \delta N} &= \sqrt{N} \left\{ 1 + \frac{1}{2} \left(\frac{\delta N}{N} \right) - \frac{1}{8} \left(\frac{\delta N}{N} \right)^2 + \dots \right\} \\ &\doteq \sqrt{N} + \frac{1}{2} \end{aligned}$$

That is, the standard deviation takes a constant value of 1/2 regardless of the measured intensity to make the assessment simple. The Am9511 is used for these computations and for high-speed numerical processing when the plotter is used.

4. Data Processing (I)

The D/max-A invariably required the aid of a host computer for search-match with a large file containing few tens of thousand or for general data analysis. Whereas, with the D/max-B, a personal computer can also handle data processing, as out-lined below.

The processing of data obtained by the diffractometer may broadly be classified into two. One is smoothing, peak search and search-match, which are frequently used. The other is different types of data analysis, the procedure of which varies largely depending on each user. Beside, in the case of the former, what is computed fundamentally is simple but operation should be made many times repeatedly. On the contrary, in the case of the latter, various operations are designed that high-speed operation is aimed for the former by use of assembler language subroutines, while for the latter the programing is made easier with C or Fortran. The case of especially time-consuming operations due to a vast amount of calculation, it is advisable to get the help of a floating point processor 8087 dedicated to computation. Table 2 shows the actually measured time required for frequently used sub-routines. Fig. 1 shows data for test. Some additional explanation is given in the following.

- a) Data read: As mentioned before, high-speed data reading from disk can be made as measured intensities are condensed to 2 bytes each.
- b) CRT graphic display: Direct writing into VRAM (Random Access Memory for Video) is made with an assembler sub-routine. When the number of data is greater than the size of abscissa for VRAM, display is made with a vertical line connecting the maximum value to the minimum value in the corresponding data region. Consequently, the required time increases with data having large statistical fluctuation, taking several times as much time in some cases.
- c) $K\alpha_2$ stripping: For search-match it is desirable to remove $K\alpha_2$ peaks. Therefore the modified Rachinger method¹⁾ which uses 3 parameter pair is employed for conversion from $K\alpha_1$ profile to $K\alpha_2$ profile. Since our intensity data are in the square root format, it is necessary for operation to execute square of the axis of ordinate, convolution and square root processing in addition to a sine conversion of the axis of abscissa, thus taking a relatively long time. To cope with this, a sine table is prepared for high-speed operation.
- d) Optimum smoothing points search: The number of smoothing points affects the signal-to-noise ratio to be obtained. The optimum number is

Table 2. Execution Time for Data Processing Subroutine

Content of Operation	Required time	Condition
Data read	0.87 sec	5" floppy diskette
	0.73 sec	20 MB 5" hard disk
CRT graphic display	1.0 sec	Fig. 1
$K\alpha_2$ stripping	5.4 sec	Modified Rachinger ¹⁾ (3 parameter pair)
Optimum smoothing points search	10 sec	Number of smoothing points with which the peak has 85% height to that raw height
Smoothing/Differentiation	1.1 sec	Savitzky ²⁾ method Q/C function, same time for 5~25 points
Background calculation	0.25 sec	32-points moving averaging+Sonneveld ³⁾ method
Peak Search	0.16 sec	Sorting by 2nd derivative, peak height and peak width
Search-match		Modified Johnson-Vand ⁴⁾ method Used file: inorganic 31799 phases Number of unknown lines: 72
	59 sec	No designation of elements
	37 sec	Designation of 6 elements

10 K

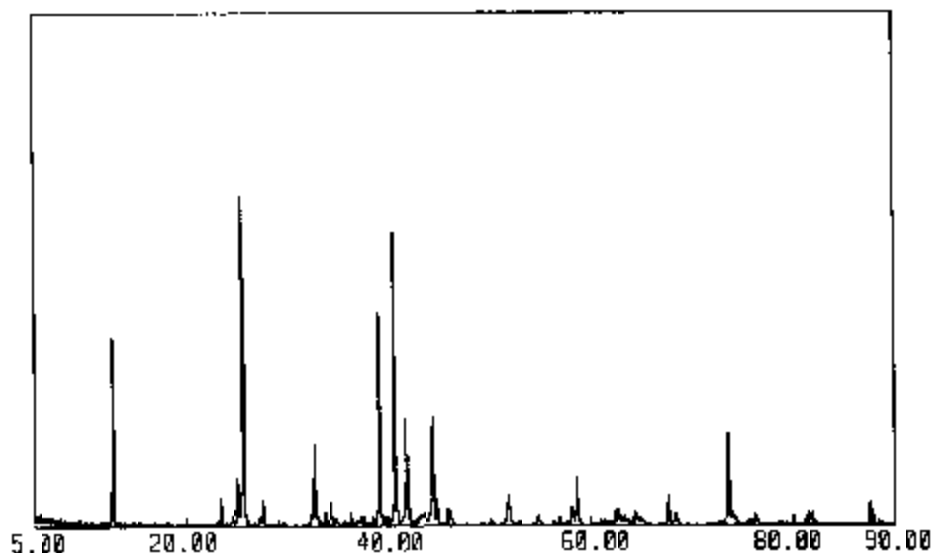


Fig. 1. CRT Display of Data used for Execution Time Test
Sampling: 0.02 (20), Number of data: 4250, Number of peaks: 72

considered that the width of a smoothing function to be used is roughly equal to the peak width. On this occasion the original peak height decreases to about 85 percent. This program is such that trial runs of smoothing are made by varying the number of smoothing points so as to obtain the optimum number of points from the mean value of a decrease in the peak height.

- e) Smoothing/Differentiation: A quadratic/cubic coefficient of the Savitzky²⁾ method is used. Since, in this case, the coefficient of the weight function takes a quadratic equation, its 3rd order difference becomes zero except for three pairs on both sides. Accordingly, convolution with the three pairs followed by integration for twice will bring the same result as with convolution with the original coefficient. This operation method keeps the operation time constant independent of the number of points for use, and therefore is advantageous especially when there are numerous points to deal with.
- f) Background calculation: First, the moving average of 32 points is carried out to eliminate the effect of statistical fluctuation, and then the Sonnevlt³⁾ method is used. The default value of the repetition is 16.
- g) Peak search: Although there are many literatures^{5),6),7)} on the peak search, no definitive one exists because of so large effects involved due to

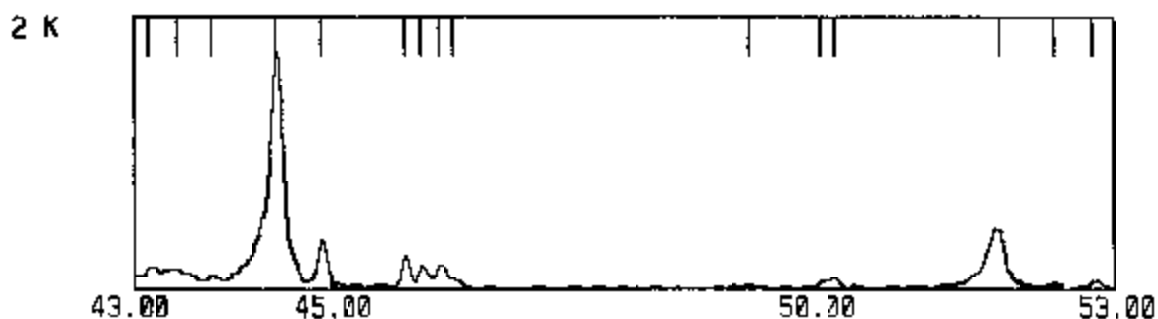
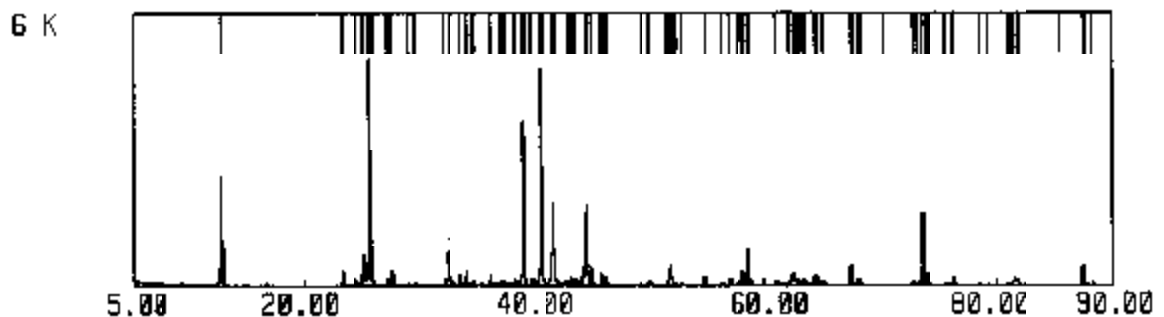
the nature of data. This matters in particular in the case of data having a poor S/N ratio. In our case a decision is passed by referring to the 2nd derivative coefficient, peak height and peak width. The criterion of decision is such that in the region where the peak height comes higher than the background by 6σ or more, those whose minimum value of the 2nd derivative exceeds 6σ as well as those whose peak width is approximately 1/2 of the convolution range or more are decided as peaks. These values were obtained through studies of correlation between various peaks found visually and their processed data, and virtually agrees with the human's decision when the optimum number of points is used. As the value of σ the following theoretical value is used. That is, the standard deviation obtained by the convolution on a set data whose standard deviations are σ_i s and the weighting function W_i is given by an expression below, where σ_i is assumed to be invariably equal taking the value of 1/2.

$$\sigma = \sqrt{\sum \sigma_i^2 W_i^2} \approx \frac{1}{2} \sqrt{\sum W_i^2}$$

Table 3 shows the σ values when the Savitzky's Q/C smoothing or the processing for the 2nd derivative coefficient is conducted on the square root data. Part of the search result by this technique is magnified shown in Fig. 2.

Table 3. Standard Deviations occurring with Smoothing/2nd derivative

Number of points	5	7	9	11	13	15	17	19	21	23	25
Smoothing	0.3485	0.2887	0.2527	0.2278	0.2091	0.1944	0.1821	0.1725	0.1640	0.1569	0.1502
2nd derivative	0.4751	0.2562	0.1699	0.1229	0.0946	0.0759	0.0627	0.0529	0.0454	0.0396	0.0349



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**** Peak Search conditions ****
SAMPLE NAME      = NO-1
THRESHOLD LEVEL  = 7.5  deg
THRESHOLD 2nd-der = 977  c/s/deg^2
THRESHOLD WIDTH  = .09  deg
    
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No.	2-THETA	INT.	WIDTH	d	1/d				
1	12.760	2196	0.120	6.922	52				
2	23.300	356	0.120	3.814	7				
3	24.480	172	0.120	3.633	3				
26	41.640	1654	0.120	2.167	19				
27	43.140	107	0.105	2.095	3				
28	43.440	94	0.090	2.081	3				
29	43.780	55	0.120	2.066	2				
30	44.440	1695	0.120	2.037	40				
31	44.900	335	0.090	2.117	8				
32	45.760	224	0.090	1.961	6				
33	45.920	157	0.090	1.975	4				
34	46.100	164	0.105	1.967	4				
35	46.260	69	0.090	1.961	2				
36	49.320	31	0.090	1.847	1				
37	50.020	55	0.090	1.822	2				
38	50.180	84	0.120	1.616	2				
39	51.840	416	0.180	1.762	10				
40	52.400	36	0.135	1.743	1				
41	52.780	56	0.105	1.733	2				
70	81.880	137	0.105	1.175	4				
71	87.620	400	0.120	1.113	10				
72	88.380	72	0.120	1.105	3				

Fig. 2. Result of Automatic Peak Search

h) Search-match: This technique is roughly the same as that of Johnson-Vand.⁴⁾ Namely, an error window is provided to compare peaks of the unknown specimen with the lines of the reference data, and by collectively checking the matching degree in terms of the number of peaks, $1/d$ and I ,

the reliability factor is to be obtained. Generally, the accuracy of search-match depends upon the accuracy of peak data, which is also affected by the specimen state, but, in any event, the peak data always contain errors, Hence correct solutions are not necessarily concentrated in the top-ranked

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Sample name = NC-1
First Search Match condition
Standard file name: INDRG          Standard card numbers: 11799
Error window: 3
d & I use (0:No use, 1:d use 2:d&I use): 1
Min. match number: 0
Minimum match percent: 30
Number of print out: 30
AND Reliability factor: 50
Major element: 1 CR      2 B      3 MO      4 ZR      5 NI
                6 TI      7          8          9          10
                11       12       13       14       15
                16       17       18       19       20
Minor element: 1         2         3         4         5
                6         7         8         9         10
                11       12       13       14       15
                16       17       18       19       20
Undetermined element: 1 O      2 F      3 H      4 N      5 CL
                6 S      7 C      8          9          10
                11       12       13       14       15
                16       17       18       19       20
Repeat of search: 1
Change of error window: 0
Change of Min. match : 0
Change of percent: 0

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JCPDS	FILE NAME	INDRG	U	S	CHEM	CHEMICAL FORMULA	R.F.
1	40809	4	4	***	(MO)	598	
2	50508	18	18	***	MO O3	544	
3	140357	3	3	***	NI3 S2	500	
4	60504	11	12	***	CR2 O3	406	
5	90361	12	13	***	(CR B)	404	
6	60610	10	10	***	(ZR B2)	395	
7	80121	10	10	***	(TI B2)	395	
8	40850	3	3	***	NI	334	
9	60694	3	3	***	CR	334	
10	120754	5	7	***	TI O	241	
11	110065	4	5	***	CR N	223	
12	170104	4	5	***	(MO O C)	223	
13	190857	12	14	***	(NI ZR)	212	
14	60614	4	5	***	(TI C)	168	
15	140020	2	3	***	NI C	167	
16	60528	7	8	***	(TI2 B5)	163	
17	200684	4	6	***	ZR O	159	
18	170314	8	10	***	(ZR H2)	159	
19	60228	13	18	***	(MO2 B5)	158	
20	60612	7	11	***	(CR2 ZR)	142	
21	80119	6	8	***	(CR B2)	139	
22	100280	6	9	***	(NI3 N)	134	
23	11252	5	6	***	CR2 N	118	
24	80378	4	5	***	(ZR H)	117	
25	120041	13	17	***	NI S	112	
26	190850	3	4	***	(NI TI)	100	
27	190834	13	18	***	(NI3 B)	99	
28	80254	4	7	***	CR O	89	
29	60546	9	16	***	(MO C)	87	
30	150500	3	3	***	(B N)	84	

Fig. 3. Example of Search-Match result

area of the search-match result. It is for this reason that the result of primary search-match should be finally examined by man's visual check, i.e. through secondary search-match. A comparison between the use of all lines registered in JCPDS and the use of only strong peaks in primary search-match tells that the probability of false matching increase with the former, and thus one cannot say that a good result always comes out from it. We are

using 18 lines based on our experience. This is advantageous in that it can lead to a reduction in time in primary search-match. Needless to say, since it is meaningful to have many lines in secondary search-match, space is reserved to allow an increase in the number of lines up to 34 lines.

Further, most of the time required for search-match is spent on a comparison between lines. In

other words, what governs here is the product of the number of peaks of the unknown specimen and the total number of the reference peaks. With a efficient program written in assembler language, it has proved that a high-speed run can be achieved than with a general-purpose mini-computer, such that it takes only 59 seconds without element designations and 37 seconds with designation of 6 elements for a specimen having as many as 72 lines in the search of the inorganic file of 31799 phases. The speed will of course slow down with as increase in the maximum number of lines per phase, but since the average number is around 30, an increase to 34 lines, for example, will result in an extension of time by no more than some 50 percent. Fig. 3 shows an example of the result of the primary search-match.

5. Data Processing (II)

Referred to next is an example of general analysis program which involves a number of numeric calculations. What affects in this case is the computer speed itself. Among various benchmark test available for the evaluation, the one by Whetstone⁸⁾ seems suitable for scientific computations. Table 4 shows the result of our test. As may be known from this result, the 8086 alone is likely to enough meet the requirement with the aid of the coprocessor 8087.

By way of example of the analysis program, Fig. 4 shows the result by Visser's indexing program.⁹⁾ JCPDS's TiO₂ (brookite) was used as data together with a Fortran program. A hard disk was used for both input and output of data in the test in order to avoid possible effects of the printer, etc. As a result, it took 2 min. 52.1 sec. with the 8086 alone and 1 min. 40.6 sec. with the additional use of the coprocessor 8087.

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TI02 (BROOKITE)

THE BEST SOLUTION IS NOW USED TO TRY AND INDEX ALL LINES.

TWO CYCLES OF REFINEMENT WITH ALL LINES HAVE BEEN CARRIED OUT.
THE FIGURE OF MERIT IS      29.0
THE NUMBER OF UNINDEXED LINES AMONG THE FIRST 20 INDEXED LINES IS   0=X20
THE NUMBER OF LINES CALCULATED UP TO THE 20ST. INDEXED LINE IS   51=N20
THE TOTAL NUMBER OF LINES CALCULATED IS      90

LIST OF ALL OBSERVED AND CALCULATED LINES UP TO AND INCLUDING THE 36ST.
IF THE TWO THETAS DIFFER MORE THAN .060 DEGREES, A BLANK LINE IS INSERTED.

  TWO THETA      D      H      K      L      Q
    9.62      9.183      0      1      0      118.6
   16.23      5.457      1      0      0      335.8
   17.23      5.143      0      0      1      378.1
   18.90      4.691      1      1      0      454.4
   19.32      4.591      0      2      0      474.4
   19.77      4.487      0      1      1      496.7
   23.75      3.743      1      0      1      713.9
   25.33      3.513      1      2      0      810.2
   25.35      3.510      *OBSERVED      811.7

                                THE DIRECT CONSTANTS OF THESE LATTICES

      A      B      C      ALPHA      BETA      GAMMA      VOLUME
      5.457      9.183      5.143      90.000      90.000      90.000      237.70
END OF PROGRAM

```

Fig. 4. Result of Visser Program Run

Table 4. Whetstone Benchmark Test using Fortran

Model	10 ³ Whetstone instruction per second
Rigaku: 8086 only	35.1
8086/8087	130.1
PDP-11/23 with floating point processor	37.0

These values are well practical ones indicating a better result than in the benchmark test.

6. Concluding Remark

As shown above, the recent development of microprocessor is noteworthy, verifying their effective characteristics as a terminal unit of the D/max-B system. Accordingly, there is no need for a host computer unless the analysis program to be run is exceedingly large. Likewise, the necessity of 8087 co-

processor appears slim so far as routine applications are concerned.

In closing, we wish to thank Dr. Fujio Izumi at National Institute for Researches in Inorganic Materials for providing us with his precious data along with kind suggestions.

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