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COMPUTER CONTROLLED X-RAY SPECTROMETERIC ANALYSIS OF GEOLOGICAL MATERIALS

by

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ABSTRACT

One of the more recent developments in X-ray fluorescent spectrography is the use of a general-purpose digital computer to automatically operate the spectrometer and process the data for elemental analysis.

For the quantitative, elemental analyses of geological samples collected for the National Aeronautics and Space Administration's Remote Sensing Project, this laboratory is using a Siemens SRS-1 spectrometer interfaced to a Digital Equipment Corporation PDP-8 computer.

This paper describes the various operating parameters controlled by the computer including the sequence field, the count-limit and repetition-limit options, method of calculation and general mode of operation.

INTRODUCTION

The quest for automatic analysis of various materials by x-ray fluorescence has led to such developments as the "peg-board" type of programming and recently to the use of a general-purpose digital computer. Both types set the operating parameters for each determination and provide a printed read-out. The extra knowledge gained by the use of a computer is that it will also process the data.

In 1964, the National Aeronautics and Space Administration approached the Geology Department staff of the Mackay School of Mines in Reno to see if they would be willing to participate in a joint study for their Remote Sensing Project. Briefly, this project concerns a fly-over by a specially equipped airplane utilizing ultra-violet, infra-red, microwave, and radar equipment to determine topographic features and identify geologic formations and structures. This technique would be used in outer space and by orbiting satellites around earth. The department's role in this project is to provide detailed geological mapping of certain pre-selected areas, which in turn requires a large number of quantitative chemical data.

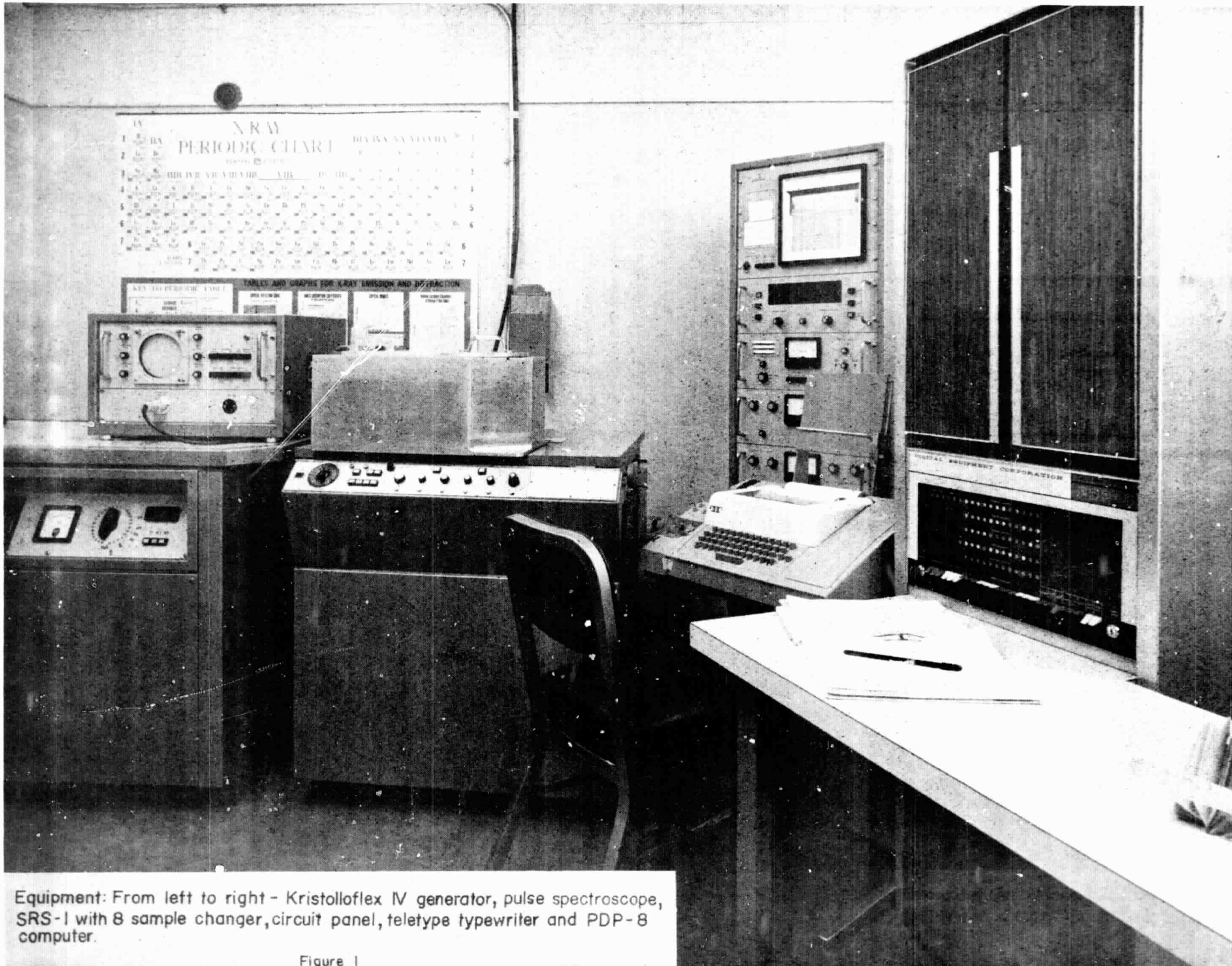
With a limited staff, the best possibility for the analysis of a large number of samples for variety of elements appeared to be by automatic x-ray spectrography.

EQUIPMENT

The analytical equipment being used for this project (fig. 1) include Siemens Kristalloflex IV generator (60KV, 80 mA), Universal sequential spectrometer (SRS-1) with eight position sample changer, high intensity tubes (Cr-2400W, Au-2800W), pulse spectroscope and circuit panel with two pulse height analizer (PHA) window pots. The x-ray instruments are interfaced to a Digital Equipment Corporation Standard Programmed Data Processor-8. The PDP-8 is designed for use as a small scale, general purpose computer and is a one-address, parallel type with 12-bit, 4096 word core memory. The cycle time is 1.5 μsec and standard input-output facilities include teletype typewriter and perforated tape equipment.

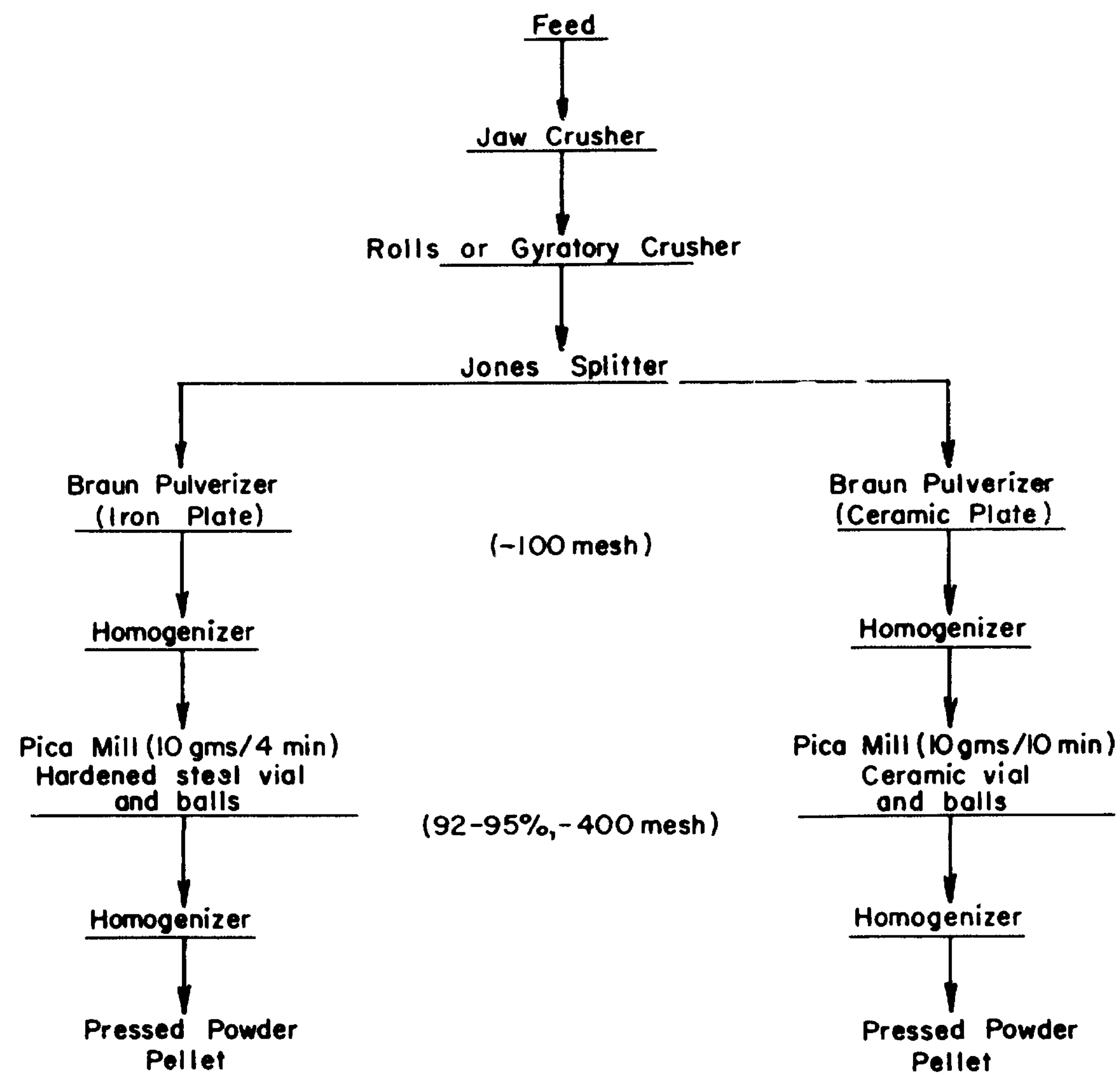
SAMPLE PREPARATIONS

For bulk samples, the sample preparation technique used has been previously described (Volborth, 1963, Weyler, 1966). Briefly, the method consists of dual grinding a sample as shown in figure 2 and making a pressed powder pellet. In making the pellet, a gram of sample is placed in a special die, a small amount of bakelite is poured around and on top of the powder and then compressed at 30,000 psi. No binder is



Equipment: From left to right - Kristolloflex IV generator, pulse spectroscope, SRS-1 with 8 sample changer, circuit panel, teletype typewriter and PDP-8 computer.

Figure 1



SAMPLE PREPARATION FLOW DIAGRAM

Figure 2

used in the sample itself. For small samples, such as those scraped from the surface of a rock, a fusion method (Rose, 1964) is preferable.

ELEMENTS

For igneous rock, the elements normally determined are: major elements - sodium, magnesium, aluminum, silicon, potassium, calcium, and iron; minor elements - phosphorous, titanium, and manganese and the rest of the elements in the periodic table are treated as trace constituents. The selection of which trace elements to analyze is dependent on the particular area, rock type, etc. Elements usually determined in carbonate rocks are calcium, magnesium, aluminum, silicon, iron, barium, and strontium.

COMPUTER PROGRAM

Siemens provided with the unit two software programs which they have named Multel I and Concentra I. Multel I provides for the automatic execution of the analysis for different elements in different samples with varying operating conditions. The operating conditions controlled and operated by the Digital Control Unit are the 2θ setting of the goniometer, collimator (2 choices), analyzing crystal (8 choices - 1st and 2nd order reflections of four crystals), sample rotation (on-off), sample location (8 samples) and detector (2 choices). Those conditions not controlled automatically and which must be preset before a run are the kilovoltage (KV) and milliamperage (mA) for the x-ray tube, the pulse height analyzer settings and counting mode. As mentioned before, the PHA has two window pots, one for scintillation and one for flow proportional detector. When the detector is selected, a preset window width is set simultaneously. Thereafter, through the use of a sine-function preamplifier coupled to the spectrometer, the position of the counting pulse-band is set automatically in the window. The counting mode is automatic in a sense which is described later.

The Multel I program has a sequence filed of 256_{10}* places in locations 1200_8 to 1577_8. The addresses of the operating conditions are stored there in the sequence in which the elements are to be measured. Also, depending on the matrix and on the concentration range, different conditions and values can be specified and stored separately. A total of 128_{10} storage positions are available for these values and each storage location is addressed by a letter (A through G) and the element number (2 digits).

Concentra I provides the facility to calculate elemental concentrations from the intensity values by determining the slope and background constants and is used in conjunction with Multel I.

These programs are read into the computer by the punch tape reader along with the Binary Loader. Digital Equipment Corporation supplies a selection of system programs, function routines and utility programs with the computer. The Binary Loader is a short routine for reading and storing the information from binary-coded tapes.

Figure 3 is a block diagram showing the components of such a system and their relationship to each other. The large dashed block on the left, termed the Digital Control Unit, represents the computer equipment and the other three blocks are the x-ray equipment. If the diagram was also considered as a flow chart, the normal starting point would be the typewriter or punch reader. The software programs are read in, starting address is set on the switch register, the load address key is depressed and then the start key. The individual program containing desired elements, sequence, measuring conditions and so forth are then read in on the

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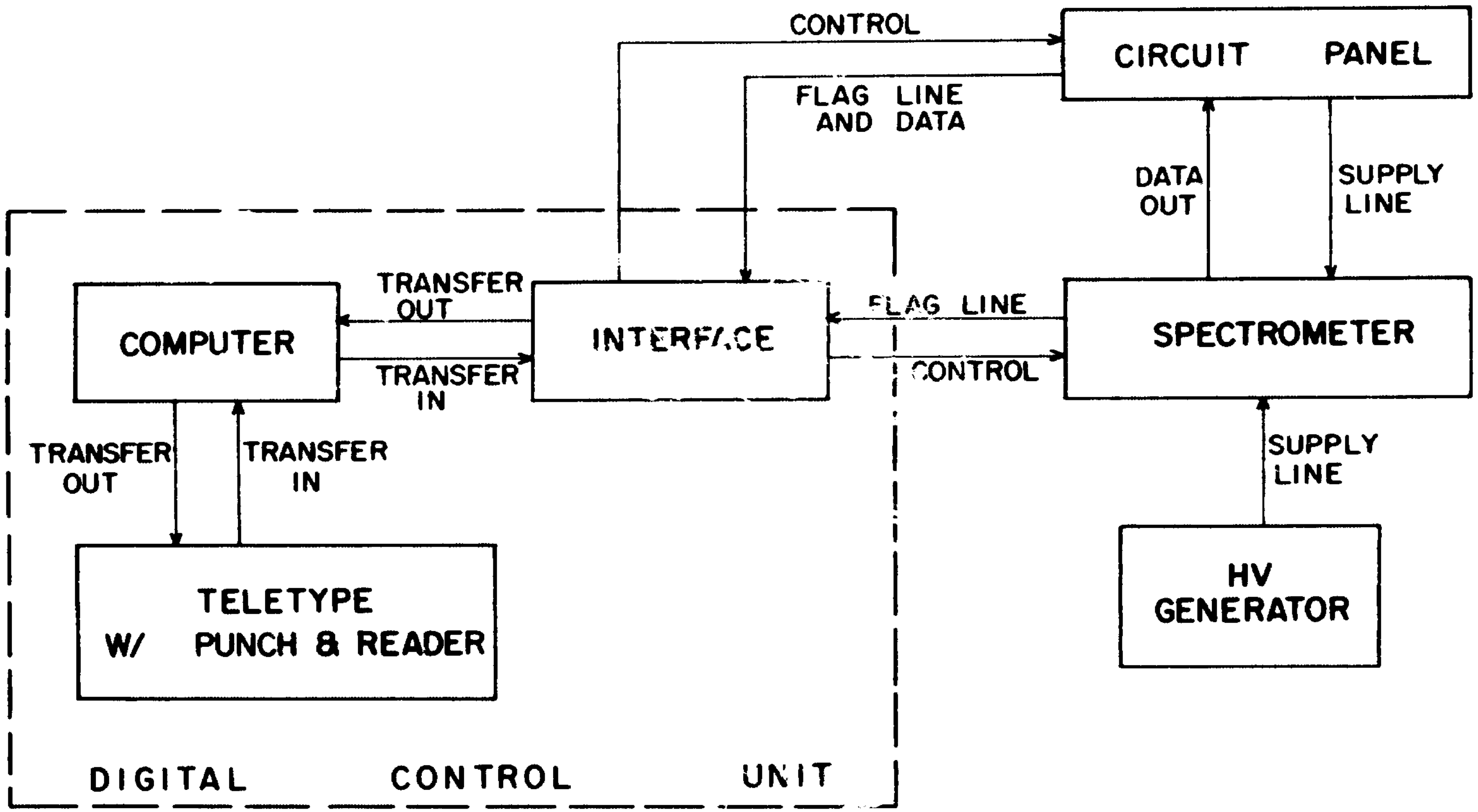
*Subscript denotes number system: 10 - decimal, 8 - octal, 2 - binary. The computer memory units are flip-flop devices utilizing the binary system. For simplification and convenience, the octal number system is used in programming.



BLOCK DIAGRAM

COMPUTER CONTROLLED X-RAY SPECTROMETER

Figure 3

typewriter or, after a program is established, it could be put on punched tape and read in.

The computer relates these commands to the interface to set the wanted conditions in the spectrometer and circuit panel. The interface is a translator between the computer and the peripheral equipment. The major components in the interface are Device Selectors, which are standard modules made by Digital Equipment Corporation and altered for the particular need.

After an x-ray measurement is taken, the data is fed back to the computer.

Two lines that possibly need defining are the Flag Lines returning to the interface from the spectrometer and the circuit panel. A flag is a term denoting that certain conditions must be met before continuance of the next sequence and usually involves some sort of time delay. For conditions such as changing crystals, collimators or detectors, a flag is set and not removed until a signal is given that the change is complete. Since computers must be cycling all the time, some type of looping in the program is required. As an example, the goniometer is driven at 300 2θ per minute and every revolution of the shaft is 1° 2θ. An incremental encoder is directly coupled to the goniometer shaft and gives 1,000 pulses per revolution of the shaft. This calculates out to 1 pulse every 200 μsec. Typical additions on the PDP-8 take 38 μsec and the cycle times for the functions amounts to 7 μsec. Therefore the computer has to wait 155 μsec between each pulse and in the program then there is a small loop in which the computer is cycling.

```
IOT 1Ø1
SKP
JMP. -2
Count
```

The PDP-8/S is being used on more recent equipment, mainly due to cost. The PDP-8/S is a slower (longer cycle time) computer but has the same storage capacity. Since the cycle time is longer, an encoder giving 100 pulses per revolutions of the goniometer shaft must be used and the 2θ is set to the closest 0.01°. Experiments by Siemens show that an encoder of 500 pulses can be used with the PDP-8/S and would allow settings of 0.005° 2θ. The Digital Equipment Corporation is now making a PDP-8/I which has the same cycle time as the PDP-8 but is less expensive. A choice of computers is available to fit the users requirements.

Interface devices to control a function such as changing collimators are quite readily adapted. However, to control and insure the goniometer setting is slightly more complicated. As I just mentioned, an encoder or pulse generator is coupled to the goniometer. In addition to this, a cam operated microswitch is also installed and initially set to activate at some set angle; for example 45°.

After the cam activates the microswitch, a flag is set and as soon as the first zero pulse from the encoder is received, the goniometer will stop. This point is called the reference angle. Before starting a measuring sequence, the 2θ should be checked to coincide with the computer contents.

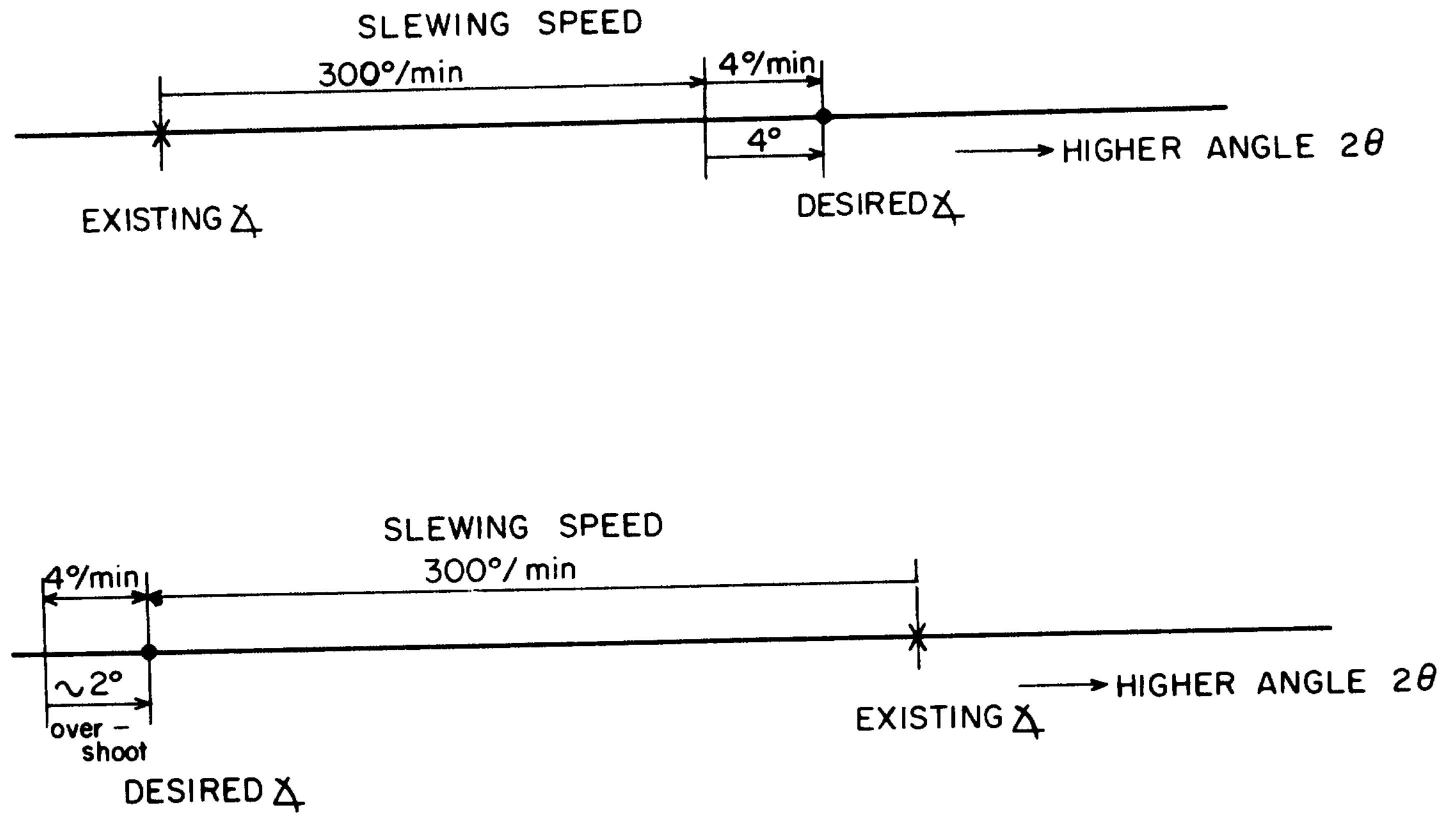
As an illustration; say that the internal counter reads 97° but the goniometer is at 60°. By manual operation the goniometer is set at approximately 97°, the SRS is switched to automatic, the DCU is switched on again and an equal sign types. The goniometer will slow down to 43°, reverse itself and start searching for a zero pulse from the encoder. Only when the cam trips the microswitch, will this pulse be sent to the DCU. After completion the DCU will store this 2θ value and this is the starting point for the first sample change. After every eight measurements, the DCU will perform an automatic absolute angle check insuring the operator that the 2θ is the proper one and there is no mechanical error.

Figure 4 shows a change of 2θ to a higher angle and to a lower angle. Note that the desired angle is always approached from the same side to prevent any backlash errors. The total number of degrees that the goniometer is operating at slow speed may be changed in the program.

The program also provides a method to combine preset time with preset counts. Figure 5 shows three samples with varied intensities. Sample "a" had sufficient concentration to give us the desired quantity of counts in one time period, sample "b" took three time periods and sample "c" never got to the preset count-limit. The print out for "b" and "c" will be their average (one basic time). Rather than waiting too long for "c" to reach the desired counts, the preset repetition-limit was set at four. Where to set these limits depends on the individual analysis and the statistics required. Although this facility is provided and is extremely useful, elements are usually picked that are compatible in their count rates for each inlist program.

The limits are set in the switch register and deposited in certain locations or by means of the ODT II debugging program.

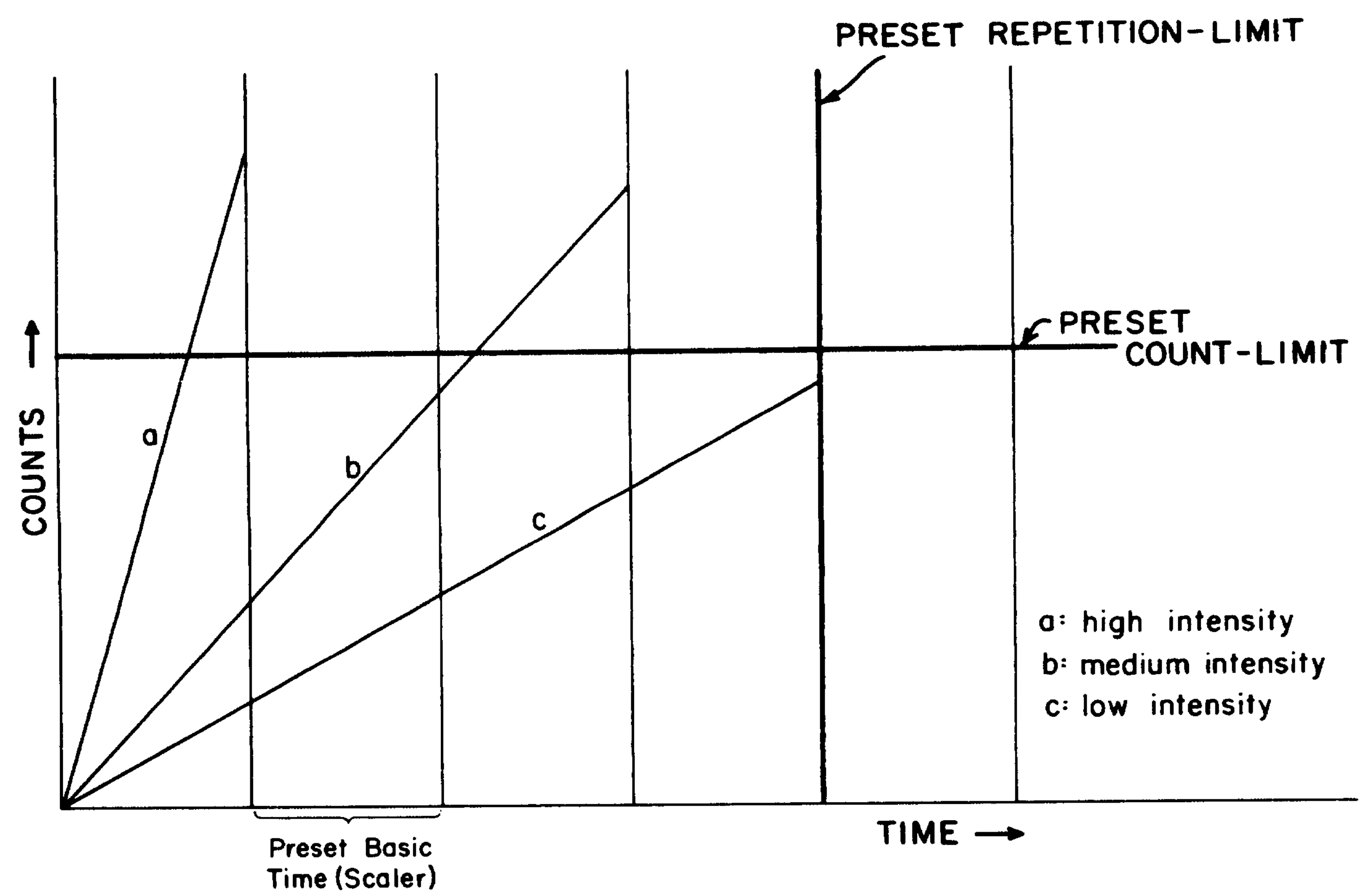
Another feature provided in the software are options controlled by the operator at the switch register of the computer, figure 6. These options determine method of calculation and whether to repeat the sequence or not. In the first method of calculation, the standards are always in position, their concentrations are stored and the unknowns are compared directly to them. In the second method, all samples are treated as unknown and the slope and background constants for each Matrix-Element combination have been stored previously.



GONIOMETER CONTROL

2θ SETTING

Figure 4



REPETITION, COUNT-LIMIT SCHEMATIC

Figure 5

SWITCH				MODE
Ø	1	2	4	
UP				Pos. Ø and Pos. 1 contain standards
DOWN				All samples are unknowns
	UP			Calculate slope and background constants and store in Matrix-Element-Field
	DOWN			Store concentration of Standards in Matrix-Element-Field
		UP		Continuous repetition of measuring-sequence
		DOWN		Stop after completion of measuring-sequence To repeat depress "CONT." key

SWITCH OPTIONS

Figure 6

Figures 7 and 8 show examples of the input-output listings. In the first example, the unknowns are being compared directly to the standards while in the second example, the composition of the standards have been stored previously.

TABLE I

Measuring Conditions - Code

No.	Collimator	Counter	Rotation	No.	Crystal	Order
0	0.4°	FC	No Rot	0	LiF	1st
1	0.4°	FC	Rot	1	LiF	2nd
2	0.4°	SC	No Rot	2	PET	1st
3	0.4°	SC	Rot	3	PET	2nd
4	0.15°	FC	No Rot	4	AdP	1st
5	0.15°	FC	Rot	5	AdP	2nd
6	0.15°	SC	No Rot	6	KAP	1st
7	0.15°	SC	Rot	7	KAP	2nd

Recently Siemens has altered the program so that the 2θ on the spectrometer can be set at the teletype typewriter, the value of the absolute angle can be changed to coincide with that read by eye by typing it in and they have changed the switch options. Also, at our request, they have incorporated into the program a method for taking background measurements, averaging and subtracting from the peak count before calculating the slope of the curve. The output lists the background count, peak, the other background count, net count, and concentration.

INPUT - LIST

```
>
1201←1200
POS. Ø MATRIX: A ELEMENT: 14 ( MC: DEF.52 2Ø=1Ø9.Ø6Ø ↑ %=52.64Ø ↑ /
POS. 1 MATRIX: A ELEMENT: 14 ( MC: 52 2Ø=1Ø9.Ø6Ø %=72.65Ø ↑ /
POS. 2 MATRIX: A ELEMENT: 14 ( MC: 52 2Ø=1Ø9.Ø6Ø /
POS. 3 MATRIX: A ELEMENT: 14 ( MC: 52 2Ø=1Ø9.Ø6Ø /
POS  4 MATRIX: A ELEMENT: 14 ( MC: 52 2Ø=1Ø9.Ø6Ø /
POS. 5 MATRIX: A ELEMENT: 14 ( MC: 52 2Ø=1Ø9.Ø6Ø /
POS. 6 MATRIX: A ELEMENT: 14 ( MC: 52 2Ø=1Ø9.Ø6Ø /
POS. 7 MATRIX: A ELEMENT: 14 ( MC: 52 2Ø=1Ø9.Ø6Ø .
```

THE CONDITIONS LISTED SHOW THAT THERE ARE EIGHT SAMPLES AND ARE IN COMPUTER LOCATIONS 12ØØ TO 12Ø7. COMPUTER WANTED TO START AT LOCATION 12Ø1 BUT WAS CHANGED TO 12ØØ.

THE MATRIX WAS DEFINED AS A, ELEMENT IS SILICA.

MEASURING CONDITIONS: 52 THE FIVE DEFINES Ø.15° COLLIMATOR, FLOW PROPORTIONAL COUNTER AND SAMPLE ROTATION. THE TWO DEFINES CRYSTAL POSITION 2, FIRST ORDER (PET).

OUTPUT - LIST

```
<
12ØØ TO 12Ø7
A14      A14      A14      A14      A14      A14      A14      A14
142264   223216   2Ø7742   2Ø1442   2Ø4628   21Ø952   2Ø88Ø2   2Ø6Ø88
52.64Ø*  72.65Ø*  68.642   66.293   67.657   68.881   69.Ø36   69.Ø7Ø
```

FIRST LINE IS COUNTS PER TIME INTERVAL.
SECOND LINE IS PERCENT COMPOSITION OF SILICA. "*" DEFINES STANDARD.

ALL INFORMATION THAT MUST BE TYPED BY THE OPERATOR IS UNDERLINED.

EXAMPLE OF INPUT-OUTPUT LIST

Figure 7

INPUT - LIST

```
≥
1210↑
POS. Ø MATRIX: B ELEMENT: 19 ( MC: DEF.52 2Ø=5Ø.642 ↑ %=Ø.64Ø ↑ ∠
POS. 1 MATRIX: B ELEMENT: 19 ( MC: 52 2Ø=5Ø.642 %=5.43Ø ↑ _

≥
1212↑
POS. Ø MATRIX: B ELEMENT: 2Ø ( MC: DEF.52 2Ø=45.151 ↑ %=1.36Ø ↑ ∠
POS. 1 MATRIX: B ELEMENT: 2Ø ( MC: 52 2Ø=45.151 %=1Ø.94Ø ↑ _

≥
1214↑
POS. Ø MATRIX: C ELEMENT: 26 ( MC: DEF.7Ø 2Ø=57.524 ↑ %=1.96Ø ↑ ∠
POS. 1 MATRIX: C ELEMENT: 26 ( MC: 7Ø 2Ø=57.524 %=11.1ØØ ↑ _

≥
1216↑
POS. Ø MATRIX: B ELEMENT: 19 ( MC: 52 2Ø=5Ø.642 )
                          2Ø ( MC: 52 2Ø=45.151 ∠
POS. 1 MATRIX: B ELEMENT: 19 ( MC: 52 2Ø=5Ø.642 )
                          2Ø ( MC: 52 2Ø=45.151 ∠
POS. 2 MATRIX: B ELEMENT: 19 ( MC: 52 2Ø=5Ø.642 )
                          2Ø ( MC: 52 2Ø=45.151 ∠
POS. 3 MATRIX: C ELEMENT: 26 ( MC: 7Ø 2Ø=57.524 ∠
POS. 4 MATRIX: C ELEMENT: 26 ( MC: 7Ø 2Ø=57.524 _
```

EXAMPLE OF INPUT LIST

Figure 8

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