X-RAY DIFFRACTION AUTOMATION AND ITS USE IN CLAY MINERALOGY

by

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ABSTRACT

THE STANDARD Philips X-ray Diffraction equipment has been fully automated for continuous unmonitored operation. Modifications of the equipment include a sample-changing device, goniometer-driven divergence slits, pulse motor drive with eight-speed option, selective scan speed as a function of *hkl* intensity, range change device, and electronic programming of the complete operation. In addition, simultaneous readout on the Brown Recorder strip chart and magnetic tape provide records for visual and computer processing.

Computer programs have been developed for the processing of the digital output that is in the form of cumulative pulse counts for the angular position and the intensity of the reflection. These data are converted to *hkl* spacings in angstroms and intensities after removal of the background count. An identification program has been developed that identifies the minerals and prints out the spacings and intensities used for the identification. Solvation and heat treatment data are utilized to aid in the identification of the clay minerals.

Selected data from sediments are used to illustrate the output of the automated instrument and the increased resolution and speed of the equipment.

INTRODUCTION

ROUTINE examination and identification of sediments for mineral content are slow by existing commercially available equipment. Two alternative methods for increasing sample output are available: duplication of existing equipment, or automation of existing equipment. The repetitive nature of X-ray diffraction analysis of similar material makes automation procedures feasible and practicable. Duplication of equipment requires more space, as well as a much larger investment in equipment.

At its Richardson, Texas, research facilities, the Sun Oil Company has developed a completely automated procedure from sample changing to computer identification of the mineral content. The present paper will deal specifically with the mechanical and electronic automation procedure. The computer procedures are illustrated and will be reported in detail when the interpretive program has been more thoroughly tested. The identification program is currently being used but is being checked with chart output patterns to verify minor constituents.

https://doi.org/10.1346/CCMN.1964.0130114 Published online by Cambridge University Press

INSTRUMENTATION

The basic Philips Wide Angle Diffractometer was modified to accommodate the sample-changing mechanism and the automation features described.

Since the stability of alignment is critical in the diffraction procedure, a means of providing stable alignment was developed first. In Plate 1, letters designate significant features of the assembly. The $\frac{1}{2}$-in. aluminum jig plate, a, is used as a base mounting instead of the relatively unstable tripod mount of the commercial instrument. Adjustments are made using a precision alignment jig, b, for the mechanical alignment. The centers of points e, f, and g define the X-ray path. Points e and f are adjusted with the plate bosses until the close-fit machined rods are free. Point g is adjusted by moving the detector arm. All points are finally adjusted using the collimator alignment bosses at c and d and the knurled knob at the end of the alignment boss (just to the right of point g). When mechanical alignment is completed, the jig table (a) is firmly bolted to the table before the removal of the jig. Collimators are positioned relative to the bosses c and d. These adjustments are secured before removing the alignment jig.

Optical alignment is accomplished in the normal way using the alignment gauge and fine slits. When maximum intensity is attained, the 2 : 1 alignment gauge is used to make this final adjustment. The adjustable slits (referred to later as a and c in Plate 6) are set at the same zero-angle slit apertures. Once the alignment is completed, it is stable for months.

The sample-changing device (Plate 2) consists of a circular magazine (a), magazine holder (b), and electronic controls for injecting and ejecting slides and rotating the magazine to position a new slide. The magazine holds 100 thin petrographic slides ($26 \times 46 \times 0.96$–1.04 mm). Thin slides made from ceramic with the same tolerance can be used in this instrument. Thicker slides can be used, if the slide guides and magazine dimensions are changed to accommodate them.

Slides are positioned sequentially and returned to the magazine by the control unit (Plate 4). Three clock motors and switches (rear Plate 3) are controlled by a series of stepping switches in the control assembly. Motor M-3 (Plate 3) rotates and positions the magazine, M-1 injects the slide and is homed after the switch at M-2 is closed. Motor M-2 ejects the slide. When the injector rack is homed, it closes the switch and actuates the goniometer from its 2° 2θ position to begin the diffraction background scan to the 64° position. Before the upper limit switch is closed and the diffraction scan begun, the background intensity level at 63.5° 2θ value is set at the fastest preselected scan speed (c in Plate 4). The lower limit switch is closed when the diffraction scan is completed and initiates the next cycle of sample change and scan.

Synchronous control of the goniometer (Plate 3), Brown Recorder (Plate 5) and magnetic tape print-out system (Plate 8) is achieved by the use of Slo-Syn pulse motors. These motors are stepping motors and step one revolution for each 200 pulses on their input circuitry. Mode of operation switches allow for automatic, manual or oscillatory operation (b in Plate 4) of the diffraction

system. These modes can be locked together in three ratios of goniometer–recorder speeds. Ratio 1 is a 1 : 1 relationship with both at the same speed; 1 : 2 provides for goniometer speed twice the recorder speed and 0.5 gives a recorder speed twice the goniometer speed. The 1 : 1 arrangement is normally used for the automatic scan.

Eight scan speeds are available in each of four range speed selector switch positions (c in Plate 4). Speed 1 is 240 pulse frequencies per second or 60° per minute scan and speed 8 is a 15 per 32° per minute scan. These speeds are accomplished through seven stages of binary flip-flops connected in series as successive divide by 2 circuits. The fastest preset speed is set as the operational speed prior to the actual diffraction scan. Sample scanning will continue at the fast speed until the count per second rate received exceeds a set value for each of the remaining three selected speeds. These threshold values are controlled by the magnetic clutch-cam switch assembly (a in Plate 5). Thus, the scan rate is decreased to the preset values sequentially as the count rate rises. This gives increased resolution of the peak position because of the decreasing scan speed with increasing intensities of a peak. As the count rate falls to the previously set background limit, the speed sequentially returns through the same scan speeds until the fast speed is again attained. If the count rate falls below the present fast scan threshold, the scan speed value is automatically reset to this new low threshold value. When the intensity exceeds the full scale deflection on the chart, the range change device on the Brown Recorder is actuated (b in Plate 5). The range change modification of the Brown Recorder provided four full scale ranges by putting in 9 m.v. bucking voltage for each of the four ranges provided. This control is provided by the two micro-switches at b in Plate 5.

An automatic driven slit system was developed and geared to the goniometer to provide the correct collimation slit openings at each angular position of scan. Plate 6 shows the slit assembly developed and the chain drive (a, b, c), which is driven by the goniometer and controlled by the sample position angle. The slits are made of molybdenum metal. In Plate 6, d shows the sample holder with its two rubber fingers used to position the slide firmly to the underside of the metal sample holder. The semicircular opening at the center is the ejection rod opening. This rod releases the tension on the sample by depressing the rubber finger when the ejection cycle is initiated.

Output from the detector is fed simultaneously to the Brown Recorder and the magnetic print-out system (Plate 8). Both systems are tied to the upper limit goniometer switch through the control assembly and initiate simultaneous print-out as the diffraction scan begins. The chart drive continues to operate through the sample change cycle to provide a straight line between patterns. The tape recorder operates for sufficient time to provide $\frac{3}{4}$in. of magnetic tape between the end of record and the initiation of the new sample data. By using the dual output, visual observation of the patterns and digital data for computer identification are available.

Plate 7 shows a safety device developed to protect instrumentation. The

https://doi.org/10.1346/CCMN.1964.0130114 Published online by Cambridge University Press

time clock is preset to accommodate the normal operation cycle for sample change and scan. If the elapsed time exceeds the set limit, the clock turns off the X-ray tube power (leaving the cooling system operational) and the electronic control assembly (Plate 4). The magnetic tape unit and the Brown Recorder are left energized. The by-pass mode in Plate 7 is used when the machine is under visual observation during the day.

APPLICATION TO X-RAY DIFFRACTION

The automatic instrumentation described was developed to further the research efforts in clay mineralogy and to provide a rapid accurate method of observing large numbers of samples. Previous X-ray diffraction pattern output with Philips equipment was limited to 15–20 patterns per day. Present output of better quality patterns is 135–180 patterns in 24 hr. This output posed a serious interpretation and data handling problem using Brown Recorder output charts. The time required for manual indexing and interpretation of data was excessive for the size of staff available.

Initially the patterns were digitized using a Benson-Lehner Oscar F Digitizer to obtain the angular positions and intensities on IBM cards. This method was partially satisfactory but saved little time and provided several more sources of error. As a result, the Instrumentation Group developed a magnetic tape print-out unit for simultaneous digital output from the X-ray diffraction unit. Data are digitized as cumulative numbers of pulses from the Slo-Syn drive, which establishes the angular position, and as intensities in counts per second. These data are obtained prior to being fed to the integrating circuitry of the Philips electronics.

A computer program has been developed that smooths the data, removes the background, converts angles to angstrom units, picks peaks and records intensities. These data can be printed out or fed directly to the mineral identification program. The identification program currently contains 187 minerals and clay mineral complexes. A subsequent paper will deal with this phase after sufficient sophistication is achieved. Computer data processing has resulted in a large volume of high quality data on the mineralogy of sediments at a very low per sample cost. The speed change during scanning, the range change and the automatic driven collimator slits have all improved the resolution and speed per determination. The sample changing assembly has greatly extended the total number of samples per day.

EXPERIMENTAL RESULTS

Examples of X-ray patterns run on the automated diffraction equipment are presented to illustrate the quality of the patterns obtained. For comparison, the magnetic tape digital print-out has been programmed into a graphical plot. Representative illustrations of the computer identification output are presented.

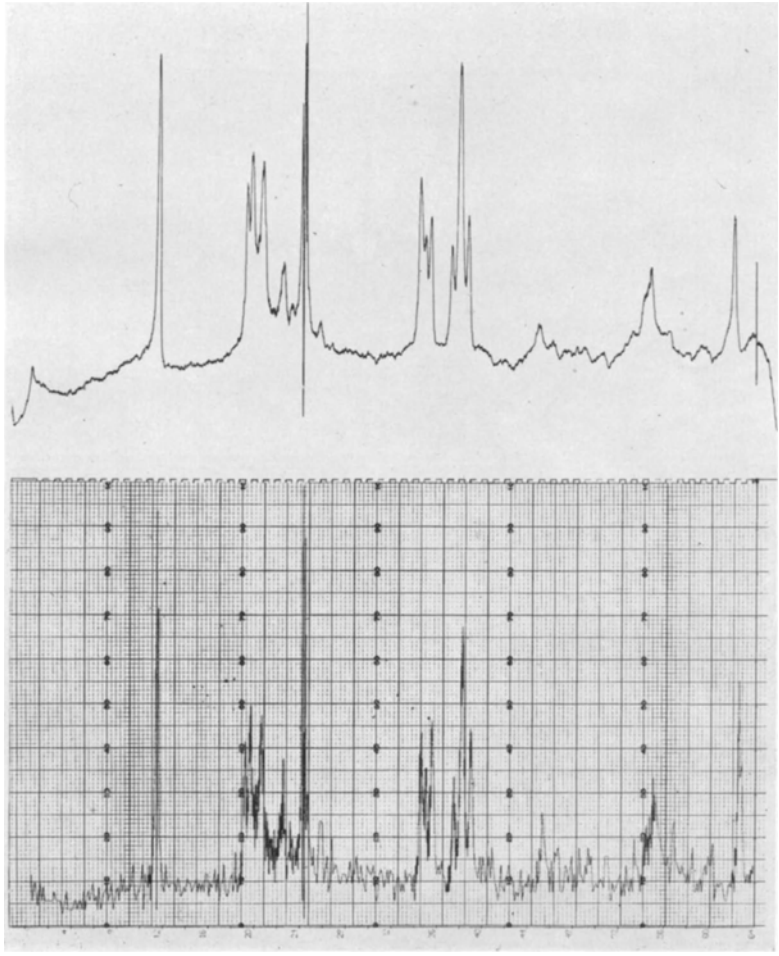

FIG 1. Brown Recorder and magnetic tape output for kaolinite no. 477.

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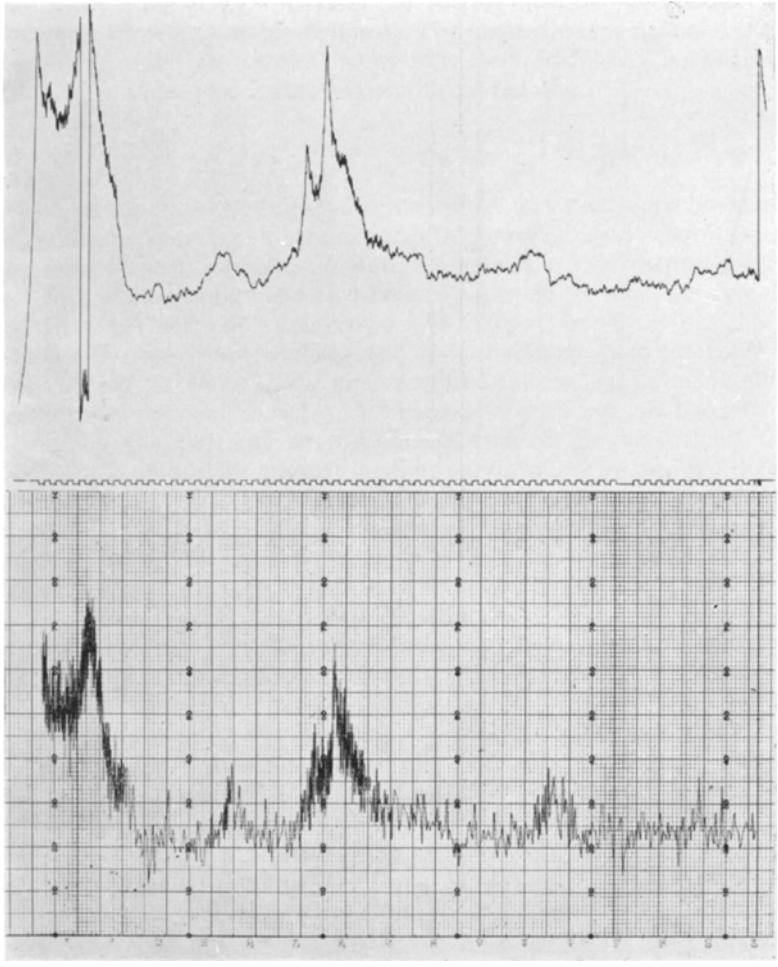

FIG 2. Brown Recorder and magnetic tape output for Gulf of Mexico sediment

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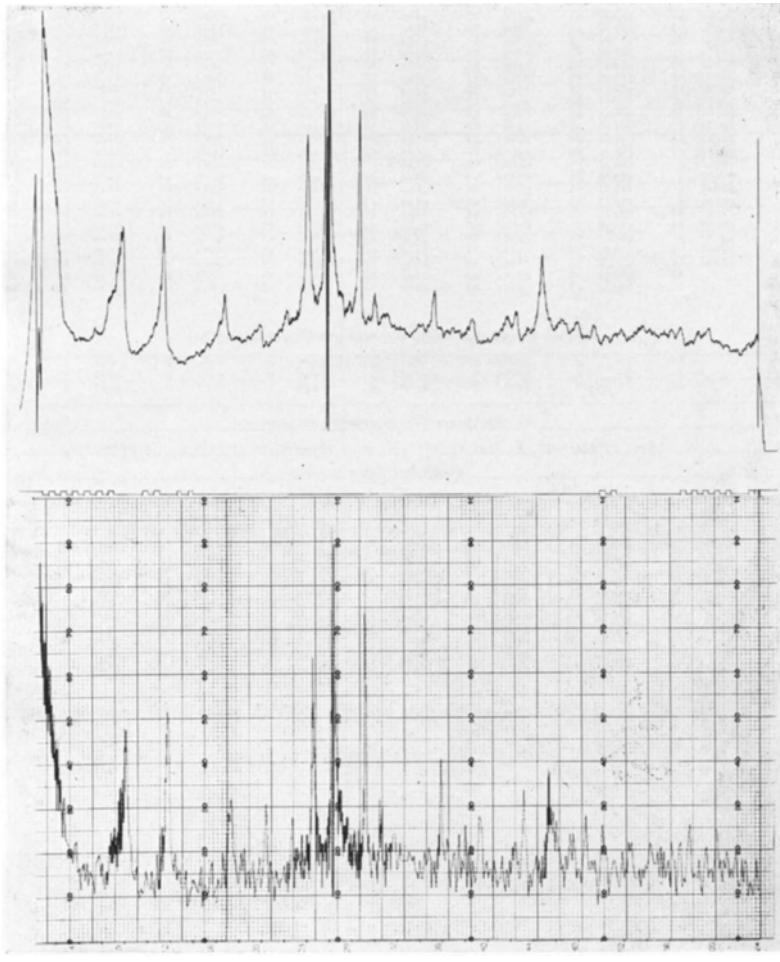

FIG. 3. Brown Recorder and magnetic tape output for Athabasca Silt

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RECORD NUMBER 1
998 DATA POINTS IN THIS PATTERN

24	12	9397	16	5943	42	4758	45	8448	12	9713	37	10413	18	12199	9
40	14	9338	10	5947	36	4762	36	8500	10	9721	14	10417	24	12231	10
56	12	9344	11	5951	34	4766	27	8532	12	9729	14	10421	26	12263	14
72	13	9340	12	5955	33	4770	32	8564	12	9737	12	10425	30	12295	8
88	10	9376	8	5959	32	4774	32	8596	12	9745	11	10429	22	12327	9
104	12	9410	12	5963	26	4778	28	8628	10	9753	14	10433	24	12359	16
120	10	9442	14	5967	25	4782	26	8660	10	9761	11	10437	26	12391	20
150	12	9474	14	5971	26	4786	26	8692	12	9769	12	10441	26	12423	72
182	10	9506	20	5975	22	4790	20	8724	14	9777	14	10445	30	12449	104
218	12	9538	8	5979	20	4794	30	8756	14	9785	22	10449	30	12452	104
2923	15	5702	10	6500	12	8092	13	9609	16	10361	20	11783	10	14733	6
2931	20	5734	14	6532	15	8084	14	9617	12	10365	22	11815	11	14765	6
2939	20	5746	11	6544	12	8116	8	9625	16	10369	24	11847	8	14797	9
2947	17	5708	12	6596	14	8148	10	9633	13	10373	20	11879	9	14829	6
2955	18	5810	14	6628	12	8180	11	9641	20	10377	22	11911	8	14861	10
2963	23	5842	18	6660	16	8212	14	9649	19	10381	24	11943	7	14893	8
2971	20	5804	33	6692	32	8244	10	9657	18	10385	32	11975	10	14925	9
2979	14	5913	42	6728	41	8276	12	9665	19	10389	37	12007	11	14957	10
2987	20	5921	44	6776	44	8308	16	9673	22	10393	20	12039	8	14989	10
2995	18	5927	36	6742	47	8340	12	9681	15	10397	24	12071	10	15021	6
2003	18	5931	46	6746	42	8372	13	9689	24	10401	32	12103	10	15053	12
2011	14	5935	36	6750	40	8404	10	9697	16	10405	24	12135	10		
2019	12	5939	40	6754	36	8436	15	9705	16	10409	27	12167	10		

THE LOW VALUES PICKED FROM THE ABOVE DATA ARE AS FOLLOWS

841	6	3370	8	5360	6	7508	6	11143	6	12576	6	-1	-1
1259	8	4286	8	6418	8	7892	6	11943	7	12712	4	-1	-1
3018	6	4998	6	7040	6	8884	8	12209	8	14413	8	-1	-1

THE EQUATION FOR EVALUATING BACKGROUND IS

BACKGROUND = 7.8114 + -7.7329E-04 X + 1.5006E-07 X**2 + -8.1195E-12 X**3

WHERE X = RAW ANGLE DATA.

THE 88 PEAKS PICKED FROM THE ABOVE DATA, USING AN INTENSITY CHANGE OF (3) OVER THE ADJACENT LOW VALUE, ARE AS FOLLOWS

982	37	2670	11	4234	15	5931	48	7796	13	9824	36	11230	13	13192	12
342	56	2946	14	4496	26	6197	68	8044	12	10010	22	11390	12	13254	9
777	10	2930	10	4614	11	6243	34	8212	14	10178	24	11623	11	13384	10
875	19	2704	12	4710	12	6532	16	8308	16	10277	44	11815	11	13480	10
1131	11	3080	16	4870	13	6742	47	8436	15	10401	32	12007	11	13642	9
1291	18	3446	18	5126	14	6866	36	8820	20	10497	50	12263	14	13770	10
1387	13	3658	18	5266	14	6962	44	8916	16	10621	42	12448	104	13962	8
1475	28	3754	12	5478	18	7284	13	9044	24	10812	17	12686	12	14317	8
2119	24	3618	14	5542	16	7444	12	9460	144	10857	12	12748	14	14727	9
2963	23	3946	14	5670	16	7604	13	9417	141	11047	14	12936	14	14864	10
2506	20	4106	18	5734	16	7668	13	9689	24	11175	12	13128	11	14957	10

Fig. 4. Magnetic tape raw data, low values and picked peaks print-out.

Fig. 1 (top) illustrates the Brown Recorder (BR) tracing of a kaolinite standard (Georgia Kaolin Co. no. 477) which took 11 min to traverse from the magazine through the diffraction scan and back into the magazine. The bottom half shows the magnetic tape output as graphed by the computer (MT). The increased sharpness and resolution of the MT print-out compared with the time-integrated BR output is evident. Note the difference in definition of the rounded X-ray tracings on the BR and MT output, which occur for low intensity rapid-scan positions. Resolution on the magnetic tape has not been sacrificed by the rapid scanning procedure.

STANDARDS

BOOK	PROJECT	MAGAZINE	SLIDE	SAMPLE NO
9	33	1	1	6402

TREATMENT 1

NO. OF DATA POINTS = 88

1.479	29.4	1.959	8.4	2.839	5.9	5.164	6.5
1.484	48.4	1.991	19.4	2.948	8.9	5.371	5.5
1.524	9.7	2.024	4.4	3.000	8.9	5.691	4.7
1.534	11.8	2.041	5.4	3.040	8.9	5.997	4.8
1.559	3.9	2.071	6.3	3.095	7.9	6.339	4.9
1.575	11.8	2.120	7.3	3.272	12.9	6.860	8.1
1.585	6.9	2.152	7.3	3.320	8.9	7.294	98.2
1.615	17.1	2.192	11.3	3.386	16.9	7.941	6.4
1.665	27.2	2.206	9.2	3.501	136.9	8.117	8.5
1.682	14.3	2.234	9.2	3.595	133.9	8.758	8.7
1.711	13.3	2.248	9.2	3.765	17.0	9.509	5.8
1.719	4.3	2.293	38.2	3.836	31.0	9.789	6.9
1.731	7.3	2.335	61.2	3.988	15.8	10.086	4.0
1.739	3.3	2.379	77.1	4.116	19.1	10.738	5.1
1.747	5.4	2.443	8.1	4.195	41.1	11.286	5.2
1.781	6.4	2.501	40.1	4.299	25.1	12.349	4.4
1.839	11.4	2.536	29.1	4.382	43.2	13.341	5.6
1.868	11.4	2.564	17.0	4.496	35.2	15.172	3.8
1.882	5.4	2.663	6.0	4.683	10.3	20.332	4.3
1.892	9.4	2.714	5.0	4.761	5.3	37.660	6.1
1.912	7.4	2.770	6.0	4.936	7.4	42.489	7.2
1.937	11.4	2.793	6.0	5.086	5.4	52.610	7.4

GL DATA OMITTED IN POSSIBLE IDENTIFICATION OF 14 ANGSTROM GROUP
PROGRAM EXITS TO NEXT LOOP

GL DATA OMITTED IN POSSIBLE IDENTIFICATION OF 14 ANGSTROM GROUP - MICA II
PROGRAM EXITS TO NEXT LOOP

CLAY MINERALS

KAOLIN GROUP

UN EQL 7.294 INT= 98.223 UN EQL 3.591 INT=136.943 UN EQL 2.335 INT= 61.164

THE PERCENTAGES OF THE FOLLOWING CLAYS-

CLAY	PERCENT
MONTMORILLONITE	0
CHLORITE	0
KAOLIN GROUP	100.00
ILLITE	0
MUSCOVITE	0

FIG. 5. Identification output for kaolinite no. 477.

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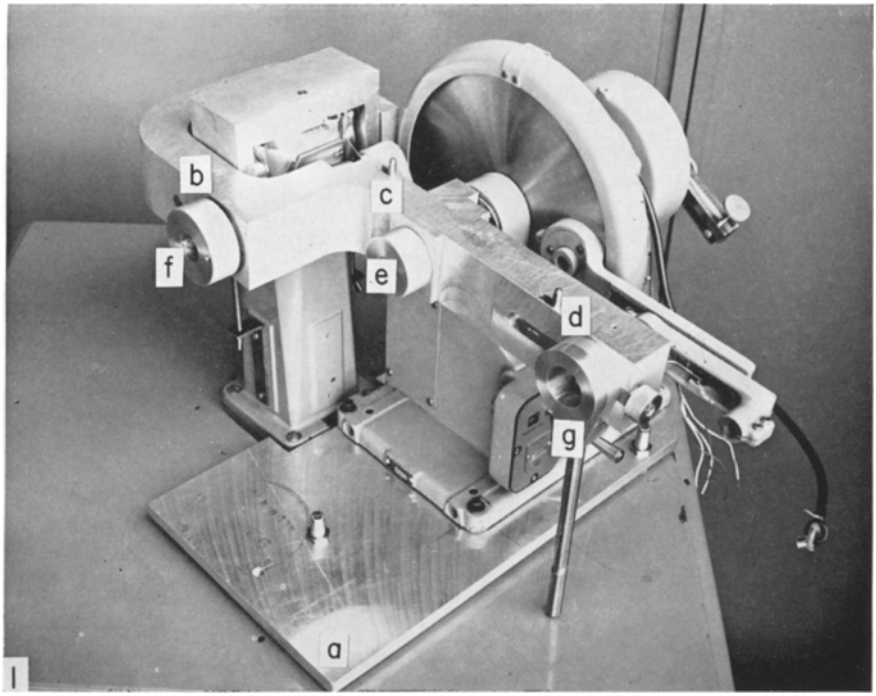

PLATE 1 Goniometer mounting base and alignment jig.

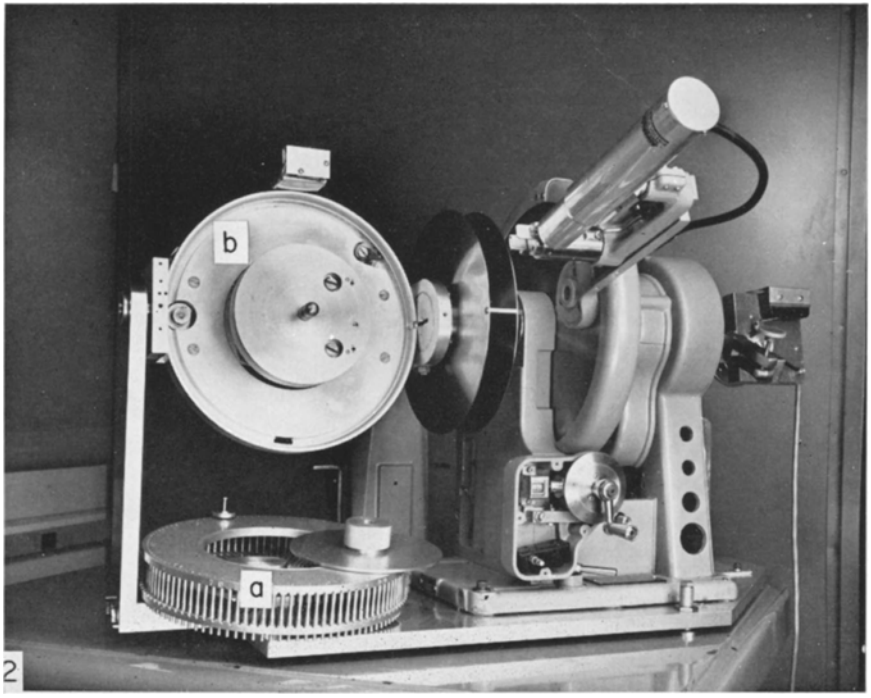

PLATE 2. Sample changer with magazine not in place.

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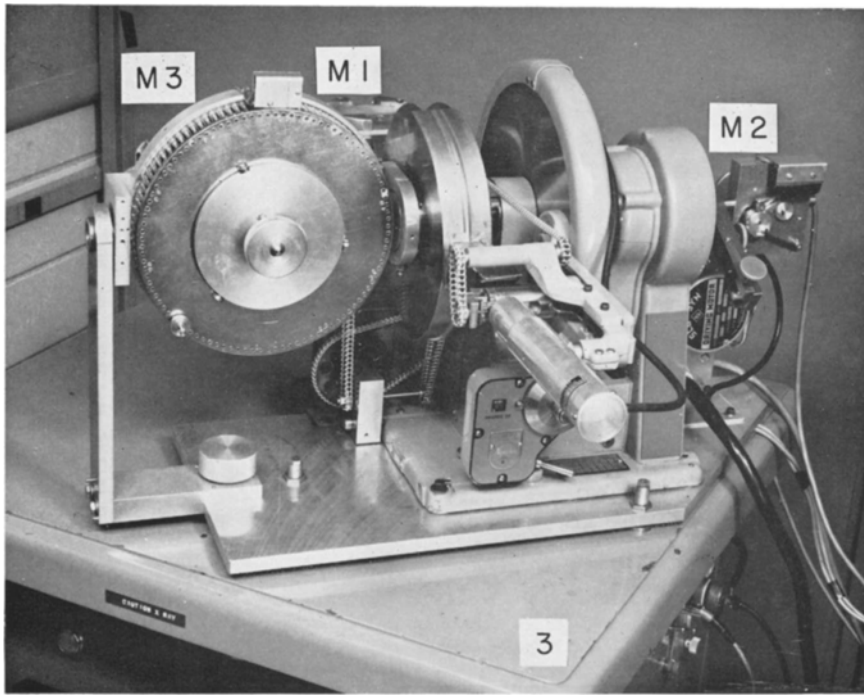

PLATE 3. Sample changer with magazine and cover in place.

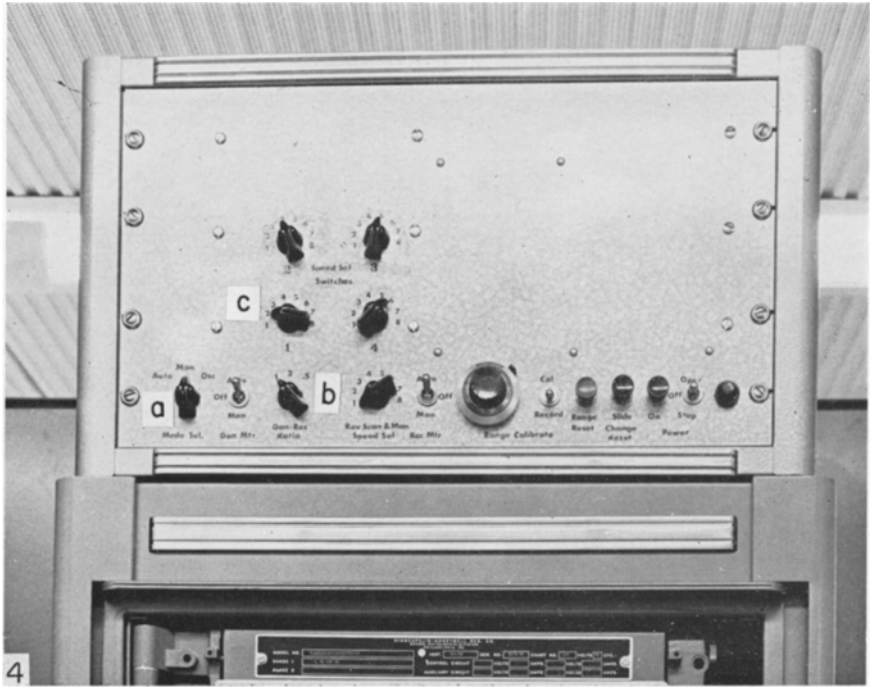

PLATE 4. Electronic control assembly.

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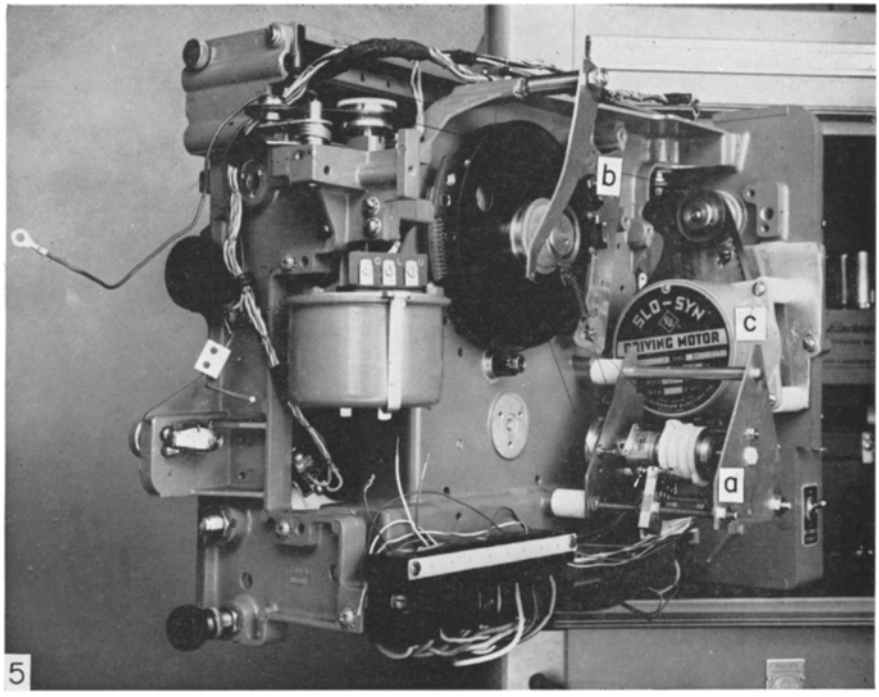

PLATE 5. Rear view of Brown Recorder modifications.

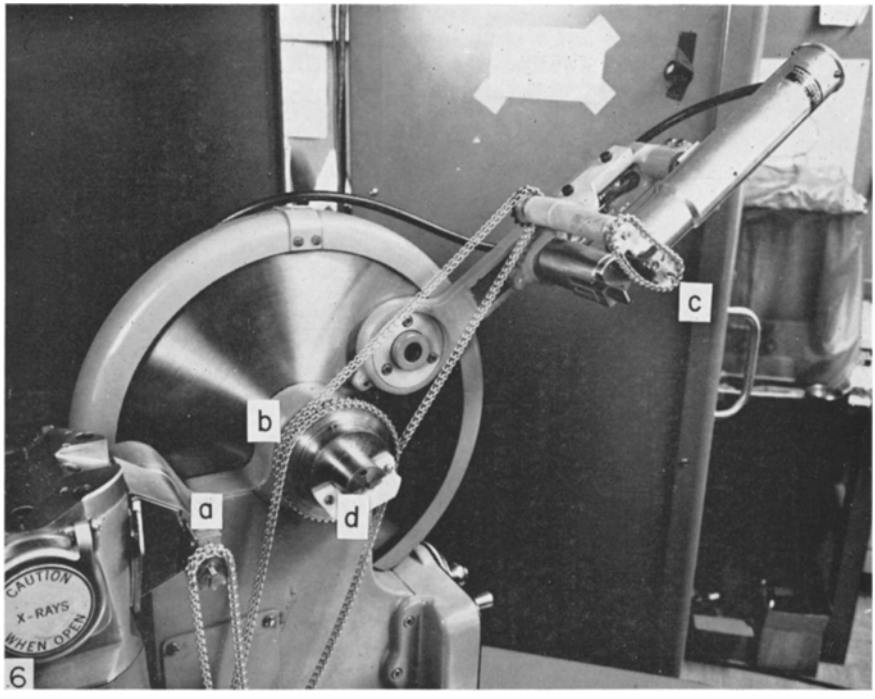

PLATE 6. Driven collimator slit assembly on goniometer.

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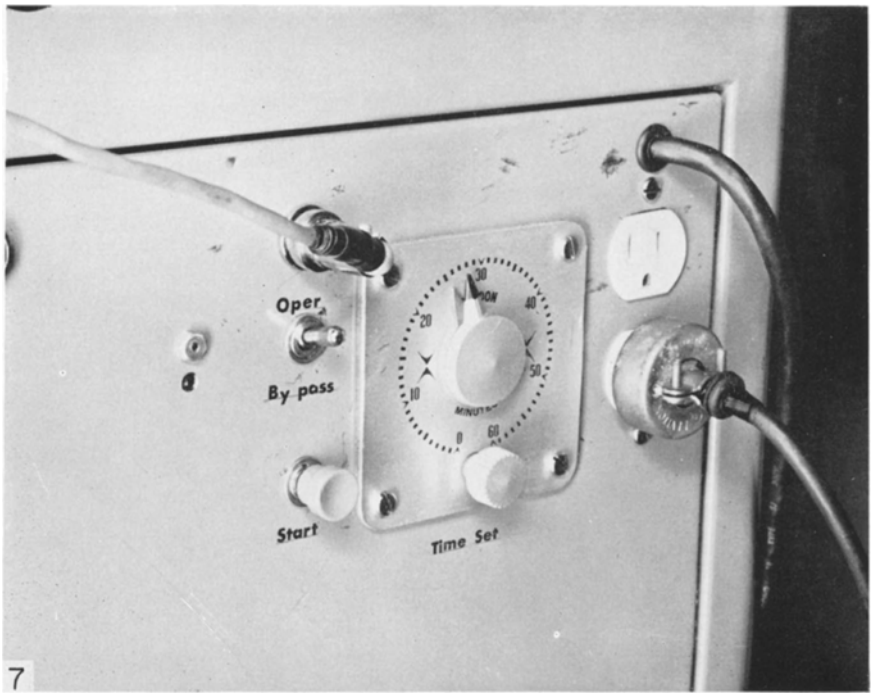

PLATE 7. Safety control modification for sample changing mechanism.

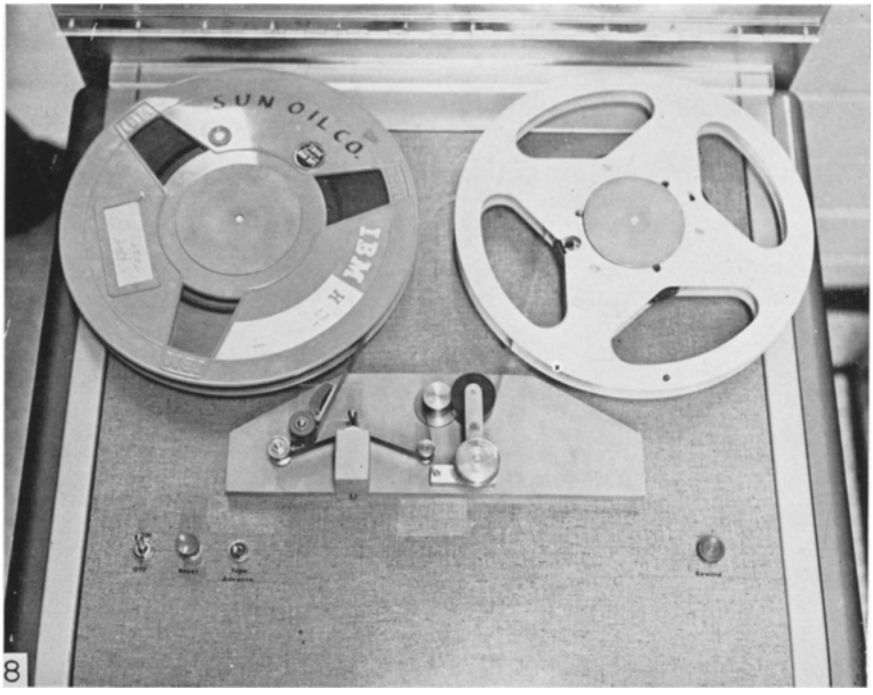

PLATE 8. Top view of digital magnetic tape print-out assembly.

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Fig. 2 shows a typical example of an X-ray diffraction pattern of a near shore Gulf of Mexico surficial sediment (top 5 cm). These materials are usually reported as being 50 per cent montmorillonite and 25 per cent each illite and kaolinite. The nature of the pattern width in the illite–montmorillonite region is typical (BR). Sample running time was 15 min. Note the amount of definition in the MT record for this area. Frequently, as many as five or more regularly stratified mixed-layer complexes are defined in the present computer programming. These are identified in the computer program by testing for ten orders of the basal spacing from 10° to 60° 2θ. If a regular sequence is present, identification is reported and shows in which tested interval the basal spacing occurs. When the MT peaks shown on the pattern are real, they can be confirmed in the sample.

Fig. 3 is another example of a complex natural mixture: the silt extracted from the Athabasca Tar Sand, Alberta, Canada. The sample is composed of calcite, quartz, kaolinite and illite with some chlorite, feldspar, anhydrite, mixed-layer clays and montmorillonite. Compare the number and sharpness of the peaks in the two types of patterns. Positive identification of all these minerals with some other minor constituents was accomplished by the identification program.

Fig. 4 is a portion of the raw data as printed out from the magnetic tape. The data pairs are the number of pulses in the left-hand column and the number of counts within the counting interval on the right. Note that there were 998 data points collected for the kaolinite pattern seen in Fig. 1 as raw data. The second block shows the low values that are used to correct the pattern for background. The equation used is presented in the next block. The bottom block shows the values picked as peaks (88) from the raw data.

Fig. 5 shows the converted data output as values in angstrom and relative intensities. The identification program uses the converted data for sequential library search. The program will test up to five treatments (1, plain; 2, glycerol; 3, heat at 450°C; 4, heat at 550°C; and 5, ethylene glycol), which may be used for refined identifications in special problem areas. Note that, below the data, two possible identifications were not made, since only treatment 1 was used. The last entry is a subroutine print-out, which computes the percentage distributions from intensities for the clay minerals. Identifications of feldspar, calcite and siderite were also made in this sample but are not included in the figure.

CONCLUSIONS

A satisfactory rapid method of automated X-ray diffraction has been attained. The addition of simultaneous Brown Recorder and digital Magnetic Tape print-out has made a computer identification program feasible. The addition of pulse height discrimination is planned, and faster counter and more sophisticated identification programming will make an automatic semi-quantitative X-ray identification method available as an inexpensive rapid routine procedure.

ACKNOWLEDGMENTS

The mechanical and electronic development of the reported instrumentation was a staff project. I should like specifically to acknowledge the efforts of Messrs. P. E. Chaney, Jack Jones and Clarence Braun, Instrumentation, and John Bennett and Carl Caldwell, Mechanical Engineering, in the development and construction of the instrumentation. Messrs. John Rice, Sidney Pitzer, Art Waggoner, Donald Welter and Richard Wong have all contributed to the computer programming and their help is gratefully acknowledged.