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RAPID DETERMINATION OF ALUMINA
IN DIASPORE CLAYS

BY

MATTHEW J. KERPER

A

THESIS

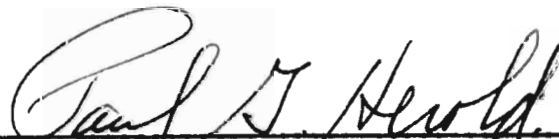
submitted to the faculty of the
SCHOOL OF MINES AND METALLURGY OF THE UNIVERSITY OF MISSOURI
in partial fulfillment of the work required for the
Degree of

MASTER OF SCIENCE IN CERAMIC ENGINEERING

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INTRODUCTION

The principal source of raw material for the production of high-alumina refractories are the diaspore clays of Missouri. These highly refractory clays contain a large percentage of the mineral diaspore, a monohydrate of alumina whose theoretical chemical formula is $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$. The clays as mined contain from 65 to 85 per cent alumina.

The alumina content of the diaspore clay is the index to its refractoriness, so it is important to know the alumina content of the diaspore clay. Diaspore is mined in comparatively small pits and naturally the alumina content will vary from pit to pit and will vary to a considerable extent in the same pit. Since a uniform finished product is desired, the alumina content of each pit must be known and frequent checks run on the output of the pits.

Chemical analysis is the standard method of determining the amount of alumina in clays. The main objections to chemical analysis is the length of time involved in the determination and the lack of information concerning the mineral form of the alumina in the sample.

Petrography, X-Ray, and the differential thermal furnace are some methods that have been suggested to overcome the deficiencies of chemical analysis. It is the purpose of this work to discuss these methods and to compare them.

REVIEW OF LITERATURE

The hydrates of alumina have so far been found to be four - dias-pore and boehmite, which are mono-hydrates, and gibbsite and bayenite, which are tri-hydrates. A di-hydrate, bauxite, was long considered as a mineral form, but it has been proven that bauxite is a mixture of the mono-hydrate and the tri-hydrate. Wohlin¹ made a thermal analysis of the various hydrates of alumina and found that dias-pore had decided heat ab-sorption at both places. He concluded that the di-hydrate was a mixture of the other two forms, thus confirming the conclusions of Cornu and Red-lich² who earlier in the twentieth century arrived at the conclusion that bauxite was a mixture of dias-pore and gibbsite.

The mono-hydrate appears as alpha-monohydrate which is dias-pore and has, as yet, not been produced artificially. Dias-pore, according to Dana³ is orthorhombic; dipyramidal. It has a hardness of $6\frac{1}{2}$ to 7, and a specific gravity from 3.35 to 3.45. It has a vitreous luster except on the cleav-age face, where it is pearly. Color is white, gray, yellowish, or green-ish. It has the formula $AlO(OH)$ and contains 85% alumina and 15% water. M. DeFladre⁴ gives the Schoenflies designation D_{2h}^{16} to dias-pore. The edges of the unit cell are a 4.40, b 9.38, c 2.83 Å. The unit cell con-tains 2 $(Al_2O_3 \cdot H_2O)$. Optically, dias-pore is biaxial positive with a very large axial angle. The indices are n 1.702, n 1.722, n 1.750. The re-

¹Wohlin, J. Sprechsal, Vol. 46, p. 719 (1913).

²Cornu, M. and Redlich, R. Zerschift Fur Chemie U. Ind. Der. Kol., Vol. 4, p. 90 (1908).

³Dana, E. S. Manual of Mineralogy, Fifteenth Edition, New York, Wiley, 1941. p. 205.

⁴DeFladre, M. Bull. Soc. Franc. Mineral., Vol. 46, pp. 140-165, (1932).

lief is high, the birefringence is strong, the crystals are length-fast, and extinction is parallel.⁵

The tri-hydrate of alumina occurs in nature as gibbsite, designated as the alpha-trihydrate. The alpha-trihydrate may also be produced by auto-precipitation from a sodium aluminate solution. The beta-trihydrate, bayenite, can be produced by saturating a sodium aluminate solution with carbon dioxide under certain conditions. Beta-trihydrate appears to be a meta-stable phase, for it goes over to the alpha form on continued shaking or on long standing in contact with alkali.⁶

As stated previously, one of the methods for proving that bauxite was a mixture of diaspore and gibbsite was the differential thermal method. The differential thermal method was suggested in 1887 by Le Chatelier.⁷ Walloch,⁸ around 1913, showed this method could be used to identify clays. In 1933, Orcel and Caillere⁹ stated that it is possible to determine better than by any other methods the similar forms of kaolinitic and montmorillanitic clays and to determine the sometimes small contents of kaolin by the temperature where the endothermic phenomena takes place. Orcel¹⁰ suggested the possibility

⁵Rogers, A. F., and Kerr, P. F. Optical Mineralogy, N.Y., McGraw-Hill, 1942. p. 202.

⁶Edwards, J. and Tosterud, M. The Oxides and Hydrates of Alumina. J. of Phys. Chem. Vol. 37, pp. 483-488 (1933).

⁷Le Chatelier, De L'Action de la Chaleur sur les Argiles. Bull. Soc. Min. Vol. 10, p. 204 (1887).

⁸Wallach, H. Analyse Thermique des Argiles. Compt. Rend. Vol. 157, p.48, 1913.

⁹Orcel, J. & Caillere, S. L'Analyse Thermique Differentielle des Argiles a Montmorillonite (Bentonites). Compt. Rend. Vol. 197, pp. 774-777 (1933).

¹⁰Orcel, J. Differential Thermal Analysis for Determination of Constituents of Clays, Laterites, and Bauxites. Congr. Internat. Mines, Met. Geol. Appl., 7^e Session, Paris, 1935, Geol. Vol. 1, pp. 359-373 (1936).

of using the differential thermal method as a quantitative measure, although no known attempt has been made along this line.

In this country most of the recent work done with the differential thermal method of analysis has been done by Dr. F. H. Norton of Massachusetts Institute of Technology. In Dr. Norton's first article on the differential thermal method of analysis¹¹, he fully describes the equipment used and the curves obtained. Of the minerals of interest here, kaolinite gave a strong endothermic peak at 610°C and a very strong exothermic peak at 980°C. All of the clays in the kaolin group that Dr. Norton analyzed gave this characteristic exothermic peak at 980°C. Gibbsite gave a strong endothermic peak at 310°C. Diaspore gave a strong endothermic peak at 550°C.

In measuring the peaks produced by the differential thermal method it was found that a measure of the area under the peak was a more reliable measure than the height of the peak, which is the maximum temperature difference between the test sample and the neutral body. The height of the peak varied with small changes in heating rate, therefore measuring the area under the peak would produce less error than measuring the height of the peak. Dr. Norton found that with care he could obtain results reproducible within two per cent. Factors that disturb the curve are the packing of the sample in the holder and the grain size of the sample used. Both of these factors would be important in a quantitative study.

¹¹Norton, F. H. Critical Study of the Differential Thermal Method for the Identification of the Clay Minerals. Jour. Amer. Ceram. Soc., Vol. 23, pp. 54-64 (1940).

To explain the peaks produced by kaolin, A. Jourdain¹² concludes that the endothermic peak that occurs from 500°C to 550°C is caused by the volatilization of water and the exothermic peak that occurs between 900° and a 1000°C results from crystallization, probably into a mixture of mullite and tridymite. Insley and Ewell¹³ state that the endothermic peak is associated with the volatilization of water and the dissociation into an exceedingly intimate mixture of amorphous alumina and amorphous silica. The exothermic peak of kaolin is associated with the formation of -alumina from amorphous alumina.

The differential thermal method of analysis is much cheaper and quicker than a chemical analysis. Differential thermal will not replace chemical analysis but it can be used in conjunction with chemical analysis and X-ray analysis to give more details about a clay mineral.

Chemical analysis by X-ray has rapidly gained widespread use since the publication of the first Hanawalt tables¹⁴ in 1938. Its field of application does not coincide with that of other forms of analysis commonly used but rather supplements them. X-ray analysis is mainly qualitative, but it only analyzes crystalline solids so its use is limited. For quantitative analysis the X-ray is far from perfect, for it is none too accurate and will only work on samples of a few

¹²Jourdain, A. Studies of the Constituents of Refractory Clays by Means of Thermal Analysis. *Ceramique*. Vol. 40, pp. 135-141 (1937)

¹³Insley, H. and Ewell, R. H. Thermal Behavior of the Kaolin Minerals. *Jour. Research Nat. Bur. Stand.* Vol. 14, p. 201 (1935)

¹⁴Hanawalt, J.D., Rinn, H.W., and Frevel, L.K. Chemical Analysis by X-Ray Diffraction. *Ind. & Engr. Chem., Analytical Ed.* Vol. 10, pp.457-512 (1938)

constituents. Clark in his book, "Applied X-Rays"¹⁵, gives some of the advantages and disadvantages of X-Ray analysis as compared to other types of analysis. Some of the advantages over chemical analysis that are of interest here are, small amounts of materials can be analyzed and these are not destroyed. The material to be analyzed need only be powdered, it does not need any other preparation, thus eliminating the difficult operation of fusing in the analysis of diaspore. The record is permanent in the case of X-ray diffraction. The results are largely independent of individual error. For qualitative analysis the main disadvantages are the high initial cost of the equipment and the special technique required. Most of the other disadvantages were due to the equipment and to a great extent have been overcome. For quantitative analysis, there are several disadvantages the chief one naturally being the limited accuracy of the results.

In 1936 Clark and Reynolds¹⁶ used X-rays as a quantitative measure to analyze mine dusts. The authors took a crystalline powder, known not to be present in the mixture being analyzed, and added it to the unknown in a definite ratio and had the X-ray diffraction pattern registered by a suitable apparatus. The ratio of the density of a line of the substance sought to that of a nearby line of the added standard is determined photometrically. The ratio thus obtained is proportional to the line intensity of the substance sought, which, in turn, is proportional to the line intensity of the substance sought, which in turn

¹⁵Clark, G. L. Applied X-Rays. N. Y., McGraw-Hill, 1940. pp. 128-129.

¹⁶Clark, G. L. and Reynolds, D. H. Quantitative Analysis of Mine Dusts. Ind. & Engr. Chemistry, Analytical Ed. Vol. 8, pp. 36-41 (1936)

is proportional to the amount of substance in the mixture. By reference to a curve which is prepared empirically using mixtures of known composition, the percentages of the constituent sought is obtainable at once.

Quartz was the material sought in the work by Clark and Reynolds. They determined that the method was accurate to within five per cent. Quartz in a sample was measurable down to as low as four per cent and as little as one per cent quartz produced a pattern. It is recommended never to use X-rays to analyze for traces. Care must be used in choosing a standard or the lines produced by the standard may interfere with the lines produced by the substance sought.

In his excellent paper on Missouri flint and diaspore clays, V. T. Allen¹⁷ states that an optical examination of the fine material in diaspore clay reveals that it is partly isotropic, with a refractive index about 1.61, and is partly opaque. Cliachite ($Al_2O_3 \cdot nH_2O$) which is the amorphous constituent of many bauxites and which frequently contains silica as an impurity, fits best the optical properties of this isotropic material. It was also noted that the refractive index of the halloysite around the diaspore needles is always higher than that of the halloysite occurring alone and suggests a change in the chemical composition of the halloysite. If this is true, it would be expected that further formation of diaspore would be accompanied by further change in the optical properties of the altered halloysite.

¹⁷Allen, V. T. Mineral Composition and Origin of Missouri Flint and Diaspore. Missouri Bureau of Geology and Mines. 1935-1941 appen. IV.

From the accompanying graph it can be seen that the refractive index of the isotropic matrix around the diaspore increases as amount of diaspore and the total alumina increases . This curve is based on values secured by determining the refractive index of the isotropic matrix of samples analyzed for total alumina.

Halloysite, according to Rogers and Kerr¹⁸, has an index of refraction of from 1.549 to 1.561, and kaolinite, which has the highest indices of the kaolin group, has an index of $n = 1.561$, $n = 1.565$, and $n = 1.566$. Since the matrix surrounding the diaspore has an index of 1.605 to 1.620, Mr. Allen (19) concludes the matrix is an intermediate stage between halloysite and clichite.

¹⁸Rogers, A. F., and Kerr, P. F., op. cit. page 2.

¹⁹Allen, V. T., op. cit. page 6.

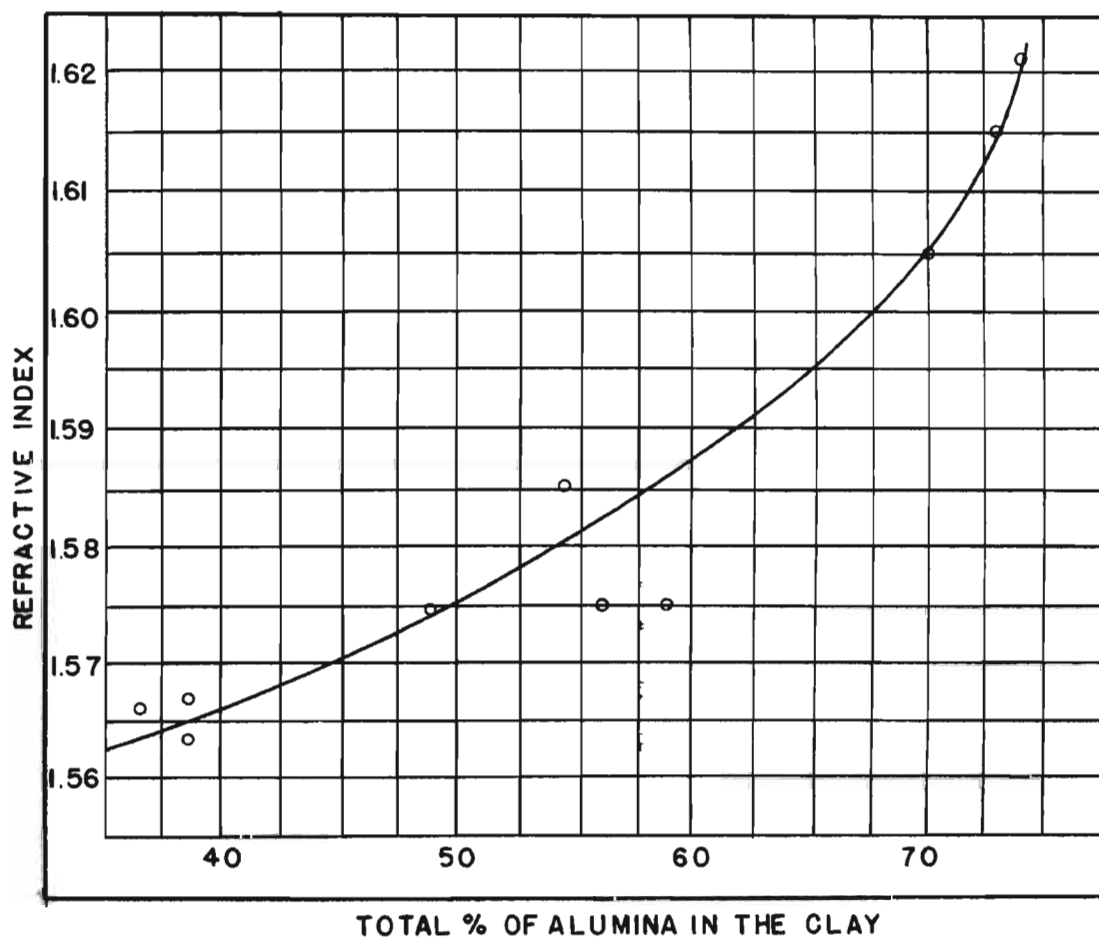


Fig. 1
RELATIONSHIP BETWEEN THE REFRACTIVE INDEX AND THE ALUMINA CONTENT OF THE CLAY

TABLE I CHEMICAL ANALYSIS

Sample	Al ₂ O ₃	SiO ₂	Fe ₂ O ₃	TiO ₂	LOI	Total
B-740	45.70	35.15	.49	3.54	13.45	98.33
B-741	69.47	12.42	1.41	1.25	14.07	98.62
B-742	61.58	18.60	1.65	3.01	13.73	98.57
B-743	50.94	30.91	.85	2.31	13.45	98.46
B-744	60.60	21.37	.85	2.63	13.62	98.47
B-745	66.10	15.86	1.01	1.72	13.98	98.67
B-746	56.30	26.90	1.01	1.09	13.23	98.53
B-747	67.90	13.40	.81	2.37	14.08	98.56
B-748	56.00	26.92	.85	1.50	13.35	98.62
B-749	56.10	25.97	.77	2.18	13.61	98.63
B-750	66.80	16.75	.85	.93	13.35	98.68
B-751	51.70	30.34	.85	2.58	12.95	98.42
B-752	66.80	15.83	.85	1.90	13.18	98.56
B-753	52.10	31.19	.77	1.21	13.20	98.47
B-754	68.90	12.59	.81	2.66	13.57	98.53
B-755	55.40	26.75	.77	2.25	13.46	98.63
B-756	68.40	14.03	.81	1.66	13.70	98.60
B-757	56.00	27.12	.81	1.50	12.95	98.44
B-758	63.50	18.63	.85	2.10	13.44	98.52
B-759	45.40	37.37	.81	1.69	13.30	98.57
B-760	56.60	26.91	.69	1.78	12.70	98.68
B-766	73.30	10.78	.89	2.54	11.00	98.51

CHEMICAL ANALYSIS

The chemical analyses were made in the chemistry laboratory of the ceramics department. The procedure followed was that prescribed by the American Society of Testing Materials for the short analysis.

The so called short analysis gives per centages of alumina, silica, iron, titanium, and loss on ignition and is all that is generally desired. The short analysis will take about seventy-two hours to complete and will cost about eight dollars.

Theoretically chemical analyses are accurate to the second decimal place, but actually in a diaspore clay plus or minus two and one half per cent accuracy in the determination of the alumina is all that can be expected.

In a chemical analysis the results are given in per cent of a substance (generally the oxide of an element) present. The analysis tells the elements present and the amount of each but does not tell the original form of the mineral in the sample. This lack of information as to original mineral form and the length of time for the completion of the analysis are the main objections to chemical analysis. However, chemical analysis remains the most accurate method of measuring amounts of alumina in a diaspore sample that we have at our disposal.

TABLE II REFRACTIVE INDEX

SAMPLE	MATRIX		DIASPORE
B-740	1.56-1.57	1.59-1.60	
B-741	1.60-1.61	1.70-1.71	
B-742	1.60-1.61	1.65-1.66	
B-743	1.58-1.59	1.63-1.64	
B744	1.59-1.60	1.65-1.66	
B-745	1.58-1.59	1.65-1.66	1.70-1.72
B-746	1.58-1.59	1.69-1.70	
B-747	1.60-1.61	1.70-1.71	
B-748	1.57-1.58	1.69-1.70	1.70-1.73
B-749	1.59-1.60	1.62-1.63	1.70-1.73
B-750	1.62-1.63	1.67-1.68	1.70-1.71
B-751	1.59-1.60	1.64-1.65	
B-752	1.60-1.61	1.67-1.68	
B-753	1.57-1.58	1.62-1.63	1.70-1.72
B-754	1.59-1.60	1.69-1.70	
B-755	1.58-1.59	1.66-1.67	
B-756	1.58-1.59	1.68-1.69	1.70-1.72
B-757	1.58-1.59	1.70-1.71	
B-758	1.57-1.58	1.66-1.67	1.70-1.72
B-759	1.58-1.59	1.64-1.65	
B-760	1.58-1.59	1.70-1.71	1.70-1.72
B-766	1.60-1.61	1.70-1.71	1.70-1.73

PETROGRAPHIC ANALYSIS

The diaspore samples were analyzed petrographically by using powdered grains. No thin sections were made. The usual optical technique was used so there would be little value in describing it here.

The ground mass in all the samples had identical appearance, varying only in the index of refraction. The matrix varied from colorless to light green or brown and infrequently showed iron red stains. In small thin fragments the ground mass was transparent but the great majority was opaque and appeared as a shapeless, granular mass. The matrix was isotropic. It can be seen in the accompanying table of index of refractions that the ground mass, or what is obviously an intimate mixture of matrix and diaspore, varied in index of refraction from 1.58 to 1.71, with the average index ranging from 1.59 to 1.63. The results found for the matrix agree, save for some higher indices, with the results found by Allen²⁰ in his work on diaspore. It is rather apparent that when the index of the ground mass runs up and into the lower diaspore limit that diaspore is so intimately mixed with the ground mass that the two cannot be separated petrographically.

The diaspore grains followed the description for diaspore given²¹ by Rogers and Kerr. No index higher than 1.73 was observed in any

²⁰Allen, V. T. Mineral Composition and Origin of Missouri Flint and Diaspore. Missouri Bureau of Geology and Mines. 1935-1941 appen. IV

²¹Rogers, A. F., and Kerr, P. F. Optical Mineralogy. N. Y., McGraw-Hill, 1942. p. 202

sample while the aforementioned authors state that for diaspore $n = 1.75$. The diaspore crystals observed were colorless, tabular in shape, and were generally minute. Cleavage was good in one direction, relief was high, and birefringence strong. Interference figures were infrequent and when obtained were poor, however the figure could be determined as uniaxial positive.

Considering the entire petrographic analysis it was noted that in general in the higher alumina diaspores the diaspore grains were more abundant than in the samples of low alumina content. In the samples of low alumina content few if any grains of diaspore were visible. It was also noted that the higher the alumina content of the sample the higher the index of refraction of the matrix for the given sample.

It must be taken into consideration that these samples were intended for chemical analysis and when received were mixed to give a representative sample. It is logical to assume that the clay as well as the diaspore could be in the sample. This is to be expected when samples are brought in for analysis.

Petrography as a means of qualitative analysis is a fairly rapid method if an experienced man does the analyzing. Working with clay minerals can produce difficulty in distinguishing between the different types of clay minerals. As a means of quantitative analysis petrography is of little value, for all petrography can do is distinguish between great amounts and small amounts.

TABLE III X-RAY DATA

B-740		B-741		B-742		B-743		B-744	
d	I/I ₁	d	I/I ₁	d	I/I ₁	d	I/I ₁	d	I/I ₁
1.37	.30	1.37	.38	1.37	.36	1.37	.19	1.37	.18
1.49	.80	1.41	.14	1.43	.27	1.49	.38	1.49	.32
1.64	.40	1.43	.24	1.49	.36	1.64	.38	1.61	.14
1.67	.30	1.49	.38	1.58	.18	2.08	.48	1.64	.50
1.90	.40	1.52	.10	1.61	.27	2.13	.29	1.81	.18
2.09	.20	1.61	.19	1.64	.55	2.20	.24	2.08	.59
2.24	.30	1.64	.67	2.08	1.00	2.33	.67	2.13	.50
2.33	.80	1.81	.24	2.12	.27	2.37	.67	2.33	.55
2.58	.90	1.90	.19	2.33	.90	2.58	.52	2.37	.50
3.62	1.00	2.09	.80	2.37	.73	3.28	1.00	2.58	.50
4.04	.80	2.15	.60	2.58	.73	4.04	.48	3.59	.68
4.50	.50	2.34	.64	3.60	.90	4.27	.29	4.03	1.00
		2.37	.52	3.90	1.00	4.47	.38	4.47	.55
		2.58	.86	4.69	.73				
		3.62	.32						
		4.04	1.00						
		4.48	.43						

TABLE III (cont.) X-RAY DATA

B-745		B-746		B-747		B-748		B-749	
d	I/I ₁	d	I/I ₁	d	I/I ₁	d	I/I ₁	d	I/I ₁
1.37	.25	1.37	.24	1.37	.30	1.37	.17	1.37	.21
1.43	.25	1.49	.41	1.41	.10	1.43	.22	1.48	.29
1.49	.33	1.64	.53	1.43	.23	1.49	.26	1.49	.29
1.53	.17	2.09	.65	1.49	.47	1.61	.17	1.52	.21
1.61	.21	2.13	.41	1.52	.17	1.64	.44	1.64	.48
1.64	.63	2.33	.65	1.56	.17	1.81	.17	2.08	.64
1.72	.13	2.38	.65	1.61	.27	2.08	.35	2.12	.43
1.81	.17	2.58	1.00	1.63	.87	2.13	.35	2.31	.36
1.90	.17	3.63	.47	1.74	.20	2.33	.52	2.37	.43
2.09	.67	4.04	.53	1.82	.20	2.36	.35	2.58	.64
2.13	.46			2.07	.87	2.58	.52	3.60	1.00
2.33	.75			2.13	.70	3.62	.57	3.96	.64
2.37	.54			2.31	.80	4.03	1.00	4.47	.43
3.59	.59			2.33	.51	4.47	.44	7.32	.86
4.04	1.00			2.56	.84	7.32	.52		
4.33	.38			3.57	.33				
				3.96	1.00				
				4.40	.37				
				4.74	.30				

TABLE III (cont.) X-RAY DATA

B-750		B-751		B-752		B-753		B-754	
d	I/I ₁	d	I/I ₁	d	I/I ₁	d	I/I ₁	d	I/I ₁
1.37	.30	1.37	.17	1.37	.38	1.37	.14	1.37	.43
1.41	.13	1.43	.30	1.49	.50	1.49	.33	1.40	.11
1.43	.27	1.49	.33	1.60	.25	1.64	.38	1.43	.22
1.49	.40	1.64	.50	1.64	.75	1.72	.14	1.49	.47
1.61	.20	1.81	.25	1.80	.38	1.90	.14	1.53	.22
1.64	.47	1.90	.17	2.09	.88	2.00	.14	1.61	.29
1.74	.20	2.09	.67	2.13	.63	2.09	.43	1.64	.90
1.81	.27	2.15	.33	2.33	.38	2.15	.33	1.70	.25
2.09	.87	2.33	.83	2.58	.50	2.33	.70	1.81	.21
2.15	.47	3.59	.83	4.04	1.00	2.58	.48	1.91	.21
2.33	.33	4.04	1.00			3.59	1.00	2.09	1.00
2.38	.33	4.47	.58			4.04	.57	2.15	.61
2.58	.67							2.33	.50
4.04	1.00							2.38	.25
4.48	.67							2.58	.75
4.74	.53							3.59	.39
								4.04	.89
								4.47	.64

TABLE III(cont,) X-RAY DATA

B-755		B-756		B-757		B-758		B-759	
d	I/I ₁	d	I/I ₁	d	I/I ₁	d	I/I ₁	d	I/I ₁
1.37	.26	1.37	.29	1.37	.20	1.37	.31	1.37	.16
1.43	.22	1.41	.17	1.43	.20	1.41	.12	1.43	.21
1.49	.43	1.43	.25	1.49	.40	1.43	.24	1.49	.42
1.61	.17	1.49	.46	1.61	.20	1.46	.24	1.61	.42
1.64	.48	1.61	.21	1.64	.60	1.49	.37	1.64	.42
1.70	.13	1.63	.63	2.09	1.00	1.64	.63	1.67	.42
1.81	.26	1.81	.21	2.15	.40	1.81	.24	1.81	.16
1.85	.17	2.09	.79	2.33	.67	1.90	.19	1.99	.26
2.09	.65	2.15	.54	2.58	.60	2.09	.88	2.07	.16
2.15	.35	2.33	.71	3.59	.87	2.15	.50	2.33	.69
2.33	.74	2.38	.63	4.04	.80	2.33	.88	2.56	.79
2.58	.65	2.58	.75			2.58	.88	3.57	1.00
3.25	.30	3.59	.58			3.59	.56	3.96	.47
3.59	1.00	4.04	1.00			4.04	1.00	4.40	.37
		4.47	.54			4.47	.50		
		4.74	.25						

TABLE III (cont.) X-RAY DATA

B-760		B-766		Diaspore		Kaolin	
d	I/I ₁	d	I/I ₁	d	I/I ₁	d	I/I ₁
1.37	.30	1.37	.32	1.00	.03	1.24	.16
1.41	.15	1.41	.12	1.037	.04	1.29	.16
1.43	.20	1.43	.32	1.063	.07	1.31	.08
1.46	.15	1.46	.32	1.09	.08	1.49	.56
1.49	.40	1.49	.44	1.14	.03	1.54	.16
1.53	.15	1.53	.20	1.17	.09	1.67	.40
1.61	.30	1.61	.24	1.20	.05	1.80	.08
1.64	.80	1.64	.64	1.215	.03	1.85	.08
1.72	.15	1.72	.20	1.24	.07	1.90	.08
1.81	.25	1.81	.28	1.26	.05	1.99	.32
2.09	.70	1.91	.24	1.29	.08	2.34	.80
2.15	.45	2.09	.76	1.33	.10	2.50	.48
2.33	.90	2.15	.52	1.37	.20	2.56	.48
2.37	.70	2.33	.76	1.40	.08	3.59	1.00
2.58	.80	2.38	.32	1.42	.27	4.04	.32
3.59	.35	2.58	.76	1.48	.33	4.20	.48
4.02	1.00	3.57	.28	1.52	.08	4.30	.64
4.48	.55	4.04	1.00	1.60	.05	4.45	.80
		4.47	.36	1.63	.83	7.20	.80
				1.71	.20	Diaspore (cont.)	
				2.06	.67	2.55	.33
				2.12	.67	3.20	.08
				2.31	1.00	3.99	1.00
				2.37	.05	4.70	.09

X-RAY ANALYSIS

The x-ray used was a Phillips North American Norelco with a Brown recording chart attached. A Coolidge type tube is used to produce the rays and a Geiger-Counter measures the intensity of the radiation.

For the analyses an iron target tube was used and good results were obtained. Later a copper target tube was used for radiation and better patterns were produced than with the iron target tube, the peaks produced were more intense and sharper and the background did not rise quite so badly. Some kaolin samples were analyzed with the two types of tubes and the same results were noted. It is recommended that for a clay mineral copper radiation be used for x-ray analysis.

Comparison of results produced by analysis of the diaspores by x-rays with Hannawalt's ²² tables showed excellent agreement with all samples. Both kaolin and diaspore lines were produced by the samples and the intensities of these lines compared favorably with the intensities of the kaolin and diaspore intensities given by Hannawalt. One line appeared on the charts of some of the samples with an intensity out of proportion to it assigned by Hannawalt. This intense line was finally attributed to a combination of a kaolin line at $d = 2.56$ with an intensity of .48 and a diaspore line at $d = 2.55$ with an intensity of .33. The line on the charts appeared around $d = 2.58$ and on some charts was the most intense line.

From simply scanning the charts and plotting kaolin peaks against diaspore peaks no determination of the amount of diaspore in a

²²Hanawalt, J.D., Rinn, H.W., and Frevel, L.K., op. cit. page 4.

sample could be determined.

The x-ray is an excellent means for qualitative analysis. It is rapid, taking no more than three hours to analyze a sample. X-ray analysis has the added feature of telling the form of the mineral in a sample and not giving simply chemical elements. If a sample is being analyzed qualitatively for an individual substance, such as diaspore, the Geiger-Counter need only traverse a few degrees to determine if a peak is present that would indicate the substance sought. This would take only a few moments.

²³

Using Clark's paper on the analysis of mine dusts as a guide an attempt was made to use the x-ray as a means of quantitative analysis. Samples were made using high alumina diaspore as the variable, zinc oxide as the filler, and Florida kaolin as the standard. Another group was tried using chemically pure flourspar as the standard. A group of eleven samples were made for each standard with the diaspore varying from zero to one gram in increments of a tenth of a gram. Zinc oxide was added to the diaspore to make one gram. The standard was kept constant in all samples at two tenths of a gram.

For the diaspore and kaolin group the diaspore line at $d = 3.99$ was used and the kaolin line at $d = 3.59$ was used. When analyzed alone the diaspore sample used did not produce a peak at $d = 3.59$ but when used in combination with Florida kaolin the peak produced at $d = 3.59$ was more intense than estimated. Apparently there is enough kaolin in the diaspore sample to augment the kaolin peaks. Naturally no conclusions could be drawn from this attempt.

²³Clark, G.L. and Reynolds, D.H. op. cit. page 5.

Using diasporite with chemically pure fluorapatite as a standard the same line at $d = 3.99$ was used for the diasporite line and a line at $d = 3.16$ was used for the fluorapatite line. Each of the samples in the series was radiated three times and each produced a slightly different result each time. Other experiments along the same line suffered the same fate so it was concluded that the variance in the voltage put into the x-ray caused the fluctuations in the peaks and the poor results.

Results that were obtained, although unusable, showed that with proper voltage control this method may prove to be an excellent means of rapidly determining the amount of alumina in diasporite.

THE DIFFERENTIAL THERMAL FURNACE

The furnace proper is a small metal cylinder, twelve and one-half inches high and ten and three-quarters inches in diameter, insulated with powdered magnesite. A small cylindrical hole, six inches long and one inch in diameter, in the bottom of the furnace is the receptical for the sample holder. The sample holder is made of cast alumina that has been fired to cone twenty. It consists of a base, column, and head. The base and column are used to hold the sample in the desired position in the furnace. The head contains the metal sample and standard cups and the thermocouple for the potentiometer. The metal cups are three-eighths of an inch in diameter and are one inch long and have an inside diameter of one-quarter of an inch. The sides and the bottoms of the cups are made of one-sixteenth of an inch thick metal. The cups have their top halves constructed of platinum and the bottom halves are made of platinum plus ten per cent rhodium. The two metals are fused together. The cups are connected at the top by a platinum wire and have platinum plus ten per cent rhodium lead wires attached to them and leading to the galvanometer. Cups of this design in addition to holding the sample and withstanding the required temperatures also act as a differential thermocouple and thereby reduce the necessity of having thermocouple wires in the sample.

A platinum wire and a platinum plus ten per cent rhodium wire fused together is placed in the head of the sample holder and acts as a thermocouple which is attached to the potentiometer for indicating temperature rise.

The sample is passed through a two-hundred mesh seive and is

placed in one of the cups. A standard of fused alumina that has been passed through a one-hundred mesh seive is placed in the other cup. The sample holder when filled is inserted in its receptical in the bottom of the furnace and is held in place by two sliding bars on the bottom of the furnace.

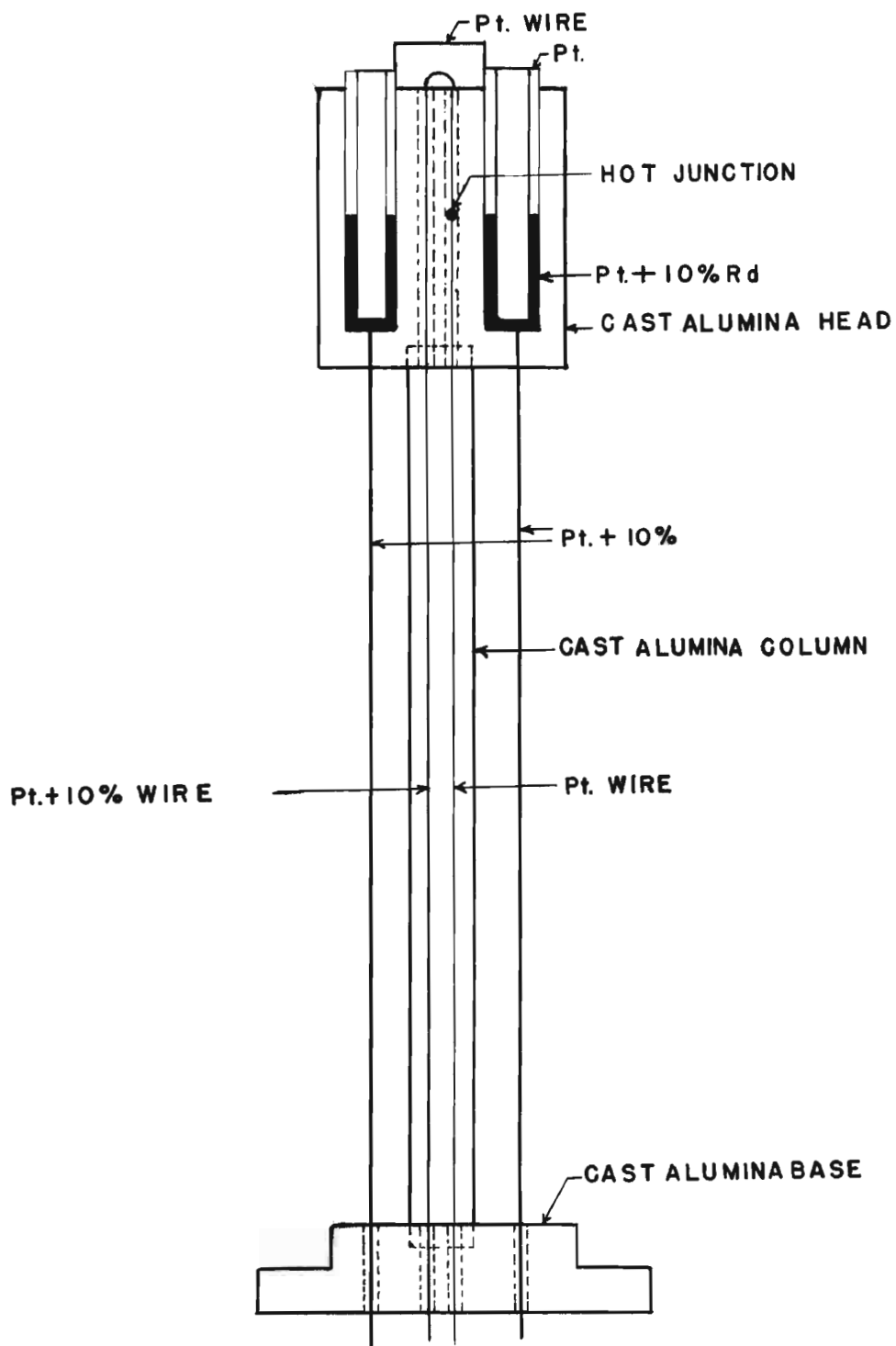
The sample is heated by one-hundred and ten volts passing through platinum coils which surround the sample. The temperature is controlled by a variac which is moved by a synchronous moter to give a temperature rise of approximately fourteen degrees per minute.

The recording box is a wooden box fourteen inches wide by fourteen inches high by four feet four inches long and contains the recording mechanisms. A galvanometer of Leeds and Northrup manufacture and having a sensitivity of .82 microvolts per millimeter, a C. D. R. X. of .22 ohms, a period of twenty-eight seconds, and a resistance of 9.6 ohms is used. It is shunted to dampen its movement and is connected to the sample and standard cups and is moved by the temperature difference between the two. The lights in the recording box and the camera moter are on a seperate one-hundred and ten volt circuit. A temperature index light is placed on the far wall from the camera next to the galvanometer in the box. A button switch closes the circuit causing the light to focus on the camera slit which produces a vertical temperature line on the sensitive paper. Temperature is recorded every fifty degrees. A light source for the galvanometer mirror is located near the center of the box and casts its light on the galvanometer mirror which reflects the light back to the camera slit causing the differential thermal curve to appear on the sensitive paper wrapped around the re-

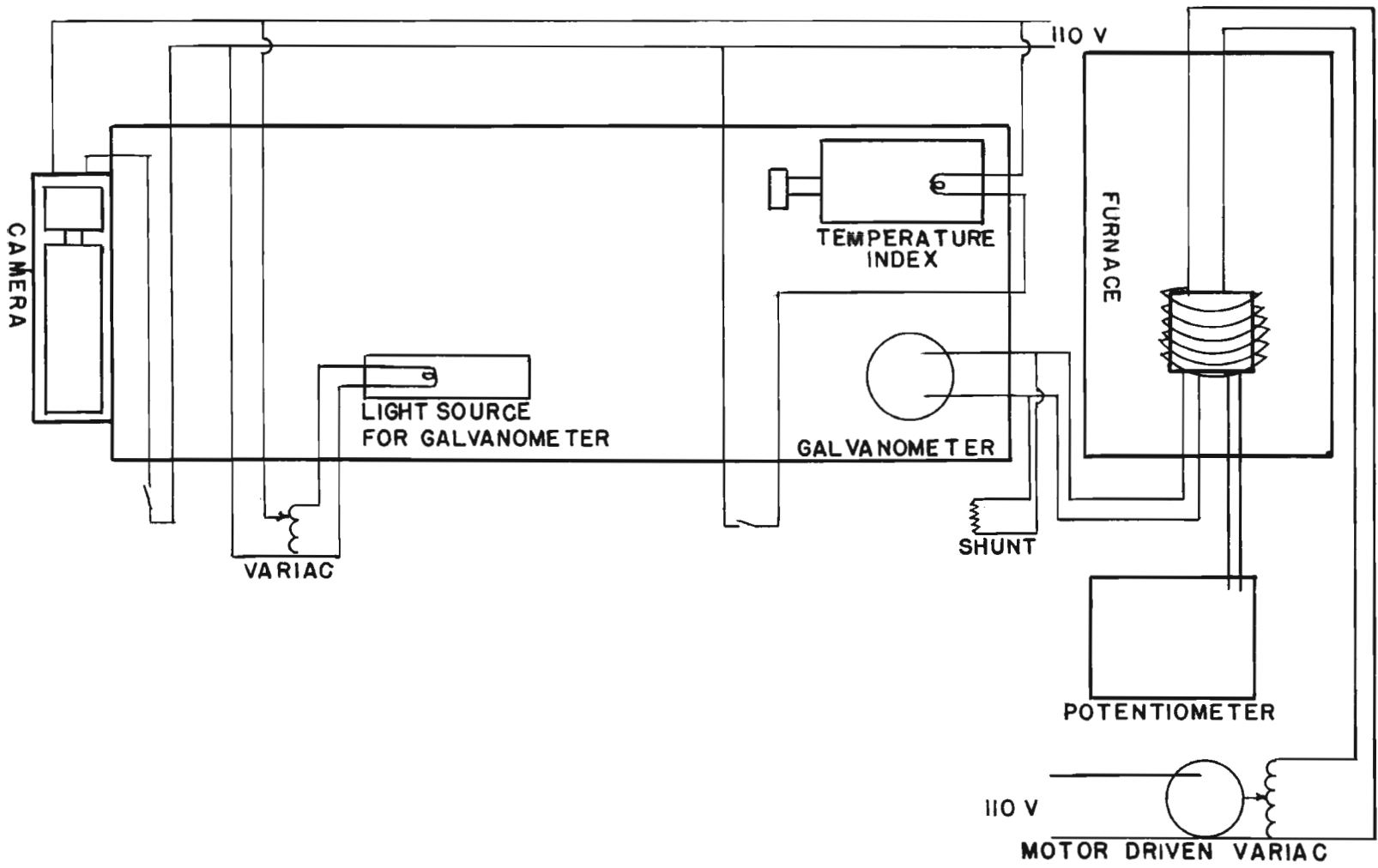
volving camera drum. A small toggle switch controls the light. A variac controls the intensity of the light and experience has proved that if the intensity of the light is increased over the range where the peaks will occur, more intense lines are produced on the peaks. If the maximum intensity is left on for the entire run the flat part of the curve is too intense. In these tests the diaspora peak and the endothermic peak of kaolin were used so the light intensity was increased at five-hundred degrees and reduced at seven-hundred degrees.

The camera is composed of a revolving cylinder, around which the sensitive paper is wrapped, and a motor. A light tight cover is placed over both the camera cylinder and the motor. There is a slit in the base of the camera, covered by a sliding panel. When the camera is placed on the end of the recording box the sliding panel is raised allowing the slit in the camera base to coincide with the slit in the recording box. The motor is geared to drive the cylinder at one revolution per hour. A small toggle switch is used to close the circuit to the camera motor.

A sensitive paper to give average to flat contrast was used and gave good results.



DETAIL OF SAMPLE HOLDER



DIFFERENTIAL THERMAL FURNACE

DIFFERENTIAL THERMAL ANALYSIS

Each sample was analyzed by the differential thermal method at least once, the majority of the samples were run twice, and some were run three times as a check. The areas under the curves were measured for comparison. When a double peak occurred, such as shown in figure 9, the area under both peaks was measured and also the diaspore peak was completed by drawing and its area measured. Both areas found were plotted against the alumina content of the sample. The areas under all curves were plotted against the corresponding alumina contents to see if they would produce a curve. The plot of the points was a scattered pattern and did not approach a curve of any kind. Of all the samples analyzed four produced duplicate results. These four when plotted did produce a nearly straight line as shown on graph 4. Further runs of other samples to bring them over to the line or to produce duplicate results did not succeed. Obviously the inability to reproduce results can be attributed to some unknown fault in the apparatus and this undoubtedly is one reason for not obtaining a usable curve.

Perhaps the varying areas may be attributed to the proximity of the kaolin and diaspore curves. Since the diaspore peak occurs at 560°C and the kaolin peak at 610°C a sample that contained both would have overlapping peaks, as shown in figure 9. The diaspore curve starts about 500°C and ends around 650°C. The kaolin peak starts about 550°C and ends about 700°C. Therefore the diaspore peak is still in evidence when the kaolin peak is starting and from 550°C to 650°C both curves are producing their effect and will reinforce each other in this range and give false results.

This theory seems born out by the fact that most of the areas are larger in proportion to the alumina content than they should be to fall on the line drawn through the four duplicate points.

The four samples that gave duplicate results have their curves reproduced in figures 4 through 7. Also included are reproductions of a high alumina curve, figure 8, a curve showing both kaolin and diaspore peaks, figure 9, and a kaolin curve, figure 10.

Other factors that may have contributed to the varying results are variance in temperature rise and lack of consistency in the amount of sample used. The temperature rise was fairly uniform but small changes were noted. Change in temperature is not supposed to produce a change in the area under the curve, only in the dimensions of the curve; however, it is possible that small errors could be introduced by variance in temperature rise. The amount of sample used and the compactness given it in the sample holder was kept as uniform as possible but undoubtedly there was a small variance in both of these factors.

An interesting point was noted in studying the results of the differential thermal analysis and that was the fact that no halloysite peak was noted. Halloysite produces three peaks when analyzed by the differential thermal method; one in the kaolin-diaspore range that would be obliterated, one at 150°C, and one at 300°C. The camera in this experiment was not turned on until 200°C was reached so the 150°C peak of halloysite would not be noted, however, the 300°C peak should have appeared if halloysite was present, especially since the apparatus used here was apparently more sensitive than that used by others.

Although the differential thermal method did not prove to be an effective means of quantitative analysis it showed promise. A table was made by comparing the sizes of the two peaks, or the absence of a peak in the case of high alumina content, and the alumina content and is shown in table IV.

TABLE IV

NO KAOLIN PEAK		DIASPORE PEAK LARGER THAN KAOLIN PEAK		KAOLIN PEAK LARGER THAN DIASPORE PEAK	
SAMP.	%Al ₂ O ₃	SAMP.	%Al ₂ O ₃	SAMP.	%Al ₂ O ₃
B-741	69.47	B-742	61.58	B-740	45.70
B-747	67.90	B-745	66.10	B-743	50.94
B-750	66.80	B-746	56.30	B-749	56.10
B-752	66.80	B-748	56.00	B-753	52.10
B-754	68.90	B-751	51.70	B-755	55.40
B-766	73.30	B-757	56.00	B-759	45.40
		B-758	63.50		
		B-760	56.60		
		B-756	68.40		

As can be noted from the table two breaks appear in the percentages of alumina and the type of curve produced. All samples of near 67 % and above, save one, produced only a diaspore curve. Those from 56% Al₂O₃ to 66%Al₂O₃ produced two curves with the diaspore predominating. Below 56% Al₂O₃ the kaolin peak was the larger of the two peaks.

As a means of qualitative analysis the differential thermal method is excellent, especially in the analysis of clay minerals when knowledge as to the type of mineral as well as the chemical composition is desired. As yet it is not known how much of a substance is needed to produce a recognizable curve.

Advantages of the differential furnace besides the fact that it identifies the mineral form are: simplicity, comparative ease of construction, economy, and speed of analysis. The furnace and auxiliary equipment in its present form cost approximately eight hundred and fifty dollars and takes about an hour to analyze a sample.

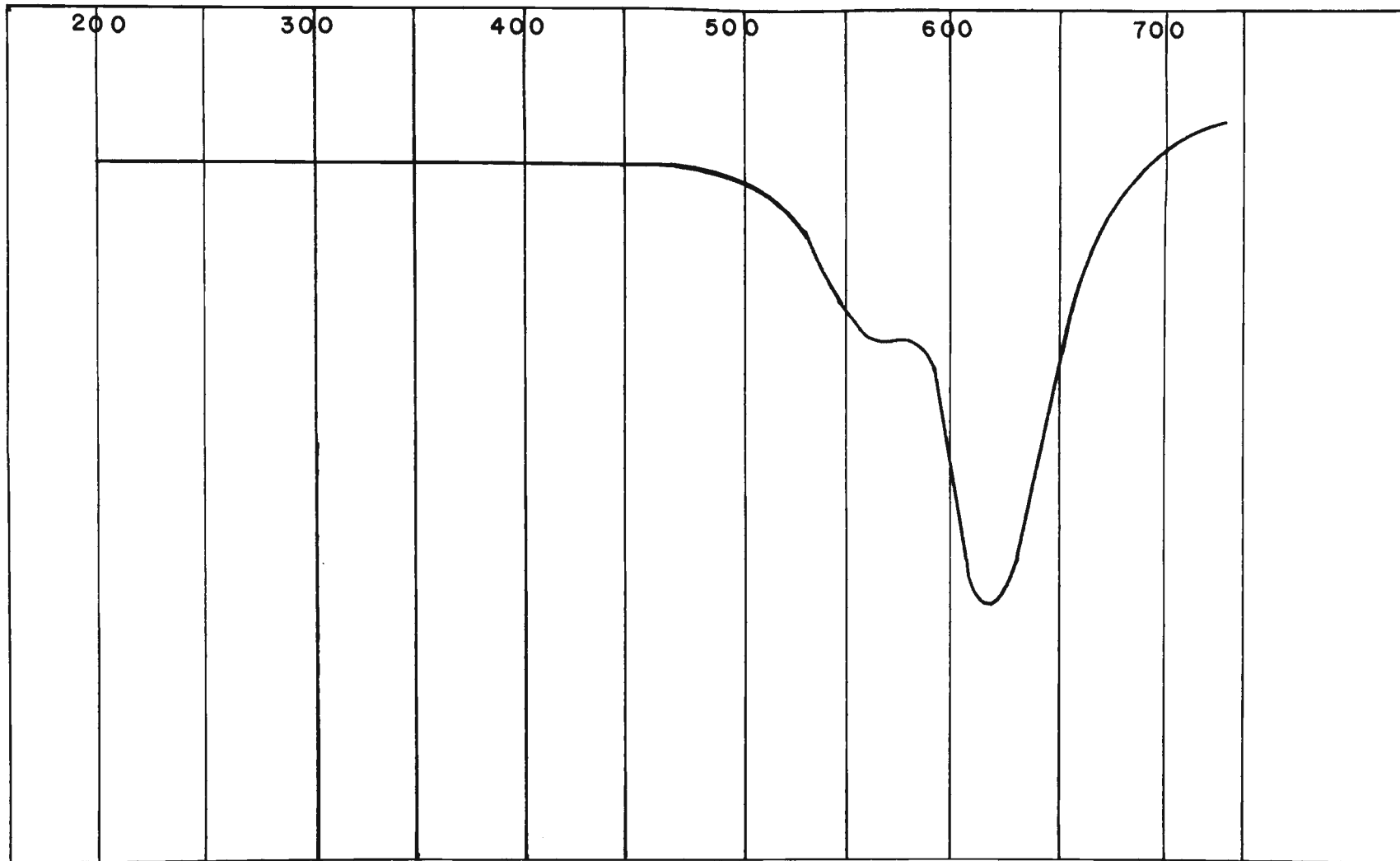
CONCLUSIONS

Of the methods reviewed, petrography, x-ray, and differential thermal, all are excellent as a means of qualitative analysis. All give the mineral form of the sample instead of the chemical composition. Petrography has the disadvantage of depending on the skill of the petrographer for accurate results and the fact that the clay minerals are sometimes rather difficult to distinguish between under the microscope. Petrography has the advantage of revealing all the minerals in a sample, even if in small amounts, providing proper analysis is made. X-ray has the disadvantages of great initial expense and the necessity of a trained operator. X-ray will not identify small amounts of a mineral in a sample unless the mineral shows very strong diffraction. For instance quartz can be determined when present in amounts as small as one-half of one per cent. Calcite on the other hand cannot be determined when present in amounts less than ten per cent. The results produced by x-ray do not depend too much on the skill of the operator

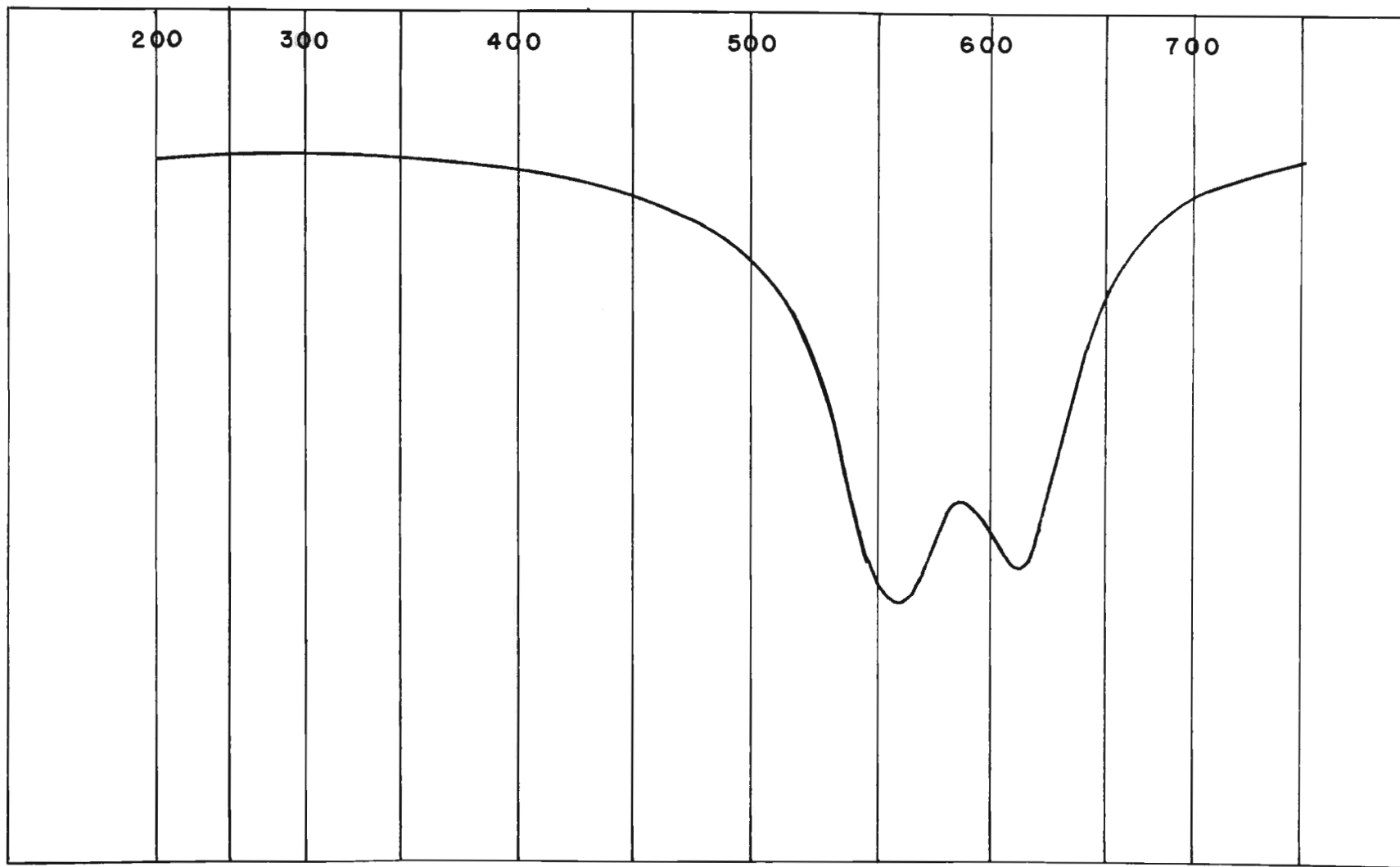
and are permanent. The differential thermal furnace, although not too widely used as yet seems to be an excellent method for analyzing clay minerals. It is not known how much of a sample is needed to produce a curve but the samples used in these runs gave excellent qualitative results. The differential thermal furnace is inexpensive and speedy and does not require a skilled technician for operation.

For quantitative analysis all methods proved ineffective. It is well known that petrography cannot be used as a quantitative measure. The x-ray should prove a useful quantitative measure when the voltage input into the tube can be kept constant.

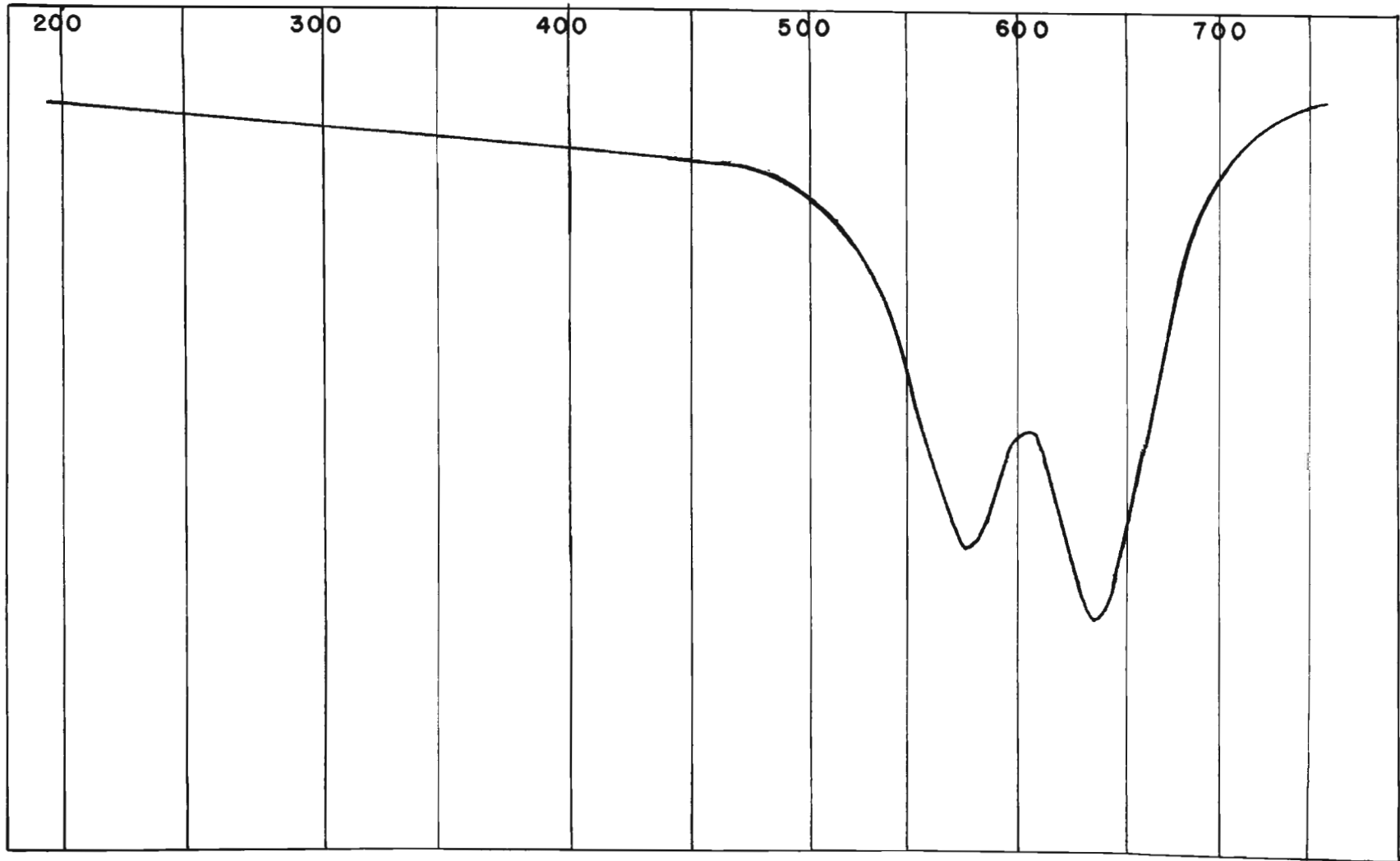
Although never used as a quantitative measure it is hoped that the differential furnace can be used in this capacity. A recording device on the apparatus to give true readings may turn the furnace into a fairly accurate quantitative measure.



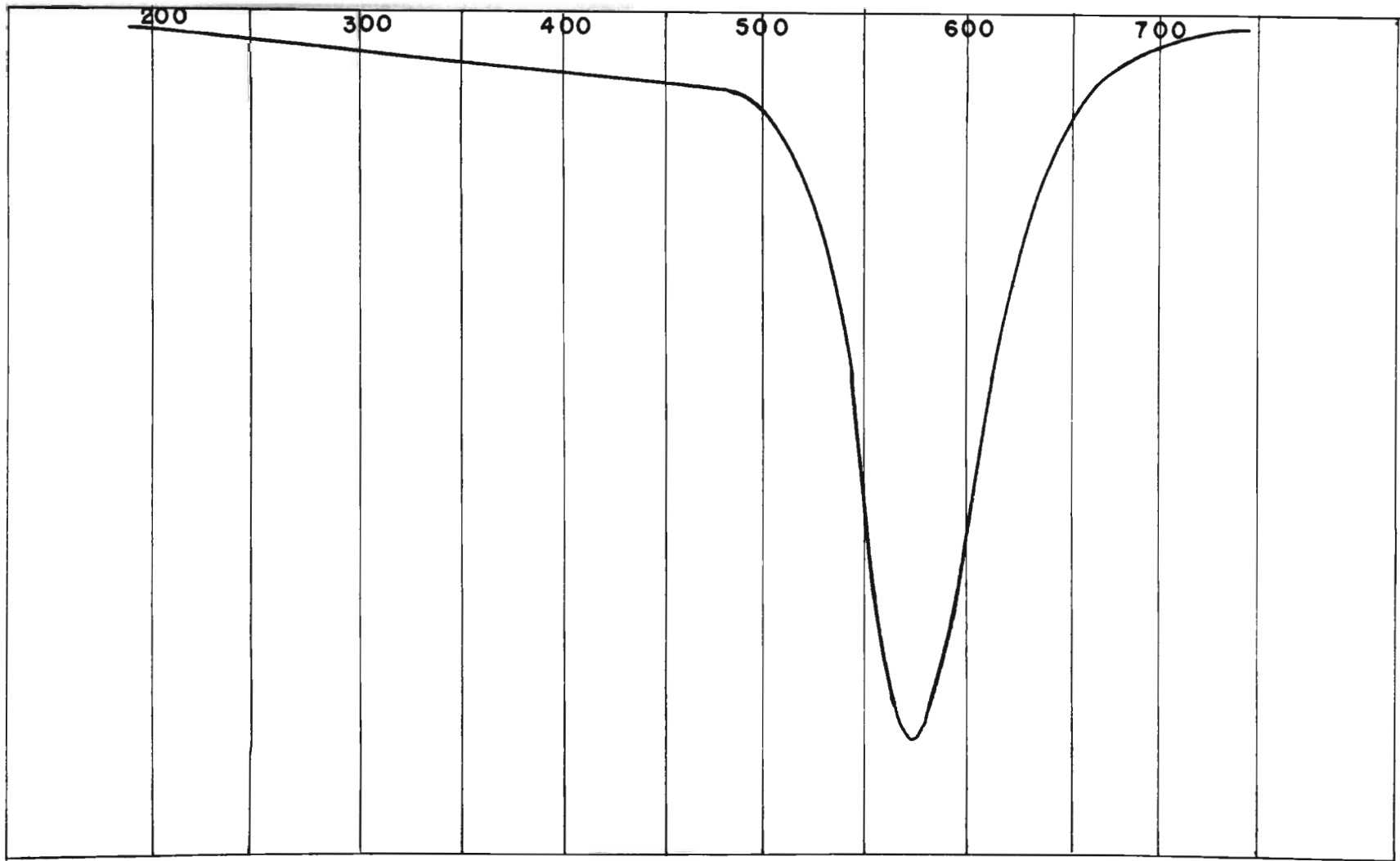
SAMPLE B-740



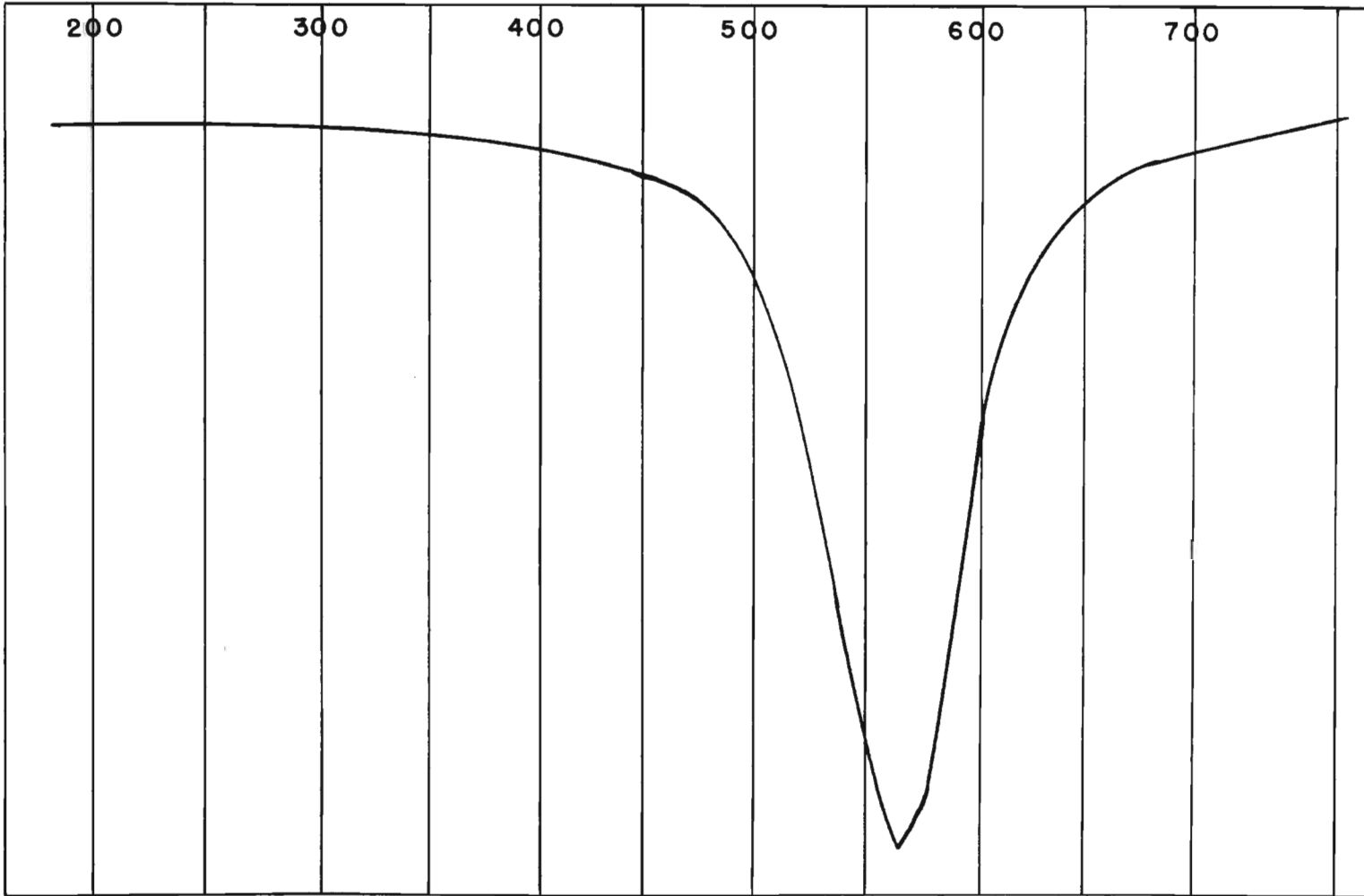
SAMPLE B-746



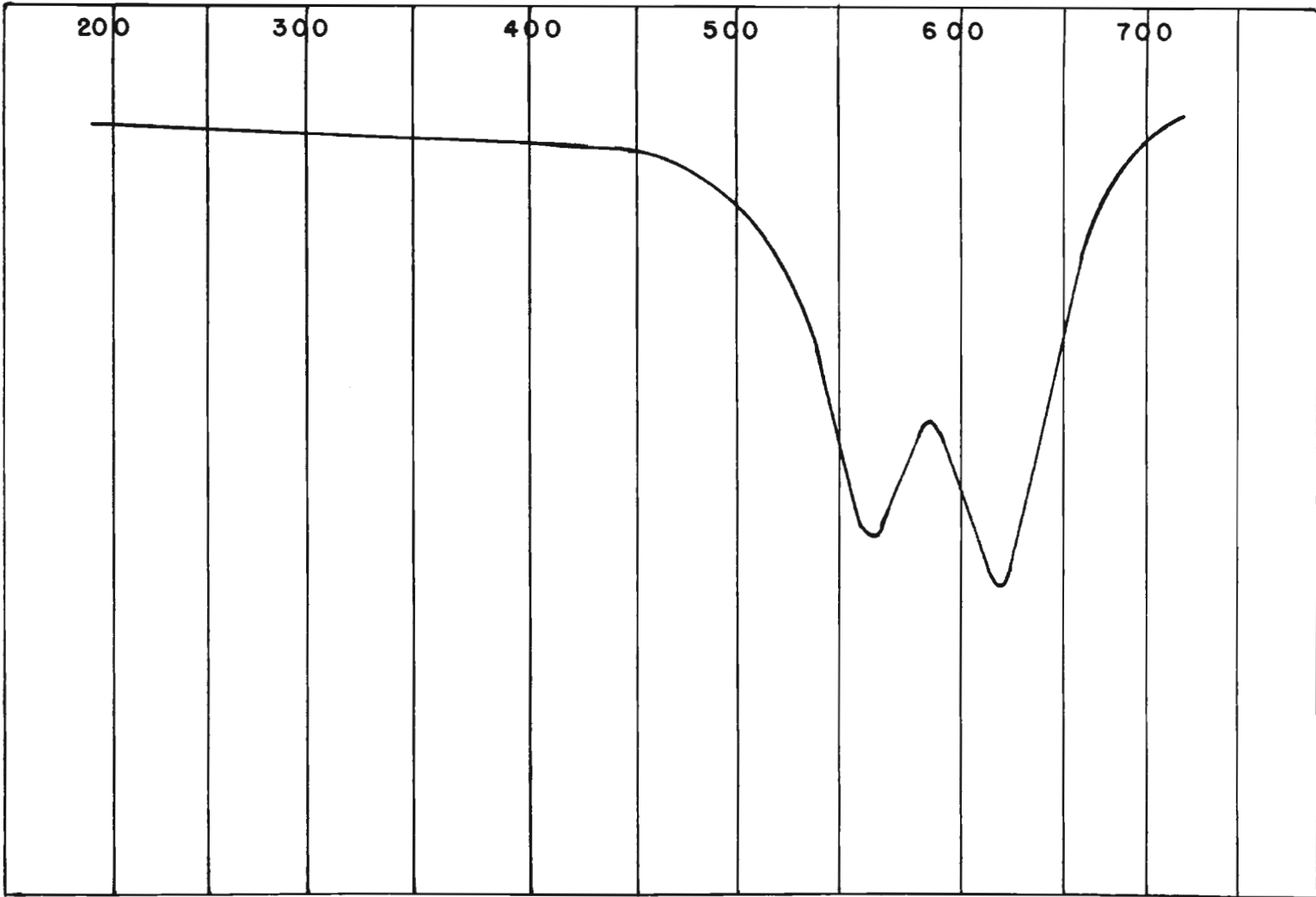
SAMPLE B-749



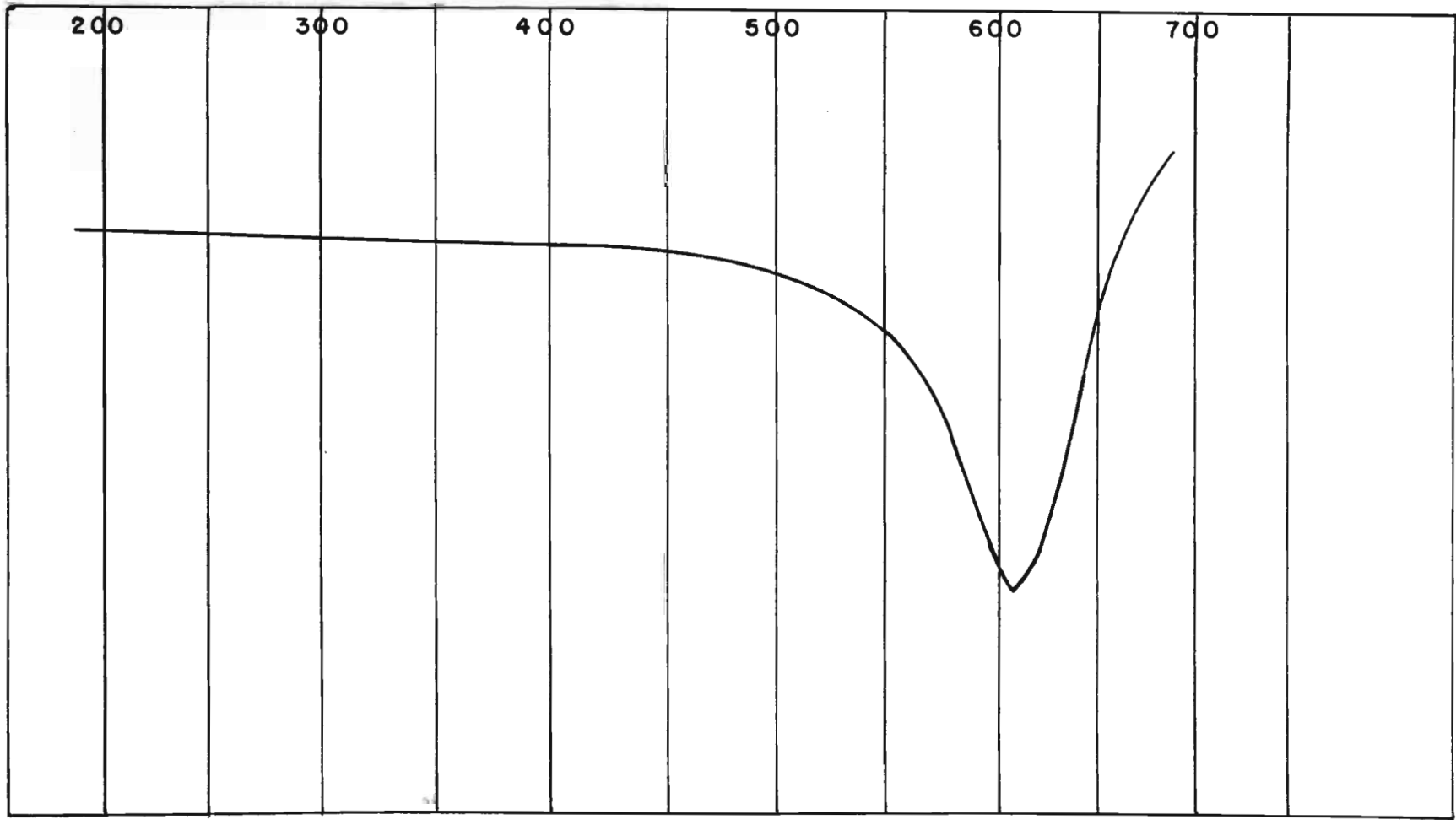
SAMPLE B-754



73.3% DIASPORE



SAMPLE B-749 SHOWING DOUBLE PEAKS



FLORIDA KAOLIN

Fig 4 Relationship of duplicate curve areas to alumina content.

70

60

% Al_2O_3

50

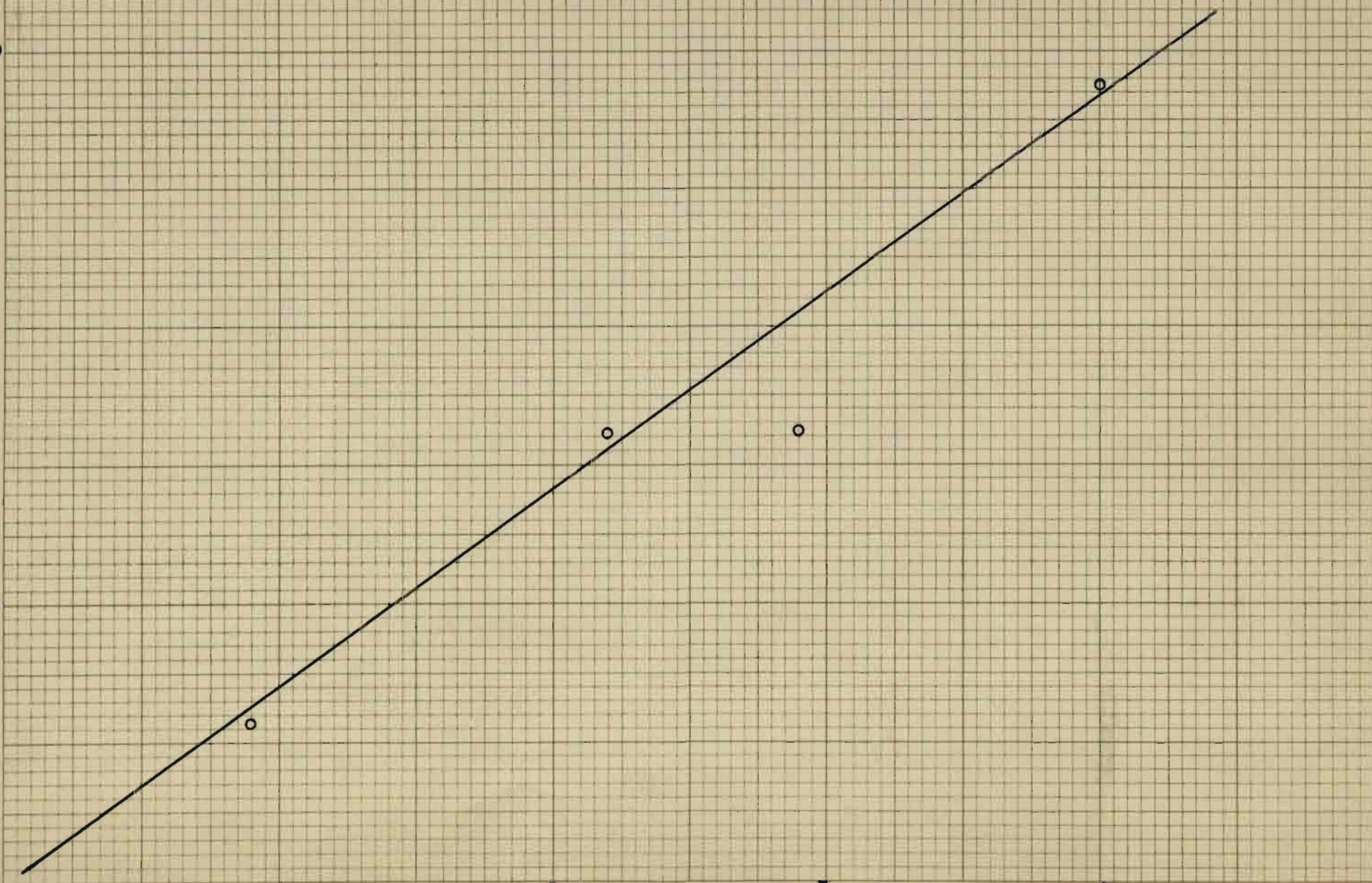
1

2

AREA IN SQ. IN.

3

4



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