

THE ANALYSIS OF CLAY MINERALS
IN KANSAS SOILS

by

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INTRODUCTION

A mantle of loessial material (believed to be Peorian loess) exists in a general east-west direction across the state of Kansas. On this loess at various parts of the state six Great Soil Groups have been identified: Sierozem-like, Brown, Chestnut, Chernozem, Prairie, and Grey-brown Podzolic.

If the mineral content at various depths (horizons) of these soils were determined, information would be obtained concerning the profile distribution of clay minerals in soils developed under different climatic conditions but of a common parent material (Peorian loess). Therefore, the ultimate objective would be the establishment of some existing relationship between climate, soil group, and clay mineral content.

Six approaches are commonly employed for the identification of clay minerals. X-ray diffraction patterns are based on the isotropic nature of the crystals. This characteristic of mineral structure is responsible for its specificity in causing a beam of X-rays (directed at the mineral target) to be diffracted at a characteristic angle. Optical properties that are studied include the orientation of crystals after drying a suspension on a glass slide, the refractive index of the crystals, the birefringence angle, and electron micrographs.

Thermal methods used for identifying clay minerals include the construction of differential thermal curves and thermal dehydration curves. Differential thermal analysis consists of heating the unknown mineral and Al_2O_3 at a given rate; the

temperature difference between the two is recorded and plotted against oven temperature. The resulting curves indicate characteristic exothermic and endothermic reactions at various temperatures. Dehydration curves are made by plotting percent loss in weight at various temperatures against the oven temperature. Characteristic breaks in the curves indicate the various mineral groups.

Several chemical methods are used to identify clay minerals. Titration curves are made by titrating the clay acid with a base. Chemical analysis may include cation exchange capacity and quantitative determinations of the more common mineral oxides. In the present study attempts were made to identify the clay minerals present in soils by means of thermal dehydration curves and chemical analyses.

REVIEW OF LITERATURE

Several investigators have already identified specific minerals and mineral groups on a number of soils. Perkins and Schrenk (2) found minerals of the beidellite-montmorillonite group in selected Kansas soils. Larson, Allaway and Rhoades (6), working on soils of the Chernozem and Chestnut Regions of Nebraska, found the montmorillonite and illite groups to be the main clay constituents with montmorillonite dominant in the five fractions and rich in iron. Russell and Haddock (1), investigating five Iowa soils, concluded that the colloids studied showed a high percentage of montmorillonites and smaller quantities of

kaolinite and illite. According to Grim (13) studies of particle size distribution of clay minerals show that kaolinite and most illites occur largely in coarse clay fractions, while montmorillonites and some illites occur in the finer size fractions. Grim and Rowland (9) state that evidence from their thermal studies indicates that most clay minerals are actually mixtures of minerals containing illite, montmorillonite, kaolinite and/or halloysite in various combinations. Sedletzky (5) points out that such minerals as montmorillonite, bentonite, beidellite, illite, kaolinite and halloysite have been found in Russian soils in fractions of $< 0.2 \mu$ size.

The use of thermal dehydration curves in the identification of clay minerals has not been as widely practiced as, for example, differential thermal curves and X-rays. However, some investigators have produced a number of dehydration curves which indicate a high degree of similarity, although the techniques applied were not identical.

Ross and Kerr (11, 12) produced dehydration curves of halloysite and kaolinite minerals from different parts of the world. They concluded that the gradual loss of water up to about 400° C. is largely due to adsorbed water, whereas a rapid loss of water between 500° and 600° corresponds to the loss of lattice hydroxyl groups. Grim, Bray and Bradley (4) produced illite dehydration curves which showed a sharp inflection or break in the curve between 400° and 450° C. This break presumably indicates the loss of lattice water. Kelley, Jenny, and

Brown (3) produced dehydration curves with halloysite, kaolinite and dickite. One set of samples was merely passed through a 10-mesh screen while the other set was ground. The authors concluded that "difference in the inflection points do not necessarily signify different lattices but may merely be the result of variation in particle size."

EXPERIMENTAL METHODS

Soil Location and Description

All soil samples were taken from the A_1 horizon of uncultivated areas. The parent material was loessial in all cases and the ground surfaces were gently sloping. Areas from which samples were taken are given in Table 1.

The Sierozem-like soil was classified as of the Prowers soil series and its A_1 horizon extended 1"-7" in depth. It contained a very poorly developed crumb structure and was calcareous but free of concretions. Its Munsell color chart classification was determined as 104R 5/4 yellowish brown. The land slope was 2-2½ percent to the southwest. The native dominant vegetation was Buffalo and Gramma grass.

The Brown soil was of the Weld series. The A_1 horizon extended downward 1"-5". It showed a weak crumb structure and was non-calcareous. Its Munsell color classification was 104R 4/3 brown or dark brown. Its slope was 1½-2 percent southwest and Buffalo-gramma sod was dominant.

The Chestnut soil was of the Keith series. The A_1 horizon

extended down 1"-10". It appeared granular, pale brown and friable. The Munsell color classification was 10R 4/2 weak red. The land slope was $1\frac{1}{2}$ percent southwest and Buffalo, Gramma and dropseed were dominant.

The Chernozem was called Hastings-like and the A₁ horizon extended down 1"-12". It was soft granular, brown-black, and friable. The Munsell color classification was 54R 3/2 dark reddish brown. The land slope was $1\frac{1}{2}$ percent southwest. Buffalo and Gramma sod were dominant.

The Prairie soil was called a Grundy-like silt loam. The A₁ horizon extended down $1\frac{1}{2}$ "-5 $\frac{1}{2}$ " and was a medium granular, dark brown, silt loam. The Munsell classification was 10R 3/1 dark reddish grey. The land slope was 0-1 percent west and the area was a native pasture with poor to fair cover.

The Grey-brown Podzolic soil was not classified as to series. The A₁ horizon extended down 1"-6" and appeared as a brown, weak granular, soft, silt loam. The Munsell classification was 104R 6/4 light yellowish brown. The land slope was 3-4 percent north. The dominant vegetation was pignut hickory and grass of prairie pasture. It was not a typical well-developed Grey-brown Podzolic soil; development was apparently influenced considerably by grasses.

Table 1. Location where soil samples were taken.

Great soil group :	County	Township	Range	Section	Exact location
Sierozem-like	Hamilton	22S	43W	SW $\frac{1}{4}$ SW $\frac{1}{4}$ Sec. 36	35'E of road 0.15 miles N of SW corner of section
Brown	Greeley	19S	41W	NE $\frac{1}{4}$ SE $\frac{1}{4}$ Sec. 1	1/10S and 250'W of E quarter corner
Chestnut	Lane	18S	29W	Center $\frac{1}{4}$ of NW $\frac{1}{4}$ Sec. 20	150' S of road 0.35 miles E of NW corner of section corner Highway 96
Chernozem	Russell	14S	15W	SW $\frac{1}{4}$ NE $\frac{1}{4}$ Sec. 11	Near oil wells 600' S and 40'W of NE corner of pasture fence
Prairie	Nemaha	3S	12E	SE $\frac{1}{4}$ SE $\frac{1}{4}$ Sec. 30	60'N and 650'W of SE corner in pasture
Grey-brown Podzolic	Leavenworth	8S	22E	SW $\frac{1}{4}$ NW $\frac{1}{4}$ Sec. 34	Caved-in road bank S of Highway 92 where creek crosses Highway 92

Separation and Fractionation of the Clay Colloids

All samples were airdried and passed through a 2mm screen (No. 10). The original samples taken for analysis were 300 gms. each except for the Chernozem which weighed 213.3 gms. Carbonates were eliminated where necessary by lowering the pH to 4 with 1N HCl. The organic matter was oxidized by treatment with 100 ml of H₂O₂ (30%) and heating on a hot plate.

Soluble salts were removed by centrifuging the samples in 1N HCl several times in an International Centrifuge at 2000 rpm for ten minutes. The samples were then sodium saturated and flocculated by treating with 2800 ml of 2% Na₂CO₃ and boiled for 5 minutes with constant agitation by means of a small motor with stirring rod attachment. The supernatant liquid was decanted and the sample transferred into 250 ml bottles for separation of the clay fraction in the International Centrifuge. It was decided to separate the colloidal clay fraction according to international size ($\leq 2 \mu$).

Separation of the clay fraction was based on the Stokes's Law principle adapted to the centrifuge by Bayer (14) where

$$t = \frac{n \log \frac{R_2}{R_1}}{3.81 N^2 r^2 (d_p - d)}$$

The centrifuge speed was set for 1000 rpm. On the basis of 20° C., t would be 161 sec. according to the above formula, since $R_2 = 21.1$, $R_1 = 11.1$, centrifuge speed = 1000 rpm, average density of particles = 2.65, and the density of water at 20° C. = 1.

This calculation ($t = 161$ sec.) agrees well with the Nomograph calculation of Tanner and Jackson (15) based on the same law. However, Tanner and Jackson offer a table of conversion factors for time changes accompanying temperature changes ranging from 16° C. to 30° C. These are very convenient to use with the International Centrifuge.

After the suspension was decanted from the centrifuge cup, about 250 ml more distilled water was added, the bottle was shaken to resuspend the sample which was recentrifuged. The centrifuging was done five times per sample to insure 90 to 95 percent recovery of the $\leq 2 \mu$ clay fraction.

After the decanted suspension containing the total clay fraction was collected, it was fractionated by passing it through a Sharples Supercentrifuge (motor drive type). The object was to first separate the particles of 2-0.2 μ size, deposited on the bowl lining, while the smaller size fractions remained in suspension. Later the remaining suspension ($\leq 0.2 \mu$) was again passed through the Sharples but at a faster rate of flow, allowing only particles of $\leq 0.08 \mu$ to remain in suspension. Both coarse (2-0.2 μ) and medium (0.2-0.08 μ) fractions were resuspended and recentrifuged four more times to ascertain more accurate separation between the three size fractions. The suspension containing particles of size $\leq .08 \mu$ was flocculated with a 1N concentration of NaCl. This procedure and its calculations were based on the work of Seay and Weeks (16). Fractionation depends on the rate of flow of the liquid suspension. The Sharples Centrifuge was operated at a rate of 25,000 rpm and

the bowl liner used was of .003" thickness. If the thickness is > or < .003" the rate of flow must be recalculated.

The simplified formula used was

$$Q_{\min} = \frac{112.7 D^2 P}{N}$$

Q_{\min} = rate of feeding soil into centrifuge (cc per minute)

112.7 = a calculated constant

D = diameter of the clay particles in cm

P = difference in density of dispersed and dispersing phases

N = viscosity of dispersion medium in poises

According to the above formula, for separation of particles 2-0.2 μ , a rate of flow of 756 cc per minute was required. For particles of 0.2-0.08 μ , a rate of 121 cc per minute was used. The fractions were dried on a hot plate, ground in an agate mortar, transferred into open bottles, and put into a 75 percent relative humidity chamber. This chamber consisted of a large glass desiccator containing about 800 ml of saturated $(\text{NH}_4)_2\text{SO}_4$ and remained in a constant temperature room of $25^\circ \text{C} \pm 2^\circ$.

Five standard minerals were chosen in order to produce standard curves. Wyoming bentonite was furnished by the American Colloid Co., Chicago. Beidellite in the form of Putnam Clay sub-soil was furnished by C. E. Marshall, University of Missouri, Columbia. Halloysite was sent by S. B. Hendricks, U.S.D.A., Washington, D. C. Kaolinite furnished by Ward's Natural Science Establishment, Inc. came from Drybranch, Georgia. Illite from Illinois was sent by W. A. White, University of Illinois, Urbana, Illinois.

The minerals were treated, separated, and fractionated as the soils. However, where an operation was unnecessary, it was eliminated; i.e., oxidation with H_2O_2 was not carried out with the standard minerals except for Putnam Clay which required this treatment.

Table 2. Results of the fractionation of soil samples representing six great soil groups.

Soil sample	: Percent : sand and : silt	: Percent : total : clay	: Percent : coarse clay : (2-0.2 μ)	: Percent : medium clay : (0.2-.08 μ)	: Percent : fine clay : (\leq .08 μ)	: Percent : soil : recovered
Sierozem-like	78.3	11.6	4.5	2.8	4.3	89.9
Brown	84.2	9.6	5.5	2.1	2.0	93.8
Chestnut	83.1	10.9	4.3	1.9	4.7	94.0
Chernozem	76.6	15.7	6.5	3.8	5.3	92.3
Prairie	75.4	15.4	4.1	2.5	8.8	90.8
Grey-brown Podzolic	85.4	9.4	4.3	2.0	3.1	94.8

Table 3. Results of the fractionation of the standard clay minerals used.

Standard Mineral	: Percent : : fraction : : 2 μ	: Percent : : total : : clay	: Percent : : coarse clay : : (2-0.2 μ)	: Percent : : medium clay : : (0.2-.08 μ)	: Percent : : fine clay : : (\leq .08 μ)	: Percent : : total : recovered
Bentonite	14.0	89.6	14.4	18.2	57.0	103.6 *
Beidellite	62.5	33.8	6.9	5.2	21.6	96.3
Halloysite	72.6	22.8	9.1	11.7	2.0	95.4
Kaolinite	52.2	46.3	30.8	13.1	2.4	98.5
Illite	68.4	8.8	4.3	2.1	2.3	97.2

* This error probably was due to an excess of NaCl used to flocculate the fine fraction.

Thermal Dehydration Curves

Thermal dehydration curves were made for all soil and standard mineral fractions using a muffle oven with a Wheelco thermostat to maintain the desired temperature. For temperatures up to and including 200° C. an Elconap oven was employed. The plotting points selected were at 50° intervals beginning with 50° C. The original samples were taken and weighed from an atmosphere of 75 percent relative humidity at a temperature of 25° C. ± 2°. Sample sizes varied from about 1/3 gm to about 1 1/4 gms.

Time of heating varied from 7 to 24 hours for the first four points, but beginning at 250° C. all fractions received the same time heating periods; from 250° C. to 450° C., 4 hours; from 500° C. to 550° C., 3 hours; from 600° C. to 750° C., 2 hours; from 800° C. to 1000° C., 1 hour. Percent loss in weight (along the vertical axis) was plotted against oven temperature (horizontal axis) to obtain the dehydration curves.

Difficulties were encountered with the muffle oven, because it did not heat equally in all parts of the oven. To overcome this, three sheets of asbestos sheeting were tied together and placed so as to fit at the door of the oven in order to increase the insulation. The thermocouple outlet at the rear of the oven was bound with a soft asbestos-like rope. In addition a small basket made of nichrome wire was constructed so that 6 crucibles placed in the oven for one heating period would be close to the oven center, 3 on each side of the thermocouple near its tip end.

The following observation was made when the thermostat was

set for 360° C.

	<u>Low Point °C.</u>	<u>High Point °C.</u>
Back of oven	365	372.5
3/4 to the rear of oven	373	384
Middle of oven	360	370
At door of oven	314.5	321.5
Thermocouple indicator (1/3 the length from the door)	357	363

Therefore it was decided to include only 6 samples at one heating period as close to the oven center and tip end of the thermocouple as possible. The thermocouple was placed between the 2 rows of 3 crucibles each.

Chemical Analysis

Cation exchange capacity was determined by the method of Rendig (17) employing the flame photometer. The determination of SiO_2 was done by the method of Robinson (18). For Fe_2O_3 , TiO_2 and Al_2O_3 , the determinations and separation given by Jackson (20) were followed. For CaO , MgO , MnO and K_2O the methods of Peech, Alexander, Dean and Reed (21) were followed.

RESULTS AND DISCUSSION

Thermal Dehydration Curves

Figures 1 through 5 represent standard mineral curves. Figures 6 through 11 represent the thermal dehydration curves for the clay minerals in six Kansas soils.

In general all curves representing coarse and medium fractions of standard minerals very closely resembled corresponding curves of Ross and Kerr (11, 12) and Kelley, Jenny, and Brown (3). However, the fine fractions of bentonite, beidellite and kaolinite show some striking differences. Whereas the coarse and medium fractions indicate the main break in the curve (loss of lattice water) extends from 500° C. to 650° C. in bentonite, the break in the fine fraction extends from 500° C. to 900° C. and shows a total water loss greater than 25 percent. Similarly, the break in the fine beidellite curve ranges from 400° C. to 700° C. with 21 percent total water loss, whereas the other two beidellite fractions break from 400° C. to 550° C. The fine bentonite curve also shows less dehydration up to 650° C.; the fine beidellite curve is higher than the other two fractions throughout its length.

The fine kaolinite curve shows a reduced break from 400° C. to 500° C. compared to its other fractions, but the portion of the curve below 400° C. shows a much greater dehydration loss than one would expect from a typical kaolinite. This divergence at the first 400° C. portion of the curve is also shown in the fine halloysite curve.

Table 4. Dehydration data for the clay fractions in the A₁ horizons of Sierozem-like and Brown soils.

Temperature in °C.	Percent loss in weight					
	Sierozem-like			Brown		
	Coarse	Medium	Fine	Coarse	Medium	Fine
50	6.93	9.32	13.04	5.86	8.94	11.13
100	9.53	12.68	17.32	8.27	12.23	15.26
150	10.26	13.65	18.29	8.81	12.89	15.97
200	10.55	14.02	18.72	9.17	13.37	16.75
250	10.94	14.65	19.39	9.58	13.98	17.65
300	11.24	15.17	19.83	9.90	14.45	18.15
350	11.45	15.50	20.19	10.11	14.73	18.47
400	11.75	15.88	20.75	10.43	15.13	18.91
450	12.77	17.00	21.95	11.47	16.44	20.22
500	13.67	18.25	23.31	12.49	17.74	21.18
550	14.34	18.93	24.41	13.05	18.32	21.85
600	14.68	19.12	24.65	13.36	18.60	22.12
650	15.05	19.46	24.92	13.55	18.81	22.30
700	15.19	19.61	25.03	13.67	18.93	22.43
750	15.24	19.67	25.17	13.65	18.92	22.38
800	15.37	19.84	25.20	13.73	19.03	22.62
850	15.46	19.92	25.23	13.86	19.18	22.65
900	15.51	19.95	25.25	13.93	19.22	22.70
950	15.49	19.93	25.25	13.85	19.20	22.68
1000	15.40	19.92	25.26	13.81	19.19	22.68

Table 5. Dehydration data for the clay fractions in the A₁ horizons of Chestnut and Chernozem soils.

Temperature in °C.	Percent loss in weight					
	Chestnut			Chernozem		
	Coarse	Medium	Fine	Coarse	Medium	Fine
50	6.35	8.52	12.37	6.88	9.62	12.80
100	8.28	10.80	15.71	8.83	12.05	16.42
150	8.64	11.27	16.30	9.16	12.48	16.98
200	9.00	11.75	16.88	9.57	12.92	17.56
250	9.56	12.61	17.63	10.02	13.69	18.26
300	9.74	13.11	18.05	10.22	14.04	18.63
350	10.08	13.63	18.41	10.49	14.40	18.99
400	10.73	14.67	19.70	11.09	15.46	20.22
450	11.84	16.09	20.55	12.04	16.64	21.11
500	12.59	16.83	21.32	12.81	17.37	21.88
550	13.10	17.28	21.83	13.31	17.86	22.44
600	13.25	17.44	22.02	13.51	18.03	22.64
650	13.44	17.63	22.18	13.69	18.22	22.79
700	13.58	17.76	22.33	13.83	18.40	22.92
750	13.62	17.81	22.38	13.88	18.44	22.98
800	13.87	18.03	22.61	14.09	18.67	23.16
850	13.92	18.07	22.61	14.16	18.77	23.18
900	13.95	18.13	22.61	14.16	18.78	23.18
950	13.98	18.15	22.62	14.19	18.80	23.20
1000	13.83	18.13	22.62	14.12	18.79	23.21

Table 6. Dehydration data for the clay fractions in the A₁ horizons of Prairie and Grey-brown Podzolic soils.

Temperature in °C.	Percent loss in weight					
	Prairie			Grey-brown Podzolic		
	Coarse	Medium	Fine	Coarse	Medium	Fine
50	3.39	6.50	12.58	1.92	5.55	12.08
100	4.41	8.17	15.87	2.59	6.96	14.99
150	4.74	8.57	16.47	2.84	7.36	15.61
200	4.94	8.87	16.85	3.07	7.75	16.04
250	5.20	9.43	17.30	3.37	8.47	16.70
300	5.44	9.83	17.66	3.52	8.79	17.13
350	5.48	10.19	18.20	3.68	9.14	17.66
400	5.85	10.75	19.01	3.86	9.58	18.24
450	7.27	13.29	21.14	5.06	11.95	20.09
500	7.82	14.02	22.11	5.84	12.70	20.75
550	8.41	14.43	22.94		13.08	21.19
600	8.63	14.67	23.30		13.36	21.50
650	8.72	14.73	23.37		13.43	21.58
700	8.85	14.89	23.51		13.58	21.78
750	9.04	15.03	23.63		13.71	21.96
800	9.11	15.06	23.73		13.84	22.15
850	9.18	15.16	23.75		13.93	22.17
900	9.22	15.24	23.76		14.03	22.21
950	9.00	15.25	23.78		14.06	22.22
1000	8.87	15.24	23.78		14.06	22.22

Table 7. Dehydration data for the clay mineral fractions of bentonite and beidellite.

Temperature in °C.	Percent loss in weight					
	Bentonite			Beidellite		
	Coarse	Medium	Fine	Coarse	Medium	Fine
50	6.28	6.00	3.91	3.32	4.74	4.06
100	9.99	10.42	7.36	5.01	7.31	7.79
150	10.13	10.62	7.59	5.31	7.74	8.41
200	10.33	10.79	7.80	5.67	8.19	8.90
250	10.54	10.96	7.99	6.06	8.78	9.37
300	10.71	11.09	8.10	6.23	9.08	9.68
350	10.93	11.30	8.36	6.50	9.46	10.22
400	11.00	11.34	8.42	6.68	9.84	11.06
450	11.14	11.48	8.66	7.60	11.94	13.33
500	11.24	11.57	8.98	9.08	13.42	14.97
550	11.60	12.01	10.14	9.71	13.96	16.52
600	13.70	14.90	11.63	9.86	14.06	17.91
650	14.35	15.27	13.67	10.03	14.30	19.12
700	14.68	15.37	17.59	10.18	14.46	20.46
750	15.15	15.48	19.70	10.34	14.71	20.64
800	15.19	15.52	21.34	10.39	14.77	20.71
850	15.19	15.47	24.43	10.42	14.81	20.74
900	15.16	15.43	25.27	10.43	14.85	20.76
950	15.16	15.45	25.45	10.43	14.88	20.86
1000	15.12	15.45	25.49	10.39	14.84	20.96

Table 8. Dehydration data for the clay fractions of halloysite and kaolinite.

Temperature in °C.	Percent loss in weight					
	Halloysite			Kaolinite		
	Coarse	Medium	Fine	Coarse	Medium	Fine
50	2.74	2.68	3.40	.85	2.00	6.83
100	3.39	3.48	4.47	1.01	2.32	8.59
150	3.68	3.80	5.12	1.03	2.44	8.95
200	4.12	4.20	6.24	1.18	2.76	10.75
250	4.49	4.73	7.57	1.29	3.08	12.65
300	5.04	5.33	8.44	1.40	3.33	13.79
350	5.70	6.02	9.53	1.57	3.70	14.81
400	6.66	7.01	11.13	1.83	4.11	15.58
450	14.10	15.85	17.47	5.18	11.43	21.70
500	15.66	16.52	17.89	13.12	14.67	22.28
550	16.08	16.89	18.28	13.59	15.10	22.70
600	16.40	17.21	18.52	13.90	15.43	23.20
650	16.67	17.44	18.73	14.16	15.68	23.38
700	16.91	17.67	18.93	14.35	15.91	23.62
750	17.08	17.84	19.12	14.50	16.10	23.80
800	17.15	17.88	19.17	14.55	16.19	23.86
850	17.15	17.88	19.22	14.52	16.20	23.89
900	17.24	17.94	19.20	14.52	16.26	23.95
950	17.28	18.00	19.30	14.56	16.33	24.06
1000	17.24	18.03	19.40	14.55	16.35	24.17

Table 9. Dehydration data for the clay fractions of illite.

Temperature in °C.	Percent loss in weight		
	Coarse	Medium	Fine
50	3.69	4.37	7.19
100	4.76	5.57	9.04
150	5.08	5.89	9.52
200	5.45	6.40	10.14
250	5.92	7.28	10.90
300	6.59	7.99	11.49
350	7.57	8.52	11.86
400	7.92	8.93	12.33
450	9.00	10.45	13.70
500	10.35	11.67	14.82
550	10.89	12.14	15.15
600	11.26	12.42	15.47
650	11.37	12.59	15.60
700	11.45	12.67	15.72
750	11.70	12.86	15.91
800	11.79	12.89	15.96
850	12.05	13.03	16.17
900	12.19	13.12	16.16
950	12.33	13.17	16.20
1000	12.39	13.20	16.25

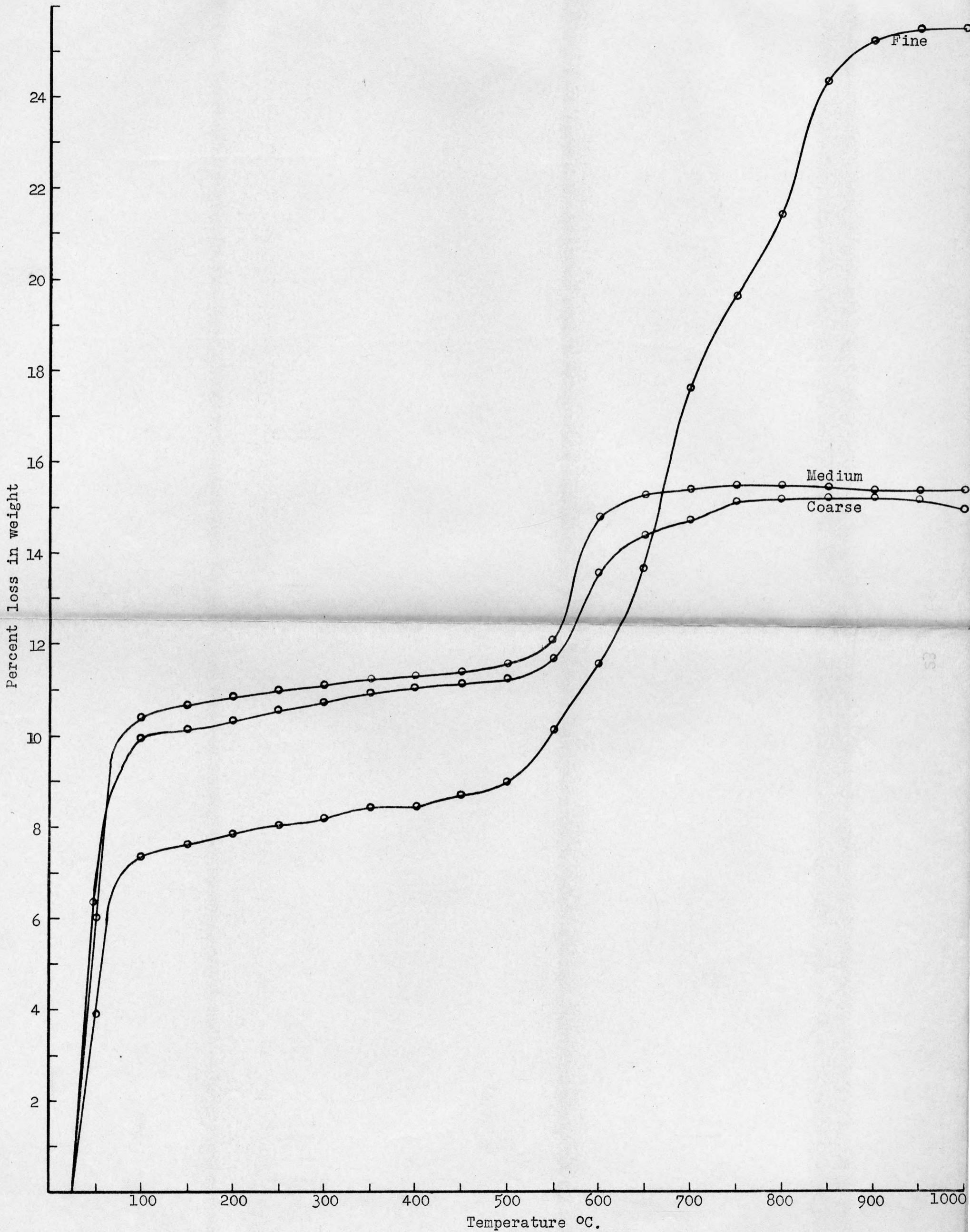


Figure 1. Thermal dehydration curves for 3 clay fractions of Wyoming bentonite.

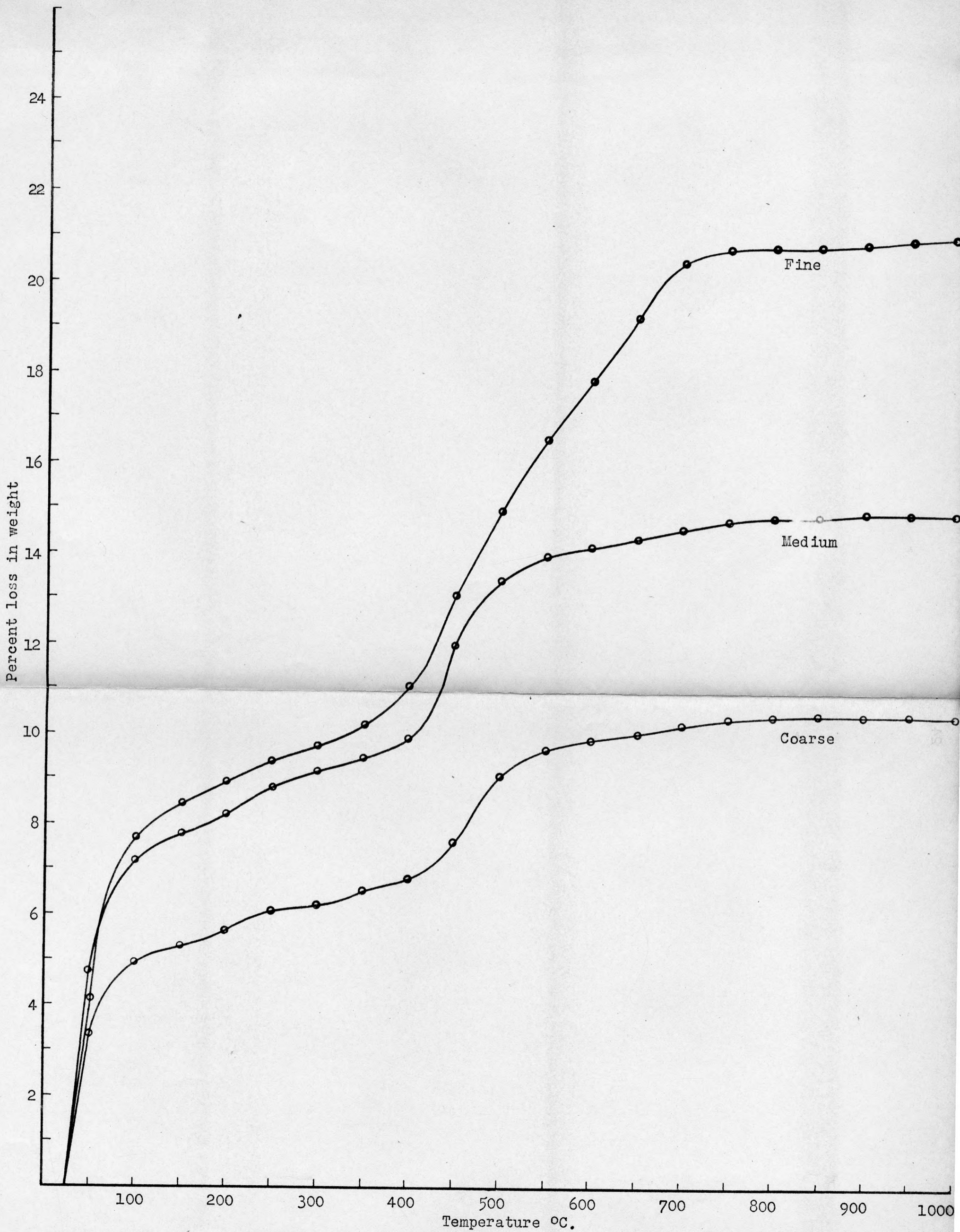


Figure 2. Thermal dehydration curves for 3 clay fractions of beidellite (Putnam Clay).

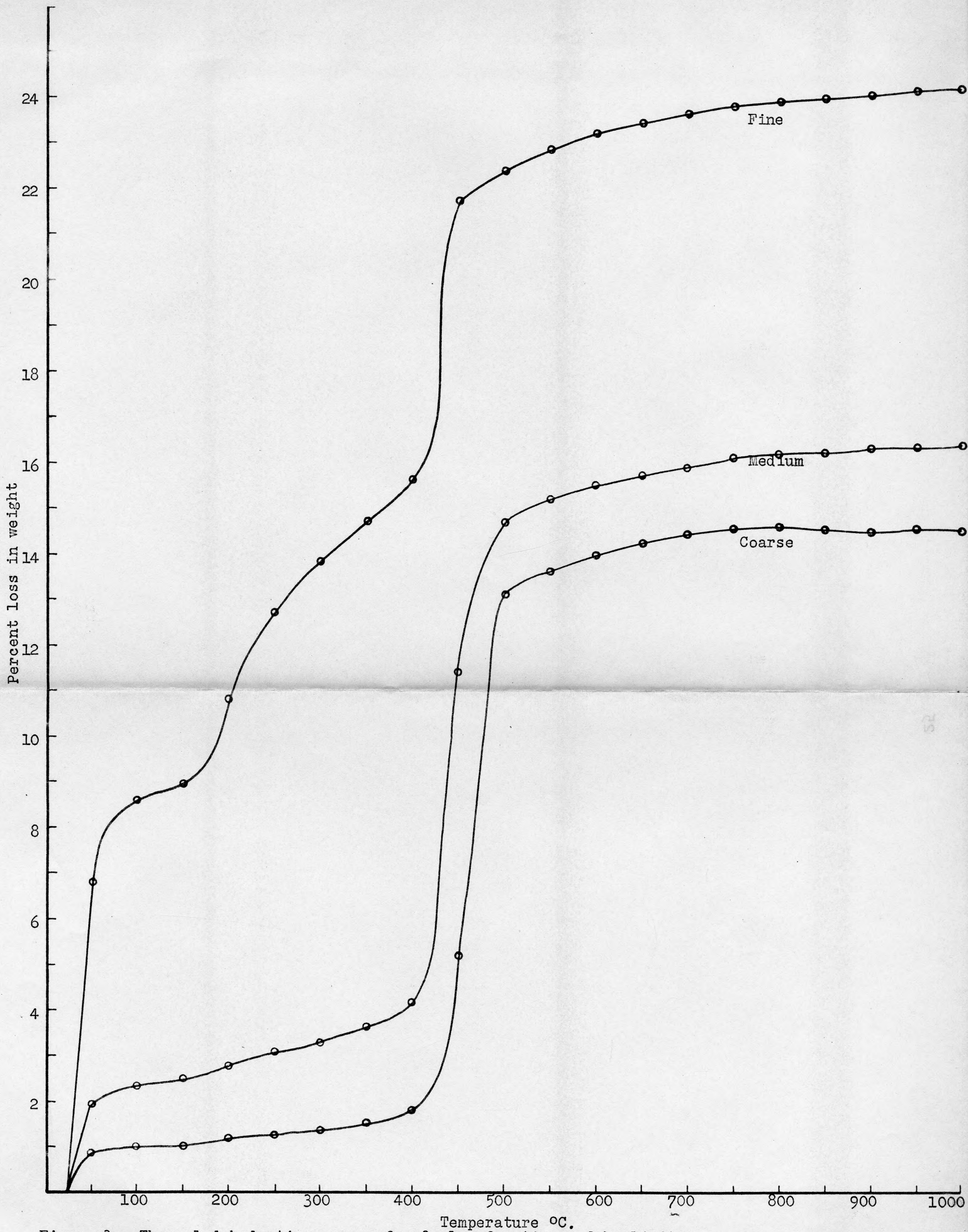


Figure 3. Thermal dehydration curves for 3 clay fractions of kaolinite.

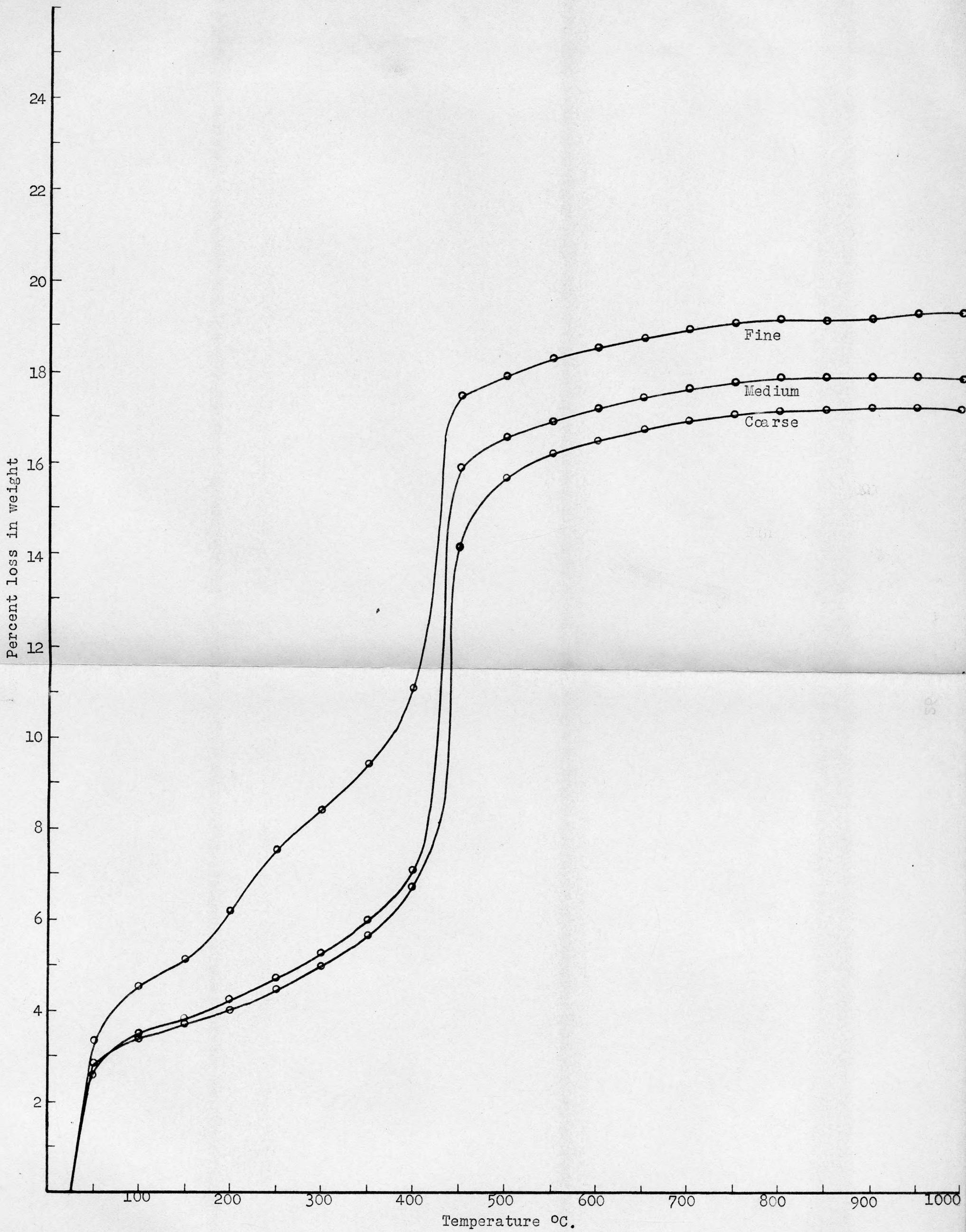


Figure 4. Thermal dehydration curves for 3 clay fractions of halloysite.

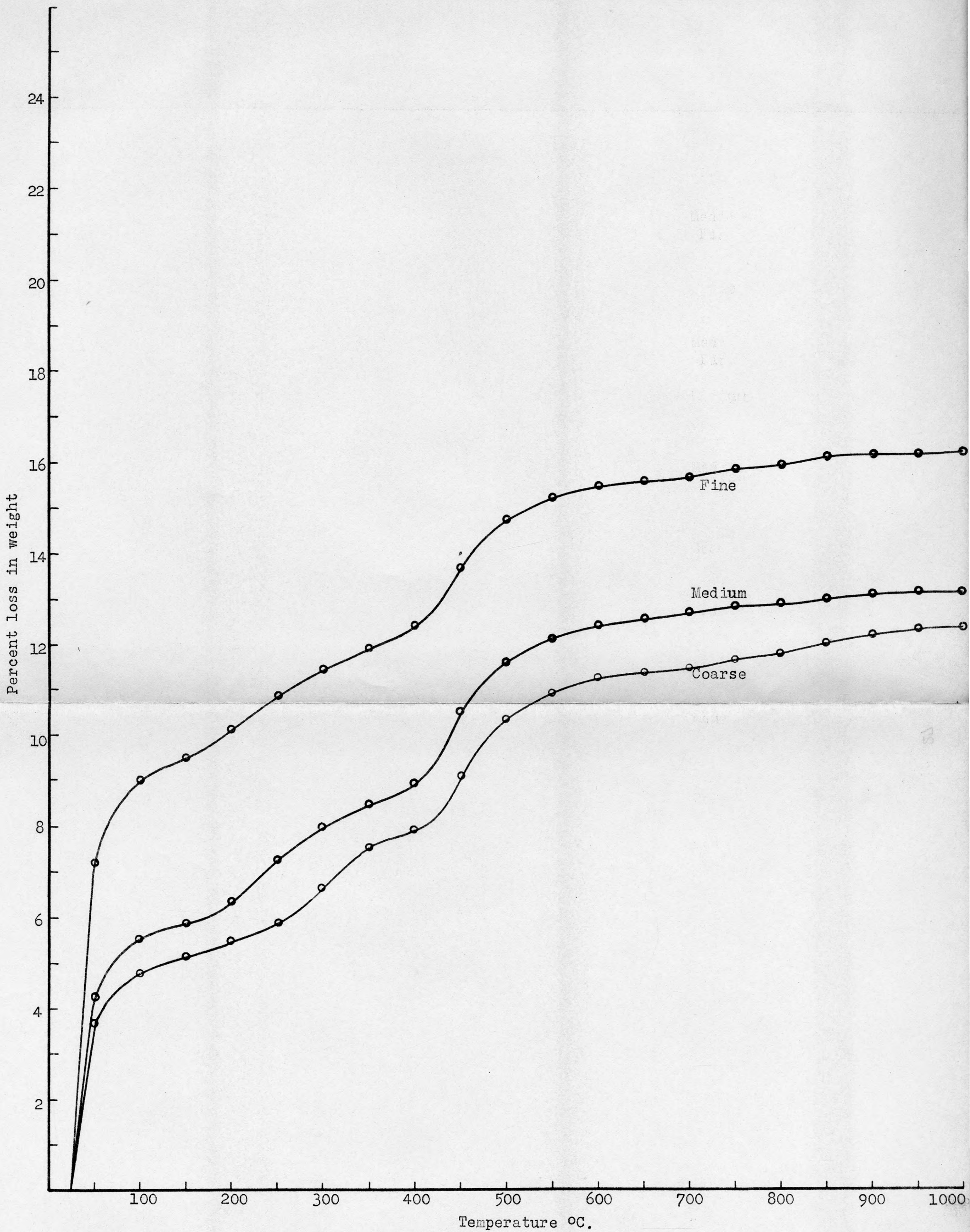


Figure 5. Thermal dehydration curves for 3 clay fractions of illite.

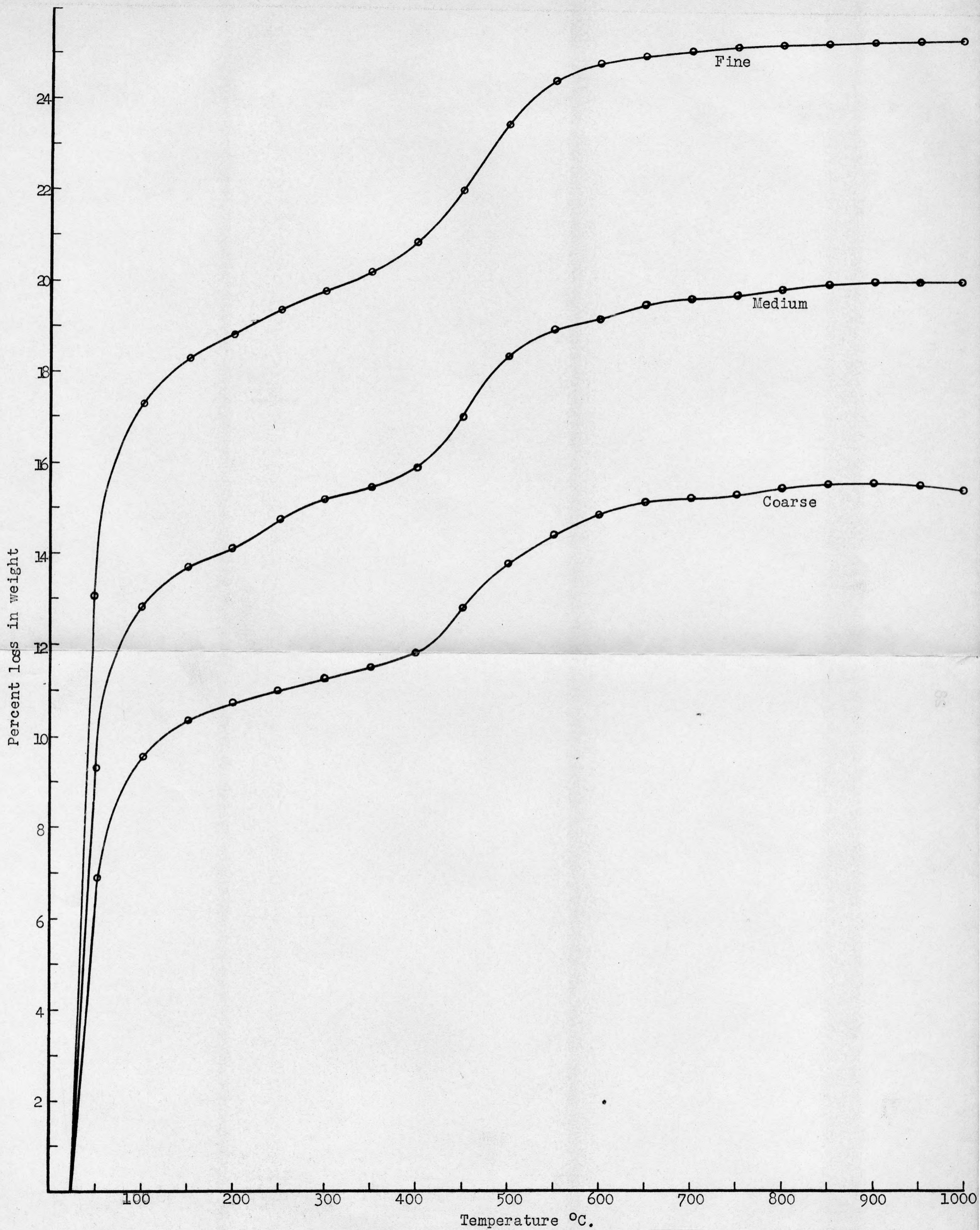


Figure 6. Thermal dehydration curves for 3 clay fractions of Sierozem-like soil.

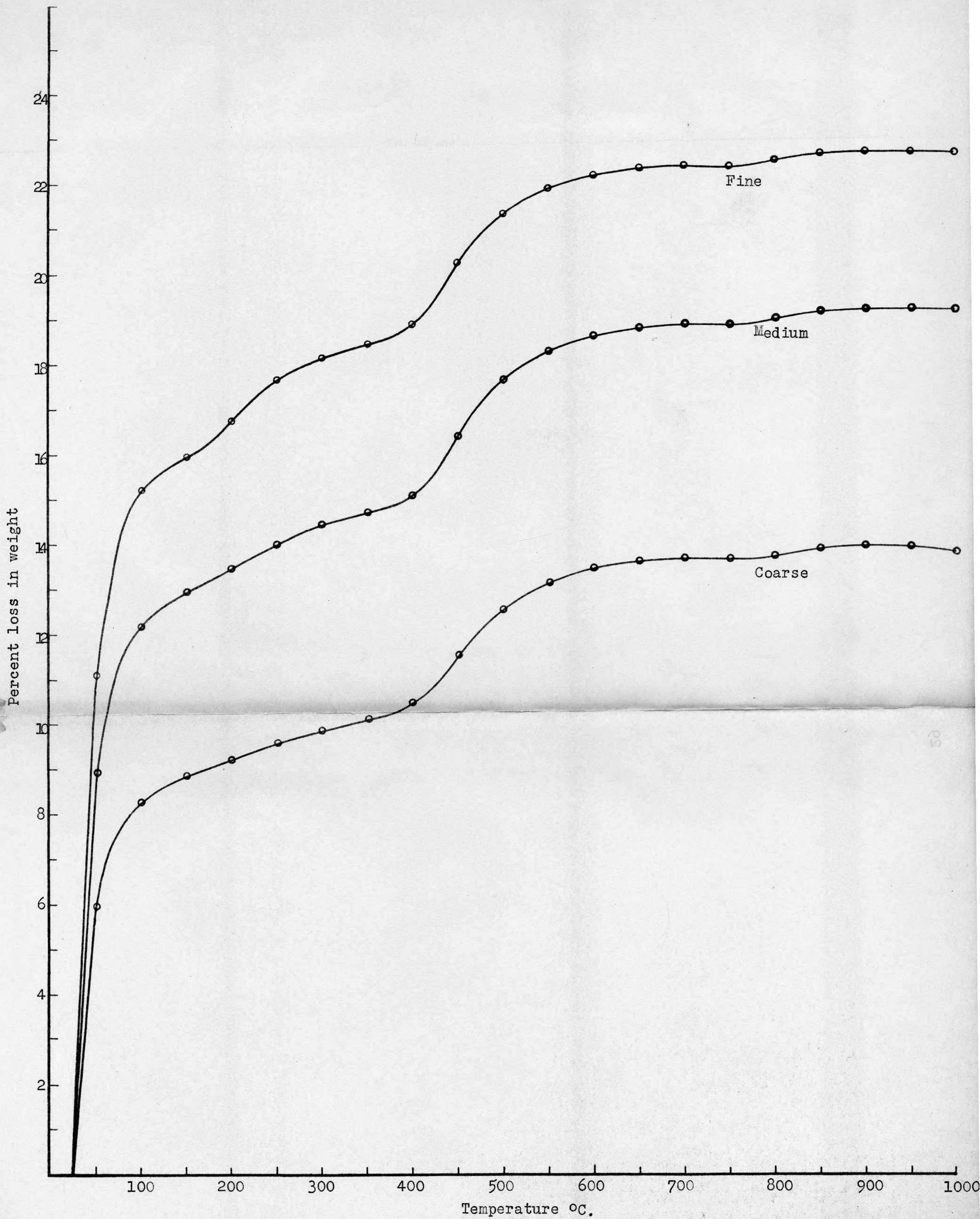


Figure 7. Thermal dehydration curves for 3 clay fractions of Brown soil.

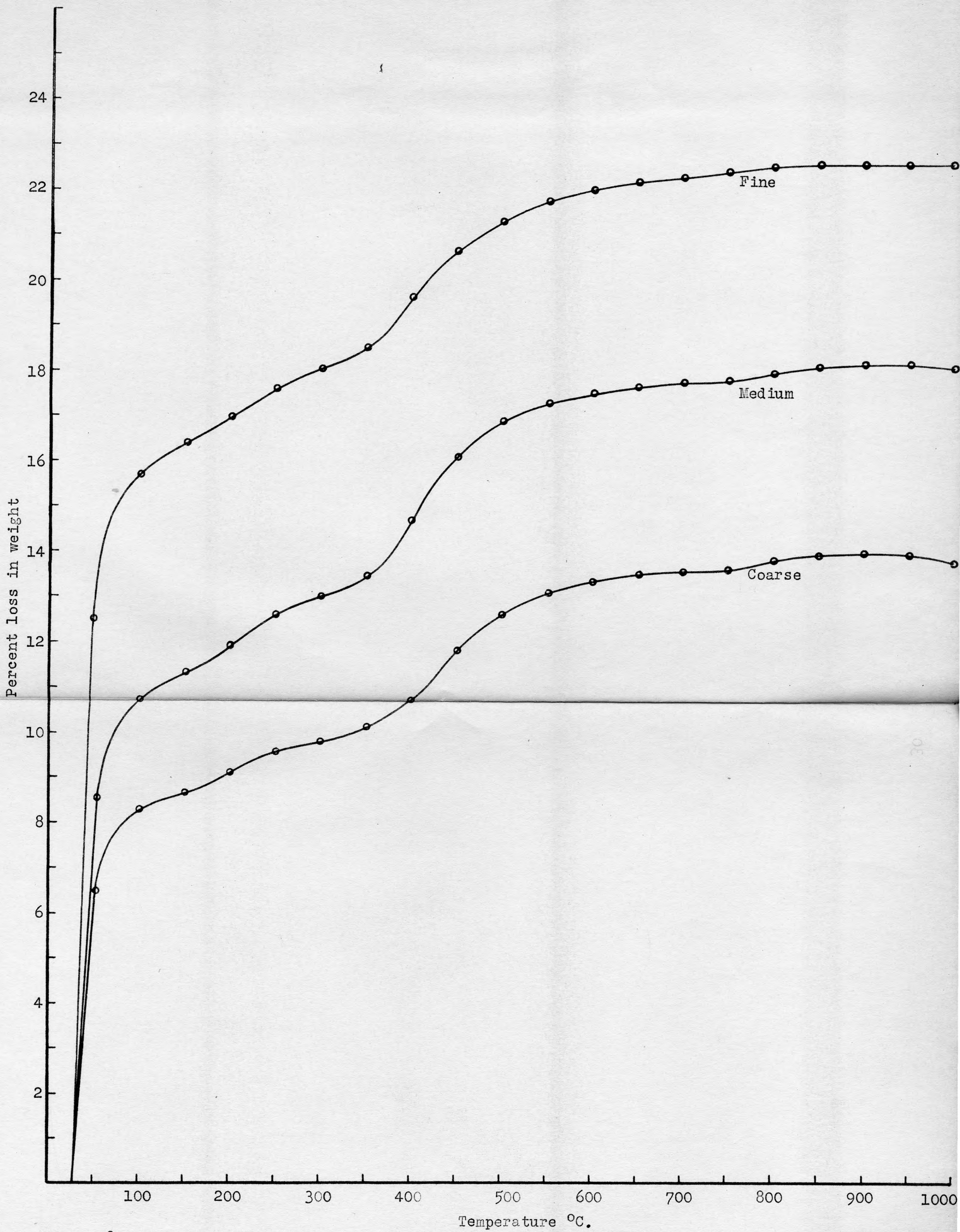


Figure 8. Thermal dehydration curves for 3 clay fractions of Chestnut soil.

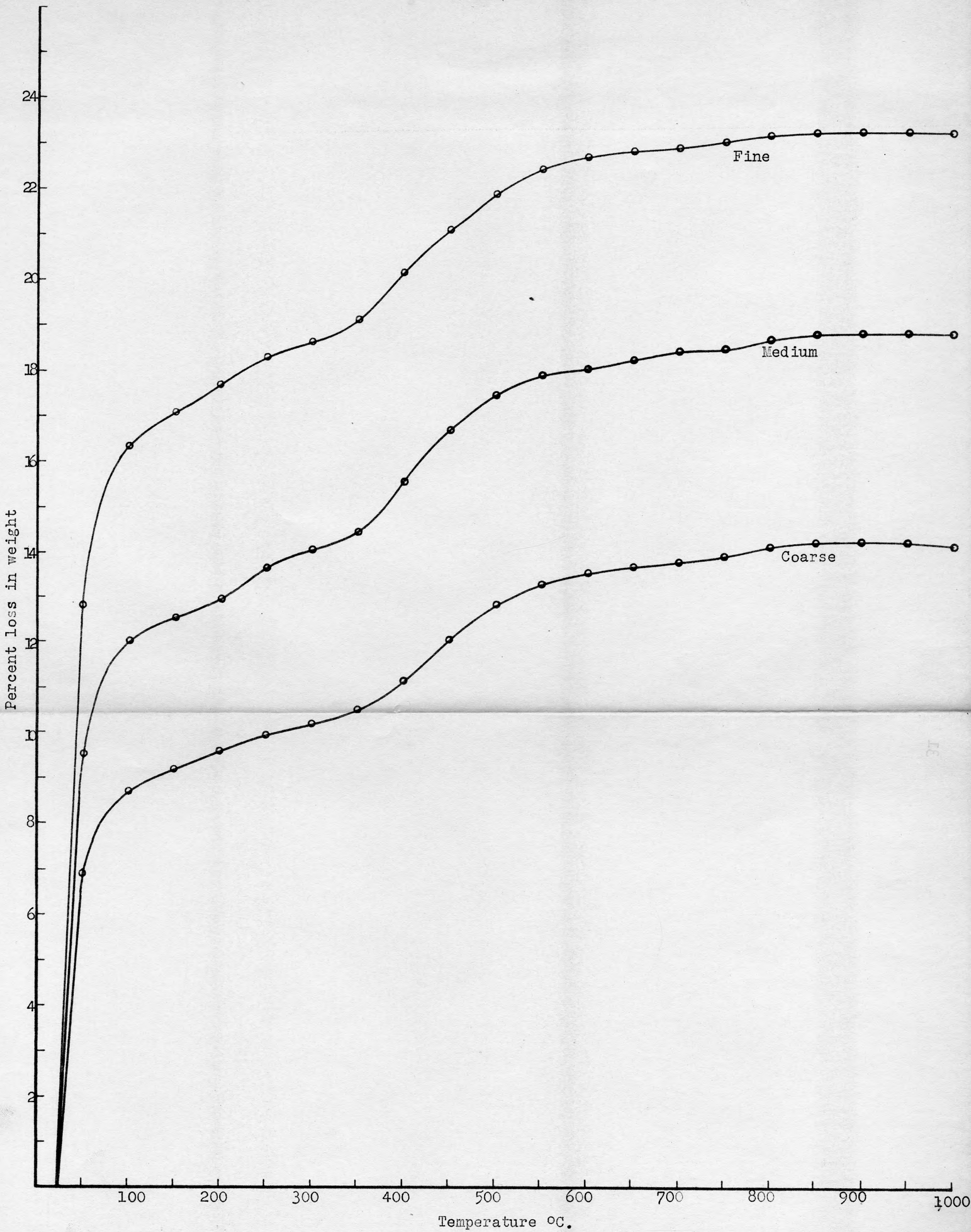


Figure 9. Thermal dehydration curves for 3 clay fractions of Chernozem soil.

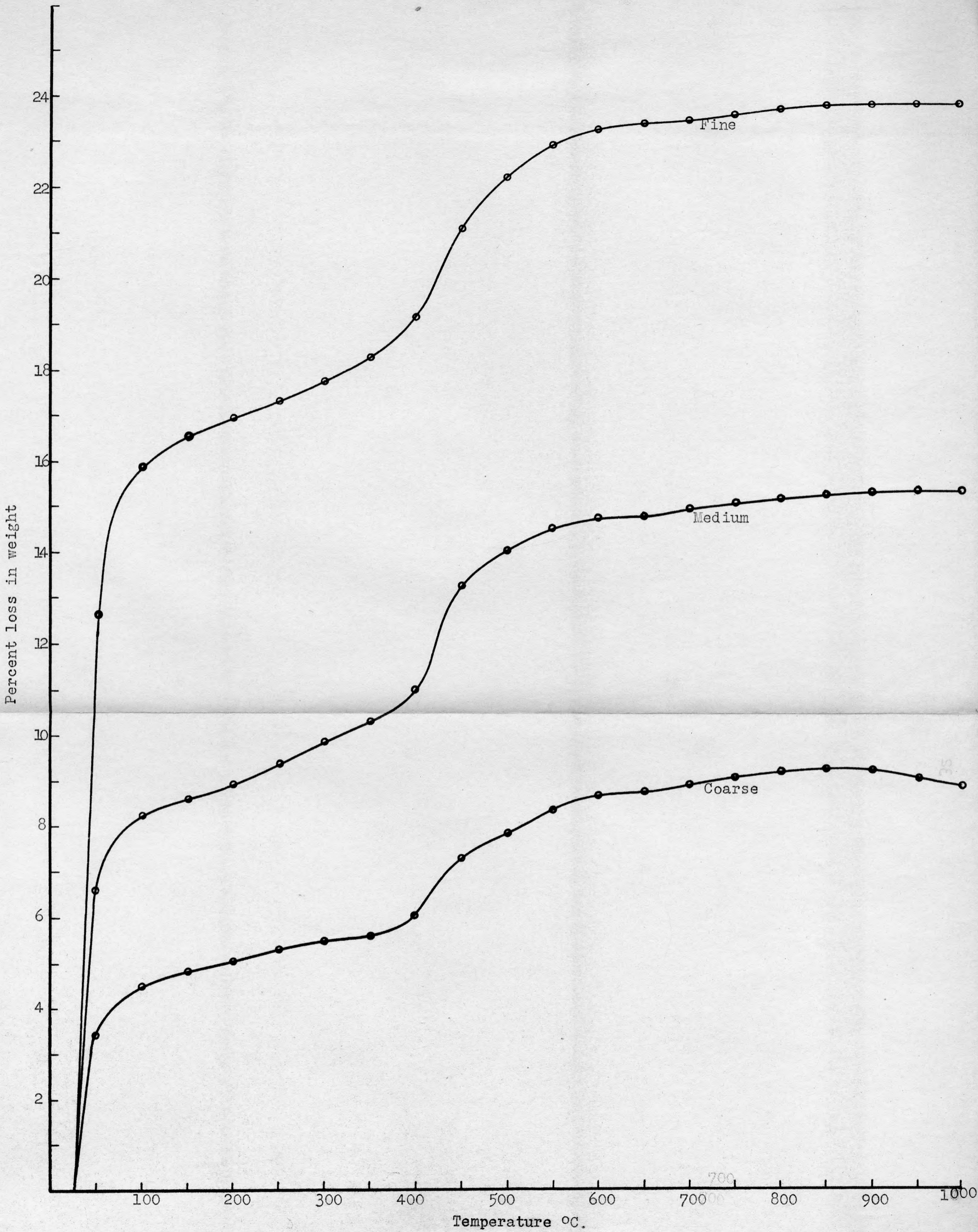


Figure 10. Thermal dehydration curves for 3 clay fractions of Prairie soil.

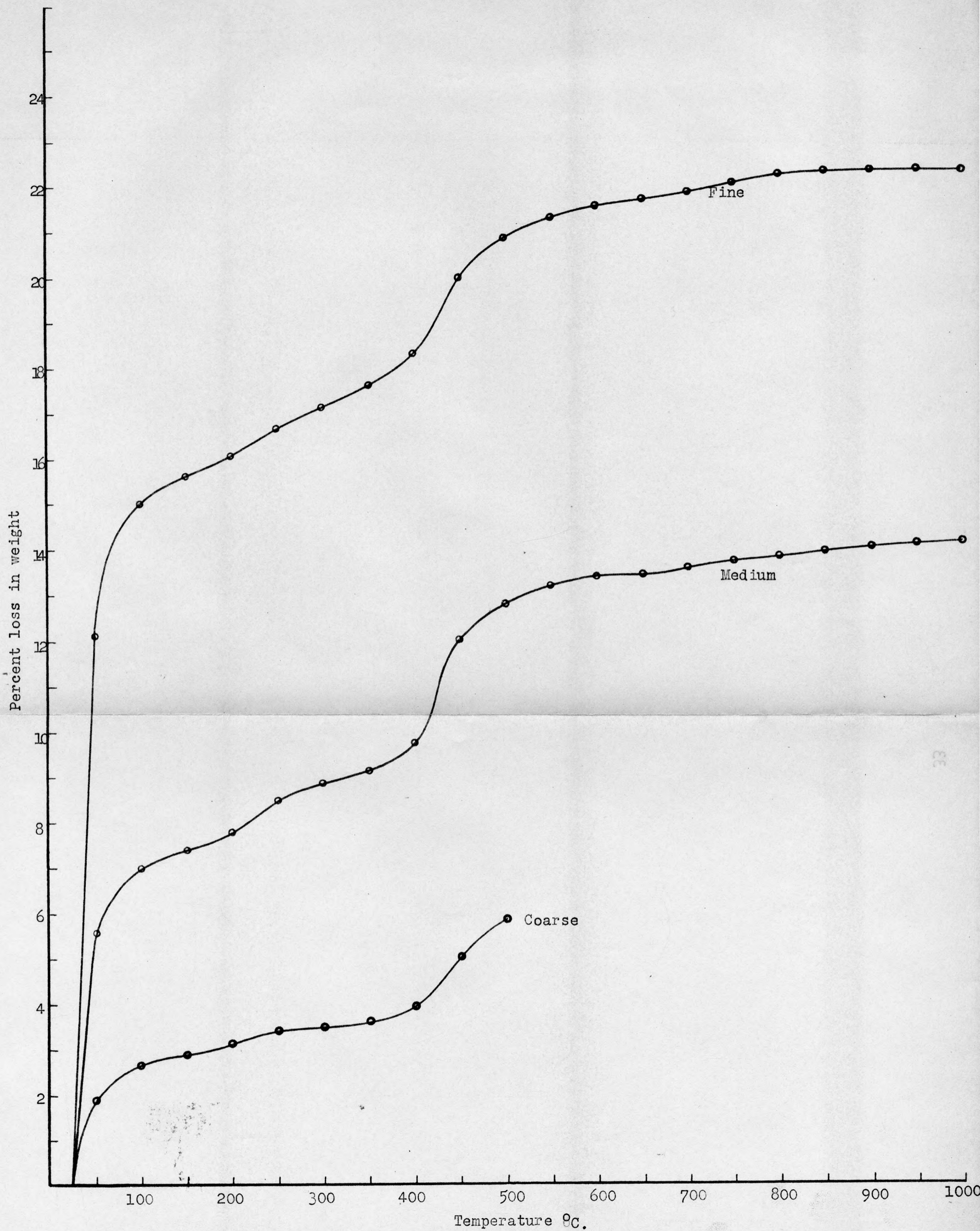


Figure 11. Thermal dehydration curves for 3 clay fractions of Grey-brown Podzolic soil.

Since the fine fractions of the standard minerals (except for illite) are not characteristic of typical curves, it would seem that some highly hydrated impurity (mineral) is more concentrated in the fine fractions of the standard minerals than in the coarse and medium fractions and that the concentration of this material is great enough to alter the characteristic shape of the curve.

If the deviation in the fine fractions were due to particle size alone, the characteristic shape would not necessarily be changed to any great extent but the points of the curve would merely indicate greater hydration than corresponding points of the other two fractions. This is indicated by the illite curves. The three illite curves have much the same shape from 100° C. to 1000° C. The difference in hydration throughout the course of the curves seems to be fairly uniform averaging about 1 percent between coarse and medium fractions and about 3 percent between medium and fine fractions.

The Department of Geology produced differential thermal analysis curves for the standard minerals used. It was concluded that the kaolinite sample contained illite in increasing amounts from the coarse to the fine fraction. Therefore the coarse and medium fractions represented the more typical curve for kaolinite as is shown in Fig. 3.

For bentonite the magnitude of the break ranges from 500° C. to 650° C. For beidellite the break comes between 400° C. and 550° C. The illite curve breaks between 400° C. and 500° C.

The kaolinite curve starts to break at 400° C. and continues to 500° C. Halloysite starts to break at about 350° C. and continues to a point between 450° C. and 500° C.

On the basis of break points in the standard curves, it is possible to indicate that certain minerals may be present in the soil samples. In Fig. 6 the Sierozem-like soil curves break from 400° to 550° C. indicating the possibility of illite and beidellite in all three fractions. The Brown soil (Fig. 7) offers the same inflection range corresponding to the same minerals. Figure 8 shows that in addition to illite and beidellite, the possibility of halloysite may be considered in the Chestnut soil, since the break starts at 350° C. The Prairie soil curves (Fig. 10) also indicate the possibility of halloysite, illite and beidellite. The Chernozem curves (Fig. 9) show the same type of break as the Chestnut and Prairie soils. The Grey-brown Podzolic soil (Fig. 11), however, indicates only illite in all 3 fractions. The termination of the coarse fraction curve at 500° C. exists because after the 500° C. point was recorded, the sample was lost and the curve, therefore, could not be continued.

The soil sample curves indicate a much greater water loss than most of the standard curves. This is believed to be due to the fact that the soils initially remained in the 75 percent relative humidity chamber for a much greater period of time than the standard minerals and probably were nearer equilibrium with the atmosphere (75 percent relative humidity) than the standard

minerals. If the initial water loss (below 100° C.) is omitted and the total water loss based on sample weight at 1000° C., then the dehydration percentage in all the soil samples ranges between 5 and 8 percent. This water percent loss is very similar to the three fractions of illite and the coarse and fine fractions of beidellite and bentonite.

Cation Exchange Capacity

Generally cation exchange capacity is believed to increase from coarse to fine fractions of the same material. However, two exceptions were noted. The bentonite fine fraction gave a lower cation exchange capacity than the other two fractions and the fine fraction of illite was less than the medium but greater than the coarse fraction. In all cases the cation exchange capacity increased from the coarse to fine fractions of the soil samples.

Tables 11, 12 and 13 show a very definite cation exchange capacity gradient, if one places the soils in the following order for all three fractions: Sierozem-like, Brown, Chestnut, Chernozem, Prairie and Grey-brown Podzolic. This is the normal geographic position of these great soil groups--from west to east--and in this order the cation exchange capacity decreases in each fraction. The only exceptions are the medium and fine fractions of the Chernozem which are somewhat higher than the Chestnut. This would seem to indicate a general decrease of the montmorillonite content of Kansas soils from west to east especially in the coarse and medium fractions.

Table 10. Cation exchange capacity of standard minerals.

Mineral	: Clay fraction	: Cation exchange capacity m.e. per 100 gms
Bentonite	coarse	88.3
	medium	99.3
	fine	79.2
Beidellite	coarse	38.4
	medium	50.5
	fine	75.7
Halloysite	coarse	13.7
	medium	13.7
	fine	49.4
Kaolinite	coarse	11.9
	medium	11.5
	fine	41.9
Illite	coarse	28.4
	medium	57.3
	fine	47.5

Table 11. Results of chemical analysis of Sierozem-like and Brown soils.

Oxides in percent	Sierozem-like soil			Brown soil		
	Clay analysis			Clay analysis		
	Coarse	Medium	Fine	Coarse	Medium	Fine
SiO ₂	58.1	49.7	52.5	57.0	51.9	52.2
Fe ₂ O ₃	3.3	3.0	2.9	2.9	3.5	3.7
Al ₂ O ₃	17.2	15.7	16.1	15.6	17.6	17.6
TiO ₂	.74	.65	.40	.77	.70	.45
CaO	.30	.27	.14	.70	.48	.30
MgO	3.7	3.6	4.1	2.3	2.7	2.5
MnO	.059	.039	.049	.035	.042	.051
K ₂ O	.71	.71	.62	.64	.71	.45
Cation * exch. cap.	60.5	76.4	96.1	56.3	72.5	95.1

* Cation exchange capacity in m.e. per 100 gms.

Table 12. Results of chemical analysis of Chestnut and Chernozem soils.

Oxides in percent	Chestnut soil			Chernozem soil		
	Clay analysis			Clay analysis		
	Coarse	Medium	Fine	Coarse	Medium	Fine
SiO ₂	58.9	59.1	50.9	57.4	49.6	48.8
Fe ₂ O ₃	3.2	3.4	4.0	3.8	4.1	3.9
Al ₂ O ₃	15.9	16.6	18.5	18.3	18.0	16.5
TiO ₂	.82	.79	.46	.92	.78	.45
CaO	.10	.43	.12	.40	.16	.18
MgO	1.74	2.00	2.15	1.97	1.99	1.75
MnO	.116	.089	.128	.071	.081	.079
K ₂ O	.65	.74	.56	.40	.53	.40
Cation exch. cap.	50.4	50.4	87.0	49.8	64.0	89.3

Table 13. Results of chemical analysis of Prairie and Grey-brown Podzolic soils.

Oxides in percent	Prairie soil			Grey-brown Podzolic		
	Clay analysis			Clay analysis		
	Coarse	Medium	Fine	Coarse	Medium	Fine
SiO ₂	62.0	51.3	46.2	59.2	47.5	47.6
Fe ₂ O ₃	2.6	3.7	4.9	3.5	4.9	5.4
Al ₂ O ₃	15.1	20.1	18.9	15.3	20.0	19.2
TiO ₂	1.02	1.11	.54	1.15	1.00	.55
CaO	.18	.55	.30	.43	.32	.15
MgO	1.12	1.97	1.75	1.26	1.74	1.72
MnO	.044	.067	.048	.082	.156	.128
K ₂ O	.56	.53	.25	.65	.60	.36
Cation exch. cap.	31.6	47.6	86.8	23.4	43.2	82.4

Chemical Analysis

The potash content of almost all soils was less in the fine than the medium and coarse fractions (Tables 11, 12 and 13). This would indicate a general decrease in illite content from coarse to fine fractions. If 5 percent were taken as the average content of K_2O in pure illite (10), then the percent of illite would range from 5 to about 16 over all the samples.

A comparison of Tables 11, 12 and 13 with Table 1 of Ross and Hendricks (24) will show a similarity of composition of these six soils and the analyses of the montmorillonite-beidellite series.

Therefore, on the basis of the dehydration curves which indicate the presence of illite, beidellite and halloysite, cation exchange capacity which indicates a high content of some member of the montmorillonite series, and chemical analysis showing similarity to the montmorillonite-beidellite series, it seems likely that all the clay fractions of the soils analyzed contain beidellite and illite as the main constituent. Small amounts of halloysite may be present in the Chestnut, Chernozem and Prairie soils.

SUMMARY

An attempt was made to determine the clay mineral content of certain Kansas soils which represent the A_1 horizons of six great soil groups. These soils were developed from a common parent material which forms a mantle east to west across the State of Kansas and is thought to be Peorian loess.

In order to analyze the clay it had to be separated from the soil by special methods. Airdry samples which had passed through a 10-mesh screen were weighed out. The carbonates were eliminated by lowering the pH to 4. Organic matter was eliminated by treatment with H_2O_2 (30%). The clay colloids were saturated with the sodium ion by treatment with 2 percent Na_2CO_3 and the replaced cations were removed by centrifuging the flocculated soils (after treatment with Na_2CO_3). The clay fraction of $< 2 \mu$ was removed by suspending the sample in distilled water and centrifuging for a given time and speed required to sediment particles $> 2 \mu$. This was carried out according to Stokes's Law as applied to the International Centrifuge.

The total clay was then fractionated into three sizes: coarse, 2-0.2 μ ; medium, 0.2-0.08 μ ; and fine, $\leq .08 \mu$. This was carried out in the Sharples Supercentrifuge in which the size of particle deposited against the bowl lining depends on the rate of flow of the soil passing through the centrifuge.

It was decided that three basic methods of analysis would be used: Thermal dehydration curves, cation exchange capacity, and chemical analysis. Thermal dehydration curves were produced

by heating the sample to given temperatures and plotting percent loss in weight against oven temperature. Cation exchange capacity was determined by replacing the exchangeable cations with potassium which was then extracted with the ammonium ion and determined by the flame photometer method. Chemical analysis consisted of quantitative determinations of the oxides of silicon, aluminum, iron, titanium, potassium, calcium, magnesium, and manganese.

In order to carry out the first two methods, data had to be obtained from standard minerals as a basis of comparison. For this purpose the minerals bentonite, beidellite, halloysite, kaolinite and illite were treated in the same manner as the soils. Chemical analyses were carried out only with the soil fractions.

Characteristic breaks in the soil colloid dehydration curves when compared to the curves of the standard minerals seemed to indicate the presence of illite and beidellite in all the soils. Lower temperature breaks found in the Chestnut, Chernozem and Prairie soils may indicate the presence also of small amounts of halloysite.

Exchange capacity data indicated that the montmorillonitic constituent increases from the coarse to the fine fractions while the illite content increases from the fine to the coarse fractions.

Chemical analyses show similarity to the analyses made by Ross and Hendricks on the montmorillonite-beidellite series.

On the basis of potassium analysis, assuming 5 percent potassium to be equivalent to 100 percent illite, the illite content of all the soil fractions ranges from about 5 to 16 percent. The remaining mineral content appears to be largely beidellite.

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LITERATURE CITED

- (1) Russell, M. B., and J. L. Haddock.
The identification of the clay minerals in five Iowa soils by the thermal method. Soil Sci. Soc. of Amer. Proc. 5:90, 1940.
- (2) Perkins, A. T., and William G. Schrenk.
The analysis and characteristics of selected Kansas soils. Contribution No. 362 of the Dept. of Chemistry, Kans. Agr. Expt. Sta., Manhattan.
- (3) Kelley, W. P., H. Jenny, and S. M. Brown.
Hydration of minerals and soil colloids in relation to crystal structure. Soil Sci. 41:259, 1936.
- (4) Grim, R. E., R. H. Bray, and W. F. Bradley.
The mica in argillaceous sediments. The American Mineralogist. 22:813, 1937.
- (5) Sedletzky, I. D.
Colloid-dispersion mineralogy, its problems and methods. Comptes Rendus (Doklady) de l'Academie des sciences de l'URSS. Vol. XXXIV, No. 6, 1942. Communicated by A. E. Fersman, member of the Academy, 12.I.1942.
- (6) Larson, W. E., W. H. Allaway, and H. F. Rhoades.
Characteristics of three soils from the Chernozem and Chestnut soil regions of Nebraska. Soil Sci. Soc. of Amer. Proc. 12:420, 1947.
- (7) Grim, R. E., and W. F. Bradley.
Rehydration and dehydration of the clay minerals. Report of Investigations No. 134, State Geol. Survey, Urbana, Ill.
- (8) Grim, R. E.
Properties of clay. Circular No. 49, State Geol. Survey, Urbana, Ill., 1939.
- (9) Grim, R. E., and R. A. Rowland.
Differential thermal analysis of clay minerals and other hydrous materials. Report of Investigations No. 85, State Geol. Survey, Urbana, Ill.
- (10) Nagelschmidt, G.
The mineralogy of soil colloids. Imperial Bureau of Soils Sci. Tech. Communication No. 42.
- (11) Ross, C. S., and P. F. Kerr.
The kaolin minerals. U. S. Dept. of Interior, Prof. Paper 165-E, 1948.

- (12) Ross, C. S., and P. F. Kerr.
Halloysite and allophane. U. S. Dept. of Interior,
Prof. Paper 185-G, 1934.
- (13) Grim, R.
Modern concepts of clay materials. Ill. State Geol.
Sur. Rept. of Invest., 80, 1942.
- (14) Baver, L. D.
Soil physics. 2nd Ed. New York: John Wiley & Sons, 1948.
- (15) Tanner, C. B., and M. L. Jackson.
Nomographs of sedimentation times for soil particles
under gravity or centrifugal acceleration. Soil Sci.
Soc. Amer. Proc. 12:60, 1947.
- (16) Seay, W. A., and M. E. Weeks.
The fractionation and properties of clays from the sur-
face soils of the Pearman and Maury series. Soil Sci.
Soc. Amer. Proc. 12:24, 1947.
- (17) Rendig, V. V.
Rapid determination of cation exchange capacity of soils
with the flame photometer. Soil Sci. Soc. of Amer.
Proc. 12:449, 1947.
- (18) Robinson, W. O.
Methods and procedure of soil analysis used in the divi-
sion of soil chemistry and physics. U.S.D.A. Cir. No. 139.
Rev. Nov. 1939.
- (19) Kolthoff, I. M., and E. B. Sandell.
Textbook of quantitative inorganic analysis. New York:
Macmillan Co., 1947 Rev. Ed.
- (20) Jackson, M. L.
Soil analysis--chemical and physiochemical methods.
Univ. of Wisconsin Agr. Expt. Sta., June 30, 1949.
- (21) Peech, M., L. T. Alexander, L. A. Dean, and J. F. Reed.
Methods of soil analysis for soil-fertility investiga-
tions. U.S.D.A. Cir. No. 757, April 1947.
- (22) Whiteside, E. P., and C. E. Marshall.
Mineralogical and chemical studies of the Putnam silt
loam soil. Univ. of Missouri Agr. Expt. Sta. Research
Bul. 386, Nov. 1944.
- (23) Grim, R. E.
Relation of the composition of the properties of clay.
Circular No. 45, State Geol. Survey, Urbana, Ill., 1939.

(24) Ross, C. S., and S. B. Hendricks.
Minerals of the montmorillonite group. U. S. Dept. of
Interior, Prof. Paper 205-B, 1945.

