

POTASSIUM FIXATION IN HAWAIIAN SOILS

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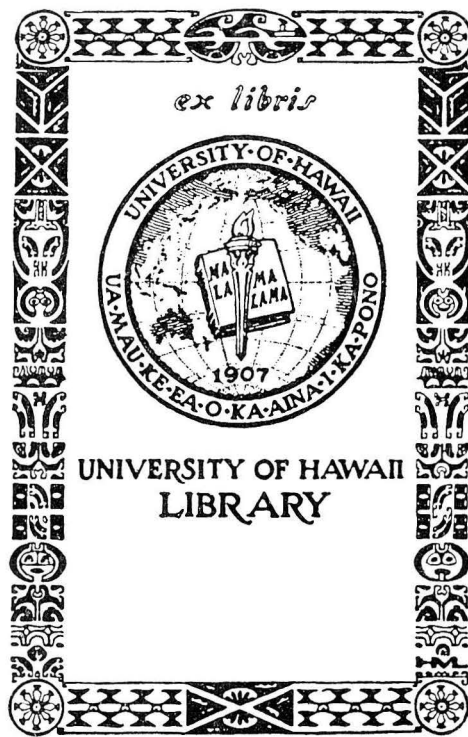


TABLE OF CONTENTS

	Page
ACKNOWLEDGEMENT.....	1
LIST OF TABLES.....	ii
LIST OF FIGURES.....	iii
INTRODUCTION.....	1
DESCRIPTION OF SOILS USED.....	3
METHODS OF ANALYSIS.....	8
EXPERIMENTAL	
Potassium Fixation Upon Moist Storage.....	9
Potassium Fixation Upon Air-Drying.....	17
Potassium Fixation Upon Oven-Drying Humic Latosol.....	21
Potassium Fixation Upon Alternate Wetting and Drying.....	23
Effect of Potassium Saturation on Fixation and Exchange Capacity.....	26
Differential Thermal Analysis of Soils Used.....	29
GENERAL DISCUSSION.....	39
SUMMARY.....	44
LITERATURE CITED.....	46

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LIST OF TABLES

	Page
Table 1. Some Properties of Soils Used.....	6
Table 2. Effect of Air-drying on Fixation of Potassium	19
Table 3. Effect of Drying to the Wilting Point on Fixation of Potassium in Low Humic Latosol (N1) Soil No. 50-225.....	20
Table 4. Effect of Oven-drying Humic Latosol Soil No. 49-35 on Fixation of Potassium.....	22
Table 5. Effect of Alternate Wetting & Drying at Room Temperature on Fixation of Potassium..	25
Table 6. Effect of Temperature on Fixation and Exchange Capacity in Potassium Saturated Soils.....	28

LIST OF FIGURES

	Page
Figure 1. Per cent of Added Potassium Fixed Upon Moist Storage of Low Humic Latosol (No. 50-91) at 266 ppm. K Application...	12
Figure 2. Per cent of Added Potassium Fixed Upon Moist Storage of Hydrol Humic Latosol (No. 49-37) at 266 ppm. K Application...	13
Figure 3. Per cent of Added Potassium Fixed Upon Moist Storage of Dark Magnesium Clay (No. 50-92) at 266 ppm. K Application...	14
Figure 4. Per cent of Added Potassium Fixed Upon Moist Storage at 416 ppm. K Application of KCl.....	15
Figure 5. Per cent of Added Potassium Fixed Upon Moist Storage at 1596 ppm. K Application of KCl.....	16
Figure 6. Differential Thermal Curve of Kaolin...	31
Figure 7. Differential Thermal Curve of Bentonite.	32
Figure 8. Differential Thermal Curves of Low Humic Latosols. (A) No. 50-91; (B) No. 50-222.....	33
Figure 9. Differential Thermal Curves of Humic Latosol (No. 51-2). (A) Presence of Organic Matter; (B) Removal of Organic Matter with Hydrogen Peroxide.....	34
Figure 10. Differential Thermal Curve of Hydrol Humic Latosol (No. 51-1).....	35
Figure 11. Differential Thermal Curve of Humic Ferruginous Latosol (No. 50-205).....	36
Figure 12. Differential Thermal Curve of Gray Hydromorphic Soil (No. 50-220)	37
Figure 13. Differential Thermal Curves of Dark Magnesium Clay. (A) No. 50-92; (B) No. 50-221.....	38

INTRODUCTION

Soil potassium exists in several forms, namely, water-soluble, exchangeable, non-exchangeable, and primary mineral forms.

Water-soluble potassium in soil solution is limited to a range of one to ten parts per million. This amount is inadequate to meet the requirements of a crop. However, there is a larger amount present in the exchangeable form associated with the colloids which is usually determined by the extraction with ammonium acetate. This form is generally considered to be readily absorbed by plant roots that make contact with it. The non-exchangeable potassium, on the other hand, is fixed and unavailable to plants. Ordinary ammonium acetate extraction will not remove the potassium. It may be extracted by HCl acid (4). Also the continuous extraction by plants will remove this non-exchangeable form under normal soil condition (6). Finally, the bulk of the soil potassium is contained in primary minerals, such as feldspars and biotite.

With the clarification of the cation exchange phenomenon in soils, these forms were identified. But, it was known for a long time that added potassium became fixed.

Fixation of potassium may be defined as the transformation of soluble and exchangeable potassium to non-exchangeable forms. Martin, Overstreet and Hoagland (17) indicated that

all the potassium fixed had functioned in replacing Ca, Mg, and Na, which appeared in the water extract; thus suggesting an exchange reaction. Wood and DeTurk (33) considered this exchange reaction very important in their concept of potassium equilibrium in soils.

Later Page and Baver (19) showed fixation of potassium within the lattice structure of montmorillonitic clays. Another theory suggests the formation of muscovite, a secondary mineral, as described by Attoe and Truog (3). This was also reported by G.W. Volk (28) as supported by X-ray patterns.

Consequently, the existence of potassium fixation has been well established by a number of investigators. Most of their work seems to indicate greater fixation by high temperature treatment and alternate wetting and drying.

In view of the fact that potassium fertilizer is used extensively in Hawaii and elsewhere in the world, the extent to which applied potassium is fixed in the soil is of vital concern. Therefore, the primary objective of this study was to determine the ability of certain Hawaiian soils to fix added potassium under various conditions and to attempt to identify the predominant minerals involved.

DESCRIPTION OF SOILS USED

Great diversity in the soils of Hawaii has resulted from variations in environmental conditions and topography. These soils have developed primarily from basaltic lava and volcanic ash (11) (12). Geologically, the age of lava and ash varies from recent flow of eruptive materials to the early formation of the Hawaiian Islands. During that period of time volcanoes in Hawaii have been very active.

The annual rainfall ranges from 10 to 15 inches in dry areas to nearly 250 inches in excessively wet areas. Drainage is generally good but areas of poor drainage are evident, especially in lowland where magnesium content is high.

Laterization is the most active and dominant soil forming process in Hawaii. In this process extensive leaching of silica and bases has taken place resulting in a low silica-sesquioxide ratio -- usually less than two.

Soil samples from six major Great Soil Groups, representing agriculturally important areas, were collected for this study. These samples were taken from the first surface foot. The six groups of soils may be briefly described as follows:

*Low Humic Latosols from Poamoho, Wahiawa, are

* U.S.D.A. Soil Survey Report (in press)

characterized by their red color. They are used extensively for growing sugar cane and pineapples. The exchange capacity ranges from 15 to 30 milliequivalents per 100 grams of soil. Organic matter is low ranging from 2 to 5 per cent. The annual rainfall varies from 15 to 60 inches. The clays are primarily kaolinite.

Humic Latosols from Tantalus, Oahu, and Laupahoehoe, Hawaii, are developed under rainfall ranging from 40 to as much as 150 inches annually. In these soils the kaolinite minerals are decomposing to a more stable aluminum oxide (22). Simultaneously, with lack of aeration, the iron oxides are being reduced and leached from the soils. The pH ranges from 4.5 to 6.0. The cation exchange capacity averages 45 milliequivalents per 100 grams of soil. Organic matter ranges from 10 to 15 per cent.

Hydrol Humic Latosols from Pepeekeo, Hawaii, are developed under excessively wet areas. The annual rainfall averages 120 to 300 inches, and in the natural condition they are continually wet. Organic matter is high ranging from 15 to 35 per cent. Due to the tremendous loss of water upon drying, their volume weights are extremely low. But they do not revert to their original form upon hydration. The clays are largely oxides.

Humic Ferruginous Latosols from Lihue, Kauai, appear rather grayish to purple. Volume weights of these soils in contrast to the Hydrol Humic Latosols, are extremely

high resulting from the accumulation of titanium and iron oxides (23)(25). Leaching is intensive which accounts for the low base saturation. The annual rainfall ranges from 35 to 150 inches. These soils probably represent the end product of soil formation for the latosols under a wet and dry climate (22).

Gray Hydromorphic Soils from Ewa, Oahu, are characterized by level topography, poor drainage, and the accumulation of magnesium. They are heavy and plastic and are easily dispersed. Large number of surface cracks appears upon drying. They are neutral to alkaline in reaction.

Dark Magnesium Clays from Ewa, Oahu, are characterized by their dark color and sticky, highly plastic consistency. They contain high accumulation of bases of calcium and particularly magnesium.

Exchange capacity is rather high. The magnesium saturation is usually more than 30 per cent. They are not truly developed solonetz but are in the process of desalinization. Montmorillonite is probably the predominant mineral. Active dolomitization is also present in small areas (24).

Some properties of the soils used are shown in table 1.

Table 1. SOME PROPERTIES OF SOILS USED

Soil Number	Soil Group	Soil Family	Location	pH	Exchangeable Cations			Exchange Capacity	Organic Matter
					Potassium m.e./100	Calcium m.e./100	Magnesium m.e./100	m.e./100	Per cent
49-35	Humic Latosol	Ookala A-5	Laupahoehoe, Hawaii	4.3	.29	.46	.20	44.4	14.00
49-37	Hydrol Humic Latosol	Akaka K8	Pepeekeo, Hawaii	4.3	2.65	.19	.39	52.9	18.00
50-91	Low Humic Latosol	Wahiawa N3	Poamoho, Oahu	5.2	3.71	4.04	1.45	11.8	2.84
50-92	Dark Magnesium Clay	Lualualei M	Ewa, Oahu	7.5	7.25	17.39	17.95	33.7	4.30
50-205	Humic Ferrugi- nous Latosol	Haiku T3	Lihue, Kauai	4.7	.09	.66	.25	17.8	7.30
50-220	Gray Hydro- morphic Soil	Honouliuli H1	Ewa, Oahu	7.4	.34	19.44	18.33	33.3	1.69
50-221	Dark Magnesium Clay	Lualualei M	Ewa, Oahu	7.3	1.09	19.19	15.95	43.3	1.90

Soil Number	Soil Group	Soil Family	Location	pH	<u>Exchangeable Cations</u>			(cont.)	
					Potassium m.e./100	Calcium m.e./100	Magnesium m.e./100	Exchange Capacity m.e./100	Organic Matter Per cent
50-222	Low Humic Latosol	Wahiawa, N3	Poamoho, Oahu	5.3	.83	3.83	1.35	11.8	2.22
51-1	Hydrol Humic Latosol	Hilo K6	Pepeekeo, Hawaii	4.5	.38	.37	1.20	47.2	16.94
51-2	Humic Latosol	Kapoho A9	Tantalus, Oahu	5.0	.48	3.06	2.99	50.4	15.68

METHODS OF ANALYSIS

Soils were leached of exchangeable cations with N ammonium acetate adjusted to pH 7.0. Peech's (20) centrifuge method was employed initially in determining potassium in the extracts. However, this method was not adapted for large quantities of potassium. The cobalti-nitrite method of Volk and Truog (30) was more suited for the analysis. Flame photometer was also used rather briefly. Calcium in the extract was determined by precipitation as the oxalate, followed by titration with potassium permanganate. Magnesium was determined by precipitation as the ammonium phosphate, followed by titration with a standard acid solution.

Cation exchange capacity was determined by leaching the soil with N ammonium acetate, followed by distillation and titration of the adsorbed ammonia. Organic matter was determined by a modification of the Walkley - Black method (31). Soil pH was determined by the use of Beckman pH meter.

POTASSIUM FIXATION UPON MOIST STORAGE

Results of both positive and negative fixation upon moist storage have been reported by investigators. Attoe and Truog (3) found no fixation after $7\frac{1}{2}$ months of moist storage. Stanford (27) reported little or no fixation of potassium by montmorillonite. On the other hand, Raney and Hoover (21), working with montmorillonite, showed as much as 23 per cent fixation. Attoe, (2) in his later work, found that fixation ranged from 0 to 17 per cent in the case of the fertilized soils.

Three important factors have been reported which influence fixation upon moist storage, namely, rate of application, time of storage, and the effect of anions.

Bray and DeTurk (8) showed increased fixation of potassium with greater addition of its soluble salts. This may be looked upon as a mass action effect whereby a state of equilibrium is attained. Wood and DeTurk (33) also noted greater fixation with heavier application, particularly with soils of high exchange capacity.

Although fixation upon moist storage is generally considered slow and gradual, Martin, et al. (17) have shown rapid fixation which was established in 48 hours. Wood and DeTurk (33) determined that the effect of time on fixation varies with different soils and differences in geological age.

The anion effect has been considered important by several investigators. Joffe and Kolodny (13) showed higher potassium fixation with increase in phosphate ions. Raney and Hoover (21) noted that at 216 ppm. K the KCl showed a higher percentage fixation, but at 2,160 ppm. K the KH_2PO_4 fixed a greater percentage.

In order to determine whether Hawaiian soils will fix added potassium, the following experiment was carried out. A series of 25 gram samples of soil was kept moist in stoppered Erlenmeyer flasks containing 20 ml. of potassium solution of three different concentrations, based on the weight of soil. The applications were 266 ppm. K, 416 ppm. K, and 1596 ppm. K. The samples were stored for one hour to eight weeks and periodically the exchangeable potassium was extracted. In addition to the study of time interval, the influence of anions and the effect of air-drying the field soil have been considered. However, differences were not observed as indicated in figures 1, 2 and 3. Fixation is determined by the difference in the amount added and that recoverable after storage.

Low Humic Latosol (No. 50-91) of figure 1 indicates no fixation. Rather than fixation, the first few days of storage showed some release of non-exchangeable potassium. Hydrol Humic Latosol (No. 49-37) of figure 2 shows no fixation also. However, Ayres and Hagihara (5) found 16 to

21 per cent fixation when potassium was applied in the form of K_3PO_4 . With KCl , K_2SO_4 , KH_2PO_4 , KPO_3 , or with mixtures of KCl and either of the superphosphate or ammophos no fixation was evident.

Dark Magnesium Clay (No. 50-92) of figure 3, unlike the other two types of soils, indicates definite fixation. With longer storage, fixation gradually increased, and at four to six weeks about 10 to 16 per cent of the added potassium was fixed.

Figure 4 indicates results obtained from the application of 416 ppm. K. These soils were collected at a later date to supplement the other samples. Gray Hydromorphic soil (No. 50-220) was also included. At this concentration and in following experiments addition of phosphate ions and the moist field soils was purposely omitted because previous study showed no effect. An exception is the Hydrol Humic Latosol. Since this soil is continually moist in the natural condition, it was never allowed to dry in storage. Evidently, at 416 ppm. K application fixation was absent.

Since fixation was not apparent for most of the soils at lower rates of application, a concentration of 1596 ppm. K was employed. It is generally believed that higher application brings about greater fixation (15) but this was not the case, as shown in figure 5. Even Dark Magnesium Clay (No. 50-92) failed to fix any potassium. Humic Ferruginous Latosol (No. 50-205) was included in this study also.

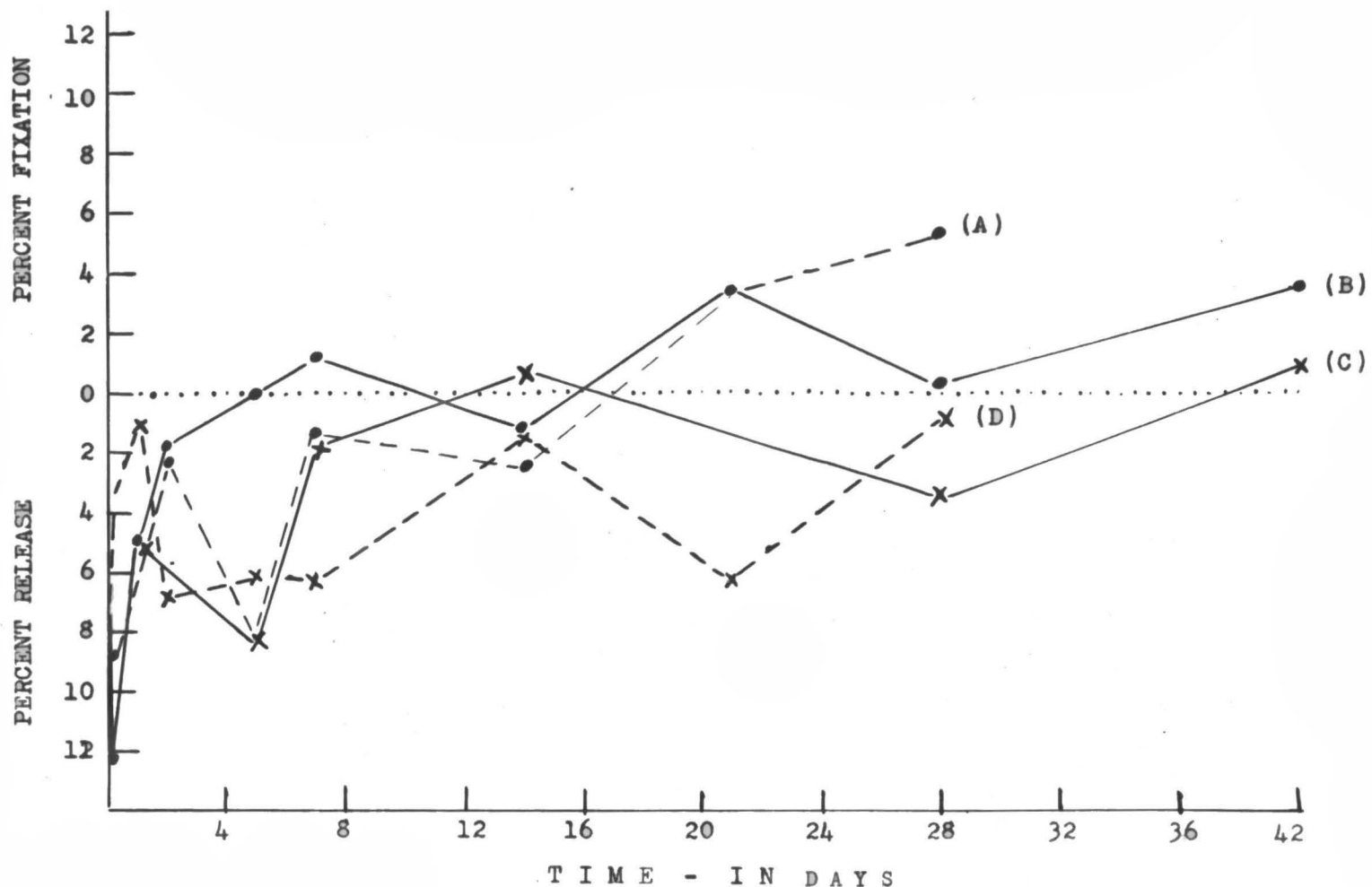


Fig. 1. Per cent of added potassium fixed upon moist storage of Low Humic Latosol (No. 50-91) at 266 ppm. K application. (A) KH_2PO_4 added to moist field soil; (B) KCl added to moist field soil; (C) KCl added to air-dry soil; (D) KH_2PO_4 added to air-dry soil.

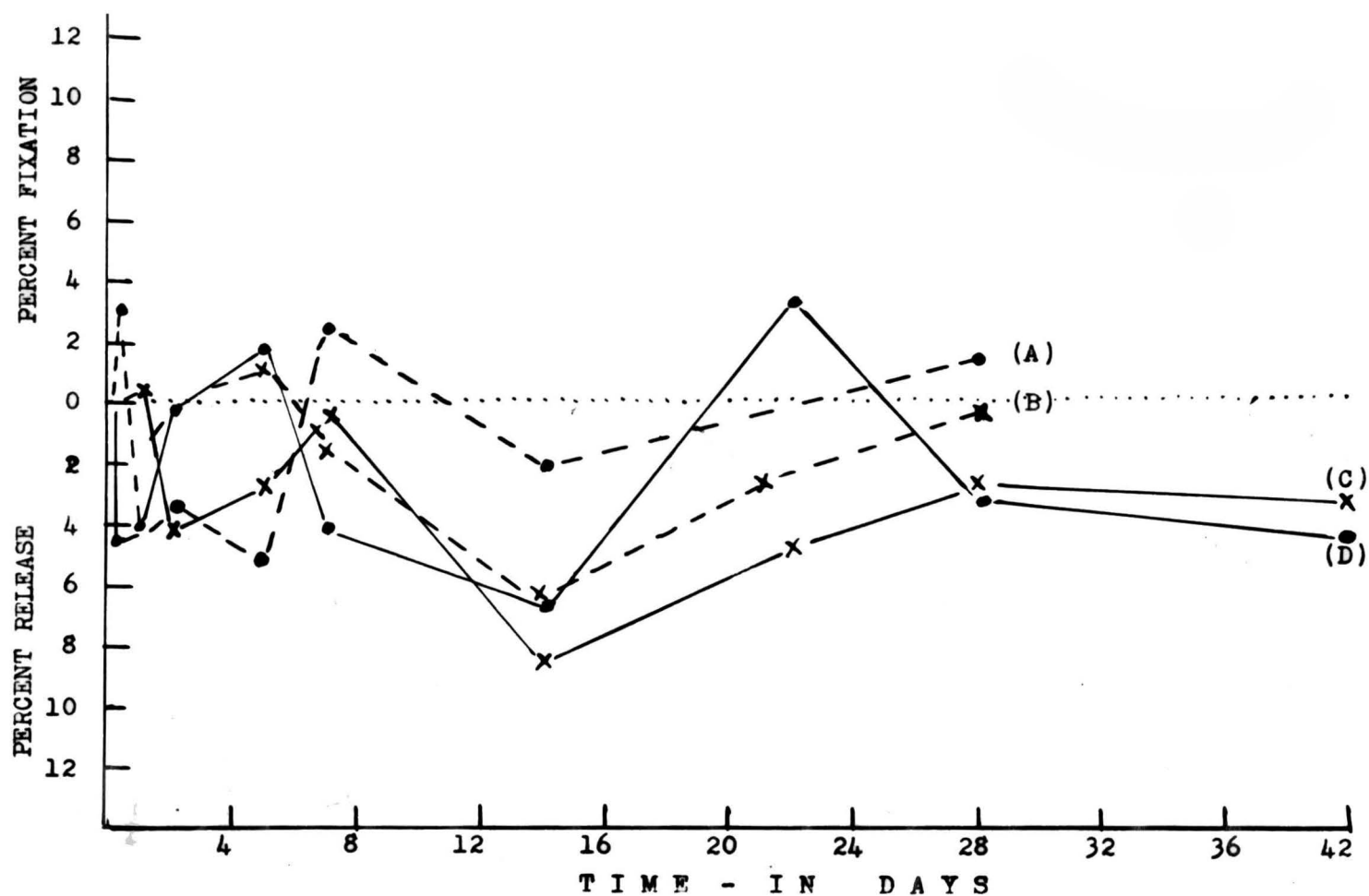


Fig. 2. Per cent of added potassium fixed upon moist storage of Hydrol Humic Latosol (No. 49-37) at 266 ppm. K application. (A) KH_2PO_4 added to moist field soil; (B) KH_2PO_4 added to air-dry soil; (C) KCl added to air-dry soil; (D) KCl added to moist field soil.

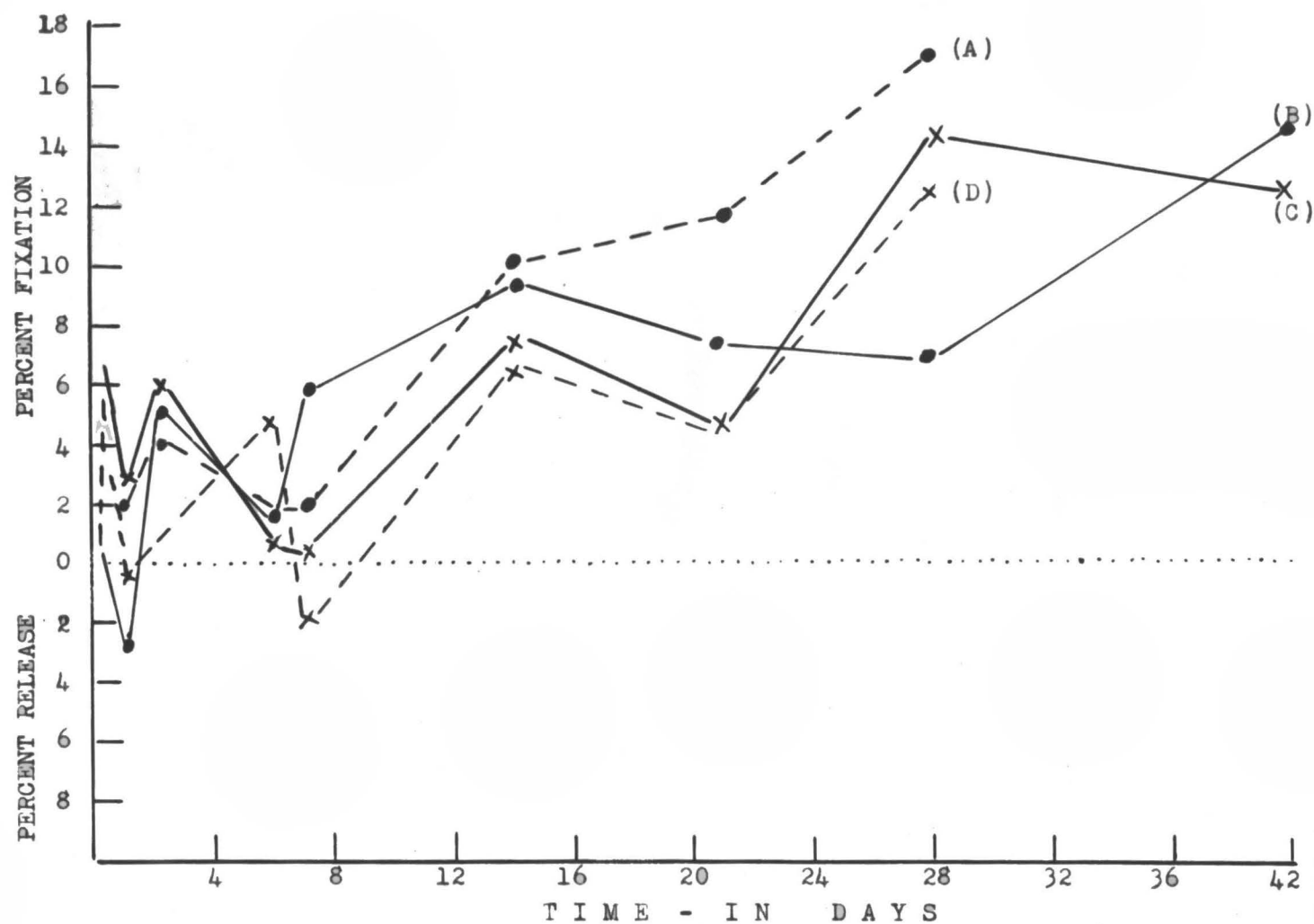


Fig. 3. Per cent of added potassium fixed upon moist storage of Dark Magnesium Clay (No. 50-92) at 266 ppm. K application. (A) KH_2PO_4 added to moist field soil; (B) KCl added to moist field soil; (C) KCl added to air-dry soil; (D) KH_2PO_4 added to air-dry soil.

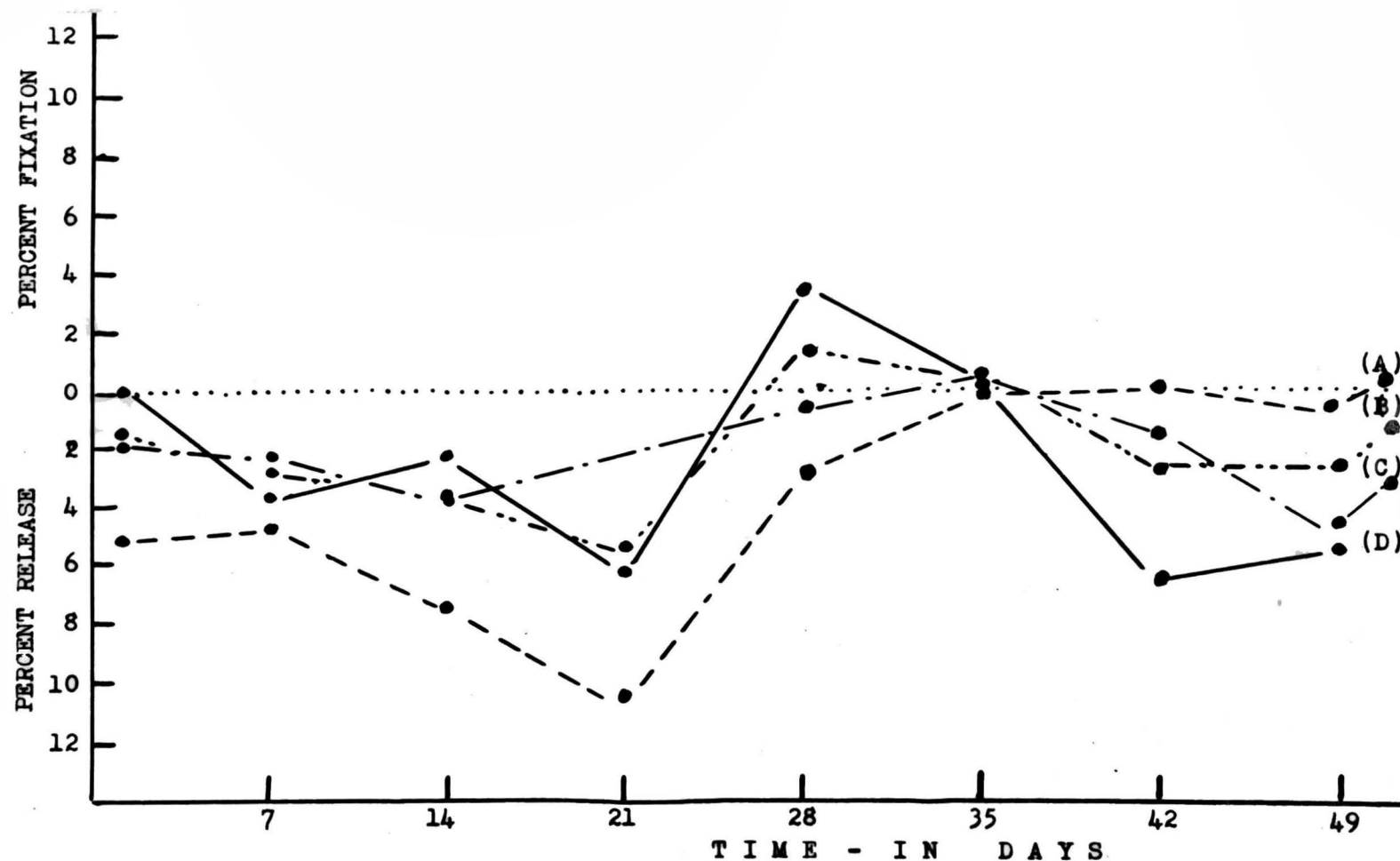


Fig. 4. Per cent of added potassium fixed upon moist storage at 416 p.p.m. K application of KCl. (A) Dark Magnesium Clay (No. 50-221); (B) Gray Hydromorphic Soil (No. 50-220); (C) Hydrol Humic Latosol (No. 51-1); (D) Low Humic Latosol (No. 50-222). Each point represents average of duplicate samples.

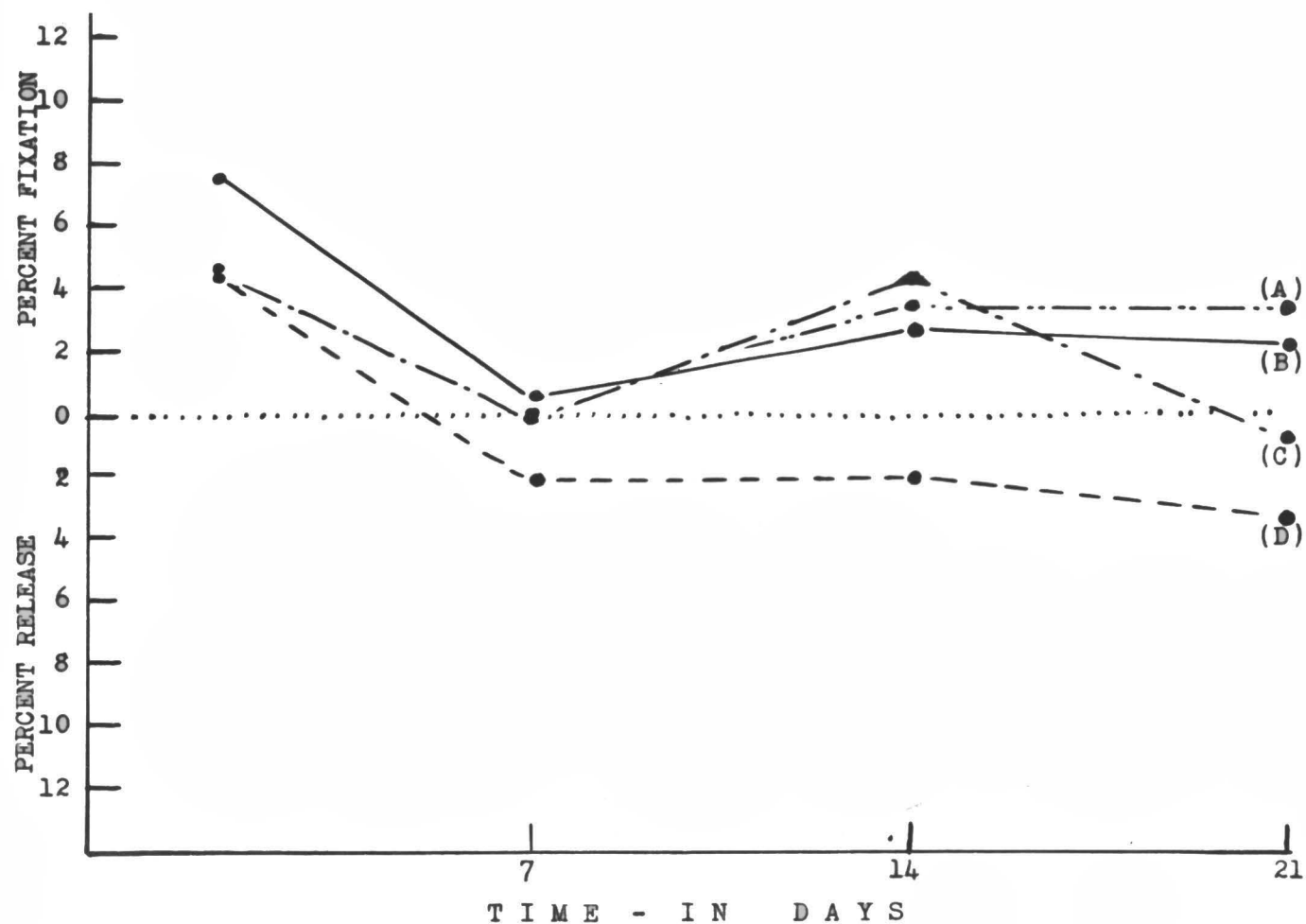


Fig. 5. Per cent of added potassium fixed upon moist storage at 1596 p.p.m. K application of KCl. (A) Humic Ferruginous Latosol (No. 50-205); (B) Low Humic Latosol (No. 50-91); (C) Hydrol Humic Latosol (No. 49-37); (D) Dark Magnesium Clay (No. 50-92). Each point represents average of duplicate samples.

POTASSIUM FIXATION UPON AIR-DRYING

Following the study on moist storage, the effect of air-drying the soils with added potassium was considered. Attoe (2) noted considerable evidence of fixation when a potassium fertilized soil was air dried. Wood and DeTurk (33) also found increased fixation upon air-drying for one week. With heavier applications, they were able to show greater fixation, particularly with soils of high exchange capacity.

To study the effect of air-drying, 25 gram portions of soil were placed in Petri-dishes. Potassium solution of different concentrations was added to the soils, and the mixture was allowed to dry at room temperature for a week. Then the exchangeable potassium was extracted. For each concentration duplicate samples were analyzed. At lower concentrations potassium was not fixed as shown in table 2. At 1596 ppm. K application potassium was fixed by Dark Magnesium Clay and Hydrol Humic Latosol. Low Humic Latosol, on the other hand, showed some release of non-exchangeable potassium.

In another approach to this subject a study was made of drying a fertilized soil to the wilting point. Low Humic Latosol (No. 50-225) was used for this experiment.

In this study, fifteen Mitscherlich pots were used as follows: 6 pots were treated with KCl solution, 6 pots were treated with KCl crystals, 2 pots were used to grow

sunflower to determine the wilting point, and 1 pot was used as a check. KCl equivalent to 1250 pounds of K_2O per acre was added to each pot. This application is somewhat comparable to an amount of 250 pounds K_2O per acre as generally practiced on plantations where KCl is narrowly concentrated.

At five different moisture levels, ranging from 17 to 28 per cent, the soil was analyzed for exchangeable potassium. Triplicate samples were taken for potassium analysis and duplicate samples for moisture determination. The wilting point of this soil, as determined by the use of sunflower, was 22 per cent.

In the first series of six pots where KCl solution was used fixation was indicated at the higher moisture level. However, below 23 per cent moisture no fixation was evidenced as shown in table 3. In another series of six pots crystals of KCl were used to simulate actual plantation practice of adding potassium fertilizer, but fixation was not apparent.

Table 2. EFFECT OF AIR-DRYING ON FIXATION OF POTASSIUM

Soil Number	Soil Group	Potassium Added ppm.	<u>Exchangeable Potassium</u>		
			Initially mgm./25g	After Drying mgm./25g	Difference mgm.
50-91	Low Humic Latosol	266	10.4	10.2	.2
50-222	"	500	17.7	17.8	.1
50-91	"	1596	43.8	45.3	1.5
50-92	Dark Mag- nesium Clay	266	13.6	13.5	.1
50-221	"	500	20.3	19.8	.4
50-92	"	1596	47.0	44.8	2.2
49-37	Hydrol Humic Latosol	266	8.2	8.1	.1
51-1	"	500	12.6	12.5	.1
49-37	"	1596	41.5	39.3	2.2
50-220	Gray Hydro- morphic	500	13.5	13.2	.3
50-205	Humic Ferruginous Latosol	500	11.8	11.0	.8
51-2	Humic Latosol	500	14.22	14.2	--

Each figure represents average of duplicate samples.

Table 3. EFFECT OF DRYING TO THE WILTING POINT ON
FIXATION OF POTASSIUM IN LOW HUMIC LATOSOL
(N1) SOIL NO. 50-225

Mitscherlich Pot Number	Moisture Per cent	Potassium Form	Exchangeable Potassium		
			Initially mgm./25g	Upon Drying mgm./25g	Difference mgm.
397	28.0	Solution	23.5	22.3	1.2
398	24.8	"	"	21.8	1.7
399	23.2	"	"	23.6	.1
401	21.5	"	"	23.3	.2
400	16.8	"	"	22.6	.9
403	27.9	Crystals	"	22.7	.8
404	26.1	"	"	23.6	.1
405	24.4	"	"	23.5	.0
407	22.4	"	"	23.2	.3
406	17.5	"	"	23.3	.2

Each figure represents average of triplicate samples.

Wilting point = 22 per cent moisture
1250 lbs. K_2O /acre application

POTASSIUM FIXATION UPON OVEN-DRYING HUMIC LATOSOL

Oven-drying offers another phase of this study which is of academic interest. Heat treatment up to 200°C tends to facilitate fixation (8)(9) because equilibrium is approached more rapidly. In treating soil samples over 200°C, Joffe and Kolodny (14) showed decrease in fixation for montmorillonite clay. At 550°C complete destruction of fixing capacity was noted.

Humic Latosol (No. 49-35) was used in this study. This soil was initially treated with various forms and combinations of potassium salts particularly the phosphates; subsequently, the soil was leached with nearly 100 inches of water. The amount of exchangeable potassium present after leaching is shown in the third column of table 4. This amount was compared with that of the same soil oven-dried at 105°C. As the results show, fixation was high ranging from 20 to 40 per cent of the exchangeable potassium.

Table 4. EFFECT OF OVEN-DRYING HUMIC LATOSOL SOIL
NO. 49-35 ON FIXATION OF POTASSIUM

Soil Depth Inches	Treatment	Exchangeable Potassium		Difference mgm.	K Fixed Per cent
		Initially mgm./25g	After* Drying mgm./25g		
0-12 surface	Check	1.2	1.3	.1	--
"	KCl+Ammophos	3.7	2.4	1.3	35.94
"	KH_2PO_4	5.8	4.2	1.6	28.45
"	$\text{KH}_2\text{PO}_4 + \text{KCl}$	6.5	4.6	1.9	29.92
"	KPO_3	5.9	4.0	1.9	32.65
12-24 Subsoil	Check	1.7	1.6	.1	--
"	KCl+Ammophos	4.4	2.7	1.7	39.93
"	KH_2PO_4	6.4	4.7	1.7	27.75
"	$\text{KH}_2\text{PO}_4 + \text{KCl}$	7.7	4.8	2.9	37.52
"	KPO_3	9.3	6.4	2.9	30.97

* Oven-dried at 105°C

POTASSIUM FIXATION UPON ALTERNATE WETTING AND DRYING

Many investigators have reported greater fixation when soils were subjected to alternate wetting and drying process. Martin, Overstreet and Hoagland (17) showed that in this process potassium fixation was not dependent on the presence of clay minerals of the expanding lattice type. This is not in harmony with Page and Baver's (19) theory, which is based on the formation of a stable structure upon dehydration of a potassium saturated system. This stable structure is formed only in the expanding and contracting lattice mineral such as montmorillonite. G.W. Volk (28) also found tremendous fixation by this type of mineral after alternate wetting and drying twenty times at 70°C. Using the same technique, N.J. Volk (29), working with 100 different soils, was able to show fixation ranging from 0 to 114 per cent of the added potassium.

In view of the high fixation data obtained by other investigators, an attempt was made to determine the effect on Hawaiian soils using this method. However, instead of drying at 70°C as Volk did, it seemed more practical to dry the soils at room temperature. Twenty-five gram portions of soil were placed in Petri-dishes and saturated with 20 ml. of KCl solutions of different concentrations. The soils were allowed to dry at room temperature for about a week; then they were rehydrated with water. This process was repeated three times. For each concentration duplicate

samples were analyzed.

Low Humic Latosol (No. 50-91 and No. 50-222) showed little fixation, 9 per cent being the highest amount fixed at 500 ppm. K application.

Dark Magnesium Clay (No. 50-92 and No. 50-221) showed a much higher fixation. At 266 ppm. K application the soil fixed an average of 11 per cent potassium and at 500 ppm. K, fixation was as much as 19 per cent. However, at 1596 ppm. K, an average of only 3 per cent was fixed.

Hydrol Humic Latosol (No. 49-37 and No. 51-1) and Humic Latosol (No. 51-2) did not fix potassium at all. Humic Ferruginous Latosol (No. 50-205) fixed an average of 8 per cent at 500 ppm. K application. Gray Hydromorphic (No. 50-220) showed an average of 7 per cent fixation.

Dark Magnesium Clay again showed the greatest amount of fixation. It is very probable that drying the soils at higher temperature would bring about further fixation.

Table 5. EFFECT OF ALTERNATE WETTING AND DRYING AT ROOM TEMPERATURE ON FIXATION OF POTASSIUM

Soil Number	Soil Group	Potassium Added ppm.	Exchangeable Potassium		Difference mgm.	K Fixed of Added Amount Per cent
			Initially	After Treatment mgm./25g		
50-91	Low Humic Latosol	266	10.4	10.1	.3	4.05
50-222	"	500	19.4	18.3	1.1	9.50
50-91	"	1596	43.8	42.6	1.2	2.85
50-92	Dark Magnesium Clay	266	13.8	13.0	.8	11.25
50-221	"	500	22.0	19.8	2.2	18.64
50-92	"	1596	47.1	46.1	1.0	2.60
49-37	Hydrol Humic Latosol	266	8.1	8.0	.1	--
51-1	"	500	14.5	14.7	.2	--
49-37	"	1596	41.4	41.4	.0	--
50-205	Humic Ferruginous Latosol	266	7.4	7.4	.0	--
"	"	500	13.0	12.1	.9	8.10
"	"	1596	40.9	40.9	--	--
50-220	Gray Hydromorphic	500	15.7	14.9	.8	6.95
51-2	Humic Latosol	500	15.4	15.1	.3	--

Each figure represents average of duplicate samples.

THE EFFECT OF POTASSIUM SATURATION ON
FIXATION AND THE EXCHANGE CAPACITY

In the fixation process the exchangeable potassium is generally converted into non-exchangeable form. Accordingly, soils saturated with potassium would seem to favor fixation. To test this point, an experiment was carried out by saturating the soils with N potassium acetate and heating the soils for 12 hours at temperatures ranging from 25°C to 100°C to facilitate the fixation process.

Wear and White (32) showed significant decreases in exchange capacity with an increase in fixation when potassium saturated soils were dried at 105°C for 12 hours. This was particularly evident in soils of 2:1 mineral structure like the bentonite. They claimed that illite, which is also of 2:1 mineral structure, did not fix as much potassium because it already contained large amount of potassium in fixed positions. Levine and Joffe (16) also noted the same relationship between fixation and the exchange complex, but not in equivalent amount. Barshad (7) was able to show that the reduction in the exchange capacity was due to vermiculite or biotite minerals in soils. Potassium in these minerals caused the crystal lattice layers to contract, thereby entrapping the potassium in the mineral structure. Ammonium, cesium and rubidium react in a manner very similar to that of potassium. The fixed cations are exchangeable only by such ions as sodium, magnesium, calcium, and barium,

which when adsorbed, caused the layers of the crystal lattices to expand.

In pursuing this study three soils were used, namely, Gray Hydromorphic (No. 50-220), Dark Magnesium Clay (No. 50-221), and Low Humic Latosol (No. 50-222). As shown in table 6, Gray Hydromorphic soil showed little fixation with increase in temperature and a slight reduction in exchange capacity. Dark Magnesium Clay showed greater fixation with increase in temperature and a considerable drop in exchange capacity. Low Humic Latosol, on the other hand, behaved somewhat differently. At 50°C fixation was at its greatest and decreased as the temperature was increased.

Table 6. EFFECT OF TEMPERATURE ON FIXATION AND EXCHANGE CAPACITY IN POTASSIUM SATURATED SOILS

Temperature	<u>Gray Hydromorphic Soil</u> (No. 50-220)		<u>Dark Magnesium Clay</u> (No. 50-221)		<u>Low Humic Latosol</u> (No. 50-222)	
	K Fixed Per cent	Exchange Capacity* m.e./100	K Fixed Per cent	Exchange Capacity* m.e./100	K Fixed Per cent	Exchange Capacity* m.e./100
25°C	0	33.8	0	42.4	0	14.7
50°C	2.37	33.5	8.54	39.4	9.79	14.5
75°C	3.56	33.4	9.39	39.6	8.99	14.4
100°C	5.85	33.0	13.79	39.4	2.65	14.7

*Exchange capacity of potassium saturated soils.

DIFFERENTIAL THERMAL ANALYSIS OF SOILS USED

Since many soils in Hawaii are made up of over 50 per cent clay fractions, the identification of clay minerals is extremely important. To a large extent these minerals determine the physical and chemical properties of soils.

Differential thermal analysis (26) provides one of the methods of identifying these minerals. This analysis was included in order to substantiate the experimental data. Briefly, this method is based upon the fact that the application of heat to a mineral causes certain physical and chemical changes that are reflected in endothermic and exothermic reactions. By comparing the change in temperature of a mineral heated at definite rate with that of a thermally inert substance (Al_2O_3) heated under the same conditions, a curve or pattern is obtained which is characteristic of the particular mineral under examination.

Two standard reference samples *, kaolin and bentonite, were run for thermal curves which represent typical 1:1 and 2:1 lattice minerals respectively as shown in figures 6 and 7. ** The vertical axes on the graphs represent galvanometer deflections of endothermic and exothermic reactions of the clays.

Kaolinite has two critical peaks, a sharp endothermic peak at about 600°C and a sharp exothermic peak at 950°C .

* Samples obtained through the courtesy of Dr. G.D. Sherman, U.H. Expt. Sta.

** Part of the analysis was done by T.A. Jones

These peaks are very distinct as shown in figures 8A and 8B of the Low Humic Latosols, which may contain nearly 80 per cent kaolinite (18). These points are also present in other types of soils but not as pronounced. Matsusaka (18) was able to identify kaolinite distinctly with quantitative data, which seem to agree fairly well with his dehydration curves. He found Kaolinite content rather low in young soils like Reddish-Brown and increased amounts in Humic Ferruginous Latosols and Hydrol Humic Latosols. Low Humic Latosols contained the highest amount.

Montmorillonites are not as easily identified in Hawaiian soils. The reference sample, bentonite, shows the endothermic peaks at about 100°C , 700°C , and 900°C . Dark Magnesium Clays of figures 13A and 13B show all three points on the curve indicating the presence of Montmorillonitic Clay and little kaolinite. Gray Hydromorphic soil of figure 11 shows greater amount of kaolinite and a questionable presence of 2:1 crystal lattice mineral.

Bauxite, goethite and limonite show large endothermic peaks at about 350°C on the differential thermal curves. These are easily identified in Humic Latosol, Hydrol Humic Latosol, and Humic Ferruginous Latosol of figures 9B, 10 and 11. Figure 9A shows the masking effect of organic matter on clay minerals as compared to figure 9B the same soil with organic matter removed by hydrogen peroxide treatment.

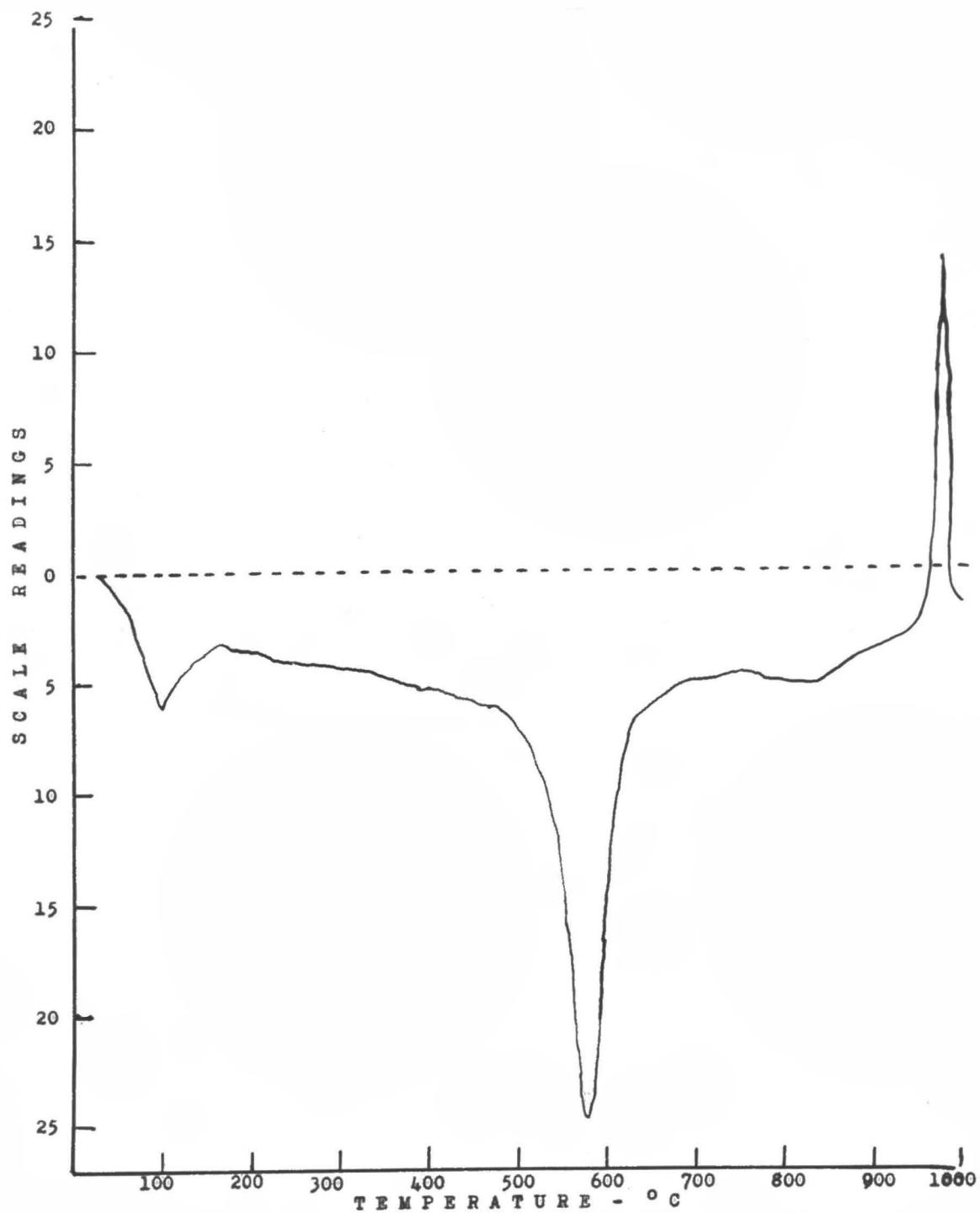


Fig. 6. Differential thermal curve of kaolin.

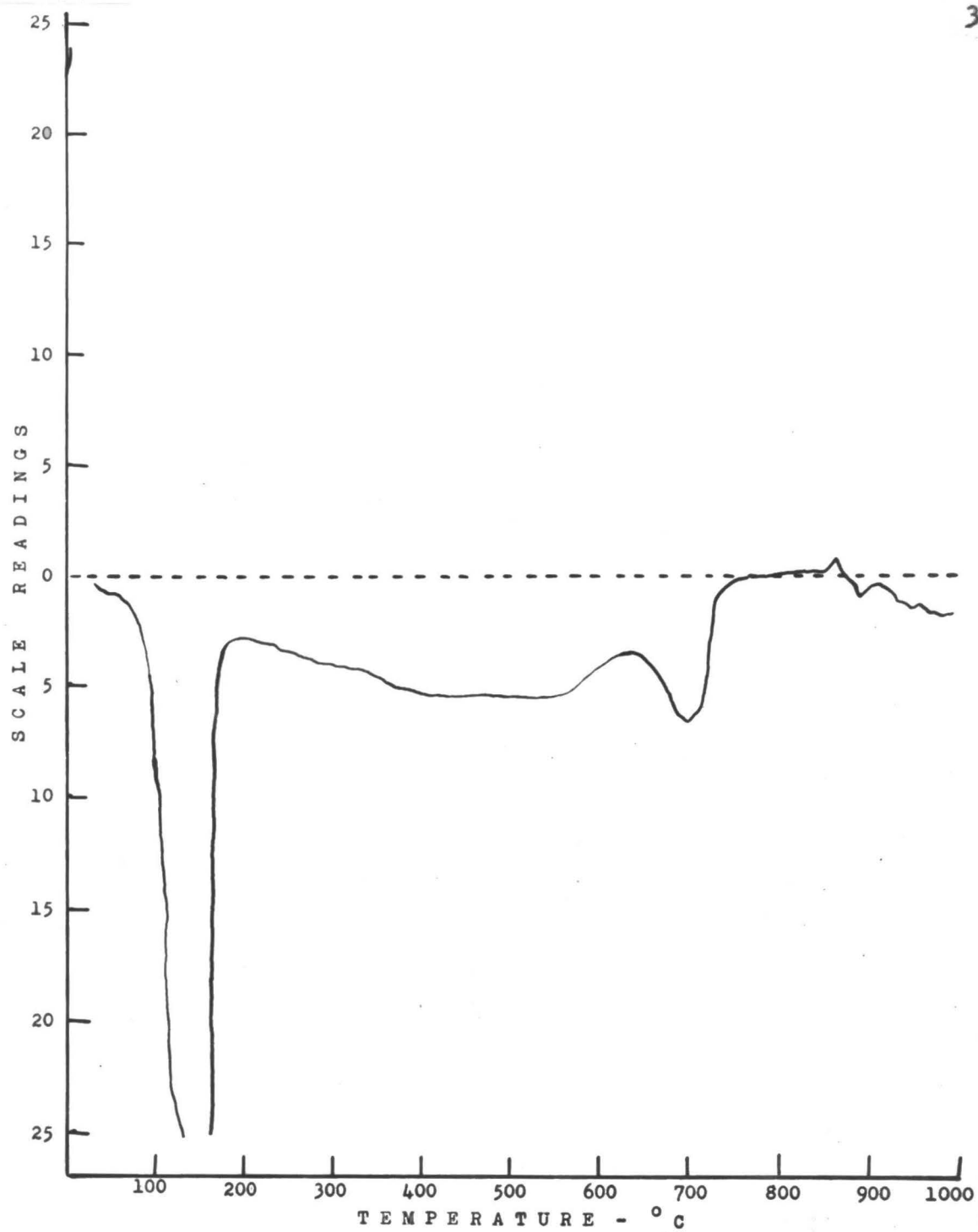


Fig. 7. Differential thermal curve of bentonite.

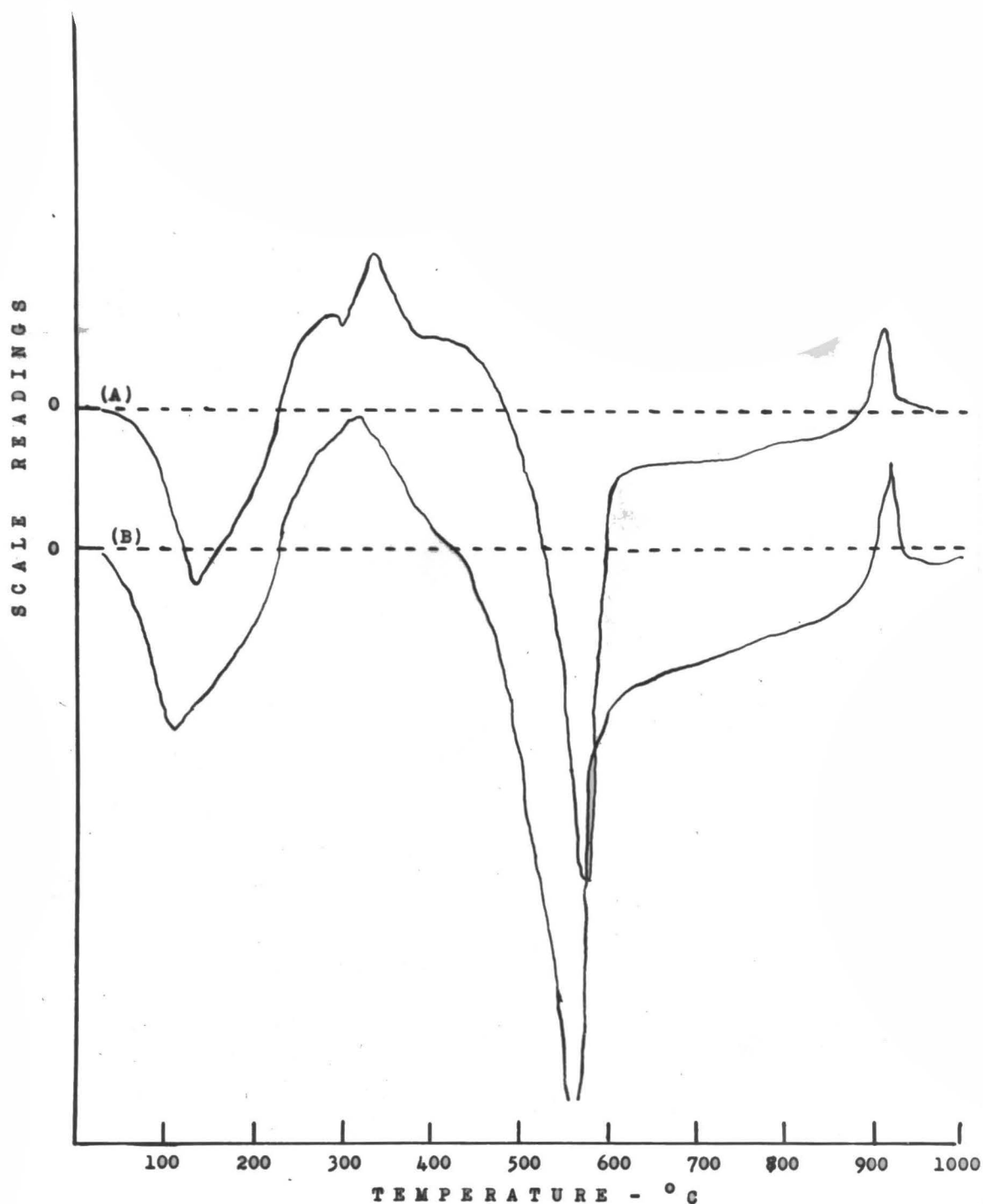


Fig. 8. Differential thermal curves of Low Humic Latosols.

(A) No. 50-91: (B) No. 50-222.

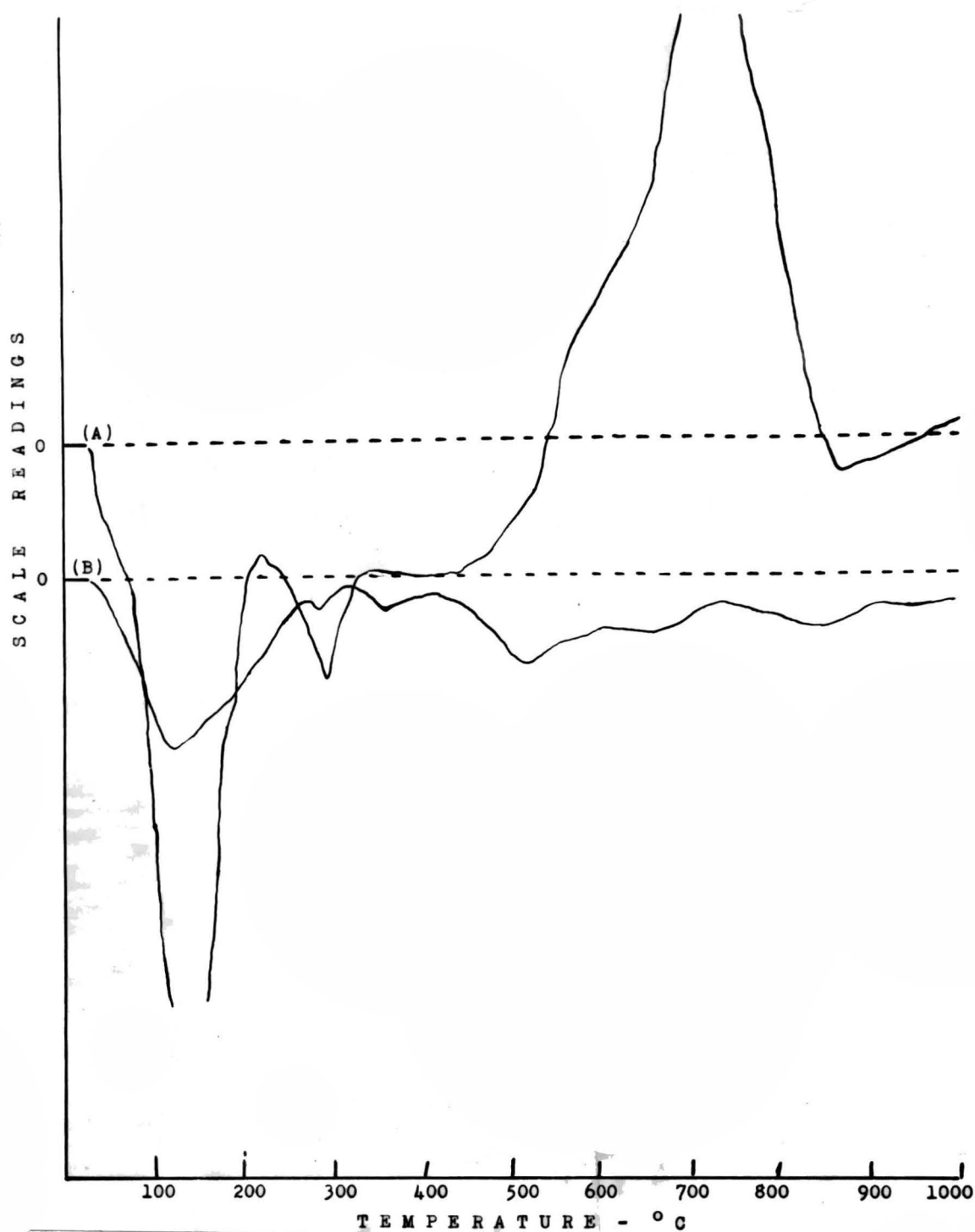


Fig. 9. Differential thermal curves of Humic Latosol (No. 51-2). (A) presence of organic matter; (B) removal of organic matter with hydrogen peroxide.

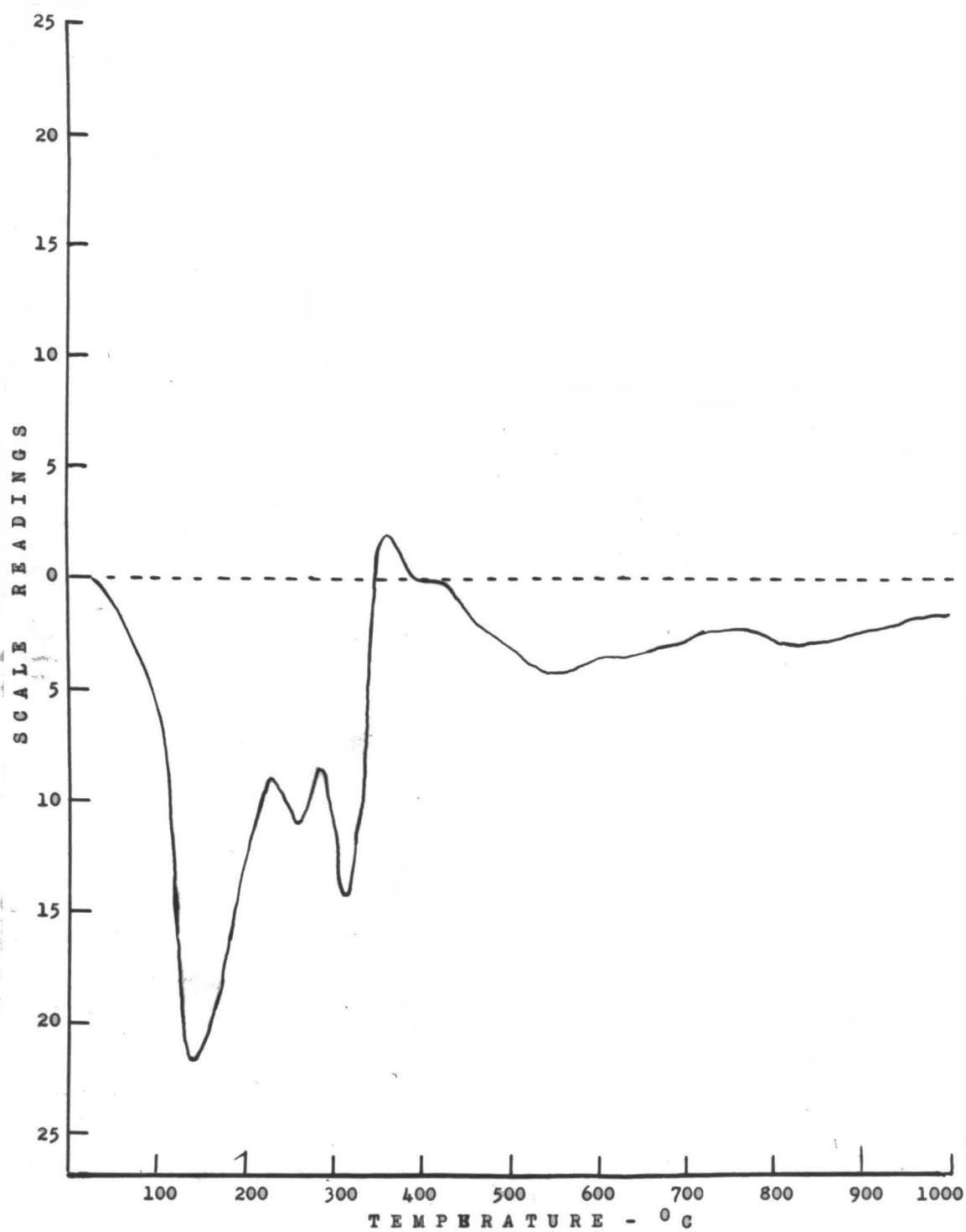


Fig. 10. Differential thermal curve of Hydrol Humic Latosol (No. 51-1).

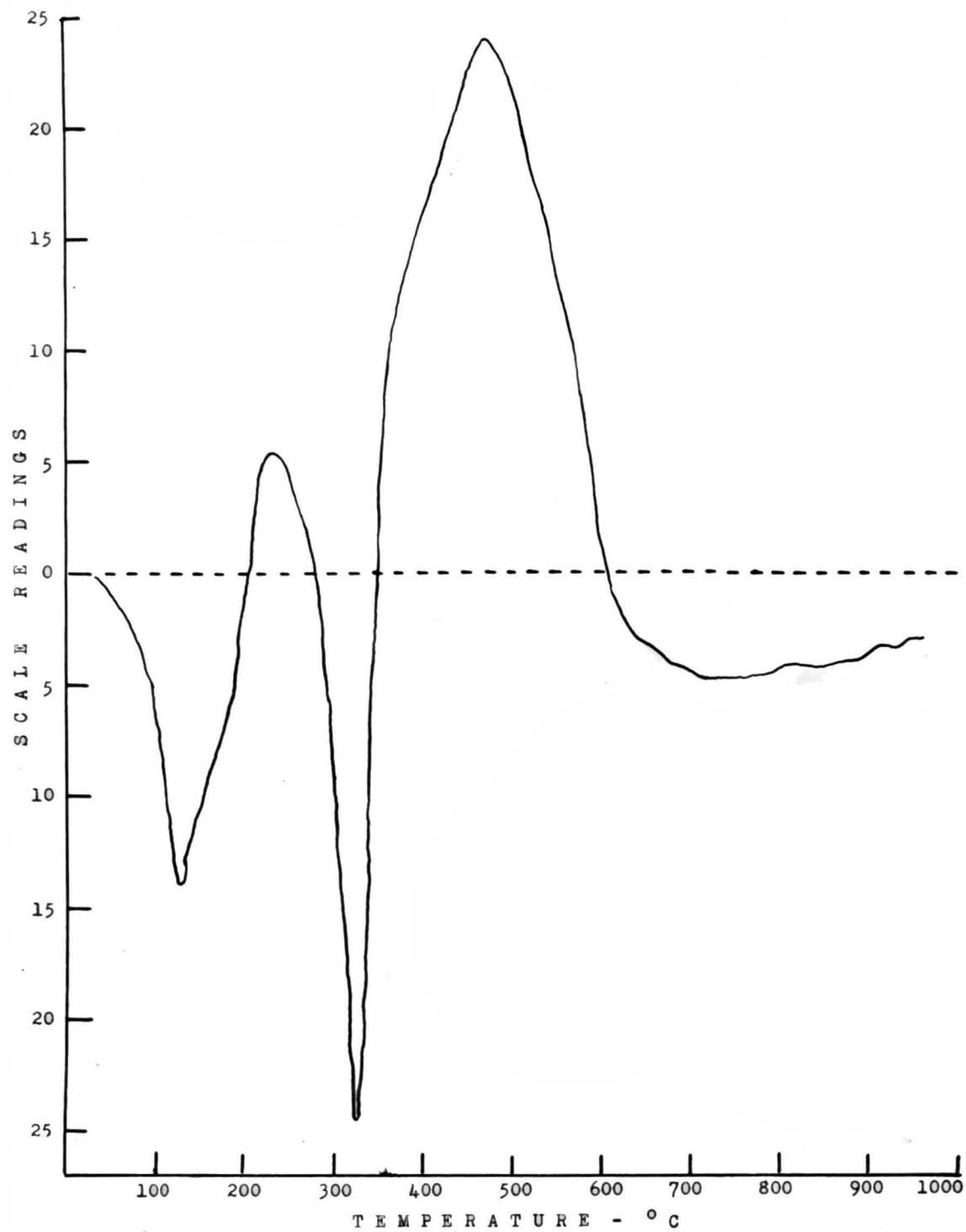


Fig. 11. Differential thermal curve of Humic Ferruginous Latosol (No. 50-205).

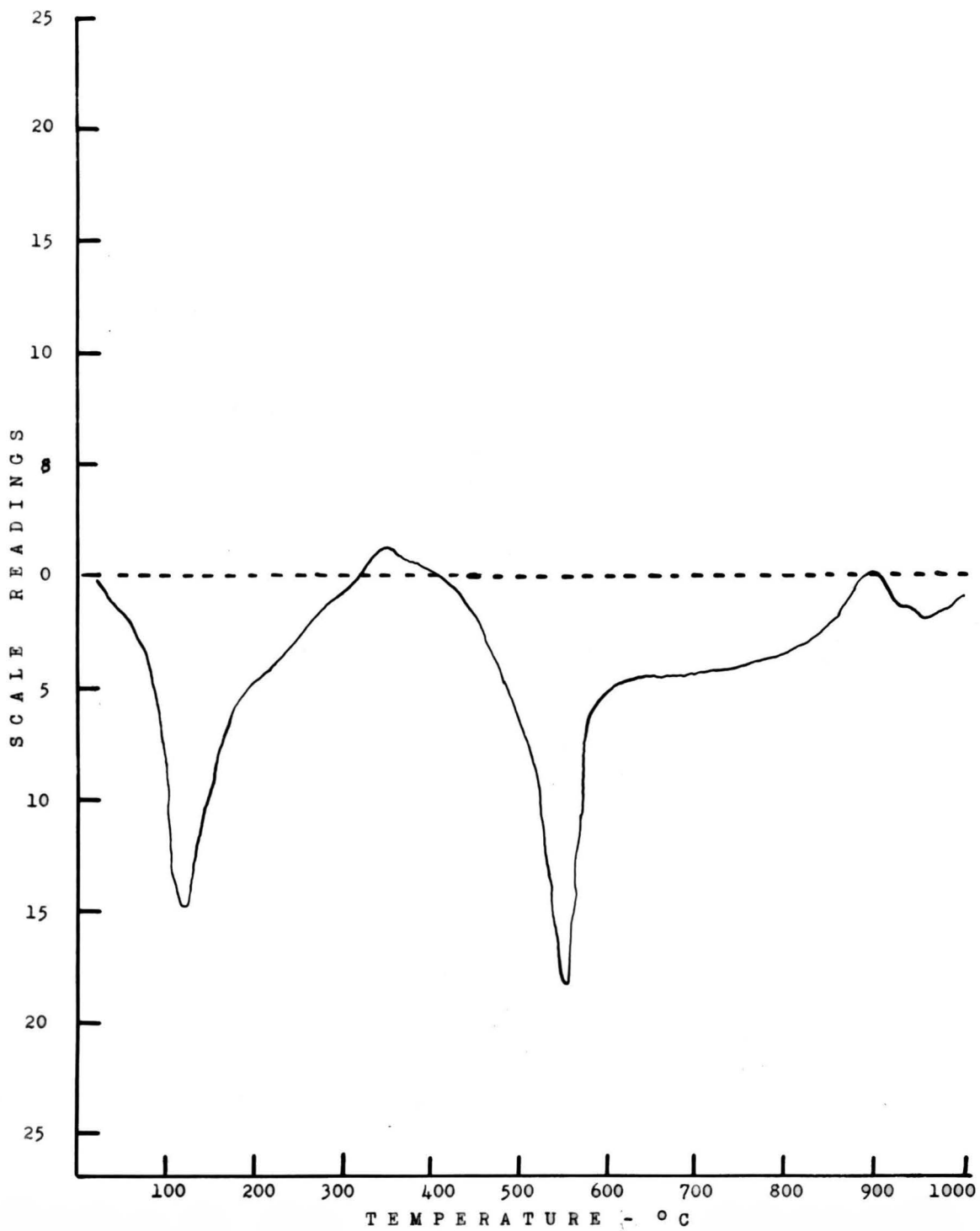


Fig. 12. Differential thermal curve of Gray Hydromorphic soil (No. 50-220).

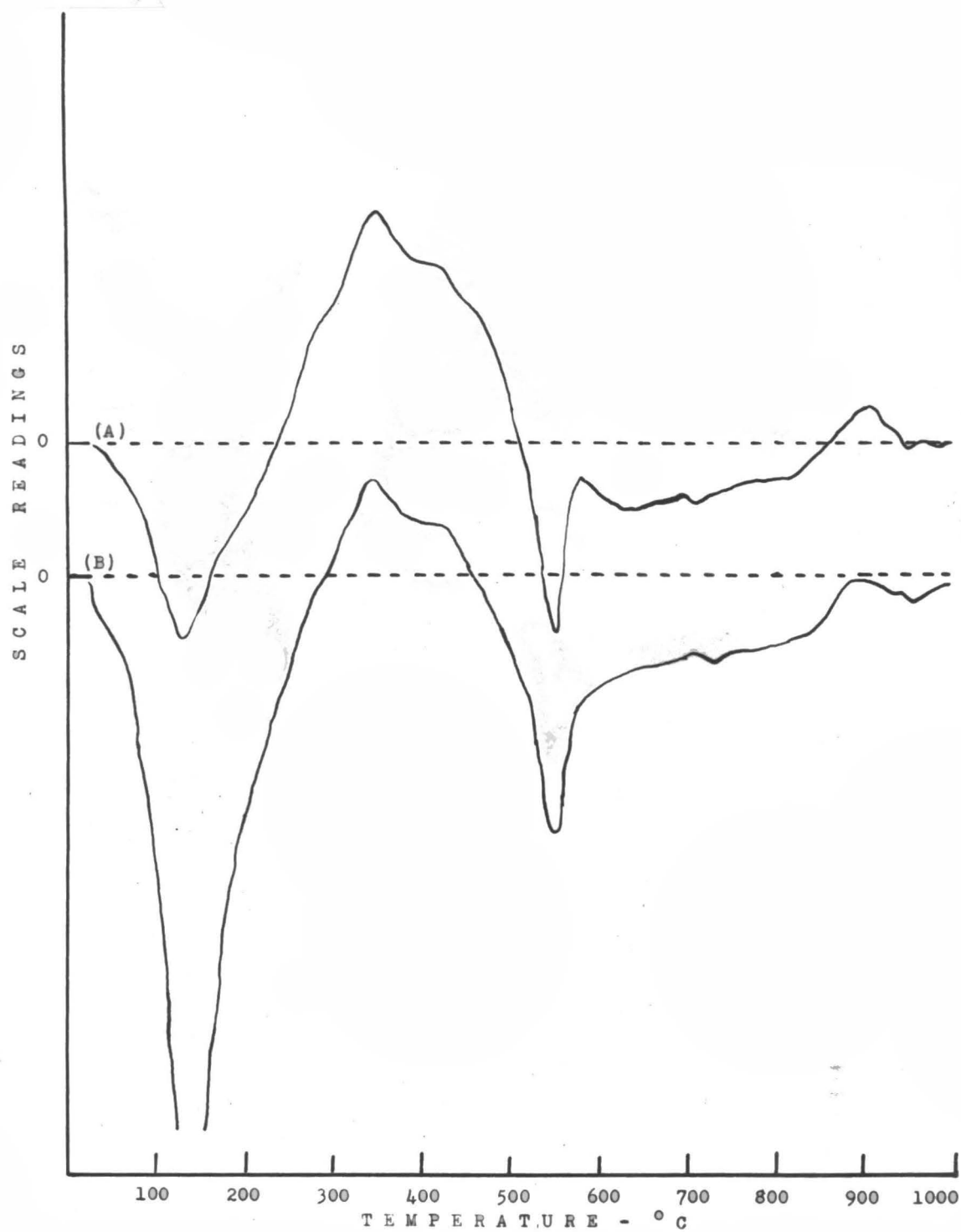


Fig. 13. Differential thermal curves of Dark Magnesium Clay. (A) No. 50-92; (B) No. 50-221.

GENERAL DISCUSSION

Principal types of Hawaiian soils do not possess the capacity to fix potassium as the Podzolic soils of the United States. In Hawaii where laterization is very active and chemical weathering accelerated, the formation of kaolinitic and oxidic minerals predominates. These minerals do not fix appreciable amounts of potassium. Haney and Hoover (21) and others have shown no fixation with lateritic colloids because the predominating mineral type consists of the non-expanding kaolinite. Page and Baver (19) related the ionic size of potassium to the expanding lattice type of mineral in describing fixation.

As part of N.J. Volk's (29) doctorate thesis, three soils from Hawaii were used. However only one showed any fixation upon alternate wetting and drying. "Laterite No. 9" as indicated in his table fixed 20 per cent of the added potassium. Using a similar procedure the Dark Magnesium Clay of this study fixed approximately the same percentage of potassium.

The results of this study conform to the findings of the above investigators. Soils under study generally showed little fixation because a large proportion of their clay fraction consisted of either kaolinite or the oxides as revealed by differential thermal curves. Low Humic Latosols, for example as shown in figures 8A and 8B, contained large amount of kaolinite. Humic and Hydrol Humic

Latosols in figures 9B and 10 consisted of oxides and kaolinite minerals. Humic Ferruginous Latosol of figure 11 consisted primarily of the oxides. Gray Hydromorphic soil, as indicated in figure 12, contained considerable amount of kaolinite and possibly 2:1 lattice mineral. Dark Magnesium Clays in figures 13A and 13B consisted of kaolinite and 2:1 lattice mineral of the montmorillonitic type. The kaolinite content was much lower in Dark Magnesium Clays than in Low Humic Latosol or Gray Hydromorphic soil.

The presence of 2:1 lattice minerals in Gray Hydromorphic and Dark Magnesium Clay, is substantiated by the properties shown in table 1. These soils possess high exchange capacities, high base saturation and high pH. As evidenced throughout this study, Dark Magnesium Clay was the only soil that consistently favored fixation.

Upon moist storage, Wood and DeTurk (33) were able to show fixation with addition of soluble potassium salts, in accordance with their equilibrium concept on different potassium forms. However, this equilibrium reaction was not observed in this current study. Fixation upon moist storage was limited to Dark Magnesium Clay at 266 ppm. K application. Abel and Magistad (1) found no equilibrium reaction of potassium for Hawaiian soils. They noted that fallowed soils showed greater release of non-exchangeable potassium than cropped soils.

Ayres and Hagihara (5) as aforementioned found 16-21 per cent fixation from K_3PO_4 upon moist storage of Humic and Hydrol Humic Latosols. Since K_3PO_4 forms a strongly basic medium upon hydrolysis, its reactions are somewhat different. According to Stanford (27) pH changes are accompanied by marked effects on fixation. The results suggest that hydrogen ions in certain positions within the mineral crystals of the acid soils are neutralized by the bases, and this process, in some manner, facilitates the entrance of potassium ions into lattice positions where fixation takes place.

Air-drying is another aspect of this study which prevails under natural condition. With higher application of potassium greater amount was fixed. The effect is definitely due to greatly increased concentration of the potassium salts. This enables a state of propinquity to exist between potassium ions and the clay fractions, resulting in the conversion of soluble and exchangeable potassium to non-exchangeable forms. Martin, et al. (17) suggest that fixation on drying may be attributed to the loss of water and to the increase in salt concentration in the liquid phase.

In another related experiment in which the Humic Latosol (No. 49-35) was dried at $105^{\circ}C$, fixation was extremely high. This may be caused by either the increase in potassium concentration, the presence of soluble phosphate, the effect

of drying at a higher temperature, or by the combination of these factors. Joffe and Kolodny (13) showed higher potassium fixation with increase in phosphate ions. Any condition which facilitates the release of phosphate aids the recombination of this phosphate with other cations, thus favoring the fixation of potassium. According to Stanford (27) the precipitation of iron and aluminum phosphates caused an increase in potassium fixation. This Humic Latosol may contain as much as 50 per cent * of its minerals as the iron and aluminum oxides, which could react chemically with the phosphates in the fixation process. With less than 10 per cent montmorillonite in this soil, it hardly seems possible that this amount will influence fixation. As a matter of fact, Stanford and others found less fixation with addition of phosphate ions to montmorillonite.

Generally speaking, therefore, moist storage and air-drying produce very little fixation.

Alternate wetting and drying presents another approach to this problem. Several workers have shown tremendous fixation. In this experiment, as much as 19 per cent fixation was noted for the Dark Magnesium Clay while the other soils showed some indications of it. Evidently this alternate wetting and drying process is more suited for the expanding and contracting mineral in facilitating the entrance of potassium ions. Page and Baver (19), as already mentioned, associated the ionic size of potassium with the expanding

* Abstract of American Journal Society Agronomy 1952 Annual Meeting "Chemical Allocation and Mineral Content of Hydrol Humic, Humic, and Brown Forest Latosols of Hawaii", T. Tamura, M.L. Jackson and G.D. Sherman.

lattice mineral. From all indications the probable reason for higher fixation by Dark Magnesium Clay is due to the presence of an appreciable amount of the expanding 2:1 lattice minerals.

Levine and Joffe (16) were able to show a relationship between the potassium which enters the complex of exchange reaction and the potassium which is fixed. It shows directly that prior to fixation potassium must be in the exchange complex. With increase in fixation greater reduction in exchange capacity was noted. Similar decreases in exchange capacity were evidenced in this study, particularly by the Dark Magnesium Clay. It, therefore, indicates a close association between the properties of fixation and exchange capacity.

Other theories have been advanced on the mechanism of fixation. For example, Joffe and Kolodny (13) and G.W. Volk (28) have suggested potassium fixation by muscovite formation as supported by X-ray pattern. Theoretically, this is possible by substituting aluminum and potassium for silica of the pyrophyllite mineral. Gorbunov (10) explained the phenomenon as being associated with the aging of the soil gel during the intermittent wetting and drying process. Rewetting does not restore the soil gel to the original state.

SUMMARY

Potassium fixation does not pose any serious problem in Hawaii. Soils representing six major Great Soil Groups comprising areas devoted primarily to agriculture were employed in this study. Of these soils Dark Magnesium Clay favored fixation in all phases of this study. Results of the experiments may be summarized as follows:

Moist storage of soils generally produced no fixation except for Dark Magnesium Clay at 266 ppm. K concentration. The anions showed no differential effects on fixation. Moist field soils showed similar results as the air-dried soils.

Little fixation was evidenced upon air-drying. An appreciable amount of potassium was fixed at the highest application by Dark Magnesium Clay and Hydrol Humic Latosol.

Oven-drying the Humic Latosol resulted in unusually high fixation which may have been due to three conditions: concentration, phosphate ions, and high temperature.

In the alternate wetting and drying process, the Dark Magnesium Clay fixed as much as 19 per cent of the added potassium. Other soils showed much less fixation.

Close relationship was noted between fixation and the exchange capacity on potassium saturated soils, but not in proportionate amount. Fixation increased with higher temperature.

Clay minerals were identified by the differential thermal analysis. The results of this analysis correlated fairly well with the data obtained in this study.

Potassium fixation is due primarily to the expanding 2:1 lattice minerals. Kaolinite and the free oxides of iron and aluminum do not favor fixation.

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