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BASE REPLACEMENT AS THE CAUSE OF ADSORPTION OF DYES BY SOILS

By

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Approved:

In charge of Major Work.

Head of Major Department.

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BASE REPLACEMENT AS THE CAUSE OF ADSORPTION OF DYES BY SOILS

INTRODUCTION

Bancroft (1) has shown that the dyeing of textiles is essentially an adsorption phenomenon; consequently, an acid dye will be more adsorbed from an acid solution because of the high adsorption of the H ion by the fiber, and a basic dye will be less adsorbed from an acid solution than it will be from a neutral or alkaline solution due to the high adsorption of OH ions from the latter. In accordance with Bancroft's theory that dyeing is an adsorption phenomenon, Beaumont (2) found that a soil containing a positive colloid will adsorb more of an acid dye than it will if it contains a negative colloid. Similarly a basic dye will be more adsorbed by a negative colloid. Rohland (3) has shown that the amount of methyl orange (an acid dye) taken up by a given soil is greater from an acid solution than from one which is neutral or alkaline. Wilkinson and Hoff (4) found also that an acid dye such as diamine blue 3B is more adsorbed by a soil in acid solution, and that the addition of a base decreases the amount of the dye taken up compared to that from the acid solution. When basic dyes such as methylene blue or neutral violet are adsorbed by soils in acid solutions they show curves which are the reverse of those for diamine blue. Even a small amount of acid decreases the dye adsorption very appreciably, but after the decrease the adsorption of the dye again increases due to the adsorption of the negative Cl ion from the HCl partly overcoming the effect of the H ion. The adsorption of dyes by soils appears to be of the same nature as the dyeing of fibers.

In addition to the adsorption of the positive dye ion by the negative colloid of the soil there is a possibility of the dye exchanging some of its positive ion for the metal ions of the soil particle and thus fixing more dye by chemical action or base exchange. Ashley (5) says that this is the way malachite green is taken up rather than by adsorption. Wilkinson and Hoff found experimentally that more Ca and Mg were brought into solution from a soil when methylene blue was adsorbed than when the same soil was treated with an equal amount of distilled water. Sante Mattson (6) investigated the electro-kinetic behavior of methylene blue toward soil colloids and found in the case of two soils that the equivalents of monovalent and divalent bases brought into solution, by treatment with methylene blue were approximately equal to the equivalents of methylene blue adsorbed. At the iso electric point Mattson assumes that all of the ionizable cations have been displaced but he shows that the dye continues to be adsorbed to some extent beyond this point and explains the fact by saying that "since there are no other cations to displace and to take the place of the methylene blue cation in the solution, the Cl ions of the dye must remain paired with the latter cations, forming another outer electrical layer on the colloid which is electronegative while the surface layer is now electropositive."

Since according to Mattson all of the ionizable cations are displaced from a certain weight of soil colloid by methylene blue, no more cations are available for base exchange. Therefore another dye such as neutral violet should displace from a new sample of the same colloid, the same equivalents of metals as the former dye.

It is the purpose of this investigation to determine quantitatively the equivalents of positive and negative ions displaced from a soil by a given dye when certain equivalents of the dye are adsorbed. 1. By comparing these results with another dye on the same soil we may reach some definite conclusion as to the capacity of a given soil colloid to exchange bases. 2. The ratio of dye which undergoes double decomposition to that which is wholly adsorbed can be found.

PREVIOUS WORK

Ashley (5) was probably the first to suggest base exchange as the cause of adsorption of dyes by soils. Lord (7) in commenting on the publication of Wilkinson and Hoff (4), stated that he had independently collected considerable data regarding the quantity of salts replaced and dye adsorbed. He makes the statement: "The results would indicate essentially a chemical reaction between the anions of the dye and cations of the electrolytes, yet, for some unexplained reason, the quantity of adsorbed dye is essentially the same as that of the recovered electrolytes." Mattson (6) showed the quantitative relationship between methylene blue and seven soils of considerable range in chemical composition. The relation between the dye and the soils was shown by the way the adsorbed dye and the exchangeable bases affected the electrical charge of the soil particles. His work is described in some detail in the next few paragraphs.

The colloidal soil materials were prepared by the supercentrifuge method (8). The variation in the electrical charge of these materials under different conditions was determined by observing the cataphoretic movement of the particles under the ultramicroscope. The apparatus consisted essentially of a straight capillary tube terminating in two chambers containing the electrodes. The wall of the tube was ground to a thickness of 0.15 mm. at the middle to bring the interior of the tube within the focal length of the objective.

The cataphoresis of each colloid was measured by preparing a series of tubes in which 25 cc. of a suspension containing 10 milligrams of the colloid were mixed with 25 cc. of solutions containing increasing quantities of dye. The tubes were then allowed to stand 24 hours before measurements were made. After a certain concentration of dye is reached slight increases affect the charge or movement of the particles profoundly. Flocculation also becomes complete at this point. By plotting milligrams methylene blue as abscissas and velocity of particles as ordinates, curves are obtained which resemble closely the neutralization curves of acids, when the pH is plotted against the quantities of base added.

The base exchange capacity of each colloid was obtained by leaching one gram with 500 cc. of neutral N. $CaCl_2$. The chloride was then removed by washing. The adsorbed Ca, which is supposed to be equivalent to the cations exchanged, was displaced by a hot solution of N. NH_4Cl, and was determined in the filtrate.

Conclusions

1. The quantities of methylene blue required to neutralize the negative charge of the soil colloids and ben-

tonite* correspond well with the quantities of exchangeable bases, but the agreement is close only under conditions of equal pH values.

2. It was found in the case of two colloids that the equivalents of monovalent and divalent bases brought into solution by treatment with methylene blue were approximately equal to the equivalents of methylene blue adsorbed.

3. When the exchangeable bases are replaced by the methylene blue cation the colloids become iso-electric.

4. The contents of exchangeable bases and the quantities of methylene blue required to neutralize the negative charge of the various soil colloids parallel the $\frac{SiO_2}{Al_2O_3+Fe_2O_3}$ ratios.

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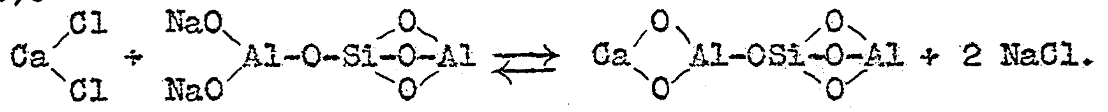
*Bentonite in its electrokinetic behavior, chemical composition and base exchange capacity is apparently similar to the colloidal soil material.

THE ZEOLITIC NATURE OF SOIL COLLOIDS

Zeolites are characterized by Thorpe (9) as hydrated silicates of aluminium with alkalies and alkali earths. These minerals hold their water of crystallization very loosely, and it is replaceable by a variety of substances such as ammonia and alcohol. When heated they swell up and appear to boil. They have been derived from the decomposition of felspar and other alkali bearing minerals. Commercial zeolites are made by fusing together soda, clay, felspar and kaolin. Zeolites exchange their bases without altering their aluminium and silicon contents, according to the following equation (10).



Calcium chloride Potassium zeolite Calcium zeolite Sodium chloride

Crystalline silicates such as felspar ($KAlSi_3O_8$) and in greater degree mica ($KH_2Al_3(SiO_4)_3$), are to a certain extent capable of exchanging their potash content for other bases.

By virtue of its colloidal nature, the clay of soils manifests the phenomenon of ionic exchange peculiar to the natural or synthetic zeolites (12). The exchangeable bases are considered by Hissink (13) as being on the surface of the particles of clay and of the humus complex in an adsorbed condition. They are thought however to be held in ionic form by chemical attraction. On the surface of the adsorbing clay and humus an electrical double layer is formed with the anion on the particle side and cation on the solution side. The cations are principally Na, K, Ca, Mg compounds being but little ionized. Parker and Pate (8) found that the exchangeable bases are only in the colloidal fraction of the soil. They state that two soils may have the same colloid content but one may contain several times as much exchangeable base as the other. Two explanations are given. (1) We may assume that some of the noncolloidal matter in a soil contains exchangeable base. If this is the case the exchangeable base content of the soil would not be directly proportional to the colloid content. (2) We may assume that exchangeable bases are found only in the colloidal material but that colloids from different soils contain different amounts of exchangeable base. The results of other investigators indicate that the second explanation is more nearly correct.

Anderegg and Lutz (14) studied base exchange in soils with the aid of the quinhydrone electrode. The results indicate that clay when oven dry is a monobasic acid, and under the conditions of their experiments, had a molecular weight of 3500.

Since soil colloids appear to be the Na, K, Mg, and Ca salts of aluminosilicic acids we could expect a dye such as methylene blue ($C_{16}H_{18}N_3SCl$) to enter into a metathetical reaction with these salts.

$$\underset{\substack{\text{Calcium}\\\text{zeolite}}}{Ca(Ze)_2} + \underset{\substack{\text{Methylene}\\\text{blue}}}{2C_{16}H_{18}N_3SCl} \longrightarrow \underset{\substack{\text{Calcium}\\\text{chloride}}}{CaCl_2} + \underset{\substack{\text{Methylene}\\\text{blue zeolite}}}{2C_{16}H_{18}N_3SZe}$$

EXPERIMENTAL

Lord (7) says that a quantitative study of base replacement in soils can be carried out more effectively by slow percolation than by the ordinary method of shaking in dilute dye solutions. His reason is that, under like conditions, the longer a colloidal mass is held in contact with a concentrated dye solution, the greater will be the yield of replaced electrolytes.

With these suggestions in mind the adsorption experiments were carried out as described by Lord (16) and Boyd (15). Five soils and two basic dyes were used. Each soil was from a different section of the state of Iowa.

No.1 - Kansanian clay from Story County.

No.2 - Webster clay loam from Wright County, upland glacial soil, normally sweet, even alkali, flat land, poorly grained.

No.3 - Marion silt loam from Van Buren County, loess, very acid under natural conditions, an orchard or small grain soil.

No.4 - Carrington loam from Hardin County, upland glacial soil, Iowan drift, most extensive general farm soil, usually shows medium lime requirement.

No.5 - Grundy silt loam from Henry County, Mount Pleasant, Iowa. Along Mississippi river, upland loess soil, very productive, good farm soil of southern Iowa.

The soils were air dried, ground in a mortar and pestle, and passed through a 48 mesh sieve.

The dyes were methylene blue and neutral violet. Because of its method of preparation, methylene blue might easily contain iron and zinc as impurities, so the commercial product was purified by two crystallizations and then analyzed. One gram of the purified dye contained 0.0027 grams of iron which is 0.1 milliequivalents of this cation. No other cations were found. Neutral violet was not analyzed for impurities since its method of preparation is quite different from that of methylene blue, and also the supply on hand was limited. Although methylene blue, $C_{16}H_{18}N_3SCl$, and neutral violet, $C_{14}H_{14}N_4HCl$, are basic dyes, they are not sufficiently ionized to give a chloride test with silver nitrate. After these dyes had been adsorbed by soils the clear filtrates in every case gave strong tests for chlorides.

In the preliminary experiments it was found that 10 grams of soil No.3 were necessary to give sufficient cations in the clear filtrate to be analyzed for easily. Because of the large samples used, the filtering tubes were enlarged sufficiently to hold the soil in the filtering column.

The filtering tubes were prepared by sealing a glass tube 5 in. long, 3/8 in. in diameter, into the round end of a test tube 8 in. long and 1 in. in diameter. A glass filtering cap one inch long was fitted on the end of the small tube or filtering column by a ground glass joint. Small filter papers, prepared from large ones by the use of cork borers, could be fastened at the joint by pressing the glass cap firmly onto the filtering column. If the joints are well ground the cap holding the filter paper will remain rigid. The filter papers can be put in place dry or wet, but the experimentor had better success fixing them when they were dry. The tubes were large enough to prevent the trapping of air bubbles in the filtering column when the soil suspensions were introduced.

A shortened test tube one inch in diameter and two inches long, with a lip on the rim, was used to introduce the soil suspensions into the filtering tubes. A definite quantity of soil was added to a small amount of the dye solution in this tube. The contents were stirred well, allowed to stand for several minutes, and then poured into the filtering tube with the aid of a short stirring rod. When the heavier soil particles had settled on the filter paper the stirring rod and tube were washed with more of the dye solution from an ordinary wash bottle. All of the supernatant liquid was allowed to filter through the soil before more of the dye solution was added. Filtration was allowed to continue until a marked discoloration appeared in the filtrate. This indicated that the soil was saturated, and the volume of the colorless filtrate was read and recorded. The filtrates were collected in graduated cylinders.

The filtrates containing the anions and cations liberated from the soil by the dye solution were analyzed according to the following scheme.

When the soils were leached with conductivity water no chlorides were displaced so the first and second steps in this procedure were omitted.

Table I.

Substance	Treatment	Precipitates formed remarks	No.
Filtrate from soil	HNO_3, $AgNO_3$	$AgCl$ - dried at 130° weighed in Gooch	1
Filtrate 1	HCl	$AgCl$, discarded	2
Filtrate 2	NH_4OH, boil	$Fe(OH)_3$, $Al(OH)_3$, SiO_2, ignited weighed	3
Filtrate 3	$(NH_4)_2C_2O_4$	CaC_2O_4 - ignited, weighed as CaO	4
Filtrate 4	$(NH_4)_2HPO_4$, NH_4OH, stand 12 hours	$MgNH_4PO_4$, ignited, weighed as $Mg_2P_2O_7$	5
Filtrate 5	$CaCl_2$	Takes out excess $(NH_4)_2HPO_4$ *	6
Filtrate 6	$(NH_4)_2C_2O_4$	Takes out excess Ca	7
Filtrate 7	HCl, evaporate to dryness in Pt dish, ignite at low red heat	Residue of $NaCl$, KCl weighed	8
Residue 8	H_2O, $HClO_4$, evaporate to white fumes on water bath add C_2H_5OH	$KClO_4$ dried at 130°, weighed in Gooch	

*This was done because $(NH_4)_2HPO_4$ is not volatile on heating. Any P_2O_5 formed would react with Pt.

Blank spaces in the tables indicate that some of the corresponding solutions or precipitates were lost.

A small amount of soil No.1 was leached with 500 cc. of N. $CaCl_2$ solution and then washed with conductivity water until the filtrate gave no test for chloride. The residue was air dried, ground with a mortar and pestle and passed through a 40 mesh sieve. This soil is referred to in the tables as soil No.6.

The reagents were analyzed for sodium and potassium. In the calculations these values were subtracted from the amounts of sodium and potassium found in the soil filtrates. Results are given in tables IV to IX.

In the calculation of the weights and equivalents of the various ions the following factors were used.

Table II

No	Ions	Value of factors	Value of 1 equivalent
1	Calcium	$\frac{Ca}{CaO} = \frac{40.07}{56.07} = 0.7146$	$\frac{Ca}{2} = \frac{40.07}{2} = 20.03$
2	Magnesium	$\frac{2Mg}{Mg_2P_2O_7} = \frac{48.64}{222.72} = 0.2184$	$\frac{Mg}{2} = \frac{24.32}{2} = 12.16$
3	Iron	$\frac{2Fe}{Fe_2O_3} = \frac{111.68}{159.68} = 0.6994$	$\frac{Fe}{3} = \frac{55.84}{3} = 18.61$
4	Sodium	$\frac{Na}{NaCl} = \frac{23}{58.46} = 0.3934$	$\frac{Na}{1} = \frac{23}{1} = 23$
5	Potassium	$\frac{K}{KClO_4} = \frac{39.1}{138.56} = 0.2821$	$\frac{K}{1} = \frac{39.1}{1} = 39.1$
6	Methylene blue color ion	$\frac{C_{16}H_{18}N_3S}{C_{16}H_{18}N_3SCl} = \frac{284}{319.45} = 0.8891$	$\frac{C_{16}H_{18}N_3S}{1} = \frac{284}{1} = 284$
7	Neutral violet color ion	$\frac{C_{14}H_{15}N_4}{C_{14}H_{15}N_4Cl} = \frac{239.15}{274.6} = 0.8709$	$\frac{C_{14}H_{15}N_4}{1} = \frac{239.15}{1} = 239.15$
8	Chlorine	$\frac{Cl}{AgCl} = \frac{35.46}{143.34} = 0.2473$	$\frac{Cl}{1} = \frac{35.46}{1} = 35.46$
9	———	$\frac{KCl}{KClO_4} = \frac{74.56}{138.56} = 0.5381$	———

The following table shows:
1. Approximate number
2. Anions displaced fr
   neutral violet (N.V
3. Reaction of filtrat

Soil	Grams soil used	Dye used	Conc. of dye solution per liter	cc. of dye solution decolorized	Grams of dye adsorbed	Acid ions displaced by conductivity wate			
						SO_4	Cl	CO_3	PO_4
1	1 gm	M.B.	2 gms.	25 cc.	0.05gms	-	slight trace	Yes	-
2	"	"	"	55 "	0.11	-	"	none	-
3	"	"	"	6 "	0.012	-	"	"	-
4	"	"	"	22 "	0.044	-	"	"	-
5	"	"	"	11 "	0.022	-	"	"	-
1	"	N.V.	4 gms.	30 cc.	0.12	-	"	"	-
2	"	"	"	40 "	0.16	-	"	"	-
3	"	"	"	6 "	0.024	-	"	"	-
4	"	"	"	15 "	0.06	-	"	"	-
5	"	"	"	8 "	0.032	-	"	"	-

ber of grams of each dye adsorbed by each soil.
ed from the soils by methylene blue (M.B.) solution,
(N.V.) solution, and conductivity water.
trates toward litmus.

Table III.

laced water		Acid ions displaced by dye solution					Reaction of fil toward litm	
PO_4	NO_3	SO_4	Cl	CO_3	PO_4	NO_3	Conductivity water	D
-	-	none	strong test	yes	-	-	Neutral	Neu
-	-	"	"	-	-	-	"	"
-	-	"	"	-	-	-	"	"
-	-	"	"	-	-	-	"	"
-	-	"	"	-	-	-	"	"
-	-	"	"	quite strong	-	-	"	Alk
-	-	"	"	none	-	-	"	Neu
-	-	"	"	"	-	-	"	"
-	-	"	"	"	-	-	"	Alk
-	-	"	"	"	-	-	"	Neu

ach dye adsorbed by each soil.
by methylene blue (M.B.) solution,
and conductivity water.
mus.

Acid ions displaced by dye solution				Reaction of filtrate toward litmus	
Cl	CO_3	PO_4	NO_3	Conductivity water	Dye solution
strong test	yes	–	–	Neutral	Neutral
"	–	–	–	"	"
"	–	–	–	"	"
"	–	–	–	"	"
"	–	–	–	"	"
"	quite strong	–	–	"	Alkaline
"	none	–	–	"	Neutral
"	"	–	–	"	"
"	"	–	–	"	Alkaline
"	"	–	–	"	Neutral

Relationship between the anions & cations of the soil and dyes.

No.	Wt. of soil leached	Hours to filter	cc. fil-trate	Gms. of dye per liter	Wt. of dye ad-sorbed	Wt. of color ion	Milli- of col ion
	1	2	3	4	5	6	7
1	2 gms.	45	50.9	2 gms. M.B.	0.1018	0.0905	0.318
2	"	43	50.7	"	0.1014	0.0901	0.317
3	"	54	51.2	"	0.1024	0.0910	0.320
4	"	55	50.5	"	0.1010	0.0897	0.316
5	5 gms.	18	31.5	8.64 M.B.	0.2722	0.2420	0.852
6	"	26	32.5	"	0.2808	0.2496	0.878
7	"	27	32.0	"	0.2765	0.2458	0.865
8	"	27	31.5	"	0.2722	0.2420	0.852
9	10 gms.	89	63.0	"	0.5443	0.4839	1.704
10	"	64	64.5	"	0.5572	0.4954	1.744
11	2 gms.	135	61.0	4 gms. N.V.	0.2440	0.2124	0.888
12	"	101	61.5	"	0.2460	0.2142	0.895
13	"	135	63.0	"	0.2520	0.2194	0.917

Cations displaced by soil No.1 by M.B.&N.V. solutions.(continuation of above results)

No.	Wt. of soil leached	Hours to filter	cc. fil-trate	Wt. of Fe_2O_3 and Al_2O_3	Wt. of Fe	Milli-equiv. of Fe	Wt. of
	1	2	3	4	5	6	7
1	2 gms.	45	50.9	0.0022	0.0015	0.082	0.0096
2	"	43	50.7	0.0020	0.0013	0.075	0.0098
3	"	54	51.2	"	"	"	0.0102
4	"	55	50.5	0.0022	0.0015	0.082	0.0088
5	5 gms.	18	31.5	trace	-	-	0.0156
6	"	26	32.5	"	-	-	"
7	"	27	32.0	"	-	-	0.0152
8	"	27	31.5	"	-	-	0.0156
9	10 gms.	89	63.0	0.0002	0.0001	0.007	-
10	"	64	64.5	0.0002	"	"	0.0342
11	2 gms.	135	61.0	0.0008	0.0005	0.030	0.0176
12	"	101	61.5	0.0006	0.0004	0.022	0.0170
13	"	135	63.0	0.0004	0.0002	0.013	0.0184

Table IV

DISPLACEMENT OF CATIONS AND ANIONS BY METHYLENE BLU
AND NEUTRAL VIOLET (N.V.) SOLUTION ON ADSORPTIC

Milli-equiv of color ion	Wt. of Cl ion	Milli-equiv. of Cl ion	Wt. of AgCl	Wt. of Cl from AgCl	Milli-equiv. of Cl from AgCl	Fe milli-equiv of adsorbed dye	Milli-equi metals disp from soil conductivi water
7	8	9	10	11	12	13	14
0.318	0.0113	0.318	0.0408	0.0100	0.284	0.010	0.010
0.317	0.0112	0.317	0.0418	0.0103	0.291	"	"
0.320	0.0113	0.320	0.0411	0.0101	0.287	"	"
0.316	0.0112	0.316	0.0410	0.0101	0.286	"	"
0.852	-	-	-	-	-	0.027	0.28
0.878	-	-	-	-	-	0.028	"
0.865	-	-	-	-	-	0.027	"
0.852	-	-	-	-	-	0.027	"
1.704	0.0604	1.704	0.2686	0.0664	1.873	0.054	0.21
1.744	0.0618	1.744	0.2674	0.0661	1.860	0.055	"
0.888	0.0316	0.888	0.1062	0.0262	0.740	-	0.25
0.895	0.0318	0.895	0.1076	0.0266	0.756	-	"
0.917	0.0326	0.917	0.1124	0.0277	0.784	-	"

Wt. of CaO	Wt. of Ca	Milli-equiv. of Ca	Wt. of $Mg_2P_2O_7$	Wt. of Mg	Milli-equiv. of Mg	Wt. of NaCl & KCl	Wt. of $KClO_4$	Wt KC fr re
7	8	9	10	11	12	13	14	
0.0096	0.0068	0.342	0.0100	0.0021	0.179	0.0116	0.0024	0.
0.0098	0.0070	0.350	0.0104	0.0022	0.186	0.0130	"	
0.0102	0.0072	0.364	0.0106	0.0023	0.190	0.0126	0.0021	
0.0088	0.0062	0.314	0.0104	0.0022	0.186	0.0116	"	
0.0156	0.0111	0.557	0.0120	-	-	0.0294	0.0038	
"	"	"	0.0138	0.0030	0.247	0.0296	0.0034	
0.0152	0.0108	0.543	0.0142	0.0031	0.255	"	0.0036	
0.0156	0.0111	0.557	0.0142	"	"	0.0308	0.0038	
-	-	-	-	-	-	-	-	
0.0342	0.0244	1.221	0.0266	0.0058	0.477	0.0724	0.0160	0.
0.0176	0.0125	0.626	0.0118	0.0025	0.211	0.0274	0.0063	0.
0.0170	0.0121	0.607	0.0110	0.0024	0.197	0.0266	"	
0.0184	0.0131	0.657	0.0118	0.0025	0.211	0.0276	"	

METHYLENE BLUE (M.B.) SOLUTION
ON ADSORPTION BY SOIL NO.1

l- uiv - d	Milli-equiv. of metals displaced from soil by conductivity water	Total milli-equiv. of metals to be subtracted (13+14)	Total milli-equiv. of metals displaced by dye solution	Milli-equiv. of metals displaced by dye alone. (16 minus 15)
	14	15	16	17
)	0.010	0.23	0.69	0.46
	"	"	0.73	0.50
	"	"	0.74	0.51
	"	"	0.67	0.44
7	0.28	0.30	-	-
3	"	"	1.20	0.90
7	"	"	1.19	0.89
7	"	"	1.23	0.93
4	0.21	0.26	-	-
5	"	"	2.40	2.14
	0.25	0.25	1.02	0.77
	"	"	0.96	0.71
	"	"	1.03	0.78

of &	Wt. of $KClO_4$	Wt. of $KClO_4$ from reagent	Wt. of: $KClO_4$ due to: dye so-: lution:	Wt. of: K	Milli-equiv. of K	Wt. of KCl (calculated from column 14)	Wt. of NaCl (column 13 minus column 19)	Wt. NaCl from agen
	14	15	16	17	18	19	20	2
16	0.0024	0.0021	0.0003	0.0001	0.002	0.0012	0.0104	0.00
30	"	"	"	"	"	"	0.0118	
26	0.0021	"	none	-	-	0.0011	0.0115	
16	"	"	"	-	-	0.0011	0.0105	
4	0.0038	"	0.0017	0.0004	0.012	0.0020	0.0274	
6	0.0034	"	0.0013	0.0003	0.009	0.0018	0.0278	
	0.0036	"	0.0015	0.1004	0.010	0.0019	0.0277	
8	0.0038	"	0.0017	0.0004	0.012	0.0020	0.0288	
	-	-	-	-	-	-	-	
24	0.0160	0.0106	0.0054	0.0015	0.039	0.0086	0.0638	0.0
74	0.0063	0.0063	none	-	-	0.0033	0.0241	0.0
56	"	"	"	-	-	"	0.0233	
76	"	"	"	-	-	"	0.0243	

- ye	Milli-equiv. of metals displaced by dye alone. (16 minus 15)
	17
	0.46
	0.50
	0.51
	0.44
	-
	0.90
	0.89
	0.93
	-
	2.14
	0.77
	0.71
	0.78

of KCl lculated n column	Wt. of NaCl (column 13 minus column 19)	Wt. of NaCl from reagents	Wt. of NaCl due to dye solution	Wt. of Na	Milli-equiv. of Na	Total milli-equiv. of metals displaced by dye solution
19	20	21	22	23	24	25
012	0.0104	0.0051	0.0053	0.0020	0.090	0.695
"	0.0118	"	0.0067	0.0026	0.114	0.727
0011	0.0115	"	0.0064	0.0025	0.109	0.738
0011	0.0105	"	0.0054	0.0021	0.092	0.674
0020	0.0274	"	0.0223	0.0087	0.381	-
0018	0.0278	"	0.0227	0.0089	0.388	1.201
0019	0.0277	"	0.0226	0.0088	0.386	1.194
0020	0.0288	"	0.0237	0.0093	0.405	1.229
-	-	-	-	-	-	-
0086	0.0638	0.0255	0.0383	0.0150	0.655	2.399
0033	0.0241	0.0153	0.0088	0.0034	0.150	1.017
"	0.0233	"	0.0080	0.0031	0.136	0.962
"	0.0243	"	0.0090	0.0035	0.153	1.034

No.	Wt. of soil leached	Hours to filter	cc. filtrate	Wt. of Fe_2O_3 & Al_2O_3	Wt. of Fe	Milli-equiv. of Fe	Wt. of CaO	Wt. of Ca	Mil equ o C
	1	2	3	4	5	6	7	8	9
1	1 gm.	90	60	0.0012	0.0008	0.045	0.0026	0.0018	0.0
2	"	96	60	"	"	"	"	"	"
3	"	84	56	"	"	"	0.0028	0.0020	0.1
4	"	72	56	"	"	"	"	"	"
5	2 gms.	65	70	0.0015	0.0010	0.056	"	"	"
6	"	90	65	0.0014	0.0009	0.052	0.0038	0.0027	0.1
7	"	95	50	0.0010	0.0006	0.037	0.0026	0.0018	0.0
8	"	95	50	0.0011	0.0007	0.041	0.0032	0.0022	0.1
9	"	72	50	0.0016	0.0011	0.060	0.0020	0.0014	0.0
10	"	75	51	0.0018	0.0012	0.067	"	"	"
11	5 gms.	70	52	0.0016	0.0011	0.060	0.0024	0.0017	0.0
12	"	70	58	0.0018	0.0012	0.067	"	"	"
13	"	26	30	0.0006	0.0004	0.022	0.0014	0.0010	0.0
14	"	31	30	0.0004	0.0002	0.013	0.0012	0.0008	0.0
15	"	26	30	"	"	"	"	"	"
16	10 gms.	55	62	"	"	"	0.0026	0.0018	0.0
17	"	65	73	"	"	"	0.0026	0.0018	0.0
18	"	65	75	"	"	"	0.0028	0.0020	0.1

Table V

CATIONS DISPLACED FROM SOIL NO.1 BY CONDU

Wt. of Ca	Milli-equiv. of Ca	Wt. of $Mg_2P_2O_7$	Wt. of Mg.	Milli-equiv. of Mg	Wt. of NaCl and KCl	Wt. of $KClO_4$	Wt. of $KClO_4$ from reagents	Wt. of due to ductiv water
8	9	10	11	12	13	14	15	1
0.0018	0.092	0.0032	0.0006	0.057	0.0310	0.0114	0.0106	0.0008
"	"	0.0028	0.0006	0.050	0.0316	"	"	0.0008
0.0020	0.100	0.0024	0.0005	0.042	0.0308	0.0118	"	0.0012
"	"	"	"	"	0.0330	0.0128	"	0.0022
"	"	0.0030	0.0006	0.051	0.0322	"	"	0.0022
0.0027	0.135	0.0042	0.0009	0.075	0.0328	0.0120	"	0.0014
0.0018	0.092	0.0024	0.0005	0.042	0.0308	0.0112	"	0.0006
0.0022	0.114	"	"	"	0.0316	0.0108	"	0.0002
0.0014	0.071	0.0038	0.0008	0.068	0.0084	0.0020	0.0021	none
"	"	0.0040	0.0008	0.071	0.0086	0.0016	"	"
0.0017	0.085	0.0044	0.0009	0.079	0.0092	0.0018	"	"
"	"	"	"	"	"	"	"	"
0.0010	0.050	0.0018	0.0003	0.032	0.0090	0.0014	"	"
0.0008	0.042	0.0016	0.0003	0.028	0.0082	0.0018	"	"
"	"	"	"	"	0.0080	0.0010	"	"
0.0018	0.092	0.0036	0.0007	0.064	0.0086	0.0014	"	"
0.0018	0.092	"	"	"	0.0088	0.0018	"	"
0.0020	0.100	"	"	"	-	-	-	"

e V

NO.1 BY CONDUCTIVITY WATER

t. of $KClO_4$ from eagents	Wt. of $KClO_4$ due to conductivity water	Wt. of K	Milli-equiv. of K	Wt. of KCl (calculated from column 14)	Wt. of NaCl (column 13 minus column 19)	Wt. of NaCl from reagents
15	16	17	18	19	20	21
.0106	0.0008	0.0002	0.005	0.0061	0.0249	0.0255
"	0.0008	"	"	"	0.0255	"
"	0.0012	0.0003	0.008	0.0063	0.0245	"
"	0.0022	0.0006	0.015	0.0068	0.0262	"
"	0.0022	"	"	"	0.0254	"
"	0.0014	0.0003	0.010	0.0064	0.0264	"
"	0.0006	0.0001	0.004	0.0060	0.0248	"
"	0.0002	0.0001	0.001	0.0058	0.0258	"
.0021	none	-	-	0.0011	0.0073	0.0051
"	"	-	-	"	0.0075	"
"	"	-	-	"	0.0081	"
"	"	-	-	"	"	"
"	"	-	-	"	0.0089	"
"	"	-	-	"	0.0071	"
"	"	-	-	"	0.0069	"
"	"	-	-	"	0.0075	"
"	"	-	-	"	0.0077	"
-	"	-	-	"	-	-

Cl ted umn	Wt. of NaCl (column 13 minus column 19)	Wt. of NaCl from reagents	Wt. Of NaCl due to conductivity water	Wt. of Na	Milliequiv. of Na	Total milliequiv. of metals displaced by conductivity water
	20	21	22	23	24	25
	0.0249	0.0255	none	-	-	0.199
	0.0255	"	"	-	-	0.192
	0.0245	"	"	-	-	0.195
	0.0262	"	0.0007	0.0002	0.011	0.213
	0.0254	"	none	-	-	0.222
	0.0264	"	0.0009	0.0003	0.015	0.287
	0.0248	"	none	-	-	0.175
	0.0258	"	0.0003	0.0001	0.005	0.203
	0.0073	0.0051	0.0022	0.0008	0.037	0.236
	0.0075	"	0.0024	0.0009	0.041	0.250
	0.0081	"	0.0030	0.0011	0.051	0.275
	"	"	"	"	"	0.282
	0.0089	"	0.0038	0.0014	0.064	0.168
	0.0071	"	0.0020	0.0007	0.034	0.117
	0.0069	"	0.0018	0.0007	0.030	0.113
	0.0075	"	0.0024	0.0009	0.041	0.210
	0.0077	"	0.0026	0.0010	0.044	0.213
	-	-	-	-	-	-

Relationship between the anions and cations of the soil and dyes.

No.	Wt. of soil leached	Hours to filter	cc. fil-trate	Gms. of dye per liter	Wt. of dye ad-sorbed	Wt. of color ion	Milli-equiv. of col or ion
	1	2	3	4	5	6	7
1	2 gms.	124	66	4.32 M.B.	0.2854	0.2537	0.893
2	"	123	66	"	"	"	"
3	"	119	65	"	0.2743	0.2438	0.858
4	"	122	67	"	0.2894	0.2573	0.906
5	"	117	63	5.08 N.V.	0.3198	0.2785	1.164
6	"	117	60	"	0.3048	0.2654	1.109

Cations displaced from soil No.2 by M.B. and N.V. solutions.(continuation of above results)

Cations displaced from soil No.2 by conductivity water

No.	Wt. of soil leached	Hours to filter	cc. fil-trate	Wt. of Fe_2O_3 and Al_2O_3	Wt. of Fe	Milli-equiv. of Fe	Wt. o CaO
	1	2	3	4	5	6	7
1	2 gms.	124	66	none	-	-	0.016
2	"	123	"	"	-	-	0.016
3	"	119	65	"	-	-	0.016
4	"	122	67	"	-	-	0.017
5	"	117	63	0.0006	0.0004	0.022	0.017
6	"	"	60	"	"	"	"
7	2 gms.	65	57	0.0004	0.0002	0.013	0.001
8	"	43	30	"	"	"	0.001
9	"	65	57	0.0002	0.0001	0.007	0.001

Table VI

DISPLACEMENT OF CATIONS AND ANIONS BY METHYLEN
SOLUTION AND NEUTRAL VIOLET (N.V.) SOLUTION ON ADS
CATIONS DISPLACED FROM SOIL NO.2 BY CONDUCT

of or	Milli-equiv. of color ion	Wt. of Cl ion	Milli-equiv. of Cl ion	Wt. of AgCl	Wt. of Cl from AgCl	Milli-equiv. of Cl from AgCl	Fe milli-equiv of adsorbed dye	Milli-equ metals di from soi conducti water
	7	8	9	10	11	12	13	14
537	0.893	0.0317	0.893	0.1168	0.0289	0.815	0.028	0.
"	"	"	"	0.1142	0.0282	0.796	"	
438	0.858	0.0305	0.858	0.1132	0.0280	0.789	0.027	
573	0.906	0.0321	0.906	0.1190	0.0294	0.831	0.028	
785	1.164	0.0413	1.164	0.1414	0.0349	0.989	-	
654	1.109	0.0394	1.109	0.1368	0.0338	0.954	-	

lli-uiv. Fe	Wt. of CaO	Wt. of Ca	Milli-equiv. of Ca	Wt. of $Mg_2P_2O_7$	Wt. of Mg	Milli-equiv. of Mg	Wt. of NaCl and KCl	Total wt. of $KClO_4$
6	7	8	9	10	11	12	13	14
-	0.0168	0.0120	0.600	0.0142	0.0031	0.255	0.0114	0.0036
-	0.0166	0.0118	0.593	0.0136	0.0029	0.244	0.0104	0.0030
-	0.0164	0.0117	0.585	"	"	"	0.0102	0.0028
-	0.0176	0.0125	0.626	"	"	"	0.0104	"
022	0.0178	0.0127	0.635	0.0122	0.0026	0.219	0.0292	0.0094
"	"	"	"	0.0126	0.0027	0.226	0.0286	0.0088
013	0.0014	-	-	0.0028	0.0006	0.050	0.0084	0.0018
"	0.0012	0.0008	0.042	0.0020	0.0004	0.035	-	-
007	0.0018	0.0012	0.064	0.0024	0.0005	0.042	0.0084	0.0018

LENE BLUE (M.B.)
ADSORPTION BY SOIL NO.2
UCTIVITY WATER

-equiv. of s displaced soil by ctivity	Total milli-equiv. of metals to be subtracted (13+14)	Total milli-equiv. of metals displaced by dye solution	Milli-equiv. of metals displaced by dye alone. (16minus 15)
14	15	16	17
0.15	0.17	0.94	0.77
"	"	0.90	0.73
"	"	0.89	0.72
"	"	0.94	0.77
"	0.15	1.05	0.90
"	"	1.04	0.89

f $_4$	Wt. of $KClO_4$ from reagents	Wt. of $KClO_4$	Wt. of K	Milli-equiv. of K	Wt. of KCl (calculated from column 14)	Total wt. of NaCl (13 minus 19)	Wt. of NaCl from reagents	Wt. Na
	15	16	17	18	19	20	21	2
56	0.0021	0.0015	0.0004	0.010	0.0019	0.0095	0.0051	0.0
30	"	0.0009	0.0002	0.006	0.0016	0.0088	"	0.0
28	"	0.0007	0.0001	0.005	0.0015	0.0087	"	0.0
	"	"	"	"	"	0.0089	"	0.0
94	0.0063	0.0031	0.0008	0.022	0.0050	0.0242	0.0153	0.0
88	"	0.0025	0.0007	0.017	0.0047	0.0239	"	0.0
18	0.0021	none	-	-	0.0011	0.0073	0.0051	0.0
	"	"	-	-	-	-	-	
18	"	"	-	-	0.0011	0.0073	"	0.0

- ye	Milli-equiv. of metals displaced by dye alone. (16minus 15)
	17
	0.77
	0.73
	0.72
	0.77
	0.90
	0.89

of KCl alculated om column)	Total wt. of NaCl (13 minus 19)	Wt. of NaCl from reagents	Wt. of NaCl	Wt. of Na	Milli-equiv. of Na	Total milli-equiv. of metals removed from the soil
19	20	21	22	23	24	25
.0019	0.0095	0.0051	0.0044	0.0017	0.075	0.940
.0016	0.0088	"	0.0037	0.0014	0.063	0.906
.0015	0.0087	"	0.0036	0.0014	0.061	0.895
"	0.0089	"	0.0038	0.0015	0.065	0.940
.0050	0.0242	0.0153	0.0089	0.0035	0.152	1.050
.0047	0.0239	"	0.0086	0.0033	0.147	1.047
.0011	0.0073	0.0051	0.0022	0.0008	0.037	0.164
-	-	-	-	-	-	-
.0011	0.0073	"	0.0022	0.0008	0.037	0.150

Relationship between the anions and cations of the soil and dyes.

No.	Wt. of soil leached	Hours to filter	cc. filtrate	Gms. of dye per liter	Wt. of dye adsorbed	Wt. of color ion	Milli-equiv. of co or io
	1	2	3	4	5	6	7
1	10 gms.	94	44	4.38 M.B.	0.1924	0.1710	0.602
2	"	96	47	"	0.2053	0.1825	0.642
3	"	94	46	"	0.2010	0.1787	0.628
4	"	93	47	"	0.2053	0.1825	0.642
5	"	55	44	5.08 N.V.	0.2232	0.1943	0.812
6	"	71	44	"	"	"	"

Cations displaced from soil No.3 by M.B. and N.V. solutions.(continuation of above results)

No.	Wt. of soil leached	Hours to filter	cc. filtrate	Wt. of Fe_2O_3 and Al_2O_3	Wt. of Fe	Milli-equiv. of Fe	Wt. o CaO
	1	2	3	4	5	6	7
1	10 gms.	94	44	-	-	-	0.005
2	"	96	47	0.0072	0.0050	0.270	0.006
3	"	94	46	-	-	-	0.008
4	"	93	47	0.0072	0.0050	0.270	0.006
5	"	55	44	0.0066	0.0046	0.242	0.008
6	"	71	44	0.0062	0.0043	0.233	"

Cations displaced from soil No.3 by conductivity water

7	10 gms.	51	47	0.0014	0.0009	0.052	0.001
8	"	65	45	"	"	"	"
9	"	53	45	"	"	"	"
10	"	51	48	0.0012	0.0008	0.045	0.001

Table VII

DISPLACEMENT OF CATIONS AND ANIONS BY METHY
AND NEUTRAL VIOLET (N.V.) SOLUTION ON ADS
CATIONS DISPLACED FROM SOIL NO. 3 BY C

f d- d	Wt. of color ion	Milli-equiv. of color ion	Wt. of Cl ion	Milli-equiv. of Cl ion	Wt. of AgCl	Wt. of Cl from AgCl	Milli-equiv. of Cl from AgCl	Fe Milli-equiv of adsorbed dye	Mi me fr co wa
	6	7	8	9	10	11	12	13	
24	0.1710	0.602	0.0214	0.602	0.784	0.0193	0.547	0.019	
53	0.1825	0.642	0.0228	0.642	0.0780	0.0192	0.544	0.020	
10	0.1787	0.628	0.0223	0.628	0.0798	0.0197	0.559	0.020	
53	0.1825	0.642	0.0228	0.642	0.0794	0.0196	0.553	0.020	
52	0.1943	0.812	0.0289	0.812	0.0954	0.0235	0.665	-	
	"	"	"	"	0.0980	0.0242	0.685	-	

of e	Milli-equiv. of Fe	Wt. of CaO	Wt. of Ca	Milli-equiv. of Ca	Wt. of $Mg_2P_2O_7$	Wt. of Mg	Milli-equiv. of Mg	Wt. of NaCl and KCl	To wt K
	6	7	8	9	10	11	12	13	
	-	0.0056	-	-	0.0080	0.0017	0.143	0.0118	0.
50	0.270	0.0060	0.0042	0.214	"	"	"	"	0.
	-	0.0086	0.0061	0.307	0.0084	0.0018	0.150	"	0.
50	0.270	0.0068	0.0048	0.242	0.0080	0.0017	0.143	0.0126	
46	0.242	0.0082	0.0058	0.293	0.0100	0.0021	0.179	0.0234	0.
43	0.233	"	"	"	0.0114	0.0024	0.204	0.0232	0.
09	0.052	0.0012	0.0008	0.042	0.0020	0.0004	0.035	0.0124	0.
	"	"	"	"	"	"	"	0.0120	0.
	"	"	"	"	"	"	"	"	0.
08	0.045	0.0010	0.0006	0.034	0.0022	0.0005	0.040	"	0.

ble VII

NS BY METHYLENE BLUE (M.B.) SOLUTION
TION ON ADSORPTION BY SOIL NO. 3.
NO. 3 BY CONDUCTIVITY WATER

Fe Milli-equiv of adsorbed dye 13	Milli-equiv. of metals displaced from soil by conductivity water 14	Total milli-equiv. of metals to be subtracted (13+14) 15	Total milli-equiv. of metals displaced by dye solution 16	Milli-equiv. o metals displac by dye alone. (16 minus 15 17
0.019	0.23	0.24	-	-
0.020	"	0.25	0.72	0.47
0.020	"	0.25	-	-
0.020	"	0.25	0.76	0.51
-	0.21	0.21	0.90	0.69
-	0.22	0.22	0.91	0.69

Wt. of NaCl and KCl 13	Total wt. of $KClO_4$ 14	Wt. of $KClO_4$ from reagents 15	Wt. of $KClO_4$ 16	Wt. of K 17	Milli-equiv. of K 18	Wt. of KCl (calculated from column 14) 19	Total wt of NaCl (13 minu 19) 20
0.0118	0.0048	0.0021	0.0027	0.0007	0.019	0.0025	0.0093
"	0.0042	"	0.0021	0.0005	0.015	0.0022	0.0096
"	0.0044	"	0.0023	0.0006	0.017	0.0023	0.0095
0.0126	"	"	"	"	"	"	0.0103
0.0234	0.0054	0.0042	0.0012	0.0003	0.008	0.0029	0.0205
0.0232	0.0056	"	0.0014	"	0.010	0.0030	0.0202
0.0124	0.0028	0.0021	0.0007	0.0001	0.003	0.0015	0.0109
0.0120	0.0020	"	none	-	-	0.0010	0.110
"	0.0032	"	0.0011	0.0003	0.008	0.0017	0.0103
"	0.0028	"	0.0007	0.0001	0.003	0.0015	0.0105

lli- f is- y dye	Milli-equiv. of metals displaced by dye alone. (16 minus 15)
	17
	-
	0.47
	-
	0.51
	0.69
	0.69

Wt. of KCl (calculated from column 14)	Total wt. of NaCl (13 minus 19)	Wt. of NaCl from reagents	Wt. of NaCl	Wt. of Na	Milli-equiv. of Na	Total milli-equiv. of metals removed from the soil
19	20	21	22	23	24	25
0.0025	0.0093	0.0051	0.0042	0.0016	0.071	-
0.0022	0.0096	"	0.0045	0.0017	0.077	0.719
0.0023	0.0095	"	0.0044	"	0.075	-
"	0.0103	"	0.0052	0.0020	0.088	0.760
0.0029	0.0205	0.0102	0.0103	0.0040	0.176	0.898
0.0030	0.0202	"	0.0100	0.0039	0.171	0.911
0.0015	0.0109	0.0051	0.0058	0.0022	0.097	0.229
0.0010	0.110	"	0.0059	0.0023	0.100	0.229
0.0017	0.0103	"	0.0052	0.0020	0.088	0.225
0.0015	0.0105	"	0.0054	0.0021	0.092	0.214

Relationship between the anions and cations of the soil and the dyes.

No.	Wt. of soil leached	Hours to filter	cc. fil-trate	Gms. of dye per liter	Wt. of dye ad-sorbed	Wt. of color ion	Milli-equiv. of col-or ion
	1	2	3	4	5	6	7
1	5 gms.	47	62	4.22 M.B.	0.2616	0.2325	0.819
2	"	44	61	"	0.2574	0.2288	0.805
3	"	50	"	"	"	"	"
4	"	"	63	"	0.2658	0.2363	0.832
5	"	48	58	5.08 N.V.	0.2940	0.2570	1.074
6	"	68	60	"	0.3048	0.2654	1.109

Cations displaced from soil No.4 by M.B. and N.V. solutions. (continuation of above results)

No.	Wt. of soil leached	Hours to filter	cc. fil-trate	Wt. of Fe_2O_3 and Al_2O_3	Wt. of Fe	Milli-equiv. of Fe	Wt. of CaO
	1	2	3	4	5	6	7
1	5 gms.	47	62	0.0008	0.0005	0.030	0.0168
2	"	44	61	0.0002	0.0001	0.007	0.0158
3	"	50	"	0.0004	0.0002	0.022	0.0150
4	"	"	63	0.0002	0.0001	0.007	0.0162
5	"	48	58	0.0008	0.0005	0.030	0.0170
6	"	68	60	"	"	"	0.0160

ations displaced
rom soil No.4 by
onductivity water

7	5 gms.	129	59	0.0004	0.0002	0.022	0.0020
8	"	"	61	"	"	"	0.0026
9	"	"	59	"	"	"	"
110	"	126	63	0.0002	0.0001	0.007	"

Table VIII

DISPLACEMENT OF CATIONS AND ANIONS BY METHYLENE BLUE
AND NEUTRAL VIOLET (N.V.) SOLUTION ON ADSORPTION B
CATIONS DISPLACED FROM SOIL NO. 4 BY CONDUCTIVI

f	Milli-equiv. of color ion	Wt. of Cl ion	Milli-equiv. of Cl ion	Wt. of AgCl	Wt. of Cl from AgCl	Milli-equiv. of Cl from AgCl	Fe Milli-equiv of adsorbed dye	Milli-equiv metals disp from soil b conductivit water
	7	8	9	10	11	12	13	14
5	0.819	0.0291	0.819	0.1048	0.0259	0.734	0.026	0.17
8	0.805	0.0286	0.805	0.1042	0.0257	0.729	0.025	"
	"	"	"	0.1030	0.0254	0.722	"	"
3	0.832	0.0295	0.832	0.1046	0.0258	0.731	0.026	"
0	1.074	0.0370	1.074	0.1264	0.0312	0.881	-	"
4	1.109	0.0394	1.109	0.1294	0.0320	0.902	-	"

- .	Wt. of CaO	Wt. of Ca	Milli-equiv. of Ca	Wt. of $Mg_2P_2O_7$	Wt. of Mg	Milli-equiv. of Mg	Wt. of NaCl and KCl	Total wt. of $KClO_4$	Wt K fr ag
	7	8	9	10	11	12	13	14	
)	0.0168	0.0120	0.600	0.0100	0.0022	0.179	0.0118	0.0036	0.
7	0.0158	0.0112	0.564	"	"	"	0.0120	0.0038	
2	0.0150	0.0107	0.535	0.0106	0.0023	0.190	0.0100	0.0036	
7	0.0162	0.0115	0.575	0.0100	-	-	0.0090	0.0028	
)	0.0170	0.0121	0.607	0.0110	0.0024	0.197	0.0280	0.0082	0.
	0.0160	0.0114	0.573	0.0104	0.0022	0.186	"	0.0078	
2	0.0020	0.0014	0.071	0.0018	0.0003	0.032	0.0074	0.0018	0.
	0.0026	0.0018	0.092	"	"	"	0.0076	0.0017	
	"	"	"	"	"	"	0.0074	0.0018	
7	"	"	"	"	"	"	0.0076	-	

ble VIII

ONS BY METHYLENE BLUE (M.B.) SOLUTION
UTION ON ADSORPTION BY SOIL NO. 4.
L NO. 4 BY CONDUCTIVITY WATER

Fe Milli-equiv of adsorbed dye	Milli-equiv. of metals displaced from soil by conductivity water	Total milli-equiv. of metals to be subtracted (13+14)	Total milli-equiv. of metals displaced by dye solution	Milli-equiv. metals displa by dye alone. (16 minus 1
13	14	15	16	17
0.026	0.17	0.19	0.90	0.71
0.025	"	"	0.85	0.66
"	"	"	0.81	0.62
0.026	"	"	-	-
-	"	0.17	0.99	0.82
-	"	"	0.95	0.78

Wt. of NaCl and KCl	Total wt. of $KClO_4$	Wt. of $KClO_4$ from reagents	Wt. of $KClO_4$	Wt. of K	Milli-equiv. of K	Wt. of KCl (calculated from column 14)	Total w of NaCl (13 mi 19)
13	14	15	16	17	18	19	20
0.0118	0.0036	0.0021	0.0015	0.0004	0.010	0.0019	0.0099
0.0120	0.0038	"	0.0017	"	0.012	0.0020	0.0100
0.0100	0.0036	"	0.0015	"	0.010	0.0019	0.0081
0.0090	0.0028	"	0.0007	0.0001	0.005	0.0015	0.0075
0.0280	0.0082	0.0063	0.0019	0.0005	0.013	0.0044	0.0236
"	0.0078	"	0.0015	0.0004	0.010	0.0041	0.0239
0.0074	0.0018	0.0021	none	-	-	0.0011	0.0063
0.0076	0.0017	"	"	-	-	"	0.0065
0.0074	0.0018	"	"	-	-	"	0.0063
0.0076	-	-	-	-	-	-	-

i- - dye	Milli-equiv. of metals displaced by dye alone. (16 minus 15)
	17
	0.71
	0.66
	0.62
	-
	0.82
	0.78

t. of KCl calculated from column 14)	Total wt. of NaCl (13 minus 19)	Wt. of NaCl from reagents	Wt. of NaCl	Wt. of Na	Milli-equiv. of Na	Total milli-equiv. of metals removed from the soil
19	20	21	22	23	24	25
.0019	0.0099	0.0051	0.0048	0.0018	0.082	0.901
.0020	0.0100	"	0.0049	0.0019	0.086	0.848
.0019	0.0081	"	0.0030	0.0011	0.051	0.808
.0015	0.0075	"	0.0024	0.0009	0.041	-
.0044	0.0236	0.0153	0.0083	0.0032	0.141	0.988
.0041	0.0239	"	0.0086	0.0033	0.147	0.946
.0011	0.0063	0.0051	0.0012	0.0003	0.016	0.141
"	0.0065	"	0.0014	0.0005	0.023	0.169
"	0.0063	"	0.0012	0.0003	0.016	0.162
-	-	-	-	-	-	-

Relationship between the anions and cations of the soil and dyes.

No.	Wt. of soil leached	Hours to filter	cc. fil- trate	Gms. of dye per liter	Wt. of dye ad- sorbed	Wt. of color ion	Milli- equiv. of col or ion
	1	2	3	4	5	6	7
1	5 gms.	77	74	2.84 M.B.	0.2072	0.1842	0.648
2	"	82	75	"	0.2100	0.1867	0.657
3	"	81	76	"	0.2128	0.1892	0.666
4	"	78	"	"	"	"	"
5	"	64	75	1.02 N.V.	0.0764	0.0665	0.278
6	"	61	"	"	"	"	"

Cations displaced from soil No.5 by M.B. and N.V. solutions. (Continuation of above results.)

Cations displaced from soil No.5 by conductivity water.

No.	Wt. of soil leached	Hours to filter	cc. fil- trate	Wt. of Fe_2O_3 and Al_2O_3	Wt. of Fe	Milli- equiv. of Fe	Wt. of CaO
	1	2	3	4	5	6	7
1	5 gms.	77	74	0.0004	0.0002	0.022	0.0092
2	"	82	75	"	"	"	0.0096
3	"	81	76	"	"	"	0.0098
4	"	78	"	"	"	"	0.0100
5	"	64	75	0.0006	0.0005	0.027	0.0036
6	"	61	"	"	"	"	0.0034
7	5 gms.	125	74	0.0008	0.0005	0.030	0.0020
8	"	190	71	0.0006	"	0.027	"
9	"	"	"	-	-	-	0.0018

Table IX

DISPLACEMENT OF CATIONS AND ANIONS BY METHYLENE BLU AND NEUTRAL VIOLET (N.V.) SOLUTION ON ADSORPTION CATIONS DISPLACED FROM SOIL NO. 5 BY CONDUCTIV

of r	Milli-equiv. of color ion	Wt. of Cl ion	Milli-equiv. of Cl ion	Wt. of AgCl	Wt. of Cl from AgCl	Milli-equiv. of Cl from AgCl	Fe milli-equiv of adsorbed dye	Milli-equi metals dis from soil conductiv water
	7	8	9	10	11	12	13	14
42	0.648	0.0230	0.648	0.0910	0.0225	0.634	0.020	0.14
57	0.657	0.0233	0.657	0.0916	0.0226	0.639	0.021	"
92	0.666	0.0236	0.666	"	"	"	"	"
	"	"	"	0.0920	0.0227	0.644	"	"
55	0.278	0.0099	0.278	0.0368	0.0091	0.257	-	"
	"	"	"	0.0354	0.0087	0.246	-	"

l- r.	Wt. of CaO	Wt. of Ca	Milli-equiv. of Ca	Wt. of $Mg_2P_2O_7$	Wt. of Mg	Milli-equiv. of Mg	Wt. of NaCl and KCl	Total wt. of $KClO_4$	W E fr ag
	7	8	9	10	11	12	13	14	
	0.0092	0.0064	0.326	0.0098	0.0021	0.176	0.0192	0.0044	0.
	0.0096	0.0068	0.342	0.0096	0.0020	0.173	0.0188	0.0024	
	0.0098	0.0070	0.350	"	"	"	0.0192	0.0042	
	0.0100	0.0072	0.358	"	"	"	0.0188	0.0032	
	0.0036	0.0025	0.128	0.0056	0.0012	0.100	0.0104	0.0026	
	0.0034	0.0024	0.121	"	"	"	"	0.0034	
	0.0020	0.0014	0.071	0.0022	0.0005	0.040	0.0074	0.0008	0.
	"	"	"	0.0020	0.0004	0.036	0.0072	0.0016	
	0.0018	0.0012	0.064	0.0022	0.0005	0.040	0.0074	0.0010	

able IX

ONS BY METHYLENE BLUE (M.B.) SOLUTION
TION ON ADSORPTION BY SOIL NO. 5.
L NO. 5 BY CONDUCTIVITY WATER

Fe milli-equiv of adsorbed dye	Milli-equiv. of metals displaced from soil by conductivity water	Total milli-equiv. of metals to be subtracted (13+14)	Total milli-equiv. of metals displaced by dye solution	Milli-equiv. metals displ by dye alone
13	14	15	16	17
0.020	0.14	0.16	0.74	0.58
0.021	"	"	0.75	0.59
"	"	"	0.76	0.60
"	"	"	0.77	0.61
-	"	0.14	0.33	0.19
-	"	0.14	0.32	0.18

Wt. of NaCl and KCl	Total wt. of $KClO_4$	Wt. of $KClO_4$ from reagents	Wt. of $KClO_4$	Wt. of K	Milli-equiv. of K	Wt. of KCl (calculated from column 14)	Total of NaC (13 mi 19)
13	14	15	16	17	18	19	20
0.0192	0.0044	0.0021	0.0023	0.0006	0.015	0.0023	0.0169
0.0188	0.0024	"	0.0003	0.0001	0.002	0.0012	0.0176
0.0192	0.0042	"	0.0021	0.0005	0.015	0.0022	0.0170
0.0188	0.0032	"	0.0011	0.0003	0.008	0.0017	0.0171
0.0104	0.0026	"	0.0005	0.0001	0.003	0.0013	0.0091
"	0.0034	"	0.0013	0.0003	0.009	0.0018	0.0086
0.0074	0.0008	0.0021	-	-	-	0.0011	0.0052
0.0072	0.0016	"	-	-	-	"	0.0050
0.0074	0.0010	"	-	-	-	"	0.0052

Milli-equiv. of metals displaced by dye alone 17
0.58
0.59
0.60
0.61
0.19
0.18

of KCl alculated from olumn 14) 19	Total wt. of NaCl (13 minus 19) 20	Wt. of NaCl from reagents 21	Wt. of NaCl 22	Wt. of Na 23	Milli-equiv. of Na 24	Total milli-equiv. of metals removed from the soil 25
0023	0.0169	0.0051	0.0118	0.0046	0.202	0.741
0012	0.0176	"	0.0125	0.0049	0.213	0.752
0022	0.0170	"	0.0119	0.0046	0.202	0.762
0017	0.0171	"	0.0120	0.0047	0.205	0.766
0013	0.0091	"	0.0040	0.0015	0.068	0.326
0018	0.0086	"	0.0035	0.0013	0.059	0.316
0011	0.0052	0.0051	none	-	-	0.141
"	0.0050	"	"	-	-	0.134
"	0.0052	"	"	-	-	-

Table X.

DISPLACEMENT OF CALCIUM BY METHYLENE BLUE (M.B.) SOLUTION AND NEUTRAL VIOLET (N.V.) SOLUTION ON ADSORPTION BY SOIL NO.6 CALCIUM DISPLACED FROM SOIL NO.6 BY CONDUCTIVITY WATER

	No.	Wt. of soil leached	Hours to filter	cc. filtrate	Gms. of dye per liter	Wt. of dye adsorbed	Wt. of color ion	Milli-equiv. of color ion
		1	2	3	4	5	6	7
Relationship between the anions and cations of the soil and dyes.	1	2 gms.	74	45	2.2 M.B.	0.0990	0.0880	0.309
	2	"	80	48.5	"	0.1067	0.0948	0.334
	3	"	70	45.5	"	0.1001	0.0889	0.313
	4	"	47	46.5	4.26 N.V.	0.1977	0.1821	0.719
	5	"	47	45	"	0.1914	0.1666	0.696
	6	"	38	41	"	0.1746	0.1520	0.635

	No.	Wt. of soil leached	Hours to filter	cc. filtrate	Wt. of CaO	Wt. of Ca	Milli-equiv of Ca
		1	2	3	4	5	6
Ca displaced from soil No.6 by M.B. and N.V. solutions.(continuation of above results.)	1	2 gms.	74	45	0.0082	0.0058	0.293
	2	"	80	48.5	0.0090	0.0064	0.321
	3	"	70	45.5	0.0076	0.0054	0.271
	4	"	47	46.5	0.0156	0.0111	0.557
	5	"	47	45	0.0154	0.0110	0.550
	6	"	38	41	0.0138	0.0098	0.492
Ca displaced from soil No.6 by conductivity water.	7	2 gms.	276	50	0.0014	0.0010	0.050
	8	"	"	40	0.0012	0.0008	0.042
	9	"	240	45	0.0012	"	"

.B.) SOLUTION
ON BY SOIL NO.6
IVITY WATER

of ad-rbed	Wt. of color ion	Milli-equiv. of color ion	Wt. of Cl ion	Wt. of AgCl	Wt. of Cl from AgCl	Milli-equiv. of Cl from AgCl	Milli-equiv. of Ca displaced from soil by conductivity water
5	6	7	8	9	10	11	12
0990	0.0880	0.309	0.0110	0.0378	0.0093	0.263	0.04
1067	0.0948	0.334	0.0119	0.0408	0.0100	0.284	"
1001	0.0889	0.313	0.0112	0.0362	0.0089	0.253	"
1977	0.1821	0.719	0.0256	0.0876	0.0216	0.611	"
1914	0.1666	0.696	0.0248	0.0874	0.0216	0.609	"
1746	0.1520	0.635	0.0226	0.0784	0.0193	0.547	"

of Ca	Milli-equiv of Ca
5	6
0.0058	0.293
0.0064	0.321
0.0054	0.271
0.0111	0.557
0.0110	0.550
0.0098	0.492
0.0010	0.050
0.0008	0.042
"	"

. of gCl	Wt. of Cl from AgCl	Milli-equiv. of Cl from AgCl	Milli-equiv. of Ca displaced from soil by conductivity water	Milli-equiv. of Ca displaced by dye solution	Milli-equiv. of metals displaced by dye alone
9	10	11	12	13	14
.0378	0.0093	0.263	0.04	0.29	0.25
.0408	0.0100	0.284	"	0.32	0.28
.0362	0.0089	0.253	"	0.23	0.23
.0876	0.0216	0.611	"	0.56	0.52
.0874	0.0216	0.609	"	0.55	0.51
.0784	0.0193	0.547	"	"	0.49

Four 2-gram samples of soil No.1 were leached with methylene blue solution until they became saturated with the dye. The soil was then washed with conductivity water until the amount of dye in the filtrate from each sample became constant.

Sample No.1 was leached with 50 cc. of conductivity water, No.2 with 50 cc. of a water solution of M. CaCl$_2$, No.3 with 50 cc. of ninety percent ethyl alcohol, and No.4 with 50 cc. of an alcoholic (90%) solution of M. CaCl$_2$. The dye in the filtrate was determined by the colorimetric method. Table XI shows that the aqueous CaCl$_2$ solution displaces two and one-half times as much dye as the pure water, while alcoholic CaCl$_2$ displaced more than three times as much dye as an equal amount of alcohol. Results are given below.

Table XI

Solutions used	Pure water	M. CaCl$_2$ in H$_2$O	Ethyl alcohol	M. CaCl$_2$ in ethyl alcohol
Sample	1	2	3	4
Gms. M.B. displaced by 50 cc. of solutions	0.0002	0.0005	0.0050	0.0160

Table XII

Table showing: (a) equivalents of methylene blue (M.B.) and neutral violet (N.V.) ions adsorbed by the soil.
(b) equivalents of anions and cations displaced during adsorption.
(c) ratio of dyes reacting metathetically to the total amount taken up.

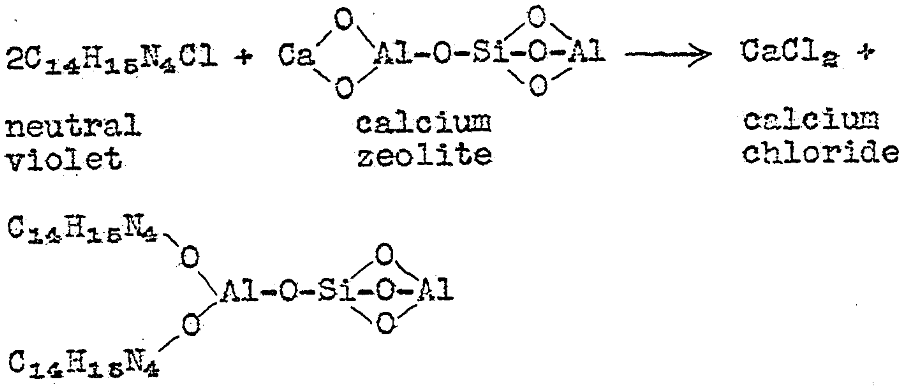
Soil	Wt. of soil used	Dye used	Milli-equiv. of color ion used	Milli-equiv. of metal ions displaced by dye solution	Milli-equiv. of Cl ion from dye solution	Milli-equiv. of Cl ion found in filtrate	Ratio of milli-equiv. of dye reacting metathetically to total milli-equiv. taken up	Ratio of milli-equiv. of dye not reacting (columns 7 & 8 calculated from col 5 & 6
	1	2	3	4	5	6	7	8
1	2 gms	M.B.	0.32	0.46	0.32	0.28	0.87	0.13
	"	N.V.	0.89	0.77	0.89	0.74	0.83	0.17
2	2 gms	M.B.	0.89	0.77	0.89	0.81	0.91	0.09
	"	N.V.	1.16	0.90	1.16	0.99	0.85	0.15
3	10 gms	M.B.	0.64	0.47	0.64	0.55	0.86	0.14
	"	N.V.	0.81	0.69	0.81	0.66	0.81	0.19
4	5 gms	M.B.	0.82	0.71	0.82	0.73	0.89	0.11
	"	N.V.	1.07	0.82	1.07	0.88	0.80	0.20
5	5 gms	M.B.	0.65	0.58	0.65	0.63	0.97	0.03
	"	N.V.	0.28	0.19	0.28	0.26	0.93	0.07
6	6 gms	M.B.	0.31	0.25	0.31	0.26	0.84	0.16
	"	N.V.	0.72	0.52	0.72	0.61	0.84	0.16

DISCUSSION

Mattson (6) found that the equivalents of metals displaced from a soil colloid by a N. $CaCl_2$ solution were approximately equal to the equivalents of methylene blue adsorbed by an equal amount of the same colloid, only when the pH of the two solutions was nearly the same. A solution containing two grams of methylene blue per liter gave a pH value of about 5.03 by the electrometric method, while a N. $CaCl_2$ solution saturated with CO_2 had a pH concentration of about 4.4. The H ion concentration of the various solutions used in this investigation was not determined.

In his work on subgrade clays Lord (7) found essentially a chemical reaction between the anions of the dye and cations of the soil colloids. Consequently, the number of equivalents of cations displaced from the soil colloid should be equal to the number of dye cations taken up. However, for some unexplained reason Lord found that the quantity of adsorbed dye was really the same as that of the recovered electrolytes. In this investigation the weights of the total electrolytes, displaced from the soils by the dye solutions, were not taken. All calculations are based on the equivalents of each ion displaced.

Table XII shows conclusively that between 0.8 and 0.9 of methylene blue and neutral violet is taken up by the soils because of a double decomposition reaction between the dyes and the soil colloids. Assuming that the soil colloids are zeolitic in nature the following reaction is representative.



neutral violet zeolite.

The only case where more equivalents of metals are displaced from a soil than equivalents of dye taken up is where methylene blue is adsorbed by soil No.1. Table III shows that this soil differs from the others since, the filtrates give a test for carbonate, when the soil is leached with the dye solutions and conductivity water. By comparing columns 4 and 6 of Table XII it is seen that in nine out of twelve determinations the equivalents of Cl ion found in the filtrate is slightly greater than the equivalents of cations found. The exceptions are soil No.1 on adsorption by neutral violet and methylene blue, and soil No.3 on adsorption by neutral violet. This would indicate that some of the positive ions which might have been liberated were not detected.

Various quantities of soil No.1 were leached with conductivity water. Results are shown in Table V. It is unusual to note that in equal volumes of filtrates, ten-gram samples give approximately the same equivalents of cations as one-gram and two-gram samples. This is explained however by observing that the time of filtration for the ten-gram sample is much less than for the other samples. When the smaller samples were used it was necessary to hasten the filtration by pressure. The time of filtration was not easily controlled since too much pressure packed the soil more firmly in the filtering column, and easily ruptured the wet filter papers. The nature of the soil caused a wide variation in the time of filtration. Some soils were quite pervious to water but very impervious to the dye solutions, while others were just the opposite. No amount of pressure could overcome a time factor with an impervious soil. The most outstanding example of this is in Table X where soil No.6 was leached with the dye solutions and conductivity water.

When a given quantity of a dye solution passes through a homogeneous soil sample certain equivalents of cations are displaced due to the solvent action of the water in contact with the soil colloids. By passing the same quantity of conductivity water through a new sample of the same soil in approximately the same time, the cations displaced by the water alone are found. The difference between these two values gives the equivalents of cations displaced by the dye alone. Results are given in Tables IV to X.

Since the time factor is important and is controlled with difficulty, we are not justified in drawing definite conclusions when the time of filtration for the dye solutions and conductivity water vary by a wide margin. Therein lies the greatest source of error in this investigation.

Other sources of error are: (a) Loss due to the evaporation of the filtrates during long periods of filtration. (b) Large samples of soil lengthened the filtering column. The dye solution had a tendency to creep down one side of the column of soil and give a highly colored filtrate long before all of the soil sample was saturated with the dye. In such cases the filtration was stopped and the filtrates analyzed. Too much dye in the filtrate gave colored residues in the determination of calcium and magnesium.

By leaching a soil colloid with $CaCl_2$ solution Mattson (6) assumed that the adsorbed calcium was equivalent to the cations exchanged. The adsorbed calcium was then displaced by hot NH_4Cl solution, and determined in the filtrate. The quantities of methylene blue required to neutralize the negative charge of a new sample of the same colloid corresponded well with the calcium displaced by the NH_4Cl solution. Therefore Mattson rightfully concludes that methylene blue is adsorbed by the soil colloids with an equivalent exchange of cations.

As was previously stated soil No.6 is soil No.1 after treatment with $CaCl_2$ solution. By observing columns 7 and 13 of Table X it is seen that the value for equivalents of calcium displaced by methylene blue is practically equal to the equivalents of the dye adsorbed. This is in agreement with Mattson's conclusions, but when the value for conductivity water is subtracted the agreement is not so good. The value for water is probably too high since the time of filtration is four times as long as for the methylene blue solution.

The point to be made in connection with Table X is that from the same weight of soil No.6 twice as many equivalents of calcium are displaced by neutral violet solution as by methylene blue solution. This is contrary to Mattson's idea since he says that at the iso-electric point all of the exchangeable bases in a soil colloid are displaced by methylene blue. When a soil has been saturated with methylene blue as in Table X the iso-electric point has been reached and exceeded.

The conclusions from the data of Table X are: (a) The power of a certain soil colloid to exchange bases depends on the nature of the dye adsorbed. (b) The electro-kinetic behavior of a certain soil colloid toward methylene blue is not an exact measure of its base exchange capacity.

CONCLUSIONS

1. The number of equivalents of neutral violet and methylene blue adsorbed by a soil colloid depends on the nature of the soil.
2. (a) From 84 to 97% of methylene blue react metathetically with the soil colloids, on adsorption by six different soils. (b) From 80 to 93% of neutral violet react metathetically on adsorption by the same six soils.
3. The number of equivalents of cations displaced from a soil colloid is approximately proportional to the number of equivalents of dye cations adsorbed by the soil.
4. The power of a soil colloid to exchange bases with a dye solution depends on the nature of the dye adsorbed.
5. The electro-kinetic behavior of a soil colloid toward methylene blue is not an exact measure of its base exchange capacity.
6. Lord's method of slow percolation for the determination of base exchange, on adsorption of dyes by soils, has the following advantages:

   (a) In general the longer a dye solution is in contact with a soil colloid the greater will be the yield of replaced cations.

   (b) The dye solution does not reach equilibrium until after 72 hours (17).

(c) The longer a soil is in contact with water the greater the yield of soluble salts.

(d) The liquids filter through the soil solumn giving clear filtrates with no colloidal suspensions.

7. Lord's method introduces the following difficulties:

(a) The time of filtration is not easily controlled since some soils are quite pervious to water but very impervious to the dye solutions, while others are just the opposite.

(b) The dye solutions have a tendency to creep down one side of a long soil column and give highly colored filtrates before the sample is completely saturated with the dye.

(c) Loss due to the evaporation of the filtrates during long periods of filtration.

8. 50 cc. of alcoholic M. $CaCl_2$ solution displaced 0.0160 gram of methylene blue from two grams of soil No.1 after the soil had adsorbed 0.1 gram of the dye from a water solution.

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