



**University of Arizona**  
College of Agriculture  
Agricultural Experiment Station

THE USE OF ALCOHOLIC SALT  
SOLUTIONS FOR THE DETERMI-  
NATION OF REPLACEABLE BASES  
IN CALCAREOUS SOILS

By O. C. MAGISTAD AND P. S. BURGESS

PUBLISHED BY  
**University of Arizona**  
UNIVERSITY STATION  
TUCSON, ARIZONA

## ORGANIZATION

### BOARD OF REGENTS

#### EX-OFFICIO MEMBERS

HIS EXCELLENCY, GEORGE W. P. HUNT, Governor of Arizona ..... Phoenix  
HON. CHARLES O. CASE, State Superintendent of Public Instruction .... Phoenix

#### APPOINTED MEMBERS

HON. ROBERT E. TALLY, Chancellor..... Jerome  
HON. LOUIS R. KEMPF, LL.B., Secretary..... Tucson  
HON. CLEVE W. VAN DYKE..... Miami  
HON. CHARLES M. LAYTON..... Safford  
HON. GEORGE M. BRIDGE..... Somerton  
HON. ROY KIRKPATRICK..... Globe  
HON. THEODORA MARSH, Treasurer..... Nogales  
HON. FRANKLIN J. CRIDER, M.S., Vice-Chancellor ..... Superior

BYRON CUMMINGS, A.M., LL.D., Sc.D. .... President of the University

#### AGRICULTURAL EXPERIMENT STATION

JOHN J. THORNER, A.M. .... Dean and Director  
JAMES G. BROWN, Ph.D. .... Plant Pathologist  
WALKER E. BRYAN, M.S. .... Plant Breeder  
PAUL S. BURGESS, Ph.D. .... Agricultural Chemist  
WALTER S. CUNNINGHAM, B.S. .... Dairy Husbandman  
HARRY EMBLETON, B.S. .... Poultry Husbandman  
RALPH S. HAWKINS, M.S. .... Agronomist  
ALLEN F. KINNISON, M.S. .... Horticulturist  
GEORGE E. P. SMITH, C.E. .... Agricultural Engineer  
ERNEST B. STANLEY, M.S. .... Animal Husbandman  
CHARLES T. VORHIES, Ph.D. .... Entomologist  
\*JAMES F. BREAZEALE, B.S. .... Research Specialist in Agricultural Chemistry  
WILLIAM G. MCGINNIES, B.S. .... Grazing Range Specialist  
MARGARET C. SMITH, Ph.D. .... Research Specialist in Home Economics  
DAVID W. ALBERT, M.S. .... Associate Horticulturist  
RICHARD N. DAVIS, B.S. .... Associate Dairy Husbandman  
OSCAR C. MAGISTAD, Ph.D. .... Associate Agricultural Chemist  
ELIAS H. PRESSLEY, M.S. .... Associate Plant Breeder  
HAROLD C. SCHWALEN, M.S. .... Associate Agricultural Engineer  
RUBERT B. STREETS, Ph.D. .... Associate Plant Pathologist  
IAN A. BRIGGS, M.S. .... Assistant Agronomist  
STANLEY P. CLARK, B.S. .... Assistant Agronomist  
WILLIAM F. DICKSON, M.S. .... Assistant Animal Husbandman  
HUBERT B. HINDS, M.S. .... Assistant Poultry Husbandman  
HOWARD V. SMITH, M.S. .... Assistant Agricultural Chemist  
MALCOLM F. WHARTON, M.S. .... Assistant Horticulturist  
ANDREW A. NICHOL, B.S. .... Assistant Entomologist  
G. GORDON POHLMAN, M.S. .... Assistant Agricultural Chemist  
CARLTON L. ZINK, B.S. .... Assistant Agricultural Engineer  
ARTHUR G. CARNS, B.S. .... Field Assistant in Irrigation and Horticulture  
†KENNETH P. PICKRELL, B.S. .... Field Investigator in Animal Husbandry  
CHARLES HOBART, M.S. .... Research Assistant  
GEORGE H. SERVISS, M.S. .... Field Assistant in Cotton Studies

\*In cooperation with the United States Department of Agriculture, Bureau of Plant Industry.

†In cooperation with the New Mexico Agricultural Experiment Station and the United States Department of Agriculture, Bureau of Animal Industry.

## CONTENTS

Introduction .....	481
Experimental .....	482
Solubility of barium chloride and barium bromide in alcoholic solutions ...	483
Equilibria in alcoholic and aqueous solutions.....	485
Rates of reaction and other factors affecting the determination of base-exchange capacity.....	485
The use of 0.1 N barium chloride in methyl alcohol.....	494
The methods finally adopted for determining replaceable bases in calcareous soils .....	496
Conclusions .....	497

## TABLES

	Page
Table I.—Solubility of $BaCl_2 \cdot 2H_2O$ in Varying Concentrations of Methyl and Ethyl Alcohol.....	483
Table II.—Solubility of $BaBr_2 \cdot 2H_2O$ in Varying Concentrations of Methyl and Ethyl Alcohol.....	483
Table III.—The Solubilities of $CaCO_3$ , $MgCO_3$ , and $CaSO_4 \cdot 2H_2O$ in 0.1 N Barium-chloride Solutions in Alcohols and Water.....	484
Table IV.—Replacement of Calcium by Barium Chloride and Ammonium Chloride in Aqueous and in Alcoholic Solutions.....	486
Table V.—Base-exchange Capacity of 50 Grams of Modified Mission Soil Containing no $CaCO_3$ , Using Different Displacing Solutions.....	487
Table VI.—Base-exchange Capacity of 25 Grams Modified Mission Soil Containing 4 Percent Calcium Carbonate, Using Different Displacing Solutions.....	489
Table VII.—Replaceable Calcium in University Farm Soil and in Yuma Sand, both Calcareous, Using Different Displacing Solutions.....	492
Table VIII.—Amounts of Calcium Dissolved from Apatite, Floats, and Hornblende by Aqueous and Alcoholic Salt Solutions.....	493
Table IX.—A Comparison of Ethyl- and Methyl-alcohol Solutions of 0.1 Normal Barium Chloride for Base-exchange Determinations on Calcareous Soils.....	494
Table X.—Exchangeable Calcium in a Modified Mission Soil Determined by Shaking and Filtering with 0.1 N Barium Chloride in Various Solvents .....	495

# THE USE OF ALCOHOLIC SALT SOLUTIONS FOR THE DETERMINATION OF REPLACEABLE BASES IN CALCAREOUS SOILS

By O. C. Magistad and P. S. Burgess

## INTRODUCTION

The importance of base-exchange reactions in soils is, at the present time, too well recognized by students of soil science to require an extensive discussion. The absorption of bases by growing plants, the retention and liberation of fertilizer salts, the formation and reclamation of alkali lands, soil-acidity phenomena and the use of sulphur, lime, and other soil amendments are some of the more essential soil processes which are largely dependent upon base-exchange reactions. When the importance of base-replacement was fully realized, the next logical step was to perfect quantitative methods for the determination of the positive ions thus held in soils. During the past 10 or 12 years a number of such attempts have been made, but thus far none has proved satisfactory for calcareous soils. The difficulty arises from the fact that calcium and magnesium carbonates are appreciably soluble in all the displacing solutions used, giving rise to several classes of errors. These are: (1) A portion of the calcium appearing in the filtrate is dissolved calcium (mainly from calcium carbonate) and is not exchangeable calcium. The correct amount of this calcium to be deducted from the total cannot accurately be determined. (2) The constant presence of dissolved calcium prevents the replacing action from going to completion. (3) An error may arise from the mechanical loss of the dispersed base-exchange complex, whenever exchangeable bases are determined by filtration or percolation methods. The ammonium-chloride method, probably the most widely used method of today, is open to severe criticism on the foregoing points, together with the fact that it dissolves from the soil considerable amounts of organic matter.

In the spring of 1926 these factors were discussed and methods were proposed\* for the determination of replaceable bases in the soils of arid and semi-arid regions which are usually calcareous and often carry considerable amounts of water-soluble salts (alkali). Since that time, a large amount of work has been done upon this subject in our laboratories.

---

\*See, "Methods for determining the replaceable bases of soils, either in the presence or absence of alkali salts," by P. S. Burgess and J. F. Beazdale, Arizona Agr. Expt. Sta. Tech. Bul. No. 9.

This has resulted in a decided modification of the methods formerly used, especially where calcareous soils are being investigated. The results of these later studies on methods, together with the procedure finally adopted, form the subject matter of this bulletin.

### EXPERIMENTAL

Experiments in our laboratories had indicated that base-exchange reactions took place about as readily in alcoholic salt solutions as in aqueous solutions. This suggested to the authors the use of alcoholic solutions of the common replacing salts, with the hope that calcium carbonate would be less soluble in them than in the corresponding water solutions.

Base-exchange reactions follow the type equation  $X=KC^{1/p}$  where  $X=$  the amount of base exchanged,  $C=$  concentration of replacing solution,  $K$  is a constant, and  $1/p$  is a constant usually having a value below 0.5. This equation clearly shows that doubling the concentration of the replacing solution increases the amount of  $X$  replaced but slightly. Experimental confirmation of this was given by aqueous, calcium-nitrate solutions reacting with a synthetic sodium zeolite. In this experiment, when 1.292 M. E. calcium was opposed to 1.780 M. E. of sodium, it caused a liberation of 1.135 M. E. of sodium, or 64 percent of the total. Increasing the concentration of calcium nearly fourfold to 5.175 M. E. caused a liberation of 1.375 M. E. of sodium, or 77 percent. This indicates that concentrated replacing solutions are very little more efficient than relatively weak ones; in fact they are very disadvantageous because such large quantities of the replacing salt are present in the filtrate or percolate that accurate determination of the replaced bases is rendered difficult. The authors consider 0.1 N barium-chloride solutions and 0.5 N ammonium-chloride solutions more satisfactory than are more concentrated ones.

In our search for a method using a barium salt in alcoholic solution, we arbitrarily decided upon 0.1 N  $BaCl_2$ . With this concentration the absorption of calcium, upon subsequent precipitation of the barium as chromate, is slight. Burgess and Breazeale \* found little or no absorption of calcium, while Von Sigmond† recovered 0.2609 gram Ca (0.2616 having been added) from a solution containing 5.3 grams  $BaCl_2$ . This is an error of 0.27 percent. The volume of the solution was not given, but estimating it to have been 500 cc., the solution would have been 0.1 normal with respect to barium chloride.

\*Loc. cit.

†Von Sigmond, A. A. S., 1927, "Über die Verschiedenen Methoden zur Bestimmung von 'S' und 'V'." Transactions of the Second Commission of the Int. Soc. of Soil Science, Vol. B pp. 123-145.

## SOLUBILITY OF BARIUM CHLORIDE AND BARIUM BROMIDE IN ALCOHOLIC SOLUTIONS

Since barium chloride is not soluble to the extent of a 0.1 N solution in either methyl or ethyl alcohol, solubility studies were made to determine how strong the alcoholic solutions could be and just dissolve enough barium chloride or barium bromide to form a tenth-normal solution. Such tests were made by adding an excess of the salt to the solvent, shaking for 2 to 6 hours, and allowing to stand overnight. In the morning an aliquot of the supernatant liquid was pipetted off and the halogen content obtained by titrating with silver nitrate, using potassium chromate as indicator. The results so obtained are given in tables I and II.

TABLE I.—SOLUBILITY OF  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$  IN VARYING CONCENTRATIONS OF METHYL AND ETHYL ALCOHOL.

	Specific gravity at 15°/15°	Percent alcohol by weight	Normality	Temperature of solubility determinations Degrees C.
Ethyl alcohol	0.7911	99.76	0.0002	18
	.8048	96.3	.003	18
	.8336	85.7	.010	18
	.8625	73.9	.080	18
	.8701	70.7	.101	23
	.8746	68.8	.132	23
Methyl alcohol	.811	94.8	.054	20
	.828	88.7	.077	20
	.845	82.4	.096	28
	.848	81.3	.104	25
	.849	80.8	.116	25
	.851	80.1	.118	25

TABLE II.—SOLUBILITY OF  $\text{BaBr}_2 \cdot 2\text{H}_2\text{O}$  IN VARYING CONCENTRATIONS OF METHYL AND ETHYL ALCOHOL.

	Specific gravity at 15°/15°	Percent alcohol by weight	Normality	Temperature of solubility determinations Degrees C.
Ethyl alcohol	0.800	98.0	0.028	15
	.812	92.0	0.135	28
Methyl alcohol	.798	99.0	1.7	18
	.813	93.5	1.68	15

The data in tables I and II show that 0.1 N solutions of barium chloride can be obtained in 68 to 70-percent ethyl alcohol or in 80-percent methyl alcohol, and that 0.1 N solutions of barium bromide can be made in 92-percent ethyl alcohol and in 100-percent methyl alcohol.

The solubilities of C. P. precipitated  $\text{CaCO}_3$ ,  $\text{MgCO}_3$ , and  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  were determined in these solutions as follows: An excess of the carbonate or gypsum was added to the displacing solution and shaken for 2 to 6 hours at  $20^\circ\text{C}$ ., allowed to stand overnight, an aliquot of the supernatant liquid pipetted off, the alcohol evaporated, taken up with about 200 cc. water, the barium precipitated as the chromate, and the Ca or Mg determined in the filtrate by the soap-titration methods. The solubilities so determined are given in Table III.

TABLE III.—THE SOLUBILITIES OF  $\text{CaCO}_3$ ,  $\text{MgCO}_3$ , AND  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  IN 0.1 N BARIUM-CHLORIDE SOLUTIONS IN ALCOHOLS AND WATER. ALL DETERMINATIONS WERE MADE AT  $20^\circ\text{C}$ ., AND ARE EXPRESSED AS PARTS PER MILLION OF Ca OR Mg.

	BaCl <sub>2</sub> in 67.8% EtOH	BaCl <sub>2</sub> in 80% MeOH	BaBr <sub>2</sub> in 95% EtOH	BaBr <sub>2</sub> in 95% MeOH	BaCl <sub>2</sub> in water
CaCO <sub>3</sub> ---	15.4 14.0	10.9	15.6	141 ---	72 ---
MgCO <sub>3</sub> ---	229	131	110	239	442
CaSO <sub>4</sub> ·2H <sub>2</sub> O		955	675	612	645

The solubilities in Table III indicate that  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$  in methyl alcohol should be the best displacing agent, followed very closely by  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$  in ethyl alcohol. Burgess and Breazeale\* have called attention to the fact that the amount of  $\text{CaCO}_3$  dissolved by a displacing solution from soil, is considerably less than that dissolved from precipitated  $\text{CaCO}_3$ . This may be caused by the fact that complete equilibrium does not take place, because precipitated  $\text{CaCO}_3$  is more finely divided, or because of side-reactions in which salts may be set free which diminish or increase the solubility of the calcium carbonate. Complete equilibrium cannot take place if the displacing solution is leached through rapidly and the calcium carbonate is present in relatively large particles. To obtain a comparison of the solubility of the calcium carbonate in a barium-chloride solution when leached through a calcareous soil, with that of precipitated calcium carbonate, a silty, clay soil was leached with barium chloride in alcohol to convert all of the zeolite to barium zeolite. It was then further leached with more barium chloride in alcohol and the amount of calcium appearing in the filtrate determined. The amounts were 13.0 p.p.m. with ethyl alcohol and 9.2 p.p.m. with methyl alcohol, compared with 14 and 11 respectively when precipitated calcium carbonate was used.

\*Loc cit

Many investigators prefer to use ammonium salts for displacement purposes rather than barium salts and for that reason the authors simultaneously investigated the possibilities of ammonium-chloride solutions in alcohol. Normal solutions of ammonium chloride can be obtained in 71-percent ethyl alcohol and 75-percent methyl alcohol at 25°C. At colder temperatures less concentrated alcoholic solutions must be used. The solubility of calcium carbonate in normal ammonium chloride in 71-percent ethyl alcohol was found to be 45 to 47 p.p.m. Ca at 20°C. This solubility is only one-fourth as great as the corresponding solubility in an aqueous solution of this salt. In a 75-percent methyl-alcohol solution of normal ammonium chloride the solubility of calcium carbonate was found to be 60 p.p.m. Ca. The solubility of calcium carbonate is thus greater in methyl-alcohol solutions than in the ethyl-alcohol solutions. Magnesium carbonate had solubilities of 180 and 548 p.p.m. Mg in the ethyl- and methyl-alcohol solutions respectively.

#### EQUILIBRIA IN ALCOHOLIC AND AQUEOUS SOLUTIONS

The same equilibrium does not result when equal amounts of zeolite or soil are treated with equal amounts of 0.1 N barium chloride in water, ethyl alcohol, or methyl alcohol. In the first experiment proving this, 2 grams air-dry calcium zeolite, 0.5 gram air-dry calcium zeolite, and 5 grams calcium-zeolite soil, were each treated with 150 cc. of 0.1 N solutions of barium chloride in water, 68-percent ethyl alcohol, and 80-percent methyl alcohol. The bottles containing the materials were shaken by machine for 12 hours, allowed to stand overnight, and the supernatant solutions analyzed for calcium. In a similar way trials were made using normal ammonium chloride in water and in 70-percent ethyl alcohol as the replacing agents. The results appear in Table IV.

The figures in Table IV show that replacement in ethyl-alcohol solutions is very nearly equal to that in water solutions. This is true with both barium chloride and ammonium chloride. Replacement in methyl-alcohol solutions is somewhat less than in ethyl-alcohol solutions.

The data in Table IV indicate equilibrium at the end of a considerable time period, 12 hours or longer, but show nothing about the rate at which these equilibria were established. We know that base-exchange reactions in water are almost instantaneous; there is, however, a slow time effect superimposed upon the rapid initial reaction as final equilibrium is approached.

#### RATES OF REACTION AND OTHER FACTORS AFFECTING THE DETERMINATION OF BASE-EXCHANGE CAPACITY

In order to obtain data on the rapidity and completeness of base exchange by the various methods, a series of percolation tubes, each contain-

ing 50 grams of modified Mission soil, was leached with successive 250-cc. portions of the various replacing solutions. The zeolite in the soil had previously all been converted into calcium zeolite and the soil washed free from chlorides. No calcium carbonate was present. The calcium appearing in the filtrate was, therefore, all replaceable calcium and was determined by soap-titration methods. The data are given in Table V, in which each figure is an average of duplicate percolations.

TABLE IV.—REPLACEMENT OF CALCIUM BY BARIUM CHLORIDE AND AMMONIUM CHLORIDE IN AQUEOUS AND IN ALCOHOLIC SOLUTIONS.

Replacing agent	2 grams CaZ			0.5 gram CaZ			5 grams soil		
	Ca replaced M. E.	Ca left M. E.	Percent replaced	Ca replaced M. E.	Ca left M. E.	Percent replaced	Ca replaced M. E.	Ca left M. E.	Percent replaced
0.1 N BaCl <sub>2</sub> in water	2.97	4.69	38.8	0.88	1.04	45.8	1.55	0.75	67.4
0.1 N BaCl <sub>2</sub> in 68% ethyl alcohol	2.95	4.71	38.5	0.87	1.05	45.4	1.51	0.79	65.7
0.1 N BaCl <sub>2</sub> in 80% methyl alcohol	2.77	4.89	36.1	0.73	1.19	38.0	1.27	1.03	55.3
1.0 N NH <sub>4</sub> Cl in water	3.52	4.14	46.1	0.95	0.97	49.4	1.24	1.06	54.0
1.0 N NH <sub>4</sub> Cl in 70% ethyl alcohol	3.37	4.29	44.0	0.93	0.99	48.4	1.17	1.13	50.9

The data in Table V show that barium chloride in alcohol did not extract quite as much calcium in the first 250 cc. as did barium chloride in water. After 750 cc. of replacing solution had percolated through the column, most of the exchangeable calcium had been taken out by barium chloride in water while barium chloride in alcohol was then extracting relatively large amounts. After six or seven portions had been leached through, the total calcium extracted was the same by both methods.

In the trials with ammonium chloride, almost identical action was obtained with water and alcohol. There was only a very slight tendency for the alcoholic solutions to replace calcium less rapidly than did the water solutions.

TABLE V.—BASE-EXCHANGE CAPACITY OF 50 GRAMS OF MODIFIED MISSION SOIL CONTAINING NO  $\text{CaCO}_3$  USING DIFFERENT DISPLACING SOLUTIONS.

(Grams Ca. in each 250-cc. portion)

Replacing salt	Solvent	First portion	Second portion	Third portion	Fourth portion	Fifth portion	Sixth portion	Seventh portion	Total
0.1 N $\text{BaCl}_2$	Water	0.2921	0.0930	0.0090	0.0950	0.0320	0.0010	0.0005	0.4025
0.1 N $\text{BaCl}_2$	68% ethyl alcohol	0.2267	0.0855	0.0410	0.0235	0.0150	0.0105	0.0035	0.4050
N $\text{NH}_4\text{Cl}$	Water	0.3900	0.0130	0.0035	0.0009				0.4074
N $\text{NH}_4\text{Cl}$	70% ethyl alcohol	0.3860	0.0145	0.0045	0.0010				0.4060

The fact that practically identical total amounts of calcium were obtained by the four methods shows that all are accurate for non-calcareous soils. One of the reasons for the slightly less rapid replacing action in alcoholic solutions may be the greater rate of percolation of the alcoholic solutions. In nearly all trials in this laboratory, the alcoholic solutions percolated much faster than did the water solutions. Cutting down the rate of percolation by means of rubber tubing and clamps increased the amount of replaced calcium per 100 cc. Thus 0.1 N  $\text{BaCl}_2$  in water replaced 0.112 gram Ca in 100 cc. while equally strong  $\text{BaCl}_2$  in alcohol replaced only 0.079 gram when percolating at the rate of 1 drop in 3 seconds. When the rate of leaching of the alcoholic solution was cut down to 1 drop in 20 seconds, the amount of calcium replaced per 100 cc. rose to 0.107 gram. This amount is but little less than the amount extracted by the water solution.

Alcoholic as well as aqueous solutions of barium chloride and ammonium chloride having been found to be satisfactory as replacing agents for non-calcareous soils, their application to calcareous soils was next investigated. The same soil was used as before (modified Mission soil), except that 4-percent C. P. calcium-carbonate powder was incorporated with it. A series of percolation tubes, each containing 25 grams of this soil was set up and leached with 250-cc. portions of the replacing salt solutions. The data are recorded in Table VI, each figure being an average of duplicates.

It should be remembered that the results reported in Table VI were with the same soil as previously used, only that 4 percent calcium carbonate had been added. One hundred grams of this soil thus contained the same amount of replaceable calcium as did 96 grams of the original soil. The base-exchange capacity of the soil used in Table VI was, therefore, 0.782 gram per 100 grams soil, or 0.195 per 25 grams soil. The total amounts of calcium found in the percolates from the 25-gram portions of soil were all greater than 0.195 gram. This was caused by the fact that some of the calcium appearing in the percolate was dissolved calcium. Here then we have the unique situation of knowing the base-exchange capacity of the soil and can find the amount of calcium dissolved from the calcium carbonate present by each replacing solution, thus 0.0239, 0.0077, 0.1807, and 0.0374 gram calcium were dissolved by 0.1 N barium chloride in water, 0.1 N barium chloride in alcohol, normal ammonium chloride in water, and normal ammonium chloride in alcohol respectively. These figures are equivalent to 19.1, 6.2, 144, and 30 p.p.m. of Ca in the solutions. These amounts are much lower than the solubility of calcium carbonate in these salt solutions upon continued shaking. The solubilities on continued shaking with precipitated  $\text{CaCO}_3$  are approximately 60, 14, 200, and 47 p.p.m. respectively.

TABLE VI.—BASE-EXCHANGE CAPACITY OF 25 GRAMS MODIFIED MISSION SOIL CONTAINING 4 PERCENT CALCIUM CARBONATE, USING DIFFERENT DISPLACING SOLUTIONS.

(Grams Ca. in each 250-cc. portion)

Replacing salt	Solvent	First portion	Second portion	Third portion	Fourth portion	Fifth portion	Total
0.1 N BaCl <sub>2</sub>	Water	0.1970	0.0097	0.0047	0.0038	0.0037	0.2189
0.1 N BaCl <sub>2</sub>	68% ethyl alcohol	0.1895	0.0053	0.0037	0.0024	0.0018	0.2027
N NH <sub>4</sub> Cl	Water	0.2350	0.0512	0.0473	0.0422	0.0420	0.3757
N NH <sub>4</sub> Cl	70% ethyl alcohol	0.1944	0.0132	0.0125	0.0060	0.0063	0.2324

This indicates that the replacing solution passing through the soil does not become completely saturated with calcium carbonate. Obviously it is impossible to determine the correct blank in each case to be subtracted from the total calcium found in order that replaceable calcium may be ascertained. One cannot assume that the replacing agent becomes saturated with dissolved calcium carbonate for the foregoing experiment has proved this to be fallacious. In this case the barium-chloride solutions were only one-third to one-half saturated while the ammonium-chloride solutions were about two-thirds saturated. With another soil and source of calcium carbonate, this relationship might not hold.

Various methods and principles have been used in determining the amount of calcium dissolved by replacing solutions. Gedroiz\* has analyzed the soil for carbonates before and after the base-exchange determination, but such a method may lead to a large error. Hissink † leaches the soil with 1 liter of ammonium-chloride solution and considers, very correctly, that this liter has removed practically all replaceable bases. The soil is then leached with a second liter of ammonium chloride and the calcium contained therein considered equal to the amount of dissolved calcium in the first liter. Such a procedure leads to errors because the first liter in passing through the soil column dissolves the finely divided calcium carbonate, while the second liter, passing through at the same rate, attacks the remaining large particles of calcium carbonate and hence cannot dissolve similar amounts. Again with soils containing a small amount of carbonate, for instance one-half percent, the major portion of the calcium would be dissolved by the first liter of ammonium chloride and practically all of the remainder, by the second. The second, however, might readily have far less calcium than it could dissolve were more of the carbonate present.

In the past it has been the practice of some, in the case of certain replacing solutions, to subtract blanks equal to the solubility of calcium carbonate in those solutions at equilibrium, when determining the replaceable bases in calcareous soils. Others have subtracted no blanks, and especially is this true where replacing solutions such as barium chloride, sodium chloride, and salts other than ammonium chloride have been used. The least chance of error arises when a salt solution having only a negligible or very small  $\text{CaCO}_3$  solubility is used, such as barium chloride in ethyl or methyl alcohol.

An attempt was made to determine replaceable calcium in a fine, sandy-loam soil from the University Farm and in a Yuma fine sand with the

\*Gedroiz, K. K. 1918. "Contribution to the method of determining the zeolite bases in the soil." *Zhur. Opit. Agron.* Vol. 19, pp. 226-244.

†Hissink, D. J. 1922. "Beitrag zur Kenntniss der Adsorptionsvorgänge im Boden." *Intern. Mitt. f. Bod.* Vol. 12, pp. 102-104.

four solutions employed above on the modified Mission soil. These soils were chosen because they are very low in replaceable Ca but fairly high in  $\text{CaCO}_3$ . In these tests, 50 grams of the University Farm soil were used and 100 grams of the Yuma sand. The former contains 4.5 percent of  $\text{CaCO}_3$  and the latter 6 percent. Two-hundred-and-fifty-cc. portions of the several solutions were used each time. All trials were made in duplicate and each figure in Table VII, reporting the data, is an average of two trials.

The total calcium found in the percolates must be corrected for dissolved calcium. Taking the Yuma sand treated with barium chloride in alcohol, the maximum correction when at equilibrium for dissolved calcium would here be 15 p.p.m. or 0.0037 gram per 250 cc. of the replacing solution. This correction would leave 0.0418, 0.0009, 0.0, 0.0, and 0.0, as the amounts of replaceable calcium in the five successive portions. But we have shown that in leaching operations final equilibrium between the salt solution and the calcium carbonate present in the soil is seldom if ever attained. An average of many determinations indicates that approximately two-thirds of the possible  $\text{CaCO}_3$  present in a saturated solution, when found in the percolate, is due to *dissolved* rather than *replaced* Ca. Table VII also shows that, with all the displacing solutions, replacement is complete after the third 250-cc. portion has passed through the soils, the amounts of Ca in the fourth and fifth portions in all cases being approximately two-thirds of the solubilities of  $\text{CaCO}_3$  in the several salt solutions used. Considering the solubilities of  $\text{CaCO}_3$  in these alcoholic and aqueous salt solutions, and using the total Ca extracted by the first three 250-cc. portions (see Table VI, last column), we find that the amounts of replaced Ca per 100 grams soil would lie between the following limits for the University Farm soil:

		Range
0.1 N $\text{BaCl}_2$ in water	0.0084 gm. to 0.0274 gm.	0.0190
0.1 N $\text{BaCl}_2$ in alcohol	0.0098 gm. to 0.0164 gm.	0.0066
1.0 N $\text{NH}_4\text{Cl}$ in water	0.0186 gm. to 0.1536 gm.	0.1350
1.0 N $\text{NH}_4\text{Cl}$ in alcohol	0.0079 gm. to 0.0400 gm.	0.0321

The amounts of replaced Ca per 100 grams soil lie between the following limits for the Yuma fine sand:

		Range
0.1 N. $\text{BaCl}_2$ in water	0.0477 gm. to 0.0684 gm.	0.0207
0.1 N $\text{BaCl}_2$ in alcohol	0.0463 gm. to 0.0529 gm.	0.0066
1.0 N $\text{NH}_4\text{Cl}$ in water	0.0393 gm. to 0.1717 gm.	0.1324
1.0 N $\text{NH}_4\text{Cl}$ in alcohol	0.0323 gm. to 0.0645 gm.	0.0322

TABLE VII.—REPLACEABLE CALCIUM IN UNIVERSITY FARM SOIL AND IN YUMA SAND, BOTH CALCAREOUS, USING DIFFERENT DISPLACING SOLUTIONS.

(Grams Ca in each 250-cc. portion.)

University Farm Replacing salt	Solvent	First portion	Second portion	Third portion	Fourth portion	Fifth portion	Total in first 3 portions
0.1 N BaCl <sub>2</sub>	Water	0.0111	0.0111	0.0052	0.0063	0.0066	0.0274
0.1 N BaCl <sub>2</sub>	68% ethyl alcohol	0.0112	0.0030	0.0022	0.0019	0.0024	0.0164
N NH <sub>4</sub> Cl	Water	0.0538	0.0520	0.0478	0.0486	0.0482	0.1536
N NH <sub>4</sub> Cl	70% ethyl alcohol	0.0149	0.0146	0.0105	0.0108	0.0106	0.0400
Yuma sand							
0.1 N BaCl <sub>2</sub>	Water	0.0530	0.0078	0.0076	0.0073	0.0075	0.0684
0.1 N BaCl <sub>2</sub>	Alcohol	0.0455	0.0046	0.0028	0.0023	0.0022	0.0529
N NH <sub>4</sub> Cl	Water	0.0840	0.0453	0.0424	0.0409	0.0420	0.1717
N NH <sub>4</sub> Cl	Alcohol	0.0422	0.0117	0.0106	0.0113	0.0098	0.0645

The first figure in each case represents what we consider to be the most nearly accurate amount of exchangeable Ca as determined by that particular replacing solution, while the last figure represents the total amount of Ca obtained in the first three extractions and contains replaceable Ca plus dissolved Ca. In calculating the first figures the blank subtracted in each case is an average of the Ca contained in the fourth and fifth portions. It will be obvious that the most accurate method will have the narrowest range. This range is the difference between the limits and approximately represents the solubilities of  $\text{CaCO}_3$  in the solutions. It will be seen from these data that the narrowest range is obtained in the case of the barium chloride in alcohol and for that reason it should be the best method for accurate, base-replacement determinations in calcareous soils.

It must be borne in mind that the soils used were exceptionally low in exchangeable calcium, making accurate determinations somewhat difficult. With soils high in exchangeable calcium such as the Mission soil, the percentage error by the various methods would be much less.

In soils free from readily soluble salts, bases may be dissolved from minerals other than carbonates by the replacing solutions and appear in the percolate as replaceable base. Excellent examples of this are the solubilities of apatite, floats, and hornblende in our replacing solutions. In the case of floats and hornblende only, the calcium going into solution was measured, while both calcium and phosphorus were measured in the case of apatite. All minerals were ground to pass a 100-mesh sieve and 4 grams were shaken in 150 cc. of the replacing solution several hours. The data are recorded in Table VIII.

TABLE VIII.—AMOUNTS OF CALCIUM DISSOLVED FROM APATITE, FLOATS, AND HORNBLLENDE BY AQUEOUS AND ALCOHOLIC SALT SOLUTIONS.

	Apatite		Floats	Hornblende	
	p.p.m. Ca	p.p.m. P	p.p.m. Ca	p.p.m. Ca	p.p.m. Mg
0.1 N $\text{BaCl}_2$ in $\text{H}_2\text{O}$ .....	47	N.D.	18	4	1
0.1 N $\text{BaCl}_2$ in alcohol.....	N.D.	N.D.	14	N.D.	N.D.
N $\text{NH}_4\text{Cl}$ in $\text{H}_2\text{O}$ .....	190	16	74	19	4
N $\text{NH}_4\text{Cl}$ in alcohol.....	N.D.	N.D.	29.4	N.D.	N.D.
Water .....	10	N.D.	N.D.	N.D.	N.D.

In making base-exchange determinations on acid soils one usually

assumes that all of the calcium obtained in the percolate is replaceable calcium and that none has been dissolved. From the foregoing table we see that if the soil contains calcium compounds as apatite, hornblende, or floats, a small amount of the calcium may have been dissolved from these minerals. In the case of the apatite, a phosphorus determination on the filtrate showed that calcium and phosphorus were not dissolved in chemically equivalent amounts. In making base-exchange determinations on calcareous soils, the calcium dissolved from these minerals is very little compared with the amounts dissolved from calcium carbonate, and hence can be neglected.

#### THE USE OF 0.1 N BARIUM CHLORIDE IN METHYL ALCOHOL

Table III showed that the solubility of calcium carbonate in 0.1 N barium chloride in 95-percent methyl alcohol was about 10 p.p.m. which is about five p.p.m. less than where ethyl-alcohol solutions are used. Because of the greater cost of methyl alcohol to educational institutions and because the rate of base-exchange is slightly less in methyl-alcohol solutions, its use as a replacing solution was not fully investigated. A single percolation test on soils was made with 0.1 N barium chloride in methyl alcohol, and also in ethyl alcohol with results as given in Table IX.

TABLE IX.—A COMPARISON OF ETHYL- AND METHYL-ALCOHOL SOLUTIONS OF 0.1 NORMAL BARIUM CHLORIDE FOR BASE-EXCHANGE DETERMINATIONS ON CALCAREOUS SOILS.  
(Grams calcium in each 100-cc. portion.)

	First portion	Second portion	Third portion	Fourth portion	Fifth portion	Total
68% ethyl alcohol . . .	0.079	0.069	0.045	0.030	0.013	0.236
95% methyl alcohol . . .	0.077	0.068	0.045	0.026	0.016	0.232

A difference of 5 p.p.m. solubility of Ca in the two replacing solutions is equivalent to 0.002 gram Ca when 500 cc. of solution is used. This would make the two methods equivalent in their action within the limits of experimental error. For laboratories and institutions unable to secure ethyl alcohol duty-free, the use of methyl alcohol as a solvent for barium chloride is suggested.

The foregoing experimental work has been done using percolation methods. These take considerable time and are objectionable when a few analyses only are wanted. With the idea of trying these displacing solutions in the more rapid shaking and filtering method, the following experiment was performed. Twenty-five grams of modified Mission soil having 0.0202 gram of replaceable calcium were put into each of four

800-cc. bottles. To each of the last three bottles 1 gram calcium carbonate was added. Five hundred cc. of displacing solution were next added to each bottle, numbers 1 and 2 receiving 0.1 N barium chloride in water, and numbers 3 and 4 receiving 0.1 N barium chloride in ethyl and methyl alcohol respectively. The bottles were shaken 1 hour in a machine and the soil material decanted onto filters. The soil remaining in the bottles was washed onto the filters with additional replacing solution and washing continued until four 250-cc. portions of filtrate were obtained for each. Calcium was then determined in each of the portions of filtrate. The results are given in Table X.

TABLE X.—EXCHANGEABLE CALCIUM IN A MODIFIED MISSION SOIL DETERMINED BY SHAKING AND FILTERING WITH 0.1 N BARIUM CHLORIDE IN VARIOUS SOLVENTS.  
(Grams calcium)

	First portion 500 cc.	Second portion 250 cc.	Third portion 250 cc.	Fourth portion 250 cc.	Fifth portion 250 cc.	Total Ca	Ex- change- able calcium
Water. No CaCO <sub>3</sub> present . . .	0.155	0.020	0.011	0.004	0.002	0.202	0.202
Water. CaCO <sub>3</sub> present . . .	0.165	0.025	0.013	0.009	0.008	0.220	0.145
68% ethyl alcohol CaCO <sub>3</sub> present . . .	0.160	0.022	0.013	0.008	0.004	0.207	0.185
95% methyl alcohol CaCO <sub>3</sub> present . . .	0.145	0.023	0.017	0.012	0.007	0.204	0.189

The theoretical amount of dissolved calcium carbonate in 0.1 N barium chloride in water at equilibrium is equal to approximately 60 p.p.m. of calcium. Thus the amount of calcium dissolved in 250 cc. would approach 0.015 gram as a limit. As the third, fourth, and fifth portions contain less than this, they carry dissolved calcium only. Subtracting 0.045 from the sum of the calcium in the first two portions (500 cc. and 250 cc.) we obtain 0.145 gram as the exchangeable calcium by this method.

By similar calculations using solubilities of 15 p.p.m. and 10 p.p.m. of calcium in ethyl- and methyl-alcohol salt solutions we have exchangeable calcium equal to 0.185 and 0.189 gram calcium respectively.

The correct figure 0.202 is not attained in any case where  $\text{CaCO}_3$  is present. The difficulty arises in that  $\text{CaCO}_3$  does not dissolve to form a completely saturated solution in these replacing agents, yet deductions are almost always made on that basis where shaking procedures are employed. The greatest accuracy occurs with 0.1 N barium chloride in methyl alcohol but a greater amount of displacing solution must be used here than with the other solvents as the reaction is slower.

THE METHODS FINALLY ADOPTED FOR DETERMINING REPLACEABLE BASES IN CALCAREOUS SOILS.

A. Percolation Method: Adapted for routine analyses where large numbers of determinations are required.

Fifty grams (25 grams if high in clay) of air-dry soil are placed in a glass percolating tube, (in this laboratory specially blown Pyrex tubes 24 cm. long, 3 cm. inside diameter are used. These tubes have a 9 cm stem attached), and leached with 500 cc. of the displacing solution. Additional 250-cc. aliquots are percolated through the soil column until the amount of calcium found in the percolate does not exceed the solubility of calcium from finely divided  $\text{CaCO}_3$  in the displacing solution. One liter is usually sufficient. The alcoholic percolates are evaporated to dryness, taken up with water, and the replaced bases determined as set forth in detail by Burgess and Breazeale\*. A small amount of waxy material may be dissolved from the soil by the alcohol, but it does not interfere with the determinations. The small cost of alcohol per determination makes it unprofitable to recover it by distillation.

It is understood that soils containing soluble salts and gypsum must first be leached to remove these salts.

With heavy soils several days may be required for percolation, but very little of the analyst's time is required except in making the actual determinations.

For very accurate work, the total calcium found is corrected by subtracting the dissolved calcium. This equals 0.015 gram per liter of percolate if 0.1 N  $\text{BaCl}_2$  in ethyl alcohol is used, 0.010 gram per liter with 0.1 N  $\text{BaCl}$  in methyl alcohol, and 0.045 gram per liter with normal  $\text{NH}_4\text{Cl}$  in ethyl alcohol. For ordinary work, unless replaceable calcium is very low, the solubility of  $\text{CaCO}_3$  in the barium chloride in alcohol-displacing solutions may be neglected.

B. Filtration Method: Adapted to use where small numbers of determinations are required.

\*See, "Methods for determining the replaceable bases of soils either in the presence or absence of alkali salts," by P. S. Burgess and J. F. Breazeale. Arizona Agr. Expt. Sta. Tech. Bul. No. 9, pp. 197-203.

Fifty grams soil (25 grams if high in clay) are shaken in a bottle for 1 hour with 500 cc. of the displacing solution and filtered through paper. The material remaining in the bottle is washed onto the filter with more of the displacing solution until all the soil is brought onto the filter and the whole leached with the displacing solution until 250 cc. filtrate are obtained. Enough 250-cc. portions of filtrate are secured until the last one does not contain more calcium than can be accounted for by solubility of calcium carbonate. Usually 1 liter is sufficient; sandy soils require less. The filtrates are evaporated to dryness, taken up in water and analyses made as under A.

### CONCLUSIONS

The importance of the base-exchange complex (zeolites) to soil economy is pointed out and the necessity for a method whereby replaceable bases can be determined accurately in calcareous soils is discussed. Some of the faults of the earlier procedures when applied to calcareous soils are mentioned.

The method here proposed for making quantitative determinations of replaceable bases in calcareous soils employs alcoholic (ethyl or methyl) salt solutions as the displacing agents. We prefer 0.1 N barium chloride in 68-percent ethyl alcohol. It is found that the activity of such a solution approaches that of an aqueous solution and that the solubility of  $\text{CaCO}_3$  in the alcoholic solution is extremely low (between 10 and 15 p.p.m.). By percolation methods, a large number of determinations can be made at once with a minimum of time and effort on the part of the analyst. The alcohol is evaporated, the Ba precipitated as the chromate and the Ca, Mg, and other bases determined in the supernatant liquid by the soap-titration and by precipitation methods. Where alkali salts are present, these must be leached out with water before percolation with the alcoholic salt solution is begun.

