

ART. IV.—*On the Influence of Strength of Acid and Time of Digestion in the Extraction of Soils*; by R. H. LOUGHRIDGE, of Oxford, Miss.

THE following investigation was undertaken with a view of determining the extent to which the variations likely to occur in the extraction of soils by hydrochloric acid, for the purpose of analysis, can influence the ultimate results; the special object being to ascertain the comparability of the analyses made in connection with the Agricultural Survey of Mississippi, both amongst themselves, and with those made by similar methods, by Dr. Peter, of soils collected by the Surveys of Kentucky and Arkansas.

In beginning the analyses of Mississippi soils in 1859, Dr. Hilgard adopted the following method, which has also been adhered to by his successors in this work, in over two hundred analyses made.

The soil (*i. e.*, "fine earth") is pulverized with a wooden pestle and thoroughly mixed. The hygroscopic moisture is determined, after exposing it in a space saturated with vapor, in a layer not exceeding 1^{mm} in thickness, for twelve hours, by drying at 200° C. in a paraffine bath. Of this dried substance from two to three grams are usually used in the general analysis, the methods employed being in general those adopted by Dr. Peter.* In another portion, after ignition, the phosphoric acid is determined by digestion for five days with nitric acid at 100° C., evaporation, precipitation by ammonium molybdate, digestion at 100°, solution in ammonia and precipitation by magnesium sulphate.

For general analysis the soil is digested in hydrochloric acid of strength 1.115 (as a rule) at 100°. It is then evaporated to complete dryness, this adding another day to the digestion.

In the insoluble residue the soluble silica is determined by boiling with sodic carbonate. The alumina and ferric oxide are precipitated according to Rose's method of boiling, for the complete separation of manganese, magnesium and calcium. The mixed precipitate is treated with potassic hydrate.

After precipitation of the lime by ammonic oxalate, the ammoniacal salts are destroyed by Lawrence Smith's method, with aqua regia; and the residue converted into nitrates, from which sulphuric acid is precipitated by barium nitrate. The alkalies are then separated by treatment with oxalic acid, ignition and washing. In the residue, barium, manganese and magnesium are separated as usual.

* Ky. Report, vol. iii.

With the aid of a Bunsen's filtering apparatus we can, by this method, complete an analysis in five days, exclusive of digestion; and three analyses may be in progress at the same time.

The substance experimented upon was a subsoil, a typical representative of the best yellow loam uplands of Mississippi, from the table lands of Benton Co., Miss.; No. 219 of the Survey Collection.*

To determine the question as to whether such variations in the *strength* of the acid, as might possibly have occurred in the use of the steam-distilled (i. e., from a retort surrounded by steam) product, without previously ascertaining its concentration, portions of the subsoil were digested five days with hydrochloric acid of the strength, severally, of 1.100, 1.115 (the normal concentration) and 1.160.

As to the *time* during which the soil must be digested in hydrochloric acid that the (sensible) limit of its solvent action upon the important soil ingredients may be reached, Dr. Peter's practice has been to digest for about ten days, in his 800 analyses of Kentucky and Arkansas soils; while for reasons of convenience, half that time has been adopted in the analyses of the Mississippi Survey. The question whether, under these circumstances, the two series can be deemed comparable, was approached by digestions, for periods of one, three, four, five and ten days, of the same soil with the same large excess of acid of 1.115; all precautions being taken to accomplish each analysis as nearly as possible under the same circumstances.

For the digestions, use was made of porcelain beakers (the use of glass being objectionable because of its solubility); the same amounts (40^{ccm}) of acid were used, and steam kept up about twelve hours each day.

The hour of "putting down" was carefully noted, and at the end of the allotted time the solution was poured off from the insoluble residue, and each evaporated to dryness separately and reunited in solution, to prevent any further action of the acid.

This result points to the conclusion, that while lime and magnesia (being readily dissolved) are probably present chiefly as carbonates or hydrocarbonates, potash as well as alumina, and to some extent lime, are present as silicates, and for that reason are not as fully extracted by acid of low strength as by that of 1.115; although the former acts more powerfully than that of 1.160

The latter fact (the coincident result of two analyses), though unlooked for, is not without analogies, although its precise

* The analysis of the subsoil of a neighboring tract is given in Hilgard's Report, 1860, p. 292.

cause, in this case, still requires elucidation. Whether the maximum of action is exerted by acid of 1·115, is another question of some interest, to be determined hereafter.

The results of the investigation as to strength of acid are as shown in the following table:

Ingredients.	Sp. Gr. of Acid.		
	1·10	1·115	1·160
Insoluble Residue,-----	71·88	70·53	74·15
Soluble Silica,-----	11·38	12·30	9·42
Potash,-----	·60	·63	·48
Soda,-----	·13	·09	·35
Lime,-----	·27	·27	·23
Magnesia,-----	·45	·45	·45
Br. Ox. Manganese,-----	·06	·06	·06
Ferric Oxide,-----	5·15	5·11	5·04
Alumina,-----	6·84	8·09	6·22
Sulphuric Acid,-----	·02	·02	·02
Volatile Matter,-----	3·14	3·14	3·14
	100·02	100·69	99·29
Amt. of Soluble Matter,--	24·00	27·02	22·27
Amt. of Soluble Bases,--	13·50	14·70	12·83

It thus appears that in the strongest acid the amount of insoluble residue is far greater than in either of the others, and that the difference lies chiefly in the soluble silica and alumina (i. e., clay), together with potash and lime. The other ingredients seem to be indifferent as to the strength of the acid.

Between the acids of strength 1·10 and 1·115 the difference is not so great, but the advantage is clearly with the latter, the amounts of silica, potash and alumina being greater, while the lime remains the same in both.

As for the comparability of the analyses as affected by the probable variations of strength of acid, I remark that the acid used for distillation by Dr. Peter, as Dr. Hilgard informs me, was the "C. P." of commerce, whose strength rarely much exceeds or falls below that of 1·115; while that used by us was usually the crude, diluted nearly to the same strength. The first and last portions coming over were habitually, I believe, rejected in either laboratory. Under these circumstances, it is very improbable that either of the extremes of sp. gr. above discussed ever actually occurred; especially as regards the stronger acid, which being in small quantity, would always be mixed with the succeeding weaker distillates.

It is therefore not probable that the percentage of potash or other important ingredients could have been so far underestimated in either of the series of analyses, as to seriously influence their comparability, either within themselves, or with each other.

The experiments on the influence of the time of digestion, made with acid of 1·115, resulted as follows :—

Ingredients.	No. of Days Digested.				
	1.	3.	4.	5.	10.
Insoluble residue, -----	76·97	72·66	71·86	70·53	71·79
Soluble Silica, -----	8·60	11·18	11·64	12·30	10·94
Potash, -----	·35	·44	·57	·63	·62
Soda, -----	·06	·06	·03	·09	·28
Lime, -----	·26	·29	·28	·27	·27
Magnesia, -----	·42	·44	·47	·45	·44
Br. ox. manganese, -----	·04	·06	·06	·06	·06
Ferric oxide, -----	4·77	5·01	5·43	5·11	4·85
Alumina, -----	5·15	7·38	7·07	7·88	7·16
Phosphoric acid, -----				·21	·21
Sulphuric acid, -----	·02	·02	·02	·02	·02
Volatile matter, -----	3·14	3·14	3·14	3·14	3·14
Total, -----	99·63	100·68	100·55	100·69	99·80
Amount of soluble matter.	19·67	24·88	25·57	27·02	24·87
“ “ “ bases,	11·05	13·68	13·91	14·49	13·68

It thus appears, that the amount of dissolved ingredients increases up to the fifth day, the increase becoming, however, very slow as that limit is approached. It is also found that the ingredients offering the greatest resistance to this action are the same as those whose amounts were sensibly affected by the strength of acid, viz., silica, potash and alumina.*

In regard to lime and magnesia, one day's digestion not being sufficient for full extraction, it is evident that they do not exist in the soil as carbonates or hydric oxides only, as has been supposed ; but also as silicates.

A comparison of the results of the five and ten day digestions shows that the solvent action of the acid has substantially ceased, there being no further increase of the amount of dissolved matter.

So far, therefore, as the time of digestion is concerned, the analyses of the Mississippi Survey are strictly comparable with those of Arkansas and Kentucky soils, made by Dr. Peter.