

From this table it will be noticed that when the Cadmium cells are first set up they differ somewhat in E. M. F. But after about a month they come to have a normal value which is common to all. Moreover, this value is not affected by any moderate change in temperature, and so far as our experience goes, these cells are more easily made, and there is less variation in E. M. F. between them than there is between the Clark cells.

It will be noticed that the values given in Table No. 1 are simply relative, but we have made absolute determination of their E. M. F., and find for the Weston cell the value 1.01851 volts when the resistance is measured in Legal ohms; or 1.015633 volts when the resistance is measured in International ohms.

The result of our investigations lead to the following conclusions:

*First.* That the Cadmium cell is more easily constructed than the Clark cell.

*Second.* That it has practically no temperature coefficient.

*Third.* That the E. M. F. of the Cadmium cell is even less variable than that of the Latimer Clark.

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SOIL SOLVENTS FOR AVAILABLE POTASH AND PHOSPHORIC ACID. BY H. A. HUSTON AND J. M. BARRETT.

It seems to be accepted that in the case of worn soils solution in strong mineral acid gives little insight into the availability of their potash and phosphoric acid. More recently the use of dilute organic acids, such as the one per cent. citric acid used by Dr. Bernard Dyer<sup>1</sup> and the acid ammonium oxalate used by Dr. A. M. Peter<sup>2</sup>, has been tried with more promising results. The theory of the use of dilute organic acid solutions seems to rest on the idea that plant roots give off fluids containing organic acids which act on the soil in a degree comparable with the effect of the dilute acids employed in the laboratory experiments.

While I do not question that plant roots in contact with polished marble, or even granite, may make appreciable markings on the carbonate of lime and on the feldspar of the granite, the conditions of the experiment, as usually conducted, differ radically from those found in the field, for in the experiment the plants are not supplied with normal soil water. So far as I have observed, normal soil waters give an alkaline reaction. No inconsiderable part of the food of the plants comes to it dissolved in the soil waters. The work of Dr. H. J. Wheeler<sup>3</sup> shows what marked difficulty is encountered in growing plants on a well-drained soil having an acid reaction.

Soil waters rising from a subsoil are charged with more or less of mineral salts; and if the upper layers of the soil have a different composition from the lower layers in which the soil waters have been charged, we may expect chemical changes to take place according to the well established facts of soil absorption.

In view of these considerations some work was undertaken with alkaline solvents. The first solution used contained the same amount of ammonium oxalate as the solution used by Dr. Peter; but instead of the acid an amount of ammonia equivalent to the acid was added. All work is based on the same relative quantities of soil and solution as used by Dr. Peter—200 grams soil and 1,000 cc solution. In working with Dyer's solution the digestions continued at room temperature for seven days, with shaking at frequent intervals. All the other digestions were continued for five hours, with constant shaking in the apparatus described in Indiana Agricultural Experiment Station Bulletin 55, and Wiley's Principles and Practice of Agricultural Analysis, Volume II, page 142. The flasks were inverted every thirty seconds. The utmost care was used to secure clean precipitates of potassium platinic chlorid.

#### THE SOILS USED.

The Kentucky soils are those used for work by the Association of Official Agricultural Chemists for the past two years, and are described on page 31 of Bulletin 47, Chemical Division United States Department of Agriculture. Briefly stated, the soil requires the addition of potash to produce satisfactory crops of corn, potatoes and tobacco, but seems to contain enough available potash for a good wheat crop. The field tests indicate abundance of available phosphoric acid. Soil No. 1 has received phosphoric acid and nitrogen, and Soil No. 2 has received potash and nitrogen. Of the Indiana soils the one marked "Turley" is from Orange County. It is a medium clay resting on a red clay, which in turn rests on the limestone rock of the region.

The land has been under cultivation for some seventy years, and at one time was so badly worn as to be considered of very little value. The sample was drawn after plowing for corn in the spring of 1896. In 1895 wheat had been so poor on this land that hogs were turned in to eat the standing crop. In the spring of 1896 the clover was so uneven that the land was put in corn, of which it produced in this very favorable year for corn, thirty-seven bushels per acre on the unfertilized plats. The owner does not believe that it can produce a profitable crop of wheat without the use of some commercial fertilizer or manure. The usual application has been one hundred pounds ground bone per acre. The field tests this year showed marked gain in corn from the use of acid phosphate and

potash, but increasing the amount of potash from thirty to sixty pounds per acre gave no increased yield. Original timber, oak.

The soil marked "Campbell" is from Monroe County, and represents a cold, badly drained clay, resembling the so-called "crawfish" clay. Commercial fertilizers are considered necessary for wheat. Field tests this year showed marked gains on corn from the use of acid phosphate and potash, but increasing the amount of potash from thirty to sixty pounds per acre gave no increased yield. Original timber, poplar and mixed hard woods.

The station land is a second-bottom soil, resting on gravel. It is a dark, productive loam. In favorable seasons the land will produce fifty bushels of corn and thirty bushels of wheat per acre without the use of fertilizers or manure. While commercial fertilizers have some effect in increasing the crops, the use of them on this land has not been profitable. Original timber: Black walnut, oak, maple, wild cherry and some hickory. The plats from which the samples were drawn have been in wheat since 1888. Plats 3 E. 1 and 3 E. 4 have received no fertilizers; plat 3 E. 2 has received "complete" chemical fertilization, and plat 3 E. 5 has received applications of barnyard manure. In five years (1890 to 1894), 3 E. 1 lost to crop 8.1 pounds phosphoric acid, 11.3 pounds potash, and 17.8 pounds nitrogen; plat 3 E. 4 lost 7.2 pounds phosphoric acid, 10.1 pounds potash, and 15.9 pounds nitrogen; plat 3 E. 2 lost net 0.8 pounds phosphoric acid, 3.2 pounds potash, and 7.9 pounds nitrogen; plat 3 E. 5 gained 4.2 pounds phosphoric acid, 6.9 pounds potash, and 0.3 pounds nitrogen. The plats contain one-tenth acre each. Plat 3 E. 4, a blank plat, contains humus (by Huston's method) 45.3 per cent., and nitrogen in this humus 4.52 per cent. Plat 3 E. 5, which has received barnyard manure, contains humus 5.6 per cent., and nitrogen in this humus 5.71 per cent.

The mechanical analyses of the Indiana soils are shown in Table I.

TABLE I.

| SOURCE.             | Gravel. | Coarse Sand. | Sand. | Silt. | Clay. | Moisture and Organic. | Total. |
|---------------------|---------|--------------|-------|-------|-------|-----------------------|--------|
|                     | %       | %            | %     | %     | %     | %                     | %      |
| Turley.....         | 0.25    | 0.16         | 7.05  | 39.82 | 47.64 | 5.31                  | 100.23 |
| Campbell.....       | 1.57    | .67          | 12.23 | 45.02 | 35.21 | 5.08                  | 99.78  |
| Station 3 E. 4..... | 1.56    | 2.56         | 13.95 | 35.42 | 36.54 | 9.94                  | 99.97  |

Since Peter's solution and the alkaline ammonium oxalate contain a salt of ammonia, it was thought that the phenomena of soil absorption might come into play. To test this, a solution of the same alkalinity, but containing the same amount of ammonia as chloride as was contained in the other solutions in the form of oxalate, was used. To test the question of soil absorption pure and simple, a neutral solution of ammonium chlorid, 17.2 grams to the liter, the same amount of ammonium chlorid as in the previous solution was used.

The soils were also digested with ammonium hydrate, sp. gr. 0.96, containing 17.2 grams ammonium chlorid per liter, and with ammonium hydrate, sp. gr. 0.96 alone. Ammonium hydrate was tried, because, as I have previously shown<sup>5</sup>, phosphates of iron and alumina are dissolved by ammonium hydrate. At first we hoped to utilize the ammonia and ammonium chlorid mixture, but in the presence of the ammonium chlorid not a trace of phosphoric acid was dissolved.

On the Kentucky soils a number of solvents were tried at a higher temperature. This modification seemed no improvement—rather the reverse; and it was decided to use room temperature.

Table II contains the results of the work. The total potash in each soil, and the amount of potash and phosphoric acid removed by hydrochloric acid, sp. gr. 1.115, are also added for the purpose of comparison:

TABLE II.

| SOURCE OF SAMPLE.                  |                                                     | Dyer's Solution 1% Citric Acid (Room Temp.; 7 Days). | Peter's Solution (Room Temp.; 5 Hrs.) | Alkaline Am. Oxalate (Room Temp.; 5 Hrs.) | Peter's Solution (65° C.; 5 Hrs.) | Alkaline Am. Oxalate (65° C.; 5 Hrs.) | Alkaline Am. Chloride (65° C.; 5 Hrs.) | Ammonia Sp. Gr. 0.96 (Room Temp.; 5 Hrs.) | 17.2 Grams Am. Chloride in 1 Liter Ammonia Sp. Gr. 0.96 (Room Temp.; 5 Hrs.) | 17.2 Grams Am. Chloride in 1 Liter Water (Room Temp.; 5 Hrs.) | 17.2 Grams Am. Chloride in 1 Liter 1½ Hcl. (Room Temp.; 5 Hrs.) | Ammonia Sp. Gr. 0.96 (Room Temp.; 20 Hrs.) | N 15 Calcium Chloride (Room Temp.; 5 Hrs.) | Ammonia 2% (Room Temp.; 5 Hrs.) | Ammonia 2% (Room Temp.; 20 Hrs.) | Alkaline Am. Chloride (Room Temp.; 5 Hrs.) | Total Potash by J. L. Smith Method. | Soluble in Hcl. Sp. Gr. 1.115 on Steam Bath. |  |
|------------------------------------|-----------------------------------------------------|------------------------------------------------------|---------------------------------------|-------------------------------------------|-----------------------------------|---------------------------------------|----------------------------------------|-------------------------------------------|------------------------------------------------------------------------------|---------------------------------------------------------------|-----------------------------------------------------------------|--------------------------------------------|--------------------------------------------|---------------------------------|----------------------------------|--------------------------------------------|-------------------------------------|----------------------------------------------|--|
| KENTUCKY:                          |                                                     |                                                      |                                       |                                           |                                   |                                       |                                        |                                           |                                                                              |                                                               |                                                                 |                                            |                                            |                                 |                                  |                                            |                                     |                                              |  |
| No. 3 potash and nitrogen          | (P <sub>2</sub> O <sub>5</sub> ) (K <sub>2</sub> O) | .0541) .0628                                         | .0138                                 | .0492                                     | .0222                             | 0                                     | .0337                                  | 0                                         | 0                                                                            | 0                                                             | 0                                                               | 0                                          | 0                                          | 0                               | 0                                | 0                                          | 0                                   | .431                                         |  |
|                                    |                                                     | .0069) .0189                                         | .0226                                 | .0185                                     | .0173                             | .0196                                 | .0140                                  | .0162                                     | .0238                                                                        | 0                                                             | 0                                                               | 0                                          | 0                                          | 0                               | 0                                | .0176                                      | 1.485                               | .340                                         |  |
| No. 1 phos. acid and nitro-<br>gen | (P <sub>2</sub> O <sub>5</sub> ) (K <sub>2</sub> O) | .0560) .0776                                         | .0165                                 | .0565                                     | .0195                             | 0                                     | .0352                                  | 0                                         | 0                                                                            | 0                                                             | 0                                                               | 0                                          | 0                                          | 0                               | 0                                | 0                                          | 0                                   | .332                                         |  |
|                                    |                                                     | .0038) .0183                                         | .0183                                 | .0144                                     | .0200                             | .0135                                 | .0165                                  | .0148                                     | .0137                                                                        | .0218                                                         | 0                                                               | 0                                          | 0                                          | 0                               | 0                                | .0134                                      | 1.467                               | .437                                         |  |
| No. 1-No. 3                        | (P <sub>2</sub> O <sub>5</sub> ) (K <sub>2</sub> O) | .0019) .0148                                         | .0027                                 | .0073                                     | .0027                             | 0                                     | .0015                                  | 0                                         | 0                                                                            | 0                                                             | 0                                                               | 0                                          | 0                                          | 0                               | 0                                | 0                                          | 0                                   | .001                                         |  |
| No. 3-No. 1                        | (K <sub>2</sub> O)                                  | .0031) .0015                                         | .0082                                 | .0015                                     | .0038                             | .0031                                 | .0008                                  | .0025                                     | .0020                                                                        | 0                                                             | 0                                                               | 0                                          | 0                                          | 0                               | 0                                | .0042                                      | .0018                               | .023                                         |  |
| INDIANA:                           |                                                     |                                                      |                                       |                                           |                                   |                                       |                                        |                                           |                                                                              |                                                               |                                                                 |                                            |                                            |                                 |                                  |                                            |                                     |                                              |  |
| Turley                             | (P <sub>2</sub> O <sub>5</sub> ) (K <sub>2</sub> O) | .0028) .0031                                         | .0025                                 | .....                                     | .....                             | .....                                 | .0025                                  | 0                                         | 0                                                                            | .0026                                                         | .0076                                                           | 0                                          | .0077                                      | 0                               | .0131                            | 0                                          | .....                               | .056                                         |  |
|                                    |                                                     | .0321) .0370                                         | .0262                                 | .....                                     | .....                             | .....                                 | .0083                                  | .0274                                     | .0388                                                                        | .0400                                                         | .0266                                                           | .0161                                      | .0132                                      | 0                               | .0248                            | 0                                          | 2.147                               | .354                                         |  |
| Campbell                           | (P <sub>2</sub> O <sub>5</sub> ) (K <sub>2</sub> O) | .0073) .0073                                         | .0016                                 | .....                                     | .....                             | .....                                 | .0035                                  | 0                                         | 0                                                                            | .0102                                                         | .0112                                                           | 0                                          | .0125                                      | .0112                           | 0                                | 0                                          | .....                               | .045                                         |  |
|                                    |                                                     | .0244) .0232                                         | .0161                                 | .....                                     | .....                             | .....                                 | .0058                                  | .0152                                     | .0257                                                                        | .0269                                                         | .0158                                                           | .0130                                      | .0086                                      | 0                               | .0188                            | 1.898                                      | .....                               | .283                                         |  |
| EXPERIMENT STATION:                |                                                     |                                                      |                                       |                                           |                                   |                                       |                                        |                                           |                                                                              |                                                               |                                                                 |                                            |                                            |                                 |                                  |                                            |                                     |                                              |  |
| 3 E. 1 blank plat.                 | (P <sub>2</sub> O <sub>5</sub> ) (K <sub>2</sub> O) | .0047) .0267                                         | .0157                                 | .....                                     | .....                             | .....                                 | .0304                                  | 0                                         | 0                                                                            | .0074                                                         | .0249                                                           | 0                                          | .0290                                      | .0348                           | 0                                | 0                                          | .....                               | .124                                         |  |
|                                    |                                                     | .0053) .0530                                         | .0156                                 | .....                                     | .....                             | .....                                 | .0073                                  | .0177                                     | .0331                                                                        | .0251                                                         | .0098                                                           | .0123                                      | .0082                                      | 0                               | .0176                            | 1.958                                      | .....                               | .450                                         |  |
| 3 E. 2 chemical fertilizer.        | (P <sub>2</sub> O <sub>5</sub> ) (K <sub>2</sub> O) | .0053) .0258                                         | .....                                 | .....                                     | .....                             | .....                                 | .0298                                  | 0                                         | 0                                                                            | .0039                                                         | .0182                                                           | 0                                          | .0423                                      | .0364                           | 0                                | .....                                      | .....                               | .118                                         |  |
|                                    |                                                     | .0258) .0025                                         | .0180                                 | .....                                     | .....                             | .....                                 | .0067                                  | .0183                                     | .0309                                                                        | .0298                                                         | .0185                                                           | .0104                                      | .0094                                      | 0                               | .0259                            | 0                                          | 1.876                               | .470                                         |  |
| 3 E. 4 blank plat.                 | (P <sub>2</sub> O <sub>5</sub> ) (K <sub>2</sub> O) | .0025) .0246                                         | .0140                                 | .....                                     | .....                             | .....                                 | .0227                                  | 0                                         | 0                                                                            | .0016                                                         | .0205                                                           | 0                                          | .0339                                      | .0342                           | 0                                | .....                                      | .....                               | .121                                         |  |
|                                    |                                                     | .0246) .0019                                         | .0157                                 | .....                                     | .....                             | .....                                 | .0082                                  | .0186                                     | .0319                                                                        | .0318                                                         | .0119                                                           | .0112                                      | .0100                                      | 0                               | .0136                            | 1.955                                      | .....                               | .447                                         |  |
| 3 E. 5 manure.                     | (P <sub>2</sub> O <sub>5</sub> ) (K <sub>2</sub> O) | .0019) .0268                                         | .....                                 | .....                                     | .....                             | .....                                 | .0231                                  | 0                                         | 0                                                                            | .0051                                                         | .0262                                                           | 0                                          | .0358                                      | .0335                           | 0                                | .....                                      | .....                               | .107                                         |  |
|                                    |                                                     | .0268) .0314                                         | .0158                                 | .....                                     | .....                             | .....                                 | .0104                                  | .0218                                     | .0354                                                                        | .0391                                                         | .0160                                                           | .0134                                      | .0094                                      | 0                               | .0300                            | 2.035                                      | .....                               | .471                                         |  |

It will be seen that Dyer's solution and Peter's solution resemble each other in a general way in their action on the phosphates of the Kentucky soil (rich in phosphates) and on the Turley soil (poor in phosphates); while on the Campbell land (poor in phosphates), and on the station land (fairly good in phosphates) they differ radically.

In their action on potash the two solutions differ widely in the case of the Kentucky soils containing too little available potash for corn, while they resemble each other in their action on the other soils, which seem from field tests with corn to contain considerably higher available potash than the Kentucky soils.

Dyer's solution extracts more phosphoric acid from the Kentucky soil that had received phosphoric acid than from the one receiving none. From the station soil it extracts the highest phosphoric acid from the soil that had received superphosphate; but it failed to extract as much phosphoric acid from the soil receiving its phosphoric acid in the form of manure as it extracted from either of the plats that had received no fertilizers. On the average, Dyer's solution extracts no more phosphoric acid from the station soils known to contain a fair supply of available phosphoric acid than from the clay soils known to be very deficient in phosphoric acid.

Dyer's solution dissolves more potash from the Kentucky soil that had received potash than from the one not receiving any.

From the clay soils, which seem from field tests with corn to be somewhat deficient in available potash, it dissolves relatively high amounts of potash. From the station soils it dissolved no more potash from the soil that had received full applications of muriate of potash than from the soils that had received no potash.

Peter's solution would indicate that there was a good supply of available phosphoric acid in the Campbell soil, where it is known to be deficient. It would also indicate that the Turley land was higher in available potash than the station soil, although the field tests indicate to the contrary.

The acid solutions of Dyer and Peter seem to fail when applied to soils of different types, although their indications are in the right direction when applied to soils of exactly the same type, such as the Kentucky soils.

The alkaline ammonium oxalate dissolves practically as much potash from the Kentucky soil as from the station soil, although the available potash is much higher in the latter, as shown by field tests.

It dissolves about the same amount of phosphoric acid from the Kentucky soil as from the station soil, both of which have a fair amount of available phosphoric acid, although the former has a much higher total phosphoric acid content. It distinguishes these soils very sharply from the clay soils known to be deficient in phosphoric acid.

The alkaline ammonium chlorid distinguishes the fertilized from the unfertilized plats very sharply on the station soil and to a fair extent on the Kentucky soil. Its action on the clay lands is in accord with what knowledge we have in regard to the potash in these soils.

The ammonium chlorid dissolved in ammonia, sp. gr. 0.96, gives results on potash in the same general direction as the mildly alkaline ammonium chlorid, but the differences are less sharply defined. As this solution is rather troublesome to work with, I would prefer to use the mildly alkaline one.

The neutral ammonium chlorid distinguishes very well the Kentucky soil from the station soil, gives fair indications on the clay soils, but fails to show the effect of the potash salts applied to the station soil.

Ammonium hydrate, sp. gr. 0.96, gives results on potash that are quite at variance with what is known about these soils, but on phosphoric acid it gives promising results. The character of the individual results indicates that the digestion was not continued long enough to complete the reaction. Yet the results clearly distinguished the lands poor in phosphoric acid from those known to be well supplied with available phosphoric acid. The only case where it seems at fault is on plat 1 of the station soil. But every other solvent acts in the same way, indicating that the sample from this plat is really higher in phosphoric acid than the sample from the other blank plat, No. 4. Crop tests covering five years show that plat 1 has a crop-producing capacity about 15 per cent. greater than plat 4.

Ammonium chlorid in neutral and alkaline solution removes notable quantities of lime from soils. The quantities were determined and are given in Table III.

TABLE III.

PER CENT. OF CALCIUM OXID REMOVED BY VARIOUS SOLVENTS.

| SOURCE OF SAMPLE.    | By alkaline ammonium chlorid (5 hours; room temp.). | By neutral ammonium chlorid (5 hours; room temp.). | By HCl, sp. gr. 1.115 (10 hours on steam bath). |
|----------------------|-----------------------------------------------------|----------------------------------------------------|-------------------------------------------------|
| Kentucky No. 3.....  | 0.144                                               | 0.173                                              | 6<br>0.51                                       |
| Kentucky No. 1.....  | .122                                                | .196                                               | 6<br>.31                                        |
| Turley .....         | .066                                                | .122                                               | .....                                           |
| Campbell.....        | .114                                                | .143                                               | .....                                           |
| Station 3 E. 1. .... | .096                                                | .216                                               | .....                                           |
| Station 3 E. 2. .... | .089                                                | .246                                               | .....                                           |
| Station 3 E. 4. .... | .113                                                | .226                                               | .447                                            |
| Station 3 E. 5. .... | .105                                                | .227                                               | .472                                            |

It will be seen that the alkaline ammonium chlorid removes about one-fourth and neutral ammonium chlorid about one-half as much lime as the hydrochloric acid used in the customary method of soil analysis. The station soils are practically free from carbonates, containing an average of only 0.015 per cent. of carbon dioxide.

Of the solvents used we consider alkaline ammonium chlorid and neutral ammonium chlorid promising for available potash, and ammonium hydrate promising for available phosphoric acid. Alkaline ammonium oxalate seems to do very well for available phosphoric acid in some cases, but the material is rather troublesome to work with on account of the large amount of organic matter that goes into solution. Where ammonium chlorid is present the solutions are nearly free from organic matter, filter very rapidly, and the ignition is readily made, leaving only a small amount of bases to be removed before determining the potash. Tatlock's method was tried for potash, but proved unsatisfactory.

We have tried chlorids of calcium, magnesium, and sodium, but prefer to use the ammonium salt, since it introduces no involatile base which would interfere with the potash determination.

We are now at work with ammonium hydrate, continuing the digestion for a longer time and changing the strength of the solution. We are also testing ammonium chlorid dissolved in 1 per cent. hydrochloric acid. We shall also test

the question of the relative quantities of the soil and solvents used as the present amounts—200 grams soil to 1 liter of solvent—seems to involve too small a volume of solvent. While we feel encouraged by the outcome of the work reported above, it must be borne in mind that before any method of soil testing can be considered satisfactory, it must give reliable indications on soils of different types that have been subjected to investigation by field tests; and these tests must not be confined to one crop, but must relate to all the crops likely to be produced on the land under investigation. From data now at hand it seems probable that certain soils may have ample potash in an available form to produce good crops of cereals, while not having enough to produce profitable crops of corn, potatoes, or tobacco. This phase of the matter must be kept in mind in deciding upon any definite amount of soluble ingredients which shall be used as a minimum in judging of the fertilizer needs of a soil.

Purdue Agricultural Experiment Station, November, 1896.

- (1) Jour. Chem. Soc., London, March, 1894. This paper contains a resume of suggestions by various authors and special investigations by Dr. Dyer.
- (2) Chem. Div. U. S. Dept. Agr., Bull. 47, p. 32.
- (3) Rhode Island Agr. Exp. Sta., 7th Ann. Rpt., p. 152.
- (4) Chem. Div. U. S. Dept. Agr., Bull. 38, p. 84; Wiley's Agr. Analysis, vol. 1, p. 326.
- (5) Chem. Div. U. S. Dept. Agr., Bull. 31, p. 99.
- (6) Determined by Harry Snyder. See Bull. 47, U. S. Dept. Agr., Chem. Div., p. 49.

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ACTION OF AMMONIUM CITRATE AND CITRIC ACID ON BASIC SLAG. BY H.  
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[ABSTRACT.]

This is a continuation of the work carried on for several years by the authors under the general head of the availability of commercial phosphates. This paper deals with the two most prominent materials proposed for determining the availability of the phosphoric acid in the slag. The factors controlling the action of the reagents are discussed under the following heads:

- I. Influence of time of digestion.
- II. Influence of temperature.
- III. Influence of acid (citric) and alkali (ammonia).
- IV. Influence of quantity of slag used.