sugars showed that the amount of lead was so slight as to account for only 0.044 and 0.042 cc. respectively, amounts too small to affect appreciably the polariscopic reading, even in these samples of the lowest grades. In high grade sugars, which constitute by far the greater portion of the world's supply, the dilution is correspondingly small and insignificant.

It will thus be seen that these authors are in the unfortunate position of having explained away twice as much difference as ever exists, and that by indirect methods; while the most direct possible methods thoroughly demonstrate the fallacies of their claims and the superiority of the dry defecation over the process heretofore in use.

YONKERS. N. Y.

CHEMICAL METHOD FOR THE DETERMINATION OF THE AVAILABLE PHOSPHORIC ACID IN SOILS.

By ALEXIUS DE 'SIGMOND.

Though the first steps in Agricultural Sciences were based upon the chemical analysis of soils, there is still a need of methods, for the determination of available plant food in soils. The ingredient most needed in hungarian soils is undoubtedly phosphoric acid. The author, as chemist of the *Hungarian State Experiment Station of Plant Industry* in *Magyar Ovàr: Hungary*, has studied this problem during more than seven years, and has devised a method, by which he has tested nearly 100 different soils of Hungary, having made control fertilizer experiments on the same soils. The work of the author was rewarded by the prize of the *Hungarian Academy of Sciences in Budapest, Hungary*, and published recently[1] by the same scientific institute. The author here gives a brief report of this work, and a complete description of his method for the determination of the available phosphoric acid in soils.

The starting point of his investigations was, to find a *natural limit* in the solubility of the phosphoric acid in soils.

In 1899 Th. Schlösing, *jun.* in France, published some of his experiments, which seemed to divide the phosphoric acid in the soil into two distinct parts, the slightly soluble and less soluble part of phosphoric acid[2]. Schlösing tested but four different soils, and the author has repeated the experiments of Schlösing on eleven different Hungarian soils. The experiments of both authors agree in so far, that there is a distinct point which separates the phosphoric acid of soils in the above mentioned two parts. When we start with distilled water, and increase gradually

[1] Mathematikai és Természettudományi Közlemények XXIX, No. 1. 1906. A könnyen átsajátitható phosphorsav jelentösége és "meghatározása talajaink trágyaszükségletének megállapitása czéljából."—Dr. Sigmond Elek.

[2] Compt. rend., 128, 1004. Action des liqueurs acides trés éntendues sur le phösphates du sol.—Th. Schlösing fils. 1899. Paris.

the acidity of the soil solution by adding more and more nitric acid to the water, and determine the acidity of the soil solution and the amount of phoshoric acid dissolved in the solution they both have found, that *on increasing the end acidity of the solution, there is a rapid increase in the amount of soluble phosphoric acid also.* But at the point, when the end acidity of the solution reaches 200 mg. N_2O_5 per liter, on further increasing the end acidity to 1000 mg. N_2O_5 per liter. there is *practically no further increase in the amount of phosphoric acid in the solution.* And this seems to be a *natural division of the phosphates of the soil into the easily soluble and less soluble part,* for after the second limit is reached the amount of phosphoric acid dissolving, on increasing the end acidity of the solution, increases very rapidly again.

The data of Tables I and II illustrate the rule just mentioned.

For the graphical demonstration of the general rule, drawn from the above data the author constructed the following average diagram.
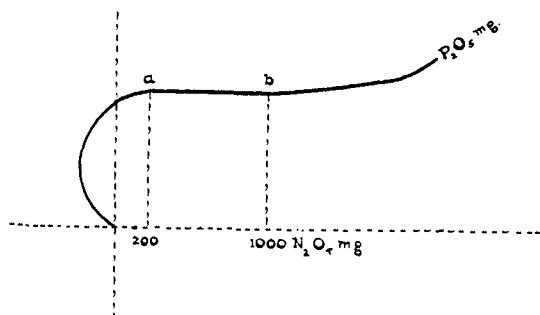
According to this diagram the straight part *a-b* of the curve represents the level, which divides the phosphates in the soil into two natural and distinct parts, the easily and slowly soluble parts.

The next problem to study was, to find out if there is some relation between the availability and the amount of the easily soluble phosphoric acid in soils. To solve this question, the author collected by the help of the *Experiment Station of Plant Industry* at *Magyar Ovàr, Hungary,* nearly 100 different Hungarian soils, one part of which was tested by field experiments, the other by pot experiments and some of them by both *i. e.* field and pot experiments.

The most of the pot experiments were carried out with the complete variation of the three chief plant foods, N. P. K., and each experiment repeated three or four times. According to this, there were made about 24-32 pot experiments with each soil; in all there were tested 51 soils by pot experiments and there were made about 1200-1600 pot experiments. On the other hand 55 soils were tested in fields, 12 being the same tested also by the pot experiments. In all 94 soils were tested by fertilizing

TABLE I.

N₂O₅ mg. used for the solution	End acidity of the solution tion N₂O₅ mg.	P₂O₅ mg in 1 liter of the solution		N₂O₅ mg. used for the solution	End acidity of the solution tion N₂O₅ mg.	P₂O₅ mg. in 1 liter of the solution
1. Couporay, loamy soil				2. Neauphle. loamy soil		
0	—25.0	0.38		0	—30.5	0.74
25	—11.9	0.52		90	— 5.0	2.74
50	3.5	1.07		180	20.0	3.64
100	9.9	1.66		270	72.0	3.41
200	69.3	1.89		520	262.0	3.63
300	148.5	1.97		770	515.0	. . .
400	245.0	1.79		1260	956.0	3.71
500	354.0	1.92		2260	1844.0	4.65
1220	1090.0	1.95		5260	4780.0	6.60
2220	1990.0	3.89		10260	9630.0	8.70
				20260	19300.0	10.49
3. Toinville, sandy soil 5 % CaCO₃				4. Boulogne. soil very rich in CaCO₃		
0	—64.	0.51		0	— 60.	0.61
250	—95.6	1.72		50	—116.	0.84
500	—20.2	3.33		100	—164.	. . .
750	58.0	4.42		200	—229.	1.46
1000	285.5	4.82		500	—358.	2.63
1250	529.0	4.94		1000	—404.	4.34
1500	766.5	4.97		2500	—238.	8.90
1750	1023.0	4.97		3000	— 84.	11.30
2000	1248.	5.16		3100	6.	13.00
2500	1793.	5.23		3200	18.6	14.19
5000	4310.	5.59		3300	57.	14.75
10000	9212.	6.31		3400	124.	17.06
				3600	319.	17.42
				3800	416.	17.97
				4000	632.	17.59

TABLE II

Name and physical character of the soil	Per cent. CaCO₃	Acidity of the solution calculated in mg. N₂O₅ per liter at the beginning	at the end	In 25 g. soil sample mg. P₂O₅	Per cent soluble P₂O₅
Pa Bashalom (loam)		658.8	+ 16.2	4.6	0.018
		1182.6	+ 313.2	6.0	0.024
		1463.0	+ 626.0	6.0	0.024
		2959.2	+1987.0	8.0	0.032
Hansag (peaty soil)		658.8	— 108.	2.4	0.010
		1182.6	— 415.	6.2	0.025
		1463.0	∓ 675.	5.6	0.022
		1738.8	— 896.	7.3	0.029
		2959.2	+ 2052.	8.6	0.034
Léva (clay)		745.2	— 567.	3.2	0.013
		1441.8	+1193.	3.2	0.013
		2959.2	∓ 2743.	4.5	0.018
Kalocsa (loam)		658.8	— 156.6	. .	. . . .
		1463.0	— 86.4	. .	. . . .
	22.91	5891.0	neutral	. .	. . . .
		6339.6	— 635.4	20.5	0.082
		6998.4	— 637.2	21.1	0.084
Pa Poó (loam)		745.2	— 54.0	traces	. . . .
		1441.8	∓ 199.8	11.3	0.045
	3.11	1738.8	— 367.2	18.7	0.075
		2959.2	— 1485.0	20.5	0.082

experiments, and the same samples were also tested by the chemical method of the author.

This method consists of the following determinations:

1.   The Determination of the Basicity of the Soil.—Titrating 25 grams of soil with a standard solution of nitric acid, containing 100 mg. N_2O_5 per liter, and boiling the soil, to drive out all the carbonic acid, we get at the basicity of the soil, *that is the amount of nitric acid neutralized by the soil.*   The author uses the term basicity for the number of mg. N_2O_5 for complete neutralization of 25 g. of the soil.

Weigh 25 g. air dried soil in a beaker, add a small amount of water and 10 cc. of the standard nitric acid solution.   Then boil the solution until the carbonic acid escapes. test, with litmus paper, and if the reaction is not distinctly acid, add again 10 cc. of nitric acid, boil, and test again with litmus paper.   Repeat this until there is a distinct excess of acid.   Then pour the whole contents of the beaker into a standard flask of 500 cc., fill up, shake, filter and determine in 50 cc. the excess of acid with a standard solution of potassium hydroxide such that 1 cc. neutralizes 10 mg. N_2O_5.   Use methyl orange as indicator.   By calculating the number of mg. of N_2O_5 neutralized by 25 g. of soil, we get the basicity of the soil.

With soils, which on adding some acid effervesce distinctly, the author has found it better to use only 5 g. instead of 25 g.

2.   Making of the Soil Solution.—In making the soil solution, we wish to get a solution with an end acidity ranging 200-1000 mg. N_2O_5 per liter of the soil solution.   The *end acidity* means the acidity of the soil solution after the solution is ready for the determination of phosphoric acid.

From the basicity of the soil, we can nearly calculate the amount of standard acid wanted, for the soil solution.   Namely:

1.   If the soil contains practically no traces of carbonates, or the basicity runs below the value of 1000 mg. N_2O_5: use but 10 cc. of the standard nitric acid solution to 25 g. of soil.

2.   If the soil contains carbonates, but the basicity ranges but 1000-4000 mg. N_2O_5: use just as many cc. of the standard acid as are required for the full neutralization of the basicity of the soil to 25 g. of soil.

3.   If the soil is very much loaded with carbonates or the basicity runs above 4000 mg. N_2O_5, and the soil is almost loamy or clay, use 5-10 cc. less of the standard acid than would be required for the complete neutralization of the basicity.   But in the case of sandy and loose, peaty soils, the author has found it best to use the amount of acid according to 2.

Now for making the soil solution weigh 25 g. of air dried soil in a standard flask of one liter, add about 100 cc. distilled water and standard nitric acid according to the above detailed rules.   With soils rich in carbonates, take care of the effervescence; then fill up to 1000 cc., close the

flask and put it in a rotatory apparatus. After half an hour of slow rotation (one rotation lasting about one-half minute) take out the flask, carefully remove the stopper and allow the solution to stand at room temperature ($12°$-$23°$) for about 16 hours. Then put the flask again in the apparatus and rotate one half of an hour again. Now filter the solution and take 25 cc. for the determination of the end acidity of the solution.

This is done by titrating it with the above mentioned standard potash solution, using methyl orange as indicator. If the end acidity would not fall between the 200-1000 mg. N_2O_5 as wanted, repeat the preparation of the solution according to the results of the end acidity. If the end acidity is right, the solution is ready for the determination of phosphoric acid.

3. The Determination of Phosphoric Acid in the Solution.—Evaporate 800 cc. of the filtered solution to about 50 cc. using a small amount of a 20 per cent. ammonium nitrate solution, for the precipitation of silicic acid. When the solution is evaporated as far as about 100 cc., filter, add 50-100 cc. ammonium molybdate solution, heat gently until the precipitation is complete, filter the solution, wash the precipitate with some nitric acid of 5 per cent., dissolve the molybdate precipitate with ammonia, add hydrochloric acid in excess, and again ammonia in excess, and precipitate with the usual magnesia mixture. The small amount of magnesium phosphate precipitates sometimes very slowly and 48 hours should be allowed for complete precipitation. Dry and burn the filter paper in a platinum crucible, ignite, and weigh the magnesium pyrophosphate as usual. The amount of P_2O_5 found, multiplied by 5, gives the per cent. in the soil.

This is exactly the method used by the author in his studies. The exactness of the method may be shown by the data of the following Table III.

TABLE III.

Name of the soil	End acidity of the solution a.	b.	Gm. P_2O_5 in 800 cc of the solution a.	b.	Mg. P_2O_5 easily soluble in 100 g. soil a.	b.	average
Tolna	o	o	0.0009	0.0009	4.5	4.5	4.5
Pél	—150	—150	0.0015	0.0015	5	5	5
Puszta-Somorja	— 10.8	— 16.2	0.0029	0.0033	14	16	15
M-Ovári akad. kisérleti tér	— 10.6	— 10.8	0.0047	0.0042	23	21	22
Vajka	— 60	— 80	0.0045	0.0047	22	23	22.5
Kisbér	—430	—470	0.0052	0.0053	26	26	26
Nagy-Bossány	—320	—350	0.0054	0.0055	27	27	27
F-Puszta Alsó-takarmányos	— 75	— 75	0.0066	0.0066	33	33	33
Kajmád	—220	—210	0.0066	0.0068	33	34	33.5
Vajka	—320	—400	0.0068	0.0066	34	33	33.5
Mezöhegyes	—290	—280	0.0109	0.0113	54	56	55
M-Ovári akad. kisérletitér	—140	—130	0.0111	0.0115	55	57	56
Lucsonyi kisérl. tér (Carlau)	—180	—240	0.0113	0.0119	56	59	57.5
Fáczánkert	—235	—240	0.0152	0.0153	76	77	76.5
F- Pusztaréti tábla	— 21.6	— 27.6	0.0173	0.0171	86	85	85.5
F- Pusztaréti tábla	—120	—130	0.0245	0.0246	122	123	122.5

It may be mentioned, that by using other methods of exact determination for the phosphoric acid, as for instance the official volumetric method of the U. S. Official Chemists, or any other exact method, the results would agree with those of the method of determination above mentioned. It may be stated also, that the author used only the fine part of the soil, passed through a sieve with holes of 1 mm. diameter. All these soils were of very fine structure, so that practically the whole mass passed the sieve. But if the soil were rich in coarse particles, the amount of P_2O_5 should be calculated for the original soil.

Using the above described method, and comparing the analytical data with the results of fertilizing experiments in pots as well as in fields, the author arrived at the following conclusions:

1. Among the 94 soils tested, there were 11 soils on which the phosphatic fertilizer had practically no effect on the yield of crops. In all these soils the amount of the soluble phosphoric acid, determined according to the above description, ranged 0.074-0.085 per cent. P_2O_5, *i. e.* 74-85 mg. P_2O_5 in 100 g. air dried soil, or more. See the following table.

TABLE IV.

No.	Name of Soil	Basicity		Mg. easily soluble P_2O_5 in 100 gr. soil.		Result of the fertilizing experiments.
1	Szeghalom (Székes)	525	....	234	....	
2	Fáczánkert	825	....	76.5	....	
3	Csákóva, csákovári dülö III	843	....	159	....	All these soils were
4	Csanád - apácza (Mokry)	1004	....	91	....	tested in pot experiments, and the phos-
5	Puszta-Poo	1372	....	75	....	phoric acid did not
6	Puszta-Vacs belsö kerület.	1733	....	159	....	have any practical effect either alone, or
7	Puszta-Gyónt.....	2412	....	121	....	with nitrogen or potas-
8	F-Puszta, réti talaj Tihany (1-8).	3365	....	136	....	sium fertilizers combined.
9	Tihany (1-8)	4165	....	136	....	
10	Lucsony kerti talaj	5978	....	82	....	
11	Györ homok	7615	....	74	....	

2. The remaining 83 soils were all lacking in available phosphoric acid, because in the fertilizing experiments there was always a marked effect of the phosphatic fertilizer on the yield of crops. The amount of soluble phosphoric acid was also in each case below the above given limit. But in classifying the soils according to their basicity, there was a marked relation between the basicity of the soil and the content of soluble phosphoric acid. In general the amount of soluble phosphoric acid increased with the increasing of the basicity of the soil. The author concluded from this fact, that the greater the basicity of the soil, the less available are the phosphates in the soil, though their solubility may be the same from the chemical standpoint. It seemed probable that the chemical compounds of the soil, to which is due the basicity, especially the carbonates of calcium or magnesium, lessen the availability of the phos-

phates of the soil.   The most probable explanation for this seems to be that the acid sap of the plant roots is more or less neutralized by the basicity of the soil, and at the same time is less effective in dissolving the phosphates in the soil, than if the basicity of the soil runs lower.   To show this rule the author classified the 83 soils, in which the stock of available phosphates was not sufficient for the production of the maximum yield of crops, in five groups.   The limits of these groups are as follows:

	Basicity N_2O_5 mg.	Average soluble P_2O_5 mg.	Maximum Soluble P_2O_5 mg
1. Group	0– 300	5.5	6.0
2. Group	300– 600	13.0	30.0
3. Group	600– 900	27.6	45.0
4. Group	900–4000	36.4	60.0
5. Group above	–4000	49.1	72.0

The detailed data are given in the following table :

TABLE VI.

No. of the soil sample	Name	Basicity	Mg easily soluble P_2O_5 in 100 g. soil	Effect of P-fertilizers Result of fertilizing Experiments Method used	Percentage increase in crop per cent.
			Group 1.		
12.	Pa. Podluzsáng	270	5	pot exp.	28
13.	Széplak (rye-fields)	240	6	field exp.	32
14.	Kehida	287	5	pot exp.	27
			Group 2.		
15.	Cseberk	340[1]	15	pot exp.	67.6
22.	Orvzi	325	30	field exp.	75
30.	Urföld (sand)	403	19	pot exp.	29
35.	Szeghalom	530	22	pot exp.	19[2]
			Group 3.		
37.	Mezökovácsháza	615	45	field exp.	43
45.	Pusztaszer	700	20	field exp.	37
47.	Bábohra (F)	853	29	pot exp.	41[2]
49.	Bábohra (B)	870	41	pot exp.	103[2]
			Group 4.		
52.	Somogyvár(Vidárnh.)	967	48	field exp.	P successfully used
61.	Kis-Szállás	1300	57	field exp.	22
64.	Paks	1585	44	pot exp.	149[2]
73.	Ságvár	3500	53	field exp.	21
			Group 5.		
76.	Solt	4400	70	field exp.	21
87.	Magarovár	7257	57	pot exp.	103[2]
88.	Diószeg	7825	67	field exp.	P successfully used
92.	Pa. Somorja	11232	44	pot exp.	77

It may be noted, that in Group 5. the maximum of 72 mg. P_2O_5 is very close to the limit, which was given for rich soils.   But this maximum is also exceptionally high and does not occur very often.   Therefore in these rare instances, when the soil is very rich in carbonates, the limit of 74 is uncertain, and in those very exceptional cases, the fertilizing experiments have to decide if there is a need of available phosphates in the soil.   It may be, that by the further evolution of our knowledge we may

[1] Calculated value.

[2] The fertilizing experiments in pots were controlled in fields, and the effect of P was practically the same.

classify the soils not only according to their basicity, but also according to their physical character, and the ratio of the available plant food.

The soil No. 11, for instance, is a very poor sandy soil in which the high amount of soluble phosphoric acid seems to be in excess, though the availability may be weakened considerably by the high basicity of the soil.

On the other hand, all the soils of Disózeg, (Nos. 86, 88 and 89), are heavy, loamy, or clay soils, manured very rich with nitrogenous fertilizers. In consequence of this the soil is very rich in available potassium and nitrogen, but relatively poor in available phosphoric acid. Let us hope, that in the early future we will have similar chemical, or partly bacteriological methods for the determination of available potassium and nitrogen in the soil. Then we will be able to find out the right ratio of the available plant food in the soil, and calculate with more certainty than we do now by using the ratio of the total amount of plant food in the soil.

Considering the marked harmony on the whole between the results of fertilizing experiments and the amount of soluble phosphoric acid determined by this new method, the author feels justified in calling this stock of phosphoric acid in the soil, as available.

The author would be very glad if his method could be tested by numerous chemists and on different, but well-known soils. The author has found in some instances, that taking into consideration the basicity of the soil Dyer's citric acid method may be, perhaps, also successful.

The author concludes with the hope, that in the future more attention will be paid to the chemical analysis of soils, and in drawing our conclusions we may take more and more in consideration the classification of the soils according to their chemical as well as their physical character. It is is a mistake to say that the chemical analysis of the soil has no practical value for the farmer, and the agricultural chemist should be very busy in the near future in finding reliable methods for the determination of the stock of available plantfood in the soil. The solution of this problem has perhaps more practical and international value than most other problems of the soil chemistry.

Budapest, Hungary.

THE CHEMICAL CARD INDEX OF THE PATENT OFFICE.

BY EDWIN A. HILL.

In 1899 the U. S. Patent Office commenced the preparation of a bibliographic card index of chemical substances for use in its official work. This index, prepared by the Classification Division, now comprises nearly 500,000 cards drawn from more than 80 chemical publications, and is believed to possess sufficient magnitude to justify an attempt to