HYDROGEN-ION CONCENTRATION—SOIL TYPE—COMMON POTATO SCAB

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In a former paper (9) we called attention to a characteristic difference of hydrogen-ion concentration shown by the extracts of soils of the types Caribou loam and Washburn loam. These types, which have similar texture, are derived from the same glacial till, and seem to owe their striking dissimilarity to local topographic differences, which affect particularly the drainage. In the Soil Survey of the Caribou Area, Maine, by Westover and Rowe (22), reference is made to the fact that potatoes grown on the Washburn loam are in general very subject to common scab, whereas potatoes grown on the Caribou loam (and Caribou silt loam) are of fine quality and are produced in notable yield. We found the Caribou loam more intensely acid than the Washburn; though both types are acid, as is locally recognized by the use of litmus paper. The Caribou loam is characterized by the yellowish-brown color of the surface soil and even brighter subsurface soil (indicative of good drainage); whereas the surface of the Washburn loam is dark gray to black in color, and is underlain by a light gray to a dull yellow and gray mottled subsurface soil, the latter being very characteristic of poorly-drained soils. Other differences have already been described (9).

In connection with a study carried on coöperatively between the United States Department of Agriculture and the Maine Agricultural Experiment Station, we collected during the season of 1917 and examined a large number of samples of these two types, including also soils intermediate in character between the Caribou and the Washburn loams, or otherwise not typical of either soil type. A search was made for soils exceptional in their behavior toward the scabbing of potatoes, and some soils of the Caribou series (not typical Caribou loam) were found producing scab, as well as three samples of Washburn loam from which clean or only slightly infected potatoes were harvested.¹

In every case except when otherwise noted, the presence or absence of scab was determined and the sample taken at the time of digging, and the sample of soil was therefore known to represent the soil condition in question. It

¹ Very little or no powdery scab was found in Aroostook County in the summer of 1917, and all reference to scab in this paper applies to the common (corky) scab, actinomycosis.

was not possible to determine the hydrogen-ion concentrations on the soil fresh from the field, and the soils were air-dried in a place free from laboratory fumes. The surface soil was sampled, down to the change of color, or the average plow depth, the average depth being 7 or 8 inches.

ELECTROMETRIC DETERMINATIONS

The electrometric determinations were made by the use of the electrode vessel previously described (7). This vessel was designed especially with regard to the nature of the material to be examined and the difficulties to be overcome, and the recommendations of Hasselbalch (11) and Cumming and Gilchrist (6) were followed. This vessel avoids the error due to the entrance of potassium chloride into the soil suspension when the liquid contact is made by means of a tube of agar with potassium chloride (13). A high-grade potentiometer was used in connection with a galvanometer. The low-resistance galvanometer coil regularly supplied was not sufficiently sensitive when used for hydrogen electrode chains of high resistance. Another coil, having a resistance of about 400 ohms, was substituted by the manufacturers, and was very satisfactory both for soil work and for solutions of good conductivity in the Clark electrode vessel (1). Commercial switches and heavily insulated "fixture" wire were used.²

In figure 1 is shown the electrode vessel together with the electrode in position, the soil and water mixture, and the approximate location of the junction between the saturated potassium chloride solution and the soil extract. Mechanical shaking was provided. During the shaking the vessel turned from an inclination of 3° to the horizontal to an inclination of about 33°; the presence of the soil mass prevented the rising of bubbles of hydrogen into the soil extract in the neck of the vessel. The shaker consisted of a horizontal cross-piece (passing through α perpendicular to the vessel as shown) actuated by an eccentric. Two metal arms were fastened to the cross-piece, the arms were covered with rubber tubing, and the vessel was laid lengthwise along the arms and fastened with strong rubber bands. The electrode vessel had a capacity of about 65 cc., measured from the stopcock to the brim (for a vessel of different dimensions a different quantity of soil suspension would have to be chosen, in order to secure satisfactory agitation of the mass with hydrogen). A small motor was used to drive the shaker, the speed being reduced in two

² The least satisfactory part of the electrical system formerly used (12) was not the much-abused capillary electrometer, but the voltmeter, which is not graduated in enough subdivisions for precision and which also requires calibration. (The one in question required a correction of about 1.5 per cent.) The capillary electrometer gave very good service. The capillary was not so fine as "thermometer tubing," and the instrument was short-circuited through soldered connections and platinum contacts, and put in good condition once in a while by applying for a few minutes an electromotive force of about 0.8 volt in the direction to make the mercury contract in the capillary (19). Electrical shielding (23) was necessary with this former system.

steps by light pulleys so that the vessel was rocked at the rate of 70 to 90 complete swings per minute.

Hydrogen was generated from caustic potash solution with iron electrodes (somewhat better with a platinum anode and a nickel cathode) using the lighting circuit of 220 volts with a lamp-bank in series. Current for coating and treating the electrode was taken off from the terminals of the hydrogen generator. The coating bath was prepared by adding a trace (about 0.03 per cent) of lead acetate to the commercial solution (3 per cent) of palladium chloride; from time to time the volume was restored by addition of distilled water, or the color restored by adding more palladium chloride. The cleaning bath was dilute sulfuric acid. Platinum anodes about 1 inch square were used for both baths. *The palladium coating was not appreciably scoured off*

FIG. 1. THE FILLED ELECTRODE VESSEL

by the action of the soil, but it *was always renewed, after complete removal of the previous coating, for each determination*, in order to exclude the possibility of an accumulative poisoning of the electrode. The time required for (lightly) coating the electrode was about 5 seconds, and after thorough washing in a stream of distilled water the electrode was then put into the cleaning bath and hydrogen liberated from the electrode for 5 to 10 seconds, after which the electrode was again thoroughly washed.

The hydrogen electrode is shown in figure 2. A sheet of platinum was used which measured 2.5 by 3.3 cm. (An electrode 1 inch square also was satisfactory.) In constructing the electrode it was necessary to support the sheet of platinum at both top and bottom, and also to provide leads for the current at two opposite points in order to secure an even deposit of palladium black. This was accomplished by welding platinum wires at opposite ends

and sealing the wires into the glass tube, which was supplied with mercury. During the shaking the electrode was never entirely out of contact with the soil suspension.

The rest of the apparatus was simple. A glass T-tube was affixed to an upright piece of board. Through one arm of the T-tube saturated potassium chloride solution could be drawn through a stopcock; another arm (which was horizontal) could be connected with the end-tube *a* of the electrode vessel by means of a rubber tube; and the third arm (also horizontal) connected with a saturated potassium chloride calomel electrode (17) through a stopcock greased at the edges, but not in the middle (1). After the apparatus was once set up it was unnecessary ever to open this last-mentioned stopcock.

The course of the determination is as follows. Fifteen grams of the air-dried soil are introduced into a test-tube 17 by 3 cm. containing 30 cc. of distilled water, the tube is closed and shaken vigorously by hand 50 times, and permitted to stand 20 minutes or longer for sedimentation. (A number of samples are thus treated at once.) The previous coating of palladium black is removed from the electrode by placing this in a beaker of strong nitric acid (or a cold mixture of nitric and hydrochloric acids). While the coating is

FIG. 2. THE HYDROGEN ELECTRODE

being dissolved the electrode vessel is cleaned and filled. The neck of the electrode vessel, including the bore of the stopcock, is filled with the comparatively clear soil extract; the stopcock is closed and the end-tube *a* is filled with saturated potassium chloride solution by means of a capillary pipette; the rubber tube leading to the calomel electrode is filled with potassium chloride solution and slipped over the end-tube *a*, avoiding the entrance of air-bubbles; and the vessel is fastened to the shaker. The rest of the soil mass is well agitated and poured into the vessel. The bare electrode is coated and cleaned as described above, the electrode is put into the rubber stopper, and this stopper, which fits well and carries tubes for the entrance and exit of hydrogen, is put into the electrode vessel, as shown in figure 1. The entrance and exit of hydrogen is controlled with light pinch-cocks. A generous volume of hydrogen (about 150 cc.) is rapidly swept through the space over the soil mixture, the current of hydrogen stopped by closing the exit, the flexible wire leading to the potentiometer is put into the mercury tube of the electrode, and the electrode vessel is shaken for 5 minutes, the stopcock being closed. Without stopping the motor the liquid contact can be made and the potential measured. To effect liquid contact the rubber tube connecting the vessel with the calomel electrode is pinched, forcing potassium chloride solution through the stopcock in the arm of the T-tube back into the reservoir, this

stopcock is closed, and the stopcock of the electrode vessel is opened, drawing some of the soil extract down into the end-tube *a* of figure 1. The boundary formed is not sharp like the line shown in figure 1. From the measured difference of potential and the room temperature, which was not permitted to change excessively, the hydrogen-ion exponent was calculated from the figures given by Michaelis for the saturated electrode (17). The calomel electrode has been checked many times against "standard acetate" and Clark and Lubs' buffer mixtures.

If the electrode vessel is not shaken during the measurement the potential is not constant, but becomes numerically greater, sometimes so fast that any measurement would be a forced one. This is due to the presence of nitrates (21, 10) (and possibly other oxidizing agents). In order to see whether a substantially correct potential is obtained (when shaking is continuous), the stopcock was closed and the vessel shaken 5 minutes longer, liquid contact made as before and the potential determined, the vessel still being shaken continuously. The changes of potential due to the extra 5 minutes' shaking are recorded in table 1.

TABLE 1

A frequency table showing the number of times each change of potential was observed. (For 58 determinations the mean change was -0.9 millivolt, the minus sign signifying a fall of potential)

	CHANGE OF POTENTIAL IN MILLIVOLTS												
	-5.5	-4.0	-3.5	-3.0	-2.5	-2.0	-1.5	-1.0	-0.5	0.0	0.5	1.0	1.5
Number of times each change was observed...	1	2	1	1	1	5	5	12	11	13	5	0	1

Three larger changes were seen (+8, -5, and -12 millivolts) and the results were disregarded and the determinations of hydrogen-ion exponent repeated with better results. The changes shown on the repetition are included in table 1 (the first value, -5.5, is one of these). Table 1 shows how "constant" the potential may be expected to be. The second measurement of potential is a simple control. If the vessel were not shaken during the measurements, and a final potential reading were taken after the potential seemed to become constant, the results in some cases would be quite erroneous, and it would appear that in general such results would be more or less in error.³

³ Kappen applies the hydrogen electrode to the extract separated from the soil, as appears from the following, taken from an abstract (14). "Only soils reacting acid to litmus raised the hydrogen-ion concentration (H-Zahl) of the extract (Schuettelwasser), soils reacting weakly or neutral decreased it, with one exception. The presence of solid soil particles in the extract increased the hydrogen-ion concentration." In the preliminary work in this laboratory it was observed that the hydrogen-ion concentration of the extract comparatively free from soil particles was less acid, but also indefinite and meaningless, and this was the reason for operating on a suspension and for shaking the electrode vessel during

COLORIMETRIC DETERMINATIONS

Since the former comparison of methods (7) the colorimetric method for the determination of hydrogen-ion concentration has been improved, and for the bacteriologist, standardized, by Clark and Lubs (3). Their method was used in the present work, 5 cc. of solution to be examined and 5 cc. of buffer mixtures being used instead of 10. The comparator was used throughout and the yellow screen light recommended by them was used for measurements with brom-cresol-purple and brom-phenol-blue. The use of dipropyl red (2) was discontinued because the colors of the standards faded rapidly, though a few measurements with it gave excellent results. In the former work (7) all the indicators were used in alcoholic solution. In this work methyl red was used as the free indicator in alcoholic solution, and the other indicators in water solution as the monosodium salts. This choice is in accordance with the recommendations of Clark and Lubs and with their implied doubt as to the suitability of methyl red as the sodium salt in buffer-poor solutions, and is theoretically better than the use of all the indicators in the free state, or all as the monosodium salts, since methyl red is a weak acid, whereas the sulfone-phthalein indicators have a highly ionized hydrogen atom (15). We used the sodium salt of methyl red in our previous work on the Caribou and Washburn loams, without electrometric control, and have found that the exponents so obtained with that indicator are about 0.3 to 0.4 too high. Some of the trouble was due simply to the use of the sodium salt, and some probably to impurities. Dr. Lubs states that the commercial product is likely to contain acetate. He kindly gave us some which he had synthesized and recrystallized from toluol, and this preparation, dissolved in redistilled alcohol (and water added), was used for the measurements reported, with excellent results. We have not determined whether such a solution will keep indefinitely. The monosodium salts of the sulfone-phthalein indicators were prepared by treating the free indicators with standard sodium hydroxide solution. Clark and Lubs use 1.1 equivalents of alkali for brom-phenol-blue and brom-thymol-blue, and in the case of the brom-cresol-purple, they use 1.5 equivalents (4). We were not able to get the last-named into solution in 1.5 equivalents of sodium hydroxide with moderate stirring or shaking, unless the mixture was heated, in which case the substance seemed to undergo slight decomposition, as the colors yielded by such a preparation in buffer mixtures were not quite so deep and brilliant as those produced by the same quantity of indicator brought into solution with alcohol. This decomposition was apparently minimized by the use of gentle heat applied for a short time to the indicator and sodium hydroxide solution in small volume. The quantities of the measurements. The cause of the difference is the presence of nitrates in a solution weak in buffer action (21, 10). In some cases the ammonia formed locally about the hydrogen electrode is sufficient to change the reaction of the whole fluid, so that the change can be detected with indicators. So far as is known, extracts of normal soils cannot be measured electrometrically, but only by the indicator method.

N/10 sodium hydroxide solution required to furnish the given equivalents for the three indicators, in the order named, were 1.64, 1.76, and 2.78 cc., for decigram portions of the indicators.

When comparing the colors it is important to avoid using a given indicator for too great a range of hydrogen-ion exponent. When a highly turbid or colored extract is being examined, the mere fact that no difference can be seen in color, when indicator has been added and comparison is made with the colors of the buffer standards, does not prove that the value of the exponent has been located; on the contrary, it is absolutely necessary that the color is seen to differ definitely when either a more acid or a less acid standard is used for the comparison. If this is not done, it is easy to locate the value at the end or near the end of the range of a given indicator, when as a matter of fact the true value lies entirely outside the range. The useful ranges of the various indicators are somewhat shorter for colored or turbid solutions than for clear solutions.

The indicator solutions were of the same strength as recommended by Clark and Lubs, namely 0.04 per cent for the three sulfone-phthalein indicators, and 0.02 per cent for methyl red, which is prepared by dissolving 0.1 gm. in 300 cc. of redistilled alcohol and diluting to 500 cc. with distilled water.

The procedure for the examination of soil was as follows. Fifteen gm. of the air-dried soil was added to 30 cc. of distilled water, in a large test-tube, the tube was closed and vigorously shaken by hand 50 times (just as for the electrometric determinations), the mixture was centrifuged, and the extract drawn off in a pipette provided with a rubber tube and mouthpiece. Five-cubic-centimeter portions were distributed into test-tubes, two or three drops of indicator added, and the color compared with the colors of the buffer mixtures containing the same quantities of indicator, a comparator being used for the comparison. One 50-cc. pipette and 6 test-tubes were used for the soil extracts; they were scrupulously clean, and rinsed well with distilled water. The rinse-water was shaken out of the test-tubes, and allowed to drain out of the pipette; it was not necessary to dry the glassware, since small variations in the volume produce no sensible error.

It is very convenient to have a selection of test-tubes, chosen so that a given volume (say 10 cc., delivered from an automatic pipette) corresponds to nearly the same height in all the tubes, say between 8 and 8.5 cm. The portions of buffer or of soil extract are then measured by filling up to a given height, using a tube for comparison containing the desired volume. Such a method of *constant height* leads to no greater error than the method of *constant volume*.

COMPARISON OF METHODS

A good though not perfect agreement was previously found between colorimetric and electrometric results (7). Such an agreement is of considerable

importance, because various objections could be brought against either method, which might appear to have force if either method had been used alone, without ever having been supported by the other. Against the colorimetric method it might be urged that the color changes were due to adsorption by the small quantity of colloidal material present in the unfiltered though centrifuged extracts, just as the action of soil on litmus paper was formerly rather widely attributed to adsorption. Against the electrometric method, on the other hand, it might be objected that strictly constant potentials would not be observed if the classical (unshaken) electrode vessel were used. Shaking the electrode vessel during the measurements has not been practised in purely physico-chemical investigation, but is a device of the biological chemist to reduce errors admittedly inherent in the measurement of blood, sea-water, and also soils. It is furthermore regarded by everyone as an absolute necessity to avoid the soiling of the electrode with the fingers, lest the electrode be poisoned and lose its characteristic catalytic property, and though this precaution was of course taken, yet it seems almost futile when it is considered that the electrode is plunged into a soil suspension. Such a poisoned electrode might give very erroneous results, and might seem to show a constant potential (especially if the potential can be observed only to centivolts) when approximate equilibrium was far from being attained.

It is therefore of interest to compare again the results obtained by the two methods, obtained by the technique described above, which embodies improvements in the colorimetric procedure.

Table 2 affords a comparison between the results given by the two methods. Fifty-seven soils were studied, including some samples not discussed in this paper, and 88 colorimetric determinations made. The results are compared by assuming the electrometric result to be correct, and tabulating the errors of the colorimetric results. To a certain extent this is unfair to the colorimetric method, since any comparison of the two methods includes the error of duplicating the sample. As judged by duplicate colorimetric determinations with the same indicator, the error of sub-sampling from a sample collected from the field, air-dried, and mixed well but without special precautions, may cause an error of about 0.1 in the value of the hydrogen-ion exponent, which would correspond to an error of about 6 millivolts. It will be seen that the difference between colorimetric and electrometric results is at the most 0.3 exponent, or about 18 millivolts, and not very often so large. Only a few electrometric determinations have been done in duplicate; those so done have given results agreeing within 2 or 3 millivolts, except in those cases already mentioned above, where the potential varied excessively during the second shaking. It has recently been reported almost impossible to obtain duplicates electrometrically agreeing within 20 millivolts (0.02 volt) (20). This was taken to indicate lack of uniformity of mixing, but may rather indicate an electrometric procedure faulty in some detail.

The average error for all indicators was 0.08 in the value of the exponent, and the mean error was -0.001 . In almost all cases the results obtained by the two methods agree within what the experimenter feels to be the uncertainty of the color distinctions. This uncertainty depends on the indicator used and on the color and turbidity of the soil extract. The color standards employed differ from one another by intervals of 0.2. The two methods may be said to give the same result, within the experimental error.

The data of table 2 dispose of such objections as have been mentioned above, but it does not follow that any and all procedures for measuring hydrogen-ion concentration are equally applicable to soil, and it would seem

TABLE 2
Errors of the colorimetric determinations

ERROR	NUMBER OF TIMES THE ERROR OCCURRED				
	Brom-phenol-blue	Methyl red	Brom-cresol-purple	Brom-thymol-blue	Total for all the indicators
0.30	0	0	1	0	1
0.25	1	1	0	0	2
0.20	1	0	2	0	3
0.15	1	0	3	3	7
0.10	2	1	4	5	12
0.05	6	7	2	0	15
0.00	0	11	2	2	15
-0.05	0	5	3	1	9
-0.10	0	4	8	0	12
-0.15	0	2	4	0	6
-0.20	0	0	2	0	2
-0.25	0	0	1	0	1
-0.30	0	0	3	0	3
Number of determinations.....	11	31	35	11	88
Average error.....	0.05	0.05	0.10	0.09	0.08
Mean error.....	+0.05	-0.01	-0.04	+0.08	-0.001

advisable, if only one of the methods can be used, to adopt a procedure very similar to one which has been tried out, and not to vary the procedure without means for checking modifications. The colorimetric method has recently been applied to filtered soil extracts (18). Though we have not exhausted the possibilities, our results with soil extracts filtered through filter paper have been incorrect and variable, according to the brand and treatment of the paper.

In addition to the observations summarized in table 2, we have often measured the same soil extract by means of two different indicators, and have thus been able to check one indicator against another without introducing any error of sampling. These checks have been most satisfactory. Not only have

the indicators mentioned above been checked against one another in this way, but also phenol-sulfone-phthalein has been checked against brom-thymol-blue. When the hydrogen electrode is not available, this method of checking the suitability of the indicator solutions is very useful and important.

EFFECT OF DILUTION ON THE REACTION

Sharp and Hoagland (21) examined electrometrically soil suspensions prepared with various ratios of water to soil, the lowest ratio in any case being 2 to 1 (2 cc. of water per gram of soil). They concluded that the change of hydrogen-ion concentration was small compared with the wide variations in the ratio. The ratio cannot be reduced much below 2 in electrometric determinations; in colorimetric determinations, however, good duplicates can be obtained with a ratio 1 to 1. We stated (9) that the average difference obtained by varying the ratio from 1 to 1 to 2 to 1 (through an error, "2 to 2" was printed) was 0.14 in the value of the exponent for 9 soils. This was unexpectedly large, and on extending the experiment to a larger number of soils

TABLE 3

A frequency table showing the effect on the hydrogen-ion exponent of changing the ratio of water to soil from 1 cc. of water per gram of soil to 2 cc. per gram

	DIFFERENCE OF EXPONENT DUE TO DILUTION								
	-0.15	-0.10	-0.05	0.00	0.05	0.10	0.15	0.20	0.25
Number of times each difference occurred.....	7	14	3	11	9	3	6	6	3

we have not been able to confirm so large a difference. We have studied 43 soil samples, showing exponents from 4.5 to 6.2, and have made 62 measurements of the difference, using methyl red and brom-cresol-purple. Table 3 shows the values thus obtained for the difference of exponents caused by varying the ratio of water to soil from 1 to 1 to 2 to 1. A positive difference means that the extract was less acid when more water was used.

The differences are distributed like errors about a mean value of $+0.04$, which seems to be a real value, not an error itself. (There was no apparent correlation between the actual values of the exponent and the difference caused by dilution.) We therefore think, with Sharp and Hoagland, that the error caused by adding to the soil the quantity of water actually necessary for the determinations is probably not serious. Plummer (20) has recently examined soil suspensions and also the soil solution obtained by the oil-pressure method. He concluded that the reaction of the soil solution so obtained is qualitatively the same as that of the suspension, but different quantitatively. The quantitative differences found are in some cases rather large. The oil-pressure method requires considerable time for the collection of the solution; in the experiments under discussion this time was from 2 to

4 days. In the absence of air anaerobic processes might in some cases be set up, and the control experiments did not exclude the possibility that anaerobic processes occurred involving changes of reaction.⁴

HYDROGEN-ION EXPONENT AND THE OCCURRENCE OF POTATO SCAB

We have already indicated that the relative freedom of the Caribou loam from potato scab may be due to its greater hydrogen-ion concentration (9) and that the acidity of the Caribou loam is often sufficiently intense to exert a restraining influence on the organism causing the common (corky) potato scab (8). The data to be presented in this paper are sufficient for a more searching inquiry into this relationship.

The hydrogen-ion exponents found electrometrically are given, together with the notes as to the occurrence of scab and the soil type, in table 4. The soils are numbered in order of decreasing acidity. As the exponent increases, the hydrogen-ion *concentration* decreases, neutrality being reached at about the exponent 7. The second decimal has little significance but has been retained for convenience in ordering.

A glance at table 4 shows a general correlation between hydrogen-ion exponent and the occurrence of potato scab, the more acid soils at the head of the list being free of scab, and the less acid or neutral soils at the foot of the list exhibiting scabby potatoes. With the exception of soil no. 9, the exponent for which is 4.9, and from which the potatoes were only slightly scabby, no scab is recorded until the exponent 5.16 is reached, at no. 20. From then on to 5.5 the scabbing is irregular. From the exponent 5.5 down through the rest of the soils, scabbing is present in every instance except in the case of no. 36, where the land has just been cleared and put into potatoes, and in which case the potato scab organisms had not had opportunity to spread through the soil. Three fields, as shown in the notes in table 4, yielded scabby potatoes in one portion of the field and clean potatoes on another portion; these differences being correlated with differences of hydrogen-ion exponent and also of soil type. The notes illustrate the characteristic freedom of Caribou loam from potato scab and the characteristic infection of potatoes grown on the Washburn loam, there being a few exceptions.

One of us has recently studied the growth of different strains of the potato scab organism at different hydrogen-ion exponents (8) and found that the exponent 5.2 represents a degree of acidity sufficient to delay or inhibit the growth; in some cases a slow but finally a good though abnormal growth occurred in a highly nutritive medium which had at the beginning the exponent 4.8, but it was shown that the acidity was being decreased in such cases during the growth, and the manner of growth indicated that successful growth depended on local decrease of acidity.

⁴ We do not understand how the solutions could have been measured electrometrically, unless denitrification had occurred.

TABLE 4

Hydrogen-ion exponents for the samples collected, with notes as to their type and the occurrence of scabby potatoes

SOIL NUMBER	HYDROGEN- ION EXPONENT	OCCURRENCE OF COMMON SCAB	SOIL TYPE
1	4.50	No scab	Typical Caribou loam
2	4.64	No scab	Not Caribou loam but similar
3	4.76	No scab (see nos. 8 and 20)	Typical Caribou loam
4	4.77	No scab	Typical Caribou loam
5	4.80	No scab	Typical Caribou loam
6	4.80	No scab	Typical Caribou loam
7	4.81	No scab	Typical Caribou loam
8	4.90	No scab (see no. 20)	Typical Caribou loam
9	4.93	Potatoes only slightly scabby	Rather typical Caribou loam
10	4.98	No scab	Washburn loam
11	4.99	No scab	Typical Caribou loam
12	4.99	No scab	Caribou loam
13	5.00	No scab	Typical Caribou loam
14	5.03	No scab	Typical Caribou loam
15	5.04	No scab (see no. 39)	Fairly typical Caribou loam
16	5.09	No scab (rest of field scabby, see no. 37)	Caribou loam, not typical
17	5.10	No scab	Caribou loam
18	5.12	No scab	Typical Caribou loam
19	5.16	No scab	Caribou loam
20	5.16	Moderate infection of scab	Fairly typical Caribou loam, collected from same field as nos. 3 and 8, only 20 feet from no. 8.
21	5.18	No scab a month before digging	Rather typical Caribou loam
22	5.21	Little or no scab	Washburn loam
23	5.30	Potatoes very scabby	Caribou loam, not typical
24	5.38	No scab	Mucky phase of Washburn loam.
25	5.39	Potatoes slightly scabby	Washburn loam
26	5.44	Potatoes not scabby (new land)	Belongs with the Washburn loam, taken from a swale in Caribou loam
27	5.52	Slight infection of scab in spots of the field	Caribou loam, not typical
28	5.52	Medium infection of scab, in places only slight	Caribou loam, not typical
29	5.64	Very scabby potatoes	Caribou loam, not typical, possibly Caribou shale loam
30	5.68	Scabby potatoes	Washburn loam
31	5.75	Scabby potatoes	Washburn loam, not typical but somewhat like Easton loam
32	5.79	Scabby potatoes	Washburn loam
33	5.89	Very scabby potatoes	Caribou shale loam
34	6.00	Very scabby potatoes	Washburn loam
35	6.17	Potatoes very scabby the previous season (1916)	Washburn loam

TABLE 4—*Continued*

SOIL NUMBER	HYDROGEN-ION EXPONENT	OCCURRENCE OF COMMON SCAB	SOIL TYPE
36	6.22	No scab a month before digging (new land)	Washburn loam
37	6.24	Scabby potatoes	Washburn loam, from same field as no. 16
38	6.30	Very scabby potatoes	Mucky phase of Washburn loam
39	6.31	Scabby potatoes	Washburn loam, from same field as no. 15
40	6.45	Scabby potatoes	Washburn loam
41	6.48	Scabby potatoes	Washburn loam
42	6.63	Scabby potatoes	Washburn loam
43	6.66	Scabby potatoes	Washburn loam
44	6.69	Potatoes said to be always scabby	Washburn loam, not typical
45	7.14	Very scabby potatoes	Washburn loam, not typical
46	7.15	Very scabby potatoes	Washburn loam, not typical
47	7.21	Very scabby potatoes	Caribou shale loam

The limiting zone of hydrogen-ion concentration seems to be about the same in soil as in culture media, and this would appear to serve as a rough biological check on the methods used for determining the hydrogen-ion concentration of the soil.⁵

The above results, while obtained for soils of the types Caribou loam and Washburn loam, appear to have a more general application. A field of Norfolk sandy loam near West Norfolk, Va., has a record of clean potatoes, and the July crop of this year has been observed by Mr. B. E. Brown of this office to be very free from scab. Liming is not practised. We sampled this field in March of this year in six places, and found the hydrogen-ion exponent to be uniformly 5.1 in the surface soil. Two samples of sand from Florida were sent to the laboratory, which were much alike, aside from color, but one yielded clean potatoes and the other scabby ones. Mineral analysis by Dr. L. E. Wise showed the two soils to have very similar ultimate composition. The clean soil showed the exponent 5.0; the scabby soil, 6.3. We have collected some samples of Everglade muck and peat; a muck field, which is yielding good crops of clean potatoes, was sampled in four places, and showed the exponents 4.7, 5.0, 5.1, 5.1; whereas the peat field, which is in general a poor soil and in yielding a poor crop of scabby potatoes, showed the exponent 5.6. Two samples of soil from the same field were collected near Milford, Conn., one of which was limed in 1906, the other received no lime. The soils

⁵ This does not mean that the use of air-dried soils is to be generally recommended, in fact fresh soils should as a rule be used where it is practicable. If a problem involves a critical zone of hydrogen-ion concentrations near the neutral point it would seem quite essential to use fresh soils. The sensitiveness of the hydrogen-ion exponent to carbon dioxide depends in general on the value of the exponent, and is comparatively small at the exponent 5 (17, p. 142, 13) though large in the case of soils at the exponent 7 (13).

were a reddish-brown loam, well drained and well suited to the growing of potatoes. The limed soil produced in 1906 very scabby potatoes, and again produced similarly scabby potatoes when next cultivated with potatoes in 1918; whereas the unlimed soil produced clean potatoes both years. The hydrogen-ion exponents were determined this year and were found to be 5.7 for the limed soil and 5.05 for the unlimed soil. If these results were incorporated in table 4, they would fit perfectly, and they confirm the conclusion, which can be based on the agreement between the soil observations and the culture medium experiments (8), that the results shown in table 4 are not limited to any particular soil type or condition, but are of general application.

It should be recalled that the organism causing scab on beets is supposed to be the same as that causing the potato scab (16) and the same relation should therefore apply also to beets. We have no direct evidence as to this.

HYDROGEN-ION CONCENTRATION AND SOIL TYPE

The relation between hydrogen-ion exponent and soil type is not easily discerned from the notes given in table 4, and can best be seen from the frequency diagrams shown in figure 3. From the upper diagram we can determine, for instance, that 9 soils of all those measured showed the exponent 5.0 (that is, from 4.95 to 5.15), and of these, one was a Washburn loam. From the lower diagram we see that eight Caribou loams showed the exponent 5.0, and of these eight, four were typical Caribou loams. The exponent 4.8 is characterized by the greatest number of typical Caribou loams; that is to say, the *mode* is 4.8. The mode for all the Caribou loams, typical or not, is 5.0 and is not so sharply defined as the mode for the typical Caribou loam. The mode for the Washburn loam is 6.4 and is still less sharply defined. It is probably more than a coincidence that the Washburn loam is found in the field to be more variable, even over small areas, than the Caribou. Two samples of Washburn loam overlapped the typical Caribou region; as noted previously, these two showed little or no scab. The frequency diagram for all the soils examined (upper diagram, taking into account all the blocks irrespective of the shading) shows two modes; that representing the Washburn loam, however, is not very marked. It will be recalled that in collecting the samples intermediate and atypical specimens (except shale loams) were especially sought. The Caribou shale loam is naturally less acid than the Caribou loam, since here the limestone shale which underlies the soils of this region comes near the surface and is mixed with the surface soil. An explanation for the difference of reaction between Caribou and Washburn loam cannot as yet be offered.

The soils of this region are never limed, for fear of the potato scab, and the Washburn and Caribou loams present a possibility for differentiation of type by hydrogen-ion measurements which is not afforded by limed soils.

The reaction of most of the samples of Washburn loam was suitable for the growth of the potato scab organism. We are in general agreement with the statement of Westover and Rowe (22), that potatoes grown on this soil

FIG. 3. FREQUENCY DIAGRAMS SHOWING THE NUMBER OF SAMPLES HAVING ANY GIVEN HYDROGEN-ION EXPONENT

type "are inferior and usually scabby, so that it is not advisable to grow them on this soil," even though in a few cases clean potatoes were found and the hydrogen-ion concentration was such as to suggest that in these cases further crops of clean potatoes may be expected.

ACID-LAND AGRICULTURE

In a very interesting bulletin Coville (5) discussed the relative sensitiveness of various crops to soil acidity. He showed that soil acidity is not always an objectionable condition which invariably requires an application of lime, in fact that soil acidity may be beneficial in controlling plant diseases or in preventing malnutrition, and that under certain economic conditions a complete system of acid-land agriculture, based on the selection of acid-tolerant crops in the rotation, is practical and desirable. He concluded that the extent to which our cheap eastern acid lands can be utilized with small applications of lime, or under some conditions without its use, is an important subject for detailed investigation, from which may reasonably be expected results of far-reaching economic importance. He had in mind for the most part soils on which red clover will not grow satisfactorily, but it is now clear that acid-land agriculture is a question of degree, and that an acid-land agriculture is actually being practised in northern Maine, especially on the Caribou loam, upon which potatoes and various truck crops are successfully raised. Liming is not practised. Clover is grown on both Caribou and Washburn loams, a mixture of red clover and alsike generally being sown. In general, red clover does somewhat better on the Washburn loam than on the more intensely acid Caribou loam, but fairly good stands of clover are obtained on the Caribou loam.⁶

Experience with litmus paper has sometimes led to the opinion that a degree of acidity tolerable on one soil type may be excessive on a different soil type; it has been shown, however, that litmus paper can not be relied upon for distinctions of acid intensity in soils (10). There seems to be no reason to suspect that we are dealing, in the case of the Caribou loam, with an exceptional condition in which the degree of acidity represented by the exponent 5 is less harmful than in other soils; on the contrary, other soils having the exponent 5 have come to our attention which do not require liming to produce good yields of potatoes and various truck crops and which include mucks and sands from Florida and some specimens of Norfolk sand.

Because of these facts it is difficult for us to agree with Sharp and Hoagland (21) that "the rational treatment of acid soils requires that sufficient lime be added to bring the soil to a neutral or slightly alkaline reaction." They were taking the exponent 7 as the index of neutrality. In the absence of sufficient evidence, to adopt the exponent 7 as the end-point to be reached in liming would seem quite as arbitrary as to adopt the end-point indicated by any one of several lime-requirement methods, because the exponent 7, though it denotes neutrality in the physico-chemical sense, has no other special

⁶ This season (summer of 1918) red clover is doing very poorly in many cases on the Caribou loam; the great difference between the growth of red clover on the two types can almost be used safely for distinguishing the types in the field.

significance.⁷ It is quite possible that the exponent 5 may be a sufficient approach to neutrality for many soils and systems of cropping, *whether this intensity of acidity belongs naturally to the soil or is reached by partial liming*. We do not propose the exponent 5 as a standard end-point; on the contrary, we wish to urge that the need is for observation and experiment, not for convention.

SUMMARY

Satisfactory procedures for the determination of hydrogen-ion concentration in soils colorimetrically and electrometrically have been described. It is necessary to add one or two cubic centimeters of water per gram of air-dry soil, but this addition of water does not seem to be a serious limitation.

The electrometric and colorimetric results on a large number of soils agreed within the experimental error.

Examination of a large number of soils from northern Maine showed an excellent correlation between hydrogen-ion concentration and occurrence of common potato scab. Soils having a hydrogen-ion exponent as low as 5.2 rarely produced scabby potatoes, soils having exponents much higher generally did produce scabby potatoes. Similar results were found for a few soils of different origin and type. The limiting zone of hydrogen-ion exponent for the potato scab organism appears to be about the same for the soil as had previously been found for culture media.

The characteristic difference of hydrogen-ion exponent between the Caribou and the Washburn loams has been confirmed. The typical Caribou loam has a hydrogen-ion exponent of about 4.8 and is free from scab, whereas the Washburn loam is generally less intensely acid (shows larger exponents) and potatoes grown on it are usually scabby.

A considerable number of soils having the exponent 5 are successfully cultivated in potatoes and truck crops without liming, showing that the exponent 7 (which indicates physico-chemical neutrality) can hardly be taken in general as "the rational" end-point in lime-requirement tests. No such standard end-point is suggested, this being left for future determination with specific crops.

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⁷ For instance, it emphatically does not mean that the freely-soluble acid substances in the soil are completely neutralized, though this might be inferred from a recent discussion (13, p. 139-140), or that no more hydrogen ions are present (we do not understand the force of the expression "free hydrogen ions," which is sometimes used), or that conditions are optimal for the growth of acid-sensitive microorganisms.

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