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UNIVERSITY OF ILLINOIS

Agricultural Experiment Station

CIRCULAR No. 185

A LIMESTONE TESTER

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URBANA, ILLINOIS, FEBRUARY, 1916

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"Necessity is the mother of invention," and the following simple method for analyzing limestone for relative purity was designed by the writer because of the frequent need for definite information as to the comparative value or relative purity of limestone from different sources. The method can also be used for ascertaining the amount of limestone in soils.

Probably there is not a teacher of agriculture or a county agricultural adviser or demonstration agent in the humid sections of the United States who could not make such analyses with satisfaction and credit to himself and with profit and large educational value to the farmers of his county; and many farm boys will make accurate analyses after some practice.

This method is not patented, but is designed and offered to the public for the service it may render in helping to place American agriculture on a more scientific and profitable basis. The tester can be assembled from apparatus and chemical supply houses at a cost of $6 or $8. This includes the apparatus as illustrated and the mortar, balance and weights, but not the blocks or acid, thermometer, or barometer.

As a rule, whatever character of service a public employe undertakes to render to one citizen should also be rendered to all citizens if they desire it. Consequently care and reason must be exercised in making plans and promises. It is impossible as well as unwise for the experiment station chemist to analyze soil samples collected and sent in by all the farmers of the state. Furthermore, farmers are not entitled to such expensive private service at public expense. The cost of a soil analysis varies from $10 to $25 per sample, depending upon the laboratory equipment and the number of samples analyzed, while the average tax upon the individual farm for the adequate support of soil investigations would not exceed ten to twenty-five cents.

Analyses of miscellaneous samples of soil, collected by unauthorized and untrained persons, by inaccurate and nonuniform methods, usually imperfectly representing even a definite stratum from a single field, or sometimes a mere patch of ground, might be of little value even to the owner of the piece of land, and probably of no value to the agriculture of a state; while to attempt to do such private work at the state experiment station would only delay the progress of the systematic soil investigations which should be made to cover every type of soil on every farm. Experiment stations may very properly undertake to answer letters from every farmer, but they should analyze soils for none as private citizens.

But farm advisers can test soil for acidity on every farm visited; they can also make the qualitative test for carbonates; and with this simple tester they can easily test every local limestone deposit of possible interest for soil improvement and every carload of limestone shipped into the county, and thus ascertain the relative purity and value of all such materials.

SOME SIMPLE CHEMISTRY

As explained in "Farm Truth No. 1," "Ground Limestone for Southern Soils," ordinary limestone is calcium carbonate, $CaCO_3$, and dolomitic limestone is calcium magnesium carbonate, $CaMg(CO_3)_2$. It should be known that the atomic or combining weights of these elements are:

40 for calcium	12 for carbon
24 for magnesium	16 for oxygen

Consequently the molecular weight for calcium carbonate is **100**; and, since the calcium and magnesium atoms have equal power to neutralize acidity, 184 pounds of pure dolomite have the same power as 200 of pure calcite. In both cases the basicity of the compound may be measured by its content of carbon dioxid, and the relative purity may be expressed in terms equivalent to calcium carbonate.

If a carbonate be treated with a strong acid, it will be decomposed, with the formation of salts of the strong acid and the liberation of carbonic acid, H_2CO_3. Thus,

$$CaCO_3 + 2HCl = CaCl_2 + H_2CO_3, \text{ or}$$
$$CaMg(CO_3)_2 + 4HCl = CaCl_2 + MgCl_2 + 2H_2CO_3$$

(These reactions are easily understood when it is known that hydrogen and chlorin have single bonds of attraction, while calcium, magnesium, and oxygen atoms have two bonds each, and carbon has four bonds.) The carbonic acid produced at once decomposes into water, H_2O, and carbon dioxid, CO_2, which is a gas and is easily measured by volume.

The limestone tester should include the following:

1 small balance, capacity 50 grams, sensitive to 5 milligrams or less.
1 set of weights from 10 milligrams to 20 grams.
1 cylinder of 500 cubic centimeters capacity, graduated to 5 cubic centimeters.
1 small wide-mouth bottle, about 200 cubic centimeters.
1 large wide-mouth bottle, about 800 cubic centimeters.
1 bulb tube, about 20 cubic centimeters.
3 pieces of bent glass tubing to fit apparatus.
2 rubber stoppers to fit bottles and having suitable holes.
2 pieces of rubber tubing to fit connections and long enough to allow necessary adjustments in position of apparatus.

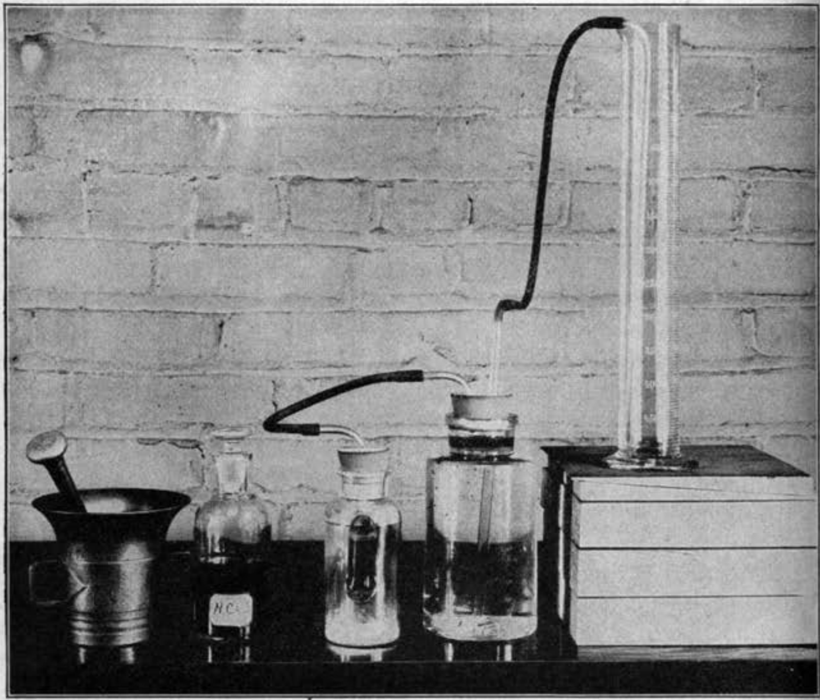

FIG. 1.—LIMESTONE TESTER; BEFORE REACTION

The only chemical needed is concentrated commercial hydrochloric acid (less properly called "muriatic" acid), which is best secured from a local drug store and ought not to cost more than 15 cents a pint. This amount should be sufficient for about fifty analyses. Before using the acid, it may be diluted with one pint of water.

DIRECTIONS FOR MANIPULATION

Set up the balance and tester on a firm, level desk or table. Place the proper glass tube in the cylinder and then fill with water to the 500-cc. mark. Pinch the rubber connection and raise the tube or lower the cylinder till the end of the glass tube is near the surface of the water. Again read the water-level and record the difference as the "tube correction" for the full height. Transfer the water to the large bottle and nearly fill it. Then add enough oil (clean nonvolatile oil) to cover the water with a film about 1/10 inch thick. Insert the stopper firmly, and by blowing on the short connecting tube force the water into the cylinder, which should be so adjusted on wood blocks (which are better than books and pamphlets) that the

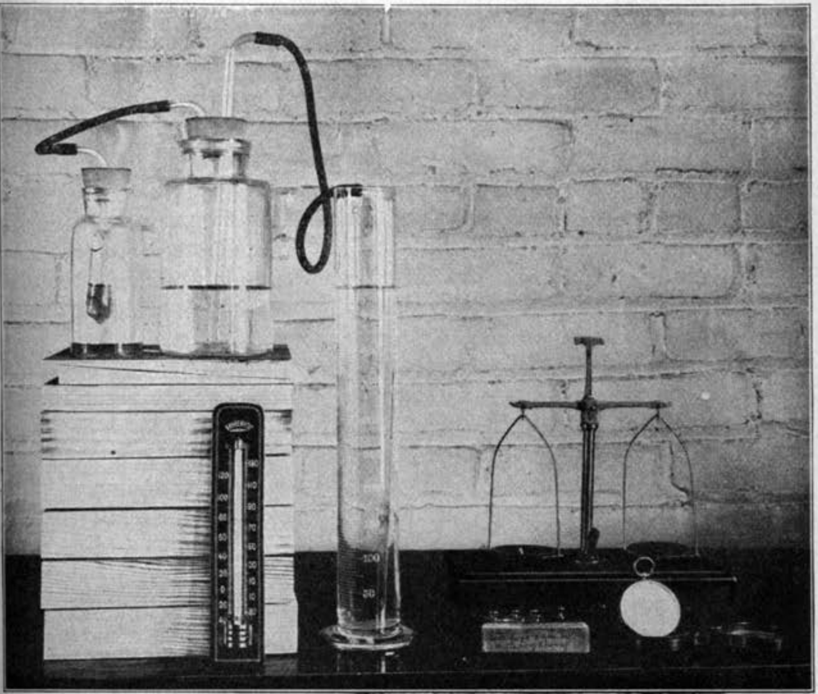

FIG. 2.—LIMESTONE TESTER; AFTER REACTION

water will safely cover the end of the delivery tube in the bottom of the cylinder and maintain a syphon connection between the bottle and the cylinder, the water seeking its level under atmospheric pressure. (See left-page illustration.)

Place a 2-gram weight on one pan of the balance and then with a knife blade add the powdered limestone to the other pan till the pointer shows equilibrium. Thus, if when put in gentle motion the pointer swings 3 spaces to the left of the zero point, then 2½ spaces to the right, and then back 2 spaces to the left, the weight is correct. Rinse out the small bottle, and without drying transfer to it the 2 grams of limestone. Insert the stopper carrying the acid tube partly filled with hydrochloric acid. Then close the connection between the bottles and record the water-level in the cylinder.

Now lower the cylinder an inch or two by removing one of the blocks, and then tip the small bottle and allow a few drops of acid to fall on the stone. If the material is common limestone, the foaming or evolution of gas will be rapid, but with dolomite it may be quite slow, and with pure dolomite it is well to warm the small bottle by holding the bottom in the palm of the hand or in a glass of hot water. Add more acid from time to time, lowering the cylinder or raising the bottles so as to preserve nearly atmospheric pressure in the bottles. When the addition of acid ceases to liberate carbon dioxid, the chemical action is complete. Adjust the apparatus so as to re-establish perfectly the water-level and thus place the gas under the local atmospheric pressure, as shown in the right-page illustration. (If the small bottle has been warmed, it must be allowed to cool to room temperature before the final adjustment.)

Record the water-level in the cylinder, and subtract from this the original reading and the proper "tube correction." The remainder represents the volume in cubic centimeters[1] of gas liberated from the stone and the small volume of water vapor associated with it. The weight (in milligrams[2]) of 1 cubic centimeter of carbon dioxid under the local conditions multiplied by the number of cubic centimeters found, gives the weight of carbon dioxid liberated from the stone; this weight divided by .44 gives the corresponding weight of calcium carbonate; and, of course, this divided by 2000 (the number of milligrams of stone taken) gives the purity, best expressed in percentage.

The accompanying tables give the weight of 1 cubic centimeter of carbon dioxid (corrected for water vapor) for a wide range of temperature and atmospheric pressure.

For the highest degree of accuracy, the analyst should have access to a thermometer and barometer, both of which are very common instruments in nearly every community. The tables may be used with either centigrade or Fahrenheit thermometers, and with barometers graduated either in millimeters or in inches.

The Computation Explained

As an example, suppose the "tube correction" for the full 500 cubic centimeters is 10 cubic centimeters (1 in 50); that the initial reading (before the reaction) is 6 cubic centimeters; and that the final reading is 464 cubic centimeters, with the room temperature at 70° F. and the barometer reading 30.08 inches. Then the net "tube correction" is practically 9 cubic centimeters, and

$$464 - (6 + 9) = 449 \text{ cc. at } 70^\circ \text{ and } 30.08''$$

Referring to the last column and the bottom line of the second part of the table, we find that for 69.8° and 30.08″ (the nearest figures to the actual readings) the weight of 1 cubic centimeter of carbon

[1]10 millimeters make 1 centimeter,
100 centimeters make 1 meter (39.37 inches),
1000 meters make 1 kilometer (about ⅝ mile),
1000 cubic centimeters make 1 liter (about 1 quart), and
1 liter of water weighs 1000 grams.

[2]1000 milligrams make a gram,
1000 grams make 1 kilogram, and
1000 kilograms make 1 metric ton (2205 pounds).

dioxid is 1.791 milligrams. (Easy interpolation will give even greater exactness.) This multiplied by 449 gives 804 milligrams of carbon dioxid; and this divided by .44 (calcium carbonate contains 44 percent of carbon dioxid) gives 1828 milligrams, or 1.828 grams, of calcium carbonate equivalent,—which divided by 2 (the weight of stone taken) shows .914, or 91.4 percent, as the relative purity. (In practice one divides by .88 instead of by .44 and then by 2.)

While the film of oil lessens the rapidity of absorption or diffusion, it is well to run a preliminary analysis and allow some carbon dioxid to stand over night in the bottle in order that equilibrium may be established. Of course, the same water may then be used for weeks, with occasional slight addition to replace evaporation.

With high temperature or low barometer, or with very pure limestone, especially dolomite, the volume of gas from a 2-gram sample may exceed 500 cubic centimeters. If not too much, the height above the mark can be measured on a card and the measure applied to the scale below the mark in order to ascertain the volume. Or, by tipping the cylinder, some water can be transferred to a glass, to be returned and measured later.

With very impure limestone it is well to take 4 grams or more for analysis, noting the weight, of course, and making the corresponding change in computing the percentage of purity. Coarse pieces of stone can easily be powdered in an iron or brass mortar, or, if necessary, with a hammer and flatiron in a tin can.

LIMESTONE SAMPLES AND SOIL

In collecting samples of limestone deposits, it is better to chip off many small pieces from different parts of the stratum than to select one large piece to pulverize. The author has found variations from 55 percent to 106 percent in the calcium carbonate equivalent of different limestones considered for soil improvement. Of course, only dolomite could show more than 100 percent equivalent, as more fully explained in Farm Truth No. 1.

In determining the limestone in soils, 2 to 50 grams of soil may be used (varying with the amount of limestone present). The weight of calcium carbonate found must be divided by the weight of soil used, care being taken with the decimal point in the computations converting to percentages or to pounds in 2,000,000. Each .1 percent corresponds to 1 ton in 2,000,000 pounds of soil, the weight of the plowed soil of an acre to a depth of about 6⅔ inches.

THE GAS LAWS

It is of interest to the thoughtful analyst to remember that gas expands with rising temperature and shrinks with increasing pressure;

WEIGHT OF CARBON DIOXID IN MILLIGRAMS PER CUBIC CENTIMETER
(Corrected for water vapor, etc.—Parr's Table: J. Am. Chem. Soc., 31, 237)

°C. \ mm.	720	722	724	726	728	730	732	734	736	738	740	742	744	°F.
10	1.779	1.784	1.789	1.794	1.799	1.804	1.809	1.814	1.819	1.824	1.829	1.834	1.839	50.0
11	1.771	1.776	1.781	1.786	1.791	1.796	1.801	1.806	1.811	1.816	1.820	1.825	1.830	51.8
12	1.762	1.767	1.772	1.777	1.782	1.787	1.792	1.797	1.802	1.807	1.812	1.817	1.822	53.6
13	1.754	1.759	1.764	1.769	1.774	1.779	1.784	1.789	1.794	1.799	1.804	1.809	1.813	55.4
14	1.746	1.751	1.756	1.761	1.765	1.770	1.775	1.780	1.785	1.790	1.795	1.800	1.805	57.2
15	1.737	1.742	1.747	1.752	1.757	1.762	1.767	1.772	1.777	1.782	1.786	1.791	1.796	59.0
16	1.729	1.734	1.739	1.744	1.748	1.753	1.758	1.763	1.768	1.773	1.778	1.783	1.788	60.8
17	1.720	1.725	1.730	1.735	1.740	1.745	1.750	1.755	1.759	1.764	1.769	1.774	1.779	62.6
18	1.712	1.717	1.722	1.726	1.731	1.736	1.741	1.746	1.751	1.756	1.760	1.765	1.770	64.4
19	1.703	1.708	1.713	1.718	1.723	1.727	1.732	1.737	1.742	1.747	1.752	1.756	1.761	66.2
20	1.694	1.699	1.704	1.709	1.714	1.719	1.723	1.728	1.733	1.738	1.743	1.748	1.752	68.0
21	1.686	1.690	1.695	1.700	1.705	1.710	1.715	1.719	1.724	1.729	1.734	1.739	1.743	69.8
22	1.677	1.682	1.686	1.691	1.696	1.701	1.706	1.710	1.715	1.720	1.725	1.730	1.734	71.6
23	1.668	1.673	1.677	1.682	1.687	1.692	1.696	1.701	1.706	1.711	1.716	1.720	1.725	73.4
24	1.659	1.664	1.668	1.673	1.678	1.683	1.687	1.692	1.697	1.702	1.706	1.711	1.716	75.2
25	1.650	1.654	1.659	1.664	1.669	1.673	1.678	1.683	1.688	1.692	1.697	1.702	1.706	77.0
26	1.640	1.645	1.650	1.654	1.659	1.664	1.669	1.673	1.678	1.683	1.687	1.692	1.697	78.8
27	1.631	1.636	1.640	1.645	1.650	1.654	1.659	1.664	1.669	1.673	1.678	1.683	1.687	80.6
28	1.621	1.626	1.631	1.635	1.640	1.645	1.649	1.654	1.659	1.664	1.668	1.723	1.677	82.4
29	1.612	1.616	1.621	1.626	1.630	1.635	1.640	1.644	1.649	1.654	1.658	1.663	1.668	84.2
30	1.602	1.607	1.611	1.616	1.620	1.625	1.630	1.634	1.639	1.644	1.648	1.653	1.658	86.0
Inches	28.34	28.42	28.50	28.58	28.66	28.74	28.82	28.90	28.98	29.06	29.13	29.21	29.29	....

Weight of Carbon Dioxid in Milligrams per Cubic Centimeter

(Corrected for water vapor, etc.—Parr's Table: J. Am. Chem. Soc., 31, 237)

°C. \ mm.	746	748	750	752	754	756	758	760	762	764	766	768	770	°F.
10	1.844	1.849	1.854	1.859	1.864	1.869	1.874	1.879	1.884	1.889	1.894	1.899	1.904	50.0
11	1.835	1.840	1.845	1.850	1.855	1.860	1.865	1.870	1.875	1.880	1.885	1.890	1.895	51.8
12	1.827	1.832	1.837	1.842	1.847	1.852	1.857	1.862	1.867	1.872	1.877	1.882	1.887	53.6
13	1.818	1.823	1.828	1.833	1.838	1.843	1.848	1.853	1.858	1.863	1.868	1.873	1.878	55.4
14	1.810	1.815	1.820	1.825	1.830	1.834	1.839	1.844	1.849	1.854	1.859	1.864	1.869	57.2
15	1.801	1.806	1.811	1.816	1.821	1.826	1.831	1.836	1.840	1.845	1.850	1.855	1.860	59.0
16	1.792	1.797	1.802	1.807	1.812	1.817	1.822	1.827	1.832	1.837	1.841	1.846	1.851	60.8
17	1.784	1.789	1.793	1.798	1.803	1.808	1.813	1.818	1.823	1.828	1.833	1.837	1.842	62.6
18	1.775	1.780	1.785	1.790	1.794	1.799	1.804	1.809	1.814	1.819	1.824	1.828	1.833	64.4
19	1.766	1.771	1.776	1.781	1.785	1.790	1.795	1.800	1.805	1.810	1.814	1.819	1.824	66.2
20	1.757	1.762	1.767	1.772	1.776	1.781	1.786	1.791	1.796	1.801	1.805	1.810	1.815	68.0
21	1.748	1.753	1.758	1.763	1.767	1.772	1.777	1.782	1.787	1.791	1.796	1.801	1.806	69.8
22	1.739	1.744	1.749	1.753	1.758	1.763	1.768	1.773	1.777	1.782	1.787	1.792	1.797	71.6
23	1.730	1.735	1.739	1.744	1.749	1.754	1.759	1.763	1.768	1.773	1.778	1.782	1.787	73.4
24	1.721	1.725	1.730	1.735	1.740	1.744	1.749	1.754	1:759	1.763	1.768	1.773	1.778	75.2
25	1.711	1.716	1.721	1.725	1.730	1.735	1.740	1.744	1.749	1.754	1.759	1.763	1.768	77.0
26	1.702	1.706	1.711	1.716	1.721	1.725	1.730	1.735	1.739	1.744	1.749	1.754	1.758	78.8
27	1.692	1.697	1.701	1.706	1.711	1.716	1.720	1.725	1.730	1.734	1.739	1.744	1.748	80.6
28	1.682	1.687	1.692	1.696	1.701	1.706	1.710	1.715	1.720	1.724	1.729	1.734	1.739	82.4
29	1.672	1.677	1.682	1.686	1.691	1.696	1.700	1.705	1.710	1.714	1.719	1.724	1.728	84.2
30	1.662	1.667	1.672	1.676	1.681	1.686	1.690	1.695	1.700	1.704	1.709	1.714	1.718	86.0
Inches	29.37	29.45	29.53	29.61	29.68	29.76	29.84	29.92	30.00	30.08	30.16	30.24	30.31	....

or, conversely, the weight of a constant volume of gas increases with increasing pressure, and decreases with rising temperature, as may be seen from the table of weights of carbon dioxid.

At standard temperature (0°C.) and pressure (760 mm.), 1 cubic centimeter of dry carbon dioxid weighs 1.97 milligrams. The weight (W) of a given volume of the moist gas may be computed from the following formula,[1] in which V is the observed volume, P the barometric pressure in millimeters, p the water-vapor pressure, and t the room temperature, centigrade:

$$W = \frac{V\,(P - p)\,1.97}{760\left(1 + \frac{1}{273}t\right)}$$

The expansion with rising temperature relates to the absolute zero, which is —273° C. The vapor pressure of water is as follows.

°C.	10	11	12	13	14	15	16	17	18	19	20
mm.	9	10	10	11	12	13	14	14	15	16	17
°C.	21	22	23	24	25	26	27	28	29	30	
mm.	18	19	21	22	24	25	27	28	30	32	

Thus in the above example,

$$W = \frac{449\,(764 - 18)\,1.97}{760 \times \frac{294}{273}} = 806 \text{ mg. } CO_2$$

$$\text{And } \frac{.806}{2 \times .44} = .916, \text{ or } 91.6\% \text{ } CaCO_3 \text{ equivalent}$$

Of course, thermometers are found everywhere, and good aneroid barometers, which cost only $5 or $10, are quite common; and they are satisfactory if properly set by a standard barometer. In case no barometer is accessible, the local pressure may be assumed, with the understanding that this appreciably reduces the accuracy of the work. In this case one may use 29.92 inches (760 millimeters) for normal atmospheric pressure at sea level, and for each 100 feet elevation above sea level deduct .10 inch, or 2.5 millimeters. Thus, for normal barometric pressure at an elevation of 600 feet above sea level, use

[1]Some minor complex sources of error are not taken into account in this formula.

29.32 inches, or 745 millimeters, but extreme variations of 1 inch (25 millimeters) above or below this normal may occur.

It is well for the amateur analyst to secure a sample of limestone of known content of carbon dioxid from his agricultural experiment station in order to test both the tester and himself.

It may be added that eight minutes is the total time required by the author for completing an analysis, including the weighing of the 2 grams of stone, placing acid in the acid tube, conducting the chemical operation, adjusting the apparatus, measuring the displaced water, recording and subtracting corrections, noting temperature and pressure, and computing the results (with the help of the tables given) to show the percentage purity of the stone.

ADDED NOTE

This limestone tester, exactly as described above, was designed by the writer in April, 1914, while connected with the Southern Settlement and Development Organization, engaged in the investigation of methods for the improvement of the agriculture of the southern states, during a year's leave of absence from the University of Illinois. With the addition of a dozen words, the above description and directions are taken verbatim from "Farm Truth No. 2" of that organization, which was in press in 1914, the page proof having been read before the termination of the writer's leave of absence on October 31, 1914. (The publication of Farm Truth No. 2 has been much delayed.)

The method of transferring the displaced water and measuring its volume in an ordinary graduated cylinder was original with the writer; also the arrangement of Parr's tables so as to permit the use of either scale on thermometers and barometers; but the acid tube, with an opening on the side near the top of the bulb, is illustrated in an article describing an inaccurate method for determining carbonates in soils by Doctor Max Passon in the *Deutsche Landwirtschaftliche Presse*, May 29, 1901. Passon's method has been commercialized in the United States as a "soil tester," but it has very little value for this purpose because carbonates are normally absent and the "test" is negative. A hundred such negative tests can be made with five cents' worth of hydrochloric acid. Where carbonates are present (as they are occasionally in humid regions and very commonly in arid regions), a drop or two of acid applied directly to the soil will produce foaming by liberating carbon dioxid gas; and where this simple test shows carbonates naturally present, the carbonates are almost invariably in such great abundance that no further test is necessary. But normally the most valuable simple soil tester is sensitive blue litmus paper which shows acidity by turning red when pressed between two pieces of soil. This test should also be applied to the subsoil. Usually five minutes is time enough to leave the paper in the soil, and five cents' worth of litmus paper will suffice for a hundred tests. This reddening of blue litmus paper shows that the soil is not only devoid of carbonates, but that it is sour, and, consequently, that ground limestone should be applied.

A "calcimeter" described in Circular No. 9 of the Kentucky Agricultural Experiment Station, issued under date of October, 1915, may have been an unconscious outgrowth of a description which the writer gave at that institution in June, 1914, of the method and apparatus he had then been using for two months, or it may have been a wholly independent design. In either case there is no reflection, for most frequently one cannot trace to its origin his own thought, and the writer fully agrees with Emerson that "thought is the property of him who can entertain it."

Upon request the Illinois Experiment Station will furnish quotations as to the exact cost of the limestone tester.