

Soil Research — Bodenkundliche Forschungen Recherches sur le Sol

Supplements to the Proceedings of the International
Society of Soil Science — Beiheft zu den Mitteilungen
der Internationalen Bodenkundlichen Gesellschaft —
Suppléments aux Comptes Rendus de l'Association de
la Science du Sol

Vol./Bd. II

1930

No 2

Report of the Committee on Soil Reaction Measurements

Second International Commission

President: Prof. Dr. Alex. A. J. von 'Sigmond

Part II. Conclusions and Recommendations

The Committee has already published (Soil Research, Vol. 2, 1930, p. 77—139) the methods and the results of its work. It has held one meeting on July 8th, 9th, 10th and 11th 1930, in the Geologische Landesanstalt, Berlin.

The following members were present: Dr. D. J. Hissink, Groningen (Holland) (Chairman); Dr. E. M. Crowther, Harpenden (England); Dr. S. B. Hooghoudt, Groningen (Holland); Prof. Dr. S. Tovborg-Jensen, Lyngby (Denmark); Dr. S. Kühn, Budapest (Hungary); Dr. M. Trénel, Berlin (Germany) and Dr. Fresenius, Berlin (Germany) (representing Prof. Dr. O. Lemmermann, Berlin, Germany).

Detailed comments and statistical analyses of the results had previously been circulated by several members, and, after a full discussion, it was unanimously agreed to make the following report and recommendations.

Comparison of methods

With a few exceptions, the pH values obtained by four independent methods in several Institutes showed satisfactory agreement.

Quinhydrone method

Since this Committee was set up primarily as the result of criticisms at Budapest of the quinhydrone method, we have directed our attention primarily to this method. Our work has shown conclusively that many soils give much higher (more alkaline) equilibrium pH values by the

quinhydrone than by other methods (see Heintze and Crowther's paper, Budapest Trans. A) and, further, that these soils are the ones which show a rapid increase in pH within the first few seconds after the addition of quinhydrone (see Kühn and Scherf's paper, *ibid.*). All Institutes obtained similar equilibrium pH values for these erratic soils. Out of a total of 28 soils examined, 8 gave erroneous results by the quinhydrone method, the excesses of the Qh pH over the H₂ pH being 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.8, 1.3. In some of the Institutes each of the 8 erratic soils, but none of others, showed a marked initial potential drift from 15 (or 8) seconds to 60 seconds after adding the quinhydrone. One Institute failed to detect this initial drift because the soil and quinhydrone were shaken together for several seconds before the time readings commenced. At Rothamsted similar errors in these 8 soils when quinhydrone was added in colorimetric measurements.

Proposed Quinhydrone Method

Apparatus: The quinhydrone, electrodes, and KCl bridge should be prepared in accordance with the instructions in Part 1 of this Report (Soil Research, Vol. 2, 1930, p. 81—83). The ratio of soil to liquid has not been examined by us and we therefore retain the 1 : 2.5 ratio adopted at the Groningen Conference.

Preliminary approximate measurement

It is necessary to make a rapid measurement in order to ascertain whether or not the soil is suitable for the quinhydrone method. The soil and water are shaken together for one minute, the quinhydrone added, and the mixture is immediately shaken vigorously for not more than 2 seconds. All time intervals are measured from the time of adding the quinhydrone to the soil. The electrode and KCl bridge are introduced and the potential measured at 10 (or at most 15), 30 and 60 seconds.

Final more accurate measurement

Where the increase in apparent pH value from 10 to 60 seconds in the preliminary measurement is less than 0.2, the soil may be regarded as suitable for the quinhydrone method, but the determination should be repeated with less rapid manipulation. The soil and water are shaken for one minute, as in the preliminary measurement, but, after adding the quinhydrone, the mixture is shaken for 10 seconds and the potential measured at 60 seconds.

Where the increase in apparent pH value from 10 to 60 seconds in the preliminary measurement is more than 0.2, the soil is unsuitable for the quinhydrone method and it is better to use some other method. In this case approximate pH values may, however, be obtained by the quinhydrone method if the preliminary measurement is repeated on a new soil sample and the reading taken at 10 seconds.

In recording such approximate results it should be clearly stated that they are „10 second values“.

Hydrogen electrode

We have found that the sintered glass crucibles of Schott, Jena, are convenient as hydrogen electrode vessels. The flask and funnel shown in Fig. III, p. 99 of Part I of this Report are not necessary and may with advantage be replaced by a rubber stopper inserted below the sintered glass plate (Fig. I). Alternatively a Schott, Jena, sintered glass funnel may be used (Fig. II). Constant potentials may be obtained within about one minute provided that:

- a) the filter is sufficiently coarse-grained to allow a rapid stream of hydrogen;
- b) the film of platinum or palladium deposited on the electrode is very thin and
- c) only a few millimetres of the electrode are immersed in the suspension.

The KCl bridge should not be lowered into the suspension until immediately before the potential measurement. With alkaline soils, especially in the naturally moist state, the removal of carbon dioxide by the current of hydrogen introduces an error and it is better to use a vessel of the Clark type.

Commercial hydrogen, preferably electrolytic, is often suitable for use without further purification.

Colorimetric Measurements

Some Institutes found very good agreement between colorimetric and electrometric measurements, but others did not. Although it is possible to obtain satisfactory results by working with great care, the colorimetric method is not at present a simple one. The selection of the appropriate indicator is of the highest importance. It is essential that indicators such as methyl red, which are adsorbed by the soil, should not be used in soil suspensions. We have found that the barium sulphate method of Kühn for clearing the suspension is very useful

and we recommend its trial in other laboratories. Several of the cooperating Institutes propose to repeat the colorimetric determinations with a better technique.

Antimony Electrode

We make at present no proposals on this method as it has not been sufficiently tested.

Aqueous and potassium chloride suspensions

We would urge the more general adoption of the Groningen recommendation that reaction measurements should be made both in aqueous and in 1 N KCl suspensions. The pH values in 1 N KCl appear to be less influenced by changes in biological and meteorological conditions and thus measure a more permanent characteristic of the soil. Aqueous suspensions should, of course, be used in studying seasonal and similar fluctuations.

Berlin, July 11th 1930

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Bericht des Ausschusses zur Prüfung der Methoden zur Bestimmung der Bodenreaktion

Zweite Internationale Kommission

Vorsitzender: Prof. Dr. Alex. A. J. von Sigmund

II. Teil. Beschlüsse und Vorschläge

Die Ergebnisse der internationalen Prüfung der Methoden zur Bestimmung der Bodenreaktion sind bereits in Soil Research, Bd. II, 1930, S. 77—139 veröffentlicht worden. Die Sitzung wurde am 8. bis 10. Juli auf Einladung von Dr. Trénel in der Geologischen Landesanstalt, Berlin, abgehalten. Anwesend waren als Vorsitzender Dr. D. J. Hissink, Groningen (Holland); Dr. E. M. Crowther, Harpenden (England); Dr. S. B. Hooghoudt, Groningen (Holland); Professor Dr. S. Tovborg-Jensen, Lyngby (Dänemark); Dr. S. Kühn, Budapest (Ungarn); Dr. M. Trénel, Berlin (Deutschland) und Dr. Fresenius, Berlin (Deutschland) als Vertreter von Prof. Dr. O. Lemmermann, Berlin (Deutschland).