

Technical paper

A Conventional Method for Valid „Actual Soil pH“ Measurement

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Abstract

After recognition of the Suspension Effect problem in potentiometric measurements in aqueous suspensions, no scientific consensus about its cause and nature was obtained. Numerous conventional methods of soil pH measurement were therefore introduced for practical soil pH determination. Most of the results of these methods are not valid with regard to the international pH scale. The method proposed in the present work rejects improper procedures and introduces correct soil sampling and a suitable pH measuring technique, as follows: the indicator glass electrode, substituting for roots in the soil, is inserted in a partly diluted sample suspension of the original soil and the modified reference electrode contacts the sample in a manner that eliminates the abnormal liquid junction potential. „Actual soil pH values“ measured in this way are valid but the method used is a conventional one. Namely, the irreversible potential of the glass electrode includes the suspension effect of the first kind (SE1) and is a mixed steady-state potential. It is considered by convention as a substitute for and equivalent to the equilibrium potential which as a rule does not exist in a suspension. The soil pH values measured by the proposed conventional method are reproducible and valid with regard to the international hpH scale. They could be considered as the pH values, with uncertainty of ± 0.1 pH unit, to which the roots are exposed.

Keywords: Actual soil pH, Steady-state mixed electrode potential, Suspension effect

1. Introduction

For the successful growth of plants, the roots must be in soil of an appropriate pH value. Potentiometric pH measurement of the soil, which is an aqueous suspension of mostly inorganic particles, is complicated because of the appearance of the suspension effect (SE).

After the year 1930, when the SE was first mentioned in the literature, many scientific publications appeared, but no consensus was attained about its cause and nature. Several conventional methods were introduced into practical routine for soil pH measurements. Many publications on the results of these conventional methods discussed the measured pH values, but the results remained invalid.

The causes of their invalidity are:

- a) improper preparation of soil samples
- b) improper techniques of potentiometric pH measurement.

In Figure 1 a visual representation of pH differences obtained with different methods of measurement is given.

The differences are due to different soil sample preparation methods and to different techniques of measurement.

Recently the question asked repeatedly was what is the essence of the Suspension Effect „puzzle“. Therefore a short simple and clear answer should be given in the light of experiments referring to this effect. The SE arose in connection with pH measurement and the „puzzle“ should be solved with the same experimentation, as follows.

In a beaker containing very diluted HCl solution, an amount of strong ion exchange resin in H – form is added and mixed so that a diluted suspension is obtained. Particles of the ion exchanger are spherical ($d \sim 0.1\text{mm}$) and surrounded by a diffused double layer containing H^+ counter ions. The particles come to equilibrium with the dispersion solution, named the equilibrium solution (eqs). The whole suspension is in this way in equilibrium.

Indirect pH measurement An amount of (eqs) is separated from the suspension and the pH measured in it by a glass – and a reference electrode, calibrated together

with a pH meter. The measured pH value is, for example, $pH_{eqs} = 5.0$. The glass – electrode potential is a reversible potential from which the pH value is deduced. It is obtained in accordance with electrochemical theory, therefore it could be named the „theoretical pH value“, which is valid for the whole suspension. The above used technique is an indirect method for the pH measurement of the suspension.

Direct pH measurement (SE1 and SE2 included)

For a direct pH measurement of a suspension, the glass electrode and the salt bridge of the reference electrode are inserted in the original suspension and the pH measured with the same procedure as with the indirect method. Thus the directly measured pH value is, for example, $pH_{SE1,SE2} = 3.5$. The difference between the directly and indirectly measured pH values, $\Delta pH_{SE1,SE2} = -1.5$, is defined as the „Suspension Effect,“. Instead of $\Delta pH_{SE1,SE2}$, the potential difference of the cells ($\Delta E_{SE1,SE2}$) can be given. The $\Delta pH_{SE1,SE2}$ value can be negative or positive. A positive $\Delta pH_{SE1,SE2}$ can be due to the ion exchange reaction occurring in the contact regions, if e.g. an Sb or Bi pH indicator electrode replaces the glass pH electrode which shows a negative $\Delta pH_{SE1,SE2}$ value.

Interpretation The interpretation of these difference was published already in 1991 (1) and more thoroughly explained in 2007 (2). Because it is meaningful for soil pH definition it should be shortly summarized.

Indirect and direct pH measurements are performed on the same suspension or on a part of a separated (eqs) with the same electrodes calibrated together with a pH meter and differing only in the installation of electrodes. From the salt bridge of the reference electrode inserted in the suspension, KCl solution flows or diffuses. When it reaches the particles it causes the appearance of an abnormal liquid junction potential at the particles/KCl solution border. This is the cause of the appearance of the suspension effect of the second kind (SE2). With increasing electrolyte concentration in (eqs), SE2 decreases. SE2 must be eliminated (e.g. by a modified reference electrode, which has a double salt bridge), when the potential of the glass electrode or the pH derived from it is measured. In the above exemplary measurement, the elimination of SE2 causes the pH difference $\Delta pH_{SE2} = -1.0$, as will be shown later.

Direct measurements (SE1 included) If, on the other hand, the pH is measured for example in the same suspension by using the glass electrode but together with the modified reference electrode, the measured pH value is $pH_{SE1} = 4.5$. The difference between $pH_{SE1,SE2} = 3.5$ and $pH_{SE1} = 4.5$, $\Delta pH_{SE2} = -1.0$, is due to elimination of SE2 and the difference between $pH_{SE1} = 4.5$ and $pH_{eqs} = 5.0$, $\Delta pH_{SE1} = -0.5$, is due to the potential of the glass electrode in contact with the original suspension. In this case the particles participate in the glass electrode potential, causing the inclusion of SE1 in the glass electrode potential.

Interpretation When the particles contact the elec-

trode surface their double layers overlap the (eqs) double layer on the glass electrode surface. In the sporadically formed contact regions different electrochemical reactions with regard to the reactions in the (eqs) double layer. The glass electrode potential depends on two kind of electrochemical reactions. Therefore it is an irreversible mixed potential, which is stable and reproducible enough to be named a steady state mixed potential(4).

From such potential of the glass electrode, which includes SE1, the soil pH is deduced, though it is a non – equilibrium potential. It could be taken as a substitute for the equilibrium potential, because the latter cannot exist in a suspension.

Instead of the pH values used as examples in the above comparisons, the corresponding pH values, taken from Figure 1, can be used where the experimental pH data are given for several soils.

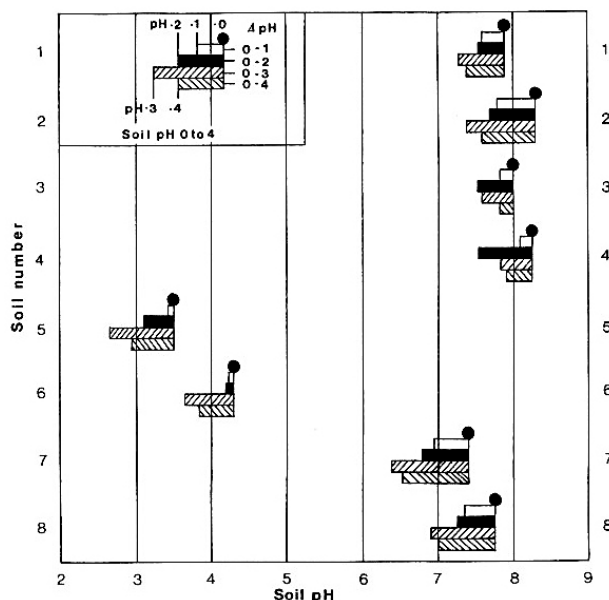


Figure 1. Soil pH values of wetted soils measured with five (pH 0 to pH 4) different methods, using the glass electrode and SCE. The differences ΔpH between pH. 0 (●) and the other pH values are given for comparison. The inset shows the legend of the symbols. pH. 0 = „theoretical“ soil pH, pH. 1 = „actual soil pH“, pH. 2 = directly measured pH including SE, pH. 3 = „theoretical“ pH of sample with added KCl solution, pH. 4 = „Theoretical“ pH of sample with $CaCl_2$ solution.

The scheme of the operational cell for pH SE1 measurement is:



In this way the soil pH_{SE1} obtained is an „actual soil pH value“. For the above used examples its pH value is: $pH_{SE1} = 4.5$ and $\Delta pH_{SE1} = -0.5$. Any other object contacting the suspension, able to react electrochemically with

the suspension (e.g. a root inserted in soil), would also gain a potential, dependent on the characteristics of the suspension.

The roots react to pH changes as can be concluded from Figure 2. This shows that the root potential changes with the HCl concentration (or pH) in solution, but the root is not an ion selective electrode.

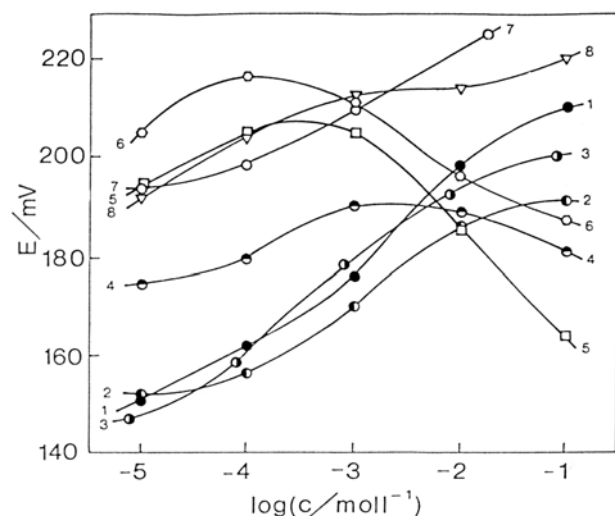


Figure 2. Voltages of the cell Ag | AgCl | Knop's Solution : Horse-beam root : Sample Solution | KCl sat. | AgCl | Ag As a function of the concentrations of sample solutions of: KCl 1, And NaCl 2, NH_4Cl 3, CaCl_2 4, AlCl_3 6, HCl 7 and Ascorbic Acid 8.

It is clear with regard to the above statements and explanations that the actual soil pH_{SE1} value is the correctly argued pH value characterizing the soil pH to which the roots growing in this soil are exposed.

2. Procedures of Soil pH Measurement

2. 1. Preparation of the Soil Sample

The aim of the method is to measure just the pH of the original soil, unchanged except for adding water to obtain a $1/1_w$ dry soil/water ratio, with the water activity $a_w = 1$, without any attempt to obtain other information about the soil. Therefore every manipulation of the soil sample is redundant, and possibly changes the original soil pH.

From an amount of homogenised original soil (e.g. ca. 60 g) some 20 g are separated, weighted and heated in a suitable container to dryness. The dry soil is weighed and the percentage of water in the soil calculated. The rest of the initial soil sample is weighed and the percentage of dry substance calculated. Then an amount of water is added such that the weights of the dry soil and of the total

water in the sample are equal ($1/1_w$). The suspension obtained in this way is mixed to be homogeneous and allowed to equilibrate. A part of this suspension (e.g. 20 g) is separated as (eqs) from the rest of the suspension. If this sample cannot be measured promptly, it should be transported in the form of the suspension in a suitably closed container and measured after 24 hours at the most.

2. 2. pH Measurement of the Soil Sample

The soil sample, electrodes and pH standard solutions should be equilibrated to the ambient temperature (e.g. 25 °C). The end salt bridge of the modified reference electrode should be filled with (eqs) of the soil suspension to be measured, inserted together with the glass electrode in a pH standard solution for pH meter calibration. After calibration the electrodes are cleaned and inserted in the soil sample (eqs). The pH value should be read after a stable value is obtained.

The actual soil pH value measured in this way is valid and in accordance with the international pH scale.

3. Discussion

For potentiometric determination of ion activity in a clear solution, the reversible potential of the corresponding indicator electrode must be measured. This is possible also in the (eqs) of a suspension, but not in the original suspension where only the irreversible steady state mixed potential of the indicator electrode, which includes SE1, exists. Because this mixed potential is stable and reproducible and near to the „theoretical“ electrode potential of the suspension, we propose that it replace the role of the equilibrium potential.

From the irreversible potential of the glass electrode used for direct soil pH measurement, the actual soil pH deduced is characteristic of the measured soil. It is the pH value to which a root growing in the measured soil is actually exposed. We therefore propose that it be declared as the valid pH value of the measured soil sample.

Today used methods for soil pH measurements could still be employed in the future, but to guide users about the reliability of the pH results. It would be necessary to cite the methods used for obtaining soil pH data.

4. Conclusions

As a consequence of the improper preparation and of unsuitable potentiometric measurement techniques applied to soil samples, the soil pH values obtained by different conventional methods are mostly invalid with regard to the actual soil pH value. The conventional method here proposed excludes these improper operations and replaces the roots by a pH glass electrode inserted in the soil toget-

her with a modified reference electrode with a double salt bridge is used, eliminate the abnormal liquid junction potential. The potential of the glass electrode is influenced by the H^+ ion activity of the equilibrium solution and of the particles of the soil suspension. Therefore occurring at the electrode potential is a steady state mixed potential which can be regarded (though a non - equilibrium potential) as replacing the function – by convention – of the equilibrium electrode potential in suspensions. The pH values obtained with this method can be considered as valid characteristic, actual soil pH values of the measured sample as they can occur in nature at the same conditions (water content and temperature) to which the roots are exposed.

Povzetek

Po prepoznanju problematičnega suspenzijskega efekta (SE) pri potenciometričnih meritvah v vodnih suspenzijah ni bilo doseženo soglasje znanstvenikov o njegovem vzroku in naravi. Zato so bile uvedene v praktično merjenje pH zemlje številne konvencionalne metode pH merjenja. Večina rezultatov teh metod ni veljavna, z ozirom na dejansko pH vrednost. Predlagana metoda zavrača njihove neprimerne postopke in uvaja pravilno vzorčevanje zemlje in primerno tehniko pH merjenja, kot sledi.

Indikatorska steklena pH elektroda, ki naj nadomešča korenine v zemlji je vtaknjena v vzorec razredčene suspenzije originalne zemlje, modificirana referenčna elektroda pa se dotika vzorca na način, s katerim je preprečen nastanek nenormalnega tekočinskega potenciala. Na ta način merjene »dejanske pH vrednosti zemlje« so veljavne, vendar je uporabljena metoda konvencionalna. Ireverzibilni potencial steklene elektrode vključuje namreč suspenzijski efekt prve vrste (SE1) in je mešan, stabilen (steady state) potencial. Po konvenciji se lahko smatra sicer neravnotežni potencial kot nadomestilo za ravnotežni potencial, ki pa v suspenziji ne obstaja. S predlagano metodo merjene pH vrednosti zemlje so ponovljive in veljavne z ozirom na mednarodno pH skalo. Te meritve se lahko smatra kot pH vrednosti katerim so izpostavljene korenine, ki rastejo v merjeni zemlji.

5. Acknowledgment

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Professor Dr. Srečko Oman

Professor Dr. Srečko Oman celebrated his 90th birthday in July of this year. His contribution in this issue of ACS is a testament to his exceptional physical and mental condition. Prof. Oman continued with his research even after his formal retirement 20 years ago. In the 90th he chaired the IUPAC committee that was founded to form the recommendations for measuring of the pH in the suspensions. The results of this work were published in two papers that met with a wide response, in both prof. Oman is the first author. Since his retirement he has been regularly visiting the Department of Physical Chemistry, where till recently he was researching the nature of the suspension effect, the topic that has been of particular interest in the last few years. He continues to follow up on the progress of the department. He is especially happy and proud of the scientific achievements by his former co-workers. He was critically and attentively observing the process of introducing the Bologna Reform of the study program at our faculty, as well as at the University. He has been stressing constantly the importance of teaching the students the basic natural science subjects, as well as the independence, critical thinking and understanding. He constantly repeats the words: Basics, Basics, and, again, Basics. He is firmly convinced that the task of every good school is to qualify students for independent work, as well as for future education at all levels.

Srečko Oman was born in Ljubljana in 1922. In 1941 he enrolled in the chemistry department of technical faculty at the University of Ljubljana from which he graduated in 1953. During his studies, in 1948, he started working as a teaching assistant, and became regularly employed at the institute of physical chemistry in 1953. He obtained his PhD in 1965. In the same year he obtained a title of assistant professor, became an associate professor in 1978, and full professor for physical chemistry in 1983. He was

lecturing subjects of physical chemistry analysis, as well as instrumentation methods, which he updated with a new modern practical course. Certain experiments from this course, that illustrate the basics of measuring of the physical-chemical quantities and were introduced by professor Oman, are still part of the curriculum today. He was researching the physical and chemical properties of polyelectrolytes and was particularly interested in measuring the pH in practice, as well as developing a variety of potentiometric sensors. For this, in particular, he obtained wide recognition in Slovenia, as well as abroad. He was paying particular attention to the pH measurements in non-ideal conditions, such as in suspensions, cosmetic products, skin, meat, and fruits. He advised solutions to the problems in pH measurement to the industry experts, as well as to his fellow researchers. He was developing his own electrodes for pH measurements. With this activity, he was helping many chemistry laboratories in the whole former SFRJ, especially with manufacturing excellent glass electrodes during the time when the acquisition of chemical measuring instruments from abroad was hindered due to the lack of funds. He elaborated the technical documentation for producing the glass electrodes and in this way enabled their fabrication in Iskra company. He was also developing and producing other kinds of ion-selective and gas electrodes. His Cu²⁺, Cl⁻, Br⁻, and I⁻ electrodes reached the quality of the acknowledged foreign makers. For his work he received several national awards. To conclude, professor Oman is the foremost expert for potentiometry in our country.

On the occasion of his high jubilee, his friends and former co-workers wish him many more healthy years.

Ciril Pohar