

INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY

ANALYTICAL CHEMISTRY DIVISION\*

# GUIDELINES FOR POTENTIOMETRIC MEASUREMENTS IN SUSPENSIONS PART A. THE SUSPENSION EFFECT

## (IUPAC Technical Report)

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# Guidelines for potentiometric measurements in suspensions

## Part A. The suspension effect

### (IUPAC Technical Report)

*Abstract:* An explanation of the origin and interpretation of the suspension effect (SE) is presented in accordance with “pH Measurement: IUPAC Recommendations 2002” [*Pure Appl. Chem.* **74**, 2169 (2002)]. It is based on an analysis of detailed schemes of suspension potentiometric cells and confirmed with experimental results. Historically, the term “suspension effect” evolved during attempts to determine electrochemically the thermodynamically defined activity of  $H^+$  (aq) in suspensions. The experimental SE arises also in determining other pIon values, analogous to pH values.

The SE relates to the observation that for the potential generated when a pair of electrodes (e.g., reference electrode, RE, and glass electrode) is placed in a suspension, the measured cell voltage is different from that measured when they are both placed in the separate equilibrium solution (eqs). The SE is defined here as the sum of: (1) the difference between the mixed potential of the indicator electrode (IE) in a suspension and the IE potential placed in the separated eqs; and (2) the anomalous liquid junction potential of the RE placed in the suspension. It is not the consequence of a boundary potential between the sediment and its eqs in the suspension potentiometric cells as is stated in the current definition of the SE.

*Keywords:* operational definition of suspension effect; suspension effect; pH; suspension potentiometric cell; IUPAC Analytical Chemistry Division; pIon; boundary potential; mixed potential; soil pH; anomalous liquid junction potential.

## 1. THE SUSPENSION EFFECT EXPLAINED ON THE BASIS OF ANALYSIS OF POTENTIOMETRIC CELLS

### 1.1 Introduction

Potentiometry is an electroanalytical technique based on the measurement of the potential of an electrochemical cell, composed of a measuring and a reference electrode (RE), both immersed in the measuring solution to be measured.

In homogeneous solutions, direct potentiometry is used for the estimation of ion activities (e.g., pH) and potentiometric titrations for determination of the amount concentration of ionic species. These measuring techniques are also applied to suspensions or sols of different materials (containing positively or negatively charged particles) in aqueous dispersion media. Although pH measurement in soil suspensions is highly relevant to this work, ion exchanger suspensions were chosen preferentially as models due to their simplicity.

The most frequently applied direct potentiometric method is the measurement of pH. Therefore, the determination of pH is selected to explain the essential procedures and experimental set-up for the potentiometric techniques applied to suspensions or sols.

The most recent definitions, procedures, and terminology relating to pH measurements in dilute aqueous solutions in the temperature range 5–50 °C are given in the IUPAC Recommendations 2002 [1]. In this reference, the glass electrode cell V is proposed for practical pH measurements [1, p. 2187]:

reference electrode | KCl ( $c \geq 3.5 \text{ mol dm}^{-3}$ ) || solution pH(X) | glass electrode (cell V)

Typically, the galvanic cells used for practical pH measurements conform to the characteristics of cell V; therefore, the results obtained in these practical pH measurements approximate results obtained by cell V.

Although “the quantity pH is intended to be a measure of the activity of hydrogen ions in [homogeneous] solutions” [1], and measurements using cell V include an unknown liquid junction potential, cell V is also used for practical measurement of pH in suspensions with the electrodes usually positioned in different phases.

When pH is measured in (i) a suspension (or its sediment) or (ii) in its equilibrium solution (eqs), the measured pH value in each of these constituent parts is different, even though the total system is in equilibrium. None of these pH values represents the (thermodynamically) true  $\text{H}^+$  activity in a suspension. This observation has caused serious problems for the theory and practice of pH measurements, problems which remain unresolved.

## 1.2 Consideration of the “glass electrode cell” containing a suspension

The term “suspension” should mean a *uniform equilibrated multiphase system*. It can be separated into the eqs and the sediment. If, when separated, the eqs and the sediment remain in physical and electrical contact, they represent a *combined suspension system*. The separated supernatant, obtained by sedimentation, centrifugation, or filtration, does not necessarily give absolutely equivalent solutions, yet they can be considered eqs, because the differences between them can be neglected with respect to the characteristics of the measured values.

In this work, the term “suspension” means the dispersion of electrically charged solid particles in water or in an aqueous solution. The origin of the charges can be adsorption or ionization, or as a property of the ion exchanger beads. The positively or negatively charged particles of different sizes found in soils provide another example. However, for this document (and in the literature that it relies upon) ion exchanger particles (which, depending on solution pH lower than 7 will be mostly in the  $\text{H}^+$  form) were chosen as a representative example for the study of pH measurements in suspension. These particles reduce the experimental effort and make a simple approach possible. Experiments showed essentially the same results when particles of other types were used [2].

The bulk liquid (of any electrolyte concentration) in the suspension will be identical to the supernatant of this suspension, when it is separated in whatever manner into two parts. It is different from that in the diffusion layers of individual particles, which are responsible for the mixed electrode potential when they are in contact with the glass electrode part of the pH electrode (Section 1.4). The diffusion layer of individual particles contributes to the anomalous liquid junction potential observed in pH measurements in suspensions.

The two separated parts are (i) the *sediment*, which can be considered the most concentrated suspension possible, and (ii) the clear (homogeneous, non-turbid) solution above it. This solution is called the eqs, if the suspension is equilibrated before separation. It is proposed to call the combination of an eqs and sediment, which are in physical and electrical contact, a *combined suspension system*.

For pH measurement in a combined suspension system, the following specific positions for the glass and REs are possible:

1. both electrodes are positioned in the eqs;
2. both electrodes are in the sediment;
3. the glass electrode is in the sediment and the RE is in the eqs; or
4. the electrodes are in the reverse position from that in 3.

In addition, it is possible to measure the pH in each *separated suspension component*, which means that:

5. both electrodes are in the separated “eqs” or
6. both electrodes are in the separated sediment.

The pH measurement is possible also with

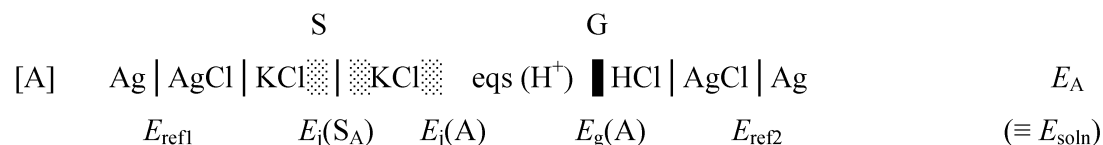
7. both electrodes in the original, (nonseparated) equilibrated suspension, the concentration of which should (ideally) be practically constant during the measurement.

In a suspension in equilibrium, the electrochemical potential  $\tilde{\mu}_{\text{H}^+}$  is equal throughout the system, therefore, the different electrode arrangements 1 to 7 could be expected to give the same pH values. Nevertheless, the electrode combinations 1 and 2 and the analogous pair 5 and 6 show large (and nearly equal) pH differences, as do the combinations 3 and 4. These pH differences were named the *suspension effect* (SE) for the first time in 1930 [5,6]. Subsequently, the nature of this effect has been studied intensively by many authors; a list of references may be found in reviews, e.g., [4,7–9]. However, there has been no consensus on the origin of, or explanation for, the SE.


An acceptable explanation of this phenomenon follows from a detailed analysis of the suspension cells (combinations 1 and 2, or 5 and 6) and from their cell potential differences,  $\Delta E$ , from which the corresponding pH differences can be calculated; this explanation is supported by recent experimental observations [3].

### 1.3 Detailed schemes for potentiometric cells used in suspensions

Scheme 1 shows both electrodes in the eqs (combined with sediment, system 1, or separated, system 5).

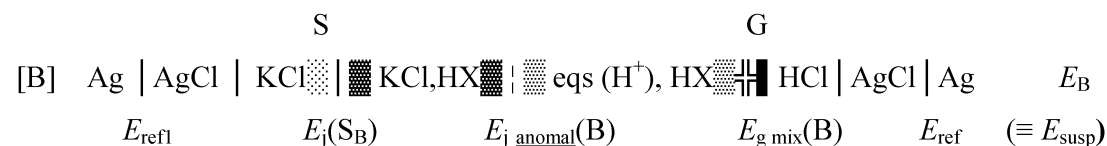


**Scheme 1**

Here, *S* indicates the separator (membrane) of the salt bridge and *G* the glass membrane of the glass electrode. The symbol  represents the region of the KCl solution in the separator and that in the contact range of eqs with KCl solution diffused from the RE. (The extent of the KCl layer in eqs is exaggerated in the scheme.)  $E_{\text{ref}}$  is the potential of the RE,  $E_{\text{g}}$  is the potential of the glass electrode.  $E_{\text{j}}(\text{S}_{\text{A}})$  and  $E_{\text{j}}(\text{A})$  are the liquid junction potentials; these are of negligible magnitude due to the approximately equal transport numbers of  $\text{K}^+$  and  $\text{Cl}^-$ , as established by potentiometric measurements [3,13].

This scheme is equivalent to that for cell V (above), but considers the interphases in detail.

Scheme 2 shows both electrodes in the sediment (combined with eqs, or separated, systems 2 and 6, respectively).



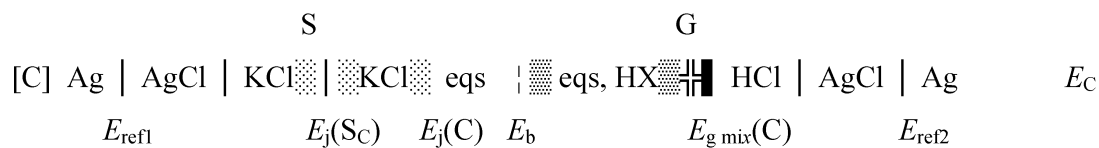
**Scheme 2**

Again, *S*, *G*, and  $\text{KCl}$  have the same meaning as in scheme [A]. The symbol  $\text{KCl}$  represents the ion exchanger *X* (sediment of *X* in  $\text{H}^+$  form) bathed in  $\text{KCl}$  solution which diffuses from the RE, and the symbol  $\text{KCl}$  means the ion exchanger *X* (in  $\text{H}^+$  form) dispersed in eqs. The sign  $\text{HCl}$  represents the glass electrode in intimate contact with the suspension particles (HX) and entrained eqs; this evokes the mixed electrode potential.  $E_{j,\text{anomal}}$  is the anomalous liquid junction potential and  $E_{g,\text{mix}}$  is the mixed potential of the glass electrode.  $E_j(\text{S}_B)$  is negligible [3], and  $E_{\text{ref}}$  is defined as in [A].

When comparing cells [A] and [B], the first component of the potential difference arises from junction potentials, viz.  $E_j(\text{A}) + E_j(\text{S}_A) - E_{j,\text{anomal}}(\text{B}) - E_j(\text{S}_B)$ , which can be approximated to  $E_j(\text{A}) - E_{j,\text{anomal}}(\text{B})$ , as  $E_j(\text{S}_A)$  and  $E_j(\text{S}_B)$  are negligible [3]. This difference occurs because in cell [B] the filling solution, which diffuses from the salt bridge into the suspension, exchanges  $\text{K}^+$  for the  $\text{H}^+$  counterions of the particles, which changes the ion arrangement in the suspension and most importantly affects the approximate equality of ion transport numbers in the  $\text{KCl}$  diffusion front. This effect is termed an anomalous liquid junction potential and represents the *suspension effect of the second kind*, SE 2, as defined in [2,3,10]. The second component of the potential difference is  $E_{g,\text{mix}}(\text{B}) - E_g(\text{A})$ ; this results from the small suspension particles making intimate contact with the electrode surface, and is called the *suspension effect of the first kind*, SE 1 [3,11]. This arises because the electrode is in contact with the (true) eqs and at the same time in intimate contact with charged particles. In the latter contact regions, an overlapping of the double layers of the particles and the electrode occurs and causes a different  $\text{H}^+$  activity in comparison with the activity existing in contacts of eqs with the electrode. This gives rise to a mixed potential [2,3,12], as discussed in Section 1.4.

It is evident that the cell potentials  $E_A$  and  $E_B$  will differ in two component potentials: (1)  $E_j(\text{A})$  and  $E_{j,\text{anomal}}(\text{B})$  and (2)  $E_g(\text{A})$  and  $E_{g,\text{mix}}(\text{B})$ . As both electrodes are in the same phase there can be no boundary potential component  $E_{\text{boundary}}$ , either in  $E_A$  or in  $E_B$ .

Scheme 3, System 3, shows the glass electrode in the sediment and RE in the eqs of a “combined suspension system” in equilibrium.



Scheme 3

The boundary potential is represented by  $E_b (= E_{\text{boundary}})$ ; all other symbols have the analogous meanings as above. The cell potential  $E_C$  differs from the potential  $E_A$  (Scheme 1) only in the potential of the glass electrode because, as discussed below,  $E_b$  is negligible [3]. In [A] the potential of the glass electrode  $E_g(\text{A})$  is a single potential, because the electrode is in contact with a homogeneous solution. However, in [C] it is a multiple or mixed electrode potential, as in [B].

The potential  $E_b$  (also known as a Donnan potential) at the eqs/sediment boundary is often considered, without foundation, as arising from an effective semipermeable membrane. It has been established experimentally [2,3] that when, for example, the movable electrode penetrates the sediment phase (“perforates” the “fictitious membrane”) no measurable step-change of the electrode potential occurs. Thus,  $E_b = 0$  and can be neglected. However, the electrode potential changes proportionately with progressive immersion of the electrode in the sediment. This is in accordance with the above interpretation that a mixed potential forms.

A Donnan potential exists at the solid–solution interface around individual particles (because the fixed ions inside the particles cannot cross the interfaces), but it does not exist where the bulk eqs is constricted in the interstitial eqs channels between the particles.

#### 1.4 Analysis of the schemes and findings

*Potential at the eqs/sediment boundary.* Analysis of the above cell schemes shows that the effect of suspended sediment material on two electrochemical processes is responsible for the SE. The SE is not a result of a hypothetical membrane and the corresponding potential, which might be ascribed to the boundary between the eqs and the sediment. It has been established experimentally that  $E_b \approx 0$  [2,3] both in control experiments, which included an appropriate agitation of the RE in the suspension, and in experiments in which a restrained flow of the solution filling the salt bridge was used or the direction of the flow was reversed.

*Liquid junction potential.* The liquid junction potential formed at the contact of the RE salt bridge with the sediment can show a much greater value than when in contact with the eqs.

The experiments carried out using a "movable electrode" to establish the existence of the "hypothetical membrane" between eqs and the sediment [10] showed that the *cause* of this change in liquid junction potential is, in fact, ion exchange between the sediment particles and the electrolyte solution flowing from the salt bridge [10]. This change in cell potential begins even before the tip of the salt bridge of the movable RE penetrates the interface [10]. This explanation is also accepted in Galster's monograph on pH measurement [13].

The ions of the diffused filling solution may exchange with counterions (e.g.,  $H^+$ ) in the (colloid) particle double layers and change the solution composition in the particle environment, which will affect *the approximately equal ion transport numbers of the diffusing electrolyte solution*. This is the fundamental reason for the development and maintenance of the *anomalous liquid junction potential*, which can be regarded as the *nature* of the changed potential. This potential can be considered as a systematic error of measurement and can be eliminated (as described in Section 2.6). The magnitude of this potential is usually of the order of some tens of mV, but it can attain more than 100 mV [2,3,7,8].

*Indicator electrode (IE) potential and its duration.* The change of the IE potential when the electrode comes into intimate contact with the charged particles can also be followed by means of the above-mentioned movable electrode. Experiments confirm the interpretation that the overlapping of the electrode double layer with the double layers of particles is the *cause* of the potential change of the IE when introduced into a suspension [3,4,11,12]. If in the combined suspension system, a movable IE perforates the fictitious membrane, where a phase boundary potential difference between supernatant and the slurry phase should exist, an instantaneous electrode potential change would occur, but it does not! By a step-by-step movement of the electrode into the bulk of the suspension, a progressive increase of the electrode surface in contact with particles occurs and the electrode potential changes in parallel. This leads to the interpretation that the electrode potential change in the suspension depends on surface processes at the electrode and not on effects associated with a membrane. With further penetration of the electrode into the suspension, the contact regions on the electrode surface increase and with this the influence on the value of the mixed potential.

After the introduction of the electrode into the suspension and establishment of contacts with the particles, the electrode potential becomes an *irreversible mixed potential* [12], because two electrochemical reactions proceed simultaneously on the same electrode surface. This potential remains essentially constant for a period of time which exceeds the time required for a potentiometric measurement. This mixed potential can be regarded as the *nature* of the changed IE potential in suspensions, which cannot be eliminated from any measurement. The mixed potential in cells [B] or [C] depends on the species, smoothness of the electrode and the particles, the ionic strength of the solution, and the particle charge and size [11,12]. Its value is usually not greater than some tens of mV.

*The potentiometric cell, represented schematically by cell [C],* is generally adopted as the most suitable for soil pH measurements. The analysis of its scheme shows that  $E_j(B)$  (required in cell [B]) is replaced by  $E_j(C)$  (which is  $\approx 0$ ) and  $E_b$  (which is  $= 0$ ). The cell potential  $E_C$  changes measurably only when the mixed potential of the IE  $E_g(C_{mix})$  changes. The systematic RE error is eliminated from the cell potential because the filling solution of the RE does not flow into the suspension. From the steady-

state potential  $E_C$ , a useful approximation of the pH of a suspension can be calculated, because  $E_C$  depends on the contribution to the  $H^+$  activity from both the particles and the eqs. If the eqs is not completely free from colloidal particles, this may represent (at most) a small uncertainty which must be taken into account.

The interpretation of the experimental results obtained in the study of hydrogen ion activity in suspensions [12] is applicable in general to a potentiometric estimation of ion activities in suspensions measured with different ion-selective electrodes (ISEs) in combination with the RE. For the latter measurements, the symbol pH used in this work should be replaced by the symbol pIon.

## 1.5 Conclusions

In the publication "Measurement of pH: IUPAC Recommendations 2002" [1], cell V is recommended for practical pH measurement *in solutions*. Because this cell is identical to the pH cells most frequently used in laboratory measurements in the past, the results from both are equivalent and in accordance with the recommendations. Cell V and some other cells are used also for pH measurements *in suspensions*, with the electrodes positioned usually separately, the glass electrode in the sediment, and the RE in its eqs. The pH values measured separately in the suspension (or in its sediment) or in the eqs are different, even though the suspension and solution are in equilibrium. This pH difference, which can be expressed in terms of the corresponding differences in the cell potentials,  $\Delta E$ , is called the "suspension effect".

An analysis of the detailed schemes for the potentiometric cells used in such suspension measurements provides an acceptable explanation of the SE. The SE is the sum of two galvanic potential changes, which occur when the electrodes are transferred from the eqs to the suspension (or sediment):

1. the change in potential of the IE, which changes to an *irreversible mixed potential probe* (a consequence of the overlapping of the diffuse double layers of the electrode with the double layers of particles, when the electrode makes intimate contact with them) and
2. the change in the liquid junction potential that exists between the salt-bridge solution of the RE and either the eqs or the suspension. In the latter case, contact of the flowing electrolyte from the salt bridge with the suspension particles gives rise to an *anomalous junction potential*.

Each of these phenomena has been confirmed with experiments [2–4,10–12].

Measurements on the suspension potentiometric cell [B] shows no evidence for a potential boundary (as is also the case in cell [A]), characterized as a "semipermeable membrane". Experiments have established that there is *no measurable boundary potential* existing between the eqs and the sediment. Therefore, the SE does not include a measurable boundary potential; the SE cannot be interpreted as a boundary or Donnan potential.

## 2. GUIDELINES FOR PRACTICAL pH MEASUREMENTS IN SOIL SUSPENSIONS

### 2.1 Introduction

The revised view of potentiometric measurements in suspensions (Section 1), which takes into account the currently presented definition of the SE and its interpretation in "Guidelines for potentiometric measurements in suspensions: Part B. Guidelines for practical pH measurements in soil suspensions (IUPAC Recommendations 2007)" [*Pure Appl. Chem.* **79**, 81 (2007)], provides an explanation for the results obtained by different potentiometric measurement techniques when applied to suspensions. This is important especially in the determination of soil pH.

Each of the different methods used provides a soil pH value, which is often neither clearly defined nor understood. The results can involve a large uncertainty and may only approximate the actual pH value. Only one experimental method is considered to provide a pH value with acceptable uncer-

tainty in regard to the influence of soil solution components on a plant. However, a comparison of results obtained by several potentiometric methods can give a meaningful insight to the true  $H^+$  activity in the suspensions.

The SE that contributes to the measurement value should not be considered a very significant characteristic of a suspension, but rather it is a troublesome difference between two cell potentials, both of which affect the determination of the *actual pH value of the suspension*. The *thermodynamically defined  $H^+$  ion activity in a suspension* cannot be equated with any potentiometrically determined pH value.

The methods for pH measurement in dilute aqueous solutions, as in IUPAC Recommendations 2002 [6], are taken as the basis for pH measurements of suspensions. From the definition and interpretation of the SE presented here, a revised view of pH measurements in suspensions becomes possible. The effects, which occur in the measurement system due to the suspension characteristics, are analyzed below for five different measurement protocols applied to cells which contain the eqs or the suspension. These effects influence the potential difference measured in suspension potentiometric cells. Each of these measurement protocols is applicable to soil pH measurements. Advice is given on the reasonable choice and use of electrodes in suspension measurements.

To codify the different expressions of the suspension pH (soil pH), measured by cell [C] or cell V, some expressions can be proposed that specify the technique used.

The term “direct suspension pH” is used when the original sample is measured directly by cell V [1], with both electrodes in the original suspension (or soil), analogous to the pH measurement in solutions (noted as, e.g., “direct soil pH”). The term “modified direct pH” is used when the suspension is modified in any way before measurement (e.g., with water or electrolyte solution added to the original sample); this must be explicitly noted (e.g., “modified direct soil pH (1:2 w)”) and the notation explained.

The term “effective suspension pH” can be used in the case where the original suspension is separated into two parts (combined suspension system) and the pH is measured with the IE in the sediment and the RE in the eqs of the cell [C], either without any prior modification of the suspension (“effective soil pH”) or with a modification of the suspension (“modified effective” suspension pH). In this case, any water or solution added to the original sample must be noted explicitly (e.g., “modified effective soil pH (1:5 KCl)”). Each of these measurements is considered to give an approximation to the true pH in soil solution, that is the pH to which an object immersed in this suspension (e.g., a root) could be exposed.

The *true* pH means the pH value measured in the clear eqs separated from the equilibrated original suspension (e.g., “true soil pH”). Analogous to the above, the term “modified true” is used when the sample was modified before measurements (e.g., “modified true soil pH (1:2  $CaCl_2$ )”). These values, in combination with the direct pH values, are used for determination of the SE.

For routine work, the corresponding abbreviations are proposed:

- D soil pH, MD soil pH (1:2 w)
- E soil pH, ME soil pH (2:5 KCl)
- T soil pH, MT soil pH (1:5  $CaCl_2$ ), etc.

The values should be valid for measurements at 20 °C; “w” means distilled water, “KCl” 1 mol  $kg^{-1}$  solution and “ $CaCl_2$ ” 0.01 mol  $kg^{-1}$  solution of salts, if not indicated otherwise.

## 2.2 Nature of suspensions and their relation to the pH electrode potential

In this report, the aqueous suspensions considered are defined as *charged solid particles* of not strictly determined sizes, which are dispersed in an aqueous *dispersing medium* (water or aqueous solution). This medium surrounds the particles permanently, even when they are settled and form a suspension *sediment*. In a suspension of, for example, ion exchanger beads (declared to be in  $H^+$ -form), which are



in equilibrium with the surrounding eqs, the particles together with their double layers may contain a larger or smaller concentration of  $H^+$  than that existing in the bulk solution. These charged particles could be regarded as reservoirs of ions that are blocked from the eqs by an equilibrium Donnan potential. Thus, a suspension contains at least two phases of either similar or different activity of  $H^+$ .

The electrochemical potential  $\tilde{\mu}_{H^+}$  is the same throughout the whole equilibrated suspension system. Therefore, *the pH of the eqs* can be considered to be the true pH value of the whole interstitial solution in a suspension or sediment (which is not disturbed by the measurement). The pH of the eqs can be measured practically by means of cell V, defined in IUPAC Recommendations 2002 [1]. In the case of an equilibrated soil suspension, it could be considered as the true soil pH value.

When the pH electrode is placed into the suspension, the particles do not influence its electrode potential during the measurement [7,10] until the reservoirs come into intimate contact with the electrode, resulting in an overlapping of the double layers of both. As a consequence of contact regions, the number depending on the particle size, the IE potential changes [12]. The change is proportional to the ratio of contact surfaces to the total electrode surface and to the double-layer thicknesses.

Whereas the potential of the pH glass electrode positioned in the eqs follows the Nernst equation, it changes to an *irreversible mixed (or corrosion) potential* when the electrode is transferred to the *corresponding suspension or sediment*, as described in Section 1.4. Different electrodes may show different mixed potentials in the same suspension, and the same electrode may show different mixed potentials when it contacts particles of different sizes in the same suspension.

The contents of reservoirs can be estimated approximately by selected methods given in Section 2.5.

### 2.3 Nature of suspensions and their relation to the reference electrode potential

The *heterogeneous character of suspensions* also influences the potential of the reference part of the potentiometric cell (represented by the RE connected with the salt bridge), which is immersed in the suspension. The liquid junction potential between the RE and its salt bridge remains unchanged during the cell potential measurement. The liquid junction potential between the filling solution of the salt bridge (containing cations and anions of approximately equal transport numbers) and the eqs can practically be neglected. In contrast, the liquid junction potential between the diffused filling solution of the salt bridge and the suspension particles can be significant. It is called the *anomalous liquid junction potential*. In regard to the measurement technique, it represents a systematic error of measurement, and can be eliminated only by avoiding the salt-bridge filling solution from coming in contact with the suspension particles.

### 2.4 Relationship between the suspension–equilibrium solution–sediment and the positioning of the electrodes

Because the origin and cause of the SEs have not been clarified since the beginning of their study (in 1930), different modified techniques were introduced into routine determination of soil pH which give different and not clearly explained, nevertheless useful, results.

With regard to the electrode positioning in a uniform or in a combined system, the following classification of potentiometric techniques is possible: both electrodes placed (1) in the original suspension system, (2) in the eqs of the suspension, (3) in the suspension sediment, or (4) the IE in the sediment and RE in the eqs of the suspension, and (5) in the reverse mode to (4).

In these methods, the above-mentioned relations between the electrodes and the measured medium must be considered, and for 4 and 5 also the possible influence of the boundary between the sediment and the eqs on the measured cell potential. As described in Section 1.5, no measurable (Donnan) boundary potential exists at this interface; thus, it is not a “virtual continuous semipermeable membrane”, as has been shown in control experiments [3,12]. Nevertheless, in spite of this fact, in some

recent publications it is erroneously assumed that a boundary potential between the eqs and the sediment is the main contributor to the SE [16–18].

## 2.5 Discussion of modified methods of pH measurements in soil suspensions

This part provides guidelines for pH measurement. With the aid of the proposed definition and interpretation of the SE in “Guidelines for potentiometric measurements in suspensions: Part B. Guidelines for practical pH measurements in soil suspensions (IUPAC Recommendations 2007)” [*Pure Appl. Chem.* **79**, 81 (2007)], processes and techniques are discussed and the significance of the results obtained is explained.

The in situ “soil pH” can be measured only in wet soil if it contains enough water so that the *water activity*  $a \approx 1$ . If this is not the case, deionized or rain water is added to the soil to obtain a homogenized wet *soil paste*, similar to the original wet soil. In these cases, the suspension is not separated into the eqs and the sediment. Measurements of pH with both electrodes in nearly dry soils are meaningless from a sheer physicochemical point of view.

In *routine pH measurements*, a greater amount of water is added to the soil to form a diluted aqueous suspension. This must be *equilibrated and separated into sediment and the corresponding eqs*. In laboratory measurements, a complete separation is performed by centrifugation, otherwise the separation is obtained by sedimentation, in which case the imperfect separation must be taken into account in assessing the uncertainty of the result. For better-defined results, the air-dried pulverized soil is sieved, mixed with deionized water in known proportions by mass, and the pH is measured in the eqs after separation. The result for a 1:2 soil/water system can be given as “soil pH (1:2 w)”. Different soil/water proportions show different pH values, which need a suitable interpretation to give useful information. Protocols for the sampling of soil populations are described in “Terminology in soil sampling (IUPAC Recommendations 2005)” [19].

### Method 1 (cell potential $E_1$ )

The *direct pH measurement of the original suspension* by means of cell V (analogous to IUPAC Recommendations 2002, which is recommended for measurement in homogeneous solutions), with *both electrodes placed in the soil suspension*, gives a result which is different from those obtained with other methods. This  $\text{pH}_1$  value has *no reasonable pH meaning*, because it is calculated from a cell potential  $E_1$ , which contains the unknown mixed potential of the IE and the anomalous liquid junction potential, the latter representing a systematic error of the measurement (Scheme 2 in Section 1.3). These two potentials are responsible for the SE. Nevertheless,  $\text{pH}_1$  can be used in comparison with other  $\text{pH}_n$  values as a repeatable suspension characteristic. Also, the *pH of a soil paste* can be considered as a result of Method 1 with the same significance.

### Method 2 (cell potential $E_2$ )

In this method, a known amount of water or of salt solution is added to the soil sample and the equilibrated suspension separated into the eqs and the sediment. For pH measurement, *both electrodes are positioned in the eqs*, which may, or may not, be in contact with the sediment. The cell potential  $E_2$  is equivalent to the difference of the electrode potentials  $E_A$  of the cell [A] in Section 1.3. The value  $\text{pH}_2$  calculated from  $E_2$  is not influenced by the diffuse layer of the suspended particles. This pH value can be adopted as the pH of the whole suspension system if the suspension is not disturbed by the measurement.

The amount of water added to the original suspension must be reported with the results. The air-dried soil-to-liquid mass ratio of the suspension should be reproducible with acceptable precision as it determines the measured cell potential. The ratio should be expressed explicitly; e.g., for the ratio 1:2 as  $E_2(1:2 \text{ w})$  for water, or  $E_2(1:2 \text{ KCl})$  for KCl solution and  $E_2(1:2 \text{ CaCl}_2)$  for  $\text{CaCl}_2$  solution, whichever is used as the dispersing medium. The comparison of  $E_2$  values, obtained in water-eqs and solution-eqs, respectively, allows an estimation of the amount of  $\text{H}^+$  set free from particles for different

soil-to-liquid ratios after these were exchanged by  $K^+$  or  $Ca^{2+}$  [7]. In routine work, the measured  $E_2$  values are expressed as corresponding  $pH_2$  values. These can be regarded as the best defined, “true pH” value measured for a suspension.

### Method 3 (cell potential $E_3$ )

The measurement is performed with *both electrodes in the separated sediment* of a suspension and is equivalent to that in Method 1, except for the fact that the particle concentration is the maximum possible. The sediment may, or may not, be in contact with the separated part of eqs. The cell scheme is given in Section 1.3, Scheme 2. Both  $E_j$  and  $E_g$  contribute to  $pH_3$ , and it cannot be used for pH evaluation of a suspension, but it is used for the determination of the total SE as described in the definition of the SE.

### Method 4 (cell potential $E_4$ )

4(a) The electrode position in Method 4 is obtained by transferring *the IE* from the eqs, as it is positioned in Method 2, *into the sediment, while the RE remains in eqs*. As can be seen from the cell [C] (Scheme 3 in Section 1.3), the IE potential changes to a mixed potential, the value of which depends on the pH of the eqs and on the  $H^+$  activity of the diffuse layer of the contacting suspension particles. Because the RE potential and the diffusion potential remain unchanged, the measured cell potential  $E_4$  differs from  $E_2$  by the potential difference  $\Delta E$  known as SE 1 (Section 1.3). For an equilibrated suspension soil/water ratio of  $1/2$ , this is given by  $\Delta E_{4-2}$  (1:2 w) =  $E_4 - E_2$ . The  $pH_4$  values obtained with the same IE in different (soil) suspensions allow an *approximate comparison* of the  $H^+$  activity to which a (charged) surface similar to that of the IE (e.g., of a root in the measured soil) could be exposed, when coming in contact with the particles of these soils. Any change in  $pH_4$  indicates a change of the electrode mixed potential, which depends on the particle contacts with the electrode surface.

Except for a method only applicable to the laboratory, where the filling solution of the salt bridge is exposed to a negative pressure [2], three other variations of Method 4 are used in routine practice, 4(b), (c), and (d). In these, the amount of the separated eqs is minimal and contact of the salt-bridge filling solution with the particles is avoided.

4(b) In this method, only a small amount of the eqs is needed for a measurement. It employs an RE connected with the suspension by two salt bridges in series (double salt bridge), of which the second one is filled with eqs.

4(c) In this modification, a strip of filter paper wetted with eqs is used for the electrolytic connection between the suspension and the salt bridge. When brought into contact with the suspension [9], a minimal amount of the clear eqs diffuses along the strip to the salt bridge.

4(d) In this method, a special combination electrode is used which, during the measurement, has only the pH sensing element in contact with the suspension. The eqs “climbs up” the specially prepared surface of the electrode stem to form the contact with the salt-bridge solution. In this case, the combination electrode does not *measure pH without the SE*, as it is often declared, because the presence of the SE 1 is unavoidable.

Method 4 is used very frequently in routine work, because the measured  $pH_4$  values, though not absolutely repeatable, depend on the sum of  $H^+$  activities contributed from the eqs and from the particles.

### Method 5 (cell potential $E_5$ )

In this method, the IE is placed in the eqs and the RE in the sediment. It is used solely when the anomalous liquid junction potential (i.e., the systematic error of measurement), equal to the cell potential difference  $\Delta E_{5-2} = E_5 - E_2$ , is to be determined. The derived  $pH_5$  value is not very relevant in routine work.

From the methods discussed above, the most appropriate one can be used to obtain the information of interest. An illustration of the above methods applied to soil pH measurement is presented in [7]. It is seen that different soils show different  $pH_2$  values (and pH differences), which can be used for the characterization of these soils in agronomy. The treatise relating to soil pH measurement can be ap-

plied—*cum grano salis*—to the general potentiometric pI<sub>on</sub> measurement in soils and in other suspensions. It should be emphasized once more that, by measurement of the voltage of any suspension galvanic cell no thermodynamically defined quantity can be obtained.

## 2.6 Devices and their application in practical “soil pH” measurements

Because these guidelines are based on the IUPAC Recommendations 2002 [1], the definitions given in that Glossary for pH measurement in real solutions, are also valid when applied to pH measurement in suspensions. Nevertheless, some additional points should be noted.

The *electrodes* used may be “single” or “combination”, but combination ones are suitable only in some cases.

*Single IEs* used in suspensions should be glass or other solid-state ISE, having smooth surfaces and providing fast responses and reproducible results. Electrodes of the second kind (e.g., Ag/AgCl, Sb/Sb<sub>2</sub>O<sub>3</sub>) do not have smooth surfaces, and for this and other reasons they show a greater or unexpected contribution to the SE [12].

The *single RE* may be constructed with one salt bridge which is filled with the same filling solution as the electrode (“half bridge”). Two salt bridges in series (a double salt bridge) are also feasible. The term “double salt bridge” in this case is more appropriate than the term “double junction” electrode. Both kinds of salt bridge are sealed with a separator (capillary, porous ceramic plug, frit, ground glass sleeve, or other). From the separator of the single salt bridge, which is in contact with the measured medium, its filling solution (e.g., saturated KCl solution of the RE half-cell) always flows or diffuses, even if the filling solution is gel-stabilized [10,14,15]. This can give rise to an anomalous liquid junction potential when it contacts the suspension particles. This can be minimized if the final half of the double salt bridge and the separator are filled with, for example, the eqs of the measured suspension for both the test solution measurements and the electrode calibration. It must be emphasized that the filling solution which flows from the separator to the sediment boundary can cause large systematic errors, even if the separator is placed in eqs near this boundary [10]. This can be minimized with a shielding tube, which is pulled onto the salt bridge and perforated by a small side-aperture (about 1.5 cm above the bottom of the tube), providing liquid and electrical contact between the two sides [11].

*Combination electrodes* are often used for measurements in suspensions. They are not suitable for measurements in *combined suspension systems*, except if the electrode is placed so that its indicator half-cell is connected with the sediment and the reference half-cell with the eqs so that SE 2 is minimized. The cell voltages measured with combination electrodes, the IE of which is immersed in a suspension, always include SE 1, notwithstanding that the electrodes are often declared to “measure soil pH without suspension effect”, as found in advertisements. Only some combination electrodes of special construction could possibly eliminate SE 2. *ISFET (combined) electrodes* also cannot avoid the SE in suspension measurements as the experiments showed; the results are therefore equivalent to those obtained with method 1.

For measurements in suspensions, the electrodes must be *placed* in the suspension in such a way that any differentiation in particle sizes around the sensing element of the electrode is avoided and a stable position of the electrodes is assured.

The instruments for voltage measurement should have a high input resistance (as pH meters generally have). The potential differences of the suspension potentiometric cells, which have relatively small ohmic inner resistances (e.g., cells with the metal or solid membrane used as a halogenide IE), can be measured with voltmeters of smaller input resistance, but the readings are not stable and are difficult to interpret.

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