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**Guidelines for Potentiometric Measurements in Suspensions A. THE
SUSPENSION EFFECT (IUPAC Technical Report) B. GUIDELINES FOR
PRACTICAL pH MEASUREMENTS IN SOIL SUSPENSION (IUPAC
Recommendations 2006)**

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INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY

ANALYTICAL CHEMISTRY DIVISION

**GUIDELINES FOR POTENTIOMETRIC
MEASUREMENTS IN SUSPENSIONS**

**A. THE SUSPENSION EFFECT
(IUPAC Technical Report)**

**B. GUIDELINES FOR PRACTICAL pH MEASUREMENTS IN
SOIL SUSPENSION
(IUPAC Recommendations 2005)**

Prepared for publication by

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Guidelines for Potentiometric Measurements in Suspensions

A. The Suspension Effect (IUPAC Technical Report)

Abstract: An explanation of the origin and interpretation of the Suspension Effect is presented in accordance with the “IUPAC Recommendations 2002, pH measurement” [1]. It is based on an analysis of detailed schemes of suspension potentiometric cells and confirmed with experimental results. Historically the term Suspension Effect (abbreviated as SE) evolved during attempts to electrochemically determine the thermodynamically defined activity of the H^+ ions in suspensions. The experimental Suspension Effect arises also in determining other pIons, analogous to pH.

The Suspension Effect relates to the observation that when a pair of electrodes (e.g. reference electrode and glass electrode) is placed in a suspension, the measured cell voltage is different from that measured when they are both placed in the separated equilibrium solution (defined in Section A1.2). The Suspension Effect is defined here as the sum of 1) the difference between the mixed potential of the indicator electrode in a suspension and the indicator electrode potential placed in the separated equilibrium solution, and 2) the anomalous liquid junction potential of the reference electrode, placed in the suspension. It is not the consequence of a boundary potential between the sediment and its equilibrium solution in the suspension potentiometric cells as is stated in the current definition of the Suspension Effect.

A 1.1 INTRODUCTION – THE SUSPENSION EFFECT EXPLAINED ON THE BASIS OF ANALYSIS OF POTENTIOMETRIC CELLS

Potentiometry is an electroanalytical technique based on the measurement of the potential of an electrochemical cell, comprised of a measuring and a reference electrode, both immersed in the measuring solution.

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 applied also 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.

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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, 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 H^+ activity in a suspension. This observation has caused serious problems for the theory and praxis of pH measurements, problems which remained unresolved.

A 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 equilibrium solution and the sediment. If, when separated, they 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 as equilibrium solutions (abbreviated as “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 which are found in soils are another example. However for this document (and in the literature that it relies upon) ion exchanger particles (which, depending on solution pH will be mostly in the H^+ form) were chosen as the representative example for the study of pH measurements in suspension. These particles allow the possibility of designing simple experiments for the

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3 measurements. Experiments showed essentially the same results, when particles of other
4 types were used [2].
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9 The bulk liquid (of any electrolyte concentration) in the suspension will be
10 identical to the supernatant of this suspension, when it is separated in whatever manner
11 into two parts. It is different from that in the diffusion layers of individual particles which
12 are responsible for the mixed electrode potential, when they are in contact with the glass
13 electrode part of the pH electrode (section A 1.4). The diffusion layer of individual
14 particles contributes to the anomalous liquid junction potential observed in pH
15 measurements in suspensions.
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23 The two separated parts are (i) the “*sediment*”, which can be considered as the
24 most concentrated suspension possible, and (ii) the clear (homogeneous, non-turbid)
25 solution above it. This solution is called the “*equilibrium solution*” (“eqs”), if the
26 suspension is equilibrated before separation. It is proposed to call the combination of an
27 equilibrium solution and sediment, which are in physical and electrical contact, a
28 “*combined suspension system*”.
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35 For pH measurement in a “combined suspension system” the following specific
36 positions for the glass and reference electrode are possible:
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39 1) both electrodes are positioned in the equilibrium solution,
40 2) both electrodes are in the sediment,
41 3) the glass electrode is in the sediment and the reference electrode is in the
42 equilibrium solution,
43 4) the electrodes are in the reverse position from that in 3).
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48 In addition it is possible to measure the pH in each “*separated suspension component*”,
49 which means that
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- 51 5) both electrodes are in the separated “*equilibrium solution*” or
52 6) both electrodes are in the separated sediment.
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7) both electrodes in the original, (non-separated) equilibrated suspension, the concentration of which should (ideally) be practically constant during the measurement.

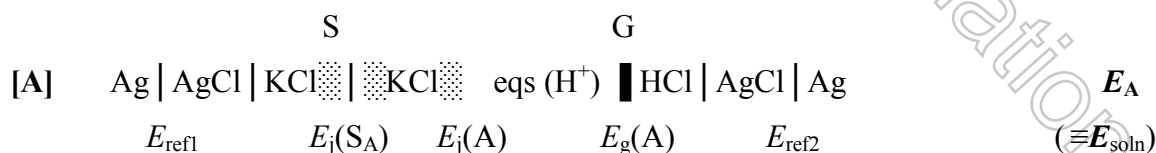
In a suspension in equilibrium the electrochemical potential $\tilde{\mu}_{\text{H}^*}$ is equal throughout the system, therefore the different electrode arrangements 1) to 7) could be expected to give the same pH values. Nevertheless the electrode combinations 1) and 2) and the analogous pair 5) and 6) show large (and nearly equal) pH differences, as do the combination 3) and 4). These pH differences were named the “**Suspension Effect (SE)**” for the first time in the year 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. [4,7,8,9]. 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, ΔE , from which the corresponding pH differences can be calculated; this explanation is supported by recent experimental observations [3].

A 1.3 DETAILED SCHEMES FOR POTENTIOMETRIC CELLS USED IN SUSPENSIONS

Scheme 1:

Both electrodes in the equilibrium solution (combined with sediment, system 1, or separated, system 5):

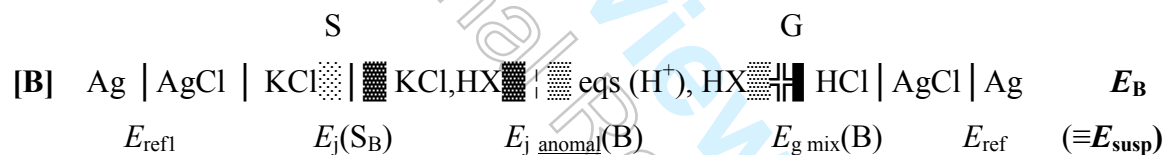


Here, “S” indicates the “separator (membrane)” of the salt bridge and “G” the glass membrane of the glass electrode. The symbol KCl represents the region of the KCl solution in the separator and that in the contact range of “eqs” with KCl solution diffused from the reference electrode. (The KCl layer in “eqs” is exaggerated in the scheme.) E_{ref} is the potential of the reference electrode, E_g is the potential of the glass electrode. $E_j(\text{S}_A)$ and $E_j(\text{A})$ are the liquid junction potentials; these are of negligible magnitude due to the equitransference numbers of K^+ and 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:

Both electrodes in the sediment (combined with equilibrium solution, or separated, systems 2) and 6) respectively)



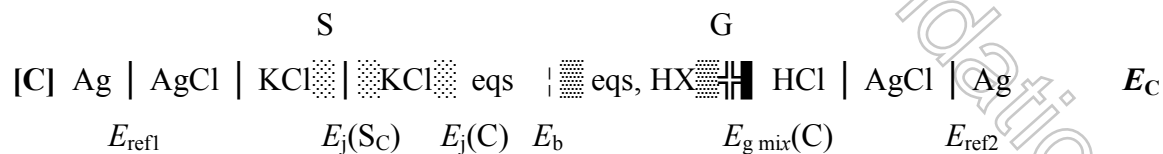
Again, “S”, “G” and KCl have the same meaning as in scheme [A]. The symbol KCl, HX represents the ion exchanger X (sediment of X in H^+ form) bathed in KCl solution which diffuses from the reference electrode, and the symbol $\text{eqs (H}^+) \text{, HX}$ means the ion exchanger X (in H^+ form) dispersed in “eqs”. The sign 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_{ref} is defined as in [A].

When comparing cells [A] and [B] the first component of the potential difference arises from junction potentials, *viz.* $E_j(A) + E_j(S_A) - E_{j\text{ anomal}}(B) - E_j(S_B)$, which can be approximated to $E_j(A) - E_{j\text{ anomal}}(B)$, as $E_j(S_A)$ and $E_j(S_B)$ are negligible [3]. This difference occurs because in cell [B] the filling solution, diffusing from the salt bridge into the suspension, exchanges K^+ for H^+ counterions of particles, which changes the ion arrangement in the suspension and most importantly affects the equitransference of ions in the “KCl” diffusion front. This 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 $E_{g\text{ mix}}(B) - E_g(A)$; 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) equilibrium solution and at the same time in intimate contact with charged particles. In the latter contact regions an overlapping of the particle and electrode double layers occurs and causes a different H^+ ion activity in comparison with the activity existing in contacts of “eqs” with the electrode. This gives rise to a mixed potential [2,3,12]. This is discussed in section A 1.4.

It is evident that the cell potentials E_A and E_B will differ in two component potentials: 1) $E_j(A)$ and $E_{j\text{ anomal}}(B)$ and 2) $E_g(A)$ and $E_{g\text{ mix}}(B)$. As both electrodes are in the same phase there can be no boundary potential component E_{boundary} , neither in E_A nor in E_B .

Scheme 3:

System 3): glass electrode in the sediment and reference electrode in the equilibrium solution of a “combined suspension system” in equilibrium:



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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 $E_g(A)$ 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 of the mixed potential formed.

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.

A 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 “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 reference electrode in the suspension, and in experiments in which a restrained flow of the salt bridge filling solution was used or the direction of the flow was reversed.

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Liquid junction potential - The liquid junction potential, formed at the contact of the reference electrode salt bridge with the sediment, can show a much greater value than when in contact with “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 the 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 reference electrode 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 ion equitransference 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 is a “systematic error of measurement” and can be eliminated (as described in paragraph A 2.6). The magnitude of this potential is of the order of some tens of mV but it can attain more than 100 mV [2,3,7,8].

Indicator electrode potential and its duration - The change of the indicator electrode potential, when the electrode comes into intimate contact with the charged particles, can also be followed by means of the above mentioned movable electrode. The experiments confirm the interpretation that the overlapping of the electrode double layer with double layers of particles is the **cause** of the potential change of the indicator electrode when introduced into a suspension [3,4,11,12]. If in the combined suspension system a movable indicator electrode 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-

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by-step movement of the electrode into the suspension bulk 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 establishing 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 indicator electrode 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 $E_j(\text{B})$ (required in cell [B]) is replaced by $E_j(\text{C})$ (which is ≈ 0) and E_b (which is $= 0$). The cell potential E_C changes measurably only when the mixed potential of the indicator electrode $E_g(\text{C}_{\text{mix}})$ changes. The systematic reference electrode error is eliminated from the cell potential because the filling solution of the reference electrode 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 H^+ ion activity contribution 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 reference electrode. For the latter measurements the pH term used in this work should be replaced by the term “**pI_{ion}**”.

A 1.5 CONCLUSIONS

In the publication "IUPAC Recommendations 2002, Measurement of pH" [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, glass electrode in the sediment and the reference electrode in its equilibrium solution. The pH values measured separately in the suspension (or in its sediment), or in the equilibrium solution, 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, ΔE , 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 Suspension Effect. The SE is the sum of two galvanic potential changes, which occur when the electrodes are transferred from the equilibrium solution to the suspension (or sediment):

1) the change in potential of the indicator electrode, which changes to *an irreversible mixed potential probe* (being 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 reference electrode and either the equilibrium solution or the suspension. In the latter case the 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 [2,3,4,10,11,12].

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

A 2.1 INTRODUCTION – GUIDELINES FOR PRACTICAL pH MEASUREMENTS IN SOIL SUSPENSION

The revised view of **potentiometric measurements in suspensions** (Part A 1), which takes into account the currently presented definition of the Suspension Effect (SE) and its interpretation below (Part B), 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”.

The different methods used each provides a “soil pH” value, which is often not clearly defined nor understood. The results can involve a large uncertainty and may only approximate to the actual pH value. Only one experimental method is considered to provide a pH value with acceptable uncertainty 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^+ ion activity in the suspensions.

The SE which 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*”

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3 *value of the suspension*". The thermodynamically defined H^+ ion activity in a suspension
4 cannot be equated with any potentiometrically determined pH value.
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9 The methods for pH measurement in dilute aqueous solutions, recommended by
10 IUPAC Recommendations 2002, [6], are taken as the basis for pH measurements of
11 suspensions. From the definition and interpretation of the Suspension Effect presented
12 here a revised view of pH measurements in suspensions becomes possible. The effects,
13 which occur in the measurement system due to the suspension characteristics, are
14 analysed below for five different measurement protocols applied to cells which contain
15 the equilibrium solution or the suspension. These effects influence the potential
16 difference measured in suspension potentiometric cells. Each of these measurement
17 protocols is applicable to "soil pH" measurements. Advice is given on the reasonable
18 choice and use of electrodes in suspension measurements.
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28 To codify the different expressions of the "suspension pH", ("soil pH"), measured
29 by cell [C] or cell"V", some expressions can be proposed that specify the technique used.
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33 The term "**direct**" suspension pH is used when the original sample is measured
34 directly by cell "V" [1], with both electrodes in the original suspension (or soil),
35 analogous to the pH measurement in solutions, (noted as, e.g. "direct soil pH").
36 "**Modified direct**" is used when the suspension was modified in any way before
37 measurement (e.g. with water or electrolyte solution added to the original sample); this
38 must be explicitly noted (e.g. "modified direct soil pH (1:2_w)") and the notation
39 explained.
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48 The term "**effective**" suspension pH can be used in the case where the original
49 suspension is separated into two parts ("combined suspension system") and the pH is
50 measured with the indicator electrode in the sediment and the reference electrode in the
51 "eqs" cell [C], either without any prior modification of the suspension ("effective soil
52 pH") or with a modification of the suspension, ("**modified effective**" suspension pH). In
53 this case, any water or solution added to the original sample must be noted explicitly (e.g.
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3 “modified effective soil pH (1:5 KCl)”. Each of these measurements is considered to give
4 an approximation to the true pH in soil solution, that is the pH to which an object
5 immersed in this suspension (e.g. a root) could be exposed.
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10 The “true” pH means the pH value measured in the clear “eqs” separated from
11 the equilibrated original suspension (e.g. “true soil pH”). Analogous to the above, the
12 “modified true” term is used when the sample was modified before measurements (e.g.
13 “modified true soil pH (1:2 CaCl₂)”. These values in combination with the “direct pH
14 values” are used for determination of the Suspension Effect.
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20 For routine work the corresponding **abbreviations** are proposed: **D soil pH, MD**
21 **soil pH (1:2 w), E soil pH, ME soil pH (2:5 KCl), T soil pH, MT soil pH (1:5 CaCl₂)** etc.
22 The values should be valid for measurements at 20 °C and “w” should mean distilled
23 water, “KCl” 1 mol kg⁻¹ solution and “CaCl₂” 0.01 mol kg⁻¹ solution of salts, if not
24 indicated otherwise.
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35 **A 2.2 NATURE OF SUSPENSIONS AND ITS RELATION TO THE pH** 36 **ELECTRODE POTENTIAL** 37 38 39

40 In this article the aqueous **suspensions** considered are defined as *charged solid*
41 *particles* of not strictly determined sizes, which are dispersed in an aqueous *dispersing*
42 *medium* (water or aqueous solution). This medium surrounds the particles permanently,
43 even when they are settled and form a suspension *sediment*. In a suspension of e.g. ion
44 exchanger beads (declared to be in H⁺-form) which are *in-equilibrium* with the
45 surrounding “equilibrium solution” (“eqs”), the particles together with their double layers
46 may contain a larger or smaller concentration of H⁺ ions than that existing in the bulk
47 solution. These charged particles could be regarded as “reservoirs” of ions, blocked from
48 the “eqs” by an equilibrium Donnan-potential. Thus a suspension contains at least two
49 phases, of either similar or different activity of H⁺ ions.
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5 The electrochemical potential $\tilde{\mu}_{\text{H}^+}$ is the same throughout the whole equilibrated
6 suspension system. Therefore *the pH of the equilibrium solution can be considered the*
7 *true pH value of the whole interstitial solution in a suspension or sediment (which is not*
8 *disturbed by the measurement).* The pH of the “eqs” can be measured practically by
9 means of the cell V, defined in IUPAC Recommendations 2002 [1]. In the case of an
10 equilibrated soil suspension it could be considered as the “true soil pH” value.
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18 When the pH electrode is placed into the suspension, the particles do not
19 influence its electrode potential during the measurement [7,10], until the “reservoirs”
20 come into an intimate contact with the electrode, resulting in an overlapping of the
21 double layers of both. As a consequence of contact regions, the number depending on the
22 particle size, the indicator electrode potential changes [12]; the change is proportional to
23 the ratio of contact surfaces to the total electrode surface and to the double layer
24 thicknesses.
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32 Whereas the potential of the pH glass electrode positioned in the “eqs” follows
33 the Nernst equation, it changes to an *irreversible mixed (or corrosion) potential* when the
34 electrode is transferred *to the corresponding suspension or sediment*, as described in
35 Part A 1.4. Different electrodes may show different mixed potentials in the same
36 suspension, and the same electrode may show different mixed potentials when it contacts
37 particles of different sizes in the same suspension.
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44 The contents of “reservoirs” can be estimated approximately by selected methods
45 given in section A 2.5.
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49 **A 2.3 NATURE OF A SUSPENSION AND ITS RELATION TO THE** 50 **REFERENCE ELECTRODE POTENTIAL** 51 52 53 54

55 The *heterogeneous character of suspensions* also influences the potential of the
56 reference part of the potentiometric cell, represented by the reference electrode connected
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with the salt bridge, which is immersed in the suspension. The liquid junction potential between the reference electrode and its salt bridge remains unchanged during the cell potential measurement. The liquid junction potential between the filling solution of the salt bridge (comprising almost equitransferent cations and anions) 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*”. It can be eliminated only by avoiding the salt bridge filling solution from coming in contact with the suspension particles.

A 2.4 RELATIONSHIP BETWEEN THE SUSPENSION – EQUILIBRIUM SOLUTION – SEDIMENT AND THE POSITIONING OF THE ELECTRODES

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

With regard to the **electrode positioning** in a uniform or in a combined system classification of potentiometric techniques is possible: both electrodes placed 1) in the original suspension system, 2) in the equilibrium solution of the suspension, 3) in the suspension sediment, or 4) the indicator electrode in the sediment and reference electrode 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 Part A 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

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3 publications it is erroneously assumed that a boundary potential between the “eqs” and
4 the sediment is the main contributor to the SE [16,17,18].
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8 9 **A 2.5 DISCUSSION OF MODIFIED METHODS OF pH MEASUREMENT IN** 10 **SOIL SUSPENSIONS** 11

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14 This section provides Guidelines for pH measurement. With the aid of the
15 proposed definition and interpretation of the SE in Part B, processes and techniques are
16 discussed and the significance of the obtained results explained.
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21 The *in situ* “soil pH” can be measured only in wet soil, if it contains enough water
22 so that the *water activity* $a \approx 1$. If this is not the case, deionised or rain water is added to
23 the soil, to obtain a homogenised wet *soil paste*, similar to the original wet soil. In these
24 cases the suspension is not separated into the “eqs” and the sediment. Measurements of
25 pH with both electrodes in nearly dry soils are meaningless from a sheer physicochemical
26 point of view.
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34 In *routine pH measurement* a greater amount of water is added to the soil to form
35 a diluted aqueous suspension. This must be ***equilibrated and separated into sediment***
36 ***and the corresponding equilibrium solution***. In laboratory measurements a complete
37 separation is performed by centrifugation, otherwise the separation is obtained by
38 sedimentation in which case the imperfect separation must be taken into account in
39 assessing the result uncertainty. For better-defined results, the air-dried pulverized soil is
40 sieved, mixed with deionised water in known weight-proportions and the pH is measured
41 in the “eqs” after separation. The result for a 1:2 soil/water system can be given as “soil
42 pH (1:2_w)”. Different soil/water proportions show different pH values, which need a
43 suitable interpretation to give useful information. The IUPAC Recommendation 2005,
44 *Terminology in Soil Sampling*, describes protocols for the sampling of soil populations
45 [19].
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Method 1 (cell potential E_1)

The *direct pH measurement of the original suspension* by means of cell V, (analogous to the 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 **pH₁** value has **no reasonable pH meaning**, because it is calculated from a cell potential E_1 , which contains the unknown mixed potential of the indicator electrode and the anomalous liquid junction potential, the latter representing a systematic error of the measurement (scheme [B] in Part A 1.4). These two potentials are responsible for the “Suspension Effect” (SE). Nevertheless pH₁ can be used in comparison with other 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 Part A 1.4. The value **pH₂** 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 manipulation.

The amount of water added to the original suspension must be reported with the results. The air-dried soil to liquid weight-ratio of the suspension should be reproducible with acceptable precision as it determines the cell potential measured. The ratio should be expressed explicitly; e.g. for the ratio 1:2 as $E_{2(1:2w)}$ for water, or $E_{2(1:2KCl)}$ for KCl solution and $E_{2(1:2CaCl)}$ for CaCl₂ 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 H^+ ion amount set free from particles for different soil to liquid ratios, after these were exchanged by the K^+ - or Ca^{2+} - ions [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 Part A 1.4 scheme [B]. 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 Suspension Effect 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 indicator electrode* from the “eqs”, as it is positioned in Method 2, *into the sediment, while the reference electrode remains in “eqs”*. As can be seen from the cell [C] (scheme 3 in Part A 1.4) the indicator electrode potential changes to a mixed potential, the value of which depends on the pH of the “eqs” and on the H^+ ion activity of the diffuse layer of the contacting suspension particles. Because the reference electrode potential and the diffusion potential remain unchanged, the measured cell potential E_4 differs from E_2 by the potential difference ΔE known as “SE 1” (section A 1.3). For an equilibrated suspension of 1/2 soil/water ratio this is given by $\Delta E_{4-2(1:2W)} = E_4 - E_2$. The pH_4 values obtained with the same indicator electrode in different (soil) suspensions allow an *approximate comparison* of the H^+ ion activity to which a (charged) surface similar to that of the indicator electrode (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 a reference electrode connected with the suspension by two salt bridges in series (“double salt bridge”), of which the final 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], the 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 Suspension Effect*”, 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^+ ion activities contributed from the “eqs” and from particles.

Method 5 (cell potential E_5)

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In this method the indicator electrode is placed in the “eqs” and the reference electrode 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 **pH₅** 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 pH₂ values (and pH differences) which can be used for the characterisation of these soils in agronomy. The treatise relating to “soil pH measurement” can be applied – *cum grano salis* – to the general potentiometric **pIon** measurement in soils and in other suspensions. It should be emphasized once more, that by means of the voltage measurement of any suspension galvanic cell no thermodynamically defined quantity can be obtained.

A 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 indicator electrodes 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/Sb₂O₃) do not have smooth surfaces and for this and other reasons they show a greater or unexpected contribution to the SE [12].

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The *single reference electrode* 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, there **always flows or diffuses its filling solution**, e.g. saturated KCl-solution of the reference electrode half cell, even if the filling solution is gel-stabilized [10,14,15]. This can give rise to the 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 e.g. the equilibrium solution 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].

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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 indicator electrode 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”. The *ISFET (combined) electrodes* also cannot avoid the SE in suspension measurements; 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 resistance, (e.g. cells with the metal or solid membrane used as a halogenide indicator electrode) can be measured with voltmeters of smaller input resistance but the readings are not stable and are difficult to interpret.

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B. GUIDELINES FOR PRACTICAL pH MEASUREMENTS IN SOIL SUSPENSIONS

(IUPAC Recommendations 2006)

Abstract: The measured cell potentials for suspension potentiometric cells have been interpreted and explained by a detailed analysis of the schemes for these cells (Part A). Some former disagreements amongst investigations have been clarified. A new unambiguous operational definition of the Suspension Effect is presented. It is defined as the difference in cell potential for two suspension potentiometric cells, one with both electrodes in the separated equilibrium solution and the other with both electrodes in the sediment or suspension. This potential difference is the sum of the change in the indicator electrode potential and the change in the liquid junction potential of the reference electrode, when the electrodes are used for measurement, once in the sediment of the suspension and then in its equilibrium solution.

B 1 INTRODUCTION - RECOMMENDED DEFINITION OF THE SUSPENSION EFFECT (RECOMMENDED TERMINOLOGY FOR THE pH (pION) MEASUREMENT IN SUSPENSIONS)

Two disputable definitions of the Suspension Effect (SE) can be found in current IUPAC recommendations, [1,2], both erroneously assuming that a boundary potential is the essential part of the SE. The existence of such a potential is not supported by experimental evidence [9,14]. The findings presented in Part A regarding the origin and interpretation of the SE [5] require modification of the definition of the SE.

B 2 RECOMMENDATION OF THE OPERATIONAL DEFINITION OF THE SUSPENSION EFFECT

Considering the IUPAC Recommendation 2002 of pH measurement [6] and the analysis of the schemes of suspension potentiometric cells, presented in Part A [5], the **operational definition of the Suspension Effect (SE)** at any temperature and pressure is:

the SE is the potential difference $\Delta E_{SE} = E_{susp} - E_{soln}$ of two suspension cells, presented in the following cell diagrams and measured both under the same conditions of temperature and pressure and with the same indicator- and reference electrode (with salt bridge filling solution):

Reference electrode	salt bridge	:: equilibrium solution	pH (ISE)	E_{soln}
	filling solution :: of suspension "X"		electrode	($\equiv E_A$)

Reference electrode	salt bridge	:: suspension "X"	pH (ISE)	E_{susp}
	filling solution :: or sediment of "X"		electrode	($\equiv E_B$)

From ΔE_{SE} the SE values can be calculated and expressed as ΔpH_{SE} , as was the case in the first definition of the SE [3], or as $\Delta pIon_{SE}$, when any ion selective indicator electrode (ISE) is used for the potentiometric measurements in suspensions.

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The cell containing the equilibrium solution of the suspension (original or modified) gives the best-defined E_{cell} (and the corresponding pH value), obtainable with any suspension potentiometric cell [13]. Thus it is the appropriate reference potentiometric cell for comparison of results obtained by modified methods for potentiometric measurements in suspensions.

When the SE determinations on different suspensions are intended for the comparison of characteristics of these suspensions, saturated KCl solution is the recommended salt bridge filling solution. The separation of the suspension into its sediment and its clear equilibrium solution can be performed by any suitable separation method.

B 3 INTERPRETATION OF THE SUSPENSION EFFECT

The interpretation of the SE, supported by analysis of schemes for the suspension potentiometric cells, with the aid of which the SE is defined, gives consideration to the previous study of numerous SE researchers and above all to the more recent experimental findings on SE.

As a result of the present analyses, the SE is considered as the sum of two independent potential changes that arise when the electrodes are transferred from the equilibrium solution to the suspension. The first potential change is the change of the indicator electrode potential (**Suspension effect of the first kind**). The second potential change is the change of the liquid junction potential when the reference electrode makes contact with the suspension (**Suspension effect of the second kind**). Experiments indicate that there is no measurable boundary potential between the sediment and the separated equilibrium solution. Therefore there is no boundary (or Donnan-) contribution to the SE.

The “*Suspension Effect of the first kind*” (“SE 1”) is caused by the transformation of the pH electrode (or ISE) from being a single electrode, when immersed in the

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equilibrium solution of a suspension, into a multiple electrode, when immersed in a suspension or sediment. (The *cause of “SE 1”*). This transformation is the consequence of the overlapping of the electrode diffuse double layer with the particle diffuse double layers. The overlapping happens when particles make intimate contact with the electrode surface [7]. The primarily Nernst electrode potential formed in the equilibrium solution, changes to an **irreversible mixed (steady state) electrode potential**, when the electrode is introduced into the appertaining suspension or sediment. (The *nature of “SE 1”*). This mixed potential is mostly constant during practical potentiometric measurements. The “SE 1” cannot be eliminated in potentiometric measurements where the indicator electrode is in contact with the suspension.

The “*Suspension Effect of the second kind*” (“SE 2”) arises from the diffusion or outflow of the (saturated KCl) filling solution from the salt bridge of the reference electrode into the suspension or sediment. (The *cause of “SE 2”*) [8]. When KCl solution contacts the dispersed charged particles, an ion exchange with the particle counterions or a change of ion arrangement around the particles may occur. This can annul the ability of the KCl solution to moderate the liquid junction potential of the reference electrode and may increase it enormously. This is caused by the K^+/Cl^- diffusion front of the KCl solution being replaced by an H^+/Cl^- diffusion front, which results in a larger diffusion potential. These effects result as an appearance of the “**anomalous liquid junction potential**”. (The *nature of “SE 2”*). The “SE 2” represents the *systematic error* of the suspension measurement by potentiometric methods. The “SE 2” can be eliminated by a reference electrode which is equipped with a “double salt bridge”; that means a reference electrode having the suspension-contacting part filled with the equilibrium solution of the measured suspension or by an equivalent arrangement.

More explanatory information on the above themes is obtainable in Refs. [9] to [5].

B 4 GLOSSARY (TERMS AND DEFINITIONS)

This Glossary presents recommended terminology related to the Suspension Effect:

Suspension of solid charged particles

A dispersion of solid electrically charged particles, commonly larger in size range than colloidal particles (of approximate diameter range 1 to 1000 nm) [*dispersed phase*], in water or an aqueous solution [*continuous, liquid phase*].

Note. It can be a *Uniform System*, an optically equable (uniform) mixture of both phases, or a *Combined System* in which a part of the liquid phase of the equilibrated suspension [*Equilibrium solution*] is separated from the rest of the suspension. By sedimentation of particles a concentrated phase [*Sediment*], can be formed, in which particles are still surrounded by the intrinsic liquid phase, the equilibrium solution. Both parts remain in physical and electrical contact.

Suspension potentiometric cell

A galvanic cell containing, as its essential component, a *uniform* or *combined suspension* or one of its separated parts alone, "*the equilibrium solution*" or "*sediment*".

Anomalous liquid junction potential

The electrochemical potential which arises at the reference electrode – measurement solution interface when, during a potentiometric measurement, the salt bridge filling solution of the reference electrode contacts the charged particles of a suspension.

Note. Its value can significantly exceed the liquid junction potential, common in solution potentiometry, depending on the suspension species and the concentration of the filling solution. The contact between the reference electrode (or its salt bridge) electrolyte and the charged particles can change the ion arrangement around the particles and cancel the equitransference of ions in the electrolyte diffusion front (e.g. by ion exchange of H^+ or OH^-); this ion exchange will diminish the suppression of the diffusion potential.

Suspension Effect

Improved SE definition: the potential difference of two potentiometric cells, where the potential-measuring electrodes are first placed both in the sediment of the suspension and then both in its equilibrium solution.

This replaces the original definition of the SE [3]: the difference in pH in suspensions of different particle concentrations, measured by a potentiometric method.

Note 1. The suspension effect is the sum of two potential differences:

1) The *Suspension effect of the first kind*, "SE 1", which arises at the indicator electrode and is the difference between the mixed potential generated in the sediment and the electrode potential generated in the equilibrium solution, and

2) The *Suspension effect of the second kind*, "SE 2", which arises at the reference electrode salt bridge interface with the measurement suspension and is the difference between the liquid junction potential of the reference electrode when placed in the sediment and when placed in the equilibrium solution.

The *cause of "SE 1"* is the intimate contact of the electrode surface with the particle diffuse double layers. Its *nature* is an irreversible mixed (steady state) potential.

The *cause of "SE 2"* is the outflow of the salt bridge filling solution from the reference electrode and the interaction of this electrolyte with particles, with which some ion exchange may occur. The *nature of "SE 2"* is the resulting abnormal liquid junction potential, possibly of a very high value.

Note 2. The potential differences mentioned can also be given as the corresponding pH (or pIon) values.

Suspension (soil) pH

Readings on a pH-meter scale, obtained for a suspension of soil (in water or electrolyte) by any method for potentiometric "pH measurement", performed in a manner analogous to the pH measurement in solutions.

Note. Most of these “Suspension (soil) pH” values have no known quantitative connection with the hydrogen ion activity in suspensions; nevertheless, they are more or less repeatable characteristic values of the measured suspensions.

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