

Desk study to assess the feasibility of a draft horizontal standard for pH

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SUMMARY

In this desk study international standards for pH determination in soil (ISO 10390), sewage sludge (EN 12176), treated biowaste (EN 13037) and waste (EN 12506) are reviewed and compared. The standard for soil differs from the other standards in two important respects: (1) Soil samples are dried before extraction, while fresh samples are used in the other standards; (2) In addition to water, 0.01M CaCl₂ or 1M KCl are used as soil extractants. pH declines in CaCl₂ or KCl extracts compared to water extracts are well documented and several comparative studies have been made of the different soil extractants. The drying of soil may have a great impact on pH as indicated in several studies. A complete horizontal standard is hardly possible, because the different sample categories will need different pretreatments, or concerning liquid sludge, no pretreatment at all. If we still want to approach a horizontal standard it will be important to have the same extractant for soil, sewage sludge, treated biowaste and waste. We recommend that pH determinations in soil should preferably be made on fresh samples using water as an extractant, in order to make the determinations more comparable with those of the other materials.

1. INTRODUCTION

pH, which is an indirect estimate of the H^+ concentration (or rather the H^+ activity) in a pure water or salt solution, is one of several fundamental measurements which are used to characterize general soil conditions. The pH value is dependent on the liquid/solid ratio and type of extractant as well as on the measuring methodology. Different researchers and laboratories have developed their own methods to measure pH and sometimes the results are not easy to compare. Therefore it has been important to standardise the methods to get comparable results and an international standard for determination of pH in soils, ISO 10390 has been developed. Later on, other standards for pH measurements in sewage sludge and treated biowaste have been developed, For these latter materials somewhat different methods concerning sample preparation and measurements are used. There is a need to harmonise the methods used into a horizontal standard for the different materials mentioned, which is an aim of the EU-project HORIZONTAL. In this desk study we have reviewed the standards for soil, sewage sludge, treated biowaste and waste. We have also reviewed a number of comparative studies concerning the methodology, but these comparisons have only been made for soil samples.

2. EXISTING STANDARDS OR DRAFT STANDARDS

2.1 Soil

The methods of pH measurement in soil solutions are described in ISO 10390 which was first published in 1994 and revised in 2002. This standard specifies that a soil suspension should be prepared with one of three reagents: deionized H₂O, 1 M KCl or 0.01 M CaCl₂ (Table 1). A suspension is made at a soil:solution volume ratio of 1:5 (V/V) using air-dried soil which should be dried at a temperature not higher than 40°C and sieved at 2 mm. This pre-treatment is also specified in ISO 11464. In the first edition of ISO 10390 the suspension should be shaken for 5 min and let to stand for at least 2 h, but not longer than 24 h in order to reach equilibrium. In the revised edition the shaking time was increased to 60 min and the suspension should be let to stand at least 1 h before measurement but not longer than 3 h (Table 1). The pH value is measured in the suspension just after the recommended time period or whilst being stirred until a stable reading is obtained (should not vary more than 0.02 pH-units within 5 s).

Another standard method for pH measurement is described by SSSA (Soil Science Society of America). In brief, 10 mL of deionized water, 1 M KCl or 0.01 M CaCl₂ is added to 10 g of air-dried soil and mixed. The suspension is standing for 10 min before the measurement (Thomas 1996) (Table 1). The measurement could be done in the clear supernatant or in the suspension under stirring. The author points out that the measurement should be done in a consistent way since the different measuring methods may result in different pH values (Thomas 1996).

2.2 Sludge

According to EN 12176 pH in sludge samples should be measured directly in the sludge if the sample is sufficiently wet, i.e. contains less than 50 g dry matter per kg sludge. If the sludge sample contains more dry matter it should be diluted with water. A sample corresponding to appr. 5.0 g dry matter is diluted to a total weight of 100 g and then shaken for 15 min (Table 2). The sample should be swirled before measurement. The pH reading should be done after approximately 30 to 60 s.

2.3 Treated biowaste

The standard EN 13037 (soil improvers and growing media) describes a similar extraction method as in the soil standard ISO 10390, but fresh samples that have passed through a 20 mm or 40 mm sieve according to EN 13040 are used. The samples should be diluted 1:5 (V/V) and shaken for 1 h (Table 2). The suspension is agitated before the measurement and pH is measured in the sedimented suspension when stabilisation is reached (varying not more than 0.1 pH-units within 15 s).

2.4 Waste

The determination of pH in waste material (ENV 12506) is different from what is described in the other standards, since the pH should be measured in eluates obtained from waste samples after batch extractions. The preparation steps are described in EN 12457, which consists of four parts. In these four parts methods for different liquid to solid ratios and grain sizes are covered. The principle is that the sample is brought into contact with water under defined conditions with the assumption that equilibrium or near-equilibrium is achieved between the liquid and solid phases by agitation during the duration of the batch extraction. Generally the duration is 24 h. After the extraction the suspended solids are allowed to settle for 15 min and the eluate is filtered over a 0.45 µm membrane filter. pH in the eluate is then measured immediately according to the standard for measuring pH in water samples (ISO 10523) (Table 2).

TABLE 1. METHODS FOR MEASURING pH IN SOIL SAMPLES

Method	Preparation	Reagents	Soil:extractant-ratio	Extraction method	Extraction time	Time before measuring	Measuring procedure	Comments
ISO 10390	Air-dried <40°C, the sample is passed through a sieve with 2 mm aperture	1. Water with $\kappa < 0.2$ mS/m, pH > 5.6 Or 2. 1 M KCl or 3. 0.01 M CaCl ₂	5 ml sample volume ratio 1:5	Shaking	60 min	1 to 3 h	Suspension shaken just before the measurement. Measuring in the settling suspension. Reading the pH after stabilisation is reached (varying not more than 0.02 pH-units within 5 s)	Drying of soil may affect the pH, especially in samples containing sulfides, the oxidation of which can lower the pH substantially. 2 and 3: the stabilisation is reached more quickly in a salt solution than in water. The pH value should be rounded off to two decimal places
Thomas, (1996) SSSA	Air-dried, Temperature or sieving not specified	1. Deionized water Or 2. 1 M KCl or 3. 0.01 M CaCl ₂	10 g sample + 10 ml extractant	Stirring or shaking	Not specified	10 min	Swirling of the suspension before measurement. pH-electrode in supernatant above soil, directly in the sedimented soil, or the suspension is stirred during the pH determination.	Water pH: values taken in the supernatant generally will be slightly higher than in the stirred suspensions. Salt pH: no differences between the techniques.

TABLE 2. METHODS FOR MEASURING pH IN SEWAGE SLUDGE, BIOWASTE AND WASTE

Method	Preparation	Reagents	Soil:extractant-ratio	Extraction method	Extraction time	Time before measurement	Measurement	Comments
EN 12176	Liquid sludge: none	Water with $\kappa < 0.2$ mS/m, pH > 5.6	Liquid sludge: no extra addition of liquid. Paste-like and solid sludges: Adding water to a sample equivalent to 5.0 g dw to a total weight of 100 g	Shaking	15 min if water is added	Not specified	Sludge sample dispersed by swirling immediately before the measurement. Reading of the steady pH value after approximately 30 – 60 s.	pH value should be rounded off to one decimal place
EN 13037	In accordance with EN 13040 Coarse material > 40 or 20 mm is removed	Water with $\kappa < 0.2$ mS/m, pH > 5.6	Volume ratio 1:5	Shaking	1 h	Not specified	Suspension agitated before the measurement. Read after stabilisation i.e. pH not changing more than 0,1 pH unit over 15 s	pH value should be rounded off to one decimal place
EN 12506	An eluate is made by leaching the material according to EN 12457	Eluation with water $\kappa < 0.5$ mS/m, pH 5 to 7.5	Three different liquid to solid ratios (L/S) are specified in EN 12457: 2 L/kg, 8 L/kg and 10 L/kg.	Leaching	Agitation for 24 h (two step method: first step 6 h, second step 18 h) then settle for 15 min and filtration over a 0.45 μ m membrane filter	Immediately after preparation of eluate	Method according to ISO 10523:1994, treated as a water sample. Solution swirled before measurement which is done without stirring	pH value should be rounded off to two decimal places

3. EVALUATION OF DRAFTING A HORIZONTAL STANDARD

The methods used in the different standards are briefly described in Tables 1 and 2. In principle one could say that we are dealing with two kinds of procedures, namely extraction of solid material such as soil and soil improvers followed by pH measurement in the resulting suspension, or leaching of waste material, where the leachate is treated as an ordinary water sample. In some cases, sludge samples could probably be treated as water samples as well. If the sludge is more like a paste it should be more diluted than a soil extract according to EN 12176. Therefore, we have to conclude that there are just a few steps that are common for all the methods. One common thing is that the solid material should be sieved before extraction but the particle size cut-off varies from 2 mm (soil) to 40 mm (treated biowaste). Another most important difference is that soil samples should be air-dried according to ISO 10390 but the other materials (sludge, treated biowaste and waste) should be pre-treated and measured for pH under fresh conditions. There are three different extractants recommended in the soil standard (deionized H₂O, 1 M KCl and 0.01 M CaCl₂) while in the other standards only deionized H₂O is used. Samples are usually shaken to approach a pH equilibrium in the suspensions, but the shaking time recommended for sludge is considerably shorter (15 min) than for soil and treated biowaste (60 min). The time needed to reach an equilibrium in the liquid-solid suspension might be rather critical. Still, in the standards for sludge and treated biowaste this question is not addressed at all. Moreover, the allowed variability of an individual pH measurement differs between the standards.

Since the standards for pH measurements in sludge and waste only consider water as an extractant, the simplest horizontal standard method for all materials would be pH measured on fresh samples using solid-water suspensions. The effect of dilution on the pH value seems to be more important for water than for salt solutions. One might therefore consider a parallel standard based on 0.01 M CaCl₂. For waste material any horizontal standard is difficult to apply since waste material is widely different from both soil and sewage sludge in most respects, e.g. in terms of the number of active exchange sites per unit mass or surface area, which calls for separate pre-treatment and extraction methods.

4. CRITICAL POINTS AND RECOMMENDATIONS

4.1 Critical points

4.1.1 Soil, pre-treatment

According to ISO 10390 the soil samples should be air dried as described in ISO 11464. The use of air dried soil samples is also recommended by SSSA (Soil Science Society of America) but whether the drying will affect the pH value is not discussed (Thomas 1996). Dried soil material is often more easy to handle with respect to sieving and homogenizing, and the drying of the sample decreases the microbial activity which makes it possible to store the soil sample before analysis. However, the drying affects several soil chemical processes such as the oxidation – reduction processes, solubility of organic matter and the concentration of nutrients (Barlett & James 1980, van Erp et al. 2001), which means that the properties of the soil solution including pH, will change compared to fresh samples, when the soil is rewetted. One investigation of moist and dried soil samples collected from Canadian podzols showed that pH decreased after drying and the difference was larger for pH measured in water (pH_{H_2O}) than for pH measured in a 0.01 M $CaCl_2$ solution (pH_{CaCl_2}) (Courchesne et al. 1995). The liquid/solid ratio was 20 mL to 2 g for the organic forest floor material (O horizon) and 20 mL to 10 g for the mineral soil layers. The authors found that there was a positive relationship between pH changes after drying and the organic carbon content in the soil samples. According to the authors this supported the hypothesis put forward by Barlett & James (1980), that drying increases the solubility potential of organic material because hydrogen bonds are broken and fresh organic surfaces become exposed. van Erp et al. (2001) investigated how pH measured in $CaCl_2$ suspensions of three different soils (sand, noncalcareous clay and calcareous clay) was affected by drying at different temperatures (20°C and 40°C), with or without forced air ventilation. For sand and noncalcareous clay all the drying treatments significantly lowered the pH compared to the moist soil while for the calcareous clay only drying without forced air ventilation at 20°C significantly decreased the pH. The authors also found that higher drying temperatures (70°C and 105°C) affected the pH more than drying at 20°C and 40°C and therefore recommended that if soil drying is preferred the drying temperature should not exceed 40°C. However, Davey & Conyers (1988) found smaller effects on pH of air drying in some acid Australian soils except for one sandstone soil in which pH decreased by 0.05 pH units.

Rewetting a dried soil does not seem to restore the original pH found in the fresh soil. In a study of Bt horizons from three Ultisols, dried soil samples were rewetted and incubated for 1-107 days (Walworth, 1992). The pH values in the centrifuged soil solutions increased by 0.5 pH units after rewetting compared to the original pH of the fresh samples.

4.1.2 Soil, extraction solution

Water extraction implies a dilution of the soil solution and thereby also a decrease of the ionic strength, but the pH measured could still be said to reflect the actual pH of the soil solution. The resulting value of the equilibrium pH depends on the charge properties of the soil particles and their ion exchange reactions and the composition of the dissolved chemical species in the soil solution. The pH will also vary throughout the growing season, mainly depending on the proton fluxes associated with the nutrient uptake by the plants and the net nitrification in the soil.

To minimise the seasonal variations, Schofield & Taylor (1955) proposed the use of a 0.01 M $CaCl_2$ solution which was supposed to have an ionic strength close to that found in soil solutions of ordinary arable soils. This is actually not true, since the $CaCl_2$ solution is usually found to exchange H^+ ions from the soil colloids for Ca^{2+} ions in the electrolyte, resulting in a lowering of the measured pH value as compared to a water suspension. The difference between pH_{H_2O} and pH_{CaCl_2} may decrease at low pH values since proportionally more H^+ ions are already in the soil solution. Several Australian researchers have investigated the relationship between pH_{H_2O} and pH_{CaCl_2} . The relationship has been described with a linear equation by Conyers & Davey (1988) and Brennan & Bolland (1998). Ahern et

al. (1995) found a linear relationship in slightly leached soils, while more weathered soils showed a distinctly curvilinear relationship at low pH. Henderson & Bui (2002) pooled data from 70465 observations of Australian soils in an attempt to obtain a general calibration curve for $\text{pH}_{\text{H}_2\text{O}}$ and $\text{pH}_{\text{CaCl}_2}$. They found that the whole data set showed the best fit when using an additive model. The additive model is a generalisation of the familiar linear regression model whereby smooth functions of the individual predictors are allowed (Henderson & Bui 2002). For this material the authors could also see that fine textured soil diverged from the calibration curve at $\text{pH} > 8$ and the model indicated a reduction of the difference between $\text{pH}_{\text{H}_2\text{O}}$ and $\text{pH}_{\text{CaCl}_2}$ as the pH declined (Henderson & Bui 2002). There are few corresponding comparisons between pH_{KCl} and $\text{pH}_{\text{H}_2\text{O}}$. van Lierop (1981) found a good relationship ($r=0.999$) between soil pH measured in 0.01 M CaCl_2 and 1 M KCl extracts from an organic soil. The soil-liquid volumetric ratio was 1:2.

4.1.3 Soil, dilution effects and shaking time

Dilution will affect the pH in that the dissociation of H^+ from the soil surfaces tends to increase with dilution in acid soils, and in addition there is an increasing hydrolysis of dissolved Al according to equilibrium reactions such as



Both effects will help to buffer the solution and maintain a rather stable pH (Thomas 1996). However, Conyers & Davey (1988) compared the effect of the solution/soil ratios 2:1, 2.5:1 and 5:1 for water and 0.01 M CaCl_2 and 0.1 M KCl extracts from some air-dried Australian soil samples. They found that $\text{pH}_{\text{CaCl}_2}$ was insensitive to dilution while pH_{KCl} and $\text{pH}_{\text{H}_2\text{O}}$ increased by 0.1 and 0.2 pH units, respectively, when the dilution increased from 2:1 to 5:1.

4.1.4 Relevance of pH determinations

pH is important as an indicator of the soil acidity conditions. The pH value may also be a critical parameter for determining the limit values for the heavy metal concentrations in soil, which means that a lower pH value will decrease the acceptable limit value. However, for some trace metals e.g. mercury, lead and copper the organic matter content may also be an important susceptibility indicator together with pH, because of the tendency of these trace elements to form strong organic complexes (Ross 1994).

As mentioned above, the reason for using 0.01 M CaCl_2 as an extractant, was partly the assumption of an ionic strength similar to that in the soil water of arable soils, which turned out to be an oversimplification.

Another issue is how important a pH determination is for sludge samples as such. It should be considerably more important to know the resulting pH after mixing sludge and topsoil.

4.2 Recommendations

Based on the existing knowledge, we have identified two main factors that might influence the determination of pH, namely the pre-treatment of the samples and the extraction medium used. This could be summarised as dry versus fresh samples, and the use of H_2O or a 0.01 M CaCl_2 solution as an extractant. The extraction time and measurement time may be less important but should be harmonised by using the same time frames for all materials.

The basic philosophy behind the preliminary recommendations below is that the chemical status of the samples should be as similar as possible to that found under ambient field conditions. Therefore drying (including air-drying) should be avoided and the ionic strength of the extractant should approach ambient conditions. The latter goal will be obtained by using water as an extractant. Due to this choice of extractant the temporal variability in measured pH will unavoidably be high, depending on varying soil moisture conditions or nutrient uptake by crops. Therefore repeated sampling on an annual or longer time basis should preferably be done at a similar time (month) of the year.

4.2.1 Pre-treatment

Literature data (Barlett & James 1980; Davey & Conyers 1988; Courchesne et al. 1995; Van Erp et al. 2001) indicated that drying affects the pH of soil samples. The dried soil sample might not represent the natural conditions in the soil. The use of fresh samples should be preferred to dried samples, as quite extensive and partly irreversible pH changes may occur as a result of the drying process. Since the standards for sludge and biowaste are based on measurements performed on fresh material it would be preferable to measure pH on fresh soil as well, to get 'a more horizontal' standard. For practical reasons soil samples cannot always be treated in the same way especially when comparisons are made with old dried samples. On the other hand, drying of sludge is probably even more impractical. However, homogenizing and sieving of fresh soils, especially clayey soils without drying might be more complicated and make it more difficult to get a representative sample from the soil. Clayey samples are notoriously difficult to sieve under moist/wet conditions and powerful mechanical devices for destroying aggregates and facilitate the sieving procedure have to be developed. For fresh mineral soil, the liquid/solid proportion (based on volume/volume ratio) in the preparations could be the same as described in ISO 10390. There will also be problems with samples with a high organic matter content (peat samples), whose volume will markedly change depending on the water content, which means that the same V/V (volume/volume) ratio cannot be used as for mineral soil. Series of different V/V ratios of added water and sample should be tested to find the optimal ratio for obtaining reproducible pH values at different initial water contents. For mineral soil samples in general sample/water ratios should also be tested even if the effect of differences in initial water content on pH values will be much smaller than for peat samples.

Our recommendation is therefore to develop a standard like ISO 11464 for pre-treatment of fresh soil samples without drying. In order to obtain that goal, more comparative studies of dried and fresh samples of soil and sludge should be carried out.

4.2.2 Extraction procedure

For soil both H₂O and 0.01 M CaCl₂ could be used. This might also be applicable for biowaste but here we need more comparative studies. Concerning sewage sludge, it is doubtful whether extraction with a CaCl₂ solution is of any relevance since sludge is more like a water sample than a soil sample.

The use of water (pH > 5.6; κ < 0.2 mS/m) as a general extractant is a very attractive alternative, as the purpose of a pH measurement should be to obtain a reasonable estimate of the pH in the soil solution, rather than a pH value resulting from a partial desorption of protons and aluminium species in a 0.01 M CaCl₂ or 1 M KCl extract. Besides these salt extractants, water is presently one of the extractants recommended for soils (ISO 10390). According to present standards the pH of sewage sludge is either measured directly (liquid sludge) or water is added to paste-like and solid sludge (EN 12176). Moreover, water is also used for biowaste (EN 13037) and waste (EN 12506).

4.2.3 Measurement of pH

The actual measurement of pH is comparatively easy to standardise concerning the shaking of the suspension before measurement and the stabilisation time needed before the reading of the pH value. However, it might be necessary to investigate the stabilisation times of different suspensions.

The shaking time may also need to be adjusted for soil samples, while we do not suggest any changes concerning the shaking time for the other sample categories.

4.2.4 Conclusive recommendations

We believe, that a completely horizontal standard for pH measurements comprising all the sample categories mentioned, cannot be defined. It is obvious that the necessary sample preparations of soil, sludge, biowaste or waste cannot possibly be identical. However, our proposal is "horizontal" both with respect to the use of fresh samples, and the general use of water of high purity as a general extractant.

Draft Standard (CEN template)

A brief proposal for a standard

Preparation

For all materials there should be the same preparation steps as before, but the preparation of fresh soil samples should also be included (for mineral soil the same solid/liquid proportions as for dried soil can be used, but for samples rich in organic matter the proportions should probably be changed).

Extraction

Extraction with water ($\kappa < 0.2$ mS/m, pH > 5,6).

Shaking time: The shaking time (60 minutes) may need to be adjusted for soil samples, while we do not suggest any changes concerning the shaking time for the other sample categories.

Measurement

Settling time: 1h for soil but also the same time for sludge and treated biowaste?

Swirling of the sample just before the measurement for all materials

The reading should be done after the similar stabilisation time.

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