

Application Bulletin 71/4 e

pH value and oxidation reduction potential in soil samples

Determination according to EN 15933, ISO 10390, and ASTM D4972

Branch

Water, wastewater, air, environmental protection; research and education

Keywords

Soil; pH value; redox potential; oxidation reduction potential; exchange acidity; acidity; ORP; EN 15933; ISO 10390; ASTM D4972; branch 2; branch 17; pH Meter; 913; flat-membrane electrode; spearhead electrode; combined Pt-ring electrode; Pt1000; 6.0256.100; 6.0226.100; 6.0454.100; 6.1114.010; environmental; agriculture

Summary

The pH value and oxidation reduction potential (ORP) of soil provide important information about soil properties, such as solubility of minerals and ion mobility. Knowledge of these properties allows making predictions concerning plant growth, bacterial activity, nutrients that may be needed, possible corrosive effects on buildings, etc.

Here, the determination of the pH value is described according to ISO 10390, EN 15933 and ASTM D4972. The oxidation reduction potential determination is carried out in a suspension.

Instruments

- pH Meter

Electrodes

Flat-membrane electrode for pH measurements in the laboratory	6.0256.100
Spearhead electrode for pH measurements in the field	6.0226.100
Combined Pt-ring electrode	6.0451.100
Pt1000 Temperature Sensor steel	6.1114.010

Reagents

- Buffer solution pH 4.00, e.g. Metrohm 6.2307.100
- Buffer solution pH 7.00, e.g. Metrohm 6.2307.110
- Buffer solution pH 9.00, e.g. Metrohm 6.2307.120
- Calcium chloride dihydrate, $\text{CaCl}_2 \cdot 2 \text{H}_2\text{O}$
- Redox standard 250 mV, e.g. Metrohm 6.2306.020

Solutions

$c(\text{CaCl}_2) =$ 0.01 mol/L	1.47 g $\text{CaCl}_2 \cdot 2 \text{H}_2\text{O}$ is weighed into a 1000 mL volumetric flask and dissolved in distilled water. The flask is then filled up to the mark with distilled water.
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Sample preparation

ISO 10390

The soil sample is dried at a temperature not higher than 40 °C. The sample should be passed through a sieve with 2 mm mesh size.

EN 15933

Soil is prepared according to EN 16179. Sludge and treated biowaste do not need any sample preparation.

ASTM D4972

The sample is air-dried or dried in a drying oven at 105 °C and screened over a 2.00 mm sieve.

Analysis

Calibration of pH electrode

The electrode is calibrated using the buffer solutions pH 9, pH = 7 and pH = 4.

pH measurement in the field

The spearhead electrode is inserted into the soil while turning the electrode slightly. If the soil is sandy or very dry, it should first be moistened with dist. water. The final pH value can be read after about 1 min.

pH measurement in the laboratory

ISO 10390 and EN 15933

Determination of pH-H₂O

This method determines the acidity of the sample.

A minimum of 5 mL air-dried soil sample and five times the sample volume of distilled water are mixed. The suspension is intensively stirred or shaken for 1 h and then allowed to stand for at least 1 h, but not more than 3 h. During this time the suspension should not get in contact with air. After this, the pH value of the suspension is measured. During the measurement the suspension should be stirred in a way that no stirring funnel is created. The final pH value is usually obtained after about 1 min. The flat membrane electrode is recommended for this analysis because its membrane shape minimizes scratching from particles in the solution.

In case of calcium- and / or magnesium carbonate-rich soils, the adjustment of a pH equilibrium may last longer than 3 h.

Determination of pH-CaCl₂

The same procedure as described under Determination of pH-H₂O is used, but c(CaCl₂) = 0.01 mol/L instead of distilled water is added. In CaCl₂ solution, a stable potential is reached faster than in distilled water.

If the measurement is carried out after the addition of calcium chloride, the exchange acidity will be obtained. Calcium chloride causes an exchange of aluminum and iron ions out of the silicates. These in turn form hydrogen ions by hydrolysis.

For the reasons given above (cation exchange), the pH values obtained will be somewhat lower than when distilled water is used. Depending on the composition of the soil, the difference may be up to 1 pH unit.

ASTM D4972

Determination of pH-H₂O

This method determines the acidity of the sample.

10 ± 0.1 g, 20 ± 0.1 g or 40 ± 0.1 g prepared sample is weighed into a suitable beaker and filled up with the same amount of water (e.g., for 10 g sample 10 mL distilled water is used). The suspension is stirred thoroughly and allowed to stand for 1 h. After that, the pH of the supernatant aqueous phase and then the pH of the suspension is measured. The measured temperature should correspond more or less to the room temperature (between 15 to 25 °C).

If the prepared sample contains clay and prevents the formation of an aqueous phase, the amount of added water should be doubled (e.g., for 10 g sample 20 mL distilled water is used).

Determination of pH-CaCl₂

The same procedure as described under Determination of pH-H₂O is used, but c(CaCl₂) = 0.01 mol/L instead of distilled water is added. In CaCl₂ solution, a stable potential is reached faster than in distilled water.

If the measurement is carried out after the addition of calcium chloride, the exchange acidity will be obtained. Calcium chloride causes an exchange of aluminum and iron ions out of the silicates. These in turn form hydrogen ions by hydrolysis.

For the reasons given above (cation exchange), the pH values obtained will be somewhat lower than when dist. water is used. Depending on the composition of the soil, the difference may be up to 1 pH unit.

After a series of 10 determination or after the end of the determination series, the electrode has to be inserted into pH 7.00. The measured pH should lie in between pH 6.9 and 7.1.

Measurement of the oxidation reduction potential in the laboratory

25 mL of the air-dried soil sample is mixed with 50 mL distilled water in an Erlenmeyer flask and the suspension is shaken for 5 min. After this time, the Pt-ring electrode is immersed in the suspension and the oxidation redox potential is measured. It is important to stir the sample during the measurement to keep the suspension from settling. Depending on the composition of the soil, the final value will be reached after 30 – 50 min. For this reason, the reading should only be taken after 50 min have elapsed.

Parameters

Calibration of pH electrode

Mode	CAL MEAS pH
Stirring rate	8
Min. waiting time	10 s
Max. waiting time	110 s
Measuring interval	2 s

pH measurement

Mode	MEAS pH
Stirring rate	Depends on sample (no settling)
Signal drift	10 mV/min
Min. waiting time	0 s
Max. waiting time	120 s
Measuring interval	2 s

Potential measurement

Mode	MEAS U
Stirring rate	Depends on sample (no settling)
Signal drift	10 mV/min
Min. waiting time	0 s
Max. waiting time	3000 s
Measuring interval	2 s

Example determination

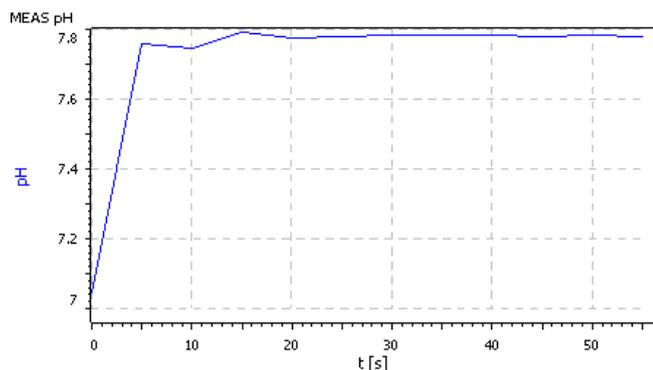


Fig. 1: pH measurement curve of soil suspension with distilled water

Comments

- A frequent calibration of the pH electrode is necessary. The frequency of the calibration depends on the number of samples. If the electrode has not been used for a while, a calibration is necessary.
- The flat membrane electrode is recommended for pH measurement in suspension, because its shape minimizes scratching of the membrane from particles in the solution.
- A fixed sample volume instead of a fixed sample weight has to be taken because of the different possible soil qualities.
- The Pt-ring electrode has to be checked from time to time (see Application Bulletin No. 48) and cleaned if necessary.

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