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**Soil quality — Determination of redox  
potential — Field method**

*Qualité du sol — Détermination du potentiel d'oxydoréduction — Méthode  
de terrain*

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## Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 3.

Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

Attention is drawn to the possibility that some of the elements of this International Standard may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

International Standard ISO 11271 was prepared by Technical Committee ISO/TC 190, *Soil quality*, Subcommittee SC 3, *Chemical methods and soil characteristics*.

Annexes A, B, C and D of this International Standard are for information only.

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## Introduction

The redox potential is a physicochemical parameter used to characterize soil aeration status in a global way. Under field conditions, it gives information on the condition of oxidation or reduction of those compounds which, depending on the case, play an important part in plant nutrition, can induce toxicity phenomena or intervene in gas transfer to the atmosphere (greenhouse effect). It can also be used to a certain extent to follow soil performances in case of sludge disposal or composting, and to adjust applications accordingly. Under laboratory conditions, it can be used in order to study oxygen diffusion phenomena to aggregate level.

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# Soil quality — Determination of redox potential — Field method

## 1 Scope

This International Standard specifies a field method for the determination of soil redox potential ( $E_h$ ).

NOTE The electrochemical measurement of redox potential described here is possible only if the relevant soil horizon has a moisture status defined as fresh or wetter according to the classes presented in annex D.

## 2 Normative reference

The following normative document contains provisions which, through reference in this text, constitute provisions of this International Standard. For dated references, subsequent amendments to, or revisions of, this publication do not apply. However, parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent edition of the normative document indicated below. For undated references, the latest edition of the normative document referred to applies. Members of ISO and IEC maintain registers of currently valid International Standards.

ISO 3696:1987, *Water for analytical laboratory use — Specification and test methods*

## 3 Term and definition

For the purposes of this International Standard, the following term and definition apply.

### 3.1

#### redox potential

$E_h$

electrochemical potential reflecting the oxidation-reduction status of a liquid chemical system (in this case of the soil solution)

## 4 Principle

Redox potential is an electrochemical equivalent of the free energy of redox reactions, and for an equilibrated single redox system of the general form:



is given by the Nernst equation:

$$E_h = E^0 + \frac{RT}{nF} \ln \frac{A_{\text{ox}}}{A_{\text{red}}} - \frac{2,303mRT}{nF} \text{pH} \quad (2)$$

where

$A_{\text{ox}}$  and  $A_{\text{red}}$  are the activities of the oxidized and reduced forms of the element, respectively;

$e^-$  refers to the electron(s) involved in the reaction;

$\text{H}^+$  refers to the proton(s) involved in the reaction;

- $n$  and  $m$  are the numbers of electrons and protons involved in the reaction, respectively;
- $E^0$  is the standard value of the potential, i.e. when  $A_{\text{ox}} = A_{\text{red}}$  and  $\text{pH} = 0$ ;
- $R$  is the universal gas constant ( $8,314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ );
- $T$  is the absolute temperature;
- $F$  is the Faraday constant ( $96 \text{ 500 C} \cdot \text{mol}^{-1}$ );
- 2,303 is the natural log of 10.

Redox potential is related to electron activity ( $e^-$ ) in the system as follows:

$$E_h = - \frac{RT}{F} \ln(e^-) \quad (3)$$

NOTE Users of this International Standard unfamiliar with these electrochemical concepts should consult appropriate texts, or seek professional advice.

The electrometric determination of redox potential is analogous to the determination of pH. The determination of  $E_h$  follows the principle of measuring potential differences between an inert measuring electrode (usually a platinum electrode), i.e. an electrode not reacting with the solution *per se*, with respect to the standard hydrogen electrode used as the reference electrode. Many redox systems are involved in the soil solution, and the resulting potential is a mixed potential depending on the existing electroactive redox couples. For practical reasons, a silver-silver chloride electrode is usually used as the reference electrode, the potential of which is added to the measured potential difference (see annex C) in order to obtain the values expressed on the basis of the standard hydrogen electrode.

## 5 Apparatus

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**5.1 Millivoltmeter**, with an input resistance not less than  $10 \text{ G}\Omega$  and sensitivity of  $1 \text{ mV}$ .

**5.2 A set of redox-electrodes**, constructed as in A.1.

All electrodes should be sufficiently robust for field use.

**5.3 Reference electrode**: silver/silver chloride reference electrode in  $1 \text{ mol/l}$  or  $3 \text{ mol/l}$  potassium chloride solution.

Other reference electrodes such as the calomel electrode can also be used, but are not recommended because of the health hazard connected with the use of mercury. The potential of such reference electrodes with respect to the standard hydrogen electrode is given in annex B. Reference electrodes should be stored in a potassium chloride solution (6.4) of the same concentration as that present in the electrode, or directly in the salt bridge (5.5) containing the same concentration of potassium chloride. It should be noted that lower concentrations of potassium chloride will reduce contamination of the soil with this salt.

**5.4 Rigid rod**, (stainless steel has been found suitable),  $20 \text{ cm}$  to  $100 \text{ cm}$  in length, with a diameter  $2 \text{ mm}$  greater than that of the redox electrodes (5.2).

The rod shall have a length which allows the redox electrodes to be inserted to the desired depth in the soil.

**5.5 Salt bridge**, to connect the reference electrode with the soil (see A.2).

**5.6 Hand auger**, with a diameter  $3 \text{ mm}$  to  $5 \text{ mm}$  greater than that of the salt bridge.

**5.7 Electrode cleaning materials**: finest grade of steel wool, scouring powder and some cotton cloth have been found suitable.



**5.8 Thermometer**, to measure the temperature at the location of the reference electrode (see clause 8) with an accuracy of 1 °C.

## 6 Reagents

**6.1 Redox buffer solution**, to calibrate the redox electrodes.

Use either buffered quinhydrone solution (prepared by adding quinhydrone to a pH buffer to obtain a suspension), or an equimolar solution of potassium hexacyanoferrate(III) and potassium hexacyanoferrate(II) (see annex B).

**6.2 Water**, conforming to grade 2 of ISO 3696.

**6.3 Agar**,  $\rho = 0,5 \%$ , in a potassium chloride solution of the same concentration as that in the reference electrode.

**6.4 Potassium chloride solution**, of the same concentration as that chosen in 5.3.

NOTE This solution is used to store the reference electrode and to add to the salt bridge, as needed.

## 7 Site selection and sampling

The selection and description of the place of measurement, and of samples for laboratory measurement, should follow the guidelines given in ISO 10381-1, — and ISO 11464.

## 8 Procedure

### 8.1 Care, cleaning and testing of the redox electrode system

The platinum electrodes shall be stored in air and kept clean. They shall be inspected for damage and/or contamination at intervals of not more than one year, and every time they are used. Oils, fats and waxes, and other chemicals likely to adhere are particularly damaging to electrode performance. If contaminated with soil material they shall be cleaned gently with a cotton cloth, and rinsed with distilled water. In cases of severe contamination, e.g. with oils, etc. (above), an appropriate solvent followed by scouring material (5.7) shall be used (see Note below).

The reference electrode(s) shall also be inspected at the same time as the platinum electrode(s). Any visible change in the colour or transparency of the potassium chloride electrolyte solution indicates probable trouble. In such cases the reference electrode shall not be used. Crystals of potassium chloride are, however, a normal feature of saturated potassium chloride solutions, and are no reason to reject the electrode in question.

The electrodes shall be checked prior to each series of measurements, by determining their response in the redox buffer solution (6.1). The measured redox potential values shall be as given in annex B. Any electrode differing by more than 10 mV from the required value shall be cleaned and tested again, and discarded if cleaning fails to correct the problem.

NOTE Experience has shown that the use of strong oxidizing agents, e.g. nitric acid or hydrogen peroxide solution, as cleaning agents for platinum electrodes can result in high redox potentials. The use of such agents is therefore not recommended.

In practical terms, the reference electrode potentials can be checked against each other. An electrode which gives a reading differing by more than 10 mV from the other(s) is likely to be faulty, and should be discarded. This check procedure requires a minimum of three reference electrodes, connected in turn.

Reference electrodes can be checked in absolute terms only against a standard hydrogen electrode. This can be done only in specialist laboratories. It is usually more convenient to buy electrodes only from a reputable source.

## 8.2 Preparation of site and measurement of redox potential

At the place of measurement, drive a hole into the soil using the rigid rod (5.4) to a depth 2 cm to 3 cm less than the desired measurement depth. Immediately insert the redox electrode into the hole to a depth deeper by 2 cm to 3 cm than that of the hole. At least two electrodes should be installed for each measurement depth. Leave the platinum electrodes in the soil for at least 30 min following installation before connecting them to the millivoltmeter.

At a distance of 10 cm to 100 cm from the redox electrode, auger a hole down to a fresh (or wetter) soil layer (see annex D), and install the salt bridge so as to obtain good contact between the ceramic cup of the salt bridge and the soil. Measure the potential difference,  $E_m$ , in millivolts between the platinum electrode and the reference electrode after 1 h, using the millivoltmeter (5.1). The measurement period can be shorter (but not  $< 30$  min) only if the difference between successive measurements at 10 min intervals is  $\leq 2$  mV. Measure the temperature (5.8) at the location of the reference electrode at the time of measurement of the potential difference,  $E_m$ .

It is recommended that the platinum electrode be disconnected from the millivoltmeter between readings. Potassium chloride can leak from the salt bridge and reach significant amounts after about 2 h. If this is undesirable, then the salt bridge should be removed from the soil and re-installed prior to each set of measurements.

Protect the reference electrode from direct heating by the sun. Keep in mind that the temperature of the reference electrode and not that of the soil should be taken into account when deriving the reference electrode potential.

## 9 Evaluation

The measured voltage,  $E_m$ , shall be related to the voltage of the standard hydrogen electrode by adding the potential of the reference electrode,  $E_r$ , (see annex C) to the reading  $E_m$  [equation (4)]. The voltage obtained in this way is designated the redox potential,  $E_h$ .

$$E_h = E_m + E_r \quad (4)$$

NOTE The redox potential in soils ranges from  $-400$  mV (extremely reduced conditions) to  $+900$  mV (highly oxidized conditions).

## 10 Expression of results

The value of the redox potential shall be quoted rounded to the nearest 10 mV.

### a) Example of calculation:

Measurement of  $E_m$ :  $+327$  mV, measured against a silver/silver chloride electrode in 1 mol potassium chloride solution. The temperature of the location of the reference electrode at the time of measurement is  $17$  °C, which means its potential with respect to the standard hydrogen electrode is  $+241$  mV (annex C). Thus:

$$E_h = +327 \text{ mV} + 241 \text{ mV} = +568 \text{ mV}$$

### b) Example of presentation of results:

Redox potential ( $E_h$ ) =  $570$  mV.

## 11 Test report

The test report shall contain the following information:

- a reference to this International Standard;
- complete identification of the test site, including the depth of measurement, and the soil moisture status, for example according to Table D.1;
- the result of the determination;
- any details not specified in this International Standard, which are optional, as well as any factor(s) which might have affected the results.

## Annex A (informative)

### Description of the construction of redox electrodes, of the salt bridge, and their arrangement during measurement

#### A.1 Redox electrode

Several types of redox electrode are available commercially. Two types of redox electrode which have been found convenient for field use are shown in Figure A.1. In the first [Figure A.1 a)], the platinum wire (usually of 0,5 mm to 1,5 mm in diameter) or sheet is soldered or welded directly to a rigid rod (diameter  $> 2$  mm) of copper or of a brass alloy. The weld is sealed with a waterproof epoxy resin. Other kinds of construction are suitable, such as high-temperature glass/metal seals. The choice will depend on the facilities available, but materials chosen should have a similar coefficient of expansion to that of platinum to ensure viable seals. It is essential that the weld and the copper above it are completely isolated from the surrounding medium after the electrode is installed. It is desirable to cover the weld with insulation (heat-shrinkable plastic tubing is the most practical) after coating with epoxy, and then to apply epoxy to the ends of the insulation. Ceramic jacketing of dental material, covered with a plastics material, has also been found to provide a good seal.

The exposed platinum surface should have a minimum area of  $1 \text{ mm}^2$ .

The second type of electrode, shown in Figure A.1 b), consists of a bundle of platinum wires (with the tips exposed) embedded in a conical epoxy tip built into a hard metal (e.g. stainless steel) body equipped with a handle for introducing the electrode into the soil. This electrode is convenient to work with, although it is more difficult to construct. It has been found that if problems occur with sealing between the platinum wire and the electrode body (glass or plastics), a small amount of melted sealing wax is effective as a further sealant.

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