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

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

Reference number
ISO 11271:2002(E)

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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.

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

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

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 ($8,314\ 1\ \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$);
T	is the absolute temperature;
F	is the Faraday constant ($96\ 500\ \text{C} \cdot \text{mol}^{-1}$);
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

5.1 Millivoltmeter, with an input resistance not less than $10\ \text{G}\Omega$ and sensitivity of 1 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 mol/l or 3 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 cm to 100 cm in length, with a diameter 2 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 mm to 5 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 ≤ 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)

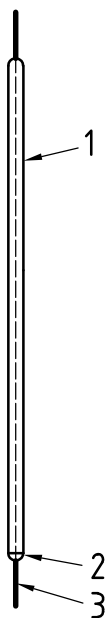
Description of the construction of redox electrodes, of the salt bridge, and their arrangement during measurement

A.1 Redox electrode

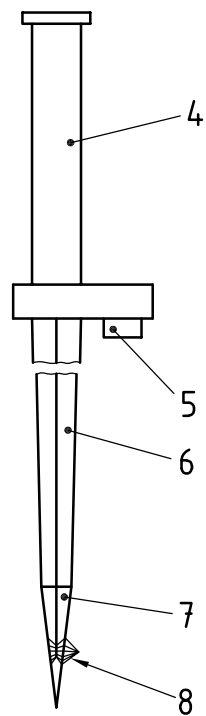
Several types of redox electrode are available commercially. Two types of redox electrode which have been found convenient for field use are shown in Figure A.1. In the first [Figure A.1 a)], the platinum wire (usually of 0,5 mm to 1,5 mm in diameter) or sheet is soldered or welded directly to a rigid 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 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.



a) Redox electrode



b) Point-tip redox electrode

Key

- 1 Insulation
- 2 Copper rod
- 3 Platinum wire
- 4 Handle
- 5 Socket
- 6 Steel rod
- 7 Epoxy
- 8 Platinum wires, exposed

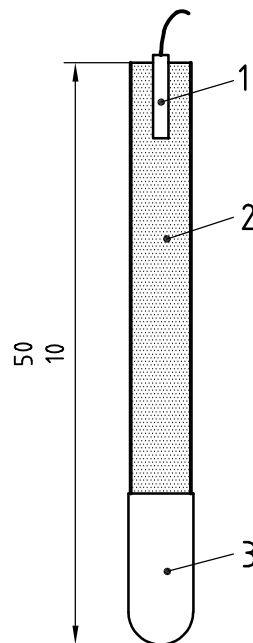
Figure A.1 — Construction of redox electrodes

A.2 Salt bridge (Figure A.2)

The purpose of the salt bridge is to close the electrical circuit during the redox measurement by connecting the reference electrode to the soil without contamination of the inner solution of the electrode. A suitable salt bridge is shown in Figure A.2, and consists of a transparent plastics tube of internal diameter 20 mm to 30 mm connected to a porous hydrophilic ceramic cup (similar to those used in tensiometers), thus providing liquid contact with the soil. The bridge is filled with agar ($\rho = 0,5 \%$) in potassium chloride solution, the latter of the same concentration as that in the reference electrode (see 5.3).

The agar is prepared by boiling the chosen potassium chloride solution with agar ($\rho = 0,5 \%$) for several minutes to obtain a clear solution. This is poured hot into the tube with the ceramic cup. The length of the salt bridge should be enough to reach the fresh (or wetter) soil layer as defined in annex D. A length up to 50 cm should be satisfactory for most applications. It should be noted that short bridges are more convenient to use. The open upper end of the tube should be closed with a stopper having a hole for the reference electrode. If the salt bridge is transported without the reference electrode (which in that case should be stored in separate potassium chloride solution), then the upper end of the tube should be completely closed. Other kinds of salt bridge construction, e.g. integrated bridge-electrode systems, can also be suitable. Solid electrolyte systems are suitable for use only in saturated soils, because of the inherent problem of the nature of the electrical junction between such electrolytes and soil particles in drier soils.

Dimensions in centimetres



Key

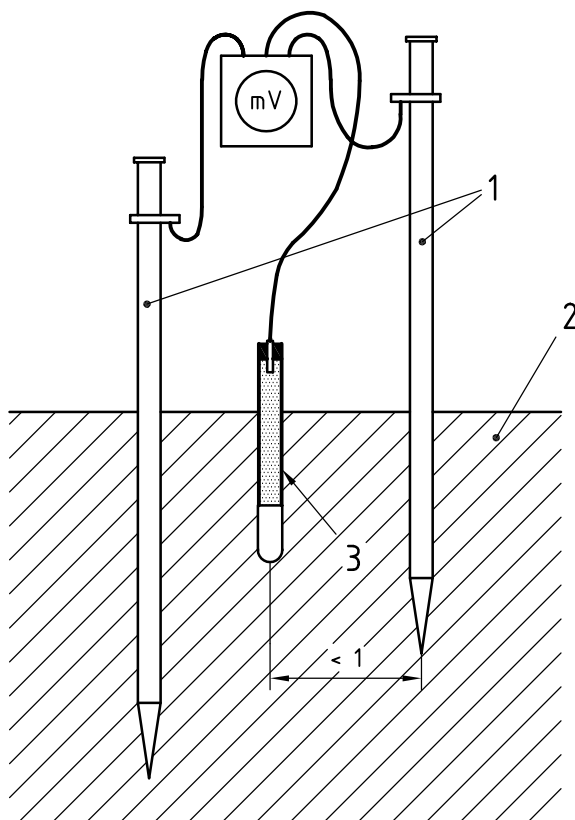
- 1 Silver-silver chloride electrode
- 2 Agar solution ($\rho = 0,5 \%$) in potassium chloride
- 3 Ceramic cup

Figure A.2 — Construction of the salt bridge for redox potential measurements

A.3 Arrangement of the electrodes during measurement (Figure A.3)

The distance between the redox and the reference electrodes should be within the range 0,1 m to 1 m. The soil layers into which both electrodes are inserted shall have a moisture status defined as fresh (or wetter) according to the wetness classes given in annex D. If, for example, the surface soil horizon is dry, the salt bridge should be placed in a hole augered down to a fresh (or wetter) layer.

Dimensions in metres



Key

- 1 Redox electrodes
- 2 Soil
- 3 Salt bridge

Figure A.3 — Arrangement of the redox and reference electrodes during measurement of redox potential at two depths in the soil (single electrode at each depth)

Annex B (informative)

Potentials of platinum electrodes in different solutions

Table B.1 — Potential of platinum electrode in quinhydrone dissolved in pH buffers versus indicated reference electrodes at temperatures 20 °C, 25 °C and 30 °C

Reference electrode	at pH 4			at pH 7		
	mV			mV		
	20 °C	25 °C	30 °C	20 °C	25 °C	30 °C
Ag-AgCl saturated	268	263	258	92	86	79
Saturated calomel	223	218	213	47	41	34
Standard hydrogen	471	462	454	295	285	275

Table B.2 — Equilibrium potential of the iron(II-III) couple at equal activities of iron(II) and iron(III)

pH	E_h mV	pH	E_h mV
0	771	8	160
1	770	9	30
2	750	10	–150
3	710	11	–320
4	620	12	–480
5	500	13	–560
6	390	14	–620
7	270		

Table B.3 — Redox potential of equimolar mixtures of potassium hexacyanoferrate(III) and potassium hexacyanoferrate(II) as measured against a standard hydrogen electrode

mol ^a	E_h mV
0,01	415
0,007	409
0,004	401
0,002	391
0,001	383

^a mol = 0,01 indicates that the concentrations of both potassium hexacyanoferrate(III) and potassium hexacyanoferrate(II) are equal to 0,01 mol/l, etc.

NOTE The measurement with the 0,001 mol/l solution is the most exact.

Annex C (informative)

Potentials of reference electrodes

Table C.1 — Potentials of commonly used reference electrodes versus the standard hydrogen electrode at different temperatures

Potentials in millivolts

°C	Calomel 0,1 mol/l KCl	Calomel 1 mol/l KCl	Calomel saturated KCl	Ag/AgCl 1 mol/l KCl	Ag/AgCl 3 mol/l KCl	Ag/AgCl saturated KCl
50	331	274	227	221	188	174
45	333	273	231	224	192	182
40	335	275	234	227	196	186
35	335	277	238	230	200	191
30	335	280	241	233	203	194
25	336	283	244	236	205	198
20	336	284	248	239	211	202
15	336	286	251	242	214	207
10	336	287	254	244	217	211
5	335	285	257	247	221	219
0	337	288	260	249	224	222

NOTE The difference between the potential of the calomel and the silver-silver chloride electrodes is 46 mV at 25 °C at the same potassium chloride (KCl) concentration.

Annex D (informative)

Soil moisture status

Table D.1 — Evaluation of soil moisture status

Soil evaluation	Definition	Diagnosis in soils with	
		> 17 % clay	< 17 % clay
Dry	Water content is less than the moisture retained at wilting point	Solid, hard, cannot be moulded, darkens strongly when moistened	Light in colour, darkens strongly when moistened
Shrinkage limit			
Fresh	Water content is intermediate between field capacity and wilting point	Semi-solid, can be moulded, cracks and crumbles when rolled by hand to 3 mm thread, darkens slightly when wetted	Darkens slightly when wetted
Moist	Water content near field capacity; free water absent	Plastic, rollable to a 3 mm thread without cracking; colour constant when wetted	Fingers get slightly moist, no water escapes soil pores upon compression, colour constant when wetted
Wet	Free water present, saturating part of soil pore space	Soft, rollable to a thread < 3 mm diameter	Fingers moisten rapidly when soil worked, visible outflow from soil pores upon compression
Saturated	All pores full, free water present	All pores full, free water present	All pores full, free water present
Inundated	Soil surface covered by water	Soil surface covered by water	Soil surface covered by water

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