



OXYGEN DIFFUSION METER

OPERATING INSTRUCTIONS



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On these operating instructions



If the text follows a mark (as shown on the left), this means that an important instruction follows.



If the text follows a mark (as shown on the left), this means that an important warning follows relating to danger to the user or damage to the apparatus. The user is always responsible for its own personal protection.

Text

Italic indicated text indicates that the text concerned appears in writing on the display (or must be typed).

Introduction

The oxygen diffusion rate (ODR) meter measures the mobility of oxygen in the soil. This mobility is of significance to the availability of oxygen to the plant roots. The method involves the measurement of the electric current needed for the reduction of all available oxygen at the surface of a cylindrical Pt-electrode in the soil. Thus the oxygen flux through the air-filled pores and the waterfilm on the electrode to a zero concentration at the electrode surface is measured.

The transport of oxygen is much faster in air than in water. In a given type of soil the diffusion rate will therefore depend strongly on the air to water ratio in the pores of the soil-structure. Plant roots require for their growth a sufficient afflux of oxygen as will be provided by moderately or well aerated soils. Care should be taken to avoid any change of aeration at the point of measurement. The ODR-sensor must not cause any compression of the soil.

The soil is a very complex system. The results of an ODR measurement in a soil are highly sensitive to the voltage between the Pt-electrode and the soil. For comparable results the conditions of measurement should be well defined and closely controlled. The ODR meter has been designed to provide a stabilised voltage of 0.65 V between the Pt-electrode and the Ag-AgCl reference electrode, and, hence, of 0.428 V between the Pt-electrode and the soil (at 25 °C).

There may be some effect of pH on the outcome of an ODR measurement, but this is usually small for $\text{pH} \geq 3.5$.

The design of the ODR meter comprises a voltmeter with a high input impedance. To further exploit this facility the selector switch has been provided with a special position for the measurement of the Redox potential of the soil.

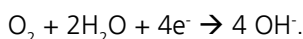


For an ODR measurement, the platinum electrode should be completely covered by a water film. In practice this means that readings should only be taken if the moisture content of the soil is at field capacity. In drier soils a Redox measurement offers a good alternative to characterise the soil, because the Redox potential is measured in a high impedance circuit, with a very low electrical current anyway. The user should be aware that soil is a heterogeneous environment, in which measurements will vary. Only average values of several, upto ten or more, measurements have meaning.

1 Description

1.1 Oxygen diffusion rate

The instrument measures the electric current needed for a quantitative reduction of the oxygen flowing from the airspaces in the soil to the platinum electrode. The chemical reaction is given by:



The reduction of one mole of oxygen thus requires four mole electrons which is equivalent to a charge of $4 \times 96500 = 386000$ Coulombs.

If ODR is the reduction rate of oxygen expressed in grams per second per square meter, this can be done as follows:

$$\text{ODR} = \frac{i \times 32}{386000 \times A}$$

In which i is the current readout in micro-amperes and A the surface area of the electrode in square meters. In the equation i should be used as a dimensionless value.

Given the surface of the electrode is about $2.37 \times 10^{-5} \text{ m}^2$ (or 0.0000237 m^2) this results in:

$$\text{ODR} = i \times 3.5 \text{ micrograms/m}^2/\text{s}$$

in which i is the dimensionless value of the instrument readout.

So if you read the value 40 in the display ODR becomes $40 \times 3.5 = 140 \text{ micrograms/m}^2/\text{s}$

1.2 ODR meter

The measurement system consists of a carrying case containing an indicating instrument (read-out unit), a plastic bottle with an Ag-AgCl reference electrode with a KCl salt bridge and a brass counter electrode. The Pt-electrode and a Riverside auger are delivered separately.

In this configuration the two functions of the counter electrode are separated: the reference electrode is used to measure and monitor the potential difference between the Pt-electrode and the soil, and the brass electrode is used to close the electric circuit for the current needed to reduce the oxygen. The basic circuit is shown in figure 1 on page 8.

The electro-chemical processes in the soil depend largely on the applied voltage. At a voltage of about 0.5 volt between the Pt-electrode and the soil the reduction of oxygen is the dominant process. The magnitude of the current will vary significantly with the voltage. It is therefore important to specify the applied voltage and to keep the voltage within narrow tolerances during measurements.

The potential of the Pt-electrode is measured with respect to an Ag-AgCl reference-electrode that is in electrical contact with the soil over a salt bridge. This measured value is used to control a voltage regulator circuit that stabilises the voltage between the Pt-electrode and the reference electrode at a value of 0.65 V.

As the anodic counter-electrode a brass electrode is used, also placed in direct contact with the soil.

1.3 Pt-electrode

The Pt-electrode is a 6 mm length of Pt wire, hardened with a 10 % addition of Ir. The wire has a diameter of 1,2 mm. The wire is mounted at the tapered end of a 750 mm long rod that facilitates the placement of the electrode at various depths in the soil. At the top of the rod is a female BNC connector for the connection of the cable to the read-out unit. A BNC cap is provided to protect the connector from soil, dirt and water when not in use. The electrode is outlined in figure 2 on page 11.

1.3.1 Preparation

Take the electrode assembly and connect a signal cable to the BNC connector. Take the cover tube from the tip. Rub the platinum tip with the glass fibre penn to remove any oxide (invisible but very disturbing on redox measurements). For accurate redox measurements follow the instructions of manual M2.18.21.27.E and/or ISO standard 11271.

Drill a hole to the desired depth minus 10 mm and insert the electrode-rod into the hole. Exert a slight pressure on the top of the assembly to bring the electrode to its correct position. Take care not to damage the electrode.



It is important that the electrode is positioned in undisturbed ground.

1.3.2 Maintenance

Wipe the electrode clean with a soft tissue after use and replace the cover tube. In the rare case of very persistent stains, the use of the fibre pen will suffice.



ODR electrodes should not be left in the soil for an extended period of time, since a decrease of readings may occur. It is best to take the electrodes out of the soil after the completion of one set of measurements and to reinsert them for the next one.

1.4 Reference electrode

A silver-silverchloride electrode filled with a saturated KCl solution is used as the reference for voltage measurement. The Ag-AgCl electrode system is mounted on top of a porous, ceramic cup that is filled with a saturated KCl solution to serve as a salt bridge to the soil. The connection between the electrode system and the salt bridge is a wet junction. A minute flow of KCl solution from the electrode vessel into the salt bridge and from the salt bridge into the soil should always be maintained during measurements. The pressure release screw near the top of the electrode assembly should be left open whenever the electrode is in use. Only when not in use the pressure release screw may be closed. For the electrical connection a female BNC connector is provided at the top of the electrode assembly. The electrode vessel is mounted in a screw cap that can be screwed onto a plastic bottle with a KCl solution. A spare cap is provided to close the bottle when the electrode is in use. The reference electrode and the salt bridge are depicted in figure 3 on page 11.

1.4.1 Commercial electrodes

Instead of the reference electrode supplied with the instrument, a commercial Ag-AgCl electrode fitted with a salt bridge may be used. Though the procedure will not differ much from the one given above, always follow the instructions of the manufacturer.

1.4.2 Preparation for use

Take the electrode assembly from the plastic bottle and close the bottle with the spare cap. Unscrew the pressure release screw one turn. Pull off the head of the silver electrode. Fill the vessel with a saturated solution of KCl to a level 15 mm below the brim. Check that the O-ring in the head is in good shape and replace the head.

1.4.3 Maintenance

Refill the electrode vessel with a saturated KCl solution when the level has dropped about 30 mm below the initial level or if any signs of discolouration (poisoning) of the liquid is noticed. Keep the pressure release screw closed when the electrode is not in use to prevent unnecessary leakage of KCl. Brush the ceramic of the reference electrode clean between and after use. Use a tooth brush and rinse ample water while doing this.

1.4.4 Storage



Always store the electrode/salt bridge assembly in its plastic bottle with KCl solution. See to it that the ceramic cup stays free from the bottom. The KCl solution in the storage bottle should be kept absolutely clean!

1.4.5 Preparation of a used electrode

The standard reference electrodes are supplied with a AgCl coating by Eijkelkamp. When the AgCl-coating is visually damaged or worn after use it must be renewed. The "old" AgCl coating must be removed totally and the electrode must be cleaned.

A damaged or worn AgCl coating will result in deviating measurements.

1.4.5.1 Before (re-)generating, the electrode must be cleaned

Clean the reference electrode before generating the AgCl-coating. When the electrode is very dirty (clearly visible deposit/cover) it must be polished (for instance with 0.05 micron Al_2O_3 powder).

When the electrode shows just a little surface deposits, it can be cleaned in two ways:

1. Put the Ag-electrode in a small water bath with water and soda and an aluminium foil on the bottom. The silver part must be submerged in the solution.
Heating the water and adding some kitchen salt will speed up the cleaning process.
2. Electro-chemical cleaning: Place the Ag-electrode in a 3 M KCl or 0.1 M HCl solution and anodize the electrode till 15 minutes at a current density of 0.5 till 10 mA/cm^2 (according to Bailey (1980) 5 mA/cm^2 is sufficient).
Connecting the Ag-electrode to the **negative** voltage - in relation to the counter electrode- will result in dissolution of the Ag. Doing this for a short period (30 seconds) will clean the Ag-electrode.
If necessary the electrode can be de-greased with acetone.



Always rinse with demi-water.

1.4.5.2 Generating an Ag-AgCl electrode

Method A: After cleaning, the Ag-electrode is placed in a concentrated (for example 5%) FeCl_3 solution. The electrode stays in the solution for 10 minutes to create a good AgCl coating. After removing the electrode from the solution a dull (mat) grey-black AgCl coating will be created. After 24 hours it will darken.

Method B: Electro-chemical coating in KCl or HCl.
Place the very clean Ag electrode in a 3 M KCl or 0.1 M HCl solution and anodize the electrode till 15 minutes at a current density of 0.5 till 10 mA/cm^2 (according to Bailey (1980) 5 mA/cm^2 is sufficient).
Connect the Ag-electrode to the **positive** voltage - in relation to the counter electrode (for example Ag or Pt shaft) - this will result in a smooth, dull (mat) grey-black coating.

1.5 Brass electrode

The counter electrode in the current circuit is a brass rod. It has an integral coaxial signal cable. An outline of the brass electrode is shown in figure 4 on page 11.

1.5.1 Maintenance



An occasional light polish with fine sandpaper may be required to remove an oxide layer from the brass surface. Avoid sharp bends in the signal cable. Do not use the glass fibre pen for this to avoid despositing brass on the platinum later.

2 Measurements

Check that the switch on the read-out unit is in the "OFF" position. Connect the signal cables from one, two or three Pt-electrodes to the BNC input connectors on the read-out unit, numbered 1, 2 and 3, as appropriate. Prepare a place in the soil for the reference electrode and the brass electrode. A distance of about 2 metres between these electrodes and the Pt-electrodes will usually be found satisfactory in the field, though it is by no means critical. In horticulture a distance of a few centimetres may be chosen without any problem, depending on the size of the object. Connect a signal cable to the reference electrode. Bury the salt bridge and the brass electrode in the top layer of the soil. In dry soils, it is often necessary to water the soil to improve the electrical contact between these electrodes and the soil. Watering should be limited to the immediate vicinity of the salt bridge and the brass electrode. Its effect must never extend to the Pt-electrodes. Connect the signal cables from the reference electrode and the brass electrode to the corresponding inputs on the read-out unit. Allow 2 to 4 minutes for stabilisation.

2.1 Measurement of Redox



The flow of an electric current in the soil disturbs the Redox equilibrium. Re-equilibration after an ODR measurement has been made may take between 15 minutes and several hours. So do not switch to ODR measurement before having done redox measurements.

When the switch on the read-out unit is turned from the "OFF" position to the "Redox" position the Redox potential between the soil and the Pt-electrode at input no 1 is displayed in mV. It takes some time when the electrodes have just been inserted into the soil before a steady reading can be obtained. This is often ten minutes, but in very dry soils it may rise to a few hours. Therefore we suggest to take a reading after ten minutes, wait for another ten minutes and take a second reading. When the difference is less than 20 mV, the latter reading can be taken as the equilibrium value.



In contrast to ODR electrodes, Redox electrodes can be left longer in the soil without any noticeable change of reading. After the first equilibration no further time-delays are required. It is important, though, that the part of the electrode structure that emerges from the soil is perfectly dry (no rain or dew) and does not move (stabilise against wind).

The Pt-electrodes as supplied with the ODR meter can very well be used as Redox electrodes.

2.2 Measurement of ODR

Turn the switch on the read-out unit to positions 1, 2 or 3 to read the ODR current at the corresponding electrodes. The reading will rise to a high value and then continue to fall for some time, when the already dissolved oxygen is reduced. It takes several minutes for the ODR measurement to reach an equilibrium. Therefore we suggest to take a reading after about three minutes, wait for another three minutes and take a second reading to see if an equilibrium has been reached yet.

Once the instrument is switched on, a current is maintained on all Pt-electrodes connected to either input 1, input 2 or input 3. Of course, only one Pt-electrode, determined by the position of the switch is connected to the measuring circuit. The steady flow of a current implies, though, that subsequent measurements after the first one require less time, typically 20 seconds.

One millivolt in the display corresponds to a current of one microampere. The voltage shown on the display is also available as an analogue signal between contacts 1 and 5 of the output connector. To avoid an excessive current drain from the batteries, the input impedance of any indicating or recording instrument should not be less than ten kilo-ohms.

2.3 Checking the instrument

Checking general:

1. Check if the batteries are fresh

Check Redox measurements:

1. Switch instrument to Redox position
2. Apply voltage between "Pt electrodes 1 and "ref. electrode" between 0 and 2000 mV.
For a rough check you may use a 1.5 Volt penlight battery.
3. Display reading should be within 3 mV accuracy of applied voltage.

Check ODR reference voltage:

In the kit going with the meter you will find a resistance soldered to some wires. Use this simple tool for the next check.

1. Short circuit input brass electrode to input ref. electrode.
2. Connect resistance 820 ohms between input ref. electrode and input PT electrodes 1
3. Switch instrument to position 1
4. At 820 ohms display reading should be 793
(+1 ohm -> -1 mV : 830 ohms -> reading 783 mV)
(-1 ohm -> +1 mV : 810 ohms -> reading 803 mV)

Check probe connections:

1. Check inputs and connections for corrosion and moisture (also on the instrument)
2. Check cables between middle pin connectors, resistance < 1 ohm
3. Check cables between outside connectors, resistance < 1 ohm
4. Check resistance reference electrode silver part (head without body) to middle pin connector, resistance < 1 ohm.
5. Check Pt electrode point resistance to middle pin connector, resistance < 1 ohm.
6. Check brass electrode to middle pin connector, resistance < 1ohm.

Check redox potential of electrodes:

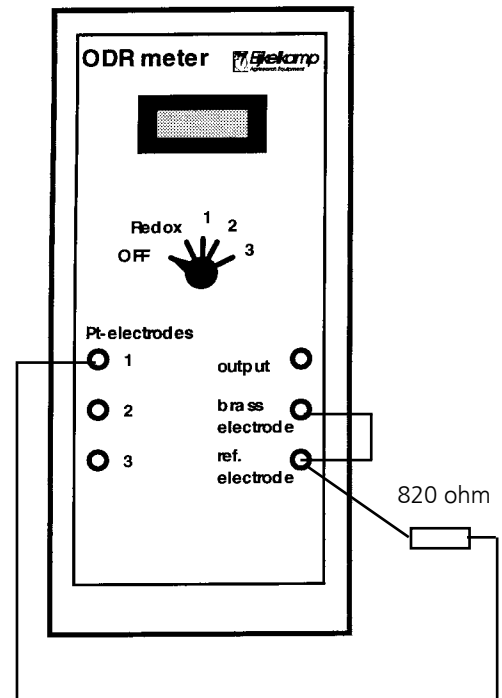
Use a Zobell kalibration solution to check the electrodes for redox measurements. The measurement value must be near the certified value of the Zobell solution (e.g lab temperature 21 °C, reference electrodes filled with 3 M KCl, measurement value must be near 228 mV). Stirr with de-aeration a little bit open.

Which value will you get ?

This depends on the temperature and type of reference-electrode. The values are shown in the table on next page. First you need to know the temperature of the (calibration) solution and the used reference temperature. Generally a field or normal lab electrode will be a Platinum-silver combination type electrode with 3 Mol KCl liquid (saturated with AgCl) as electrolyte.

Warning: The table is established using data from the Zobell-solution supplier (in Italics) and from the Austrian and DIN standard. Missing but usefull data have been extrapolated and are marked with *.

Use the grey marked column for the 3 M KCl electrodes supplied by Eijkelkamp.



Temp °C	Ag/AgCl saturated	Ag/AgCl (4M KCl)	Ag/AgCl (3M KCl)	Ag/AgCl 1M KCl	Calomel	Standard hydrogen Eh	Eref compared to Ag/AgCl (3M KCl)
-5		270 mV			234.2		
0		263.5	258*		226.0	482*	224*
5		257	251*		217.8	472*	221*
10	251	250.5	245	218	209.6	462	217
15	243	244	235	208	201.4	450	215
20	236	237.5	228	199	193.2	439	211
25	230	231	220	191	185.0	427	207
30	217	224.5	204	173	176.8	404	200
35		218			168.6		
40	210	211.5	195	164	160.4	391	196
45	203	205	187	155	152.2	379	192
50	196	198.5	178	146	144.0	366	188

3 Storage, transport



Always use the protective covers provided when electrodes or the instrument will be transported.



Always clean the electrodes before storage.



The reference electrode may be stored in the bottle with KCl for some time, up to a few months. When the instrument has to be transported over a long distance, or will be stored for a long time, the reference electrode is best emptied, cleaned and dried. When it is to be used again, the procedure as described under "1.4.2 Preparation for use" should be followed.

4 Specifications

Range:	Redox: 0 to 999 mV
	ODR: With the Pt-probe surface area of $2.37 \cdot 10^{-5} \text{ m}^2$ (0.0000237 m^2): 0 to 999 μA , corresponding to an O_2 diffusion rate of 0 to 3500 micrograms/ m^2/s , or 0 to 21 micrograms $\cdot \text{cm}^{-2} \cdot \text{min}^{-1}$
Resolution:	Redox: 1 mV
	ODR: 1 μA , corresponding to 3.5 micrograms/ m^2/s or 0.021 micrograms $\cdot \text{cm}^{-2} \cdot \text{min}^{-1}$
Accuracy:	Redox: $\pm 3 \text{ mV}$ ----- 880299
	ODR: $\pm 3 \mu\text{A}$
Climate:	Operating temperature 0 °C to 50 °C, humidity 30 to 80 % relative humidity.
Output:	Five-pin subminiature connector, voltage of 0 to 999 mV between contacts 1 and 5 for full range Redox or ODR signals. Input impedance of indicator or recorder $\geq 10 \text{ k}\Omega$. Mating cable connector is supplied with the instrument.

Power:	Four penlite (IEC-LR6) batteries; consumption 7.5 mA. Low battery-voltage level is indicated in the upper left corner of the display by a battery symbol.
Battery replacement:	Batteries can be reached through the lid at the bottom of the back of the read-out unit. Mind the polarity when replacing batteries.
Dimensions:	Carrying case 410 x 340 x 180 mm (L x W x H) Pt-electrode length 800 mm, diameter 12 mm
Weight:	Carrying case 4 kg Pt-electrode 1 kg Riverside auger 4 kg
Pt-electrode:	Wire of platinum with 10 % iridium, diameter 1.2 mm, exposed length 6 mm, length 70cm
Reference electrode:	Silver sheet 2 x 8 x 100 mm, ceramic cup, 100 ml PE plastic wide-neck bottle, probe provided with a pressure release screw.
Brass electrode:	Brass rod, diameter 8 mm, length 173 mm

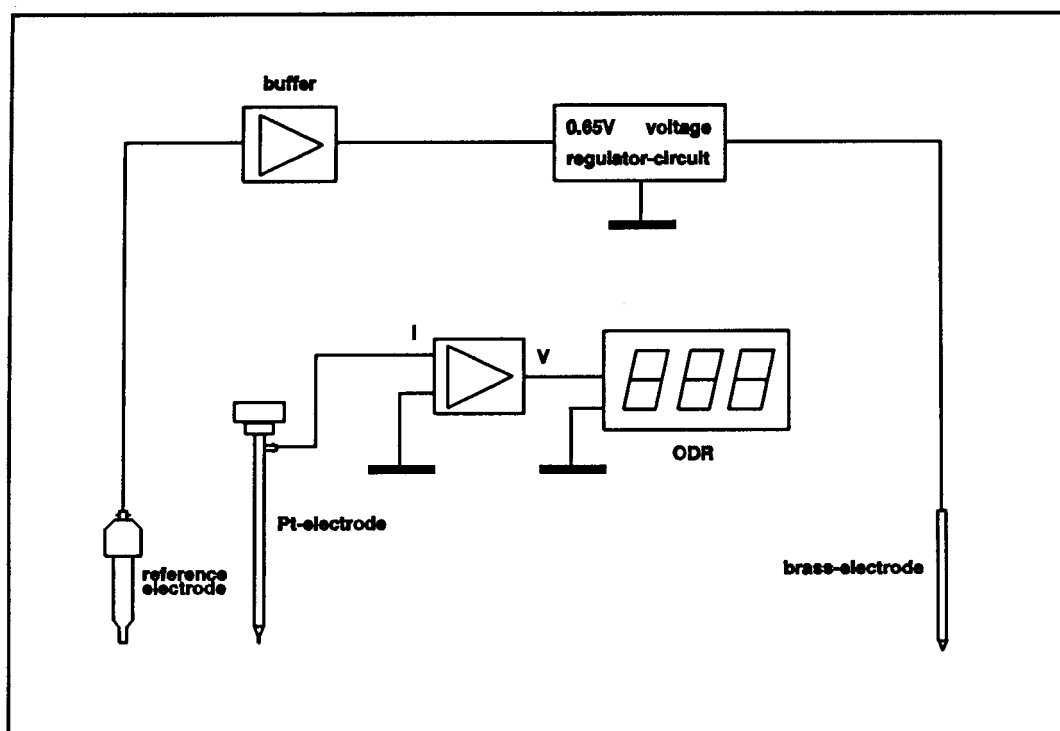
Literature

An extensive discussion of the ins and outs of an ODR measurement has been given by D.S. McIntyre (The platinum micro-electrode method for soil aeration measurement, Adv. in Agron. 22: 235 - 283 (1970)).

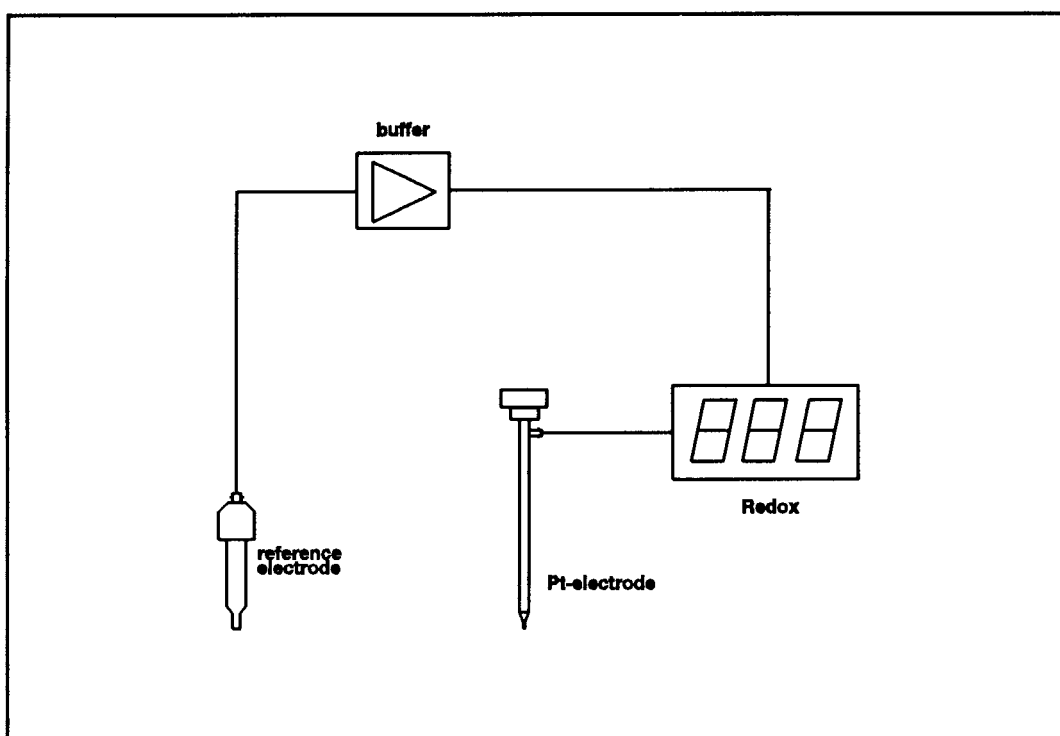
Analysis with ion-selective electrodes. Second edition, 274 pp, Bailey, 1980.

A survey of principles and procedures of both ODR and REDOX measurements is given by Jan Glinski and Witold Stepniewski in chapters 6 and 7 of Soil Aeration and Its Role for Plants, CRC Press, Inc., Boca Raton, Florida, USA, 1985.

Figure 1. Schematic diagram



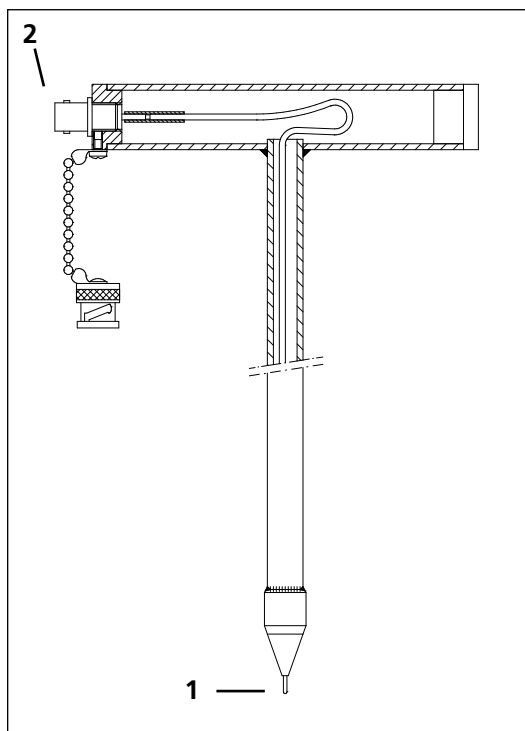
a



b

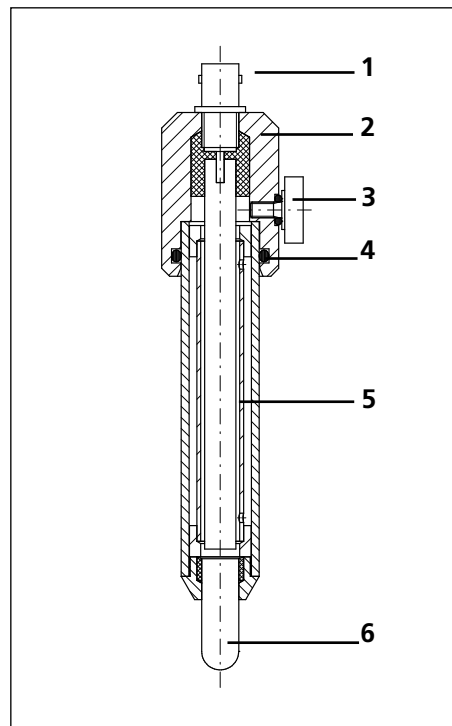
Schematic diagram of the Oxygen Diffusion Rate Meter set for ODR measurement (a) an Redox measurement (b).

Figure 2. Pt-electrode



*Pt-electrode: 1 Pt-Ir wire
2 BNC connector*

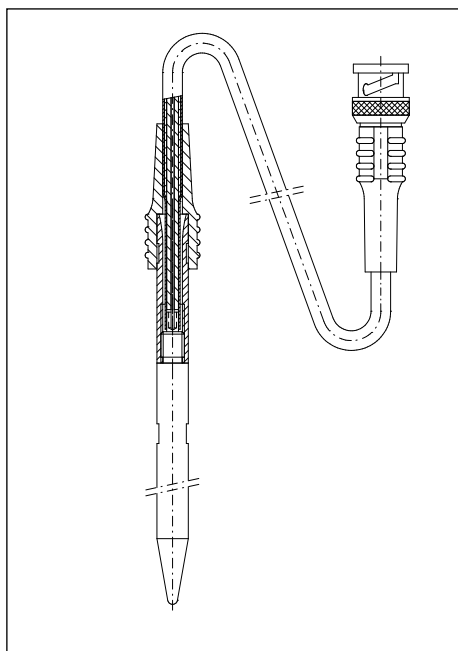
Figure 3. Reference electrode



*Reference electrode and salt bridge
1 BNC connector
2 Electrode head with silver electrode
3 Pressure release screw
4 O-ring
5 Observation
6 Porous cup*

Figure 4. Brass electrode

Brass electrode with integral cable and BNC connector.



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