HYDROLOGIE BODENKUNDE METEOROLOGIE MONITORING



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Manual redox electrodes acc. to Mansfeldt

ecoTech redox electrodes

User Manual for installation and application of redox- and reference electrodes according to Mansfeldt

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1 General

This execution of a redox electrode was developed by Prof. Dr. Mansfeldt, University of Cologne, and was optimized by ecoTech in cooperation with the Bavarian Environmental Protection Agency. It was designed for continuous operation in soils even under water-saturated conditions. Due to its small dimensions, it is appropriate for laboratory use, too (in soil columns or pot experiments).

As reference electrode an Ag/AgCl electrode is used which has electrical contact to the redox electrode by means of a salt bridge. Measurements can be made either with high-class voltmeters or with suitable data loggers (high input resistance is needed).

2 Redox electrode, Art. No. 461

2.1 Construction

Redox electrodes consist of a Platinum (Pt-) Rod (99,95 %) which is connected to a coax cable with a special sealing at the juncture. The shaft of the redox electrode consists of carbon fibre, is therefore very torsion-resistant and, in spite of its small diameter of 6 mm, can be extended up to a length of 100 cm without stability problems.



Fig. 1: Redox electrodes 461, left for laboratory use with S7-plug, right for field use with fixed cable

2.2 Number of replications

The redox potential of a soil (E_H) is measured as voltage [mV] and may alter very strongly on the millimeter scale. Very small soil regions, in contact with the platinum rod, can dominate the measuring value of the electrode. Therefore, redox potentials should be measured with small, normalized platinum surfaces. For this reason, ecoTech's redox electrode has a platinum rod with

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a diameter of only 1 mm and a length of only 5 mm. Use of 3 or more replications per depth and site is common.

2.3 Installation

ecoTech's redox electrodes have a shaft diameter of 6 mm and are installed directly in the soil

(field or lab). For this it is necessary to drill a hole into the soil, using a suitable pipe or massive post of 6 mm diameter, just short before the desired measuring depth (①). Then pull out the installation rod (②), and press the electrode, **carefully** by hand, into the desired depth (③). In doing so, the platinum part will be pushed directly into the soil. This procedure has to be done with considerable care and can be done by silting up, as an exception in rocky grounds. Preferably, the Pt-rod should be installed in undisturbed soil for better measurements.

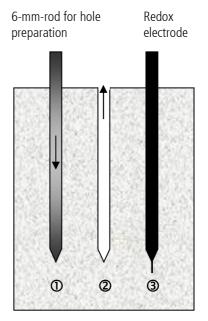
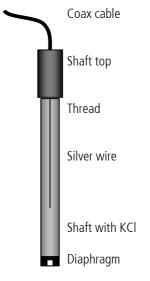


Fig. 2: Installation redox electrode

3 Reference electrodes

3.1 Construction

The reference electrode in the measurement setup described here, is an Ag/AgCl electrode. It functions as reference point for the potentials difference to the redox-(Platinum-)electrode. It consists of a silver wire which is sealed with AgCl and plunged into a 3 M solution of potassium chloride. The electrical contact of the electrolyte solution to the surrounding soil is given by a ceramic diaphragm. The diffusion which takes place through the very small pores of the ceramic diaphragm is sufficient to establish the redox equilibria on the electrodes' surfaces.







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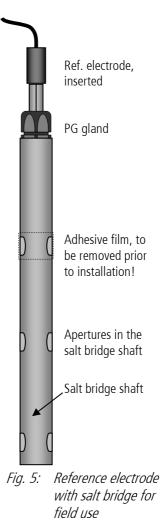
Fig. 4: Ag/AgCl reference electrode; here without salt bridge which is necessary for field investigations (see chapter 3.2)

3.2 Reference electrodes for field investigations, Art. No. 4621

With direct soil contact, the liquid KCl can issue continuously from the diaphragm into the soil and would be wasted rapidly while permanent installation of the electrode. Hence, the electrical life of the reference electrode would be reduced considerably. To avoid this, diffusion of the liquid KCl is reduced rapidly by imbedding the reference electrode into a salt bridge. The salt bridge basically consists of KCl, which is consolidated by adding agar-agar. By this means, an effective diffusion barrier is built fort the KCl electrolyte of the reference electrode. The electrical contact can be maintained while the diffusion of KCl solution out off the diaphragm is retarded.

Apertures in the shaft of the salt bridge establish the electrical contact with the soil matrix.

While the summer months and drying out topsoil a volume reduction of the agar gel volume can take place, leading to a loss of contact of the agar gel to the soil matrix and unreliable measurements. To guarantee the electrical contact of the reference electrode to redox electrode in the subsoil, the length of the salt bridge should be sufficient to reach into soil regions which stay moist for the whole year.



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3.2.1 Installation

Prior to installation, the adhesive films on the stem, which prevent the agar-gel from spilling during transport, have to be removed. The salt bridge has a diameter of 25 mm and is installed permanently in the soil, by using a drill (e.g. a 4 cm diameter Edelman-corer) and by silting up. To secure proper contact between the salt bridge and the soil, do the following: transform the cuttings into a slurry by using a stirrer and then put it back into the bore hole, so the salt bridge will be completely enclosed.

At the top of the salt bridge there is a PG gland, which is closed by a rubber plug on delivery condition. Before the beginning of measurements open the screw cap of the gland, remove the plug and push the shaft of the reference electrode through the opening of the gland into the salt bridge shaft. The electrode has to be placed several centimetres deep into the agar gel and then the screw cap of the PG gland has to be closed until the sealing of the gland is enclosing the electrode shaft water tightly. The reference electrode is now connected to the soil solution by the ceramic diaphragm and the agar gel of the salt bridge.

3.3 Reference electrodes for laboratory investigations, Art. No. 4622

Reference electrodes for laboratory investigations (right Fig.) are built basically identically as

reference electrodes for field use (see previous chap.). The reference electrode is imbedded in a salt bridge too, but the component parts were minimized considerably. The laboratorysalt bridge has got an outer diameter of 12 mm and is screwed together with the shaft's end of the reference electrode. Inside of the salt bridge there is a small reference electrode, constructed like described in Chap. 3.2, but reduced to diameter of 6 mm.



Fig. 6: Reference electrode with salt bridge for laboratory use

3.3.1 Installation

Prior to installation, the adhesive films on the stem, which prevent the agar-gel from spilling during transport, have to be

removed. To secure proper contact between the salt bridge and the soil, do the following: transform the cuttings into a slurry by using a stirrer and then put it back into the bore hole, so the salt bridge will be completely enclosed. Possibly, the predominantly horizontal installation in

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laboratory lysimeters or laboratory soil columns the installation can be done while the filling procedure of the column.

3.4 Reading adjustment

In the electrochemical series the redox potentials are related to the normal hydrogen electrode. This system was defined to have the redox potential $E_0 = 0$ V. When using a Ag/AgCl reference electrode instead of the difficult-to-use hydrogen electrode a temperature-influenced voltage difference to the standard hydrogen electrode is measured. To convert from readings measured with a redox electrode and Ag/AgCl reference electrode to standardized readings of a hydrogen electrode (E_0), a correction value has to be added to the readings. These correction values are influenced by the temperature as well as by the concentration of the KCl electrolyte. In the following table there literature values of these correction values are listed. The concentrations given in mol/L are related to 25° C.

Temp. (°C)	C (KCI)		
	1 mol L ⁻¹	3 mol L ⁻¹	Saturated
0	249,3	224,2	220,5
5	246,9	220,9	216,1
10	244,4	217,4	211,5
15	241,8	214,0	206,8
20	239,6	210,5	201,9
25	236,3	207,0	197,0
30	233,4	203,4	191,9
35	230,4	199,8	186,7
40	227,3	196,1	181,4
45	224,1	192,3	176,1
50	220,8	188,4	170,7

Tab. 1: Potentials of Ag/AgCl reference electrodes with three electrolyte concentrations in relation to the standard hydrogen electrode; as affected by temperature and electrolyte concentration

The given mV values have to be added to the measured reading, depending on the measured temperature and the used KCl concentration. To take account for the temperature dependency of the voltage readings Fiedler (1997) used two different correction factors for summer and winter with automatic temperature compensation. In many cases the reading adjustment is simply done





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by adding a value of 207 mV (0,207 V) to get readings of the standard hydrogen electrode. Considering the natural variations of redox potential readings in soil, the achievable accuracy in many cases can be smaller than the temperature-depending alteration of the correction factor. To be able to decide in a given case if a temperature compensation of the correction factor is necessary, soil temperature measurements are recommended.

4 Measurements

4.1 Measuring systems for automatic readings

4.1.1 Essential equipment

Generally, the redox electrode represents the plus-pole and the reference electrode the minuspole of the circuit. To be able to measure the potential difference between a redox electrode and a reference electrode, they have to be connected via an ion conductor (electrolyte) and an electrical conductor with a suitable measuring device, i.e. a volt meter with high input resistance.

ecoTech redox electrodes were designed for continuous operation in soils, thus automatic data acquisition with data logger is possible. To measure redox potentials automatically with data loggers, some special conditions are required. First, to measure with several electrodes simultaneously, the related measuring channels have to be electronically separated from each other, to avoid a mutual interference. Second, the input resistance of the electronic equipment has to be extremely high (Rabenhorst 2009). And finally, the sensors have to be disconnected effectively from the electronic by relays to avoid any electro-chemical processes between two measurements. For this reason we developed a special connection module for the automatic measurement of redox sensors in continuous operation which fulfills all these requirements and which communicates with our datalogger "enviLog" via the SDI12 protocol.



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4.1.2 Operation



Fig. 7: Connection module for up to 7 redox- and pH electrodes (Art. No. 4611)

The connection module 4611 offers three different operation modes. In the most simple case it is possible to connect up to 7 redox-(and pH-)electrodes (as plus poles) at the same time, together with one single common reference electrode (as minus pole). For this setup all electrodes have to be installed together at the same field site or in the same container (e.g. Lysimeter) and hence be in electrical contact. In this electronic setup 7 readings are processed.

The redox- and pH electrodes, as well as the reference electrodes are equipped with coax cables. Coax cables consist of an inner conductor and a shield, which is a cable mesh around the inner conductor. The inner conductor delivers the reading and is connected directly to the electrode, the mesh around the inner conductor protects the signal against electro-magnetic interferences. Both, the inner conductor as well as the shield, are equipped with end splices and can be connected directly to the connection module 4611. For this purpose, the end splices are pushed into the green terminal block (Fig. 8) and fixed by tightening the particular screw hand-tight with a screwdriver. Inner conductor- and shield-cable are arranged alternating.



Fig. 8: Terminal block of the connection module 4611 for redox- and pH electrodes

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If up to 7 redox- and pH electrodes are connected to the connection module 4611 in operation with a single common reference electrode (mode 7-1), the terminal block of the connection modules is assigned as follows:

Tab. 2:	Configuration of the terminal block of connection module 4611 in mode 7-1 (7 measuring
	electrodes with 1 reference electrode):

1	Redox/pH 1 Signal
2	Redox/pH 1 GND (shield)
3	Redox/pH 2 Signal
4	Redox/pH 2 GND (shield)
5	Redox/pH 3 Signal
6	Redox/pH 3 GND (shield)
7	Redox/pH 4 Signal
8	Redox/pH 4 GND (shield)
9	Redox/pH 5 Signal
10	Redox/pH 5 GND (shield)
11	Redox/pH 6 Signal
12	Redox/pH 6 GND (shield)
13	Redox/pH 7 Signal
14	Redox/pH 7 GND (shield)
15	Reference Signal
16	Reference GND (shield)

If the operation of redox- or pH electrodes in two separated containers (e.g. Lysimeters) is necessary, the connection module 4611 can be reprogrammed and measure the values of two different measuring circuits. For this purpose, a second reference electrode per module is required, and it is possible to connect up to three redox- and pH electrodes per circuit. Hence, up to 6 values are read out per module. The configuration is given in Tab. 3:

 Tab. 3: Configuration of the terminal block of connection module 4611 in mode 6-2 (2 times 3 measuring electrodes with 2 reference electrodes in two measuring circuits A and B):

1	Redox/pH 1A Signal
2	Redox/pH 1A GND (shield)
3	Redox/pH 2A Signal
4	Redox/pH 2A GND (shield)
5	Redox/pH 3A Signal
6	Redox/pH 3A GND (shield)
7	Reference A Signal
8	Reference A GND (shield)
9	Redox/pH 1B Signal
10	Redox/pH 1B GND (shield)

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11	Redox/pH 2B Signal
12	Redox/pH 2B GND (shield)
13	Redox/pH 3B Signal
14	Redox/pH 3B GND (shield)
15	Reference B Signal
16	Reference B GND (shield)

A third opportunity is to programme each module in a way that it can read out up to 4 measuring electrodes in 4 separated containers (e.g. Lysimeter). In this case, for each measuring electrode one single reference electrode is required. Hence, up to 4 values are read out per module. The configuration is given in Tab. 4:

Tab. 4: Configuration of the terminal block of connection module 4611 in mode 4-4 (4 single measuring electrodes with 4 reference electrodes in 4 measuring circuits A, B, C, and D):

1	Redox/pH A Signal
2	Redox/pH A GND (shield)
3	Reference A Signal
4	Reference A GND (shield)
5	Redox/pH B Signal
6	Redox/pH B GND (shield)
7	Reference B Signal
8	Reference B GND (shield)
9	Redox/pH C Signal
10	Redox/pH C GND (shield)
11	Reference C Signal
12	Reference C GND (shield)
13	Redox/pH D Signal
14	Redox/pH D GND (shield)
15	Reference D Signal
16	Reference D GND (shield)

Connection of more than 7 redox- and/or pH electrodes

If more than 7 redox- or pH electrodes have to be connected, several connection modules 4611 are required. In these cases it is not a requirement to have an own reference electrode for each connection module. All modules may be connected with a single, common reference electrode. For this purpose, the connection modules are linked with bridges between the ports no. 15 and 16 like shown in Fig. 9:

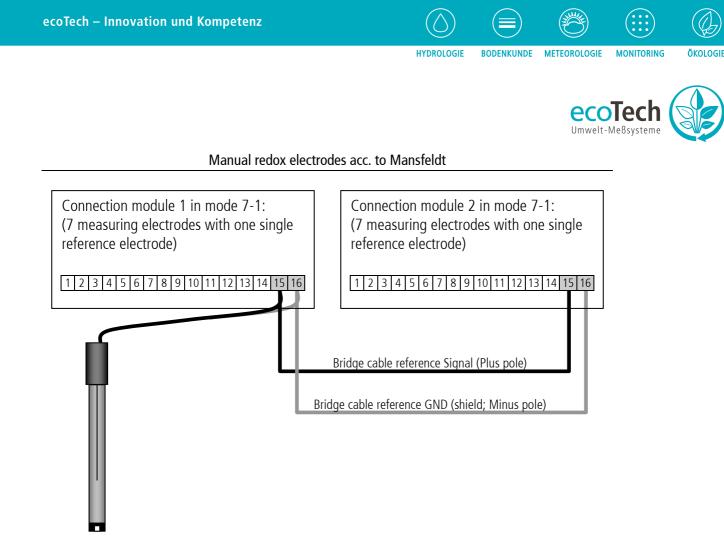


Fig. 9: Operation of more than 7 measuring electrodes with one common reference; bridge connection between ports 15 and 16 of two connection modules 4611

If more than 14 (2 x 7) measuring electrodes have to be connected with one common reference electrode, the bridge connection can be extended to further connection module in the manner shown in Fig. 9., and so on.

Ground

The redox connection module 4611 has to be grounded by means of the green-yellow cable (Fig. 7, p. 9) to ensure that the measured potential is lying in the allowed range of electrical input voltage. For this purpose with each connection module a piece of copper tube is delivered, which has to be installed in the soil. If several connection modules are used on one field site, it is enough to lay all green-yellow cables on one single ground rod.



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4.1.3 SDI-12 commands

The redox connection module is compliant to the common SDI-12 specifications version 1.3, dated January 2013. In the following, the **SDI-commands** (bold printed) are shortly explained.

Identification with any adress: **?!!** -> 011GEOPREC_REDOX_30_FFFFFF<<CR><LF> Sensor answers with adress '0'

Adress change '0' to '1': **0A1!** -> 0<CR><LF>

Identification of sensor '1': **11!** -> 111GEOPREC_REDOX_30_FFFFFF<CR><LF>

Adress change back '1' to '0': **1A0!** -> 1<CR><LF>

The operation modes (see ch. 4.1.2) have to be scanned as follows:

```
Command 'M': Inputs 1-7 are measured in relation to 8:

OM! (bzw. OMO!)

-> 00057<CR><LF>

-> 0<CR><LF>

ODO!

->0+278.8+279.6+278.6+278.9<CR><LF>

OD1!

->0+279.5+279.2+279.0<CR><LF>
```

Command 'M1': Inputs 1-3 are measured in relation to 4 and inputs 5-6 are measured in relation to 8:

```
OM1!
-> 00056<CR><LF>
-> 0<CR><LF>
OD0!
-> 0-0.1+0.6-0.3+279.5<CR><LF>
OD1!
->0+279.3+279.0<CR><LF>
```

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Command 'M2': Input 1 is measured in relation to 2, input 3 is measured in relation to 4, input 5 is measured in relation to 6 und input 7 is measured in relation to 8: **OM2!**

-> 00054<CR><LF> -> 0<CR><LF> **0D0!** -> 0-0.7-0.3+0.2+278.9<CR><LF>

When the optional temperature sensor is used, the following commands are valid:

Command 'M3': Inputs 1-7 (measured in relation to 8) and the temperature as last value:

OM3! -> 00058<CR><LF> -> 0<CR><LF> **OD0!** ->0+278.8+279.6+278.6+278.9<CR><LF> **OD1!** ->0+279.5+279.2+279.0+19.8<CR><LF>

Command 'M4': Inputs1-3 (measured in relation to 4), inputs 5-6 (measured in relation to 8) and the temperature as last value:

0M4!

-> 00057<CR><LF> -> 0<CR><LF> **0D0!** -> 0-0.1+0.6-0.3+279.5<CR><LF> **0D1!** ->0+279.3+279.0+19.7<CR><LF>

Command 'M5': Input 1 (measured in relation to 2), input 3 (measured in relation to 4), input 5 (measured in relation to 6), input 7 (measured in relation to 8) and the temperature as last value: **OM5!**

```
-> 00055<CR><LF>
-> 0<CR><LF>
OD0!
-> 0-0.7-0.3+0.2+278.9<CR><LF>
OD1!
->0+19.8<CR><LF>
```





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Command 'M6': Here only the temperature of the digital sensor is measured. **OM6!** -> 00031 < CR > < LF > -> 0 < CR > < LF > **OD0!** -> 0+20.1 < CR > < LF >

The measuring range of the temperature sensor is -55.0 °C up to + 85.0 °C. In case the sensor is not well-connected or not working properly, the error code -99.9 is displayed.

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4.1.3 Applications

When several redox connection modules are used, measurements of up to 48 redox electrodes with one single data logger are possible. Within a field site equipped in January 2005, 18 redox electrodes in different depths are being in continuous operation with one single, common reference electrode. The distances between electrodes in this experimental setup are several meters, which does not affect the accuracy of the readings as long as the electrical contact between the electrodes is established by the soil water. An adequate experimental setup is shown in Fig. 10:



Fig. 10: Field station for the investigation of As concentration in the soil water as affected by redox potential, pressure head and soil temperature; measurement and automatic data acquisition with 18 redox electrodes, tensiometers, temperature sensors and soil water extraction by suction cups in 6 soil depths

The shown measuring station transmits the readings automatically to a data server, and only the newest readings are transmitted (incremental). The system is able to send the newest readings to your PC as eMail attachment. For more details see the "enviWatch" system in the appendix.

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In contrast to the station described above with one single reference electrode for 18 redox electrodes, each container in laboratory setups has to be equipped with a single reference electrode (Fig. 11).



Fig. 11: Laboratory setup fort he measurement of redox processes in the soil water as affected by the redox potential, pressure head, and soil temperature

For laboratory setups with several containers, the connection module 4611 can be reprogrammed to operate with several reference electrodes in up to 4 different containers (see ch. 4.1.1). The configuration of the module under delivery conditions is described in your documents.

4.2 Measuring systems for mobile readings

In some cases the automatic measurement of redox potentials is not useful or not possible for cost reasons. If many field sites are necessary with only poor amounts of electrodes and with high distances between them, it may be not possible to equip all these sites with data logger and accessories. Moreover, it may be useful to measure redox potentials with a handheld temporarily with some permanently installed redox electrodes to estimate the benefit of those readings for a special interrogation. A subsequent connection of those sensors to an automatic measuring system is possible.



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4.2.1 Essential equipment

If automatic measurements of soil redox potentials with a data logger and accessories are ineligible, readings can be done mobile with a handheld. The redox electrodes can be read out with high-valued voltmeters (e.g. for pH readings). Fig. 12 shows the essential equipment for the mobile operation:



Fig. 12: Equipment for mobile measurements of the redox potential: Handheld for redox, pH and temperature (Art. No. 4612) as well as an adapter with connectors for the cable ends of the electrodes (Art. No. 4613)

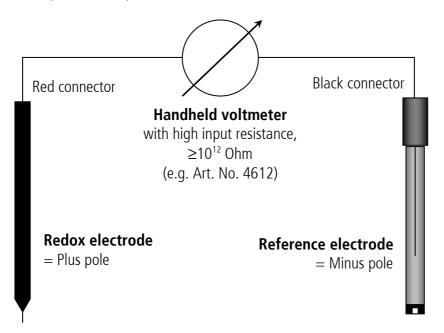


Fig. 13: Measuring setup for mobile operation





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For precise mobile readings please note the following:

- 1. At each site a reference electrode is required.
- 2. Quick measurements with recently installed electrodes only can provide indication values. Nevertheless, a tendency may already be recognized.
- 3. Redox electrodes should remain at the same place for a longer period, and be read out from time to time. With installation of an electrode, the soil system is disturbed, e.g. oxygen is transported to the measuring point. Hence, the medium is affected by the measurement itself, and a reliable measuring value is reached after a waiting period of hours or days.
- A subsequent connection of single sensors to an automatic measuring system is possible. For this purpose the cables of redox- and reference electrodes can be directly connected to the terminal block of the connection module.

4.2.2 Operation

Cable ends should be protected against the weather by placing them in a weather-proof box. Just like redox electrodes, salt bridges for reference electrode should remain in the field for a longer time. Only the reference electrode (Fig. 3 &4) can be removed from the salt bridge after reading out the values. This procedure can be useful when the measurements are made on different sites one after another. To save costs, it is possible to install salt bridges on every site but use only one single, mobile reference electrode for all of them. **Attention**: After removing the reference electrode from the PG gland of the salt bridge (Fig. 5, p. 5), the opening has to be closed water-tightly by a silicone or rubber stopper!

For the measurement the reference electrode is put into the salt bridge shaft. Afterwards, the cable ends of the redox electrode (Plus) and the reference electrode (Minus) are connected to the handheld, and the soil redox potential is displayed. For measurements of redox potentials at one site, one single salt bridge which reaches down to more or less to the depth of the deepest redox electrode is enough. All redox electrodes at this site are connected with the single reference electrode as minus pole one after another.

Range

In waterlogged soils with high amounts of available organic carbon, negative readings of several hundreds of millivolts can occur. After dehydration and ventilation, the values may rise rapidly. Readings of + 500 mV and more show that the soil has been dehydrated to an extent that a



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continuous connection of the redox and the reference electrodes via the soil water may not be guaranteed any more. Values then are subject to heavy fluctuation and need to be verified.

Caution: Only use voltmeters with high electrical entry impedance! Voltmeters suitable for pHmeasurements can be used for measuring the redox potential, but not common voltmeters for standard electrical purposes. This applies, even if the correct value of 220 mV is displayed in the instrument, while measuring in a redox buffer solution, as the offset won't be apparent, until significantly higher or lower levels. The same applies while using redox electrodes in combination with data-loggers.

5 Check-up and maintenance

It is possible to verify the system by immersing the reference and the redox electrode into a standard buffer-solution (e.g. 220 mV) and check the measured value. According to the temperature, differences of a few millivolts are possible. If considerable differences appear, the electrolyte concentration inside the reference-electrode might be the cause. The electrolyte can be exchanged easily (see below)

5.1 Maintenance of the redox electrodes

The redox electrodes are maintenance-free and can stay installed permanently.

5.2 Maintenance of the reference electrodes

5.2.1 Exchange of KCl solution

Principally, the liquid KCl electrolyte inside of reference electrodes should be exchanged after use or storage of 1 year. In a study of Fiedler (1997) the electrolyte solution was even changed all 2 months. At the **field issue of the reference electrode** (Art. No. 4621), the screw cap of the PG gland has to be unscrewed first (s. Fig. 5). Then the reference electrode is pulled out off the PG gland and cleaned. Afterwards, the transparent shaft is screwed off, the complete content is emptied and replaced by new electrolyte (3 M KCl).

The procedure at the **laboratory issue of the reference electrode** (Art. No. 4621) is similar: First, the 12 mm thick outer tube, which is the shell of the salt bridge, has to be screwed off counter-clockwise (s. Fig. 6, S. 6). The 6 mm thick inner tube has to be cleaned from agar and

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afterwards is carefully screwed off counter-clockwise, too. As above, the content is emptied and replaced by new electrolyte (3 M KCl).

As long as a reference electrode is not used, the covering cap has to be pushed onto the tip to avoid dehydration of the ceramic diaphragm.

5.2.2 Exchange of KCl gel

The agar gel of the salt bridge has to be exchanged from time to time (depending on soil conditions), as the concentration of the contained KCl is decreasing with time. Even due to dehydration and elution the amount of gel in the salt bridge shaft may decrease, so the gel has to be refilled or exchanged completely.

For this purpose the salt bridge has to be de-installed by pulling it carefully out off the soil. By moistening the soil around the shaft, friction can be decreased considerably. At the field issue of the salt bridge the cap has to be unscrewed (Fig. 5, S. 5) and the reference electrode is taken off. At the laboratory issue, the transparent outer shaft (D = 12 mm) has to be unscrewed counter-clockwise and pulled off the imbedded reference electrode.

Both salt bridges can be cleaned mechanically and washed with warm water. The gel can be refilled mechanically in small quantities on the one hand. On the other hand, liquid agar solution with 3 M KCl can be refilled carefully into the transparent tube. Please note that a) the apertures of the shaft have to be closed by adhesive films before refilling (s. Fig. 5 and 6) and b) the temperature of the liquid agar must not be too high (risk of deformation of the PVC tube). If after all maintenance procedures the correct measuring value of a buffer solution is not displayed (s. above), an exchange of the reference electrode is recommended.

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6 Technical data

Redox electrode (Art. No. 461)

- Signal mV
- Platinum element 99,95 % Pt, hard drawn out
- D = 1 mm, L = 5 mm from shaft tip
- Shaft carbon fibre, D = 6 mm
- Shaft length from 5 up to 100 cm with continuous C-fibre tube
- Extension with socket up to 200 cm possible
- 2 m cable
- S7 laboratory plug on demand
- Reference electrode Ag/AgCl (with salt bridge)
- Measurement only with high input resistance
- Validation with commercially available redox buffer solutions

Reference electrode field/laboratory (Art. No. 4621/4622)

- Ag/AgCl with salt bridge
- Ceramic diaphragm
- PVC shaft
- 2 m cable
- S7 laboratory plug on demand
- Diameter 12 mm
- Shaft length 120 mm

Redox connection module (Art. No. 4611)

- Input resistance: >1 Tera-Ohm (T Ω) = 1.000 Giga-Ohm
- Range: +/- 1250 mV
- Resolution: 0,1 mV
- Accuracy: typically 3 mV
- Damping period after power-up: 2 sec. (or more)
- Power consumption: ca. 120 mA (redox)
- Waiting period: ca. 3-4 sec.
- Accuracy of the optional digital temperature sensor in the range of -10 to 40°C: typically 0.5 °C
- Resolution of the optional digital temperature sensor: 0.1 °C
- Galvanic isolation of circuits (analog and SDI12): up to 500 V
- Isolation resistance typically > 1 Giga-Ohm

DROLOGIE BODENKUNDE METI

METEOROLOGIE MONITORING





Manual redox electrodes acc. to Mansfeldt

7 Literature

- Dorau, K. & T. Mansfeldt (2016): Comparison of redox potential dynamics in a diked marsh soil: 1990 to 1993 versus 2011 to 2014; J. Plant Nutr. Soil Sci., 179, 641-651.
- Fiedler, S. (1997): In-situ-Langzeitmessungen des Redoxpotentials in hydromorphen Böden einer Endmoränenlandschaft im württembergischen Alpenvorland; Hohenheimer Bodenkundliche Hefte, Bd. 42.
- Mansfeldt, T. (2003): In situ long-term redox potential measurements in a dyked marsh soil; J. Plant Nutr. Soil Sci., 166, 210-219.
- Mansfeldt, T. (2004): redox potential of bulk soil and soil solution concentration of nitrate, manganese, iron, and sulfate in two Gleysols; J. Plant Nutr. Soil Sci., 167, 7-16.
- Rabenhorst, M. C., W. D. Hively & B. R. James (2009): Measurements of Soil redox Potential; Soil Sci. Soc. Am. J., 73, 668-674.
- Weigand H., T. Mansfeldt, S. Wessel-Bothe & C. Marb (2005): Bulk soil redox potential and arsenic speciation in the pore water of fen soils; in W. Skierucha & R.T Walcak (eds.):
 Monitoring and modelling the properties of soil as a porous medium: the role of soil use; International conference, Lublin; 44-46.
- Weigand H., T. Mansfeldt, R. Baeumler, D. Schneckenburger, S. Wessel-Bothe & C. Marb (2010): Arsenic release and speciation in a degraded fen as affected by soil redox potential at varied moisture regime; Geoderma, 159, 371–378.

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