paleo terra

Measuring redox potential with a Campbell Scientific CR800 / CR1000

The Campbell Scientific (CS) CR800 and CR1000 datalogger are essentially the same dataloggers with similar specifications. The CR1000 is best known and has 8 differential (DIFF) analog inputs or 16 single ended (SE) analog inputs. The CR800 has less analog inputs: 3 DIFF or 6 SE. Throughout this text, only the CR1000 is referred to, but if the number of analog inputs allow, a CR800 is usually suitable as well. If a CR800 is combined with an AM16/32B multiplexer, up to 64 redox electrodes can be measured against one or two reference electrodes.

1   Input resistance

Measuring soil redox potential means measuring a potential difference between a reference electrode and a redox (usually platinum) electrode whilst 'using' as little electrons from the soil chemical system as possible. If too much current would flow due to the redox measurement itself, the redox potential would change invalidating the reading. A comparable effect can be observed when trying to start an automobile with the lights on. When the starter motor is actuated, the lights become dimmer as the terminal voltage of the battery drops.

The ISO standard 11271:2002 'Soil quality - Determination of redox potential - Field method' states that one needs a millivoltmeter with an input resistance not less than 10 GΩ . Assuming a maximum potential difference between the reference electrode and a redox electrode of 600 mV, 10 GΩ input resistance translates into 60 picoampère (pA) of current. For well redox-buffered soils, this amount of current may be easy to deliver without significantly affecting the redox potential. However, for soils with low redox buffering capacity, tens of pA may be too high.

Campbell Scientific specifies the CR1000 analog input resistance at 20 GΩ typical, so the CR1000 nicely complies with the ISO standard. However, compared to the >1 TΩ claimed input resistance of the redox specialized Hypnos datalogger, 20 GΩ seems meager. 1 TΩ input resistance translates into 0.6 pA for a reference-redox potential difference of 600 mV. When working with such low currents, 'leakages' through other pathways than the datalogger input resistance become relevant as well. These are the four main causes of 'leakage' current when working at a pA level:

- datalogger input resistance
- insufficient wiring insulation
- input capacitance (if multiplexing)
- 'ground loop' effects

To start with ground loops, these may contribute μA's of current, which would definitely affect the redox potential itself. Section 3 gives hints how to avoid them. Input capacitance is only relevant when multiplexing several redox signals to one datalogger input. More about this subject in section 4.

Wiring needs attention because general purpose PVC insulated multicore wiring has relatively low insulation resistance. A length of five meter has about 5 GΩ resistance to its surroundings. If two wires carrying different redox potentials run alongside each other, the resistance between both signals is about 10 GΩ , only half of the CR1000 analog input resistance. Single core thick sheathed PVC wiring of the same length has at least 60 GΩ insulation resistance, so these wires combine well with the CR1000 input specifications. Polyethylene (PE) or polypropylene (PP) wire insulation performs much better than PVC. A wire length of five meter has an insulation resistance over 1 TΩ . PE insulation is usually found around the inner core in coax cables and in specialized multicore cabling.

Datalogger input resistance is a complex subject. It is basically determined by the input bias current of the first op-amp of the electronic circuit that buffers the redox potential signal. Op-amps with an input bias current of 1 pA typical are generally available. This suggests a datalogger input resistance of 1 TΩ should be generally available. Some reasons why this is not the case are: 1) leakage currents of the redox signal at connectors and on the datalogger circuit board; 2) op-amp inputs are very sensitive to electrostatic discharges and the components that protect the inputs suffer from leakage currents; and 3) ultra high datalogger input resistance is only effective if the complete

path along which the redox signal travels is of equally high resistance, which is difficult to achieve in daily practice. Using Campbell Scientific equipment it is possible to achieve a higher 'time-average' input resistance . An AM16/32B multiplexer can disconnect the redox sensors from the datalogger whilst the datalogger is not measuring, usually by far most of the time.

2   Reference electrode

A reference electrode is necessary to supply a fixed chemical potential to the datalogger. Redox potentials are measured against this stable potential. Usually, a general purpose Ag|AgCl reference electrode can be used in soils. Specialized soil reference electrodes exist, e.g. the Silvion WE200. Ag|AgCl means that the reference potential of the electrode is determined by a silver/silverchloride system. It is essential that the silver and chloride ion concentrations around this system are stable. Therefore, the reference electrode contains an electrolyte, usually KCl saturated with AgCl. Several KCl concentrations are in common use, most notably 3M, 3.5M and saturated. Reference electrodes are traditionally made as a glass tube, but epoxy bodied references become common, reducing the risk of breaking the electrode in the soil.

The reference electrode internal electrolyte must be separated from the soil solution to maintain its stable composition. At the same time, ions must be able to travell in and out of the reference electrode to maintain electroneutrality inside the electrode while the Ag|AgCl system maintains the stable potential. The compromise is usually a 'frit', a porous material like a ceramic or teflon with micropores, placed between the internal electrolyte and the outside world. Still, the frit not only opens up a path for K and Cl ions out of the electrode, but also for foreign soil solution ions into the electrode. It is therefore very likely the internal electrolyte composition changes over time, affecting the potential of the electrode. Gel filled electrodes and double junction electrodes often perform better. Either the gel or double junction slows down the ingress of foreign ions into the reference system. The advantage of a longer service time however comes at a cost: these reference electrodes are more expensive and can generally not be refilled. The internal electrolyte of regular reference electrodes can be refreshed, extending their overall lifetime.

Ag|AgCl reference electrode potentials vary with the electrolyte KCl concentration, and with temperature. The following table gives some theoretical Ag|AgCl reference electrode potentials in mV versus the standard hydrogen electrode, derived from Langmuir(1971) and Bates(1973).

Temperature (°C)	3M KCl	3.5M KCl	sat'd KCl
40	198	193	184
35	202	197	189
30	205	201	194
25	209	205	199
20	213	208	204
15	216	212	209
10	220	215	213
5	222		
0	225		

When using reference electrodes in soils, expect deviations up to +/- 20mV from the theoretical reference potential over periods of weeks to months. This should usually not be a problem for soil redox measurements. Still, it may not be a good idea to depend on the potential of only one reference electrode ('primary reference electrode') in an experiment. At the very least, the potential of the reference electrode should be tested at the start and end of an experiment against a second reference electrode exclusively kept for this purpose ('master reference electrode'). Do not use the master reference in the soil, instead measure the reference electrodes against each other in clean water, of even better in a 3M KCl solution. During an experiment, monthly testing of the primary reference electrode may be appropriate.

If budget allows for a third reference electrode, it may be informative to install an extra reference electrode ('secondary reference electrode') in the soil and connect this electrode as if it were a redox electrode. Ideally, the potential of the secondary reference reads 0 mV versus the primary reference if both are of the same chemistry. The secondary reference not only acts as a check for the primary reference, it can also be used as a back-up in case the primary reference fails. Failure of the primary reference should be noted when compared to the master reference. Using the secondary reference to correct the redox potentials involves some extra calculations after the experiment, but these are not complicated: the key is to use the potential difference between the primary and secondary reference to calculate ('correct') the primary reference potential. Redox electrode potentials can then be calculated with the corrected primary reference potential. It is of course advisable to also check the secondary reference against the master reference before deciding to use the secondary reference in the redox potential calculations.

In some cases, it may be necessary or advisable to use more than one primary reference electrode per datalogger for (groups of) redox electrodes, e.g. if different experiments in isolated containers are connected to the same datalogger. This is only possible if measuring DIFF channels.

3   Datalogger wiring

Redox potential measurements are differential mV measurements between the redox sensing platinum and a reference electrode. One reference electrode can be used as a reference for many Pt electrodes. At a CR1000, the reference electrode is connected to the LOW input of all DIFF channels used for redox measurements. If more than one reference electrode is used, each reference electrode is connected to the LOW inputs of the DIFF channels it serves. The Pt electrodes are then connected to the HIGH inputs, one Pt electrode per HIGH input.

Alternatively, if no other sensors are connected to the datalogger, the reference electrode may be connected to signal ground. Then all Single Ended (SE) inputs, twice the number of DIFF inputs, are available to measure redox potential. In electro-magnetic noisy environments, this configuration is not recommended. Differential measurements feature better noise rejection.

Redox potential measurements require the potential difference between redox and reference electrode to be measured with very high input resistance. One of the consequences is that even the smallest current leak may influence the measurements. A common cause for current leaks are ground connections via e.g. power mains connections, the datalogger housing or other connected sensors. The following recommendations help prevent (small) current leaks.

- Run the datalogger off batteries, without any (charger) connection to mains power.

- Do only connect the datalogger to another device (e.g. a modem) if the device is not connected to mains power. It is safe to connect to a modem running off the same batteries as the datalogger, or a laptop that is running off its internal batteries.

- Isolate the datalogger and all connected devices from the earth. This is contrary to CS recommendations. CS advises the datalogger to be grounded to earth for maximum input protection. However, to properly measure redox potential a decrease in input protection cannot be avoided. To isolate the datalogger from the earth it is best placed inside a plastic enclosure. The plastic enclosure itself may be inside a metal enclosure if convenient. Note that not grounding the datalogger to earth reduces the safety of the system, e.g. in case of lightning. Take extra care if a thunderstorm is nearby. Do not get near the datalogger system: sensor wiring may conduct a lightning strike into the datalogger system.

- Only connect other sensors to the datalogger if these have no connection to earth ground. A safe sensor is e.g. a temperature sensor fully encapsulated in plastic. A submerged conductivity sensor is obviously connected to earth.

4   Multiplexing with an AM16/32B

Using an AM16/32B multiplexer connected to a CR1000 datalogger allows to expand the number of redox channels to 64 (sic!) if no more than four 'primary reference electrodes' are needed (see section 2 for an explanation of 'primary reference electrode'). If more than four reference electrodes are used, then a maximum of 32 redox electrodes can be connected using one AM16/32B.

Apart from expanding the number of redox channels, a multiplexer also reduces the time-average input resistance of the datalogger. Sensors are fully disconnected when the multiplexer is not active. There is however a disadvantage using a multiplexer. As different redox channels are switched to the same datalogger input, a previous redox signal will influence the next redox signal switched to the datalogger input via the input capacitance. Some charge is always stored on a datalogger input, and some of this charge must be 'absorbed' by the next redox signal if it is at a different redox potential.

Four different redox AM16/32B multiplexing schemes are summarized in the following table (more complicated setups are imaginable if other sensors are also multiplexed on the same multiplexer):

Measurement type	No. of datalogger channels needed	Max. redox electrodes	Primary reference electrode configuration
SE	2	64	1 serving all redoxes
DIFF	2	64	2 serving max. 32 redoxes each
DIFF	4	64	4 serving max. 16 redoxes each
DIFF	1	32	up to 1 for each redox

In the following descriptions, wiring of the power supply, reset and clock lines is ignored. These are well described in the AM16/32B manual. The redox electrodes are always connected to the multiplexer as follows (use the the white markings, not the blue):

redox probe 1 - multiplexer input 1 H
redox probe 2 - multiplexer input 1 L
rx 3 - 2 H
rx 4 - 2 L
...
rx 64 - 32 L

Multiplexer to datalogger connections and reference electrode connections differ between multiplexing schemes.

4.1   Up to 64 SE redox electrodes

For SE measurements, the reference electrode is always connected to signal ground on the datalogger (so not via the multiplexer).

Multiplexer ODD H is connected to datalogger SE 1, and ODD L to SE 2:

ODD H - SE 1
ODD L - SE 2

The multiplexer is in 2x32 mode. The CR1000 program measures SE1 and SE2 between each multiplexer channel switching. All odd redoxes will be measured by datalogger channel SE1, the even redoxes by channel SE2. To minimize mutual effects of redox potentials through datalogger input capacitance, the redox probes can be grouped by expected redox potential. Expected low redox potentials on SE1 (so connected to multiplexer 1H, 2H, etc.), expected high redox potentials on SE2 (so connected to multiplexer 1L, 2L, etc.). If possible, also try to order the redox probes within a group, e.g. from lowest expected redox potential to highest.

It is possible to use 4x16 mode as well for multiplexed SE measurements. The datalogger measures SE1, SE2, SE3 and SE4 between each multiplexer channel switching. This would allow for faster measurement rounds. Also, the redoxes are separated in 4 groups, which could be advantageous with respect to minimizing mutual effects through datalogger input capacitance. Multiplexer to datalogger wiring is different:

ODD H - SE 1
ODD L - SE 2
EVEN H - SE 3
EVEN L - SE 4

The redoxes are now grouped differently: group A - rx 1, rx 5, rx 9, .. rx 61; group B - 2, 6, 10, .. 62; group C - 3, 7, 11, .., 63; group D - 4, 8, 12, .., 64.

4.2   Up to 64 DIFF redox electrodes with one or two primary reference electrodes

Multiplexer to datalogger:

ODD H - DIFF 1 H
ODD L - DIFF 2 H

Reference electrodes to datalogger (ref 2 may be the same physical electrode as ref 1 if only 1 reference is needed):

ref 1 - DIFF 1 L
ref 2 - DIFF 2 L

Multiplexer in 2x32 mode. Datalogger program measures DIFF 1 and DIFF 2 between each multiplexer switching. Odd redoxes form one group connected to DIFF 1, even redoxes the second group connected to DIFF 2.

4.3   Up to 64 DIFF redox electrodes with up to four primary reference electrodes

Multiplexer to datalogger:

ODD H - DIFF 1 H
ODD L - DIFF 2 H
EVEN H - DIFF 3 H
EVEN L - DIFF 4 H

Reference electrodes to datalogger (ref 2/3/4 may be the same physical electrode as ref 1/2/3 if only 1/2/3 references are needed):

ref 1 - DIFF 1 L
ref 2 - DIFF 2 L
ref 3 - DIFF 3 L
ref 4 - DIFF 4 L

Multiplexer in 4x16 mode. Datalogger program measures DIFF 1, DIFF 2, DIFF 3 and DIFF 4 between each multiplexer switching. Redoxes 1, 5, 9, .. 61 form group A connected to DIFF 1, redoxes 2, 6, .. 62 group B connected to DIFF 2, redoxes 3, 7, .. 63 group C connected to DIFF 3 and redoxes 4, 8, .. 64 group D connected to DIFF 4.

4.4   Up to 32 DIFF redox electrodes with free choice of reference electrode

Reference electrodes to multiplexer: choose for each redox electrode which reference electrode to use, and connect to the corresponding ..L input.

Multiplexer to datalogger (2x32 mode):

ODD H - DIFF 1 H
ODD L - DIFF 1 L

Datalogger program only measures DIFF 1, then switches multiplexer, etc. There are no separate redox groups, all redoxes are measured by the same datalogger input channel. The mutual input capacitance effect can only be minimized by trying to order the redox electrodes by expected potential.

Multiplexer to datalogger (4x16 mode):

ODD H - DIFF 1 H
ODD L - DIFF 1 L
EVEN H - DIFF 2 H
EVEN L - DIFF 2 L

Datalogger measures DIFF 1, DIFF 2, then switches multiplexer, etc. The odd redoxes form one group measured by DIFF 1, the even redoxes are measured by DIFF 2.

4.5   Final note on multiplexing

By grouping of the redox electrodes it is possible to reduce the 'datalogger input capacitance effect'. However, each redox electrode is biased differently, namely by the previously measured redox potential. It may be better experimental design to bias each redox electrode with the same potential, i.e. make sure the 'capacitance charge' on the datalogger input is always the same before connecting a redox electrode. This can be accomplished by switching a reference electrode to the datalogger input after each redox electrode. To do so, every second redox electrode within a group must be replaced by a reference electrode connection (which can be one and the same reference electrode wired to up to 32 multiplexer inputs). The maximum number of redox electrodes that can be connected to an AM16/32B multiplexer is indeed half as much as before.

When using the multiplexer in 2x32 mode, the (extra) reference electrode should be connected to 2H, 2L, 4H, 4L, .., 32H, 32L. When using the multiplexer in 4x16 mode, connect the reference to 3H, 3L, 4H, 4L (all blue 2), 7H, 7L, 8H, 8L (all blue 4), .., 31H, 31L, 32H, 32L (all blue 16).

The datalogger program should measure as before, but perhaps not store all values. It is very well possible to combine the functions of 'bias reference electrode' and 'secondary reference electrode' in the same physical reference electrode.

5   Shielding

Reodx potential measurements are mV measurements with very high input resistance. Therefore, they are susceptible to electro-magnetic interference (EMI). Whether this is an issue or not depends on where the measurement setup is situated. Inside a laboratory with many electric devices around, EMI must be considered. Out in the field far away from human activities, EMI is much less of a concern. Depending on requirements, redox probes may have a cable with copper braid shielding. If a braided shield is present it will only protect against EMI if the shield is connected to the datalogger power ground, or ground lug. Take care the cable is not damaged. Exposed shield may form an unintentional connection to earth.

6   Datalogger programming

If the reference and redox electrodes are connected to differential channels, the VoltDiff () instruction must be used to read the redox potential. If the reference electrode is connected to signal ground and the redox electrodes to single ended channels, VoltSE () is to be used.

If 4 redox electrodes are connected to single ended or differential channels 1 through 4, the following configuration of the VoltSe() or VoltDiff() instruction is suggested:

- 4 repetitions

- ±2500 mV Analog Voltage Input Range

- start each scan at input channel 1

- do NOT reverse polarity to enhance the measurements (for differential measurements): this would 'feed' the redox electrodes with the reference electrode potential; for single ended measurements, do not measure the offset voltage with each execution

- default settling time (3 milliseconds)

- filter for 50Hz or 60Hz noise depending on the local grid frequency

- do not scale the raw values: multiplier = 1 and offset = 0

A very basic example program is given below, following the suggested configuration, assuming the use of differential channels, and measuring and storing four redox potentials once per minute in a country with a 50Hz grid. If single ended channels are used, uncomment the VoltSE() instruction and comment the VoltDiff() instruction.

```
'CR1000 Series Datalogger

'Declare Public Variables
Public redox(4)

'Define Data Tables
DataTable (Redox,1,-1)                        'auto-allocate memory
    DataInterval (0,1,Min,10)                 'store one sample per 1 minute
    Sample (4,redox,FP2)                      'store 4 redox values as 2-byte CS floating points
EndTable

'Main Program
BeginProg
    Scan (1,Min,0,0)                          'run a scan once per 1 minute
        'VoltSe(redox,4,mV2500,1,0,0,_50Hz,1,0)
        VoltDiff(redox,4,mV2500,1,0,0,_50Hz,1,0)
        CallTable Redox
    NextScan
EndProg
```

7 Electrode installation

The redox electrodes are designed to be pushed directly into the soil. Pre-augering may be necessary, but is not recommended as the soil environment may be influenced by the access to free air. If pre-augering is necessary, best is to use a smaller diameter, so the redox probe will make good contact with the soil later on. Probes with a nylon top cap and cable from the side can be hammered into the soil, but this must be done with care. If too much force is exerted on the top of the probe, the probe may start splitting over the length.

Most reference electrodes are not designed to push into the soil directly, so it is usually necessary to remove some soil first. Although in principle no current flows during redox potential measurements, this is not completely true. A very small current (picoampères) will flow between the reference electrode and redox electrodes. Therefore, the resistance of the soil must be reasonably low, to prevent an ohmic error in the measurements. Typical CR1000 input resistance is 20 GΩ . Assuming a 1 V potential difference between reference and redox electrode, 50 pA will flow between the electrodes. If a 1 mV measurement error is acceptable, the soil resistance between both electrodes should remain below 20 MΩ . As long as the soil is not very dry and the distance between the electrodes is reasonable (not more than tens of meters) the soil resistance will be reasonably low. If the topsoil may dry out, it is sensible to bury the reference electrode to a level where the soil does not completely dry out. Another option is to hang the reference electrode into the groundwater in a dipwell. Apart from minimal soil resistance this may enhance the reference lifetime as the groundwater may be cleaner than the soil water.

8 Calculation of redox potential versus the Standard Hydrogen Electrode

The results stored in datalogger memory are mV differences between the reference electrode and platinum electrode(s). If the reference electrode is connected to the LOW inputs and the redox electrode to the HIGH inputs, a reading of +200 mV means the redox potential is at 200 mV above the reference electrode potential. (This is also true if the reference electrode is connected to signal ground and the redox electrode to a SE channel.) When using an Ag|AgCl 3M KCl reference electrode at 15°C, the reference electrode potential is +216 mV versus the Standard Hydrogen Electrode (SHE). If the datalogger reads a value of +200 mV, then the redox potential is at +216 + 200 = +416 mV versus the SHE.