# *Redox Potential Measurements*

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**Redox potential is an electrical measurement that shows the tendency of a soil solution to transfer electrons to or from a reference electrode. From this measurement we can estimate whether the soil is aerobic, anaerobic, and whether chemical compounds such as Fe oxides or nitrate have been chemically reduced or are present in their oxidized forms (Vepraskas and Faulkner, 2001).**

**Making these measurements requires three basic pieces of equipment:**

1. **Platinum electrode**
2. **Voltmeter**
3. **Reference electrode**

**The basic set-up is shown below:**

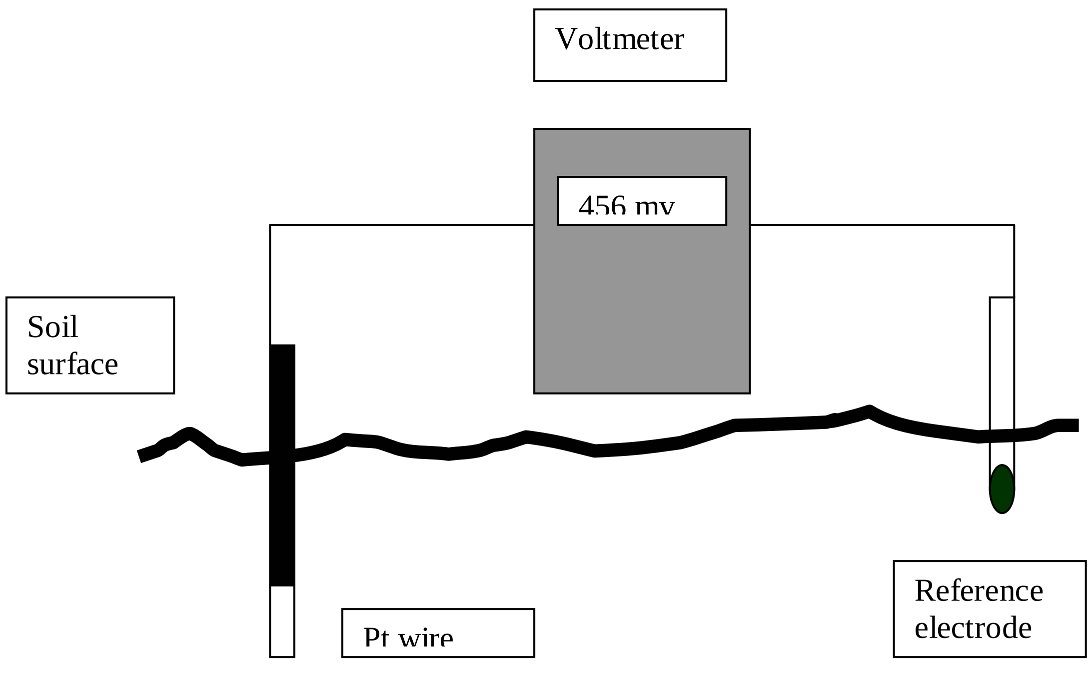



Fig. 1. The Pt wire is buried into the soil to be in contact with the soil solution. The reference electrode must also be in contact with the soil solution. It has a ceramic tip which can be placed in the soil, or the electrode can be placed in a salt bridge which is itself placed in the soil. Wires from both the Pt electrode and reference electrode are connected to the voltmeter.

## Pt Electrodes

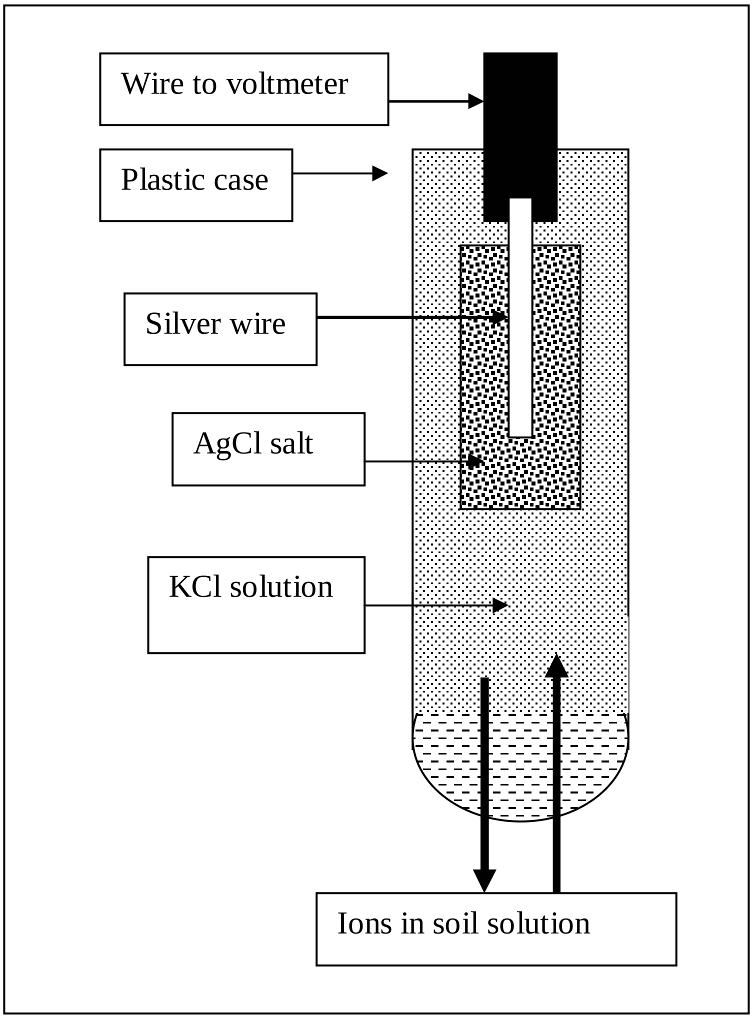
Platinum electrodes consist of a small piece of platinum wire that is soldered or fused to wire made another metal. Platinum conducts electrons from the soil solution to the wire to which it is attached.

Platinum is used because it is assumed to be an inert metal. This means it does not give up its own electrons (does not oxidize) to the wire or soil solution. Iron containing materials such as steel will oxidize themselves and send their own electrons to the voltmeter. As a result the voltage we measure will not result solely from electrons being transferred to or from the soil.

Metals such as copper and aluminum will oxidize and also cannot be used for redox potential measurements. Stainless steel also may oxidize, but to a small extent, and should not be used**.**

## Reference Electrodes

Reference electrodes provide a standard redox reaction that will accept or give up electrons to the soil solution. Two types of reference electrodes are in use: Ag/AgCl and Calomel.



The Ag/AgCl electrode consists of a Ag metal wire and a AgCl salt. The basic reaction is:

$Ag \rightarrow Ag^{+} + e^{-}$

When the reaction goes to the right (Ag is oxidized) the electron is sent to the voltmeter and could be transmitted to the Pt wire to reduce chemicals in the soil solution if the voltmeter were not present. If the reaction goes to the left then an electron comes from the voltmeter into the electrode.

The Ag and $Ag^{+}$ are surrounded by a solution of KCl which maintains electrical neutrality. When the reaction above goes to the right, then a $K^{+}$ is released to the soil through the ceramic tip of the electrode. When the reaction goes to the left then a $Cl^{-}$ anion is released through the ceramic tip.

Another type of reference electrode in common use is the calomel which contains Hg. The basic reaction is:

$Hg \rightarrow Hg^{+} + e^{-}$

This electrode works the same as the Ag/AgCl.

Correction Factors

While both kinds of reference electrodes give reliable data, the voltages measured with each electrode are interpreted slightly differently. It is for this reason that users must know which electrode they have.

The voltage measured in the field must be corrected to what would have been obtained with a different reference electrode, called the standard hydrogen reference electrode. This electrode cannot be used in the field, but our interpretations of redox potential measurements are based on values determined with it. Therefore, all voltages measured in the field with either the Ag/AgCl or calomel reference electrode have to be adjusted to the value that would have been obtained had a standard hydrogen electrode been used. The basic correction factors are:

| Reference Electrode | Correction Factor (mv) |
|---|---|
| Ag/AgCl in saturated KCl solution | +200 |
| Calomel | +250 |

These correction factors are temperature dependent, but in most instances the effect of temperature is must less than the variability in the data for a given time. Therefore, in my opinion a temperature correction is not necessary unless very precise measurements are required.

Formula for Converting Field Data to Redox Potential:

Field Voltage + Correction Factor = Redox Potential (Eh)

The symbol Eh or EH is used to indicate a voltage that has been corrected to what would have been obtained with a standard hydrogen electrode.

## Voltmeters

Voltmeters measure the amount of voltage needed to stop electrons from flowing between the Pt electrode and the reference electrodes. These meters should not let electrons flow, otherwise stable readings will not be obtained.

Voltages produced by oxidation-reduction reactions are small, and range from +1 to –1 volts (+1000 to –1000 mv). The voltmeter selected must be capable of measuring these small voltages.

Two basic kinds of voltmeters are available: 1) laboratory grade Eh-pH meters and 2) commercial voltmeters. The lab grade meters are probably the most accurate of the two to use. They can be expensive (>$300) and are preferred for research use.

Commercial voltmeters that measure millivolts seem to be adequate for routine use. These are available for <$100.

## Sources of Equipment

The following supplies provide equipment. We have used all with good results or know of others who have used these with good results.

### Voltmeters

- **Fisher Scientific Equipment Company**
- **Radio Shack**

### Reference Electrodes

- **Fisher Scientific Equipment Company**
- Jensen Instruments (2021 7$^{th}$ St., Tacoma, WA 98045; phone: 253-572-2659)

### Platinum Electrodes

- Constructed in-house using one of the procedures shown below.

- Jensen Instruments: have constructed excellent electrodes in the past, but there may be a delay in delivery of up to 9 months.

- Louisiana State University: contact Dr. Wayne Hudnall. We have not used electrodes from this laboratory but they have a good reputation.

**Platinum Electrode Construction**
**For Redox Potential Measurements**

**Over the last 10 years, graduate students and technicians in the Soil Science Department have constructed their own Pt electrodes using the procedures described below. The methods have evolved over time, and we expect will continue to evolve. Two methods are described below. Method A uses epoxy to insulate and seal the brass rod from the environment. Method B uses a rigid heat-shrink tubing in place of the epoxy. Method A has been tested for a number of years and found to be reliable. The epoxy is messy and therefore, Method B is easier to use. However, our experience with Method B is limited and while we use it now, it is still being evaluated.**

## Materials:

## Method A: Insulate with Epoxy

1/8" diameter brass brazing rod (available at many welding supply companies)

18 gauge platinum wire (available from Fisher Scientific. Phone # 1-800-766-7000)

Batterns flux (available at many welding supply stores)

1/4" and 3/16" initial diameter adhesive-lined polyolefin heat-shrink tubing (available from McMaster-Carr Supply @ www.mcmaster.com)

Marine-Tex brand waterproof epoxy (available from most hardware stores)

Propane torch with adjustable flame attachment (available from most hardware stores)

Heat-shrink hot air gun (available from McMaster-Carr Supply @ www.mcmaster.com)

18 gauge multi-stranded wire (order different colors for different depths etc. Also available from McMaster-Carr Supply. )

Latex gloves and a pair of heat resistant gloves for handling propane torch.

Needle nose pliers

Sandpaper: 70 grain and 150 grain, 1 pack of each.

Soldering iron and solder.

## Method B: Insulate with Rigid, Heat-Shrink Tubing*

Rigid Heat Shrink Tubing (available from McMaster-Carr Supply @ www.mcmaster.com part # 72675K51)
*All other materials are the same as for Method A.

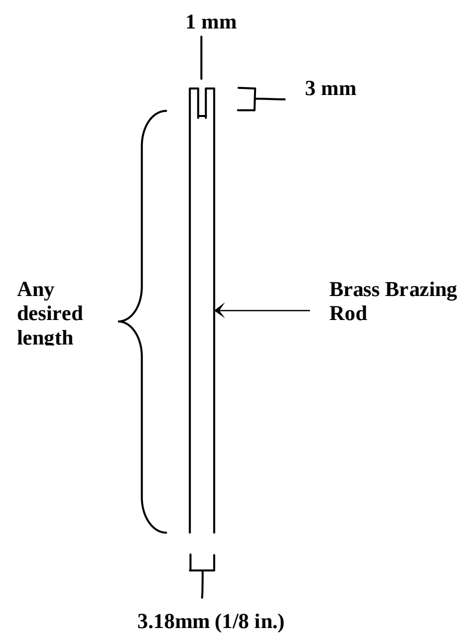



**Fig. A (steps 1-3)**

**Methods:**

1) Cut brass brazing rod to desired length of electrode.

2) Drill a 1 mm hole 3 mm deep in the end of the brass-brazing rod.

3) Cut platinum wire into 13 mm lengths.

4) Brush the drilled end of the brass-brazing rod with the flux and also dip a piece of the platinum wire in the flux.

5) Insert one end of the platinum wire into the hole on the brass-brazing rod. Hold wire in place with pliers.

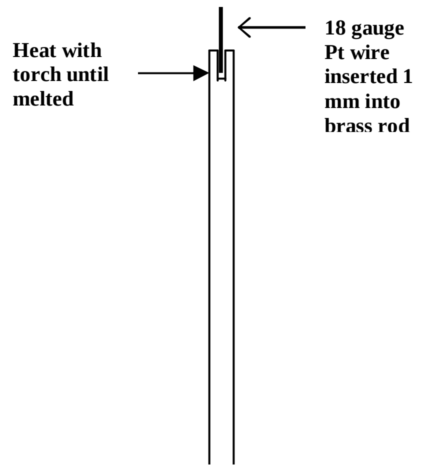



**Fig. B (steps 5 & 6)**

6) While holding the wire in place, direct the tip of the hot blue flame from the propane torch at the area of the rod where the platinum wire was inserted. Continue to heat the rod until it melts, thereby creating a bond between the rod and the platinum. Hold the wire in place until the rod cools. (Note: Rod must be held in a vertical position while performing this procedure to avoid sagging of the molten metal.) Once the rod cools, be sure to check the Platinum/brass interface by tugging on platinum wire with a pair of pliers.

7) Cut heat shrink tubing approximately 5 cm shorter than the length of the rod. Set aside.

## Sealing with Epoxy: Method A

Waterproofing the Pt-brass joint can be done with either epoxy or rigid heat-shrink tubing. Both methods will be described.

8a) Mix Marine-Tex epoxy according to manufacturer's
directions.

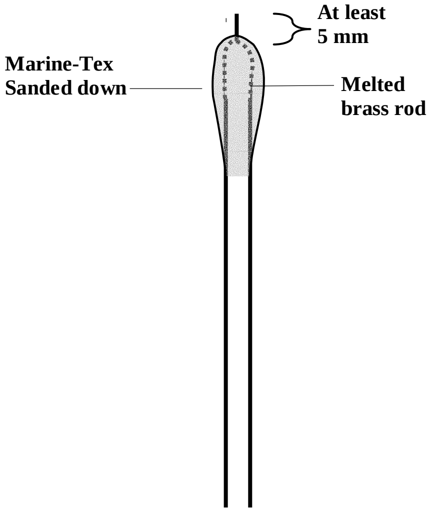



**Fig. C steps (9, 10 & 11)**

9a) Cover the junction between the rod and platinum wire with the Marine-Tex epoxy. Spin the rod so that the entire junction is adequately covered and/or use a Popsicle stick or plastic knife to smooth out the Marine-Tex mixture. Leave at least

5 mm of the tip of the wire uncovered.

10a) Let the Marine-Tex set up until the Marine-Tex can be touched with a latex glove without adhering to the glove. Smooth the Marine-Tex with gloved fingers. Work the Marine-Tex down the rod until at least 5 mm of the Marine-Tex is thin enough for the heat shrink tubing to slide over. Leave excess Marine-Tex above this thinned area.

11a) After enough time has passed to allow the Marine-Tex epoxy to harden (24 hrs.) You must sand down the epoxied tip to smooth out any rough spots in the epoxy. Starting with a 60 or 70-grain sandpaper, smooth out the larger bumps in the epoxy. Once the larger bumps have been smoothed use the 150-grain sandpaper to give the epoxy a smooth finish. Be sure to leave enough epoxy to allow for a watertight seal around the platinum wire.

12a) Slide a pre-cut piece of heat shrink tubing on the rod from the end without the platinum wire. Shove the tubing over at least 5 mm of the Marine-Tex.
Starting with the end of the tubing that is in the Marine-Tex, shrink approximately 5 cm of the tubing.
Slowly continue heating the rest of the tubing.
Let harden.

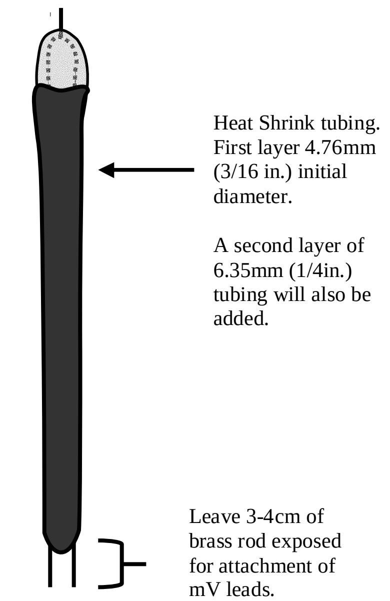



**Fig. D steps (12 & 13)**

# Sealing with Rigid Heat Shrink Tubing: Method B

8b) Next, slide a terminal insulator over the brass-Platinum interface, being careful to leave enough of the platinum exposed for proper contact with the soil. Then, using the heating gun, heat the insulator until the adhesive lining becomes liquefied and the insulator shrinks around over the platinum. Allow insulator to cool.

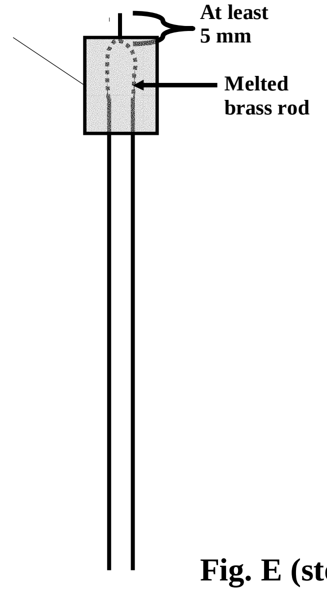



Fig. E (step 8b)

9b) Slide a pre-cut piece of heat shrink tubing on the rod from the end without the platinum wire. Shove the tubing over at least 5 mm of the terminal insulator. Starting with the platinum end of the tubing, shrink approximately 5 cm of the tubing. Slowly continue heating the rest of the tubing. Let harden.

10b) Finish shrinking the rest of the tubing on the rod.

11) If needed, trim tubing from end of rod to leave enough room (approx. 5 cm) for the attachment of mV leads (18 gauge copper wire). For electrodes to be installed between 30 and 60 cm cut off approximately 6 feet of the copper wire (use more copper wire for electrodes to be installed at deeper depths). Set aside.

12) With a knife or pair of electricians pliers strip about 4 cm off the end of the wire. Wrap the 4 cm of exposed copper wire around the exposed 5 cm of the brass rod and hold in place. Apply a liberal coat of solder all along where the copper wire and brass rod meet and let cool. To check the soldered connection once the solder has cooled, tug on the copper wire gently. Apply a second layer of heat shrink tubing, making sure to cover the soldered area where the m V leads were attached to the brass rod and extend it approximately 15 cm up the

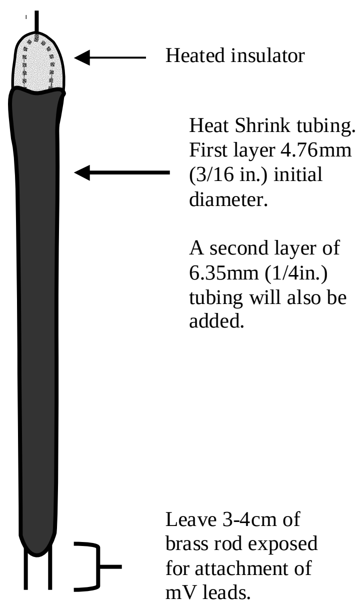



Figure F. (steps 9, 10, 11)

copper wire. You may apply a third layer of tubing at the point where the brass rod and copper wire meet for added protection and stability.

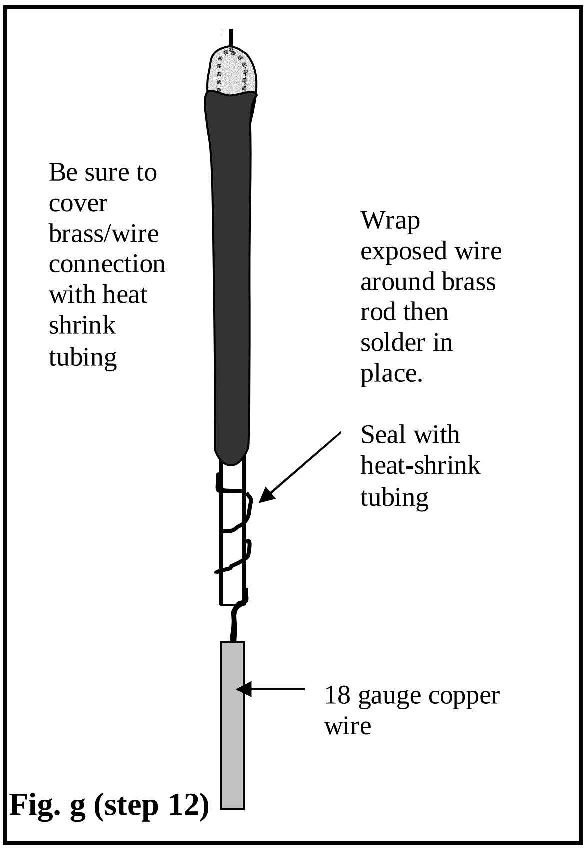



**Fig. g (step 12)**

**Procedure for Making Ferrous-Ferric solution (Light's Solution) for Oxidation-Reduction Potential Measurements and testing of electrodes.**

Once constructed the electrodes have to be checked for accuracy. This is first done using a solution of known and stable redox potential. The solution we have used was described by Light (1972) and is prepared from scratch. The ingredients are shown below.

| **Composition:** | **Concentration:** |
|---|---|
| **Ferrous ammonium sulfate**<br>39.21 g/l $Fe(NH_4)_2(SO_4)_2 \cdot 6H_20$ | 0.100M |
| **Ferric ammonium sulfate**<br>48.22 g/l $FeNH_4(SO_4)_2 \cdot 12H_20$ | 0.100M |
| **Sulfuric Acid**<br>56.2 ml/l concentrated $H_2SO_4$ | 1.00 M |
| | |

To test an electrode for accuracy:

First, scratch the platinum tips of each electrode with steel wool. Second, fill a beaker halfway with the Light's solution you have made. Fill a second beaker with tap water. Using a redox potential meter outfitted with a Ag, AgCl reference electrode you will take an mV reading of each electrode individually in both the buffer solution and in tap water. The buffer solution should read at +476mV (+/- 20 mV). The tap water reading will vary from the buffer reading but should not vary by more than 100 to 150 mV from other electrodes. If an electrode is varying more than 150 mV, there may be something wrong with that electrode. Problems with electrode readout include; electrode not being water tight, platinum not having a good connection to brass rod, and copper wire not being soldered on correctly.

## Sample Results of Redox Electrode Test

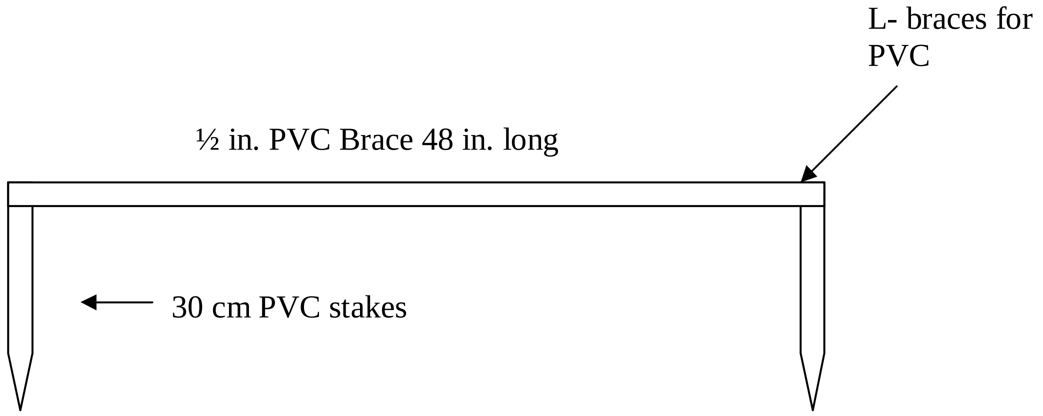
| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | | | | | |
| **Electrode#** | **Light-soln reading** | **Deionized H20 reading** | **Deionized H20 reading #2** | | **Electrode#** | **Light-soln reading** | **Deionized H20 reading** | **Deionized H20 reading #2** |
| 1 | 482 | 420 | 431 | | 47 | 476 | 375 | 386 |
| 2 | 480 | 383 | 387 | | 48 | 444 | 410 | 413 |
| 3 | 471 | 290 | 294 | | 49 | 482 | 280 | 283 |
| 4 | 478 | 250 | 254 | | 50 | 478 | 370 | 373 |
| 5 | 470 | 303 | 307 | | 51 | 476 | 440 | 443 |
| 6 | 472 | 270 | 274 | | 52 | 482 | 410 | 413 |
| 7 | 465 | 360 | 364 | | 53 | 480 | 350 | 353 |
| 8 | 482 | 383 | 387 | | 54 | 480 | 250 | 253 |
| 9 | 482 | 441 | 445 | | 55 | 481 | 360 | 363 |
| 10 | 482 | 312 | 316 | | 56 | 481 | 410 | 413 |
| 11 | 482 | 367 | 371 | | 57 | 482 | 260 | 263 |
| 12 | 482 | 457 | 461 | | 58 | 480 | 350 | 353 |
| | | | | | | | | |

## Installation of Redox Electrodes

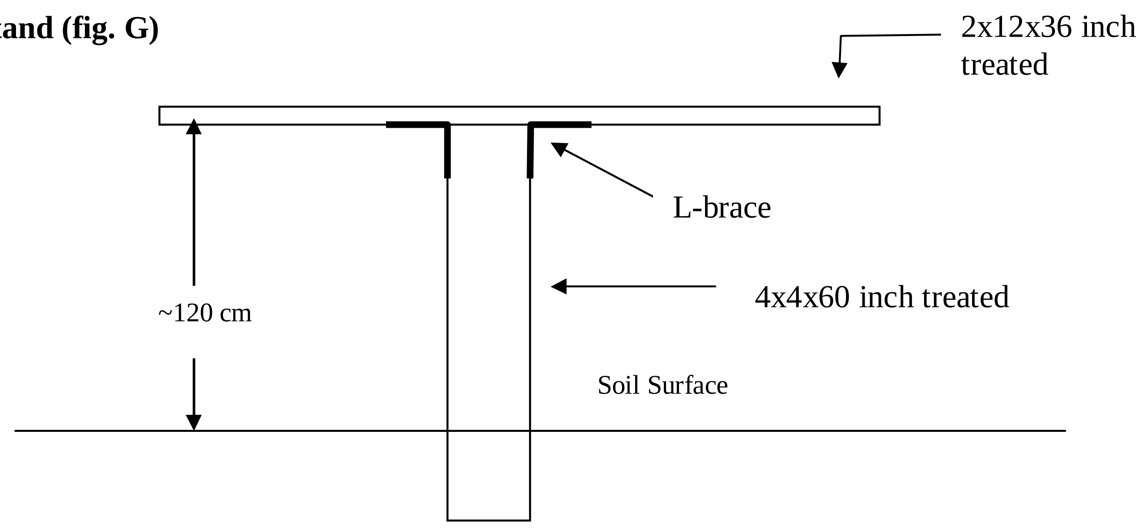
- PVC braces (2-3) were constructed for each plot (see figures F&G).
- The stand was installed in a 10 cm diameter hole at approximately 45 cm depth.
- The braces were arrayed around the stand on three sides at approximately one meter from the stand base. The braces were installed with a push probe so that the cross brace was about 15 cm above and parallel to the soil surface.
- The platinum-tipped electrodes were installed with a push probe at various depths. In a bucket, soil from the push-probed holes was mixed with water to form a slurry. The slurry was used to backfill the hole. The electrode platinum tip was scraped before insertion into the soil and was then inserted through the slurry and into undisturbed soil. The probes were secured to the brace with plastic cable ties.

- Using a staple gun, the copper wire leads of the electrodes were attached to the stand. The extensions were arranged on the stand in the same order the electrodes are to be read.

**Brace (fig. F)**




**Stand (fig. G)**



**Salt Bridge Construction**

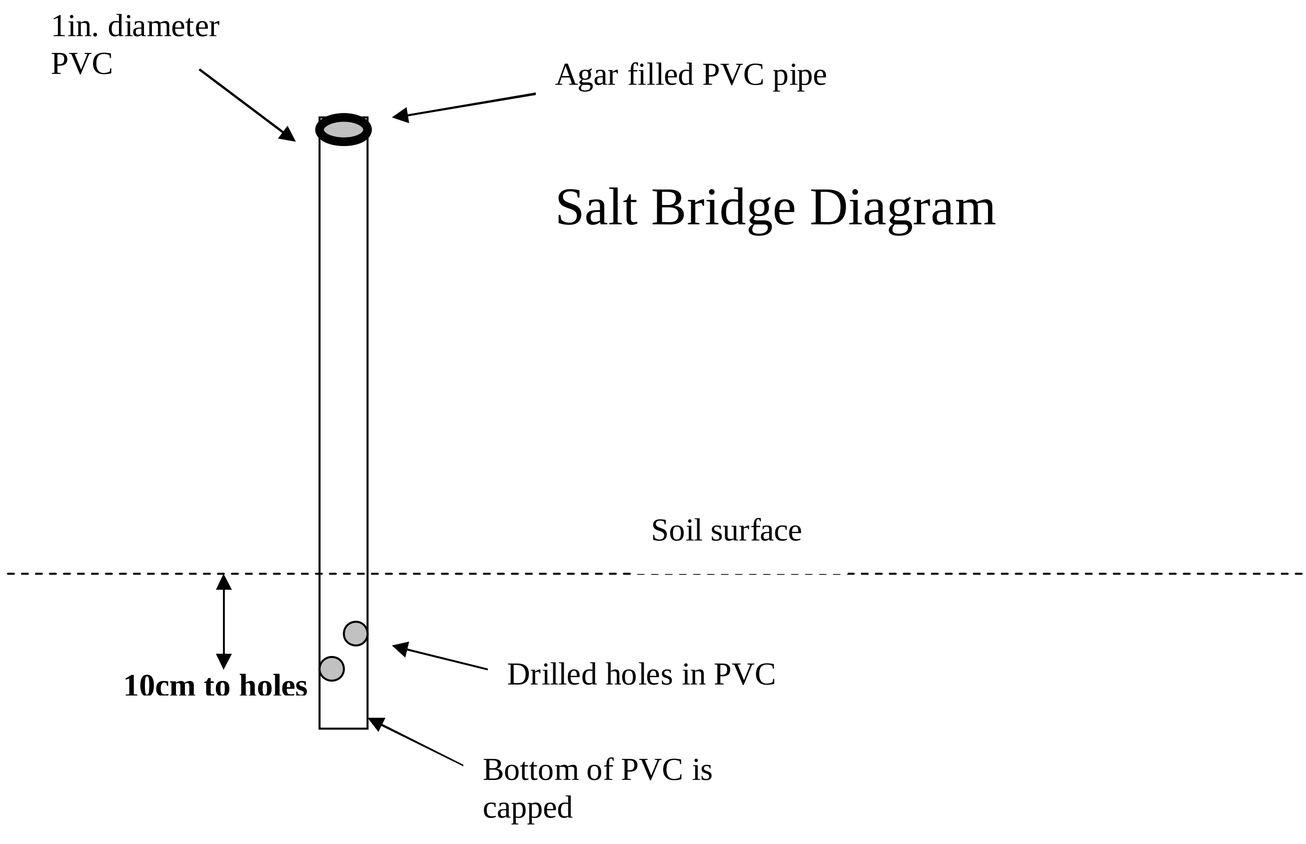
- Salt bridges, one per brace, were constructed and installed to aid redox potential readings.

- The salt bridges were constructed using 1-inch PVC, Potassium Chloride and Agar.

- The salt bridge is composed of:

  (1) 25 – 30 g Agar and…
  (2) 250 mL of saturated KCL solution mixed with…
  (3) 1L of boiling deionized water.

- These ingredients are allowed to cool until a pour able gel forms. This gel is then poured into the 1-inch PVC tubes until they are full and then allowed to cool. The salt bridges were installed using a 1-inch auger. A hole about 60 cm deep was drilled between the stand and the nearest brace. The hole was 30 to 50 cm from the brace and placed approximately in line with is center. 2 holes were drilled into the PVC approximately 10 cm from the bottom of the pipe to allow the agar to come into contact with the soil. Then the salt bridge was installed into the pre-drilled hole.



# APPENDIX B

## Procedure for Making Thermocouples to Measure Soil Temperature

## Procedure For Making Thermocouples To Measure Soil Temperature

### Materials

- Thermocouple Wire - Omega EXPP-T-20 (copper/constantan)
- Electrical Solder - 40% tin 60% lead (rosin core)
- 3/4” Schedule 40 PVC pipe
- 3/4” Schedule 40 PVC couple
- 3/4” Schedule 40 PVC end cap
- #3 rubber stopper
- 50-80 grit sandpaper
- 20 gauge stainless steel wire
- Marine-Tex brand epoxy (white)
- Sand

### Methods

**Wire:**

- Cut a pair of wires to 25” and 37” for each PVC pipe.
- On one end of each wire, strip outer and inner insulation back 1”.
- Twist copper and constantan wires together.
- Solder the twisted wires together.
- Trim soldered wire to 1cm.
- On the other end of each wire, strip outer insulation back 1”-2” and strip inner insulation of both the copper and constantan back 1cm.
- Tie a knot in the short wire of each pair near the non-soldered end (this allows for the differentiation of the shallow and deep thermocouples in the field).
- Test each pair of wires against a mercury thermometer at $O^{o}C$ (ice water) and at room temperature to verify that each wire is within established tolerance range.

**PVC:**

- Cut PVC pipe to 36” lengths.
- Make a mark 14” down from the top end of pipe (this represents the soil surface).
- From this mark measure down 6” and 20” and make a mark (this will be the depths of temperature measurement).

Drill a 3/8” hole in the side of the

## References

Lights, T.S. 1972. Standard solution for redox potential measurements. Analytical Chemistry 44 (6): 1038-1039.

Vepraskas, M. J. and S. P. Faulkner. 2001. Redox chemistry of hydric soils. p. 85 to 105. In J.L. Richardson and M.J. Vepraskas (eds.) Wetland soils CRC Press, Boca Raton, FL.