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Application Note

Tip Log #121

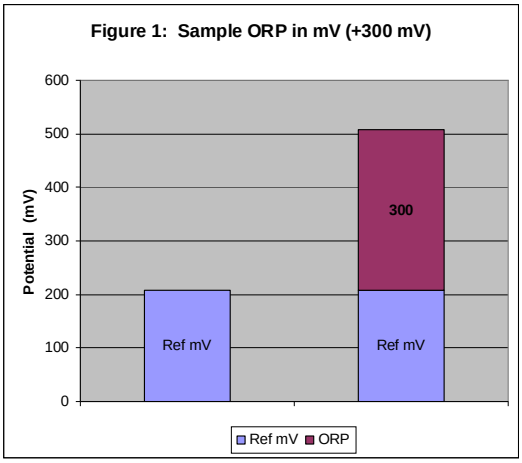
Applications Tip of the Week
ORP – mV, RmV, and Eh (oh my!)

Just like walking through a dark wood in The Wizard of Oz movie (lions, tigers, and bears, oh my!), trying to figure out the various ORP measurement units can be a little scary. Here's some help with that.

ORP expressed as mV

In many online and lab applications, ORP is commonly expressed in units of mV. The measurement proceeds as follows: the user checks the electrode calibration by reading a standard, then measures the sample and reads the ORP measurement in mV from the analyzer/meter. Simple.

What may not be obvious is this: the sample ORP reading in mV shown on the meter is the potential of the sample *as compared to* the potential of the standard reference half-cell of the electrode. That means that if the sample reads +300 mV ORP, the potential of the sample is +300 mV higher than the standard potential of your reference half-cell for the electrode. See Figure 1 at the right.

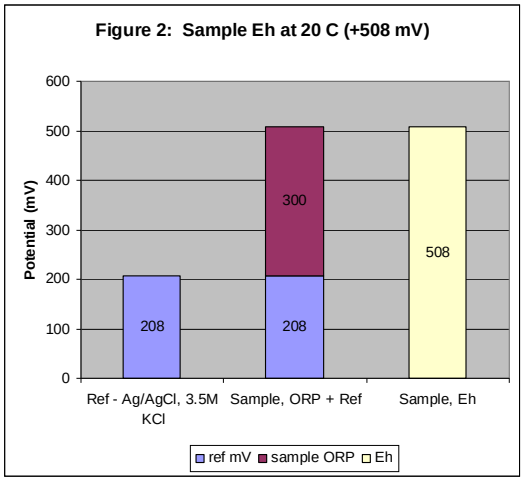


So why do we need to know that? See below.

ORP expressed as Eh

For other applications, ORP is more commonly expressed in units of Eh, for example, soil or water quality measurements. The Eh value corresponds to the potential of the sample *as compared to* the potential of the Standard Hydrogen Electrode (SHE) which is 0.0 mV. The measurement may proceed as follows: the user measures ORP as noted above. Then, the user adds the mV of the standard reference half-cell of their electrode (vs. SHE) to calculate Eh, like this:

Eh of sample = ORP sample reading (mV) on the meter + standard reference half-cell potential (mV)



So, let's calculate the Eh of the sample we discussed above, which measured ORP as +300 mV. If the ORP electrode has a silver:silver chloride reference half-cell and uses a filling solution of 3.5M KCl (saturated with AgCl), then the standard reference half-cell potential at 20C is 208 mV (0.208 V). [Note: Standard reference half-cell potentials can be found in many references or ORP methods. See Table 1 at the end of this Tip]. To calculate Eh:

Eh of sample = +300 mV + 208 mV = 508 mV as Eh

Figure 2 on the left demonstrates this calculation. If you have a meter that allows for a relative mV calibration or Eh calibration, then measuring Eh becomes easier.

ORP readings in RmV

Many meters allow for calibration of the ORP measurement. This is a handy feature. After calibration, the reading on the meter may display as RmV, to indicate that the reading has been offset. The offset may display live on the meter or in the calibration log. The calibrated offset is commonly used in one of two ways:

1. To calibrate the ORP reading to be more accurate, or
2. To calibrate the reading to display Eh directly (no calculation step required).

Calibration scenario 1: Calibrate the standard reading to match the expected ORP reading for that standard. For example, if using a Thermo Scientific Orion 2102 monitor and Orion 110250 ORP electrode with the Orion ORP Standard (Orion 967901) at 25C, calibrate the reading to +220 mV (the expected value when using the Orion 900011 filling solution). The calibrated offset is usually small, e.g., < +/- 5 mV. After calibration, the Orion ORP Standard reading will display as +220 RmV. Sample measurements will display in units of RmV. Note: Some meters will simply display "mV" after calibration.

Temperature (°C)	E_H Value (mV)	Absolute Value with Cat. No. 900011 Filling Solution (mV)	Absolute Value with Cat. No. 900001 Filling Solution (mV)
0	+ 438	218	176
5	+ 435	218	176
10	+ 431	219	175
15	+ 428	219	175
20	+ 424	219	174
25	+ 420	220	173
30	+ 415	220	172
35	+ 411	220	171
40	+ 406	220	170
45	+ 401	220	169
50	+ 396	220	167

Calibration scenario 2: Calibrate the standard reading to match the expected Eh reading for that standard. See the table at right. For example, if using an Orion 9180 electrode with the Orion ORP Standard (Orion 967901) at 25C, the meter will auto-calibrate the reading to +420 mV as indicated on the standard. Note that the calibrated offset will be quite similar to the standard reference half-cell potential. In this case, the offset will be about +200 mV, which is the standard reference half-cell potential for this electrode. After calibration, the Orion ORP Standard reading will display as +420 RmV or Eh ORP. See Figure 3 below. [Note: Check your meter instruction manual for expected units.] After calibration, sample measurements will read Eh directly. No calculations are required.

Temperature (°C)	E_H Value (mV)	Absolute Value with Cat. No. 900011 Filling Solution (mV)	Absolute Value with Cat. No. 900001 Filling Solution (mV)
0	+ 438	218	176
5	+ 435	218	176
10	+ 431	219	175
15	+ 428	219	175
20	+ 424	219	174
25	+ 420	220	173
30	+ 415	220	172
35	+ 411	220	171
40	+ 406	220	170
45	+ 401	220	169
50	+ 396	220	167

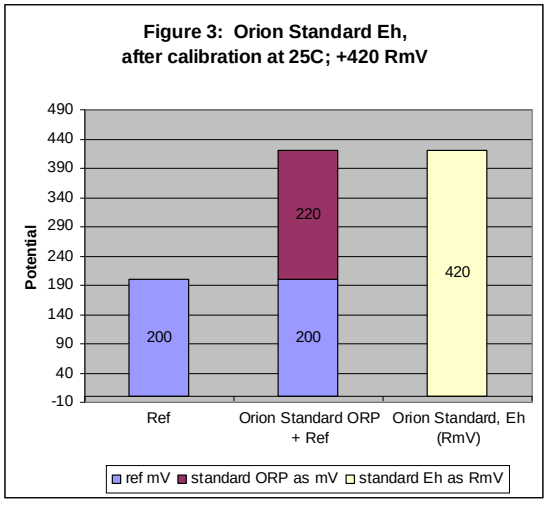


Table 1: Standard half-cell potentials of selected reference electrodes

Temp °C	Silver:silver chloride			Calomel [1]			
	3M KCl [1]	3.5M KCl [2]	Saturated KCl [2]	3M KCl [2]	3.5M KCl [2]	4M KCl [2]	KCl saturated [2]
10	0.220	0.215	0.214	0.260	0.256	—	0.254
15	0.216	0.212	0.209	—	—	—	0.251
20	0.213	0.208	0.204	0.257	0.252	—	0.248
25	0.209	0.205	0.199	0.255	0.250	0.246	0.244
30	0.205	0.201	0.194	0.253	0.248	0.244	0.241
35	0.202	0.197	0.189	—	—	—	0.238
40	0.198	0.193	0.184	0.249	0.244	0.239	0.234

For details, see Table 6.5-2 at: http://water.usgs.gov/owq/FieldManual/Chapter6/6.5_contents.html