Introduction:

Oxidation-reduction potential (ORP), also known as redox potential, refers to the capacity of a solution to oxidize (accept electrons) or reduce (donate electrons). ORP sensors work by measuring the voltage across a circuit formed between the indicator and reference electrodes. When an ORP electrode is placed in a solution containing oxidizing or reducing agents, electrons are transferred back and forth on the measuring surface, generating an electrical potential.

Common applications for the ORP method include monitoring water chlorination processes for water disinfection, distinguishing between oxidizers and reducers present in wastewater, and metal screening. ORP measurements are practical for water disinfection monitoring since waters are routinely treated with oxidizers (e.g. chlorine) to minimize bacterial growth. An ORP of between 650mV and 700mV generally indicates a low level of contamination, as many spoilage bacteria, E.coli and Salmonella are killed within seconds at this level. Additionally, spoilage yeasts and some fungi are killed within a few minutes at this ORP level.

ORP measurements are also useful in metal screening processes, as it can be used to identify the approximate concentration of metal ions in water. Neutral waters with a redox potential of less than 390mV are not likely to contain a concentration of metal ions greater than 0.005 mg/L, or 5ppb. Metals are often involved in oxidation-reduction reactions as their activity levels are directly proportional to their dilute concentrations in solution. As the concentration of metal ions increases, the redox potential also increases. The general reaction for a redox reaction involving metals at equilibrium, where M represents the metal, and n is the oxidation state, is written as:

$$M = M^{n+} + ne^-$$

ORP electrodes cannot be calibrated over a range of redox potentials as can pH, and so standard solutions with known redox potentials are used to ensure that the electrode is responding accurately. There are two common redox standard solutions, Zobell’s and Light’s solutions. The redox potentials of these solutions depend upon the type of indicator and reference electrode used for measurement. The most common type of indicator electrode is the platinum electrode, however gold or graphite can also be used. In terms of reference electrodes, the standard hydrogen electrode is rarely used because of its extreme fragility and so silver:silver-chloride or calomel reference electrodes are common. The data obtained in this document was obtained using a combination ORP electrode, with a platinum indicator electrode and silver:silver-chloride reference electrode.
The redox potential of the platinum electrode versus the silver:silver chloride electrode in Zobell’s and Light’s solutions at 25°C are +228 and +475, respectively. Because redox potentials are temperature dependent, expected ORP values are generally reported as a function of temperature. ORP values can also fluctuate with pH if hydrogen or hydroxide ions are involved in the redox half-cells. ORP values tend to increase as pH decreases, and decrease as pH increases.

This method is a quick, simple, and accurate way to determine the redox potential of a sample. Please contact your local MANTECH sales representative to find out how this method can work for you.

Conforms to: Standard Methods, Method 2580
ASTM, Method D1498-00

Sample: All water samples

Concentration Range: Tested between 200 – 500mV

Apparatus:
1. Redox Electrode
2. Electrode Cable
3. Interface
4. TitraSip (optional)
5. Autosampler
   a) AutoMax73, 73 sample locations from a 50mL tube
   b) AutoMax122, 122 sample locations from a 50mL tube
   c) AutoMax 197, 197 sample locations from a 50mL tube

Reagents:
1. Redox Standard Solutions:
   a. Zobell’s Solution: 1.4080g potassium ferrocyanide + 1.0975g potassium ferricyanide + 7.4555g potassium chloride (KCl) diluted up to 1L with deionized (DI) water
   b. Light’s Solution: 39.21g ferrous ammonium sulphate + 48.22g ferric ammonium sulphate + 56.2mL sulphuric acid (H2SO4) diluted up to 1L with DI water

Procedure:
Sample Analysis:
1. Pour ~25mL of sample into tubes, and place in the autosampler.
2. Run a schedule that measures the redox potential of a sample.
3. The sampler moves to the rinse station, and all probes and the TitraSip cell are rinsed with deionized (DI) water prior to analysis.
4. The sampler moves to the first sample position, and the sample line is primed.
5. 10mL of sample is pumped into the 35mL TitraSip cell, and the stirrer turns on.
6. The redox potential of the sample is recorded in millivolts (mV).
7. The sampler moves to the rinse station, and all probes and the TitraSip cell is rinsed with DI water before moving to the next sample.
8. Steps 4 to 7 are repeated for all remaining samples.
*Note the volumes described above will vary by configuration

**Calculations:**
No calculations are necessary as the potential of the sample is read as a direct mV reading for this type of electrode.

**Quality Control:**
Light’s solution (expected value = +475mV) and a purchased ORP standard (expected value = +220mV) were analyzed for their redox potential, with statistical data reported below.

*Light’s solution:*

![Figure 1: Control Limits Plot for Light’s Solution](image)

<table>
<thead>
<tr>
<th>Control Limits – Individuals</th>
<th>95% Confidence Limits</th>
<th>99.7% Confidence Limits</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\mu = 476.706$</td>
<td>$\mu - 2\sigma = 476.131$</td>
<td>$\mu - 3\sigma = 475.843$</td>
</tr>
<tr>
<td>$\sigma = 0.288$</td>
<td>$\mu + 2\sigma = 477.281$</td>
<td>$\mu + 3\sigma = 477.569$</td>
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<tr>
<td>CV = 0.006%</td>
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</tbody>
</table>
Purchased ORP Standard:

Control Limits – Individuals  95% Confidence Limits  99.7% Confidence Limits
µ = 224.069    µ-2σ = 223.594    µ-3σ = 223.357
σ = 0.238    µ+2σ = 224.544    µ+3σ = 224.781
CV = 0.106%

Hints/Suggestions:
1. Ensure that the electrode is completely filled with 4M KCl fill solution before each run. Tests indicate that a diluted reference fill solution will alter the ORP measurements.
2. Analyze samples immediately after sampling; do not attempt to store samples for future analysis. Atmospheric contact and delayed analysis both contribute to disrupted ORP measurements, especially for samples with very low concentrations of oxidizing or reducing agents.
3. Due to the influence of temperature on ORP readings, it is important that temperature fluctuations are minimized.
4. Zobell’s reference solution is light sensitive and should be stored in an amber bottle in the refrigerator to reduce decomposition. If stored accordingly, it is generally stable for several months.
5. Rinse all sample beakers with deionized water prior to sample addition to prevent contamination of samples due to tap water impurities.
6. During testing, the electrodes seemed to stabilize very quickly (with incorrect outcomes), but when left in solution for a longer period of time, the mV readings fell into line with what was expected. Therefore, it seems as though the electrodes are slower to respond and therefore it is suggested that the stability settings be set quite strict with a high time-out value. Below are some important settings needed to run the Redox method:
### Calibration / UDV Settings

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<table>
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<tr>
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<tbody>
<tr>
<td>Electrode port</td>
<td>2.0V</td>
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<tr>
<td>Delta mV</td>
<td>0.1mV</td>
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<tr>
<td>Delta Time</td>
<td>30s</td>
</tr>
<tr>
<td>Stability Time Out</td>
<td>360s</td>
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