



ORP versus amperometry for TRO measurement.

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A technical comparison of oxidation-reduction potential (ORP) and amperometric measurement for total residual oxidant — why ORP falls short as a quantitative method and where amperometry delivers the accuracy that water treatment demands.

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ORP tells you something is there. Amperometry tells you how much.

Two technologies compete for total residual oxidant (TRO) measurement: oxidation-reduction potential (ORP) and amperometry. ORP is inexpensive and widely used as a qualitative indicator, but its logarithmic response, sensitivity to pH, temperature, and interfering substances, and susceptibility to electrode poisoning make it fundamentally unsuitable for accurate concentration measurement. Amperometry provides a linear, direct measurement of the oxidant itself — delivering the quantitative accuracy that water treatment, ballast water compliance, and pool safety require.

Linear response

Amperometric signal is directly proportional to oxidant concentration — ORP is logarithmic, amplifying error

±30%+ error

Typical ORP measurement accuracy of ±5 mV translates to >30% concentration error due to logarithmic math

Zero = zero

In amperometry, zero current always means zero chlorine — no baseline shift between water sources

200 mV spread

ORP baseline varies by nearly 200 mV between different water sources at the same chlorine level

H O W O R P W O R K S

Measuring voltage, not concentration

ORP stands for oxidation-reduction potential — a measurement, in millivolts, of the tendency of a chemical substance to oxidize or reduce another. An ORP sensor consists of an inert metal electrode (typically platinum) and a reference electrode; a voltmeter measures the potential difference between them. The

electrode gives up electrons to an oxidant (chlorine) or accepts electrons from a reductant, developing a potential proportional to the overall redox state of the solution.

The typical accuracy of an ORP measurement is ± 5 mV. This is further complicated by the fact that different probes from the same manufacturer often show a 20 to 50 mV difference in the same water sample. Manufacturers test their sensors in Zobell solution, which contains a high level of redox couples — in this solution sensors read close to each other. In real-world drinking water samples, they do not.

Why ORP fails as a quantitative method

Electrode poisoning

ORP electrodes are easily poisoned by organic molecules. In testing with synthetic perspiration in a 300-gallon spa using bromine sanitizer, an ORP sensor registered negative values after approximately 12 hours of exposure and did not recover for 29 hours. Had the ORP sensor been controlling sanitizer feed, this would have caused massive over-bromination of the spa.

Baseline varies with water source

Five different water samples tested at the same chlorine level showed ORP baselines varying by nearly 200 mV. According to the World Health Organization, there is a wide variation between 720 mV in different waters (1 ppm to 15 ppm chlorine) due to varying baseline ORP at zero chlorine. In seawater, baseline ORP can range from -275 to +350 mV, greatly exacerbating the problem. With amperometric sensors, zero current is always zero chlorine — no zero calibration or baseline adjustment is needed.

Logarithmic response amplifies errors

The Nernst equation governing ORP produces a coefficient of only 29.58 mV per tenfold change in concentration. A typical ± 5 mV measurement accuracy translates to more than $\pm 30\%$ error in calculated concentration — before accounting for reference electrode drift, temperature effects, or pH changes. Any of these additional factors further compound the error.

pH and chloride dependence

ORP depends on chloride ion and pH as much as it does on hypochlorous acid. Any change in chloride concentration or pH affects the ORP reading. To derive an accurate chlorine concentration from ORP, chloride and pH must be measured to high accuracy or held constant — conditions rarely achievable in real-world water treatment.

No temperature compensation

Temperature changes affect ORP readings, but this effect is not compensated by standard ORP instruments, introducing yet another source of uncontrolled error in the derived concentration.

THE FUNDAMENTAL PROBLEM

ORP measures the aggregate redox state of the solution — not the concentration of any specific oxidant. Multiple redox couples, pH, temperature, chloride, and organic loading all influence the reading. Attempting to derive a specific chlorine concentration from this composite signal requires assumptions that rarely hold in practice.

Direct, linear measurement of the oxidant

In an amperometric sensor, a fixed voltage is applied between electrodes, and a reaction takes place at the working electrode (cathode) in which the oxidant (hypochlorous acid) is reduced back to chloride. The current that flows as a result is directly proportional to the oxidant concentration presented to the sensor — a linear relationship, in contrast to ORP's logarithmic response.

CHARACTERISTIC	ORP	AMPEROMETRY
Signal relationship	Logarithmic	Linear
Measures	Aggregate redox potential	Specific oxidant concentration
Zero calibration	Varies with water source (up to 200 mV)	Zero current = zero chlorine, always
pH dependence	Significant — affects reading directly	Compensated or minimal
Electrode poisoning	Easily poisoned by organics (hours to recover)	Self-cleaning; resistant to fouling
Accuracy at ± 5 mV	$>\pm 30\%$ concentration error	$\pm 4\%$ or better (Halogen MP5)
Seawater baseline	-275 to +350 mV range	Zero current = zero, regardless of matrix
Best use	Qualitative indicator	Quantitative concentration measurement

Three-electrode vs. two-electrode designs

Most membrane chlorine sensors use a two-electrode configuration. In general, two-electrode readings are less stable and electrodes do not last as long as the three-electrode method used in the Halogen MP5. The three-electrode design provides better long-term stability and accuracy.

Where the difference matters most

Swimming pools and spas

Cyanuric acid (CYA) is used in virtually all outdoor pools to prevent UV degradation of chlorine. CYA levels frequently exceed 200 ppm and can reach 350 ppm in sun-belt states. At these levels, ORP electrodes are rapidly poisoned and must be cleaned every three days. One ORP manufacturer recommends pools should not exceed 40 ppm CYA — far below the 100–200 ppm limits most health departments allow. The Halogen sensor is the only amperometric sensor that operates reliably with CYA levels above 200 ppm.

ORP also produces false readings when the sun goes down, as CYA releases some bound chlorine, raising the ORP signal. The controller then reduces chlorine feed. When the sun rises the next morning, dangerously low chlorine levels are detected, triggering alarms. This daily cycle wastes water (from unnecessary dilution to lower CYA), creates safety risks, and generates needless maintenance calls.

Wastewater treatment

A Water Environment Research Foundation (WERF) study comparing ORP and amperometric sensors in wastewater applications found significant limitations with ORP: chemicals other than chlorine can elevate ORP without producing effective microbial kill; other chemicals can interfere with ORP function; and field ORP calibrations cannot be effectively checked because lab ORP probes are easily fouled by wastewater components. The study scored ORP only 2 out of 5 for ability to provide information to meet effluent coliform requirements.

Ballast water treatment

Ballast water treatment systems using electro-chlorination require accurate TRO measurement for IMO compliance. The challenges of ORP in seawater — baseline variation from -275 to $+350$ mV, sensitivity to the lower oxidation potential of bromine (the dominant oxidant in seawater), and electrode fouling — make amperometry the preferred measurement method for ballast water compliance monitoring.

HALOGEN'S APPROACH TO ORP

Halogen includes ORP measurement in its multiparameter sensor — but as a qualitative indicator for contamination events, not as a concentration measurement. While the MP5's chlorine measurement covers 0.05 to 15 ppm, ORP can detect contamination or cross-connection events by identifying drops below the baseline ORP level. Halogen's self-cleaning system eliminates the poisoning issues that plague conventional ORP sensors, providing a reliable qualitative reading.

C O N C L U S I O N

The right tool for the right measurement

ORP has a legitimate role as an inexpensive qualitative indicator — it can confirm that some oxidant is present. But the disadvantages for quantitative measurement are fundamental, not incremental: logarithmic response that amplifies errors, sensitivity to pH, temperature, and interfering substances, electrode poisoning from organics, and baseline variation between water sources that can span hundreds of millivolts.

Amperometry measures the oxidant directly, with a linear signal proportional to concentration, a stable zero baseline regardless of water source, and resistance to the fouling and poisoning that compromise ORP readings. For any application that requires knowing how much oxidant is present — regulatory compliance, disinfection control, ballast water treatment — amperometry is the appropriate measurement technology.

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A B O U T T H E A U T H O R

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Michael Silveri is the founder of Halogen Systems, Inc. and inventor of the company's amperometric sensor technology. With over two decades of experience in electrochemical water quality measurement, he has led the development of reagent-free chlorine analyzers deployed across municipal water treatment plants, building water systems, and industrial applications worldwide.