ORP (redox) measurement. Metallic electrodes. A little theory

ORP Redox potential
Oxide-reduction potential, ORP, also known as redox potential, indicates the oxidising or reducing properties of a substance.
To measure ORP, a pH-meter which measures mV and a metallic electrode made of platinum or gold are used.
Platinum is recommended for highly-oxidising solutions that contain chlorides, redox titrations, etc.
Gold is recommended for highly acidic solutions, titrations of ampicillin or penicillin with mercury nitrate, for redox titrations where chrome or iron etc, are present.
Silver electrodes are also available.
Silver is mainly used in argentometric titration.

Calibration of metallic electrodes
Metallic electrodes do not present significant drift of potential, which is why they are not calibrated.
However, some deviations of potential may occur after continued use of the electrode as a result of alterations of the metallic surface or contamination of the reference electrode. Redox standard solutions are available to check that these electrodes are working well, *see page 53*.

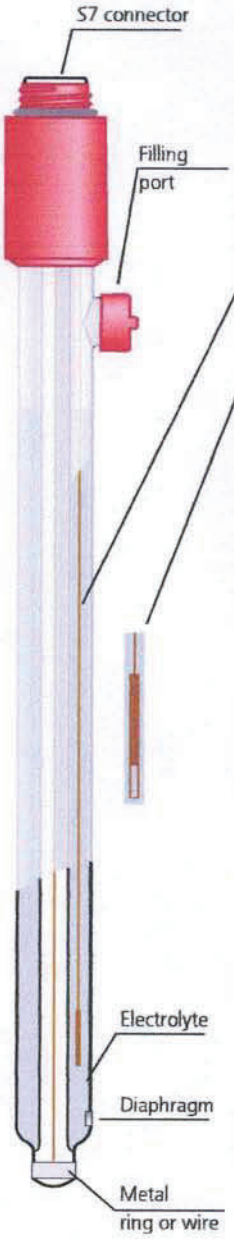
Effects of temperature on ORP (redox) measuring...

... on the electrode
Temperature has no significant effect whatsoever on metal electrodes.

... on a given sample
The oxidation-reduction potential of a sample depends on temperature.
However, pH-meters do not provide any type of compensation.
In this case, connecting a temperature sensor to the pH-meter will serve only to find out the temperature of the sample.

Combined metallic electrodes Essential components

Insofar as their connectors, reference elements, electrolyte and diaphragms are concerned, combined metallic electrodes are the same as pH electrodes. However, the glass membrane is replaced with a ring or wire made from a noble metal.



Connector
With S7 screw cap, to attach the cable.

Body material
Normally made of glass.

Reference element
This is a cell that supplies a stable potential (mV). There are a number of types:

Silver wire (Ag)
Galvanically coated with AgCl, it is the typical reference element.

Encapsulated AgCl crystals
The silver wire comes into contact with a portion of the AgCl crystals inside a small glass tube.

Electrolyte
This is a concentrated saline solution in contact with the reference element.
Metallic electrodes are available with **liquid electrolytes**.

Diaphragm
This is the point of union between the electrolyte and the sample. It is the critical part of the electrode as it has a direct influence on its life-span.
A wide range of diaphragms are available. They vary according to manufacturer, application, quality of electrode and price.
This catalogue features electrodes with sleeve, ceramic and open diaphragms.

The sleeve diaphragm consists of a hole in the body of the electrode, half-closed by a PTFE ring which provides a high level of electrolyte flow..

The ceramic diaphragm is a chemically-inert, porous ceramic plate. These are the traditional diaphragms. It allows a tiny amount of electrolyte to flow through.

Metal wire or ring
May be made of either silver, platinum or gold.

Practical considerations

Immersion depth
To obtain a correct measurement of the ORP, the electrode must be immersed until the diaphragm is covered.

Minimum volume of sample
This will depend on the shape of the measuring recipient.

Price-quality ratio
In practice, the quality of the electrode used has a direct bearing on the reliability of a measurement. CRISON only supplies top quality electrodes because experience has proven them to be a better investment in the medium and long-term.

Common problems
Use of the wrong electrode, or mis-use of the electrode, causes a series of problems that will substantially reduce the lifespan of the electrode. The most common problems, along with their causes and consequences, are:

- Diaphragm blockage.
  Open measuring circuit. Unstable readings...
- Reference system contamination.
  Drift of mV values.
- Build-up of dirt on metallic surface.
  Slow response and wrong measurements.
- Slow response.
  As described above.

Guarantee
CRISON electrodes are guaranteed for a six-month period.
The guarantee only covers manufacturing defects and does not cover defects that could arise from incorrect use, handling, application or maintenance, or as a result of premature wear inherent to certain samples.

Applications for metallic electrodes

Application	Electrode	Metal	Electrolyte	Observations
General ORP measurement	52 61	Platinum	CRISOLYT A	
	50 55	Platinum	Gel	The 50 55 model, especially for the PH 25.
...in waste water	52 62 / 50 55	Platinum	CRISOLYT	This type of sample may contain elements which contaminate the diaphragm, which is why CRISON recommends electrodes with a clog-resistant diaphragm.
... in galvanizing baths	52 62 / 50 55	Platinum	CRISOLYT	
	52 63	Gold	CRISOLYT	
Redox titrations in general	52 61	Platinum	CRISOLYT A	
...COD analysis	52 66	Platinum	CRISOLYT A	These are special-length electrodes, which makes them appropriate for taking measurements directly in COD tubes. Mainly used with CRISON'S special COD samplers (Sampler 20).
	52 70	Gold	CRISOLYT A	
...in microsamples	52 65	Platinum	CRISOLYT A	Ideally-sized for working with small volumes of sample. Also appropriate for working with CRISON's Sampler 45.
...in the presence of chrome or iron	52 63	Gold	CRISOLYT A	Gold is recommended as an indicator.
	52 69	Gold	CRISOLYT	
Argentometric titrations	52 60	Silver	KNO_3 1M	An electrode with silver as an indicator metal should be used. In the case of the micro electrode, it can be used to work on microanalysis with the CRISON Sampler 45.
Argentometry in microsamples	52 68	Silver	KNO_3 1M	
KF Titrations	52 64	Double platinum	-	The technique used in this type of analysis is bipotentiometry. They are indicator electrodes. The presence of a reference electrode is not required.
SO_2 Analysis	52 64	Double platinum	-	