

Application Bulletin



Of interested for:

General chemical laboratories, Effluent treatment plants,
Chemical process technology

No. 48/1 e

Checking the condition of platinum or gold electrodes used for redox-potential measurements

Summary

Data are given for checking the condition of redox electrodes. Their potentials can be calibrated either with ready-to-use METROHM Standard Redox Solution, or by measurement in buffer solutions saturated with quinhydrone followed by comparison with calculated values. Redox potential is the potential appearing on a precious-metal electrode immersed in a reduction-oxidation (redox) system. When the electrode responds properly, calibration is unnecessary. However, contaminated precious-metal electrodes can give false potential indications, and the reference-electrode potential may also be erroneous. For these reasons it is often desirable to check the potentials of redox electrode-assemblies, for which purpose solutions with a definite redox potential are required.

1st method

Check the electrode with the ready-to-use METROHM Standard Redox Solution at a potential of $U = +250 \pm 5$ mV at a temperature of 20°C. (**Metrohm 6.2306.020, Brinkmann 20 09 612-8**)

2nd method

A saturated solution of quinhydrone in an acid or neutral (but not alkaline) buffer solution has a well-defined redox potential. The potential U appearing on a precious-metal (gold or platinum) electrode immersed in such a solution is given by the following equation:

$$U = U_{\text{St.qh.}} - 0.1984 \cdot (273.16 + t) \cdot \text{pH}$$

where t is the temperature in degrees Centigrade and $U_{\text{St.qh.}}$ is the standard redox potential of quinhydrone, which is itself temperature-dependent and can be obtained from the following table:

t (°C)	$U_{\text{St.qh.}}$ (mV)
5	+714.3
10	+710.7
15	+707.0
20	+703.4
25	+699.7
30	+696.0

The potential U' of an electrode assembly is the difference between the potentials of the component electrodes, in this case that of the precious-metal electrode (U) and that of the reference electrode (U_R).

$$\pm U' = U - U_R$$

The sign of U' gives the polarity of the electrode assembly with respect to the precious-metal electrode, and must therefore be taken into account.

Some reference electrode potentials

t (°C)	U_R calomel/KCl sat. (mV)	U_R Ag/AgCl/KCl 3 mol/L (mV)
10	+254.1	+218.9
20	+247.7	+211.5
25	+244.4	+207.6
30	+241.1	+203.6

The above potentials include the diffusion potentials appearing at the diaphragm at medium pH values.

Checking the condition of platinum or gold electrodes used for redox-potential measurements

Method

Two buffer solutions (e.g. pH 4 and pH 7) are taken, and pure (analytical grade) quinhydrone is added, with shaking, until no more dissolves. Some excess solid quinhydrone must remain. The electrode assembly under test is immersed in the solutions and the potentials so produced are measured, the potentials of the precious-metal electrode then being calculated. Should any deviation occur from the expected values, the potential of the reference electrode should first be checked against that of another reference electrode known to be reliable. The reference electrode of the assembly under test is in order if no potential difference is found. A precious-metal electrode which gives an erroneous redox potential must be contaminated in some way. Directions for cleaning such electrodes are given in the appropriate operating instructions.

The potentials of platinum or gold electrodes in perfect condition at 20°C are as follows:

pH value	U (mV)
4.00	+470.8
7.00	+296.3

The potentials of electrode assemblies (precious-metal electrode / reference electrode) are:

pH value	U' calomel/KCl sat. (mV)	U' Ag/AgCl/KCl 3 mol/L (mV)
4.00	+223.2	+259.4
7.00	+48.7	+84.9

The measured values may often vary from the calculated ones by a few mV owing to variations in the diffusion potential at the diaphragm of the reference electrode, and variations in the quality (i.e. purity) of the quinhydrone.

Cleaning and Conditioning

Reagents

1. Alcohol : methyl, ethyl, or isopropyl.
2. Ammonium hydroxide, NH₄OH, concentrated.
3. Mixed acid cleaner : mix concentrated H₂SO₄ and HNO₃ in 2:1 ratio.

Procedure

1. Gently wipe the metallic portion with alcohol (avoid bending a platinum tip).
2. Submerge the lower 1-cm portion in the acid cleaner for a period as listed in Table 2 below.
3. Remove electrode and rinse thoroughly with de-ionized H₂O.
4. For **combination electrodes only** : Soak the lower 1-cm portion in concentrated NH₄OH for 15 minutes (longer if the slope falls below 0.950). Remove electrode and rinse thoroughly with de-ionized H₂O.
5. Store only the combination electrodes in de-ionized H₂O or other recommended aqueous media (e.g., 3M, 4M, and sat'd. KCl , sat'd KNO₃, pH-buffered solutions 4 and 7) for at least 10 minutes before use. Platinum indicator electrodes are stored dry.

Checking the condition of platinum or gold electrodes used for redox-potential measurements

Table 2 : Acid cleaning periods

<u>Electrode condition</u>	<u>Soaking period</u>
• For daily cleaning, and between titrations in non-aqueous media.	1 ----- 5 min.
• After storage for more than 2 weeks.	10 ----- 15 min.
• Uas exceeds ± 15 mv and pHas falls outside of 6.75 and 7.25	15 min.
• Re-conditioning after prolong use in oily and viscous mwterials	0.5 ----- 12 hrs.

Brinkmann Instruments

Support and Services Directory

Contact Information

United States

Canada



Business Hours:

8:30 a.m. to 6:00 p.m. EST

8:30 a.m. to 6:00 p.m. EST



Phone:

800-645-3050
516-334-7500

800-263-8715
905-826-5525

Fax:

516-334-7506

905-826-5424



Address:

One Cantiague Road
P.O. Box 1019
Westbury, NY 11590-0207

6670 Campobello Road
Mississauga, ONT L5N 2L8



Website:
E-mail:

www.brinkmann.com
info@brinkmann.com

www.brinkmann.com
canada@brinkmann.com



Customer Support:

800-645-3050, menu option 2
custserv@brinkmann.com

800-263-8715, ext. 237
custserv@brinkmann.com



Repair:

800-645-3050, ext. 2404
techserv@brinkmann.com

800-263-8715, ext. 232
techserv@brinkmann.com



BioSystems Lab:

800-645-3050, ext. 2258
bioapps@brinkmann.com

516-334-7500, ext. 2258 (U.S.)
bioapps@brinkmann.com

Analytical Systems Lab:

800-645-3050, ext. 2421
apps@brinkmann.com

516-334-7500, ext. 2421 (U.S.)
apps@brinkmann.com

brinkmann
— an eppendorf company —