

Application Bulletin 48/4 e

Check of Silver, Platinum and Gold electrodes

Branch

General analytical laboratories

Keywords

Branch 1; check; test; silver electrode; gold electrode, platinum electrode; ring electrode; Titrode; rod electrode; metal electrode: potential measurement; titration; bivalentammetric titration; redox standard solution; ready-to-use redox standard; 6.2306.020

Summary

It is essential to know before starting the sample analysis if the electrode is in a good state or not. A well working electrode will increase the quality of your results, as the accuracy and precision will be increased. Furthermore, tedious error tracking can be omitted and no sample is wasted due to a defect or old electrode.

There exist several ways how to check metal electrodes, e.g., measurement of redox potentials, potentiometric titration or bivalentammetric titration. This bulletin describes the best methods for the various by Metrohm available metal electrodes.

Check of Pt and Au electrodes with redox standard solution

Instruments

- pH meter
- Stirrer
- Water bath

Electrodes

Combined Pt-ring electrode	6.0451.100 6.0451.300 6.00403.300
Combined Au-ring electrode	6.0452.100
Separate Pt-ring electrode*	6.0351.100
Separate Au-ring electrode*	6.0352.100
Pt rod electrode*	6.0331.000 6.1247.010 + 6.1241.040
Au rod electrode*	6.1248.030 + 6.1241.040

*for a separate metal electrode a reference electrode (e.g., 6.0750.100) with the reference electrolyte c(KCl) = 3 mol/L must be used.

Reagents

- Electrolyte solution c(KCl) = 3 mol/L: Metrohm No.: 6.2308.020
- Redox standard U = + 250 ± 5 mV: Metrohm No.: 6.2306.020

Or

- Ultra pure quinhydrone
- Buffer solution pH = 7.00: Metrohm No.: 6.2307.110
- and/or Buffer solution pH = 4.00: Metrohm No. 6.2307.100

Solutions

Quinhydrone redox standard	Buffer solution (pH 4.00 or 7.00) is mixed with ultrapure quinhydrone until a saturated buffer solution is obtained. Some excess of undissolved quinhydrone must remain.
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Sample preparation

No sample preparation is required.

Analysis

Check with ready-to-use redox standard solution (e.g., 6.2306.020)

The electrode is checked with a ready-to-use, certified redox standard solution (e.g., Metrohm No. 6.2306.020). For example, the Metrohm redox standard has a redox potential of $U = +250 \text{ mV} \pm 5 \text{ mV}$ at $20 \text{ }^\circ\text{C}$ against the reference system $\text{Ag}/\text{AgCl}/c(\text{KCl}) = 3 \text{ mol/L}$.

To perform the measurement, the redox standard is first tempered to $20 \text{ }^\circ\text{C}$ using a water bath. When $20 \text{ }^\circ\text{C}$ has been reached, the electrode to be tested is immersed in the solution and the potential of the solution is measured while gently stirring. The measured value should not deviate from the certified value of the standard by more than 5 mV. For example, the measured value of a certified redox standard with a potential of 253.5 mV should range between 248.5 and 258.5 mV.

Check with self-made redox standard solution

A saturated solution of quinhydrone in acidic or neutral (but not alkaline) buffer solution represents a well-defined redox system.

The electrode to be tested is immersed in the solution and the potential of the solution is measured while gently stirring. The obtained potential is then compared to the calculated theoretical values in Table 1. The deviation of the measured value to the theoretical value should not exceed 5 mV.

Table 1: Theoretical potential of a Pt- or Au-electrode in a buffer solution saturated with quinhydrone.

Metrohm pH buffer, saturated with quinhydrone	T / $^\circ\text{C}$	U / mV*
pH 4.00 (6.2307.100)	5	+ 273.2
	15	+ 264.9
	20	+ 260.8

pH 7.00 (6.2307.110)	25	+ 266.1
	30	+ 252.0
	5	+ 102.7
	15	+ 90.5
	20	+ 84.6
	25	+ 78.6
	30	+ 72.2

* the potentials given here are only correct for a reference system which is filled with $c(\text{KCl}) = 3 \text{ mol/L}$. Otherwise the potential of the reference system has to be taken into account.

Parameters

Mode	MEAS U
Signal drift	2 mV/min
Min. waiting time	0 s
Max. waiting time	52 s

Example determination

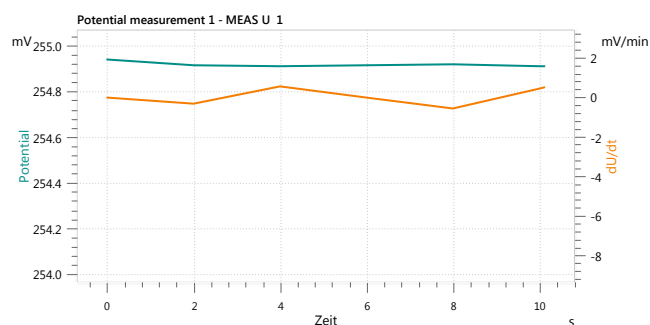


Fig. 1: Potential measurement performed with a Pt ring electrode using a standard redox solution.

Comments

- Only Pt- and Au-electrodes can be tested with the redox standard solutions due to oxidation of less noble metals such as silver.
- Only combined metal ring-electrodes or separate metal electrodes can be tested with the redox standard solution as a stable potential of an $\text{Ag}/\text{AgCl}/c(\text{KCl}) = 3 \text{ mol/L}$ reference is required.
- If deviations from the theoretical value exceed 5 mV, the potential of the reference electrode used, must be measured against a second reference electrode known to be reliable. The reference electrode being tested is in a good shape, if the measured potential is zero.
- A metal electrode that measures an incorrect potential is either defective or contaminated in some way. Directions for cleaning such electrodes are given in the corresponding leaflets or monographs.

Check of Au electrodes by titration

Instruments

- Titrator with MET mode
- 10 mL burette
- Stirrer

Electrodes

Combined Au-ring electrode	6.0452.100
Micro Au Titrode	6.0435.110 6.00435.120
Separate Au-ring electrode*	6.0352.100
Au rod electrode*	6.1248.030 + 6.1241.040

*for a separate metal electrode a reference electrode (e.g., 6.0750.100) with the reference electrolyte $c(\text{KCl}) = 3 \text{ mol/L}$ must be used.

Reagents

- Sodium thiosulfate, $\text{Na}_2\text{S}_2\text{O}_3$, p.a.
- Sulfuric acid $c(\text{H}_2\text{SO}_4) = 0.1 \text{ mol/L}$

Solutions

Iodine solution	$c(\text{I}_2) = 0.05 \text{ mol/L}$ If possible this solution should be bought from a supplier.
Titrant	$c(\text{Na}_2\text{S}_2\text{O}_3) = 0.1 \text{ mol/L}$ 15.8 g sodium thiosulfate is weighed into a 1000 mL volumetric flask. 400 mL deion. water is added and the sodium thiosulfate is dissolved. Afterwards the volumetric flask is filled up to the mark with deion. water.

Sample preparation

No sample preparation is required.

Analysis

A 100 mL beaker is filled with 50 mL deion. water. 1 mL sulfuric acid is added and then 2 mL $c(\text{I}_2) = 0.05 \text{ mol/L}$ is pipetted to the solution. The sample is titrated while stirring with $c(\text{Na}_2\text{S}_2\text{O}_3) = 0.1 \text{ mol/L}$ until after the equivalence point. Afterwards, the titration equipment is rinsed well with deion. water. It is recommended to run each test in triplicate.

Parameters

Mode	MET U
Signal drift	50 mV/min
Min. waiting time	0 s
Max. waiting time	26 s
Volume increment	0.1 mL
Dosing rate	Maximum
Stop volume	3 mL
Stop U	Off
Stop EP	9
EP recognition	All

Evaluation

There are several parameters that are evaluated for the electrode performance. Titration duration and titrant consumption until the equivalence point, reproducibility and the potential jump.

The potential jump is calculated as follows using fixed point evaluation:

$$\text{FP}\{1\} = V_{\text{EP}1} \times 0.9$$

$$\text{FP}\{2\} = V_{\text{EP}1} \times 1.1$$

$$\Delta U_{90-110\%} = \text{FP}\{2\} - \text{FP}\{1\}$$

$V_{\text{EP}1}$:	Titrant consumption of sample determination until first equivalence point in mL
$\text{FP}\{1\}$:	Potential in mV at 90% of the consumed titrant volume
$\text{FP}\{2\}$:	Potential in mV at 110% of the consumed titrant volume
$\Delta U_{90-110\%}$:	Potential difference between fix point 1 and 2

The following criteria must be met for an electrode passing the test:

- Only one EP should be found per titration.
- The relative standard deviation of the three repetitions of the titration should be less than 0.5% ($n = 3$).
- The titrant consumption until the equivalence point (EP) should be between 1.95 and 2.05 mL.
- The titration duration should be no longer than 160 s.
- The potential jump $\Delta U_{90-110\%}$ should be $\geq 70 \text{ mV}$.

Example determination

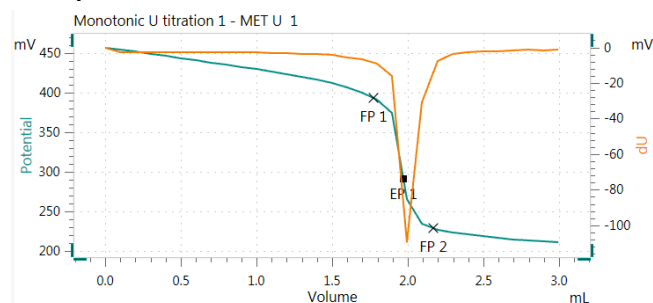


Fig. 2: Titration curve obtained for the check of an Au ring electrode.

Comments

- An electrode that measures an incorrect value is defective or contaminated in some way. Directions for cleaning of such electrodes are given in the corresponding instructions for use and monographs.
- If the titrant consumption until the equivalence point (EP) is not between 1.95 and 2.05 mL, please check first the buret if it is correctly dosing.

Check of Pt electrodes by titration

Instruments

- Titrator with DET mode
- 10 mL burette
- Stirrer

Electrodes

Pt Titrode	6.0431.100
	6.0471.300
	6.00401.300
Combined Pt ring electrode	6.0451.100
	6.0451.300
	6.00403.300
Micro Pt Titrode	6.0431.100
Separate Pt ring electrode*	6.0351.100
Pt rod electrode*	6.1248.000 + 6.1241.040
	6.0331.000

*for a separate metal electrode a reference electrode (e.g., 6.0750.100) with the reference electrolyte $c(\text{KCl}) = 3 \text{ mol/L}$ must be used.

Reagents

- Sodium thiosulfate, $\text{Na}_2\text{S}_2\text{O}_3$
- Sulfuric acid $c(\text{H}_2\text{SO}_4) = 0.1 \text{ mol/L}$

Solutions

Iodine solution	$c(\text{I}_2) = 0.05 \text{ mol/L}$ If possible this solution should be bought from a supplier.
Titrant	$c(\text{Na}_2\text{S}_2\text{O}_3) = 0.1 \text{ mol/L}$ 15.8 g sodium thiosulfate is weighed into a 1000 mL volumetric flask. 400 mL deion. water is added and the sodium thiosulfate is dissolved. Afterwards the volumetric flask is filled up to the mark with deion. water.

Sample preparation

No sample preparation is required.

Analysis

A 100 mL beaker is filled with 50 mL deion. water. 1 mL sulfuric acid is added and then 2 mL $c(I_2) = 0.05$ mol/L is pipetted to the solution. The sample is titrated while stirring with $c(Na_2S_2O_3) = 0.1$ mol/L until after the equivalence point. Afterwards, the titration equipment is rinsed well with deion. water. It is recommended to run each test in triplicate.

Parameters

Mode	DET U
Signal drift	50 mV/min
Min. waiting time	0 s
Max. waiting time	26 s
Meas. point density	4
Min. increment	10 μ L
Dosing rate	Maximum
Stop volume	3 mL
Stop U	Off
Stop EP	9
EP recognition	All

Evaluation

There are several parameters that are evaluated for the electrode performance. Titration duration and titrant consumption until the equivalence point, reproducibility and the potential jump.

The potential jump is calculated as follows using fixed point evaluation:

$$FP\{1\} = V_{EP1} \times 0.9$$

$$FP\{2\} = V_{EP1} \times 1.1$$

$$\Delta U_{90-110\%} = FP\{2\} - FP\{1\}$$

V_{EP1} :	Titrant consumption of sample determination until first equivalence point in mL
$FP\{1\}$:	Potential in mV at 90% of the consumed titrant volume
$FP\{2\}$:	Potential in mV at 110% of the consumed titrant volume
$\Delta U_{90-110\%}$:	Potential difference between fix point 1 and 2

The following criteria must be met for an electrode passing the test:

- Only one EP should be found per titration.
- The relative standard deviation of the three repetitions of the titration should be less than 0.5% ($n = 3$).
- The titrant consumption until the equivalence point (EP) should be between 1.95 and 2.05 mL.

- The titration duration should be no longer than 150 s.
- The potential jump $\Delta U_{90-110\%}$ should be ≥ 70 mV.

Example determinations

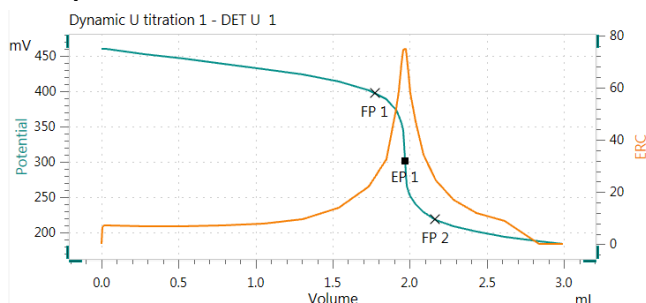


Fig. 3: Titration curve obtained for the check of a Pt ring electrode.

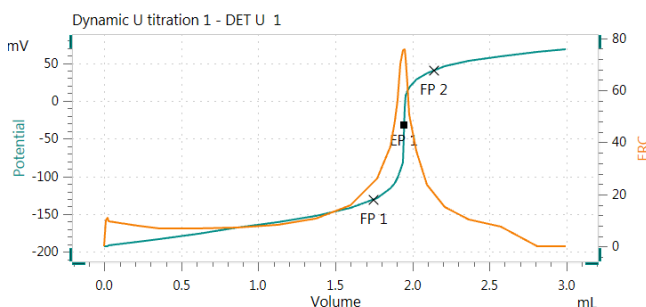


Fig. 4: Titration curve obtained for the check of a Pt Titrode.

Comments

- An electrode that measures an incorrect value is defective or contaminated in some way. Directions for cleaning of such electrodes are given in the corresponding instructions for use and monographs.
- If the titrant consumption until the equivalence point (EP) is not between 1.95 and 2.05 mL, please check first the buret if it is correctly dosing.

Check of Ag electrodes by titration

Instruments

- Titrator with DET mode
- 10 mL burette
- Stirrer

Electrodes

Ag Titrode	6.0430.100(S, Br, Cl)
	6.00430.100(S, Br, Cl)
	6.0470.300(S, Br)
	6.00470.300(S, Br)
	6.00400.300
	6.00404.300
Combined Ag ring electrode	6.0450.100(S, Br, Cl)
	6.00450.100(S, Br, Cl)
	6.0450.300
	6.00450.300
	6.00402.300
Micro Ag Titrode	6.0433.100
Separate Ag ring electrode*	6.0350.100(S)
	6.00350.100(S)
Ag rod electrode*	6.1248.010(S) +
	6.1241.040
	6.0331.010(S)

*for a separate metal electrode a reference electrode (e.g., 6.0750.100) with the reference electrolyte $c(\text{KNO}_3) = 1 \text{ mol/L}$ must be used.

Reagents

- Hydrochloric acid $c(\text{HCl}) = 0.1 \text{ mol/L}$

Solutions

Silver nitrate $c(\text{AgNO}_3) = 0.1 \text{ mol/L}$	$c(\text{AgNO}_3) = 0.1 \text{ mol/L}$ If possible, this solution should be bought from a supplier.
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Sample preparation

No sample preparation is required.

Analysis

A 100 mL beaker is filled with 50 mL deion. water. 2 mL $c(\text{HCl}) = 0.1 \text{ mol/L}$ is pipetted to the water. The sample is titrated while stirring with $c(\text{AgNO}_3) = 0.1 \text{ mol/L}$ until after the equivalence point. Afterwards, the titration equipment is rinsed well with deion. water. It is recommended to run each test in triplicate.

Parameters

Mode	DET U
Signal drift	50 mV/min
Min. waiting time	0 s
Max. waiting time	26 s
Meas. point density	4
Min. increment	10 μL
Dosing rate	Maximum
Stop volume	3 mL
Stop U	Off
Stop EP	9
EP recognition	All

Evaluation

There are several parameters that are evaluated for the electrode performance. Titration duration and titrant consumption until the equivalence point, reproducibility and the potential jump.

The potential jump is calculated as follows using fixed point evaluation:

$$\text{FP}\{1\} = V_{\text{EP}1} \times 0.9$$

$$\text{FP}\{2\} = V_{\text{EP}1} \times 1.1$$

$$\Delta U_{90-110\%} = \text{FP}\{2\} - \text{FP}\{1\}$$

$V_{\text{EP}1}$:	Titrant consumption of sample determination until first equivalence point in mL
$\text{FP}\{1\}$:	Potential in mV at 90% of the consumed titrant volume
$\text{FP}\{2\}$:	Potential in mV at 110% of the consumed titrant volume
$\Delta U_{90-110\%}$:	Potential difference between fix point 1 and 2

The following criteria must be met for an electrode passing the test:

- Only one EP should be found per titration.
- The relative standard deviation of the three repetitions of the titration should be less than 0.5% ($n = 3$).
- The titrant consumption until the equivalence point (EP) should be between 1.95 and 2.05.

- The titration duration should be no longer than 150 s.
- The potential jump $\Delta U_{90-110\%}$ should be ≥ 70 mV.

Example determinations

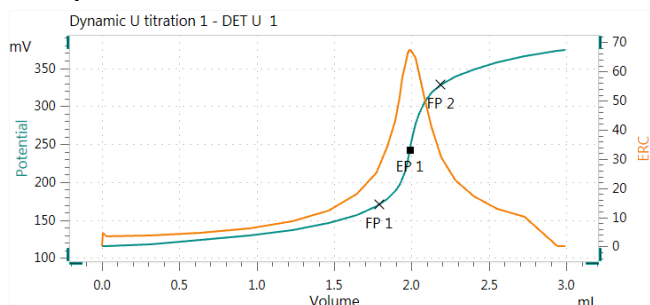


Fig. 5: Titration curve obtained for the check of an Ag ring electrode.

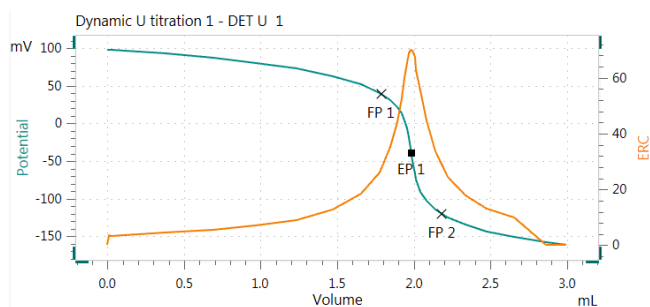


Fig. 6: Titration curve obtained for the check of an Ag Titrode.

Comments

- An electrode that measures an incorrect value is defective or contaminated in some way. Directions for cleaning of such electrodes are given in the corresponding instructions for use and monographs.
- If the titrant consumption until the equivalence point (EP) is not between 1.95 and 2.05 mL, please check first the buret if it is correctly dosing.
-

Check of metal electrodes by bivalentammetric titration

Instruments

- Titrator with MET Ipol mode
- 10 mL burette
- Stirrer

Electrodes

Double Pt sheet electrode	6.0309.100
Double Pt wire electrode	6.0338.100
	6.0340.000
	6.0341.100
Double Au ring electrode	6.00353.100

Reagents

- Sodium thiosulfate, $\text{Na}_2\text{S}_2\text{O}_3$
- Sulfuric acid $c(\text{H}_2\text{SO}_4) = 0.1$ mol/L

Solutions

Iodine solution	$c(\text{I}_2) = 0.05$ mol/L If possible this solution should be bought from a supplier.
Sodium thiosulfate solution	$c(\text{Na}_2\text{S}_2\text{O}_3) = 0.1$ mol/L 15.8 g sodium thiosulfate is weighed into a 1000 mL volumetric flask. 400 mL deion. water is added and the sodium thiosulfate is dissolved. Afterwards the volumetric flask is filled up to the mark with deion. water.

Sample preparation

No sample preparation is required.

Analysis

A 100 mL beaker is filled with 50 mL deion. water. 1 mL sulfuric acid is added and then 2 mL of $c(\text{I}_2) = 0.05$ mol/L is pipetted to the solution. The sample is titrated while stirring with $c(\text{Na}_2\text{S}_2\text{O}_3) = 0.1$ mol/L until after the equivalence point. Afterwards, the titration equipment is rinsed well with deion. water. It is recommended to run each test in triplicate.

Parameters

Mode	MET Ipol
I(pol)	1.0 μ A
Signal drift	50 mV/min
Min. waiting time	0 s
Max. waiting time	26 s
Volume increment	0.1 mL
Dosing rate	Maximum
Stop volume	3 mL
Stop U	Off
Stop EP	9
EP recognition	All

Evaluation

There are several parameters that are evaluated for the electrode performance. Titration duration and titrant consumption until the equivalence point, reproducibility and the potential jump.

The potential jump is calculated as follows using fixed point evaluation:

$$FP\{1\} = V_{EP1} \times 0.9$$

$$FP\{2\} = V_{EP1} \times 1.1$$

$$\Delta U_{90-110\%} = FP\{2\} - FP\{1\}$$

V_{EP1} : Titrant consumption of sample determination until first equivalence point in mL

$FP\{1\}$: Potential in mV at 90% of the consumed titrant volume

$FP\{2\}$: Potential in mV at 110% of the consumed titrant volume

$\Delta U_{90-110\%}$: Potential difference between fix point 1 and 2

The following criteria must be met for an electrode passing the test:

- Only one EP should be found per titration.
- The relative standard deviation of the three repetitions of the titration should be less than 0.5% ($n = 3$).
- The titrant consumption until the equivalence point (EP) should be between 1.90 and 2.10.
- The titration duration should be no longer than 200 s.
- The potential jump $\Delta U_{90-110\%}$ should be ≥ 100 mV.

Example determination

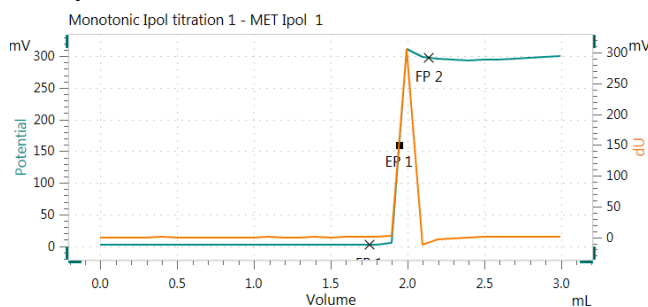


Fig. 7: Titration curve obtained for the check of a Pt wire electrode.

Comments

- An electrode that measures an incorrect value is defective or contaminated in some way. Directions for cleaning of such electrodes are given in the corresponding instructions for use and monographs.
- If the titrant consumption until the equivalence point (EP) is not between 1.95 and 2.05 mL, please check first the buret if it is correctly dosing.

References

- Leaflet for metal electrodes (8.109.8047)
- Monograph: Electrodes in Potentiometry (8.105.5013)
- Monograph: Practical Titration (8.029.5003)
- Metrohm Application Bulletin AB-025 Coatings on silver electrode

Date

December 2018

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