CEFRACOR
CENTRE FRANÇAIS DE L'ANTICORROSION

Committee for Cathodic Protection and Associated Coatings

Recommendations for the verification of reference electrodes

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1. SCOPE

This operating procedure describes the use of the test bench for reference electrodes or measurement electrodes.

2. FIELD OF APPLICATION

This recommendation applies to the conditions of use of electrode verification benches used in the field or electrochemical laboratories. They may be used for any type of electrode, for instance: Copper/Saturated copper sulfate (Cu/Saturated $CuSO_4$), Silver/Silver chloride/Saturated potassium chloride (Ag/AgCl/Saturated KCl) also referred to as Silver/Saturated silver chloride, Silver/Saturated silver chloride /sea water (or Chlorinated silver rod/sea water) et Saturated Calomel (Hg/Hg_2Cl_2/Saturated KCl).

It must be noted that, for environmental reasons, the calomel electrode is only used in laboratories because of the risk of rupture.

3. DEFINITIONS AND CLASSIFICATION OF THE ELECTRODES

- **Primary standard (reference) electrode** : standard hydrogen electrode (S.H.E.)

- **Secondary standard (reference) electrode**: reference electrode used in laboratories. It is used in the laboratory of the user, for the checking of field reference electrodes. It self is periodically calibrated with respect to the H.S.E. in an external notified laboratory. A validity period is given by the calibration certificate. This period depends on the conditions of use and storage of the secondary standard electrode.

- **Field reference electrode**: reference electrode used for the verification of measurement electrodes on site.[1]

- **Measurement electrode**: measurement electrode used in the field or in the laboratory in order to carry out a potential measurement by means of a voltmeter. This electrode may be a reference electrode (e.g. Cu/Saturated $CuSO_4$) or not (e.g. Ag/AgCl/sea water or Zn/ sea water).

- **M.A.E. (Maximum Allowable Error)**: this corresponds, during verification, to the maximum acceptable gap between the potential of the electrode to be checked and that of the secondary standard (reference) electrode.[2]

4. PRINCIPLE OF THE VERIFICATION OF AN ELECTRODE

The principle consists in measuring the potential difference between the electrode to be checked and an electrode taken as a reference and called "secondary standard (reference) electrode".

The secondary standard (reference) electrode used is a saturated calomel electrode for laboratory purpose. The Silver/Silver chloride/saturated potassium chloride laboratory electrode will not be used because of its always possible deviation of its potential caused by its exposure to the light.

Potential differences to be taken into account between the electrode to be checked ant the secondary standard (reference) electrode

The potential of the secondary standard electrode of saturated Calomel (E_1) is indicated on the calibration certificate delivered by the external notified body that has carried out the calibration (see **§ 7**).

The theoretical or calculated potentials of the $Cu/CuSO_4$, Ag/AgCl and Calomel electrodes are the following:

Type of electrode	Cu/Saturated $CuSO_4$	Ag/Saturated AgCl (laboratory type)	Ag/AgCl /sea water	Saturated Calomel
Potential [(a)] (at 25°C)	+ 316 mV [(b)]	+ 200 mV [(c)]	+ 250 mV [(c)]	+ 242 mV [(d)]

[(a)] With regard to the standard hydrogen reference electrode
[(b)] Calculated theoretical value
[(c)] Value taken from the annex A of standard EN 13509,
[(d)] Value indicated on the calibration certificate (see **§ 7**). The calculated theoretical value is equal to + 241,5 mV

For the Ag/AgCl/sea water electrode the correction of the potential shall be carried out according to the concentration of chloride.

[1] The field reference electrode may also be used for potential measurements in the field when a higher accuracy is required than that obtained with a measurement electrode. In this case it shall be recalibrated before it can be used again for verification.

[2] The notion of M.A.E. applies also to the verification, on site, of the measurement electrode with regard to the field reference electrode.

The potential difference that **theoretically** should be read on the voltmeter of the calibration bench is given by:

$$\Delta E = E_2 - E_1,$$

Where :

- E_1 : potential of the secondary standard reference electrode
- E_2 : the **theoretical** potential of the electrode to be checked.

4.1. Influence of the temperature during the verification

The temperature correction of a reference electrode is given by:

$$E = Eo + \frac{dE}{dt}(t - 25)$$

Where :

- E_O : is the potential of the electrode at 25 °C.

The data regarding the « dE / dt » ratio of the electrodes vary according to the sources. In a first stage, the values given in the following table can be adopted, knowing that contradictory data exist and which require an enhanced study:

TYPE OF ELECTRODE	**dE / dt, expressed in « mV / °C »**
Saturated Calomel	- 0,76
Copper/ saturated copper sulfate	+ 0,90
Silver/Silver chloride (Saturated KCl)	- 0,65
Silver/Saturated silver chloride /sea water	- 0,33

Note : For information, a pipeline measured at -900 mV with regard to a Cu/ saturated $CuSO_4$ electrode at 25 °C will present a potential of -909 mV with regard to the same electrode when the latter is at a temperature of 35 °C (supposed that the pipeline is at a constant temperature).

Application to the verification of a $Cu/CuSO_4$ electrode with regard to the saturated calomel electrode

The secondary standard electrode (saturated calomel) and the $Cu/CuSO_4$ electrode to be verified undergo each a deviation in case of variation of the temperature.

In practice, it is not mandatory to maintain the verification bench at a constant temperature. It is however recommended to bring the electrode to be checked at the same temperature as the test bench and to record the temperature (ambient air or solution of the test bath) at the moment of the measurement in order to calculate the temperature correction.

4.1.1. Calculation of the accuracy of the measurement chain

The accuracy of the measurement chain depends on:

- the quality of the secondary standard electrode (saturated calomel) of which the potential is given on the calibration certificate (in § 7 at : ± 3 mV)
- the accuracy of the voltmeter used for the measurement, which is (see § 6.2) ±0,1 % plus ±1 digit, or for the range « ±200 mV » : ((0,1 % x74) + 0,1) = ± 0,17 mV
- the temperature measurement error which is ±1°C, leading to an error of ± 1.66mV

The **accuracy of the measurement chain, at 25 °C,** is equal to: 3 + 0,17 + 1.66= **± 4.8 mV**

5. MAXIMUM ALLOWABLE ERROR (M.A.E.)

The maximum allowable error taken into account for the verification of an electrode depends on the type of the electrode considered. The closer this electrode is ranked to the secondary standard electrode, the smaller is the M.A.E.

In practice the value of the M.A.E. is determined by the user depending on the experience feedback and the written procedures he follows.

The measurement electrode used shall have an M.A.E. smaller or equal to 20 mV after checking on site of the measurement electrode with regard to the field reference electrode.

In order to achieve this result, the M.A.E.'s tested on the verification bench can be the following:

± 5 mV for the « field reference" electrode

± 15 mV for the "measurement" electrode

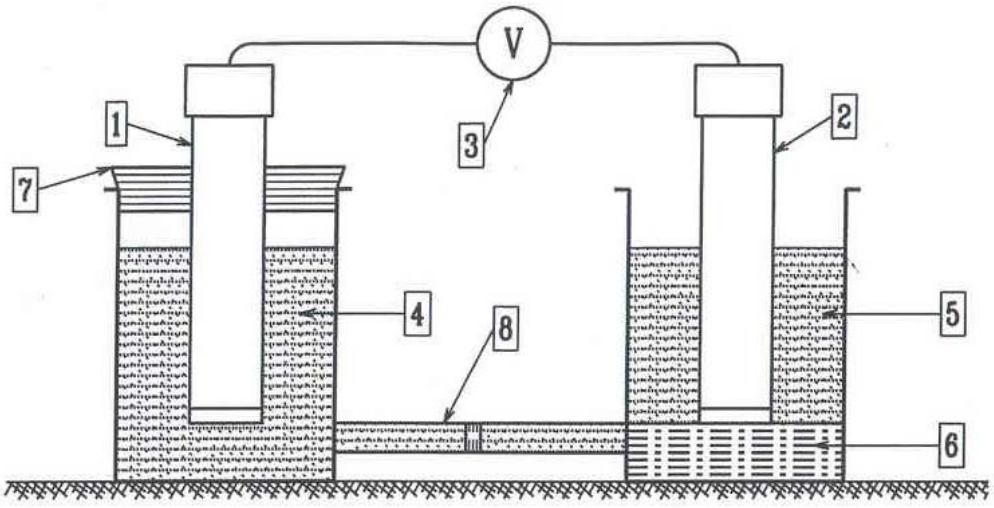
It must be noted that:

- The M.A.E of the electrode comprises the accuracy of the measurement device,
- For the measurements of potential gradients it is recommended to use matching electrodes (having similar M.A.E.'s).

6. ELECTRODE VERIFICATION BENCH

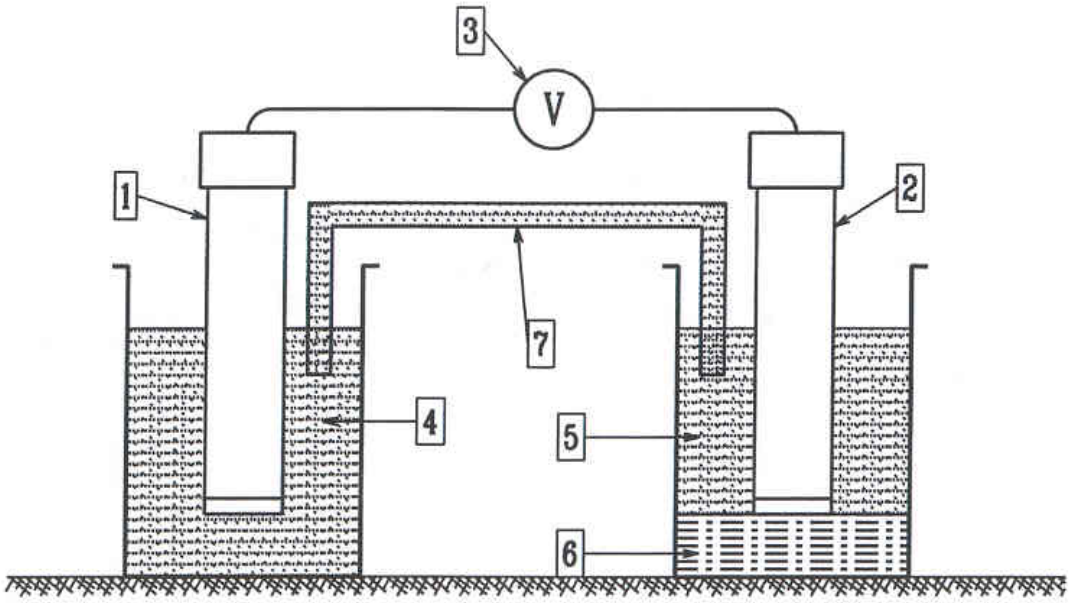
6.1. Schematics of the principles

Three typical schematics of verification benches are proposed.



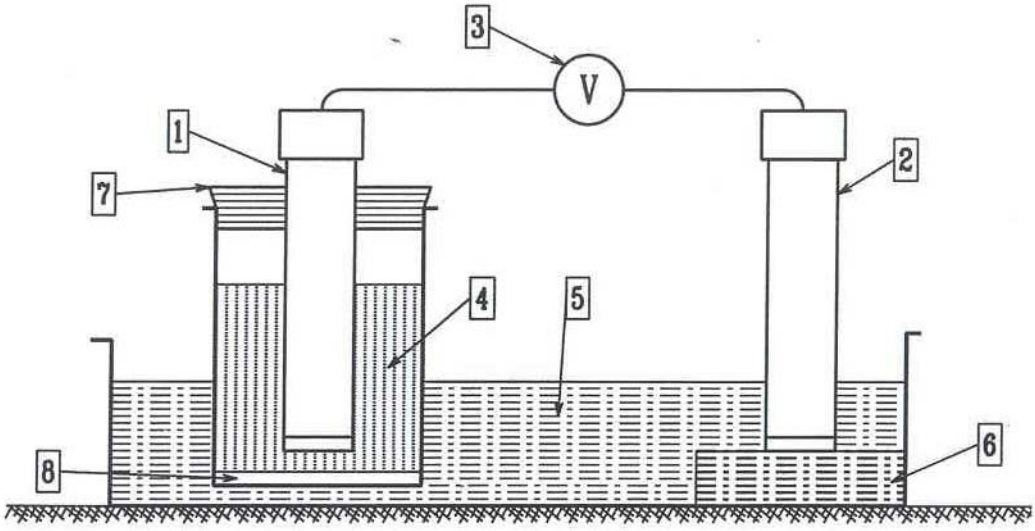
Typical schematic n° 1

1: Secondary standard electrode (saturated calomel), E1
2: Electrode to be verified, E2
3: Voltmeter (direct current position)
4: Saturated solution of Potassium Chloride (KCl)
5: Saline solution (KCl or $CuSO_4$ according to the type of electrode)
6: Sponge
7: Cap
8: Electrolytic bridge with sintered glass separation



Typical schematic n° 2

1: Secondary standard electrode (saturated calomel), E1
2: Electrode to be verified, E2
3: Voltmeter (direct current position)
4: Saturated solution of Potassium Chloride (KCl)
5: Saline solution (KCl or $CuSO_4$ according to the type of electrode)
6: Sponge
7: Removable electrolytic bridge



Typical schematic n° 3

1: Secondary standard electrode (saturated calomel), E1
2: Electrode to be verified, E2
3: Voltmeter (direct current position)
4: Saturated solution of Potassium Chloride (KCl)
5: Saline solution (KCl or $CuSO_4$ according to the type of electrode)
6: Sponge
7: Cap
8: Electrolytic junction

6.2. Designation of the equipment

- Set of glassware :

Typical schematic n° 1

- It comprises two glasses connected by a permanent electrolytic bridge. The separation of the electrolytes of each glass is achieved by a sintered glass of a porosity equal to 5.

Typical schematic n° 2

- It comprises two glasses connected by a removable electrolytic bridge.

Typical schematic n° 3

- It comprises a single receptacle (e.g. crystallizer). The secondary standard reference electrode is protected against contamination by an electrolytic junction.

- Measurement device:
  - A laboratory type voltmeter with a high impedance (exceeding 100 MΩ), is set in the position ‘’VOLT direct current”. This voltmeter is every year calibrated by an external notified laboratory.

  - The following characteristics are given as an example :
    - Positions 0,2 V et 2 V with an input impedance of 10^{12} Ω
    - Range 0 ± 200,0 mV : resolution of 0,1 mV
    - Range 0 ± 2,0 V : resolution of 1 mV
    - Accuracy : ± 0,1 % ± 1 digit in case of a digital voltmeter

- Secondary standard electrode:
  - The saturated Calomel electrode(Hg/Hg_2Cl_2/saturated KCl) must be immerged for at least 35 millimeters.
  This electrode must never be used for another purpose than the verification bench.

- Connection cables :
  - Two supple liaison cables (HO7VK type) with suitable connectors are used to connect the secondary standard reference electrode as well as the electrode to be tested to the voltmeter.

- Miscellaneous accessories :
  - A natural sponge may be used to damp the shocks while handling the electrode to be verified.
  - It is recommended to install a lid on the receptacles in order to avoid the evaporation of the electrolyte and maintain the levels.

- Thermometer
  - It is recommended to use a thermometer having a read-out accuracy of ± 1°C.

6.3. Conservation of the secondary standard electrode

• As it involves a saturated Calomel electrode, the secondary standard electrode with the liquid junction, should be stored permanently immerged in a saturated solution of potassium chloride (KCl).

• Never store the secondary standard electrode at temperatures above 40°C, or below 10°C. Avoid abrupt variations of the temperature.

• Make sure that the filling and storage solutions are saturated by checking the permanent presence of some KCl crystals (in the electrode and in the glass).

• If necessary periodically adjust the level of the filling and storage solutions.

6.4. Preparation and conservation of the saturated potassium chloride solution

• *saturated potassium chloride solution (for 1 liter of solution) :*

- add approximately 400 g of potassium chloride ("pure "quality) to 1 liter of demineralized water,
- shake energetically,

- it is possible to warm up the water (to approximately 60°C) in order to speed-up the solution of the crystals but, in this case, one shall ensure that the solution has cooled down to ambient temperature before its use,
- an excess of de potassium chloride crystals must remain in the solution, otherwise 50 g shall be added.

• *Conservation of the solution:*

It shall be stored in a tightly closed container and shielded from the light. The container shall be labeled (name of the product, concentration, date of preparation).

The maximum duration of conservation of this solution is one year.

6.5. Operating procedure for verification of an electrode

6.5.1. Preliminary verifications

- *Verification of the saline solutions :*

• The renewal of the saline solutions shall be carried out, as a minimum, at each change of the secondary standard reference electrode, and at least once per year, which corresponds to the time of conservation of the solution.
More over, the electrolyte shall be replaced at any modification of coloration.

Note: During the operation of replacement of the saline solution all care shall be taken to avoid deterioration of the secondary standard electrode.

- *Check of the saturation and the level of the filling solution (saturated Potassium Chloride) of the secondary standard electrode (saturated calomel) :*

• Make sure that the filling solution is saturated by checking the permanent presence of some potassium chloride crystals (KCl).

• Adjust periodically the level of the electrolyte filling solution with a saturated solution of potassium chloride (saturated KCl).

• Make sure of the absence of air bubbles in the glass body of the electrode.

6.5.2. Verification operating procedure

• If necessary, clean the electrode to be checked with city water and a brush in order to avoid any pollution of the electrolyte solution.

• Connect the electric lead of the secondary standard electrode to the common terminal of the voltmeter.

• connect the electrode to be verified to the positive terminal (red) of the voltmeter and place it in its receptacle. It shall be immerged for at least 35 millimeters.

• Switch-on the voltmeter and select the "DC Voltage" mode.

• Await stabilization of the display of the voltmeter.

• Read and register the displayed value of the voltmeter.

• Rinse the wood of the electrode in a receptacle filled with demineralized water.

6.5.3. Expression of the result

The obtained results are recorded by writing on the compliance certificate.

It is recommended to file this document for a duration of two years.

6.6. Labeling of the electrodes

Each electrode shall be suitably labeled.

For the "field reference" electrode, the following label is attached to the electrode:

CONTROL

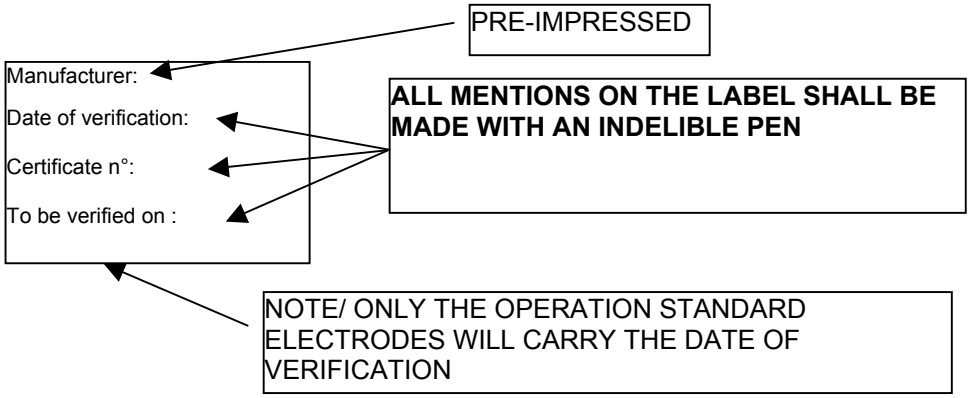
For the "measurement" electrode, the following label is attached to the electrode, however this is not mandatory:

MEASURE

If the M.A.E. of the "measurement" electrode is higher than the expected value, the following label is attached to the electrode:

DISCARD

The following label is attached to the electrode:



Note: The metrological standard EN ISO 10012 (September 2003) impose to seal the standard electrode in order to avoid it to be opened between two verifications.
The use of a tamper proof sticker between the lid and the body of the electrode is recommended.

7. MODEL OF A CALIBRATION CERTIFICATE DELIVERED BY A NOTIFIED BODY

Certificat d'étalonnage
XG2002-081

Certificat délivré à :

Date d'étalonnage : 06 mars 2002
Prochain étalonnage proposé : Septembre 2002

Electrode de référence type : TR100 (Electrode calomel, remplissage KCl saturé)
n° de série : 040-11-048
Fabricant :

Chaîne de raccordement
Système d'électrode à hydrogène :

Electrode étalon de travail : TR100 n° 448-18-022
directement raccordée à l'électrode à hydrogène.
pH-mètre : LPH530T n° 625R01N001 étalonné électriquement,
certificat XS2001-173
Sonde de température : T201 n° 936-12-049 étalonnée, certificat XS2001-171
Solution de mesure : Solution saturée de KCl, ref. KS100 lot n° A00361.

Etalonnage
Potentiel à 25 ±0.1 °C par rapport
à l'électrode à hydrogène : **242.4 ± 3.0 mV (k = 2)** hors potentiel de jonction
cette incertitude élargie inclut toutes les incertitudes types liées au processus d'étalonnage.

Responsable métrologie : Signature

Opérateur : Signature

8. STATEMENT OF COMPLIANCE OF A VERIFIED ELECTRODE

The statement of compliance comprises as a minimum:

- Identification of the electrode to be verified :
  - Identification number
  - Type of electrode
  - Manufacturer

- Verification procedure data:
  - Implemented operating procedure
  - Date of the verification operation
  - Periodicity of the verification
  - Ambient temperature

- Identification of the secondary standard electrode
  - Identification number of the secondary standard electrode
  - Calibration certificate number of the secondary standard electrode
  - Date of the calibration operation of the secondary standard electrode
  - Periodicity of calibration of the secondary standard electrode

- Assessment of compliance of the electrode to be verified :
  - Compliant :
    - ❑ YES
    - ❑ NO
  - Measured value at t°C
  - Corrected value at 25°C
  - Inferred error with respect to the calculated theoretical value (measured value – calculated theoretical value) at 25°C
  - Maximum Allowable Error
  - Accuracy of the measurement chain
  - Decision :
    - ❑ Approved for service
    - ❑ Approved for service with restriction
    - ❑ Repair
    - ❑ Downgraded
    - ❑ Discarded

- Name and signature of the operator

9. EXAMPLE OF POTENTIAL VARIATION OF A COPPER/COPPER SULFATE ELECTRODE

(WITH RESPECT TO THE STANDARD HYDRIOGEN REFERENCE ELECTRODE) AT APPROXIMATELY 20°C, WITHOUT TEMPERATURE CORRECTION