



Designation: G220 – 20

Standard Practice for Replacing Saturated Calomel Reference Electrode (SCE) for Measuring Electrode Potentials¹

This standard is issued under the fixed designation G220; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This practice provides the steps necessary to prepare revisions to standards that specify the saturated calomel reference electrode (SCE) for measuring or controlling electrode potentials.

1.2 The SCE contains mercury and, as a result, it may not be available in locations where mercury has been banned. This practice covers the selection and use of an alternative reference electrode.

1.3 In test methods where the SCE is specified, it will be necessary to develop a new precision statement using the alternative reference electrode.

1.4 This practice will not apply to electrometric pH determinations where the SCE has been used. (Electrometric pH measurement is an analytical method that is covered elsewhere.)

1.5 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.6 **Warning**—Mercury has been designated by many regulatory agencies as a hazardous substance that can cause serious medical issues. Mercury, or its vapor, has been demonstrated to be hazardous to health and corrosive to materials. Use caution when handling mercury and mercury-containing products. See the applicable product Safety Data Sheet (SDS) for additional information. The potential exists that selling mercury or mercury-containing products, or both, is prohibited by local or national law. Users must determine legality of sales in their location.

1.7 This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety, health, and environmental practices and determine the applicability of regulatory limitations prior to use.

¹ This practice is under the jurisdiction of ASTM Committee G01 on Corrosion of Metals and is the direct responsibility of Subcommittee G01.11 on Electrochemical Measurements in Corrosion Testing.

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1.8 This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.

2. Referenced Documents

2.1 *ASTM Standards*:²

E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method

G3 Practice for Conventions Applicable to Electrochemical Measurements in Corrosion Testing

G215 Guide for Electrode Potential Measurement

2.2 *NACE/ASTM Standard*:²

G193 Terminology and Acronyms Relating to Corrosion

3. Terminology

3.1 *Definitions*—For definitions of terms used in this practice, see NACE/ASTM Terminology G193.

4. Summary of Practice

4.1 In test methods and practices where the SCE is specified for electrode potential measurement or control, the KCl saturated silver/silver-chloride reference electrode, Ag/AgCl (sat KCl), shall be used as an acceptable alternative.

4.2 If the Ag/AgCl (sat KCl) reference electrode is used in a test method, all previous electrode potential values referred to the SCE can be converted to the Ag/AgCl (sat KCl) scale by adding 0.045 V to the SCE values.

4.3 New precision statements are required for test methods where the alternative reference electrode, Ag/AgCl (sat KCl), is now specified. The interlaboratory test program and analysis of results will be required within 5 years of completing the standard incorporating the new Ag/AgCl (sat KCl) reference electrode requirement.

² For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

5. Significance and Use

5.1 Electrode potential measurement is an essential step in many electrochemical corrosion test methods and practices.

5.2 The SCE has been widely specified for laboratory tests because it is reliable, accurate, simple to use, and it has been readily available. However, because this device contains mercury, and mercury has recently been banned by some governmental agencies, it may not be available in locations where mercury is banned. As a result, test methods using the SCE may not be possible in locations where mercury is banned. Therefore, it is necessary to establish an alternative reference electrode for these standards.

5.3 The KCl saturated, silver/silver chloride reference electrode, Ag/AgCl (sat KCl), is a satisfactory replacement for the SCE in laboratory test methods and practices. This reference electrode should provide comparable performance and accuracy to the SCE.

5.4 It will be necessary to carry out interlaboratory test programs for each test method where the Ag/AgCl (sat KCl) electrode is specified to replace the SCE, in order to develop the precision of the method using the new reference electrode.

NOTE 1—In cases where a test method specifies that either the SCE or the Ag/AgCl (sat KCl) reference electrode may be used, and the ILS program used to develop the precision of the method included significant numbers of participants using each of these reference electrodes, no additional testing is required.

6. Comparison of Ag/AgCl (sat KCl) Electrode to SCE

6.1 The SCE has been the most widely used reference electrode for laboratory corrosion testing where it has been necessary to measure or control the specimen electrode potential. This reference electrode was standardized for use in pH meters before electrochemical corrosion testing became widely practiced. As a result, it was both commercially available and sufficiently accurate for corrosion testing. See Practice G3 and Guide G215 for more information on the care and use of these devices.

6.2 The silver/silver chloride reference electrodes have been used in electrochemical measurement systems for many years.³ Traditionally these reference electrodes were used with either a 1.0 M KCl or a 0.1 M KCl fill solution. The 0.1 M solution had a higher silver ion content that made it less susceptible to polarization errors from measurement devices. The fixed concentration fill solution does not vary in concentration with temperature changes as does a KCl saturated solution, so its potential variation with temperature only reflects the characteristics of the silver/silver ion system.

6.3 The KCl saturated reference electrodes require that KCl crystals be present in the fill chamber to assure that the solution is saturated. This requirement also allows the fill solution to remain saturated in spite of minor infusion of water from the test environment. The saturated solution also minimizes the infusion of contaminating ions from the test environment through the liquid junction.

6.4 The issue of polarization of the reference electrode from the measuring instrument is seldom a concern with modern electronics.

6.5 The fact that test methods and practices specify the SCE, and these standards have acceptable precision and stability shows that the saturated KCl fill solution is not an issue for these standards. Therefore, this solution should be adequate for the silver/silver chloride reference electrode.

6.6 Although silver ions are problematic in many environments, the concentration of silver ions in a saturated KCl solution is less than 10^{-10} M at ambient temperature. Contamination of the test environment from leakage from an Ag/AgCl (sat KCl) liquid junction with silver ions is unlikely to ever be a problem. The concentration of mercurous ions (Hg_2^{++}) in a saturated KCl solution is less than 10^{-18} M at ambient temperature, also indicating that the SCE does not cause mercury contamination of test environments. See Appendix X1 for the details on the calculations of these concentrations.

6.7 Although the silver/silver chloride electrodes have been used for many years, the methods of manufacture have not been standardized. As a result, there may be variations in the standard potential resulting from different manufacturing methods.

7. Procedure

7.1 Test methods and practices that specify the SCE shall be revised to include the Ag/AgCl (sat KCl) as an alternative reference electrode. All previous electrode potential values referred to the SCE can be converted to the Ag/AgCl (sat KCl) scale by adding 0.045 V to the SCE values. Appendix X2 shows the derivation of this change.

7.2 An interlaboratory test program shall be set up and carried out to determine the precision of results using the new Ag/AgCl (sat KCl) reference electrode. The interlaboratory test program shall follow the guidance of Practice E691, and must be completed within 5 years of having the revision accepted as a standard. A new precision statement shall be written based on the results of the interlaboratory test program.

8. Verification of Ag/AgCl (sat KCl) Electrode

8.1 The procedures described in Guide G215 shall be used to verify that the Ag/AgCl (sat KCl) reference electrodes are operating properly. In cases where testing laboratories have established protocols for validating reference electrodes, these procedures apply to the Ag/AgCl (sat KCl) reference electrodes. In cases where an SCE master electrode is present, this electrode can be used to check Ag/AgCl (sat KCl) electrodes. In this case, the Ag/AgCl (sat KCl) electrodes should show a -0.045 V, ± 0.005 V reading when the SCE is connected to the positive terminal of the potentiometer or electrometer.

9. Maintenance of Ag/AgCl (sat KCl) Electrode

9.1 The guidance provided in Guide G215 for maintenance of reference electrodes shall be followed.

³Ives, David J. G., and Janz, George J., *Reference Electrodes, Theory and Practice*, Academic Press, New York, NY, 1961.