4.2 Silver/Silver Chloride (Ag/AgCl) Reference Electrodes

BAS offers several models of Ag/AgCl reference electrodes (Figure 4.2). Each reference electrode is individually inspected and tested for adherence to an acceptable range relative to a standard calomel electrode.

Figure 4.2.

The model RE-6 (MF-2078) is the shortest (3 cm), and fits into the thin-layer flowcell used in current model LCEC detectors. It features glass-body construction with a porous ceramic frit at the solution interface. The filling solution is 3 M NaCl gel that has been saturated with AgCl; the gel is semi-solid and will appear cloudy with occasional particles.

The model RE-5b (MF-2052 or MF-2079) has the same diameter as the RE-6, but uses a porous Vycor frit at the solution interface. The filling solution is aqueous 3 M NaCl that has been saturated with AgCl.

Use of a reference electrode with bubbles lodged in the tip may prevent electrical contact with the sample solution and cause damage to the working electrode. Bubbles can be dislodged by holding the top of the electrode with one hand and tapping the electrode near the Vycor tip with the other hand until the bubbles rise to the top.
Removing the Sheath

Every Ag/AgCl reference electrode is shipped with a colored plastic sheath that covers the porous tip and retards drying. IMMEDIATELY UPON RECEIPT, REMOVE THIS SHEATH BY ROLLING IT DOWN FROM THE GLASS BODY TO THE TIP (see Figure 4.3). The plastic will roll down and slide off the end of the electrode. Do not tug at the sheath or hold the electrode by the pin while you are doing this. If you have trouble removing the sheath, make a small cut at the upper edge of the sheath using small scissors, and try again.

**CAUTION:** Be extremely careful when removing the plastic sheath from the RE-5b reference electrode. The Vycor frit is attached to the glass body with heat-shrink Teflon, which can be pulled off. The best method is to cut the length of the plastic sheath with scissors. A scalpel may be used, but there is greater chance of damaging the heat-shrink tubing.

ONCE THE SHEATH IS REMOVED, STORE THE ELECTRODE TIP IN 3 M NaCl AS SHOWN IN FIGURE 4.4. The Ag/AgCl reference electrodes are easily ruined by drying. Keep the tips wetted at all times and store in 3 M NaCl when not in use. A reference electrode storage vial is available from BAS (MR-5275).

Figure 4.3. Removing the RE-6 reference electrode’s colored plastic sheath.
**Storing Ag/AgCl Reference Electrodes**

Be sure that you check the electrodes periodically and replace the solution in the storage vessel with fresh 3 M NaCl to keep the tips wet. **DO NOT ENTIRELY IMMERSE REFERENCE ELECTRODES.** Keep the connecting pins dry, or they will corrode and contaminate the reference electrode.

Reference electrodes will naturally change with use due to the transport of ions and solvent across the junction (ceramic or Vycor tip). The rate of change is a function of the difference in composition between the sample solution (i.e., mobile phase in liquid chromatography) and the filling solution (3 M NaCl gel). In LCEC usage, it is advisable to change to a new reference electrode frequently, at least once per month. [See Current Separations Vol. 11 No. 1/2 for more about the role of a reference electrode.] Storing the reference electrode in 3 M NaCl between experiments will extend its lifetime. In spite of all attempts to extend their lifetimes, reference electrodes are still expendable items, so be certain to have spares on hand as needed.

**Testing the Viability of Ag/AgCl Reference Electrodes**

If you are concerned about the viability of a particular Ag/AgCl reference electrode, you can test it using a simple voltmeter, additional reference electrodes of the same type (or a calomel reference electrode), and a small beaker of 3 M NaCl (see Figure 4.5). Read the potential difference between the electrodes on the voltmeter. Ideally the difference between two electrodes of the same type would be zero. However, in actual practice there is commonly some variation.
If the two electrodes are of the same type (e.g., Ag/AgCl vs. Ag/AgCl, or calomel vs. calomel) the meter should read 0 ± 20 mV. If your reading for any pair of electrodes is significantly different, you should have another electrode of the same type handy to help distinguish which of the two is bad. When comparing an Ag/AgCl reference electrode to a calomel electrode, make the calomel the black (negative) input on the voltmeter. The meter should then read –35 ± 20 mV. A single-probe combination pH electrode is not suitable for this test.

Figure 4.5. Testing the viability of Ag/AgCl reference electrodes.

Rotation of Ag/AgCl Reference Electrodes

We recommend that three reference electrodes be rotated in your LCEC system. Keep one electrode in your system for about two weeks. Turn the detector to STANDBY before removing and replacing the electrode. (Failure to do so can ruin a glassy carbon working electrode.) Rinse excess 3 M NaCl storage solution off the replacement reference electrode before inserting it into the cell. Replace the bushing and O-ring if they show signs of wear. Turn the cell on. Place the first electrode into the storage container. In another two weeks, replace the reference electrode with the third reference electrode provided in the kit. By rotating the three reference electrodes provided with your detector on a continuous basis, you can maximize their lifetimes. Depending on the mobile phase conditions and detector use, the reference electrodes can last from 6–12 months. When you replace reference electrodes, replace all three of them at the same time.