# From Christmas Ornament to Glass Electrode


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Recent papers in *this Journal* show that it is possible to allow freshman to work with potentiometric techniques without spending much money. Ahn et al. (*1*) describe a method of making an Ag | AgCl reference electrode. Sevilla, III, et al. (*2*) suggest a more inexpensive option: a Cu | $Cu^{2+}$ reference electrode. Instead of commercial pH meters, one can use a low cost apparatus as suggested by Sevilla, III, et al. (*2*), Harris and Harris (*3*), and Paris et al. (*4*). However, pH measurements require a costly and fragile accessory: the glass electrode. Optionally, the Sb | $Sb_2O_3$ electrode may be used (*2*). Nevertheless, the glass electrode remains the more extensively used pH electrode.

A glass electrode is difficult to make because the wall of the sensing glass bulb must be very thin, and glass of special composition is needed. A thin wall is required due to the exceedingly high electrical resistance of the glass membrane. Special composition is needed to lower the resistance and to provide linear response of the electric potential at high pH values. For many undergraduate experiments, the alkaline error may be disregarded. Thus, soda lime glass may be used. However, the wall must be kept as thin as possible.

Although the glass bulb may be made by a skilled glazier, we choose a more impressive and simple way: Make the glass electrode from a Christmas-tree ornamental ball. Balls of alkaline glass with wall thickness of about 0.2 mm were suitable. The potential of the glass electrode with this ball was measured against a reference electrode with the help of a simple impedance-matching circuit and a digital multimeter. The arrangement was evaluated and found appropriate for acid–base titrations.

## Construction of the Glass Electrode

Balls of several sizes can be used. In our country, the best choice is a ball with 2.5-cm diameter that has a wall thickness of about 0.2 mm. Silver balls are preferred because they do not have an external layer of varnish. Nevertheless, the colored layer can be removed with acetone or other organic solvent. The inner silver layer is removed with 1:1 $HNO_3$:$H_2O$.

To degrease and form a hydrated gel layer on the walls, the ball is filled with and immersed in 5 M NaOH solution and boiled for 30 min. The ball is then drained and immersed in 0.1 M HCl for 5 min, followed by a thorough rinse with distilled water. An 8-cm section of 6.5-mm-o.d. glass tubing is fixed to the neck of the ball with silicone glue as shown in Figure 1. The internal Ag | AgCl reference electrode is made as described in ref *1*. The inner solution is saturated with KCl and AgCl. The silver wire is fixed to the glass tubing with poly(tetrafluoroethylene) tape.

Before using, the electrode must be conditioned by alternate immersions in 0.1 M HCl and 0.1 M NaOH solutions for 2 h in each step. Conditioning is finished when the ball has a visible, uniform liquid coating on the external surface. When not in use, the electrode must be kept in water or acidic buffer.

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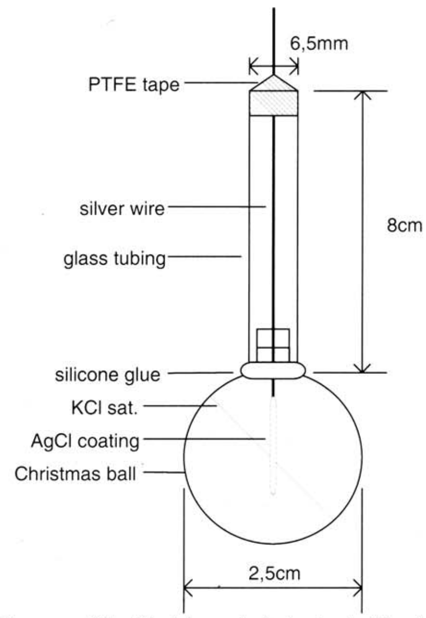


Figure 1. Diagram of the Christmas-ball electrode. The inner solution is saturated with KCl and AgCl.

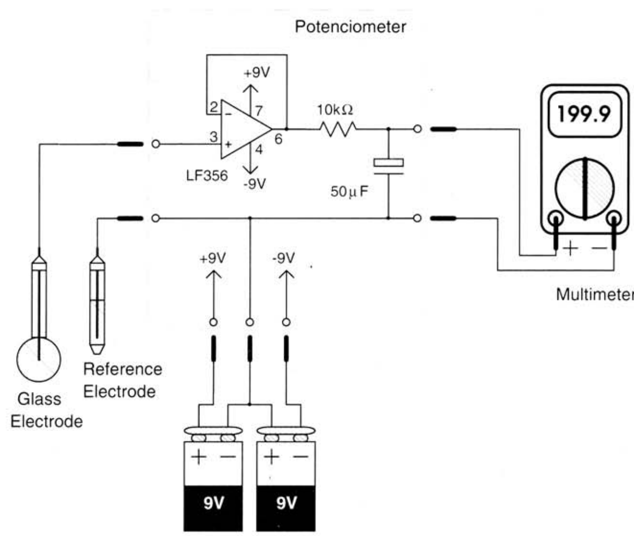


Figure 2. Diagram of the electronic circuit of the potentiometer and the arrangement for measurements with a digital multimeter.

## Construction of the Potentiometer

Due to the high impedance of the electrode, the potential cannot be accurately measured by a conventional multimeter. To avoid the use of an expensive potentiometer or a pH meter, a simple circuit was constructed with an LF356 operational amplifier arranged in a voltage-follower mode. Figure 2 shows the circuit that is powered by two 9-V batteries. The resistor and capacitor at the output of the operational amplifier constitute a noise filter, which improves the stability of the readings. A multimeter with 1-

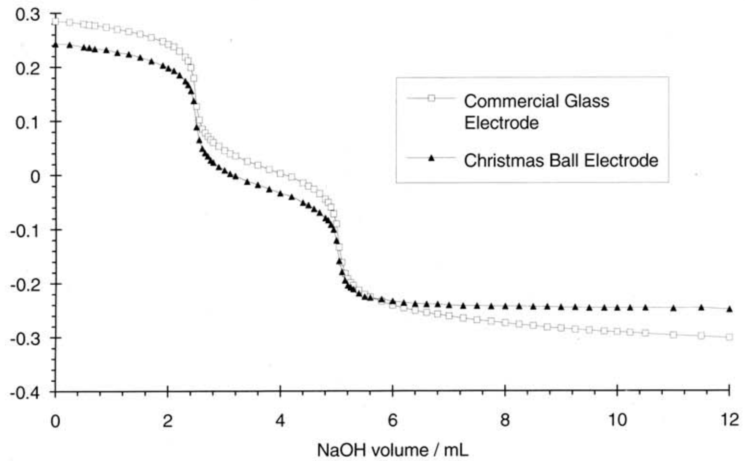


Figure 3. Potentiometric titration curves of 50 mL of about 0.05 M $H_3PO_4$ with 1.006 M NaOH using Christmas-ball and commercial-glass electrode (Metrohm). In both cases, a commercial Ag|AgCl reference electrode (Metrohm) was used.

or 2-V dc range is used to measure the electromotive force of the cell. The external reference electrode may be a commercial one or that cited in ref *1*.

## Evaluating the Glass Electrode

The tape on the top of the electrode does not make a good seal, which may lead to changes in the concentration of the internal solution. However, the inner pH is stable enough to allow many hours of use after calibration. Response time is slightly greater than for good commercial glass electrodes. However, for many applications, such as titrations, this is not a critical problem.

Figure 3 shows potentiometric titration curves of 50 mL of about 0.05 M $H_3PO_4$ with 1.006 M NaOH solution using Christmas-ball and commercial-glass electrodes. In both cases, the same Ag | AgCl reference electrode was used to facilitate comparison of the glass electrodes. The stoichiometric points for the first inflection are 2.47 and 2.47 mL; for the second inflection they are 5.03 and 5.02 mL for commercial and Christmas-ball electrodes. These results are obtained from the first derivative, and the estimated error is 0.03 mL. The alkaline error becomes evident after the second inflection. As expected, even with the commercial-glass electrode, neutralization of the third hydrogen is not noticed.

The composition and thickness of the balls change greatly from one manufacturer to another, but because the price is low, several balls can be tested. The silicone glue, used to attach the ball to the glass tubing, should not be exposed to hot, strongly alkaline, strongly acidic, or oxidizing media.

## Conclusion

The glass electrode described cannot substitute for commercial electrodes in all experiments. Drawbacks include great size, fragility, alkaline error, and slow response time. However, the low cost allows the student to do many experiments. For example, to carry out titrations, check its response in different buffers, exchange inner solution or reference electrode, or even break one! This is a helpful way to demystify the most common and frequently misunderstood electroanalytical sensor.

## Literature Cited

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