Reduction of Sample Volume and Waste Generation in Acid/Base Titrations Using Microelectrodes

by

A. A. Ekechukwu

Westinghouse Savannah River Company
Savannah River Site
Aiken, South Carolina 29808

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REDUCTION OF SAMPLE VOLUME AND WASTE GENERATION IN ACID/BASE TITRATIONS USING MICROELECTRODES (u)

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SUMMARY

The Analytical Development Section (ADS) has developed microelectrode methods for use with pH titrations and pH determinations. These microelectrode methods offer increased sensitivity and enable analyses to be done with smaller sample and buffer volumes than are used with standard size electrodes. This report establishes the technical validity of the methods and describes the application of these methods to decreased detection limits, decreased waste generation, and decreased radiation exposure.

INTRODUCTION

Hydrogen ion concentration, pH, is one of the most frequently made measurements in the ADS Wet Chemistry laboratory. In addition to the absolute measurement of solution pH, many of the analyses performed in the wet chemistry laboratory are titrations which use pH to determine the titration endpoint. The measurement of total and free acid, total and free base, aluminate, carbonate, and alkalinity all use solution pH to determine the endpoint of titration. In a typical pH titration, an aliquot of sample is added to a volume of buffer or water. The pH of this solution is monitored as titrant, a standardized acid or base, is added. The "break-point" (region where the pH of the solution changes rapidly) of the titration is noted, and the analyte concentration is calculated from the concentration of the titrant and the volume of titrant used to reach the break-point. The titration curve for a typical pH titration, determination of total hydroxide concentration, is shown in Figure 1.

Although the measurement of absolute pH is one of the simplest laboratory analyses, it is frequently done incorrectly, particularly with unbuffered samples. The most commonly made error is not allowing the electrode to equilibrate sufficiently in the

sample. Therefore it is important to measure an adequate sample volume (20 to 25 mL with a standard size 12 mm electrode) and to repeat the measurement with fresh volumes of sample until successive measurements agree within 0.1 pH unit. In general, 50 to 100 mL of sample are required to accurately determine pH. Since the required sample volume is proportional to the size and sensitivity of the electrode, reduction of the solution volume and generated waste can be accomplished by using smaller, more sensitive electrodes known as microelectrodes.

Microelectrodes are small working surface electrodes, ranging in size from 5 mm to less than 1 mm in diameter. A standard size electrode, which is usually 12 mm in diameter, typically requires clearance in solution of twice the electrode diameter in order to obtain accurate data. If a smaller solution volume is used, the electrode experiences electrochemical feedback from the sides of the reaction vessel. This feedback distorts the electrochemical response and corrupts the acquired data. Smaller electrodes require proportionally less clearance in solution and thus smaller volumes of solution. In addition, reducing the size of the electrode surface decreases the electrochemical noise caused by the unequal distance of all points on the surface of the electrode to the reference or counter electrode. For these reasons, smaller electrodes offer lower detection limits and require correspondingly lower sample volumes. ADS made use of these microelectrodes to decrease the analysis system size and enhance the sensitivity of the pH measurements and pH titrations performed in the lab.

EXPERIMENTAL

Equipment Description
pH measurements for pH determinations were made using a Beckman IS12 pH Meter. The electrode used was a Beckman Futura 4 mm combination pH electrode. For titrations, a Radiometer Autotitration system was used with a Radiometer model pHC4400 combination pH electrode. The term "combination" refers to an electrode which incorporates both the working electrode and the reference electrode in one unit.

Standards and Calibration
The measuring systems were calibrated using National Institute of Standards Technology (NIST) traceable buffers, pH 4 and pH 7. Check standards, listed in Table 1, were prepared and analyzed to verify the validity of the pH calibration.

Length of Time Required for Analysis
For titrations, the length of time required for analysis depends upon the amount of analyte present in the sample to be titrated. In titration methods performed in the ADS wet chemistry lab, the maximum volume of titrant is expended in 5 minutes. Samples which are more concentrated and require additional titrant are diluted and reanalyzed. In general, a titration takes 1 to 4 minutes to complete. In pH determinations, the electrode stabilizes in solution in less than one minute. Generally three to four successive determinations are required to obtain an accurate reading.

Accuracy and Precision of Measurements
Using the calibration standards listed above, the precision of the titration methods and pH measurement is between +/- 1 and 3% RSD. This is comparable to precision using the standard size electrode. The precision and accuracy are dependent upon the sample matrix so may be slightly higher for actual samples. Table 1 shows the results for check standards and pH buffers run with the various titration methods.

DISCUSSION

pH Titrations
The titration vessel used with the standard size pH electrode required a minimum sample volume of 25 mL to adequately cover the surface of the electrode. Using a narrower microelectrode, the analysis could be performed in a 10 mL titration vessel which requires only 5 mL of sample to adequately cover the electrode surface. Data validation tests on standards and samples showed the precision and detection limits to be comparable to that obtained using a standard size electrode and 25 mL of solution. Table 2 shows the results of five samples which were analyzed using both the standard size electrode and the microelectrode. The results are equivalent within the accuracy of the method (+/- 3%).

pH Measurement
The standard size pH electrode which had been in use in the lab required 20 to 25 mL of solution to adequately cover the electrode. The 4 mm diameter microelectrode requires only 5 mm clearance to generate accurate data. Using a 10 mL vial, accurate pH measurements can be made using 1.5 mL of sample. Table 3 shows the data for five samples and buffer standards. The pH results agreed within 0.1 pH unit and so are considered essentially equivalent within the precision of the method.

Comparison of Standard Size and Microelectrodes
Aside from the obvious size difference, standard and microelectrodes differ in sensitivity and accuracy. Ideal electrochemical behavior (referred to as a Nernstian response) is obtained with a point-to-point interaction between the electrodes in a cell. As the surface of the electrode expands and becomes more than a point, this ideal response is distorted. An analogous situation is found in spectrophotometry. As the grating used to distinguish between wavelengths becomes larger, there is less definition between wavelengths and thus less resolution in the measurement. Since noise effects smaller measurements more, this distortion increases the detection limits. Microelectrodes are accurate in the nanoamp and even picoamp range whereas standard size electrodes are accurate only in the milliamp to microamp range.

The increase in sensitivity comes at a cost of durability of the electrode. Microelectrodes are physically more fragile than their standard size counter parts. They are therefore not well suited to field work. Microelectrode surfaces are more easily fouled (coated with non-conductive material such as organics or redox byproducts) than larger electrodes because it doesn't take as much material to coat the electrode surface. They are more difficult to fabricate and are hence more

expensive. These differences must be taken into account when evaluating the use of the electrode.

CONCLUSION AND PATH FORWARD

ADS has successfully implemented microelectrodes for use in pH measurements and acid base titrations. The microelectrode methods generate less than half the waste of the standard size electrodes. This change decreased the liquid waste generated from the titration methods by 60% and the waste generated from pH determinations by more than 90%. The method mechanics are the same for both types of electrodes. The precision and accuracy of the data are relatively unchanged within the limits of the method. ADS is currently evaluating microelectrodes for use in the potentiometric and ion selective electrode methods performed in the lab.

Figure 1: pH Titration Curve for Total Hydroxide Measurement
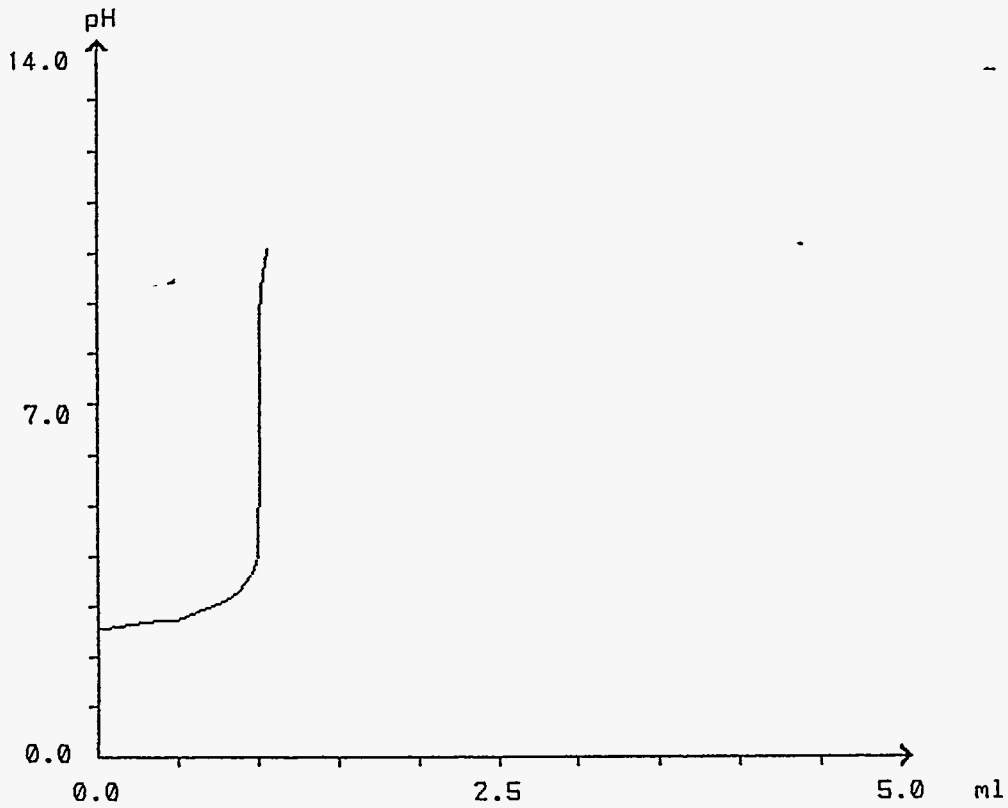

```
RADIOMETER TITRALAB        DATE:  96-02-28  12:41


    3 TOTAL ACID                          IP

          Sample number              1

    Stack   Identification     Amount  Unit  Smp factor
    No.     STD                0.1000   ml    1.0000

            ----------------------------------

    Start pH:     2.575
    ---------------------------------------------------
      No. !   pH   !    ml      !  Result (mol/l  )
    -----+--------+------------+----------------------
           !        !           !
    IP 1 !   7.627!   1.0181    !    1.0181
           !        !           !
    IP 2 !--------!  ---------  !----------------
         '         '            !
```

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