

# Simple and Automated Coulometric Titration of Acid Using Nonisolated Electrodes

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**S** Supporting Information

**ABSTRACT:** Coulometric titrations involve the quantification of analyte by measurements of current and time. In most coulometric titrations, the anode and cathode are placed in isolated cells that are connected by a salt bridge. By contrast, the experiments described here involve coulometric titrations (of acidic protons in solution) using a silver anode and graphite cathode placed in the same reaction vessel. The chemistry of the electrode reaction generating the reactant is described. This use of non-isolated electrodes allows for simplified experimental procedures (some of which are described) and faster titration times. Additional streamlining of the experiment is achieved by the use of MicroLab data acquisition instrumentation. This laboratory is appropriate for an analytical course.

**KEYWORDS:** Second-Year Undergraduate, Upper-Division Undergraduate, Analytical Chemistry, Laboratory Instruction, Computer-Based Learning, Hands-On Learning/Manipulatives, Acids/Bases, Electrochemistry, Instrumental Methods, Laboratory Computing/Interfacing



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Coulometric titrations are an important part of both the analytical chemistry<sup>1</sup> and instrumental analysis<sup>2</sup> curricula. As a result, a large number of coulometric titrations have been reported in this *Journal*,<sup>3–9</sup> including determinations of cyclohexene,<sup>4</sup> acid,<sup>7</sup> iodide,<sup>8</sup> and sulfites in wine.<sup>9</sup> Coulometric titrations simplify the titration process because they eliminate the need for the preparation of primary standard solutions<sup>1,2</sup> and allow for facile generation of unstable reagents such as Br<sub>2</sub>.<sup>4,8</sup> Unfortunately, the coulometric titrations previously reported include<sup>3–9</sup> the use of expensive coulometers, complicated experimental apparatus, and complex circuitry. A coulometric titration experiment is described that uses nonisolated electrodes to simplify the experimental setup and the MicroLab data acquisition instrumentation to simplify the electronics.

## BACKGROUND

Coulometric titrations involve the quantification of analyte through measurements of electric current,  $I$ , and the time,  $t$ , that the current passes through a solution containing the analyte. Because the flow of electric current is easier to control and measure than the flow of reagent, coulometric titrations serve as the basis of many automated titration systems. From the measurements of current and time, the total charge,  $q$  that passed through solution may be calculated through eq 1 in the case of constant current

$$q = It \quad (1)$$

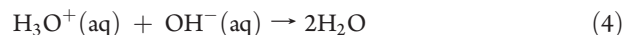
or eq 2 if current is not held constant throughout the titration

$$q = \int_0^t I dt \quad (2)$$

Once the charge transferred is calculated, Faraday's constant ( $F = 96,485 \text{ C/mol e}^-$ ) is used to determine the amount of electrons transferred. For example, in the experiment presented here, electrons from a power source react with water at an inert carbon electrode to produce hydroxide ions:

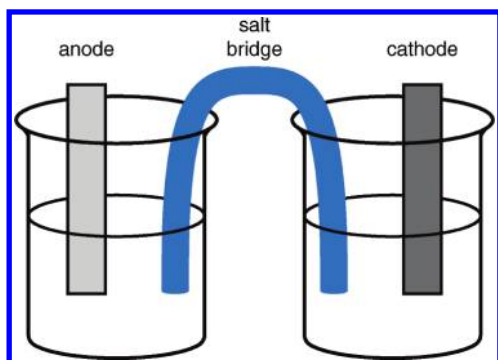


The hydroxide is generated by current in an equimolar fashion: 1 mol of electrons produces 1 mol of reagent hydroxide. The hydroxide reacts with analyte acid:



Taken together, eqs 3, 4, and the Faraday constant provide a relationship between the number of electrons supplied and the amount of acid consumed.

Hydroxide generation occurs at the working electrode, so termed because it is at this electrode where the reactions of interest (production of hydroxide and concomitant consumption of analyte acid) occur. In this experiment, the working electrode



**Figure 1.** Isolated electrodes. Anode and cathode are separated by a salt bridge to reduce transport of material from anode to cathode (or vice versa) that would interfere with reaction(s) of interest.

is the cathode because reduction occurs at the cathode by definition. In this experiment, the oxidation of silver provides the electron source,



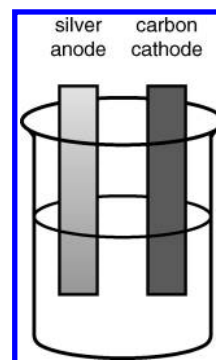
where a strip of solid silver serves as the counter electrode. The counter electrode is the anode, as oxidation occurs at the anode by definition.

A complicating feature of coulometric titrations is that species generated at the counter electrode can interfere with reactions at the working electrode. For example,  $\text{Ag}^+$  generated at the anode can migrate to the working electrode and be reduced in place of water:



Reduction of  $\text{Ag}^+$  at the working electrode presents a problem if it is assumed that each electron causes the production of a single hydroxide ion. (In general, more than one reaction can take place at an electrode, and accurate quantification is possible only if there is one reaction at the working electrode.) In the great majority of coulometric titrations reported in this *Journal*,<sup>3,5-9</sup> this problem is dealt with by isolating the anode and cathode compartments into separate cells so as to minimize diffusion of redox active species between electrodes (Figure 1). To maintain electric conduction, the isolated cells are connected by a porous barrier such as a salt bridge or glass frit. Although a porous barrier provides a solution to the migration problem, such an arrangement is not perfect.<sup>10-13</sup> First, the introduction of the barrier generally decreases the current, increasing the time it takes to complete a titration. Second, because ions must still pass through the barrier to maintain electrical conduction, perfect isolation of the electrodes from interfering species is difficult to achieve. Finally, the presence of two cell compartments complicates experimental design and restricts attempts to miniaturize or automate titration systems.<sup>12,13</sup> In the experiment presented here, the anode and cathode are not separated but are maintained in a single compartment (Figure 2).

To remove interfering  $\text{Ag}^+$ , NaBr is dissolved in the analyte solution.<sup>2,14</sup> The presence of 0.1 M  $\text{Br}^-$  precipitates AgBr and lowers the solubility of AgBr to  $\sim 10^{-6}$  M,<sup>15</sup> ensuring that no measurable  $\text{Ag}^+$  is free to migrate to and be reduced by the working electrode. Thus, a carbon working electrode (cathode) and silver counter electrode (anode) in a single cell may be constructed for fast, facile, and quantitative coulometric titration of acid. Further simplification of the process is achieved by means



**Figure 2.** Nonisolated electrodes.

of using a MicroLab data acquisition system and model 270 electrochemistry accessory module to provide a power source and to collect data. This eliminates the need to construct home-built electronics to drive and monitor the process.<sup>16</sup>

## EXPERIMENTAL SETUP

A 50 mL solution that contains 0.1 M  $\text{KNO}_3$  (supporting electrolyte) and 0.05 M NaBr is added to a 150 mL glass beaker. A small magnetic stir bar is added to the beaker, which is set on a stir plate. A small strip of silver foil (Flinn Scientific) and a graphite rod (Flinn Scientific) are clamped to a ring stand so that they are not touching and are immersed in the solution.

The MicroLab FS-522 is used as an electric power source and is connected to the model 290 module, to which each electrode is attached by an alligator clip. The MicroLab interface is programmed to provide power and record current and time; the potential between electrodes is set to provide sufficient current to the electrochemical system to drive the reaction in a convenient quantity of time (see the Supporting Information for detailed instructions). A suitable indicator, such as phenolphthalein, is added to the solution. After the analyte (HCl, vinegar, or toilet bowl cleaner) is pipetted to the beaker (40–500  $\mu\text{L}$ ), stirring is commenced and the program is started, which initiates the electrolyzing potential and records the current and time data while plotting the data in real time. The program is stopped when the indicator changes color. The time from the initiation of current to the first observable color change is recorded. The current–time data are exported into a spreadsheet such as Microsoft Excel. The time to reach the end point is used as the upper limit of integration when integrating the current versus time data to determine the charge delivered.<sup>17</sup>

## HAZARDS

Hydrochloric acid is corrosive and causes burns to body tissue.

## RESULTS AND DISCUSSION

The coulometric titration of 469  $\mu\text{L}$  of a 0.1000 M standard solution of HCl (Fisher Scientific) was conducted with this experimental system. As the reaction proceeded, an increasing quantity of visible, white, AgBr precipitate accumulated within the reaction vessel. The current remained fairly constant throughout the titration (Figure 3). First and second derivative data<sup>18</sup> of pH versus time data may be collected during the experiment. The first derivative analysis (Figure 4) displayed a definite end point at 141 s, coinciding with the solution pH reaching 7.3. Integration

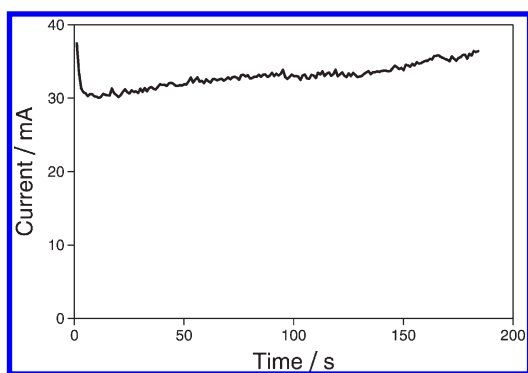


Figure 3. Time dependent current in the coulometric titration of 469  $\mu\text{L}$  of a 0.1000 M standard solution of HCl.

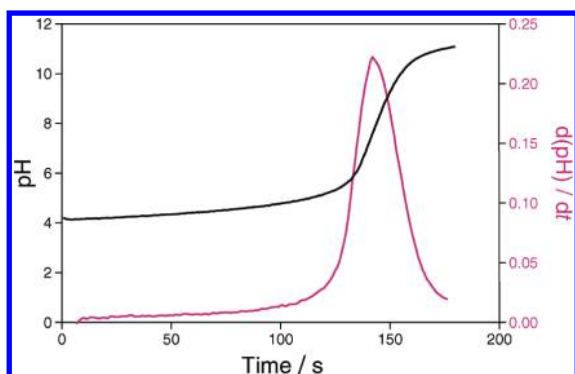


Figure 4. Time dependent pH in the coulometric titration of 469  $\mu\text{L}$  of a 0.1000 M standard solution of HCl (black trace) and corresponding first derivative plot (red trace).

of the current versus time data (Figure 3) to 141 s yielded an experimental concentration of 0.101 M. The results of several student trials measured the HCl concentration to be  $0.102 \pm 0.003$  M. In the titrations of vinegar and toilet bowl cleaner, the same method was used as for the titration of 0.1000 M HCl, except in these cases only 250  $\mu\text{L}$  of vinegar or 40  $\mu\text{L}$  of toilet bowl cleaner were pipetted into the solution system. The results of several student trials measured the HCl percentage in the vinegar to be  $4.97 \pm 0.12\%$  and the HCl percentage in the toilet bowl cleaner to be  $16.01 \pm 0.09\%$ . These measurements are in good agreement with the manufacturer's claims of 5% acetic acid in vinegar and 16% HCl in toilet bowl cleaner. It should be noted that in the titration of acid in vinegar (data not shown), the end point did not coincide with the solution pH reaching 7, because acetic acid is a weak acid.

The oxidation of  $\text{Br}^-$  at the anode



must be considered because the potential used in this experiment, 2.5 V, was greater than the potential to oxidize bromide. Any  $\text{Br}_2$  formed could migrate to the working electrode to compete with the reduction of water:



Although the  $\text{Br}^-$  oxidation would be an issue with a Pt electrode, the rate of oxidation of  $\text{Br}^-$  at an Ag electrode is going to be much lower than the rate of oxidation of Ag. This is because the

$\text{Br}^-$  would have to encounter the electrode to be oxidized. However, the bromide will first encounter the layer of surface  $\text{Ag}^+$ , and thus, precipitation of  $\text{AgBr}$  is going to be favored over  $\text{Br}^-$  oxidation.

## CONCLUSION

The use of nonisolated electrodes in the coulometric titration of acid described here simplifies experimental setup. In addition, the use of the MicroLab data acquisition system to simultaneously provide a power source and collect data provides an uncomplicated electronic system to run the titration. As a result, this experiment (using indicator end point detection) has been performed in a lab of 15 analytical chemistry students. The titrations of HCl solution, vinegar, and toilet bowl cleaner takes most students less than 3 h to complete, giving students lab time to work on data analysis. A recent survey of the analytical chemistry students indicates that over 85% of students prefer coulometric to volumetric titration of acid. The less time-consuming nature of the coulometric titration was the main reason cited for preference.

## ASSOCIATED CONTENT

### Supporting Information

Student handout and notes for the instructor. This material is available via the Internet at <http://pubs.acs.org>.

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- (16) Other power sources may be used to drive the process. For example, we have also conducted this titration using simple and

inexpensive materials such as a 9 V battery, alligator clips, small graphite rods, a silver strip, a beaker, a stopwatch, and a digital voltmeter with an appropriate current range. However, in this simplified configuration, students cannot set the voltage applied to the cell nor integrate a changing current to determine coulombs of charge delivered. See the Supporting Information.

(17) The MicroLab computer interface includes a well-regulated dc power source. It can be set reproducibly to within 1 mV over the 0–4V range. It also has a straightforward programming routine that will immediately calculate derivatives and integrals of data; other software (Logger Pro, for example) can also calculate derivatives and integrals. This feature provides an attractive method of data analysis for students in chemistry courses not requiring calculus or robust analysis of data.

(18) To collect time-dependent pH data, a bit more complicated procedure is necessary, but it affords students the opportunity to analyze a titration curve to find the time to reach the end point. Two separate MicroLab interfaces are required, one to measure pH versus time and the other to apply voltage and read current versus time. A separate interface is required to avoid interference produced on the pH probe by the voltage and current sensors. See the Supporting Information.