

09

AMPEROMETRIC TITRATION FOR THE DETERMINATION OF FERROUS ION
(REDOX TITRATION)

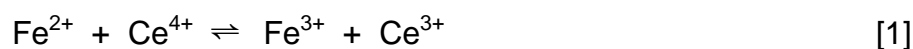
End-point indication using amperometric titration is inherently more accurate than indication using visual indicators. The accuracy of the end-point determination is primarily given by the accuracy of titrant delivery. There are other suitable electrochemical methods, but amperometric titrations possess greater sensitivity than conductometric and potentiometric titrations. In addition, equipment needs for amperometric titrations are much simpler than typically required for other electrochemical methods. Typical analyses are in the range of 0.1 mol/l -- 0.0001 mol/l, with analyte not needing to be an electroactive species; the titration can be conducted by utilizing redox system present either before or after the end point.

In amperometry, the potential of the working electrode (vs. the reference electrode) is held at a constant value and the resulting current is measured. The electrodes are usually in a stirred or flowing solution. Alternatively, the electrode may be realized in the form of an ultramicroelectrode, where stirring is not essential. Analytical determinations are made from the current, which is proportional to the concentration of the electroactive species. Usually, the potential is held at the limiting current region of the electroactive species of interest. Amperometry is now commonly used as a means of detection for flow injection analysis (FIA) and liquid chromatography. In these techniques, the sample is injected into a flowing stream of electrolyte, and a current peak is recorded as the sample passes through the electrochemical cell.

In its conventional and/or most common form, the arrangement for the amperometric titration consists of a polarizable electrode, *e.g.*, a platinum flag or wire, in combination with a large surface non-polarizable reference electrode. A constant potential is impressed across the indicating system such that it is on the diffusion current plateau for the titrant, reactant or both. During the titration experiment the current flowing through the system is recorded as a function of the volume of titrant. With modern instrumentation a three-electrode system is used, where the reference electrode only senses potential, but does not carry any current, and the current circuit is completed by using a third electrode, called a counterelectrode.

With its three electrode-configuration, the CV-27 voltammograph (a potentiostat) (Bioanalytical Systems, West Lafayette, IN) is a suitable controller for this application. Additionally, a second potentiostat by PINE instruments was purchased for the teaching laboratory. Some of you will be using the BAS instrument and some of you will get to use the PINE instrument. Following week, when another experiment using a

potentiostat is performed, you will get to use the other instrument. The use of these instruments will be illustrated with the titration of ferrous ion using the ceric ion as titrant. The net reaction is given below.



Standards and sample solutions

0.010 mol/l ceric ammonium sulfate in 1.0 mol/l sulfuric acid

0.010 mol/l ferrous ammonium sulfate

0.0010 mol/l ferrous ammonium sulfate

unknown solution (containing iron(II) from the TA

Note: The one molar sulfuric acid in the standards is sufficiently corrosive to harm your eyes, skin and clothing. Wear adequate protection.

Procedure

In a clean beaker, dispense a known volume of the 0.010 mol/l Fe (II) standard solution. Place a platinum working electrode and a Ag/AgCl reference electrode in the beaker. Place the counter electrode in a tube with a fritted disk at its bottom and put the tube in the beaker. Deliver enough deionized water into the beaker to cover all the electrodes (the solution should flow slowly through the fritted disk into the counter electrode compartment). Add 1 ml of phenanthroline indicator to the solution to guide you visually in the process of the titration.

Instruction for the BAS instrument: Connect all three electrodes to the CV-27 (**RED**-auxiliary, **BLACK**-working, and **WHITE**-reference). Fill clean dry burette with the Ce(IV) titrant solution. Record the initial volume reading. Turn the **CELL MODE** to **STANDBY**. Turn the **POWER** switch to the **ON** position and adjust E1 to +0.8 V. Switch the DISPLAY to I out position. Turn on the magnetic stirrer. Turn the **CELL MODE** switch to **CELL**. Read and record the cell current (I out) at zero volume of titrant. (The current will be read conveniently by the connected computer.

Add 0.50 ml of titrant to the sample solution and record the current reading from the CV-27. Continue to add the titrant and record the current at each volume increment. Note the volume of titrant that produces an indicator end-point (from orange to light blue or clear). Continue adding 0.5 ml of titrant and recording the current until 10 ml past the indicator end-point.

Repeat the titration for the 0.0010 mol/l Fe(II) solution, and for the unknown solution. Smaller volume increments may be needed.

Instructions for the PINE instrument: The instrument is brand new and some of the details of the operation are still being developed. Much of the procedure is the same as for the BAS CV-27. The TA will tell you which electrode connects to which color connection. The operation is computer-driven and should be reasonably obvious.

Results

Plot the current versus volume of the titrant added for all titrations. Determine the end point for the known solutions and compare how the end-point volume agrees with the volume expected for titration with the known cerium standard. Also, how does the amperometric end-point agree with the visual end point as determined by your observation?

Calculate and report the Fe(II) concentration in your unknown.

Discuss the possible sources of error in your result. Is there any discrepancy between the indicator endpoint and the amperometric endpoint? If so, explain why.

Why is the counter electrode placed in the fritted tube?

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