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# Study of Potentiometric titration and volumetric method used to measure potential

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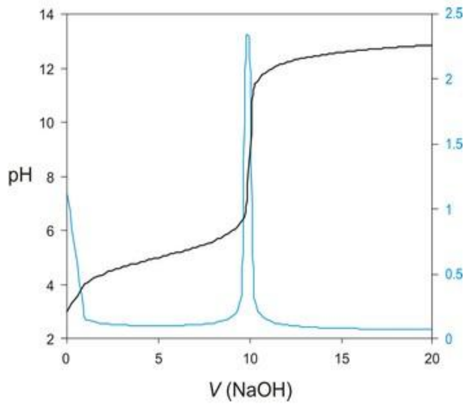
Abstract : Potentiometric titration is a volumetric method in which the potential between two electrodes is measured (referent and indicator electrode) as a function of the added reagent volume. Types of potentiometric titrations for the determination of analytes in photoprocessing solutions include acid-base, redox, precipitation, and complexometric. Potentiometric titrations are preferred to manual titrations, since they are more accurate and precise. They are also more easily adapted to automation, where automated titration systems can process larger volumes of samples with minimal analyst involvement.

## Titration Curve

A titration curve has a characteristic sigmoid curve. The part of the curve that has the maximum change marks the equivalence point of the titration. The first derivative, $\Delta E/\Delta V$, is the slope of the curve, and the endpoint occurs at the volume, V', where $\Delta E/\Delta V$ has the maximum value.



## General Principles

The Nernst equation tells us that a measurable quantity - voltage or potential - is related to the concentration of species in solution. In many cases, the measured potential is due to a number of species, and hence the concentration of one can be difficult or impossible to determine. Electrodes have been designed to respond only to one (or a very small number of) species, thus allowing the measurement of its concentration. This is known as direct potentiometry, and will be discussed in the next chapter. In other cases, the analyte can be determined by means of a titration, and the change in its concentration monitored by measurement of the solution potential. This is known as a potentiometric titration. In titration measurements, the errors (activity differences and junction potentials) mentioned in the previous chapter are not a problem because we are not interested in relating a single voltage measurement to the solution concentration: we are only interested in identifying the endpoint volume of the titration by the change in voltage from one volume addition to the next. Figure 2.1 shows the typical shape of a potentiometric titration curve. Titrant Volume mV endpoint break endpoint volume .Typical potentiometric titration curve.

**Features of the titration curve :**

• the wave-like shape occurs because of the rapid change in voltage around the endpoint of the reaction

• the endpoint break is the large change in voltage around the endpoint

• the endpoint break should be as large as possible to improve accuracy of detection: this is done by choosing the titrant carefully. • the endpoint volume is defined as the volume half-way up the endpoint break • the voltage values before the endpoint are due to the analyte.

• the voltage values after the endpoint are due to the titrant.

**Choosing a Potentiometric Titration**

Compared to titrations using an indicator to detect the endpoint, potentiometric titrations are:

• more expensive – you need a stirrer and bar, electrodes, and a voltmeter

• slower to set up – making sure the electrodes are correctly in place and functioning properly, getting the burette above the beaker and out of the way of the electrodes, making sure the stirrer bar isn't going to smash the end off the electrode

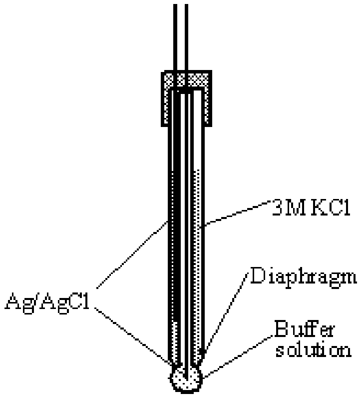
• slower to perform – having to record all the data (in most cases)

• slower to get the endpoint volume – you just don't read the volume off the burette at the end (in most cases), you have to process the data in some way.

Electrodes used in potentiometric titrations

The experimental setup for potentiometric measurement comprises a set of an indicating and reference electrodes or two identical indicating electrodes, which should be treated carefully. Do not place the electrodes anywhere except attached to the electrode holder. At the end of the experiment rinse the electrodes and place each one in its housing as required.

Glass electrode. Combined glass reference electrode consists of indicator and reference electrodes in the same body. Great care should be taken of it: never touch the glass part of the electrode with anything except soft tissue paper. While in use, the bulb of the glass electrode and the diaphragm of the reference electrode should be immersed in solution. For short-term storage the combined glass electrode should be immersed in solution of 2 M KCl. Buffer solutions of known pH are used for the pH calibration. The pH values of some buffers are temperature dependent. For high accuracy, calibration and measurements are to be performed at the same temperature.



Combined glass and reference electrode

Ion-selective electrodes are used for detection of specific ions in a mixture of ions. The sensor element, ion-selective membrane, has a construction similar to that of glass electrode. For calibration of ion-selective electrodes a standard addition method is often employed.

Silver indicating electrodes are silver wires with 1-2 mm diameter. When used in precipitation titration, the silver-salt precipitate should be occasionally removed from the electrode surface (mechanically with fine grade emery paper, or chemically immersing the electrode in NH3 solution). It is simpler, however, to prevent the coating of the electrodes by addition of a surfactant as polyvinyl alcohol (1 drop 0.3% PVA to every 5 ml of solution).

Mercury-coated indicating electrodes are reported to be prepared by lightly amalgamating a gold wire. The disadvantage in use of gold is that it is consumed with time by the amalgam formation. Silver wire used instead of gold, however, can serve many years. The preparation of mercury-coated silver electrode is done by the instructor in a hood (mercury vapors are poisonous!). The silver wire (~1.5 mm diameter) is (a) rubbed with emery paper, rinsed with distilled water and dried with tissue; (b) dipped into mercury to form an amalgame; (c) the mercury is gently spread on the wire with soft tissue. This electrode may be used during several runs of titrations without any renewal. For renewal, step (a) may be omitted.

Platinum redox electrodes are used in redox potentiometric titrations. In excess of oxidant oxide films are formed on the platinum electrodes. The potential response of the electrode is distorted, and the film must be removed. Efficient pretreatment is achieved by cathodically polarizing the platinum electrode in 0.5 M H2SO4 at current density of 0.5 mA/cm2 for 5 - 15 min. Platinum wire is recommended to use as an auxiliary electrode.

Gold redox electrodes are seldom used in potentiometric titrations. According to our recent experience, the gold electrodes are better behaved than platinum electrodes in view of rate of response and stability toward formation of oxides. These features are of high importance in continuous mode of titration. A good example is the use of gold electrodes in the titration of ascorbic acid with bromine in continuous mode, where the response of the platinum electrode is unsatisfactory.

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