

# Potentiometric Titrations for Photoprocessing Solutions

ULM-0003-01

## INTRODUCTION

Titrations involve the addition of accurately known volumes of standardized titrant to a solution containing the sample. The concentration of the analyte(s) being determined by titration can be calculated based on the volume of titrant used to reach the endpoint (also referred to as the equivalence point or break) of the titration. The titration endpoint can be determined manually or potentiometrically. In a manual titration the endpoint is determined by use of a visual indicator that changes color when the endpoint of the titration has been reached. In a potentiometric titration the endpoint is determined by use of a pair of electrodes or a combination electrode. The endpoint occurs where there is a maximal rate of change of potential at the endpoint of the titration. In the portion of the curve corresponding to this large change in potential, there is a point at which the curve changes its direction of curvature. This point is an inflection point or break in the curve and ideally it occurs at the equivalence point of the titration. However, in certain cases, there may be a bias in the analysis, and the break may be slightly displaced from the true equivalence point. The analysis of known samples may indicate that the bias is large enough to require a correction.

The electrode pair for potentiometric titrations includes an indicator and reference electrode. The combination electrode contains the indicator and reference electrode configured in a single electrode. The electrodes for potentiometric titrations are chosen so that a change in potential of the titration solution, caused by titration of the analyte(s) of interest, is optimally detected. 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.

Use of this method requires handling of potentially hazardous chemicals. Material Safety Data Sheets should be consulted for each chemical before use. These can be obtained from the chemical's supplier.

## TYPES OF TITRATIONS

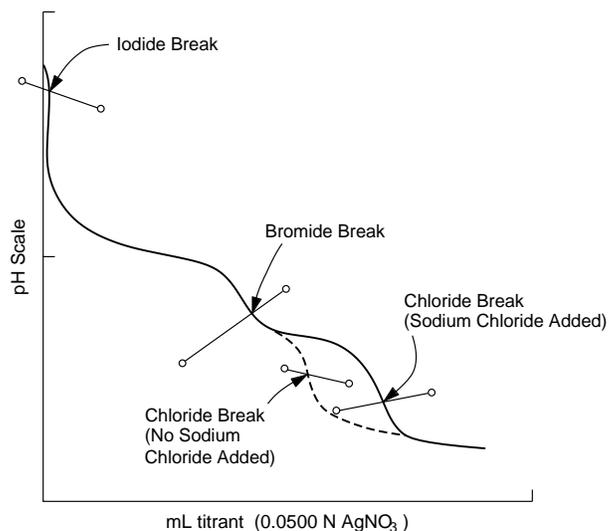
Types of potentiometric titrations for the determination of analytes in photoprocessing solutions include acid-base (total alkalinity and total acidity), redox (HI/HY and cerate), precipitation (halides), and complexometric (free EDTA and Antical #5). The specific titrimetric method, including which electrode(s) to use, can be found in individual analytical methods for each photographic process.

Since silver halide titrations are not explained in more detail in most methods, they will be discussed here. An Orion double junction electrode with an outer filling solution of potassium nitrate is used as the reference electrode for titrations of halides with silver nitrate. A silver electrode is used as the indicating electrode for halide titrations, because

its potential is a function of the silver ion concentration in the titration solution. The potential between the electrodes is measured and recorded manually when a potentiometer or a pH meter is used; this is done automatically when an automatic titrator is used. These potential measurements are read on a millivolt scale.

Difficulties may occur when more than one halide is present in a solution. One of the difficulties in titrations with silver nitrate is in knowing which particular halide caused the inflection point on the curve. Where iodide, bromide and chloride are present the first break should be that of the iodide, because it has the lowest solubility. However, if little or no iodide is present in the sample, the first break will be that of the bromide, followed by a break for chloride. See Figure 1, *Typical Bromide Titration Curve*. When little chloride is present, the bromide and chloride in the sample may co-precipitate. If so, one break may easily be confused with the other. This situation is avoided in several bromide methods by the addition of more chloride to the sample before titration, to pull the chloride break away from the bromide break.

Figure 1 Typical Bromide Titration Curve



F002\_0987AC

## TITRANT PREPARATION AND STANDARDIZATION

Titration preparation and standardization methods can be found in *Processing KODAK Motion Picture Films, Module 4, Reagent Preparation Procedures*.

## PREPARATION AND STORAGE OF ELECTRODES

### Preparation of Indicator-Electrodes

1. Silver Bar or Silver Billet Electrodes
  - a. Clean the silver electrode to brightness using Silver Polish, obtainable from Fisher Scientific Co. (catalog number 9-311-309), on a damp tissue. Rinse the electrode well with reagent water, Type 1. For a definition of reagent water, Type 1, see ASTM standard B 1193.
  - b. Do an initial titration. This allows the electrode the opportunity to become equilibrated in the system in which it will be used. Discard the results from this initial titration.
  - c. Rinse the silver electrode well with reagent water, Type I and wipe it with a tissue between subsequent titrations of similar samples (e.g. a silver electrode equilibrated in a bromide system may be used only for subsequent bromide titrations or until it no longer performs before recleaning to brightness).

The silver electrode should be stored dry in air when not being used.
2. Electroplated Silver-Silver Iodide Electrode

Follow instructions provided in Method 900, *Procedure for Electroplating a Silver-Silver Iodide Electrode*, or any subsequent revision.

The silver iodide electrode should be stored dry in air when not being used.
3. Platinum Disc Electrode

Whenever a deposit or coating collects on the disc, clean the disc using an aluminum oxide polishing strip, made by Moyco and obtainable from Orion, part number 301044-001. Thoroughly rinse the electrode with reagent water, Type 1.

The platinum electrode should be stored dry in air when not being used.
4. Glass Electrodes

See Method ULM-191-2, *pH Measurement of Photographic Processing Solutions*, (or any subsequent method for determining pH) for instructions on care and storage of glass indicator electrodes.
5. Ion specific electrodes (Copper, Silver Sulfide, Potassium Iodide, Calcium)

Refer to the analytical procedure or manufacturers directions for proper electrode cleaning and storage.

### Reference Electrodes

1. Calomel Electrodes for Use with a Glass Indicator Electrode

See Method ULM-191-2, *pH Measurement of Photographic Processing Solutions*, (or any subsequent method for determining pH) for instructions on care and storage of calomel electrodes.
2. Calomel Electrodes for Use with Silver Bar or Billet and Platinum Disc Electrodes
  - a. Remove the potassium chloride fill solution and substitute saturated potassium nitrate solution when titrating with silver nitrate.

**Note:** Refer to the specific method when determining whether to use 3.5 N potassium chloride or saturated potassium nitrate solution in the calomel electrode, for titrations with titrants other than silver nitrate.
  - b. There should be a few potassium nitrate crystals present in the calomel electrode after filling with saturated potassium nitrate solution. The electrode should be checked to ensure that the solution is flowing through the inverted sleeve or fiber tip, before using.
3. Ag/AgCl Double Junction Electrodes

It is recommended that the manufacturers supplied solution be used for the inner chamber (AgCl) and that it be emptied and refilled weekly. The outer chamber should be filled with an appropriate solution for the analysis being carried out, usually a 10 percent potassium nitrate solution, which should be emptied and refilled daily.

Ag/AgCl electrodes can be stored in reagent water, Type 1 for up to one week. For longer periods of time drain the electrode, rinse with water and store dry.

### PERFORMANCE CHECK OF ELECTRODE / INSTRUMENT SYSTEM

Analysis of samples containing known amounts of the analyte being measured can be an effective way of determining whether the system will produce reliable results on samples containing unknown amounts of the same analyte.

### BLANK DETERMINATION

Some test methods call for the determination of a blank (e.g. HI/HY and cerate titrations). The titration blank should be determined under the same conditions as the sample, including temperature, equipment parameters, and titration speed. The blank should include everything except the analyte being measured.

When measuring titration blanks for a potentiometric analysis, the blank value to be subtracted from the sample titration should correspond to the volume of titrant required to titrate the titration matrix (containing everything except the analyte of interest being measured). This volume

difference corresponds to the potential of the equivalence point of the sample or standard being measured.

## DETERMINATION OF THE END POINT FOR POTENTIOMETRIC TITRATIONS

### Microprocessor Controlled Titrators

Microprocessor controlled titrators are programmed to pick end points automatically using algorithms.

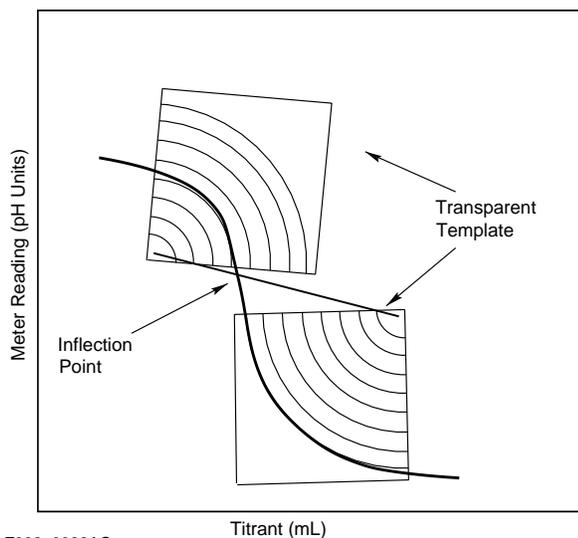
### Concentric Arcs Method

One way of manually locating the endpoint of a titration curve is by using a concentric arcs template. This template is semi-rigid and transparent. A series of arcs is scribed upon it  $\frac{1}{4}$ -inch apart.

Locate the approximate position of the endpoint, which is in the part of the curve representing the greatest rate of potential change. Place the template on the curve on one side of the approximate endpoint, superimposing one of the arcs on the curve. Try different arcs to find the largest one that best fits the curve. Then make a dot on the graph through the small hole in the template.

Place the template on the curve on the other side of the approximate endpoint and repeat the procedure. The arc that best fits this part of the curve is not necessarily the same arc that best fit the first part of the curve. Draw a straight line between the two dots. The point where the straight line intersects the curve is the end point. See Figure 2, *Use of Concentric Arcs Template to Determine the End Point of a Potentiometric Titration*.

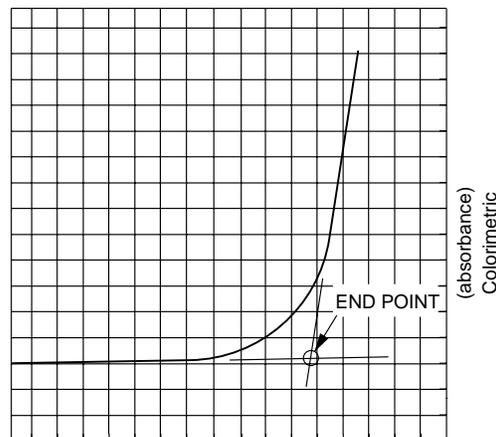
Figure 2 Use of Concentric Arcs Template to Determine the End Point of a Potentiometric Titration



### Colorimetric Endpoint Determination

Some titrations use color change end point detection instead of potentiometric (e.g. Antical #5 in RA-4 and free EDTA). Colorimetric endpoints should be determined using a Brinkmann 701 colorimeter, or equivalent, and optical probe at the optimal wavelength. Endpoints are best determined using a strip chart recorder and using the intersecting tangents method for determining the endpoint. See Figure 3, *Colorimetric – Intersecting Tangents*.

Figure 3 Colorimetric – Intersecting Tangents



Directions:

1. Use a straight edge to draw a line tangential to the bottom half of the curve.
2. Draw another line tangential to the top half of the curve.
3. The endpoint is measured where the lines intersect.

## TITRATION PROCEDURE

### Preparation for Titration

**Note:** See the particular instrument (pH meter or automatic titrator) manual for specific operating instructions and appropriate settings.

1. Attach the appropriate electrode pair or combination electrode to the instrument according to the specific method. Electrodes with side caps (plugs) should be uncapped before use to allow appropriate “weeping” of fill solutions.

**Note:** All titrations must be run with the indicator electrode in the indicator jack of the instrument and the reference electrode in the reference jack. Refer to the instructions included with specific combination electrodes used, as they do not all attach to the titrator in the same manner.

2. Fill the burette with the proper titrant, making sure the delivery tip has been “seasoned” (purged several times with small aliquots of fresh titrant). Rinse all excess titrant from the delivery tip with reagent water, Type 1 from a wash bottle into a “waste” beaker.
3. Prepare the sample with its necessary reagents as indicated in the specific method. Add a magnetic stir bar. Be sure to leave enough space at the bottom of the beaker so the magnetic stir bar does not damage the electrodes.

4. Stir the sample on a magnetic stirrer and immerse the electrodes and burette tip in the sample.

**Note:** The titrant delivery tip should be placed so that the titrant flows past the reference electrode before the indicator electrode. Set the stirrer speed to stir rapidly without splashing or creating a vortex.

5. Add reagent water, Type 1, if necessary, to cover at least the lower  $\frac{1}{2}$ -inch of the electrodes. Keep the solution level below the electrode fill solution level to insure proper “weeping” of electrode fill solution.
6. Remove the delivery tip from the solution as soon as titration is complete to prevent contamination of titrant by sample solution diffusion.

### Actual Titration

**Note:** Make the necessary instrument and recorder adjustments before starting the titration.

#### 1. Manual Titration Using a pH Meter

- a. Add the titrant in 0.20-mL increments, unless otherwise indicated in the specific method. After each addition, wait until the needle stops moving and record burette and meter readings.
- b. Titrate until each succeeding 0.20 ml increment produces less change in the meter reading than the preceding addition. Make at least five more additions of titrant before ending the titration. Plot on graph paper, ml of titrant on the x axis versus millivolts on the y axis.

**Note:** For bromide titrations, titrate until the chloride endpoint has been passed, unless more than 10 ml of titrant is required.

- c. Remove the electrode assembly from the beaker. Rinse the electrodes with reagent water, Type 1. If rinsing does not remove all deposits, gently blot the electrodes with a tissue and rinse them again. Place the electrodes in their appropriate storage media.
- d. Determine the endpoint by the *Concentric Arcs Method*.

#### 2. Automatic Titration Using Recording Titrators and Microprocessor Controlled Titrators

**Note:** Automatic titrators should be set to the parameters found in the specific method being performed.

- a. When using a recording titrator (such as a Metrohm E-536) turn the titrator drive on and allow the titration to proceed through the desired break(s). Turn the titrator drive off. Microprocessor controlled titrators have other operating directions, which can be found in the instrument manuals.
- b. Remove the titration beaker and rinse the delivery tip and electrodes. (if rinsing does not remove all deposits, gently blot the electrodes and delivery tip with a tissue and rinse them again.) Place the electrodes in their appropriate storage media.
- c. Microprocessor controlled titrators will automatically pick the endpoint(s). For recording titrators, determine the endpoint by the *Concentric Arcs Method*.