# ANALYTICAL CHEMISTRY

# Precipitation Titration

by

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# Chapter Description

- Expected Outcomes
  - Describe the fundamental of precipitation titration
  - State the types and limitations of precipitation titration
  - Describe the precipitation titration curve involving silver ion

*Precipitation Titration*
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*http://ocw.ump.edu.my/course/view.php?id=467*

# Contents

- Introduction
- Types of Precipitation Titration
- Limitation of Precipitation Titration
- Precipitation Titration Curves Involving Silver Ion

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# INTRODUCTION

- **Precipitation titration**: titration of analyte with a standard solution of a precipitating agent. e.g. $Cl^-$ can be determined when titrated with $AgNO_3$.

- Titrations with **silver nitrate** are sometimes called **argentometric titrations**.

- **End point** is determined by either the appearance of excess titrant or the disappearance of the reactant (color indicator @ instrumental methods).

- **Silver nitrate**, is the most widely used and important precipitating reagent for the determination of the halogens.

# METHODS IN PRECIPITATION TITRATION

## Detection of end point:

### Chemical

-Precipitation Type - Mohr's method
-Adsorption – Fajan's method
-For silver analyses – Volhard method

### Sensors –Potentiometric or amperometric

**The chemical types are also classified into:**

1. Indicators reacting with titrant forming specific color.
2. Adsorption indicators.

# SEVERAL PRECIPITATION TITRATION -MOHR METHOD-

This method utilizes **chromate as an indicator**.
The method is applicable to the determination of $Cl^-$ and $Br^-$, but not for $I^-$ or $SCN^-$.

Titration: $Ag^+ (aq) + Cl^- (aq) \rightarrow AgCl (s)$
End point: $Ag^+ (aq) + CrO_4^{2-} (aq) \rightarrow Ag_2CrO_4 (s)$

The first drop of excess $Ag^+$ will react with the chromate indicator (reddish precipitate) after all $Cl^-$ has been consumed to formed AgCl.

This method can incur relatively greater titration error because it is difficult to observe the red color ($Ag_2CrO_4$ precipitate) over the yellow color ($CrO_4^{2-}$ ion). At present, this method is not widely used as other end point detection method are now available.

# SEVERAL PRECIPITATION TITRATION -MOHR METHOD-

- Direct titration
- **Basis of endpoint:** formation of a colored secondary precipitate
- Indicator: soluble chromate salt ($Na_2CrO_4$, $K_2CrO_4$)

# SEVERAL PRECIPITATION TITRATION -MOHR METHOD-

Endpoints for Argentometric Titrations

*Precipitation Type - Mohr's method*

***$Ag_2CrO_4$ precipitation in neutral pH solution..***

***Product is coloured***

*Colour forms just after AgCl or Ag I forms .*

*Small error involved.*

# SEVERAL PRECIPITATION TITRATION -MOHR METHOD-

- Has to be performed at a neutral or weak basic solution of pH 7-9 (or 6-10)
- In a lower pH (acid solution)

$$CrO_4^{2-}(aq) + H^+(aq) \rightarrow H_2CrO_4$$

$$H_2CrO_4 \leftrightarrow 2H^+(aq) + CrO_4^{2-}(aq)$$

- In a higher pH (basic solution)

$$Ag^+(aq) + OH^-(aq) \rightarrow AgOH(s)$$

By Lara Djelevic

Clear yellow colour of chromate indicator solution before addition of any silver nitrate

**Before endpoint**

- Addition of silver ions
- Formation of AgCl (white precipitate
- Chromate indicator → faint yellow colour

**At the endpoint**

- All $Cl^-$ has been comsumed
- Excess $Ag^+$ react with chromate ion → slight reddish colour

**After endpoint, excess $Ag^+$**

- Increase formation of silver chromate (stronger reddish precipitate)

# SEVERAL PRECIPITATION TITRATION -MOHR METHOD-

## Mohr Method for $Cl^-$ determination

- Relies on $K_{sp}$ differences for two insoluble silver salts

$$Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s) \quad \text{(titration rxn)}$$

$$2Ag^+(aq) + CrO_4^{2-}(aq) \rightarrow Ag_2CrO_4(s) \quad \text{(indicator rxn)}$$

- AgCl is less soluble than $Ag_2CrO_4$ so it will precipitate first
- $Ag_2CrO_4$ is **brick red in color** so a color change is observed at the endpoint

# SEVERAL PRECIPITATION TITRATION -MOHR METHOD-

**The problem should be pay attention to:**

★ The consumption of the indictor : **$5 \times 10^{-3}$ mol/L** .

If the concentration of the $K_2CrO_4$ is **too high**, the end point is advance, result is low

If the concentration of the $K_2CrO_4$ is **too low** ,the end point is delay ,result is high .$K_2CrO_4$ exert titration produce positive error, the measured concentration is low, it need a blank test.

# SEVERAL PRECIPITATION TITRATION -VOLHARD METHOD-

This method is to determine $Cl^-$ by titrating with $Ag^+$ using back titration. First, $Cl^-$ is precipitated by excess standard $AgNO_3$ (known quantity).

$$Ag^+ (aq) (excess) + Cl^- (aq) \rightarrow AgCl (s)$$

The precipitate is isolated and the excess $Ag^+$ is titrated with standard thiocyanate (KSCN) solution in the presence of $Fe^{3+}$.

$$Ag^+ (aq) + SCN^- (aq) = AgSCN (s)$$

After all of the $Ag^+$ has been consumed, the $SCN^-$ reacts with $Fe^{3+}$ to form a red complex.

$$Fe^{3+} + SCN^- = Fe(SCN)^{2+}$$

The indicator system is very sensitive and usually good results are obtained.

# SEVERAL PRECIPITATION TITRATION -VOLHARD METHOD-

**Problem 1**: The end point slowly fades because AgCl is more soluble than AgSCN. The AgCl slowly dissolves and is replaced by AgSCN.

**This problem can be overcome by :**

- Filter off the solid AgCl and only the $Ag^+$ left in the filtrate.

- Add a few mL of $C_6H_5NO_2$ with the AgCl precipitate and shake.

Problem 2: Possibility of $Fe^{3+}$ to hydrolyze to form $Fe(OH)_3$ under alkaline conditions.

**This problem can be overcome by :**

- Perform titration under slightly acidic conditions.

# SEVERAL PRECIPITATION TITRATION
# -VOLHARD METHOD-

## Endpoints for Argentometric Titrations

Chemical method for silver analyses

Volhard's method using thiocyanate , $CNS^-$, as titrant.

Iron (III) is the indicator as it forms a red complex ion with thiocyanate , $CNS^-$, $Fe(CNS)^{2+}$

The method can be adapted to Chloride analyses.

**$AgNO_3$ is added in excess. The AgCl precipitate is often filtered off. Then the excess $Ag^+$ backtitrated with thiocyanate , $CNS^-$.**

Iron (III) acts as the indicator as above.

**Before endpoint**

- Addition of $SCN^-$ ion
- Formation of silver thiocyanate precipitate
- Faint yellow colour observed

**At the endpoint**

- All $Ag^+$ completely consumed
- Excess $SCN^-$ react with $Fe^{3+}$ ions
- Ferric ammonium sulfate indicator → slight orange/red colour

**After endpoint (excess of $SCN^-$)**

- Further formation of ferric thiocyanate (stronger dark red colour)

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# SEVERAL PRECIPITATION TITRATION -FAJANS METHOD-

**Before equivalence point**

- Addition of $Ag^+$ to $Cl^-$
- Formation of colloidal AgCl

**At equivalence point**

- All $Ag^+$ has been consumed

**After equivalence point**

- Anion dyes (fluorescein and its derivatives – adsorption indicator) adsorbed on AgCl surface
- Excess $Ag^+$ react with $FI^-$ → reddish preciptate

- Fluorescein and its derivatives – weak acids.
- Solution should be slightly alkaline, so that indicator keep in anion form.
- Only slightly alkaline to avoid Ag+ is converted to AgOH
- Strong acids of other fluorescein derivatives (eosin) can be used in acidic pH.
- Simple method with reproducible results.

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# SEVERAL PRECIPITATION TITRATION -FAJANS METHOD-

## Endpoints for Argentometric Titrations

Chemical

- Adsorption – Fajan's method
- A **red dye** attaches to the silver salt, on the surface of the analyte precipitate particle.
- **This happens only when the silver ion $Ag^+$ is in excess, i.e just after the equivalence point.**

# LIMITATION OF PRECIPITATION TITRATION

- ❑ A few number of ions such as halide ions ($Cl^-$, $Br^-$, $I^-$) can be titrated by precipitation method.
- ❑ Co-precipitation may be occurred.
- ❑ It is very difficult to detect the end point.

# APPLICATIONS OF PRECIPITATION TITRATION

1. The determination of the chlorine contained in natural water : Mohr and Volhard Method

2. The determination of Silver contained in silver alloy: Volhard method

3. The determination of halogen contained in organic compounds such as food, organochlorine pesticides, used Volhard method.

$$C_6H_6Cl_6 + 3OH^- = C_6H_6Cl_3 + 3Cl^- + 3H_2O$$

4. The determination of sodium chloride contained in MSG:
   Mohr method, no more than 20%
   glutamate more than 95% grade level
   glutamate more than 80% second level

# APPLICATIONS OF PRECIPITATION TITRATION

5. The precipitation can be observed when the salt is occurred and indicators is used to see the pH range: mostly used for neutralization reactions

6. Precipitation titration is used for such reaction when the titration is not recognized by changing the colors. during the reaction a salt is precipitated as the titration is completed.

7. Precipitation titration is an Amperometric titration in which the potential of a suitable indicator electrode is measured during the titration.

8. It is used for determination of chloride by Mohr's Method using Silver nitrate.

# PRECIPITATION TITRATION CURVE INVOLVING SILVER ION

- The most common method of determining the halide ion concentration of aqueous solution
- To construct titration curve, 3 types of calculation are required, each of which corresponds to a distinct stage in the
- reaction:
  - Pre-equivalence
  - Equivalence
  - Post-equivalence

# APPLICATIONS OF STANDARD SILVER NITRATE SOLUTIONS

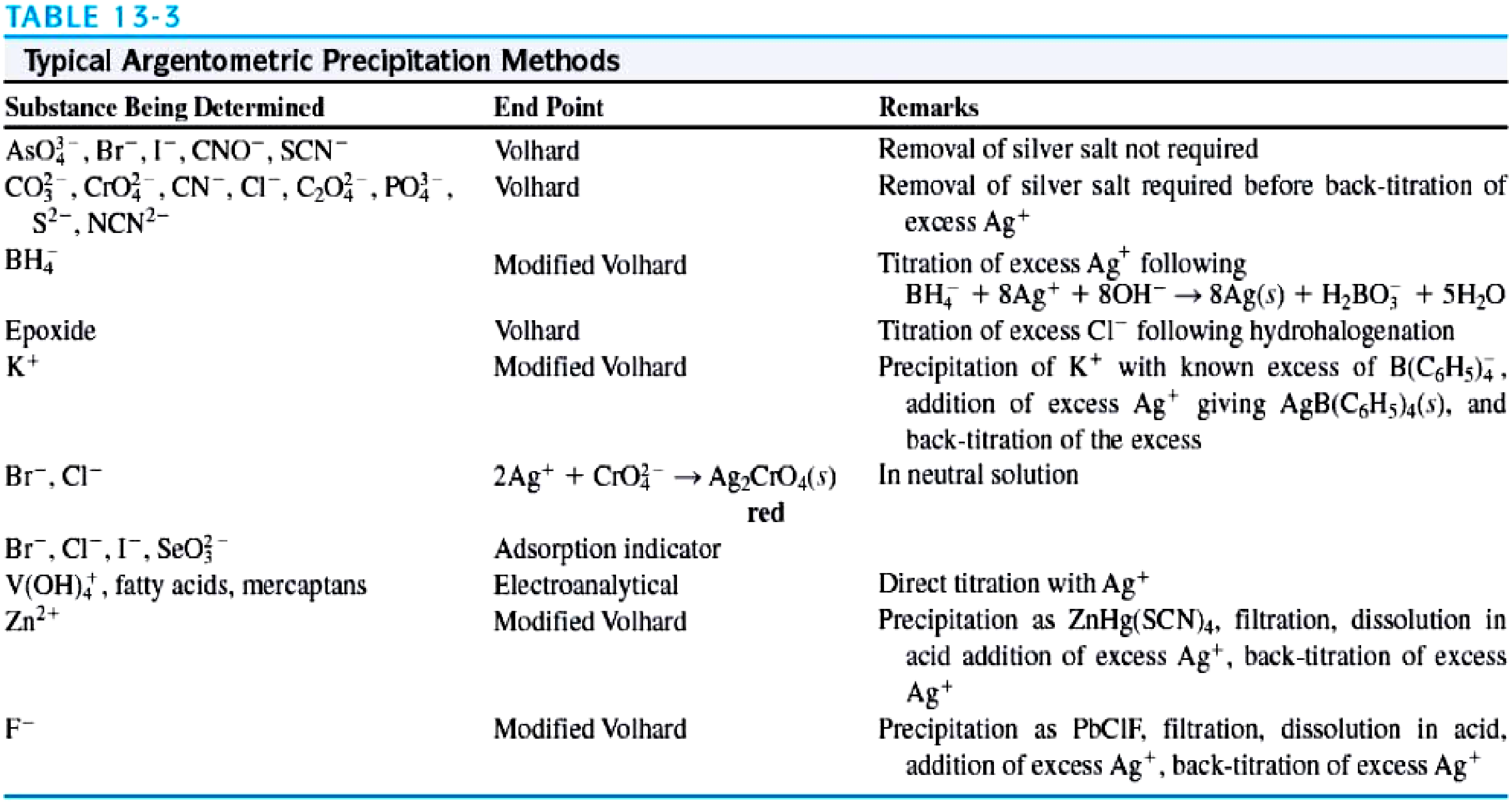


**TABLE 13-3**

**Typical Argentometric Precipitation Methods**

| Substance Being Determined | End Point | Remarks |
|---|---|---|
| $AsO_4^{3-}$, $Br^-$, $I^-$, $CNO^-$, $SCN^-$ | Volhard | Removal of silver salt not required |
| $CO_3^{2-}$, $CrO_4^{2-}$, $CN^-$, $Cl^-$, $C_2O_4^{2-}$, $PO_4^{3-}$, $S^{2-}$, $NCN^{2-}$ | Volhard | Removal of silver salt required before back-titration of excess $Ag^+$ |
| $BH_4^-$ | Modified Volhard | Titration of excess $Ag^+$ following $BH_4^- + 8Ag^+ + 8OH^- \rightarrow 8Ag(s) + H_2BO_3^- + 5H_2O$ |
| Epoxide | Volhard | Titration of excess $Cl^-$ following hydrohalogenation |
| $K^+$ | Modified Volhard | Precipitation of $K^+$ with known excess of $B(C_6H_5)_4^-$, addition of excess $Ag^+$ giving $AgB(C_6H_5)_4(s)$, and back-titration of the excess |
| $Br^-$, $Cl^-$ | $2Ag^+ + CrO_4^{2-} \rightarrow \underset{\textbf{red}}{Ag_2CrO_4(s)}$ | In neutral solution |
| $Br^-$, $Cl^-$, $I^-$, $SeO_3^{2-}$ | Adsorption indicator | |
| $V(OH)_4^+$, fatty acids, mercaptans | Electroanalytical | Direct titration with $Ag^+$ |
| $Zn^{2+}$ | Modified Volhard | Precipitation as $ZnHg(SCN)_4$, filtration, dissolution in acid addition of excess $Ag^+$, back-titration of excess $Ag^+$ |
| $F^-$ | Modified Volhard | Precipitation as PbClF, filtration, dissolution in acid, addition of excess $Ag^+$, back-titration of excess $Ag^+$ |

# CALCULATING THE TITRATION CURVE

Calculate the titration curve for the titration of 50.0 mL of 0.0500 M NaCl with 0.100 M $AgNO_3$.

$$Ag^{+}(aq) + Cl^{-}(aq) \rightleftharpoons AgCl(s)$$

When the equilibrium constant of the reaction is so large:

$K=(K_{sp})^{-1}=(1.8 \times 10^{-10})^{-1} = 5.6 \times 10^{9}$

assume that $Ag^{+}$ and $Cl^{-}$ react completely.

**Step 1:** Calculate the volume of $AgNO_3$ needed to reach the equivalence point. Tips: shows that we need 25.0 mL of $Ag^+$ to reach the equivalence point.

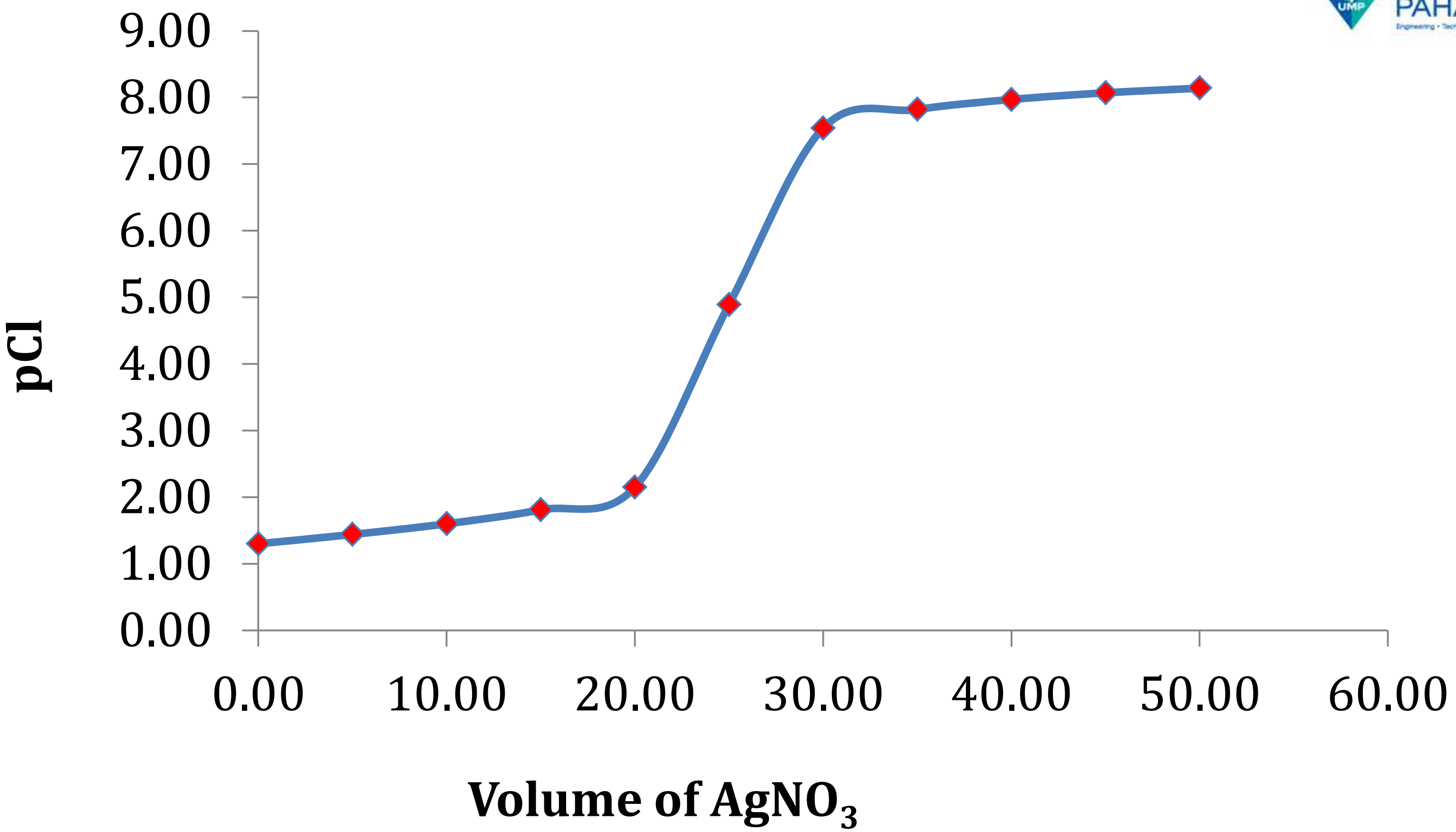
**Step 2:** Calculate pCl before the equivalence point (determine the concentration of unreacted NaCl). Tips: Before the equivalence point the titrand, $Cl^-$, is in excess. The concentration of unreacted $Cl^-$ after adding 10.0 mL of $Ag^+$ which corresponds to a pCl of 1.60.

**Step 3:** Calculate pCl at the equivalence point (use $K_{sp}$ for AgCl to calculate the concentration of $Cl^-$). At the titration's equivalence point, concentrations of $Ag^+ = Cl^-$. To calculate the concentration of $Cl^-$ we use the $K_{sp}$ expression for AgCl; thus solving for $x$ gives $[Cl^-]$ as $1.3 \times 10^{-5}$ M, or a pCl of 4.89.

**Step 4:** Calculate pCl after the equivalence point (calculate the concentration of excess $AgNO_3$ and then calculate the concentration of $Cl^-$ using the $K_{sp}$ for AgCl).

After the equivalence point: calculate the concentration of excess $Ag^+$ and then use the $K_{sp}$ expression to calculate the concentration of $Cl^-$. For example, after adding 35.0 mL of titrant or a pCl of 7.81. Additional results for the titration curve.

| Volume of $AgNO_3$ (mL) | pCl | Volume of $AgNO_3$ (mL) | pCl |
|---|---|---|---|
| 0 | 1.30 | 30 | 7.54 |
| 5 | 1.44 | 35 | 7.82 |
| 10 | 1.60 | 40 | 7.97 |
| 15 | 1.81 | 45 | 8.07 |
| 20 | 2.15 | 50 | 8.14 |



Titration curve for the titration obtained.

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