Environmental Chemistry

Week 2

Gravimetric and Volumetric Analyses

1) Gravimetric Analysis

Gravimetric analysis is one of the most accurate and precise quantitative methods used to determine how much of a certain material is in a sample. Gravimetric analysis is based on the measurement of the weight (gravity). Determination of total solids, suspended solids, fixed solids or volatile solids is made easily by gravimetric analysis. The two gravimetric methods are precipitation and volatilization.

In precipitation method, the analyte is converted to an insoluble product. When precipitation is completed, insoluble product (precipitate) is filtered and then heated (dried) until its mass becomes constant. The primary purpose of this is to drive off any solvent and any other volatile species that may be present. The temperature and time required to produce a suitable product varies from precipitate to precipitate. The thing to remember is that heating may change the chemical composition of the precipitate. After heating, the dried precipitate is cooled prior to weighing. This avoids convection currents from altering the mass measurement. The hot sample is placed into a desiccator during the cooling stage to reduce adsorption of water from the air. The mass of the precipitate is determined by weighting. The solid weight is determined by difference between final weight and tare weight.

In volatilization methods the analyte is heated and the analyte or its decomposition product is collected. The resulting loss of mass is determined.

Gravimetric measurement requires crucible or dish to hold the residue or precipitate. The weight of this container (tare) must be known and deducted from the gross weight to obtain net weight the material being measured. Weighting can be performed with the accuracy of 0.1 or 0.01 g of balance. Porcelain or high-silica crucibles or aluminum dishes are commonly used for gravimetric measurement. Platinum ware also can be used but it is preferred for special measurement because of its high cost. Before gravimetric analysis, wares should be conditioned to remove the dirt (dust) or adsorbed moisture on the wares. In the gravimetric analysis, use of wares without proper conditioning would lead to relatively large errors in final results.
During the conditioning, crucibles and dishes are cleaned with water and then heat-treated under desired temperature at the same conditions as in gravimetric analysis. After cooling in the desiccator, containers are balanced to obtain final weight of precipitate.

The efficiency of the gravimetric analysis is based on some factors such as:

- There must be a phase change so that the product can be separated from the reaction solution. This is satisfied when the product is a solid precipitated from solution.
- The reaction must be significantly complete. This is satisfied when the Ksp of the product is small. It also means that there are no competing equilibria that might re-dissolve the product.
- The final product must be pure and must be of a definite chemical composition.
- The rate of reaction must be fast enough to be practical.

Gravimetric calculations are based on the fundamental stoichiometric calculations. The basic form of the calculation is:

\[
\% \text{ analyte} = \frac{(\text{weight precipitate})(\text{gravimetric factor})(100)}{\text{weight sample}}
\]

The gravimetric factor (GF) comes from a combination of the mole ratios and the formula weights used in the stoichiometric calculation.

\[
\text{gravimetric factor} = \frac{\text{substance sought}}{\text{substance known}}
\]

2) Volumetric analysis

Volumetric (titrimetric) analysis is a quantitative analytical technique which employs a titration in comparing an unknown with a standard. Volumetric analysis has a standard solution and an analyte. A standard solution (titrant) is one whose solute concentration is accurately known or containing a known concentration of reactant. On the other hand, an analyte is a substance to be determined of unknown
concentration. For volumetric methods of analysis to be useful, the reaction must reach completion in a short period of time.

The most common apparatus used in volumetric analysis are the pipette, buret, measuring cylinder, volumetric and conical (titration) flask. Reliable measurement of volume is often done with the help of a pipet, buret, and a volumetric flask. The conical flask is preferred for titration because it has a good “mouth” that minimizes the loss of the titrant during titration.

In a titration, a measured and controlled volume of a standardized solution from a buret is added incrementally to an analyte. The titration proceeds until analyte is just consumed or completed stoichiometrically at the equivalence point. Whether or not the equivalence point comes when equimolar amounts of reactants have been mixed depends on the stoichiometry of the reaction. For example, in the reaction of HCl and NaOH, the equivalence point does occur when one mole of HCl has reacted with one mole of NaOH. However, in the reaction of H₂SO₄ and NaOH, the equivalence point occurs when two moles of NaOH have reacted with one mole of H₂SO₄. The titration technique can be applied to many types of reactions, including oxidation-reduction, precipitation, complexation, and acid-base neutralization reactions.

For detecting the equivalence point of the reaction, an indicator is added to the reaction mixture. Indicator changes colour in response to a chemical change. An acid-base indicator (e.g., phenolphthalein) changes colour depending on the pH. A drop of indicator solution is added to the titration at the start and the titrant reacts with the indicator. After completely reacting with the analyte in solution and the indicator undergoes a color change and enables the end point to be observed. The point in the titration at which the color change occurs is called the end point. The titration will be accurate only if the end point and the equivalence point coincide fairly closely, thus, the indicator used in a titration must be selected carefully. A large number of indicators are commercially available and finding the right one for a particular titration is not a difficult task.

In some reactions, the solution changes colour without any added indicator. This is often seen in redox titrations, for instance, when the different oxidation states of the product and reactant produce different colours.
Compared to gravimetric analysis, volumetric analysis consume less time. Volumetric analyses are used for many determinations such as dissolved O₂, biochemical oxygen demand (BOD), chemical oxygen demand (COD), chlorides and hardness.
Environmental Chemistry

Week 2

Gravimetric and volumetric analyses
Gravimetric Analysis

- Quantitative method
- Gravimetric analysis is based on the measurement of the weight (gravity).
- Amount of total solids, suspended solids, fixed solids, volatile solids, precipitate
- Gravimetric methods: precipitation and volatilization

**Precipitation:**
- Analyte is converted to an insoluble product.
- Insoluble product (precipitate) is filtered and then heated (dried).
- The mass of the precipitate is determined by weighting
- Use stoichiometry to determine the amount of analyte

**Volatilization**
- Analyte is heated
- Analyte or its decomposition product is collected.
- The resulting loss of mass is determined.
Factors effection efficiency of gravimetric analysis

✓ The rate of reaction must be fast enough to be practical.
✓ The reaction should be completely or significantly completed
✓ At the end of the reaction the analyte must be separated from the reaction
✓ There must be no competing equilibria that might re-dissolve the product
✓ The final insoluble product (precipitate) must be a pure compound.
✓ The precipitate must be easily filtered
**Apparatus**

- Beaker for precipitation reaction
- Heating system (optional)
- Crucible or dish to hold the residue or precipitate
- Filter
- Drying instrument (oven, water bath)
- Desiccator
- Balance (0.1 or 0.01 g accurate)

Net weight = Gross weight - Tare weight (weight of container)
Apparatus
Gravimetric Analysis of ion solution

- Add precipitation agent in excess amount
- Monitor the complete precipitation
- Heat for increasing particle size (optimal)
- Filter precipitate
- Dry and weight the weight
- Use stoichiometry to determine the amount of analyte

For example: Determination of chlorides
Ag⁺, Pb²⁺, and Hg₂²⁺ form insoluble chlorides. Silver chloride (AgCl) is insoluble (99.9% of the silver is converted to AgCl). It is pure and is easily filtered.

\[ Ba^{+2} + SO_4^{2-} \rightarrow BaSO_4 \]

\[ Ag^+ + Cl^- \rightarrow AgCl \] (white solid)
Before gravimetric analysis, wares should be conditioned to remove the dirt (dust) or adsorbed moisture on the wares.

In the gravimetric analysis, use of wares without proper conditioning would lead to relatively large errors in final results.

During the conditioning, crucibles and dishes are cleaned with water and then heat-treated under desired temperature at the same conditions as in gravimetric analysis. After cooling in the desiccator, containers are balanced to obtain final weight of precipitate.
Amount of analyte is calculated based on stoichiometry of reaction.

\[ \% \text{ analyte} = \frac{\text{weight precipitate}(\text{gravimetric factor})(100)}{\text{weight sample}} \]

Gravimetric factor = \( \frac{\text{substance sought}}{\text{substance known}} \)

\[ \text{Ag}^+ + \text{Cl}^- \rightarrow \text{AgCl} \]

\[
\frac{\text{molar mass of Cl}}{\text{molar mass of AgCl}} = 0.24737
\]

\[ \text{Ba}^{+2} + \text{SO}_4^{2-} \rightarrow \text{BaSO}_4 \]

What is the gravimetric factor for Ba?
A 2.00g sample of limestone was dissolved in hydrochloric acid and all the calcium present in the sample was converted to Ca\(^{2+}\)\(_{\text{aq}}\).

Excess ammonium oxalate solution, \((\text{NH}_4)_2\text{C}_2\text{O}_4\)\(_{\text{aq}}\), was added to the solution to precipitate the calcium ions as calcium oxalate, CaC\(_2\text{O}_4\)\(_{\text{s}}\).

The precipitate was filtered, dried and weighed to a constant mass of 2.43g.

Determine the percentage by mass of calcium in the limestone sample.

1. Write the balanced chemical equation for the precipitation reaction:
   \[
   \text{Ca}^{2+}\(_{\text{aq}}\) + \text{C}_2\text{O}_4^{2-}\(_{\text{aq}}\) \rightarrow \text{CaC}_2\text{O}_4\(_{\text{s}}\)
   \]

2. Calculate the moles of calcium oxalate precipitated.
   \[
   n(\text{CaC}_2\text{O}_4\(_{\text{s}}\)) = \frac{\text{mass}}{\text{MM}}
   \]
   \[
   n(\text{CaC}_2\text{O}_4\(_{\text{s}}\)) = \frac{2.43g}{(40.08 + 2 \times 12.01 + 4 \times 16.00)}
   \]
   \[
   n(\text{CaC}_2\text{O}_4\(_{\text{s}}\)) = \frac{2.43}{128.10}
   \]
   \[
   n(\text{CaC}_2\text{O}_4\(_{\text{s}}\)) = 0.019 \text{ mol}
   \]

3. Find the moles of Ca\(^{2+}\)\(_{\text{aq}}\).
   From the balanced chemical equation, the mole ratio of Ca\(^{2+}\) : CaC\(_2\text{O}_4\(_{\text{s}}\) is 1 : 1
   So, \(n(\text{Ca}^{2+}\(_{\text{aq}}\)) = n(\text{CaC}_2\text{O}_4\(_{\text{s}}\)) = 0.019\text{mol}

4. Calculate the mass of calcium in grams
   \[
   \text{mass (Ca)} = n \times \text{MM}
   \]
   \[
   \text{mass (Ca)} = 0.019 \times 40.08 = 0.76\text{g}
   \]

5. Calculate the percentage by mass of calcium in the original sample:
   \[
   %\text{Ca} = \frac{\text{mass Ca} + \text{mass sample}}{100}
   \]
   \[
   %\text{Ca} = \frac{0.76 + 2.00}{100} = 38\%
   \]
Volumetric Analysis

- Volumetric analysis = Titrimetric analysis = Titration
- A quantitative analytical technique
  - A standard solution (titrant) is that containing a known concentration of reactant
  - An analyte is a substance to be determined of unknown concentration
  - The basis of the titration is a chemical reaction of a standard solution with an analyte

In a titration, a measured volume of a standard solution (A) from a buret is added incrementally to an analyte (B). The titration proceeds until B is just stoichiometrically completed at the equivalence point.

\[ aA + bB \underset{\text{equivalence point}}{\rightarrow} AaBb \]
Compared to gravimetric analysis, volumetric analysis consume less time.

Volumetric analyses are used for many determinations such as dissolved O2, biochemical oxygen demand (BOD), chemical oxygen demand (COD), chlorides and hardness.
The most common apparatus used in volumetric analysis
- pipette
- buret
- Measuring (graduated) cylinder
- Volumetric and conical (titration) flask
The Mohr pipet has graduations that allow it to deliver a range of volumes. The volumetric pipet has a single graduation that allows it to deliver one specific volume accurately.
Volume reading

- 6.63 ml

Measurement:
- 1.40 ml
- 1.42 ml
Glassware standards

B class volumetric flask
Flask is calibrated to contain 1000±0.80 mL of liquid at 20 °C. According to ASTM E287-02, tolerance of A class 1000 mL volumetric flask should be ±0.300, that means ±0.600 for B class flask (twice A class tolerance).

This flask is marked DIN - Deutsches Institut für Normung - and DIN standard is slightly different.
Maximum relative errors for A class volumetric glassware

<table>
<thead>
<tr>
<th>capacity mL</th>
<th>pipette tolerance mL</th>
<th>pipette relative (%)</th>
<th>burette tolerance mL</th>
<th>burette relative (%)</th>
<th>flask tolerance mL</th>
<th>flask relative (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.006</td>
<td>0.60</td>
<td></td>
<td></td>
<td>0.010</td>
<td>1.00</td>
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<tr>
<td>2</td>
<td>0.006</td>
<td>0.30</td>
<td></td>
<td></td>
<td>0.015</td>
<td>0.75</td>
</tr>
<tr>
<td>3</td>
<td>0.010</td>
<td>0.33</td>
<td></td>
<td></td>
<td>0.015</td>
<td>0.50</td>
</tr>
<tr>
<td>4</td>
<td>0.010</td>
<td>0.25</td>
<td></td>
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</tr>
<tr>
<td>5</td>
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<td>0.20</td>
<td></td>
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<td>0.020</td>
<td>0.40</td>
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<td>10</td>
<td>0.020</td>
<td>0.20</td>
<td>0.020</td>
<td>0.25</td>
<td>0.020</td>
<td>0.20</td>
</tr>
<tr>
<td>15</td>
<td>0.030</td>
<td>0.20</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>20</td>
<td>0.030</td>
<td>0.15</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>0.030</td>
<td>0.12</td>
<td>0.030</td>
<td>0.15</td>
<td>0.030</td>
<td>0.12</td>
</tr>
<tr>
<td>50</td>
<td>0.050</td>
<td>0.10</td>
<td>0.050</td>
<td>0.13</td>
<td>0.050</td>
<td>0.10</td>
</tr>
<tr>
<td>100</td>
<td>0.080</td>
<td>0.08</td>
<td>0.100</td>
<td>0.13</td>
<td>0.080</td>
<td>0.08</td>
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<td>200</td>
<td>0.100</td>
<td>0.05</td>
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<td>0.100</td>
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<td>250</td>
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<td>0.120</td>
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<tr>
<td>500</td>
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<td>0.150</td>
<td>0.03</td>
</tr>
<tr>
<td>1000</td>
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<td>0.300</td>
<td>0.03</td>
</tr>
<tr>
<td>2000</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.500</td>
<td>0.03</td>
</tr>
</tbody>
</table>
For detecting the equivalence point of the reaction, an indicator is added to the reaction mixture. The titrant reacts with the *indicator*, after completely reacting with the analyte in solution and the indicator undergoes a color change and enables the end point to be observed. The point in the titration at which the color change occurs is called the **end point**.

<table>
<thead>
<tr>
<th>Indicator</th>
<th>Acid color</th>
<th>Base color</th>
<th>pH Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl violet</td>
<td>Yellow</td>
<td>Violet</td>
<td>0–2</td>
</tr>
<tr>
<td>Malachite green (acidic)</td>
<td>Yellow</td>
<td>Blue-green</td>
<td>0–1.8</td>
</tr>
<tr>
<td>Thymol blue (acidic)</td>
<td>Red</td>
<td>Yellow</td>
<td>1.2–2.8</td>
</tr>
<tr>
<td>Bromphenol blue</td>
<td>Yellow</td>
<td>Blue</td>
<td>3.0–4.6</td>
</tr>
<tr>
<td>Methyl orange</td>
<td>Red</td>
<td>Yellow-orange</td>
<td>3.1–4.6</td>
</tr>
<tr>
<td>Brom cresol green</td>
<td>Yellow</td>
<td>Blue</td>
<td>3.8–5.4</td>
</tr>
<tr>
<td>Methyl red</td>
<td>Red</td>
<td>Yellow</td>
<td>4.4–6.2</td>
</tr>
<tr>
<td>Litmus</td>
<td>Red</td>
<td>Blue</td>
<td>4.5–8.3</td>
</tr>
<tr>
<td>Brom thymol blue</td>
<td>Yellow</td>
<td>Blue</td>
<td>6.0–7.6</td>
</tr>
<tr>
<td>Phenolphthalein</td>
<td>Yellow</td>
<td>Red</td>
<td>6.8–8.4</td>
</tr>
<tr>
<td>Met cresol purple</td>
<td>Yellow</td>
<td>Purple</td>
<td>7.6–9.2</td>
</tr>
<tr>
<td>Thymol blue (alkaline)</td>
<td>Yellow</td>
<td>Blue</td>
<td>8.0–9.6</td>
</tr>
<tr>
<td>Phenolphthalein</td>
<td>Colorless</td>
<td>Red</td>
<td>8.2–9.8</td>
</tr>
<tr>
<td>Thymolphthalein</td>
<td>Colorless</td>
<td>Blue</td>
<td>9.3–10.5</td>
</tr>
<tr>
<td>Alizarin yellow</td>
<td>Yellow</td>
<td>Lilac</td>
<td>10.1–11.1</td>
</tr>
<tr>
<td>Malachite green (alkaline)</td>
<td>Green</td>
<td>Colorless</td>
<td>11.4–13.0</td>
</tr>
</tbody>
</table>
## Titration types

<table>
<thead>
<tr>
<th></th>
<th>Type of chemical to be analysed</th>
<th>Type of reagent used</th>
<th>Monitoring method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid/base</td>
<td>acid or base</td>
<td>alkali or acid</td>
<td>pH indicator or pH meter</td>
</tr>
<tr>
<td>Precipitation</td>
<td>ion that forms insoluble salts</td>
<td>compound containing the other ion needed to form the insoluble salt</td>
<td>conductivity</td>
</tr>
<tr>
<td>Redox</td>
<td>oxidising or reducing agent</td>
<td>suitable reducing or oxidising agent</td>
<td>natural colour change or redox indicator</td>
</tr>
<tr>
<td>Complexometric</td>
<td>metal ion that forms complexes</td>
<td>complexing agent</td>
<td>metal ion indicator</td>
</tr>
</tbody>
</table>
Acid base reactions

A strong acid reacts with a strong base to form a neutral (pH=7) solution. A strong acid reacts with a weak base to form an acidic (pH<7) solution. A weak acid reacts with a strong base to form a basic (pH>7) solution.

What will be if weak acid and weak base are titrated?
Precipitation reaction
Methyl orange

pH = 2

pH = 7

Phenolphthalein

pH = 7

pH = 10

Good Endpoint

Bad Endpoint (Overly Titrated)
Calculation

equivalent mass = molar mass/\(a\)

where "\(a\)" for an acid is the number of moles of \(H^+(aq)\) supplied by one mole of acid in the reaction taking place, and for a base "\(a\)" is the number of moles of \(OH^-(aq)\) supplied by one mole of base in the reaction taking place.

(1) \(HCl + NaOH \rightarrow NaCl + H_2O\)
Equivalent mass \(HCl\) = Molar mass \(HCl\) = 36.5 g
Equivalent mass \(NaOH\) = Molar mass \(NaOH\) = 40.0 g

(2) \(H_2SO_4 + 2NaOH \rightarrow Na_2SO_4 + 2H_2O\)
Equivalent mass \(NaOH\) = Molar mass \(NaOH\) = 40.0 g
Equivalent mass \(H_2SO_4\) = (Molar mass \(H_2SO_4\))/2 = 49.0 g

(3) \(H_3PO_4 + 3NaOH \rightarrow Na_3PO_4 + 3H_2O\)
Equivalent mass \(NaOH\) = Molar mass \(NaOH\) = 40.0 g
Equivalent mass \(H_3PO_4\) = (Molar mass \(H_3PO_4\))/3 = 32.7 g

(4) \(H_3PO_4 + 2NaOH \rightarrow Na_2HPO_4 + 2H_2O\)
Equivalent mass \(NaOH\) = Molar mass \(NaOH\) = 40.0 g
Equivalent mass \(H_3PO_4\) = (Molar mass \(H_3PO_4\))/2 = 49.0 g

What is equivalent mass of \(Al(OH)_3\)?
Normality = (equivalents of solute)/Liter of solution

# equivalents of A = (Volume of A) \times (Normality of A)

\[ N = aM \]

(1) \[ \text{HCl} + \text{NaOH} \rightarrow \text{NaCl} + \text{H}_2\text{O} \]
1.0 \( M \) HCl = 1.0 \( N \) HCl

(2) \[ \text{H}_2\text{SO}_4 + 2\text{NaOH} \rightarrow \text{Na}_2\text{SO}_4 + 2\text{H}_2\text{O} \]
1.0 \( M \) H\(_2\)SO\(_4\) = 2.0 \( N \) H\(_2\)SO\(_4\)

(3) \[ \text{H}_3\text{PO}_4 + 3\text{NaOH} \rightarrow \text{Na}_3\text{PO}_4 + 3\text{H}_2\text{O} \]
1.0 \( M \) H\(_3\)PO\(_4\) = 3.0 \( N \) H\(_3\)PO\(_4\)

(4) \[ \text{H}_3\text{PO}_4 + 2\text{NaOH} \rightarrow \text{Na}_2\text{HPO}_4 + 2\text{H}_2\text{O} \]
1.0 \( M \) H\(_3\)PO\(_4\) = 2.0 \( N \) H\(_3\)PO\(_4\)
At the equivalence point of an acid-base titration the equivalents of acid equals the equivalents of base:

\[ V_{\text{acid}}N_{\text{acid}} = V_{\text{base}}N_{\text{base}} \]

10.0 mL of an unknown acid required 20.0 mL of 0.125 \( N \) NaOH to reach the equivalence point.
(a) Calculate the normality of the unknown acid.
(b) What is the molarity of the unknown acid if one mole of acid reacts two moles of base in the neutralization process?

**Answer:** (a) equivalents of acid = equivalents of base

\[ V_{\text{acid}}N_{\text{acid}} = V_{\text{base}}N_{\text{base}} \]

Therefore \( N_{\text{acid}} = (20.0 \text{ mL})(0.125 \text{ \( N \))}/(10.0 \text{ mL}) = 0.250 \text{ \( N \)} \)

(b) \( M_{\text{acid}} = 0.250 \text{ \( N \)}/2 = 0.125 \text{ \( M \)} \)