Introduction to Analytical Chemistry

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D.A. Skoog, D.M. West, F.J. Holler, S.R. Crouch, "**Fundamentals of Analytical Chemistry**", 9th Edition, Thomson Brooks/Cole, 2014.

Part I: Tool of Analytical Chemistry
Part II: Chemical Equilibria
Part III: Classical Methods of Analysis
Part IV: Electrochemical Methods
Part V: Spectrochemical Methods
Part VI: Kinetics and Separations

What is Analytical Chemistry?

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Analytical chemistry involves separating, identifying, and determining the relative amounts of the components in a sample of matter. It is a measurement science consisting of a set of powerful ideas, instruments and methods that are useful in all fields of **science**, **engineering** and **medicine**.

- **Qualitative analysis** reveals the **identity** of the elements and compounds in a sample.
- **Quantitative analysis** indicates the **amount** of each substance in a sample.

1A The Role of Analytical Chemistry

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- Analytical chemistry is applied throughout industry, medicine, and all the sciences. Ex.
- Quantitative analytical measurements also play a vital role in chemistry, biochemistry, biology, geology, physics, and the other sciences.
- Many scientists devote much time in the laboratory gathering quantitative information about systems that are important and interesting to them.

1A The Role of Analytical Chemistry

Figure 1-1
The relationship between analytical chemistry, other branches of chemistry, and the other sciences. The central location of analytical chemistry in the diagram signifies its importance and the breadth of its interactions with many other disciplines.

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1B Quantitative Analytical Methods

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The results of a typical **quantitative analysis** are computed from two measurements:

1) One is the mass or the volume of sample to be analyzed.

2) The second is the measurement of some quantity that is proportional to the amount of **analyte** (分析物) in the sample, such as mass, volume, intensity of light, or electrical charge.

1B Classifying Quantitative Analytical Methods

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We classify analytical methods according to the nature of this final measurement 2).

1. **Gravimetric methods** determine the mass of the analyte or some compound chemically related to it.
2. **Volumetric method** determines the volume of a solution containing sufficient reagent to react completely with the analyte.
3. **Electroanalytical methods** involve the measurement of such electrical properties as voltage, current, resistance, and quantity of electrical charge.
4. **Spectroscopic methods** are based on measurement of the interaction between electromagnetic radiation and analyte atoms or molecules or on the production of such radiation by analytes.

1B Classifying Quantitative Analytical Methods (cont.)

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Miscellaneous methods:

- mass-to-charge ratio
- rate of radioactive decay
- heat of reaction
- rate of reaction
- sample thermal conductivity
- optical activity
- refractive index.

Flow Diagram Showing the Steps in a Quantitative Analysis

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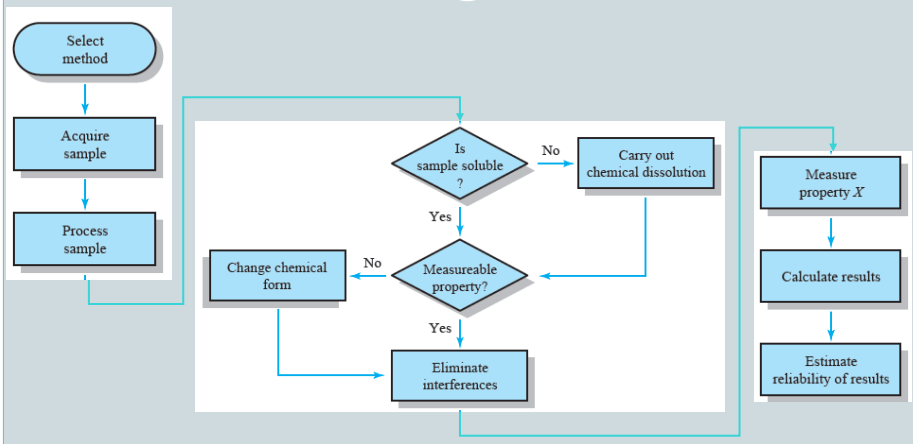

1C-1 Picking a Method

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- One of the first questions to be considered in the selection process is the **level of accuracy** (準確性) required.
- A second consideration related to **economic factors** is the number of samples to be analyzed.
- The complexity of the sample and the number of components in the sample always influence the choice of method to some degree.

1C-2 Acquiring the Sample

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- A material is ***heterogeneous*** if its constituent parts can be distinguished visually or with the aid of a microscope. (silver ore)
- An ***assay*** (檢驗，鑑定) is the process of determining how much of a given sample is the material indicated by its name (for example, a zinc alloy is assayed for its zinc content).
- We *analyze* samples and we determine ***substances***.

  ex: analyze blood samples to determine blood gases or glucose.

1C-2 Acquiring the Sample

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- **Sampling (取樣，抽樣)** is the process of collecting a small mass of a material whose composition accurately represents the bulk of the materials being sampled.
- Sampling is frequently the most difficult step in an analysis and the source of greatest error. The final results of an analysis will never be any more reliable than the reliability of the sampling step.

1C-3 Processing the Sample

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- Under certain circumstances, no sample processing is required prior to the measurement step. (pH measurement of water)
- Under most circumstances, we must process the sample in any of a variety of different ways.
- The first step in processing the sample is often the preparation of a laboratory sample.

1C-3 Processing the Sample

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- Preparing a **Laboratory Sample**
  - A solid sample is ground, mixed to ensure homogeneity, and stored for various lengths of time before analysis begins.
  - Because any loss or gain of water changes the chemical composition of solids, it is a good idea to dry samples just before starting an analysis.
  - Alternatively, the moisture content of the sample can be determined at the time of the analysis in a separate analytical procedure.

1C-3 Processing the Sample

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- Preparing a Laboratory Sample (Cont.)
  - Liquid samples are subject to solvent evaporation
  - If the analyte is a gas dissolved in a liquid, analyte must be kept inside a second sealed container to prevent contamination by atmospheric gases.
  - Extraordinary measures, including sample manipulation and measurement in an inert atmosphere, may be required to preserve the integrity of the sample.

1C-3 Processing the Sample

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- **Replicate samples** (複製樣本), or **replicates**, are portions of a material of approximately the same size that are carried through an analytical procedure at the same time and in the same way.
- Replication improves the quality of the results and provides a measure of their reliability.
- Quantitative measurements on replicates are usually averaged, and various statistical tests are performed on the results to establish their **reliability** (信賴度，可靠度).

1C-3 Processing the Sample

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- Preparing **Solutions**: Physical and Chemical Changes
  - Ideally, the solvent should dissolve the entire sample, including the analyte, rapidly and completely.
  - The sample may require heating with aqueous solutions of strong acids, strong bases, oxidizing agents, reducing agents, or some combination of such reagents.
  - It may be necessary to ignite the sample in air or oxygen or perform a high-temperature fusion of the sample in the presence of various fluxes.

1C-4 Eliminating Interferences

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- Few chemical or physical properties of importance in chemical analysis are unique to a single chemical species.
- Species other than the analyte that affect the final measurement are called **interferences**, or interferents.
- An ***interference*** is a species that causes an error in an analysis by enhancing or attenuating (making smaller) the quantity being measured.
- Techniques or reactions that work for only one analyte are said to be ***specific (特異性)***. Techniques or reactions that apply for only a few analytes are ***selective (選擇性)***.
- The ***matrix (基質)***, or *sample matrix*, is all of the components in the sample containing an analyte.

Remain Steps of A Typical Quantitative Analysis

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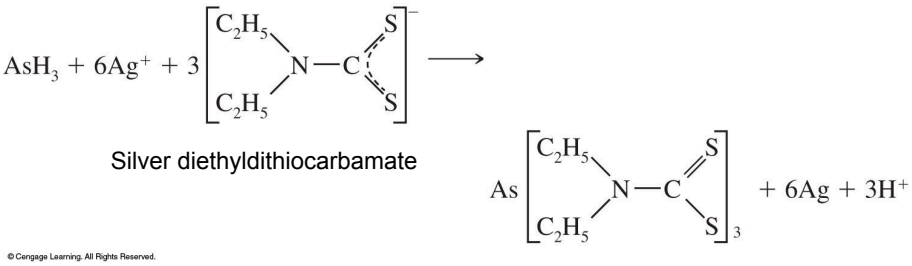
- **1C-5 Calibration (校正) and Measurement**
  - Ideally, the measurement of the property (*X*) is directly proportional to the concentration. $C_A = kX$

    where *k* is a proportionality constant

    Calibration: the process of determining the proportionality between analyte concentration and a measured quantity.
- **1C-6 Calculating Results**
  - Computing analyte concentrations are based on the raw experimental data collected in the measurement step, the characteristics of the measurement instruments, and the stoichiometry of the analytical reaction.



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Use spectrophotometer (光譜儀) to measure the absorbance of the sample.

Beer's Law: A = εbc

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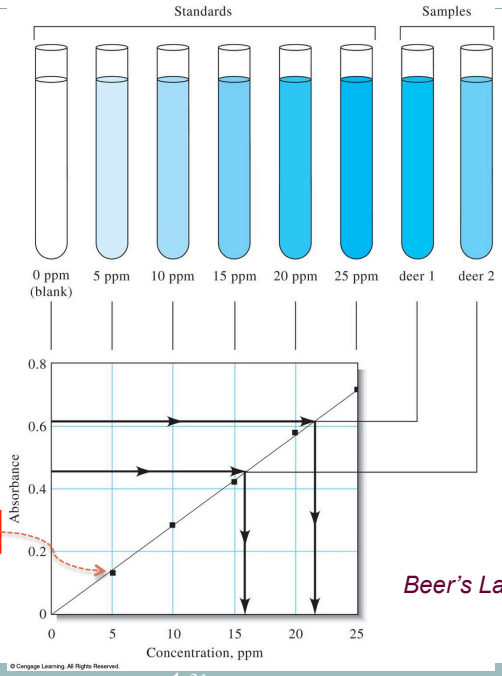
Calibration



Calibration curve

Beer's Law: $A = \varepsilon bc$

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Remain Steps of A Typical Quantitative Analysis

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- **1C-7 Evaluating Results by Estimating Their Reliability**
  - Analytical results are incomplete without an estimate of their reliability. (p. 12)

1D An Integral Role For Chemical Analysis: Feedback Control Systems

Analytical results may be used to control a patient's health, to control the amount of Hg in fish, to control the quality of a product, to determine the status of a synthesis, or to find out whether there is life on Mars.

- Chemical analysis is the measurement element in all of these examples and in many other cases.
- The process of continuous measurement and control is often referred to as a ***feedback system***, and the cycle of measurement, comparison, and control is called a ***feedback loop***.

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Feedback Control Systems

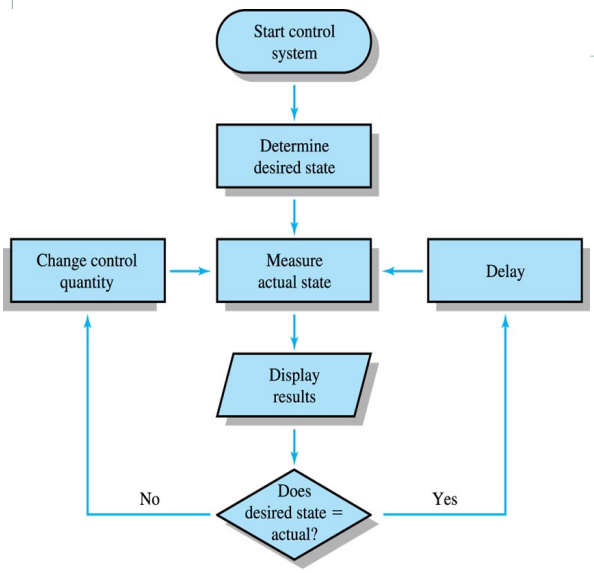

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Figure 1-3 Feedback system flow diagram. The desired state is determined, the actual state of the system is measured, and the two states are compared. The difference between the two states is used to change a controllable quantity that results in a change in the state of the system. Quantitative measurements are again performed on the system, and the comparison is repeated. The new difference between the desired state and the actual state is again used to change the state of the system if necessary. The process provides continuous monitoring and feedback to maintain the controllable quantity, and thus the actual state, at the proper level. The text describes the monitoring and control of blood glucose as an example of a feedback control system.

THE END