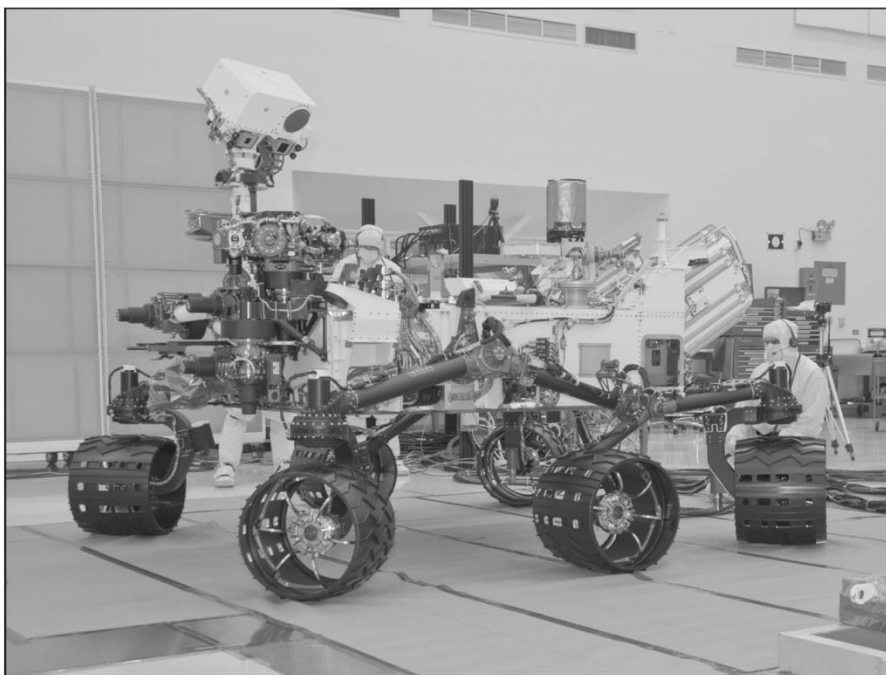# Chapter 1: The Nature of Analytical Chemistry

Overview

- "Analytical chemistry is a measurement science consisting of a set of powerful ideas and methods that are useful in all fields of science and medicine."

NASA/JPL-Caltech

Some exciting illustrations of the power and significance of analytical chemistry
have occurred,
are occurring, and
will occur
during NASA's rover explorations of the planet Mars.

NASA/JPL-Caltech

- On July 4, 1997, the Pathfinder spacecraft delivered the Sojourner rover to the Martian surface.

- Analytical instruments returned information on the chemical composition of rocks and soil.

- Investigations by the lander and rover suggested that Mars was at one time in its past warm and wet with liquid water on the surface and water vapor in the atmosphere.
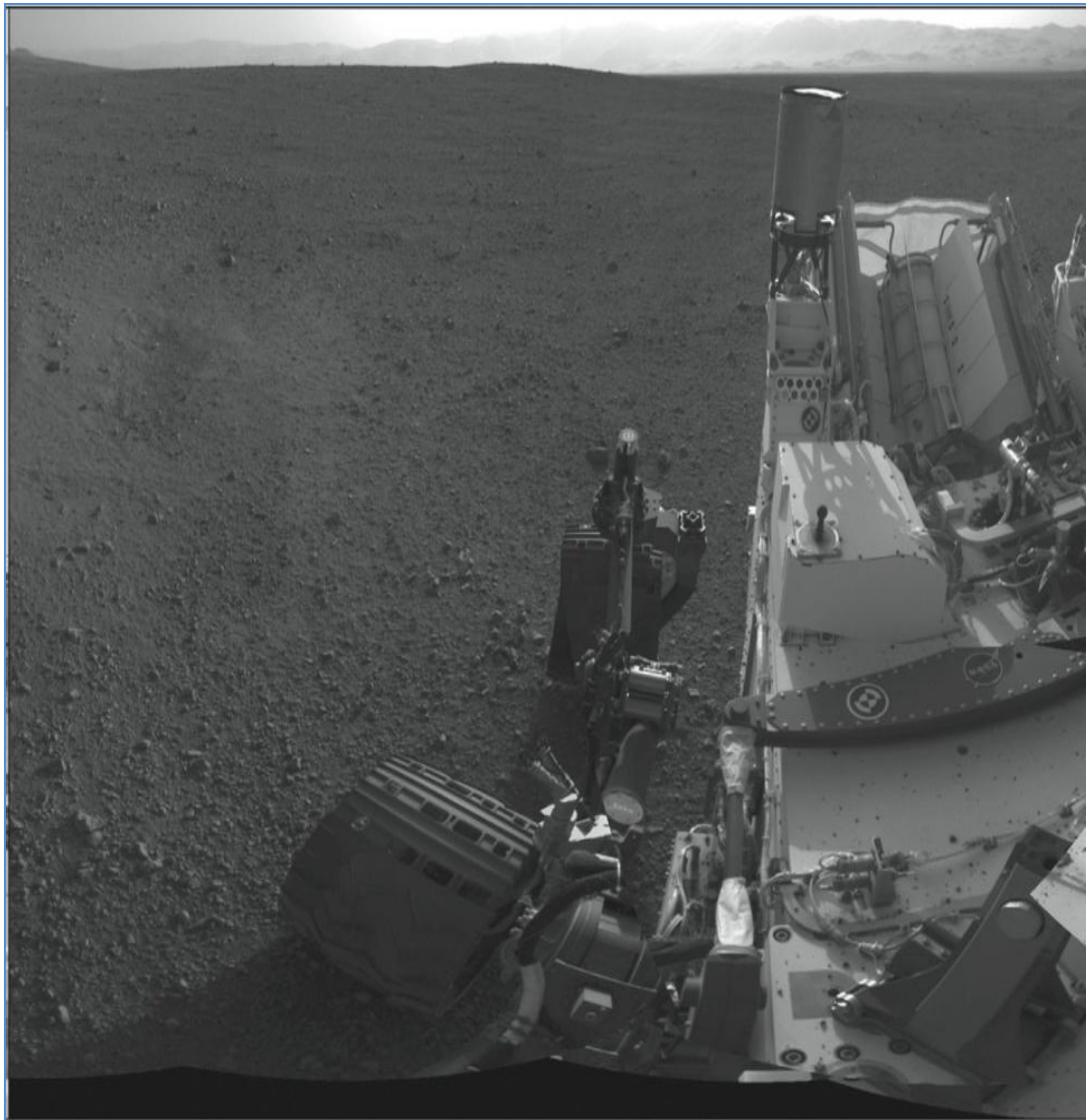
NASA/JPL-Caltech

- In January 2004, the Mars rovers Spirit and Opportunity arrived on Mars for a 3 month mission.

- A major result from Spirit's alpha particle X-ray spectrometer (APXS) and Mossbauer spectrometer was finding concentrated deposits of silica and, at a different site, high concentrations of carbonate.

- Spirit continued to explore and transmit data until 2010, outliving even the most optimistic predictions.

- Even more amazing, Opportunity continues to travel the surface of Mars and, by March, 2012, had covered more than 21 miles exploring and transmitting images of craters, small hills, and other features.
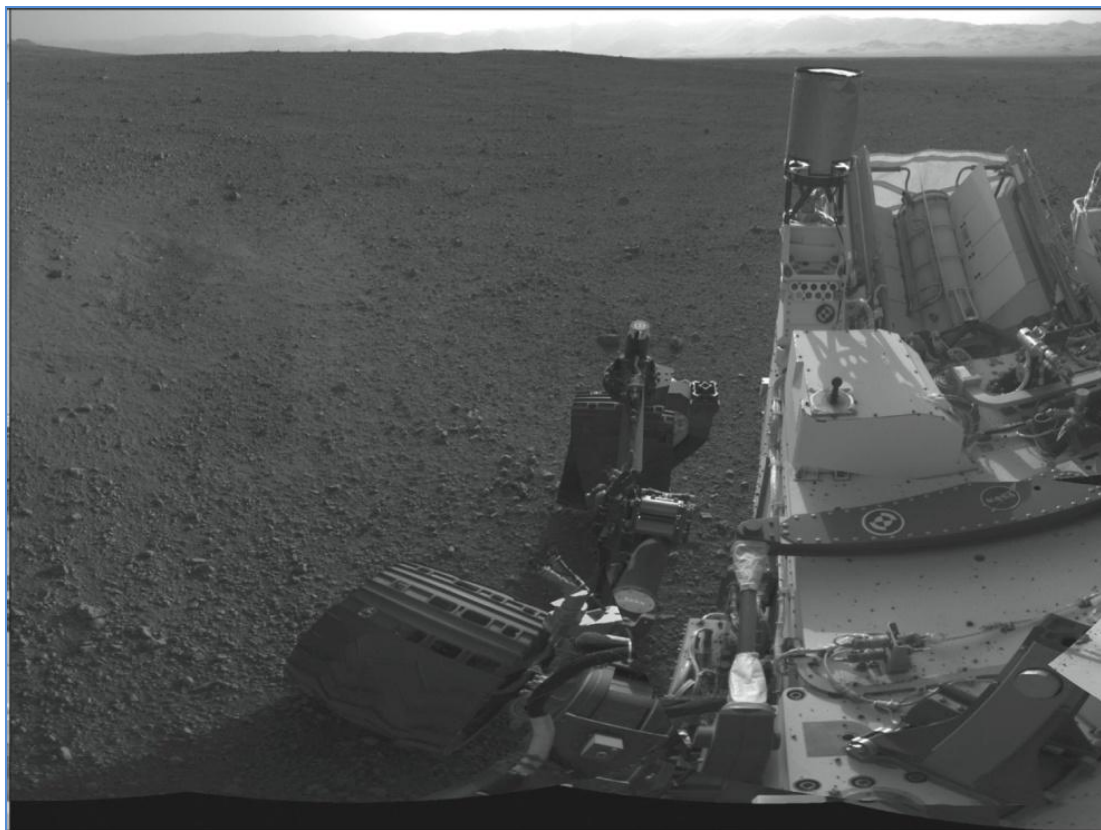
NASA/JPL-Caltech

- In late 2011, the Mars Science Laboratory aboard the rover Curiosity. It arrived on August 6, 2012 with a host of analytical instruments on board.

- The Chemistry and Camera package (CHEMCAM) (LIBS) + remote micro imager. The LIBS instrument will provide determination of many elements with no sample preparation. It can determine the identity and amounts of major, minor, and trace elements and can detect hydrated minerals. The sample analysis package contains a quadrupole mass spectrometer, a gas chromatograph, and a tunable laser spectrometer. Its goals are to survey carbon compound sources, search for organic compounds important to life, reveal the chemical and isotopic states of several elements, determine the composition of the Martian atmosphere, and search for noble gas and light element isotopes.

- These examples demonstrate that both qualitative and quantitative information are required in an analysis.

  - 1. Qualitative Analysis – reveals chemical identity of elements and compounds in a sample.

  - 2. Quantitative Analysis – determines the relative amounts of each substance in a sample.

  - 3. Analytes – components of a sample that are to be determined.

1.A The Role of Analytical Chemistry

•Analytical chemists use science and technology to solve practical problems.

•Analytical chemistry is applied in all areas of science, industry, and medicine.

–The concentrations of O_2 and of CO_2 in blood samples.

– Quantities of hydrocarbons, NOx, and CO in automobile exhaust gases for emission-control devices.

–Quantitative measurements of ionized Ca in blood serum help diagnose parathyroid disease in humans.

– Quantitative determination of N in foods: protein content and thus their nutritional value.

– Analysis of steel during its production for carbon, nickel, and chromium to achieve a desired strength, hardness, corrosion resistance, and ductility.

– The mercaptan content of household gas supplies to warn of dangerous leaks.

– Farmers tailor fertilization and irrigation schedules to meet changing plant needs during the growing

Chemistry: The Central Science; all sub-disciplines rely on analytical chemistry to function.
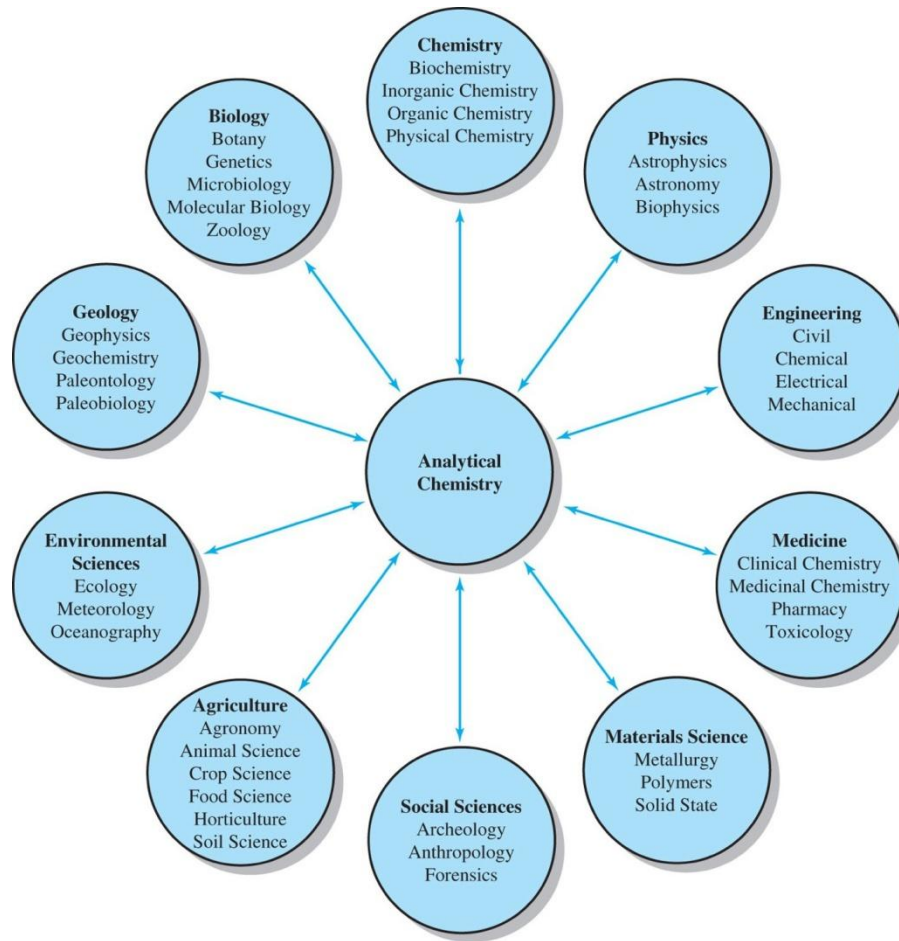
The interdisciplinary nature of chemical analysis
makes it a vital tool in medical, industrial, government, and
academic laboratories throughout the world.

Figure 1-1 p3

"TODAY EVERYONE HAS TO KNOW 'WHAT'S IN THE FOOD?', 'WHAT'S IN THE WATER?', 'WHAT'S IN THE AIR?' THIS IS TRULY THE GOLDEN AGE OF ANALYTICAL CHEMISTRY."

1B- Quantitative Analytical Methods

- Four general areas of analytical methods:

1. Gravimetric methods: determine the mass of analyte or some compound chemically related to it.

2. Volumetric methods use the volume of a solution containing sufficient reagent to react with the analyte.

3. Electroanalytical methods measure electrical properties (potential, current, resistance) to find composition of samples.

4. Spectroscopic methods based on interaction of electromagnetic radiation with analyte atoms & molecules, or on the production of radiation by analytes.

1C A Typical Quantitative Analysis
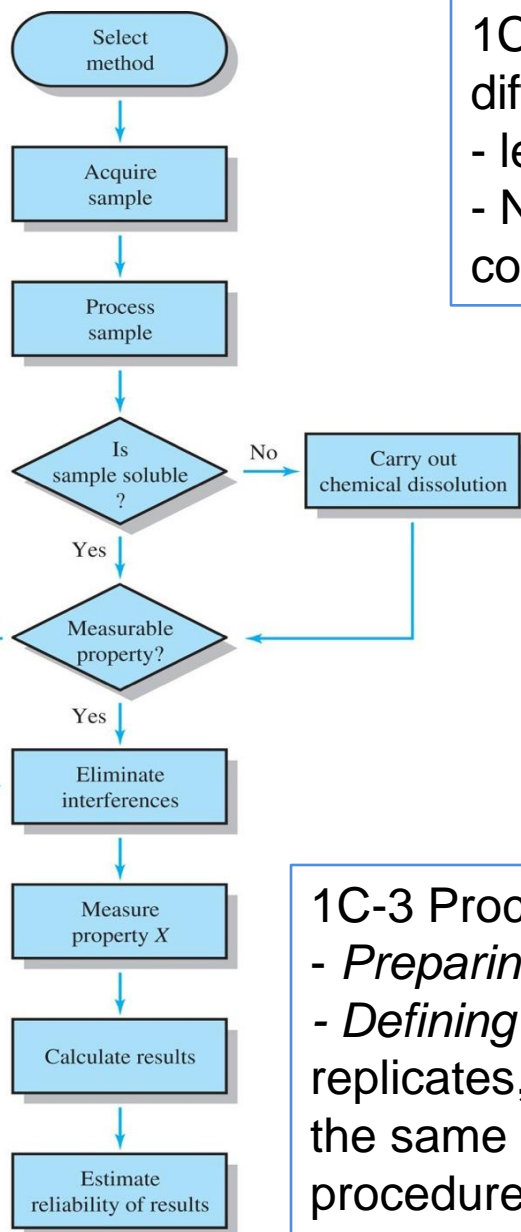
1C-1 Choosing a Method: The choice is sometimes difficult and requires experience as well as intuition.
- level of accuracy :investment on time and money
- Number of samples analyzed and number of components in the sample

1C-2 Acquiring the Sample:
- an analysis must be performed on a sample that has the same composition as the bulk of material from which it was taken. When the bulk is large and heterogeneous, great effort is required to get a representative sample.
- The collection of specimens from biological sources represents a second type of sampling problem.

1C-3 Processing the Sample:
- *Preparing a Laboratory Sample: grounding, mixing, storing*
- *Defining Replicate Samples:* Replicate samples, 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.

1C A Typical Quantitative Analysis

Cont' 1C-3 Processing the Sample:
Preparing Solutions: Physical and Chemical Changes
-Converting the sample into a soluble form:acid-base addition, ignition, high temperature fusion.
- converting the sample into a form suitable for the measurement step. Mn → MnO$_4$ colored solution

1C-4 Eliminating Interferences: An interference or interferent is a species that causes an error in an analysis by enhancing or attenuating (making smaller) the quantity being measured. The matrix, or sample matrix, is the collection of all of the components in the sample containing an analyte.

1C-5 Calibrating and Measuring Concentration: *Ideally, the measurement* of the property is directly proportional to the concentration, that is, $c_A = kX$
where *k is a proportionality constant.* The process of determining *k is* called a calibration.

1C-6 , 1C-7 Calculating and Evaluating Results
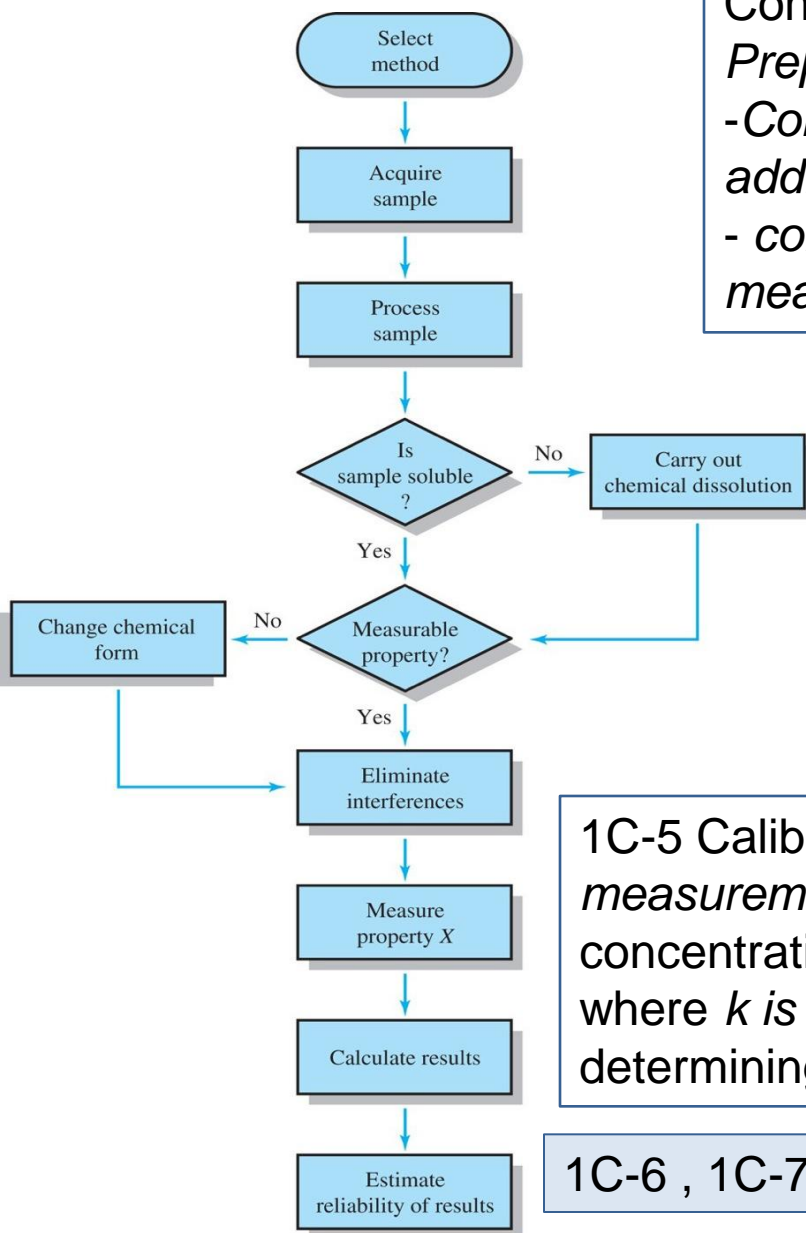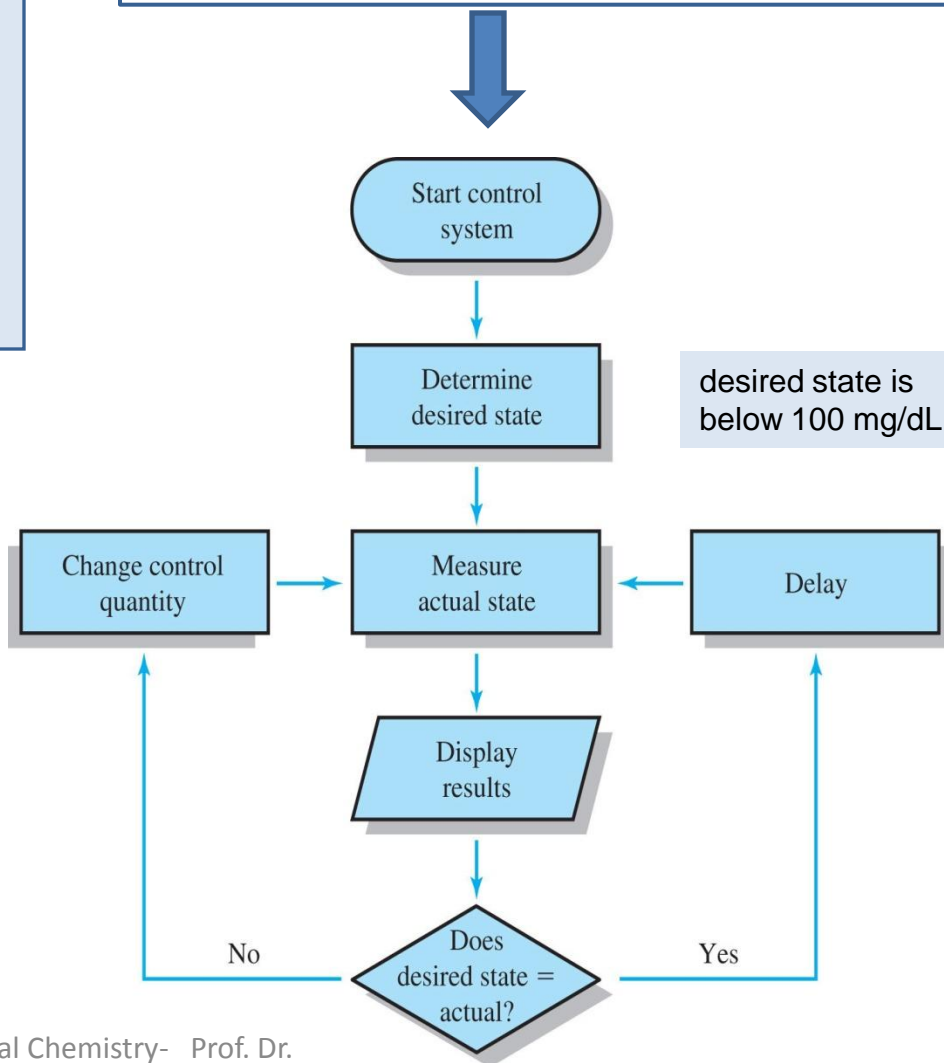
1D- Feedback Control Systems

The analytical results may be used to

- help control a patient's health,
- control the amount of mercury in fish,
- control the quality of a product,
- determine the status of a synthesis, or
- find out whether there is life on Mars.

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.
- *Mn conc. in steel*
- *Cl conc. in swimming pool*

determination and control of the concentration of glucose in blood.

Start control system

Determine desired state

desired state is below 100 mg/dL

Change control quantity → Measure actual state ← Delay

Display results

Does desired state = actual?

No   Yes

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# Deer Kill: A Case Study Illustrating the Use of Analytical Chemistry to Solve a Problem in Toxicology

The Problem :
A dead whitetailed deer near a pond in the Land between the Lakes National Recreational area in Kentucky

•to find the cause of death so that further deer kills might be prevented, they searched 2 acres of area.
• The investigators noticed that grass surrounding nearby power line poles was wilted and discolored. They speculated that a herbicide might have been used on the grass. A common ingredient in herbicides is arsenic in any one of a variety of forms, including arsenic trioxide, sodium arsenite, monosodium methanearsenate, and disodium methanearsenate.

Selecting a Method

A scheme for the quantitative determination of arsenic in biological samples is found in the published methods of the Association of Official Analytical Chemists (AOAC).
In this method, arsenic is distilled as arsine, AsH_3, and is then determined by colorimetric measurements.
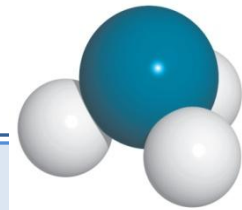
Processing the Sample: Obtaining Representative Samples

Back at the laboratory, the deer were dissected, and the kidneys were removed for analysis. The kidneys were chosen because the suspected pathogen (arsenic) is rapidly eliminated from an animal through its urinary tract.

Processing the Sample: Preparing a Laboratory Sample

Each kidney was cut into pieces and homogenized in a high speed blender. This step served to reduce the size of the pieces of tissue and to homogenize the sample.

Processing the Sample: Defining Replicate Samples

Three 10-g samples of the homogenized tissue from each deer were placed in porcelain crucibles. These served as replicates for the analysis.

Doing Chemistry: Dissolving the Samples

- to convert organic matrix to carbon dioxide and water: **dry ashing.**
- This process involved heating each crucible and sample cautiously over an open flame until the sample stopped smoking. The crucible was then placed in a furnace and heated at 555°C for two hours. Dry ashing served to free the analyte from organic material and convert it to arsenic pentoxide. The dry solid in each sample crucible was then dissolved in dilute HCl, which converted the As_2O_5 to soluble H_3AsO_4.

Eliminating Interferences

-Arsenic can be separated from other substances that might interfere in the analysis by converting it to arsine, AsH_3, a toxic, colorless gas that is evolved when a solution of H_3AsO_3 is treated with zinc. The solutions resulting from the deer and grass samples were combined with Sn^{2+}, and a small amount of iodide ion was added to catalyze the reduction of H_3AsO_4 to H_3AsO_3 .

- The H_3AsO_3 was then converted to AsH_3 by the addition of zinc metal as follows:

$$H_3AsO_3 + 3Zn + 6HCl \rightarrow AsH_3(g) + 3ZnCl_2 + 3H_2O$$

- The entire reaction was carried out in flasks equipped with a stopper and delivery tube so that the arsine could be collected in the absorber solution as shown in **Figure 1F-1. The** arrangement ensured that interferences were left in the reaction flask and that only arsine was collected in the absorber in special transparent containers called cuvettes.
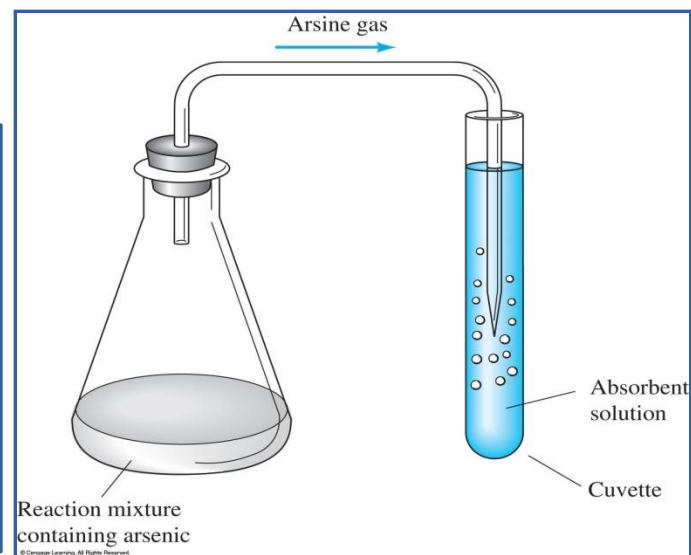
Arsine bubbled into the solution in the cuvette reacts with silver diethyldithiocarbamate to form a colored complex compound according to the equation:
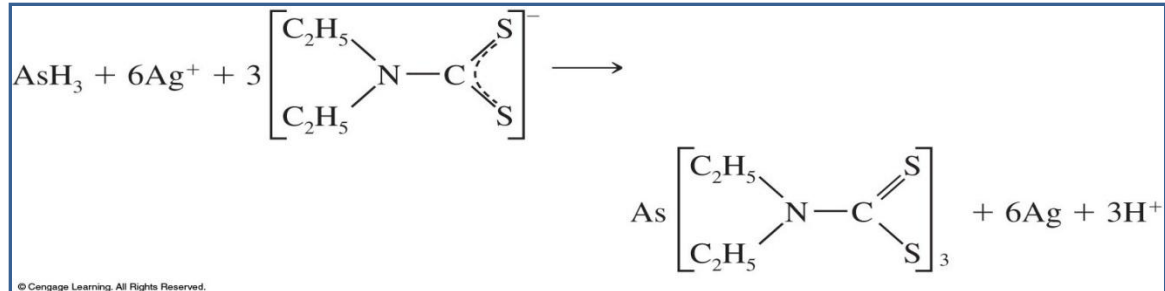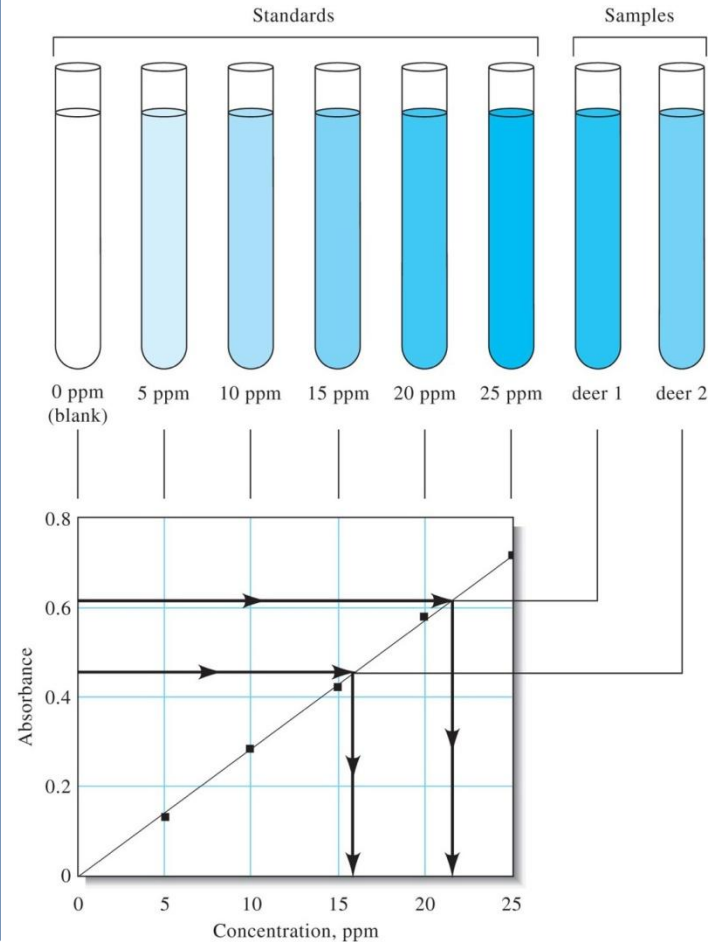
Measuring the Amount of the Analyte

The amount of arsenic in each sample was determined by measuring the intensity of the red color formed in the cuvettes with an instrument called a spectrophotometer.

A spectrophotometer provides a number called absorbance that is directly proportional to the color intensity, which is also proportional to the concentration of the species responsible for the color. To use absorbance for analytical purposes, a calibration curve must be generated by measuring the absorbance of several solutions that contain known concentrations of analyte. The upper part of Figure 1F-2 shows that the color becomes more intense as the arsenic content of the standards increases from 0 to 25 parts per million (ppm).

Figure 1F-2 Constructing and using a calibration curve to determine the concentration of arsenic. The absorbance values are plotted against the concentrations of the solutions in the cuvettesFinally, the concentrations of the unknown solutions are read from the plot, as shown by the dark arrows.

Conclusion:

Arsenic in kidney tissue of an animal is toxic at levels above about 10 ppm, so it was probable that the deer were killed by ingesting an As compound. The tests also showed that the samples of grass contained about 600 ppm arsenic.