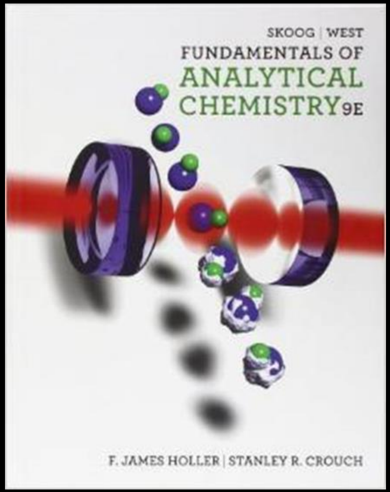


Fundamentals of
Analytical Chemistry

9th edition

Skoog / West / Holler / Crouch

Chapter 1

The Nature of Analytical Chemistry

부산대학교 자연대 화학과 (심 윤 보)

교수목표 및 강의계획

1.교수목표 및 강의계획 (course objectives & Description)

1) 교수목표:
A sound physical understanding of the principles of analytical chemistry and applications

1) 분석화학에 중요한 화학적 원리들을 (chemical principles) 숙지시키는데 있다.

2) 실험자료의 정확성과 정밀성을 판단할 수 있는 능력을 개발시키며, 통계적 방법을 사용하여 판단을 명확히 할 수 있는 능력 함양.

3) 분석화학 문제를 정량적인 방법으로 푸는데 필요한 능력 배양 및 최근의 분석화학에서 사용하고 있는 다양한 습식 분석기술 숙지.

2) 강의계획
습식분석법의 기초가 되는 화학평형, 화학량론 및 이를 사용한 응용에 대해 강의

2. 주교재 (Required textbook)

Quantitative Chemical Analysis, Daniel C. Harris, 8^{th} eds. W.H.Freeman and Company, 2010.

3.평가방범 (Requirements & Grading)

중간고사 40%, 기말고사 40%, 보고서10%, 출석10%

4. 참고문헌 (References)

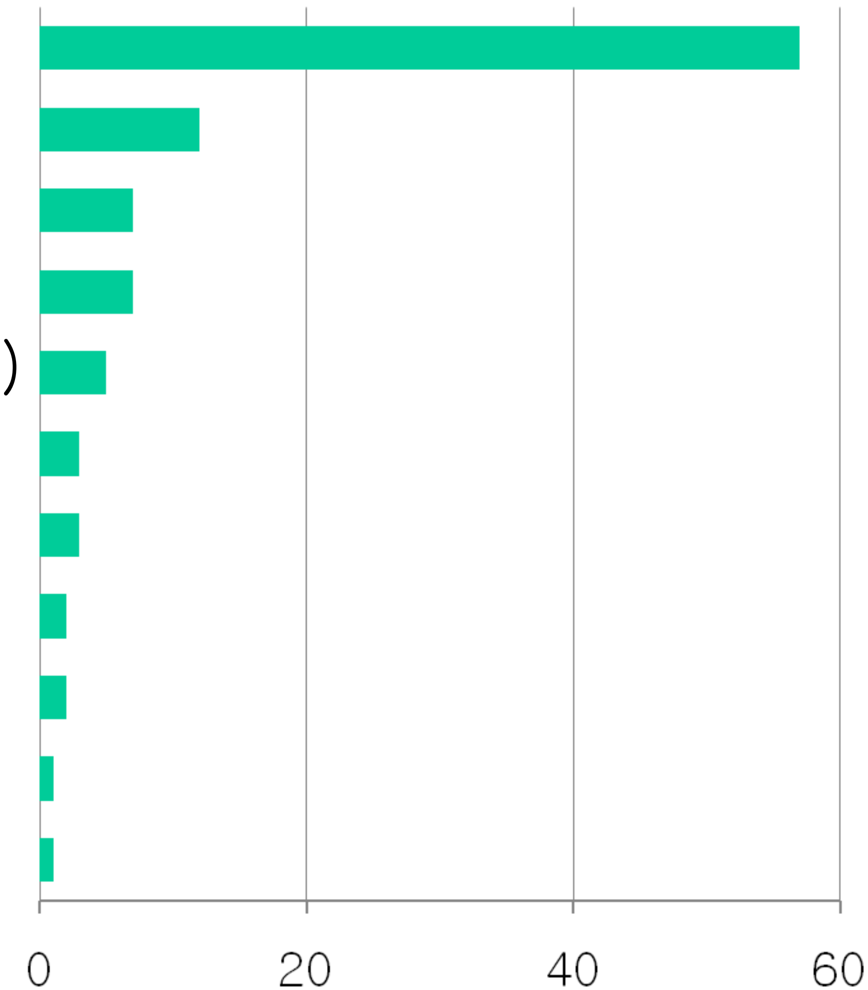
-Exploring Chemical Analysis, D.S.Harris, W.H.Freeman and Company, New York, 2001,
- Fundamental of Analytical Chemistry, Skoog, West, Holler, Crouch, 8th edition, Saunders

Time Table

weeks	contents
제 1주	1) Introduction and Chemical Measurements
제 2주	2) Tools of the Trade
제 3주	3) Experimental Error
제 4주	4) Statistic and Quality Assurance and Calibration Methods
제 5주	5) Chemical Equilibrium (임시고사)
제 6주	6) Gravimetric Analysis and Precipitation Titration
제 7주	7) Activity and the Systematic Treatment of Equilibrium
제 8주	8) Monoprotic Acid-Base Equilibria
제 9주	9) Polyprotic Acid-Base Equilibria
제 10주	10) Acid-Base Titrations (중간고사)
제 11주	11) EDTA Titrations
제 12주	12) Advanced Topics in Equilibrium
제 13주	13) "
제 14주	14) Fundamentals of Electrochemistry
제 15주	15) Redox Titrations
제 16주	16) 기말고사

-. Relative number of Chemists working for their major employers

- Industry(57%)
- Local authority(12%)
- Central government(7%)
- University(7%)
- Nationalised industry(5%)
- Other employer(3%)
- Regioal authority(3%)
- Atomic energy(2%)
- Self-employed(2%)
- Area authority(1%)
- Consulting(1%)



-. A more breakdown of the field of employment of chemists

- Education (including universities, polytechnics, colleges, and schools (18%)
- Pharmaceutical (13%)
- Other chemical (8.5%)
- Other industry (including transport, communications, mining, building, automotive, aerospace, textile, tobacco, photographic, etc.) (8%)
- Plastic (6.5%)
- Research institute (6%)
- Food, drink (5%)
- Oil (5%)
- Water supply (5%)
- Central or local government (4.5%)
- Gas and electricity supply (3.5%)
- Electronic (2.5%)
- Metallurgical (2%)
- Detergents (2%)
- Paper and printing (2%)
- Consulting (1.5%)
- Cosmetics (1.5%)
- Other services (1.5%)
- Hospital (1.4%)
- Glass (1.3%)
- Other (1.3%)

“The quality of life heavily depends on the chemical industry”

1. Chemistry :

* Fields :

  * **Manufacturing** ; metal, cement, glass, plastics, adhesives, nails, screws, polish, paint
  * **Clothes** ; fiber, paint, detergents
  * **Food** ; drink, spices and preservatives
  * **Agriculture** ; pesticides ,fertilizer, animal feeds, supplements
  * Pharmaceutical industry ;

What Is Analytical Chemistry?

Analytical chemistry is the science of obtaining, processing, and communicating information about the composition and structure of matter: it is the art and science of determining what matter is and how much of it exists.

*In 2012 (salary survey data), analytical chemistry was the most popular field of work for ACS chemists.

Principle of classical method; 1) stoichiometry 2) equilibrium state

Definitions of analytical chemistry

“ Analytical chemistry is a science of chemical characterization and measurement.”

H. A. Laitinen, 1982

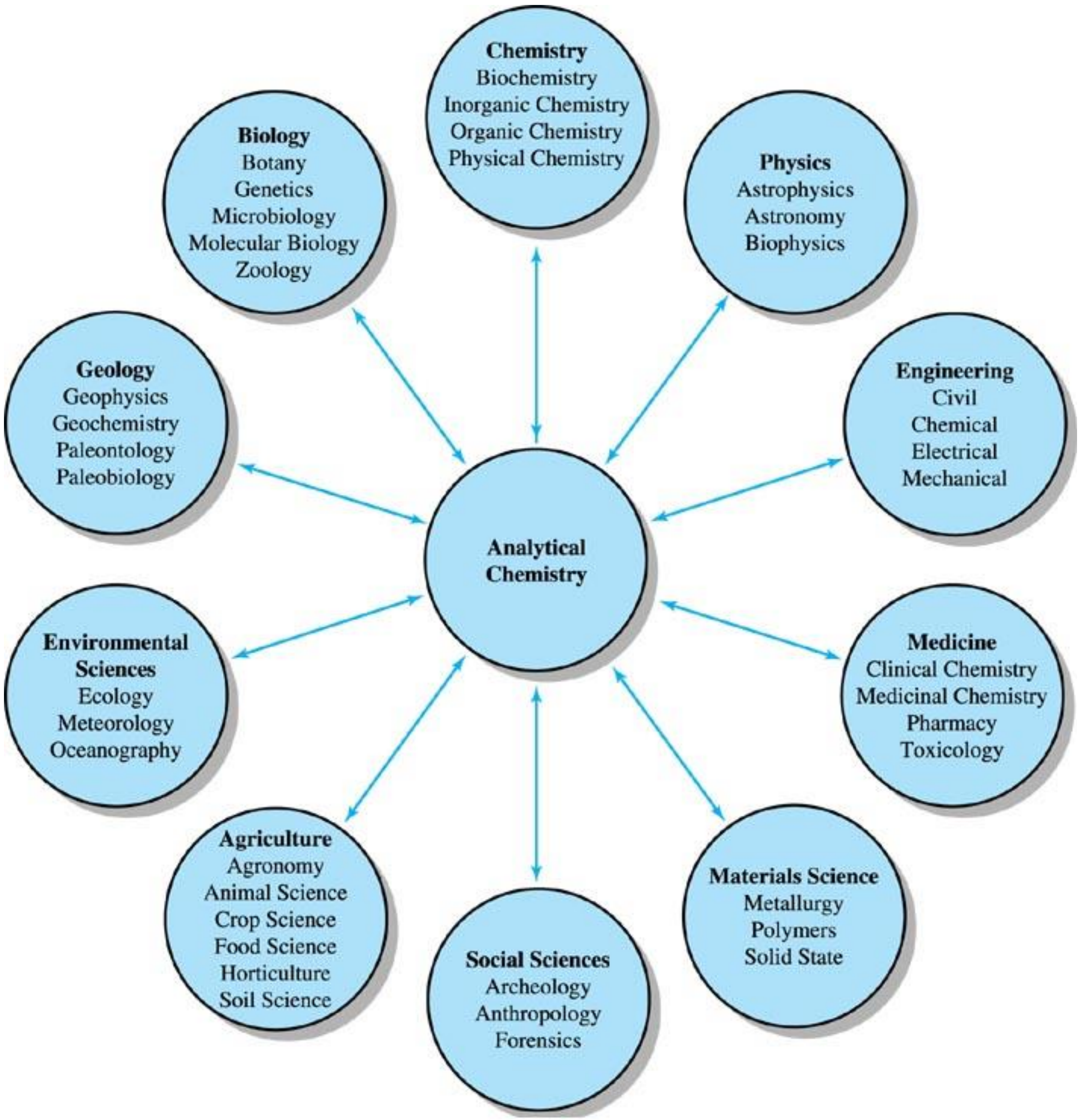
“ Analytical chemistry is a science of signal production and interpretation.”

E. Pungor, 1987

“ In the course of determination, chemical, physiochemical, and physical methods are used. All of them, however, have the same feature: it is the dependence of signal on analyte concentration. The important task of analytical chemistry is therefore the discovery and implantation of these dependencies into analytical procedures.”

A. Lewenstam, J. Zytkow, 1987

Several different areas of analytical chemistry



1. Clinical analysis - blood, urine, feces, cellular fluids, etc., for use in diagnosis.
2. Pharmaceutical analysis - establish the physical properties, toxicity, metabolites, quality control, etc.
3. Environmental analysis - pollutants, soil and water analysis, pesticides.
4. Forensic analysis - analysis related to criminology; DNA finger printing, finger print detection; blood analysis.
5. Industrial quality control - required by most companies to control product quality.
6. Bioanalytical chemistry and analysis - detection and/or analysis of biological components (i.e., proteins, DNA, RNA, carbohydrates, metabolites, etc.).
7. Archeology, Geology, Food Analysis, ………………………………

What do analytical chemists do? (RSC)

A. **Manufacturing company** : need to employ analytical chemists whose job it is to devise ways of measuring the relative amounts of the various chemical species that go to make up the particular material.

Example,

1) the concentration of elements like carbon and nickel in the case of a steel sample

2) the amount of drug in a pill

3) the concentration of certain molecules such as the vitamins in a breakfast cereal

Analytical chemist in industry:

a)sampling and testing raw materials

b)testing intermediates

c) monitoring product quality

d) monitoring effluent quality.

B. Helping to save lives (clinical chemists) in hospital

1) The analysis of samples of patients' blood, urine, etc.
2) Monitoring the concentrations of certain key components of the blood or urine.
3) Analysis for the particular active ingredient or its metabolites.
4) Patient must be checked regularly to see that the level of drug circulating in the body is correct.

C. Helping to protect the consumer and the environment ; ex) 1) food and drink checking

2) the environment checking

Example,

Analytical Chemists work in central and local government;

1) Analysis of food, water, drink, medicines, pesticides, beer, wines, spirits, oils, petrol, tobacco products, and a variety of contraband including drug,
2) The level of toxic and hazardous substances in the work-place environment.
3) Monitoring-asbestos fibers, mercury vapour, or lead dust

D. Helping the Farmer (agricultural chemist) ;

1) Monitoring the levels of nutrients in soils & Fisheries

2) Level of potentially harmful materials will be monitored in the soil, crops and animals.

E. Helping to catch criminals (forensic scientists) ;

"Every contact leaves its traces"

F. Helping to ensure fair play ; Drug abuse

G. Helping in other ways ; 1) geological surveys 2) coal and gas supply 3) electricity generation 4) prospecting and so on.

What Do Analytical Chemists Do? (ACS)

Analytical chemists use their knowledge of chemistry, instrumentation, computers, and statistics to solve problems in almost all areas of chemistry and for all kinds of industries.

For example, **their measurements are used to**

1) assure the safety and quality of food, pharmaceuticals, and water,
2) assure compliance with environmental and other regulations,
3) support the legal process,
4) help physicians diagnose diseases,
5) provide measurements and documentation essential to trade and commerce.

Analytical chemists often work in service-related jobs and are employed in industry, academia, and government.

• They conduct basic laboratory research; 1) perform process and product development; 2) design instruments used in analytical analysis; 3) teach; and 4) work in marketing and law.

Professional Organizations

- (KCS and) ACS Division of Analytical Chemistry
- Subdivision of Separations Chemistry (SCSC)
- Analytical Chemistry Springboard
- Analytical Sciences Digital Library (ASDL)
- National Registry of Certified Chemists (NRCC)
- Society for Applied Spectroscopy (SAS)

Analytical Chemistry

1. Classical method -> mass and volume
2. Instrumental method -> others

a. Qualitative Analysis -> organic ; functional group and structure

*organic mixture : Separation prior to this

-> inorganic ; ion detect

b. Quantitative

* Properties of samples affected by coexist elements.
* Quantity of contents of sample

---상량 분석 (5%이상)

---반미량 분석 (-0.1%)

---미량 분석 (0.1%이하)

---흔적량 (0.01%-0.0000001%)

b. 정량분석

* 시료의 성질 및 특징 : 공존 원소

* 시료의 량 및 성분 함량

---상량 분석 (5%이상)

---반미량 분석 (-0.1%)

---미량 분석 (0.1%이하)

---흔적량 (0.01%-0.0000001%)

- Steps in the analysis process;

1) Sampling

bulk material로 부터 시료의 제조 -분쇄, 혼합,건조,등

2) Preparation of solutions

--- 시료의 종류, 분석 목적에 따라.

3) Separation

--- 측정 성분 또는 방해 성분의 분리

4) Measurement

---기기와 방법에 따라 2,3 과정 차이

5)Report

General Steps in a Chemical Analysis

1. Formulating the question
2. Selecting analytical procedures
   - literature survey, devise new procedures, internet, references…
3. Sampling
   - *process of selecting representative material*
   - "garbage in—garbage out!"
4. Sample preparation
   - dissolving, concentrated, remove **interferences**, **masking**…
5. Analysis
   - Replicate measurements (Measure the concentration of analyte in several identical **aliquots**)
   - "The uncertainty of a measurement is as important as the measurement itself."
6. Interpretation and drawing conclusions
7. Reporting

Feature 1-1

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

The Problem

The incident began when a park ranger found a dead whitetailed deer near a pond in the Land between the Lakes National Recreation Area in western Kentucky. The ranger enlisted the help of a chemist from the state veterinary diagnostic laboratory to find the cause of death so that further

White-tailed deer have proliferated in many parts of the country.

The ranger and the chemist carefully inspected the site where the badly decomposed carcass of the deer had been found. Because of the advanced state of decomposition, no fresh organ tissue samples could be gathered. A few days after the original inquiry, the ranger found two more dead deer near the same location.

The investigators then conducted a careful examination of the surrounding area in an attempt to find clues to establish the cause of death.

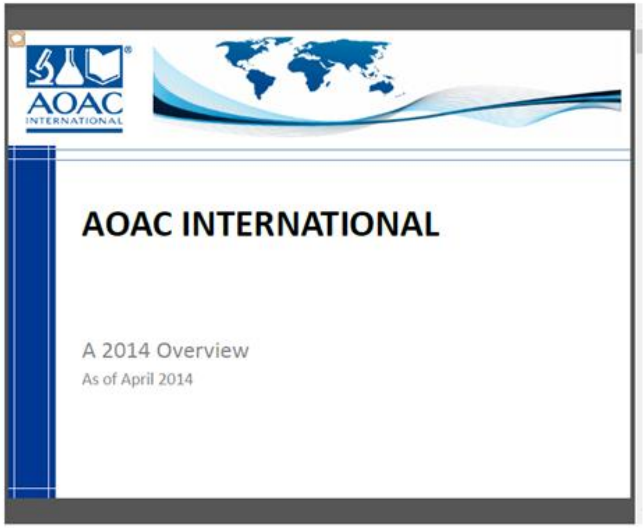
The search covered about 2 acres surrounding the pond. The investigators noticed that grass surrounding nearby power line poles was wilted and discolored. They speculated that a herbicide might have been used on the grass.

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. The last compound is the disodium salt of mthanearsenic acid, CH3AsO(OH)2, which is very soluble in water and thus finds use as the active ingredient in many herbicides.
The herbicidal activity of disodium methanearsenate is due to its reactivity with the sulfhydryl (S3H) groups in the amino acid cysteine. When cysteine in plant enzymes reacts with arsenical compounds, the enzyme function is inhibited, and the plant eventually dies. Unfortunately, similar chemical effects occur in animals as well.

The investigators, therefore, collected samples of the discolored dead grass for testing along with samples from the organs of the deer. They planned to analyze the samples to confirm the presence of arsenic and, if present, to determine its concentration in the samples.

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**).[3]
In this method, arsenic is distilled as arsine, AsH_3, and is then determined by colorimetric measurements.


AOAC INTERNATIONAL

A 2014 Overview

As of April 2014

[3] *Official Methods of Analysis*, 18th ed., Method 973.78 , Washington, DC: Association of Official Analytical Chemists, 2005.

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 highspeed blender. This step served to reduce the size of the pieces of tissue and to homogenize the resulting laboratory 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

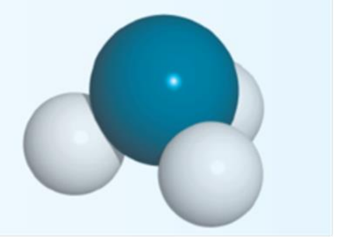
To obtain an aqueous solution of for analysis, it was necessary to convert its organic matrix to carbon dioxide and water by the process of **dry ashing**. This process involved heating each crucible and sample cautiously over an open flame until the sample stopped smoking. The crucible was then placed 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.

Here we show arsine, AsH_3. Arsine is an extremely toxic, colorless gas with a noxious garlic odor.
Analytical methods involving the generation of arsine must be carried out with caution and proper ventilation.



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 according to the following reaction:

$$H_3AsO_4 + SnCl_2 + 2HCl \rightarrow H_3AsO_3 + SnCl_4 + H_2O$$

The H_3AsO_3 was then converted to AsH3 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

s.

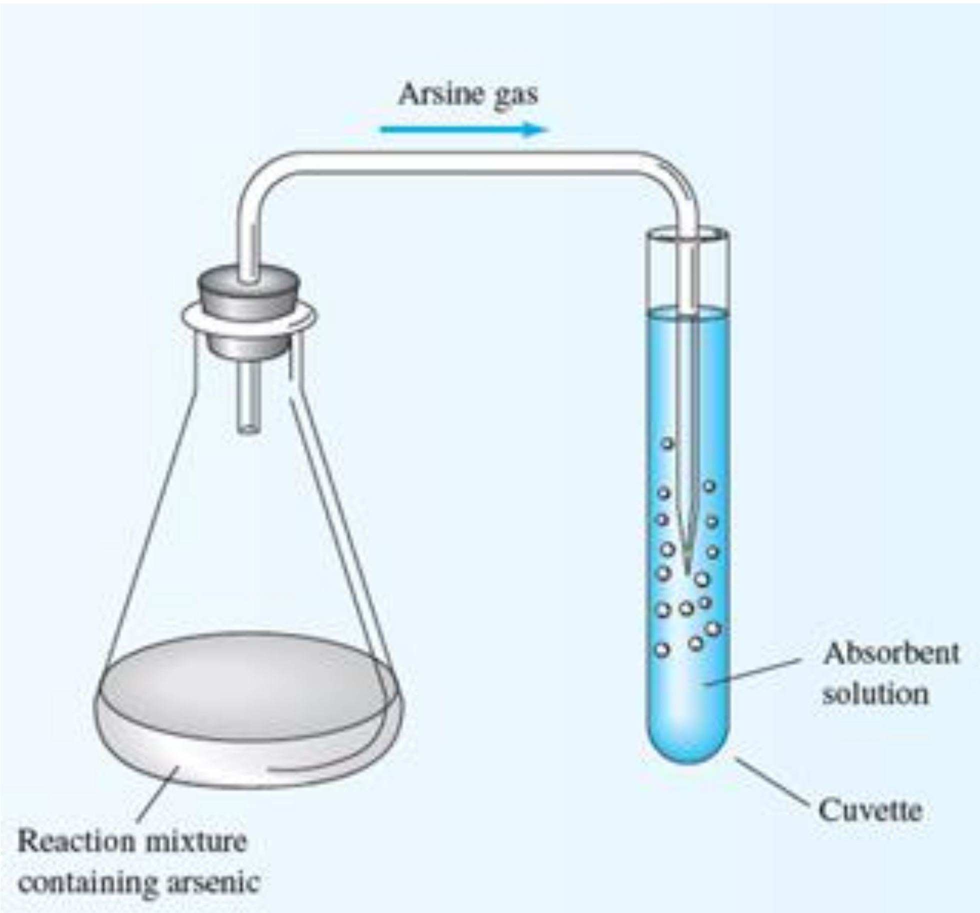
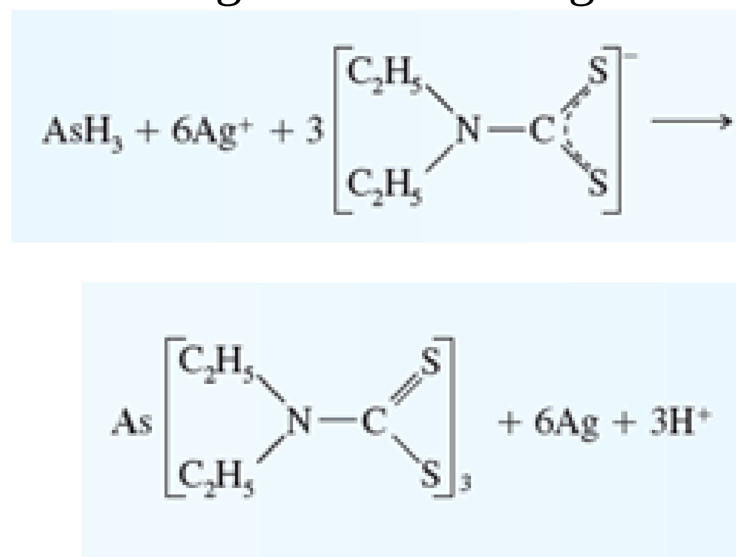


Figure 1F-1 An easily constructed apparatus for generating arsine, AsH_3.

Arsine bubbled into the solution in the cuvette reacts with silver diethyldithiocarbamate to form a colored complex compound according to the following



Molecular model of diethyldithiocarbamate.
This compound is an analytical reagent used in determining arsenic.

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.

As shown in Chapter 26, 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.

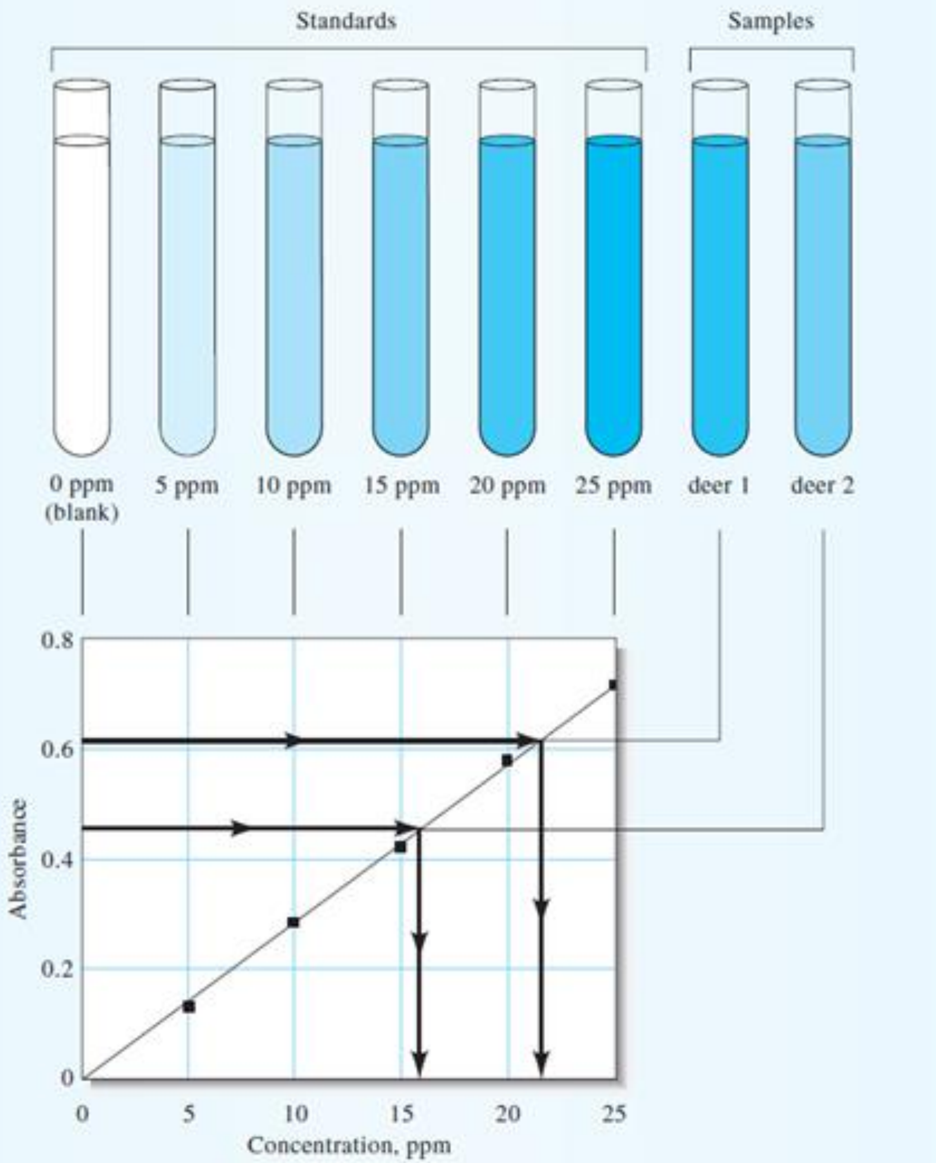


Figure 1F-2 Constructing and using a calibration curve to determine the concentration of arsenic. The absorbances of the solutions in the cuvettes are measured using a spectrophotometer. The absorbance values are then plotted against the concentrations of the solutions in the cuvettes, as illustrated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

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).

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.

Calculating the Concentration

The absorbance for the standard solutions containing known concentrations of arsenic are plotted to produce a calibration curve (Figure 1F-2). Each vertical line between the upper and lower parts of Figure 1F-2 ties intensity of each solution is represented by its absorbance, which is plotted on the vertical axis of the calibration curve.

Note that the absorbance increases from 0 to about 0.72 as the concentration of arsenic increases from 0 to 25 parts per million. The concentration of arsenic in each standard solution corresponds to the vertical grid lines of the calibration curve as shown. This curve is then used to determine the concentration of the two unknown solutions shown on the right. We first find the absorbances of the unknowns on the absorbance axis of the plot and then read the corresponding concentrations on the concentration axis. The lines leading from the cuvettes to the calibration curve show that the concentrations of arsenic in the two deer samples were 16 ppm and 22 ppm, respectively.

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 arsenic compound. The tests also showed that the samples of grass contained about 600 ppm arsenic. This very high level of arsenic suggested that the grass had been sprayed with an arsenical herbicide. The investigators concluded that the deer had probably died as

Estimating the Reliability of the Data

The data from these experiments were analyzed using the statistical methods described in Chapters 5- 8. For each of the standard arsenic solutions and the deer samples, the average of the three absorbance measurements was calculated.

The average absorbance for the **replicates** is a more reliable measure of the concentration of arsenic than a single measurement. **Leasts quares analysis** of the standard data (see Section 8D) was used to find the best straight line among the points and to calculate the concentrations of the unknown samples along with their **statistical uncertainties** and **confidence limits**.

Conclusion

In this analysis, the formation of the highly colored product of the reaction served both to confirm the probable presence of arsenic and to provide a reliable estimate of its concentration in the deer and in the grass. Based on their results, the investigators recommended that the use of arsenical herbicides be suspended in the wildlife area to protect the deer and other animals that might eat plants there.
The case study of Feature 1-1 illustrates how chemical analysis is used in the identification and determination of quantities of hazardous chemicals in the environment.
Many of the methods and instruments of analytical chemistry are used routinely to provide vital information in environmental and toxicological studies of this type.
The system flow diagram of Figure 1-3 may be applied to this case study. The desired state is a concentration of arsenic that is below the toxic level.
Chemical analysis is used to determine the actual state, or the concentration of arsenic in the environment, and this value is compared to the desired concentration.
The difference is then used to determine appropriate actions (such as decreased use of arsenical pesticides) to ensure that deer are not poisoned by excessive amounts of arsenic in the environment, which in this example is the controlled system. Many other examples are given in the text and in features throughout this book.