

Analytical chemistry. Role in the development of a modern science and technology

Analytical chemistry

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.

Scoog, 2004

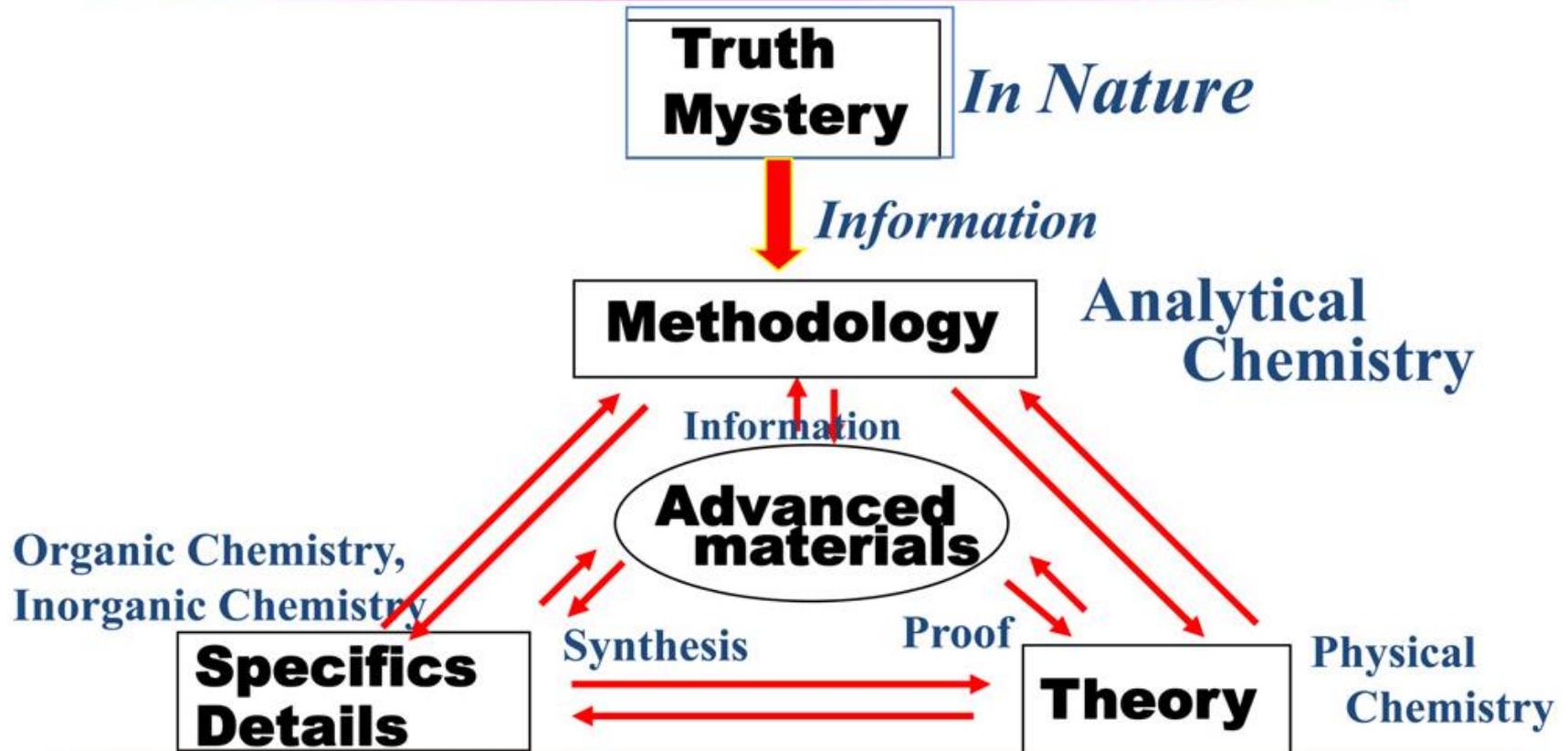
“Analytical chemistry is what analytical chemists do”

Murray, Analytical Chemistry, 1994

Definition: *it is the science of extraction, identification, and quantitation of an unknown sample. It also deals with methods for determining the chemical composition of samples.*

What is analytical chemistry

What is Analytical Chemistry ?



Aims of analytical chemistry

To develop methodology for getting information on Truth and Mystery in Nature

To enhance intellectual assets through discovery of novel substances, search and identification of substances, establishment of new methodology for analysis

Looking at current activities in chemical measurement, one would have to say that the analytical chemistry field is as vibrant, innovative, significant, and productive an area of science as one could imagine.

Enke, Talanta, 2011

SPARS

Sensitivity and selectivity

Precision

Accuracy

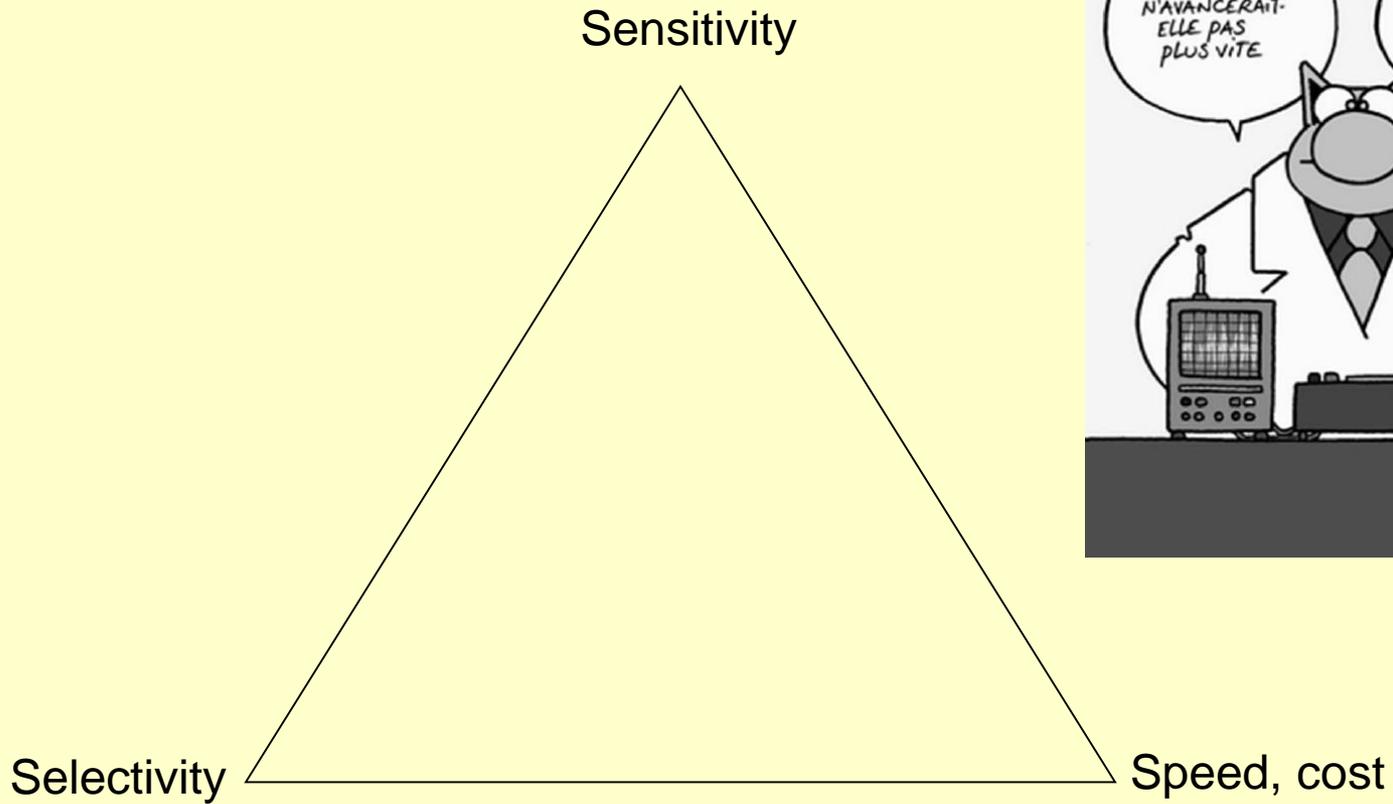
Rapidity

Simplicity

ZEC

Zero emission concept

Analytical triangle *



***Thanks to JF Focant**

Analytical chemistry has a major role in the following areas

Analytical chemistry plays an important role in nearly all aspects of chemistry. There are many fields that depend on analytical chemistry.

For example:

- **In medicine:** analytical chemistry is the basis for clinical laboratory tests which help physicians diagnose disease.
- **Industry:** analytical chemistry provides the means of testing raw material and assuring the quality of finished products. Such as paints and detergents, etc.
- **Environmental quality:** the air in the cities must be analyzed for detecting carbon monoxide or ocean contamination.
- **Forensic analysis:** analysis related to criminology for example; finger print detection and blood analysis.

Some examples of application of analytical chemistry

The concentration of oxygen and of carbon dioxide are determined in millions of blood samples every day and used to diagnose and treat illness

Quantities of hydrocarbons, nitrogen oxides and carbons monoxide present in automobile exhaust gases are measured to assess the effectiveness of smog-control devices

Quantitative determination of nitrogen in foods establishes their protein content and thus their nutritional value

Analysis of steel during its production permits adjustment in the concentrations of such elements as carbon, nickel and chromium to achieve a desired strength, hardness, corrosion resistance and ductility

The mercaptan content of household gas supplies is monitored continually to ensure that the gas has a sufficiently noxious odor to warn of dangerous leaks

What areas of application of analytical chemistry do you know?





Some examples of application of analytical chemistry

- Cancer diagnostics

<https://www.facebook.com/ScienceNaturePage/videos/983478985117693/>

- Analysis of space and other planets

<https://www.youtube.com/watch?v=P4boyXQuUIw>

- DNA analysis

<https://www.youtube.com/watch?v=Enn3BHE3v4s>

Possible jobs

- Scientist (e.g., analytical chemist)
- Head of analytical laboratory
- **Analyst (laboratory technician or engineer)**
- Sales of analytical instrumentation
- Many other possibilities in the nearby areas

Aim of the course

***To learn how to do chemical
analysis of any given sample***

Target skills

- Preparation of samples with a desired concentration of analyte and its uncertainty
- Identification of compounds present in sample on its physical properties and using qualitative reactions
- Determination of concentrations of analytes in samples using titrimetric and gravimetric methods
- Estimation of uncertainties in measurements

Required skills

- Equalizing chemical reactions
- Solving algebraic equations and their systems
- Converting between different units of measurement
- Calculating concentrations

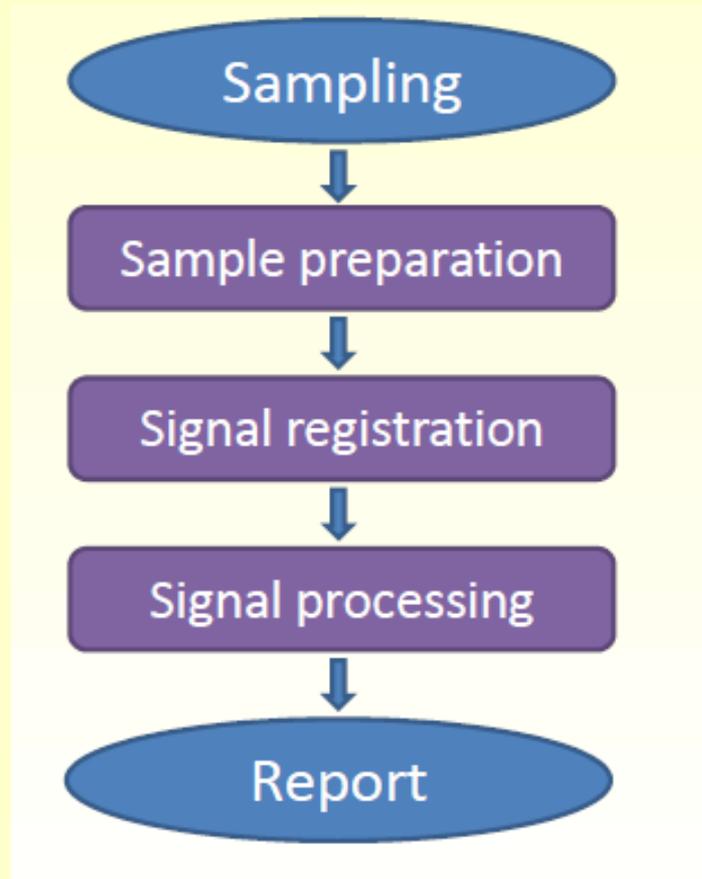
Main definitions

- **Sample** – object to be analyzed
- **Analyte** – compound to be determined/identified
- **Matrix** – other compounds present in a sample

Examples

- **Sample** - air
- **Analyte** – carbon dioxide
- **Matrix** – oxygen, nitrogen, argon

General procedure of analysis



Analytical chemistry can be divided into two main type

- **Qualitative analysis;**

An analysis in which we determine the identity of the constituent in a sample.

- **Quantitative analysis;**

An analysis in which we determine how much of a constituent is present in a sample.

Analytical chemistry is a science about measurements in chemistry

Comparing between quantitative and qualitative analysis:

Qualitative Analysis

- Deals with the identification of elements, ions and compounds in a sample (we may be interested in whether a given substance is present or not).

Quantitative Analysis

- Deals with the determination of how much of one or more constituent is present within a sample.
- There are two kinds of quantitative analysis:
 1. classical Chemical Analysis
 2. Instrumental Analysis

Quantitative analysis can be divided into:

- Classical chemical analysis:

It depends on simple classical technique to determine the mass, volume, and the corresponding techniques used in this type of analysis are:

- ❖ Volumetric (measurement in volume).
- ❖ Gravimetric (measurement in mass).

- Instrumental analysis:

This analysis depends on the physical properties of the sample where there is no reaction involved. Unlike the classical analysis instrumental analysis depends on more complex devices such as spectroscopic (interaction of light with matter) and electro analytics (measures electrical potential, resistance, etc) which can help in estimate the sample precisely especially in low concentrations.

Analytical approach to solving problems

Step 1. Identify and Define Problem

What is the problem's context?
What type of information is needed?

Step 5. Propose Solution to Problem

Is the answer sufficient?
Does answer suggest a new problem?

Step 2. Design Experimental Procedure

Establish design criteria.
Identify potential interferents.
Establish validation criteria.
Select analytical method.
Establish sampling strategy.

Step 4. Analyze Experimental Data

Reduce and transform data.
Complete statistical analysis.
Verify results.
Interpret results.

Step 3. Conduct Experiment & Gather Data

Calibrate instruments and equipment.
Standardize reagents.
Gather data.



Analytical methods

- Chemical and electrochemical
- Physical
- Biochemical

Methods to learn

- Titrimetry
- Gravimetry
- Potentiometry
- Spectrophotometry
- Chromatography

Basic tools of analytical chemistry

- In analytical chemistry measurements are made using appropriate instruments or equipment. The array of these equipment is impressive ranging from the simple and inexpensive to the complex and costly. Each instrument has its own purpose of use in the analysis, for example, there are equipment to measure the mass, volume where other are used for transferring solution during an experiment .

Equipment for measuring the mass:

An object mass is measured using a balance. The most common type is the electronic balance which had replaced the mechanical ones.



Electronic balance



Mechanical balance

Equipment for measuring the volume:

- Analytical chemists use a variety of glassware to measure a liquid's volume. The choice of what type of glassware to use depends on how accurately we need to know the liquid's volume and whether we are interested in containing or delivering the liquid.

cylinder:

- A graduated cylinder is the simplest device for delivering a known volume of a liquid reagent. The graduated scale allows you to deliver any volume up to the cylinder's maximum



Volumetric Pipette

- is used to deliver a specified volume of solution. Several styles of pipets are available as shown below



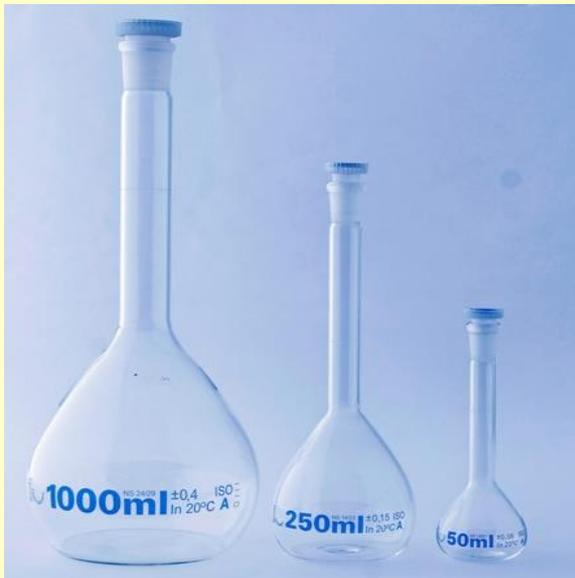
pipettes



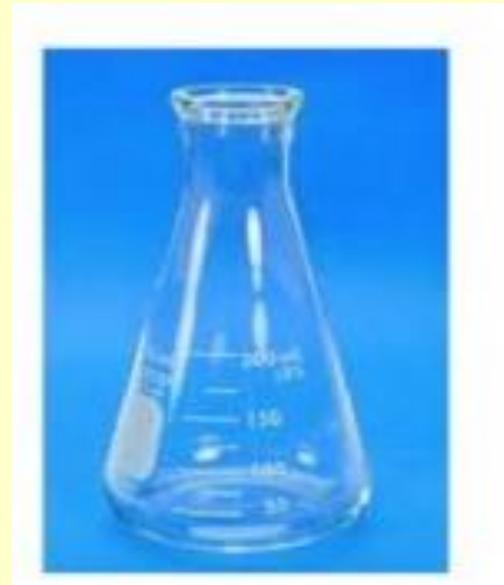
Micro pipettes

Volumetric Pipette

- Graduated cylinders and pipets deliver a known volume of solution. A volumetric flask, conical flasks, on the other hand, contains a specific volume of solution



Volumetric flask



Conical flask

Table 2.1 Fundamental SI Units of Importance to Analytical Chemistry

Measurement	Unit	Symbol	Definition (1 unit is...)
mass	kilogram	kg	...the mass of the international prototype, a Pt-Ir object housed at the Bureau International de Poids and Measures at Sèvres, France. [†]
distance	meter	m	...the distance light travels in $(299\,792\,458)^{-1}$ seconds.
temperature	Kelvin	K	...equal to $(273.16)^{-1}$, where 273.16 K is the triple point of water (where its solid, liquid, and gaseous forms are in equilibrium).
time	second	s	...the time it takes for 9 192 631 770 periods of radiation corresponding to a specific transition of the ^{133}Cs atom.
current	ampere	A	...the current producing a force of 2×10^{-7} N/m when maintained in two straight parallel conductors of infinite length separated by one meter (in a vacuum).
amount of substance	mole	mol	...the amount of a substance containing as many particles as there are atoms in exactly 0.012 kilogram of ^{12}C .

[†] The mass of the international prototype changes at a rate of approximately 1 µg per year due to reversible surface contamination. The reference mass, therefore, is determined immediately after its cleaning by a specified procedure.

Table 2.2 Derived SI Units and Non-SI Units of Importance to Analytical Chemistry

Measurement	Unit	Symbol	Equivalent SI Units
length	angstrom (non-SI)	Å	$1 \text{ Å} = 1 \times 10^{-10} \text{ m}$
volume	liter (non-SI)	L	$1 \text{ L} = 10^{-3} \text{ m}^3$
force	newton (SI)	N	$1 \text{ N} = 1 \text{ m} \cdot \text{kg}/\text{s}^2$
pressure	pascal (SI)	Pa	$1 \text{ Pa} = 1 \text{ N}/\text{m}^2 = 1 \text{ kg}/(\text{m} \cdot \text{s}^2)$
	atmosphere (non-SI)	atm	$1 \text{ atm} = 101,325 \text{ Pa}$
energy, work, heat	joule (SI)	J	$1 \text{ J} = \text{N} \cdot \text{m} = 1 \text{ m}^2 \cdot \text{kg}/\text{s}^2$
	calorie (non-SI)	cal	$1 \text{ cal} = 4.184 \text{ J}$
	electron volt (non-SI)	eV	$1 \text{ eV} = 1.602\,177\,33 \times 10^{-19} \text{ J}$
power	watt (SI)	W	$1 \text{ W} = 1 \text{ J}/\text{s} = 1 \text{ m}^2 \cdot \text{kg}/\text{s}^3$
charge	coulomb (SI)	C	$1 \text{ C} = 1 \text{ A} \cdot \text{s}$
potential	volt (SI)	V	$1 \text{ V} = 1 \text{ W}/\text{A} = 1 \text{ m}^2 \cdot \text{kg}/(\text{s}^3 \cdot \text{A})$
frequency	hertz (SI)	Hz	$1 \text{ Hz} = \text{s}^{-1}$
temperature	Celsius (non-SI)	°C	$^{\circ}\text{C} = \text{K} - 273.15$

Table 2.3 Common Prefixes for Exponential Notation

Prefix	Symbol	Factor	Prefix	Symbol	Factor	Prefix	Symbol	Factor
yotta	Y	10^{24}	kilo	k	10^3	micro	μ	10^{-6}
zetta	Z	10^{21}	hecto	h	10^2	nano	n	10^{-9}
eta	E	10^{18}	deka	da	10^1	pico	p	10^{-12}
peta	P	10^{15}	-	-	10^0	femto	f	10^{-15}
tera	T	10^{12}	deci	d	10^{-1}	atto	a	10^{-18}
giga	G	10^9	centi	c	10^{-2}	zepto	z	10^{-21}
mega	M	10^6	milli	m	10^{-3}	yocto	y	10^{-24}

Deer Kill: A Case study illustrating the use of analytical chemistry to solve a problem in toxicology

try

The Problem

The incident began when a park ranger found a dead white-tailed deer near a pond in the land between the Lakes National Recreation Area in western Kentucky. The park ranger enlisted the help of a chemist from the state veterinary diagnostic laboratory to find the cause of death so that further deer kills might be prevented.

The ranger and the chemist investigated 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 chemist was summoned to the site of the kill, where he and the ranger loaded the deer onto a truck for transport to the veterinary diagnostic laboratory. The investigators then conducted a careful examination of the surrounding area to find clues to the cause of death.



© D. Robert Franz/Corbis

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

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 methanearsenic acid, $\text{CH}_3\text{AsO}(\text{OH})_2$, 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 (S—H) 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 This method involves the distillation of arsenic as arsine, which 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 reduced the size of the tissue pieces and homogenized the resulting laboratory sample.

Processing the Sample: Defining Replicate Samples

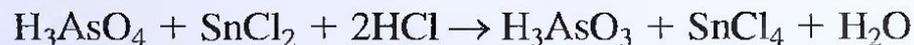
Three 10-g samples of the homogenized tissue from each deer were placed in porcelain crucibles.

Doing Chemistry: Dissolving the Samples

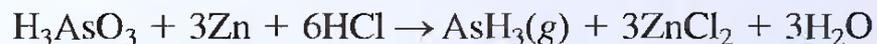
To obtain an aqueous solution of the analyte for analysis, it was necessary to dry ash the sample in air to convert its organic matrix to carbon dioxide and water. This process involved heating each crucible and sample cautiously over an open flame until the sample stopped smoking. The crucible was then placed in a furnace and heated at 555°C for 2 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 As₂O₅ to soluble H₃AsO₄.

Eliminating Interferences

Arsenic can be separated from other substances that might interfere in the analysis by converting it to arsine, AsH₃, a toxic, colorless gas that is evolved when a solution of H₃AsO₃ is treated with zinc. The solutions resulting from the deer and grass samples were combined with Sn²⁺, and a small amount of iodide ion was added to catalyze the reduction of H₃AsO₄ to H₃AsO₃ according to the following reaction:



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



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.

Analytical chemistry. Role of analytical chemistry

Arsine bubbled into the solution in the cuvette, reacting with silver diethyldithiocarbamate to form a colored complex compound according to the following equation:

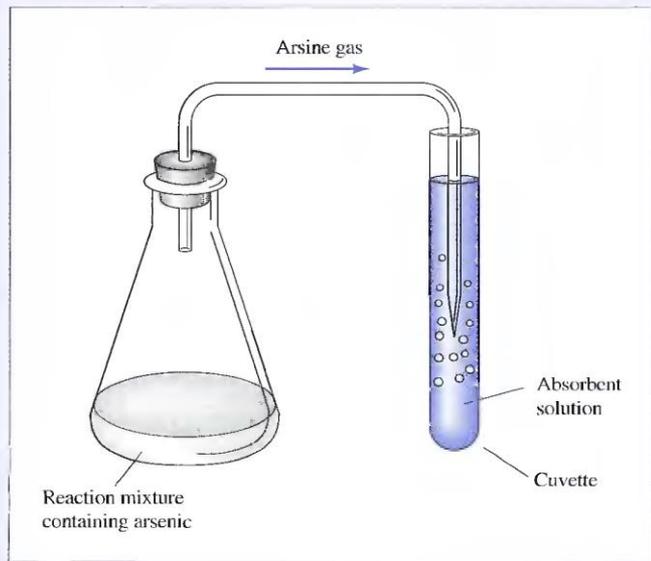
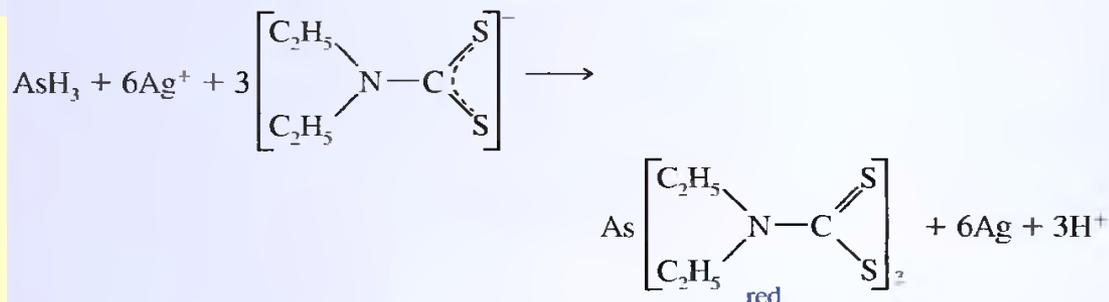


Figure 1F-1 An easily constructed apparatus for generating arsine, AsH_3 .



Measuring the Amount of the Analyte

The amount of arsenic in each sample was determined by using an instrument called a spectrophotometer, to measure the intensity of the red color formed in the cuvettes. As discussed 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. 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).

Calculating the Concentration

The absorbances for the standard solutions containing known concentrations of arsenic are plotted to produce a calibration curve, shown in the lower part of Figure 1F-2. Each vertical line between the upper and lower parts of Figure 1F-2 ties a solution to its corresponding point on the plot. The color 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 ppm. The concentration of arsenic in each standard solution corresponds to the vertical grid lines of the calibration curve. 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 were 16 ppm and 22 ppm, respectively.

Arsenic in the 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 a result of eating the poisoned grass.

Estimating the Reliability of the Data

The data from these experiments were analyzed using the statistical methods described in Chapters 5, 6, and 7. 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. Least-squares analysis of the standard data (see Section 8C) 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.

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. On the basis of 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.

Analytical chemistry. Role of analytical chemistry

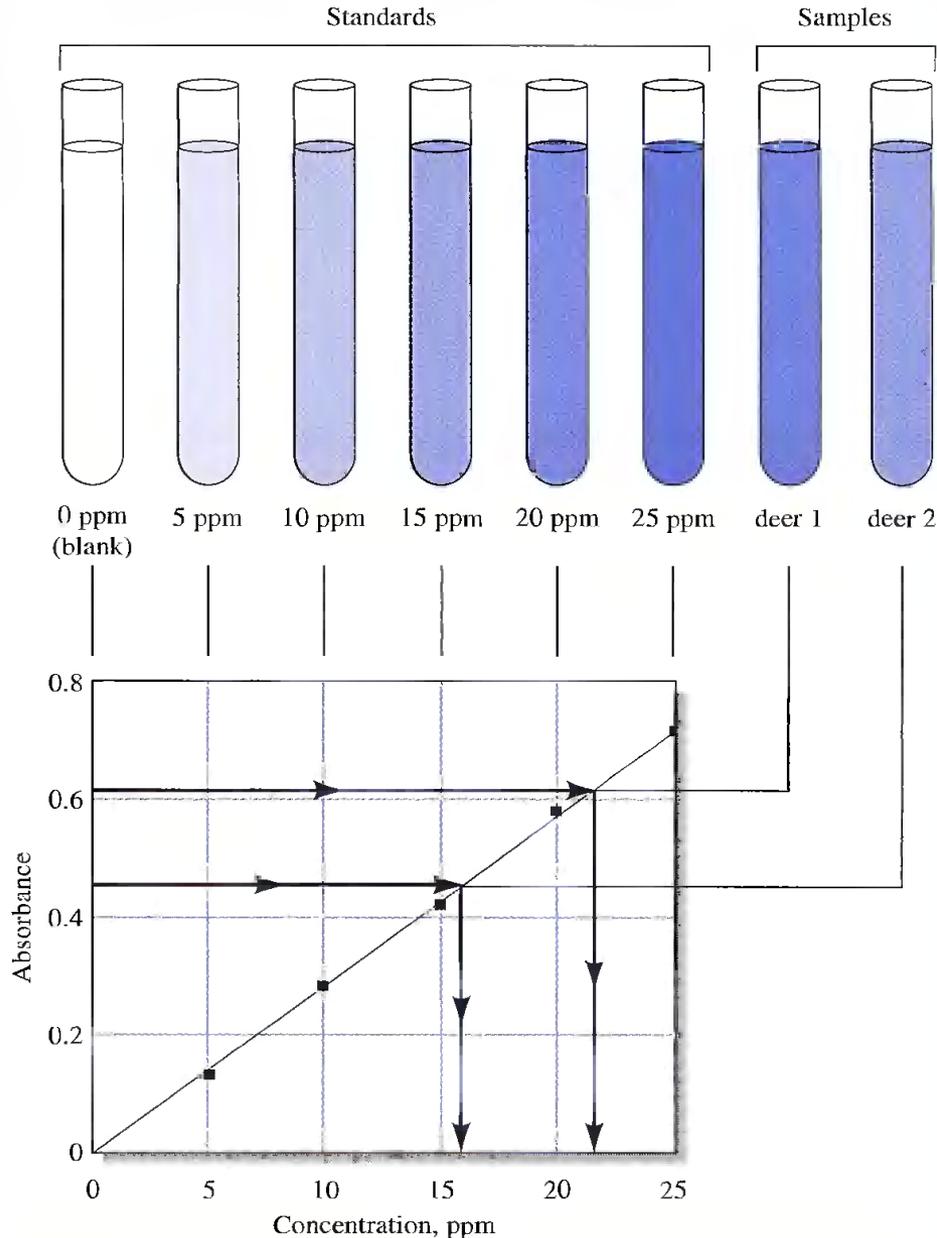


Figure 1F-2 Constructing and using a calibration curve to determine the concentration of arsenic. The absorbances of the solutions in the cuvettes are measured using a spectrophotometer. The absorbance values are then plotted against the concentrations of the solutions in the cuvettes, as illustrated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

This case study illustrates how chemical analysis is used to identify and determine 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 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 with 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.

Practice Exercise 1.1

As an exercise, let's adapt our model of the analytical approach to the development of a simple, inexpensive, portable device for completing bioassays in the field. Before continuing, locate and read the article

“Simple Telemedicine for Developing Regions: Camera Phones and Paper-Based Microfluidic Devices for Real-Time, Off-Site Diagnosis”

by Andres W. Martinez, Scott T. Phillips, Emanuel Carriho, Samuel W. Thomas III, Hayat Sindi, and George M. Whitesides. You will find it on pages 3699-3707 in Volume 80 of the journal *Analytical Chemistry*, which was published in 2008. As you read the article, pay particular attention to how it emulates the analytical approach. It might be helpful to consider the following questions:

- What is the analytical problem and why is it important?
- What criteria did the authors consider in designing their experiments?
- What is the basic experimental procedure?
- What interferences were considered and how did they overcome them?
- How did the authors calibrate the assay?
- How did the authors validate their experimental method?
- Is there evidence of repeating steps 2, 3, and 4?
- Was there a successful conclusion to the problem?

Don't let the technical details in the paper overwhelm you. If you skim over these you will find that the paper is well-written and accessible.