Analytical Chemistry

Analytical Chemistry

Is About Obtaining Information about Materials.

Analytical chemistry is the science of obtaining, processing, and communicating information about the chemical composition and the structure of matter; based on measurements.

In other words, it is the art and science of determining *what substance(s), a sample of a material is made of* and *how much of the substance(s) of interest (i.e. mass/concentration) is in the sample of the material under investigation*.

Analytical Chemistry: Identification and quantification of *substance(s)* (also termed as *solutes, analytes, components*) of interest in a material.

Qualitative analysis – What analyte(s) are present in a sample?
or Is an analyte(s) of interest present?

Quantitative analysis – How much of the analyte(s) is there?

Analysis of molecular/chemical composition of materials of interest often (not always) necessitates the separation/isolation of an analyte(s) of interest from the sample (= mixture) before any type of further analysis (chromatography, extractions etc.).

An ***analyte*** is a substance or chemical constituent of a sample that is to be measured by an analytical method.

Methodology of chemical analysis:

* 1. Classical wet techniques; gravimetry and titrimetry.
  2. Instrumental methods; methods involving instrumentation; electrochemical-analysis, chromatography, spectroscopy. (may involve wet chemistry).

*classical wet techniques necessarily employs chemical reactions and the reaction stoichiometry as the basis of analysis, exclusively .

Stoichiometry is the relationship between the number of moles of the reactants and products of a balanced chemical reaction.

Classical wet techniques in particular (gravimetric and titrimetric) depend on those chemical reactions which proceed to a near completion.

The amount of the product formed of such reactions is determined by the *limiting reactant* (reagent).

Such reactions are limited, however reactions that would proceed from moderate to a high degree of completion under normal conditions could be pushed forward to the product side so as to be useful for quantitative analysis.

Whether an analysis is routine (as in manufacturing industry) or otherwise, the main objectivein chemical analysis is to obtain information involving matter.

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General Approach to Chemical Analysis.

1. Selecting an analytical method (search literature for existing protocols or devise new methods)*.
2. Selecting a *representative composite sample* for analysis. (Sampling).
3. Making a *laboratory sample* from the *representative composite sample* amenable for analysis protocol (homogeneous solution; masking of interfering species if necessary).
4. Analyzing the laboratory sample with the selected procedure in replicate, 3 – 6, 8 replicates. May use more than one analytical procedure (method) to confirm the result.
5. Perform the statistics on results.
   Report results, interpretation/conclusions

1. Analytical Method Selection (to analyze - *laboratory sample*):

based on,
- accuracy and precision expected
- time constraints
- cost/number of analyses
- complexity of sample (possible interferences)

2. Sampling:

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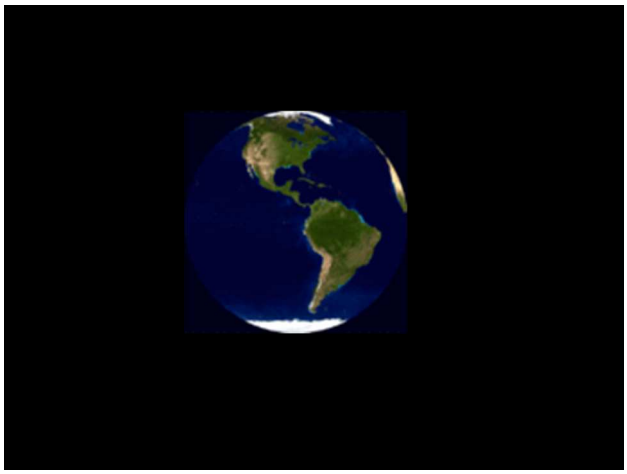
Often the actual 'subject' under analysis is much larger than the laboratory sample.

Truck load of coal (*metal impurities*)
A Lake (for dissolved *oxygen*)
Blood (*lead*)
Stratosphere (ozone)
.

} **Lot**

Sampling is the process of obtaining a *representative composite sample (=bulk sample)* from the **lot**.

It is followed by the preparation of the *laboratory sample.*



Lot - normally heterogeneous; in the extreme - highly segregated

From the Lot ⇒ bulk sample = *representative-composite* of the lot

Bulk sample ⇒ *laboratory sample* – a homogeneous solution

3. Laboratory sample: Dissolve a known mass of the bulk sample in a volumetric flask. Divide the solution into smaller parts (viz. *aliquots* 25.00mL).

4. Analyze: Each *aliquot* is subjected to a well defined procedure, where *interfering* components (*interferents*) are *'masked'* (removed from reaction sphere) if necessary.

- replicate the procedure many times, *n*, (minimum, triplicate *n*=3) to produce a raw data set.

Interferents are species that coexists with the analyte and affect the final measurement by enhancing or attenuating the signal.

5. Data treatment: Calculations to find amount/concentration from the data set and analysis of the data using statistics.

3. Laboratory sample:

Random bulk sampling:
overall un-segregated lot
Random homogeneous lot

1	5	9	13	17	21	25	29
2	6	10	14	18	22	26	30
3	7	11	15	19	23	27	31
4	8	12	16	20	24	28	32

Divide the lot into small equal regions (matrix); use a 'map'. Number (label) the regions. (Set up all numbers in a 'lotto' type *random drawing*). Draw a few numbers (regions) randomly.

Obtain equal amounts of material from the randomly picked regions; combine them; *bulk sample*.

Random bulk sampling:
inhomogeneous (*segregated*) lot

1	5	9	13	17	21	25	29	33
2	6	10	14	18	22	26	30	34
3	7	11	15	19	23	27	31	35
4	8	12	16	20	24	28	32	36

20% 10% 40%

Divide bulk ..... Pick numbers randomly.

Collect from the different areas *proportionally*.

e.g. 1:2:7 number of samples from the three areas.

Laboratory sample for analysis is a *homogeneous solution*, most of the time.

Analyze equal aliquots of prepared lab sample in replicate.

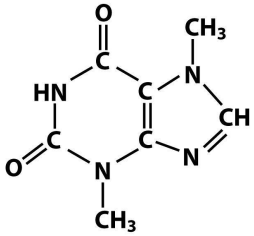
(instrumental methods involve generating calibration curves/ internal standards/ standard addition techniques)

Workout the uncertainty/error (statistics) of the results.

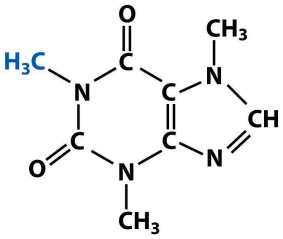
Report results, interpretation/conclusions.

4. Analysis

Example; Chemical Analysis

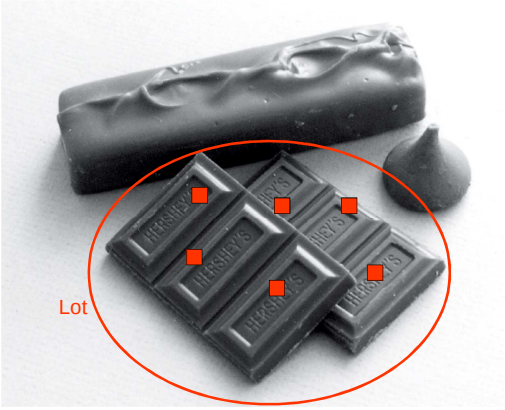


Theobromine

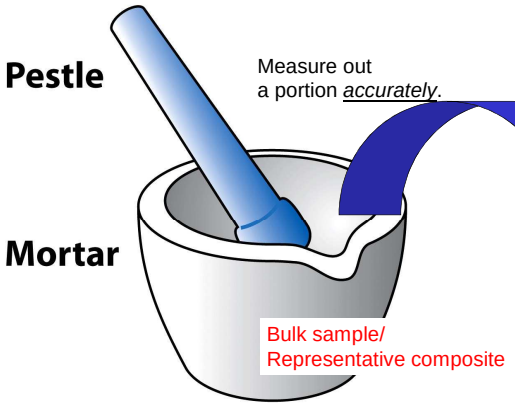


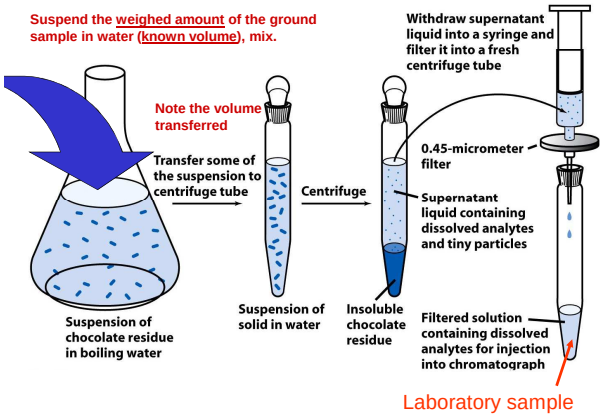
Caffiene

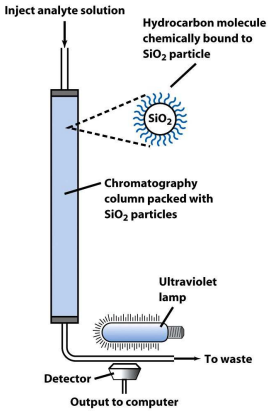
Both, soluble in water.

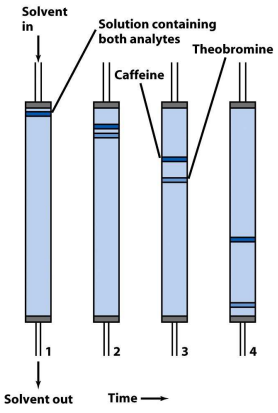


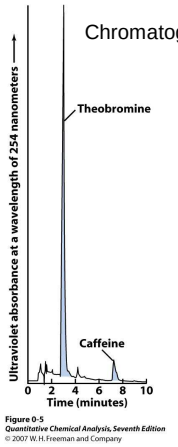
Recent photograph from a Colorado Chocolate Factory.









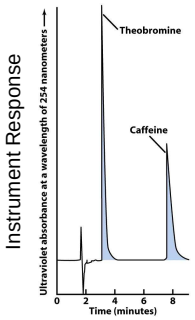


Chromatogram (graphical output from chromatograph)

Successful qualitative analysis.

The signal from the chromatograph by itself is not of valuefor *quantitative analysis*.

Different substances detected by the same detector produces different responses for the same quantity of different materials.



Different substances detected by the same detector produces different responses for the same quantity of different materials. That is the sensitivity of each analyte is unique.

The signal from the chromatograph *by itself is not of value for quantitative analysis*.

It is necessary to generate a calibration plot(s) for the analyte(s) of interest to quantify the analytes.

To generate a calibration plot, prepare a series of solutions of known concentrations of the analyte(s) (standards) and *subject the standards to analysis under the same experimental conditions*. Obtain the instrument responses for each analyte. (Details later).

A calibration plot relates the signal/response intensity to the concentration of the analyte (linear graph).

Sensitivity of an analyte for detection = slope of calibration plot.

5. Data treatment:

Calibration plot

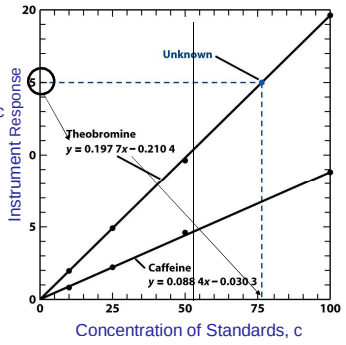
Instrument Response vs. c

Instrument Response $\propto$ c

$y \propto c$; $y = m\,c$

$y = m\,c + b$

Height or area of the peaks; y.



Different response factors (slope=sensitivity) of substances necessitates the generation of *a calibration plot for each analyte*.

Table 0-1 Analyses of dark and white chocolate

	Grams of analyte per 100 grams of chocolate	
Analyte	**Dark chocolate**	**White chocolate**
Theobromine	0.392 ± 0.002	0.010 ± 0.007
Caffeine	0.050 ± 0.003	0.000 9 ± 0.001 4

Uncertainties are the standard deviation of three replicate injections of each extract.

Summary of results:

Sample standard deviation, s, is a measure of the reproducibility of the analysis (at a preliminary level).

Smaller s, indicates a better analysis (better precision).

Relative standard deviation is a measure of the quality of the analysis; the smaller the better.

Table 1-1 Fundamental SI units

Quantity	Unit (symbol)	Definition
Length	meter (m)	One meter is the distance light travels in a vacuum during $\frac{1}{299\,792\,458}$ of a second.
Mass	kilogram (kg)	One kilogram is the mass of the prototype kilogram kept at Sèvres, France.
Time	second (s)	One second is the duration of 9 192 631 770 periods of the radiation corresponding to a certain atomic transition of ^{133}Cs.
Electric current	ampere (A)	One ampere of current produces a force of 2×10^{-7} newtons per meter of length when maintained in two straight, parallel conductors of infinite length and negligible cross section, separated by 1 meter in a vacuum.
Temperature	kelvin (K)	Temperature is defined such that the triple point of water (at which solid, liquid, and gaseous water are in equilibrium) is 273.16 K, and the temperature of absolute zero is 0 K.
Luminous intensity	candela (cd)	Candela is a measure of luminous intensity visible to the human eye.
Amount of substance	mole (mol)	One mole is the number of particles equal to the number of atoms in exactly 0.012 kg of ^{12}C (approximately $6.022\,141\,99 \times 10^{23}$).
Plane angle	radian (rad)	There are 2π radians in a circle.
Solid angle	steradian (sr)	There are 4π steradians in a sphere.

Table 1-2 SI-derived units with special names

Quantity	Unit	Symbol	Expression in terms of other units	Expression in terms of SI base units
Frequency	hertz	Hz		1/s
Force	newton	N		m · kg/s²
Pressure	pascal	Pa	N/m²	kg/(m · s²)
Energy, work, quantity of heat	joule	J	N · m	m² · kg/s²
Power, radiant flux	watt	W	J/s	m² · kg/s³
Quantity of electricity, electric charge	coulomb	C		s · A
Electric potential, potential difference, electromotive force	volt	V	W/A	m² · kg/(s³ · A)
Electric resistance	ohm	Ω	V/A	m² · kg/(s³ · A²)
Electric capacitance	farad	F	C/V	s⁴ · A²/(m² · kg)

Table 1-3 Prefixes

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

Units:

Molar mass = **Formula mass**, g/mol
Formality = moles of substance per liter of solution, mol/L.
*Molarity (M) - moles of a substance per liter of solution, *often used to mean formality,* mol/L.
*Molality (m) - moles of substance per kg of solvent.

Osmolarity - moles of particles per liter of solution, mol/L.

*assumes the chemical form of the substance *is unchanged* !?

Percent Composition (parts per hundred);

$$wt\% = \frac{m_{analyte}}{m_{sample}} \times 10^{2}$$ *Mass of analyte per 100g of sample*

$$vol\% = \frac{vol_{analyte}}{vol_{sample}} \times 10^{2}$$ *Volume of analyte per 100mL of sample*

$$wt\%_{o} = \frac{m_{analyte}}{m_{sample}} \times 10^{3}$$

$$\text{ppb} = \frac{m_{analyte}}{m_{sample}} \times 10^{9}$$

$$\text{ppm} = \frac{m_{analyte}}{m_{sample}} \times 10^{6}$$ *Mass of analyte per 10^6 g of sample.*

$$\text{ppt} = \frac{m_{analyte}}{m_{sample}} \times 10^{12}$$

For *aqueous solutions*, often 1ml is assumed to weigh 1g. therefore;

$$1\,ppm = 1g/10^{6}\,g = 1\mu g/g = 1\mu g/mL = 1g/10^{3}\,L = 1mg/L$$
$$1\,ppb = 1g/10^{9}\,g = 1ng/g = 1ng/mL = 1g/10^{6}\,L = 1\mu g/L$$

'Parts per' expressions can be used for volumes of analytes as well.

$$pX = -\log_{10} X$$

Please revise the procedure for unit conversions.