ENVIRONMENTAL CHEMICAL ANALYSIS

ANALYSIS Identification and Quantitation

CHEMICAL The Analyte: A Discrete Chemical Species or
A Collection of Related Chemical Species (i.e., An Aggregate)

ENVIRONMENTAL Analyte of Environmental Significance and/or
Analyte in an Environmental Matrix (e.g., Soil, Sludge or Water)

Examples of discrete chemical analytes	**Examples of environmental matrix**
Heavy metals (elemental) **Hg**, **Pb**, **Cd**	Adipose tissue
Monoatomic ions H^+, Ca^{2+}, F^-	Well water
Polyatomic ions SO_4^{2-}, NH_4^+, CN^-	Sea water
Molecular gases O_2, NH_3, Cl_2	Aquaculture water
P (as available PO_4^{3-}) or **P** (total)	Irrigation water
Specific organic molecules; e.g. 2,4-dichlorophenol, octachlorodibenzodioxin	Pulp mill effluent

Examples of Aggregate Parameters

TDS	Total dissolved solids	Na^+, Cl^-, Ca^{2+}, HCO_3^-, …
Total Alkalinity	Total acid neutralizing capability	OH^-, HCO_3^-, CO_3^{2-}, NH_3, …
Total Hardness	Total divalent metal cations	Ca^{2+}, Mg^{2+}, Fe^{2+}, Mn^{2+}, …
TOC	Total organic carbon	All carbon present in various organic molecules
Turbidity	Total light scattering due to suspended solids	All suspended (undissolved) material; e.g. silt, clay, algae, …

CHEMCIAL ANALYSIS

Quantitation (obtaining a number) is only one of many important steps in the process of Chemical Analysis

"The Chemical Analysis Process"

1. Definition
2. Method
3. Sampling
4. Preparation
5. Quantitation
6. Evaluation

1. Definition: Defining the Analytical Question that needs to be solved

Choosing the analyte/s that will answer the question

E.g., heavy metal toxicity in shellfish
amount of detergent in effluent
value of precious metals in sediment
the concentration of a performance enhancing drug in athelete's urine
primary productivity of natural lake

What motivates the analysis
E.g., regulatory guidelines
liability to litigation
profile margins
awarding Olympic medals
research

2. Method: Choosing an Appropriate Method of Analysis

There is no single ‘best’ method in analytical chemistry.

There are many methods available for any particular analyte.

Choosing the most appropriate method depends on a number of factors

- Accuracy
- Detection limits/sensitivity
- Speed
- Cost
- Legality (e.g., US EPA approved)

Consult *Standard Methods for the Analysis of Water and Wastewater* and on-line databases (e.g., EPA methods)

New analytical methods are constantly being developed. Therefore, a review of the literature is essential. The following periodicals publish peer-reviewed articles involving emerging analytical methods.

- *Analytical Chemistry*
- *Analytical Methods*
- *Trends in Analytical Chemistry*
- *International Journal of Environmental Analytical Chemistry*
- *Journal of Chromatography*
- *Progress in Analytical Chemistry*
- *Environmental Science and Technology*

3. Sampling: Obtaining a representative bulk Sample

Representative meaning that sample taken reflects the entire body from which it came.

The bulk sample may be further treated or split into a number of laboratory samples depending on the method of analysis.

Spatial Variation

Homogeneous - analyte spread uniformly throughout

(e.g., ethanol in blood, **As** in mixed drinking water)

Heterogeneous - analyte concentration varies depending on location

(e.g., $\mathbf{H_2S}$ in stratified lake, **I**-131 in whole organism)

Temporal Variation

Stable - analyte concentration remains constant

(e.g., $\mathbf{Ca^{2+}}$ in seawater, **S** in coal)

Variable - analyte concentration varies depending on when sample collected

(e.g., $\mathbf{O_2}$ in surface water, turbidity in stream)

Sample bottles, preserving agents and storage protocols are also important, particularly for trace analysis. Protocols vary depending on the analyte and jurisdiction. Details are summarized elsewhere.

4. Sample Preparation: Preparing sample for a particular analytical method and eliminating interferences.

Extract from the bulk sample, a homogeneous laboratory sample.

Convert the laboratory sample into a form suitable for analysis, which generally means dissolving the sample in solution. Samples with very low analyte concentrations (trace analysis) may need to be concentrated prior to analysis.

Remove or mask species that interfere with chemical analysis.

Sample preparation steps might include

- Treating with acid
- Filtering
- Centrifugation
- Distillation
- Chromatography

Interference occurs when a species other than the analyte increases or decreases the response of the analytical method.

Masking is the transformation of an interfering species into a form that is not detected.

If the analyte cannot be separated from an interferent, a 'masking agent' is often employed.

E.g., In the spectrophotometric analysis of $\mathbf{F^-}$,
$\mathbf{Fe^{2+}}$ and $\mathbf{Al^{3+}}$ will interfere
Therefore citrate ion is added to 'mask' these species by forming strong iron and aluminum complexes, which effectively removes them from interfering with the analysis of fluoride ion.

5. Quantitation: Performing the measurement – Calibration and Determination

Small test portions of the lab sample are used for individual analysis and are called aliquots.

Some measured physical quantity (e.g., titrant volume, colour intensity, electrical current) is related to the concentration of the analyte.

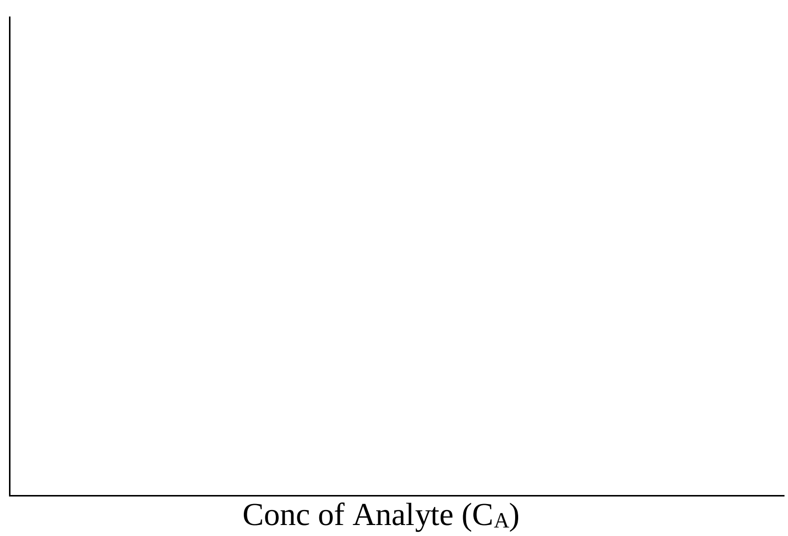
The concentration of analyte (C_A) is proportional to a measured quantity or signal (S)

$C_A \propto S$
and
$C_A = \kappa \times S$
Where κ is proportionality constant.

For gravimetric and volumetric analysis, the value of κ can be determined from the stoichiometry and the dilution factors.

For other analytical methodologies, the relationship between C_A and S is determined empirically via a process known as calibration.

A calibration curve is generated by measuring samples of known analyte concentration (standards).



Replicate measurements to assess uncertainty of method.

6. Evaluation: Interpreting the Results

Results must be reported with associated units of measure and some indication of the associated uncertainty.

Statistical methods can be used to comment on confidence levels (e.g., 95% certainty that x is between certain limits).

Statistical methods can also be used to determine the precision of an analytical method and the number of samples that must be analyzed to obtain a result within specified limits.

Results must be interpreted within the context of the original question.

E.g.,
- health and environmental protection
- drinking water guidelines vs maximum acceptable limits
- legal permit limits
- profit margins