CHM 6110 – Goals for the Semester

Become familiar with various modern instrumental methods

Be able to decide on appropriate instrument to carry out an analytical determination

Be able to improve existing methods, or to develop new methods to achieve the desired objective

Be able to appreciate analytical perspective on decision making, and

Analytical Chemist → Analytical Scientist } differ in their approach to the problem

The Analytical Scientist vs. Chemist

Analytical Chemist → **Analytical Scientist** } differer in their approach to the problem

- Qualitative analysis
- Quantitative analysis
- Characterization

- Method development
- Multidisciplinary
- Problem solving
- Broader perspective

DOMAINS

- Routine analysis
- Protocol typically exist
- More classical than instrumental
  - Titrations, Gravimetry, etc.
  - Measurement of physical properties
    - melting point, boiling point, viscosity, density, odor, color, etc.

- Cutting edge research and technology
- Modern instrumental methods, less classical
- Electronics, computers and statistics

Areas Needing Analytical Scientist

(A) New demands/challenges evolve with time that expands/broadens analytical chemistry

1. *To cope with these challenges, the analytical scientist is required to up with other disciplines including physics, mathematics, optics, computers, communication, engineering, etc.*

2. *A scientist's role in a method of analysis is thus more than understanding and making measurements.*
   - It requires experience, broad knowledge, intuition, and the <u>problem solving skills of a detective</u>
   - The analyst must deal with the:
     i. nature and origin of the sample,
     ii. desired accuracy and precision,
     iii. limitations in costs and time for the analysis, and
     iv. selection of appropriate techniques

3. *Significant interactions with collaborating investigators are typically required, not only for the analyst to acquire the necessary information to solve the problem, but also to communicate the information that can realistically be provided, given the nature of the sample and measurement techniques available*

Areas Needing Analytical Scientist

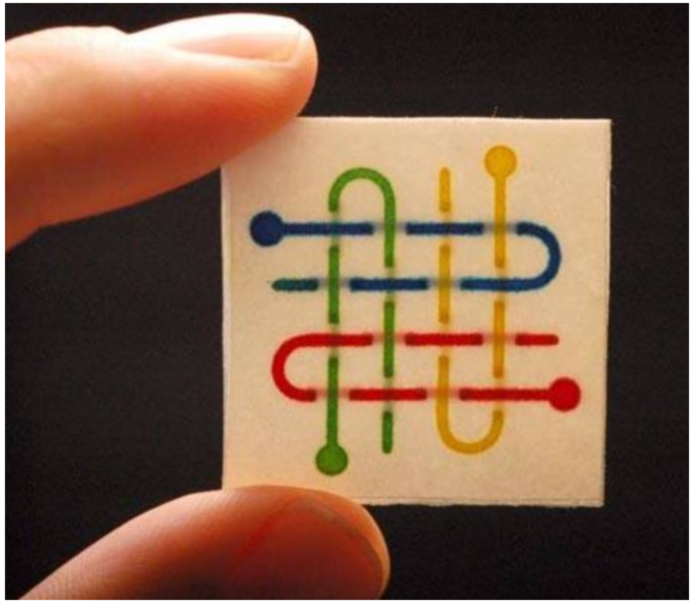
(B) Trace elements/gases (e.g., fluorochlorocarbons) in the atmosphere

(C) ppb levels of impurities in soil, drug metabolites in human bodies

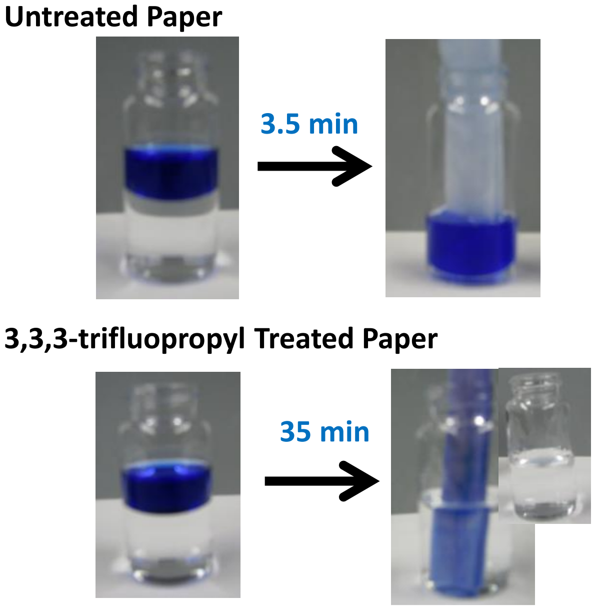
(D) Evaluation of pesticide exposure to farmers, children, pregnant women

(E) Development of rapid and sensitive devices for chemical/biological warfare agents

(F) Real time modeling and monitoring of oil spill near a port



Paper Device for Disease Diagnosis

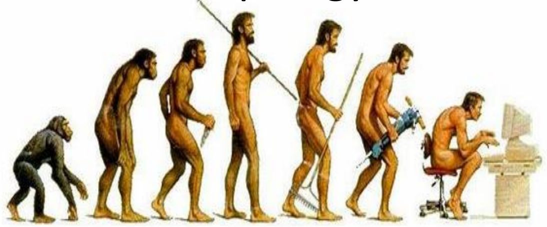


Paper for Selective Oil Absorption

Areas Needing Analytical Scientist

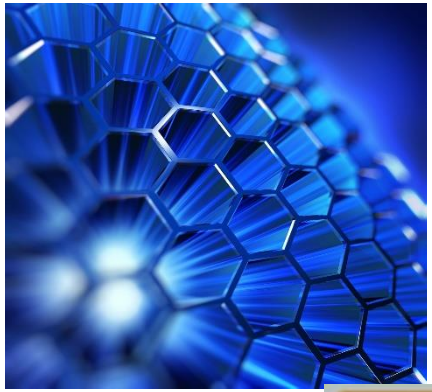
Archaeology

Anthropology



Geology

Material Science

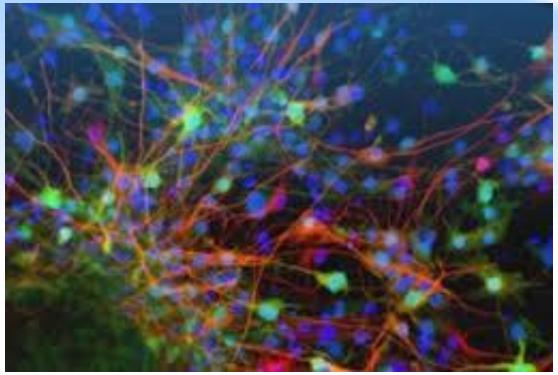


Analytical Chemistry

Forensic Science

Toxicology

Molecular Biology



Pharmacology

Scope of Analytical Instrumentation

Determination of quantity of substances in a sample

It is a science of invention

Application of concepts, principles, and devising strategies for measuring the characteristics of chemical systems and species

Extreme limits: limited access to space, time, volume, cost, amount precision, etc.

These challenges exist at *Cutting Edge Research*

Analytical Perspective/Approach

1. Identification and defining of the problem
2. Designing experimental procedure:
   Sampling, pre-treatment and analysis
3. Performing experiments and collecting data
4. Analysis of collected data
5. Presenting a solution to the problem

Steps 1 and 5 involve many people

Define the Problem

The first important step in the development of a chemical method is to clearly define the problem.

It requires:

- a solid understanding of analytical techniques,
- problem-solving skills, and
- experience and intuition

Several key points must be addressed:

1) the intent of the measurement,
2) the necessary considerations in sampling and sample preparation,
3) the best technique for making the measurement,
4) evaluation of the data,
5) reporting the results, and
6) the resources needed to accomplish the analysis

Define the Problem

Representative Questions to Define the Problem

- What is the nature and background of the problem?
- What is known about the history of the sample?
- What analyte is important in the sample?
- What is the concentration range of the analyte?
- What degree of accuracy and precision is demanded?
- What other components are present in the sample (concomitants)?
- What are the physical and chemical properties of the sample, analyte, and concomitants?
- Have prior, similar efforts been documented in the literature?
- What instruments and equipment are available for the determination?
- How much time is needed to perform the work?
- How soon does the work need to be done?
- How much money is available to accomplish the work?
- How many samples must one measure?
- Are there limitations to the amount of sample that can be used?

Analyte is:

Major >1%

Minor 0.01 – 1%

Trace 10^{-2} – 10^{-6}%

Ultra-trace 10^{-6} – 10^{-9}%

Designing Experimental Procedure

1. Properties of sample
   1. Phase
   2. Available amount
   3. Homogeneity

2. Properties of analyte
   - Instruments rely on specific properties (physical or chemical) of analytes
   - Knowledge of these unique properties, combined with an understanding of the nature of the analyte-instrument interaction, determines the appropriate measurement technique

3. Anticipated concentration range of analyte
   - The expected concentration of analyte must be compared to the concentration range within which an instrument can reliably measure (dynamic range)
   - Use literature or preliminary experiment to guide you in your decision

Designing Experimental Procedure

Sampling Considerations

- who collects samples

- amount (always take more than needed):
  - solid samples – amount needed is determined by required precision, the particle size of the solid material, and the distribution of the analyte
  - liquids and gases, smaller sample sizes are generally needed, as homogeneity for liquids and gases can be improved with mixing prior to sampling

- location:
  - important for cases where homogeneity cannot be achieved through mixing

- Transportation and storage:
  - chemical changes, volatilization, absorption of moisture, contamination, and adsorption/desorption processes with sample container walls

Two sources of experimental error:

- ✓ Sampling and instrumental
- ✓ Many data analysis techniques assume normal distribution → all errors are due to instrument.
- ✓ It is your duty to evaluate sampling contribution to overall precision (standard deviation) of the method

Designing Experimental Procedure

Sampling Preparation

- samples must be treated to make them compatible with the instrumental techniques

- Implementation requires the biggest investment of time:

- Transformation types:
    - Solids: many instruments require sample to be in a liquid phase
        - Dissolution, extraction and digestion
    - Liquids and gases:
        - Filtration → removes particulate matter
        - Extraction → remove an analyte from a complex matrix
        - Chromatographic separation → remove interferences from the analyte

- Enrichment and pre-concentration

Perform Experiment and Collect Data

Measure replicate samples to establish the precision of the method

- if possible perform all experiment for a given replicate samples within a single day

Large sample population is needed to reach the “true” value

- Usually not possible (because of cost, time, etc.) to repeat experiments that many times
- Typically the replicates must to be tested to ensure that they are part of the large population
- The confidence level must also be reported
- The limit of detection of the developed method must always be reported

Presentation of Results

Results must be presented from two different perspectives:

- Internal
  - technical and meaningful presentation is required for peer review and approval
- Collaborators (external)
  - non-technical presentation to peers outside the institution that performed the studies

Forms of Presentation

- Formal oral papers
- Poster presentations
- Research articles
- Theses or dissertations
- Progress reports

Important Information

- Surprises, conclusions, and recommendations related to the original problem must always be stated

Types of Instrumental Methods

Classical: Non-electrical → Non-electrical

Instrumental: Non-electrical → (stimulus) → Electrical → (transducer) → Non-electrical

All measurements begin and end in non-electrical domain

Instrumental methods REQUIRE inter-domain conversions

Instrument	Stimulus (energy source)	Analytical Information	Information Sorter	Transducer
Mass Spectrometer	Ion source	Mass-to-charge	Mass analyzer	Electron multiplier
Atomic Emission Spectrometer	Heat/Plasma	UV-visible radiation	Monochromator	Photomultiplier

Instrument Classification

(1) Those involving the interaction of analyte with electromagnetic radiation

- Emission of radiation → radiant energy is produced by analyte after stimulation

- Absorption of radiation
- Scattering of radiation
- Refraction of radiation
- Diffraction of radiation
- Rotation of radiation

} involves changes if electromagnetic radiation brought about by its interaction with the sample

(2) Those involving electrical properties

- Electrical potential
- Electrical charge
- Electrical current
- Electrical resistance

(3) Miscellaneous

- Mass
- Mass-to-charge
- Rate of reaction
- Thermal
- Radioactivity
- Retention time