ENVIRONMENTAL CHEMICAL ANALYSIS II

Instrumental Methods of Analysis

Analytical Chemistry

Analytical chemistry involves the determination of chemical composition of samples

- ***Qualitative analysis*** = involves identification of species in the sample
  - What elements are in wastewater?
- ***Quantitative analysis*** = involves determination of the amount of species in the sample
  - How much *lead* and *copper* are in the wastewater sample?

Analyte = species of interest
Ex. Lead and copper in the example above

Types of Analytical Methods

Classical methods (or ***wet chemical methods***) such as *titration* and *gravimetry*

- Analysis is based on <u>mass</u> (or <u>volume</u>) *relationships* in a chemical reaction involving the analyte

Example: Acid-base ***titration*** for the determination of alkalinity
Gravimetric determination of Cl^- by precipitation as AgCl (and weighing the precipitate)

Instrumental methods- involve the use of modern analytical instruments for chemical analysis

HOW? Instruments serve as communication device between chemical species and the chemist

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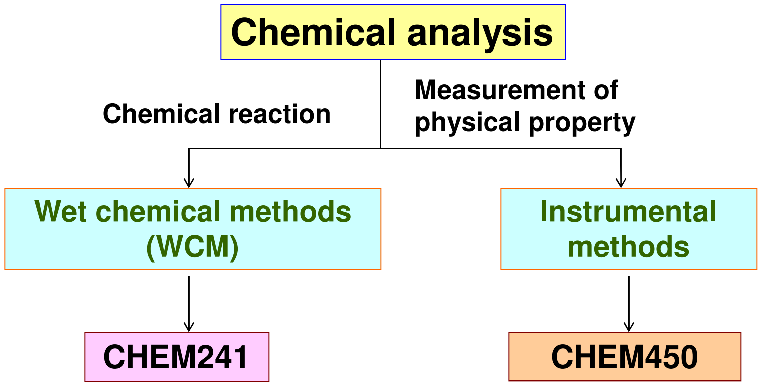
Types of chemical analysis based on method



Chemical analysis

Chemical reaction

Measurement of physical property

Wet chemical methods (WCM)

Instrumental methods

CHEM241

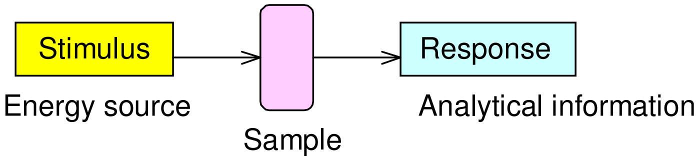
CHEM450

Instrumental methods

Various instrumental methods are designed to perform:

- Primarily qualitative analysis – such as IR, NMR
- Primarily quantitative analysis – such as titration, UV/vis spectroscopy
- Both qualitative and quantitative – such as GC/MS

Instrumental analysis generally involves two steps:



Stimulus → Sample → Response

Energy source

Sample

Analytical information

1. **Stimulation** of the analyte - to elicit a response (e.g. a change in physical property) that relates to ID or concentration of analyte

   Example: Shining UV radiation to a solution of benzene results in molecular excitation

2. **Conversion** (encoding) of information from the analyte to the instrument

   Example: Electrical signal from the benzene molecules released during de-excitation is converted into a numeric display, such as absorbance (of UV light)

Instrumental Analysis, Cont.

Instrumental Methods for the Analysis of Environmental Samples

Spectroscopic Methods

- utilize electromagnetic radiation (light) to extract chemical information from the analyte

  - ❖ Molecular UV/Vis Spectroscopy
  - ❖ Atomic Absorption (AA) Spectroscopy
  - ❖ Inductively Coupled Plasma (ICP) Spectroscopy

Chromatographic Methods= separations techniques based on differential migration of solutes or analytes in a column

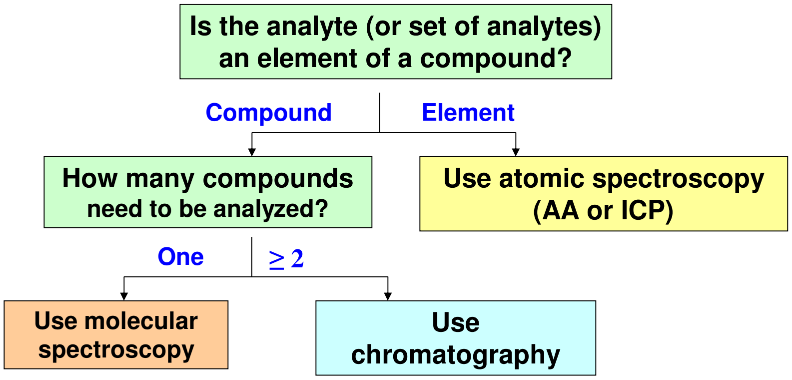
- ❖ Gas Chromatography (GC)
- ❖ High Performance Liquid Chromatography (HPLC)

Instrumental Analysis, Cont.

Q. How do we know which of these instrumental methods to use?

- ❖ It depends on a lot of factors, including the nature of the analyte, the type of information (qualitative or quantitative) desired, the amount of sample available, etc.
- ❖ Use the following as general guidelines when selecting an instrumental method (It does not apply to every type of analysis)

General guidelines for selecting an instrumental method (**Note: The following *does not apply to every type of analysis)***



Is the analyte (or set of analytes) an element of a compound?

Compound

Element

How many compounds need to be analyzed?

Use atomic spectroscopy (AA or ICP)

One

≥ 2

Use molecular spectroscopy

Use chromatography

Some Advantages of Instrumental Methods Over Wet Chemical Methods

1) Speed and automation

- WCM always utilizes chemical reactions - lengthy and tedious steps involved
- IM usually measures a physical property of the analyte, which allows for faster analysis
  - Minimizes labor costs
  - Increases productivity

Some Advantages of Instrumental Methods – Cont.

2.) Low detection limits, which allows for the determination of minor components (i.e. *low-level analysis*) vs. WCM, which only determines major components

Detection limit (also called limit of detection or **LOD**) indicates the lowest analyte concentration that can be determined to be statistically different from the blank (99% confidence). [Note: Lower LOD is better]

Precision and accuracy? Not always.

IMs are usually not as precise and accurate as a carefully executed WCM.

Quantitation Using the Calibration Method

Goal of calibration: To determine the relation between analyte signal and its concentration

$$\boxed{S_{analyte} = f(c_{analyte})}$$

Analyte signal **Analyte concentration**

Most instrumental methods attempt to make the relationship, $f(c_{analyte})$, linear. That is,

$$\boxed{S_{analyte} = m(c_{analyte}) + b}$$

Looks familiar?

Straight line equation: $y = mx + b$

m = slope of calibration curve
b = y-intercept

SPECTROSCOPIC METHODS

Spectroscopic Methods

- Based on the interaction of light or *electromagnetic radiation* with analytes in solution

Ex. UV, visible, and infrared light

Spectroscopy or **spectrometry**

- Involves measurement of amount of light ***absorbed*** or ***emitted*** by analytes in solution

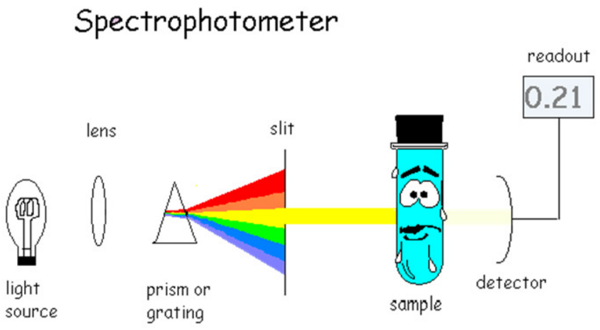
Molecular or atomic absorption spectroscopy

Molecular or atomic emission spectroscopy

Spectroscopic Methods, Cont.

Schematic diagram of a typical UV/Vis **spectrophotometer**.

Image available at http://www.electrical-res.com/pager/1/511/



Quantitation based linear relation between absorbance of light and solution concentration

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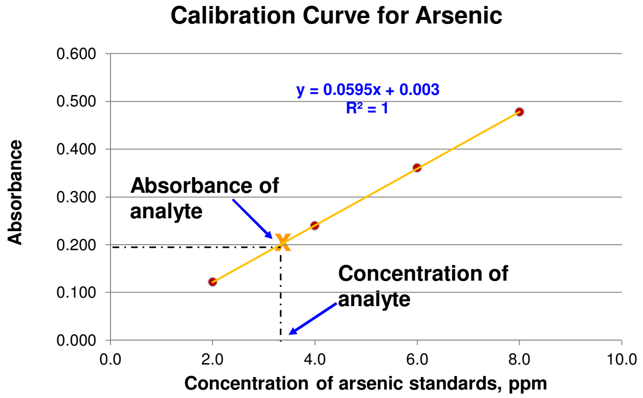
Linear Relationship Between Absorbance and Concentration (**Beer's Law**)

Calibration Curve = plot of absorbance of light, **A**, versus concentration, **c**, of standard solutions



Extrapolation gives the …

UV/Vis Absorption Spectroscopy

- Application: Quantitation of ***molecular species*** in solution

  Molecules must absorb either UV or visible light
  - UV – multiple bonds (Ex. Benzene, PAHs)
  - Visible –colored compounds

Benchtop UV/Vis spectrometer: Image available at http://chemicoscientific.com/analytical_instruments.html

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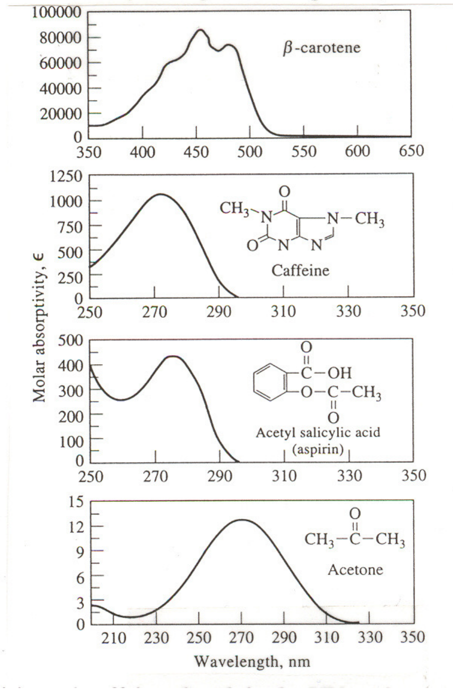

Other UV/vis absorption spectra of organic compounds

Increasing conjugation; shift to ***longer wavelength*** of absorption. WHY?

- It takes less energy (longer λ) to excite molecule with conjugated electron systems

Atomic Spectroscopy

Quantitation based on the absorption or emission of light by atoms and monatomic ions

Widely used for the analysis of elements in environmental samples

- ➢ Analyte must be in solution (Ex. soluble metal ions) or can be solubilized, e.g. by acid digestion

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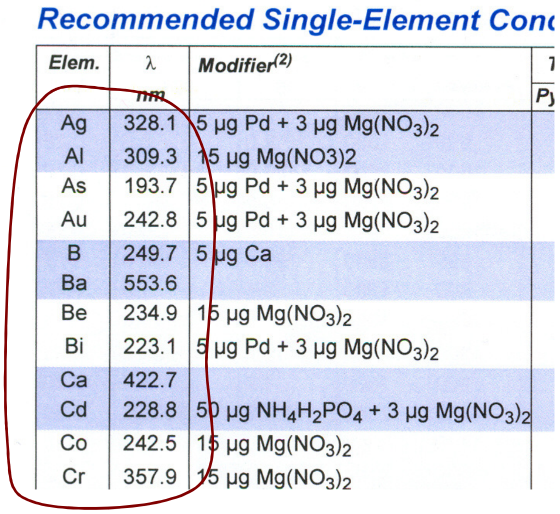
Atomic absorption spectroscopy

Uses flame of tiny furnace to atomize elements in the sample

If we have the lamp (excitation source) for it, we can analyze it



Recommended Single-Element Conc

Elem.	λ	Modifier$^{(2)}$	T
	nm		P
Ag	328.1	5 μg Pd + 3 μg $Mg(NO_3)_2$	
Al	309.3	15 μg Mg(NO3)2	
As	193.7	5 μg Pd + 3 μg $Mg(NO_3)_2$	
Au	242.8	5 μg Pd + 3 μg $Mg(NO_3)_2$	
B	249.7	5 μg Ca	
Ba	553.6		
Be	234.9	15 μg $Mg(NO_3)_2$	
Bi	223.1	5 μg Pd + 3 μg $Mg(NO_3)_2$	
Ca	422.7		
Cd	228.8	50 μg $NH_4H_2PO_4$ + 3 μg $Mg(NO_3)_2$	
Co	242.5	15 μg $Mg(NO_3)_2$	
Cr	357.9	15 μg $Mg(NO_3)_2$	

Wavelength of max. absorption for various elements

Inductively Coupled Plasma Mass Spectrometry (ICPMS)

- Widely used for the simultaneous analysis of multiple elements in a sample (vs. atomic absorption's single element capability)

- Plasma = very hot, ionized argon gas; > 6000 ^{0}C temp.
  - Atomizes and ionizes virtually all elements in the P.T.
  - Mass spectrometer separates and detects ionized elements by mass-to-charge ratio

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ICP torch

- The plasma is so **hot (>6000^{0}K)** that it serves both as excitation source and as atomizer as well

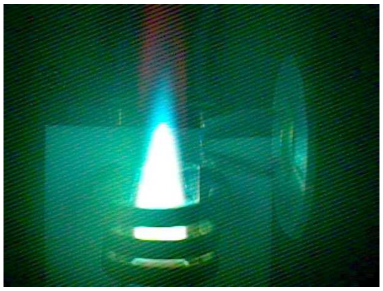


Photo of argon plasma in operation
Photo by: Steve Kvech

Image available at http://www.cee.vt.edu/ewr/environmental/teach/smprimer/icpms/icpms.htm

For a demonstration of Perkin-Elmer's NexION ICP-MS spectrophotometer go to: http://www.perkinelmer.com/Catalog/Family/ID/NexION

Summary of Atomic Spectroscopic Techniques

TABLE 9.2 Detection Limits for Selected Elements ($\mu g/L$)

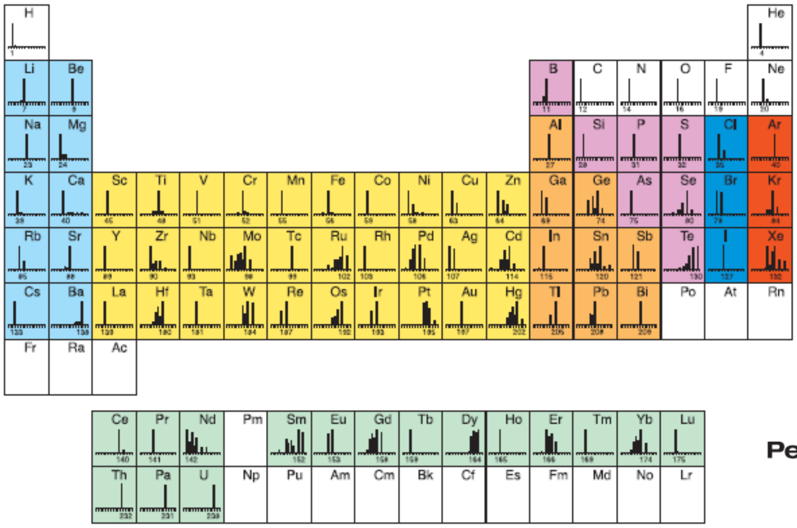
Element	Flame AA	Graphite Furnace AA	ICP	Cold Vapor Hg	Hydride
Arsenic	150	0.05	2	—	0.03
Bismuth	30	0.05	1	—	0.03
Calcium	1.5	0.01	0.05	—	—
Copper	1.5	0.014	0.4	—	—
Iron	5	0.06	0.1	—	—
Mercury	300	0.6	1	0.009	—
Potassium	3	0.005	1	—	—
Zinc	1.5	0.02	0.2	—	—

Source: From Perkin Elmer Instruments literature. With permission.

Note that GFAAS has the best sensitivity among the 3 methods discussed

Elements analyzed by ICP-MS (in color)

The 30-minte guide to ICPMS. Available at
http://www.perkinelmer.com/PDFs/Downloads/tch_icpmsthirtyminuteguide.pdf



PerkinElmer
For the Better

Figure 1. Elements analyzed by ICP-MS (in color).

Applications: ICP- MS

(1) **Identification** and/or **quantitation** of elements in a mixture

- **Concentrations of elements in water in ppb; # replicates = 10**

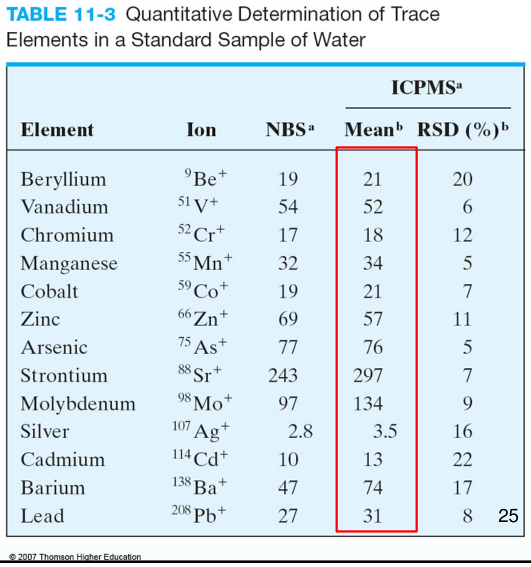


TABLE 11-3 Quantitative Determination of Trace Elements in a Standard Sample of Water

			ICPMS^a	
Element	**Ion**	**NBS^a**	**Mean^b**	**RSD (%)^b**
Beryllium	$^{9}\text{Be}^+$	19	21	20
Vanadium	$^{51}\text{V}^+$	54	52	6
Chromium	$^{52}\text{Cr}^+$	17	18	12
Manganese	$^{55}\text{Mn}^+$	32	34	5
Cobalt	$^{59}\text{Co}^+$	19	21	7
Zinc	$^{66}\text{Zn}^+$	69	57	11
Arsenic	$^{75}\text{As}^+$	77	76	5
Strontium	$^{88}\text{Sr}^+$	243	297	7
Molybdenum	$^{98}\text{Mo}^+$	97	134	9
Silver	$^{107}\text{Ag}^+$	2.8	3.5	16
Cadmium	$^{114}\text{Cd}^+$	10	13	22
Barium	$^{138}\text{Ba}^+$	47	74	17
Lead	$^{208}\text{Pb}^+$	27	31	8

(1) **Quantitation** of elements in a mixture – Cont.

- Ex. Determining the levels of long-lived radionuclides in the environment (Ex. surface water)

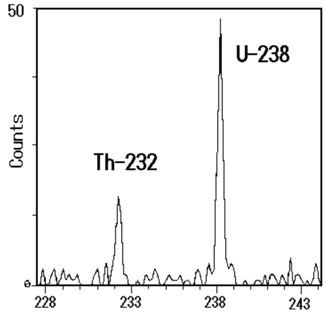


Image available at http://www.nirs.go.jp/ENG/project4.htm
ICP-MS of U and Th in rain water.

Applications of ICP-MS – *Cont.*

(2) **Surface analysis** (i.e. determination of structure and composition of solid surfaces)

- Ex. Elemental composition of rock sample
- Ex. Determining surface impurities in alloys

(3) Determination of **isotopic ratios** of atoms in samples

- Ex. $^{12}C/^{14}C$ (radiocarbon dating); isotopes used in medical imaging, such as ^{11}N, ^{15}O