

Chapter 1 Introduction

Problems : 1-10

1A Classification of Analytical Methods

Classical (wet lab)

Instrumental

1A-1 Classical Methods

Mostly titrimetric methods (doing titrations)

Or Gravimetric methods (weigh what you isolated)

Use of these methods is slowly declining

1A-2 Instrumental Methods

Use of instruments to separate and quantitate different components

use is skyrocketing as instrument become more dependable and less

expensive

1B Types of Instrumental Methods

Overhead of table 1-1

Discuss what each of the characteristic properties are or mean

Point out the few methods that we will actually be able to cover in this class

Be aware that for any particular analysis the choice between instrumental methods, or between instrumental and classical method is not clear.

Always a trade off between sensitivity, selectivity, expense, and possible interferences

Also notice that table does not include any separation methods. Just about any instrumental method can be hooked up to some chromatographic method to purify and quantitate simultaneously

1C Instruments for Analysis

On the most abstract and simplest term all instruments look like this

Energy Source or **Stimulus** → **Sample** → **Response**(analytical Information)

Put in that way you can break most instruments down as in Table 1-2

We can further subdivide instruments based on how we obtain and interpret the response

this leads use to the concept of Data Domains

1C-1 Data Domains

How is the data recorded on the instrument?

Electrical Signals (Voltage, current charge or a combination) etc

Other

Thus broadly class in 2 categories, Electrical and non-electrical

1C-2 Non Electrical Data Domains

Mass (on a non-electrical balance hard to find now-a-days)

Length or volume

Actually most non-electrical are being replaced with electrical analogs!

1C-3 Electrical Domains

Signal transduction

- In most electrical instruments the signal will change forms or be transduced several times into several different forms (see example 1-3)
- The first few chapters of the book deal with electrical transductions, IE electrical circuits that transduce signal form one form to another. This is important if you are designing your own instrument, or repairing a broken instrument, but is not a focus of this class so we will skip

Analog and Digital domains

- Electrical circuitry is divided into 2 major types of designs, Analog and Digital
- Analog- signal varies continuously and the magnitude of the signal is followed in a continuous manner in the circuit
 - susceptible to noise
 - entire chapter devoted to minimizing noise in analog signals
- Digital - magnitude of signal is determined for one instant in time, interpreted into a series of bits, then bit pattern is manipulated by the instrument with computer (digital) circuits
 - Digitizing signal
 - Digital circuits only 2 discontinuous values, High and low
 - Dealing with digital circuits all of chapter 4
 - Once data is digitized it is immune to noise
 - But still lots of techniques for minimizing noise in a set of signals

Time domain

- May be interested in just the absolute magnitude of some signal
- Or may be interested in how the values changes with time
- Following a signal as a function of time is called the time domain
- May measure a time domain signal with either analog or digital instruments so overlaps both analog and digital domains

1C-4 Detectors, Transducers and Sensors

Actually 3 different terms, but often confused due to sloppy usage

Detector - mechanical, electrical, or chemical device that identifies, records, or indicates a change in a single variable. Properly just a single, simple component. Due to sloppy usage term often applied to a complete instrument like a UV detector on an HPLC system.

This text will use the term Detection system for this complete system application

Transducer - Should be specifically a device that changes information from a non-electrical domain into an electrical domain signal .

Sensor - In this book a device capable of monitoring a specific chemical species continuously and reversibly. Often a transducer coupled with some other device to make it sensitive to a single kind of signal. Several examples in text but examples don't mean much at this time.

1C-5 Readout devices

A transducer that converts an electrical signal into some form that can be understood by a human. Examples Dials, digital readouts, oscilloscopes, strip chart recorders, etc

1C-6 Microprocessors and Computers

Most instrument contain one or more simple to sophisticated electrical device

Sensors, transducers, operational amplifiers, and integrated circuits in the analog domain, then analog-to-digital converters counters microprocessors and entire computers in the digital domain

To truly understand in instrument need to be familiar with all of these devices. An introduction is given in chapters 3 and 4, but we won't have time to look at in this course

1D Selecting an analytical method

Have a wide range of instruments, said earlier there is no magic 'best' instrument
How do you begin to pick the best one?

1D-1 Define the Problem

Question you need to ask

- What accuracy do you need?
- How much sample do you have?
- What is the concentration of the sample?
- What components in the sample can interfere?
- What are the physical and chemical properties of the sample?
- How many time do you have to do the analysis?

Once you know these answers then you can start looking at the individual instrumental methods and choosing the one that has all the answers

1D-2 Performance characteristics of instruments - Figures of Merit

In answering the above questions it is necessary to evaluate an instrument based on the criteria shown in Table 1-3

For each criteria there is usually a specific mathematical relationship that

can give you a number, or Figure of Merit to characterize how well an instrument meets a specific criterion. Lets look at each criterion and its figure of merit

- Precision- Degree of mutual agreement between independent determinations of a value - F of Ms: Standard Deviation, Relative standard Deviation, standard deviation of the mean, coefficient of variation and variance (see table 1-5 for definitions)
- Bias - the presence of systematic or determinate error in a measurement. Bias equation: bias = $\mu - \bar{X}_t$, where μ is the population mean in a sample with a true mean of X_t . Bias is usually determined by trying your method on a known reference material. You usually need 20-30 measurement to get a good determination of the population mean (μ). Ordinarily you try to remove any bias in an instrumental method via a good calibration.
- Sensitivity - The ability to discriminate between small difference in analyte concentration. Since most methods depend on some kind of linear calibration curve ($Y=mX + b$), the sensitivity depends both on the slope, and on the noise or standard deviation in any particular measurement. The best figure of merit for sensitivity is the one of Mandel and Stiehler : Analytical Sensitivity(γ) = m/s_s , where m is the slope and s_s is the standard deviation of the measurement.
- Detection limit - The minimum concentration of an analyte that can be detected in an instrument. Relates to how big the signal is vs the standard deviation of the blank.

$S_m = \bar{S}_{bl} + ks_{bl}$ S_m is the minimum analytical signal, S_{bl} (bar) is the average blank signal, k is some number of standard deviations, and s_{bl} is the standard deviation of the blank

- Dynamic Range - (see figure 1-7)What range of concentrations can the method handle. The low end of the dynamic range is set by the *limit of quantitation (LOQ)* Which is generally taken as the average blank values + 10x the standard deviation of the blank. The upper limit of the dynamic range is taken from the *limit of linearity (LOL)*, or the place where you calibration curve departs from a straight line. You usually need a dynamic range of 100 to 1000, but some instruments have dynamic ranges in the 1,000,000's
- Selectivity - Degree to which method is free from interference from other components in the sample. Figure of merit is the selectivity coefficient k .

Suppose you are measuring a sample containing components A and B, using our linearity assumption $Signal = m_A[A] + m_B[B] + S_{bl}$ Where m_a and m_b are the response slopes for a and b, and S_{bl} is our blank value. The selectivity coefficient for A with respect to B is $k_{B,A} = m_B/m_A$

1E Calibration methods

Almost all instrumental methods except gravimetric and coulometric method require some kind of calibration. The most common calibration methods are: Calibration Curves, Standard Additions and Internal standards. Let's look at briefly so you are familiar with these methods

1E-1 Calibration Curves

- Prepare a blank and several standards with known concentrations of the analyte
- Measure response of instrument for each sample and make a *calibration curve* (also called *working curve* or *analytical curve*)
- Preferably the calibration curve is linear over the range in which the samples will fall
- Non-linear calibration curves can be used, but it generally takes more points to achieve a good calibration
- Success of calibration method can depend critically on how well calibration samples match analysis samples
 - Ideally they are exactly matched, IE there is no difference except that you know the concentrations of the analyte in the sample ahead of time
 - The problem is that sample may contain other substances that change the response of the instrument to you sample (may either interfere and reduce the response, or enhance and increase response). If your calibration samples don't contain these other components, they you don't have a good calibration curve.
 - Achieving a good match can be difficult

1E-2 Methods of Standard Addition

- If above calibration curve doesn't work because of other materials in the sample, the alternative is to spike the sample with additional, known amounts of the analyte
- Measurements are performed on unspiked sample and the sample at several different levels of spike.
- From known amounts in each spike and known volumes of sample and spike, can extrapolate back to original concentration
- Since each sample contained all the components of the original sample, this method automatically compensates for any interfering substances

1E-3 Internal Standard

- An internal standard is a substance, other than the analyte, that is added to all samples, blanks, and calibration samples.
- Calibration involves comparing your analyte response to the standard response
- Hard part is finding a good internal standard. response of instrument to standard should be very similar to response for analyte but must be

sufficiently different that you can tell one from the other.