CHEMISTRY 3080 4.0
Instrumental Methods of Chemical Analysis

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Office Hours: - by appointment or
- T, R @ 11:30-12:30pm (DO NOT COME 1 HOUR BEFORE LECTURE)

Course Grading

Laboratories	30%
Research Essay	10%
Tests (3)	24 %
Pop Quiz or Assignments	6 %
Final Exam	30%

Important Dates:

Classes:	Jan 04 - Apr 04 (24 classes)
Exams:	Apr 06 - Apr 29
Labs start:	Jan 18-21 (start)
Tests:	Thurs Feb 3, Thurs March 3, Tues March 29
Research Essay:	Article Approval – Tues Feb 22, Due Date – Thurs March 10
Reading Week (no classes):	Feb 14-18
Chemistry Ski Day:	Feb 17 or 18 (Mount St. Louis)
Meet the Profs night :	Jan 27 (evening)

Course Details

Textbook: "Principles of Instrumental Analysis", 5th edition,
1998 by Skoog, Holler & Nieman, Harcourt Brace Publishers

Reference Books (on reserve in Steacie Science Library):

"Electronics and instrumentation for scientists", Malmstadt, Enke, Crouch.
"Electrochemical methods : fundamentals and applications", Bard, Faulkner
"Instrumental methods of analysis", Willard, Merritt, Dean.
"Gas chromatography : a practical course" Schomburg.
"Fundamentals of Analytical Chemistry", 7th ed., Skoog,West,Holler
"Quantitative Chemical Analysis", 2th ed., D.C. Harris
"Quantitative Analysis", 6th ed., R.A. Day and A.L. Underwood
"Analytical Chemistry - Principles and Techniques", L.G. Hargis

Laboratories: manuals are available from the lab coordinator, C.Hempstead, 360CCB
all laboratory conflicts go through Carolyn .

Note: the laboratory portion if the course represents a significant fraction of your final grade. To complete the experiments and reports satisfactorily, you must read and understand the experiment in the manual and the background information in the textbook before coming to the lab. The demonstrators may quiz you on your knowledge of the experiment at the beginning of the laboratory. Marks may be deducted for those who are not prepared.

Chemistry 3080 4.0 Course Outline

	Topic	Chapter
1)	***Introduction***	1
	• instrumental analysis	
	• figures of merit	
	C calibration methods	
2)	***Electronics, signals and noise***	**2, 3, 4, 5**
	• basic electronics and devices	
	• digital electronics	
	• computers & interfaces	
	• signals and noise	
3)	***Analytical Separations***	**26, 27, 28**
	• principles of chromatography	
	• gas chromatography	
	• high performance liquid chromatography	
	• other methods	
4)	***Analytical Spectroscopy***	**6 (Review)**
	• components for optical spectroscopy	7, 8, 9, 10, 13, 14
	• UV/VIS absorbance spectrophotometry	
	• luminescence (fluor-, phosphor- and chemilumin-escence)	
	• atomic emission and atomic absorption	
5)	***Electroanalytical Methods***	**22, 23, 25**
	• potentiometry	
	• voltammetry	
6)	***Mass Spectrometry***	**11, 20**
	• the mass spectrometer	
	• ion sources	
	• hyphenated methods	

Introduction

Classification of Analytical Chemistry

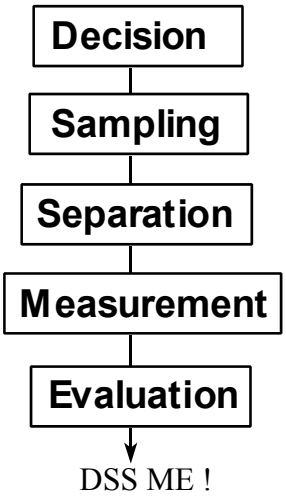
Classical methods

- separations performed by precipitation, solvent extraction or distillation.
- quantitative analysis performed by gravimetric and volumetric (titrimetric) methods
- detection limits in the ppb - % range.
- precision can often be excellent
- these methods are often labour intensive

Instrumental Analysis

- often these are semi to fully automated techniques that involve the manipulation of molecules, photons and electrons to provide simultaneous (often) qualitative and quantitative analysis.
- detection limits in the pp 10-15 - % range
- precision is dependent less on the operator and more on the instrument and sources of noise.

The Analytical Method



Subfields of Instrumental Analysis

Analytical Separations (chemical equilibrium + detectors)

- **gas chromatography**
- **liquid chromatography, ion chromatography**
- **supercritical fluid chromatography**
- **electrophoresis & capillary electrochromatography**

Electroanalytical methods (chemical potential + electrons)

- **coulometry**
- **voltammetry**
- **potentiometry**

Analytical Spectroscopy (chemical energy + photons)

- **absorbance**
- **fluorescence, phosphorescence**
- **Raman**
- **infrared**
- **photothermal**
- **atomic absorption/atomic emission**
- **inductively coupled plasma**

Cont'd

Other Methods

- **mass spectrometry (m/e ratio + ion mobility)**
- **radiochemical**
- **thermal methods**
- **surface analysis**
- **nuclear magnetic resonance (NMR)**
- **X-Ray spectroscopy**

Hyphenated Methods

separation method / detection method

- liquid chromatography + mass spectrometry (LC/MS)
-Electrophoresis + inductively coupled plasma + mass spectrometry (CE/ICP-MS)

sampling/separation/ion generation/detection method

solid phase microextraction/gas chromatography/electrospray ionization-mass spectrometry (SPME/GC/EI-MS)

Instrumental methods of Chemical Analysis (vs classical techniques)

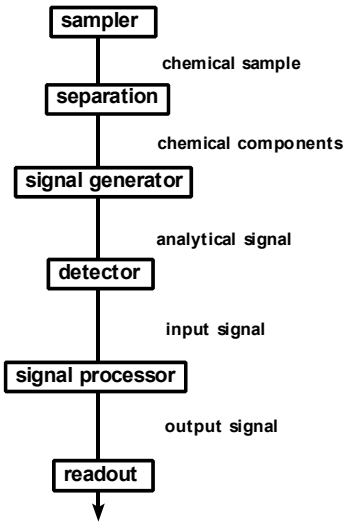
Advantages

- **less labour intensive**
- **easy to automate**
- **simultaneous multi component analysis**
- **fast analysis**
- **lower detection limits**

Disadvantages

- **higher expense**
- **harder to trouble shoot problems, more technical expertise**
- **black box syndrome**

Components of an analytical instrument



Sampler

A sampler included in an instrument can have many functions:

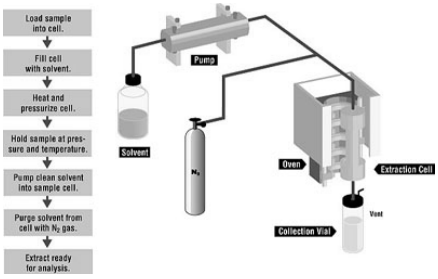
- **to transport a prepared sample to the separation or measurement region. May involve the beginning of quantitation where a highly reproducible fixed volume is delivered.**
  eg. - autosampler and injector used in HPLC or GC.

- **to transform the prepared sample in a form suitable for the measurement process.**
  eg.- an atomizer in atomic absorption will nebulize (desolvation) and atomize (break chemical bonds to produce free atoms and ions) the sample, preparing it for the absorbance measurement in the flame.

- **to process the raw sample making it ready for chemical analysis**
  eg. derivitization reactions in flow injection type apparatus will selectively react with one component of the matrix making it more distinguishable from the other components (ie- addition of an absorbing or fluorescent chromophore to the molecule)

Accelerated Solvent Extraction (ASE)

Instrumented sample preparation



ASE Saves Solvent, Time & Money

	Average Solvent Used per Sample	*Average Extraction Time per Sample*	*Average Cost per Sample**
Soxhlet	200–500 mL	4–48 hr	$27
Automated Soxhlet	50–100mL	1–4 hr	$16
Sonication	100–300 mL	30 min–1hr	$24
SFE	8–50 mL	30 min–2 hr	$23
ASE	15–40 mL	12–18 min	$14

**Based on 2000 samples per year. Costs (in U.S. dollars) are based on appropriate instrumentation per technique (including amortization of initial capital investment), apparatus, laboratory equipment (e.g., fume hood), labor, and all consumables.*

Separation

Separates components of the sample into different chemical entities, ready for the measurement process.

- chromatographic column achieves separation based upon differences in equilibrium adsorption processes.

- capillary zone electrophoresis separates components of a sample based upon their ionic mobility in the solvent medium.

- in mass spectrometry, molecular ions are separated based upon their m/z (m=mass, z = charge) ratio in a mass analyzer.

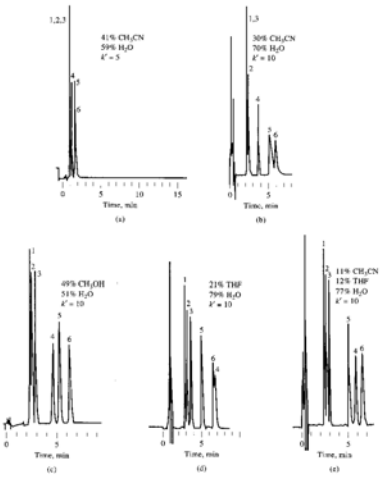


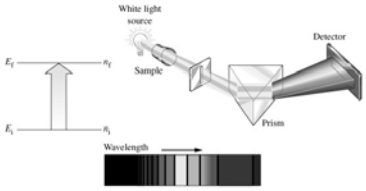
Figure 28-16 Systematic approach to the separation of six steroids. The use of water to adjust k' is shown in (a) and (b). The effects of varying α at constant k' are shown in (b), (c), (d), and (e). Column: 0.4 × 150 mm packed with 5 μm C_8 bonded, reversed-phase particles. Temperature: 50°C. Flow rate: 3.0 cm^3/min. Detector: UV 254 nm. THF = tetrahydrofuran. CH_3CN = acetonitrile. Compounds: (1) prednisone; (2) cortisone; (3) hydrocortisone; (4) dexamethasone; (5) corticosterone; (6) cortexolone. *(Courtesy of DuPont Instrument Systems, Wilmington, DE.)*

Signal generator

the instrumental components and chemical system that produce some signal that is related (hopefully linearly) to the presence and quantity of analyte.

eg.-absorption of UV/VIS radiation, the signal generator includes light source, optics, absorbance cell and the absorbing molecules.

analytical signal: $A = -\log T = \varepsilon bC$



eg. polarography - signal generator is the voltage source, mercury drop generator, cell and analyte.

analytical signal:

$$i_d = KD^{1/2} m^{2/3} t^{1/6} C$$

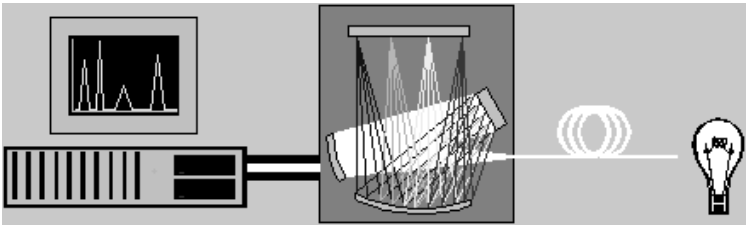
i_d = diffusion current
D = diffusion coefficient
K = constant
m = Hg mass rate
t = time of Hg drops
C = analyte concentration

Detector

a component (input transducer) that converts one form of energy to another OR converts an analytical signal to an electrical signal (usually voltage or current).

examples-photomultiplier tube (PMT), photodiode, electron multipliers (ions), voltammeter.

Photodiode Array or Charge Coupled device



Signal Processor:

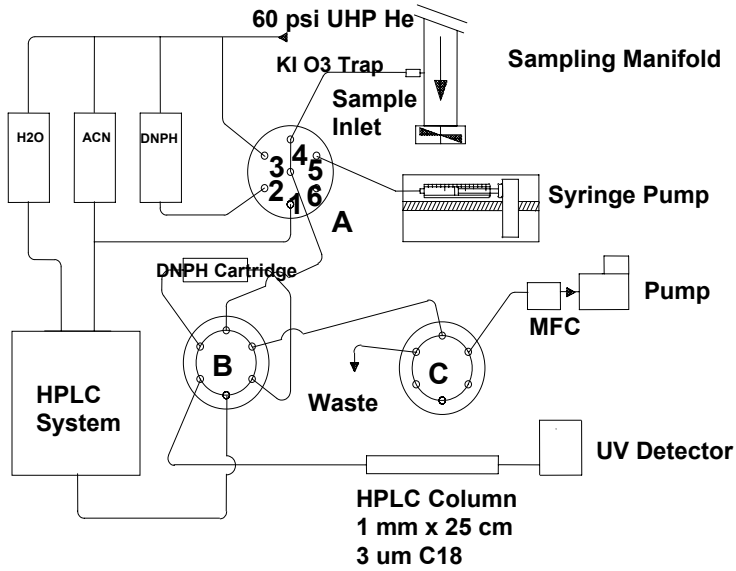
Modifies the detector signal to make it more convenient for interpretation.

The signal processor is usually an electronic module or circuit that can perform one or more of the following functions:

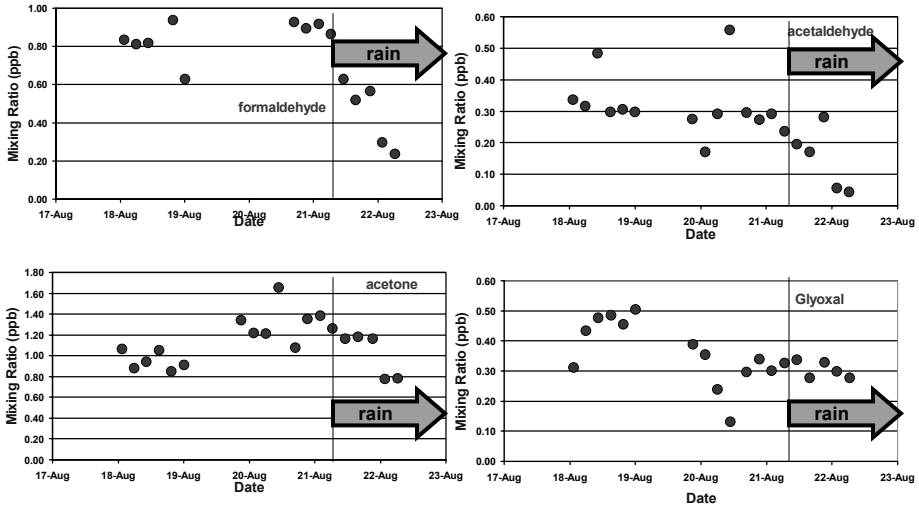
- amplification - multiplying the signal by a constant >1
- attenuation - multiplying the signal by a constant <1,
- filtering - reducing noise in a given frequency range
- rectification - change from an AC to a DC signal
- voltage to frequency conversion- change from AC to DC
- mathematical - integration, exponentiation, ratioing.

Gaseous Carbonyls by Automated DNPH Cartridge/μ-HPLC/CCD Absorption detection

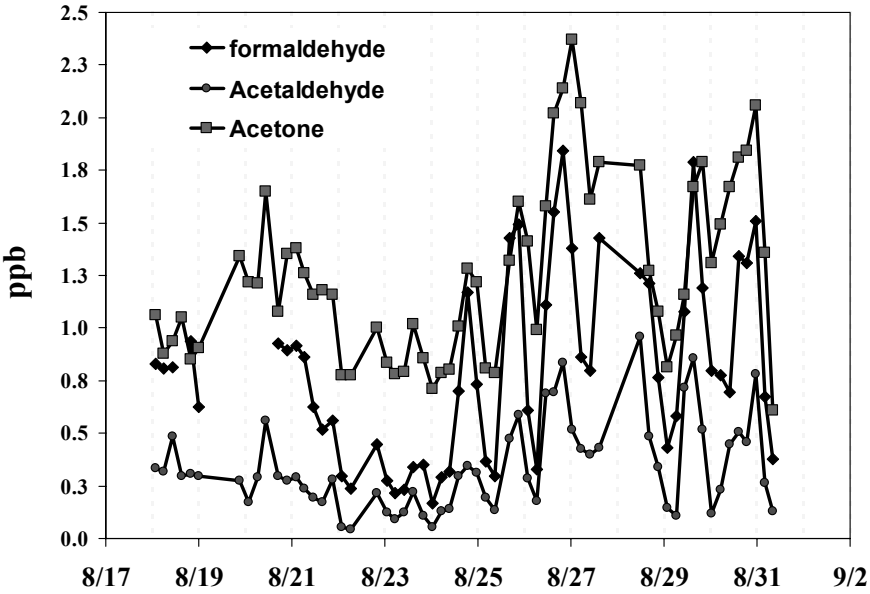
Automated DNPH/ μ-HPLC/CCD Carbonyl Measurement Instrument Schematic



Gaseous Organic Carbonyls by Automated DNPH/μ–HPLC/CCD System

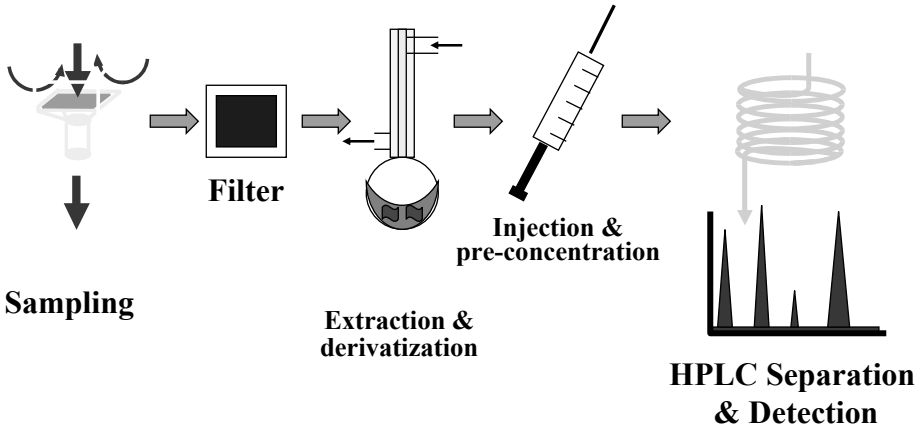


Sumas: Gas Phase Carbonyls, 2001

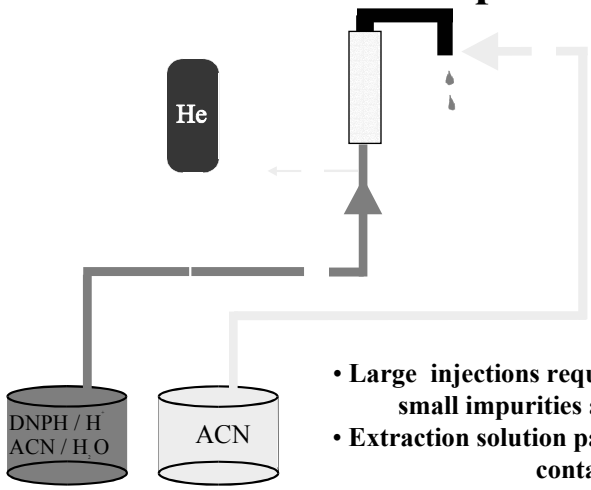


High Volume Filter Sampling for Organic Analysis of Aerosols

Organic carbonyls in Particulates

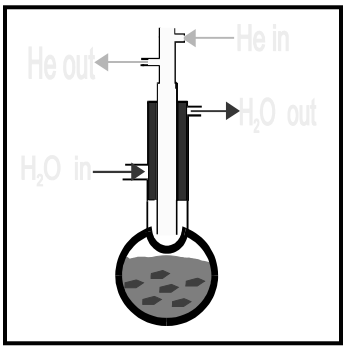


DNPH Preparation

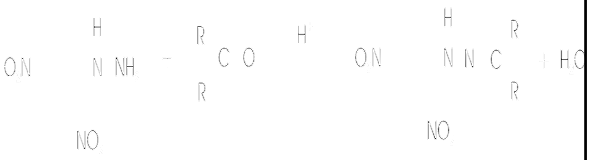


- Large injections require very pure DNPH since small impurities are pre-concentrated
- Extraction solution passed through C-18 to trap contaminants

DNPH Extractions



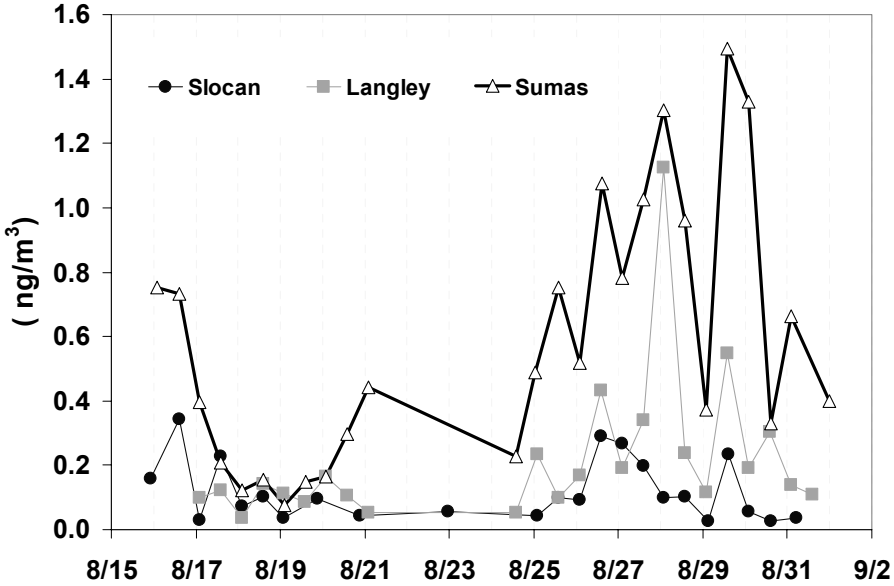
General Reaction:



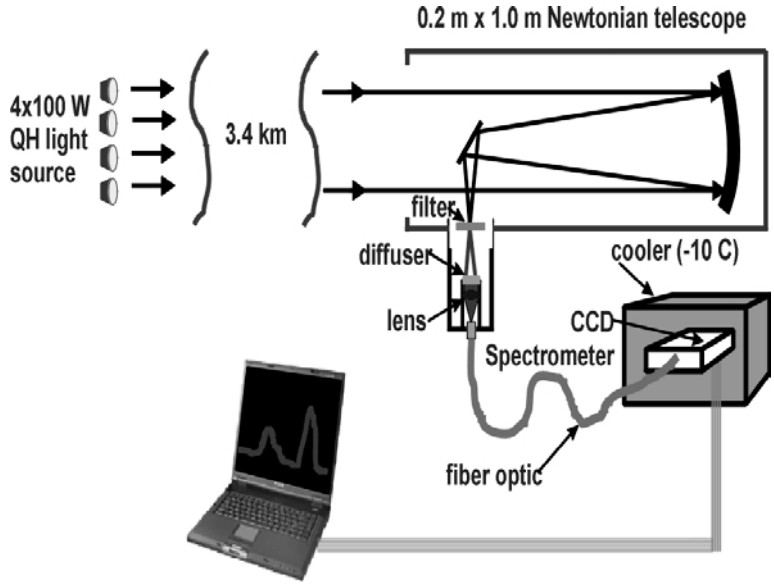
DNPH **Hydrazone**

- **25 ml of 10^{-3} M DNPH solution**
- **65% H_2O , 35% Acetonitrile, pH = 3**
- **Temp. = 85 ^{0}C**

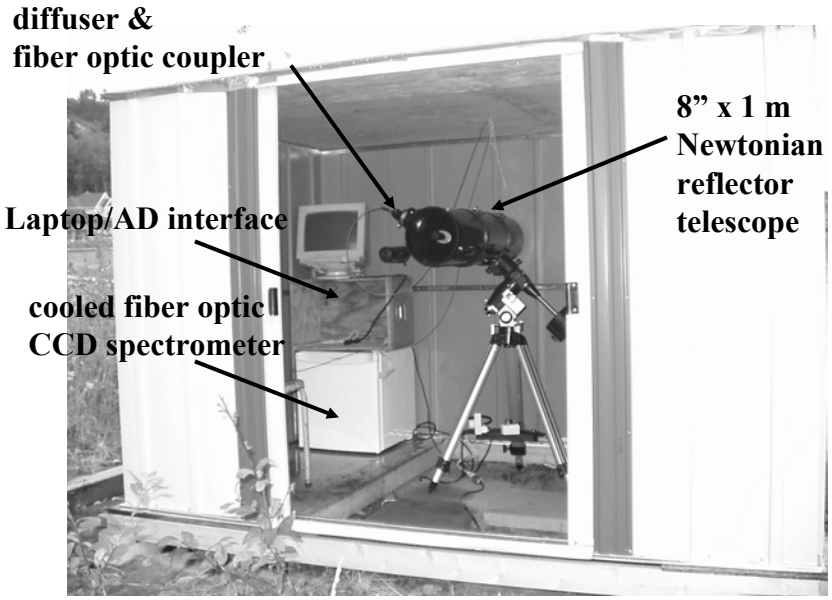
Particulate methylglyoxal in the LFV



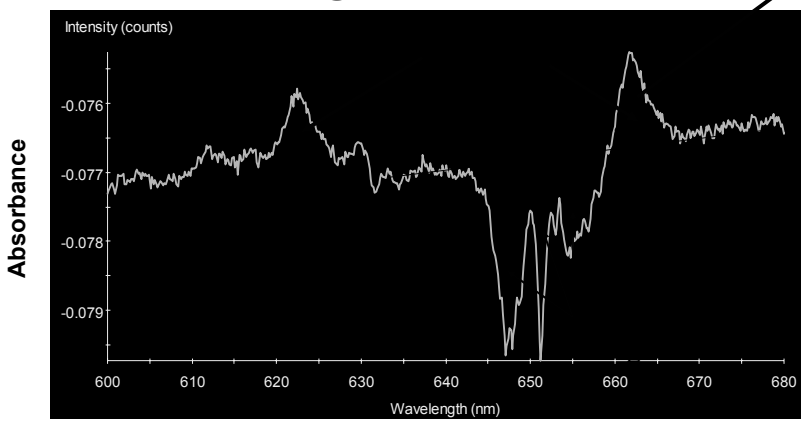
Instrumental set-up for DOAS



DOAS Receiver

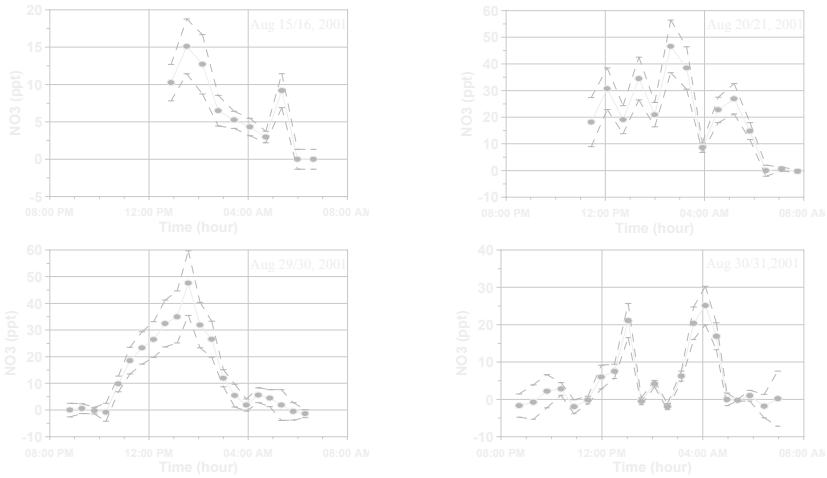


Absorption Spectrum*, Aug 31, 4:00 am.

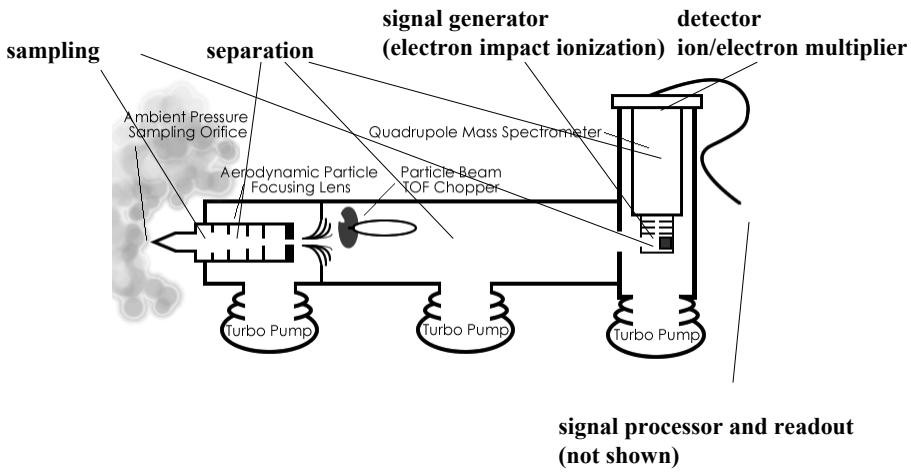


reference spectrum is an early morning spectrum just after sunrise when NO3 is at negligible levels but other atmospheric species (ie- H2O) are still present.

NO_3 Levels by DOAS: Sumas



Aerosol Mass Spectrometer



Performance Parameters: Figures of Merit

Precision: the closeness of several measurements to each other.

you should know:

- **standard deviation (population, σ and sample, s)**
- **relative standard deviation, coefficient of variation, ppt, etc.**
- **variance**
- **standard deviation of the mean**
- **confidence intervals using t stat and z stat.**

Accuracy: the closeness of a central value to the "true" value

you should know:

- **error (called *"bias"* in text).**
- **the difference between determinate (systematic) error and indeterminate (random) error.**

Sensitivity

Very frequently, the analytical signal, y, is linearly related to the concentration of the analyte, C:

$y_{analytical} = mC + y_{blank}$

where **m = slope**
C = analyte concentration
y_{blank} **= signal seen for a sample with no analyte (C=0)**

Sensitivity = slope of calibration curve = m = $\Delta y/\Delta C$ = dy/dC

(MUST have UNITS!!! ie- signal units concentration^{-1})

Limits

Detection Limits:

IUPAC definition
"the limit of detection, expressed as a concentration c_L (or amount q_L), is derived from the smallest measure, y_L, that can be detected with reasonable certainty for a given analytical procedure."
ACS definition
"the limit of detection is the lowest concentration of an analyte that an analytical process can reliably detect".

In order to distinguish the blank signal and the signal arising from a small quantity of material, we need to rely on statistics.

$y_{analytical} = mC + y_{blank}$

A detectable signal, y_{DL}, is one that is different (greater) than the blank signal by a statistically significant amount.

$y_{analytical} - y_{blank} = mC = k\sigma_{blank}$

Detection Limit, contd

$mC_{DL} = k\,\sigma_{blank}$

$$C_{DL} = \frac{k\sigma_{blank}}{m}$$

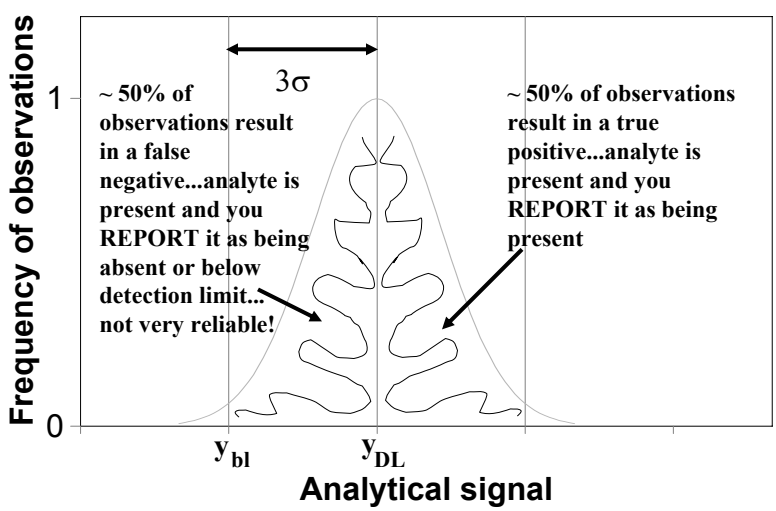
What value of k ??

If we could average significant values of the blank such that it were a well defined value with a low standard uncertainty, AND if the distribution of errors in the analytical signal are normally distributed, then a difference in signal of 2 s_{blank} is statistically significant at the 95% confidence level. BUT not all distributions are normal AND there can be uncertainty in the blank level if we do not have an infinite number of measurements. For this reason, IUPAC recommends that the detection limit be defined with a value of k=3.

$$C_{DL} = \frac{3\sigma_{blank}}{m}$$

This equation defines the concentration detection limit.
- it also defines why we continually strive to lower the instrumental noise, σ. The lower the noise, the lower is our limit of detection.
We also attempt to lower blank levels....Why? because noise increases with signal level usually...if we lower background level, we lower noise.

Working with a sample at the detection limit?



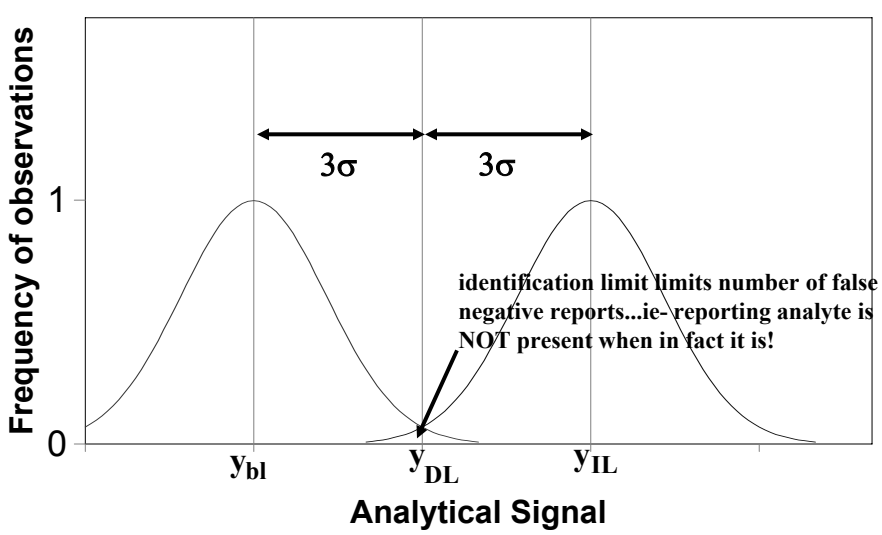
Identification Limit

the amount of material that can be *reliably* detected with a reasonable degree of confidence.

By reliably detected, we may mean for example, if a sample with this concentration were put into our instrument, we are statistically confident that we would report the sample as containing a statistically significant amount of analyte the majority of the time…

$$C_{IL} = \frac{6\sigma_{blank}}{m}$$

Identification limit



Limit of Quantification

the amount of material that can be reliably *quantified*, C_q. The signal given by this amount of material is y_q and the uncertainty in the signal is σ_q

Typically, we would like to quantify the concentration of material with a relative uncertainty less than 10%.

$$RSD = \frac{\sigma_{ql}}{y_{ql}} = 0.10 \qquad y_{ql} = \frac{\sigma_{ql}}{0.10} = 10\sigma_{ql} \approx 10\sigma_{blank}$$

If we make the approximation that $\sigma_{ql} \sim \sigma_{blank}$, and m is well known, then:

$$C_{QL} = \frac{10\sigma_{blank}}{m}$$

Analytical Ranges

Dynamic Range:
- the range over which the signal is linear, usually defined from the detection limit to the the point where the signal is no longer linear with concentration.

Useful Range:
- the range over which there is useful quantification, usually defined from the limit of quantification (or identification limit) to the the point where the signal is no longer linear with concentration. (Note - that the useful range does NOT include the detection limit, working at the detection limit is NOT reliable.)

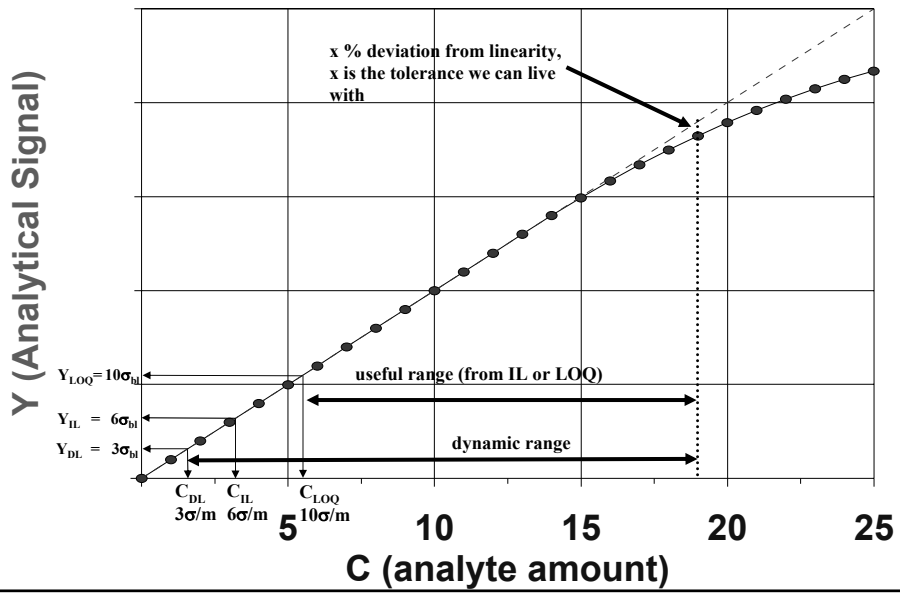
For a general instrumental method, we would like linear dynamic and useful ranges of greater than 2 orders of magnitude...the more the better usually.

-for specific applications we can sometimes get away with less than this:

eg. monitoring CH_4 in natural gas supply where we are measuring a major component that varies by a small amount.

$$85\% < CH_4 < 99\%$$

Summary of limits and ranges in Calibration of Instrumental Analytical methods



Methods of Calibration

1) normal calibration curve (analytical curve)
2) standard additions
3) internal standard

Calibration Curve
- used for simple matrixes
- instrumental signal is measured for a series of calibration solutions of varying analyte concentration.
- a least squares fit of the data to a function establishes a workable mathematical relationship.
- usually the relationship is linear, y=mC + b; if not we must use non-linear least squares analysis (ie- polynomial fit)

How to handle blanks
i) subtract blank signal from all subsequent signals to establish "corrected" or "net" instrumental signal.
ii) include blank signals in regression in which case a non zero intercept establishes the level of the blank.

REVIEW - you are expected to know linear least squares analysis and how to determine unknown concentration (with error!) from the measurement of unknown.
see Skoog Appendix 1 for review of this method.

Standard additions

- used when matrix is complex and will potentially affect the analyte response (ie- sensitivity changes, examples- measuring elemental constituents in blood).

Procedure

- prepare multiple samples of volume V_x and unknown concentration C_x. We spike each sample with a different volume, V_s, of a prepared standard of our analyte of concentration, C_s. Optionally, we further dilute each spiked sample to total volume V_t. Measure the signal for each spiked sample and plot analytical signal, y , vs. spiked sample concentration, C_s'. The original sample concentration is diluted as well as spike. The moles of spiked standard = C_sV_s

$$C_s' = C_s \times \frac{V_s}{V_t} \qquad C_x' = C_x \times \frac{V_x}{V_t}$$

The instrumental signal will be given by:

$$y = m(C_x'+C_s')+y_{blank} \qquad y = mC_s' + (mC_x' + y_{blank})$$

Plot y vs C_s' to get slope, m, and intercept, b. Note intercept, b= $(mC_x' + y_{blank})$

If y_{blank} is negligible, then b = mC_x' OR

$$C_x' = \frac{b}{m} \qquad AND \qquad C_x = \frac{b}{m} \times \frac{V_t}{V_x}$$

Standard additions – cont'd

Note: we frequently use very small spike volumes V_s and no dilution. This simplifies our analysis in that the dilution factors disappear from the above eqn's.

$V_t \sim V_x$ AND $C_x' \sim C_x$ AND $C_x = b/m$

Limitations

- instrument response must be linear over the expected concentration range and we must assume and verify that $mC_x' >> y_{blank}$.

Applications

- wherever matrix effects can be significant,

Example

5.0 mL aliquots of an unkown containing phenoarbital were delivered to 50.0 mL volumetrics. The following volumes of a standard solution of phenoarbital (2.00ug/mL) were then introduced to the volumetrics before diluting to volume:

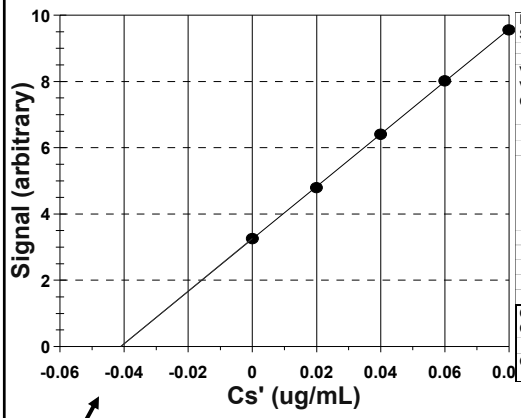
0.00, 0.50, 1.00, 1.50, 2.00 mL.

The corresponding signals on a fluorometer instrument were:

3.26, 4.80, 6.41, 8.02, 9.56 arbitrary units.

Find the concentration of phenoarbital in the original unknown.

Standard Additions – example



Example 1-11 Skoog, 5 ed.
Standard Additions

Vx (mL)	5
Vt (mL)	50
Cs (ug/ml)	2

Vs (mL)	Cs' (ug/mL)	Y (arb)	
	-0.041037		0
0.0	0.00	3.26	3.26
0.5	0.02	4.80	
1.0	0.04	6.41	
1.5	0.06	8.02	
2.0	0.08	9.56	

Regression Output:	
b	3.246
s {b}	0.026
r^2	1
N	5
DOF	3
m	79.10
s{m}	0.404

CALCULATIONS			
Cx' (b/m)	0.04104	+/-	0.0004
Cx(b/m*Vt/Vx)	0.4104	+/-	0.0039

negative x-axis intercept gives C_x'

Internal Standard method

- used when sensitive physical variables in analytical measurement are difficult to control. (ie- injection volume in GC, sample flow rate in AA)
- an internal standard is a substance added in a constant amount to all samples, or it may be a major constituent of the sample. I

Procedure
- add equal amount of int. std. to all samples and standards.
- measure analyte and int. std analytical signal for all samples and standards
- the analytical signal, corrected for fluctuations of the physical variable, can be calculated as $y_{analyte}/y_{int.\ std.}$

$$Plot \quad \frac{y_{analyte}}{y_{Int.std.}} \quad vs \quad C_{analyte}$$

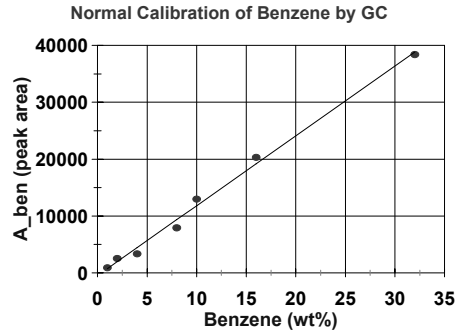
Limitations
- analyte and int. std. must behave similarly.
- analyte and int. std. signals must be proportional to the physical quantity giving rise to instrumental variations.
- method is limited to methods that can resolve the analyte and int. std. signal simultaneously.

Internal Standard-example

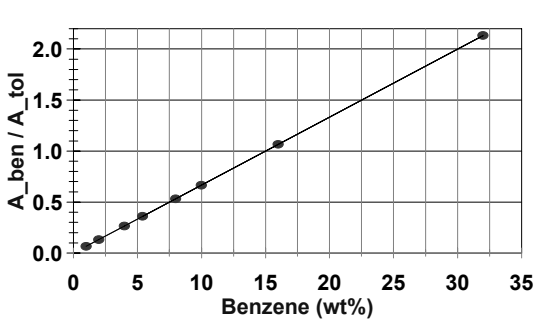
Example: Gas Chromatography

In a separation of benzene and cyclohexane in a hydrocarbon mixture, toluene can be added as an internal standard to EVERY sample and standard. The gas chromatographs will give three peaks. In a normal calibration, our analytical signal is the integrated area of the analyte peak. Using the internal standard, the peak areas for benzene, cyclohexane and toluene A_{ben}, A_{chex} and A_{tol}, are measured for each standard and unknown sample run. The ratio, A_{ben}/A_{tol} is then calculated for each standard and sample (similar for cyclohexane). A least squares analysis of A_{ben}/A_{tol} vs C_{ben} will yield a straight line. The measurement of A_{ben}/A_{tol} for the unkown gives us the concentration of benzene in the unknown sample(s).

Vinj	wt% ben	A_ben	A_tol	A_ben/A_tol
0.93	1	930	13950	0.066667
1.27	2	2540	19050	0.133333
0.842	4	3368	12630	0.266667
0.99	8	7920	14850	0.533333
1.297	10	12970	19455	0.666667
1.27	16	20320	19050	1.066667
1.2	32	38400	18000	2.133333
1.222	5.4	6598.8	18330	0.36
0.178466	<---------	relative std deviation in injection volume		



normal calibration shows large variation, which will contribure uncertainty to our analysis of the unknown.



internal standard method removes ALL variation associated with the physical variable.... reduces the uncertainty in our analysis of the unknown.

Basic Electronics

Analog signals : an analog signal is continuously varying.
Digital Signals: signal has discrete digitized levels.

Information may be stored in an analog signal through the *magnitude* of three quantities :

Quantity	*Symbol*	*Unit of measure*
current	I	Amperes (coulomb s^{-1})
charge	Q	coulomb
voltage	V	Volts

Information may also be stored in the *time dependence* of these quantities, ie- in the frequency domain.

direct current (DC): not varying in time, current flows in one direction.
eg.- circuitry in a car runs off a DC source (12V)

alternating current (AC): the current is periodic in time, switching direction every ½ period. eg.- North American household power source (120V peak, 60Hz)

$V(t) = 120V \cos(2\pi f t) = 120V \cos \omega t$ **f = frequency = 1/period**
w = angular frequency (radians/sec)

Review of Basic Components and Laws

R - resistance (ohms – Ω)

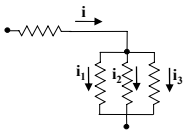
Ohm's Law: If we apply a voltage across a resistor, the current that flows is inversely proportional to the resistance.

$I = V/R$ **or** $V = IR$ **(voltage *drop* across a resistor)**

Power Law: the power (joules s^{-1}) dissipated in a resistive element is given by:

$P = I^2R = IV = V^2/R$

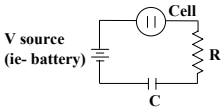
Kirchoff's Current Law: the algebreic sum of all currents encountered at any instant at a junction must be zero.



$I = i_1 + i_2 + i_3$

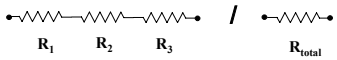
Kirchoff's Voltage Law: the algebreic sum of the voltages in a closed loop must be zero.

$V_{source} = \Delta V_{cell} + \Delta V_R + \Delta V_C$



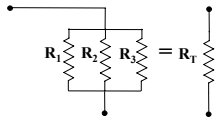
Series, Parallel Circuits and Voltage Dividers

Series Circuits: **all electrical components in the same current path. For resistors in series...**



$$R_{total} = \Sigma R_i = R_1 + R_2 + R_3$$

Parallel Circuits: **components in parallel current paths with a common voltage. For resistors in parallel.**



$$\frac{1}{R_T} = \sum_i \frac{1}{R_i} = \frac{1}{R_1} + \frac{1}{R_2} + \frac{1}{R_3}$$

Voltage Dividers: **a combination of elements in series will act as a voltage divider where only a fraction of the total voltage appears across an individual element.**

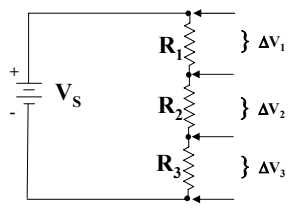
$\Delta V_1 = IR_1 \quad \Delta V_2 = IR_2 \quad \Delta V_3 = IR_3$

$V_T = V_S = \Delta V_1 + \Delta V_2 + \Delta V_3 = I\,(R_1 + R_2 + R_3)$

$$\frac{\Delta V_1}{V_T} = \frac{\Delta V_1}{V_S} = \frac{IR_1}{I(R_1 + R_1 + R_1)} = \frac{R_1}{R_{total}}$$

$$\Delta V_1 = \frac{R_1}{R_{total}} \times V_S \quad AND$$

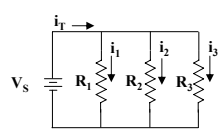
$$\Delta V_i = \frac{R_i}{\sum_i R_i} \times V_S$$



Current Dividers

- a combination of resistors in parallel will act as a current divider. Highest current is through the path of least resistance.

$V_S = \Delta V_1 = \Delta V_2 = \Delta V_3 \qquad I_t = i_1 + i_2 + i_3$



$I_t R_t = i_1 R_1 = i_2 R_2 = i_3 R_3$

$$\frac{i_1}{I_t} = \frac{\frac{V_S}{R_1}}{\frac{V_S}{R_T}} = \frac{\frac{1}{R_1}}{\frac{1}{R_T}} = \frac{\frac{1}{R_1}}{\frac{1}{R_1} + \frac{1}{R_2} + \frac{1}{R_3}}$$

$$i_1 = \frac{\frac{1}{R_1}}{\sum_i \frac{1}{R_i}} \times I_T$$

Example: V = 15V, $R_1 = 100\ \Omega$, $R_2 = 200\ \Omega$, $R_3 = 300\ \Omega$. What is I_t, i_1, i_2, i_3, R_t?

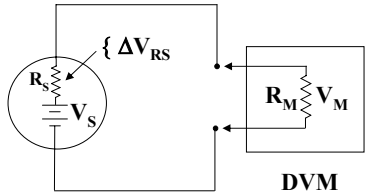
Answers. $I_t = 0.275A$; $i_1 = 0.150A$, $i_2 = 0.075A$, $i_3 = 0.050A$, $R_t = 54.5\ \Omega$.

The highest current is through the resistor with the lowest resistance.

Voltage Measurements and Loading Errors

The goal in any signal measurement is to minimize the effect of the measurement process on the measured quantity itself. The small error that can result in a voltage measurement is known as a loading error. Any voltage we are measuring could be represented by a voltage source, characterized by the voltage, V_s, and the source impedance, R_s.

Voltage measurements:



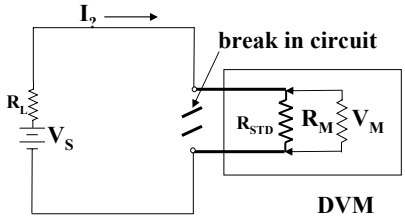
$V_s = \Delta V_{RS} + V_M$

The internal impedance (resistance) of the voltage measurement device (ie- a digital volt meter (DVM) meter, R_M, must be much greater than the impedance of the voltage source we are measuring, R_S. This is necessary to ensure that $V_M >> \Delta V_{RS.}$
The error in the voltage measurement is given:
V_{error} = measured voltage – actual source voltage = $V_M - V_S = (V_s - \Delta V_{RS}) - V_s = -\Delta V_{RS}$
The relative error (loading error) in the voltage measurement is given by:

$$err(\%) = \frac{-\Delta V_{RS}}{V_S} \times 100 = \frac{\frac{-R_s}{(R_s + R_M)} \times V_s}{V_s} \times 100 = \frac{-R_s}{(R_s + R_M)} \times 100$$

Current measurements

Current is measured by inserting a standard resistor, R_{STD}, (part of a DMM) into the current path of the circuit being measured. The standard resistor, R_{STD}, must be much smaller than the load resistance, R_L, (and the internal impedance of the voltage measurement circuit of the DMM, R_M) so as not to perturb the magnitude of the current in the circuit before we made the break. Note that the meter becomes part of the circuit, and the current, $I_?$ flows through the load resistor, R_{STD}.



$$Error = -\frac{R_{STD}}{(R_{STD} + R_L)} \times 100\%$$

Err → 0 as R_{STD} → 0 (Note: we know that $R_M >> R_{STD}$)

Resistance measurements

the meter produces a known constant current, I_{STD}, and the voltage drop across the unknown resistor, R_x, is then determined. $R_x = V_x/I_{STD}$. The meter must be capable of producing a constant current that is independent of the unknown resistance. This is usually done in scales.

Digital Multimeters and Oscilloscopes

The heart of the DMM includes a dc digital voltmeter circuit, with the addition of other front end component circuits for R_to_V, V_to_V, I_to_V conversion and an AC to DC convertor for the measurement of AC signals.

GRAPHIC MISSING

Valuable laboratory apparatus for measuring ac and dc waveforms. One can measure the voltage, waveform shape, phase lag between signals and create x-vs-y plots. An analog oscilloscope is shown below.

GRAPHIV MISSING

Capacitors

Capacitors: **a passive electrical component consisting of two metal foils separated by an electrically insulating dielectric medium. The capacitor is capable of storing charge but will not allow current to pass. The amount of charge stored is proportional to the applied voltage difference:**

$$Q = CV$$

where Q = charge (coulombs)
V = voltage (volts)
C = capacitance (farads) (typical = pF - mF).

Although capacitors will not allow dc current to *pass*, they will allow AC current to flow in a circuit because of the current required to alternately charge and discharge the capacitor as the voltage changes. ie- differentiating wrt time, we get:

$$I = \frac{dQ}{dt} = \frac{d(CV)}{dt} = C\frac{dV}{dt}$$

Note that the larger dV/dt, the faster the voltage changes with time, the larger the current that flows to the capacitor. As dV/dt → 0, I → 0. ie- if we apply a constant voltage (DC) across a capacitor, no current will flow (at steady state).

Capacitive Reactance:
Capacitors, like resistors, impede the flow of current. Their reactance (also called "impedance", in ohms) is given by:

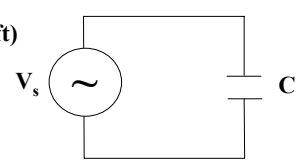
$$X_C = \frac{1}{2\pi fC} = \frac{1}{\omega C}$$

Note that as f → 0, X_C → 4 Ω. As f → 4, X_C → 0 Ω

Capacitor Circuit

Now consider the following circuit: $V_s = V_p \sin(2\pi ft)$

The voltage source is time dependent. What is the time dependent voltage across the capacitor and the time dependent current through the circuit?



$V_c = V_s = V_p \sin(2\pi ft)$ $\quad Q = CV_c$

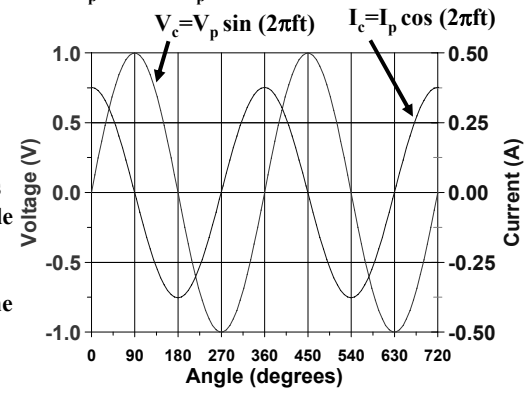
$I_c = dQ/dt = d(CVc)/dt = C\, dV_c/dt = C\, d/dt\, [V_p \sin(2\pi ft)] = C\, 2\pi f\, V_p \cos(2\pi ft)$

$I_c = I_p \cos(2pft)$ $\quad$ where $I_p = 2\pi fC\, V_p$

Notes:

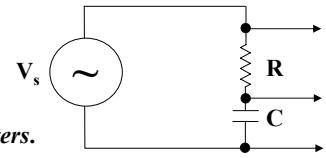
1. $X_c = V_p/I_p = V_p/(CV_p\, 2\pi f)$
   $= 1/(2\pi fC) = 1/(wC)$
   (we had stated this previously)

2. **The voltage across the capacitor is in phase with the voltage source,while the current through the capacitor is out of phase with the voltage by 90° (π/2 radians). The current "leads" the voltage by 90°.**

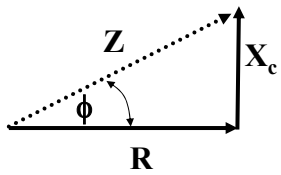


RC Series Circuits

These types of circuits are useful as *filters,* allowing either high or low frequency components to "pass through", while filtering out the undesirable frequencies. Therefore, they are known as either *high-pass* or *low-pass filters*.



As shown previously, the voltage lags the current through a pure capacitor by 90°. We say the phase difference, $\phi = 90°$. For a pure resistor, V = IR at all times and thus, there is no phase difference, $\phi = 0°$ between the voltage across the resistor and the current through the resistor. For a series RC circuit, the phase difference between the source voltage and the current can be predicted along with the total *impedance* of the circuit, Z, using the vector analogy for addition of the impedance of the capacitor and the resistor.

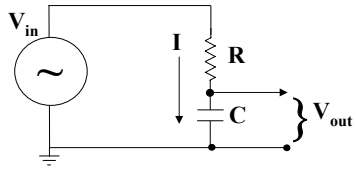


$$\phi = \tan^{-1}\left(\frac{X_c}{R}\right)$$

$$Z = \sqrt{R^2 + X_c^{\,2}} = \sqrt{R^2 + \left(\frac{1}{2\pi fC}\right)^2}$$

Low Pass Filter

An electronic configuration used to filter out high frequency signals while allowing low frequency signals to pass through.



We wish to express the voltage ratio, V_{out}/V_{in} as a fraction.

We can use the analogous form of Ohms Law, replacing R with the Imedance, Z of the RC combination, in order to find the magnitude of the current.

$$I = \frac{V_{in}}{Z} = \frac{V_{in}}{\sqrt{R^2 + \left(\frac{1}{2\pi fC}\right)^2}}$$

$$\frac{V_{out}}{V_{in}} = \frac{I X_c}{V_{in}} = \frac{X_c}{Z}$$

$V_{out} = V_C = I X_c$

$$\frac{V_{out}}{V_{in}} = \frac{\frac{1}{2\pi fC}}{\sqrt{R^2 + \left(\frac{1}{2\pi fC}\right)^2}}$$ **Low Pass Filter Equation**

As f → 0, V_{out}/V_{in} → 1.0 As f → %, V_{out}/V_{in} → 0

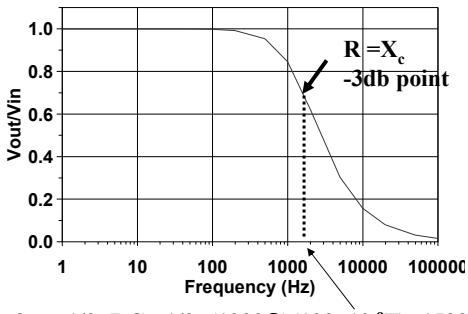
Low Pass Filter – example

The cutoff frequency of the filter is often characterized by the point at which $R = X_c$.
When $R = X_c$; $R = 1/2\pi fC$; AND

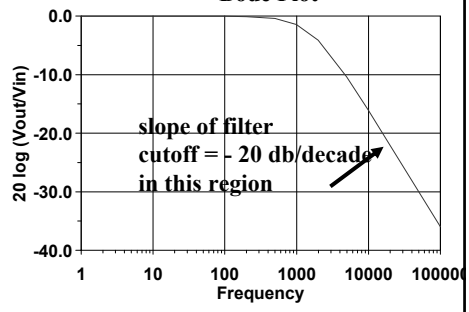
$$\frac{V_{out}}{V_{in}} = \frac{\frac{1}{2\pi fC}}{\sqrt{R^2 + \left(\frac{1}{2\pi fC}\right)^2}} = \frac{R}{\sqrt{R^2 + R^2}} = \frac{R}{R\sqrt{2}} = \frac{1}{\sqrt{2}} = 0.707 \qquad AT \quad f = \frac{1}{2\pi RC}$$

The cutoff frequency is also known as the -3db point
db = 20 log V_{out}/V_{in} db = 20 log (0.707) = -3.01 db Plot of db vs f

R = 1000 Ω C = 100 nF



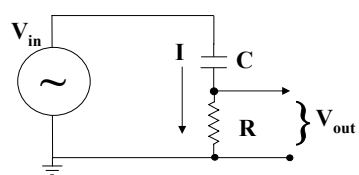
Bode Plot



$f_{3db} = 1/2\pi RC = 1/2\pi(1000\Omega)(100 \times 10^{-9}F) = 1592$ Hz

High Pass Filter

An electronic configuration used to filter out low frequency signals while allowing high frequency signals to pass through.



By analogy of the low pass filter...

$$I = \frac{V_{in}}{Z} = \frac{V_{in}}{\sqrt{R^2 + \left(\frac{1}{2\pi fC}\right)^2}}$$

$$\frac{V_{out}}{V_{in}} = \frac{IR}{V_{in}} = \frac{R}{Z}$$

$$\frac{V_{out}}{V_{in}} = \frac{R}{\sqrt{R^2 + \left(\frac{1}{2\pi fC}\right)^2}}$$

$V_{out} = V_R = I\,R$

High Pass Filter Equation

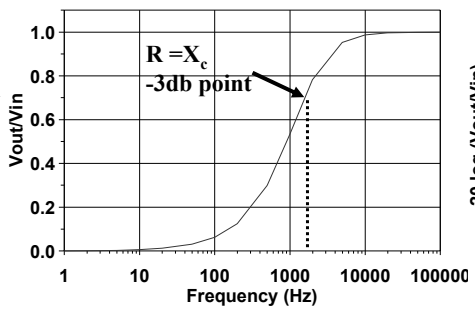
As f → 0, V_{out}/V_{in} → 0 As f → %, V_{out}/V_{in} → 1

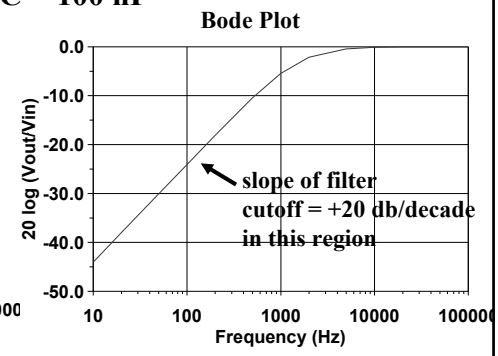
The same as the low pass filter, the cutoff frequency of the high pass filter is characterized by the - 3 db point.....

$$f_{3db} = \frac{1}{2\pi RC}$$

High Pass Filter- example

R = 1000 Ω, C = 100 nF





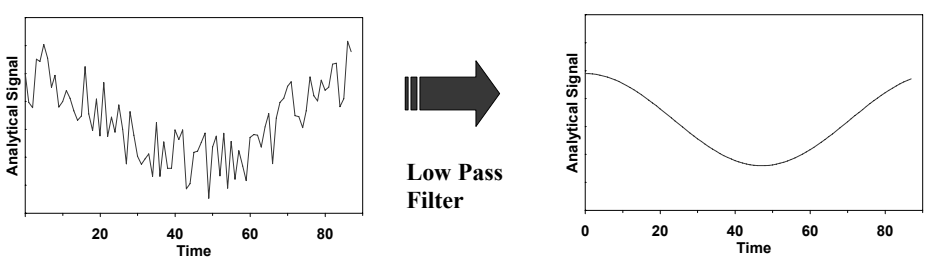
$f_{3db} = 1/2\pi RC = 1/2\pi(1000\Omega)(100 \times 10^{-9} F) = 1592$ Hz

Note that frequency plots of high pass and low pass filters with the same value of R and C appear as mirror images, with mirror plane $f = f_{3db}$

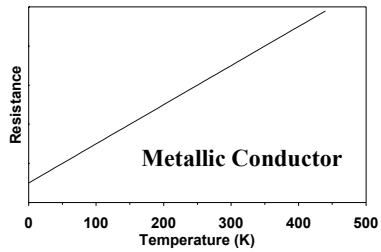
Applications of Filters

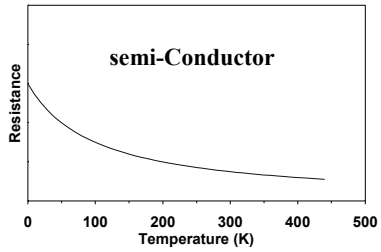
Low Pass and High Pass filters are used to eliminate noise at certain frequencies, while allowing "signal" to pass through the filter without any attenuation.

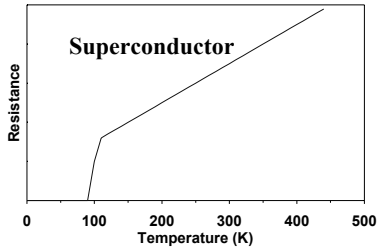
For analytical signals that vary slowly (close to DC or < 1Hz for example), use a low pass filter.



Conductors, semiconductors and Super conductors







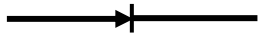
Semiconductors, Doping and Diodes

Doping

Semi-conductors conduct through thermal excitation of electrons across an energy band gap, ΔE. Conductivity increases with temperature (R decreses, see previous page) and can be enhanced in a semiconductor by doping group IV material (ie – Si) with Group V elements (As or Sb) OR Group III elements (Ga or In).

- a semiconductor doped with a group V is n-type since in the crystal lattice, there will be an extra conducting electron. It carries electricity through the movement of negative charge.
- a semiconductor doped with a group III is p-type. It carries electricity through the movement of positive holes

Diodes



- a semiconductor device that behaves as a conductor when current travels in one direction and as a large resistance when current travels the other direction. It is simple a pn junction
***PN Junctions*: When voltage is biased in one direction, charge can flow freely, electrons in one direction and positive holes in the other. When biased in the other direction, a rapid movement of holes and electrons in the reverse direction gives rise to a depletion region where there are no charge carriers. The resistance of this depletion region is very high. (see graphics in text)**

DC Power Supply

Power Supply - graphic

Power Supplies

The purpose of a DC power supply is to provide a source of power (ie- +5V, +10V, +15V) to the instrument to run various electronics and components. An ideal power supply delivers precisely regulated voltage with low output impedance, low ripple, low noise and long lifetime. Many problems in instrumentation can often trace back to the power supply.

Components of a power supply
Switch & overload protection

- the switch isolates the instrument from the source of power.

- overload protection is provided in the way of a fuse: slow blow, fast blow or circuit breaker. A constantly blowing fuse is a symptom of an electronic problem somewhere in the instrument.

fuses - graphics

Transformer

Purpose is to *step up* or *step down* the AC line voltage. This is accomplished by the way of interwound coils. A time varying current in the primary coil produces a time varying magnetic flux in the second coil, which induces an AC voltage. The transformer equation is given by:

$$V_{sec} = V_{prim} \times \frac{N_{sec}}{N_{prim}}$$

where V_{sec} **= voltage in secondary coil**
V_{prim} **= voltage in primary coil**
N_{sec} **= number of turns in secondary coil**
N_{prim} **= number of turns in the primary coil**

Normally, the transformer is used to divide the voltage. Transformers can also be used to isolate ac signals so to avoid common ground (the sec and prim wires are not connected).

graphic-transformer

Rectifiers

rectifiers produce a ~ dc voltage from an AC input voltage.
Half-Wave Rectifier
- only half (+) of the ac wave passes through the rectifier because of the bias of the diode. When current does pass through, it's voltage drop is seen across the load resistor.

graphic- ½ wave rectifier

Full Wave Rectifier
- more efficient than a HWR since there will be half of the ripple when we smooth the output. There are various types. One example is shown below. Current always flows through the load resistor in one direction, on both the positive and negative cycles. The diodes dictate the current path.

graphic- full wave rectifier circuit

Filters

- an effective way to smooth the output from the rectifier is with a low pass filter. A capacitor in parallel with the load resisitor can accomplish this.
- the larger the capacitor, the higher the average voltage and the smaller will be the ripple. Ripple may be defined by the ripple factor:

$$r = \frac{V_{AC}}{V_{DC}}$$

where V_{AC} and V_{DC} are the AC and DC components of the output voltage respectively.

graphic- RC filter

graphic- effect of capacitance on ripple

Voltage Regulation

- changes in ac line voltage (± 20%) or load current can cause the voltage output of a filtered rectifier to vary significantly. If we require 0.1 or 1% precision in the measured signal in our instrument, this would be unacceptable.

how do we regulate voltage in a power supply?

Zener Diode -this is a diode which is designed to be operated in breakdown mode.

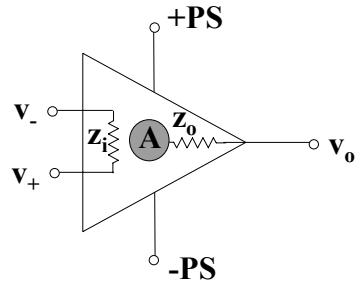
graphic- Zener Diode

Integrated Circuit Voltage Regulator
- the principle is simple as shown below. Components actually contain many internal transistors and devices. The voltage regulators are power rates and require heat sinking.

graphic- IC Voltage regulator

Operational Amplifiers
(Op-Amps)

- Integrated circuit chips used in all modern chemical instrumentation for analog signal "conditioning"



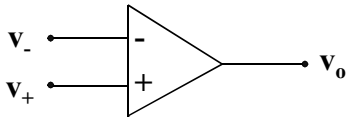
v_-	inverting input	v_o	output voltage
v_+	noninverting input	Z_i	input impedance
+PS	power supply (+15V)	Zo	output impedance
-PS	power supply (-15V)	A	open loop gain

Properties

- high open loop gain (A - ~10^4-10^8)
- high input impedance (1MΩ - 10^{13}Ω)
- low output impedance (1-100Ω)
- zero output for zero input (<0.1mV)

Op-Amps (cont'd)

Common convention



The actual for an op-amp is very complicated containing dozen(s) of transistors, resistors, diodes, etc. The description of how it operates is beyond the scope of this course. BUT, we ask that you "accept" on faith the following high level language equation which describes it's operation.....

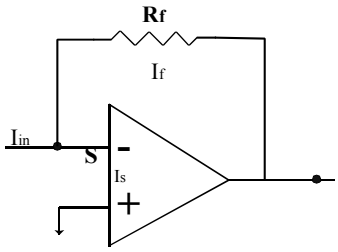
Open loop equation: $v_o = -A\,(v_- - v_+)$ (1)

Rearranging (1) we get: $v_- = v_+ - v_o/A$ OR
$v_- \approx v_+$

since $|v_o| < 15V$, $v_o/A < 1.5mV$

Golden Rule 1: The inverting and noninverting inputs can be considered to be at the same potential.

Current to Voltage Convertor



we have added "feedback". This is a basic op-amp circuit for measuring current.

Golden Rule 2: The current flowing through the inverting and noninverting inputs of the op-amp is negligible (due to high input impedance of op-amp).

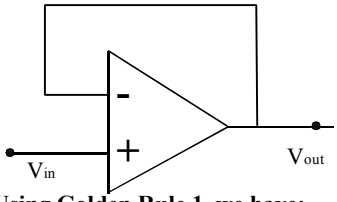
$\mathbf{I_{in} = I_f + I_s \quad . \quad I_f}$

Since Point S is at virtual ground, (ie- v_- . 0), all the current flows through R_f, and from Ohm's law, we have

$$v_o = v_- - I_f R_f \;.\; 0 - I_{in} R_f$$

$$v_o = -I_{in} R_f$$ **Important equation!**

Voltage Follower



A simple op-amp configuration with feedback between the inverting input and the output.

Can we derive the output as a function of the input voltage, v_{in} ?

Using Golden Rule 1, we have:

$v_+ \;.\; v_-$

but $v_- = v_{out}$

$v_+ = v_{in}$

so $v_o = v_{in}$ **OR** **Gain = $v_o/v_{in} = 1$**

This appears trivial…so, why use this???

One would use this in cases where the source voltage (v_{in}) impedance is very large, making it difficult to measure the voltage with a conventional measurement device without *loading errors*. Remember the output impedance of the OA is low. Thus we have converted a voltage source with high impedance into a voltage source with low impedance, making it easier to measure the voltage with s secondary device (DMM, chart recorder, analog to digital convertor…etc.

Voltage Follower – cont'd

Another way to derive the voltage follower equation from first principle is as such:

$v_o = -A\,(v_- - v_+)$,
$v_o = -A\,(v_o - v_{in})$ [since $v_- = v_o$, $v_+ = v_{in}$]

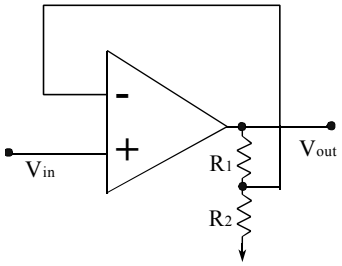
$v_o\,(1+A) = A\,v_{in}$

$$v_o = v_{in} \times \frac{A}{A+1}$$

$$v_o \approx v_{in} \times \frac{A}{A}$$

$$v_o \approx v_{in}$$

Voltage Follower with Gain (non-inverting amplifier)



$v_- = b\,v_o$ where b is a voltage divider fraction
$v_- = [R_2/(R_1 + R_2)]v_o$

$v_o = -A\,(v_- - v_+)$
$v_o = -A\,(bv_o - v_{in})$ since $v_- = bv_o$, $v_+ = v_{in}$
$v_o\,(1+Ab) = A\,v_{in}$

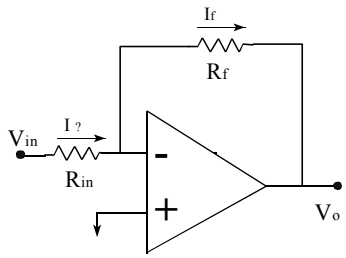
$$v_o = v_{in} \times \frac{A}{bA+1} \approx v_{in} \times \frac{A}{bA} = v_{in} \times \frac{1}{b}$$

$$v_o = v_{in} \times \frac{R_1 + R_2}{R_2}$$

One can use a potentiometer in place of R_1 and R_2 in order to get adjustable gain.

The voltage follower (with gain) has high input impedance, and low output impedance making it valuable an ideal amplifier for high impedance sources (ie- pH meters a), prior to the readout device.

Inverting Amplifier



A variation of the current to voltage convertor used for voltage amplification. With the addition of the input resistor, we have :

$v_o = -I_? R_f$,

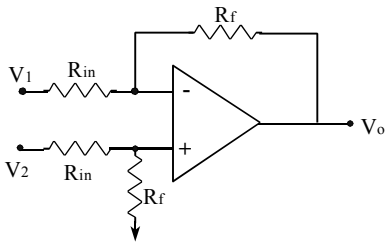
but $I_? = v_{in}/R_{in}$ because of virtual ground at v_

$$v_o = -v_{in} \times \frac{R_f}{R_{in}}$$

R_f can be changed to adjust gain.

Unlike the non-inverting amplifier, the inverting amplifier inverts the voltage signal. For AC signals, this is equivalent to a 180° phase shift.

Differential Amplifier



This is a useful configuration for amplifying small voltage *differences* between 2 inputs.

We will again derive v_o as a function of the inputs, V_1 and V_2. First we need to find what the voltages are at the inputs to the op-amp; v_ and v_+

$$v_+ = v_2 \times \frac{R_f}{(R_f + R_{in})} \qquad v_- = v_o + (v_1 - v_o) \times \frac{R_f}{(R_f + R_{in})}$$

Invoke Golden Rule #1……$v_+ = v_-$

$$v_2 \times \frac{R_f}{(R_f + R_{in})} = v_0 + (v_1 - v_0) \times \frac{R_f}{(R_f + R_{in})}$$

$$v_o = \frac{R_f}{R_{in}}(v_2 - v_1)$$

Output voltage is proportional to *difference* in input voltages!

Differential Amplifier – cont'd

Advantage of differential amplifier:

It gets rid of *"common mode noise"* , noise in the form of voltages that are common to both inputs, ie- thermal drift, induced voltages at 60 Hz or other frequencies. These common voltages are subtracted.

Common Mode Rejection ratio (CMRR)

Differential Amplifiers are characterized by how well they can reject common signals. This is called the common mode rejection ratio (the higher the better):

where A_{diff} **= amplification of difference signals (ie-** R_f / R_{in}**) and**

A_{comm} **= amplification of common signals (ie- imperfections)**

$$\text{CMRR} = \frac{A_{diff}}{A_{comm}}$$

example: $R_f = 50k\Omega$, $R_{in} = 500\Omega$.

A common voltage source is fed to both inputs by shorting the leads together, $V_1 = V_2 = 1.0$ **V. The output,** $v_o = 1mV$**, then we find CMRR as:**

$A_{diff} = R_f / R_{in} = 100$ $\qquad$ $A_{comm} = 1mV/1V = 0.001$

$\text{CMRR} = 100/.001 = 1\text{x}10^5$

Mathematical Functions

Addition and Subtraction

These circuits can be used to add voltages or currents. The derivation is easily seen from Kirchoff's law

Integrators: **In general, an integrator will attenuate noise, averaging the input voltage over a specified period of time. The output voltage is the time integral of the input signal.**

$$v_0 = -\frac{1}{R_{in}C_f}\int_0^t v_{in}\,dt$$

Differentiators: **In general, a differentiator will amplify noise. They can be used wherever the time rate of change of a signal is required.**

The derivation is easy: $v_o = -I_f R_f$

but $I_f = dq/dt = C_{in}\, dv_{in}/dt$

$$v_o = -R_f C_{in}\frac{dv_{in}}{dt}$$

Note that if the the signal is not changing, current does not flow through the input capacitor. Only ac signals will generate a response.

Mathematical Functions

see Fig 3-14 a,b,c,d

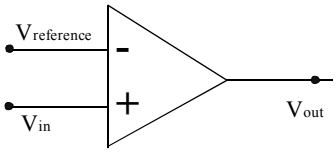
Op-amp applications

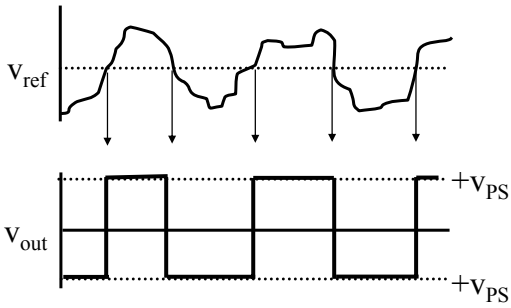
Fig 3-9, 3-10, 3-11

Comparator

a triggering device composed of an op-amp without feedback. When $v_{in} > v_{ref}$, v_{out} goes high, when $v_{in} < v_{ref}$, v_{out} goes low.

$V_{out} = -A\,(v_{-} - v_{+}) = A\,(v_{in} - v_{ref})$





This device can be used for producing a "clean" square wave from an otherwise noisy AC signal. Or as we will see, it is a useful decive in the analog to digital convertor.

Digital to Analog Convertors

Analog to Digital Convertors

Signals and Noise

Noise limits our ability to distinguish between real (ie- chemical) and background signals. As chemists making sensitive measurements, our *call to arms* is:

i) to understand the noise in the measurement system

ii) to reduce the noise in the measurement

iii) to reduce the background signal

Why are ii) and iii) synonymous?..... because noise generally increases with signal (not always).

Signal to noise ratio:

$$\frac{S}{N} = \frac{\text{mean signal}}{\text{noise}} = \frac{\bar{Y}}{\sigma_y}$$

We often measure the quality of a signal measurement by the S/N ratio...the larger the better. At S/N ratios >3, the signal is detectable. Note that,

$$S/N = \frac{\bar{Y}}{\sigma_y} = \frac{1}{\frac{\sigma_y}{\bar{Y}}} = \frac{1}{RSD}$$

Sources of Noise

Sources of Noise

Chemical Noise: usually associated with the portion of our measurement system that is external to our instrument, but not always.

- incomplete reactions

- effect of temperature fluctuations on equilibrium

- changes in pressure, relative humidity, light intensity that can alter the concentration of an analyte (these parameters could change the sampling efficiency for example)

Instrumental Noise: noise associated with the instrumental portion of our method.

- Thermal noise

- Shot noise

- Flicker noise

Thermal Noise

noise associated with thermally induced motion in charge carriers, either of the charge carriers or the lattice through which the charge carriers pass (resistor noise). The thermally induced motion results in charge inhomogeneities, giving rise to voltage fluctuations (recall that a voltage is potential energy associated with the separation of charge):

$$V_{rms} = \sqrt{4kTR\Delta k}$$

where

	k =	Boltzmann's constant (1.38054×10^{-23} JK^{-1})
	T =	temperature (K)
	R =	resistance (ohms)
	) f =	frequency bandwidth (Hz)

Note : the noise is independent of f (white noise).

How do we reduce thermal noise?

1) reduce the temperature (we get ~ factor of 2 reduction in noise by cooling from ambient to liquid N_2 temp (77K)).

2) reduce the value of the resistors used in circuits (not always practical).

3) reduce the frequency bandwidth (ie-we can add a low pass, high pass, or bandpass filter to reduce the frequencies accepted in the signal processor to only those that are necessary).

Shot Noise (electrical)

- noise associated with the movement of charge across a junction (ie- p-n junction, electrolytic cell, photocell).
- because the movement of charge across the boundary is random, the number of charges per second (ie- the current) is subject to statistical fluctuations).
- usually much smaller than thermal noise.

$$I_{rms} = \sqrt{2Ie\Delta I}$$

where I = current (amps)
e = charge on electron (1.6021×10^{-19} C)
) f = frequency bandwidth (Hz)

Note : this noise is also independent of f (white noise).

How do we reduce shot noise?

1) reduce the frequency bandwidth
2) we can reduce the relative noise, I_{rms}/I, by increasing the current.

Flicker Noise (1/f Noise)

- magnitude is inversely proportional to the frequency of the signal (1/f) or to $1/(f)^{1/2}$
- for signals that don't have a discrete frequency, the signal will have noise at all frequencies that are in the bandwidth of the detector.
- 1/f noise can frequently dominate for f < 100Hz. When f<<1Hz, we call this *drift*.
- although not well understood, 1/f noise appears to be a function of the electronic components used. Metallic film resistors have less 1/f noise than composite resistors; field effect transistors have less 1/f noise than bipolar junction transistors.

Emperical Equation:

$$V_{rms} = \sqrt{\frac{KI^2}{f}}$$

where K = constant dependent on materials used
I = dc current (A)
f = frequency (Hz)

* Willard et al., *Instrumental Methods of Analysis*, 7th ed. (1988) pg 17.

How do we reduce flicker noise?

1) avoid DC measurements, go to higher frequencies
2) use better electrical components

Photon or Molecular Shot Noise

when our experimental signal involves the counting of individual items (ie- photons or molecules) and the emission of the photon or molecule is a random event, then we have statistical noise associated with the number of counts, N.

$$\sigma_N = \sqrt{N} \qquad RSD = \frac{\sigma}{Y} = \frac{\sigma_N}{N} = \frac{\sqrt{N}}{N} = \frac{1}{\sqrt{N}}$$

The relative standard deviation is reduced, or the signal to noise ratio is increased, as the number of counts is increased.

Environmental Noise

-results from transfer of energy from our environment to the instrumental system.

-usually confined to specific frequencies

-energy can be from electromagnetic (EM) radiation, mechanical motions, or any other periodic fluctuation (ie- temperature for f <<1Hz.

-the most ubiquitous environmental noise is produced from 60-Hz transmission lines. Noise is seen at 60 Hz and at the harmonics (120, 180, 240 ...).

Distinguishing Signals from Noise

(identical signal levels, differing noise levels)

Environmental Noise

see Fig 5-3 in textbook

Methods for Signal to Noise Enhancement

Hardware methods

Shielding: used for elimination of electromagnetic radiation.

shielded boxes - circuits are often constructed inside metallic boxes which is connected to ground. The box provides a "guassian" shield. No electric fields will penetrate.

Shielded wire - the most common is coax cable. This is used for shielding signals that must be transmitted over a distance. The cable is composed of several layers as shown below

Problems - one has to worry about capacitance at high frequencies. Both sides of the shield are connected to common, resulting in ground loops that can be problematic under certain conditions.

Filtering - discussed previously. Used to eliminate noise in certain frequency ranges.

Differential Amplifiers - discussed previously. Can be used to reject common mode noise.

Modulation/Demodulation

In these methods, we improve our S/N ratio by:

i)modulation - moving our signal to a relatively quiet frequency where there is little noise,

ii) tuned amplification - selectively amplify the signal at the new frequency

iii)demodulation - recovery of the amplitude of the signal. Output is a noise free DC signal.

Example: Spectrophotometric methods

i) chopper

ii) & 3) lock-in amplifier

Software Techniques for reducing Noise (or S/N Enhancement)

Boxcar Averaging

For a single point, our signal is: $y_i \pm \sigma$ **and** $(S/N)_1 = y_i/\sigma$

For a boxcar containing n points:

$$\bar{y}_i = \frac{\sum_i y_i \pm \sqrt{\sum \sigma_i^2}}{N} = \frac{\sum y_i}{N} \pm \frac{\sqrt{N\sigma_i^2}}{N} = \bar{y} \pm \frac{\sigma}{\sqrt{N}} \qquad \left(\frac{S}{N}\right)_N = \sqrt{N} \times \frac{\bar{y}}{\sigma}$$

The noise is reduced by a factor of $1/(N)^{1/2}$ and the S/N is increased by $(N)^{1/2}$

Smoothing: both weighted and non-weighted