Goals for today …

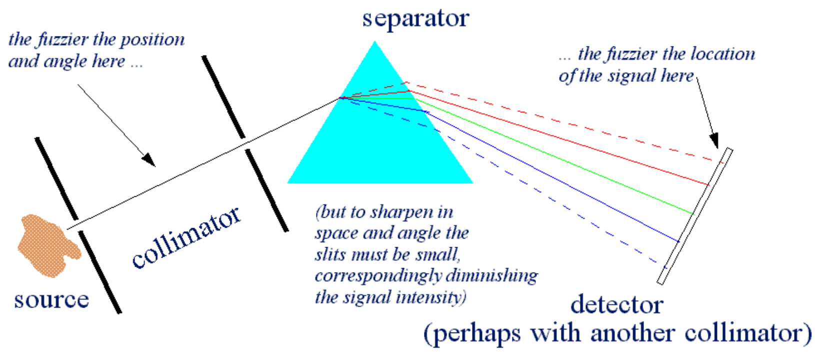
- Spectroscopic techniques and algorithms
- Instruments and algorithms for contraband detection
  - vapor detection techniques (mostly chemistry)
  - bulk detection techniques (mostly physics)

Spectroscopies

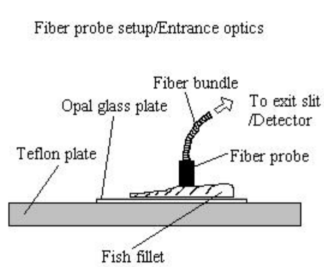
- Signal as a function of some dispersion parameter
  - retention time (chromatographies)
  - drift time (ion mobility spectroscopy)
  - wavelength (optical spectroscopy)
  - frequency (NMR, NQR, ESR)
  - photon energy (x-ray, γ-ray spectroscopies)
  - particle energy (photoelectron energy spectroscopy)
  - ion mass (mass spectroscopies)
- Always three functions, usually three modules:
  - source
  - dispersion element
  - detector

Principle of Conservation of Misery

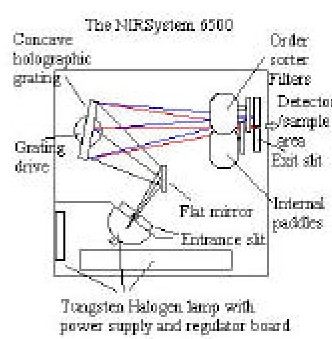
- There is an inevitable tradeoff between your ability to separate spectral components (resolution) and your ability to detect small quantities (sensitivity)



Example: VIS-NIR Diffuse Reflectance Spectrum to Measure Fish Freshness



(probe: light in and out)



(monochromator: specific color light out)

What’s This GC Gizmo?

- Pipe coated (or packed with grains that are coated) with a “sticky” liquid ...
- Inert gas (e.g., He) flows through the pipe (“column”)
- Mixture (e.g., gasoline) squirted into “head”
- Gas (“mobile phase”) carries it over the liquid (“stationary phase”)

- Mixture components move at different velocities due to different equilibria between mobile and stationary phases
- Components emerge at column “tail”: detect with a “universal” detector, or use as inlet to mass spectrometer or other instrument
- MANY similar techniques: liquid chromatography, ion mobility chromatography, electrophoresis, and (the original) color-band based chromatography (hence the name)

What's this MS Gizmo?

- *Usually* a separation based on mass of positive ions; sometimes negative ions, rarely neutrals
- *Usually* all the ions are accelerated (and filtered) to the same energy
- Velocity thus depends on mass: v = Sqrt(2 W/m)
- Velocity can be measured by time-of-flight, by trajectory in a magnetic field, etc, in many different geometries

- Smaller lower cost alternative: quadrupole mass spectrometers
  – ions move under combined influence of DC and oscillating (RF) electric fields; most orbits are unbounded, but for any particular mass there is a small region in the DC/RF amplitude plane where they are bounded (analogous to the inverted pendulum)

Spectroscopies: Algorithms

Unraveling Overlapping Spectra

- Absent separation (like GC), given the spectrum of a mixture, how best to unravel its components when the component spectra all overlap?
  - $S_1 = \{s_{11}, s_{12}, s_{13}, ..., s_{1n}\}$
    1 = hexane, {1,2,3,...,n} = peak IDs
  - $S_2 = \{s_{21}, s_{22}, s_{23}, ..., s_{2n}\}$
    2 = octane, {1,2,3,...,n} = same peak IDs
  - ... etc ....
  - $S_m = \{s_{m1}, s_{m2}, s_{m3}, ..., s_{mn}\}$
    m = Xane, {1,2,3,...,n} = same peak IDs

- Consider the inverse problem: given the concentrations, it is straightforward to predict what the combined spectrum will be:
  - $C = \{c_1, c_2, c_3, \ldots, c_m\}$, 1 = hexane, 2 = octane, ..., m = Xane
  - $S = c_1S_1 + c_2S_2 + c_3S_3 + \ldots + c_mS_m$
- Or in matrix notation:

components of the mixture

spectrum of each component of the mixture

$$\begin{bmatrix} s_{11} & s_{21} & s_{31} & s_{41} & s_{51} \\ s_{12} & s_{22} & s_{32} & s_{42} & s_{52} \\ s_{13} & s_{23} & s_{33} & s_{43} & s_{53} \\ s_{14} & s_{24} & s_{34} & s_{44} & s_{54} \\ s_{15} & s_{25} & s_{35} & s_{45} & s_{55} \\ s_{16} & s_{26} & s_{36} & s_{46} & s_{56} \\ s_{17} & s_{27} & s_{37} & s_{47} & s_{57} \\ s_{18} & s_{28} & s_{38} & s_{48} & s_{58} \end{bmatrix} \cdot \begin{bmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \\ c_5 \end{bmatrix} = \begin{bmatrix} S_1 \\ S_2 \\ S_3 \\ S_4 \\ S_5 \\ S_6 \\ S_7 \\ S_8 \end{bmatrix}$$

overlapped spectrum of all the components of the mixture

concentrations of each of the components of the mixture

- If we look at only as many peaks as there are components then the matrix is square, and it is easy: $c = s^{-1} S$
- If we have fewer peaks than components then we are up the creek.
- If we have more peaks than components then what to do?
- More peaks than components means we have "extra data" that we can use to improve the precision of our result.

Pseudo-Inverse Method

- The trick is to multiply both sides of the equation by s^T:
  - s c = S
    (n_{peaks} x $n_{components}$) ($n_{components}$ x 1) = (n_{peaks} x 1)
  - $s^T s\ c = s^T S$
    ($n_{components}$ x n_{peaks}) (n_{peaks} x $n_{components}$) ($n_{components}$ x 1) = ($n_{components}$ x n_{peaks}) (n_{peaks} x 1)
  - note that $s^T s$ is square, hence it (generally) has an inverse

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  - $c = (s^T s)^{-1} s^T S$
    ($n_{components}$ x 1) =
    ($n_{components}$ x $n_{components}$)$^{-1}$($n_{components}$ x n_{peaks}) (n_{peaks} x 1)
  - called the "pseudo-inverse method"
- Calculated component concentrations are optimal: equivalent to least squares fitting
  - i.e., algebraic least squares fit gives the same result as matrix solution using pseudo-inverse formalism
- (Yes, of course, there are degenerate cases where $s^T s$ doesn't actually have an inverse, or calculating it is unstable; then you need to use better judgement in deciding which peaks to use!)

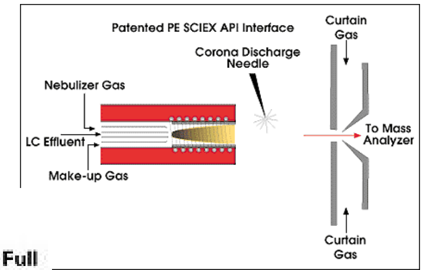
Caution ...

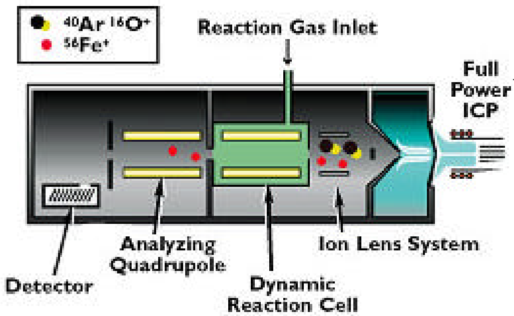
- $c = (s^T s)^{-1} s^T S$ is the same as the optimal result you would get if you minimized the sum of the squares of the differences between the components of the data set S and a "predicted" data set $S = s\ c$:
  - $\Sigma = Sum((sc - S)_i$ *over all* n_{peaks} *spectral peaks)*
    $d\Sigma / dc_j = 0$ *gives* $n_{components}$ *simultaneous equations which when you solve them for* $\{c\}$ *gives the same result as the pseudo-inverse*

- But (to keep the notation and discussion simple) *I've left something out*: as in our previous discussion about how to combine multiple measurements that have different associated uncertainties, you need to weight each datum by a reciprocal measure of its uncertainty, e.g., $1/\sigma_i^2$ (in both the least-squares and the pseudo-inverse formulations).

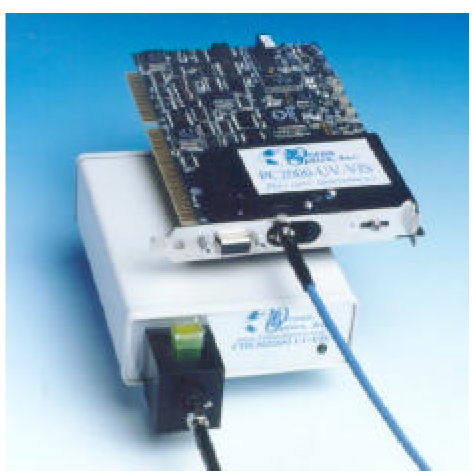
Tandem Technologies

note analogy to image processing: not one magic bullet, but a clever chain of simple unit operations





Miniaturization



Ocean Optics:
optical spectrometer optics and electronics on a PC card; separate light source (below), and fiber optic (blue) light input path

Contraband Detection

System issues when you have to detect something that probably isn't there

Pod (Probability of Detection) FAR (False Alarm Rate)

- Illustrative problem: a town has 10 blue taxis, 90 black taxis; a man reports a hit-and-run accident involving a blue taxi; tests show he correctly identifies taxi color 80% of the time; what is the probability that the taxi he saw was actually blue?
- First thought: 80%.

- Second thought: you should ask how often he is correct when he says he saw a blue cab. If the cab really was blue, he reports 8 blue cabs out of 10 blue; if the cab really was black, he reports 18 blue cabs out of 80 that are actually black. So when he reports a blue cab he is correct only (8/(8+18)) = 31% of the time!
- (see http://www.maa.org/devlin/devlinjune.html)

Bayes Theorem

- We start with an *a priori* estimate from previous experience, etc.
  Then we receive additional information from an observation.
  How do we update our estimate?
- P(blue)=0.10, P(black)=0.90 [etc., total 1., for possibilities>2]
- P(say it is blue | if it is blue) = 0.80,
  P(say it is blue | if it is black) = 0.20,
  P(it is blue | if say it is blue) = ?

$$P(itisblue \mid ifsayitisblue) = \frac{P(itisblue)P(sayitisblue \mid ifitisblue)}{P(itisblue)P(sayitisblue \mid ifitisblue) + P(itisblack)P(sayitisblue \mid ifitisblack)}$$

Bayes Theorem

$$P(X|A) = \frac{P(X)P(A|X)}{P(X)P(A|X) + P(Y)P(A|Y) + P(Z)P(A|Z)}$$

Airport Explosives Sniffer

- P(alarm | if bomb) = 0.80 (PoD)
  P(alarm | if no_bomb) = 0.01 (PFA)
  P(bomb) = 0.000001
  P(no_bomb) = 0.999999
- An alarm goes off; what is the probability of a real bomb?
- P(bomb | if alarm) = P(bomb) P(alarm | if bomb)/ (P(bomb) P(alarm | if bomb) + P(no_bomb) P(alarm | if no_bomb))

- P(bomb | if alarm) = 0.00007994 =~= 0.00008 (false alarm rate is 99,992/100,000)
- P(bomb | if alarm) = 0.5 when P(alarm | if no_bomb) = 0.8×10^{-6}

Try this one ...

- A commercial system reports NG, RDX, PETN, TNT, Semtex, HMX.
- Terrorists use P(NG)=0.15, P(RDX)=0.10, P(PETN)=0.20, P(TNT)=0.05, P(Semtex)=0.25, P(HMX)=0.05, P(OTHER)=0.20.
- The instrument characteristics are P(NG_alarm | if NG)=0.80, P(RDX_alarm | if RDX)=0.85, P(PETN_alarm | if PETN)=0.60, P(TNT_alarm | if TNT)=0.75, P(Semtex_alarm|if Semtex)=0.90, P(HMX_alarm|if HMX)=0.70, P(some_alarm | if other)=0.30, P(wrong_alarm | if any_of_the_six)=0.05, P(some_alarm | if no_explosive)=0.01

- One piece of luggage out of a million contains actual explosive.
- When an alarm goes off, what is the probabability that some explosive is actually present in the luggage?