

# chemical sensing

## linear devices

# chemical sensing

- ▶ introduction to chemical sensing and sensors
  - ◆ vapor detection techniques (mostly chemistry)
  - ◆ bulk detection techniques (mostly physics)
- ▶ in general, “spectroscopic” techniques
- ▶ in parallel, algorithmic approaches to “signal-to-symbol transformation” for these sorts of signals

# approaches to chemical sensing

- ▶ identify the *nuclei*, e.g.,  
neutron-activation or  $\gamma$ -ray spectroscopy
- ▶ identify the *atoms*, e.g.,  
flame emission spectroscopy
  - ◆ these are great for, e.g., prospecting for iron ore: you *might* not care whether you find FeO, Fe<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>S<sub>3</sub>, or any other iron compound, as long as it is Fe
  - ◆ but if you want to know, e.g., how a computer works it doesn't do you a lot of good to grind it up and analyze the dust for H, C, N, O, Si, Al, Fe, Cu, Au, Sn, Pb, etc

▶ identify positive and negative *ions* of atoms, fragments of molecules, most small molecules, some big molecules, e.g., mass spectrometry:

◆ but there are many ways to make the same mass, e.g.,  $\text{H}_3\text{COCH}_3$  (acetone) and  $\text{H}_3\text{CCH}_2\text{OH}$  (ethyl alcohol) look the same at any practical mass resolution, and both look the same as  $\text{NO}_2$  and isotopes of Ca, Sc, Ti, and V (all atomic mass 46) at low resolution, i.e., at high detection sensitivity

▶ identify effect of molecular *solubility* (partition) between two solvents on transport time through a “sticky pipe”, e.g., gas and liquid chromatography

- ◆ “retention time” not unique

- ◆ concatenated techniques, e.g.,

  - GC-MS, effective but slow and expensive

▶ identify electric-field induced *drift* rate of molecular ions through a gas, e.g., ion mobility spectrometry (IMS, plasma chromatography, ...)

- ◆ airport hand luggage sniffers

  - <http://www.sensir.com/Smiths/InLabSystems/IonScan/IonScan.htm>

- ▶ identify characteristic *x-ray* spectral attenuation of materials of particular interest in particular places
  - ◆ airport “color” x-ray machines for explosives, drugs
- ▶ and probably a hundred specialized technologies relying on ...
  - ◆ photoelectric effect
  - ◆ speed of sound
  - ◆ infrared absorption
  - ◆ etc etc etc ... taking advantage of some unusual chemical or physical property of the specific analyte

- ▶ in general, we can do quite well these days with complex instruments whose scale is room size or even desk size ... and more recently, desktop monitor size ...
- ▶ but there is a demand for low-cost hand-held (or robot-held) equivalents ...
- ▶ many are based on “chemi-resistors”, “chemi-transistors”, “chemi-capacitors”, etc
  - ◆ covered briefly on the white-board recently
- ▶ first we will discuss “laboratory” chemical analytical instruments and how they are being/might be miniaturized

# spectroscopies

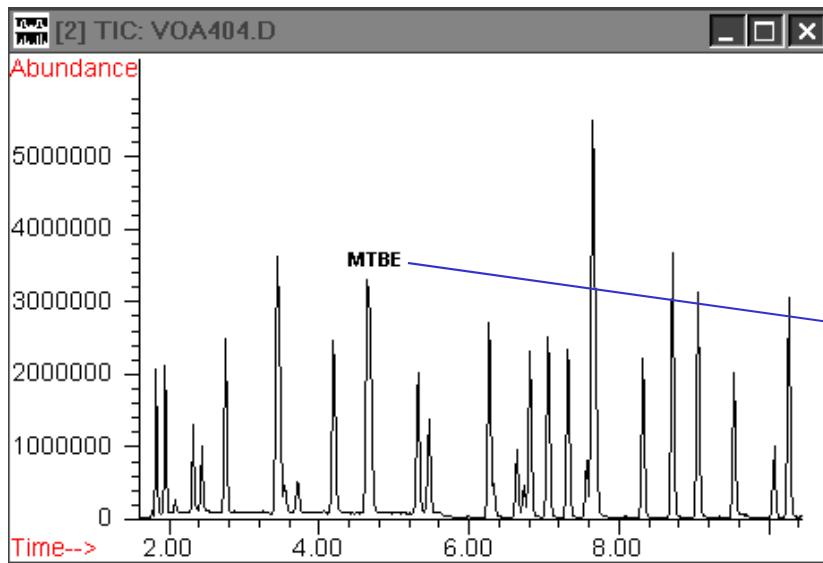


# spectroscopies

- ▶ when a single component produces a mix of separable responses ...
  - ◆ example: the *optical* spectrum of a particular isotope of iron (Fe)
    - electron state transitions between all possible energy levels of the atom (subject to some “selection rules”)
  - ◆ example: the *ion mass* spectrum of a molecule of heptane (gasoline is mostly  $C_7H_{16}$ )
    - $C^+$ ,  $CH^+$ ,  $CH_2^+$ ,  $CH_3^+$ ,  $CH_3C^+$ ,  $CH_3CH^+$ ,  $CH_3CH_2^+$ ,  $CH_3CH_2C^+$ ,  $CH_3CH_2CH^+$ ,  $CH_3CH_2CH_2^+$ ,  $CH_3CH_2CH_2C^+$ , ...,  $CH_3CH_2CH_2CH_2CH_2CH_2CH_3^+$

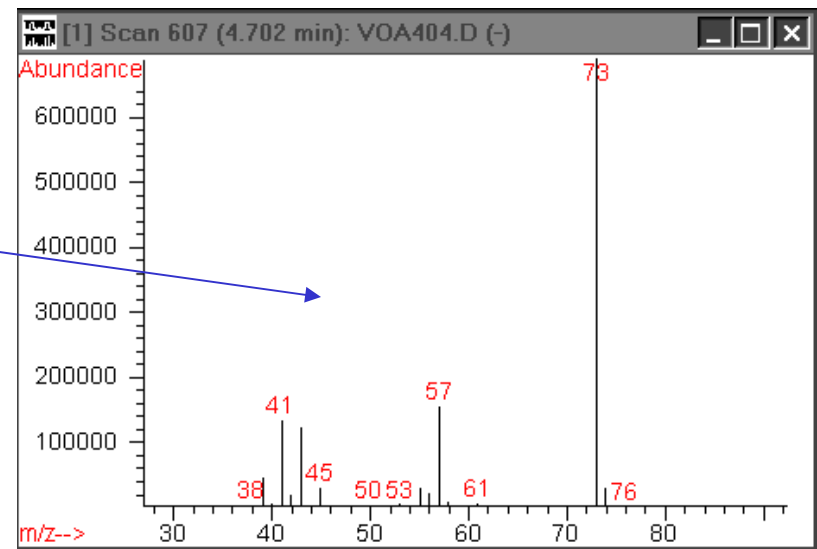
▶ or a mixture produces a complex response for each component

- ◆ can sometimes pre-separate the mixture components
  - gasoline: ..., hexane ( $C_6H_{14}$ ), heptane ( $C_7H_{16}$ ), octane ( $C_8H_{18}$ ), ... can be separated in time domain (e.g., gas chromatography)



(temporal separation by GC)

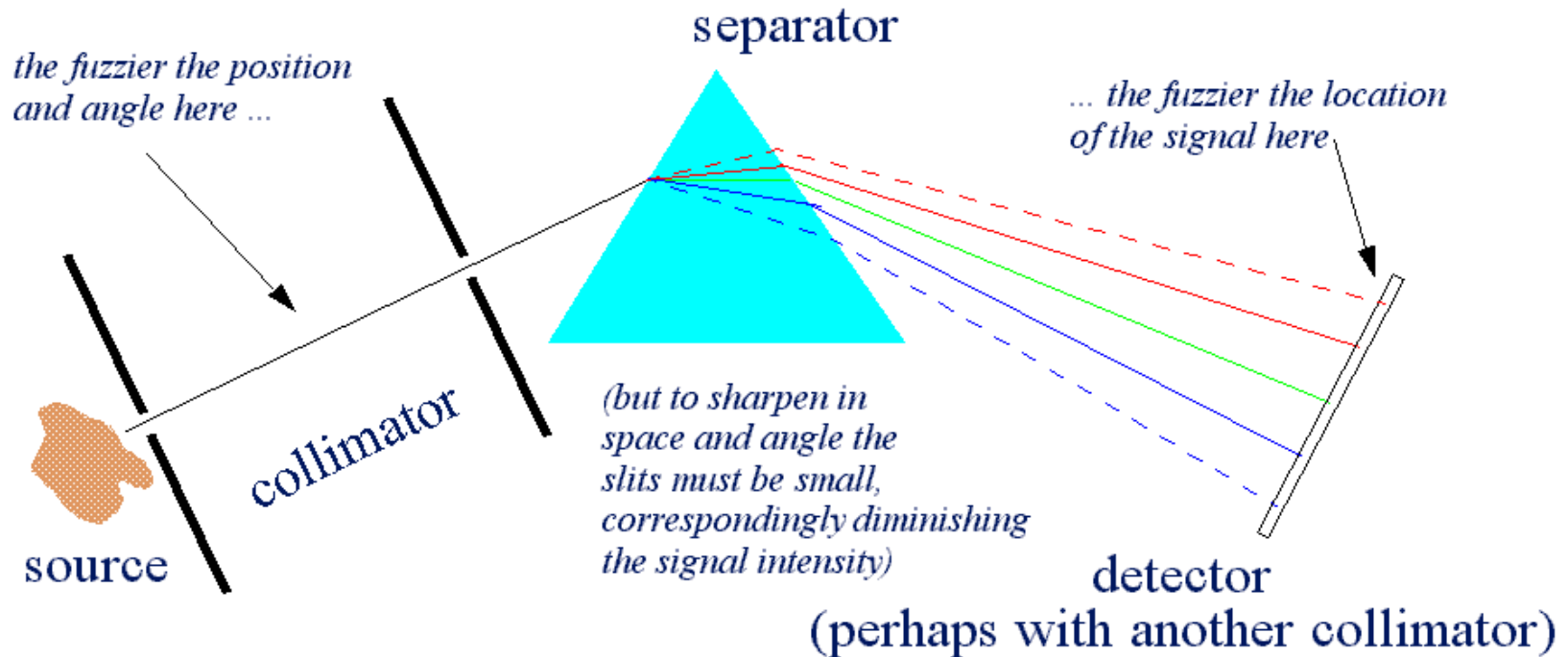
(structural separation by MS)



# optical spectroscopy

# illustrates the general principle ...

- ▶ inevitable tradeoff between your ability to separate spectral components (resolution, selectivity) and your ability to detect small quantities (sensitivity)

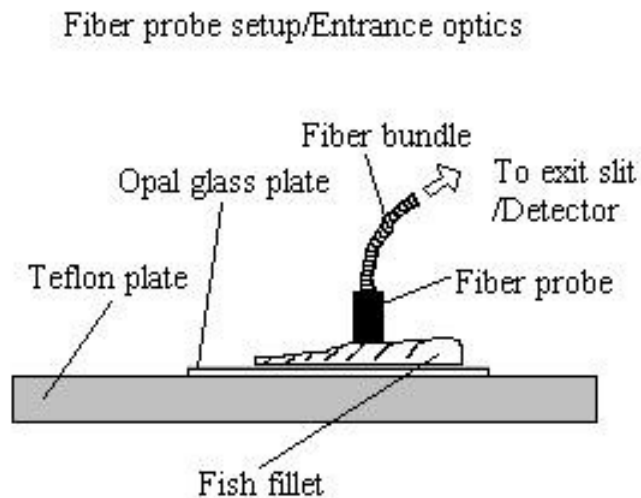


# miniaturization example

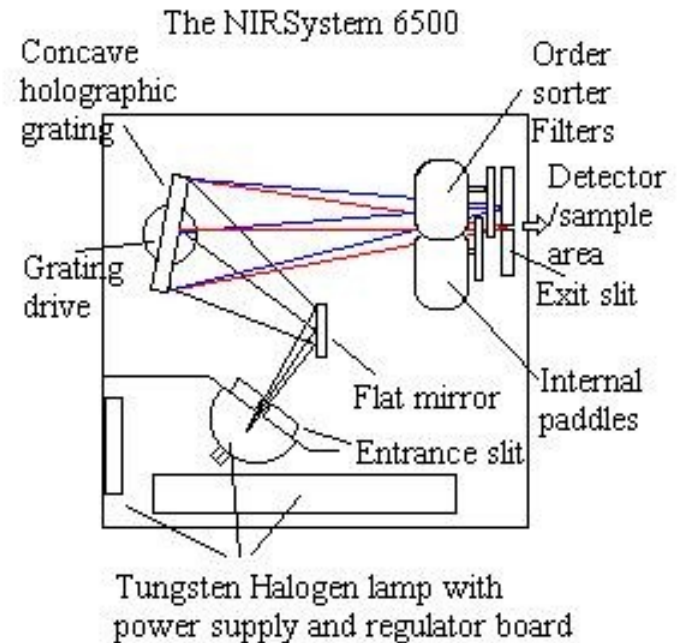


Ocean Optics:  
optical spectrometer  
optics and electronics  
on a PC card; separate  
light source (below),  
and fiber optic (blue)  
light input path

# example: VIS-NIR Diffuse Reflectance Spectrum to Measure Fish Freshness



(probe: light in and out)



(monochromator: specific color light out)

# mass spectrometry

# mass spectrometry

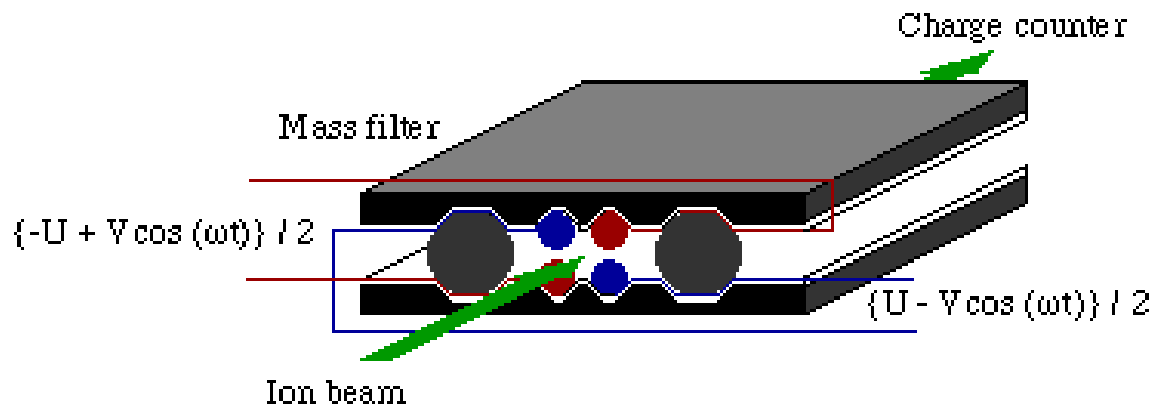
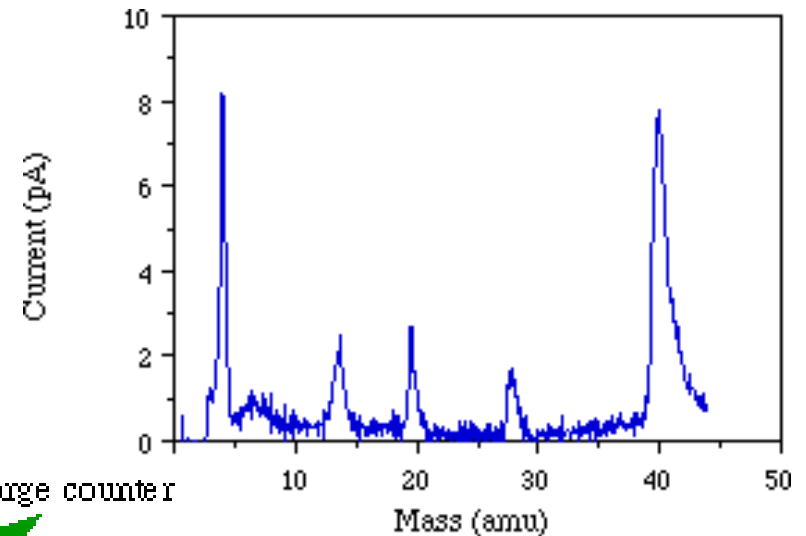
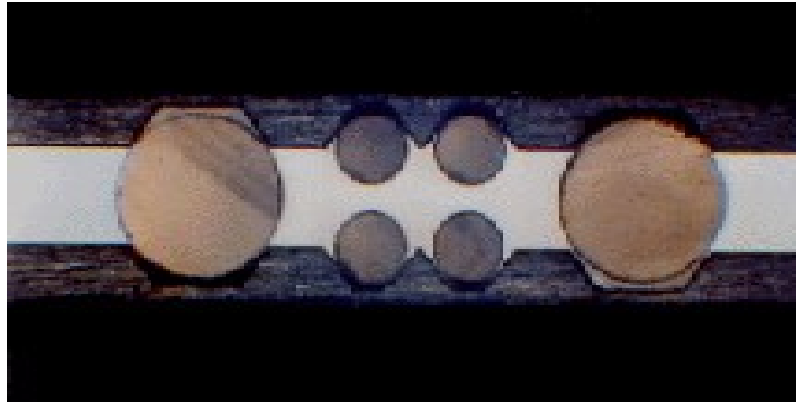
- ▶ *usually* a separation based on mass of positive ions; sometimes negative ions, rarely neutrals
- ▶ *usually* all the ions are accelerated to the same energy (and filtered to remove outliers)
- ▶ velocity thus depends on mass:  $v = (2 W/m)^{1/2}$
- ▶ velocity measured by time-of-flight, by trajectory 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
  - equations of motion analogous to the inverted pendulum
    - similar to the inverted pendulum application made famous as an example of fuzzy logic control

# miniaturization example



▶ argon/air/helium, 500 micron diameter rods, 3 cm long

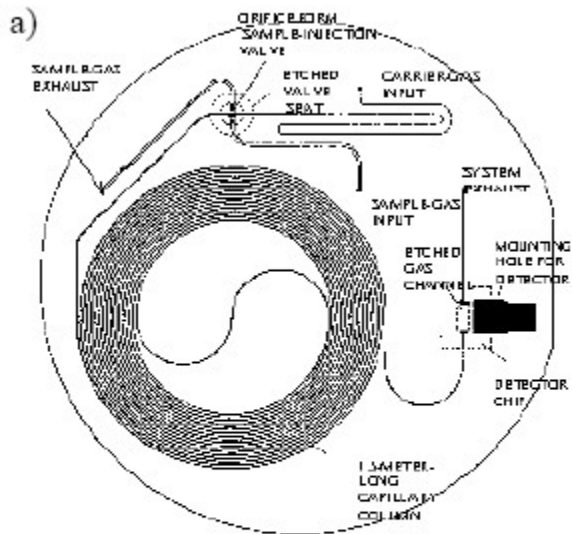
[http://www3.imperial.ac.uk/portal/page?\\_pageid=189,618267&\\_dad=portallive&\\_schema=PORTALLIVE](http://www3.imperial.ac.uk/portal/page?_pageid=189,618267&_dad=portallive&_schema=PORTALLIVE)

# chromatographies

# gas chromatography

- ▶ pipe coated (or packed with grains that are coated) with a “sticky” liquid (“stationary phase”)
- ▶ 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
- ▶ mixture components move at different effective speeds due to different equilibria between phases
- ▶ components emerge at column “tail”
  - ◆ detect with a “universal” detector
  - ◆ or use as inlet to mass or optical spectrometer, etc

# miniaturization example



**Fig.1:** a) The first integrated gas chromatograph made on 2" silicon substrate [1], b) Portable chromatograph GC MTI Quad 400; dimensions 19x52.5x52.5 cm, weight 20.4 kg, manufactured currently by Hewlett-Packard.

► <http://eetd.llnl.gov/mtc/Instruments.html>  
(another instrument – fewer details – link to this one has disappeared)

# MANY similar techniques:

- ▶ liquid chromatography
  - ◆ liquid mobile phase, solid or liquid stationary phase
- ▶ ion mobility chromatography
  - ◆ ion drift velocity through a gas under influence of an electric field (airport explosives detector principle)
- ▶ electrophoresis
  - ◆ molecules drift through a gel under influence of an electric field (used in many medical tests)
- ▶ *real old fashioned* chromatography
  - ◆ dye-like chemicals separated by different diffusion speed through a packed powder, e.g., chalk stick, or soup dribble on table cloth

# hybrid techniques

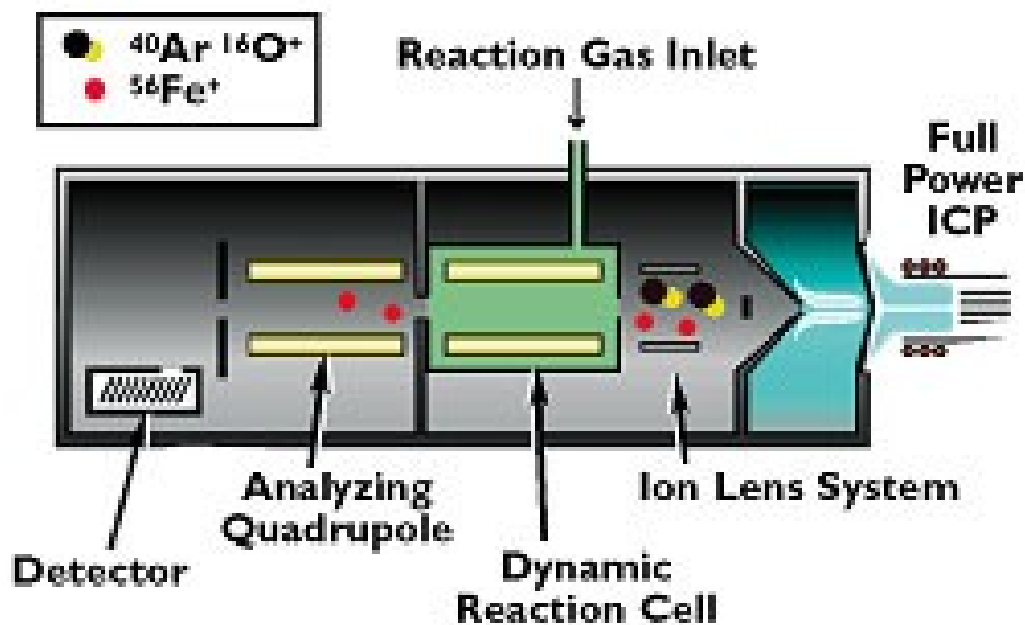
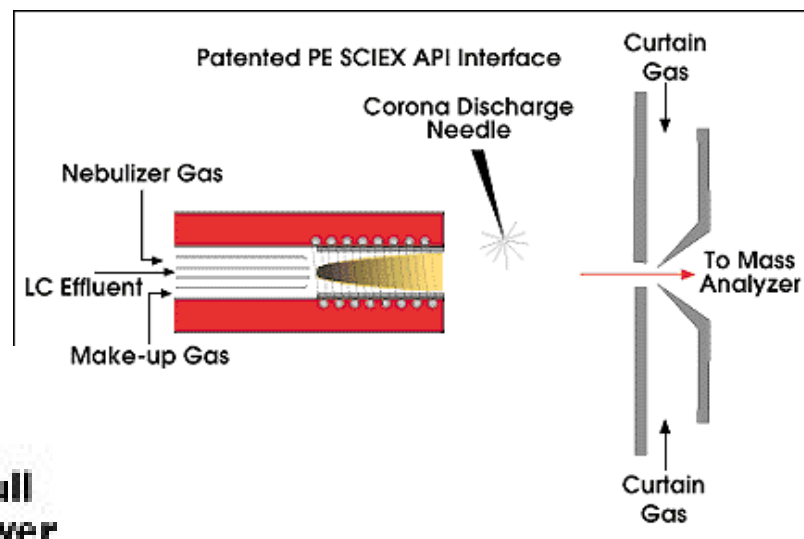
# hybrid or “tandem” techniques

- ▶ for *routinely* detecting and identifying any but the simplest chemical species, hybrid techniques are usually employed ...
  - ◆ GC – MS
  - ◆ pre-concentration – IMS (airport explosives)
  - ◆ multiple MS stages with collisional decomposition between stages
  - ◆ etc



# LC MS with high-pressure ionizer etc

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



# linearity

# linearity & superposition

- ▶ all the techniques discussed today are (nearly) linear in several senses of the word
  - ◆ output signal linear in sample concentration
  - ◆ response to multiple components present simultaneously is the sum of the responses to the individual components separately
    - i.e., little or no cross-sensitivity
- ▶ later we will discuss sensors where this is not true, e.g., solids state chemical sensors
  - ◆ like the  $\text{SnO}_2$  chemi-resistors discussed previously
- ▶ if it is true then simple pattern recognition works

# unraveling overlapping spectra (or “signatures”)

# overlapping spectra of a mixture

▶ absent separation (like GC), given the spectrum of a mixture, how best to unravel its components when the component spectra all overlap?

◆ arrange your spectrum library in a rectangular matrix:

■  $S_1 = \{s_{11}, s_{12}, s_{13}, \dots, s_{1n}\}$

1 = hexane,  $\{1,2,3,\dots,n\}$  = peak IDs

■  $S_2 = \{s_{21}, s_{22}, s_{23}, \dots, s_{2n}\}$

2 = octane,  $\{1,2,3,\dots,n\}$  = same peak IDs

■ ... etc ....

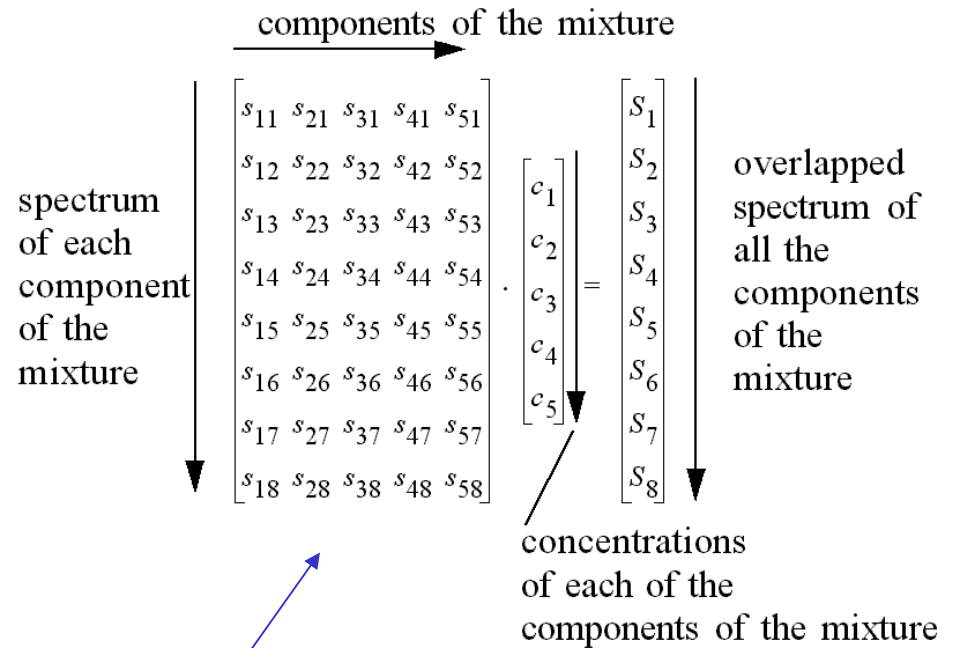
■  $S_m = \{s_{m1}, s_{m2}, s_{m3}, \dots, s_{mn}\}$

m = Xane,  $\{1,2,3,\dots,n\}$  = same peak IDs

▶ consider the inverse problem: given the concentrations, it is very easy to predict what the combined spectrum will be:

- ◆  $C = \{c_1, c_2, c_3, \dots, c_m\}$ ,  
1 = hexane, 2 = octane, ..., m = Xane
- ◆  $S = c_1 S_1 + c_2 S_2 + c_3 S_3 + \dots + c_m S_m$

▶ or in matrix notation  $s c = S$ :



- ▶ if we look at exactly as many spectral peaks as there are components in the mixture 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
  - ◆ well, we can establish some constraints ...
- ▶ if we have more spectral peaks than components in the mixture then what to do?
- ▶ more peaks than components means we have “extra data” *that we can use to improve the precision of our result – a sensor fusion opportunity*

# pseudo-inverse method

▶ the trick is to multiply both sides of the equation by  $\mathbf{s}^T$ :

$$\begin{aligned} \diamond \mathbf{s} \quad \mathbf{C} &= \mathbf{S} \\ (n_{peaks} * n_{components}) (n_{components} * 1) &= (n_{peaks} * 1) \end{aligned}$$

$$\begin{aligned} \diamond \mathbf{s}^T \quad \mathbf{s} \quad \mathbf{C} &= \mathbf{s}^T \mathbf{S} \\ (n_{components} * n_{peaks}) (n_{peaks} * n_{components}) (n_{components} * 1) \\ &= (n_{components} * n_{peaks}) (n_{peaks} * 1) \end{aligned}$$

◆ note that  $\mathbf{s}^T \mathbf{s}$  is square, so it (generally) has an inverse



$$\mathbf{c} = (\mathbf{s}^T \mathbf{s})^{-1} \mathbf{s}^T \mathbf{S}$$

$$(n_{\text{components}} * 1) =$$

$$(n_{\text{components}} * n_{\text{components}}) (n_{\text{components}} * n_{\text{peaks}}) (n_{\text{peaks}} * 1)$$

- ▶ the calculated component concentrations are optimal: *exactly* the same as 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  $\mathbf{s}^T \mathbf{s}$  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 ...

- ▶  $\mathbf{c} = (\mathbf{s}^T \mathbf{s})^{-1} \mathbf{s}^T \mathbf{S}$  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  $\mathbf{S}$  and a “predicted” data set  $\mathbf{S} = \mathbf{s} \mathbf{c}$ :
  - ◆  $\Sigma = \text{Sum}((\mathbf{s} \mathbf{c} - \mathbf{S})_i \text{ over all } n_{\text{peaks}} \text{ spectral peaks})$   
 $d\Sigma / dc_j = 0$  gives  $n_{\text{components}}$  simultaneous equations which when you solve them for  $\{\mathbf{c}\}$  gives the same result as the pseudo-inverse

- ▶ but (to keep the notation and discussion simple) *I've left out something important*: 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)
- ▶ specific ad hoc weighting schemes are often hard to justify with first-principles arguments

# exercise

- ▶ the following table shows the major peaks in the mass spectrum of a mixture of FC-43 and FC-70; you can find their individual spectra at <http://www.sisweb.com/index/referenc/mscalibr.htm>; use the “EI Positive Ion ...” data; estimate the fractions of FC-43 and FC-70 in this mixture; first do a “quick and dirty estimate”, then do it as precisely as you can given the data at your disposal; do you get the best result by using all the data, or might it be better to discard, e.g., data from some of the smaller peaks?

amu	mixture
69	100.0
100	11.3
114	4.6
119	11.4
131	22.5
169	3.5
181	11.0
219	13.3
264	3.4
269	14.9
314	2.9
414	0.9
502	0.7
514	0.6

note: amu means  
 “atomic mass units”  
 (called “daltons”, by  
 chemists and biologists)

all the peaks are  
 normalized to  
 the biggest one  
 ( $\text{CF}_3 \leftarrow 69 \text{ amu}$ )