Analytical Methods

OSHA Health Response Team

12 IHs , chemical engineers, and civil engineers

-Substantial field experience
-Unique individual skills
-Suite of specialized equipment

Generic NIOSH Method Format

NAME OF SUBSTANCE **METHOD #**

FORMULA Molecular Weight Chemical Abstracts Service # RTECS #

Method numbers are the same as those in the 3rd edition. Evaluation (Full, Partial, Unrated) is assigned as described on p. 5 of the "blue pages". Issue date reflects current version (August 15, 1993) and previous 3rd edition versions, if any.

OSHA : These exposure limit values are
NIOSH: those in effect at the time of
ACGIH: printing of the method.

PROPERTIES: Boiling/melting points, equilibrium vapor pressure, and density help determine the sample aerosol/vapor composition.

SYNONYMS: Common synonyms for the substance, including Chemical Abstracts Service (CAS) numbers; these are all listed alphabetically in the Index of Names and Synonyms ("yellow pages" in this Manual).

SAMPLING

SAMPLER: Brief description of sampling EQUIPMENT

FLOW RATE: Acceptable sampling range, L/min

VOL-MIN: Minimum sample volume (L); corresponds to Limit of Quantitation (LOQ) at OSHA PEL

-MAX: Maximum sample volume (L) to avoid analyte breakthrough or overloading

BLANKS: Each set should have at least 2 field blanks, up to 10% of samples, plus 6 or more media blanks in the case of coated sorbents, impinger solutions, or other

ACCURACY

Data are for experiments in which known atmospheres of the substance were generated and analyzed according to the method. Target accuracy is less than 25% difference from actual concentration at or above the OSHA PEL.

MEASUREMENT

TECHNIQUE: The measurement technique used

ANALYTE: The chemical species actually measured

A summary of the measurement EQUIPMENT, SAMPLE PREPARATION, and MEASUREMENT steps appearing on the second page of the method is given here.

CALIBRATION: Summary of type of standards used

RANGE: Range of calibration standards to be used; from LOQ to upper limit of measurement (Note: More concentrated samples may be diluted in most cases to fall within this calibration range.)

ESTIMATED LOD: Limit of detection (background + 3σ)

PRECISION ($\bar{S}_r$): Experimental precision of spiked samplers

APPLICABILITY: The conditions under which the method is useful, including the working range in mg/m^3 (from the LOQ to the maximum sampler loading) for a stated air volume are given here.

INTERFERENCES: Compounds or conditions which are known to interfere in either sampling or measurement are listed.

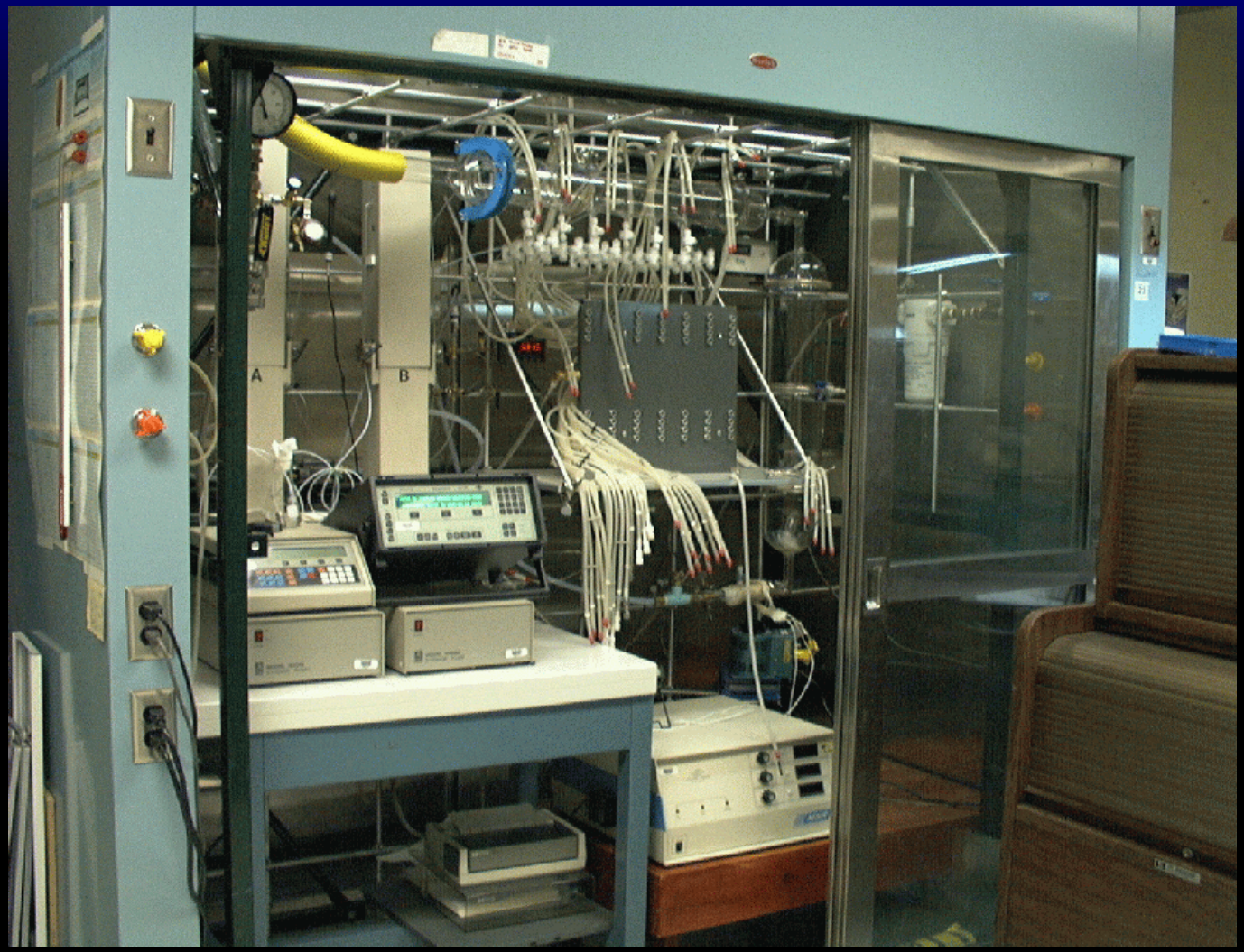
OTHER METHODS: Methods from the 2nd edition ("P&CAM" and "S" methods) which are related to this one, as well as similar OSHA and literature methods are keyed to REFERENCES.

OSHA: Enforcement

NIOSH: Research

- Some OSHA exposure standards contain monitoring accuracy requirements
- Traditional NIOSH criteria has been ±25% of the true value

OSHA Methods Development



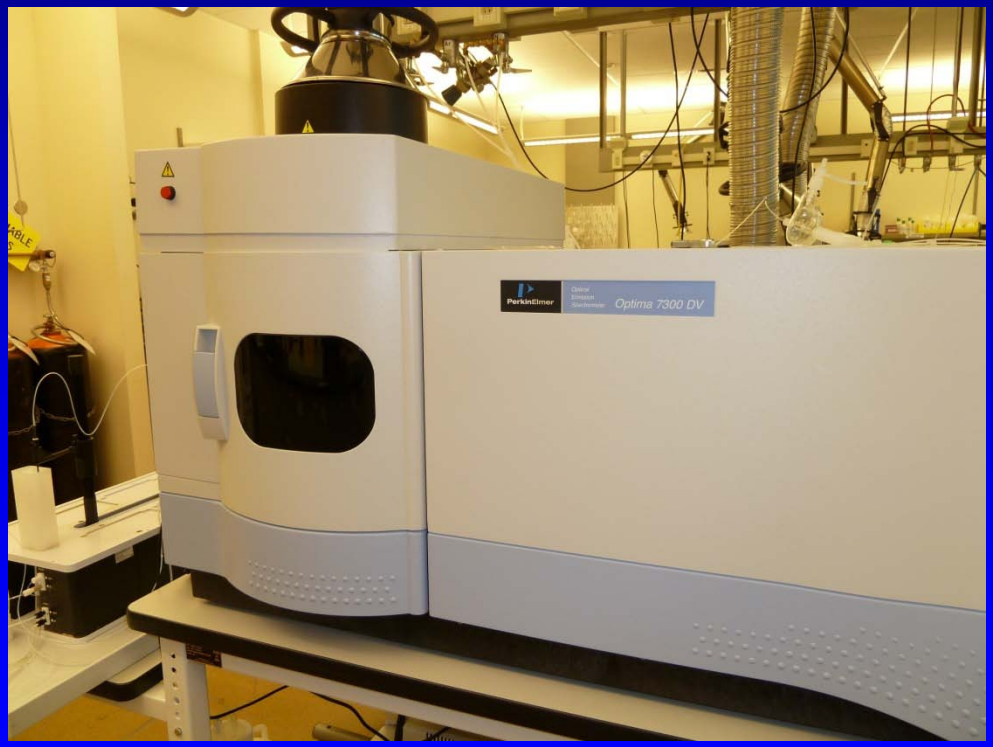
Metals

Emission Spectroscopy: simultaneous emission at discrete frequencies (element-specific) from high energy plasma; can detect multiple elements simultaneously

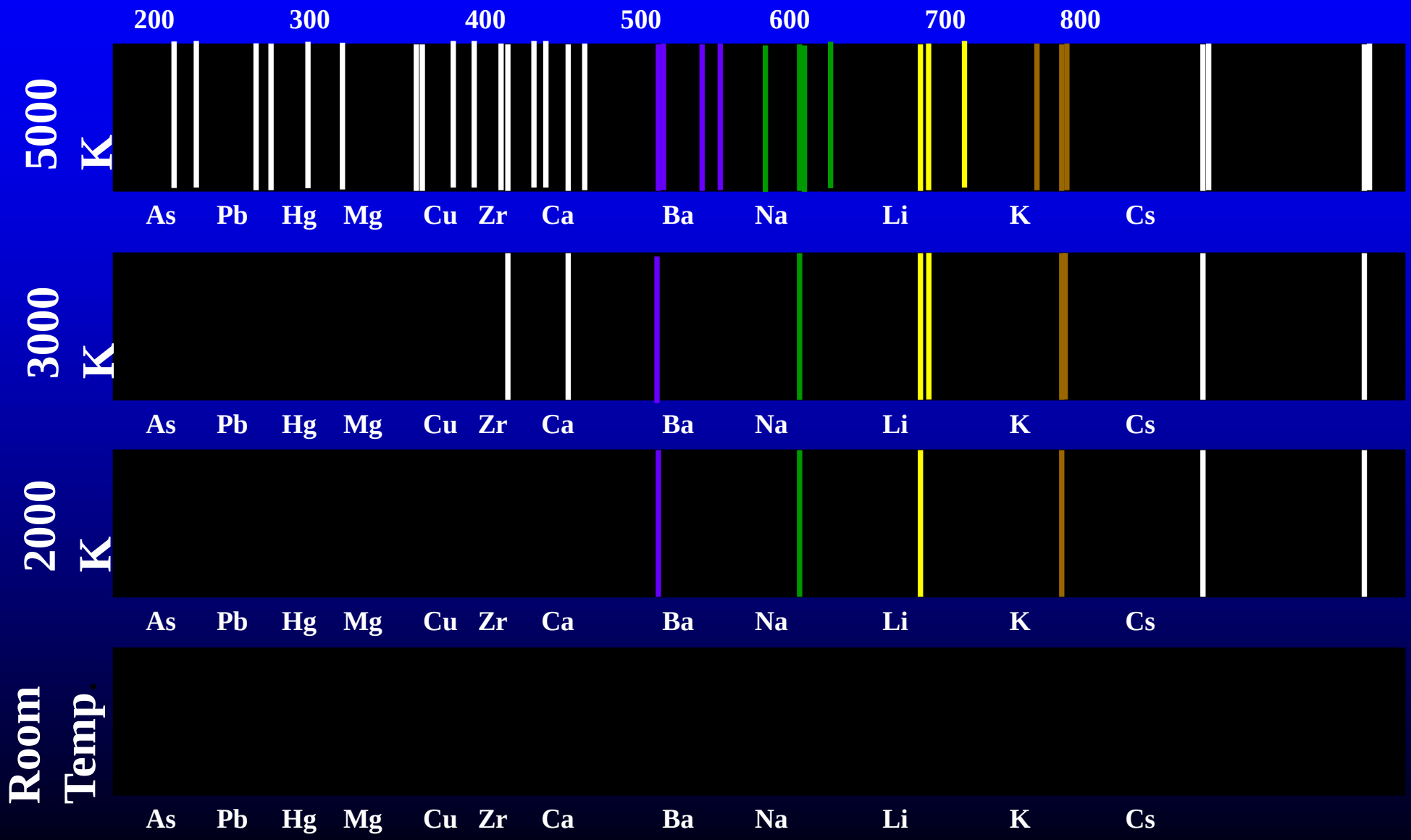
Absorption Spectroscopy: detects a single specific (can be selected) element in a high energy flame; a filament made of the same element irradiates the sample and the absorbance of the flamed sample is proportional to the concentration of that single analyte in the flame

Inductively Coupled Plasma (ICP)

ICP-OES: optical emission spectroscopy



Effect of Temperature on Emission



Inductively Coupled Plasma (ICP)

Analyze a variety of elements simultaneously

Single exposure gives entire spectrum for these

Intensities depend on temperature, excitation

High temperatures give complex spectra

Concentrations determined from calibration with reference samples

Inductively Coupled Plasma (ICP)

ICP-MS: mass spectrometry – may be used to speciate isotopes as MS detects elements once ionized, with the initial composition not particularly relevant (more on MS later)

Atomic Absorption (AA)

Great versatility – many elements can be analyzed

High accuracy, low detection limits

Microsamples can be determined

Rapid, straightforward technique

Simple, inexpensive instruments

Limited to one element at a time

Less suited for bulk samples

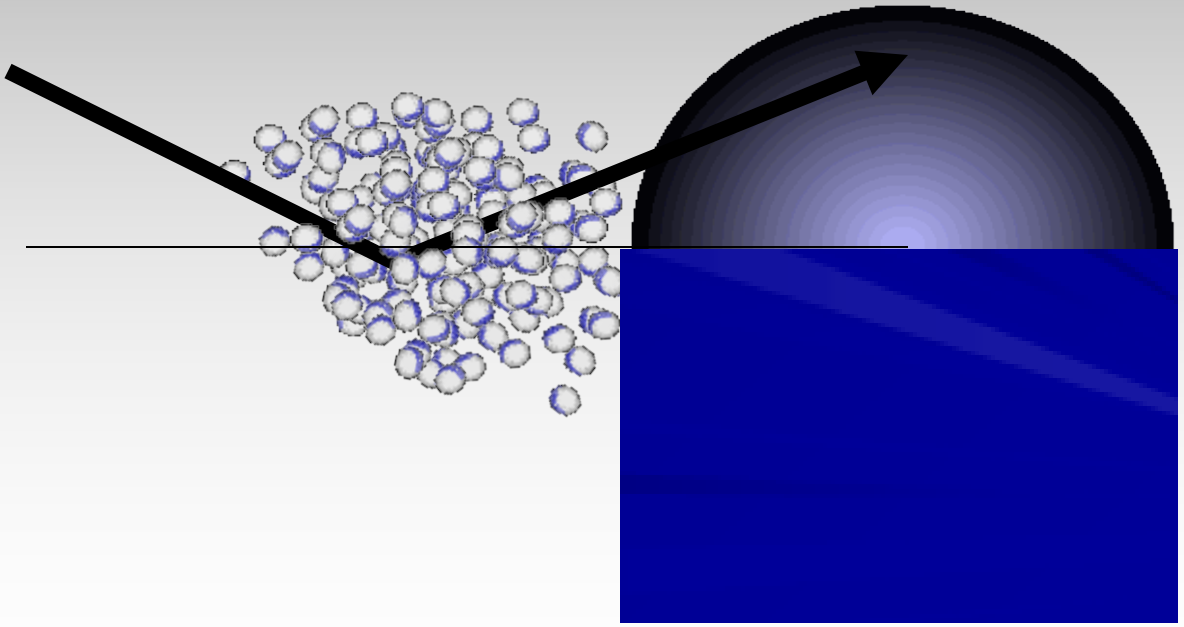
Crystalline Silica

X-Ray Diffraction -Bragg equation

$$n\lambda = 2\,d\,\sin\theta$$

Amorphous –

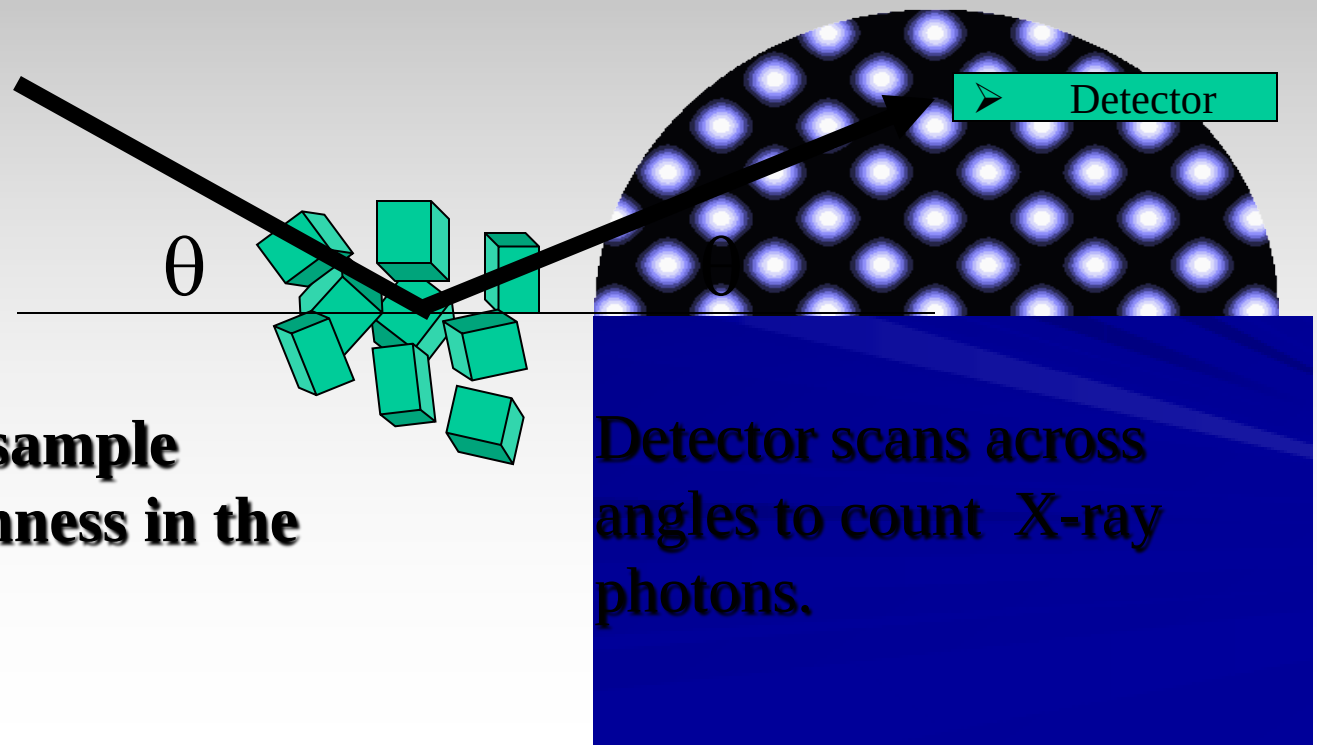
Having no real or apparent crystalline form.



Crystalline dusts –

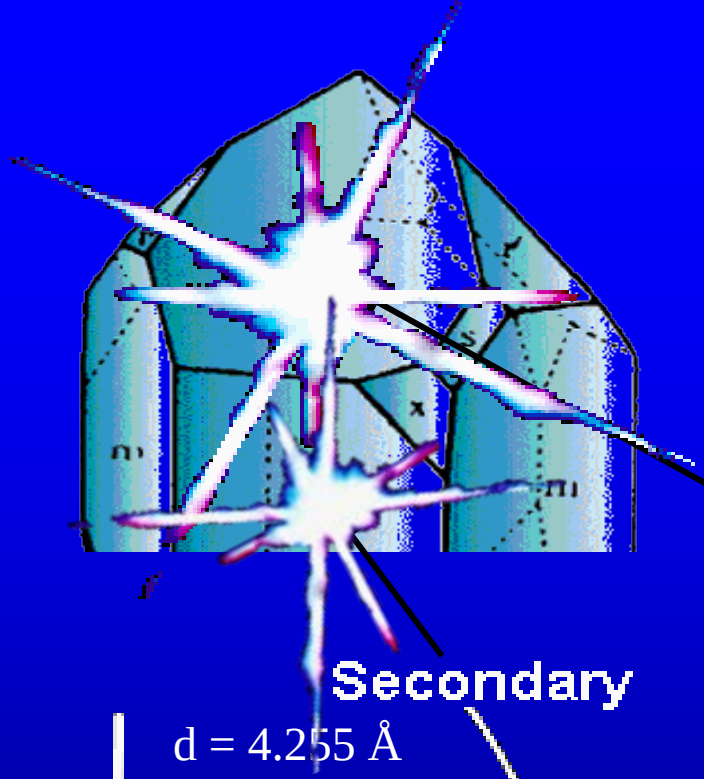
Each dust-size piece of crystal may diffract X rays producing higher intensity spots at different angles.

X-ray diffracts off millions of randomly orientated dust particles creating spots that combine to form arcs.

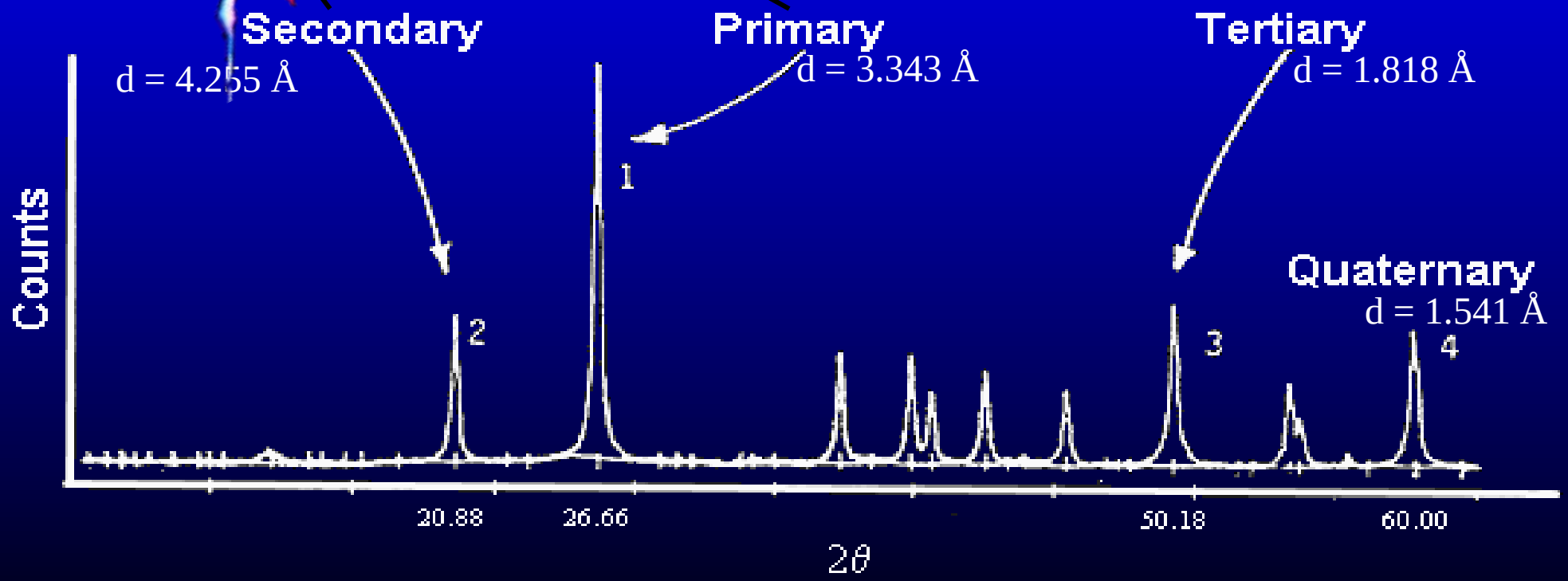


Spinning the sample improves evenness in the arcs.

Detector scans across angles to count X-ray photons.



Some of the diffraction peaks are readily associated with facets on the more common quartz crystal habits.



Frondel, Clifford: Dana's System of Mineralogy, 7th Ed. Vol. III pg 49 ff. (1962).

OSHA PEL for Respirable Dust Containing Quartz

It can be shown mathematically that when this PEL function is divided into the TWA exposure, the resulting severity calculated is the sum of the severities of the individual quartz and PNOR exposures. This is virtually the same result one would obtain using the mixture calculation for exposures to substances having an additive effect on the body or target organ system.

$$\text{Severity} = \frac{C_1}{PEL_1} + \frac{C_2}{PEL_2} + \ldots + \frac{C_n}{PEL_n}$$

OSHA PEL

OSHA Occupational Safety and Health Administration

To use the OSHA PEL for crystalline silica, two types of analyses are required.

- A gravimetric measurement is necessary to determine the total sample weight for calculating both the TWA exposure and the % Quartz.
- The mass of quartz in the sample needs to analytically determined to enable the calculation of the % Quartz.

The Quartz SAE reported out with the lab analyses applies to the mixture, i.e., the respirable dust containing quartz and provides a conservative estimate taking into account the pump error in the sampling and both the gravimetric and quartz analytical errors.

Gravimetric Methods

Total Dust: PVC Filter –MCEF adsorbs water

Total Extractables: e.g., coal tar pitch volatiles, uses benzene extraction of glass fiber filter

Organics

High Performance Liquid Chromatography (HPLC)

Gas Chromatography (GC)

HPLC

Large organics with low volatility (polar, high molecular weight, e.g. TDI)

Requires organic solvent and often aqueous mobile phase

- **Martin and Synge, 1940s (later won Nobel Prize); Chloroform (mobile phase), water-impregnated silica gel (stationary phase)**

- **Modern HPLC uses "reverse phase" (RP) non-polar columns and initially a more polar mobile phase (e.g., water with ACN) ; gradient elution**

- **Packed columns**

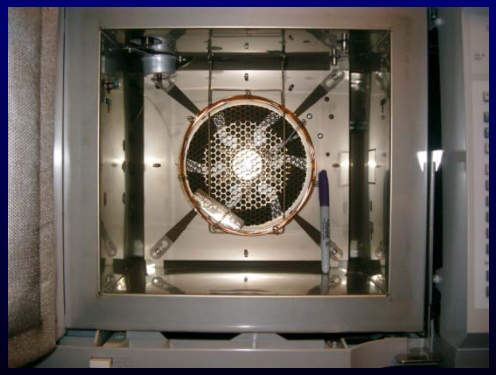
GC

Organics that may be made volatile at “reasonable” temperatures (currently up to 400 C)

Requires analytical column and a means to precisely control the column temperature

Martin and James, gas/liquid chromatography 1950s; N_2 (mobile phase), high molecular weight liquid film (stationary phase); packed columns

Modern GLC uses open tubular fused silica column with cross-linked siloxane polymer “liquid” film bonded/immobilized to the interior surface of the column



He or H_2 offer better performance (separation ability), are now the predominant carrier gases

Air-bath convection oven is usually used to heat column

Sorbents Subjected to GC Analysis

Charcoal: activated charcoal is the most widely used solid sorbent in IH applications

Silica gel: polar, hygroscopic material -humidity is important factor

Porous polymers: e.g. "Tenax" a polymer of 2,6-diphenyl-p-phenylene oxide -high thermal stability, less reactivity, also less surface area compared to charcoal

Coated materials (on-tube derivatization): e.g. aldehyde collection with coated resin

UNITY
MARKES
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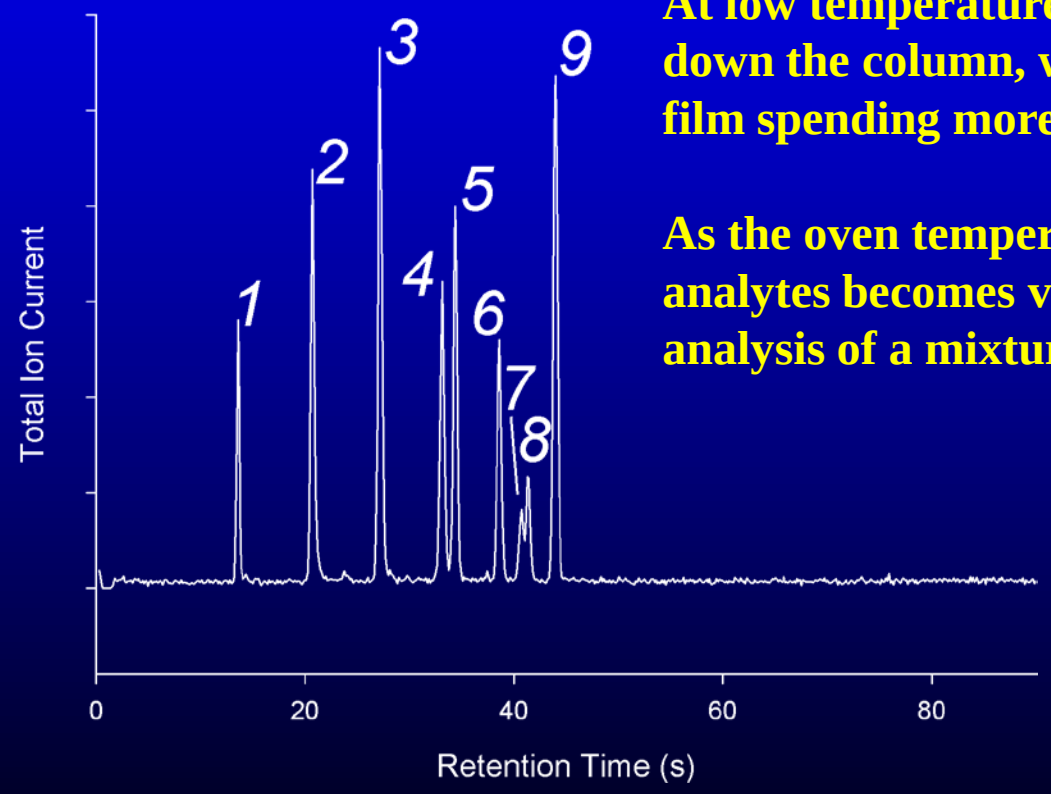
Chromatogram



Analytes have different solubility in stationary phase liquid film –however temperature dependent volatility (boiling point) is the primary factor for separation

At low temperature light analytes are volatile and they move down the column, with those that are highly soluble in the film spending more time there (eluting later)

As the oven temperature is ramped higher a wide range of analytes becomes volatile; temperature programming allows analysis of a mixture with wide volatility range

GC Detectors

Many detectors developed for GC have gone on to become stand-alone handheld detectors: FID, PID, TCD

Flame ionization detector (FID): hydrocarbons – H_2 flame creates ions which are counted at an electrometer; **stable, wide dynamic range, non-selective (universal for hydrocarbons that may be burned), CS_2 does not respond well and is thus frequently used to desorb CT samples for GC-FID analysis**

Photoionization detector (PID): selective (depends on energy of uv source used to ionize) - ions thus created are counted at an electrometer; high concentrations of water vapor or compound that does not ionize will interfere with quantitative measurements

Thermal conductivity detector (TCD): universal detector but not very sensitive - different gases or vapors have different heat transfer properties and the temperature variation of a heated cell (compared to unexposed cell) is translated to a detector signal

Electron capture detector (ECD): electronegative (halogenated) compounds or those with (e.g. nitro) functional groups-standing current from an electron source (e.g., ^{63}Ni) is disrupted when such an analyte passes through the detector; **extremely sensitive, but selectively so, short linear dynamic range**

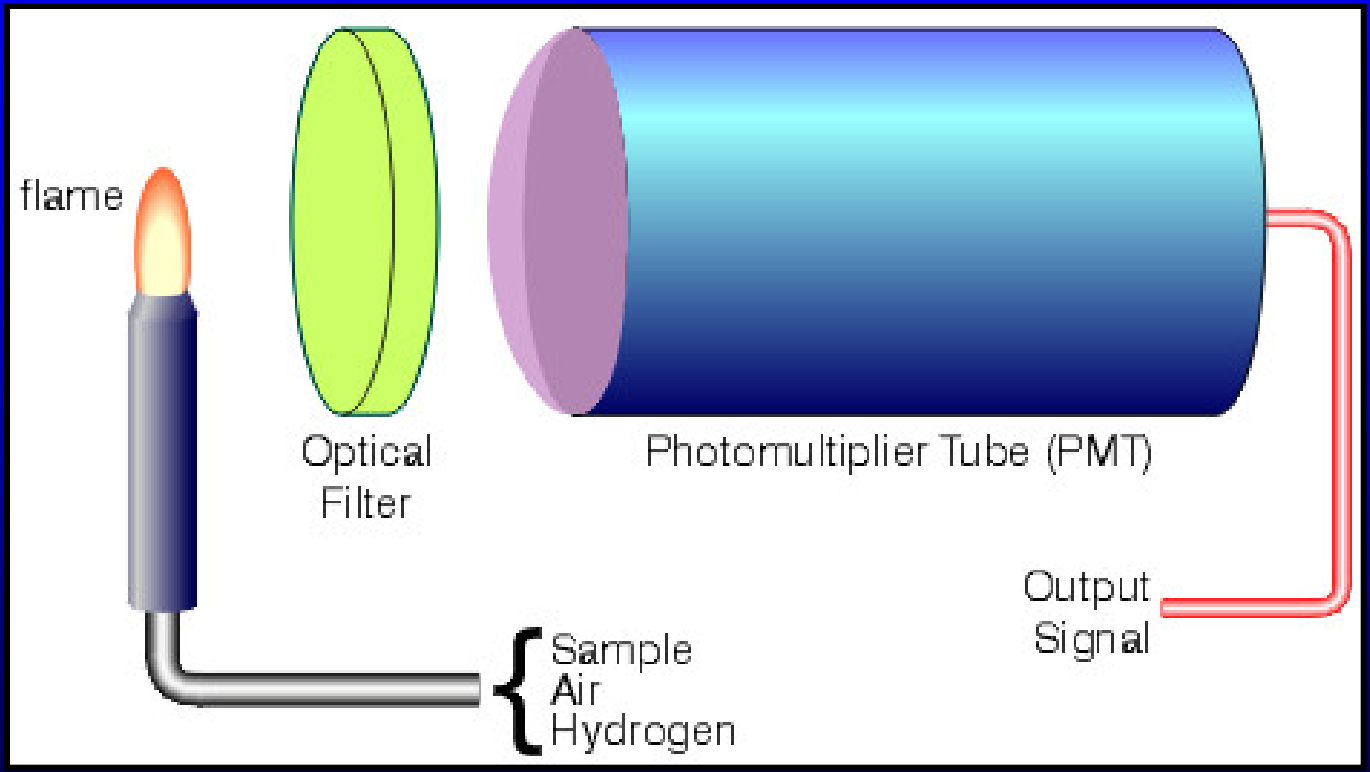
Flame Photometric Detector (FPD)

Dual channel FPD can detect compounds that contain either S or P selectively, and with great sensitivity

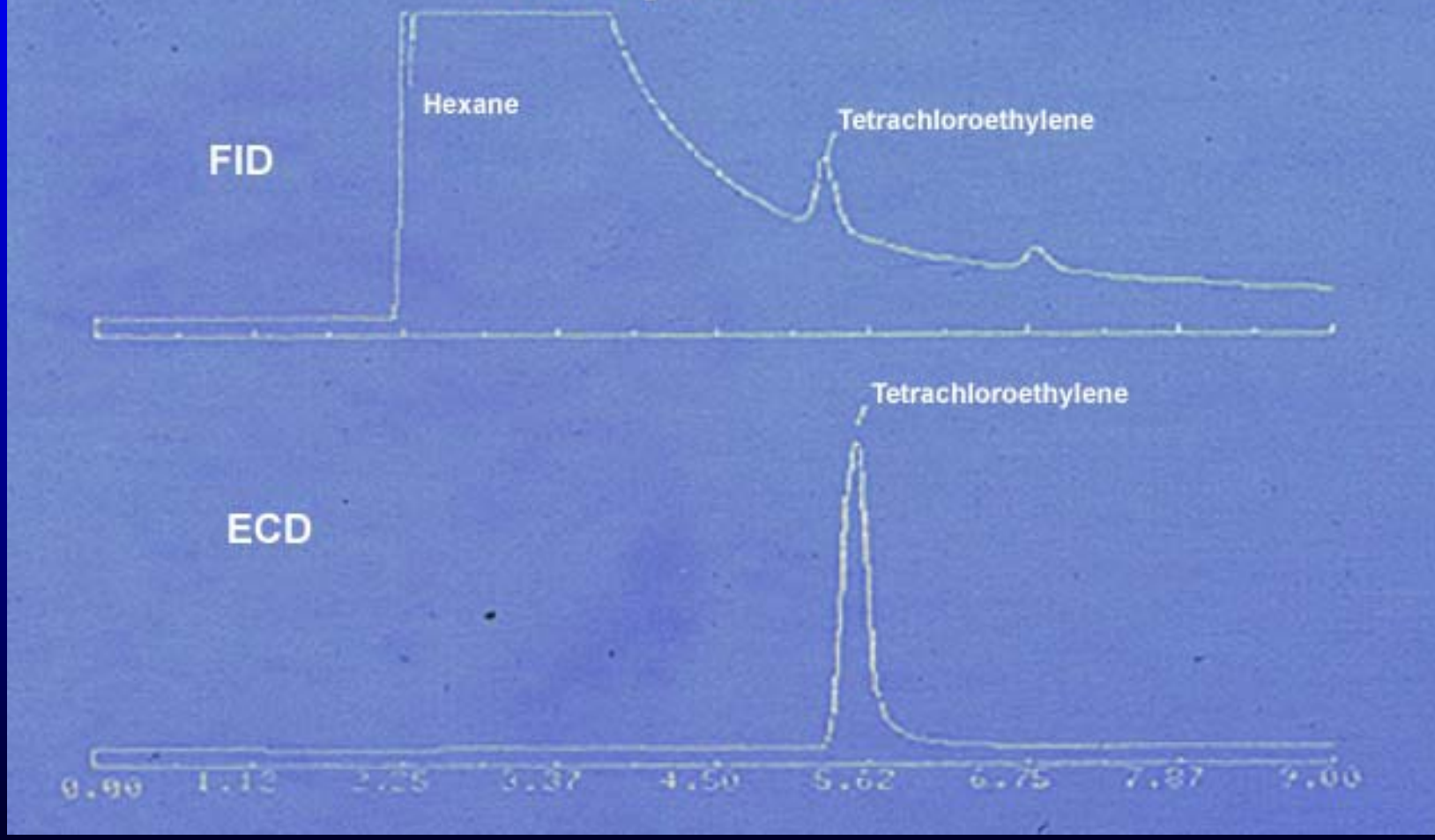
This is a specialized emission sprctroscopy method that monitors only two wavelengths (one for each element), combined with gas chromatography

A handheld FPD is also available, primarily used by military organizations to detect CWA analytes that often contain either (or both) of these elements

Flame Photometric Detector (FPD)



Comparison of Detector Responses



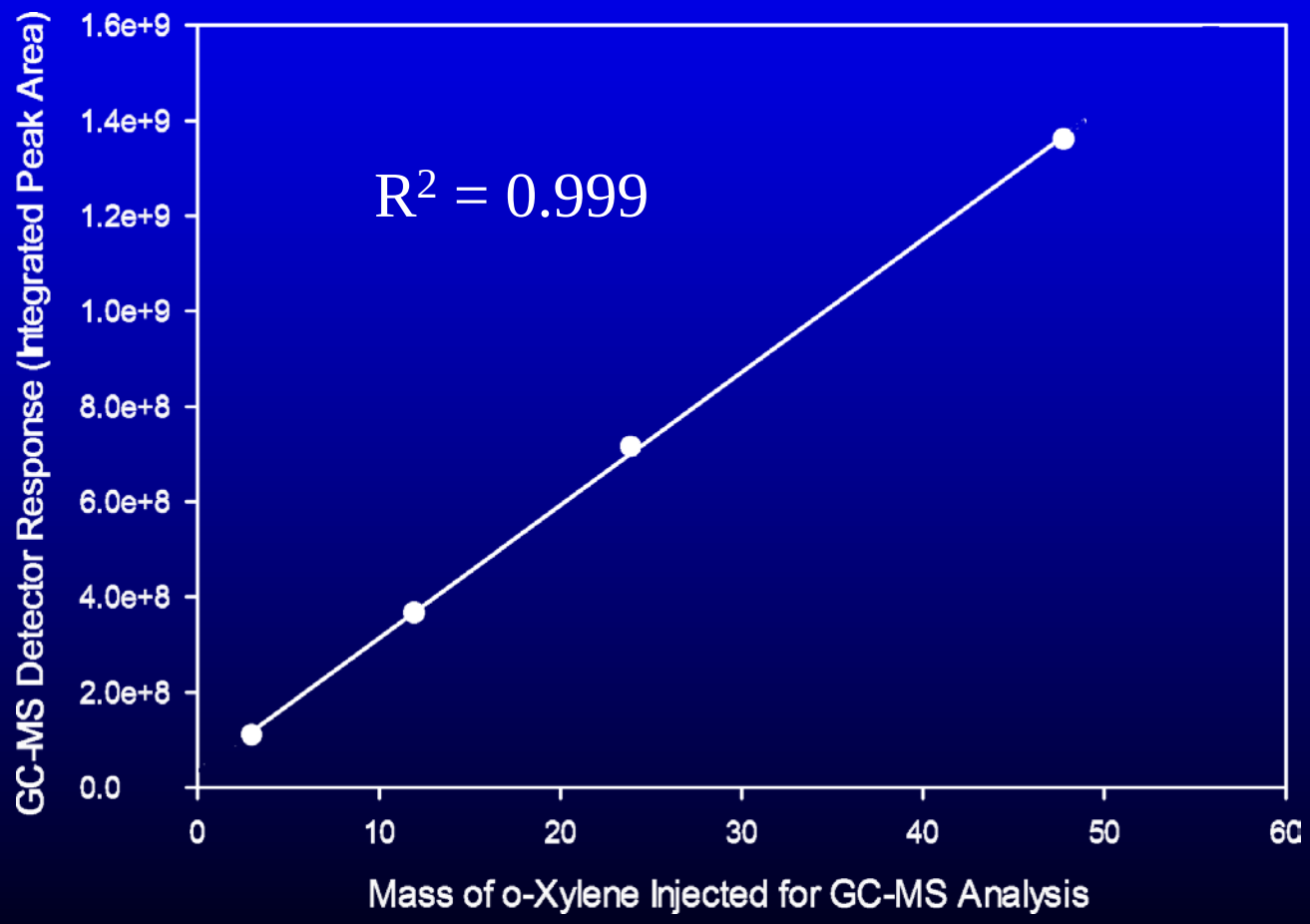
GC Column Stationary Phases

Liquid Film Types – typically used for hexane and higher analytes: polydimethylsilicone (e.g., DB-1, DB-5); polyethylene glycol (PEG); carbowax

Adsorptive (solid) types – typically used for light gases/vapors and permanent gases: Poropak, PLOT (porous layer open tubular – various sorbents), Chromosorb, Alumina

Quantitative GC

Calibration curve needed: mass of analyte injected (x-axis) plotted against GC detector response (GC peak area, y-axis)



y (peak area) is determined experimentally for unknown:

$y = mx + b$

Mass Spectrometric Detector

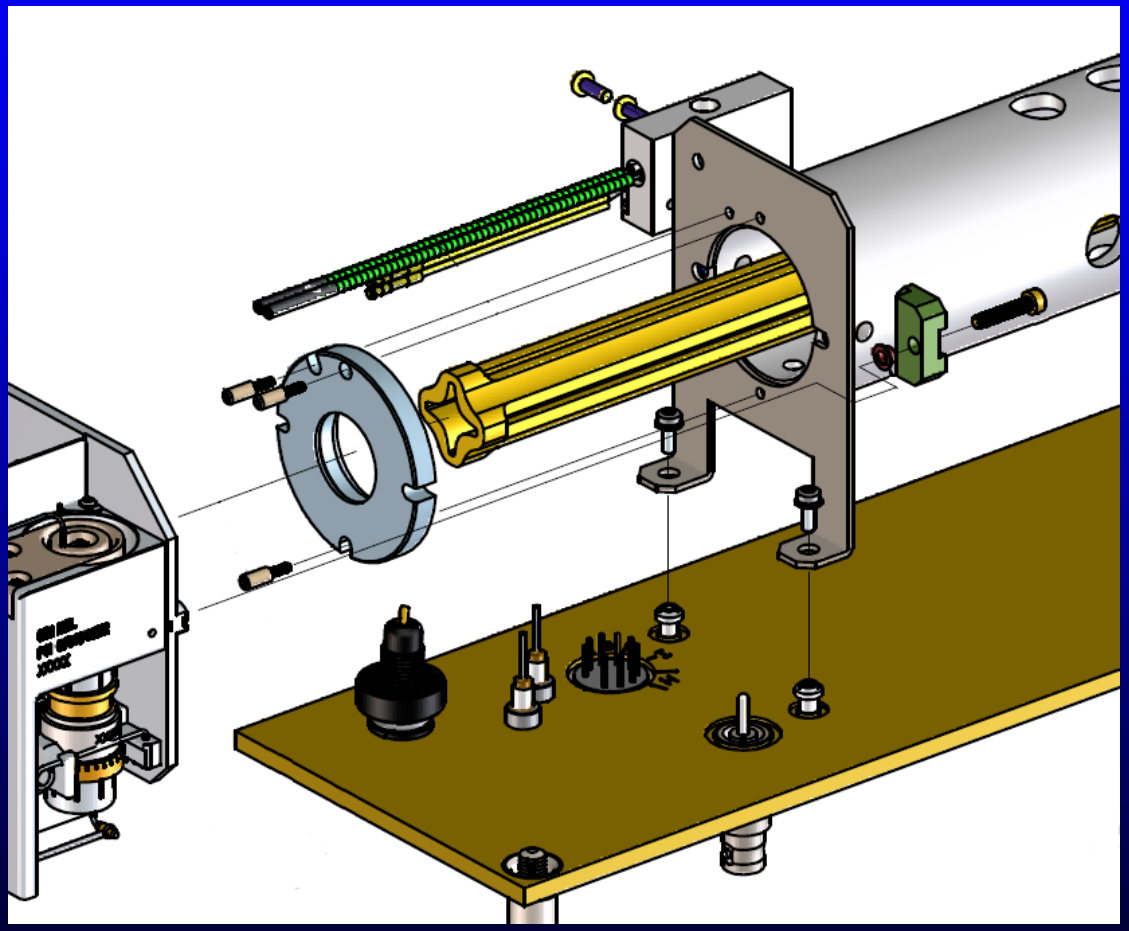
Mass spectrometry measures the mass-to-charge ratio of ions. When molecules of a pure compound are reproducibly fragmented and ionized, the method provides a mass spectrum that can be used to determine the chemical composition of the material

A mass spectrum can be interpreted following predictable rules, and can be searched against a mass spectra database to help identify initially unknown compounds

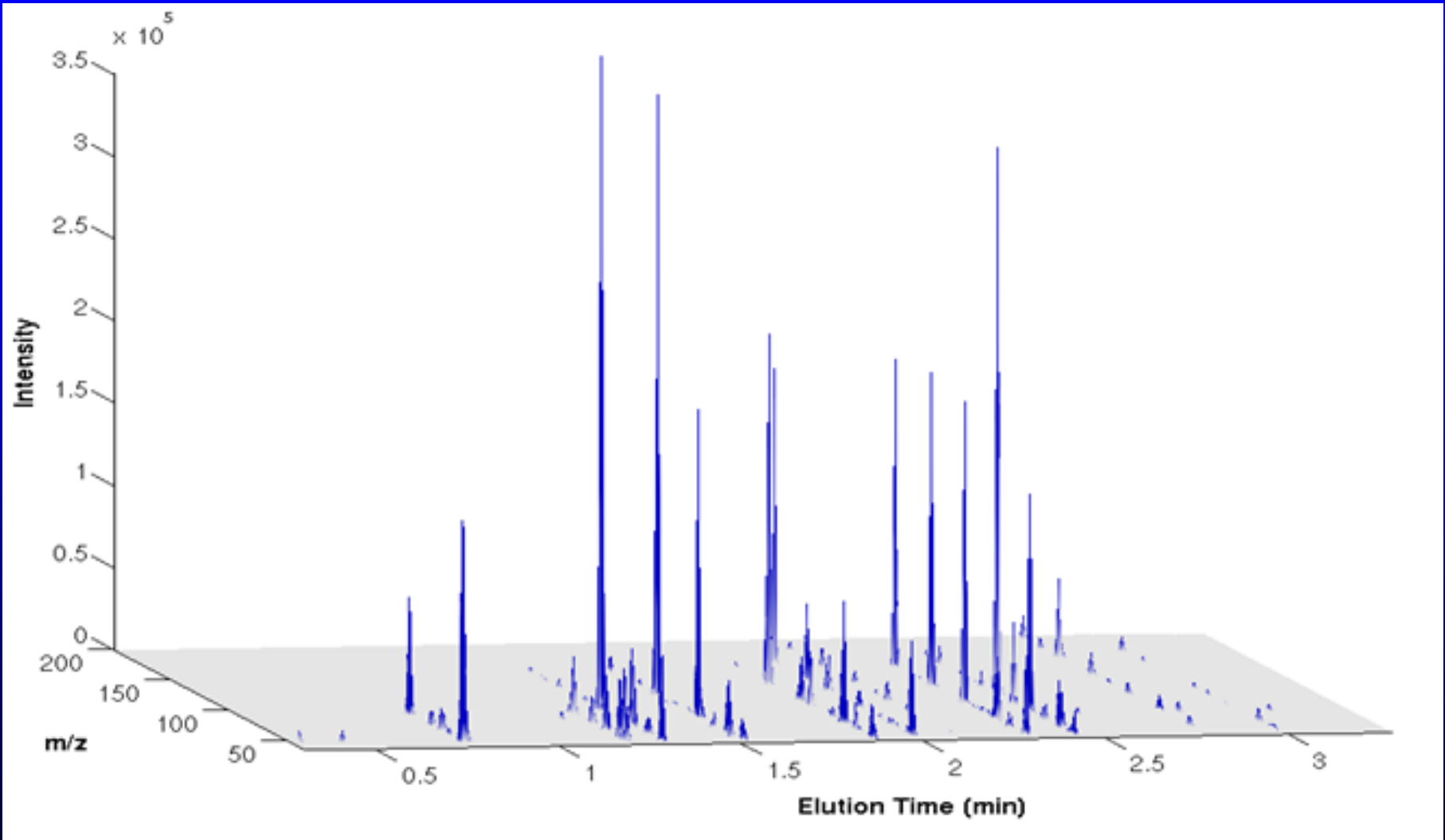
A mass spectrum can be like a “fingerprint” for a given chemical

GC/MS can provide "high-certainty" identification of chemical components - even trace-level chemicals in complex mixtures – 3-dimensional data are produced

Mass Spectrometric Detector



3-Dimensional GC-MS Data



EI Mass Spectrum

Basis for Electron Ionization MS

$CH_3OH + e^-$ $\quad 2e^- \quad + \quad CH_3OH^{\bullet+}$

32 *m/z*,molecular ion (not stable in this case)

$CH_3OH^{\bullet+}$ $\quad H^\bullet \quad + \quad CH_2OH^+$

31 *m/z*, peak with greatest intensity (100% or base peak)

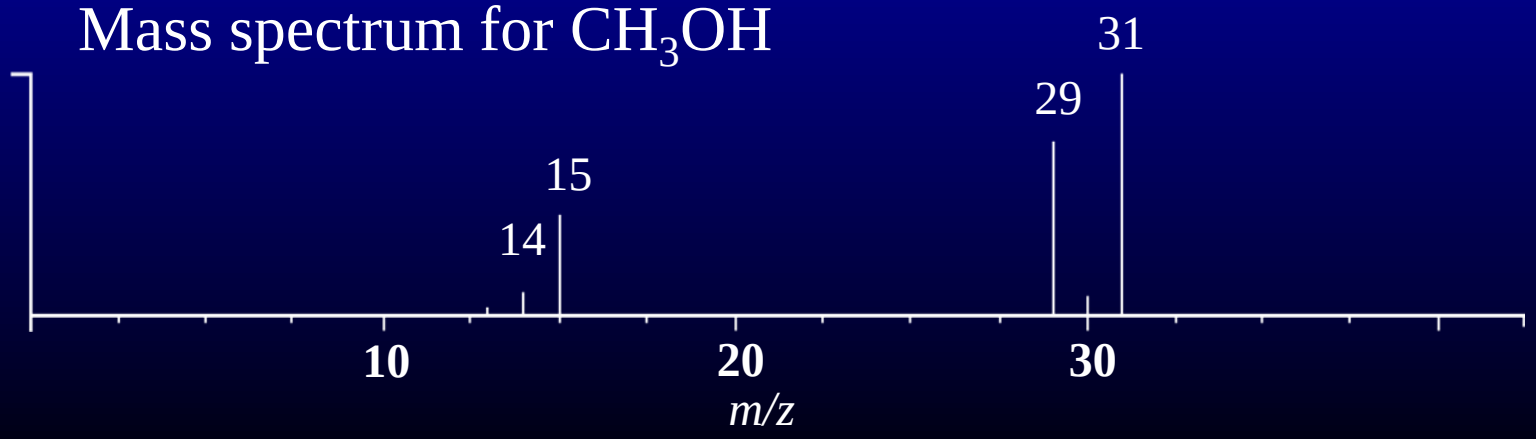
$CH_3OH^{\bullet+}$ $\quad OH^\bullet \quad + \quad CH_3^+$

15 *m/z*, (45%, relative to 31 *m/z* peak @ 100)

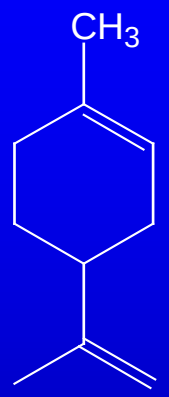
CH_2OH^+ $\quad H_2 \quad + \quad CHO^+$

29 *m/z*, (85%, relative to 31 *m/z* peak @ 100)

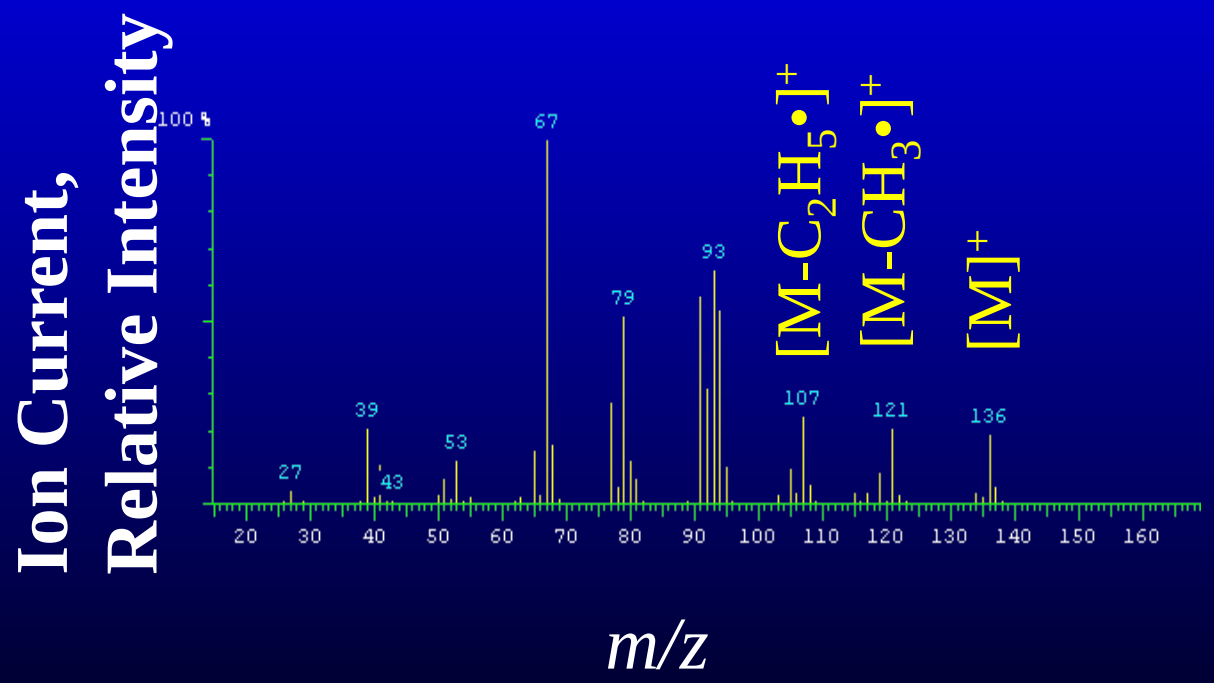
Mass spectrum for CH_3OH



Example EI Mass Spectrum



D-limonene



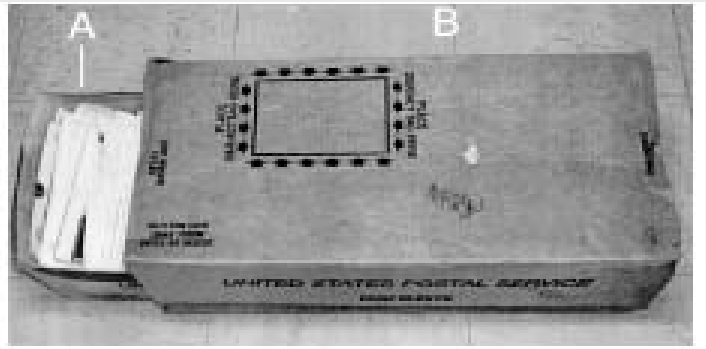
GC/MS Field Analysis Case Study

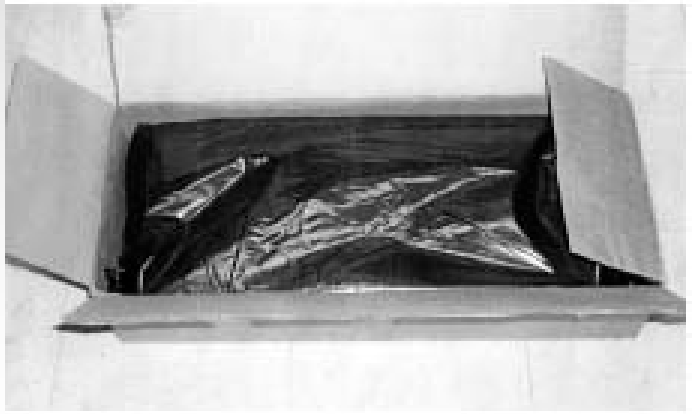
Problem: Initially unknown exposures to volatile organic chemicals among legislative workers handling mail irradiated as a protection against anthrax

Why use GC/MS for this problem?

(1) Complex mixture with many trace components

(2) Initially, composition completely unknown





GC/MS Field Analysis Case Study – Irradiated Mail

A seemingly simple question: “what’s in the sample?”

Complexities of GC/MS analysis are demonstrated by this project: initial qualitative screen needed first, then different (non-standard) column and sample introduction methods needed to definitively identify a good number of the VOCs present from mail irradiation

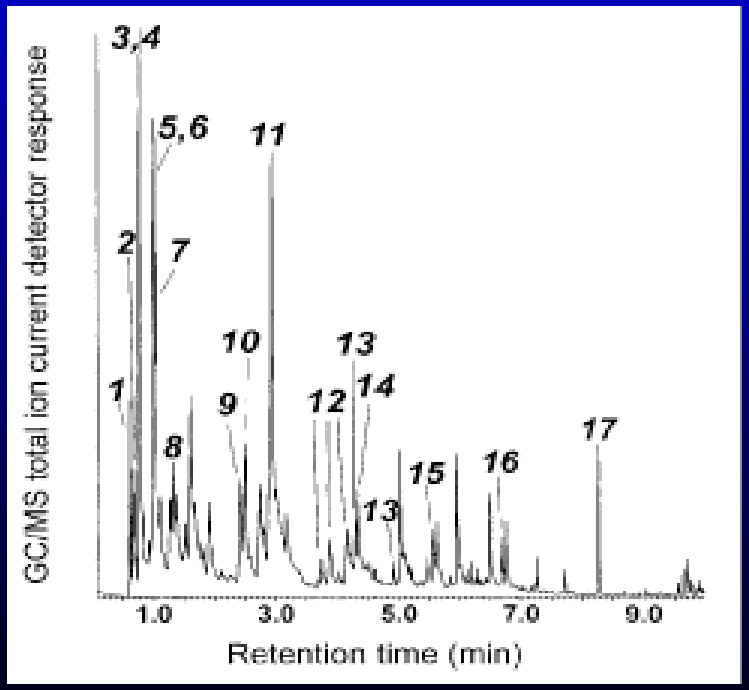
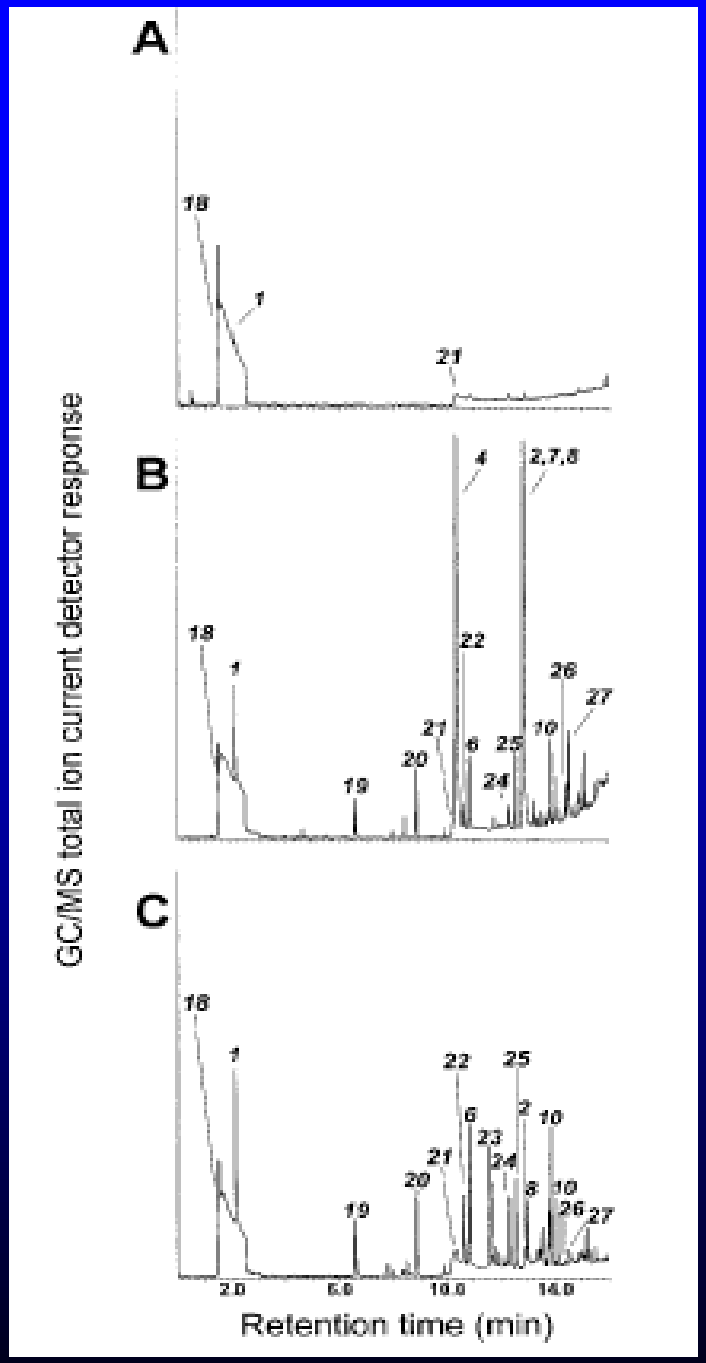
Also, quantitative sampling should not be attempted without first identifying the compounds present

Initial GC-MS Instrumentation Used

Typical GC air bath oven

GC-MS with Mobile Laboratory

Initial screening samples showed rich mix of volatile organic compounds; poor GC resolution meant that different column was needed…



GC-MS Analyses for Irradiated Mail Project Moved into Laboratory