Analytical Chemistry in the Real World

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OXFORD SUMMER COURSES

Objectives

- Learn about various chemical analytical techniques in the real world and some history
- Learn about some of the real work that chemists do in the real world
- Applications of analytical chemistry in various areas of human scientific, artistic and technical fields
- Learn about some of the most important players of analytical instrumentation

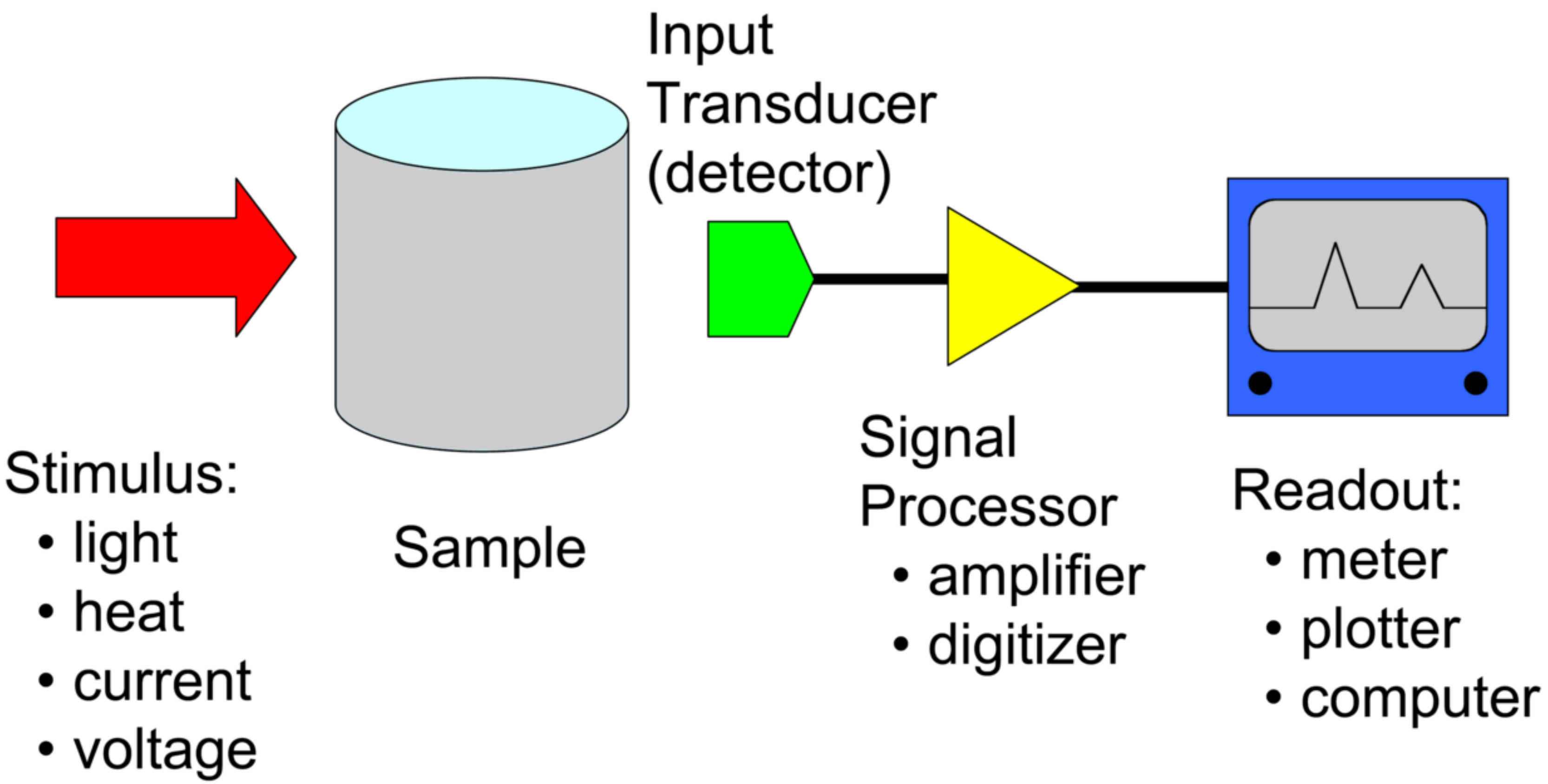
A Little Bit of History

- *History of Analytical Chemistry and how it has advanced*
- The first instrumental analysis was flame emission spectrometry developed by Robert Bunsen and Gustav Kirchhoff who discovered rubidium (Rb) and cesium (Cs) in 1860.
- Chemistry is as old as Alchemy

Analytical Techniques

- *Used to Separate, Identify and Quantify matter*
- *HPLC, LC MS, GC MS, IR, Raman, NMR, UV Vis, SEM, AFM, XRD, XRF, Titration, Dynamic Light Scattering*
- *Method Validation before application*
- *Use of software to plot data and create calibration curves and to classify data: Chemometrics and PCA*

Schematic of Analytical Instrument



Applications

- *Applications in Pharmacy and Medicine, Food Safety, The Environment, Art Conservation, Medical Lab Technology, Forensics, Polymer Science, Engineering, Water Treatment, Petrochemical industry, Sports Medicine/Doping Control, Mining, Polymer Science, Agriculture/Soil Analysis*

Pharmaceutical Analytical Chemistry

- Purify the reaction product using chromatography or filtration
- Check for impurities in the batch after it is synthesized
- Check for content uniformity
- Test for the expiration date/effect of heat and air
- Dissolution testing
- Check for metabolites in the urine and API blood levels (pharmacokinetics)

Water Analysis

- Check the conductivity
- Check what ions are in the water
- Check for harmful bacteria
- Check the turbidity
- Check for smells and tastes
- Check for hardness
- Check for number and size of particles in Ultra Pure Water
- Check for taste and odor molecules

Forensics

- Human blood or rabbit blood?
- DNA of hair or blood samples
- Materials analysis
- Identify white powders
- Poisons in the blood? Toxicology
- Explosives residue
- Detection of explosives at airports
- Detection of fake art

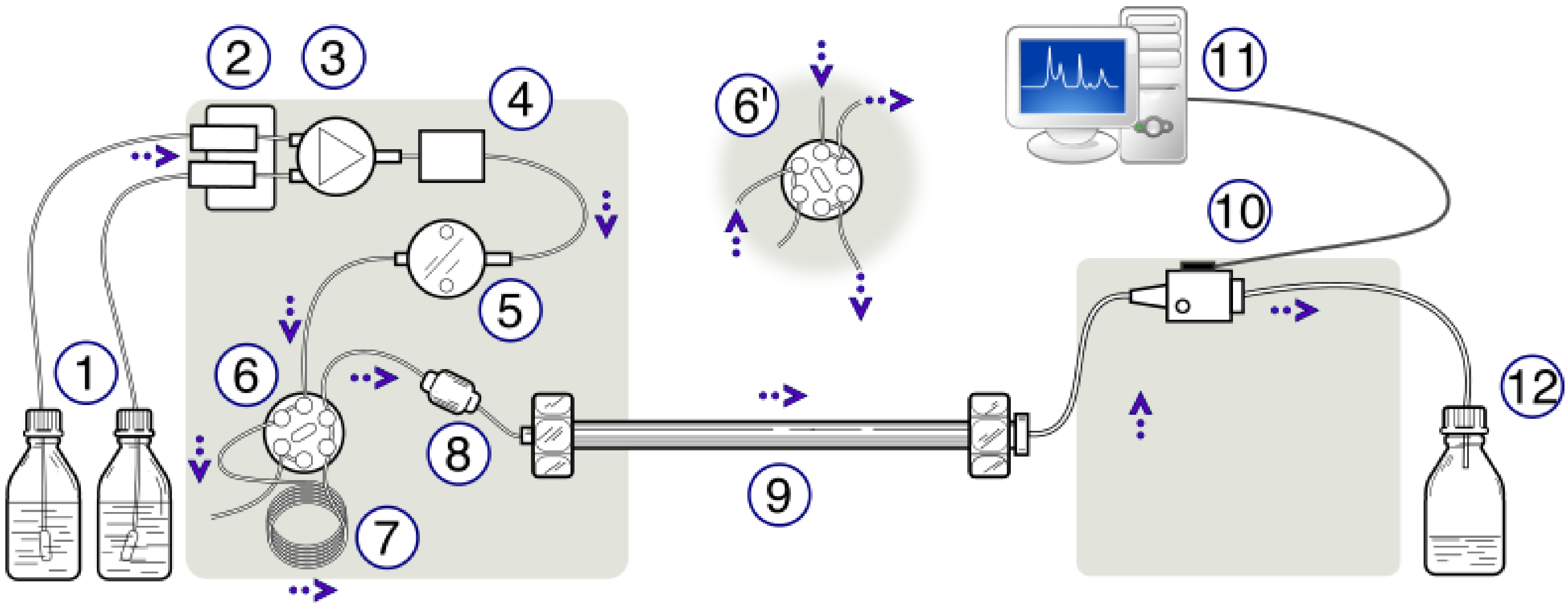
Mining

- Chemists and geochemists want to know the composition of ores
- They use techniques such as XRF for elemental analysis of the ores
- Chemists want to know the purity of the elements after they have separated such as Fe or Al or Cu or Au or Ag !!!!

Medicine

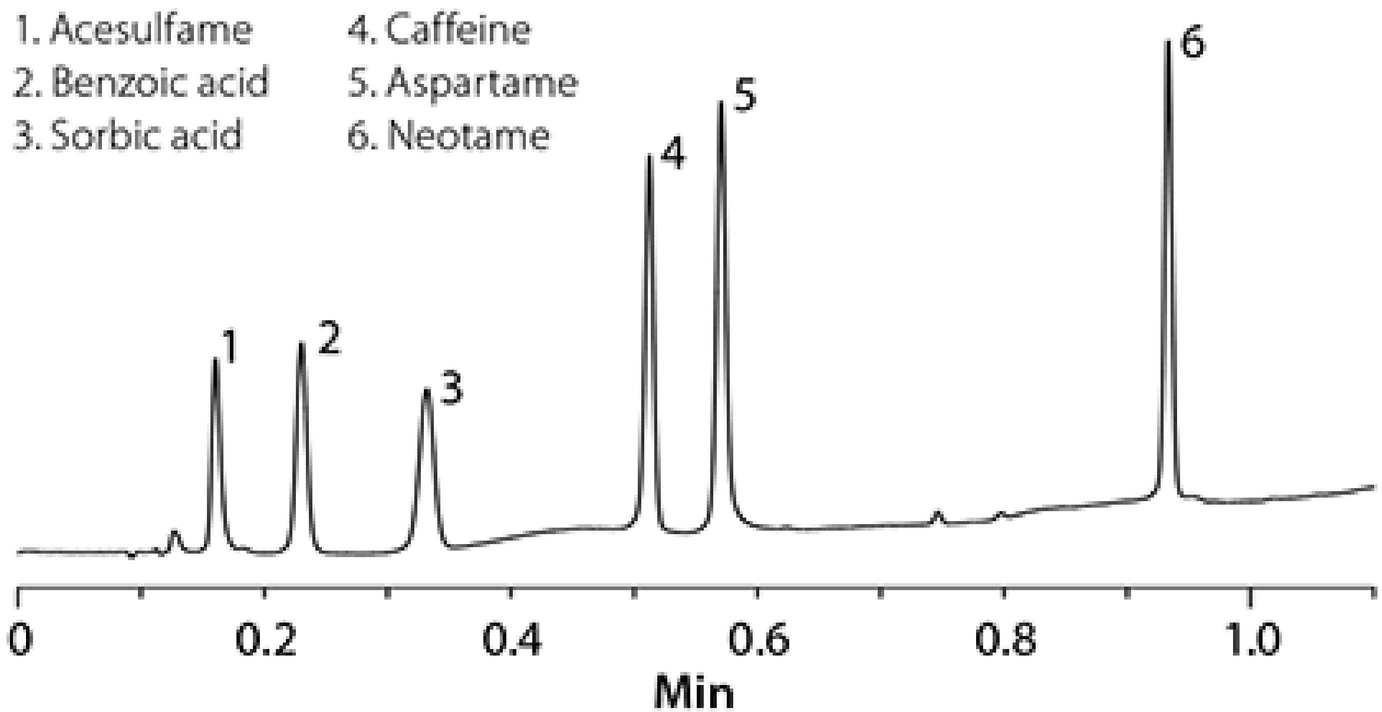
- Cholesterol in blood
- Drugs in Urine
- Drug monitoring in blood of infants
- Hormones in blood and urine
- Glucose in blood of diabetics
- Disease biomarkers
- Kidney/Liver health biomarkers in blood

HPLC Schematic

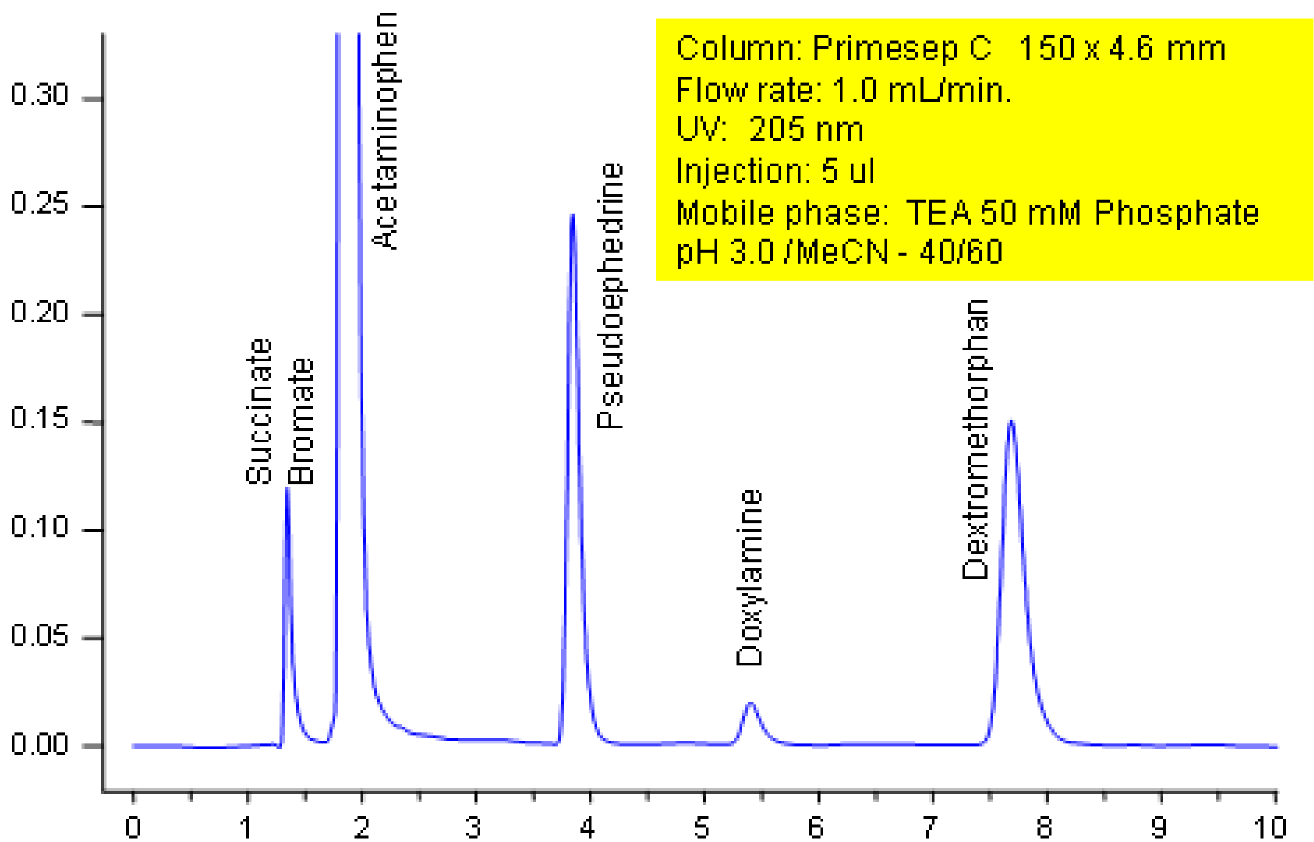


(1) Solvent reservoirs, (2) Solvent degasser, (3) Gradient valve, (4) Mixing vessel for delivery of the mobile phase, (5) High-pressure pump, (6) Switching valve in "inject position", (6') Switching valve in "load position", (7) Sample injection loop, (8) Pre-column (guard column), (9) Analytical column, (10) Detector (i.e. IR, UV), (11) Data acquisition, (12) Waste or fraction collector.

HPLC Chromatogram of a Diet Soda



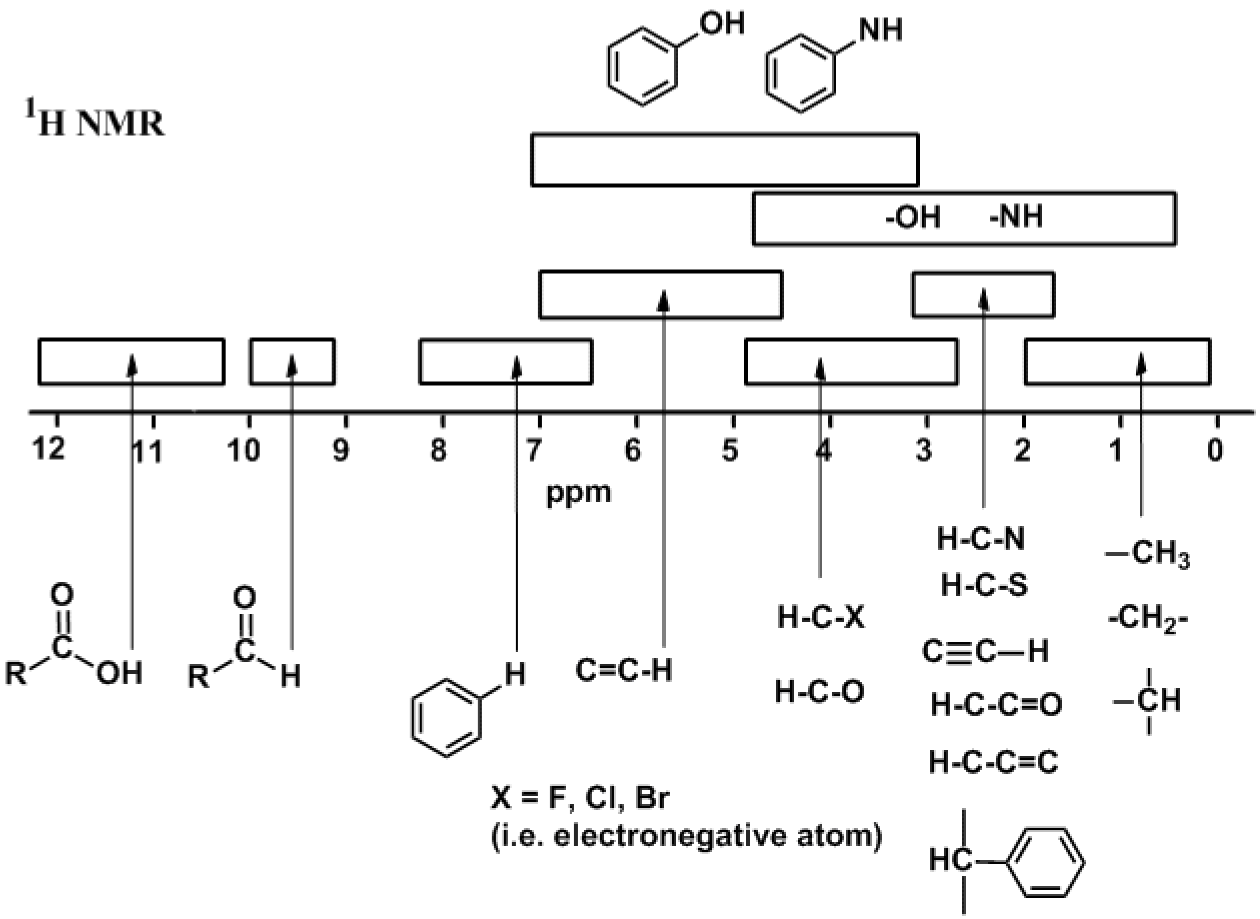
HPLC Chromatogram of Nyquil



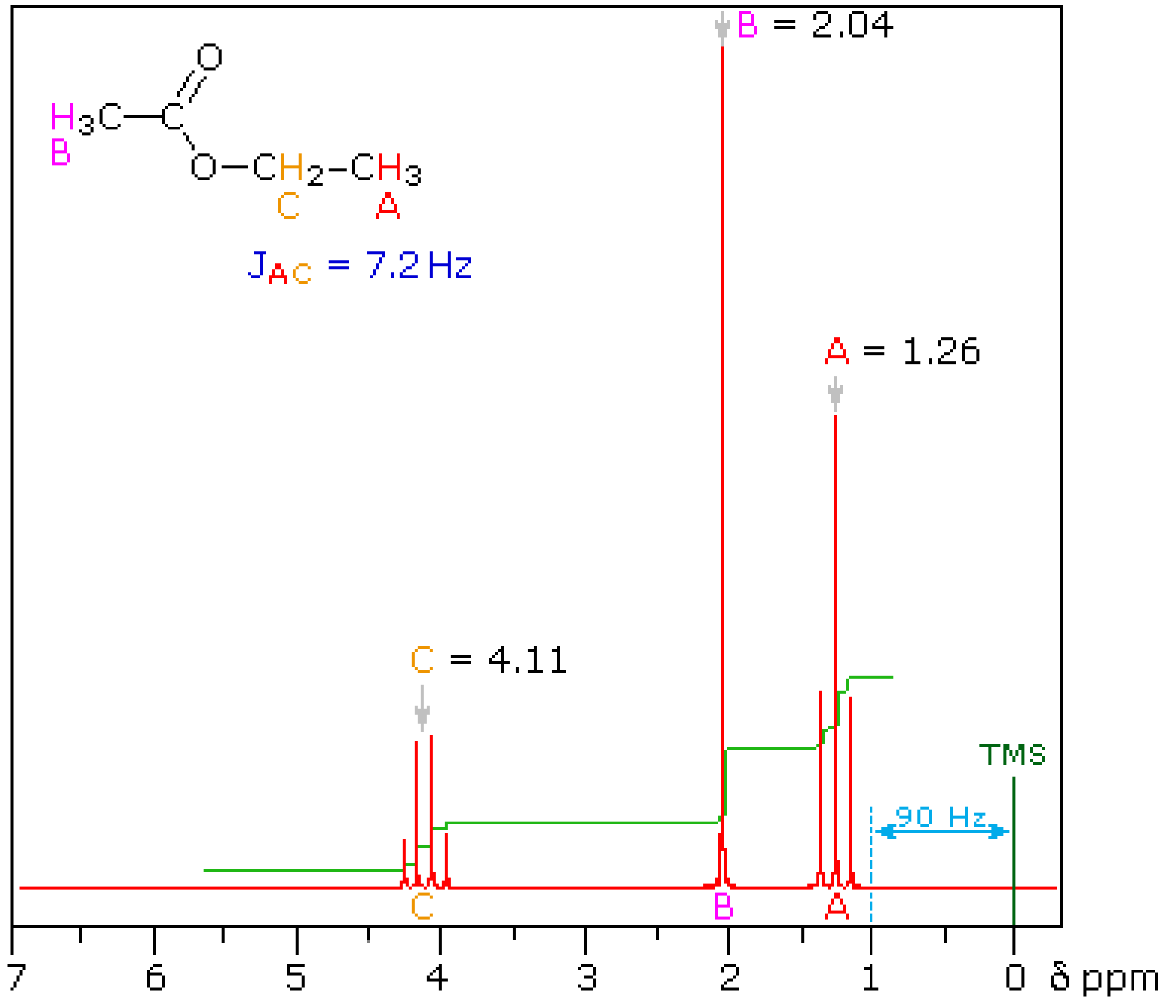
NMR Spectroscopy

- Nuclear magnetic resonance (NMR) is a physical phenomenon in which spinning nuclei in a magnetic field absorb and re-emit electromagnetic radiation at a specific resonance frequency.

H1-NMR Signal Shifts



NMR Spectrum of Ethyl Acetate



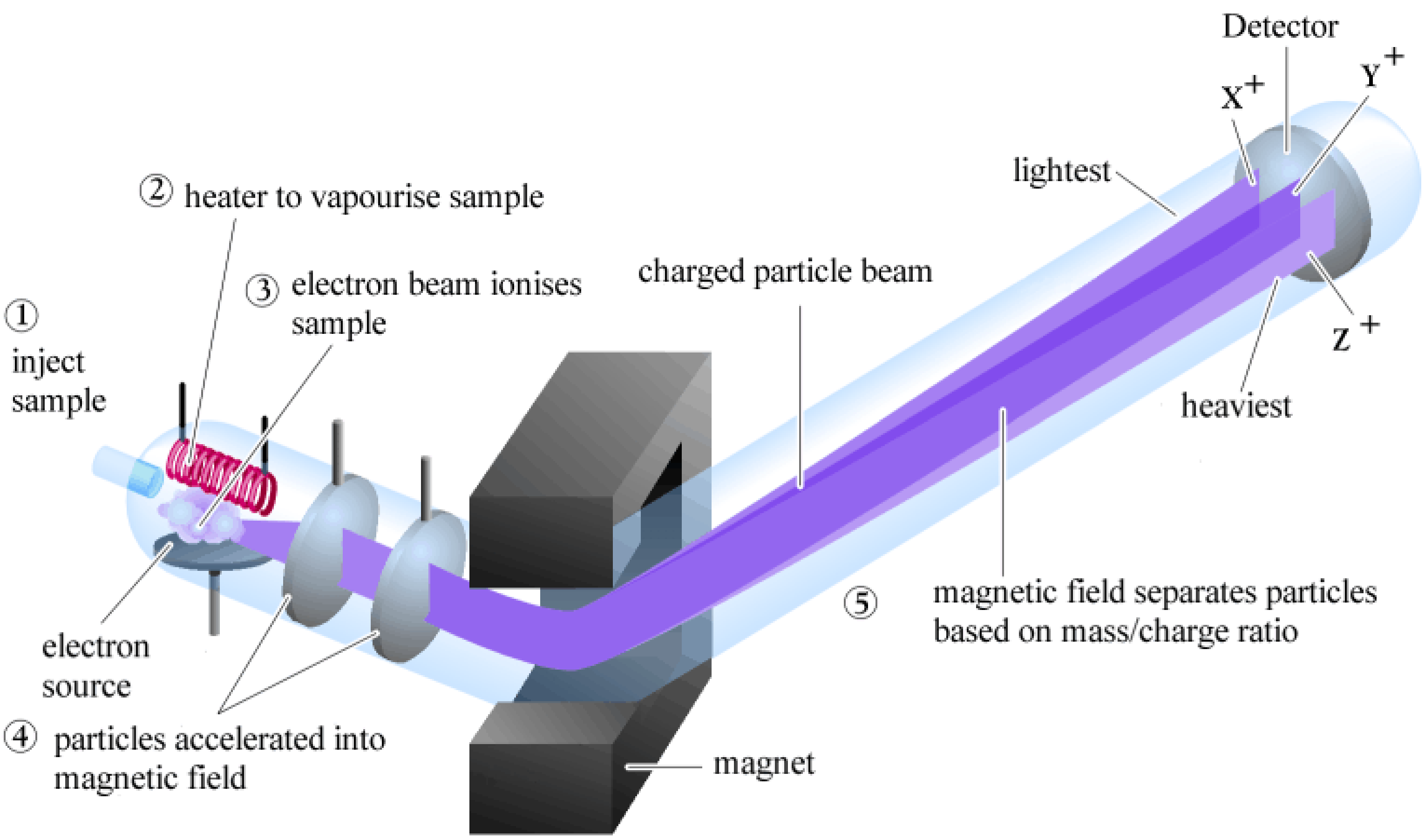
Importance of NMR

- NMR spectroscopy is used to unambiguously identify known and novel compounds, and as such, is usually required by scientific journals for identity confirmation of synthesized new compounds.

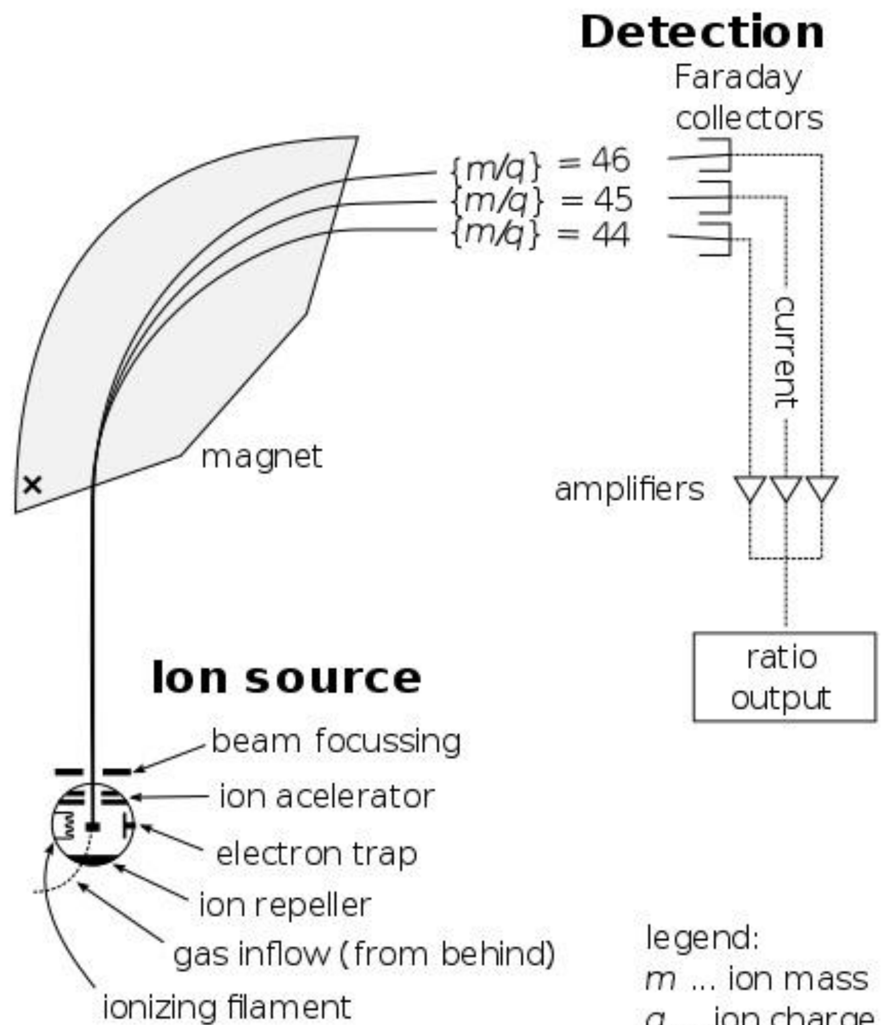
Mass Spectroscopy

- Mass spectrometry (MS) is a highly accurate and precise analytical technique that ionizes chemical molecules and sorts the accelerated charged ions in a magnetic field based on their mass-to-charge ratio.

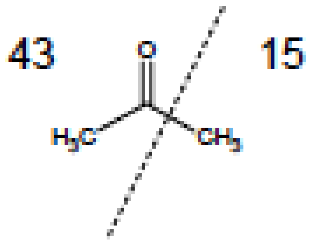
MS Mechanism



MS Schematic

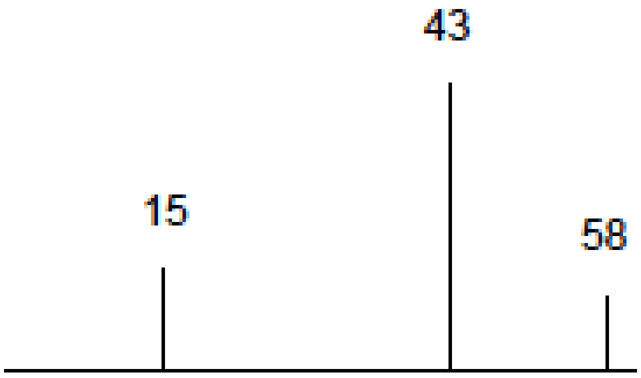


Mass Spectrum of Acetone

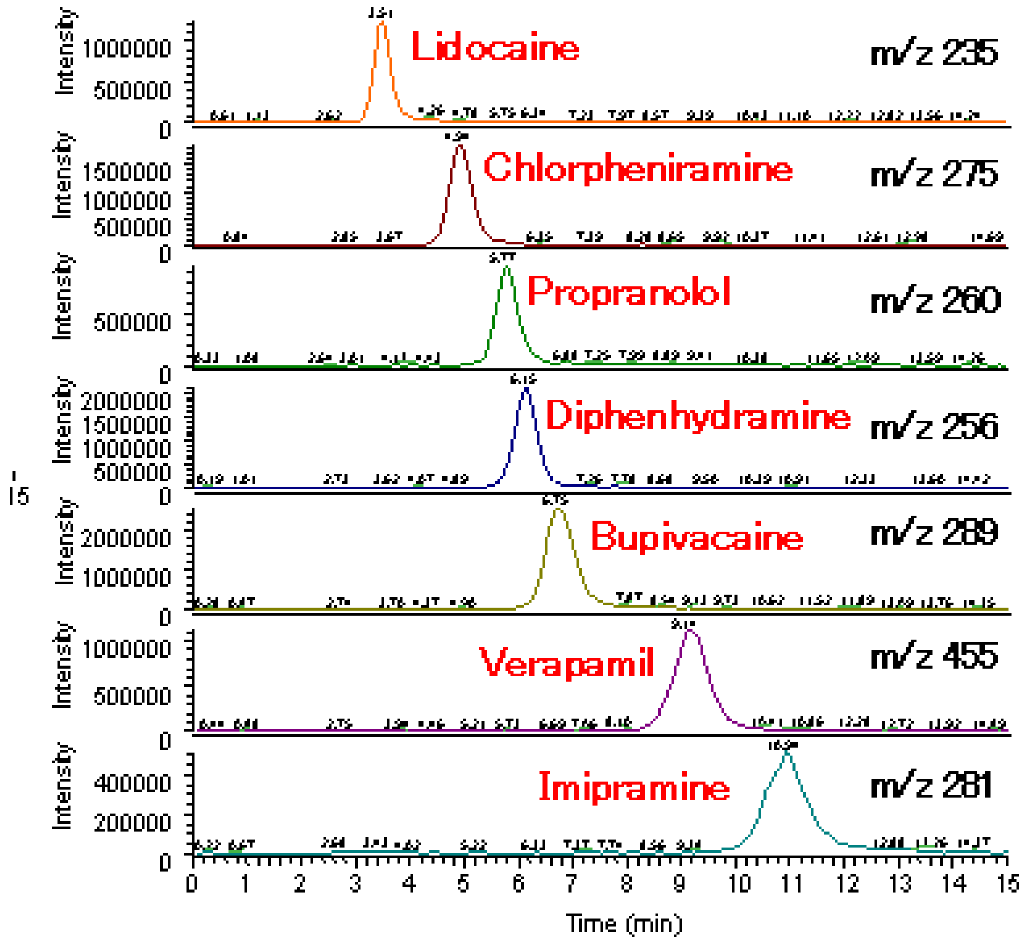


Acetone

MW=58



LC MS of a Blood Sample



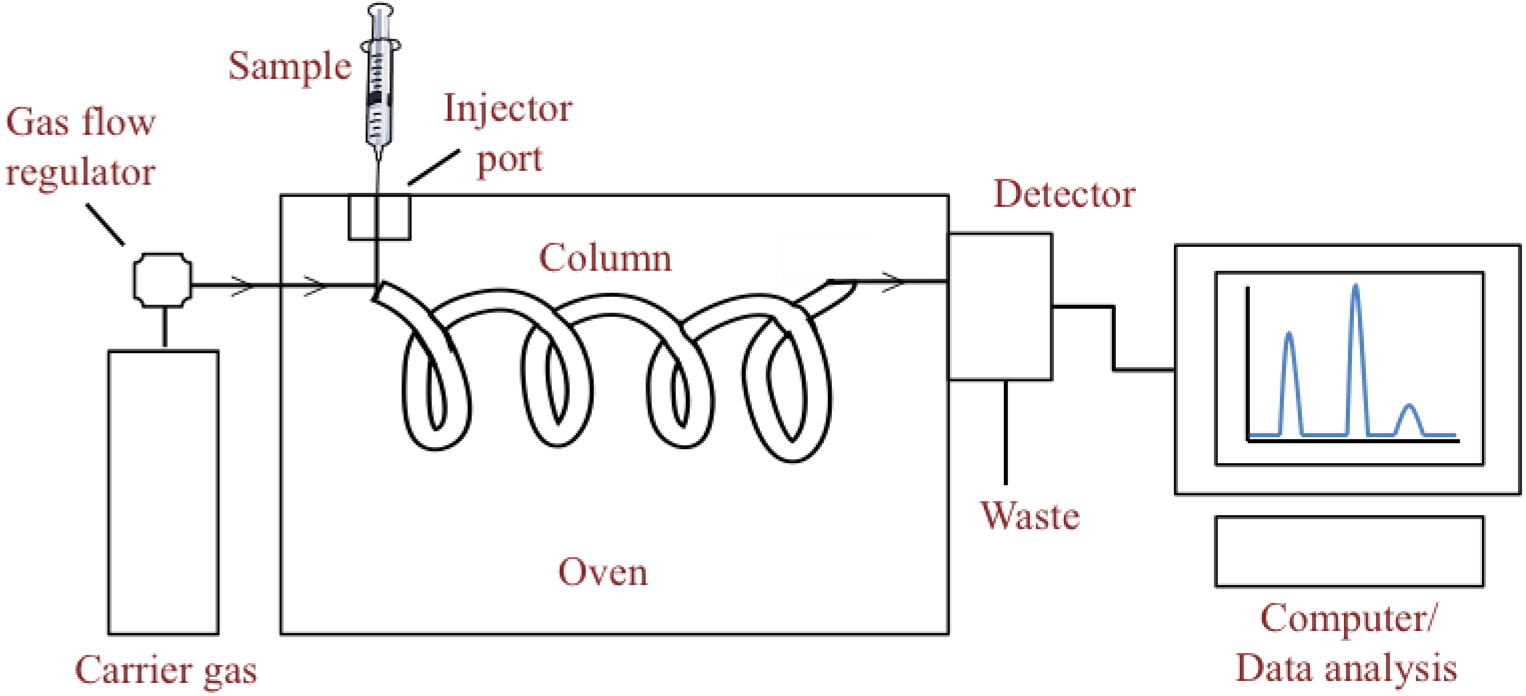
Portable MS

MX908™ leverages high-pressure mass spectrometry (HPMS) to deliver dramatically enhanced sensitivity and broader threat category coverage. This second-generation tool increases mission support with unmatched flexibility and detection power for elite responders in **chemical**, **explosive**, **drug**, and high priority **toxic industrial chemical** (TIC) scenarios. Another model Is used for CWA detection (Chemical Warfare Agents)

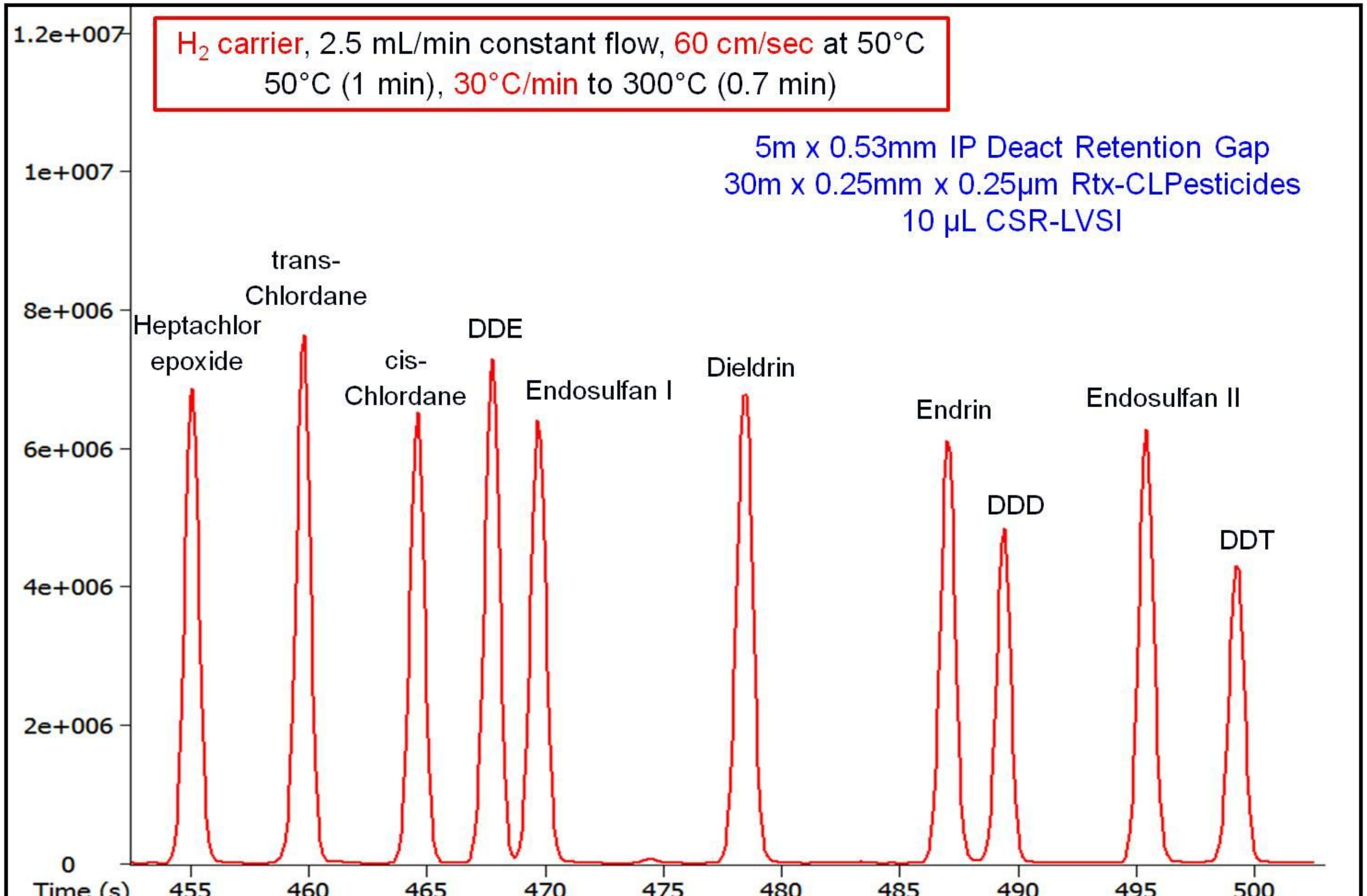
Gas Chromatography

- Separation and detection technique based on passing a mixture or pure compound through a long GC thin column made from a solid tube coated by a sticky substance (stationary phase), by pushing it through with a carrier gas (mobile phase).
- The target compound has to be volatile and have a MW between 200-800 amu

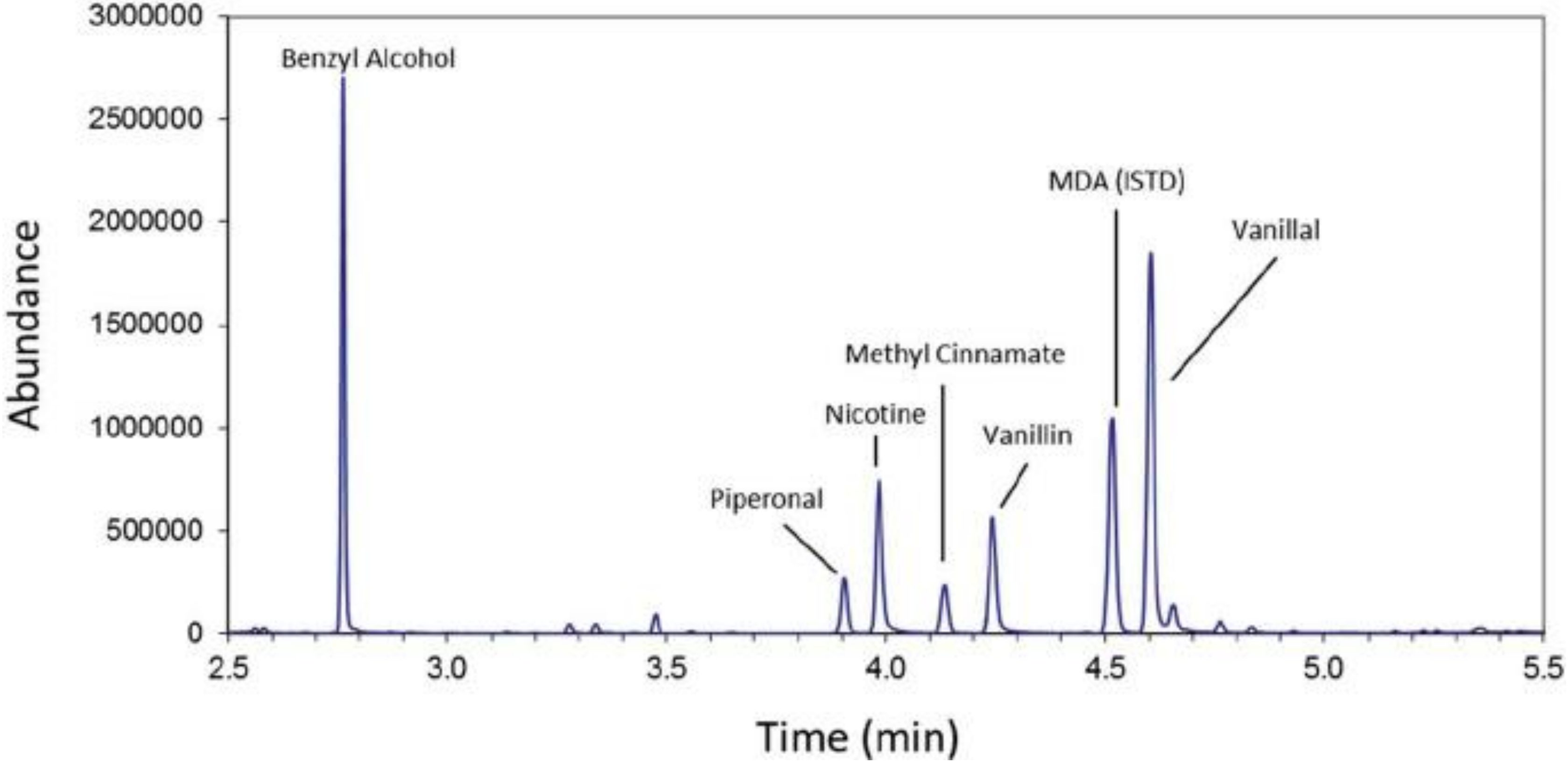
GC Schematic



Gas Chromatogram Pesticides



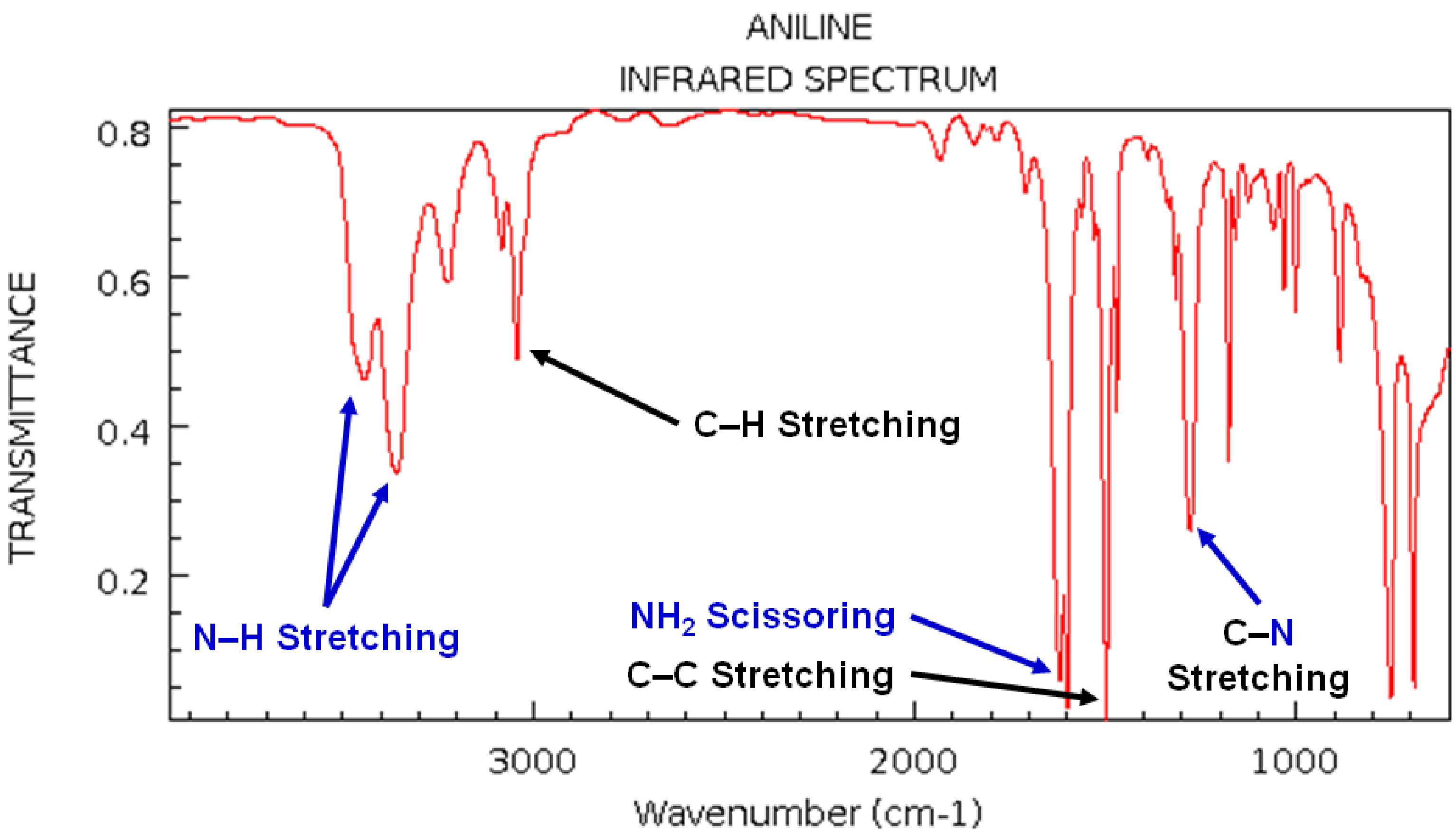
GC Chromatogram of Flavors in A Cigar



IR Spectroscopy

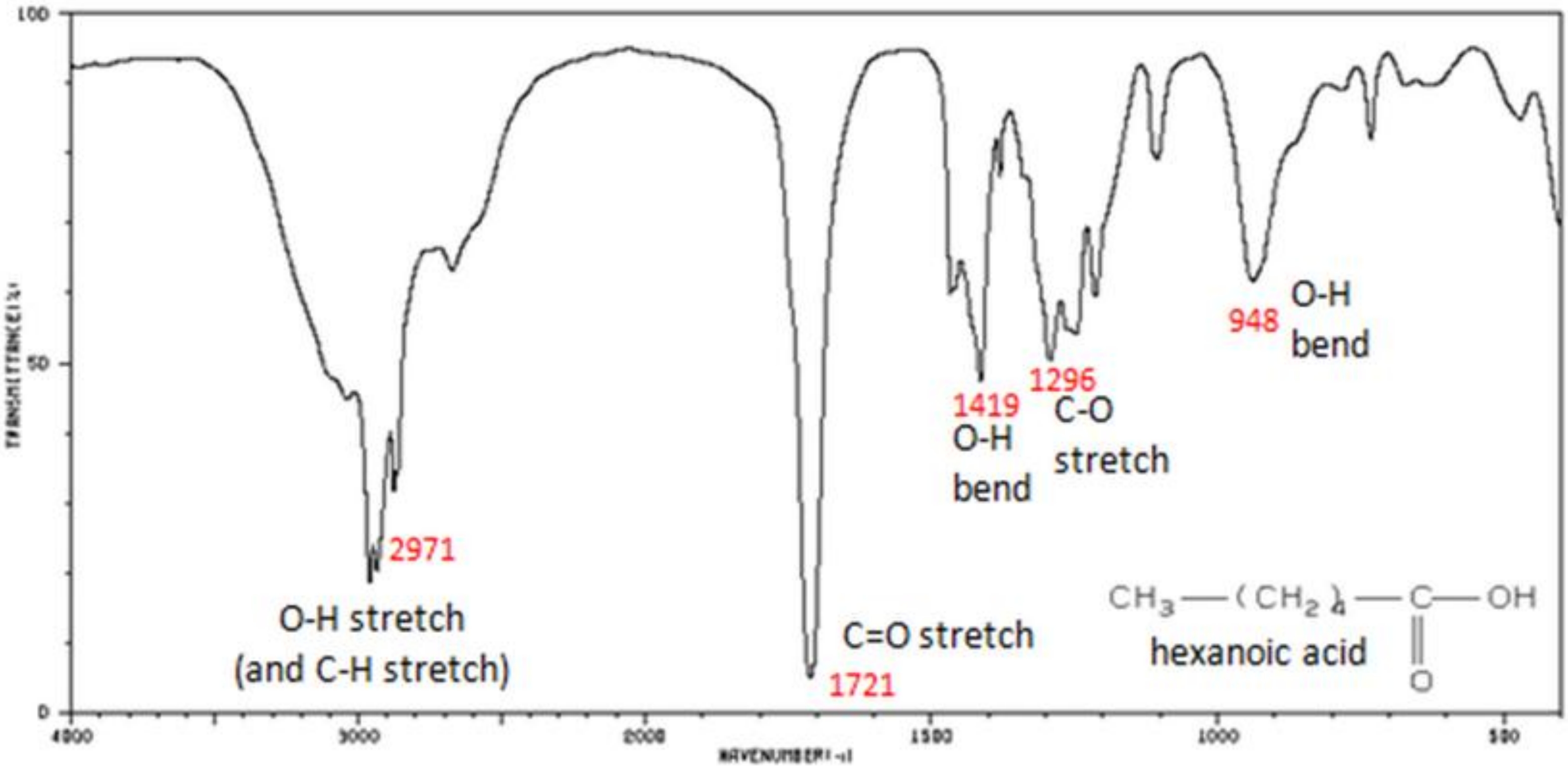
- Infrared spectroscopy involves the interaction of infrared radiation with matter. As with all spectroscopic techniques, it can be used to identify and study chemicals. Samples may be solid, liquid, or gas. The method or technique of infrared spectroscopy is conducted with an instrument called an infrared spectrometer (or spectrophotometer) to produce an infrared spectrum.

Aniline IR Spectrum

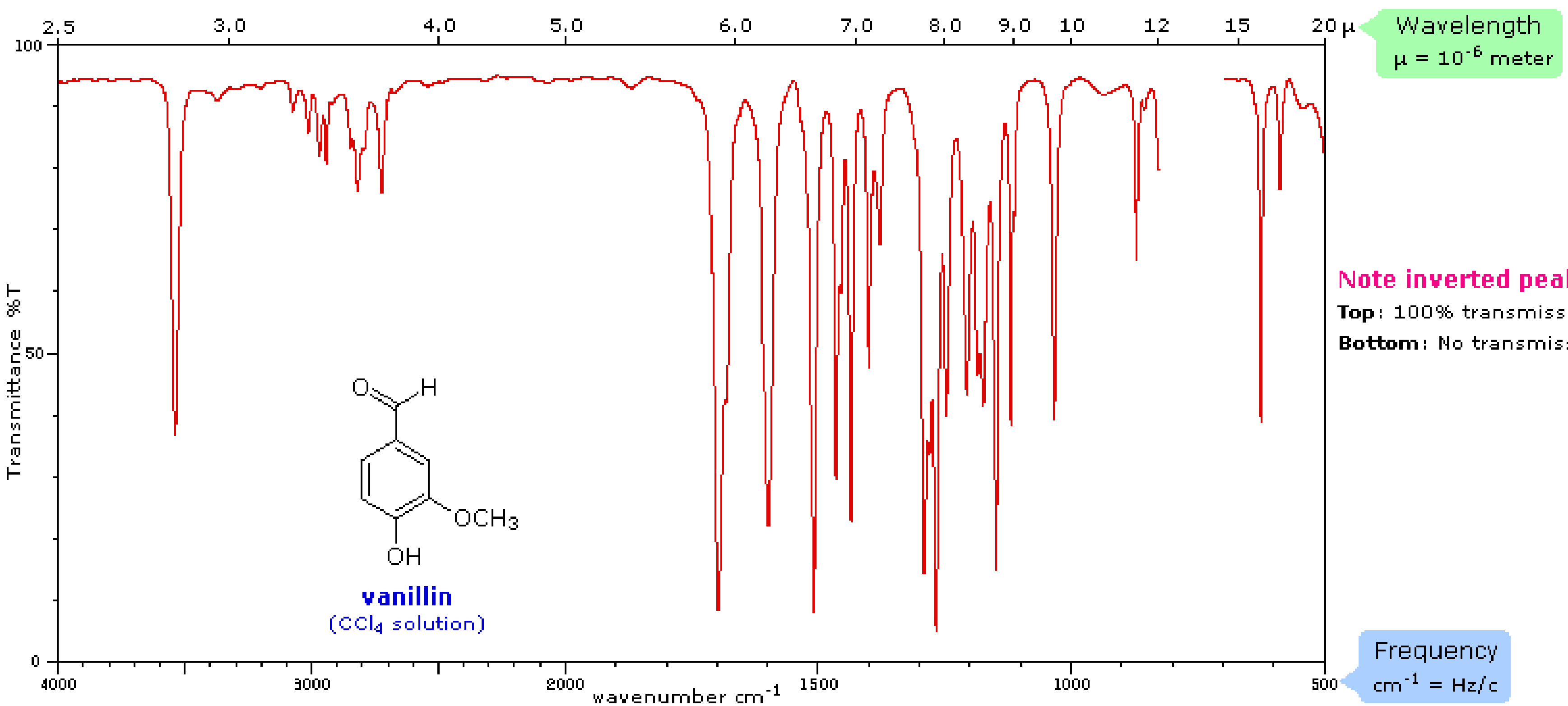


NIST Chemistry WebBook (http://webbook.nist.gov/chemistry)

IR Spectrum Hexanoic Acid



Vanillin IR Spectrum

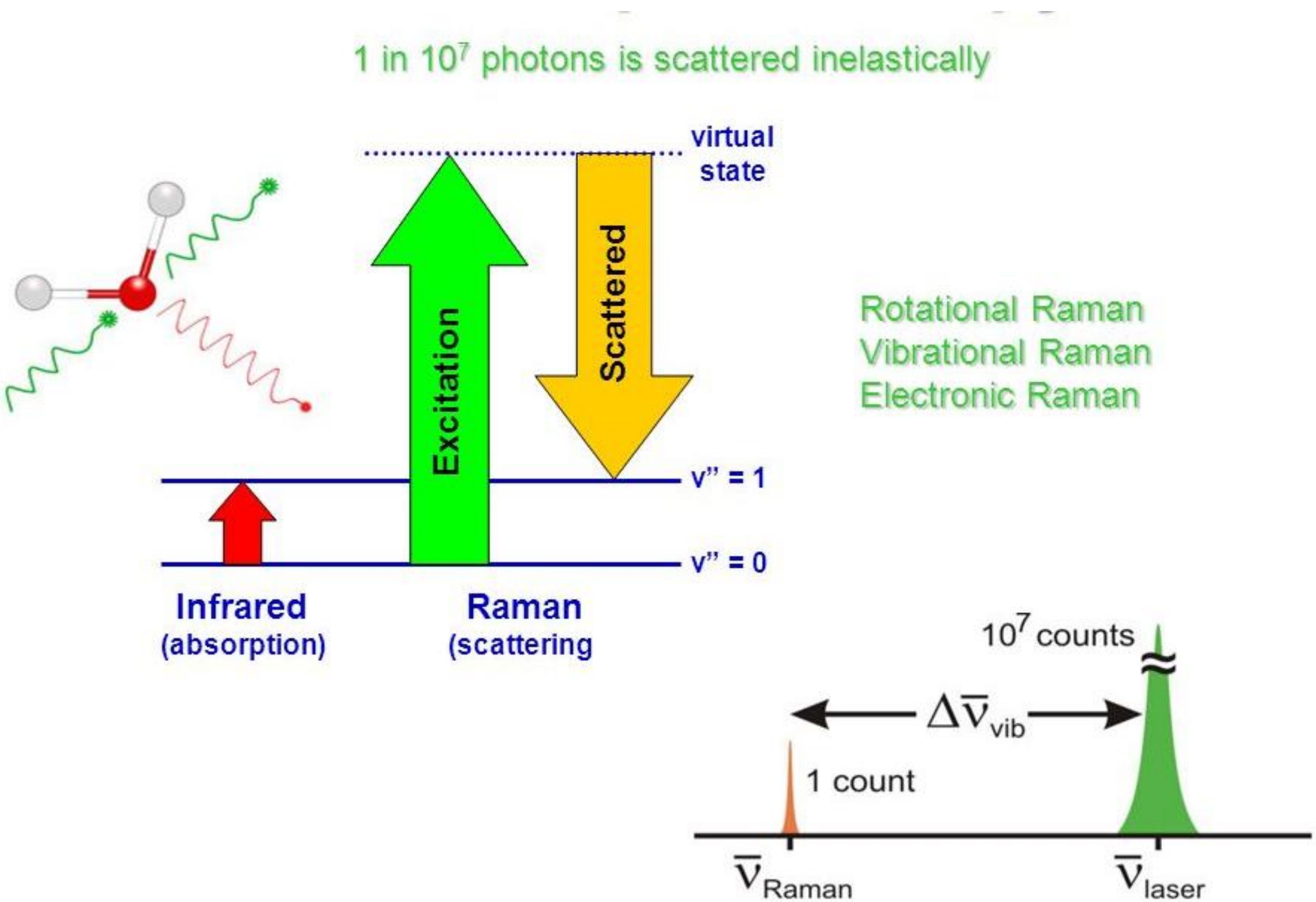


Note inverted peaks

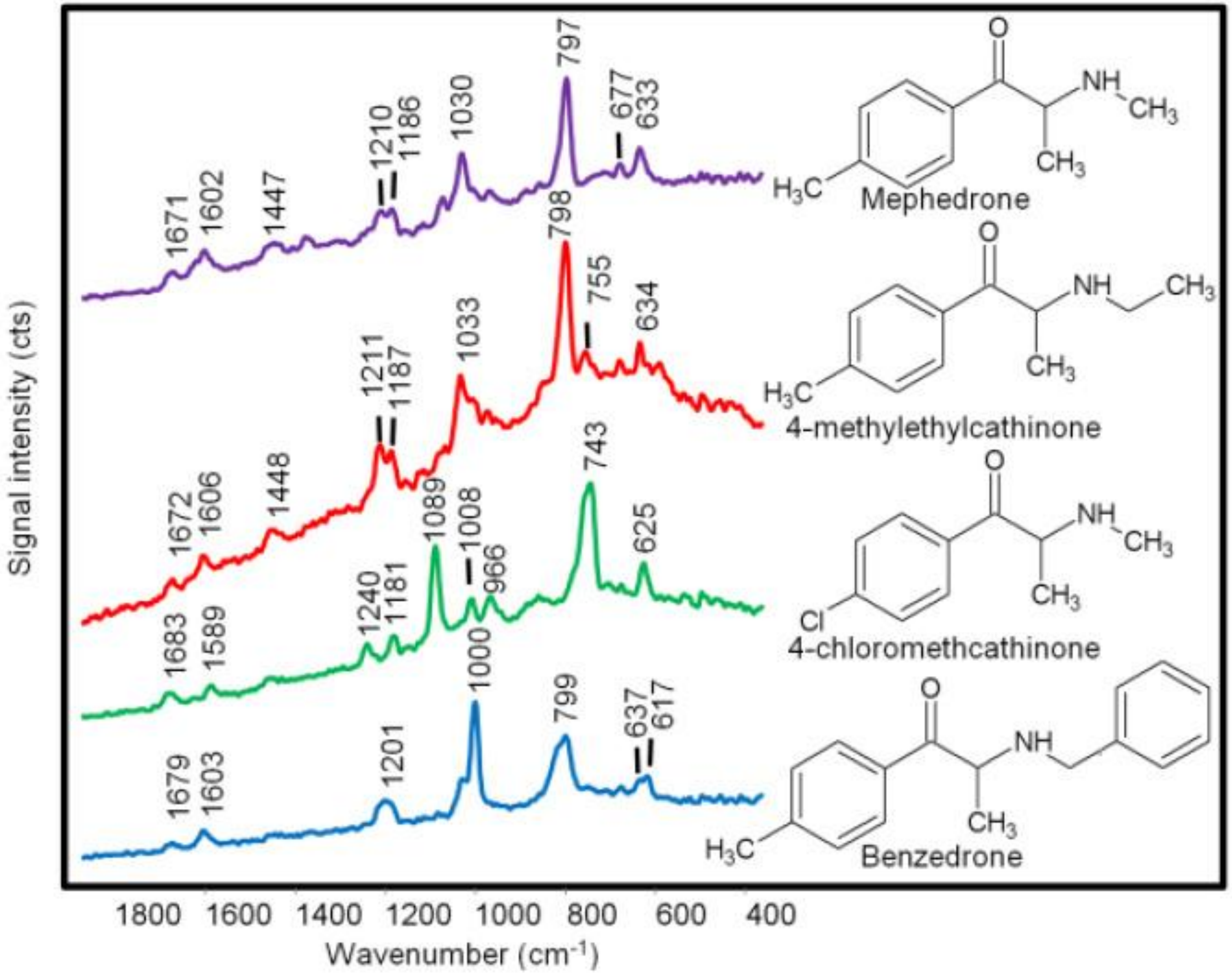
Top: 100% transmission

Bottom: No transmission

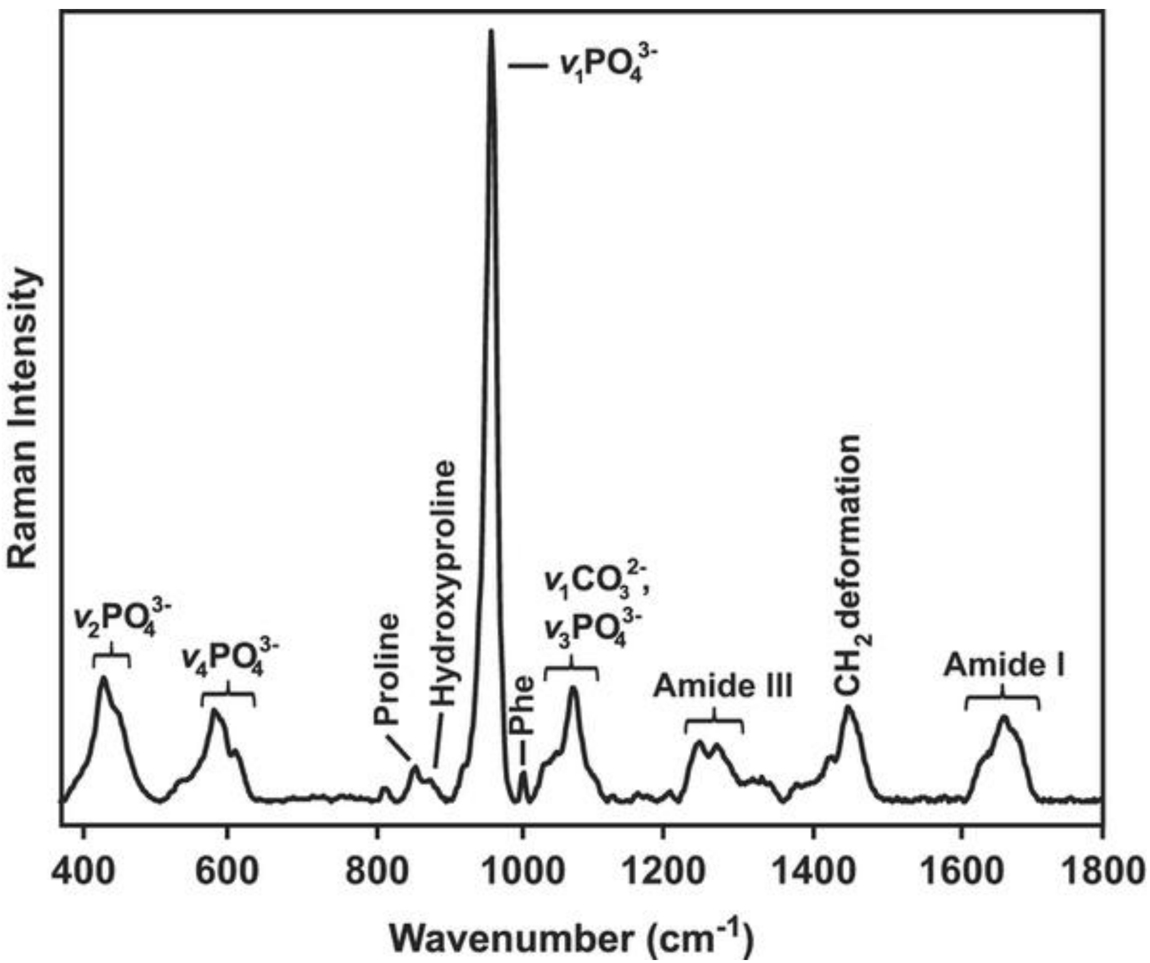
Raman Spectroscopy



Raman Spectra

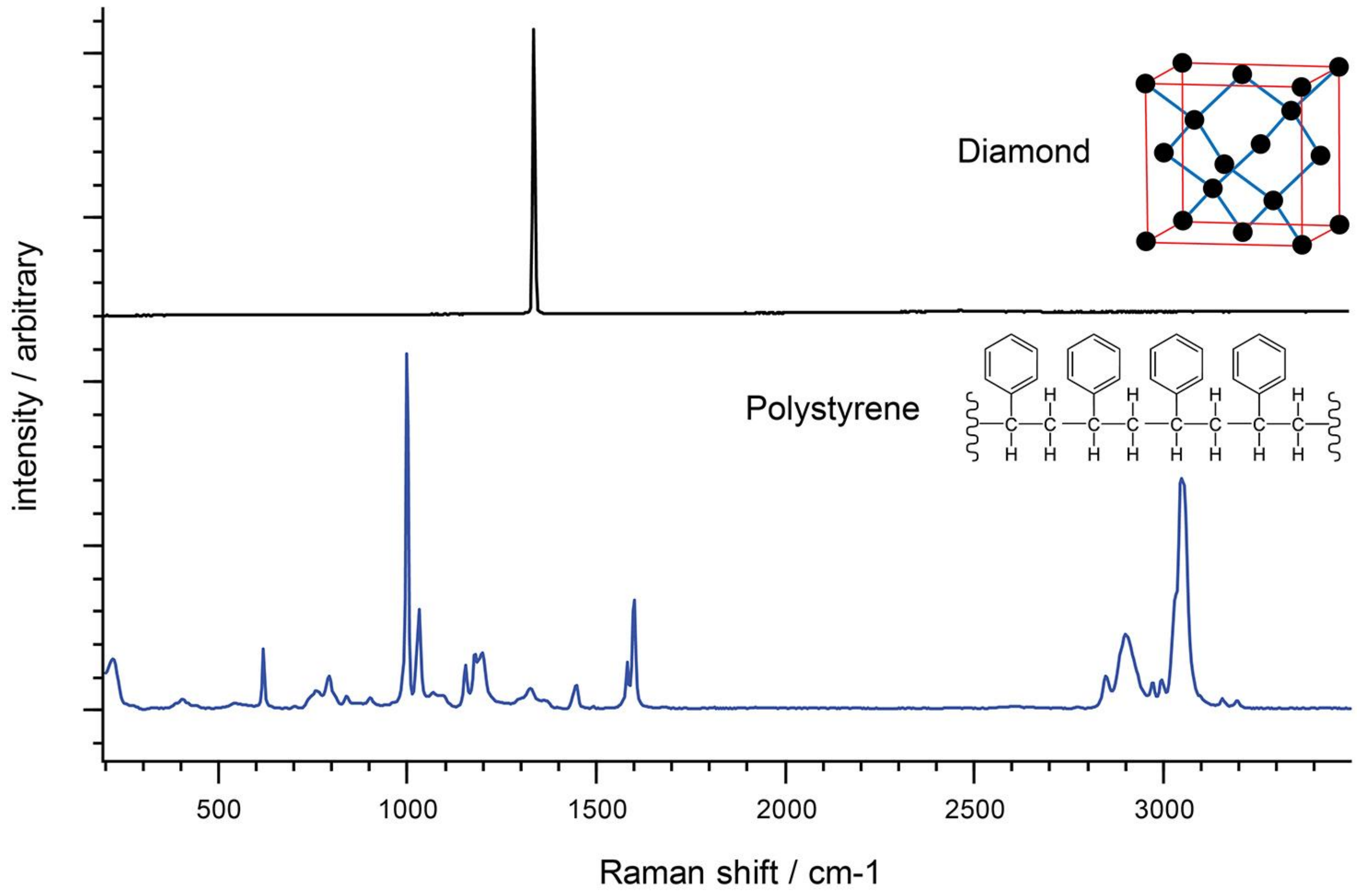


Raman Peaks Assignment



Baseline-corrected Raman spectrum of mouse cortical bone acquired using a 785-nm laser. Major bone mineral and matrix collagen band positions and associated spectral regions are marked.

Raman Spectra of Diamond and PS



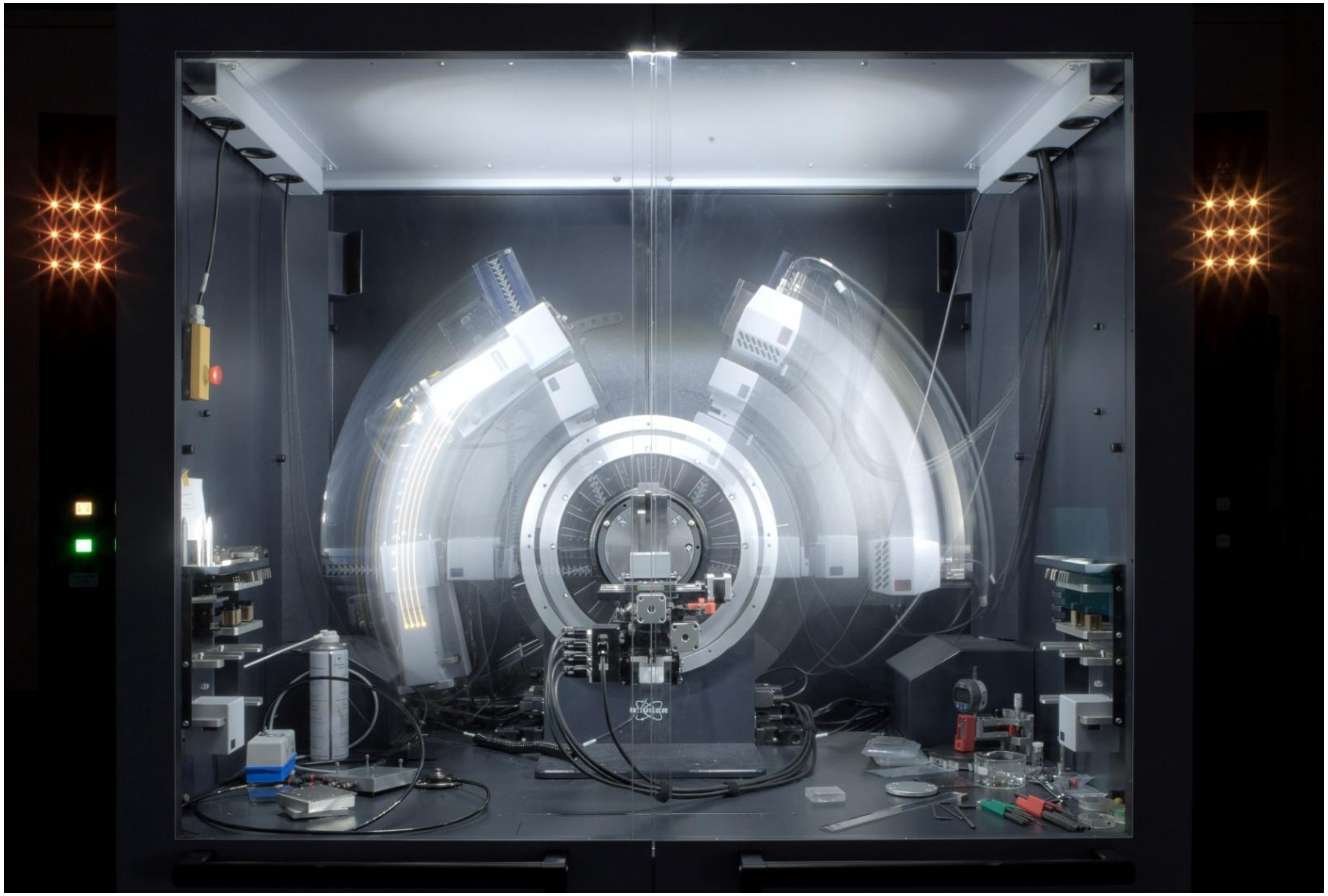
What Can/not Be Analyzed With Raman Spectroscopy?

- All solid chemical compounds that do not fluoresce including drugs, explosives, polymers
- Gems such as diamond and sapphire
- Liquids such as cyclohexane, ethanol, methanol,
- Polymorphs
- Graphene
- No metals
- No monatomic salts NaCl/KCl/KI/KBr

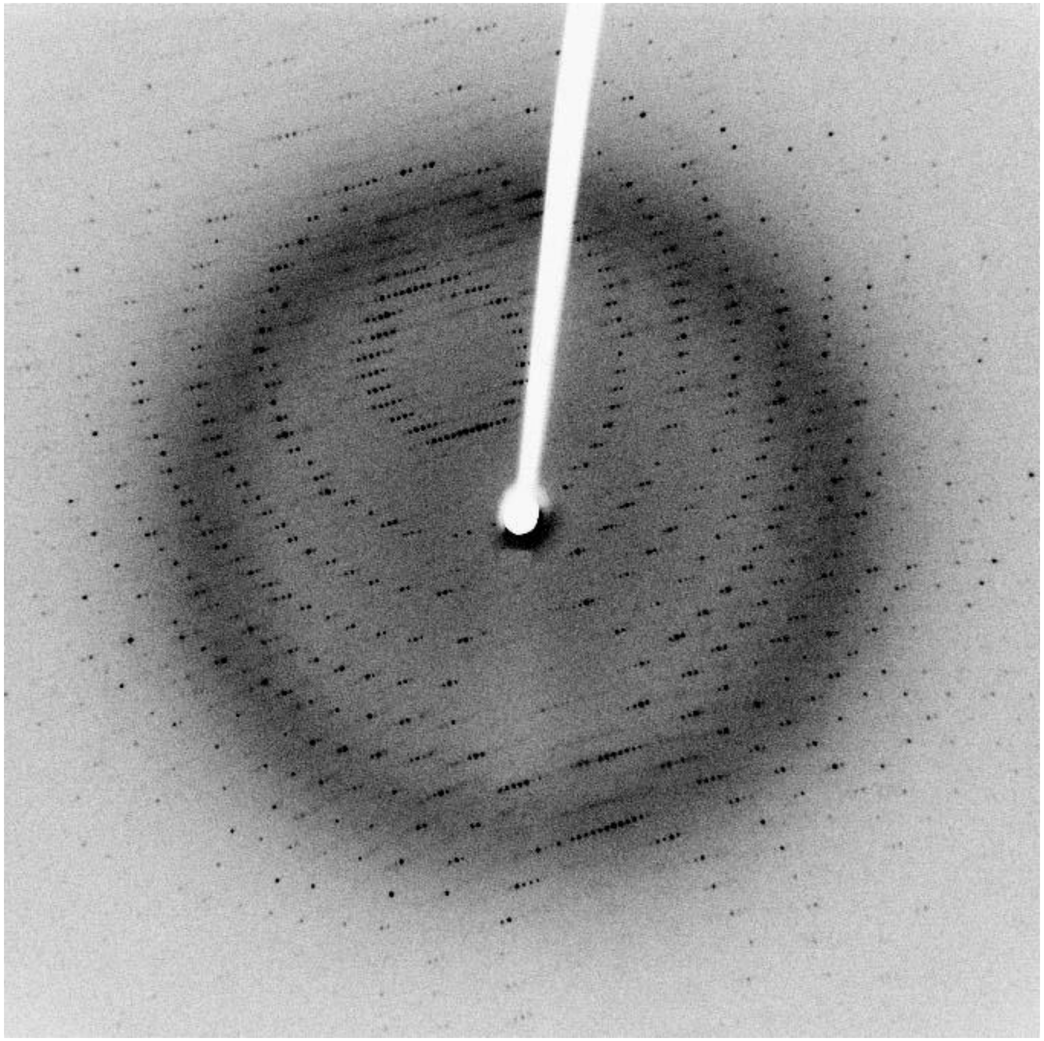
XRD

- An advanced analytical technique used for determining the atomic and molecular structure of a crystal, in which the crystalline atoms cause a beam of incident X-rays to diffract into many specific directions. By measuring the angles and intensities of these diffracted beams, a crystallographer can produce a three-dimensional picture of the density of electrons within the crystal. From this electron density, the mean positions of the atoms in the crystal can be determined, as well as their chemical bonds.

A powder x-ray diffractometer



X-Ray Diffraction Pattern



Nobel Prizes involving X-ray crystallography

1914 Max von Laue Physics "For his discovery of the diffraction of X-rays by crystals",an important step in the development of X-ray spectroscopy.

1915 William Henry Bragg and William Lawrence Bragg Physics "For their services in the analysis of crystal structure by means of X-rays",

1962 Max F. Perutz and John C. Kendrew Chemistry "for their studies of the structures of globular proteins"

1962 James Watson, Francis Crick and Maurice Hugh Frederick Wilkins Medicine "For their discoveries concerning the molecular structure of nucleic acids and its significance for information transfer in living material“

1964 Dorothy Hodgkin Chemistry "For her determinations by X-ray techniques of the structures of important biochemical substances"

1972 Stanford Moore and William H. Stein Chemistry "For their contribution to the understanding of the connection between chemical structure and catalytic activity of the active centre of the ribonuclease molecule”

1976 William N. Lipscomb Chemistry "For his studies on the structure of boranes illuminating problems of chemical bonding“

Nobel Prizes involving X-ray crystallography - II

1985 Jerome Karle and Herbert A. Hauptman Chemistry "For their outstanding achievements in developing direct methods for the determination of crystal structures"

1988 Johann Deisenhofer, Hartmut Michel and Robert Huber Chemistry "For their determination of the three-dimensional structure of a photosynthetic reaction centre"

1997 John E. Walker Chemistry "For their elucidation of the enzymatic mechanism underlying the synthesis of adenosine triphosphate (ATP)"

2003 Roderick MacKinnon and Peter Agre Chemistry "For discoveries concerning channels in cell membranes

2006 Roger D. Kornberg Chemistry "For his studies of the molecular basis of eukaryotic transcription"

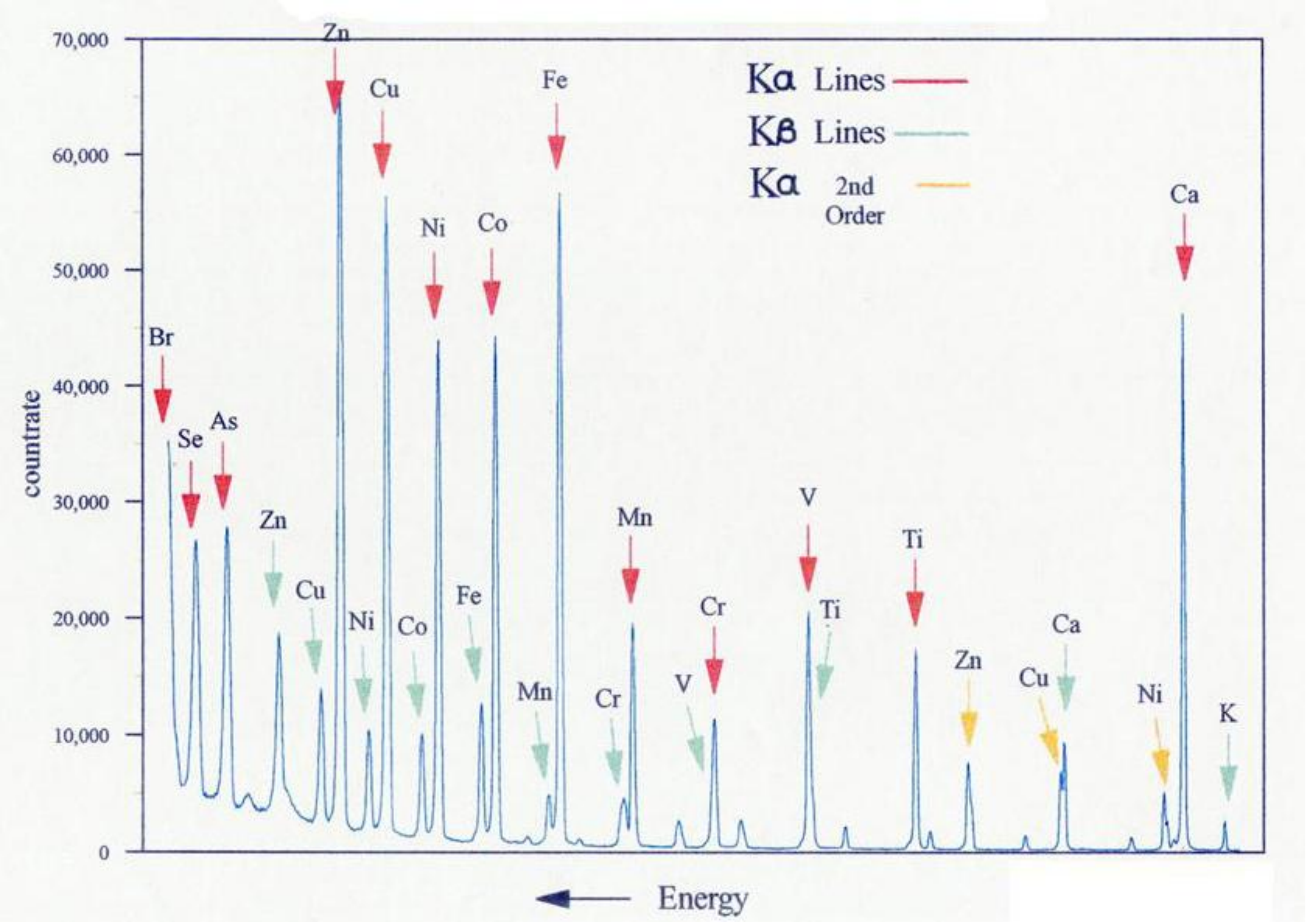
2009 Ada E. Yonath, Thomas A. Steitz, Venkatraman Ramakrishnan Chemistry "For studies of the structure and function of the ribosome"

2012 Brian Kobilka Chemistry "For studies of G-protein-coupled receptors"

XRF

- X-ray fluorescence (XRF) is the emission of characteristic "secondary" (or fluorescent) X-rays from a material that has been excited by bombarding it with high-energy X-rays. The phenomenon is widely used for elemental analysis and chemical analysis, particularly in the investigation of metals, glass, ceramics and building materials, and for research in geochemistry, forensic science, archaeology and art objects such as paintings and murals.

Typical XRF Elemental Peaks



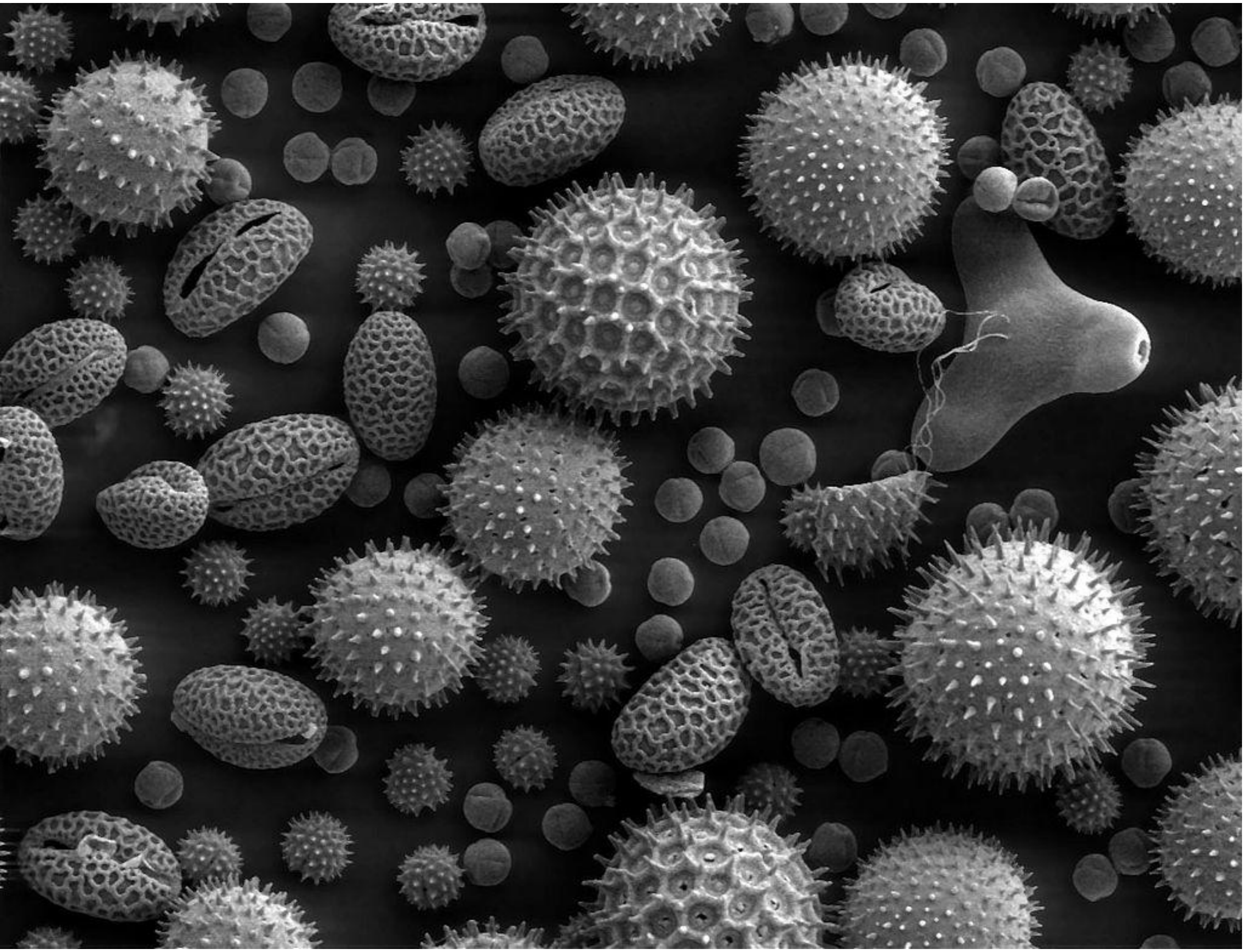
XRF for Analysis of Rocks in the Field

XRF Used in Metal Sorting

SEM

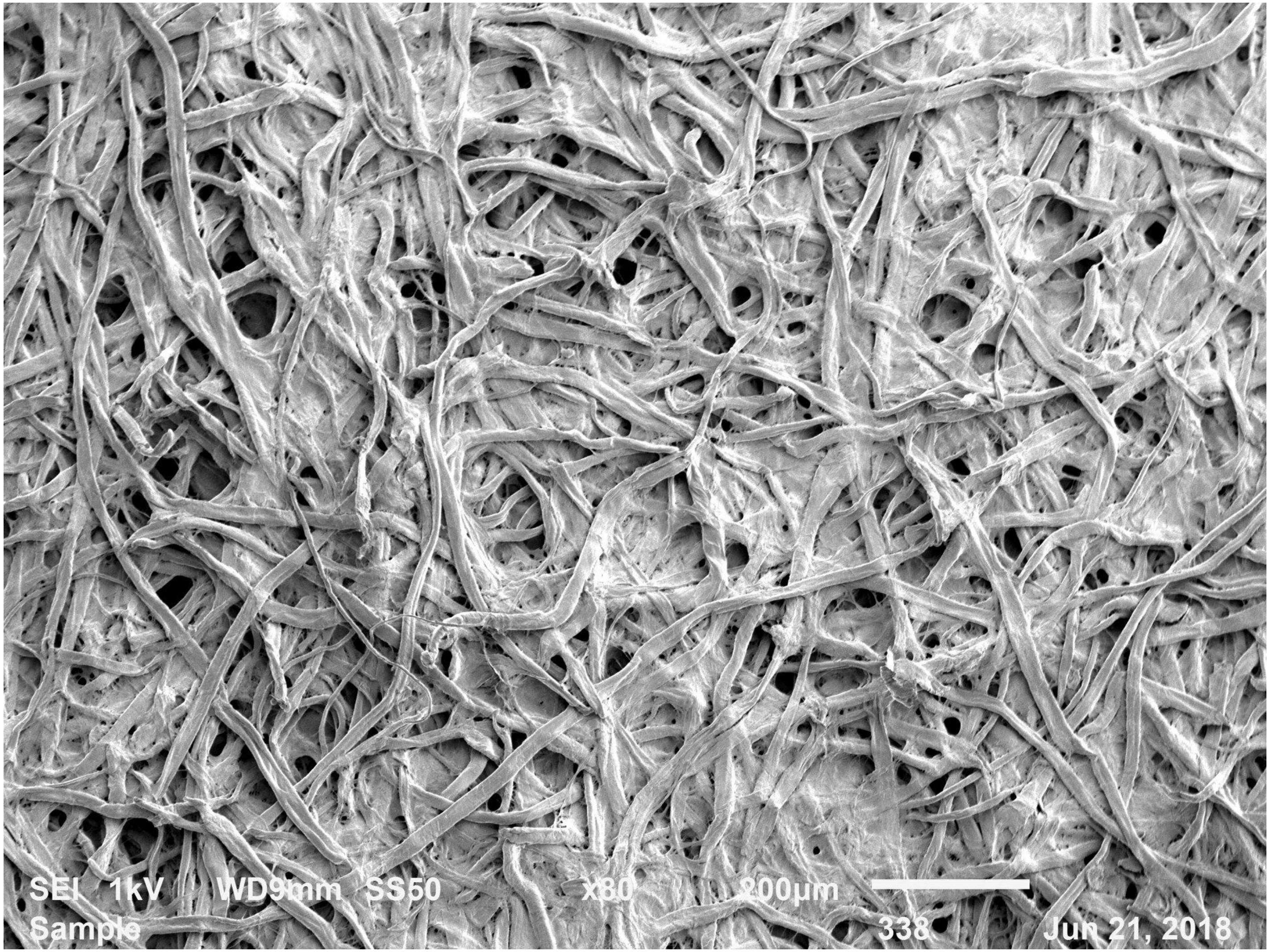
- A scanning electron microscope (SEM) is a type of microscope that produces images of a sample by scanning the surface with a focused beam of electrons. The electrons interact with atoms in the sample, producing various signals that contain information about the sample's surface topography and composition. The electron beam is scanned in a raster scan pattern, and the beam's position is interrelated with the detected signal to produce an image. SEM can achieve resolution better than 1 nanometer.

SEM Inmage of Pollen

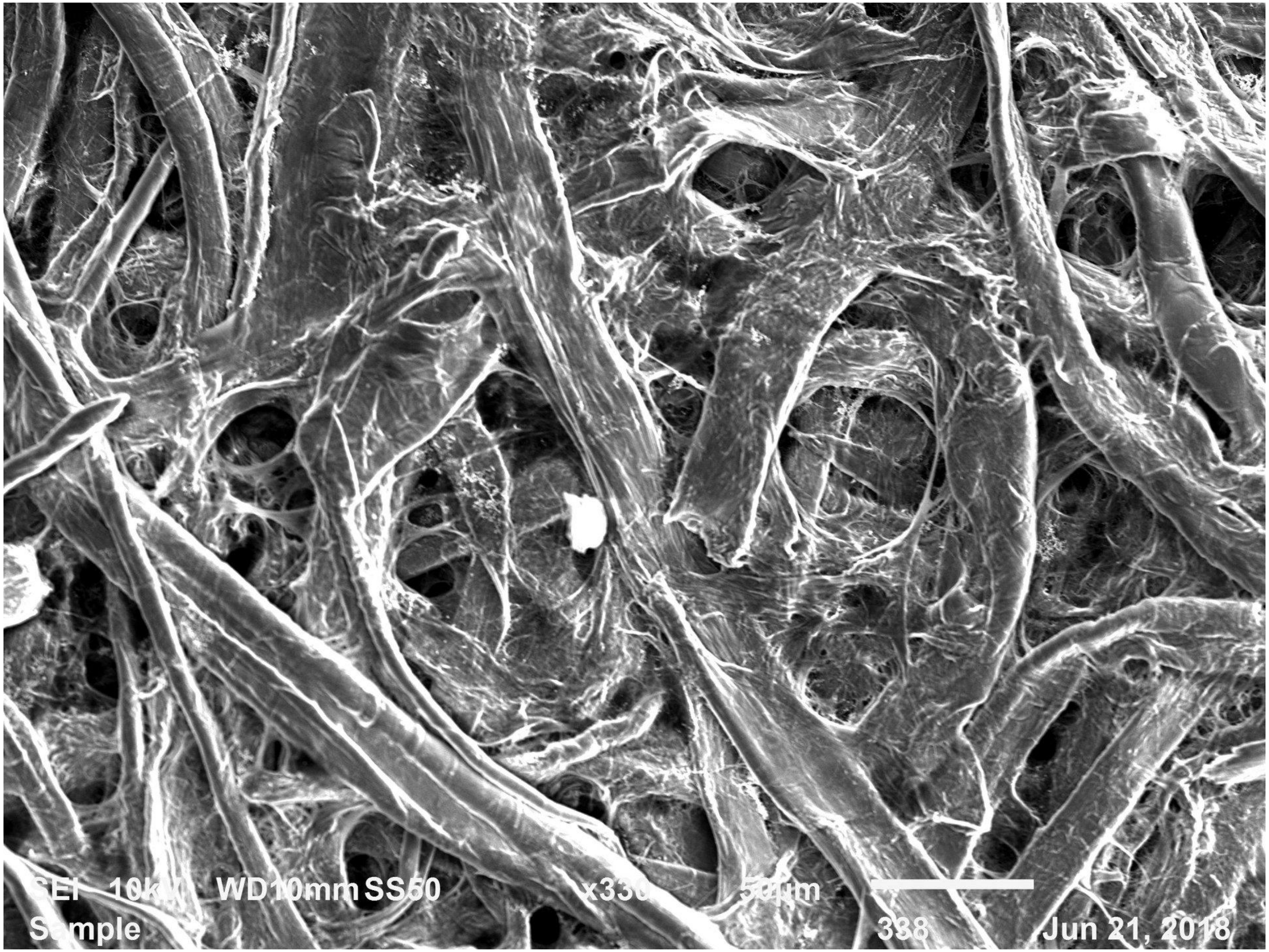


SEM image of pollen grains shows the characteristic depth of field of SEM images

SEM Image of Cellulose Fibres



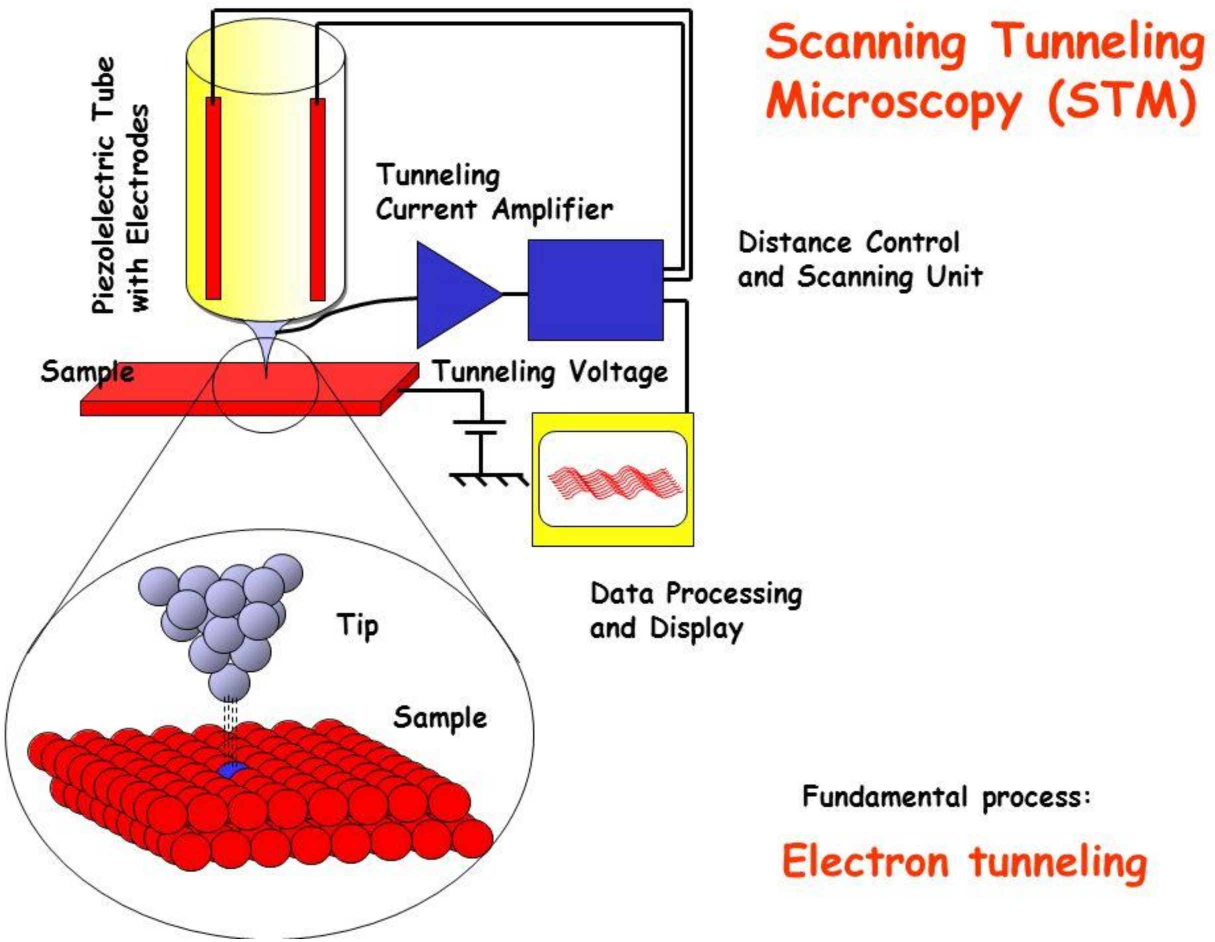
Cellulose Fibers and Small Ag Nano Particle



STM

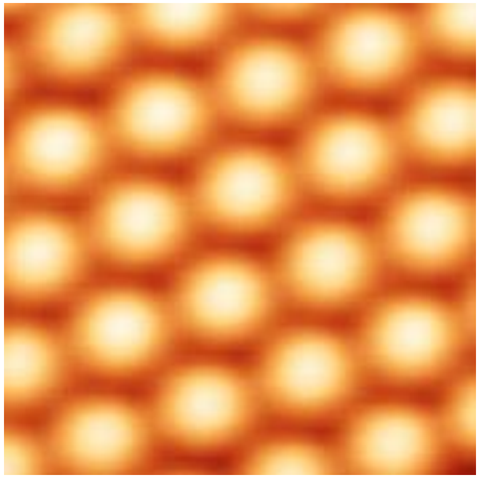
- A scanning tunneling microscope (STM) is an instrument for imaging surfaces at the atomic level. Its development in 1981 earned its inventors, Gerd Binnig and Heinrich Rohrer (at IBM Zürich), the Nobel Prize in Physics in 1986. For a STM, good resolution is considered to be 0.1 nm lateral resolution and 0.01 nm (10 pm) depth resolution. With this resolution, individual atoms within materials are routinely imaged and manipulated.

STM



Scanning Tunneling Microscopy (STM)
Piezolelectric Tube with Electrodes
Tunneling Current Amplifier
Distance Control and Scanning Unit
Sample
Tunneling Voltage
Data Processing and Display
Tip
Sample
Fundamental process:
Electron tunneling

Sample STM Image

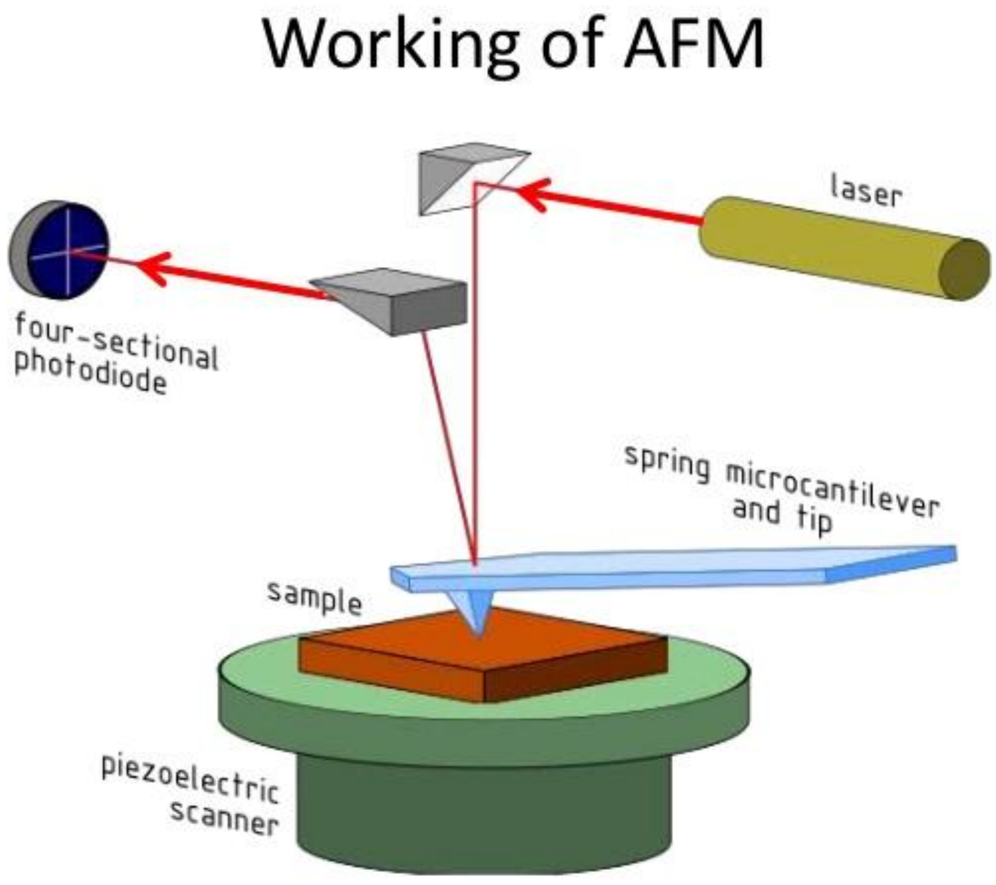


The silicon atoms on the surface of a crystal of silicon carbide (SiC).

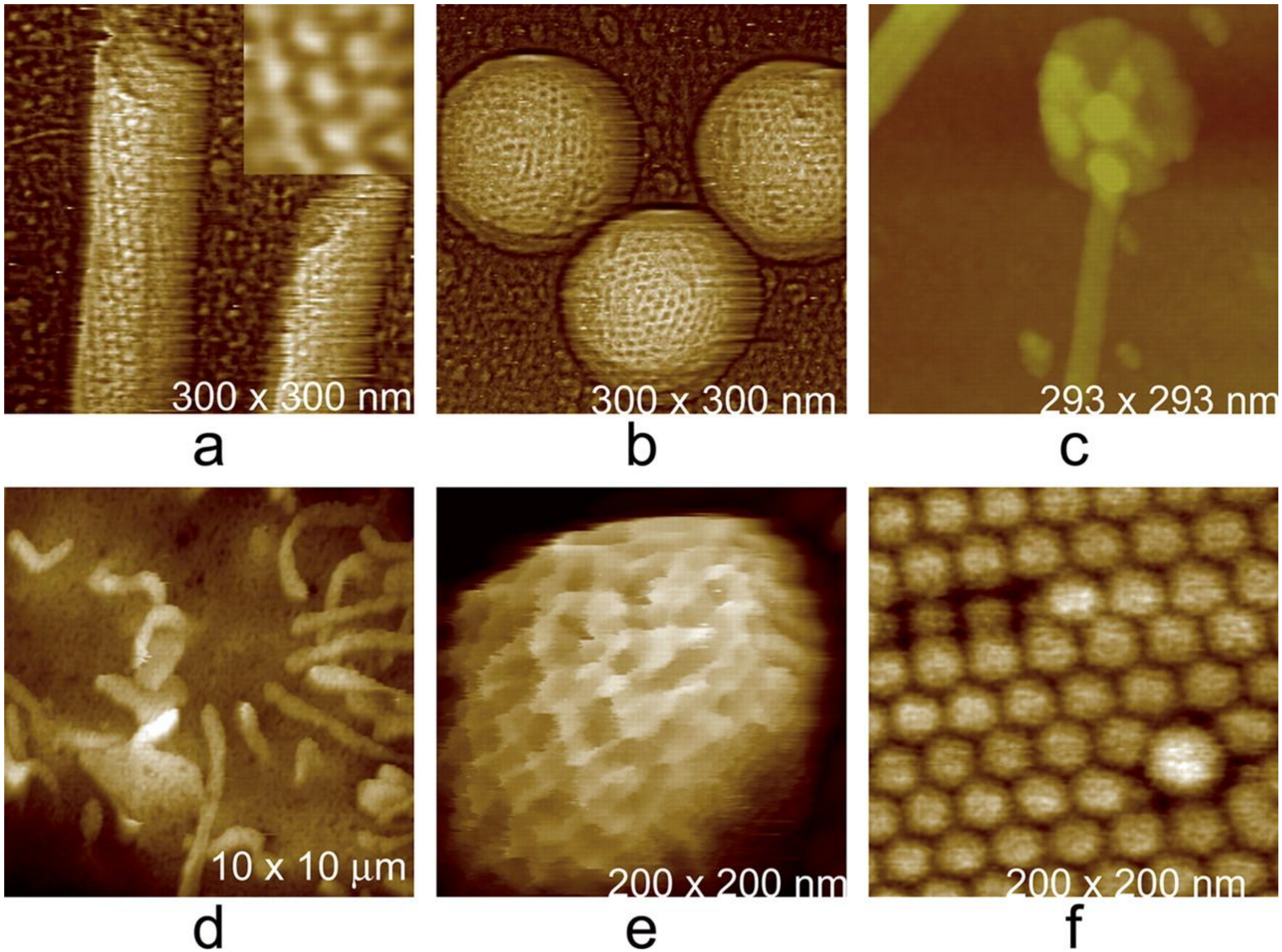
AFM

- Atomic force microscopy (AFM) is a very-high-resolution type of scanning probe microscopy (SPM), with demonstrated resolution on the order of fractions of a nanometer, more than 1000 times better than the optical diffraction limit.
- It goes deep where optical microscopes cannot go due to diffraction of light
- The information is gathered by "feeling" or "touching" the surface with a mechanical probe. Piezoelectric elements that facilitate tiny but accurate and precise movements on (electronic) command enable precise scanning.

Mechanism of AFM



AFM Images in Biology



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Further Reading

- On NMR
  https://www2.chemistry.msu.edu/faculty/reusch/virttxtjml/spectrpy/nmr/nmr1.htm
- On Mass Spectrometry

https://www2.chemistry.msu.edu/faculty/reusch/virttxtjml/spectrpy/massspec/masspec1.htm