Science and Technology

Chemical Weapons Detection

Detecting the Production of Chemical Weapons

- Can be cooperative, within the framework of CWC, or noncooperative, based on intelligence agents, remote sensing, and covertly placed monitoring devices
  - On-site inspections established by the OPCW are important.
  - Because the evaluation of intent is important, intelligence-gathering services are important.

Indicators (Signatures) of CW Production from Remote or On-site Inspections

- Detection of chemical weapons in the plant itself
- Detection of chemical weapons in the plant waste stream
- Detection of precursors
- Detection of decomposition products
- Aspects of plant design
- Testing of munitions and delivery systems
- Biomarkers in plant workers, vegetation, or other animals

Indicators (Signatures) of CW Production from Remote or On-site Inspections

- Patterns of material and equipment imports
  - Developing countries require outside help to make CW, e.g. Iraq and Libya got CW production plants from outside sources.
  - Purchase of glass-lined pipes and corrosion-resistant alloys (can be dual use)
  - Tracking precursors is difficult because many are used widely in commercial applications
  - Ratios of starting materials and catalysts might be useful
- Economic dislocations, e.g. diverting a chemical plant to CW production might lead to fewer pharmaceuticals and pesticides available

Indicators (Signatures) of CW Production from Remote or On-site Inspections

- Visual Signatures (Most external features of CW plant are the same as an ordinary commercial chemical plant)
  - Construction of large chemical plant not reported in chemical trade press
  - Plant in remote location
  - High level security
  - Large distances between buildings to complicate air attacks
  - Proximity to metal-machining factory capable of making munitions
  - Presence of trucks to carry hazardous materials
  - Lack of steel drums and other common packing materials
  - Few plants and animals near plant
  - Flurry of activity, suggesting an accident

Indicators (Signatures) of CW Production from Remote or On-site Inspections

- Internal production signatures obtained by authorized onsite inspections
  - Production equipment – no one component identifies CW production, but there are unique combinations…e.g. specialized pumps and valves with double seals
  - Unique ways of heating and cooling reaction vessels (Some intermediates react explosively with water, so use other heat-exchanging fluids and cooling towers rather than steam vents.)
  - Corrosion-resistant materials (increasingly common in chemical industry)
  - Safety and pollution-control equipment…tightly sealed enclosure, negative pressure, remote control, pumps with double or triple seals, different ventilation and emission control systems
  - Unique waste treatment and disposal

Indicators (Signatures) of CW Production from Remote or On-site Inspections

- Chemical Signatures from collection and analyzing of samples
  - Because analysis of chemicals derived from onsite visits can provide proprietary information about a company, the analysis and publication of data must balance the need to verify CW and the need to protect business information
  - CWC verification searches for specific known chemicals
  - Phosphorus-methyl (P-CH_3) bonds are characteristic of nerve agents
  - Phosphorus-fluorine (P-F) bond for sarin and soman

Reasons for Detection

- Alarm
- All-clear
- Verification and identification
- Mapping of ground contamination
- Mapping of decontamination requirement

http://www.opcw.org/our-work/assistance-and-protection/protection-against-chemical-weapons/detection/

Detection Technology

- Agent identification can be done to some extent by means of a combination of detection devices.
- Laboratory analysis of samples collected is necessary for more reliable information.

http://emedicine.medscape.com/article/833933-overview#a1

M8 Detection Paper

- Two dyes and one pH indicator on paper
- Blotted on liquids that arouse suspicion. It identifies CAs by changing colors within 30 seconds of exposure.
- Nerve agent yellow
- Mustard agent red
- VX causes the indicator to turn to blue which, together with the yellow, will become green/green-black.

M8 Detection Paper (cont.)

- Advantages – sensitive, inexpensive, quick
- Disadvantage - other substances can also dissolve the pigments.
  - Brake fluid, antifreeze, and insect repellent yield false-positive readings.
  - False readings are especially undesirable in civilian situations because they may lead to mass panic.
  - Therefore, chemical detection paper is combined with other techniques.

M9 Detection Paper

- M9 paper has adhesive backing that allows it to be attached to clothing and equipment.
- Color change (Red, Reddish brown, Pink, Purple) indicates chemical agent but does not identify a specific agent
- Tends to react faster than M8 paper
- Can be attached to vehicles. Vehicles are limited to a speed of about 20 mi/h.

M22 Detector

- Portable, operates independently after system startup, and provides an audible and visual alarm.
- Simultaneously detects nerve and blister agent vapors
- Detection leads to more precise identification using other techniques.

M256A1 Chemical Kit

- Portable kit detects nerve gas, mustard gas, and cyanide and usually is used to define areas of contamination.
- Used extensively during the Gulf War but is also available commercially.
- Contains a package of M8 paper, detailed instructions, and a vapor sampler (12 enzymatic tickets that contain laboratory filter paper for detecting CA vapors).

M256A1 Chemical Kit (cont.)

- Eight glass ampoules, six containing reagents for testing and two in an attached chemical heater.
- Ampoules are crushed between the fingers and direct the flow of liquid reagent to wet the test spots.
- Each test spot or detecting tablet develops a distinctive color for a chemical agent.
- Detects all agents at levels below those that can kill or injure people.
- Prone to false-positive results, but it has not been demonstrated to produce false-negative results.

Colorimetric Tubes

- Use enzymatic techniques to identify CAs.
- Hand pump draws a sample into a specific tube, and the concentration of the substance is read from the tube.
- Simple and inexpensive
- Different tubes for different agents.
- Requires knowledge of which CA is likely to be present in a given environment.
- A tube for each possible CA must be used for thorough detection.

Colorimetric Tubes (cont.)

- Example: test for mustard gas

$Cl(CH_2)_2S(CH_2)_2Cl$ (mustard agent)
+ pyridine-CH_2-p-phenylidene-NO_2 (colorless)

reacts at 110 °C in the presence of NaOH to give

$Cl(CH_2)_2S(CH_2)_2N$=CH-pyridine-NO_2 (blue)

Detection Tickets

- For nerve agents
- Two parts, one with enzyme-impregnated paper and the other with substrate-impregnated paper.
- When the package is broken and the enzyme paper wetted, the substrate part of the ticket is exposed to the test vapor by means of a pump.
- Two parts put together for two minutes.
- Can also be used without a pump (by waving it in the air) but this gives a slightly less sensitivity.

Detection Tickets (cont.)

- If the enzyme part of the ticket has turned a weak blue color, nerve agent is not present.
- The blue change of color requires an active enzyme - some form of cholinesterase. In the presence of nerve agents, the enzyme is inhibited and no change of color occurs.
- Detection tickets of this kind cannot distinguish between the different nerve agents.

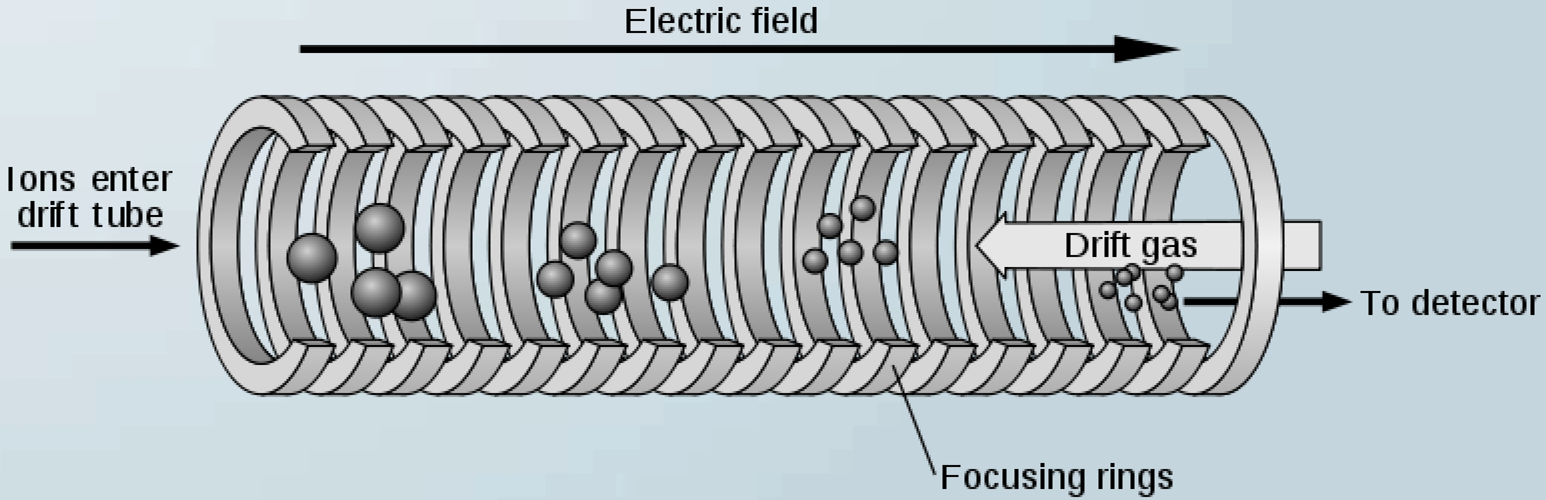
2,6-dichloroindophenylacetate (red) + cholinesterase produces 2,6-dichloroindophenol (blue)

Ion Mobility Spectroscopy (IMS)

- Used in many handheld and stand-alone detection devices
- Gaseous sample drawn into a reaction chamber using an air pump.

Ion Mobility Spectroscopy (IMS)

- Sample ionized , most commonly using radioactive beta emitters such as nickel-63 or americium-241
- Ions pulled through a tube by an electric field.
- A gas opposes the ion motion
- Ions hit detector at end of tube
- Migration time related to ion's mass, charge, and shape.

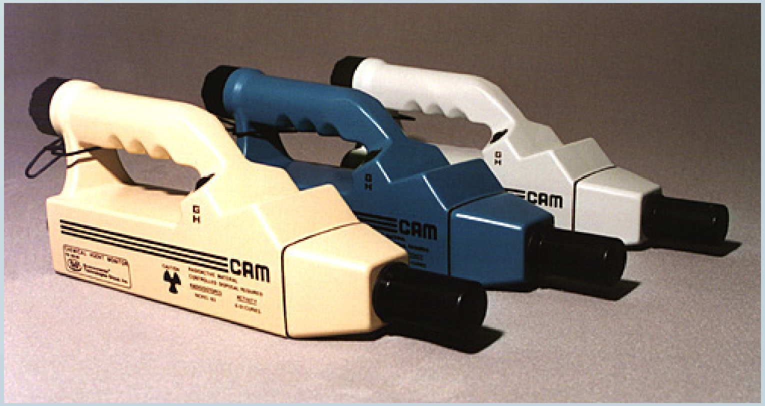


Ion Mobility Spectroscopy (IMS)

- Substances identified according to the time it takes to traverse the distance to the detector and the amount of electrical charge detected.
- Pattern compared to a sample of clean air; if different and unique to certain types of agents, the alarm sounds.
- Limitation - compounds with similar molecular masses take similar times to drift, e.g. wintergreen oil (molecular mass = 152) will be incorrectly identified as mustard gas (molecular mass = 158)
- Positive hits should be confirmed by a second technique.

Improved Chemical Agent Monitor (ICAM)

- IMS device
- Used extensively in the Gulf War, even attached to certain vehicles.
- Handheld device that continuously displays the concentration of nerve agents or mustard agents.
- Prone to erroneous detection in enclosed spaces and areas of strong vapor concentration (e.g. heavy smoke).
- Available for commercial purchase and are used by many medical response teams.

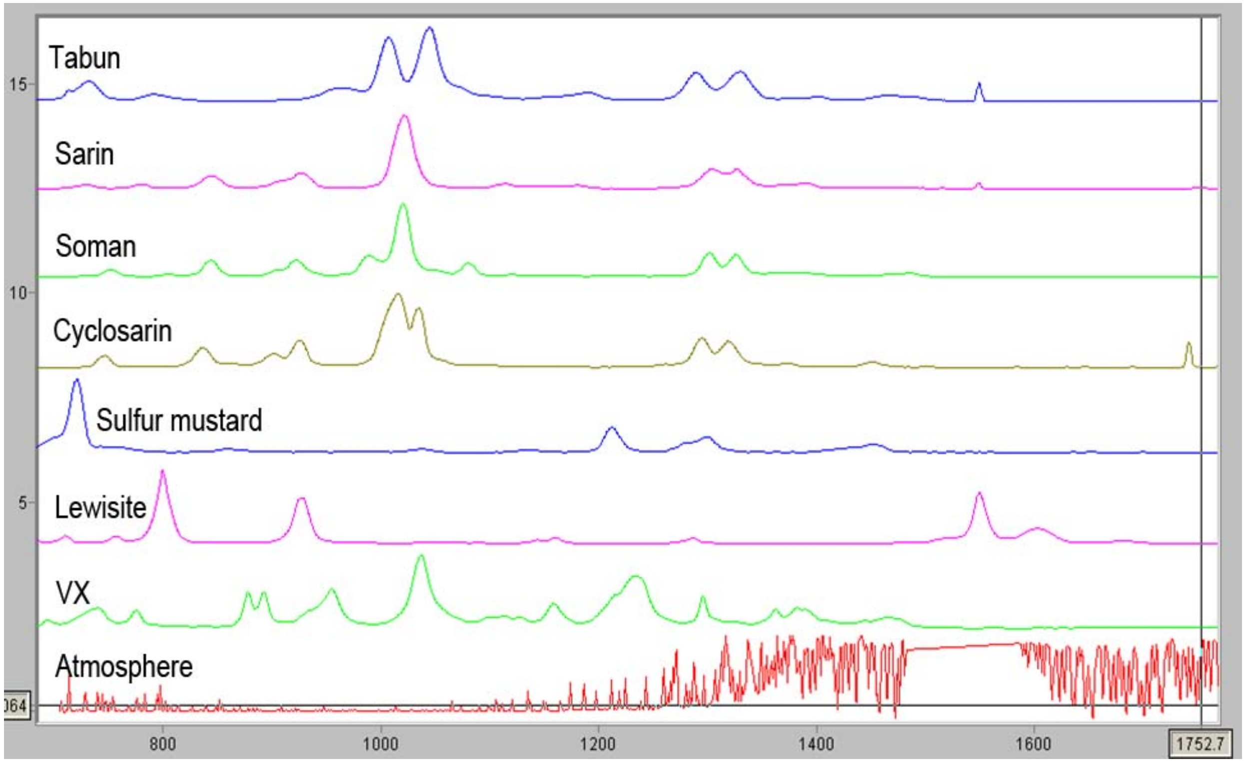


Advanced Portable Detector (APD)

- IMS device
- Sold commercially to HAZMAT response teams for domestic preparedness.
- Handheld device can be powered by batteries.
- Can detect mace and pepper spray as well as nerve agents, blister agents, and hazardous compounds.

Infrared Radiation Detection Techniques

- Long-range detectors and point detectors
- IR radiation used to excite molecules
- Each agent absorbs unique wavelengths and yields a unique pattern referred to as a fingerprint.

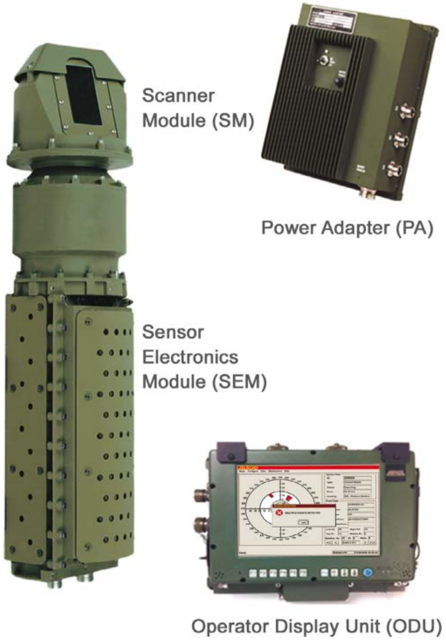


M21 Remote Sensing CA Alarm

- The military uses the M21 Remote Sensing Chemical Agent Alarm (RSCAAL)
- Based on infrared detection.
- Can detect a vapor cloud from 5 km with an 87% detection rate.
- Continuously monitors a background and notes the change in spectral information if a vapor cloud obstructs the background
- Limited in that it must be stationary and can be obstructed by snow and rain.

Joint Service Lightweight Standoff Chemical Agent Detector (JSLSCAD)

- Infrared (IR) detection system
- Passive detector of chemical agent vapors at ranges up to 5 kilometers and ultimately to 10 kilometers.
- Lightweight and fully automatic detection system
- 360-degree coverage from a variety of tactical and reconnaissance platforms



Flame Photometric Detector (FPD)

- A flame of hydrogen is used to burn a sample of air. The color of the flame is analyzed by a photometer for concentrations of sulfur and phosphorous (key components in nerve gas and mustard).
- Highly sensitive yet is prone to false-positive results by detecting other gases that contain significant concentrations of sulfur or phosphorus but are nonhazardous.
- AP2C handheld detector uses this technology.
- Federal agencies and international agencies use this for mass screenings and for confirming decontamination of casualties.

Miniature Automatic Continuous Agent Monitoring System (MINICAMS)

- Based on combining gas chromatography, which separates components, with flame photometry.
- A typical cycle lasts 3-5 minutes, enabling continuous monitoring of the environment.

Surface Acoustic Wave Detector

- Have chemically selective coated piezoelectric crystals that absorb target gases. The absorption causes a change in the resonant frequency of the crystal that is measured by a microcomputer.
- Able to identify and measure many CAs simultaneously.
- Inexpensive
- SAW MiniCAD mk II

- Joint Chemical Agent Detector (JCAD) ChemSentry

Carbon Nanotube Gas Ionization Detector

- May soon be used for chemical agents
- Nanotubes generate high electric fields
- Different gases cause different electrical conductance for the nanotubes, which can be used to identify the substance.

Department of Homeland Security Recommended Criteria for Choosing Detection Devices

http://emedicine.medscape.com/article/833933-overview#a1

Unit cost	Cost per piece of equipment including all support equipment and consumables
Chemical agents detected	Ability to detect nerve and blister agents
Toxic industrial chemicals and materials detected	Ability to detect toxic chemicals produced by industry
Sensitivity	Lowest concentration of chemical agent that results in positive response; ideally, lower than levels necessary for injury to personnel
Resistance to interferents	Ability of device to ignore agents such as smoke, moisture, or other chemicals that prevent the device from accurately providing a response

Department of Homeland Security Recommended Criteria for Choosing Detection Devices

Response time	Time it takes to collect a sample, analyze, determine if an agent is present and provide feedback
Start up time	Time to set up and initial a sampling
Detection states	Ability to detect agent in vapor, aerosol, or liquid form
Alarm capability	Visual and/or audible alarm
Portability	Ease of transport, which encompasses weight and dimensions
Power capabilities	Battery versus AC electrical power

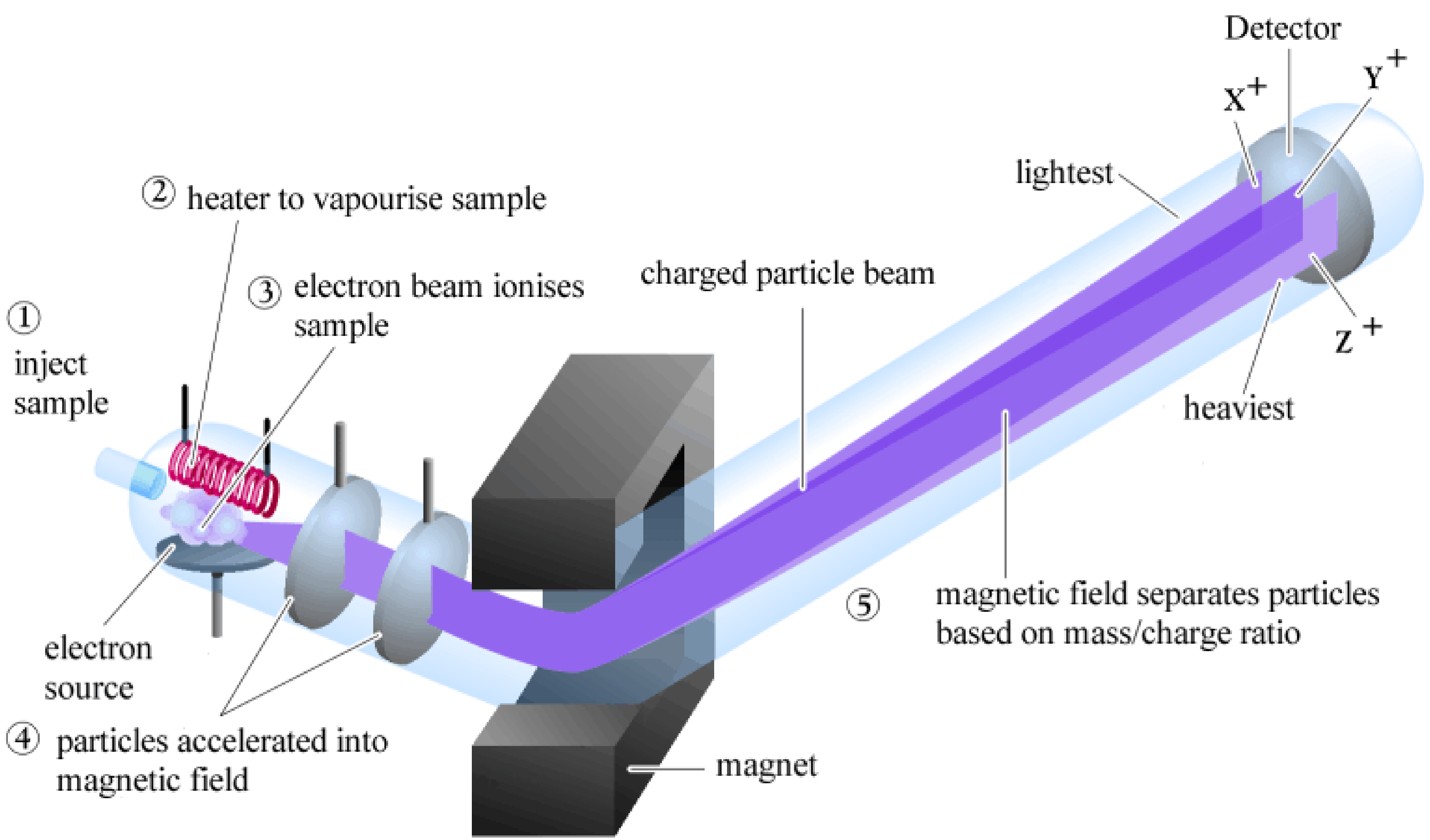
Department of Homeland Security Recommended Criteria for Choosing Detection Devices

Battery needs	Type, amount, cost, and operating life if powered by batteries
Operational environment	Extremes of conditions under which the device can operate
Durability	How well the device withstands rough handling
Operator skill level	Skill involved in using the device
Training requirements	Number of hours and type of educational background required for operation

Laboratory Instruments
Gas Chromatography/Mass Spectrometry (GCMS)

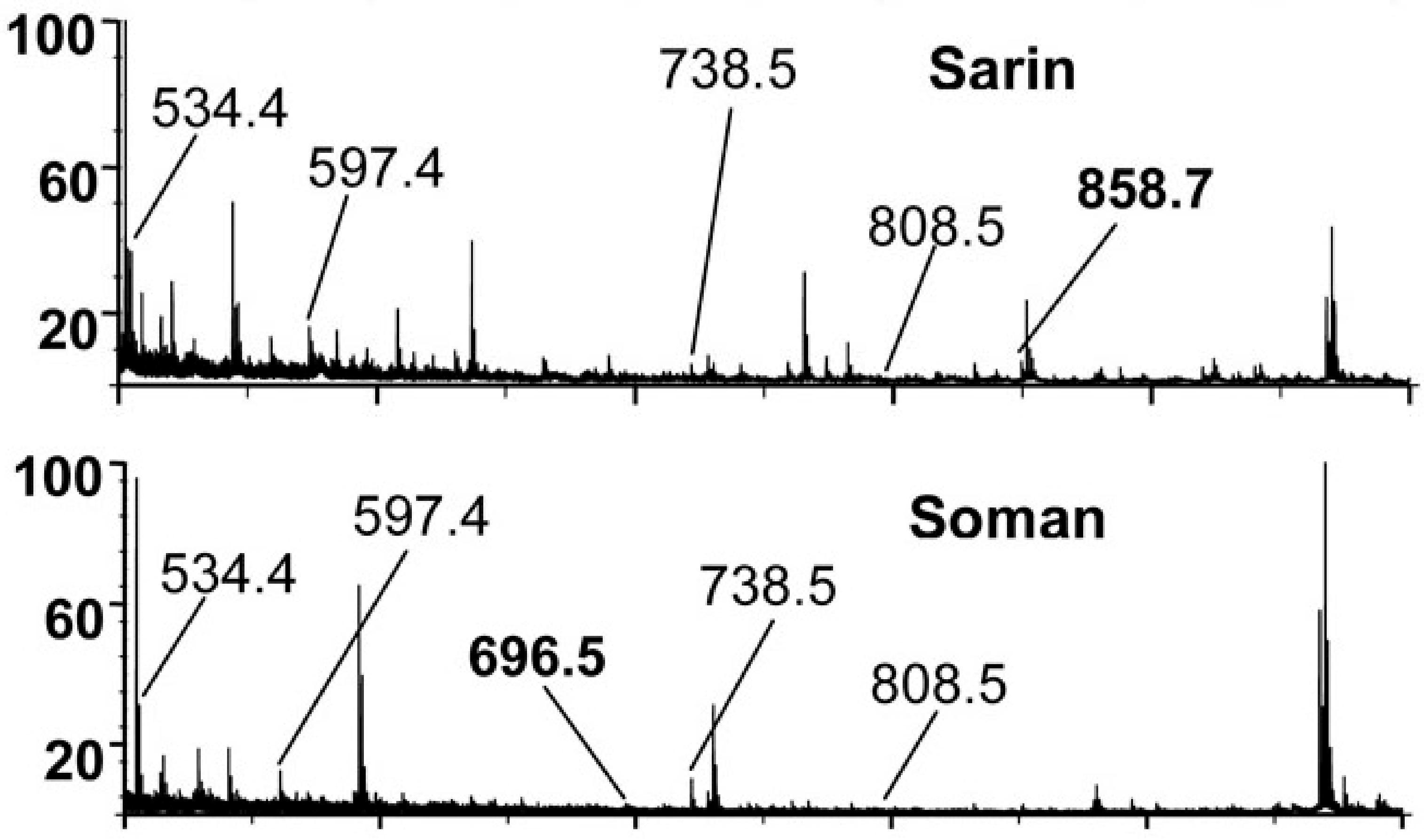
- Gas chromatograph separates components
- Mass spectrometer breaks substances into fragments and provides a mass spectrum that reflects the masses of the fragments. Comparison of mass spectrums to those of known substances helps to identify substances tested.

Mass Spectrometer



Mass Spectrum

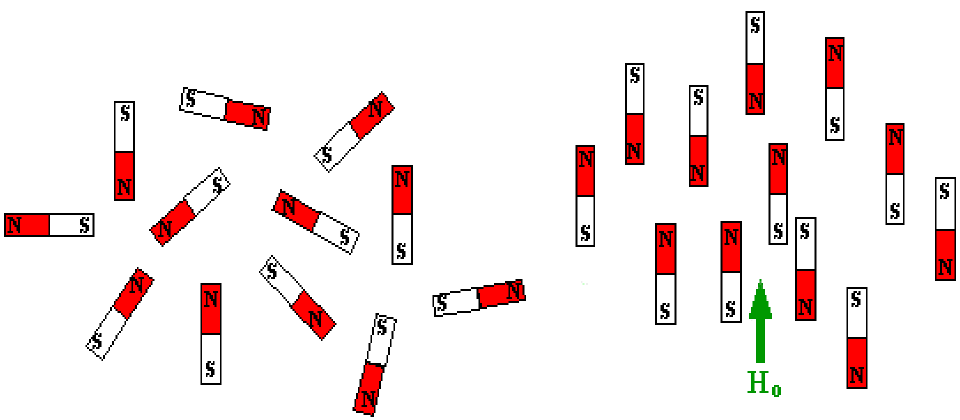
Numbers are mass to charge ratio.



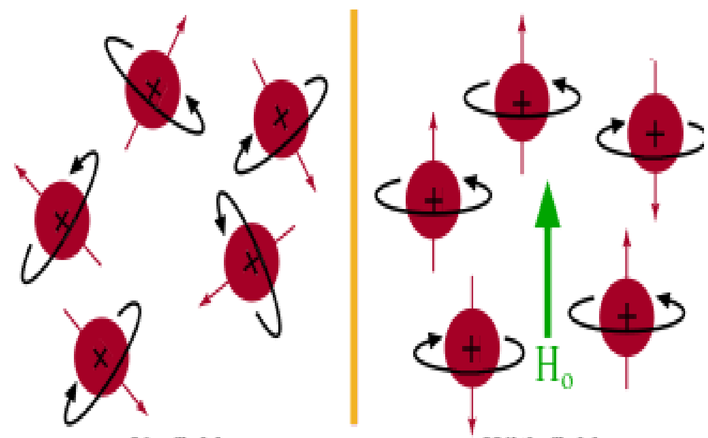
http://www.ncbi.nlm.nih.gov/pmc/articles/PMC2577157/

Laboratory Instruments - Nuclear Magnetic Resonance (NMR): Analyzing Chemicals Based on Their Nuclei's Spins Under Magnetic Force

- Nuclei with an odd mass or odd atomic number have "nuclear spin“ (includes ^{1}H and ^{13}C)
- Moving charges create magnetic fields.
- The nuclear spin sets up a magnetic field that can be influenced by an external magnetic field (H_0)
  - They behave like tiny bar magnets.
  - They line up with their spin aligned or opposed to the magnetic field.



No Field With Field

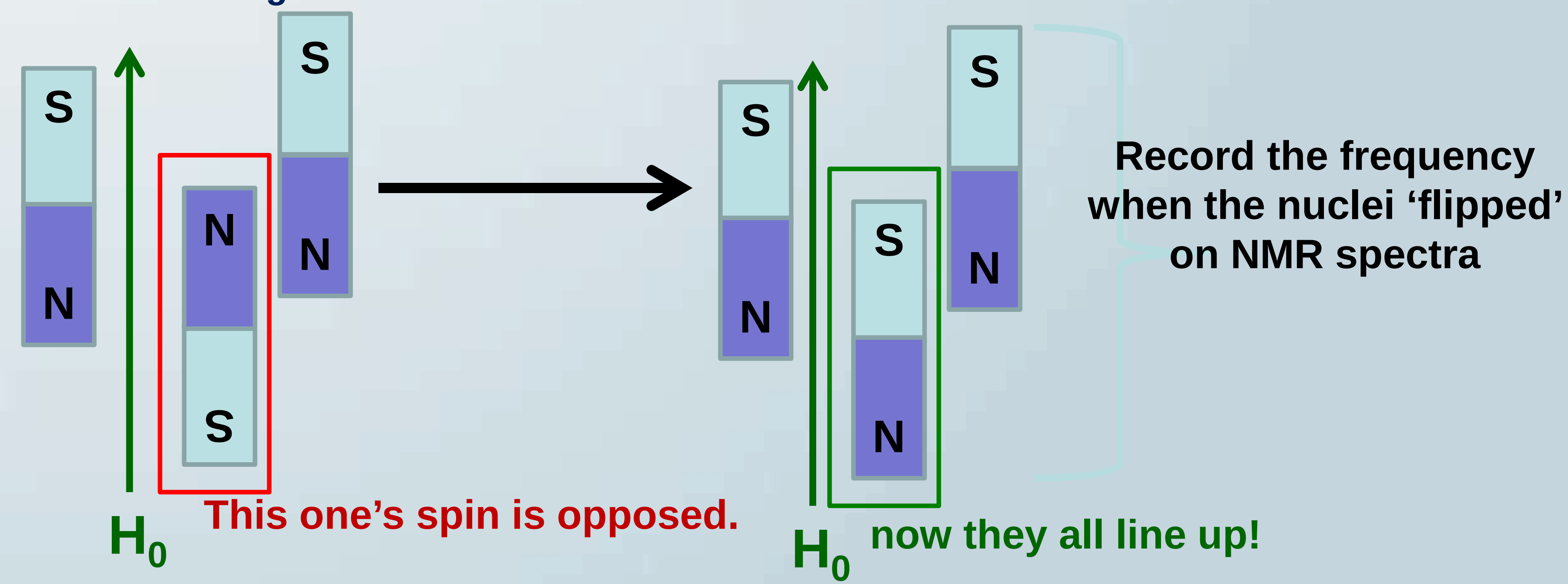


No field With field

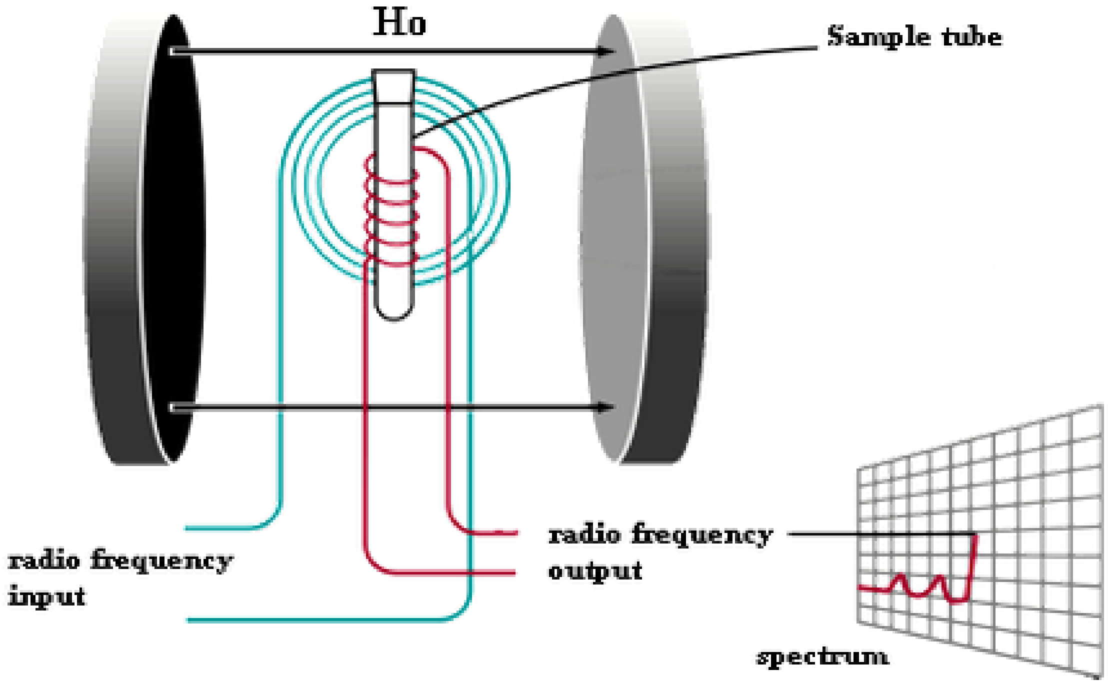
NMR: Nuclear Resonance and Chemical Shifts

- We apply energy to “flip” the spins of nuclei.
- Unique energy required for different nuclei in a compound
    - Nuclei in compounds are in different electronic environments.
    - Energy applied through radio waves…keep varying frequency until the ‘flip’ happens
    - When you hit the right frequency and spin ‘flips’, the radio wave and nucleus *resonate*.
    - You plot this resonance to learn about the chemical environment of the nuclei.

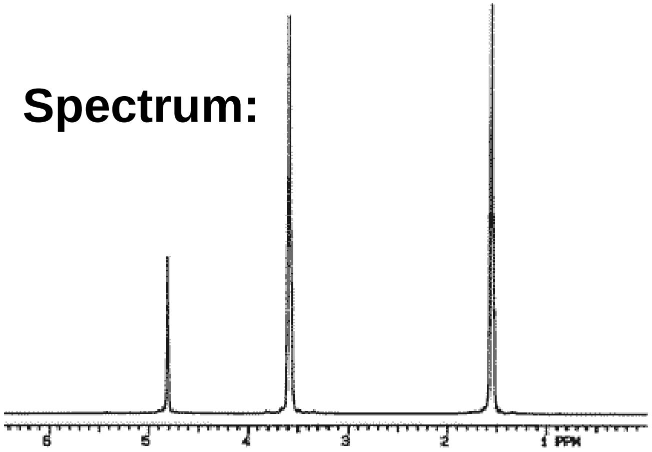
^{1}H nuclei in magnetic field:



Nuclear Magnetic Resonance



Spectrum:



Sarin NMR Spectrum

NMR Spectra for sarin: