

# Chemical Detection of Contraband

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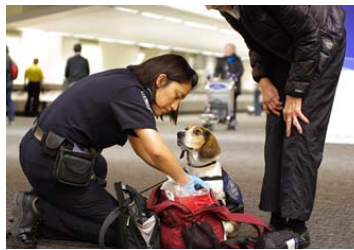


Cocaine, 84 kg, hidden in boxes of chrysanthemums.



<https://www.dailymail.co.uk/news/article-2209630/Florist-jailed-18-years-smuggling-23.5m-cocaine-UK-hidden-boxes-flowers.html>

Pants Bomber Causes Grief for Chefs Who Smuggle Salami Into America  
Wall Street Journal Jan 14, 2010



<https://www.cbp.gov/border-security/protecting-agriculture/agriculture-canine>



Feb.28, 2019  
1.6 tons cocaine  
Port of Newark

Photo: Courtesy of Customs & Border Protection

## So What, Who Cares?

We all do!

How we go about it depends on what we want to detect

- explosives
- drugs
- CWAs
- TICs, TIMs
- VOCs
- environmental pollutants

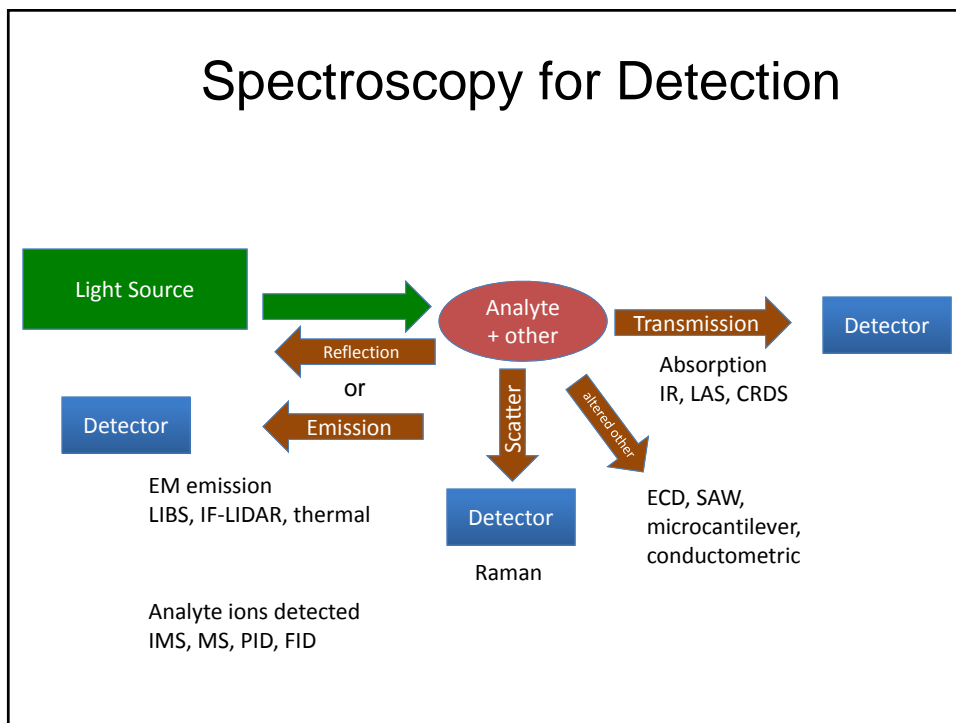
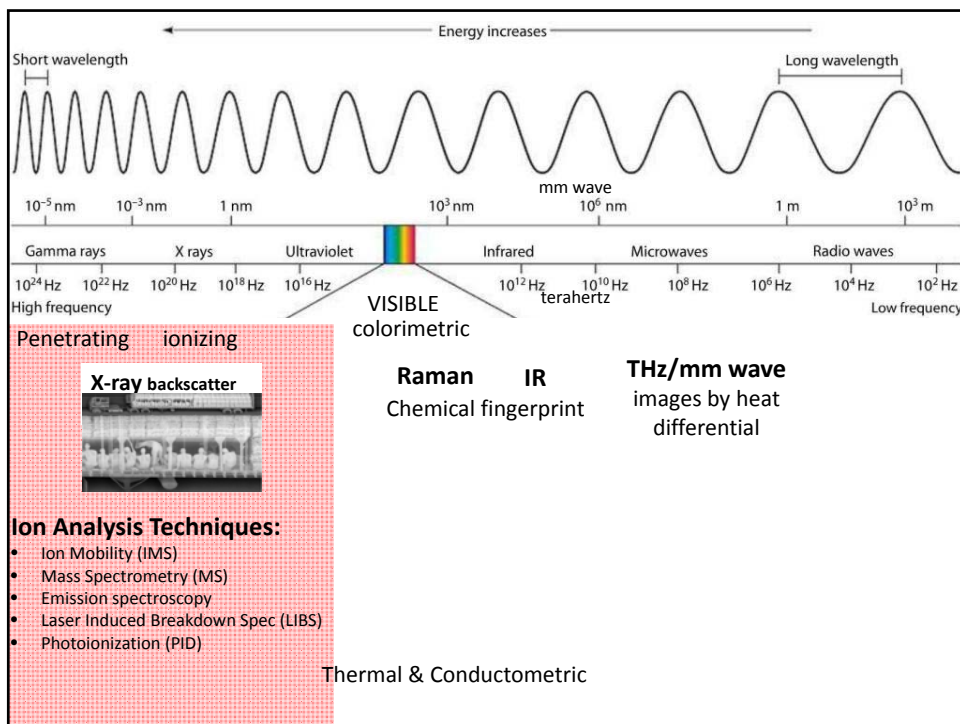


<http://www.stayathomemum.com.au/my-kids/babies/33-weird-things-you-wont-know-unless-youre-a-parent/3/>



<https://www.kidspot.com.au/baby/baby-care/nappies-and-bottom-care/smart-nappies-will-save-you-from-getting-poo-on-your-finger/news-story/32809dc5d5c6e10096257a68d934f>

Korean startup, Monit, has new bluetooth device, which tells when baby needs changing.



## What is available? Where is it used?

	collected sample	penetration of packaging	standoff	non-destructive	detects <1mg	commercial detection device	library	addition features/bugs
IMS	x				x	x	x	sample volatility
mass spectrometry	x				x	x	x	robustness?, sample volatility
fluorescence	x				x	x		
chemiluminescence	x				x	x		
Raman spectroscopy	x	can do clear containers	x	x	x	x	x	for standoff detects plumes but not for collected colored samples
infrared spectroscopy	x		x	x	x	x	x	water interferes
terahertz spectroscopy	x		x	x	x	x	x	water interferes
surface acoustic wave	x			x	x	x		specificity limited by chip
differential absorption			x	x	x	x		tuned for plumes, atmosphere interferences
hyperspectral imaging			x	x	x	x		tuned for plumes, atmosphere interferences
cavity ring-down spec.	x		x	x	x	x	x	
microcantilever	x			x	x	x		specificity limited by design
calorimetric	x						x	
colorimetric	x				x	x	x	
X-ray	x	x		x		x		
X-ray diffraction (XRD)	x	x		x		x	x	
NQR	x	x		x		x	x	

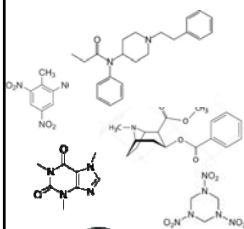
### Detection vs Analytical Instruments

	detection instrument		analytical instrument	
	seconds	ppb	ppb	minutes
TNT	8	50	10	15
PETN	3	20	15	9

Instruments for analysis and instruments for detection are different.

Many analytical procedures have been adapted for detection or identification  
For non-destructive, non-invasive sample needs to be emitting SOMETHING.

In general, vapor pressure of solid explosives are lower than drugs, making detection of a mobile analyte more difficult.



Drugs (free base)	Vapor pressures (ATM, at 25°C)
Nicotine	3.434E-05
MDMA	5.88E-06
Caffeine	1.13E-06
PCP	1.96E-07
Secobarbital	7.53E-08
Pentalbarbital	5.47E-08
Methaqualone	2.11E-08
Cocaine	1.29E-08
Morphine	1.25E-09
9-THC	1.33E-10
Heroin	7.51E-11
Fentanyl	3.17E-11

Explosives	Vapor pressures (ATM, at 25°C)
NM	4.83E-02
DADP	1.78E-04
TATP	2.44E-04
EGDN	1.02E-04

2,4-DNT	4.83E-07
NG	5.95E-07
TNT	1.58E-08
AN	5.90E-09
Picric acid	9.70E-10
Urea nitrate	3.88E-10
Styphnic acid	6.03E-11
PETN	1.85E-11
RDX	6.16E-12
DATB	5.44E-14
NH4 perchlorate	4.01E-14
Nitroguanidine	1.86E-14
HMX	4.34E-17
TATB	2.38E-18
HNS	6.09E-21
Guanidine nitrate	2.62E-23



### Raman spectroscopy

### Infrared spectroscopy

Raman & IR probe molecular bonding in similar frequency ranges by inducing stretching & bending. Molecular symmetry determines if mode is IR or Raman active or both. IR results from changes in dipole; Raman from changes in polarizability. Both give chemical fingerprints.

<https://www.wikiwand.com/fr/Lidar>

Aqueous solutions & clear containers are not a problem. Can be adapted to standoff.

### Cavity ring-down spectroscopy (CRDS)

- Laser pulse is trapped in highly reflective cavity
- Intensity of the trapped pulse will decrease by a fixed percentage each round trip in cavity due to absorption & scattering by analyte in cavity (more analyte faster decay) & reflective losses
- Effective path length of kilometers
- High sensitivity, but limited analyte detection (monochromatic laser)

### Laser Induced Breakdown Spectroscopy (LIBS)

- Laser is focused to form a plasma, which atomizes & excites samples
- LIBS can analyze matter regardless of state—solid, liquid or gas—all elements emit light of characteristic frequencies when excited to sufficiently high temperatures

<http://www.easternapplied.com/LIBS-Technology-Overview>

### Mass or Ion Mobility Spectrometers (MS or IMS)

- Sample is ionized by radioactive or high energy source or heat (MS) Ions move through high vacuum (MS) or electric field (IMS) to detector.
- Claims that IMS can be standoff.

[https://www.researchgate.net/publication/235602942\\_Computational\\_Methods\\_for\\_Merab-omic\\_Data\\_Analysis\\_of\\_Ion\\_Mobility\\_Spectrometry\\_Data\\_Reviewing\\_the\\_State\\_of\\_the\\_Art](https://www.researchgate.net/publication/235602942_Computational_Methods_for_Merab-omic_Data_Analysis_of_Ion_Mobility_Spectrometry_Data_Reviewing_the_State_of_the_Art)

### Photolization Detector (PID)

- Sample is ionized by UV light
- Positively charge ions complete circuit & signal results
- Only works for ions that can be ionized at below the energy of the UV source
- Tends to detect molecular ions but has poor to moderate sensitivity.



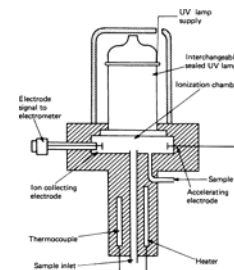
[www.defiant-tech.com/frog-4000.php?gclid=EAIaQobChMI6cEP-3d4wVax-tBh3mdgD5EAAYASAAEgKQg\\_D\\_BwE](http://www.defiant-tech.com/frog-4000.php?gclid=EAIaQobChMI6cEP-3d4wVax-tBh3mdgD5EAAYASAAEgKQg_D_BwE)

### Flame Ionization Detection (FID)

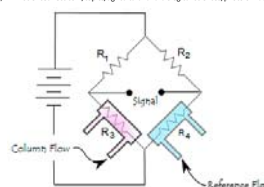
- Used for measuring hydrocarbons
- Ionizes by burning
- Does not work well with heteroatoms

### Thermal conductivity detector (TCD)

- Compares electrical current through filament in chamber with & without analyte present
- Resistance changes in filament detected
- Universal detector but less sensitive than FID & much less than PID



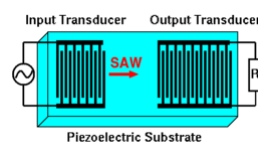
<https://www.sciencedirect.com/topics/agricultural-and-biological-sciences/photolization-detector>



<http://cdn.analyteguru.com/uploads/2015/11/TCD.png>

### Surface acoustic wave detector (SAW)

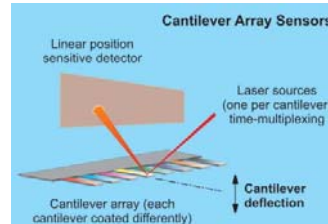
- Consists of piezoelectric substrate connecting two interdigitated transducers (IDT)
- Electrical signal from one travels thru substrate to other IDT
- Substrate transmits IDT electrical signal as surface acoustic wave; wave characteristic is modified by whatever analyte surface has absorbed
- Second IDT receives a signal, altered in characteristic fashion, and re-emits
- There are many fielded applications



[https://en.wikipedia.org/wiki/Surface\\_acoustic\\_wave](https://en.wikipedia.org/wiki/Surface_acoustic_wave)

### Cantilever beam detectors

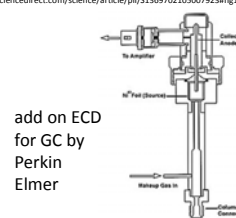
- Microcantilevers are thin silicon wafers (possibly treated)
- Bends when analyte molecules are adsorbed
- Bending is detected by deflection of a laser beam
- Resonance frequency of the cantilever can vary due to mass loading
- Often in arrays, they are small, fast, & highly sensitive.



<https://www.sciencedirect.com/science/article/pii/S1369702105007923#fig1>


### Electron capture detector (ECD)

- Electron source (e.g. a Beta emitter) irradiates N<sub>2</sub> in a cavity between two electrodes causing N<sub>2</sub> to lose e<sup>-</sup> resulting in current
- The analyte captures some e<sup>-</sup> thus reducing signal
- Very sensitive for halogen & nitro compounds




add on ECD for GC by Perkin Elmer


**Stand-off Detection**      Bees do it.    Rats do it    Elephants do it?



U Montana trained bees to associate food with odor of explosive. Bees detected DNT at 30-100 ppt. Number of bees indicate vapor plumes. Bees detect plume meters from source & navigate up the plume to source. Density of bees is mapped, by sight, camera or laser-assisted counts.

**Southern Giant Pouched Rat**

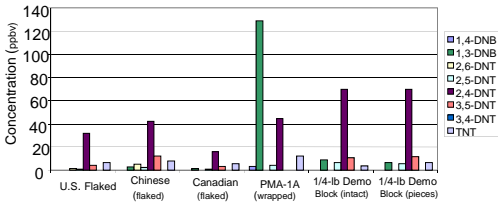




**Samples & Simulants**



Train your instrument on realistic samples. Do you have the appropriate simulant?

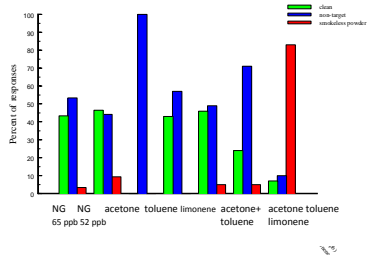
Average Static Headspace from TNT Variant Samples



Don't assume dogs "see" what instruments "see"

Where is the sample?



Did your sample actually get to the detector?

What is the detector detecting?

### Orthogonal Chemical Sensor for Trace Detection

**Rapid Detection of Threats... sensors on drones**

- ✓ sensitive...low detection limit
- ✓ small mass...a few grams
- ✓ low energy budget...a few mA
- ✓ real time processing....
- ✓ can be tailored for various threats...drugs, explosives, etc
- ✓ compatible w/communication protocols Zigbee / Bluetooth



**Chemical sensors for vapor detection**

continuous monitoring/screening...24/7  
sensitivity.....low detection limits  
selectivity.....mitigate false positives  
low profile; conform to wings surface



**Our answer:**  
**URI orthogonal sensor for trace detection**  
**Otto Gregory & Peter Ricci**

### Five Fixes from ALERT-URI division

#### Hazardous Spills of Explosive or Toxic Others Onsite

**SCHMOO** Safe Control of Hazardous Materials & Others Onsite

Part One: Desensitizes & freezes threat  
Part Two solidifies Part One  
Once solidified sample can be transported to lab  
Sample can be recovered unchanged for analysis



		
Hazardous Material (TATP)	Application of Part One	Material Isolated
		
Application of Part Two	Easy Pickup and Removal	Total Time < 1 minute

### Introduction System for Non-volatile Substances

Ambient Desorption Ionization (ADI) a sampling technique that doesn't require sample vaporizing. Sample is desorbed & ionized by high voltage & small amount of solvent.

Sample is positioned in in front of IMS or MS inlet such that a cone of ions is carried into the inlet.



### Safe Scent Aids for Dogs & Detectors



### Physical Properties Database



Partial List: Companies doing biological, CW, drugs, explosives, radiological detection

ALERT	Rapid Scan
Agilent	Rigaku
Bruker Detection	RomTech
BWTech	Shimadzu
ChemImage	Smiths Detection
Envionics Oy	Spectral Evolution
FLIR	S.E. International
Hindsight Imaging	S2 Threat Detection
IDSS	Technologies
<del>Implant Sciences</del> L3	Thermo Scientific
Metrohm	& all the colorimetric companies
Perkin Elmer	
Pendar	