TOOLS OF THE TRADE, REFRESHER ON COMMONLY USED MONITORS

Bill Lent, Patrick Ledesma

Session Code M-12

Monday, February 26, 2024

26th California Unified Program Annual Training Conference
February 26-29, 2024

What are we going to do today?

- Refresher training focused on monitors used by first responders and CUPA staff.
- Identify opportunities for agencies that don't have a robust HEMRT
- Review operational issues
- General overview with hands on for using the following equipment:
  - Combustible Gas Indicators
  - Photo Ionization Detectors

  Demonstrations for the following:
  - Radiological monitors
  - FTIR
  - Raman and other specialized instruments

What are we going to do today?

- Some hands- on training for the CGI and PID
- Response Equipment Demonstrations Raman, FTIR
- Overview of available resources and operational theory
- Tour of Type 2 Haz Mat response vehicle

How did we get here

CERCLA (1970)

- Torrey Canyon Spill (1968 England)
- Love Canal (1970, Niagra Falls, NY)
- Bhopal India (1984) methyl isocyanate
- Times Beach (1982, Missouri)
- Exxon Valdez (1989, Prince William Sound, Alaska)
- Anthrax Letters "Amerithrax" (2001, Washington DC, et al)

- Methyl Bromide release (1974, Belmont, CA)
- Bay Bridge (1982, San Francisco, CA)
- Honey Oil Explosion (2023, San Francisco, Daly City)

CALIFORNIA CUPA FORUM

ERT Over Time

Operational Issues

OK, we have an incident, grab a meter and go, right?

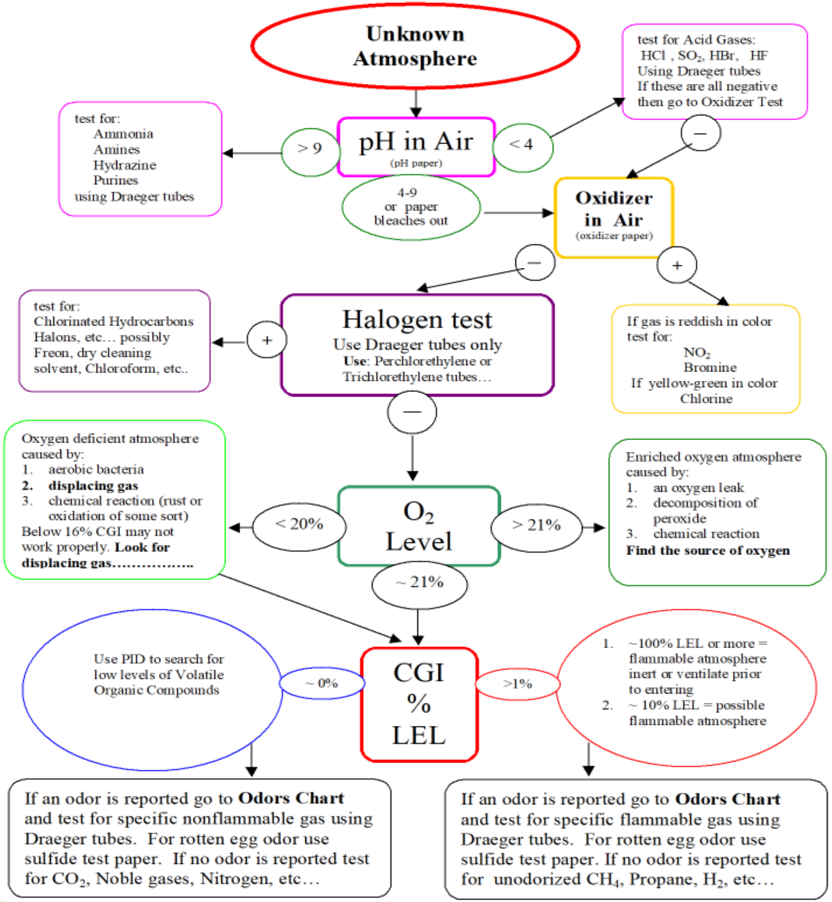
- Success is based on understanding the environment and having a plan
- What affects our success in "identifying that unknown?"

  - Size- up
  - Solid, liquid or gas?
  - A bunch of decision- making considerations

CALIFORNIA CUPA FORUM

Atmosphere Monitoring Considerations

- Strategic air monitoring
- Detection and operating ranges
- Sensitivity and limitations
- Normal atmosphere
- Type of contaminant encountered
- Unknown atmospheres
- Monitoring priorities
- Monitoring for confined spaces
- Air movement
- Locating the gas
- Distance and location relative to release
- Understanding real-time monitoring
- Datalogging
- Calibration gas
- Intrinsic safety
- Hazardous location
- Warm- up time
- Lag time
- Response time
- Recovery time
- Use considerations


Unknown Atmosphere
pH in Air
(pH paper)
> 9
< 4
4-9 or paper bleaches out
test for: Ammonia Amines Hydrazine Purines using Draeger tubes
test for Acid Gases: HCl , SO2, HBr, HF Using Draeger tubes If these are all negative then go to Oxidizer Test
Oxidizer in Air
(oxidizer paper)
+
If gas is reddish in color test for: NO2 Bromine If yellow-green in color Chlorine
Halogen test
Use Draeger tubes only
Use: Perchlorethylene or Trichlorethylene tubes…
test for: Chlorinated Hydrocarbons Halons, etc… possibly Freon, dry cleaning solvent, Chloroform, etc..
O2 Level
< 20%
> 21%
~ 21%
Oxygen deficient atmosphere caused by: 1. aerobic bacteria 2. displacing gas 3. chemical reaction (rust or oxidation of some sort) Below 16% CGI may not work properly. Look for displacing gas……………..
Enriched oxygen atmosphere caused by: 1. an oxygen leak 2. decomposition of peroxide 3. chemical reaction Find the source of oxygen
CGI % LEL
~ 0%
>1%
Use PID to search for low levels of Volatile Organic Compounds
1. ~100% LEL or more = flammable atmosphere inert or ventilate prior to entering 2. ~ 10% LEL = possible flammable atmosphere
If an odor is reported go to Odors Chart and test for specific nonflammable gas using Draeger tubes. For rotten egg odor use sulfide test paper. If no odor is reported test for CO2, Noble gases, Nitrogen, etc…
If an odor is reported go to Odors Chart and test for specific flammable gas using Draeger tubes. For rotten egg odor use sulfide test paper. If no odor is reported test for unodorized CH4, Propane, H2, etc…

Air Monitoring Equipment

- Combustible Gas Indicators
- Photo Ionization Detectors
- Radiological monitors
- FTIR
- Raman and
- Other instruments

Air Monitoring Equipment

CGI, PID, RAD, FTIR, ...

CALIFORNIA CUPA FORUM

26th California Unified Program Annual Training Conference
February 26-29, 2024

Air Monitoring Equipment

FTIR, RAMAN, SAW, IMS, GCMS….








Instrument Responses (2.4, 2.10)

- No single instrument can provide sufficient information
- Each monitor/detector has strengths & **"blind spots"**
- Monitoring strategy must employ a combination of devices

Vapors and Gases, Where Are They? (2.14)

- Vapor density
  - lighter than air?
  - heavier than air?

- The vapors of all liquids are heavier than air at normal temperatures and pressure!
- What about gases?

CALIFORNIA CUPA FORUM

Why Use Air Monitors?

- Set zones…
- Provides continuous data in real time
- Determine protective action distances
- Determine if an area is safe to enter or re-enter
- Determine the type of respiratory protection needed
- Comply with OSHA
- Provide preliminary ID of some air contaminants
- We will talk about interferences later

Unknown Atmospheres

- Instrument of the greatest use can:
  - **Measure Flammability**
  - **Measure Oxygen**
  - **Detect categories of chemicals**
  - **Detect Radiation**
  - **Detect various toxic gases**
  - **Determine presence or absence of corrosives**
- **Key: Use a combination of the above**

Air Monitoring Equipment

- **Combustible Gas Indicators**
- Photo Ionization Detectors
- Radiological monitors
- FTIR
- Raman and
- Other instruments


RKI
INSTRUMENTS
EAGLE
HEX 0 LEL%
OXY 20.9 VOL%
CO 0 PPM
RKI INSTRUMENTS, INC.
POWER/ ENTER
RESET/ SILENCE
DISP/ ADJ
LEL/ PPM
AIR/ ▲
SHIFT/ ▼

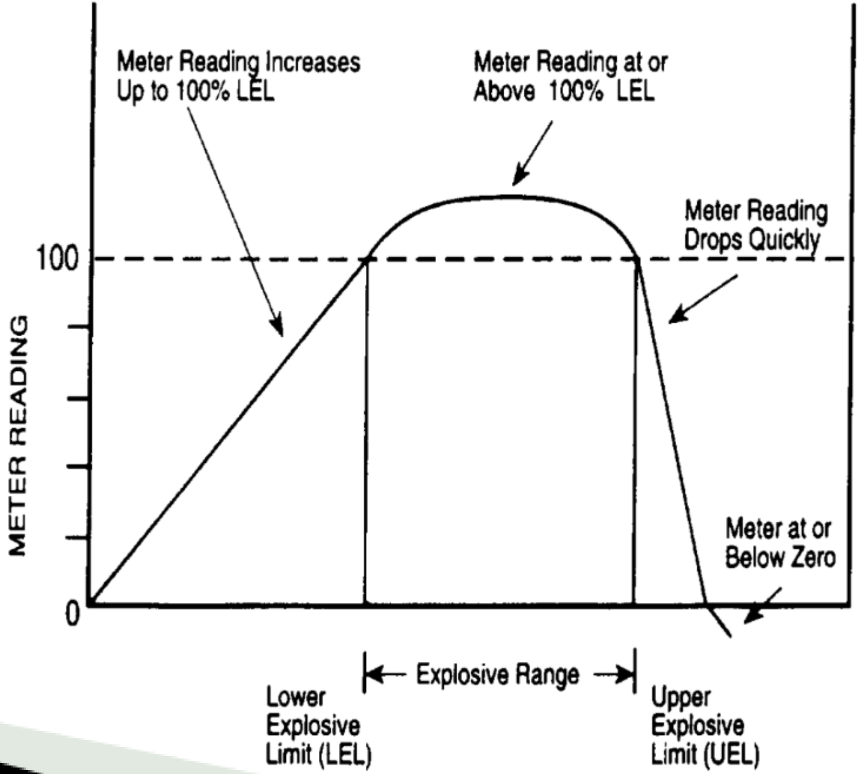
Combustible Gas Indicators (CGIs)

- Monitors a wide range of atmospheric levels in one meter
- Detects gases in the flammable range (LEL)
- Identifies potentially explosive atmospheres
- Operators must understand what the reading means
- Also called a Four Gas monitor because it detects other hazardous gases
- Depending on the hazards, CGI's can be set up to detect flammable vapors, oxygen plus toxic gases like H_2S.CO,NH_3.CO_2 .
- The reading is relative to the calibration gas for the instrument

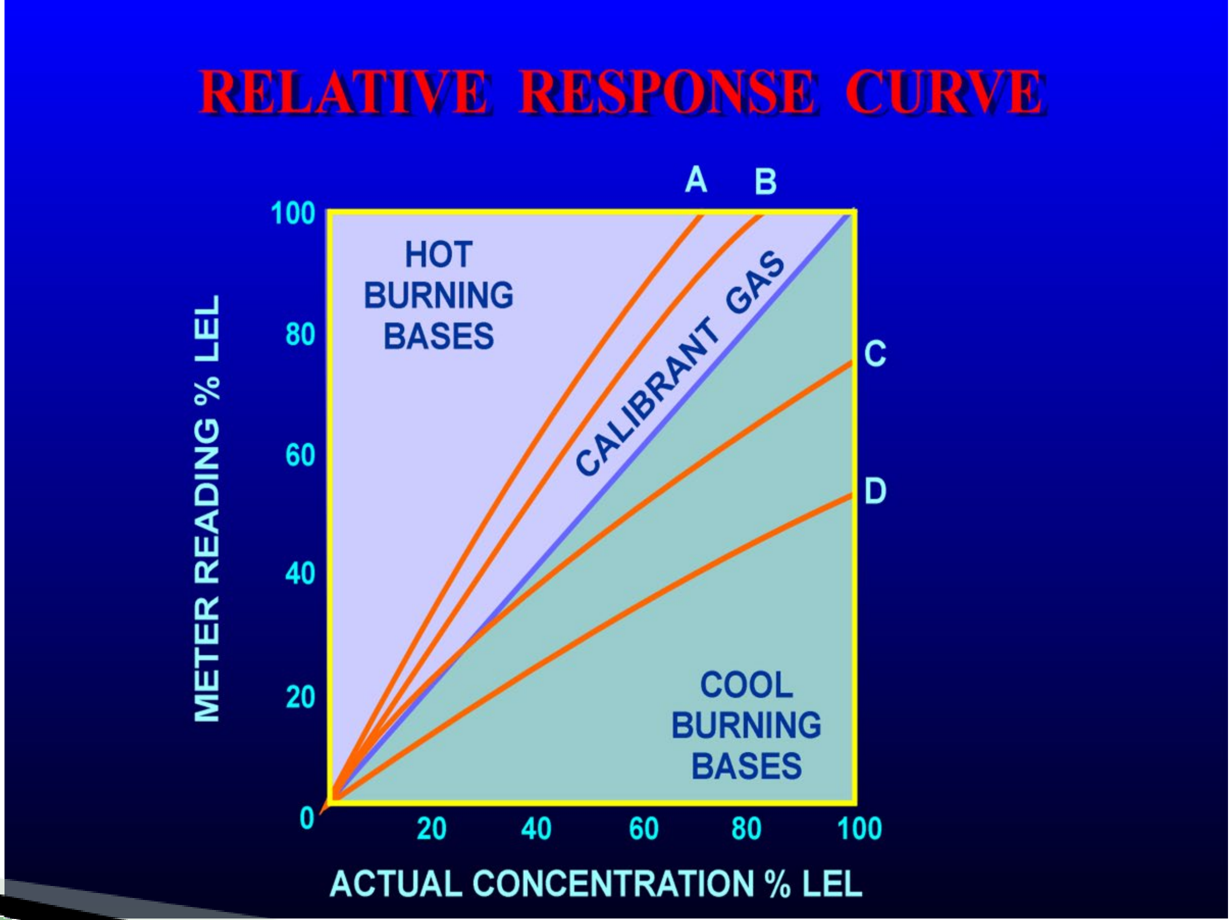
Flammable Gas Monitoring

- To Determine:
  - Risk of fire or explosion
  - CGI reading indicative of a relative high concentration of contamination
  - LEL vs PPM
  - In addition to the flammable vapors CGI's also monitor oxygen
  - Chemical specific sensors monitor for other toxic components
  - Used for confined space entry
  - CUPA staff use CGI's for UST removals and odor investigations

Flammable Gas Monitoring



- Not the cal gas? You need a correction factor
- Or it's a pucker factor!



Gas being Sampled LEL		Multiply by
Acetone	2.5	0.9
Acetylene	0.7	2.5
Benzene	1.2	1.0
Butane	1.9	0.9
Ethane	3.0	0.7
Ethanol	3.3	0.8
Ethylene	2.7	0.7
Hexane	1.1	1.2
Toluene	1.1	1.1
Xylene	1.0	1.3

You've responded to a hexane spill. You get a meter reading of 20% LEL on the RKI Eagle. What is the actual concentration of Hexane in % LEL and ppm?

___________% LEL

___________ ppm

Answer:

Actual % LEL is found by applying the conversion factor which is 1.2

1.2 x 20 % = 24 % of the LEL of hexane

Actual concentration in ppm is found by taking 24% of the LEL (1.1%) and multiplying it by 10,000.

24 % of 1.1 = 0.24 x 1.1 = 0.264

0.264 x 10,000 = 2,640 ppm

# %	=	PPM

- 0.1% = 1000 ppm
- 0.5% = 5000 ppm
- 1%   = 10,000 ppm
- 5%   = 50,000 ppm
- 10% = 100,000 ppm
- 50% = 500,000 ppm
- 90% = 900,000 ppm
- 100% = 1,000,000 ppm

CALIFORNIA CUPA FORUM

LELs of Some Common Chemicals

- Acetylene 2.5% by volume
- Benzene 1.2% by volume
- Butane 1.9% by volume
- Butyl Alcohol (Butanol) 1.4% by volume
- Diethyl Ether 1.9% by volume
- Ethane 3.0% by volume
- Ethyl Alcohol (Ethanol) 3.3% by volume
- Ethylene 2.7% by volume
- Ethylene Oxide 2.7% by volume
- Hexane 1.1% by volume
- Hydrogen 4.0% by volume
- Isopropyl Alcohol (Isopropanol) 2.0% by volume
- Methane 5.0% by volume
- Methyl Alcohol (Methanol) 6.0% by volume
- Methyl Ethyl Ketone 1.4% by volume
- n-Pentane 1.4% by volume
- Propane 2.1% by volume
- Propylene 2.0% by volume
- Styrene0.9% by volume Toluene 1.1% by volume
- Xylene 1.1% by volume

Conversion Factors

HAZARDOUS MATERIAL SPILL RESPONSE

COMBUSTIBLE GAS INDICATOR

RELATIVE RESPONSE OF A CGI TO VARIOUS GASES

(REFERENCED TO HEXANE, TOLUENE, OR METHANE)

GAS	ACTUAL LEL IN %	CONVERSION FACTOR (MULT.)		
		HEXANE	TOLUENE	METHANE
Acetone	2.15	0.65	0.63	1.55
Benzene	1.3	0.87	0.84	2.07
Butadiene	2.0	0.88	0.85	2.10
Carbon Monoxide	12.5	0.60	0.58	1.43
Ethyl Acetate	2.0	0.81	0.79	1.93
Ethyl Alcohol	3.3	0.60	0.58	1.43
Formaldehyde	7.0	1.96	1.9	4.67
Heptane	1.0	1.03	1.00	2.45
Hexane	1.1	1.00	0.97	2.38
Hydrogen Sulfide	4.0	1.96	1.9	4.67
Methyl Ethyl Ketone	1.7	0.84	0.81	2.00
Methylene Chloride	12.0	2.78	2.7	6.62
Methane	5.0	0.42	0.41	1.00
Pentane	1.5	0.71	0.69	1.69
n-Propyl Acetate	1.7	0.77	0.75	1.83
n-Propyl Alcohol	2.1	0.80	0.78	1.90
Styrene	1.1	1.24	1.2	2.95
Toluene	1.2	1.03	1.00	2.45
Trichloroethylene	12.5	0.59	0.57	1.40

Response varies from one sensor to another and the response of a sensor can change with age, so these data should be used for estimation purposes only.

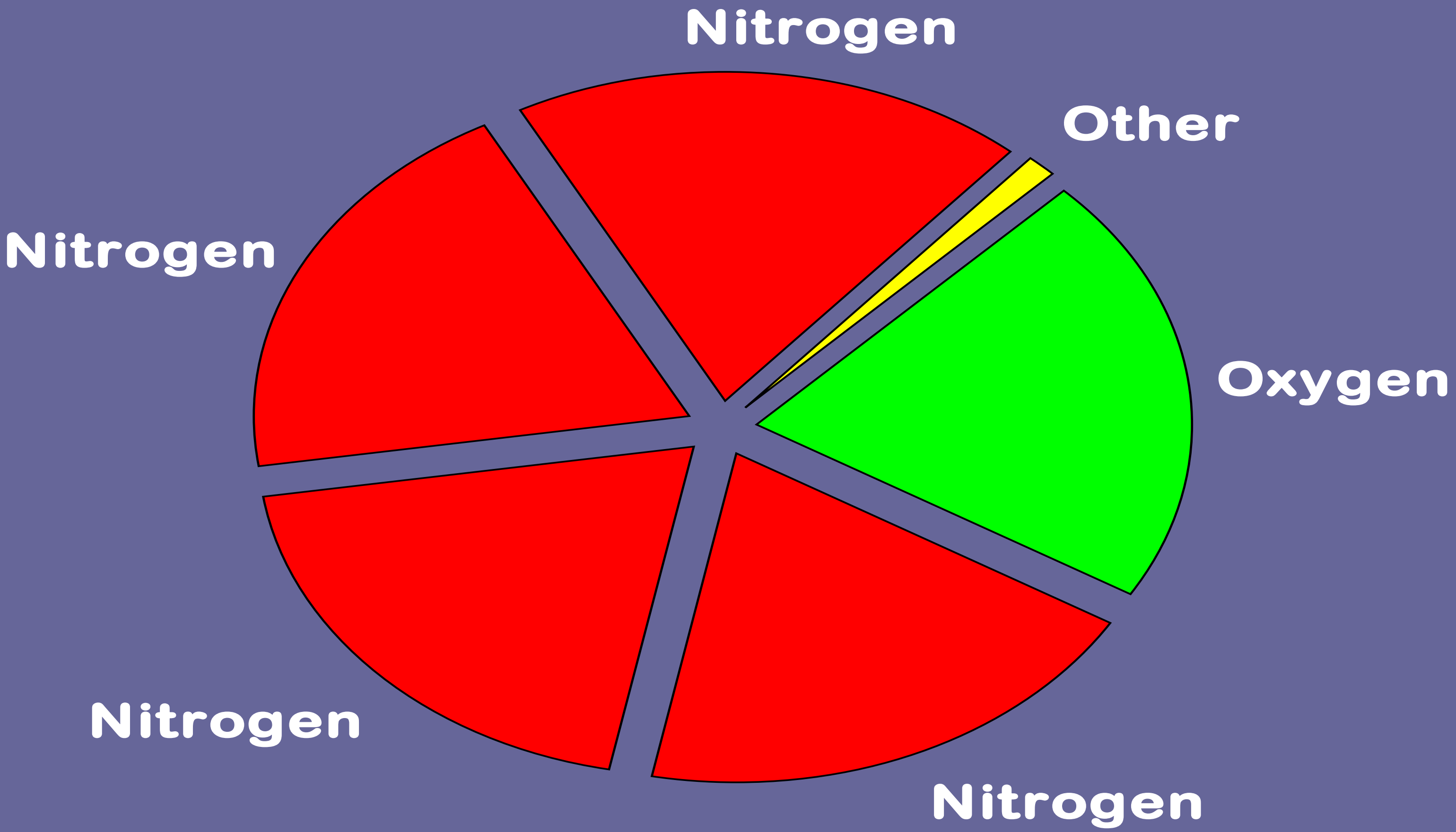
With an instrument calibrated for hexane, toluene, or methane, but used to monitor for a different gas, the equivalent response in %LEL for that gas is obtained by multiplying the observed %LEL reading by the Conversion Factor.

Earth's Atmosphere

Major Gases	Percent
nitrogen	78.08
oxygen	20.94
argon	0.93

Minor Gases	ppm
carbon dioxide	330
neon	18
helium	5
methane	2
krypton	0.5
nitrogen dioxide	0.5
xenon	0.08

Normal Atmosphere



Oxygen Displacement

- 20.9% No displacement
- 20.8% 0.1% x 5 = 0.5%
  5000 ppm contaminate in air
- 20.7% 0.2% x 5 =1.0%
  10,000 ppm contaminate in air
- 20.6% 0.3% x 5 = 1.5%
  15,000 ppm contaminate in air

Air Monitoring Equipment

- Combustible Gas Indicators
- **Photo Ionization Detectors**
- Radiological monitors
- FTIR
- Raman and
- Other instruments

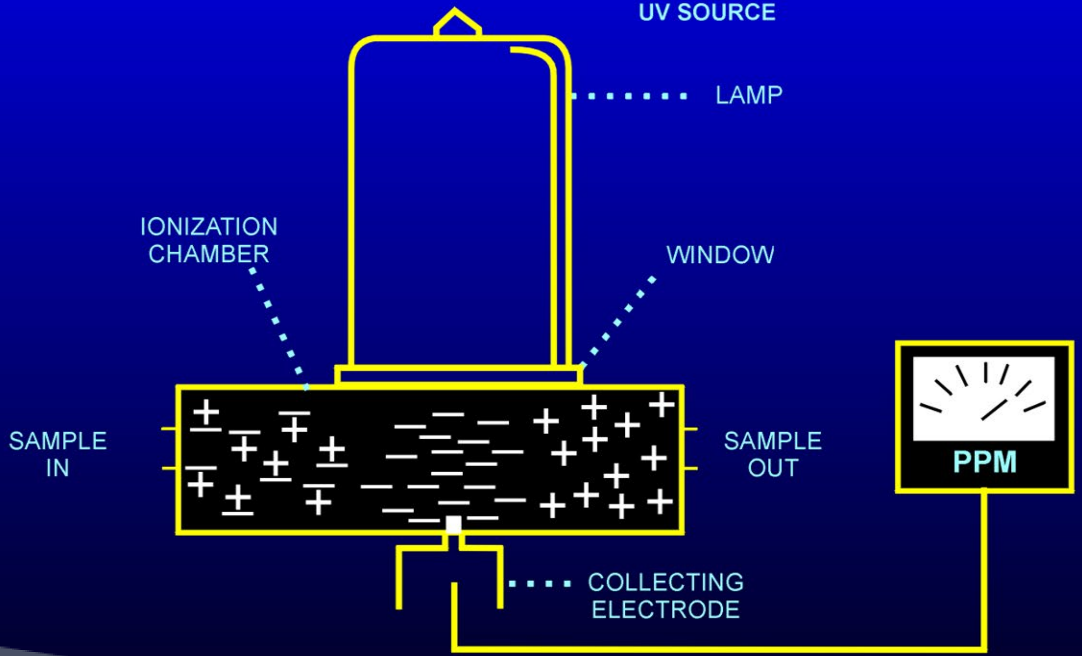
Photo Ionization Detectors

- Detects compounds by ionizing them
- Can determine compounds at very low concentrations
- Not accurate at high concentrations
- Very good with aromatic hydrocarbons (BTEX)
- Can be blind to many common gases (IP)
  - IP of chemical must be lower than the energy source in the PID (usually 10.6)
  - Methane
  - O_2, N_2, CO
  - Water vapor

Photoionization Detectors (PID)

- **Developed during the early 70's**
- **Designed to detect relatively low concentrations of VOC's**
- **can range from 0.1 to 10000 ppm**
- **as low as the parts per billion range**
- **Particularly well suited for detecting aromatic hydrocarbons (BTX)**

PHOTOIONIZATION DETECTOR



CALIFORNIA CUPA FORUM

Ionization Potential (IP)

The energy required to remove the outermost electron from a molecule

- Specific for any compound or atomic species
- Measured in electron volts (eV)

Molecule	IP (eV)
Methane	12.98
$CFLC_3$ (Freon 11)	11.77
Dichloromethane	11.35
Ammonia	10.15
Acetone	9.69
MEK	9.53
Benzene	9.24
Toluene	8.82

PID Lamps and Filaments

eV	Gas	Filaments
8.3		Magnesium Fluoride
9.5	Oxygen	Magnesium Fluoride
10.0		Calcium Fluoride
10.2	Hydrogen	Magnesium Fluoride
10.6	Nitrogen	Magnesium Fluoride
11.7	Argon	Lithium Fluoride
11.8	Neon	Lithium Fluoride

Calibration

- All readings are relative to the cal gas
- Calibration must be current
- Many units come with several calibration gases settings pre-programmed
- Dirty bulbs affect the quality of the Calibration
- Humidifying calibrant gas can compensate for water vapor – can purchase pre humidified cal gas

Applying Conversion Factors

The Meter Reads:		Conversion Factor (10.6 bulb)		
Ammonia: 25 MU	(10.6)	5.7	142.5 PPM	
Butane:(10.63) 200 MU	(10.6)	67	13,400 PPM	(LEL =1.9%)
Benzene 700 MU	(10.6)	.53	371 PPM	

Interpretation of Results

- **Meter reading represents total concentration of gases in air that the PID can ionize**
- **Most materials are not ionized as well as factory calibrant gas**
- **Sometimes suspect gas may be ionized more efficiently than calibrant gas**
- **While PIDs can detect many materials at low concentrations, they do not detect everything**

MiniRAE 2000: 0.1-10,000 ppm

pppRAE: 1-9999 ppb/ 0.1-200 ppm

Photoionization Detector

PID Summary

- PIDs – Detect organic & some inorganic chemicals
- They ionize the sample
- The ionization energy (bulb) is called IP
- The energy is measured in eV
- Results are based on the calibration gas and if the chemical has an IP within the range of the lamp it can be detected
- Measured in PPM (corrected) or meter units (uncorrected)
- Use conversion factors

Air Monitoring Equipment

- Combustible Gas Indicators
- Photo Ionization Detectors
- **Radiological monitors**
- FTIR
- Raman and
- Other instruments

CALIFORNIA CUPA FORUM

Radiological Monitors

- Survey Meter
- Fixed Area Detector
- Self- Reading Dosimeter
- Film Badge
- Multi- Channel Analyzer

Radiological Monitors

- Alpha (α), Beta (β), Gamma (γ) and Neutron (n)
  - Alpha radiation is (+) charged particle
    - Inhalation hazard
  - Beta radiation is a (–) charged particle
    - Inhalation hazard (more penetrating than alpha)
  - Gamma radiation does not have mass or a charge
    - Consists of a packet of energy (photons)
      - Penetrating exposure hazard
- Contamination v Exposure
  - Contamination = touched the source
  - Exposure = touched the energy emitting from the source

Radiological Monitors

- Measurements
  - Rate: calculated potential of a dose received over an hour
  - Dose: accumulated amount of radiation at a measuring point (REM/hr), typically mREM/hr
  - Counts per minute (radiation present or not present, relative intensity)
- Exposure Limits

Dose Limits

Whole Body Dose Limits

- Occupational = 5 rem/yr
- General Public (NRC) = 100 mrem/yr
- Emergency Worker (EPA)
  - 2 mrem/hr = Exclusion Zone Line (Emergency Response)
    - **Posted Boundaries**
    - 5 mrem/hr = all activities (defines radiation area)
    - 100 mrem/hr = high radiation area
    - >500 rad/hr (same as rem for ß/γ) = very high radiation area
  - 25 REM = max single dose (lifesaving / large population protect.)
  - >25 REM = voluntary basis only

Solid State Detectors

Radiation Spectrometer

- Is a dual-purpose instrument with a complete digital gamma spectroscopy and dose rate system

- Unit will facilitate locating sources and then identify the source via its Gamma spectrometry and radio isotope identification capability

CALIFORNIA CUPA FORUM

Air Monitoring Equipment

- Combustible Gas Indicators
- Photo Ionization Detectors
- Radiological monitors
- **FTIR**
- Raman and
- Other instruments

FTIR

- Fourier Transform Infra- red (FTIR) technology
    - Measures light absorbed by a substance
    - Wavelengths absorbed correspond to bonds
- Used to sample liquid and solid materials
    - Most common method is the Diamond ATR
    - CBRN, narcotics, TICs, precursors, common substances
- FTIR has significant limitations and can't be used as a stand- alone monitor
    - Has to be taken to the unknown chemical (decon considerations)
    - Struggles with traces levels or <10% solution
    - Can't see substances lacking covalent bonds, metals or elements

FTIR

- FTIR
  - Fast (<1 scan / second) average 15 second result
  - High quality data (good throughput) → reliable identifications
  - High specificity
  - High detection limits (~10% mixture)
  - Requires precision optics
  - Relatively high- power consumption

- ATR (attenuated Total Reflection)
  - No sample preparation
  - Diamond sensor is virtually indestructible
  - Sample must contact sensor

What Solids / Liquids Can Infrared Identify?

Must have a COVALENT CHEMICAL BOND

- Organic compounds
  - Pesticides
  - Plastics
  - Chemical WMD
  - Drugs (legal or illicit)
  - Petroleum product

- Many inorganic compounds
  - Water
  - Mineral acids (sulfuric, nitric, etc.)
  - Inorganic oxides (rust, talk, etc.)
  - Oxy compounds (nitrates, chlorates, phosphates)

What Gases / Vapors can IR Identify?

Must have a COVALENT CHEMICAL BOND

- Virtually any gas or vapor released into the air by:
  - Cylinder opening or leaking
  - Evaporation of a volatile chemical
  - Liberation from a chemical reaction
  - Off- gassing from products containing volatile chemicals
- Covalently- bonded organic and inorganic compounds:
  - Organic solvents (acetone, benzene)
  - Flammables (propane, hexane)
  - TICs and TIMs (ammonia, freon)
  - Pesticides (alachlor, warfarin)
  - Chemical WMD (VX, mustard gas)

CALIFORNIA CUPA FORUM

What Solids / Liquids can IR not Identify?

- Elemental substances
  - Metals (iron, aluminum, etc.)
  - Non-metals (sulfur, phosphorus, etc.)
- Ionic Salts (sodium chloride, calcium chloride)
- Dilute aqueous (water- based) solutions, or individual compounds or any mixture
  - IR does not separate mixtures
  - Components at less than 10% concentrations are missed
- Biological agents
  - Infrared cannot reliably speciate biological agents (spectra too similar)

What Gases / Vapors can IR not Identify?

- Noble (inert) gases
  - Helium
  - Neon
  - Argon
  - Krypton
  - Xenon
  - Radon

- Homonuclear diatomic gases (two of the same atom covalently)
  - Hydrogen (H_2)
  - Oxygen (O_2)
  - Nitrogen (N_2)
  - Fluorine (Fl_2)
  - Chlorine (Cl_2)
  - Bromine (Br_2)

- Aerosols (except for liquid droplets that can be vaporized)

HazMat ID / Elite

Air Monitoring Equipment

- Combustible Gas Indicators
- Photo Ionization Detectors
- Radiological monitors
- FTIR
- **Raman** and
- Other instruments

Raman

- Identifies solids and liquids, like FTIR
  - Measures how much light is emitted by a substance
  - Multiple wavelengths emitted at frequencies corresponding to bonds
  - Ability to detect chemicals without making direct contact
  - Can be analyzed directly through transparent or semi-transparent containers.
  - Similar limitations to FTIR (covalent/pure ionic bonds, metals, and elements
  - Uses a class 3B laser, which can ignite dark colored substances like black powder

Raman:

- Vibrating covalent chemical bonds “scatter” certain laser radiation
  - Laser energy “pushes” on electron clouds, which in turn emit slightly different frequencies as they stabilize
- The pattern of scattering for a chemical is its Raman fingerprint
- Raman spectra are compared to reference libraries to identify unknowns

- ***THESE TECHNIQUES PROVIDE COMPLIMENTARY DATA FOR SAME SAMPLE***

CALIFORNIA CUPA FORUM

Raman advantages:

- Requires no handling or preparation
- Is unaffected by strong IR absorbers (water, CO_2, glass)
- Requires no special accessories for aqueous solution (water is a very weak Raman scatter)
- Raman excitation wavelength can penetrate container materials which allows in situ analysis in evidence bags, envelopes, and glass vials

What Solids / Liquids can Raman Identify?

- Must have POLARIZABLE COVALENT CHEMICAL BOND
- Organic compounds
  - Hydrocarbons (olefins, fuels, easy polarizable electrons-double & triple bonds)
  - Organic solvents (aromatics- BTX, hexanes)
  - Chemical WMD
- Inorganic Compounds
  - Metal oxides (Peaks at lower wavenumbers than IR can see)
  - Oxy compounds (Sulfates, Nitrates, Chlorates)
- Some pure elements (sulfur, carbon, phosphorous*)
- Raman-active chemicals in WATER
  - Water is NOT Raman-active (invisible)
  - Acid / base solutions
  - Contaminants in water

What Solids / Liquids can Raman NOT Identify?

- Most pure elements
  - Metals
  - Most non-metals
- Ionic salts (sodium chloride, calcium chloride)
- Highly polar compounds
  - Water (practically invisible)
  - Carbohydrates (very weak)
  - Proteins (weak)
- Highly fluorescent compounds (from coloring or contamination)
- Individual components of any mixture
  - Like IR, Raman does not separate mixtures
  - Components at less than 10% concentration can't be seen
- Biological Agents
  - Raman cannot reliably speciate biological agents

IR and Raman Complimentary Nature

- **With both infrared and Raman, one has two techniques which can identify unknown chemicals, but they come at the identity from different angles**

- **One measurement can back up the other with independent dataorthogonal techniques – *"If it walks like a duck, and quacks like a duck, …"***

CALIFORNIA CUPA FORUM

Air Monitoring Equipment

- Combustible Gas Indicators
- Photo Ionization Detectors
- Radiological monitors
- FTIR
- Raman and
- **Other instruments**

Other Instruments

- FID (Flame Ionization Detector, aka organic vapor analyzer/OVA)
  - Uses charged particles (ions) to detect chemicals in the air, similar to PID
  - Uses a hydrogen flame to burn organic materials (unlike using UV to displiace ions, used by PID)
  - Very sensitive to carbon monoxide and methane, unlike PID
  - Hydrogen flame has sufficient energy to ionize IPs up to 12.4 eV
  - Special considerations in explosive atmospheres
- Gas Chromotography
  - Chromotography = picture of concentration over time
  - Different chemicals elute at different times

Other Instruments

- Mass Spectometry
  - Expensive and complicated
  - Following GC, gases are smashed into smaller pieces and weighed
  - Compared to standards
- ChemPro
- MX 908
- Refrigerant Leak Detector
- Oxidizer Paper
- pH Paper
- Assays

Response Equipment

- Containment
  - Boom
  - Plugs
  - Dikes
  - “Expanding Football”
- Dams
  - Underflow
  - Overflow
- Neutralizers

How do I get resources?

- https://calcupa.org/trust/index.html

The California Certified Unified Program Agency (CUPA) Forum Board established the CUPA Forum Environmental Protection Trust Fund in 2009 (Trust Regulations). This Trust was established to manage and disburse monies from enforcement case settlements to enhance the investigation, inspection and enforcement of Unified Programs throughout the State of California.

- These monies will be disbursed through a Grant process. Grant requests shall be made using the Grant Application on this page. **They must be submitted no later than March 31st of each year.** Grant requests may be approved in whole or in part and upon such terms and conditions as the Trustees deem appropriate. **Successful grant applications will be awarded for the following fiscal year beginning July 1.**

- **Grant applications must be complete before they will be considered.** All specific certifications must be checked. **The intended purpose of the grant could be as simple as the purchase of one instrument or a complex program dealing with training, equipment and implementation.** The only mandatory award criterion is that the intended purpose must benefit Unified Program implementation and enforcement.

How do I get resources?

- Trust Grant Application
- Supplemental Application for Vehicles or Emergency Response Equipment
- Trustees Contact Information
- Grant Application Hints and Tips

Any Questions?

26th California Unified Program Annual Training Conference
February 26-29, 2024