Oil and Petrochemical Industry
Gas Detection Issues and Answers

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GfG Instrumentation

World-wide manufacturer of fixed and portable gas detection solutions

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Oil and Petrochemical Site Visit
Gas Detection Questions

- "Oil Industry" is a very broad category!
- Oil industry managers deal with an extremely wide range of atmospheric hazards, monitoring applications and activities.
- Hazards can be generally present or associated with specific activities (like CS entry).
- Managers need to anticipate critical requirements ahead of time!
- Gas detection equipment must be fit for purpose!

What are your most urgent concerns and problems?

- The more detailed grasp you have of the activities and risks that involve atmospheric hazards, the better.
- Drill down to make sure you understand what is most important.
- Are you currently meeting all requirements?
- Where do you need to make improvements?
- Gas detection issues are not necessarily limited to safety!
  - Toxic exposure limits are getting lower every year!

Oil industry managers are involved with all types of safety and hygiene gas detection

- Personal exposure monitoring
- Confined space
- Hot work
- Toxic materials, vapors and gases
- Hazmat and emergency response
- Other activity-based monitoring

Fixed or Portable solution?

- Oil and chemical industry safety and facilities managers deal with extremely wide range of atmospheric hazards, monitoring applications and activities.
- When hazards are generally present or associated with specific activities (like CS entry) gas detection solutions focus more on portable instruments.
- When hazards are chronically present, or present in specific areas, fixed gas detection should be considered as well.
- Optimal solution often includes both fixed and portable instruments!

What are the major categories of oil and chemical industry sites and products?

- Different types of oil / petrochemical business have very different gas detection requirements
- "Upstream" exploration and production
  - Crude oil
  - Natural gas
  - Bitumen
- "Midstream" transportation and wholesale marketing of crude or refined products
  - Pipeline
  - Rail
  - Tanker (truck)
  - Marine transport
- "Downstream" refining and processing
  - Crude oil and bitumen into fuels (i.e. gasoline / diesel / jet fuel / fuel oil)
  - Processing and purifying raw natural gas
- Chemical plants convert "feedstock" into new products
  - Olefins
  - Aromatic hydrocarbons
  - Multitude of additional products

What are typical "Upstream" gas detection concerns?

- "Upstream"
  - Exploration and production
    - Crude oil
    - Natural gas
    - Bitumen
- What are some typical upstream concerns?
  - Personal protection
  - Lone worker
  - Confined space entry
  - Local fixed systems
- Rely on single and basic multi-gas instruments
  - H_2S
  - 4 Gas with LEL / O_2 / CO / H_2S
  - 5 Gas with PID
  - Benzene
  - Other specific toxic gases

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What are typical "Midstream" gas detection concerns?

- "Midstream"
  - Transportation and wholesale marketing of crude or refined products
    - Pipeline
    - Rail
    - Tanker (truck)
    - Marine transport
- What are some typical midstream concerns?
  - Personal protection
  - Lone worker
  - Confined space
- Rely on single and basic multi-gas instruments
  - H_2S
  - 4 Gas with LEL / O_2 / CO / H_2S
  - 5 Gas with PID
  - Other specific toxic gases (SO_2 / NO_2 / benzene / etc.)

What are some of the special concerns that affect maritime gas detection?

- Special regulations for platforms, marine terminals, loading docks, shipyards, maritime vessels and shoreside facilities
- Different toxic and safety exposure limits
  - Enforced by USCG rather than OSHA
  - Exposure limits tied more closely to TLV
  - LEL settings in high risk “Zone 0” areas often at 5% LEL rather than 10% LEL
- Different CS entry requirements
  - 1912 Sub-part B rather than 1910.146
  - Hot work requirements per NFPA 306
  - Marine chemist sign-off on “gas free” conditions prior to entry
  - Entry by “Competent Persons” only
- Instruments may require additional certifications
  - UL / CSA Zone 0 Certification
  - Marine “Steering Wheel”

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What are typical "Downstream" gas detection concerns?

- "Downstream"
  - Refining and processing of crude oil and bitumen
  - Processing and purifying raw natural gas
  - "Upstream / downstream" categorization is sometimes not clear cut
- What are some typical downstream concerns?
  - Personal protection
  - Toxic exposure monitoring
  - Confined space
  - Shut-downs
  - Fixed systems
- Rely on single and multi-gas instruments
  - H_2S
  - 4 Gas with LEL / O_2 / CO / H_2S
  - 5 Gas with PID
  - Other specific toxic gases (SO_2 / NO_2 / benzene / etc.)

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What is crude oil?

- Complex mixture of hydrocarbons that includes all liquid, gaseous and solid components.
  - Lighter hydrocarbons (methane ethane and butane) exist as gases.
  - Pentane and heavier hydrocarbons are in the form of liquids or solids.
- Oil wells predominantly produce crude oil with some natural gas dissolved in it.
  - Crude oil commonly contains at least some sulfur.
    - “Sweet” crude contains less sulfur
    - When sulfur content exceeds 0.5% (by weight) the oil is referred to as "sour".
    - Ultimately the sulfur will need to be removed from the final fully refined product.
- Gas wells produce natural gas.
  - Raw natural gas mostly methane with variable concentrations of other gases (ethane, propane, butane and “natural gas liquids” (condensates) sometimes referred to as “natural gasoline.”
  - When H_2S exceeds 4.0 ppm gas is referred to as “sour.”
  - H_2S in sour gas can sometimes reach flammable concentration and higher!

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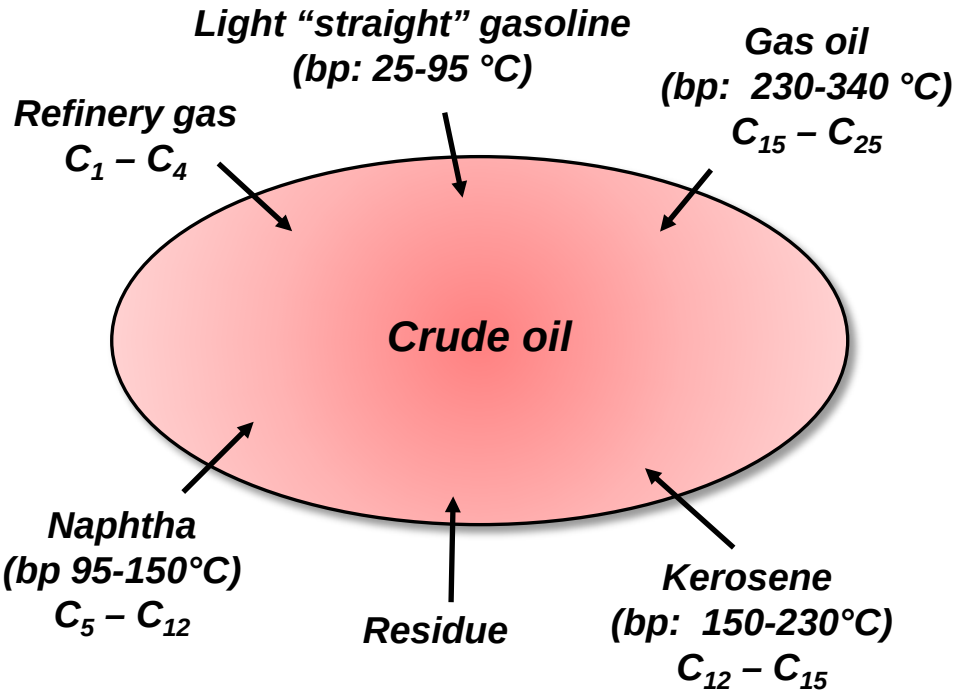
What is refining?

- Process of converting crude oil or raw natural gas into high value products.
- Most important refinery products are transportation fuels – gasoline, jet fuel, and diesel fuel.
- Other important products include liquefied petroleum gas (LPG), heating fuel, lubricating oil, wax, and asphalt.
- Crude oil is separated into various “cuts” by means of distillation and fractionation.
  - Separation is by means of boiling points, which is related to the size of the molecules.
  - Larger the molecule, the higher the BP.



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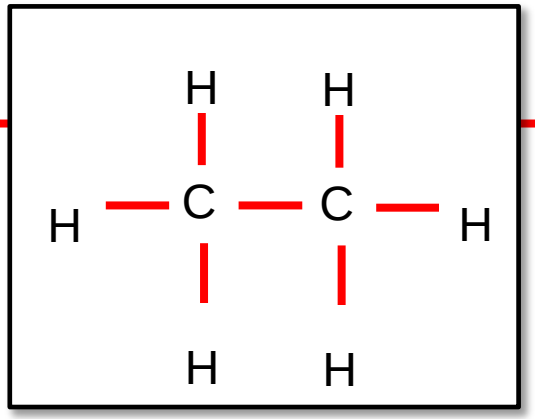
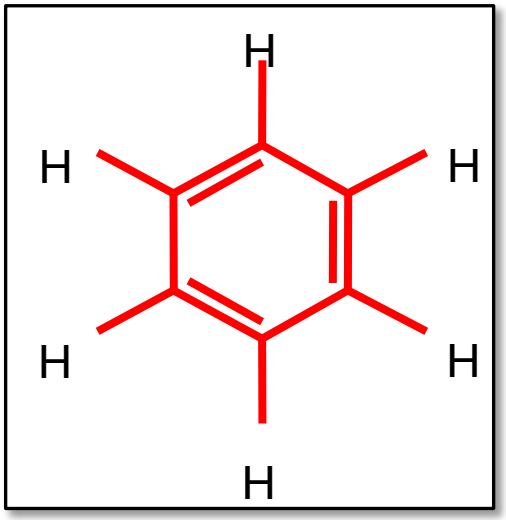
What are hydrocarbons?

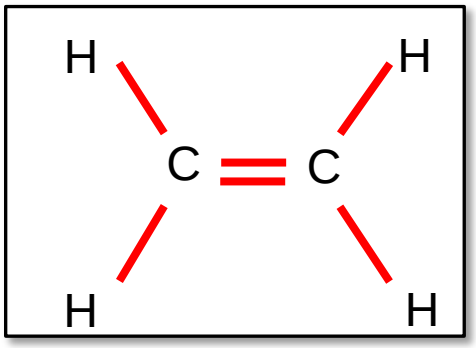
- A hydrocarbon is an organic molecule that consists entirely of hydrogen and carbon atoms.
- "Saturated" hydrocarbons contain only single bonds between carbon atoms.
  - "Alkanes" are the simplest class of hydrocarbons.
  - They are called saturated because each carbon atom is bonded to as many hydrogen atoms as possible
- "Unsaturated" hydrocarbons have at least one double or triple bond between carbon atoms.
  - "Olefins" have at least one double bond
  - "Aromatic" hydrocarbons include one or more rings



Ethane



Benzene



Ethylene

What else happens during the refining process?

- Elemental sulfur and H_2S are removed during desulfurization
  - Hydrodesulfurization process uses hydrogen
  - SO_2 as well as H_2S may be particular concern
- Oil refineries produce olefins and aromatics by fluid catalytic cracking of petroleum fractions.
  - Cracking converts high molecular weight HCs to more useful, low molecular weight ones
  - Olefins and aromatics are the building-blocks for a wide range of materials such as plastics, solvents, resins, fibers, elastomers, lubricants, detergents, and adhesives.
  - Catalytic cracking uses and produces hydrogen!
    - IR LEL sensors are unable to detect H_2.
    - H_2 may also interfere with CO sensors.
    - Make sure instrument includes sensor that can detect H_2.
    - If using IR LEL sensor, consider adding substance specific EC H_2 sensor.

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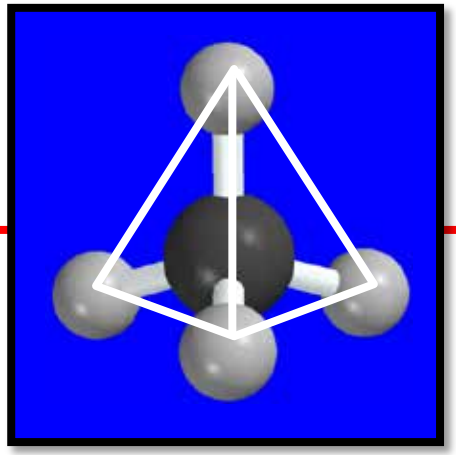
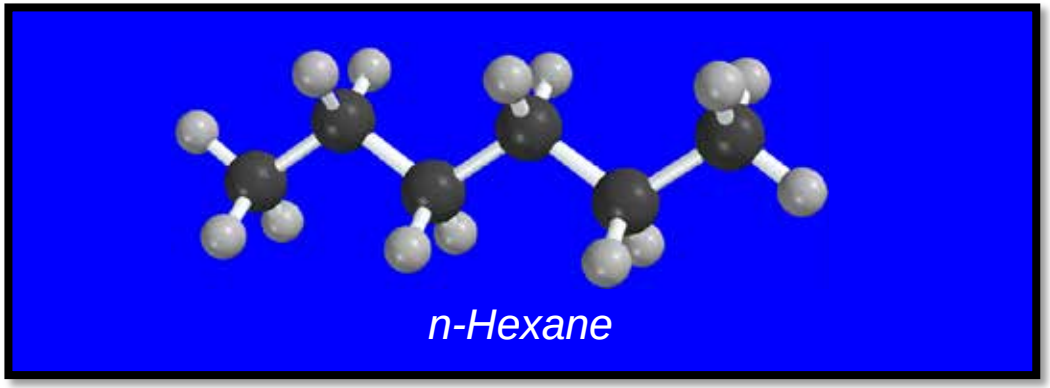
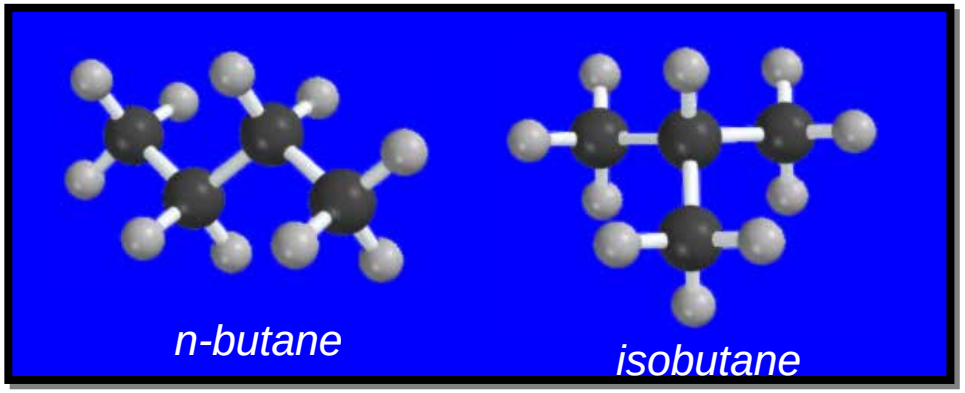
Saturated hydrocarbons can be "straight" chains or branched

- Methane is the simplest (smallest) hydrocarbon
- The most stable molecular structure is "straight" chain (designated "n")
- Branched alkanes burn more evenly
  - Modern engines unable to use "straight" gasoline
  - Gasoline used by modern vehicles is "reformed" to include branching
  - Branched hydrocarbons have better burning characteristics for automobile engines

Methane







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Oil and chemical industry gas detection requirements can include

- Personal protection
- Production
- Process
- Facilities
- Industrial hygiene
- Community (such as fence line or nuisance odor)
- Regulatory (EPA)
- Disaster response (explosion, spill or fire)
- Construction (shut-downs)
- Confined space
  - Routine entries
  - Large scale ongoing-entries
  - Entries into inerted vessels
  - Hot work
  - Special procedures (catalyst rebuilding)

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What are the most common oil industry atmospheric hazards?

- Oxygen deficiency
- Oxygen enrichment
- Presence of toxic gases
  - H_2S
  - SO_2
- Presence of combustible gases
- Typically use single-gas H_2S or a 4 gas or 5 gas detector with:
  - LEL
  - O_2
  - CO
  - H_2S
  - PID

Why is H_2S so common?

- *Produced by anaerobic sulfate-reducing bacteria*
- *The higher the sulfur content the greater the potential for H_2S*
- *Older fields more prone to H_2S than new fields*
- *Heavier than air*
  - *Collects in vessels, pits, within protective berms, or in other low-lying areas*
  - *Half-life in air = 12 to 37 hours*
  - *Eventually breaks down in sunlight*
- *Extremely toxic!*
  - *1000 ppm leads to immediate "knockdown"*
- *Particularly dangerous in oil production areas subject to cold winter temperatures*
  - *During very cold and dry conditions, half-life can exceed 37 hours*

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What are the exposure limits for H_2S?

- Latest TLV limits controversial!
- Suggested alarms:
  - NIOSH:
    - Low: 10.0 ppm
    - High: 15.0 ppm
    - STEL: 15.0 ppm
    - TWA: 10.0 ppm
  - TLV®:
    - Low: 3.0 ppm
    - High: 5.0 ppm
    - STEL: 5.0 ppm
    - TWA: 1.0 ppm

H2S exposure limits					
OSHA PEL					
	TWA	STEL	Acceptable Ceiling (C) Concentration	Acceptable Maximum Peak above Ceiling for an 8-hour shift	
				Concentration	Maximum duration
	NA	NA	20 ppm	50 ppm	10-minutes once only if no other measurable exposure occurs during shift
NIOSH REL					
	TWA	STEL	Ceiling		
	10.0 ppm	15.0 ppm	NA		
2009 ACGIH TLV					
	TWA	STEL	Ceiling		
	10.0 ppm	15.0 ppm	NA		
2010 ACGIH TLV					
	TWA	STEL	Ceiling		
	1.0 ppm	5.0 ppm	NA		

What is the best type of LEL sensor?

- It depends on the specific applications!
- There are 4 major LEL sensor options, all have advantages and disadvantages:
  - Traditional catalytic “pellistor” LEL
    - Detects gas by oxidation (heating) pellistor bead in sensor
  - Full size IR LEL
    - Detects gas by absorbance of IR light over longer optical path
  - Miniaturized (low power) MEMS IR LEL
    - Detects gas by absorbance of IR light over extremely small optical path (low power)
  - Miniaturized (low power) MEMS Molecular Properties Spectrometer (MPS)
    - Presence of a flammable gas causes changes in the thermo-conductive properties of the air/ gas mixture that are measured by the sensor transducer

What are advantages and limitations of catalytic pellistor LEL sensors?

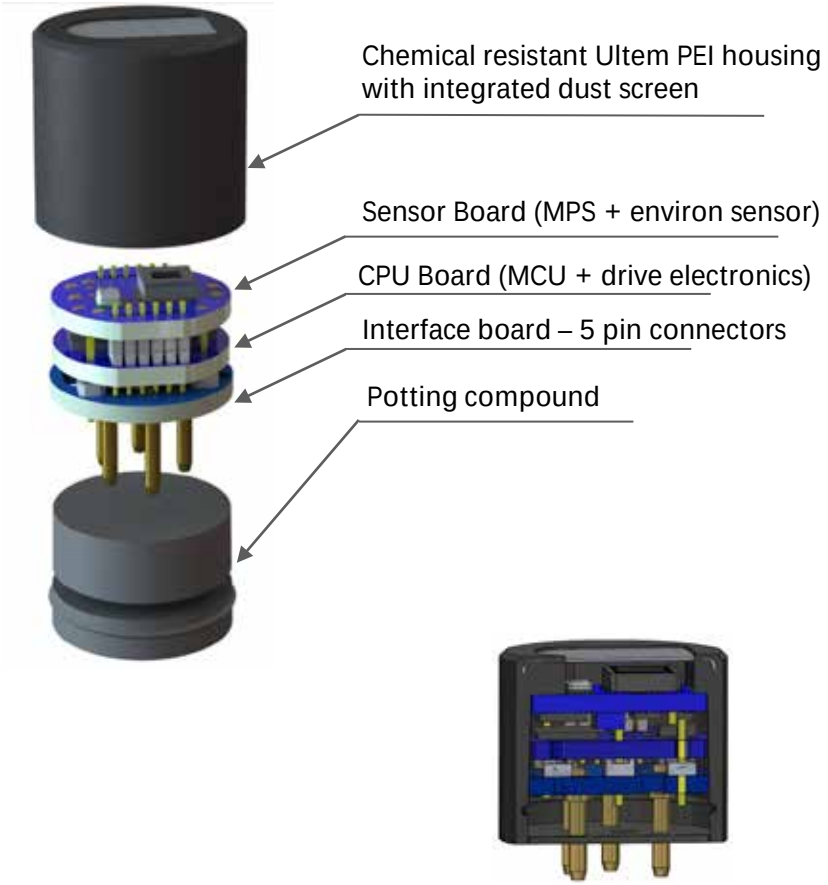
- Advantages:
  - Predictable, well understood technology
  - Predictable cross sensitivities, (most instruments have built-in CF library)
  - Able to detect H_2, acetylene and unsaturated HCs
- Disadvantages:
  - Uses more power
  - Poor response to larger molecules
  - Slower response to larger molecules
  - Easily poisoned
  - Exposure to high concentration combustible gas damaging to sensor
  - Must have minimum of 10% O_2 to accurately detect gas

What are IR LEL sensor advantages and limitations?

- Advantages:
  - Sensor cannot be poisoned
  - Does not require oxygen to detect gas
  - Can be used for high-range combustible gas measurement
  - Responds well to large hydrocarbon molecules that cannot be measured by means of standard LEL sensor
- Disadvantages:
  - Molecule must include chemical bonds that absorb at the wavelength(s) used for measurement
  - Not all combustible gases can be detected!
    - NDIR sensors with short optical path-lengths may have limited ability to measure gases with lower relative responses
    - Cannot detect hydrogen or acetylene!

What are Molecular Property Spectrometer (MPS) sensor advantages and disadvantages?

- Advantages:
  - Low power
  - Sensor cannot be poisoned
  - Does not require oxygen to detect gas
  - Detects hydrogen, acetylene and other gases, including large HC molecules
- Disadvantages:
  - Any difference in density from fresh air causes sensor response
  - Mixtures of lighter than air and heavier than air gas can cancel out
  - Responds to CO_2
  - Not recommended for confined spaces where O_2 deficiencies can be due to presence of CO_2 or other displacing gases
  - Not recommended for inert gas CS monitoring



Performance of IR LEL sensors differs from performance of catalytic LEL sensors

- Read the owner's manual!
- Make sure to verify with manufacturer before attempting to use the sensor to measure unsaturated hydrocarbons, aromatic VOCs or other gases not specifically listed in the owner's manual!

Appendix B

Detectable Combustible Gases

Gas[1]	Expected response at 20% LEL target gas[2]
Methane	20% LEL
Propane	15% LEL to 45% LEL
Butane	15% LEL to 35% LEL
Pentane	15% LEL to 45% LEL
Hexane	8% LEL to 28% LEL
Methanol/Ethanol[3]	6% LEL to 26% LEL
Hydrogen	No response
Acetylene	No response

[1] For any gases not listed, please contact Honeywell Analytics to find the best solution for your application.

[2] The BW Clip4 LEL sensor is optimized to see methane. While the unit can detect and respond to the other combustible gases listed in the above table, the accuracy of the readings may be in-consistent. If the primary need is to detect a specific combustible gas other than methane, please contact Honeywell Analytics to discuss an alternative product.

[3] Please use caution when using the BW Clip4 around Methanol and/or Ethanol. The BW Clip4 CO sensor may become inhibited by prolonged exposure to concentrations of Methanol and/or Ethanol thus causing the unit to alarm. This condition can last up to 12 hours before the CO sensor recovers to normal levels.

What are volatile organic compounds (VOCs)?

- VOCs are organic chemicals or mixtures characterized by tendency to evaporate easily at room temperature
- Familiar VOCs include:
  - Solvents
  - Paint thinner
  - Nail polish remover
  - Gasoline
  - Diesel
  - Heating oil
  - Kerosene
  - Jet fuel
  - Benzene
  - Butadiene
  - Hexane
  - Toluene
  - Xylene
  - Many others

Why use photoionization detector equipped instruments?

- For most VOCs, long before you reach a concentration sufficient to register on a combustible gas indicator, you will have easily exceeded the toxic exposure limits for the contaminant
- PID equipped instruments are generally the best choice for measurement of VOCs at exposure limit concentrations
- Whatever type of instrument is used to measure these hazards, it is essential that the equipment is used properly, and the results are correctly interpreted

Combustible sensor limitations

Contaminant	LEL (Vol %)	Flashpoint Temp (ºF)	OSHA PEL	NIOSH REL	TLV	5% LEL in PPM
Acetone	2.5%	-4ºF (-20 ºC)	1,000 PPM TWA	250 PPM TWA	500 PPM TWA; 750 PPM STEL	1250 PPM
Diesel (No.2) vapor	0.6%	125ºF (51.7ºC)	None Listed	None Listed	15 PPM	300 PPM
Ethanol	3.3%	55ºF (12.8 ºC)	1,000 PPM TWA	1000 PPM TWA	1000 PPM TWA	1,650 PPM
Gasoline	1.3%	-50ºF (-45.6ºC)	None Listed	None Listed	300 PPM TWA; 500 PPM STEL	650 PPM
n-Hexane	1.1%	-7ºF (-21.7 ºC)	500 PPM TWA	50 PPM TWA	50 PPM TWA	550 PPM
Isopropyl alcohol	2.0%	53ºF (11.7ºC)	400 PPM TWA	400 PPM TWA; 500 PPM STEL	200 PPM TWA; 400 PPM STEL	1000 PPM
Kerosene/ Jet Fuels	0.7%	100 – 162ºF (37.8 – 72.3ºC)	None Listed	100 mg/M3 TWA (approx. 14.4 PPM)	200 mg/M3 TWA (approx. 29 PPM)	350 PPM
MEK	1.4%	16ºF (-8.9ºC)	200 PPM TWA	200 PPM TWA; 300 PPM STEL	200 PPM TWA; 300 PPM STEL	700 PPM
Turpentine	0.8	95ºF (35ºC)	100 PPM TWA	100 PPM TWA	20 PPM TWA	400 PPM
Xylenes (o, m & p isomers)	0.9 – 1.1%	81 – 90ºF (27.3 – 32.3 ºC)	100 PPM TWA	100 PPM TWA; 150 PPM STEL	100 PPM TWA; 150 STEL	450 – 550 PPM

There are <u>many</u> new developments in gas detection!

- New products
- New sensors
- Wireless communication
- Integrated fixed and portable networks
- Third party support through call centers
  - Emergency response
  - Record keeping and notifications
  - Internet based maintenance programs

What brand(s) and model(s) of gas detection equipment do you currently use?

- Before making a change or investigating new products, make sure you understand your current products and requirements
  - If you are not sure, make sure to find out the brands and models currently in service.
  - Make sure you understand the capabilities; the strong points as well as the weak points, of the products you are currently using.
- Ask the manufacturers or distributors of the products you work with (or are interested in) for help.
  - Download specifications and comparison charts if the manufacturer has them.
  - Discuss ways the manufacturer and distributor can help meeting your needs with regards to product, capabilities or support.

How well is your current equipment performing?

- This is a critical starting point in the conversation.
  - Are you generally happy?
  - Are you experiencing problems?
  - How old is your current equipment?
  - What features have you heard about that you are interested in?
  - What brand(s) and model(s) of gas detectors are you considering?
  - What are the alternatives?
- Distributors are a great source for product information!
- When in doubt, or with regards to advanced technical questions, ask the manufacturer!

Avoid being overly focused on price!

- Eventually, the decision of whether to proceed involves price and affordability.
- However, there is a difference between the initial purchase price and the true cost of ownership.
  - The questioning process is designed to uncover your needs, and what would provide the optimal solution.
  - Once you fully identify the problems and how the new product is going to help, it's easier to understand the costs.
  - Once you have clarified the tradeoff between benefits and costs is when to widen or restrict choices as a function of price.

Identify "cost of ownership" issues

- Are you spending a fortune keeping your current equipment in service?
- Are you being charged a monthly fee for reports and factory support?
- Do you trust your gas detectors?
- Do you have many sensor failures?
  - If so, what kinds of sensors are failing?
- Do you have battery problems?
  - Do the instruments run long enough on a single charge or set of batteries?
- How often do you test and calibrate your instruments?
  - Do you do it yourself or use a service?
- Are there any special conditions or contaminants that are causing problems?
- <u>Do you feel you are currently getting a good deal?</u>

Do you have plans to update, replace or change the equipment you are currently using?

- If you have relationships with gas detection manufacturers and distributors you trust, get them involved!
  - Distributors generally have more than one manufacturer option.
  - Gas detection manufacturers are happy to discuss issues directly with end-user customers.
  - The Internet and social media are terrific tools for finding out what's new, and what customers have to say.
  - You have multiple sources of information!
- Gas detection decisions are often made by a group of individuals who have different roles in the decision process, including process or facilities management, safety, hygiene, purchasing, and (often) union representatives.
  - Make sure you don't leave anyone out!
  - The same issue often looks considerably different to a manager with different responsibilities.

Who is currently looking after your instruments?

- Do you do it yourself, use a third-party service, or work directly with the factory?
- If you like your current instruments, and want to keep them in service, you might want to talk about maintenance agreements or refurbishment programs.
- Ask your local distributor whether they offer calibration or repair services.
- Ask your current manufacturer whether they have factory maintenance programs, or a loaner or replacement instrument policy.
- You should expect excellent after the sale support!

Do you use your portable gas detectors for general protection for workers at the site, or confined space entry, or both?

- Portable instruments are not limited to use in confined spaces!
- Many facilities require use of personally assigned gas detectors by every employee or contractor on-site; or when working in specified areas.
- The most common personal instruments are single sensor H_2S or CO “Clips” as well as compact 4 gas instruments that measure O_2 / LEL / CO and H_2S.
- Many facilities that in the past have only monitored for H_2S are in the process of moving to multi-gas instruments.

In terms of units sold, personal protection is the largest gas detection segment

- For personal protection instruments do you mostly use:
  - Single gas H_2S?
  - 4 gas meters?
  - Other single gas meters?
  - H_2S is still the most common single gas instrument, with CO a distant second, but don't overlook other toxic gases that may be present at a particular site.
- Some of the other most commonly used personal single gas instruments include:
  - NO_2
  - SO_2
  - Ozone
  - HF
  - PID
  - As well as many others!

What sensor configurations do you currently use for confined space entry?

- Do you have the right configuration, or are you thinking about a change?
- How many / what kinds of sensors are installed in your instruments?

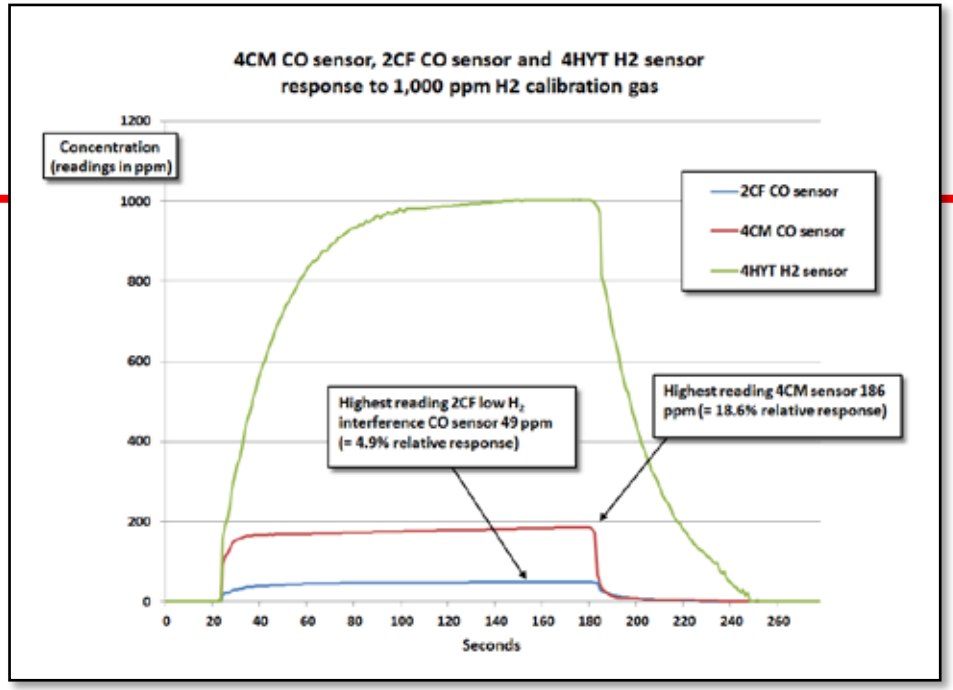
Multi-gas portable instrument considerations

- Do you have other gases of concern beyond the basic four most common atmospheric hazards (O_2, LEL, CO and H_2S)?
  - SO_2?
  - VOCs?
  - Benzene?
  - Hydrogen?
  - CO_2?
  - NO_2?
  - Other gases?
- Do you use pump equipped or diffusion for toxic gas measurement?
  - Is it possible to equip your single-gas meters with a pump?

Even more multi-gas questions

- Do you have alcohol, heavy fuels or VOCs on site?
  - VOC vapors are potentially explosive, but toxic at much lower concentrations.
  - Especially true for VOCs like benzene, hexane, toluene and xylenes.
  - Consider including a PID sensor in multi-gas instruments used for fuel spills and other situations that involve VOC vapor.
- Do you encounter VOCs during confined space entry?
  - If so, your CS instruments should have PID sensor as well.

And even more multi-gas questions



- Do you ever have problems with hydrogen?
  - Hydrogen is explosive, but the most common concern is often the interfering effect of hydrogen on CO sensors.
  - Whenever hydrogen is a concern make sure to discuss using "hydrogen nulled" CO sensors.
- <u>Hydrogen cannot be measured by IR LEL sensors!</u>
  - Hydrogen is very common at oil and chemical industry sites!
  - Consider equipping instruments with IR LEL sensors with a sensor for directly measuring H_2.
  - If you are depending on CO or COSH sensor to detect H_2, make sure you understand how the sensor responds!

Further multi-gas considerations

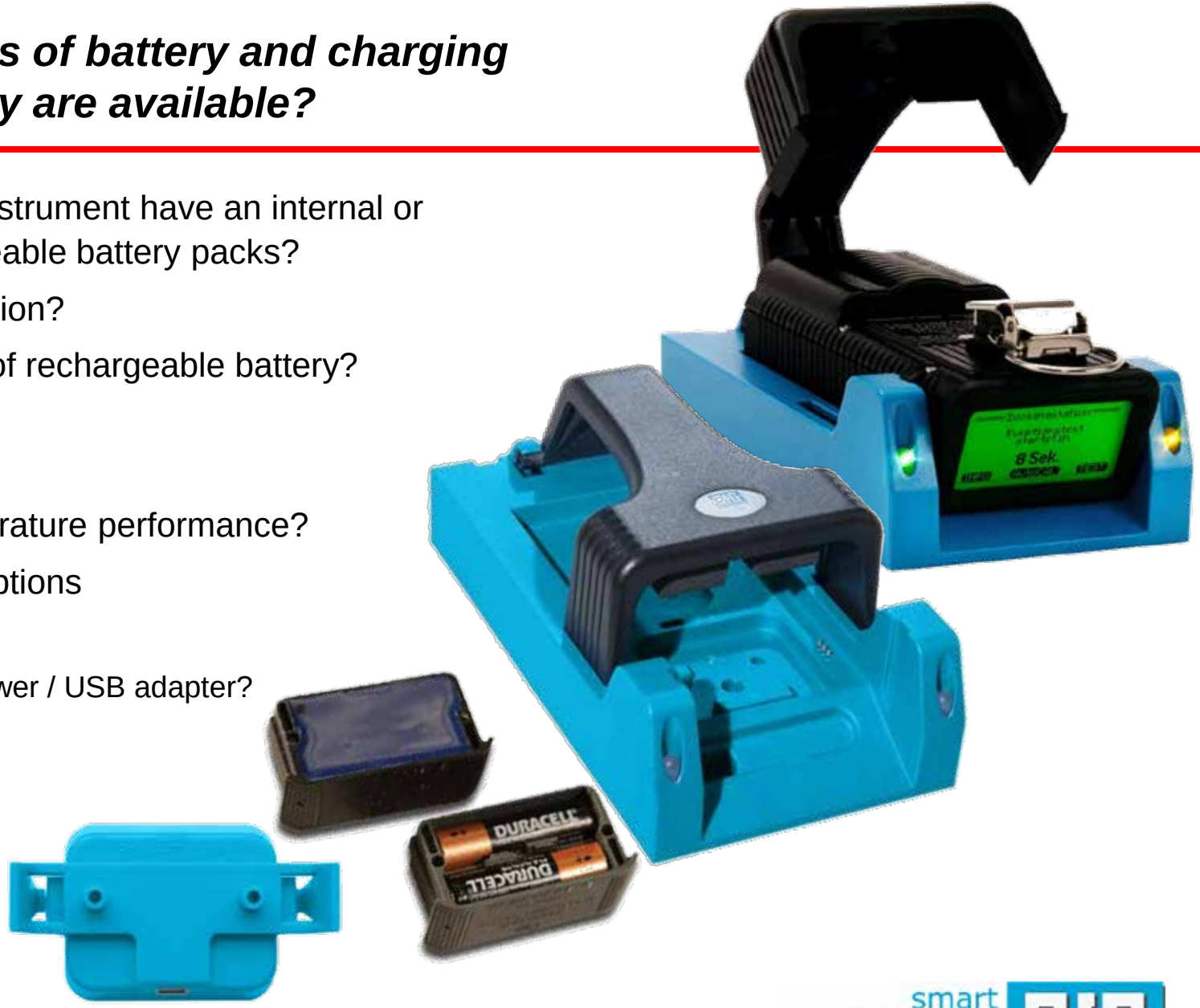
- Do you have any other contaminants or toxic gas concerns?
  - Oil and chemical industry sites have a long list of potential contaminants.
  - Consider including additional sensors in the multi-gas instrument, or
  - Use specialty sensors in separate instrument.
  - Watch out for compatibility issues!

How do you sample the atmosphere from within the confined space?

- Is the instrument a diffusion only design?
- Does the instrument have an attachable sample pump?
- Does the instrument have a built-in pump?
- Does the instrument have the option of switching from diffusion to sampling by means of the built-in pump?

What types of battery and charging technology are available?

- Does the instrument have an internal or interchangeable battery packs?
- Alkaline option?
- What type of rechargeable battery?
  - Li Ion?
  - NiMH?
- Cold temperature performance?
- Charging options
  - Cradle?
  - Wall power / USB adapter?



What about periodic testing and calibration?

- How often do you perform a bump test?
  - Before each day's use?
  - Do you keep bump test kits (with gas) with the instruments?
  - How do you prove your instruments have been bumped?
  - What do you do if you fail a bump test?
- How often do you perform a full calibration?
  - Do you use a docking station for bump tests and calibrations?
  - How do you prove your instruments are properly maintained and calibrated?
  - How do you retain maintenance and calibration records?
- Is your current strategy working?
  - Is it easy?

Are your gas detectors wirelessly enabled (or are you considering this option)?

- Most manufacturers now offer a “wireless” communication option.
  - Each manufacturer has its own strategy, with its own benefits and limitations.
  - Make sure you understand the wireless options and competitive benefits!
- Common communication methods:
  - Blue Tooth
  - Cellular
  - ISM RF
- Do you intend to use wireless communication during CS entry?
  - How do you get the information out of the space?

Have you addressed "third-party" issues?

- Do you intend to use a remote call center service to coordinate emergency response?
- Do you intend to use a third-party rescue service (such as a corporate emergency response team, or the local fire department)?
- How will you coordinate real-time emergency information with all involved parties?

What about after the sale support?

- Satisfaction is a function of ongoing support.
  - Atmospheric monitors and systems are life critical safety equipment.
  - Customers should expect excellent after the sale support.
- Don’t forget to consider:
  - Warranty
    - Sensors
    - Instrument
- Technical support
  - Is your vendor there to provide help?
- Training
  - Videos?
  - In person?
  - Internet resources?

Questions?

Thank you!

For additional information or gas detection help: www.goodforgas.com

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