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PDC 704: Methods and Applications for Chemical Detection in Real Time

Philadelphia, PA | May 21–23 | PDCs: May 19, 20 and 24

The Premier Conference and Exposition for
Occupational and Environmental Health and Safety Professionals
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AIHce EXP 2018
Philadelphia, PA
May 20-23

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The #1 Training Choice for Occupational and
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Educational transcripts will be available July 13, 2018

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PDC 704

Methods and Applications for Chemical Detection in Real Time

Intermediate | Competent, Experienced, Novice
Saturday & Sunday, May 19-20 | 8:00 AM – 5:00 PM
Credits: 14 CM Credit Hours

Topics

Exposure Assessment Strategies, Real-Time Detection Systems, Sensor Technologies

Description

The PDC is targeted towards IH, safety, and emergency response personnel who use or may be called on to use field portable detection and identification tools, or professionals who may need to understand data produced by such tools. Discussion on intra-day exposure variability and situations where knowledge of rapidly fluctuating contaminant concentrations may be important to correctly assess exposures will be presented. The operating principles and key limitations of commonly-used detection instruments will be described in detail. How such instruments may be integrated into emergency response protocols required by the OSHA Hazardous Waste Operations and Emergency Response (HAZWOPER) standard will be discussed. The hands-on portion of the PDC will include various instruments and associated data processing systems. Expert case studies presented will demonstrate how real-time chemical detection has been effectively used to answer important human exposure questions.

Prerequisites

IH-level knowledge of chemistry, interest in field-portable detection tools and the exposure assessment process

Value Added

Participants will receive case studies, flow charts and hands-on experience with portable real-time detection instruments.

Outcomes

Upon completion, participants will be able to:

- Create a field detection plan for hazards.
- Apply knowledge of real-time detection tool limitations.
- Use the hands-on experience to operate a variety of portable real-time detectors.
- Describe scenarios where field-portable detection tools are helpful.
- Select the best field detection and identification tool for a given scenario.
- Describe the toxicological relevance of intra-day variability.
- Use intra-day variability information to evaluate the need for or adequacy of control measures.
- Use correct approaches to augment traditional air samples with real-time detection data.
- Train another H&S professional on the roles for real-time detection instruments.

Outline

- Introduction
- Outline Potential Exposures
- Available Detection Tools

- Sensors to Guide Sampling for Exposure Assessment
- Operating Principles of Various Detection Systems
- Detection Systems in HAZWOPER Operations
- Interactive Exposure Assessment Scenario Discussions/Exam
- Hands-on Demonstrations and Use of Various Instruments

Transfer of Knowledge

Instructors will evaluate participants' understanding of the materials presented based on:

- Hands-on demonstrations and practicum
- Post course test

Instructors

Philip Smith, PhD, CIH, U.S. Department of Labor – OSHA, Sandy, UT.
Jim Cornish, Gasmet Technologies, Inc., Vancouver, BC, Canada.
Robert Henderson, MBA, GfG Instrumentation, Inc., Ann Arbor, MI.
William Mills, Northern Illinois University, Dekalb, IL.

Methods and Applications for Chemical Detection in Real Time

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Gasmet Technologies, Inc.
Vancouver, BC

Learning Objectives

Upon Completion the participant will be able to:

1. *Create a sound field detection plan for hazards based on costs, availability, and operating principles of important field detection and identification technologies*
2. *Correctly apply knowledge of real-time detection limitations to exposure assessment problems*
3. *Correctly use the basic functions of portable real-time aerosol detectors, and colorimetric, ionization, and absorbance-based detection tools with hands-on experience for most of these technologies*
4. *Correctly employ electrochemical sensor detection technologies and technologies used for detection of flammability/explosivity*
5. *Describe scenarios where field-portable gas chromatographic detection tools are helpful, and limitations to the usefulness of this detection tool*
6. *Select the best field detection and identification tool for a given scenario based on capabilities and limitations*

Learning Objectives (Continued)

Upon Completion the participant will be able to:

7. ***Describe the toxicological relevance of intra-day variability related to airborne exposure concentrations in the case of both fast acting and slow acting chemical and aerosol hazards***
8. ***Use knowledge of information regarding intra-day variability of airborne exposure concentrations to evaluate the need for or adequacy of control measures***
9. ***Use technically correct approaches to augment collection of traditional air samples with real-time detection data***
10. ***Teach another health and safety professional the most suitable roles for real-time detection systems and instruments in comprehensive exposure assessment***

Course Outline, Day 1

- ***I. Introduction***
- ***II. Outline potential exposures***
- ***III. Discussion of the overall range of available detection tools, capabilities and limitations, costs, and training needs***
- ***IV. Discussion on types of work processes where substantial intra-sampling period exposure concentration variability is expected, and the inadequacy of TWA sampling to identify exposure "peaks and valleys"***
- ***V. Discussion on the use of sensors to guide sampling for traditional exposure assessment (i.e., guidance to inform hanging pumps to answer difficult questions or select most likely exposed workers for traditional sampling)***
- ***VI. Discussion of operating principles, detection systems, and case studies for:***
  - ***(1) Colorimetric detectors***
  - ***(2) Electrochemical sensors***
  - ***(3) Flame ionization detector/miscellaneous detectors***
  - ***(4) Aerosol monitors***
- ***VII. Hands-on time (aerosol only)***

Course Outline, Day 2

I. Discussion of operating principles, detection systems, and case studies for:

- *(1) Combustibility/explosivity meters*
- *(2) Photoionization detector*
- *(3) FTIR*
- *(4) Field-portable gas chromatography and mass spectrometry*

II. Role of detection systems in HAZWOPER operations

III. Interactive exposure assessment scenario discussions/exam

IV. "Hands-on" time

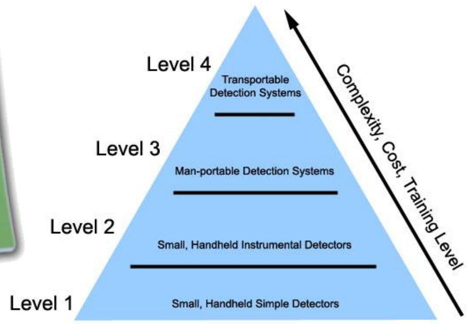
Potential Exposures for Which Real-Time Detection is Useful

1. ***In traditional industrial hygiene, to supplement professional judgment:***
   - ***Selection of locations to sample***
   - ***Real-time exposure feedback***
   - ***Track exposure changes with better temporal resolution***

2. ***For "comprehensive exposure assessment" where information regarding intra-sampling period variability is needed (e.g., "C" overexposures)***

3. ***When you need data without laboratory delay: accidental/unplanned release of "TICs" (toxic Industrial chemicals) or CW agents:***
   - ***Industrial disaster***
   - ***Tokyo subway sarin attack (1995)***
   - ***Intentional use of TICs by terrorists***

Range of Real-Time Detection Equipment Complexity/Cost/Capabilities


Level 4 — Transportable Detection Systems

Level 3 — Man-portable Detection Systems

Level 2 — Small, Handheld Instrumental Detectors

Level 1 — Small, Handheld Simple Detectors

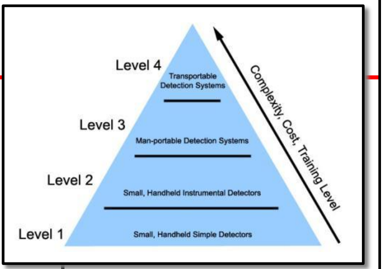
Complexity, Cost, Training Level

"Important Instrumentation and Methods"

Chapter

1. *Introduction*
2. *The Importance of Real-Time and Near Real-Time Detection Instrumentation for Human Exposure Assessment*
3. *Colorimetric Detection methods and Devices*
4. *Photoionization*
5. *Surface Acoustic Wave (SAW)-Based Instrumentation for Field Detection of Gases and Vapors*
6. *Ion Mobility Spectrometry*
7. *Specialized Detectors*
8. *Field-Portable Fourier Transform (FTIR) Spectroscopy for Gas and Vapor Analysis*
9. *Field-Portable Gas Chromatography*
10. *Mass Spectrometry*
11. *Solid Phase Microextraction*
12. *The Development and Application of Thermal Desorption - Gas Chromatography for Personal Exposure Assessment and Field Analysis*

Real-Time Detection Level



Routine Exposure Assessment	*Select Location for "Traditional Sampling"*	***1,2***
	Determine Exposure Intensity (PPE Selection)	***1,2***
	Determine Temporal Exposure Profile	***2***
	**Identify Unknown Stressors*	***3***
Emergency Situations	*Determine Exposure Intensity (PPE Selection)*	***1,2***
	Identify Unknown Stressors	***3***

**Consider laboratory-based method*

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Need for Sophisticated Technology vs. Availability

For airborne chemical exposure…

<u>Simple:</u> handheld detectors, e.g. PID, electrochemical, or length-of-stain tube detectors –simple to use, but require you to have a good idea of what you're faced with in order to provide good information

<u>Complex:</u> a spectrometric method such as mass spectrometry, along with a separation step such as gas chromatography (GC-MS) can allow identification of unknown compounds in many instances –very expensive, requires well-trained and experienced operators; cannot be overemphasized… very expensive! For air samples, concentration (often a sorbent tube or trap) and desorption methods (either heat or solvent) are needed, making GC analysis a multi-step process -gas phase FTIR instrument is less complex, but no analyte separation

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Example Equipment Details

Equipment type/cost	*Sample type*	*Operating cost*	*Training cost*	*Limitations*
Level 2 PID, $2.5k (detect/quantify gases/vapors)	*gas/vapor*	*low*	*low*	*must know chem. identity, not sensitive @ IDLH for extremely toxic chemicals; doesn’t detect analytes w/ high ionization energy*
Level 3 Portable GC-MS, $100k+ (ID, even trace components)	*organic solids, liquids, gases, vapors*	*high*	*high (approaches full-time commitment)*	*must be set up for specific analyte class; volatility-limited*

Selectivity

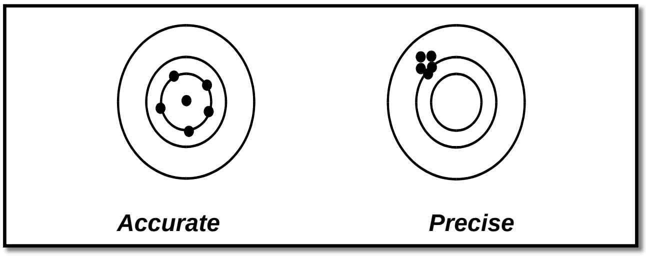
- *The ability of an analytical method to quantify an analyte of interest, even in the presence of interfering, or potentially interfering materials in the atmosphere and its principal components*
    - *PID (broad selectivity)*
    - *FID (less broad)*
    - *FPD (selective specifically for sulfur or phosphorous)*

Repeatability

- *A difficult parameter to quantify*
- *Affected by:*
    - *Analyses by different analysts*
    - *Analyses using older vs. newer analyzers*
    - *Analyses using different analytical methods*
    - *Analyses in different matrices*

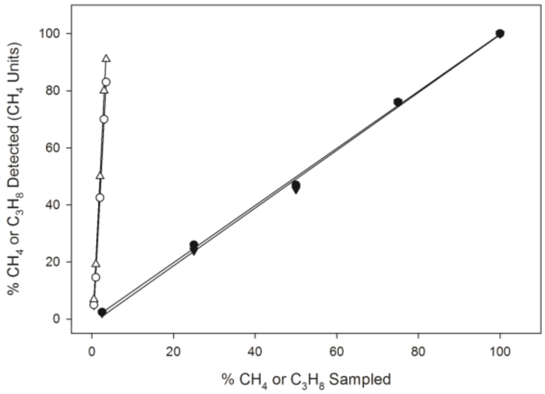
Accuracy, Precision, & Bias

• ***Accuracy:***	***Agreement between the instrument reading and the true concentration***
• ***Precision:***	***Agreement among repeated independent measurements***
• ***Bias:***	***A consistent or systematic difference between the true concentration and the measured value***

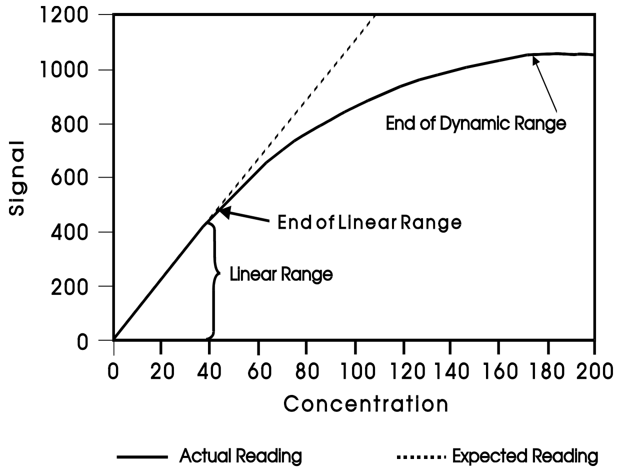


Common Terms

- ***Linearity:** Measure of how well an instrument's concentration-response curve fits the equation for a straight line*
- ***Linear Range:** The concentration range over which the instrument's concentration-response curve matches a straight line; **Dynamic Range:** Concentration range over which the instrument reading changes with a change in concentration of the target analyte*



Instrument Response Curve

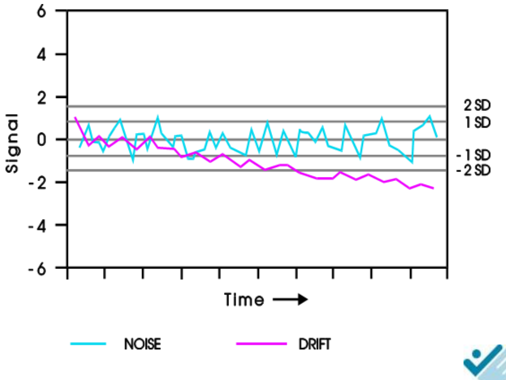


LOD and LOQ

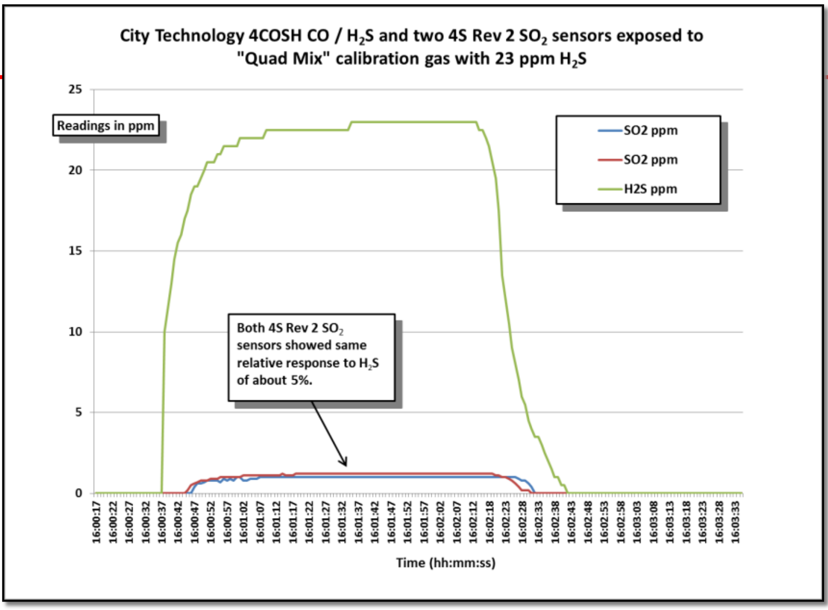
- ***LOD:** Limit of detection is the lowest concentration of the target compound that the instrument can reliably detect as different from zero*
- ***LOQ:** Limit of quantification is the lowest concentration of the target compound that the instrument can reliably measure*

Noise and Drift

- ***Noise:** Rapid random fluctuations in the instrument signal that are not caused by changes in the concentrations of the target compound*
- ***Drift:** Slow long-term changes in the instrument reading that are not caused by changes in the concentrations of the target compound*

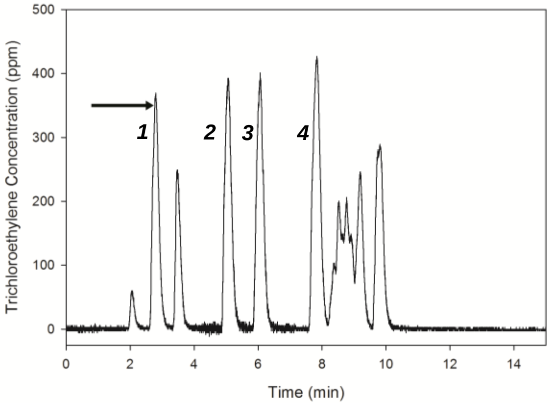


Specificity & Interference


City Technology 4COSH CO / H_2S and two 4S Rev 2 SO_2 sensors exposed to "Quad Mix" calibration gas with 23 ppm H_2S

Both 4S Rev 2 SO_2 sensors showed same relative response to H_2S of about 5%.

Intra-Sampling Period Variability



Trichloroethylene

OSHA "Peak" Standard = 300 ppm

ACGIH STEL = 25 ppm

10.6 ev PID used in flow-through Standard generator: actual 15-min TWA value = 46.3 ppm, but 4 Events > OSHA Peak Standard Occurred

From Smith, Simmons, and Toone: J. Occup. Environ. Hyg., to appear June 2018

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Exposure Measurement Variability

Nicas, Simmons, and Spear: Am. Ind. Hyg. Assoc. J. 52:553-557 (1991)

At least two sources of variability in air sampling:

(1) "Variability in the true average exposure level from period to period, e.g., day to day"

(2) "Variability in measuring a constant environmental level because of random errors in the collection and analytical method"

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Comprehensive Exposure Assessment

[1]**"Characterization of all exposures to all workers on all days"**

This explicitly includes day-to-day variability –does it also include within-shift variability?

[2]**"The best description of the exposure of a worker to an airborne agent is the instantaneous value of the breathing zone concentration throughout the duration of the workshift"**

To include both intra-sampling period <u>AND</u> day-to-day fluctuations, a comprehensive airborne exposure assessment…

Characterizes the instantaneous values of the breathing zone concentration for all workers throughout the duration of all Workshifts on all days

[1] J. Mulhausen: Introduction. In: A Strategy for Assessing and managing Occupational Exposures, 4th ed. Jahn, Bullock, and Ignacio, eds. (2015)

[2] Spear, Selvin, and Francis: The influence of sampling Time on the Distribution of Exposures. Am. Ind. Hyg. Assoc. J., 47:365-368 (1986)

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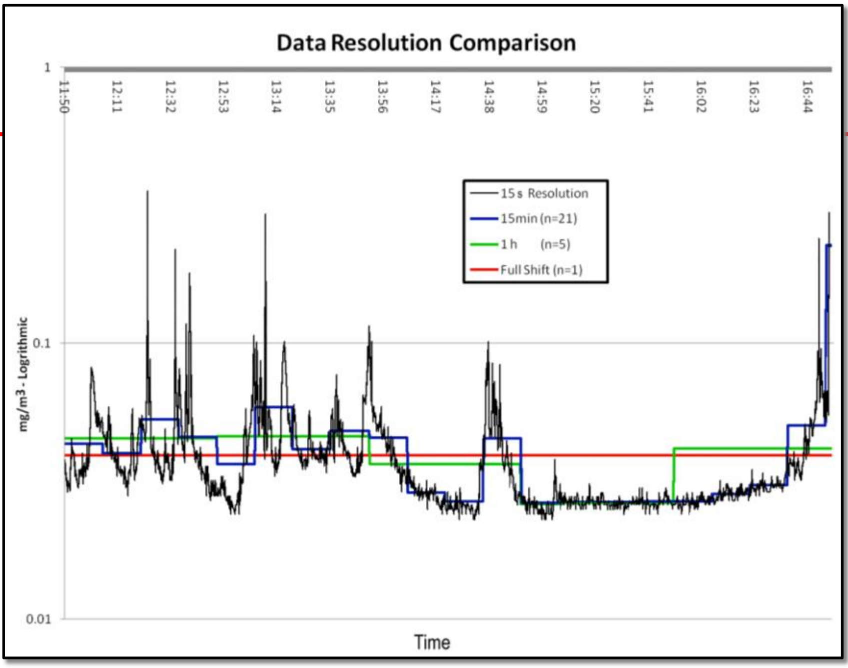


Toxicological Basis for "Ceiling" Standards

Body Burden/Target Receptor Concentration

- ***Per ACGIH TLV Booklet Introduction:***

  > ***"...there are certain substances for which it [the TWA concentration] is inappropriate…"***
  >
  > ***including "…substances which are predominantly fast-acting"***

- ***Intense exposures over short periods may produce "a high dose rate (mg/min) into the body and target tissue, which may alter metabolism, overload protective or repair mechanisms, and amplify tissue responses."***

  Smith, T.J.: Studying peak exposure –Toxicology and Exposure Statistics. In: Exposure Assessment in Epidemiology and Practice (2001)

- ***Regarding acute –acting xenobiotics "…Sample duration should be made very short, particularly when the acute effect is serious. One solution would be to use a direct-reading instrument to monitor exposures."***

  Rappaport, Selvin, Spear, and Keil, Am. Ind. Hyg. Assoc. J., 42:831-38 (1981)

Early real-time colorimetric detection

N.G. White: Hydrogen Cyanide as an Industrial Hazard: Methods of Detection and Control. Industrial Hygiene Quarterly 9:81-84 (1948).

With regard to an early real-time colorimetric detection system for HCN (indicator reagent in a liquid matrix)…

*"The color change during the sampling period in concentrations of 40 ppm or under gives results well within 10% error and enables an individual to safely enter an area of unknown concentration **if he holds his breath during the exposure.** If after sampling 100 cc he can detect no color change he may resume breathing. If 200 cc does not develop the endpoint, **he can advance into the area and remain there safely for five minutes.**"*

(emphasis added)

Target Tissue/Receptor Concept

*The overall key concept of toxicology is the **Dose-Response relationship***

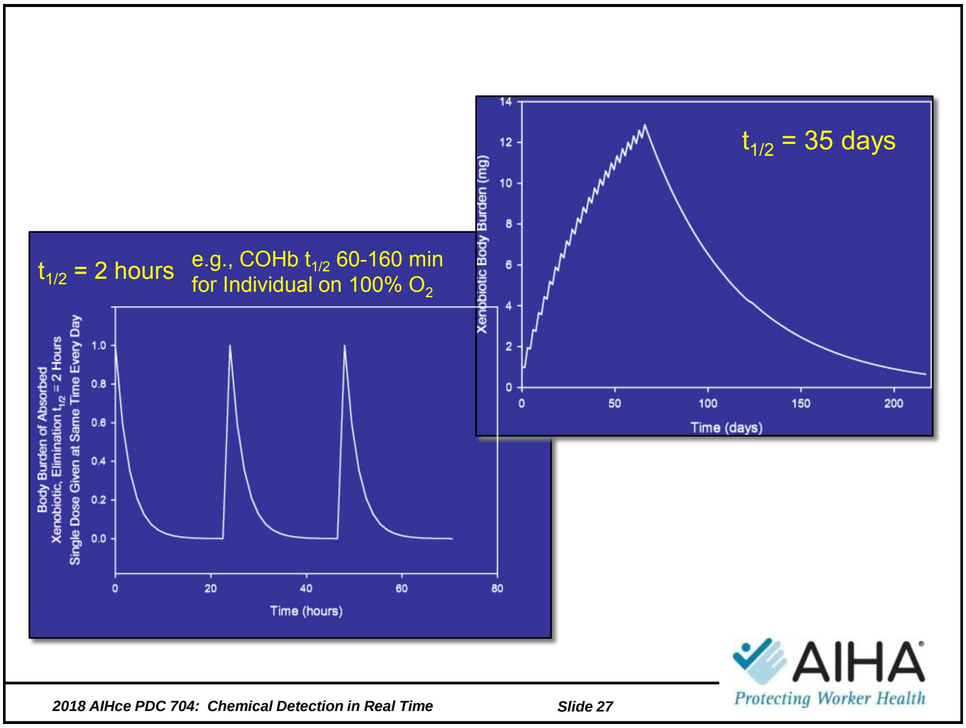
*The four key concepts of toxicokinetics are **Absorption, Distribution, Metabolism, Excretion***

*We do not measure absorption directly, but we measure **Exposure***

*Exposure X Absorption coefficient X Time = **Dose***

*Distribution of a xenobiotic occurs following absorption, including to **target tissues and/or receptors***

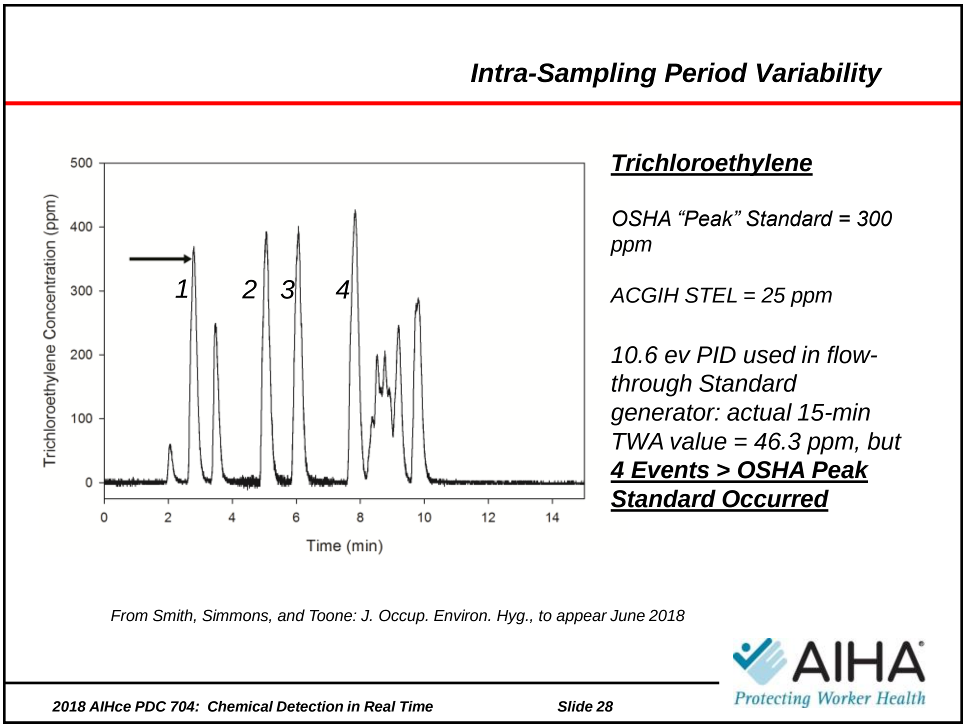
A response may be elicited if homeostasis is disrupted by the concentration of xenobiotic at the target tissue or receptor –e.g., CN^- and CO both bind to mitochondrial cytochrome c oxidase, disrupting the ability of mitochondria to produce ATP during oxidative phosphorylation, affecting the CNS (homeostasis disruption)



$t_{1/2}$ = 2 hours

e.g., COHb $t_{1/2}$ 60-160 min for Individual on 100% O_2

$t_{1/2}$ = 35 days



Intra-Sampling Period Variability

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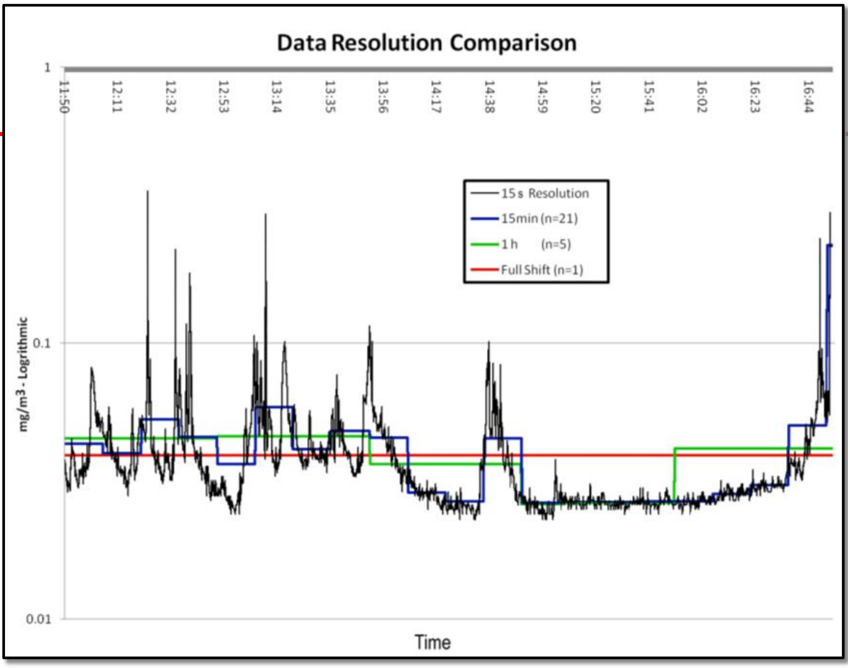
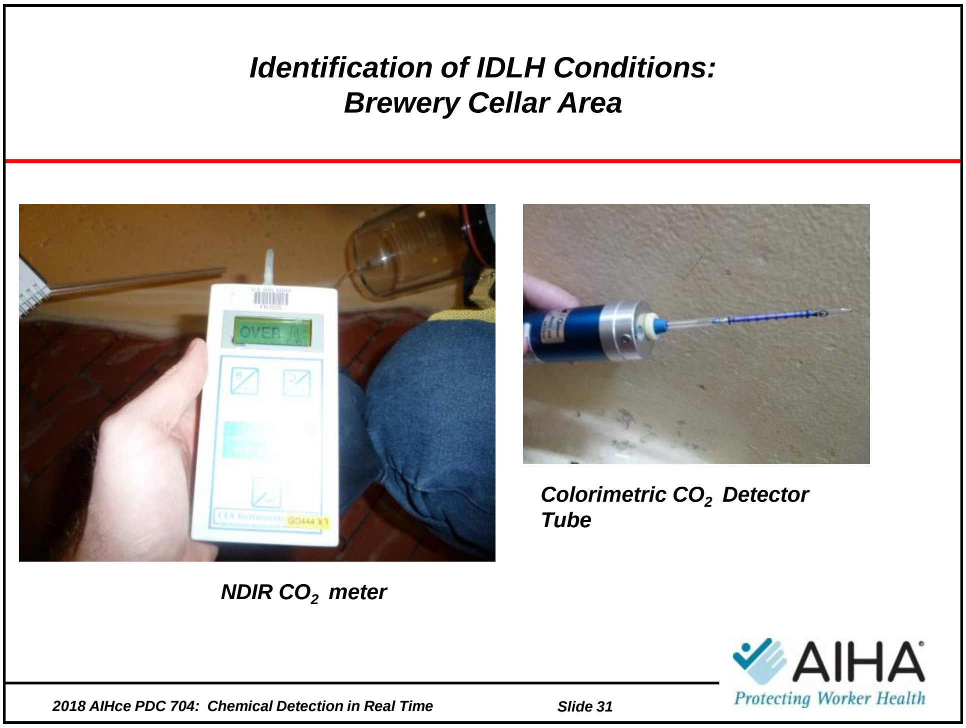
From Smith, Simmons, and Toone: J. Occup. Environ. Hyg., to appear June 2018

When Does Intra-Sampling Period Variability Matter?

1. ***For exposures to stressors with potential to produce rapid toxicity or threat to safety***
   1. ***Any gas that may be released in large amounts (*O_2* dilution –any gas other than *O_2*, innate toxicity –e.g., *CO_2*, flammability –*CH_4*)***
   2. ***Volatile solvents (narcosis)***
   3. ***"Metabolic poisons" (*H_2S*, HCN, CO, others)***
   4. ***Flammable vapors (to be discussed in detail later)***
2. ***For any exposures where knowledge regarding adequacy of controls is sought***

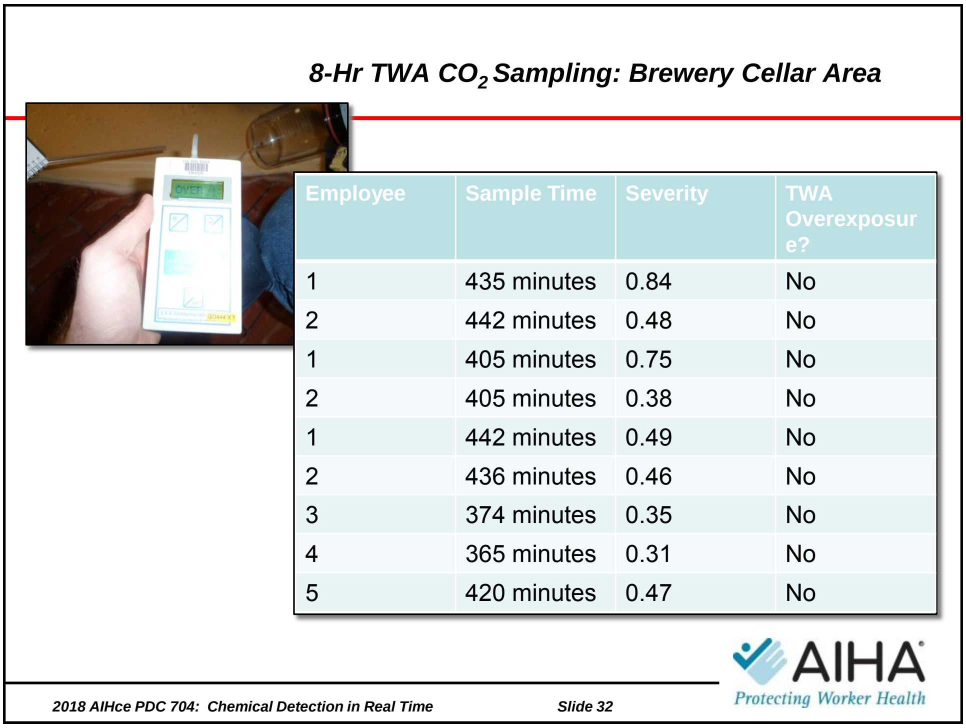




Identification of IDLH Conditions: Brewery Cellar Area

NDIR CO_2 meter

Colorimetric CO_2 Detector Tube



8-Hr TWA CO_2 Sampling: Brewery Cellar Area

Employee	Sample Time	Severity	TWA Overexposure?
1	435 minutes	0.84	No
2	442 minutes	0.48	No
1	405 minutes	0.75	No
2	405 minutes	0.38	No
1	442 minutes	0.49	No
2	436 minutes	0.46	No
3	374 minutes	0.35	No
4	365 minutes	0.31	No
5	420 minutes	0.47	No

Identification of Employees with TWA Overexposure Potential

CO_2 Concentration Reading = 0.54 %

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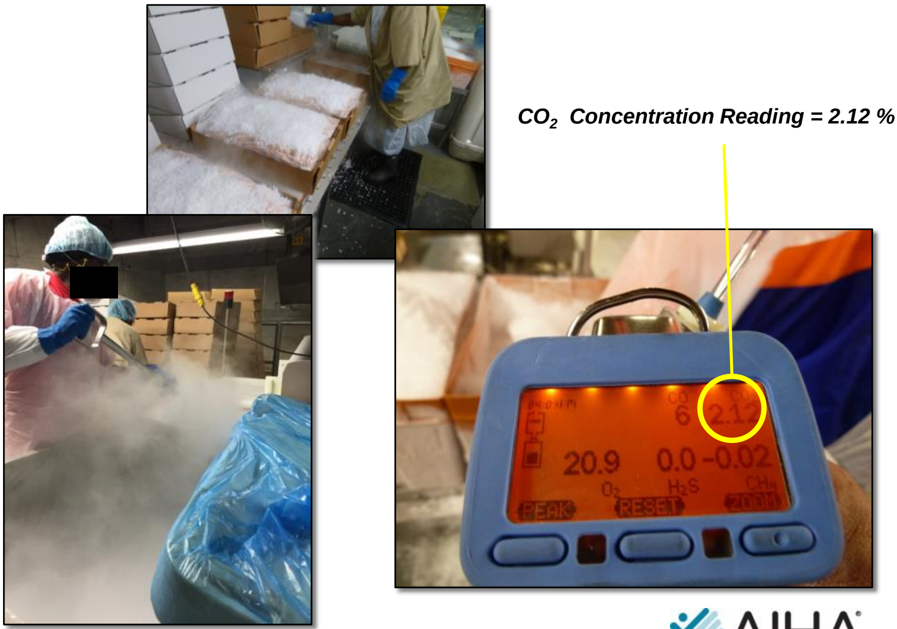
2018 AIHce PDC 704: Chemical Detection in Real Time *Slide 33*



CO_2 Concentration Reading = 2.12 %

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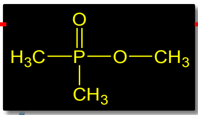
2018 AIHce PDC 704: Chemical Detection in Real Time *Slide 34*

Colorimetric Tube Detection

Example of Capabilities without Instrumentation: Colorimetric Detection

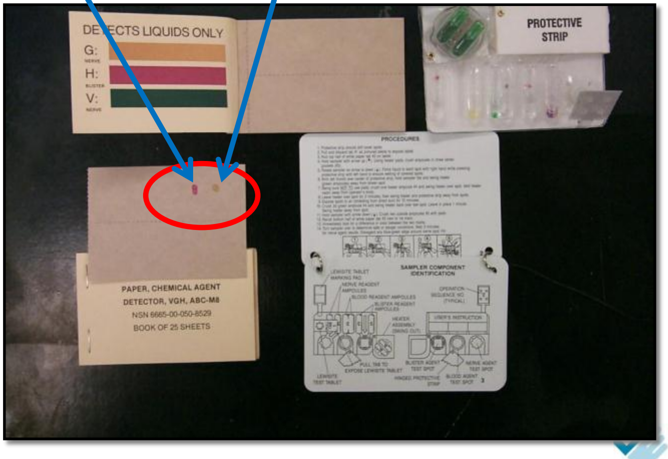
Capabilities without Instrumentation

M8 Paper (simple)



$$H_3C-\overset{\overset{O}{\|}}{\underset{\underset{CH_3}{|}}{P}}-O-CH_3$$

M256 Kit (complicated)



History

- Carbon monoxide detection
  - Hoover and Lamb, 1917
  - “Hoolamite” in 5mm tube
    - Fuming sulfuric acid with iodine pentoxide on porous inert material
    - Charcoal prefilter to remove oxidizing agents
  - Detection to 0.005% CO

What is a detector tube ?

- *A sealed glass tube containing an inert material which is coated with one or more chemicals; a color change occurs when a specific contaminant is present*
- *Dimensions are often 120 (L) x 7 mm (D, ≈ ¼")*
- *Filled with an inert solid or granular material*
  - *Silica gel, alumina, pumice, ground glass*
- *Coated with one or more chemical reagents*

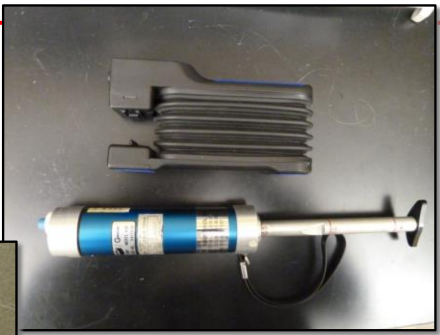
Isopropanol

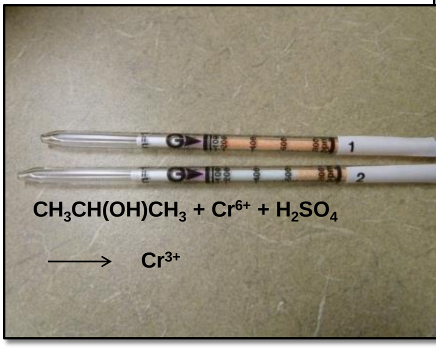
$CH_3CH(OH)CH_3 + Cr^{6+} + H_2SO_4 \longrightarrow Cr^{3+}$

How does a detector tube work ?

Air is typically sampled using a hand-operated pump

When a defined volume of air is passed through a tube the resulting length of stain indicates airborne concentration



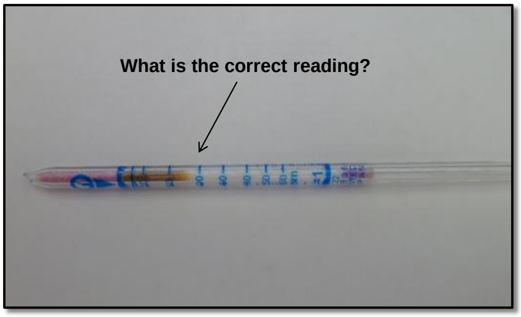


$CH_3CH(OH)CH_3 + Cr^{6+} + H_2SO_4$

$\longrightarrow Cr^{3+}$

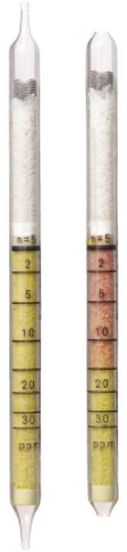
Reading detector tubes

- ***Adequate lighting - but no direct sunlight***
- ***Hold the tube against a light background***
- ***Scale tubes:***
  - ***Full length of discoloration (sum of all colors)***
  - ***Diffuse indication (end point of the slightest discoloration)***
- ***Compare with an unused tube***
- ***Color change (or stain) can take one to two minutes***
- ***Diagonal leading edge:***
  - ***Average between the shortest and longest discoloration***



What is the correct reading?

Example:
HCN Colorimetric Tube



- ***Range: 2-30 ppm***
- ***5 Strokes (takes approximately 1 minute)***
- ***Reaction Principle***

(1) $HCN + HgCl_2 \longrightarrow HCl$
(2) $HCl + \text{Methyl Red} \longrightarrow \text{Read Reaction Product}$

- ***Cross Sensitivity: phosphine***

  H_2S, NH_3, SO_2, NO_2, HCl ***– no affect to indication***

  H_2S ***– Brown prelayer***

Simultaneous Test Sets

- *Time to determine toxic industrial chemicals or chemical warfare agents for first responders is limited*
- *Simultaneous Measurement*
- *Detect and Measure Five Toxic Industrial Chemicals Simultaneously*
  - *Set I: Acid Gas, HCN, CO, Basic, NO_x*
  - *Set II: SO_2, Cl_2, H_2S, CO_2, $COCl_2$*
  - *Set III: Ketones, Aromatics, Alcohols, Aliphatics, Chlorinated Hydrocarbons*

Chemical Warfare Agents

- *Nerve Agents*
  - *Sarin, Tabun, Soman, VX*
- *Blister Agents*
  - *Mustard Gas, Lewisite*
- *Blood Agents*
  - *Hydrogen Cyanide, Cyanogen Chloride*
- *Phosgene, Cl_2*

Agent	*Detector Tube*	*Sensitivity*
Hydrocyanic Acid	*Hydrocyanic Acid*	*1 ppm*
Phosgene	*Phosgene*	*0.2 ppm*
Lewisite	*Organic Arsenic Cmpds. and Arsine*	*3 mg/m3 (org. arsenic)*
N-Mustard	*Organic Basic Nitrogen Cmpds.*	*0.1 ppm arsine*
S-Mustard	*Thioether*	*1 mg/m3*

Advantages

- ***No batteries or power source***
- ***No calibration***
- ***Always ready to use***
- ***Light***
- ***Easy to use***
- ***Measures specific gases***

2018 AIHce PDC 704: Chemical Detection in Real Time

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Limitations

- ***Should use manufacturer-specific pump***
- ***Must read and follow instructions***
- ***No alarms, no datalogger***
- ***Correction may be needed for temperature, humidity, atmospheric pressure***
- ***Not permanent – stain can degrade in a matter of hours***
- ***Limited shelf life***
- ***Interfering chemicals***
  - ***Positive – color change***
  - ***Negative – inhibit color change***
- ***May not be precise***
- ***One time sample***
- ***May be difficult to read***

2018 AIHce PDC 704: Chemical Detection in Real Time

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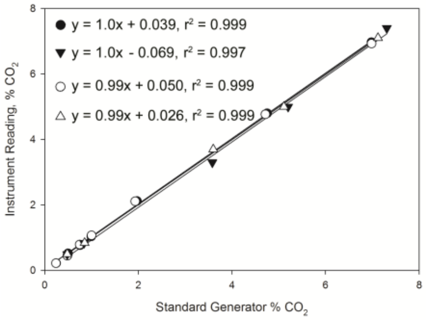
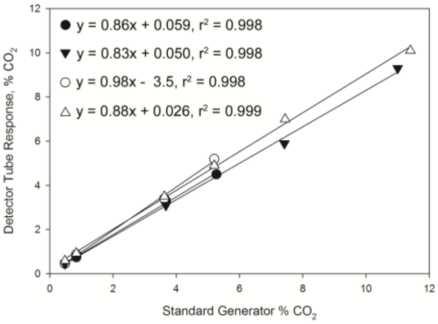
Example: Measurement of CO_2 with Colorimetric Tubes, NDIR, and FTIR

From Hill and Smith, *J. Occup. Environ. Hyg. 12*:819-828 (2015)

Triangles = NDIR, Circles = FTIR





Dark = Dry, White = 80% RH

Tube Reading Procedure for CO_2 Measurement

From Hill and Smith, *J. Occup. Environ. Hyg. 12*:819-828 (2015)

(1) Values were obtained by visually determining color change front against printed scale to the nearest 1/10th marking interval

(2) These values were then corrected

(a) Reading of 3.3% for the 2L tube (dry air with 3.67% CO_2) initially recorded as 1.4%; this value was doubled to 2.8% as only a 50 ml draw (one-half full pump stroke) was used

(b) The resulting 2.8% value was then corrected for lab atmospheric pressure by multiplying 2.8% by 760 mmHg, and dividing by 653 mm Hg (the atmospheric pressure in the laboratory)

Specific Colorimetric Tube Data for CO_2 Measurement

From Hill and Smith, *J. Occup. Environ. Hyg. 12*:819-828 (2015)

%CO_2 Concentration/ Conditions	*2L Tube % Difference Result*		*2H Tube % Difference Result*	
0.48/dry	*0.46*	*-4.3*	*0.46*	*-4.3*
0.48/humid	*0.47*	*-2.1*	*0.59*	*23*
0.84/dry	*0.75*	*-11*	*0.81*	*-3.6*
0.84/humid	*0.88*	*4.8*	*0.93*	*11*
3.67/dry	*3.3*	*-10*	*3.1*	*-16*
3.62/humid	*3.4*	*-6.1*	*3.4*	*-6.1*
5.27/dry	*4.5*	*-15*	*-*	
5.20/humid	*5.2*	*0*	*4.9*	*-5.8*
7.42/dry	*-*		*5.9*	*-20*
7.44/humid	*-*		*7.0*	*-5.9*
11.0/dry	*-*		*9.3*	*-15*
11.4/humid	*-*		*10.1*	*-11*

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Questions?

- *Thank you!*

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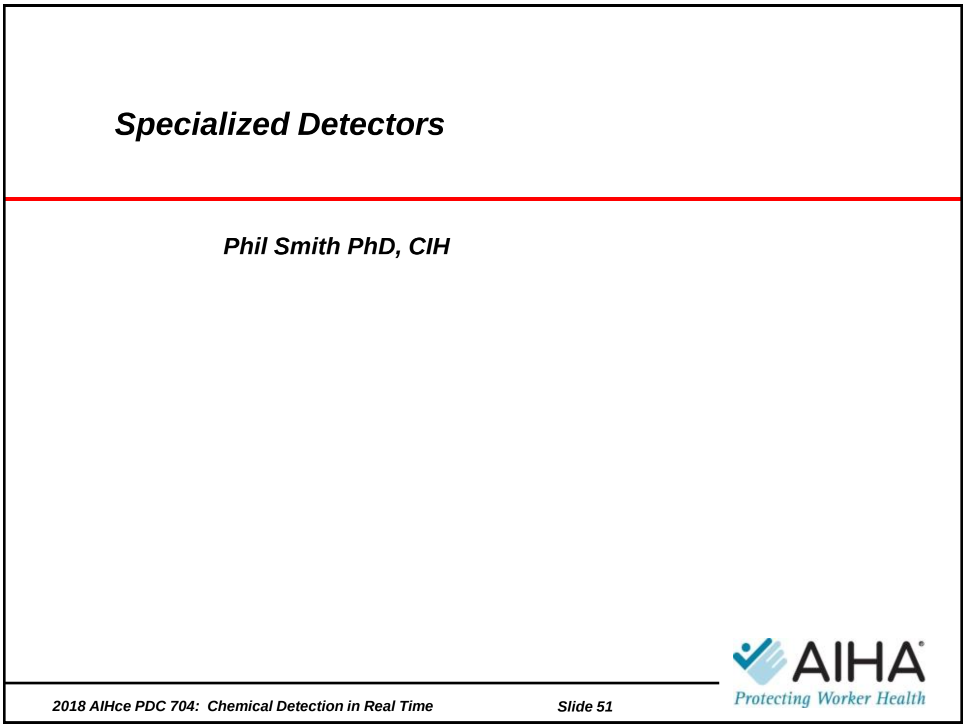
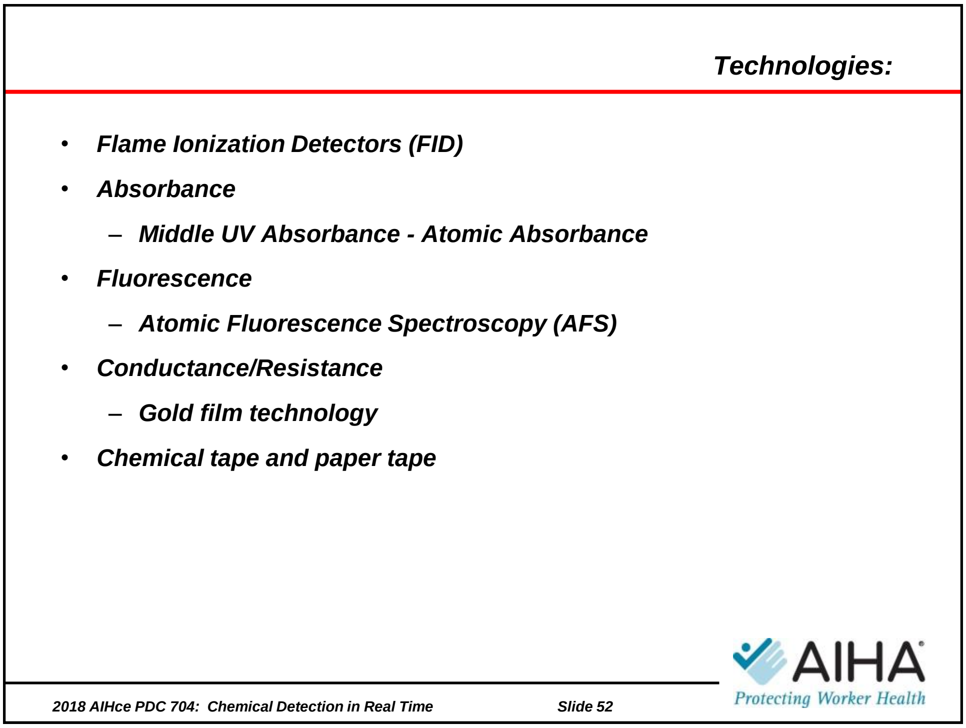


Specialized Detectors

Phil Smith PhD, CIH



Technologies:

- ***Flame Ionization Detectors (FID)***
- ***Absorbance***
  - ***Middle UV Absorbance - Atomic Absorbance***
- ***Fluorescence***
  - ***Atomic Fluorescence Spectroscopy (AFS)***
- ***Conductance/Resistance***
  - ***Gold film technology***
- ***Chemical tape and paper tape***

Flame Ionization Detectors

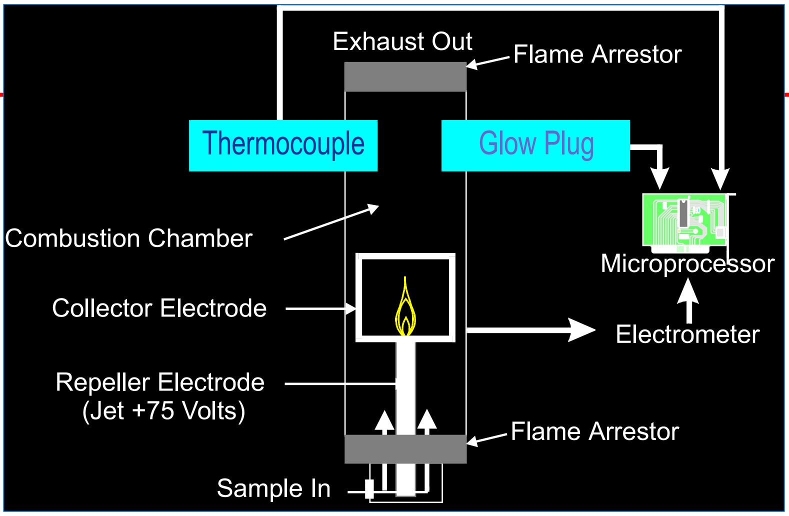
FID Principle of Detection

- *Use H_2 flame as source of ionization energy*
- *Able to detect nearly all organic compounds*
- *In clean air, H_2 flame free from ions and non-conducting*
- *Organic contaminants with carbon-hydrogen or carbon-carbon bond break down according to the following reaction:*

$$RH + O \rightarrow RHO^+ + e^- + CO_2 + H_2O$$

- *Positively charged carbon containing ions collected on a negatively charged plate*
- *The ion current proportional to the hydrocarbon concentration*

FID Schematic



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Flame Ionization Detectors (FID)

- ***Depending on instrument, FID capable of dynamic range of 1.0 ppm – 100,000 ppm (CH_4)***
- ***Used for:***
  - ***Testing for leakage from valves and flanges at oil refinery, petrochem and chemical plants (EPA Method 21 compliance)***
    - ***All point sources of leakage must be tested twice a year***
  - ***Natural gas transmission (test for leakage and / or determination of point source of leaks)***
  - ***General environmental / air quality TVOC measurement***

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EPA Method 21

- ***Determination of Volatile Organic Compound Leaks***
- ***Specifies selection and use of monitors for leak detection and monitoring "fugitive emissions"***
- ***Detector types that may be used include (but are not limited to) catalytic oxidation (pellistor), flame ionization (FID), infrared absorption (IR), and photoionization (PID)***
- ***TVOC readings expressed (or recalculated) in "carbon units" or "FID units"***

FIDs Use Hydrogen Gas as Fuel

- ***Require high pressure (16 MPa or 2300 lb/in^2) cylinder of hydrogen***
- ***Refilling and storage of H_2 cylinder significant issue***
- ***Some FID detectors not classified as to Intrinsic Safety***
- ***Other issues limiting performance:***
  - ***Carbon buildup in the detector which can lead to "flame outs", and***
  - ***Position sensitivity of detector due to use of live flame to drive ionization***

FID Operating Characteristics

- *Detects wide range compounds*
- *Sample air is O_2 source*
- *Ionizes compounds up to 15.4 eV*
- *Generally calibrated with methane*
- *Wide dynamic range, very linear*
- *Limitations:*
  - *Non specific*
  - *Not as sensitive as PID*

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FID detectable gases and vapors

- *Saturated Hydrocarbons - Methane, Ethane, Propane, n-Hexane*
- *Aromatics - Benzene, Toluene, Naphthalene*
- *Unsaturated Hydrocarbons - Acetylene, Ethylene, 1,3-Butadiene*
- *Chlorinated Hydrocarbons - Vinyl Chloride, Chloroform, Trichloroethylene, Methylene Chloride*
- *Ketones - Acetone, Methyl Ethyl Ketone, Methyl Isobutyl Ketone*
- *Alcohols - Methanol, Ethanol, Isopropanol, n-Butanol*

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FID Operating Characteristics

- ***Oxygen deficiency***
  - ***Cannot be used in O_2 deficient atmospheres***
  - ***Use in O_2 deficient atmosphere requires separate oxygen supply***
- ***High humidity***
  - ***Minimal effect***

FID vs. PID

- ***Major difference is amount of variance in sensitivity from one organic substance to another***
- ***Amount of energy (or ionization potential) necessary to dislodge an electron to create a charged fragment determines sensitivity of PID for a specific molecule***
- ***Ionization Potential varies widely from one substance to the next***
- ***For these reasons sensitivity of PID detector also varies widely between compounds***

FID vs. PID

- ***FID sensitivity does not vary as significantly from one organic substance to another***
- ***Amount of energy necessary to break specific carbon-carbon or carbon-hydrogen bonds is relatively constant***
- ***Thus, FID sensitivity more generalized, and varies less between one hydrocarbon and another***

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FID can detect methane, while PID cannot

- ***FID is preferred instrument for detection of methane and other saturated alkanes***
- ***Excellent for unsaturated hydrocarbons and alkenes at part-per-million levels***
- ***Hydroxyl (OH-) or chloride (Cl-) functional groups tends to reduce sensitivity***
- ***Inorganic contaminants such as chlorine, ammonia or hydrogen cyanide are not detected***

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PID and FID Complementary Detection Techniques

- ***Instruments containing PID and FID detectors are complementary, rather than competitive***
- ***Type of detector chosen should reflect the contaminant(s) being measured***
- ***Neither technique equally good at detecting all ionizable contaminants***
- ***Some manufacturers offer dual PID/FID analyzers in the same instrument***

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PID vs. FID: Which one to Use?

- ***Health and Safety - PID***
  - ***PID is generally more sensitive to higher toxicity compounds***
- ***Fugitive Emissions - FID***
  - ***Method 21 requires methane calibration***
- ***Haz Waste Site Monitoring - PID***
- ***Landfill Monitoring - Both PID and FID***
- ***Natural Gas Detection - FID***

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Absorbance

- ***Beer-Lambert Law***

$$A = a * b * c$$

Where:

A = absorbance (log transmitted light/log incident light (I/Io) x l

a = extinction coefficient -molar absorptivity (L/mole) x (1/cm)

b = path length (cm)

c = airborne concentration of absorbing analyte (mole/L)

Spectroscopic Detector

Components

- ***Monochromatic light source – Hg vapor, tungsten***
- ***Sample cell***
- ***Photodetector***
- ***Associated electronics***

Near UV absorbance – 300-400 nm

  - ***Ammonia, ozone, elemental mercury***
  - ***Single digit ppb values***

Frequency

- ***Each element or chemical emits a specific wavelength of light:***

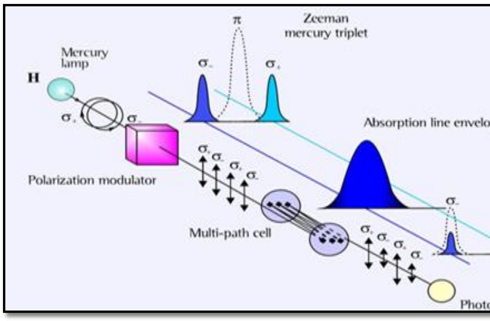
Element/Compound/ Chromophore	*Absorption Coefficient*	*l_{max} nm*	*Transition*
Mercury	*10^6*	*253.7*	
Ozone	*308.8*	*260*	
Aromatic	*2,864*	*262*	*p --p**
Ketone C=O	*14*	*253.7*	*n -- p**
-C=C-			*p --p**
Ether -O-	*1,000*	*185*	*n -- p**
Amine -NH2	*3,000*	*195*	*n -- p**
Carboxyl -COOH	*60*	*205*	*n -- p**
Aldehyde -CHO	*1000 20*	*210 290*	*n -- p**
Benzene	*7,000*	*200*	*p --p**
Toluene	*2,875*	*262*	*p --p**
Ammonia	*5,000*	*190*	

Absorption Coefficients for Selected Compounds & Chromophores in the UV region (Table from "Important Instrumentation and Methods for the Detection of Chemicals in the Field")

Mercury Detection

Light transmitted through a sample chamber which contains numerous reflective mirrors -decreased light intensity is measured

- ***Increasing the path length (b) increases absorbance (a) and thus boosts sensitivity***



Lumex RA915M Mercury Vapor Analyzer (With permission from Lumex of Ohio)

How It Works…

- *Mercury vapor is drawn into a cell where the vapor is irradiated by UV light emitted from a Hg source*
- *Small quantities of the UV light are absorbed by Hg vapor*
- *Careful background subtraction (Zeeman correction) allows detection of very low levels of mercury*
    - *Instant NIOSH 6009 indoor air Hg concentrations*

Detection Limits

- *2 ng/m^3 (0.002 µg/m^3) multi-path cell*
- *5K – 200K ng/m^3 single path*

ATSDR Suggested Clean up levels

- *1,000.0 ng/m^3 (Residential)*

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Limitations

- *Heavy and Large*
    - *7.5 Kg (16.5 lb.)*
    - *46 x 21 x 11 cm(18.1 x 8.3 x 4.3 in.)*
- *Noisy*
- *Delicate – mirrors can move*
- *Battery life*
    - *3.5 hours (use extension cords?)*

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Other Hand Portable Mercury Detectors

- ***Ion Science***
  - ***MVI Portable Mercury Detector***
    - ***Dual beam UV absorbance***
- ***(No longer manufactured or supported) Genesis Laboratory Systems***
  - ***Hg253 Portable Mercury Analyzer***
    - ***Atomic absorption***

Ion Science MVI Portable Mercury Detector

More Mercury Please

- ***Atomic Fluorescence Spectroscopy (AFS)***
- ***Arizona Instruments***
  - ***Jerome J505 Portable Atomic Fluorescent Spectroscopy Mercury Vapor Analyzer***

Atomic Fluorescence Spectroscopy (AFS)

- ***A mercury lamp excites the mercury vapor at 254nm***
- ***A detector measures the emission of the photons, at the same wavelength, as the electrons return to their stable ground states***
- ***Specific to mercury***
  - ***No interferences from hydrocarbons, H_2S, ammonia***

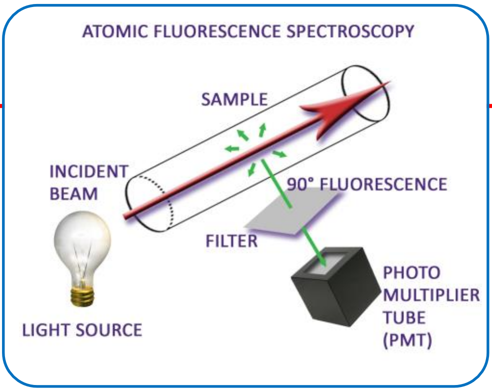


Diagram courtesy of Arizona Instruments

Resistance/Conductance

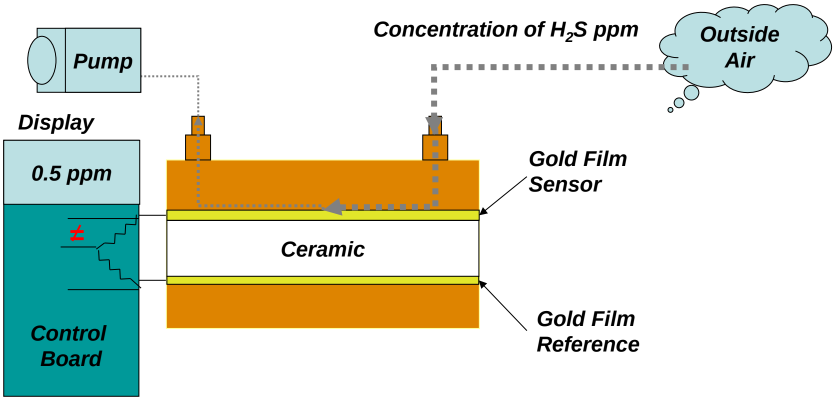
- ***Conductometric instruments measure the flow of electrical current across a liquid or solid, although it is the solid state variety (specifically a gold film design) that is very commonly used for routine field measurements***
- ***Sorbed chemicals can either enhance or reduce resistance of the conductometric material placed between electrodes, and the effect is proportional to the concentration of the chemical present in the solid material.***
- ***Metal oxide semiconductor (MOS) sensors use an oxidized metal coating of tin, zinc, lanthanum, tungsten or nickel, on a silica or alumina substrate.***

Gold Film Sensor

- ***A gold film instrument is not an MOS conductor, but the same principle related to resistivity change applies, and this approach is well-known for monitoring certain gases and vapors which cause a resistance change which can be easily measured.***
- ***Measures hydrogen sulfide or mercury***
- ***Inherently stable***
- ***Holds calibration for up to one year***
- ***Durable***
  - ***Better able to withstand shocks with little loss for accuracy***

Jerome® J605 Gold Film

- ***A thin gold film, in the presence of hydrogen sulfide, undergoes an increase in electrical resistance proportional to the mass of hydrogen sulfide in the sample.***



Use of figures and diagrams by permission of Arizona Instruments, Inc.

Resistance Technology Instruments

- ***Detection Range (H_2S):***
  - ***0.001 – 50 ppm (631)***
  - ***3.0 ppb - 20.0 ppt (J605)***
- ***Flowrate:***
  - ***0.15 L/min***
- ***Uses:***
  - ***Agriculture, landfill, storm drains/sewers, scrubber efficiency testing, source detection, ambient air analysis, water treatment***

Arizona Instruments Jerome 631

Arizona Instruments Jerome J605

Limitations

- ***Cross-sensitivities***
  - ***Chlorine, ammonia, NO_2, mercaptans (thiols)***
  - ***Optional filter removes chlorine and ammonia***
- ***5.4 pounds***
- ***Regeneration of gold film sensor is by heating to drive off trapped contaminant (H_2S or Hg)***
- ***Not explosion proof***

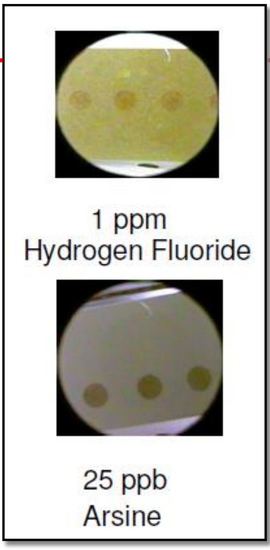
Portable Chemical Tape / Paper Tape Detectors

Honeywell ChemKey
TLD & MDA SPM

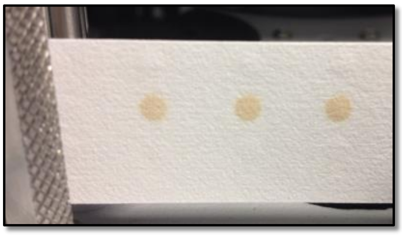
DOD Technologies
CLPX Portable Gas Monitor

How it works

- ***Chemically impregnated paper tape***
- ***Air sample drawn through the tape***
- ***Resulting color intensity related to concentration***



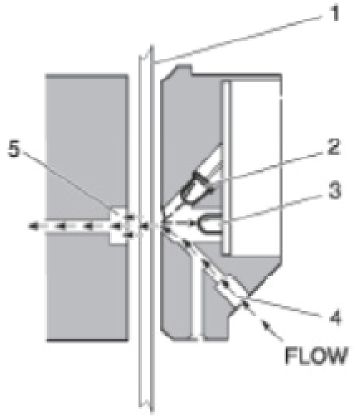
Courtesy of Honeywell Analytics



SiH4 Tape, Courtesy of DOD Technologies

Sample Detection

- *Sample is illuminated and analyzed with the Optical scanning system*
- *“Calibration free”*
  - *No need to calibrate detectors to specific concentrations*
  - *Conducts optics check or comes with a Sample or Test card to check system*



1-Tape
2-Light
3-Optics
4-Air sample inlet
5-Air sample outlet

Courtesy of Honeywell Analytics

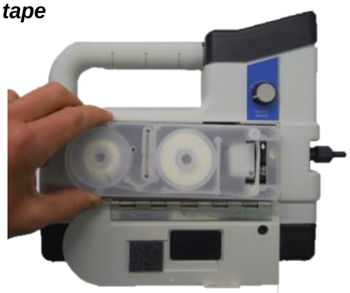
Select Detection Comparisons

Chemical	PEL	Chem Tape Detection (LDL)
Diisocyanate - TDI	0.02 ppm (C)	0.0017 ppm
Phosphine (PH_3)	0.3 ppm	0.005 ppm
Hydrazine (N_2H_4)	1.0 ppm	0.007 ppm
Hydrogen fluoride (HF)	3.0 ppm/6.0 ppm (C)	0.3 ppm
Phosgene ($COCl_2$)	0.1 ppm	4.9 ppb

Tape Basics

- *Tapes on Cassette or Reels*
  - *Two weeks continuous detection*
- *Tape TLC*
  - *Tapes should be stored in freezer*
  - *Only remove cassettes from protective packaging when ready for use*
  - *Reel may be advanced for fresh tape*

ChemCassette, Honeywell



CLPx, DOD Tech

Paper Tape Applications

- *Possible applications*
  - *Indoor/Outdoor*
  - *Corrosive/toxic gas areas*
  - *Remote sampling area*
  - *Survey work*
  - *Ventilation and exhaust systems*
  - *Emergency Response*
  - *IH surveys*
- *Common Industries*
  - *Computer chip industries*
  - *Rocket fuel propellant facilities and research*
  - *Chemical manufacturer*
  - *Metallurgical*

"Paper Tape" Capabilities and Limitations

Capabilities:

- ***Paper tape detection has existed since the early 1970's***
- ***Useful when other detection methods are not available***
- ***Individual Gas or Gas Family specific***
  - ***Very few interferences***
- ***Low detection limits/Rapid response***
  - ***Down to ppb levels as quickly as 10 seconds***

Limitations:

- ***Different tape chemistry needed for specific chemicals***
- ***Chemical tapes have limited shelf life***
- ***Exposure to direct sunlight, ambient air and elevated temperatures may decrease sensitivity of tape***
- ***9.5 – 14.5 pounds***
- ***Not intended for combustible atmospheres***

Questions?

- ***Thank you!***

Ion Mobility Spectrometry

Phil Smith, PhD, CIH

Objectives

- ***Discuss how ion mobility spectrometry works***
- ***Discuss the selectivity of IMS methods***
- ***Discuss target IMS analyte classes***

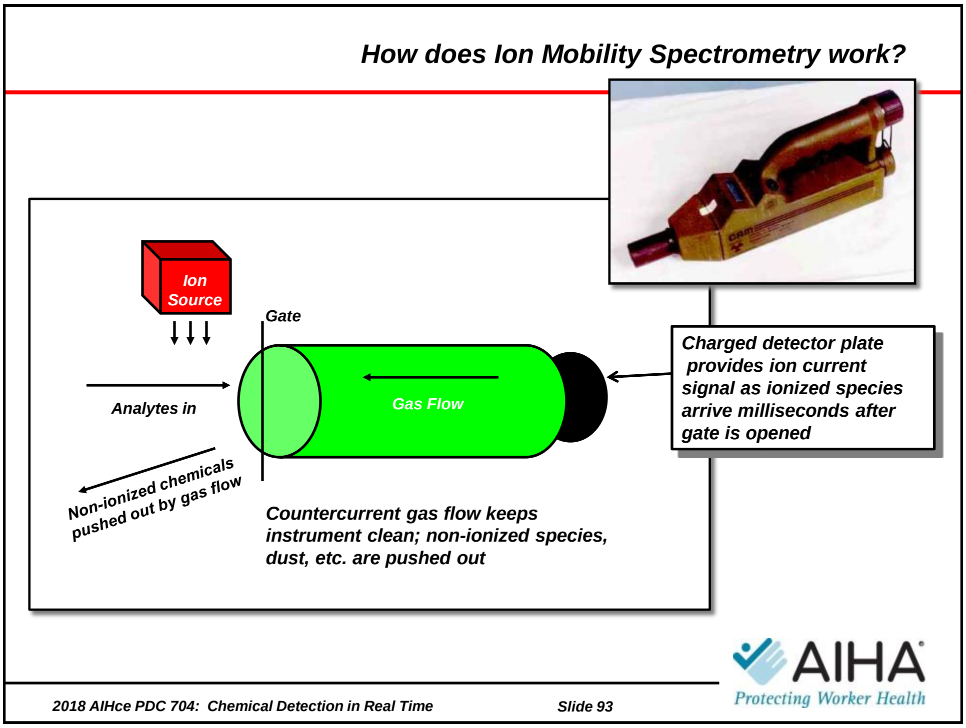
What is Ion Mobility Spectrometry?

- **At one time known as "Plasma Chromatography" (a misnomer)**
- **A simple and rugged method that uses relatively little power**
- **Relies on atmospheric pressure chemical ionization of target analytes (makes for selectivity based on ionization potential)**

How does Ion Mobility Spectrometry work?

- **IMS is a selective method because not all chemicals are ionized easily at atmospheric pressure**
- **Compounds more easily ionized typically contain heteroatoms (O,N,P,S; e.g. most pertinent CW agents or explosives with NO_2 groups)**

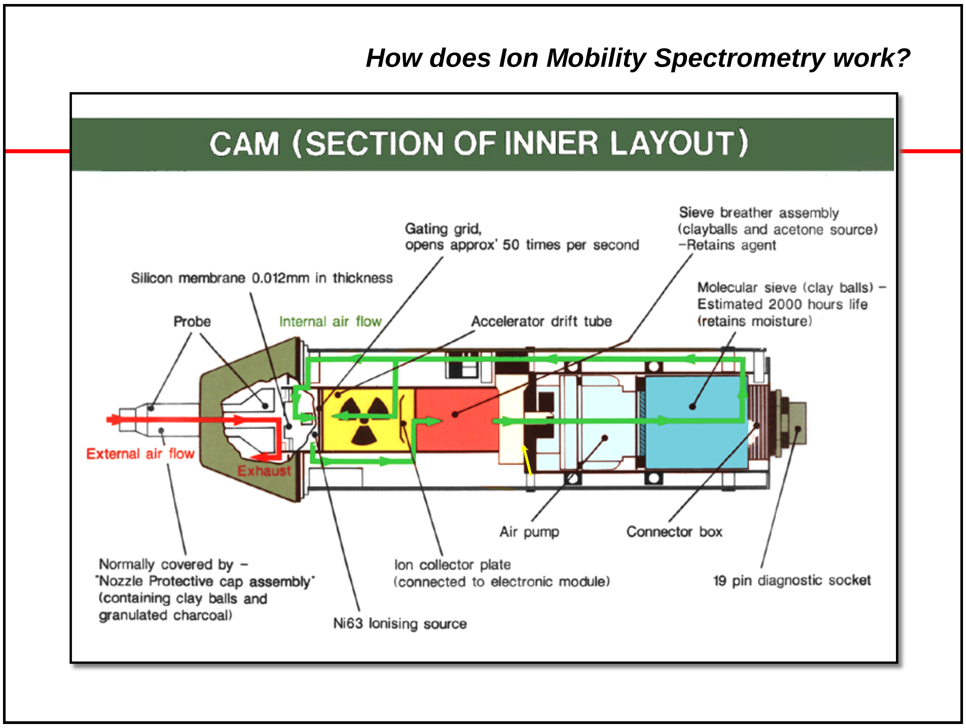
How does Ion Mobility Spectrometry work?



Charged detector plate provides ion current signal as ionized species arrive milliseconds after gate is opened

Countercurrent gas flow keeps instrument clean; non-ionized species, dust, etc. are pushed out

How does Ion Mobility Spectrometry work?


CAM (SECTION OF INNER LAYOUT)

How does Ion Mobility Spectrometry work?

- *Ionization Chemistry*
  - *Relatively abundant reactant compounds are ionized first – can be H_2O, acetone, or other compound. Using H_2O as an example reactant compound:*

    (1) $N_2 + e^-$ (67 keV from ^{63}Ni) $N_2^+ + 2e^-$
    (2) $N_2^+ + 2N_2$ $N_4^+ + N_2$
    (3) $N_4^+ + H_2O$ $2N_2 + H_2O^+$
    (4) $H_2O^+ + H_2O$ $H_3O^+ + OH\bullet$
    (5) $H_3O^+ + H_2O + N_2$ $H^+(H_2O)_2 + N_2$

    Stable reactant ion
  - *Reactant ion peak (RIP) present when no analytes are available for ionization*
  - *Reactant ions provide charge to analytes that will accept the charge*
  - *Analytes can produce either positive or negative ions following reaction with reactant ions*
    - *Sulfur mustard (HD) provides a negative ion (chlorinated compound)*
    - *Explosives also provide negative ions*
    - *G agents and VX provide positive ions*
    - *By switching polarity of Faraday plate detector, + and - detection modes are available for some instruments*

Advantages of Ion Mobility Spectrometry

- *High sensitivity*
- *Lightweight*
- *Fast (milliseconds)*
- *Low power requirement (battery OK)*
- *Somewhat selective for functional groups found in CW agents and explosives*
- *Can scan both + and – ions*

Limitations of Ion Mobility Spectrometry

- The ion source is often radioactive ^{63}Ni
- Low resolution (not useful as a separation method, e.g., as a type of chromatography)
- Poor quantitation (dynamic range limited by consumption of reactant ions and dynamic ionization process)
- Functional group selectivity limits the compounds that can be detected, allows some compounds easily ionized to mask presence of others less easily ionized

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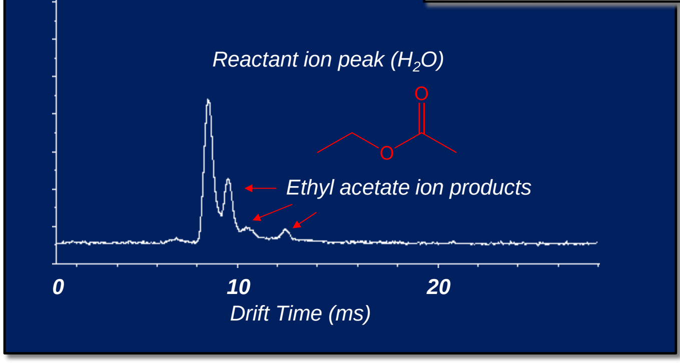
Ion Mobility Spectrometry



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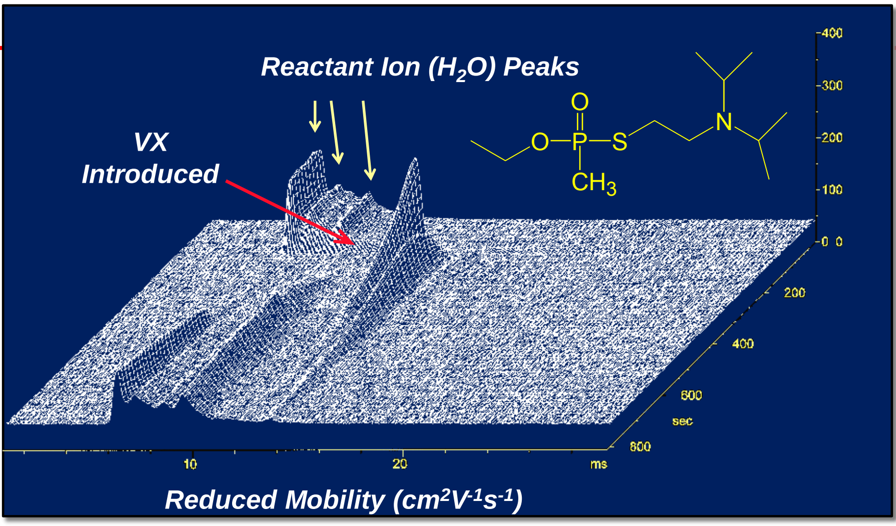
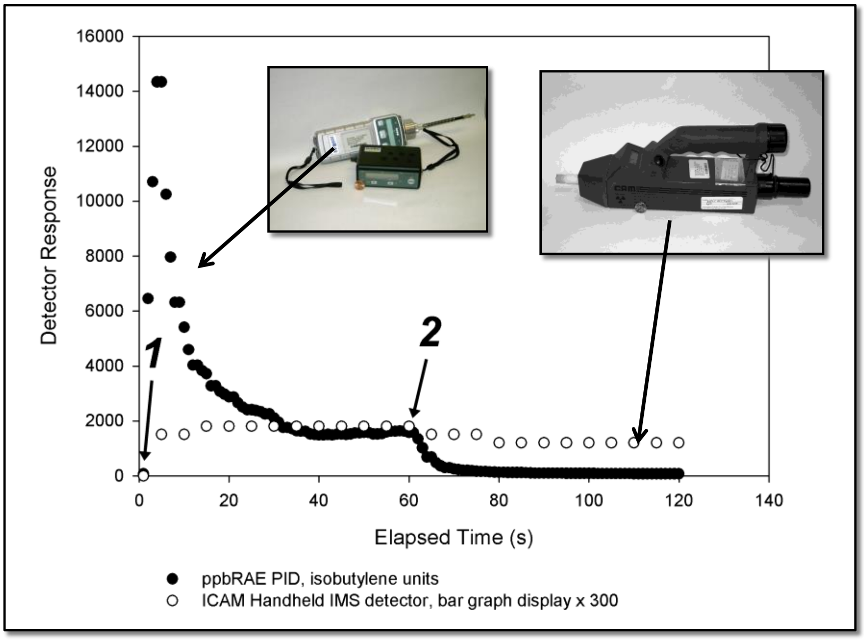
IMS analysis of VX





For Further Information on Ion Mobility Spectrometry

- **Eiceman and Karpas: "*Ion Mobility Spectrometry"* CRC Press, 1993**

Questions?

- ***Thank you!***

Real Time Particle Measurement Technologies

William J. Mills III
M.Sc. , Ph.D., CIH, C.Chem.
Northern Illinois University

Overview

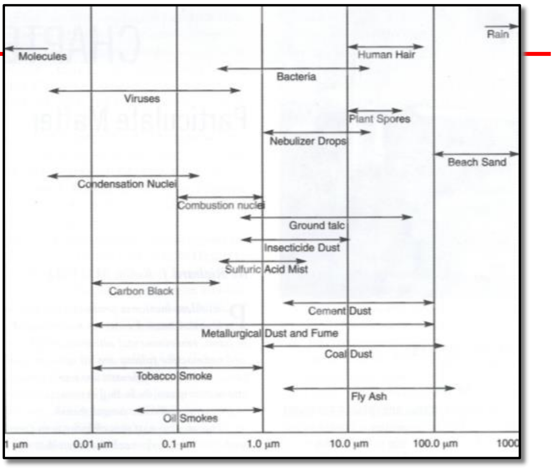
- *Introduction*
- *Particle Size and Human Exposure*
- *Tyndall Meter*
- *Photometric technology*
- *Optical Particle Counting technology*
- *Condensation Particle Counting technology*
- *Beta (β) Attenuation*
- *TEOM - Tampered Element Oscillating Microbalance*
- *Micro Aethalometer*
- *Measuring Nanoparticle Exposure*
- *Summary*
- *Questions*

Introduction

- ***Particles*** ***(or Particulate Matter(PM)) large and small, are an important factor in exposure monitoring, indoor air quality, mechanical filtration and environmental air quality.***
- ***An*** ***aerosol*** ***is*** *technically* ***a suspension (mixture) of a solid or liquid "particle" in the air . The term "aerosol" is commonly used to refer to the particulate portion of the mixture***

  (IVHHN, Seinfeld (1998),
  http://www.mfg.mtu.edu/cyberman/environment/air/pmintro.html)
- ***Tyndallmeters, Photometers, optical particle counters (OPCs) and condensation particle counters (CPCs) all measure airborne particles in real-time via MIE light-scattering physics***
  - ***Differ in sensitivity to specific particle characteristics such as size, size distribution, density, morphology and refractive index.***

PM
Particle Size Ranges



Total suspended particulate

Refers to all the particulate material suspended in the air

Typically >100 µm in diameter rapidly falls out of the air due to gravitational and inertial settling

Particles < 10 µm achieve significant penetration into the lungs

Standard Recognized Size Fractions

Environmental (US EPA)

- ***PM_{10} (≤10 µm)***
- ***$PM_{2.5}$ (≤2.5 µm)***

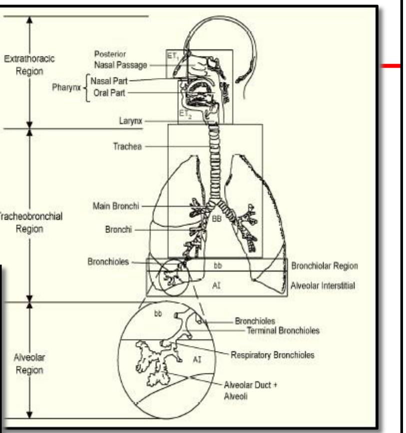
Occupational (ACGIH, ISO, CEN)

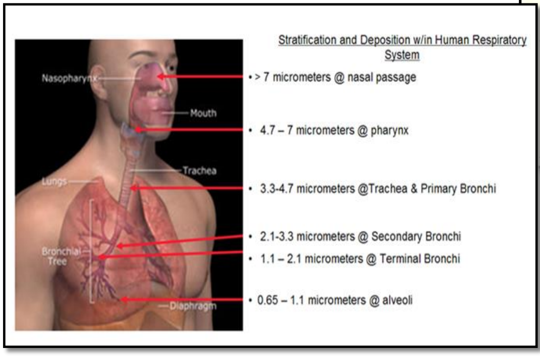
- ***Total Inhalable (≤100 µm)***
- ***Thoracic (≤10 µm)***
- ***Respirable (≤4 µm)***

(construction work, mineral extraction, wind-blown dust and soil)

Common Terms: Dust, Fume, Mist, Fog, Smog, Smoke

Human Exposure

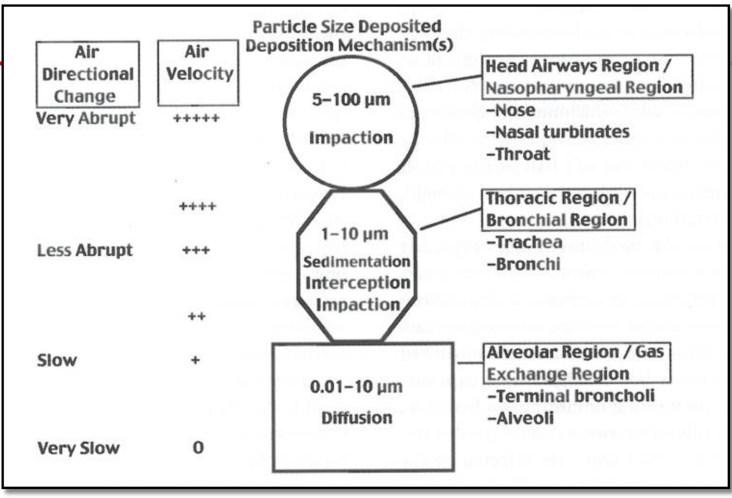




Stratification and Deposition w/in Human Respiratory System

- > 7 micrometers @ nasal passage
- 4.7 – 7 micrometers @ pharynx
- 3.3-4.7 micrometers @Trachea & Primary Bronchi
- 2.1-3.3 micrometers @ Secondary Bronchi
- 1.1 – 2.1 micrometers @ Terminal Bronchi
- 0.65 – 1.1 micrometers @ alveoli

Particle Deposition in Respiratory System



Air Directional Change	Air Velocity	Particle Size Deposited Deposition Mechanism(s)	
Very Abrupt	+++++	5–100 µm Impaction	Head Airways Region / Nasopharyngeal Region –Nose –Nasal turbinates –Throat
	++++		
Less Abrupt	+++	1–10 µm Sedimentation Interception Impaction	Thoracic Region / Bronchial Region –Trachea –Bronchi
	++		
Slow	+	0.01–10 µm Diffusion	Alveolar Region / Gas Exchange Region –Terminal broncholi –Alveoli
Very Slow	0		

A History of Particulate Detection in Real Time: The Tyndall Effect

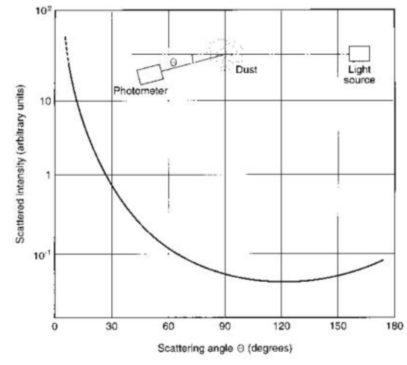


Figure 1 Intensity of scattered light as a function of angle

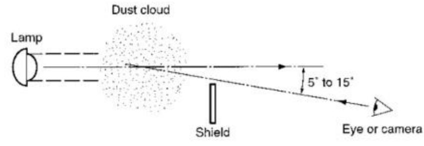


Figure 2 The use of the dust lamp to observe the presence of airborne particles

- ***The "Tyndall phenomena" has been known since the late 1800's.***
- Tyndall, J. (1864). "ON THE BLUE COLOR OF THE SKY, THE POLARIZATION OF SKY-LIGHT, AND POLARIZATION OF LIGHT BY CLOUDY MATTER GENERALLY." J.Franklin Inst.: 6.
- ***"Tyndall lighting" and use of a Tyndallmeter to determine smoke concentration have been documented since 1917 , and industrial hygiene applications since the 1920's.***
- ***Use has been replaced by direct photometric units.***

Use of Tyndall Lighting

MDHS

Methods for the Determination of Hazardous Substances
Health and Safety Laboratory

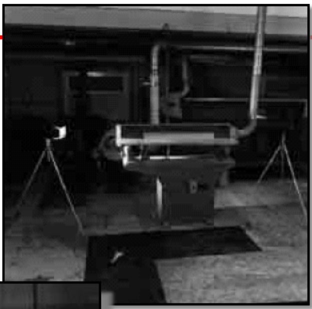
HSE
Health & Safety Executive

82

The dust lamp

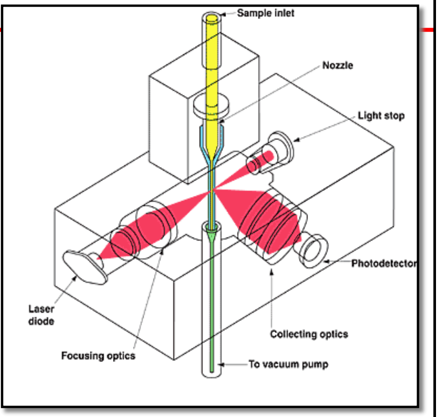
A simple tool for observing the presence of airborne particles

March 1997



- ***Works best with Dark Background.***
- ***Qualitative NOT Quantitative Particulate Concentration Information***

Photometric Technology

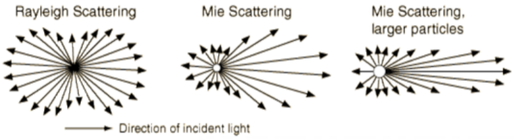


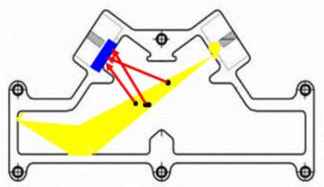
- *Photometric=Nephelometry (older term)*
- *90°, 60° or 45° light scattering laser photometry is used to determine mass concentration*
- *A continuous air sample is drawn into the sensing chamber*
- *A laser is used to illuminate the air stream*
- *Particles in the air stream scatter light in all directions*
- *A lens (Mie scattering) is placed at an angle to both the air stream & laser beam*
- *The lens collects and focuses this scattered light onto a photo-detector*
- *The photo-detector converts the light into a voltage*
- *This voltage is proportional to the amount of light scattered, which is proportional to the mass concentration of the aerosol in mg/m^3*
- *Photometers measure the total area of scattered light and cannot see particles <0.1 μm*
- *The amount of scattered light is dependent upon particle size, index of refraction, density, morphology and size distribution*
- *The photo-detectors today are capable of "seeing" 1.5 to 2 orders of magnitude in particle size range*

AIHA
Protecting Worker Health

Photometric Technology

- ***Technology calibrated to an ISO standard dust, readings provide real time measurement***
- ***Assumes aerosol being measured is same mass as calibration dust***
- ***Can employ a correction factor if measured aerosol is consistent***
- ***Known to be very precise and repeatable, but not always accurate***

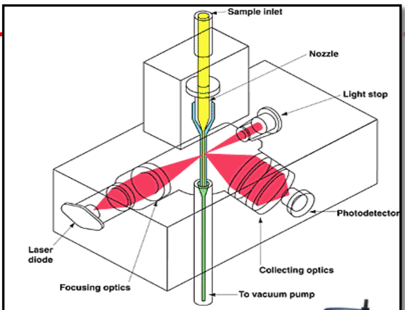




AIHA
Protecting Worker Health

Photometric Technology

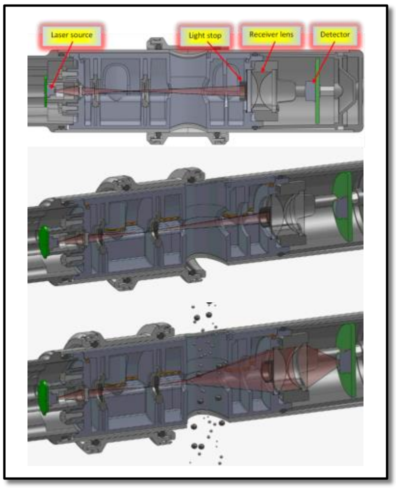
- *What types of aerosols will a photometer detect and measure?*
  - *Dusts, mists, fumes, smoke, fogs, condensates, etc…*
- *Applications*
  - *Personal exposure monitoring (WBZ)*
  - *Ambient work area monitoring*
  - *Point source monitoring*
  - *Engineering studies*
  - *Site perimeter monitoring*
  - *Emissions monitoring*
  - *Trend analysis / screening*
- *Real-time photometric readings allow you:*
  - *Get meaningful information during actual work activity*
  - *Look at engineering or process controls and validate their effectiveness*
  - *Look at human factor interactions with material handling and or processes and evaluate & validate their effectiveness*
  - *Assist in decision making for level of PPE for a task*



Photometric Technology

Principle of Operation:

- *Near Forward Light Scatter in a diffusive photometer*



Typical Applications:

- *Risk assessments for dusts and aerosols*
- *Monitoring dust levels within the workplace*
- *Industrial process monitoring*
- *Testing air filtration efficiency*
- *Environmental dust assessments*
- *Boundary monitoring for construction and demolition*

Particles enter the chamber, and diffract, refract and reflect the light beam…the dispersion product of the light beam is gathered and focused onto the sensor.

OPC Technology

- Single particles are drawn through a focused laser sheath and the resulting scattered light is collected by a mirror and focused on to a photo-detector
- Concentration is derived from the count rate and particle size is derived from the pulse heights
  - Does NOT provide Mass information
- OPCs require fairly high power laser and an expensive optical system for particle detection
- OPC size bins can be arranged to simultaneously measure PM1.0, PM2.5 and PM10 eliminating the need for inlet conditioners like impactors
- Typical particle size range: 0.3 to 20 μm
- Typical concentration range:
  - $2x10^6$ particles / ft^3 (70 particles / cm^3)
- OPCs come in hand held, table top and fixed monitor configurations
- OPCs are calibrated with PSL beads of known refractive index
  - The measured size of an unknown particle is it's light scattering equivalent size compared to PSL
- Unlike photometers, OPC performance criteria are very well defined
- For OPCs, sensitivity can be increased if the sampling flow rate is reduced
- OPC manufacturers will have different models to choose from depending upon the application in question
- Unlike photometers, OPC flow rate is very critical for reasons stated above

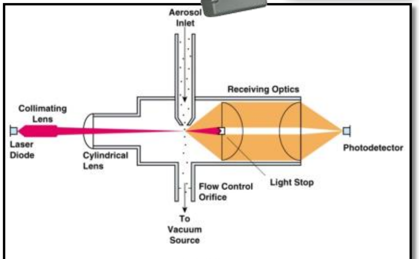


Figure 2
Flow Through an Optical Particle Counter

OPC Technology

- What types of aerosols will an OPC detect and measure?
  - Dusts, mists, fumes, smoke, fogs, condensates, etc…
- Applications
  - Clean room monitoring
  - Pharmaceutical clean room monitoring
  - Indoor Air Quality studies
  - Air pollution monitoring
- Real-time OPC readings allow you:
  - Obtain size distribution information
  - Get meaningful information about mechanical filtration performance
  - Look at the mechanical processes by which aerosols are generated
  - Look for contamination in manufacturing processes in clean room applications
  - Assist in decision making for level of mechanical ventilation and PPE for a task

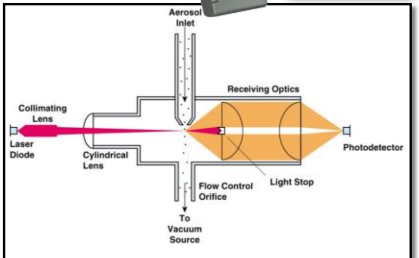


Figure 2
Flow Through an Optical Particle Counter

CPC Technology

- *A continuous air sample is drawn into the CPC*
- *Particles pass through a saturator chamber mixing with alcohol vapor*
- *This mixture passes through a condensation chamber where the alcohol condenses onto the particles causing them to grow to an optically detectable size*
- *These particles pass thru a focused laser beam producing a flash of light*
- *These flashes of light are sensed by a photo-detector*
- *Particle concentration is determined by counting the flashes of light*
- *If these particles were not grown to larger size particles they would not scatter enough light to be detected*
- *A CPC (a.k.a. - Condensation Nuclei Counter) is an instrument for detecting and counting ultrafine aerosols that are invisible to OPCs and photometers*
- *Ultrafine aerosols are defined as particles less than 0.1 μm*
- *CPC units of measure are made in particles / cm^3*
- *A CPC detects single particles, making it more sensitive than OPCs and photometers*
- *A CPC uses a method of condensation and growth of particles until they are large enough (at least 1.0 μm) to be detected by typical optical methods*

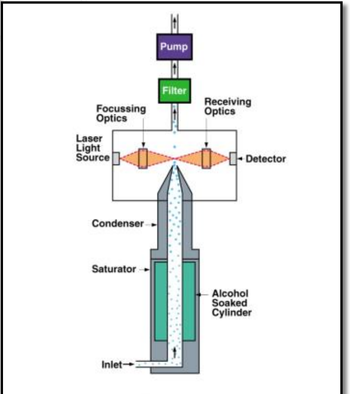


Figure 3
Flow Through a Condensation Particle Counter

CPC Technology

- *Applications*
  - *Respirator fit testing*
  - *Filter testing*
  - *Indoor Air Quality Studies*
  - *Environmental air pollution studies*
- *Real-time CPC readings allow you:*
  - *Evaluation of mechanical filtration systems*
    - *Filter testing*
    - *HVAC performance monitoring*
    - *Respirator Fit Testing*
  - *Point source monitoring*
  - *Look at engineering or process controls and validate their effectiveness*

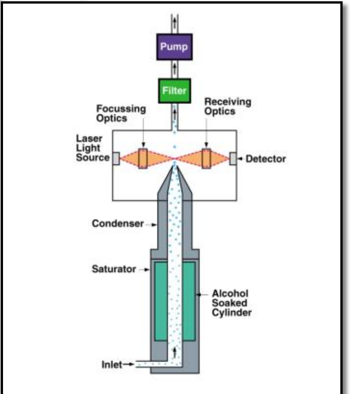


Figure 3
Flow Through a Condensation Particle Counter

Overall Comparison Of Technologies

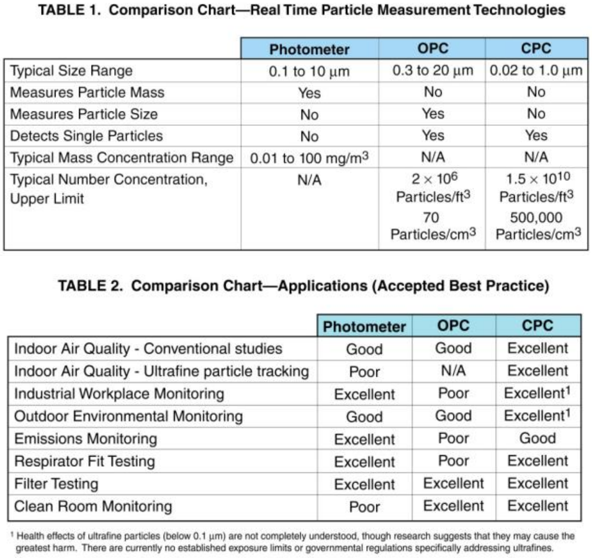


TABLE 1. Comparison Chart—Real Time Particle Measurement Technologies

	Photometer	OPC	CPC
Typical Size Range	0.1 to 10 µm	0.3 to 20 µm	0.02 to 1.0 µm
Measures Particle Mass	Yes	No	No
Measures Particle Size	No	Yes	No
Detects Single Particles	No	Yes	Yes
Typical Mass Concentration Range	0.01 to 100 mg/m^3	N/A	N/A
Typical Number Concentration, Upper Limit	N/A	2×10^6 Particles/ft^3 70 Particles/cm^3	1.5×10^{10} Particles/ft^3 500,000 Particles/cm^3

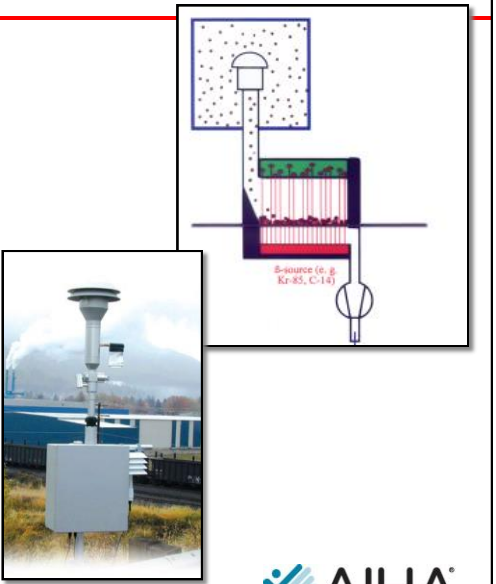
TABLE 2. Comparison Chart—Applications (Accepted Best Practice)

	Photometer	OPC	CPC
Indoor Air Quality - Conventional studies	Good	Good	Excellent
Indoor Air Quality - Ultrafine particle tracking	Poor	N/A	Excellent
Industrial Workplace Monitoring	Excellent	Poor	Excellent[1]
Outdoor Environmental Monitoring	Good	Good	Excellent[1]
Emissions Monitoring	Excellent	Poor	Good
Respirator Fit Testing	Excellent	Poor	Excellent
Filter Testing	Excellent	Excellent	Excellent
Clean Room Monitoring	Poor	Excellent	Excellent

[1] Health effects of ultrafine particles (below 0.1 µm) are not completely understood, though research suggests that they may cause the greatest harm. There are currently no established exposure limits or governmental regulations specifically addressing ultrafines.

Beta (β) Attenuation

- ***Uses a radioactive source to perform measurement***
- ***Aerosol is drawn through an inlet and deposited on a tape***
- ***As the mass of the collected aerosol increases, the beta energy decreases (attenuates)***
- ***Can provide long term unattended monitoring (usually best for fixed applications)***
- ***Measurement not immediate due to subtle differences in mass (often best with 30-60 minute averaging)***



TEOM - Tampered Element Oscillating Microbalance

- *TEOM - Tampered Element Oscillating Microbalance*
- *Deposits particulate on a metal tampered element (similar to a tuning fork) and frequency changes are used to measure true mass*
- *At present, only available for underground coal mines (MSHA), but technology offers additional utility*
- *Not suitable for extremely small mass (0.01 mg/m^3), but critical to provide real time exposure in efforts to minimize black lung disease*

Aethalometer

- *Measurement Principle: Real- time analysis by measuring the rate of change in absorption of transmitted light due to continuous collection of aerosol deposit on filter*
- *Lightweight*
- *Self contained and wearable*
- *Low power consumption*
- *High sensitivity*
- *Fast (real-time) response*
- *Adjustable sample flow rate*
- *Internal data logging and storage*
- *Simple data handling*
- *Easy to handle filter media*
- *Optional PM2.5 size selective inlet for measurement in the breathing zone*

Personal Exposure Monitoring

Cookstoves

Indoor Air Quality

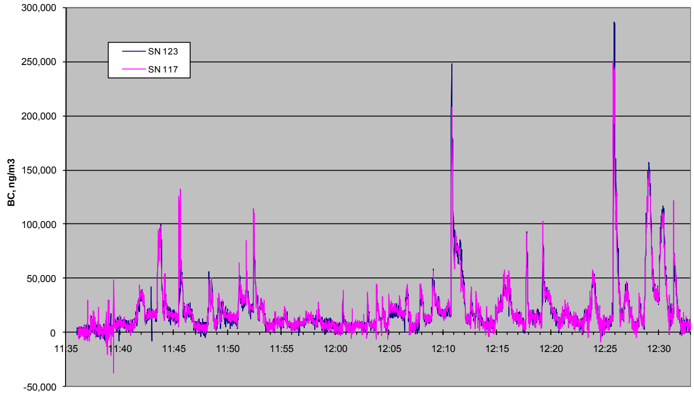
Vertical Profiling

Aethalometer

Mobile Measurements: Barcelona Street Study

microAeth® Model AE51: streets of Barcelona, Spain

Two instruments side-by-side on bicycle
Raw 1-second data exactly as recorded



Data courtesy of Project P.I., Audrey de Nazelle, Centre for Research in Environmental Epidemiology, Barcelona; D. Westerdahl, S. Fruin, Univ. Southern California.

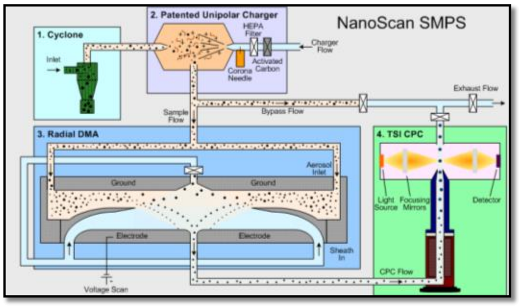
Black Carbon is a primary component of Diesel Particulate Matter (DPM). Exposure to Black Carbon occurs when people breathe in smoke and fumes from traffic related exhaust. Exposure is particularly hazardous to human health because the Black Carbon particles are very small in size (smaller than one micron or about 1:170 the size of a human hair) and have an active surface which attracts gases and other particle phase toxins. These tiny particles penetrate deep into the lungs, carrying a host of the other toxic materials which are present in smoke and vehicle exhaust.

www.aethlabs.com

Scanning Mobility Particle Size (SMPS) Technology

Features

- *High resolution and accuracy*
- *Wide size and concentration range*
    - *2.5 – 1000 nm*
    - *10 – 487 nm*
    - *10 – 420 nm*
- *Fast response time – scans in as fast as 30 sec.*
- *What type of aerosols can be detected with a SMPS?*
    - *Any aerosols within the detection range*



- ***A SMPS uses a Differential Mobility Analyzer (DMA) and a CPC to measure size and number concentration of nanopaticles***
- ***DMA separates particles according to charge and electrical mobility for size classification***
- ***CPC grows the particles to a detectible size for counting***

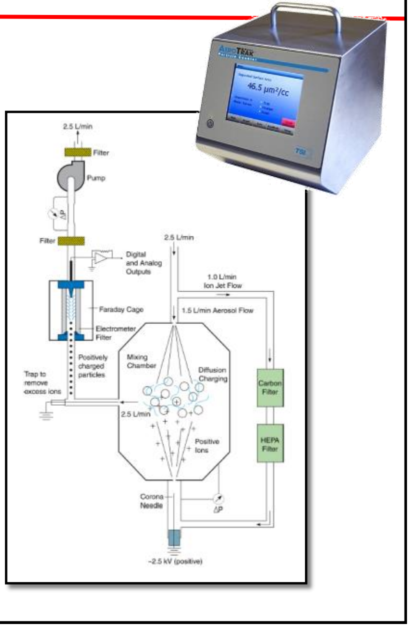
Measuring Nanoparticle Exposure

Example instrument a simple and fast solution for indicating the <u>lung deposited surface area equivalent dose</u> of particles in the size range of 10 to 1000 nanometers.

- *Based on diffusion charging of sampled particles*
- *Detection of the charged aerosol using an electrometer*
- *An aerosol sample is drawn into the instrument continuously at a rate of 2.5 L/min. The flow is split with 1 L/min passing through two filters (a carbon and a HEPA) and an ionizer and 1.5 L/min of aerosol sample flow.*
- *Flow streams are merged in a mixing chamber where particles in the aerosol flow mix with the ions carried by the filtered clean air, bringing the aerosol particles into a defined, charged state*
- *Charged aerosol then passes through an ion trap to remove excess ions and charged aerosol*
- *The aerosol then moves on to an electrometer for charge measurement*

Example Usage :

- *Monitoring workplace exposure to nanoparticles*
- *Industrial hygiene surveys*
- *Ambient work area monitoring*
- *Baseline screening and trending*
- *Engineering studies*
- *Material science and production process monitoring*
- *Inhalation toxicology research studies*
- *Epidemiology research studies*



Summary

- ***Photometers, OPCs and CPCs all have their uses***
- ***Matching the appropriate technology to your application will provide the data you need***
- ***Photometers measure mass to compare against air quality standards and guidelines***
- ***OPCs measure particle number concentrations and size ranges to validate mechanical filtration systems and to help identify sources***
- ***CPCs measure ultrafine particle concentrations than cannot be measured by photometers or OPCs for existing applications and some new applications that are now emerging as a new monitoring and exposure metric***

Some Websites

- *Important Instrumentation and Methods for the Detection of Chemicals in the Field: https://webportal.aiha.org/Purchase/ProductDetail.aspx?Product_code=01d77ed4-13ac-e211-a7f9-005056810034*
- *www.casellausa.com*
- *http://www.cdc.gov/niosh/docs/92-104/pdfs/92-104.pdf*
- *http://www.wolfsense.com/*
- *www.hazdust.com*
- *http://www.kanomax-usa.com/dust/dust%20monitor%20guide.pdf*
- *http://www.metone.com/particle-counters.php*
- *http://www.thermoscientific.com/ecomm/servlet/productscatalog_11152__89583_-1_4*
- *www.tsi.com*
- *www.aethlabs.com*
- *www.aethlabs.com*
- *http://www.flir.com/thermography/americas/us/view/?id=57067*

DISCLAIMER: This is not a comprehensive list , is provided for informational purposes only and does not constitute endorsement

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Thank You for Listening!

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  Global Product Manager – Health and Safety Instruments
- ***Alan Matta (Thermo Fischer Scientific)***
  Product Manager
- ***Rob Brauch (Casella CEL USA)***
  Business Unit Manager

The mention of any manufacturer or trade name is for informational purposes only and does not constitute endorsement or approval!

Using Multi-sensor and Photoionization Detector Equipped Instruments

Bob Henderson BS, MBA
GfG Instrumentation, Inc.

AIHA
Protecting Worker Health

Capabilities and Limitations of Multi-sensor Instruments

- First line screening tool for CS, HAZMAT and WMD response
- Many brands available (BW, MSA, ISC, GfG, RAE, etc.)
- Typically 1 – 6 sensors: O2 / LEL / PID / NDIR and / or 1 to 3 substance-specific toxic gas sensors
- Many new types of sensors available for use in these instruments

AIHA
Protecting Worker Health

Many technologies are available for use in portable real-time instruments

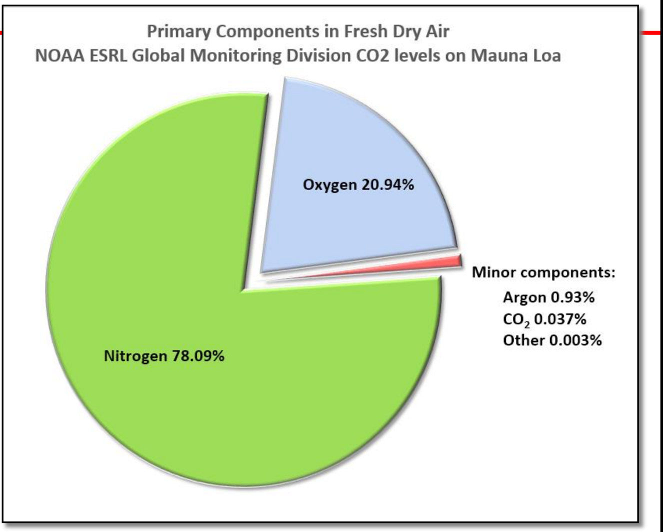
- *Oxygen deficiency and enrichment:*
  - *Fuel cell oxygen sensors*
  - *Solid polymer ("oxygen pump") sensors*
- *Combustible gases and vapors:*
  - *Catalytic % LEL ("Wheatstone bridge") sensors*
  - *Non-dispersive infrared (NDIR) % LEL and % volume sensors*
  - *Thermal conductivity (TC) sensors*
  - *Metal oxide semiconductor (MOS)*
- *Toxic gases and vapors:*
  - *Electrochemical sensors*
  - *Photoionization detectors (PID)*
  - *Non-dispersive infrared (NDIR)*
  - *Flame ionization (FID)*
  - *Ion Mobility Spectroscopy (IMS)*

- *The most commonly used technologies are highlighted in red*
- *Each type of detection has capabilities and limitations which must be understood for safe use*

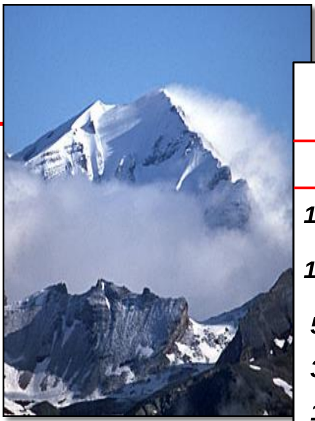
Measuring Oxygen (Deficiency and Enrichment)

Composition of fresh dry air

- *78.09 % Nitrogen*
- *20.94 % Oxygen*
- *0.93 % Argon*
- *0.037% CO2*
- *Other trace gases: less than 0.003%*


Primary Components in Fresh Dry Air
NOAA ESRL Global Monitoring Division CO2 levels on Mauna Loa

Partial Pressure O_2 vs. % Vol at Varying Altitudes

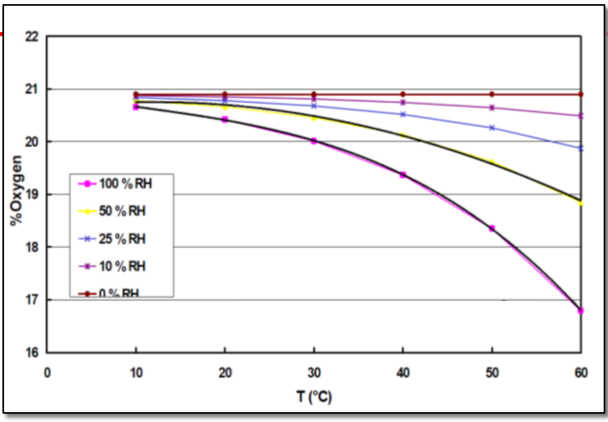


Height		Atm. Pressure	PO_2		Con.
feet	meters	mmHg	mmHg	kPa	% Vol
16,000	4,810	421.8	88.4	11.8	20.9
10,000	3,050	529.7	111.0	14.8	20.9
5,000	1,525	636.1	133.3	17.8	20.9
3,000	915	683.3	143.3	19.1	20.9
1,000	305	733.6	153.7	20.5	20.9
0	0	760.0	159.2	21.2	20.9

19.5% O_2 at sea level = 18 kPa

O_2 concentration in fresh air as function of temperature and humidity

- O_2 in dry air = 20.94%
- O_2 at 20°C and 25% RH ≈ 20.8%
- O_2 at 40°C and 90% RH ≈ 19.5%
- What should you do if the instrument is used in high temp, high RH conditions?
- Use cylinder of "Zero Air" to fresh air adjust the O_2 sensor



Fuel Cell Oxygen Sensors

- Sensor generates electrical current proportional to the O_2 concentration
- Sensor used up over time (one to three years)
- Oxygen reduced to hydroxyl ions at cathode:

$$O_2 + 2H_2O + 4e^- \longrightarrow 4OH^-$$

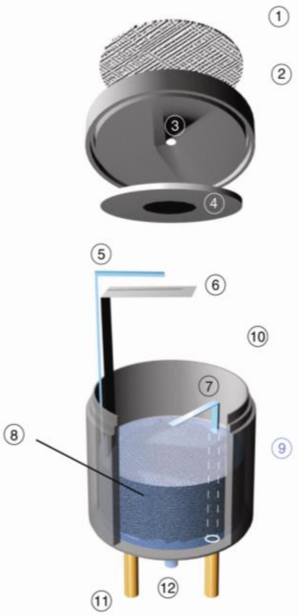
- Hydroxyl ions oxidize lead (anode):

$$2Pb + 4OH^- \longrightarrow 2PbO + 2H_2O + 4e^-$$

- Overall cell reaction:

$$2Pb + O_2 \longrightarrow 2PbO$$

Major components of a "fuel cell" type oxygen sensor



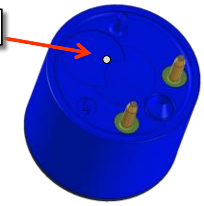
① External Moisture Barrier
② Diffusion Barrier
③ Diffusion Capillary
④ O_2 Sensing Electrode
⑤ Current Collector
⑥ Separator
⑦ Current Collector
⑧ Lead Anode (within electrolyte)
⑨ Electrolyte
⑩ Outer casing
⑪ Connector pins
⑫ Placement pin

Most O_2 sensors have a "capillary pore" used to allow sensor to self-stabilize at new pressure

- *O_2 sensors with capillary pore are true percent by volume measurement devices*
- *Are able to self stabilize to changes in pressure due to barometric pressure and altitude*
- *Stabilization at new pressure is not instantaneous, may take 30 seconds or longer*
- *Rear vent allows faster stabilization, with less stress to internal components*

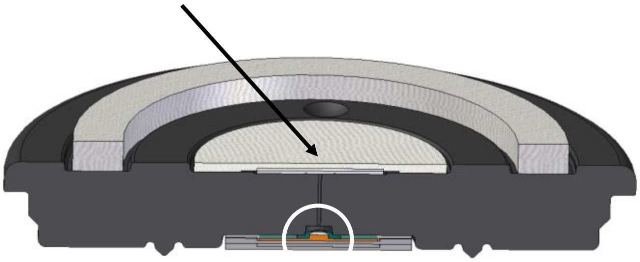
Capillary pore (located under external moisture barrier filter)

Rear vent



Capillary pore structure

- *Integrated moisture protection membrane*
- *Reduces humidity transient response and eliminates false alarms*



- *Internal anti-bulk flow mechanism*
- *Dampens transient response to step change in pressure*

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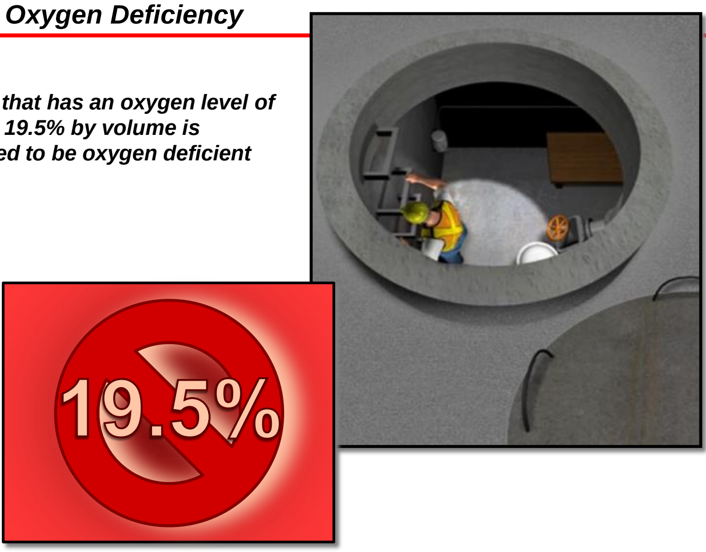
Oxygen Deficiency

- *Any area that has an oxygen level of less then 19.5% by volume is considered to be oxygen deficient*



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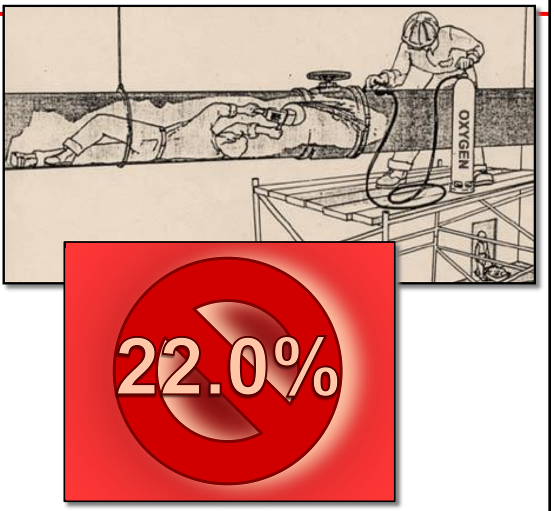
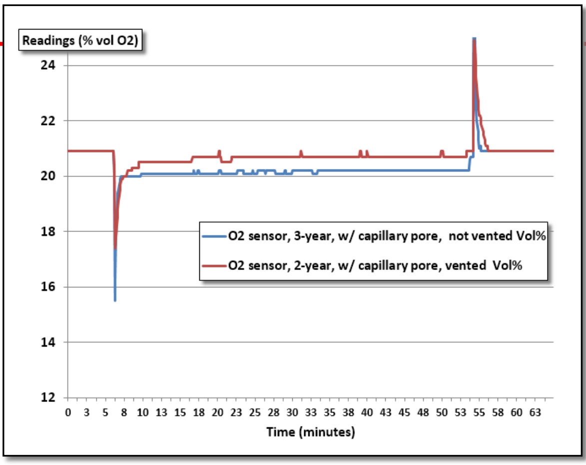
Oxygen Enrichment

- *Proportionally increases rate of many chemical reactions*
- *Can cause ordinary combustible materials to become flammable or explosive*
- *Definition varies between standards:*
  - *OSHA 1910.146, and 1926 Subpart AA reference 23.5 %*
  - *OSHA 1915-Subpart B, "Standard for shipyard employment" specifies 22 %*
  - *The latter value is consistent with non-mandatory recommendations from groups such as the National Fire Protection Association (NFPA)*
  - *The most conservative standards specify 22 % as the concentration above which the atmosphere is deemed to be hazardous due to oxygen enrichment*



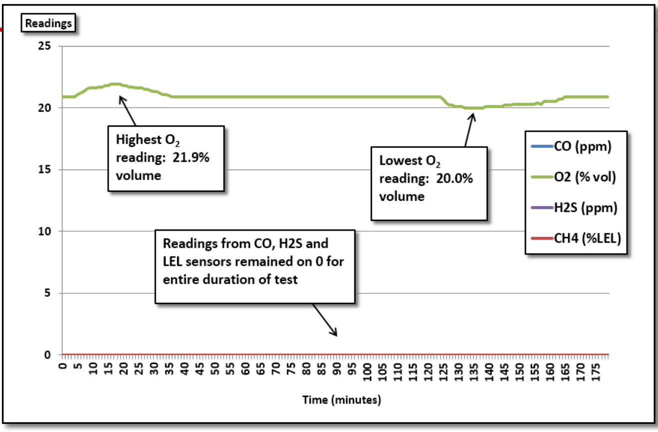
Effects of changes in pressure on O_2 sensor readings

- *Readings from instrument taken through negative pressure airlock at a nuclear generating station*
- *Both sensors equipped with capillary diffusion barrier. One sensor equipped with rear vent as well*
- *Readings of both sensors recovered to above 19.5% O_2 within 55 seconds*
- *Vented O_2 sensor took 3.3 minutes to stabilize at 20.5% O_2*
- *Vented O_2 sensor readings eventually reached 20.8% after about 10.5 minutes*
- *Non-vented sensor eventually stabilized at 20.2%, never recovered to 20.8% or higher*



Actual readings of oxygen sensor cycled from +20°C to –20°C then back to +20°C

- *While temperature dropping O_2 readings slightly high*
- *Once stabilized at –20°, readings return to 20.9%*
- *As chamber returned to room temperature O_2 readings slightly depressed*
- *Once stabilized at room temperature, O_2 readings return to 20.9%*
- *Most other common sensors (LEL, CO, H_2S) much less affected by temperature*



Highest O_2 reading: 21.9% volume

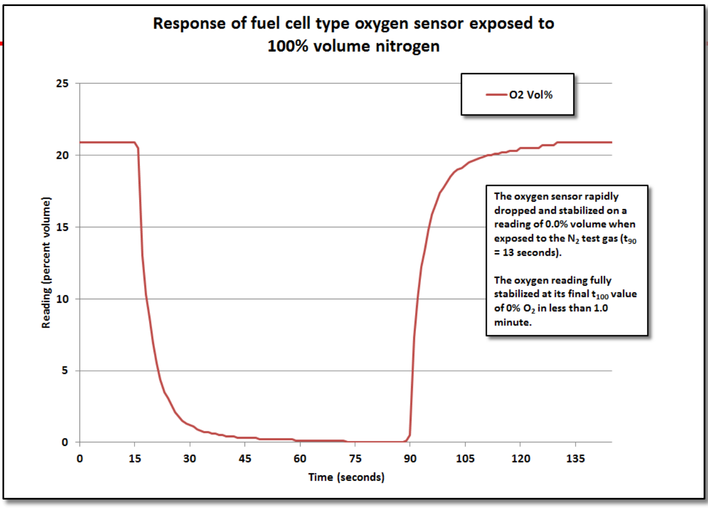
Lowest O_2 reading: 20.0% volume

Readings from CO, H2S and LEL sensors remained on 0 for entire duration of test

Protecting Worker Health

O_2 sensor response to 100% N_2

- *When exposed to 100% N_2 oxygen readings should drop to zero in a minute or less*
- *O_2 instruments used to measure near zero should be calibrated at zero as well as 20.9%*


Response of fuel cell type oxygen sensor exposed to 100% volume nitrogen

The oxygen sensor rapidly dropped and stabilized on a reading of 0.0% volume when exposed to the N_2 test gas (t_{90} = 13 seconds).

The oxygen reading fully stabilized at its final t_{100} value of 0% O_2 in less than 1.0 minute.

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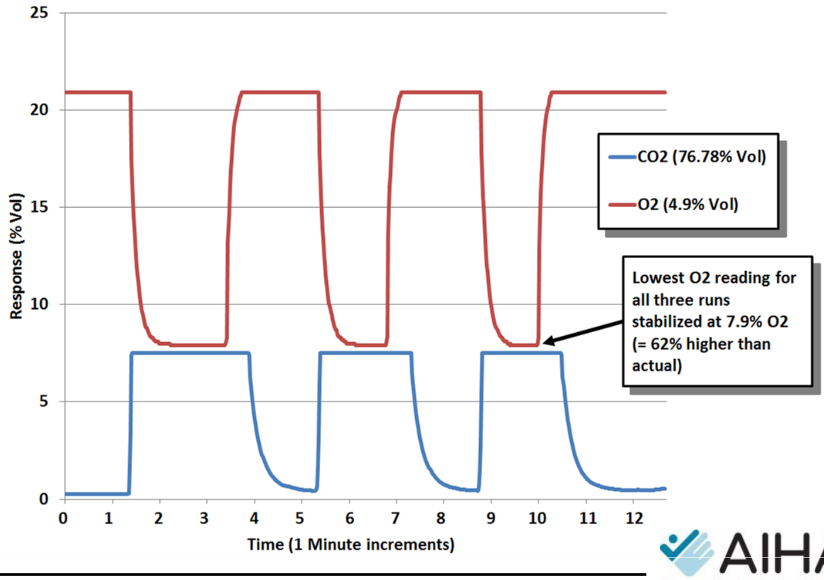
O_2 sensor response to 4.9% O_2, 18.3% N_2, 76.8% CO_2

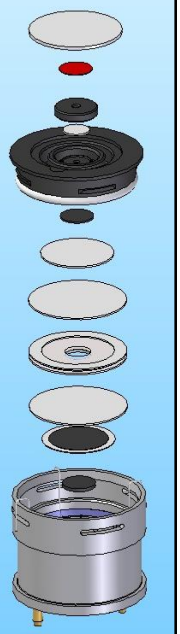


Lowest O2 reading for all three runs stabilized at 7.9% O2 (= 62% higher than actual)

Fuel cell type O_2 sensor failure mechanisms

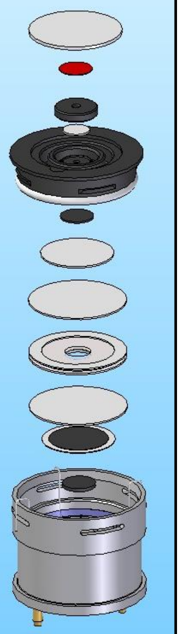
- *Lower current output:*
  - *All available surface of Pb anode converted to PbO_2*
  - *Electrolyte leakage*
  - *Loss of structural integrity of housing*
  - *Desiccation*
  - *Blockage of capillary pore*
  - *Electrolyte poisoned by exposure to contaminants*
- *Higher current output:*
  - *Short-term upward "ramping" readings due to cracks, tears or leaks allowing O_2 direct access to anode*
  - *Contraction of "bubbles" in electrolyte due to rapid temp change*
- *Readings do not change:*
  - *Loss (reduction) in platinum content in current collector and / or sensing electrode*
  - *Partial occlusion of capillary pore*
- *Test sensor before each day's use!*

Oxygen Pump
(Lead Free) O_2 Sensors



- *European Union (EU) “Reduction of Hazardous Substances” (ROHS) directive restricts use of certain substances in new electronic equipment*
    - *Pb, Cd, Hg, hexavalent chromium, polybrominated biphenyls (PBB's), and polybrominated diphenyl ethers (PBDE's)*
- *Lead containing “fuel cell” sensors specifically excluded (for the time being)*
- *“Oxygen pump” sensors are lead-free alternative to fuel cell sensors*

Oxygen Pump
Detection Principle



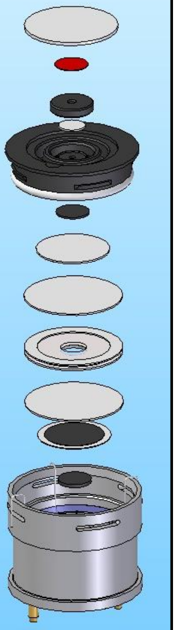
- *Oxygen passively diffuses into polymer (catalyst) substrate*
- *Power from instrument battery used to “pump” the oxygen back out*
- *Reactions: Oxidation / Reduction of target gas by catalyst*

Sensing: $O_2 + 4H^+ + 4e^- \longrightarrow 2\,H_2O$

Counter: $2\,H_2O \longrightarrow O_2 + 4H^+ + 4e^-$

- *Oxygen generated on counter electrode*
- *Amount electricity required to remove reaction product and return sensor to ground state (by generating O_2 at counter electrode) proportional to concentration of oxygen present*

Oxygen Pump Sensor
Advantages and disadvantages



- *Advantages:*
  - *Non-consuming detection technique (sensor does not lose sensitivity or consume itself over time)*
- *Disadvantages / concerns:*
  - *Detection reaction may be influenced by shifts in humidity*
  - *Sensor is net consumer of electricity (drain on power supply)*
  - *Important to ensure that reaction product (H_2O) is removed from sensor*

Case study:
Heavy vehicle exhaust in underground mines

- *Exhaust gas from diesel engine is primarily nitrogen (N_2), water vapor (H_2O), and carbon dioxide (CO_2)*
- *A relatively small part of the exhaust consists of toxic materials such as:*
  - *Particulate contaminants (soot)*
  - *Carbon monoxide (CO) from incomplete combustion*
  - *Hydrocarbons from unburnt fuel*
  - *VOCs from incomplete combustion*
  - *Nitrogen oxides (NOx)*
  - *Sulfur oxides (SOx) from fuel impurities*

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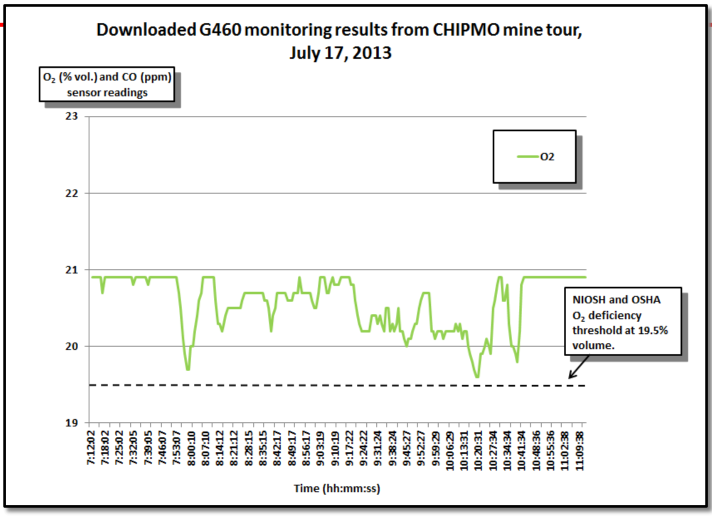
Diesel engine exhaust

- ***Diesel engines consume oxygen!***
- ***Produce a lot of carbon dioxide (CO_2)***
- ***When warm, produce very little CO***
- ***Produce carbon particulates (soot) – especially when engine cold or straining***
  - ***Unburned fuel and combustion by-products adsorbed on particles of soot, increasing danger of respirable particles carrying toxic VOCs deep into lungs***
- ***Produce oxides of nitrogen (NOx) – especially when the engine is running hot, or in reduced levels of O_2***
- ***Produce oxides of sulfur (SOx) when fuel contains high concentrations of sulfur***
  - ***"Ultra low sulfur" diesel fuel produces very little SOx***

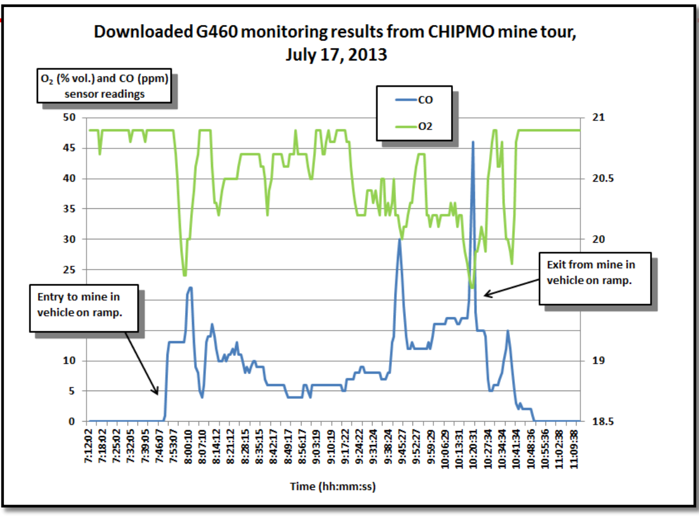
An O_2 reading lower than 20.9% indicates there is too much of some other gas present in the atmosphere



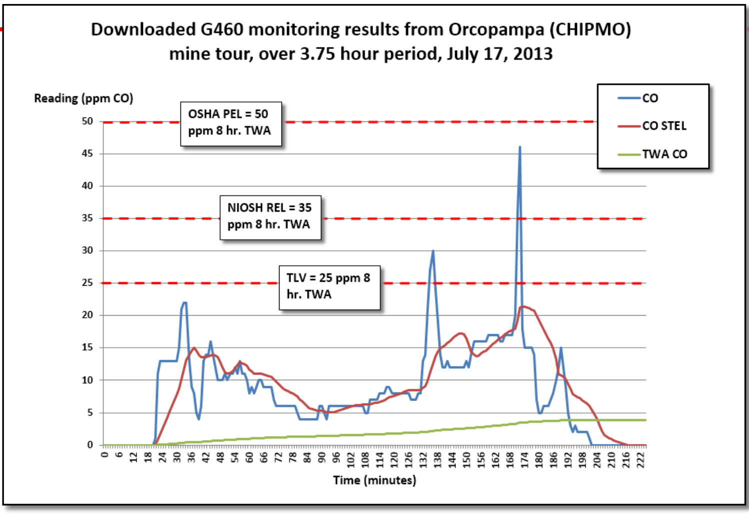
Downloaded G460 monitoring results from CHIPMO mine tour, July 17, 2013

NIOSH and OSHA O_2 deficiency threshold at 19.5% volume.

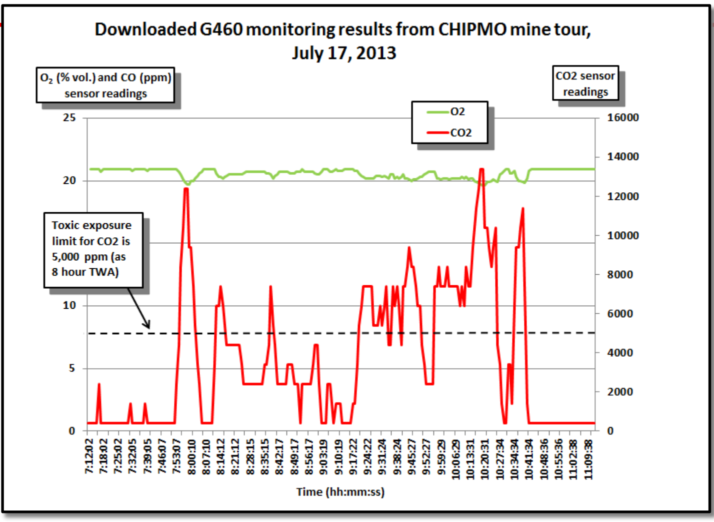
In this example as O_2 reading drops CO concentration rises


Downloaded G460 monitoring results from CHIPMO mine tour, July 17, 2013

CO concentration rises but does not come near TWA (per any standard) exposure limit during this monitoring session

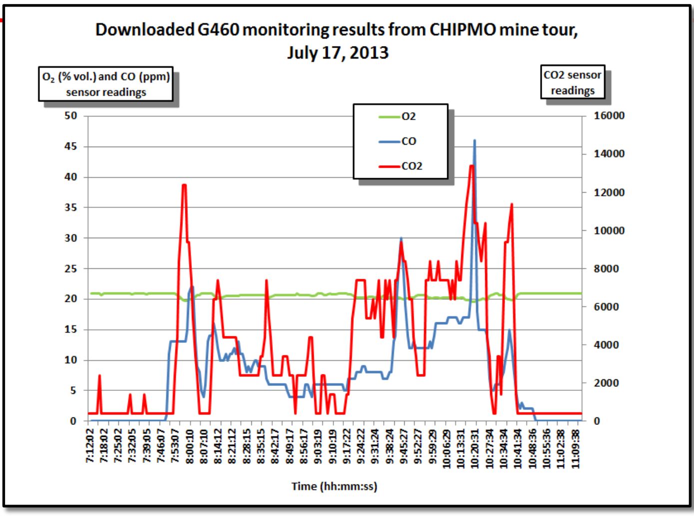

Downloaded G460 monitoring results from Orcopampa (CHIPMO) mine tour, over 3.75 hour period, July 17, 2013

CO_2 (not CO) actually the primary contaminant replacing the O_2 in the monitored atmosphere

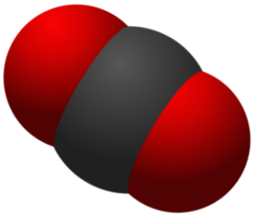

Downloaded G460 monitoring results from CHIPMO mine tour, July 17, 2013

Toxic exposure limit for CO2 is 5,000 ppm (as 8 hour TWA)

Important to directly measure <u>all</u> the contaminants that can materially affect the atmosphere

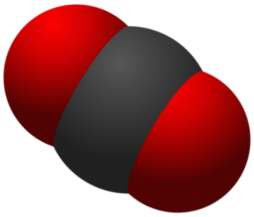

Downloaded G460 monitoring results from CHIPMO mine tour, July 17, 2013

CO_2 Properties



- *Present as a natural component in fresh air (approximately 350 ppm)*
    - *Colorless*
    - *Odorless*
    - *Tasteless*
    - *Heavier than air (density of 1.5 times that of fresh air)*
    - *When released into enclosed space it tends settle to bottom*
    - *Because of tendency to settle, as CO2 produced it can reach higher and higher concentrations*

CO_2 exposure symptoms



- *Besides displacing oxygen in fresh air, high concentrations may worsen symptoms related to oxygen deficiency, and interfere with successful resuscitation*
- *Exposure Symptoms include*
    - *Headaches*
    - *Dizziness*
    - *Shortness of breath*
    - *Nausea*
    - *Rapid or irregular pulse*
    - *Depression of central nervous system*

Even moderate concentrations of CO_2 can produce symptoms

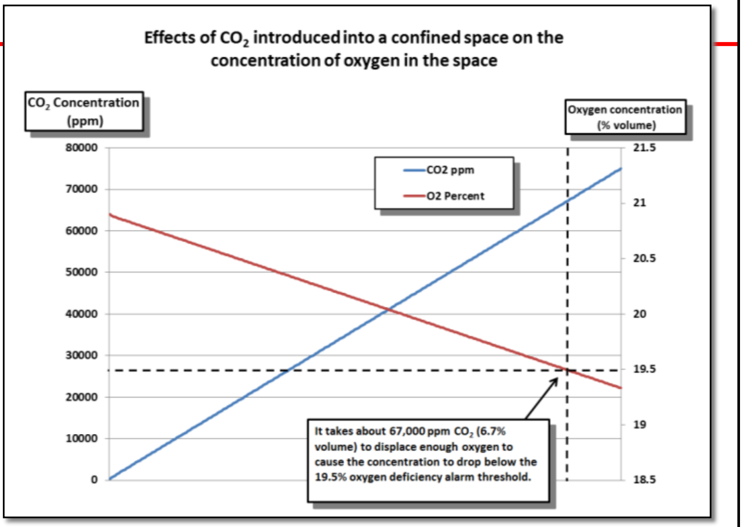
Concentration	Symptom
350 – 400 ppm	Normal background concentration in outdoor ambient air
350 – 1,000 ppm	Concentrations typical of occupied indoor spaces with good air exchange
1,000 – 2,000 ppm	Complaints of drowsiness and poor air
2,000 – 5,000 ppm	Headaches, sleepiness, and stagnant, stale, stuffy air. Poor concentration, loss of attention, increased heart rate and slight nausea may also be present
>5,000 ppm	Exposure may lead to serious oxygen deprivation resulting in permanent brain damage, coma and even death

Concentrations of 40,000 ppm CO_2 or higher should be regarded as IDLH

- *Exposure to very high concentrations (e.g. exposure to 6% volume CO_2 for several minutes or 30% volume CO_2 for 20-30 seconds), linked to permanent heart damage*
- *Concentrations greater than 10% capable of causing loss of consciousness within 15 minutes or less*

Presence of displacing gas on oxygen concentration

- *Be <u>very</u> cautious when using O_2 concentration to estimate concentration of some other displacing gas*
- *Every 5% of displacing gas introduced into a confined space reduces O_2 concentration by only about 1%*

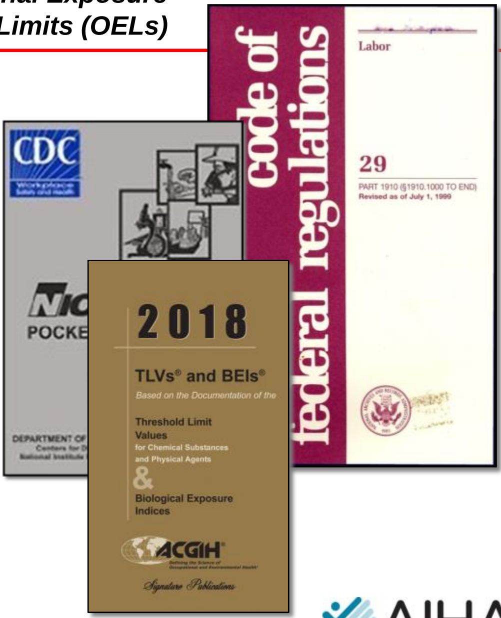


It takes about 67,000 ppm CO_2 (6.7% volume) to displace enough oxygen to cause the concentration to drop below the 19.5% oxygen deficiency alarm threshold.

Toxic Gases and Vapors

Occupational Exposure Limits (OELs)

- ***Depend on jurisdiction and activity***
- ***Sets limits for unprotected worker exposure to a listed toxic substance***
- ***Limits for gases and vapors given in "Parts-per-Million" (ppm) concentrations***
    - ***1 % = 10,000 ppm***



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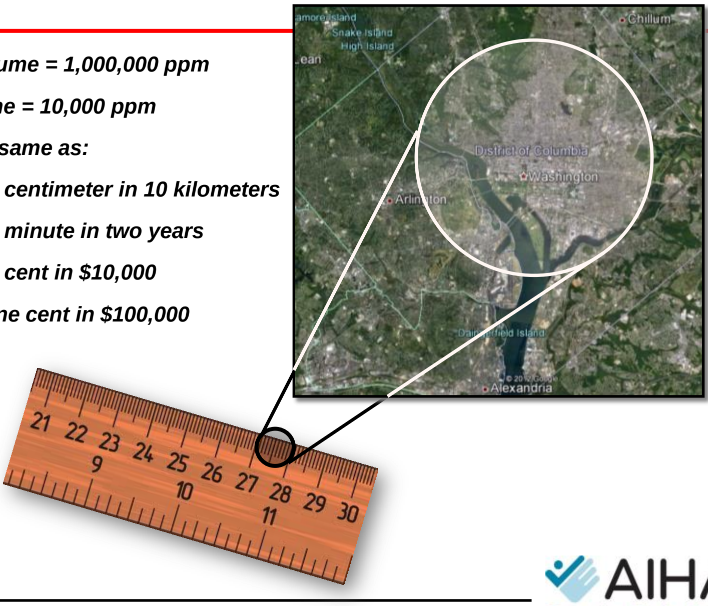
Meaning of parts-per-million (ppm)

- ***100% by volume = 1,000,000 ppm***
- ***1% by volume = 10,000 ppm***
- ***1.0 ppm the same as:***
    - ***One centimeter in 10 kilometers***
    - ***One minute in two years***
    - ***One cent in $10,000***
- ***0.1 ppm = One cent in $100,000***



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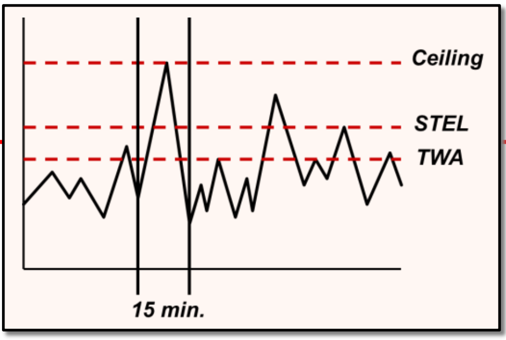
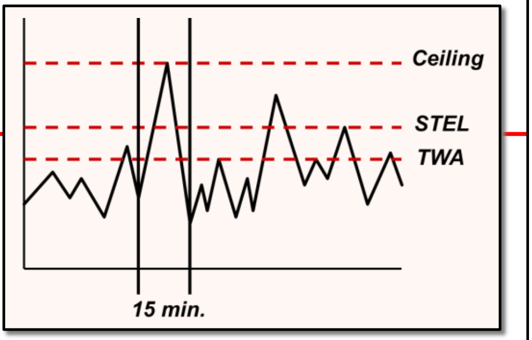
Toxic Exposure Limits



- *Toxic exposure limits are defined by means of:*
  - *8-hour TWA*
  - *15-minute STEL*
  - *Ceiling*
- *The exposure limit for a particular contaminant may include more than one part*

Toxic Exposure Limit Terms: TWA



- *TWA: The Time Weighted Average (TWA) is the exposure averaged over a full 8-hour shift*
- *When the monitoring session is less than eight hours, the TWA is projected for the full 8-hour shift*
- *When monitoring session more than 8 hours, the TWA limit is calculated on an "equivalent" 8-hour shift basis*

TWA is Projected Value

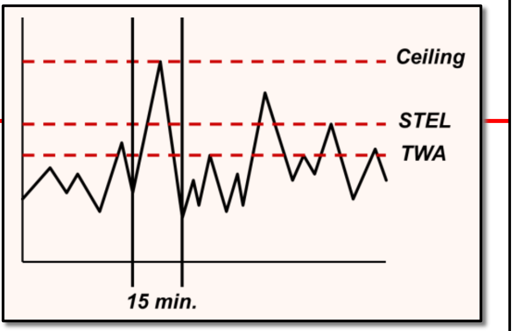
According to OSHA cumulative TWA exposures for an eight hour work shift are calculated as follows:

$$E = (C_a T_a + C_b T_b + \dots C_n T_n) / 8$$

Where:

- ***E is the equivalent exposure for the eight hour working shift***
- ***C is the concentration during any period of time T where the concentration remains constant***
- ***T is the duration in hours of the exposure at concentration C***

Toxic Exposure Limit Terms: STEL

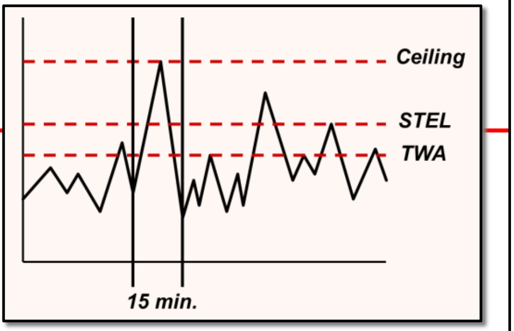


- ***Some gases and vapors (like CO and H_2S) have an allowable maximum Short Term Exposure Limit (STEL) which is higher than the 8-hour TWA***
- ***The STEL is the maximum average concentration to which an unprotected worker may be exposed during any 15-minute interval***

The average concentration may <u>never</u> exceed the STEL during any 15-minute interval

Any 15-minute interval where the average concentration is higher than the TWA (but less than the STEL) must be separated by at least 1-hour from the next, with a maximum of 4 times a shift

Ceiling Limit



- *Ceiling is the maximum concentration to which an unprotected worker may be exposed*
- *Ceiling concentration should never be exceeded even for an instant*
- *The "Low Peak" and "High Peak" alarms in most portable instruments are activated whenever the concentration exceeds the alarm setting for even a moment*

How are these calculations affected by the choice of data-logging interval?

- *They're not!*
  - *PEL calculations are continuously updated by the instrument*
  - *The datalogging interval simply specifies how often the instrument stores a "snap shot" of the current readings for the purposes of generating a printed report or database file of test results*

What are “Excursion limits?”

- ***ACGIH® “Excursion Limit” applies to TLVs® that do not have a STEL or Ceiling***
- ***Excursions may exceed 3X the TLV® TWA for no more than a total of 30 minutes during a workday, and under no circumstances should they exceed 5X the TLV® TWA***
- ***Alarm activation is based on constantly updated time-history calculations***

What should you do for extended work shifts?

- ***Most industrial hygienists use Brief and Scala model***
  - ***Corrects for increased exposure time and decreased recovery time***
  - ***Simple to use***
  - ***Very conservative***
- ***Adjusted TLV =***

$$\boxed{= \text{TLV} \times \left(\frac{8}{h}\right) \times \left(\frac{24 - h}{16}\right)}$$

Where h = # of hours worked per day

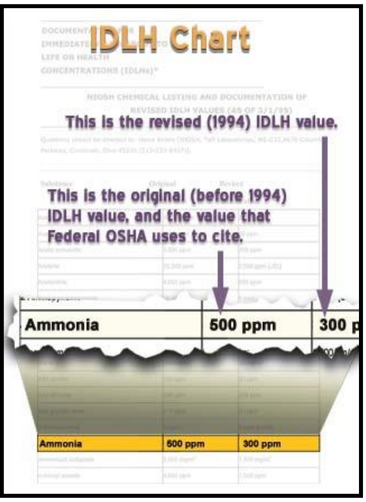
- ***Model used for chemicals where the TLV® is based on acute or chronic toxicity and <u>not</u> for chemicals that have a TLV® based on irritation (i.e. Ammonia)***
- ***For 12 hour shift according to this model the TWA TLV® limit should be reduced to one-half the 8-hour value***

Immediately Dangerous to Life and Health

- *IDLH is not part of PEL*
    - *IDLH is maximum concentration from which it is possible for an unprotected worker to escape without suffering injury or irreversible health effects during a maximum 30-minute exposure*
    - *Primarily used to define the level and type of respiratory protection required*
    - *Unprotected workers may NEVER be deliberately exposed to IDLH or ANY concentrations which exceed the PEL*

Exposure limits for ammonia

	8-Hr TWA	*STEL*	*Ceiling*
Federal USA OSHA PEL	*50*	*NA*	*NA*
State OSHA (1989) PEL (NIOSH REL)	*25 ppm*	*35 ppm*	*NA*
TLV	*25 ppm*	*35 ppm*	*NA*


IDLH Chart

This is the revised (1994) IDLH value.

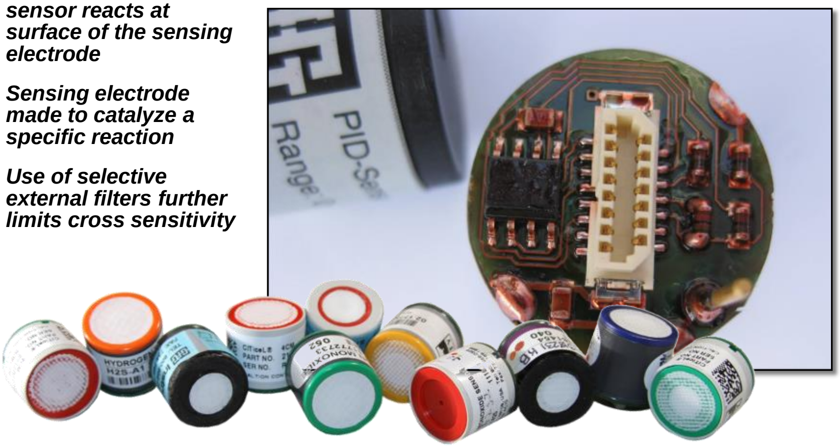
This is the original (before 1994) IDLH value, and the value that Federal OSHA uses to cite.

Ammonia 500 ppm 300 p

Ammonia 500 ppm 300 ppm

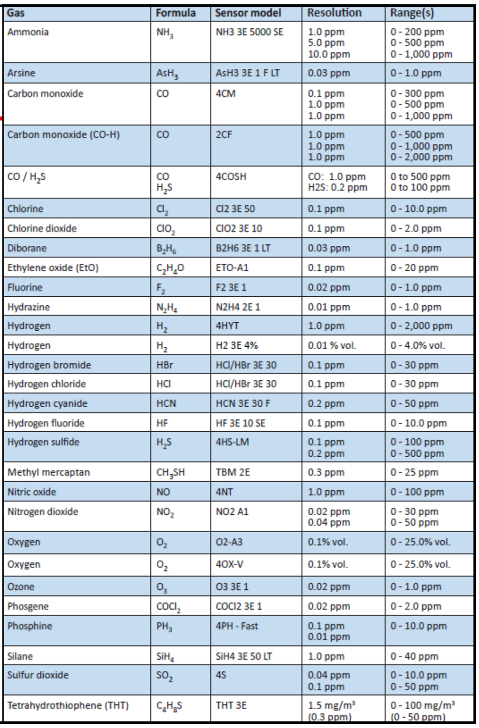
Substance-specific electrochemical (EC) sensors

- ***Gas diffusing into sensor reacts at surface of the sensing electrode***
- ***Sensing electrode made to catalyze a specific reaction***
- ***Use of selective external filters further limits cross sensitivity***



Available electrochemical sensors, standard ranges and resolution

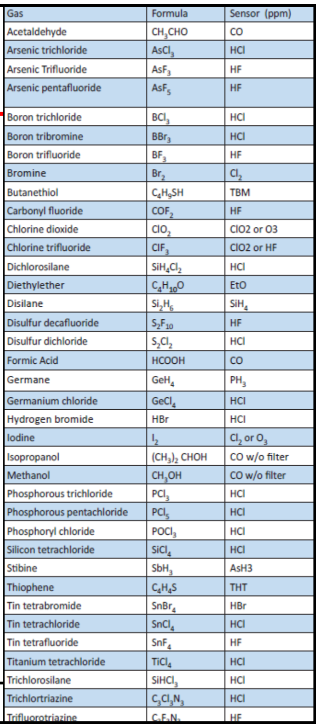
- ***More types of EC sensors available every year, both for individual toxic gases as well as sensors designed to detect a range of toxic or combustible gases***



Gas	Formula	Sensor model	Resolution	Range(s)
Ammonia	NH_3	NH3 3E 5000 SE	1.0 ppm 5.0 ppm 10.0 ppm	0 - 200 ppm 0 - 500 ppm 0 - 1,000 ppm
Arsine	AsH_3	AsH3 3E 1 F LT	0.03 ppm	0 - 1.0 ppm
Carbon monoxide	CO	4CM	0.1 ppm 1.0 ppm 1.0 ppm	0 - 300 ppm 0 - 500 ppm 0 - 1,000 ppm
Carbon monoxide (CO-H)	CO	2CF	1.0 ppm 1.0 ppm 1.0 ppm	0 - 500 ppm 0 - 1,000 ppm 0 - 2,000 ppm
CO / H_2S	CO H_2S	4COSH	CO: 1.0 ppm H2S: 0.2 ppm	0 to 500 ppm 0 to 100 ppm
Chlorine	Cl_2	Cl2 3E 50	0.1 ppm	0 - 10.0 ppm
Chlorine dioxide	ClO_2	ClO2 3E 10	0.1 ppm	0 - 2.0 ppm
Diborane	B_2H_6	B2H6 3E 1 LT	0.03 ppm	0 - 1.0 ppm
Ethylene oxide (EtO)	C_2H_4O	ETO-A1	0.1 ppm	0 - 20 ppm
Fluorine	F_2	F2 3E 1	0.02 ppm	0 - 1.0 ppm
Hydrazine	N_2H_4	N2H4 2E 1	0.01 ppm	0 - 1.0 ppm
Hydrogen	H_2	4HYT	1.0 ppm	0 - 2,000 ppm
Hydrogen	H_2	H2 3E 4%	0.01 % vol.	0 - 4.0% vol.
Hydrogen bromide	HBr	HCl/HBr 3E 30	0.1 ppm	0 - 30 ppm
Hydrogen chloride	HCl	HCl/HBr 3E 30	0.1 ppm	0 - 30 ppm
Hydrogen cyanide	HCN	HCN 3E 30 F	0.2 ppm	0 - 50 ppm
Hydrogen fluoride	HF	HF 3E 10 SE	0.1 ppm	0 - 10.0 ppm
Hydrogen sulfide	H_2S	4HS-LM	0.1 ppm 0.2 ppm	0 - 100 ppm 0 - 500 ppm
Methyl mercaptan	CH_3SH	TBM 2E	0.3 ppm	0 - 25 ppm
Nitric oxide	NO	4NT	1.0 ppm	0 - 100 ppm
Nitrogen dioxide	NO_2	NO2 A1	0.02 ppm 0.04 ppm	0 - 30 ppm 0 - 50 ppm
Oxygen	O_2	O2-A3	0.1% vol.	0 - 25.0% vol.
Oxygen	O_2	4OX-V	0.1% vol.	0 - 25.0% vol.
Ozone	O_3	O3 3E 1	0.02 ppm	0 - 1.0 ppm
Phosgene	$COCl_2$	COCl2 3E 1	0.02 ppm	0 - 2.0 ppm
Phosphine	PH_3	4PH - Fast	0.1 ppm 0.01 ppm	0 - 10.0 ppm
Silane	SiH_4	SiH4 3E 50 LT	1.0 ppm	0 - 40 ppm
Sulfur dioxide	SO_2	4S	0.04 ppm 0.1 ppm	0 - 10.0 ppm 0 - 50 ppm
Tetrahydrothiophene (THT)	C_4H_8S	THT 3E	1.5 mg/m³ (0.3 ppm)	0 - 100 mg/m³ (0 - 50 ppm)

Additional gases detectable by means of relative response

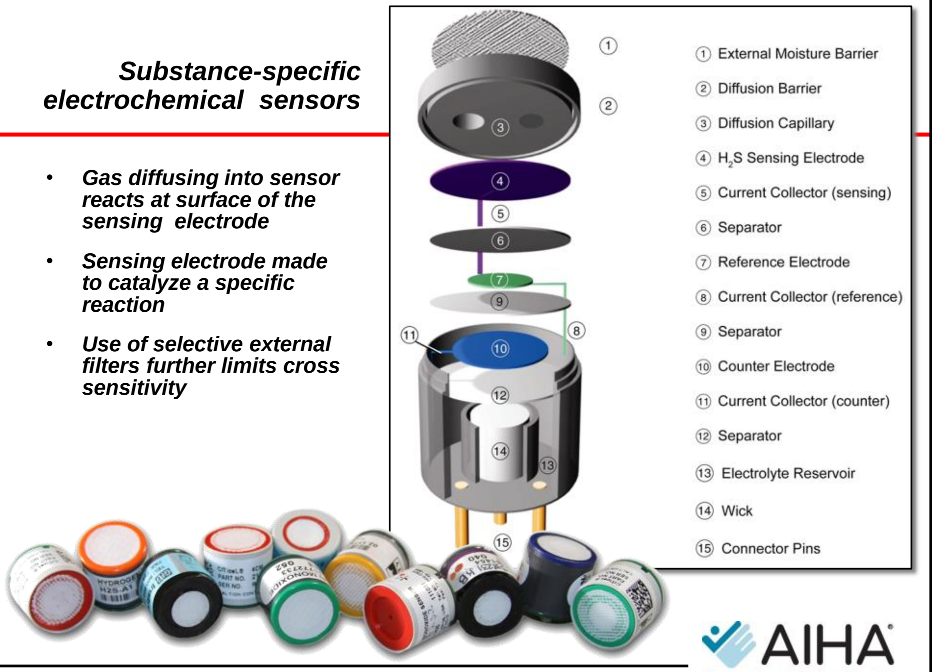
- *Electrochemical sensors are designed with specific usage requirements in mind*
- *The same manufacturer may offer multiple models of sensor for the detection of the same gas, but that are optimized for different sets of interferents and operating conditions*
- *Thus, cross sensitivities may vary widely between different models and brands of sensors!*
- *In addition, response values may differ at concentrations other than the ones listed in product documentation*
- *Discuss with manufacturer BEFORE attempting to use relative response values to measure additional gases*



Gas	Formula	Sensor (ppm)
Acetaldehyde	CH_3CHO	CO
Arsenic trichloride	$AsCl_3$	HCl
Arsenic Trifluoride	AsF_3	HF
Arsenic pentafluoride	AsF_5	HF
Boron trichloride	BCl_3	HCl
Boron tribromine	BBr_3	HCl
Boron trifluoride	BF_3	HF
Bromine	Br_2	Cl_2
Butanethiol	C_4H_9SH	TBM
Carbonyl fluoride	COF_2	HF
Chlorine dioxide	ClO_2	ClO2 or O3
Chlorine trifluoride	ClF_3	ClO2 or HF
Dichlorosilane	SiH_4Cl_2	HCl
Diethylether	$C_4H_{10}O$	EtO
Disilane	Si_2H_6	SiH_4
Disulfur decafluoride	S_2F_{10}	HF
Disulfur dichloride	S_2Cl_2	HCl
Formic Acid	HCOOH	CO
Germane	GeH_4	PH_3
Germanium chloride	$GeCl_4$	HCl
Hydrogen bromide	HBr	HCl
Iodine	I_2	Cl_2 or O_3
Isopropanol	$(CH_3)_2$ CHOH	CO w/o filter
Methanol	CH_3OH	CO w/o filter
Phosphorous trichloride	PCl_3	HCl
Phosphorous pentachloride	PCl_5	HCl
Phosphoryl chloride	$POCl_3$	HCl
Silicon tetrachloride	$SiCl_4$	HCl
Stibine	SbH_3	AsH3
Thiophene	C_4H_4S	THT
Tin tetrabromide	$SnBr_4$	HBr
Tin tetrachloride	$SnCl_4$	HCl
Tin tetrafluoride	SnF_4	HF
Titanium tetrachloride	$TiCl_4$	HCl
Trichlorosilane	$SiHCl_3$	HCl
Trichlortriazine	$C_3Cl_3N_3$	HCl
Trifluorotriazine	$C_3F_3N_3$	HF

Substance-specific electrochemical sensors

- *Gas diffusing into sensor reacts at surface of the sensing electrode*
- *Sensing electrode made to catalyze a specific reaction*
- *Use of selective external filters further limits cross sensitivity*



Oxidizing vs. reducing gases

- *Sensors for reducing gases:*
  - *Detection reaction generates current at working electrode; overall reaction consumes O_2*
    - H_2
    - H_2S
    - CO
    - SO_2
    - PH_3
- *Sensors for oxidizing gases:*
  - *Detection reaction consumes power at working electrode; overall reaction generates O_2*
    - Cl_2
    - NO_2
    - O_3
    - HCl
    - HF
    - ClO_2

Typical Electrochemical Detection Mechanism

H_2S Sensor:

Hydrogen sulfide is oxidized at the sensing electrode:

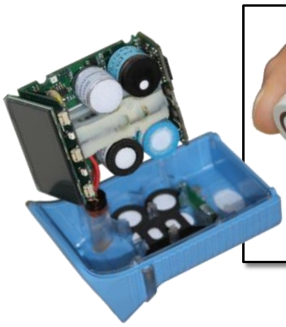
$$H_2S + 4H_2O \longrightarrow H_2SO_4 + 8H^+ + 8e^-$$

The counter electrode acts to balance out the reaction at the sensing electrode by reducing oxygen present in the air to water:

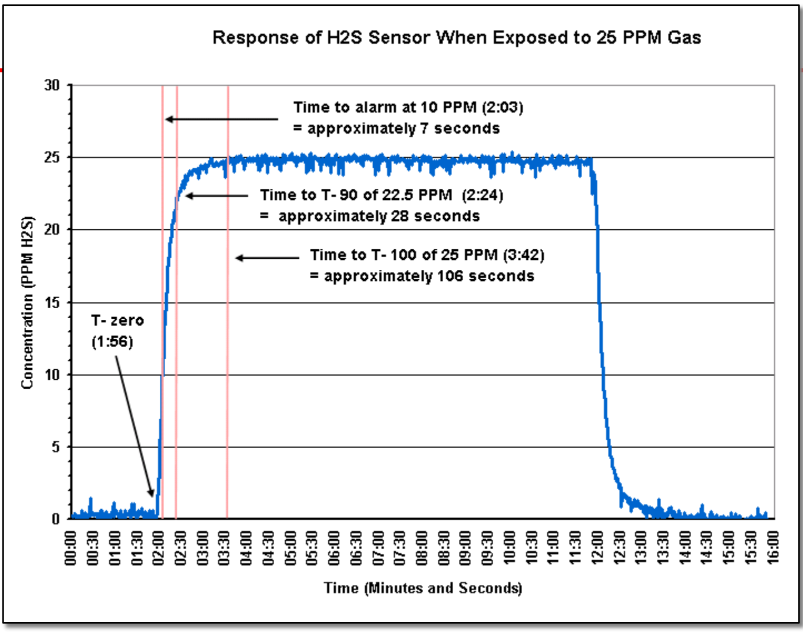
$$2O_2 + 8H^+ + 8e^- \longrightarrow 4H_2O$$

And the overall reaction is: $H_2S + 2O_2 \longrightarrow H_2SO_4$

City Technology 4HS Signal Output: 0.7 μA / ppm H_2S



Electrochemical Sensor Performance



Dual-channel COSH Sensor

H_2S Gas Reaction:

H_2S Sensing Electrode Reaction: $H_2S + 4H_2O \longrightarrow H_2SO_4 + 8H^+ + 8e^-$

H_2S Counter Electrode Reaction: $2O_2 + 8H^+ + 8e^- \longrightarrow 4H_2O$

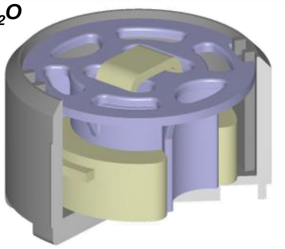
Overall reaction: $H_2S + 2O_2 \longrightarrow H_2SO_4$

CO Gas Reaction:

CO Sensing Electrode Reaction: $CO + H_2O \longrightarrow CO_2 + 2H^+ + 2e^-$

CO Counter Electrode Reaction: $\frac{1}{2} O_2 + 2H^+ + 2e^- \longrightarrow H_2O$

Overall reaction: $CO + \frac{1}{2}O_2 \longrightarrow CO_2$



H_2S signal output: 775 nA / ppm

CO signal output: 80 nA / ppm

Typical Electrochemical Detection Mechanism

Hydrogen Sensor:

Hydrogen is oxidized at the sensing electrode:

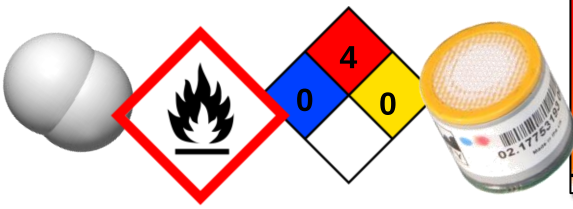
$$H_2 \longrightarrow 2H^+ + 2e^-$$

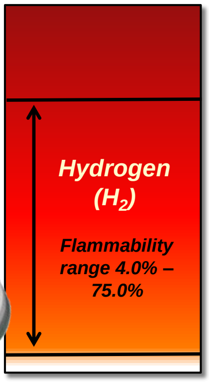
The counter electrode acts to balance out the reaction at the sensing electrode by reducing oxygen present in the air to water:

$$\tfrac{1}{2}O_2 + 2H^+ + 2e^- \longrightarrow H_2O$$

And the overall reaction is: $H_2 + 1/2O_2 \longrightarrow H_2O$

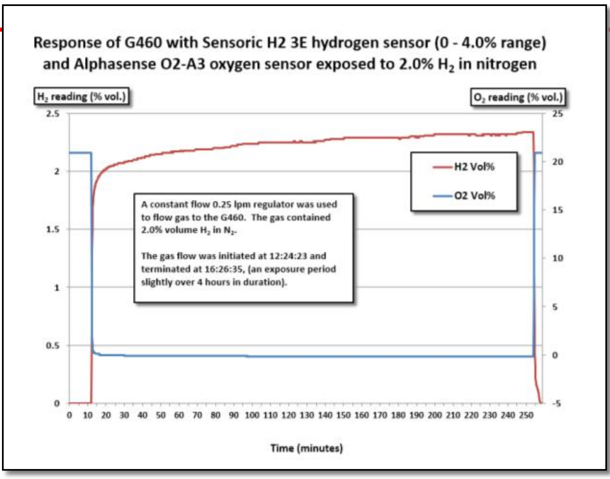
City Technology 4HYT Signal Output: 15 nA / ppm H_2





Most EC sensors can detect gas (for a while) in absence of oxygen

- *H_2 sensor electrolyte includes water, the source of oxygen when the ambient atmosphere is oxygen free*
- *As H^+ accumulates in the electrolyte, pH is altered, and sensor shows slightly increasing sensitivity*
- *Sensor recovers when returned to atmosphere that contains O_2*



Response of G460 with Sensoric H2 3E hydrogen sensor (0 - 4.0% range) and Alphasense O2-A3 oxygen sensor exposed to 2.0% H_2 in nitrogen

A constant flow 0.25 lpm regulator was used to flow gas to the G460. The gas contained 2.0% volume H_2 in N_2.

The gas flow was initiated at 12:24:23 and terminated at 16:26:35, (an exposure period slightly over 4 hours in duration).

Oxidizing gas sensor detection reaction

- ***Chlorine sensor detection reaction:***
  - ***Sensing electrode:***

    $Cl_2 + 2e^- \longrightarrow 2Cl^-$
  - ***Counter electrode:***

    $\frac{1}{2} O_2 + 2H^+ + 2e^- \longrightarrow H_2O$
  - ***Overall:***

    $Cl_2 + H_2O \longrightarrow 2Cl^- + \frac{1}{2}O_2 + 2H^+$

- ***Nitrogen dioxide detection reaction:***
  - ***Sensing electrode:***

    $NO_2 + 2H^+ + 2e^- \longrightarrow NO + H_2O$
  - ***Counter electrode:***

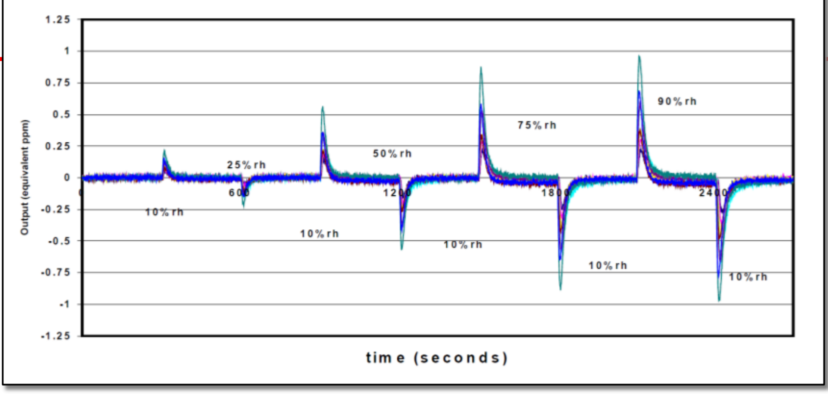
    $\frac{1}{2} O_2 + 2H^+ + 2e^- \longrightarrow H_2O$
  - ***Overall:***

    $NO_2 \longrightarrow NO + \frac{1}{2} O_2$

AIHA
Protecting Worker Health

Effects of humidity on EC sensors

Response of NO_2 sensor output as function of humidity

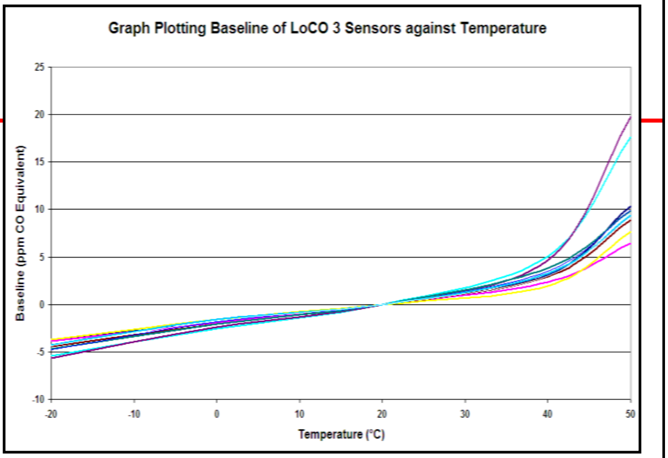


- ***Sudden changes in humidity can cause "transients" in readings***
- ***Sensor generally stabilizes rapidly***
- ***Avoid breathing into sensor or touching with sweaty hand***

AIHA
Protecting Worker Health

Electrochemical sensor performance

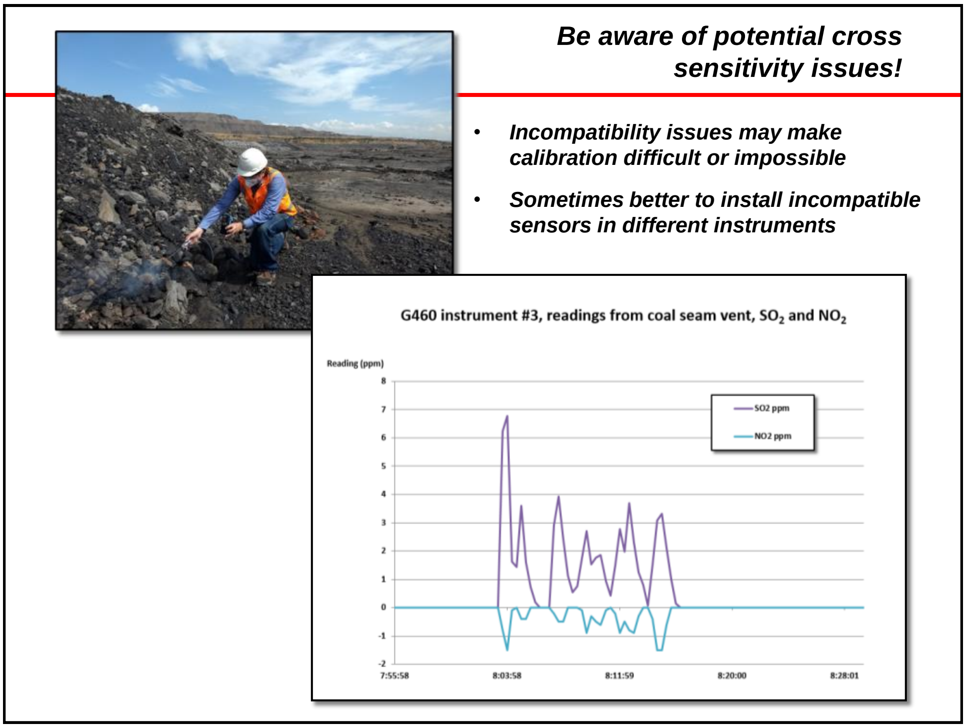
- *In general, uncorrected “zero” (baseline) output of sensor is lower in cold temperatures; higher in hot temperatures*
- *Effects mathematically predictable; can be corrected by means of temperature compensation*



Cross sensitivities of City Technology 4S – Rev. 2 sensor at 20°C

Relative responses of City Technology 4S – Rev. 2 sulfur dioxide (SO_2) sensor at 20°C

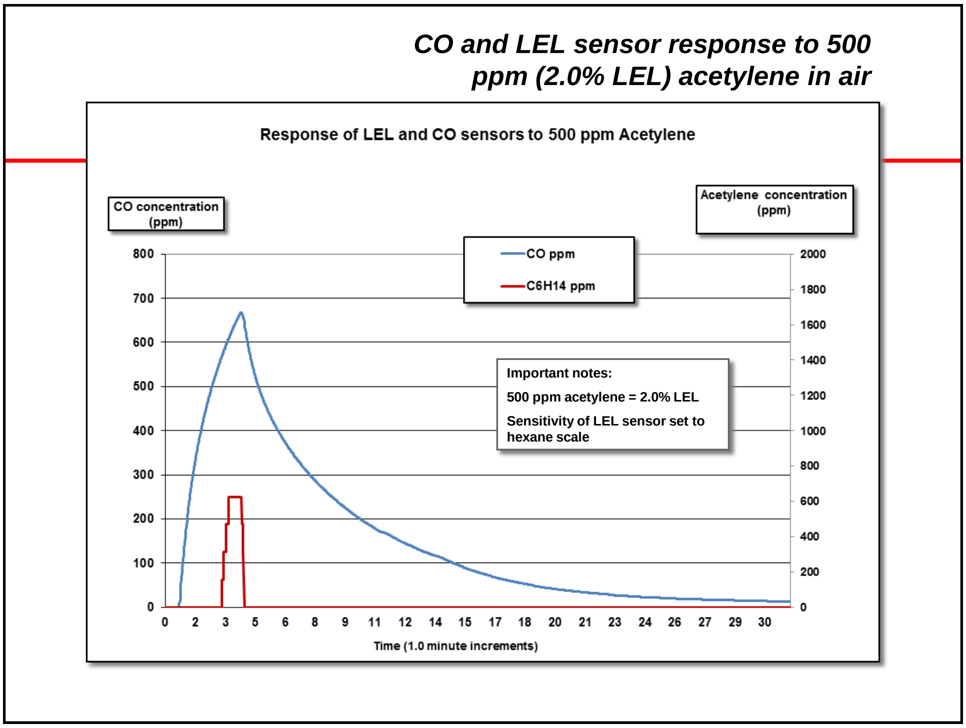
Gas	*Concentration used (ppm)*	*Reading (ppm SO2)*
Carbon monoxide (CO)	*300*	*< 1*
Nitric oxide (NO)	*50*	*0 to 5.0*
Nitrogen dioxide (NO_2)	*6*	*< −10*
Hydrogen sulfide (H_2S)	*25*	*< 0.1*
Chlorine (Cl_2)	*5*	*< −2*
Ammonia (NH_3)	*20*	*0*
Hydrogen (H_2)	*400*	*< 1*
Hydrogen cyanide (HCN)	*10*	*< 5*
Acetylene (C_2H_2)	*10*	*< 30*
Ethene (C_2H_4)	*50*	*< 45*



Be aware of potential cross sensitivity issues!

- *Incompatibility issues may make calibration difficult or impossible*
- *Sometimes better to install incompatible sensors in different instruments*

G460 instrument #3, readings from coal seam vent, SO_2 and NO_2



CO and LEL sensor response to 500 ppm (2.0% LEL) acetylene in air

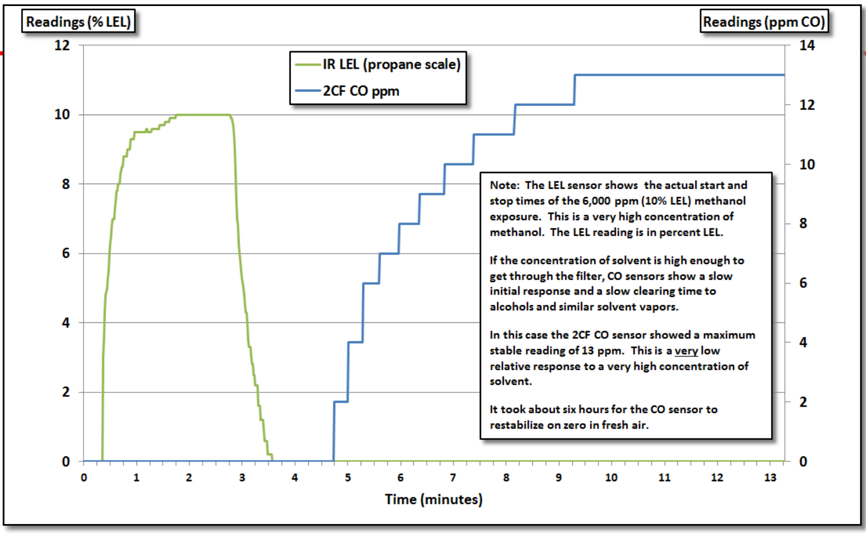
Response of LEL and CO sensors to 500 ppm Acetylene

Important notes:

500 ppm acetylene = 2.0% LEL

Sensitivity of LEL sensor set to hexane scale

Response of LEL and CO sensors to 10% LEL (6,000 ppm) methanol vapor



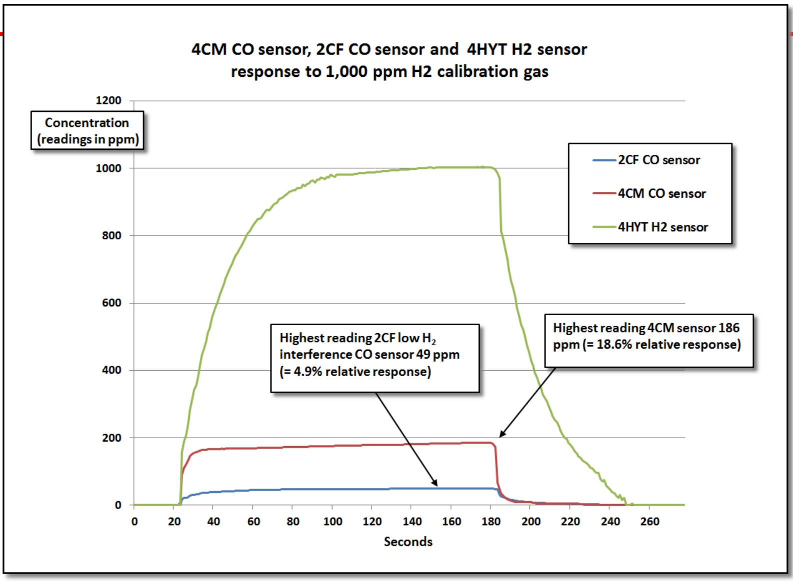
Note: The LEL sensor shows the actual start and stop times of the 6,000 ppm (10% LEL) methanol exposure. This is a very high concentration of methanol. The LEL reading is in percent LEL.

If the concentration of solvent is high enough to get through the filter, CO sensors show a slow initial response and a slow clearing time to alcohols and similar solvent vapors.

In this case the 2CF CO sensor showed a maximum stable reading of 13 ppm. This is a very low relative response to a very high concentration of solvent.

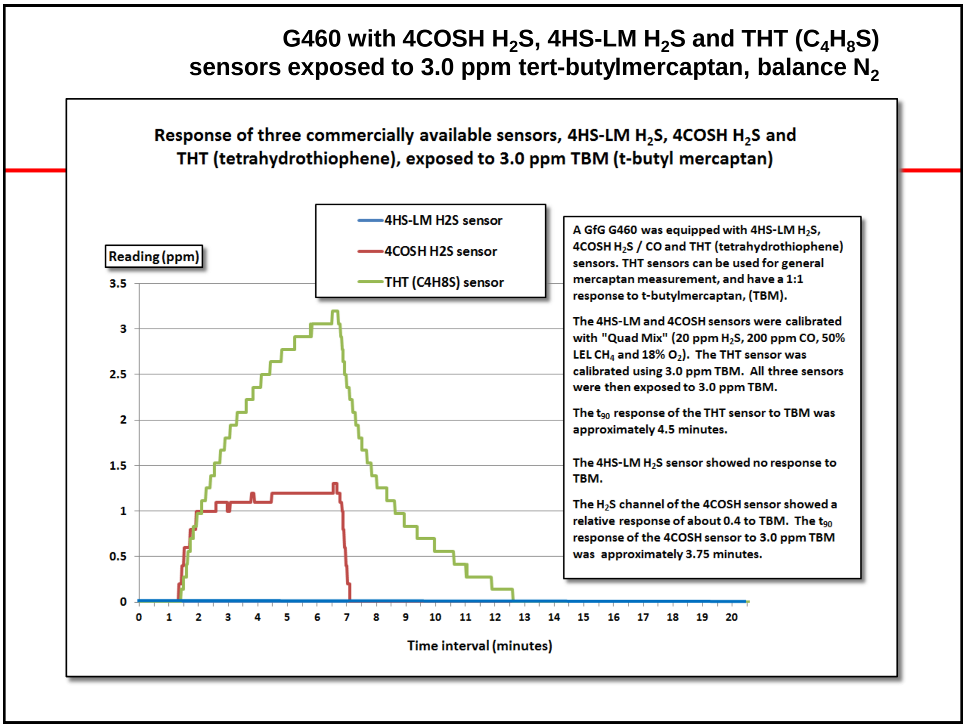
It took about six hours for the CO sensor to restabilize on zero in fresh air.

Effects of hydrogen on CO sensor readings


4CM CO sensor, 2CF CO sensor and 4HYT H2 sensor response to 1,000 ppm H2 calibration gas

Highest reading 2CF low H_2 interference CO sensor 49 ppm (= 4.9% relative response)

Highest reading 4CM sensor 186 ppm (= 18.6% relative response)



G460 with 4COSH H_2S, 4HS-LM H_2S and THT (C_4H_8S) sensors exposed to 3.0 ppm tert-butylmercaptan, balance N_2

Response of three commercially available sensors, 4HS-LM H_2S, 4COSH H_2S and THT (tetrahydrothiophene), exposed to 3.0 ppm TBM (t-butyl mercaptan)

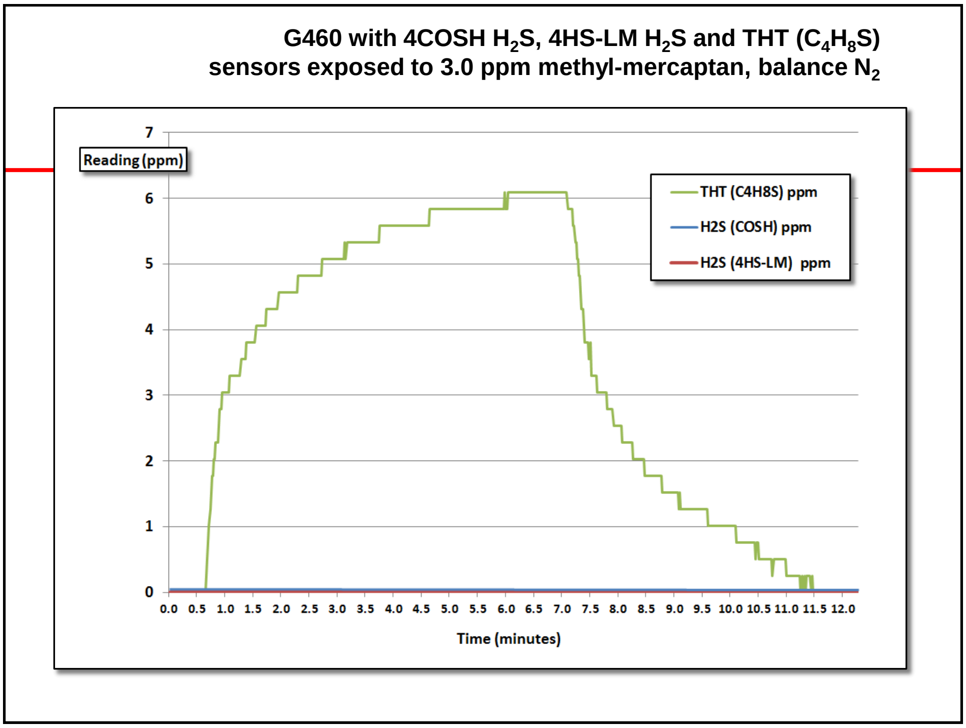
A GfG G460 was equipped with 4HS-LM H_2S, 4COSH H_2S / CO and THT (tetrahydrothiophene) sensors. THT sensors can be used for general mercaptan measurement, and have a 1:1 response to t-butylmercaptan, (TBM).

The 4HS-LM and 4COSH sensors were calibrated with "Quad Mix" (20 ppm H_2S, 200 ppm CO, 50% LEL CH_4 and 18% O_2). The THT sensor was calibrated using 3.0 ppm TBM. All three sensors were then exposed to 3.0 ppm TBM.

The t_{90} response of the THT sensor to TBM was approximately 4.5 minutes.

The 4HS-LM H_2S sensor showed no response to TBM.

The H_2S channel of the 4COSH sensor showed a relative response of about 0.4 to TBM. The t_{90} response of the 4COSH sensor to 3.0 ppm TBM was approximately 3.75 minutes.



G460 with 4COSH H_2S, 4HS-LM H_2S and THT (C_4H_8S) sensors exposed to 3.0 ppm methyl-mercaptan, balance N_2

Some EC sensors include a material or active ingredient that is consumed as gas is detected

- *The two most common "consuming" type EC sensors are ammonia (NH_3) and cyanide (HCN)*
- *Sensing electrode in HCN sensor impregnated with gold that is consumed during the detection reaction*
  - $2\ HCN + Au \rightarrow HAu(CN)_2 + H^+ + e^-$
- *NH_3 sensor filled with an organic gel electrolyte in which the reaction occurs*

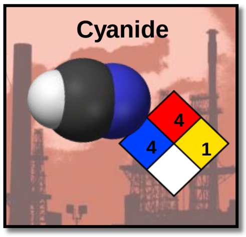
At the sensing electrode:

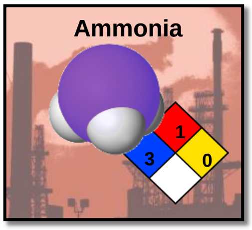
$2\ NH_3 \rightarrow N_2 + 6\ H^+ + 6\ e^-$

At the counter electrode:

$O_2 + 4H^+ + 4\ e^- \rightarrow 2H_2O$

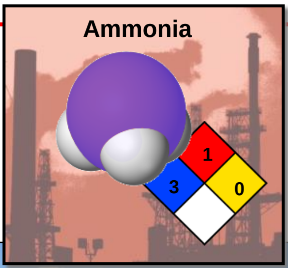
  - *Active ingredients in the electrolyte are incrementally used up as the sensor is exposed to ammonia*
  - *Once the "ppm hour" exposure life of the sensor is exceeded, it is no longer capable of detecting gas, and will need to be replaced*





Operating lifespan of consuming type sensors a function of exposure

- *Operating lifespan of "consuming" type sensors given in "ppm years"*
  - *A "2 ppm year" sensor lasts:*
    - *12 months in 2 ppm gas*
    - *6 months in 4 ppm*
    - *3 months in 8 ppm, and so on*
- *Exposure to high concentration gas during leak or emergency conditions can seriously shorten sensor life*
- *Do not use when significant concentration is normally present in ambient air!*



In poultry barn with ambient concentration of 20 ppm, NH3 sensor may only last a few weeks

Setting toxic sensor alarms

AP 1019:

Setting the alarms in electrochemical sensor equipped toxic gas instruments

Recently lowered exposure limits have made taking a more conservative approach to setting alarms mandatory for many instrument users.

Recently lowered exposure limit guidelines for H_2S, SO_2 and NO_2 have forced many instrument users to revisit where to set the alarms in their atmospheric monitors. For other gases, although the exposure limits have not changed, corporate policies as well as enforcement agency decisions have made taking a more conservative approach mandatory for many instrument users.

- **Which exposure limits apply?**

The most important obligation for any employer is to ensure that workers are not harmed by exposure to toxic materials or conditions that may be present in the workplace environment. Exposure limits like the OSHA PEL, NIOSH REL and ACGIH® TLV® provide exposure limits, which if exceeded, may lead to immediate or long term harm. These guidelines and standards set the limits above which conditions are deemed to be hazardous. They are not necessarily the concentrations that should be used when setting alarms. For instrument users there are two obligations. The first is ensuring that workers are not exposed to hazardous conditions. The second is ensuring that workers are able to leave the affected area before becoming affected by a hazardous condition. Workers should be out of the area before rather than after the concentration of toxic gas exceeds the hazardous condition threshold. Unfortunately, the PEL, REL and TLV® are not always in agreement. Which exposure limit is applicable and enforceable depends on where you are, what you are doing, and who is responsible for enforcing your workplace safety requirements. Even when the applicable (and enforceable) hazardous condition threshold concentrations are unambiguous, setting the alarms can still be a challenge.

United States Occupational Safety and Health Administration (OSHA) regulations use the term Permissible Exposure Limit (PEL) to define the maximum concentration of a listed contaminant to which an unprotected worker may be exposed as an 8 hour time-weighted average (TWA) during the course of his workplace duties. Exposure limits for gases and vapors are usually given in units of parts-per-million (ppm). Limits for mists, fume and particulate solids are expressed in units of mg/m3. In addition to the 8 hour TWA PEL, Ceiling (C), Short Term Exposure Limit (STEL), and peak exposure limits are also specified for some airborne hazards.

OSHA 8 hour TWA PEL and C values are given for some airborne contaminants in Subpart Z (Section 1910.1000), and in substance-specific standards (e.g., methylene chloride, 1910.1052 and benzene, 1910.1028).

OSHA PELs are listed in Subpart Z (Section 1910.1000) of the Code of Federal Regulations, and posted at www.OSHA.gov. Individual states may either follow the Federal regulations, or if they have their own "Approved Occupational Safety and Health Plan" may follow their own, state-specific permissible exposure limits. States may not publish or follow exposure limits that are more permissive than Federal OSHA limits. Twenty-five states (as well as Puerto Rico and the Virgin Islands) have their own approved plan. In many cases the exposure limit in these states for a particular toxic substance is more conservative than the Federal OSHA PEL.

The National Institute of Occupational Safety and Health (NIOSH) develops and periodically revises recommended exposure limits (RELs) for hazardous substances or conditions in the workplace. The NIOSH REL is an occupational exposure limit that has been recommended by NIOSH to OSHA for adoption as a permissible exposure limit. The REL represents a level of exposure that NIOSH believes would be protective of worker safety and health over a working lifetime if used in combination with engineering and work practice controls. The OSHA PELs listed in Subpart Z are the same values originally promulgated in 1971. Because NIOSH RELs are periodically reviewed and updated, they tend to be more conservative than the OSHA exposure limits. Many states with approved occupational safety and health plans use the NIOSH RELs as the basis for their state specific permissible exposure limits. This

GfG Instrumentation

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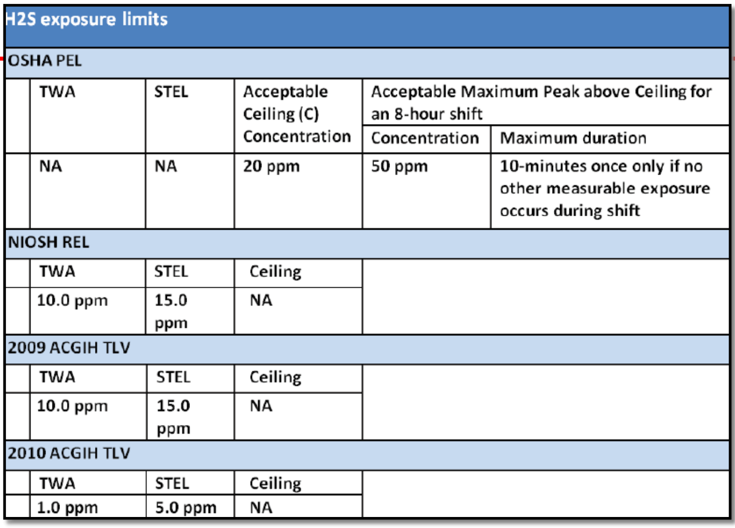
AP1019_2_7_13

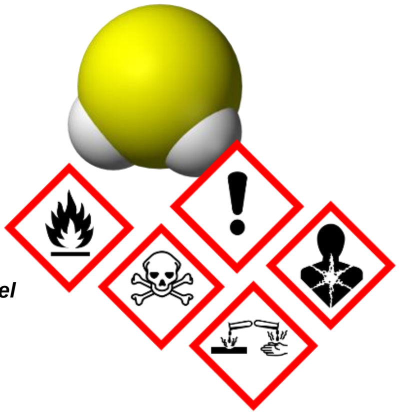
Exposure limits for H_2S



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		

Are H_2S sensors capable of measuring at the new TLV limits?

- ***The answer is "Yes" BUT with qualifications…..***
  - ***Some H_2S sensors easily capable of providing readings with 0.1 or 0.2 ppm resolution***
  - ***Instrument programming (firmware) must permit setting the alarms at the desired concentration***
  - ***May be necessary to update firmware or replace older instrument with a newer model***
  - ***Dual channel COSH sensors used to measure both CO and H_2S have a smaller measurement signal***
  - ***Depends on the manufacturer whether or not the instrument can be used with alarms set to the new TLV***



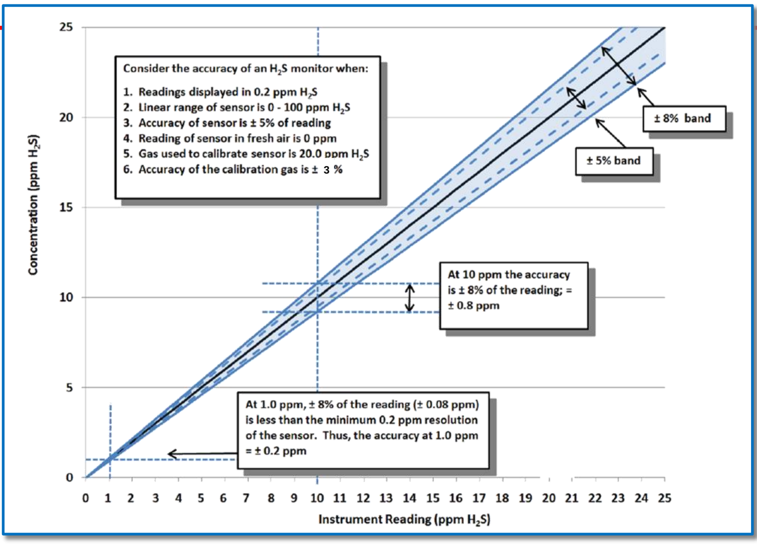
So how accurate are the readings?

- ***Instrument manufacturers frequently state accuracy of +/- 5% of readings***
- ***If the instrument is set to display readings in ± 0.2 ppm increments:***
  - ***From 0 – 4.0 ppm the accuracy is +/- 0.2 ppm; from 4.0 to 100 ppm the accuracy is +/- 5% of reading.***
- ***If the instrument is set to display readings in ± 0.1 ppm increments:***
  - ***From 0 – 2.0 ppm the accuracy is +/- 0.1 ppm, from 2.0 to 100 ppm the accuracy is +/- 5% of reading***

How does the accuracy of the cal gas affect the accuracy of the readings?

- ***Standard "Quad Mix" cal gas with 20 ppm H_2S is available with ± 3% accuracy, 6-months shelf life dating***
- ***Using ± 3% accuracy gas means that new accuracy statement for the combined instrument and cal gas system becomes (with standard setup) 0.2 ppm or ± 8% of reading, whichever is greater***
- ***So from 0 – 2.0 ppm the accuracy is ± 0.2 ppm***

Combined effects of sensor and calibration gas accuracy



Consider the accuracy of an H_2S monitor when:

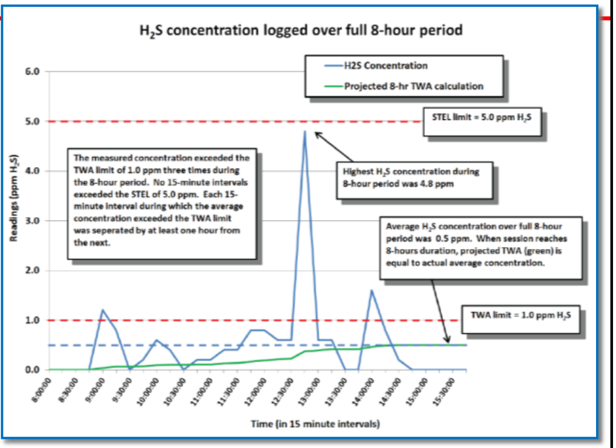
1. Readings displayed in 0.2 ppm H_2S
2. Linear range of sensor is 0 - 100 ppm H_2S
3. Accuracy of sensor is ± 5% of reading
4. Reading of sensor in fresh air is 0 ppm
5. Gas used to calibrate sensor is 20.0 ppm H_2S
6. Accuracy of the calibration gas is ± 3 %

At 10 ppm the accuracy is ± 8% of the reading; = ± 0.8 ppm

At 1.0 ppm, ± 8% of the reading (± 0.08 ppm) is less than the minimum 0.2 ppm resolution of the sensor. Thus, the accuracy at 1.0 ppm = ± 0.2 ppm

Where should practitioners who care about the TLV® set the alarms?

- *Concentrations above the TLV® TWA limit permitted as long as balanced by equal amount of time spent below the limit*
- *Exposure above the TWA up to the STEL should be less than 15-minutes, should not occur more than four times per day; and any 15-minute interval which exceeds the TWA limit should be separated by at least one hour from the next*
- *ACGIH® "Excursion Limit" applies to TLVs® that do not have a STEL*
- *Excursions may exceed 3X the TLV® TWA for no more than a total of 30 minutes during a workday, and under no circumstances should they exceed 5X the TLV® TWA*


H_2S concentration logged over full 8-hour period

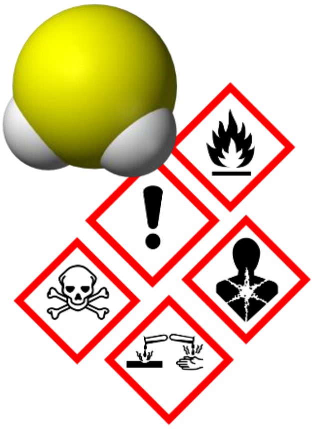
The measured concentration exceeded the TWA limit of 1.0 ppm three times during the 8-hour period. No 15-minute intervals exceeded the STEL of 5.0 ppm. Each 15-minute interval during which the average concentration exceeded the TWA limit was seperated by at least one hour from the next.

Highest H_2S concentration during 8-hour period was 4.8 ppm

Average H_2S concentration over full 8-hour period was 0.5 ppm. When session reaches 8-hours duration, projected TWA (green) is equal to actual average concentration.

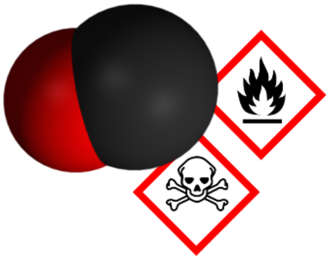
Where should you set the H_2S alarms?

- ***H_2S TLV® only includes STEL and TWA limits; does not include a Ceiling or "Peak" limit***
- ***Instruments typically have four user settable alarms for each toxic sensor (Low, High, STEL and TWA)***
- ***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***



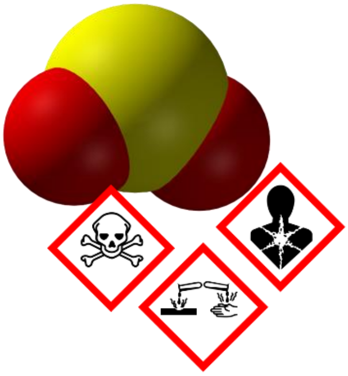
Where should you set the CO alarms?

- *The NIOSH REL for CO includes a TWA (35 ppm) and Ceiling (200 ppm); but does not include a STEL*
- *The TLV® for CO includes a TWA limit (25 ppm); but does not include a STEL or Ceiling limit*
- *Suggested alarms:*
  - *Typical factory default settings:*
    - *Low: 35.0 ppm*
    - *High: 100.0 ppm*
    - *STEL: 50.0 ppm*
    - *TWA: 35.0 ppm*
  - *TLV®:*
    - *Low: 25.0 ppm*
    - *High: 75.0 ppm*
    - *STEL: 25.0 ppm*
    - *TWA: 25.0 ppm*

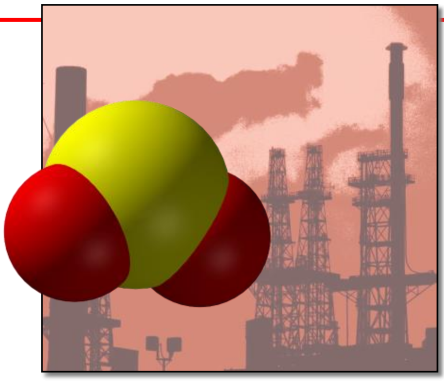


Exposure limits for sulfur dioxide SO_2

- *OSHA PEL:*
  - *TWA = 5.0 ppm*
- *NIOSH REL:*
  - *TWA = 2.0 ppm*
  - *STEL = 5.0 ppm*
- *Old TLV :*
  - *TWA = 2 ppm*
  - *STEL = 5 ppm*
- *New (2009) TLV:*
  - *STEL = 0.25 ppm*

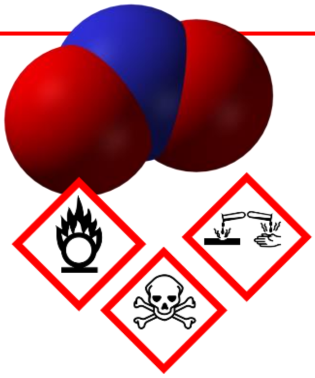


Suggested alarm settings for SO_2



- *Suggested alarms:*
  - *Typical factory settings (based on NIOSH):*
    - *Low: 2.0 ppm*
    - *High: 5.0 ppm*
    - *STEL: 5.0 ppm*
    - *TWA: 2.0 ppm*
  - *TLV®:*
    - *Low: 0.75 ppm*
    - *High: 1.25 ppm*
    - *STEL: 0.25 ppm*
    - *TWA: 0.25 ppm*

Exposure limits for NO_2



- *US OSHA PEL:*

  Ceiling = 5 ppm
- *US NIOSH REL:*

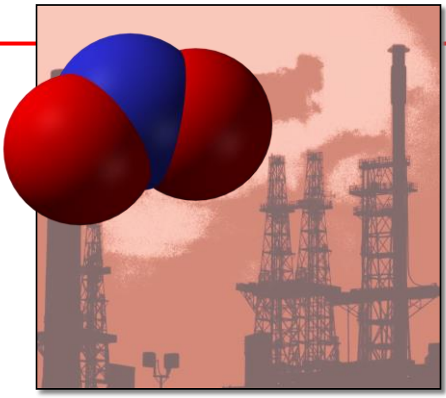
  15 min. STEL = 1 ppm
- *Old TLV:*

  8 hr. TWA = 3 ppm

  5 min. STEL = 5 ppm
- *New 2012 TLV*

  8 hr. TWA = 0.2 ppm

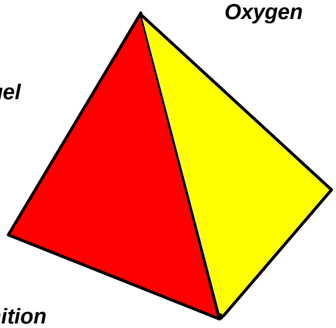
Suggested alarm settings for NO_2



- ***Suggested alarms:***
    - ***Typical factory settings (based on NIOSH):***
        - ***Low: 3.0 ppm***
        - ***High: 5.0 ppm***
        - ***STEL: 1.0 ppm***
        - ***TWA: 1.0 ppm***
    - ***TLV®:***
        - ***Low: 0.6 ppm***
        - ***High: 1.0 ppm***
        - ***STEL: 0.2 ppm***
        - ***TWA: 0.2 ppm***

Explosive or Flammable Atmospheres

Fire Tetrahedron



Oxygen

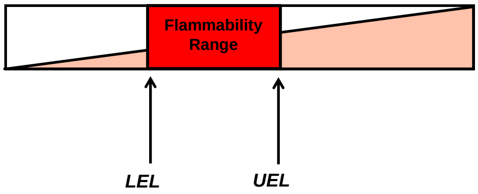
Fuel

Chain reaction

Source of ignition

Different gases have different flammability ranges

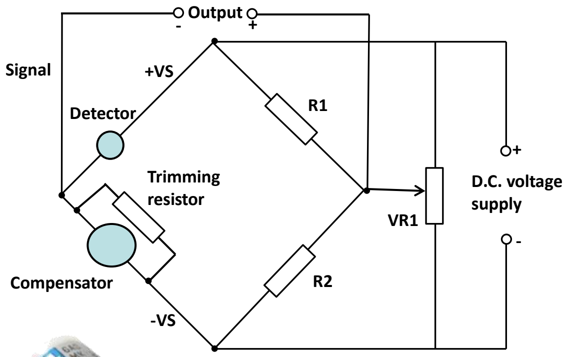
Gas Concentration

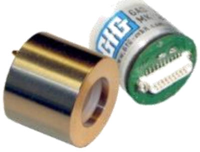


Fuel Gas	*LEL (%VOL)*	*UEL (%VOL)*
Acetylene	*2.2*	*85*
Ammonia	*15*	*28*
Benzene	*1.3*	*7.1*
Butane	*1.8*	*8.4*
Carbon Monoxide	*12*	*75*
Ethylene	*2.7*	*36*
Ethylene oxide	*3.0*	*100*
Ethyl Alcohol	*3.3*	*19*
Fuel Oil #1 (Diesel)	*0.7*	*5*
Hydrogen	*4*	*75*
Isobutylene	*1.8*	*9*
Isopropyl Alcohol	*2*	*12*
Gasoline	*1.4*	*7.6*
Kerosine	*0.7*	*5*
Methane	*5*	*15*
MEK	*1.8*	*10*
Hexane	*1.1*	*7.5*
Pentane	*1.5*	*7.8*
Propane	*2.1*	*10.1*
Toluene	*1.2*	*7.1*
p-Xylene	*1.1*	*7.0*

Catalytic “Hot Bead” Combustible Sensor

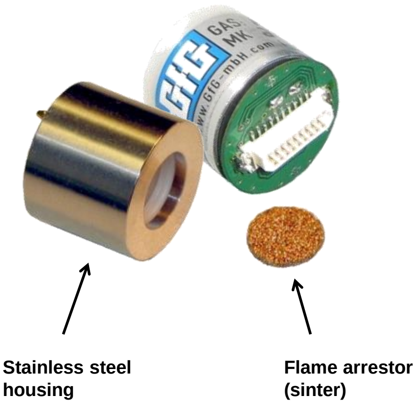
- *Detects combustible gas by catalytic oxidation*
- *When exposed to gas oxidation reaction causes the active (detector) bead to heat*
- *Requires oxygen to detect gas!*





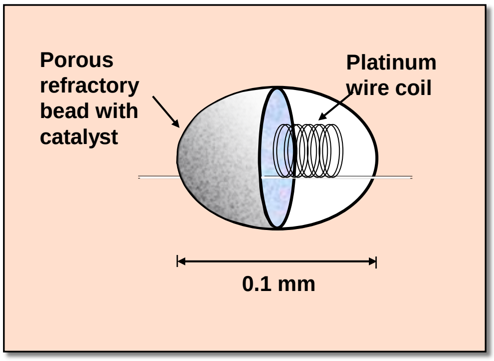
Traditional LEL sensors are “Flame proof” devices

- *Flame proof sensors depend on physical barriers such as stainless steel housings and flame arrestors to limit the amount of energy that can ever be released by the sensor*
- *The flame arrestor can slow, reduce, or even prevent larger molecules from entering the sensor*
- *The larger the molecule, the slower it diffuses through the flame arrestor into the sensor*
- *The response of the sensor is so slow to molecules larger than nonane (C9) in size that they are effectively undetectable*



Combustible Gas Sensor

- *The catalyst in the LEL sensor bead can be harmed if it is exposed to certain substances*
- *The larger the molecule, the slower it diffuses into the bead, the longer it takes to be oxidized, and the lower the relative response*



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Conditions created by oxidation of large molecules affects diffusion of molecules into the sensor

- *Oxidation occurs on step-by-step basis, and proceeds only when molecules are in physical contact with catalyst coated surfaces within the bead.*
- *The very hot reaction by-products create convective currents as they rapidly diffuse away from the catalyst surfaces in the bead.*
- *Water vapor produced by oxidation of larger molecules creates a significant net outward flux, impeding diffusion of new molecules into the bead.*
- *Oxidation of methane:* $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$

  To oxidize one molecule CH_4 *three molecules enter bead, and three molecules produced as by-products.*

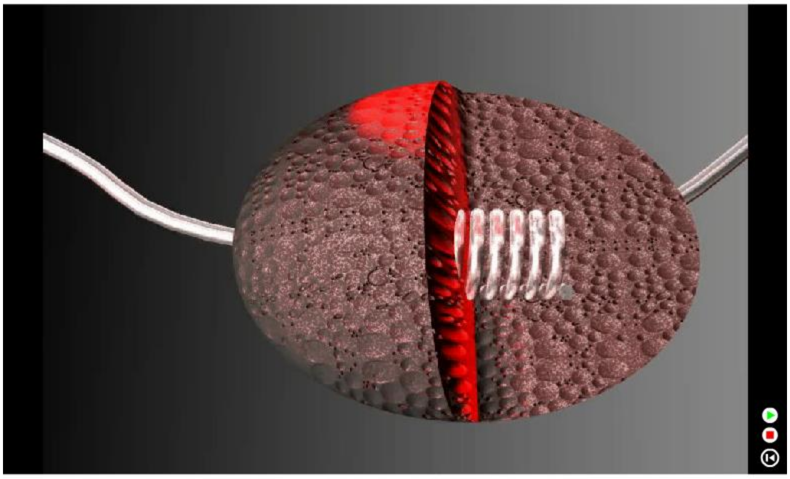
- *Oxidation of pentane:* $C_5H_{12} + 8O_2 \rightarrow 5CO_2 + 6H_2O$

  To oxidize one molecule of pentane, nine molecules enter bead, and 11 molecules produced as by-products.

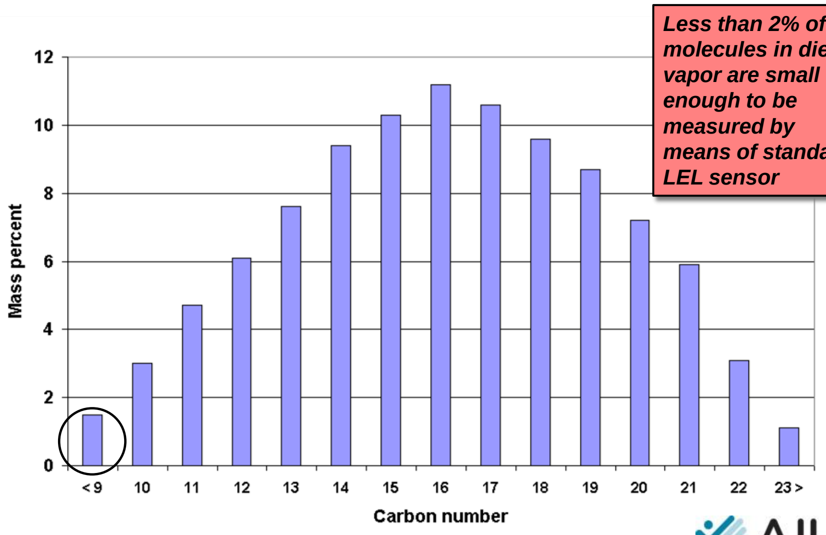
- *Oxidation of nonane:* $C_9H_{20} + 14O_2 \rightarrow 9CO_2 + 10H_2O$

  To oxidize one molecule of nonane, 15 molecules enter bead, but 19 need to leave the sensor.

Catalytic Sensor Structure



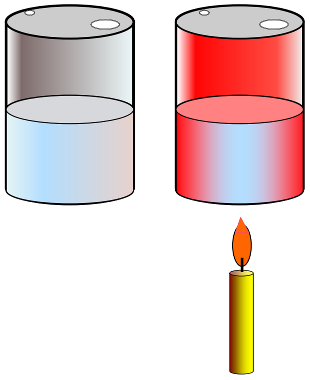
Typical carbon number distribution in No. 2 Diesel Fuel (liquid)



Less than 2% of molecules in diesel vapor are small enough to be measured by means of standard LEL sensor

Vaporization is a function of temperature

- *Vapors are the gaseous state of substances that are either liquids or solids at room temperatures*
  - *Gasoline evaporates*
  - *Dry ice (solid carbon dioxide) sublimates*
- *Increasing the temperature of the combustible liquid increases the amount of vapor produced*



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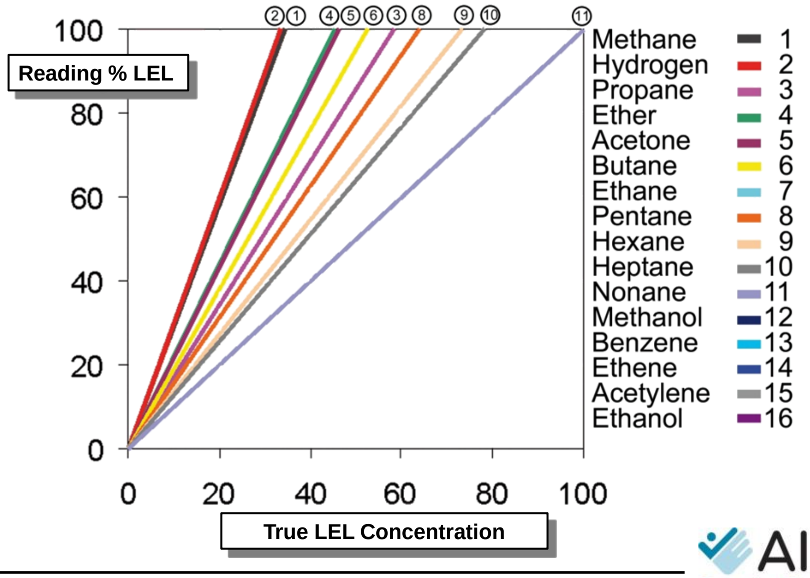
Flammable and combustible liquid classifications (OSHA 29 CFR 1910.106)

	Flash Point Temp °F	*Boiling Point °F*	*Examples*
Class IA flammable liquid	*Below 73 °F*	*Below 100 °F*	*Methyl ethyl ether* *Pentane* *Petroleum ether*
Class IB flammable liquid	*Below 73 °F*	*Above 100 °F*	*Acetone* *Ethanol* *Gasoline* *Methanol*
Class IC flammable liquid	*At or above 73 °F*	*Below 100 °F*	*Styrene* *Turpentine* *Xylene*
Class II combustible liquid	*At or above 100 °F*	*Below 140 °F*	*Fuel oil no. 44 (Diesel)* *Mineral spirits* *Kerosene*
Class IIIA combustible liquid	*At or above 140 °F*	*Below 200 °F*	*Aniline* *Carbolic acid* *Phenol* *Naphthalenes* *Pine oil*
Class IIIB combustible liquid	*At or above 200 °F*		

Typical catalytic LEL sensor relative responses

Relative responses of 4P-75 catalytic LEL sensor			
Combustible gas / vapor	**Relative response when sensor calibrated on pentane**	**Relative response when sensor calibrated on propane**	**Relative response when sensor calibrated on methane**
Hydrogen	**2.2**	**1.7**	**1.1**
Methane	**2.0**	**1.5**	**1.0**
Propane	**1.3**	**1.0**	**0.7**
n-Butane	**1.2**	**0.9**	**0.6**
n-Pentane	**1.0**	**0.8**	**0.5**
n-Hexane	**0.9**	**0.7**	**0.5**
n-Octane	**0.8**	**0.6**	**0.4**
Methanol	**2.3**	**1.8**	**1.2**
Ethanol	**1.6**	**1.2**	**0.8**
Isopropanol	**1.4**	**1.1**	**0.7**
Acetone	**1.4**	**1.1**	**0.7**
Ammonia	**2.6**	**2.0**	**1.3**
Toluene	**0.7**	**0.5**	**0.4**
Gasoline (unleaded)	**1.2**	**0.9**	**0.6**

Catalytic pellistor combustible gas response curves



Correction Factors

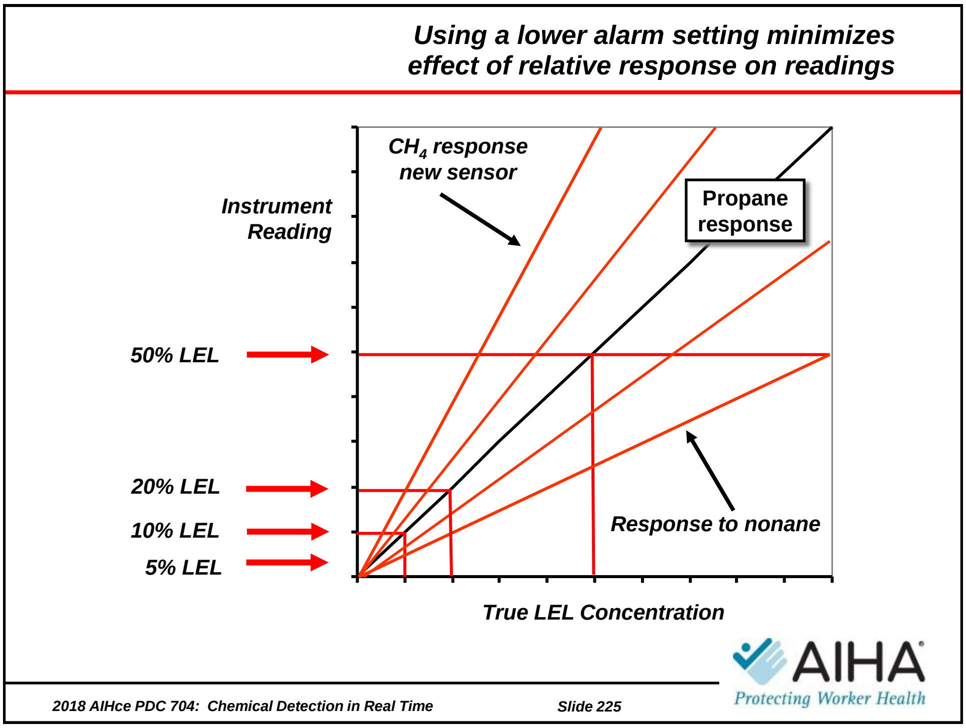
- *Correction factor is the reciprocal of the relative response*
- *The relative response of 4P-75 LEL sensor (methane scale) to ethanol is 0.8*
- *Multiplying the instrument reading by the correction factor for ethanol provides the true concentration*
- *Given a correction factor for ethanol of 1.25, and an instrument reading of 40 per cent LEL, the true concentration would be calculated as:*

40 % LEL	*X*	*1.25*	*=*	*50 % LEL*
Instrument Reading		*Correction Factor*		*True Concentration*

Catalytic combustible LEL sensor correction factors

Correction factors for 4P-75 catalytic LEL sensor

Combustible gas / vapor	Correction factor when sensor calibrated on pentane	Correction factor when sensor calibrated on propane	Correction factor when sensor calibrated on methane
Hydrogen	0.45	0.59	0.91
Methane	0.50	0.67	1.00
Propane	0.77	1.00	1.54
n-Butane	0.83	1.11	1.67
n-Pentane	1.00	1.33	2.00
n-Hexane	1.11	1.43	2.22
n-Octane	1.25	1.67	2.50
Methanol	0.43	0.57	0.87
Ethanol	0.63	0.83	1.25
Isopropanol	0.71	0.95	1.43
Acetone	0.71	0.95	1.43
Ammonia	0.38	0.50	0.77
Toluene	1.43	2.00	2.86
Gasoline (unleaded)	0.83	1.11	1.67



Using a lower alarm setting minimizes effect of relative response on readings

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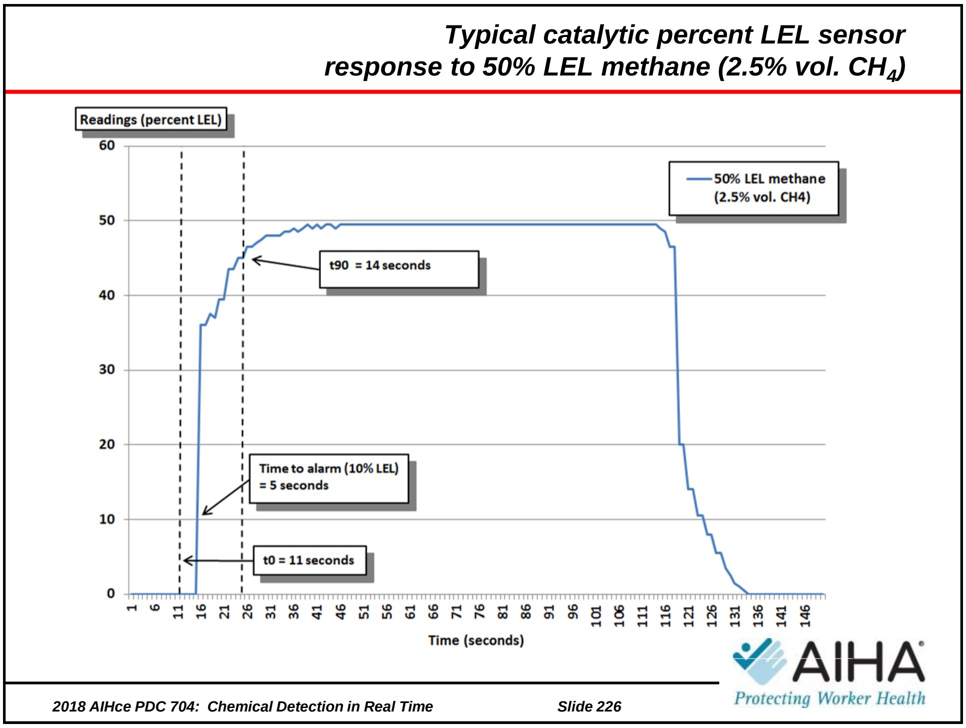

Typical catalytic percent LEL sensor response to 50% LEL methane (2.5% vol. CH_4)

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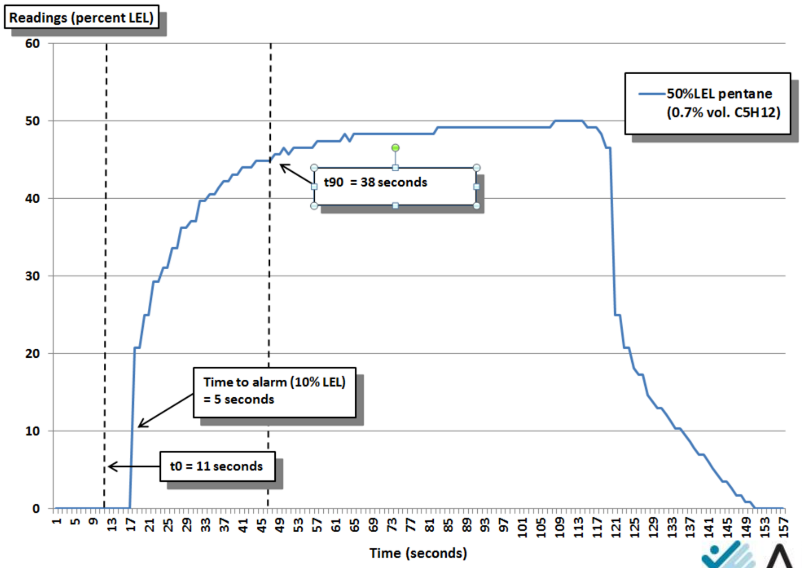
Typical catalytic percent LEL sensor response to 50% LEL pentane (0.7% vol. C_5H_{12})



t90 = 38 seconds

Time to alarm (10% LEL) = 5 seconds

t0 = 11 seconds

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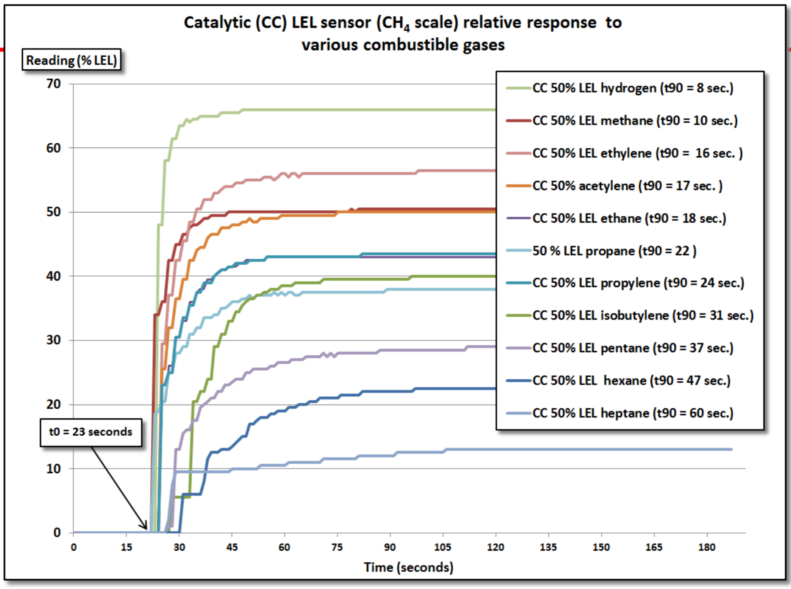
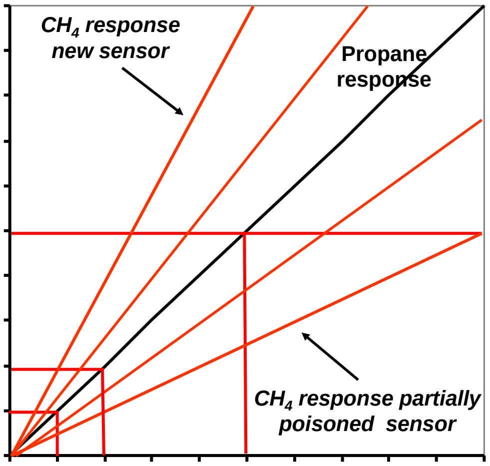
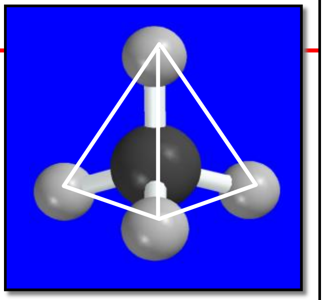
Catalytic combustible sensor exposed to various gases


Catalytic (CC) LEL sensor (CH_4 scale) relative response to various combustible gases

t0 = 23 seconds

Response to methane over life of sensor





- Relative response to methane may change substantially over life of sensor

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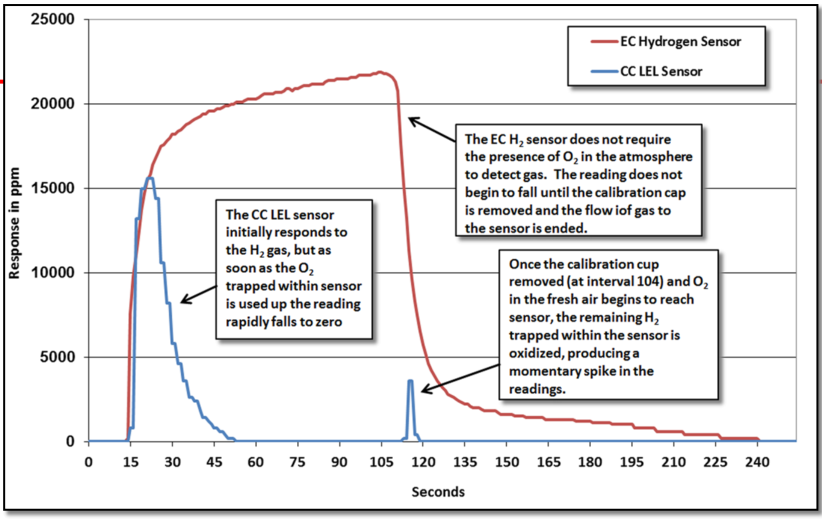
Methane based equivalent calibration gas mixtures

Combustible Gas / Vapor	Relative response when sensor is calibrated to 2.5% (50% LEL) methane	Concentration of methane used for equivalent 50% LEL response
Hydrogen	1.1	2.75% CH4
Methane	1.0	2.5% Vol CH4
Ethanol	0.8	2.0% Vol CH4
Acetone	0.7	1.75% Vol CH4
Propane	0.65	1.62% Vol CH4
n-Pentane	0.5	1.25% Vol CH4
n-Hexane	0.45	1.12% Vol CH4
n-Octane	0.4	1.0% Vol CH4
Toluene	0.35	0.88% Vol CH4

Response of electrochemical and LEL sensor to 20,000 ppm hydrogen in nitrogen



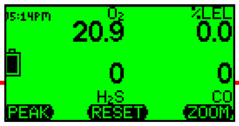
The EC H_2 sensor does not require the presence of O_2 in the atmosphere to detect gas. The reading does not begin to fall until the calibration cap is removed and the flow iof gas to the sensor is ended.

The CC LEL sensor initially responds to the H_2 gas, but as soon as the O_2 trapped within sensor is used up the reading rapidly falls to zero

Once the calibration cup removed (at interval 104) and O_2 in the fresh air begins to reach sensor, the remaining H_2 trapped within the sensor is oxidized, producing a momentary spike in the readings.

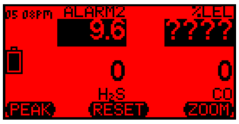
Effects of O_2 concentration on combustible gas readings

- Look at O_2 readings first!
- LEL readings may be affected if levels of O_2 are higher or lower than fresh air
- Catalytic LEL sensors require a minimum level of 10% oxygen to read LEL
- If the O_2 concentration is too low the LEL reading should be replaced with question marks



Readings in fresh air

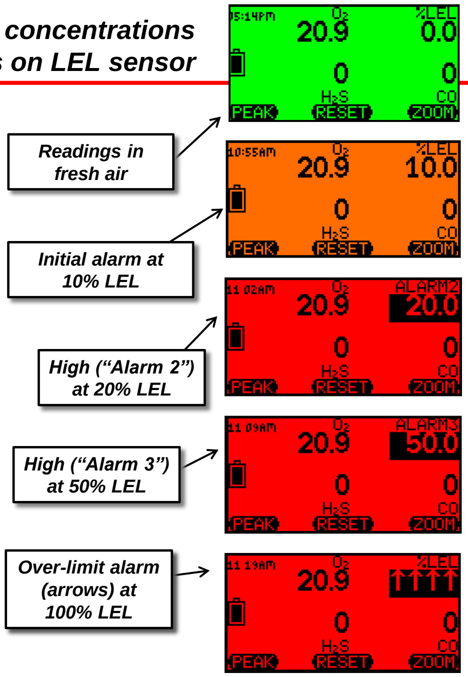
Readings in O_2 deficient air



Readings when O_2 too low for LEL sensor

Effects of high concentrations of gas on LEL sensor

- When doing atmospheric testing we concerned with the LEL not the UEL. Why is that?
  - Work is not permitted in areas where the concentration of gas exceeds safety limits!
  - If the explosive gas concentration is too high there may not be enough oxygen for the LEL sensor to detect properly
  - Concentrations above 100% LEL can damage the LEL sensor



Readings in fresh air

Initial alarm at 10% LEL

High (“Alarm 2”) at 20% LEL

High (“Alarm 3”) at 50% LEL

Over-limit alarm (arrows) at 100% LEL

Combustible sensor poisons

- Combustible sensor poisons:
  - Silicones (by far the most virulent poison)
  - Hydrogen sulfide

> Note: The LEL sensor includes an internal filter that is more than sufficient to remove the H_2S in calibration gas. It takes very high levels of H_2S to overcome the filter and harm the LEL sensor

  - Other sulfur containing compounds
  - Phosphates and phosphorus containing substances
  - Lead containing compounds (especially tetraethyl lead)
  - High concentrations of flammable gas!
- Combustible sensor inhibitors:
  - Halogenated hydrocarbons (Freons®, trichloroethylene, methylene chloride, etc.)

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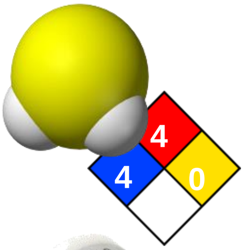
Effects of H_2S on combustible gas sensors

- H2S affects sensor as inhibitor AND as poison
  - Inhibitors like trichloroethane and methylene chloride leave deposit on active bead that depresses gas readings while inhibitor is present
  - Sensor generally recovers most of original response once it is returned to fresh air
- H2S functions as inhibitor BUT byproducts of catalytic oxidation become very corrosive if they build up on active bead in sensor
  - Corrosive effect can rapidly (and permanently) damage bead if not “cooked off” fast enough
  - How efficiently bead “cooks off” contaminants is function of:
    - Temperature at which bead is operated
    - Size of the bead
    - Whether bead under continuous power versus pulsing the power rapidly on and off to save operating energy.



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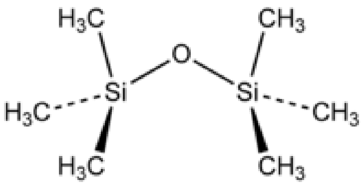
“Silicone resistant” vs. “standard” pellistor type LEL sensors

- "Silicone resistant" combustible sensors have an external silicone filter capable of removing most silicone vapor before it can diffuse into the sensor
  - Silicone vapor is the most virulent of all combustible sensor poisons
  - Filter also slows or slightly reduces response to heavier hydrocarbons such as hexane, benzene, toluene, xylene, cumene, etc.
  - The heavier the compound, the greater the effect on response



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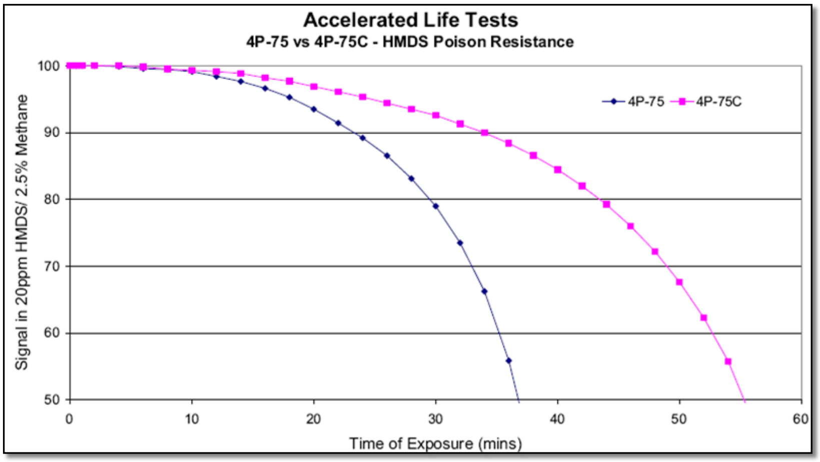
Effects of hexamethyldisiloxane (HMDS) on pellistor sensor



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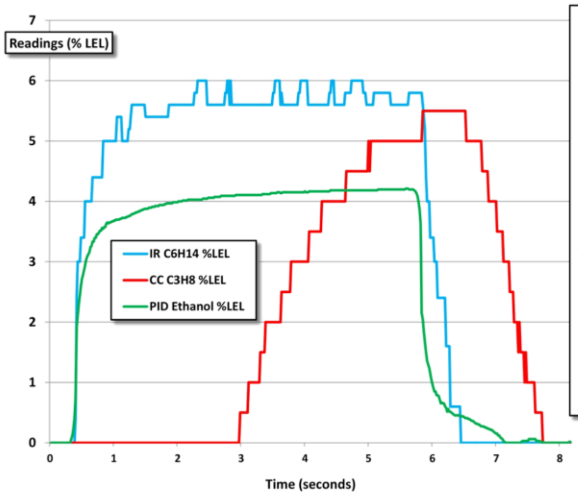
Effects of silicone filter on LEL sensor performance

Response of IR LEL, CC LEL (with sillicone filter) and PID sensors to 5% LEL (2,150 ppm) ethanol in air



Notes:

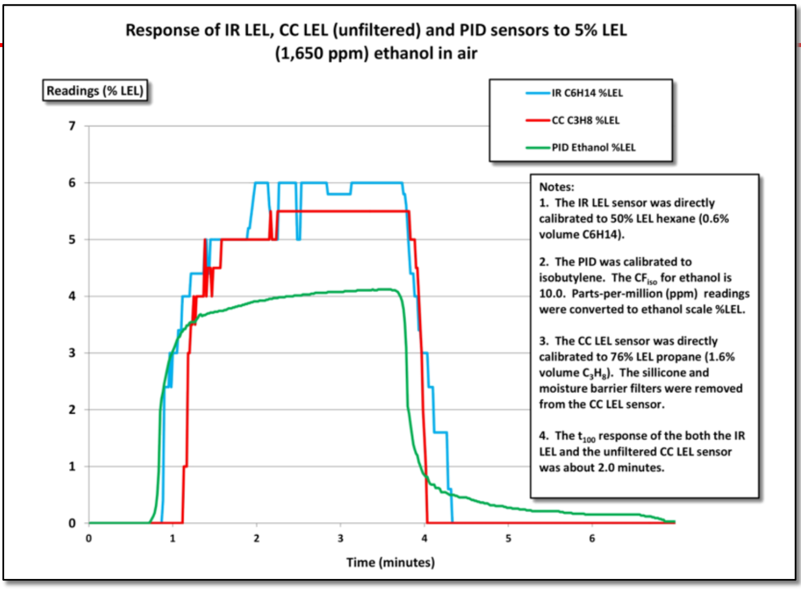
1. The PID was calibrated to isobutylene. The CF_{iso} for ethanol is 10.0. Parts-per-million (ppm) readings were converted to ethanol scale %LEL.

2. The IR LEL sensor was directly calibrated to 50% LEL hexane (0.6% volume C_6H_{14}).

3. CC LEL sensor was directly calibrated to 76% LEL propane (1.6% volume C_3H_8). The sensor was equipped with sillicone and moisture barrier filters.

4. The t_{100} response of the sillicone filter equipped CC LEL sensor was almost 5.0 minutes. The t100 response of the IR LEL sensor was about 2.0 minutes.

Effects of silicone filter on LEL sensor performance



Notes:

1. The IR LEL sensor was directly calibrated to 50% LEL hexane (0.6% volume C6H14).

2. The PID was calibrated to isobutylene. The CF_{iso} for ethanol is 10.0. Parts-per-million (ppm) readings were converted to ethanol scale %LEL.

3. The CC LEL sensor was directly calibrated to 76% LEL propane (1.6% volume C_3H_8). The sillicone and moisture barrier filters were removed from the CC LEL sensor.

4. The t_{100} response of the both the IR LEL and the unfiltered CC LEL sensor was about 2.0 minutes.

Standard "catalytic" LEL sensor advice

- ***Whatever the brand, allow enough time for full stabilization prior to performing fresh air zero***
  - ***Always perform fresh air zero, even if display shows reading of 0% LEL***
    - ***Digital filtering near zero may mask readings that are slightly above or below zero***
  - ***Do not perform auto-zero as part of automatic start-up sequence***
    - ***Wait at least 5 minutes after initially turning instrument on before performing a fresh air zero***
    - ***Especially important to allow sensor to stabilize fully when there is a large difference in temperature between where the instrument is turned on (usually indoors) and actually used***
- ***Perform functional test before each day's use!***
  - ***Use methane based test gas mixture OR if you use a different gas (e.g. propane or pentane) challenge the sensor with methane periodically to verify the sensor has not lost sensitivity to methane***

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Bump test and calibration requirements

AP 1007:
Calibration and Bump Test Requirements for Direct Reading Portable Gas Monitors

Manufacturers and regulatory agencies agree the safest and most conservative approach is to perform a functional test by exposing your gas detector to test gas before each day's use.

Oxygen deficiencies, explosive atmospheres, and exposure to toxic gases and vapors injure hundreds of workers every year. The atmospheric conditions that lead to these accidents and fatalities are usually invisible to the workers who are involved. The only way to ensure atmospheric conditions are safe is to use an atmospheric monitor. The only way to know whether an instrument is capable of proper performance is to expose it to test gas. Exposing the instrument to known concentration test gas verifies that gas is properly able to reach and be detected by the sensors. It verifies the proper performance of the instrument's alarms, and (if the instrument is equipped with a real-time display), that the readings are accurate. Failure to periodically test and document the performance of your atmospheric monitors can leave you open to regulatory citations or fines, as well as increased liability exposure in the event that a worker is injured in an accident.

There has never been a consensus among manufacturers regarding how frequently direct reading portable gas detectors need to be calibrated. However, manufacturers do agree that the safest and most conservative approach is to verify the performance of the instrument by exposing it to test gas before each day's use. Performing a functional "bump test" is very simple and takes only a few seconds to accomplish. It is not necessary to make a calibration adjustment unless the readings are found to be inaccurate. The regulatory standards that govern confined space entry and other activities that include the use of direct reading instruments are in agreement with this approach.

However, the definition of "bump test" has always been a little slippery. Some manufacturers differentiate between a "bump test" that provides a qualitative evaluation of the instrument's ability to detect gas and a "calibration check" that verifies that the response of the sensor(s) when exposed to known concentration test gas are within the manufacturer's requirements for accuracy. All manufacturers agree that instruments that fail either a "bump test" or "calibration check" should be put through a "full calibration" before further use.

ISEA Statement on Validation of Operation for Direct Reading Portable Gas Monitors

The International Safety Equipment Association (ISEA) is the leading international organization of manufacturers of safety equipment, including environmental monitoring instruments. The ISEA is dedicated to protecting the health and safety of workers through the development of workplace standards and the education of users on safe work practices and exposure prevention. In 2010 the ISEA updated their protocol for, *"Validation Procedures of Operation For Direct Reading Portable Gas Monitors"* to clarify the Association's recommendations for the procedures used to verify proper operation, and the accuracy of the readings.

The protocol was designed to reemphasize to OSHA and other standards writing bodies the importance of verifying the calibration of instruments used to monitor the atmosphere in potentially hazardous locations, to clarify the differences

Figure 1: Performing a functional "bump test" by exposing the instrument to test gas takes only a few moments perform.

GfG Instrumentation
Worldwide Manufacturer of Gas Detection Solutions
www.goodforgas.com

Instruments should be tested by exposure to calibration gas on a regular basis!

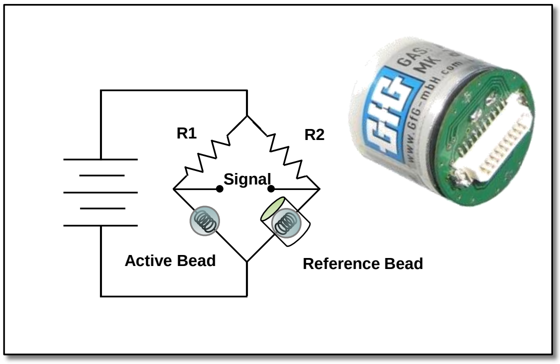
- ***Gas detection instruments can only keep workers safe when they are maintained and used properly***
- ***Regulations in the USA, Canada, Mexico and Europe require that gas detectors must be tested by exposure to known concentration gas <u>before each day's use</u>***
- ***No exceptions!***

Perform a bump test or calibration check before each day's use!

- ***"Bump test" (function check) is <u>qualitative</u> check in which the sensors are exposed to test gas for a time and at a concentration to activate all of the alarms to at least the lower alarm settings***
  - ***The test does not verify the accuracy of the readings or output of the sensors when exposed to gas***
- ***"Calibration check" is a quantitative test using a traceable source of known concentration test gas to verify response of the sensors is within the manufacturer's acceptable limits.***
  - ***Different manufacturers are free to publish different requirements***
- ***"Full calibration" includes adjustment of the instrument's response to match a desired value compared to a known traceable concentration of test gas***
  - ***Calibration interval and other requirements specified by manufacturer***
- ***If instrument fails bump test or calibration check perform full calibration before use***

Thermal conductivity (TCD) combustible gas sensors

- ***Specialized type of sensor most frequently used to detect high range concentrations of combustible gas (especially natural gas)***
- ***Very similar to Wheatstone type LEL sensor, EXCEPT the active bead is not treated with catalyst***
- ***Depend on differences in density of atmosphere to measure gas***



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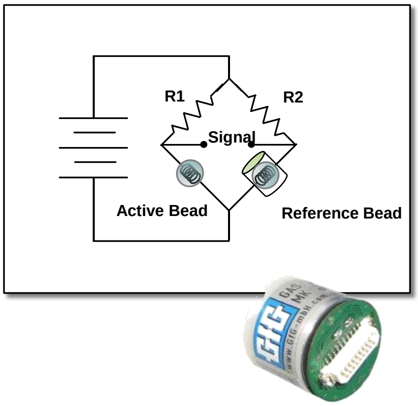
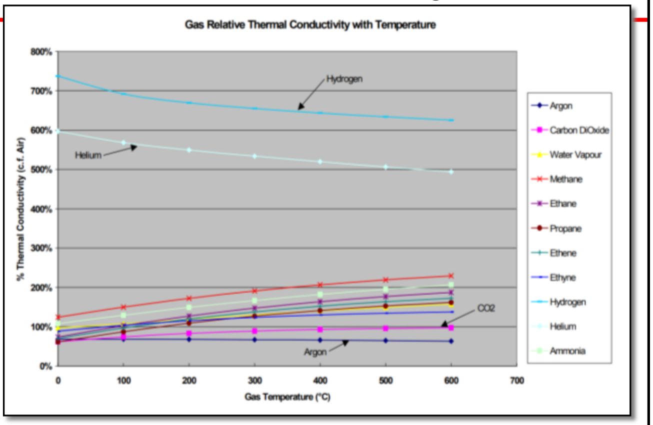
Thermal conductivity (TCD) combustible gas sensors

- ***Two beads strung onto opposite arms of Wheatstone bridge circuit***
- ***Neither bead treated with catalyst***
- ***Reference bead isolated from the air being monitored in sealed or semi-sealed chamber***
- ***Active bead exposed to atmosphere being monitored***
- ***Beads heated to operating temperature***
- ***Detection depends on "air-conditioning" effect of gas on the active bead***
  - ***Lighter than air gas (such as hydrogen or methane), attenuates the atmosphere, causing the active bead to dissipate heat more efficiently***
  - ***If a heavier than air gas is present (such as propane) the bead is insulated by the denser atmosphere***
- ***Difference in temperature between the two beads is proportional to the amount of combustible gas present in the atmosphere being monitored***



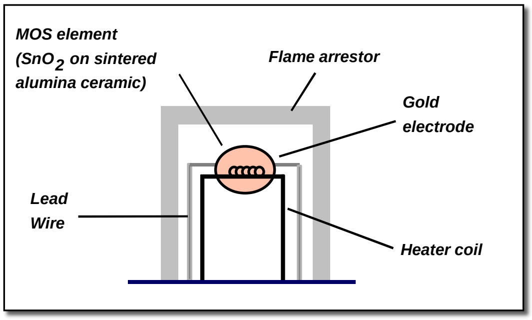
Thermal conductivity (TCD) combustible gas sensors



- ***Benefits***
  - ***Able to detect gas up to 100% volume concentration***
  - ***Gases with similar densities (such as methane and ethane) have similar response***
  - ***Often included in same instrument as catalytic LEL sensor***
  - ***Do not use if background gas mixture is unknown or variable***
- ***Limitations***
  - ***Changes in the makeup of the air being tested can affect readings***
  - ***Not recommended for use in confined spaces where there is the potential for oxygen deficiency, or air that contains elevated concentrations of nitrogen or carbon dioxide***
  - ***Generally only use when measured gas is present in fresh air***
  - ***Do not use if background gas mixture is unknown or variable***

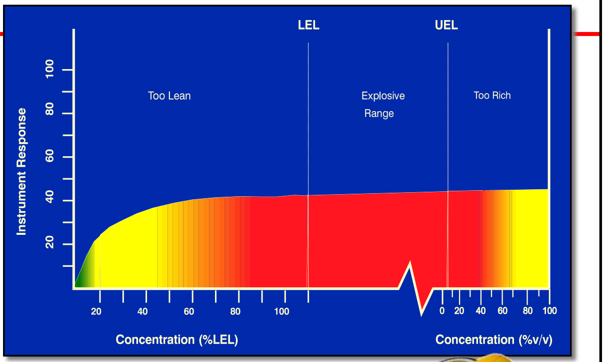
MOS Detection Mechanism

- ***Sensing element:***
  - *Tin dioxide (SnO2) on sintered alumina ceramic*
  - *In clean air electrical conductivity low*
  - *Contact with either oxidizing or reducing gases (such as CO, combustible gas and ammonia) increases conductivity*
  - *Sensitivity to specific gases depends on temperature of sensing element*



MOS sensor capabilities and limitations

- ***Benefits:***
  - *Broad range response (including refrigerants and halogenated solvents)*
  - *Detection in ppm range or lower concentration*
  - *Inexpensive*
  - *Good for qualitative measurement or leak detection*
  - *Long life*
- ***Limitations:***
  - *Non-linear signal*
  - *Qualitative rather than numerical reading*
  - *Affected by temperature and humidity conditions (sensor can "go to sleep" in very low humidity)*
  - *Damaged by same inhibitors and poisons that harm catalytic LEL sensors*



Non-dispersive infrared (NDIR) sensors

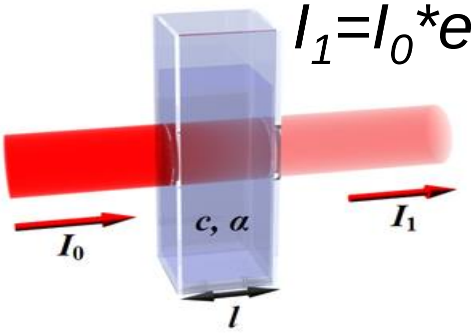
- *Many gases absorb infrared light at a unique set of wavelengths*
- *In NDIR sensors the amount of IR light absorbed is proportional to the amount of target gas present*
- *IR absorption has advantages of high sensitivity, low cross-sensitivity, long life, and resistance to contamination*
- *IR absorption employed in both very high-performance laboratory analyzers and in very low-performance systems (e.g. inexpensive, non-intrinsically safe hand-held CO_2 detectors)*

Non-dispersive infrared (NDIR) sensors

- *When infra-red radiation passes through a sensing chamber containing a specific contaminant, only those frequencies that match one of the vibration modes are absorbed*
- *The rest of the light is transmitted through the chamber without hindrance*
- *The presence of a particular chemical group within a molecule thus gives rise to characteristic absorption bands*
- *Non-dispersive IR sensors measure at a specific range of wavelengths associated with a particular gas or class of gases*

Beer-Lambert Law

$$I_1=I_0*e^{-\alpha Lc}$$



Optical path-length matters…

- I_0 is the intensity of the incident light
- I_1 is the intensity after passing through the material
- L is the distance that the light travels through the material (the path length)
- c is the concentration of absorbing species in the material
- α is the absorption coefficient or the molar absorptivity of the absorber

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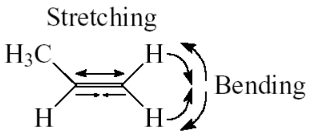
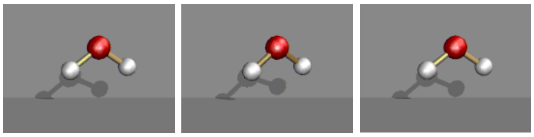
Energy Absorbed by "Bond Stretching" and "Bending" Vibration

- Must have a COVALENT CHEMICAL BOND

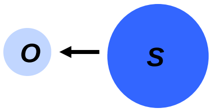




Symmetric Stretch

Asymmetric Stretch

Bend

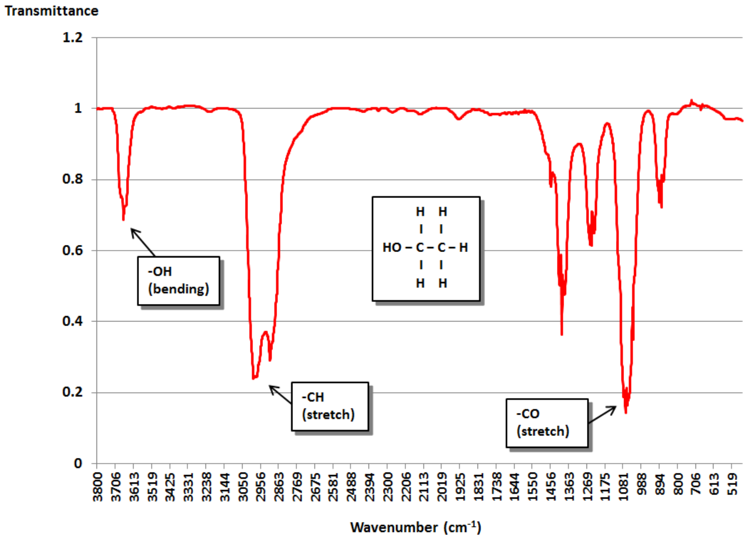


Nonlinear Molecules

Linear molecules: SO

Geometry and specific bonds in molecule give rise to IR spectrum

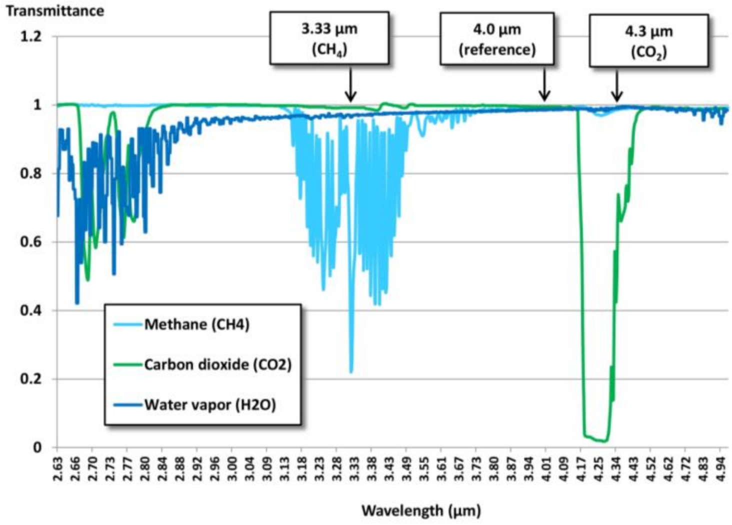
Infrared transmittance spectrum for ethanol
(3800 to 500 cm^{-1} range)



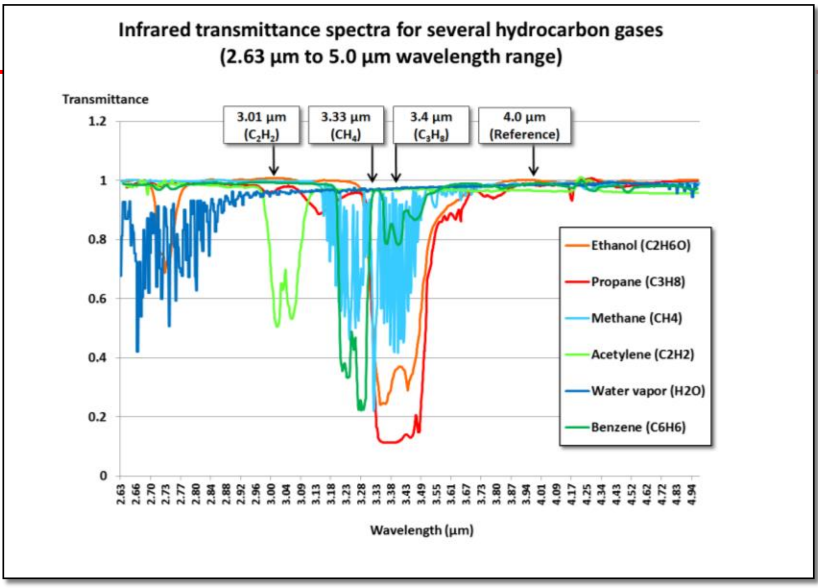
Requirements for IR Absorption

- *Lower quantum levels must be "populated"*
- *Dipole moment (degree of charge imbalance) must change with the vibrational "motion"*
- CO_2 *and* CH_4 *absorb IR*
- *Homonuclear diatomics such as hydrogen DO NOT absorb IR*
- *IR-transparent gases:*
  - H_2
  - N_2
  - O_2
  - F_2
  - Cl_2
  - Hg_2
  - *Ar*

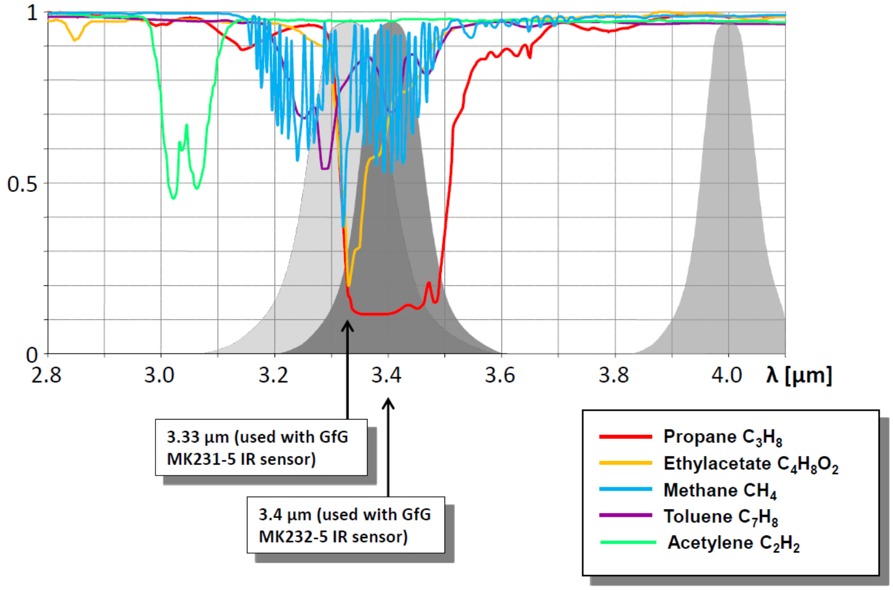
Infrared transmittance spectra for methane, water (vapor) and carbon dioxide (2.63 µm to 5.0 µm wavelength range)



Wavelengths typically used for IR LEL measurement



LEL measurement at 3.33µm vs. 3.4µm



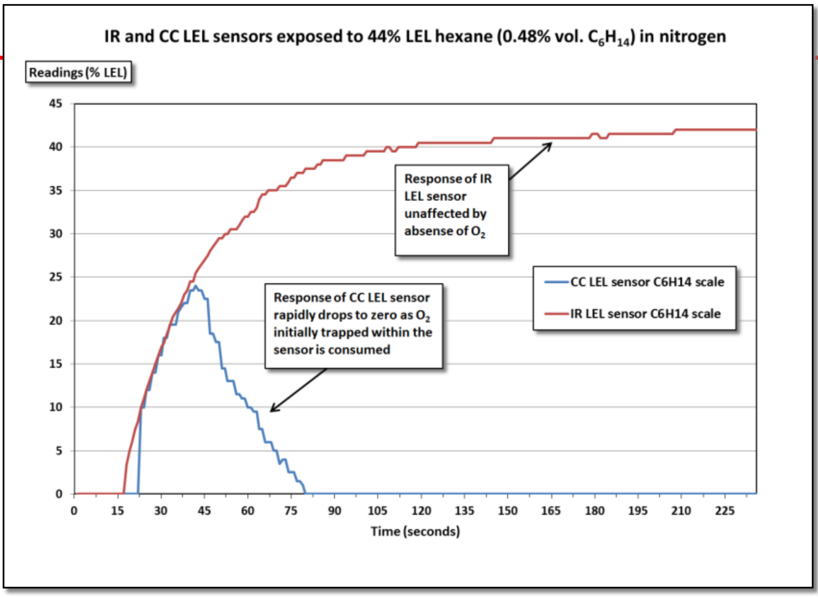
3.33 µm (used with GfG MK231-5 IR sensor)

3.4 µm (used with GfG MK232-5 IR sensor)

Combustible gas NDIR sensor advantages and limitations

- ***Limitations:***
  - ***Molecule must include chemical bonds that absorb at the wavelength(s) used for measurement***
  - ***Not all combustible gases can be detected!***
    - ***"Diatomic" molecules like hydrogen (H_2) cannot be detected at all***
    - ***Gases with double and triple bonds (like acetylene) detect poorly or not at all at some measurement wavelengths***
    - ***NDIR sensors with short optical path-lengths may have limited ability to measure gases with lower relative responses***
- ***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***

IR LEL sensor performance unaffected by the absence of oxygen

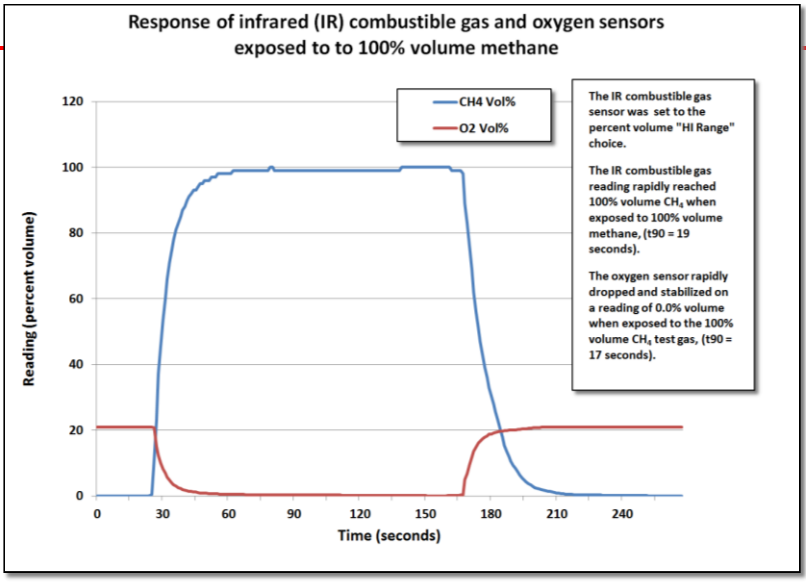


IR and CC LEL sensors exposed to 44% LEL hexane (0.48% vol. C_6H_{14}) in nitrogen

Response of IR LEL sensor unaffected by absense of O_2

Response of CC LEL sensor rapidly drops to zero as O_2 initially trapped within the sensor is consumed

IR combustible sensors can be used for high range measurement up to 100% volume gas

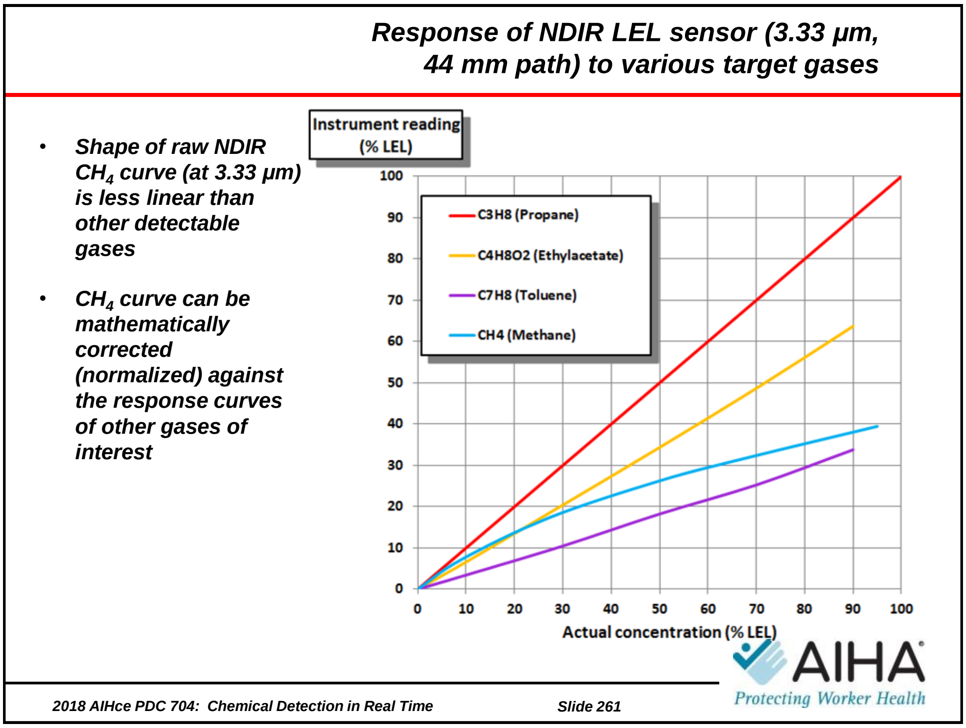


Response of infrared (IR) combustible gas and oxygen sensors exposed to to 100% volume methane

The IR combustible gas sensor was set to the percent volume "HI Range" choice.

The IR combustible gas reading rapidly reached 100% volume CH_4 when exposed to 100% volume methane, (t90 = 19 seconds).

The oxygen sensor rapidly dropped and stabilized on a reading of 0.0% volume when exposed to the 100% volume CH_4 test gas, (t90 = 17 seconds).



Response of NDIR LEL sensor (3.33 µm, 44 mm path) to various target gases

- ***Shape of raw NDIR CH_4 curve (at 3.33 µm) is less linear than other detectable gases***
- ***CH_4 curve can be mathematically corrected (normalized) against the response curves of other gases of interest***

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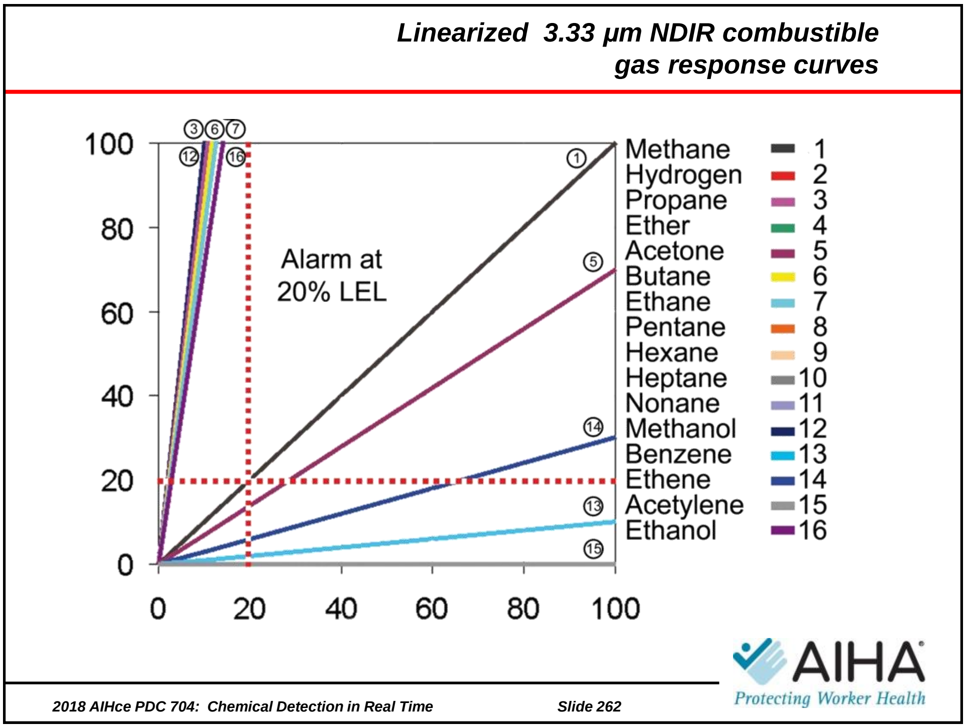

Linearized 3.33 µm NDIR combustible gas response curves

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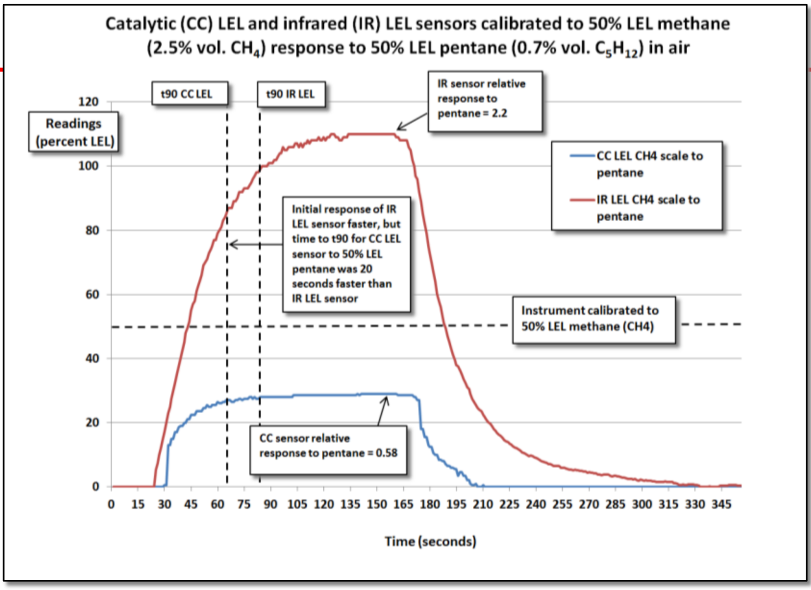
Relative response of pellistor and infrared sensors to n-Pentane



Catalytic (CC) LEL and infrared (IR) LEL sensors calibrated to 50% LEL methane (2.5% vol. CH_4) response to 50% LEL pentane (0.7% vol. C_5H_{12}) in air

IR sensor relative response to pentane = 2.2

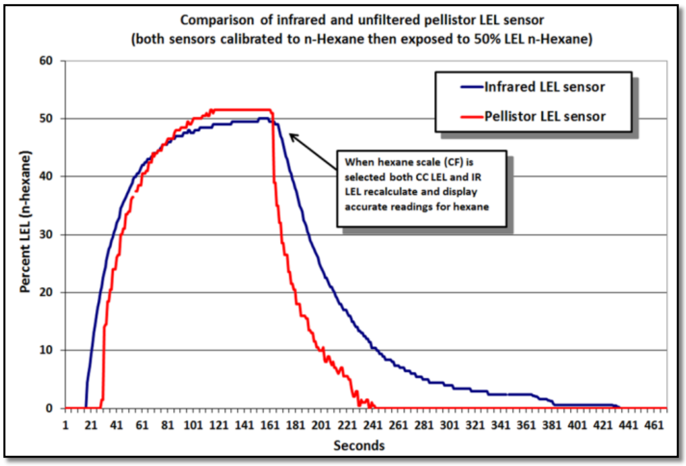
Initial response of IR LEL sensor faster, but time to t90 for CC LEL sensor to 50% LEL pentane was 20 seconds faster than IR LEL sensor

Instrument calibrated to 50% LEL methane (CH4)

CC sensor relative response to pentane = 0.58

Corrected response of catalytic LEL and IR LEL sensors to 50% LEL n-Hexane

- ***Both sensors were calibrated to 50% LEL n-Hexane***
- ***Readings for both sensors are now very close to the true 50% LEL concentration***
- ***Initial response of IR sensor is slightly quicker than the pellistor sensor***
- ***However, the time to the final stable response (T100) is virtually identical for both sensors, (about 150 seconds)***



Comparison of infrared and unfiltered pellistor LEL sensor (both sensors calibrated to n-Hexane then exposed to 50% LEL n-Hexane)

When hexane scale (CF) is selected both CC LEL and IR LEL recalculate and display accurate readings for hexane

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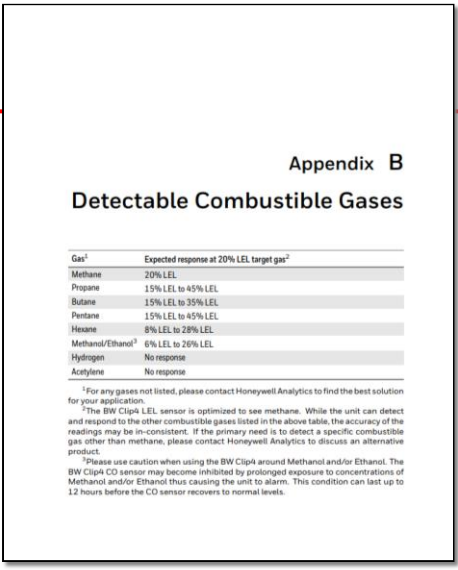
Performance of IR LEL sensors differs from performance of catalytic LEL sensors

- ***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.

Photoionization Detectors

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*

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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*

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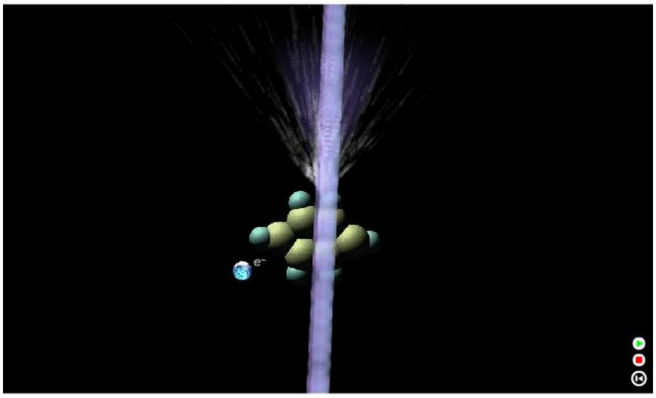
Combustible sensor limitations

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

PID - Operating Principle

- PIDs used for measuring solvent, fuel and VOC vapors in the workplace environment
- PIDs use ultraviolet light as source of energy to remove an electron from neutrally charged target molecules creating electrically charged fragments (ions)
- This produces a flow of electrical current proportional to the concentration of contaminant
- The amount of energy needed to remove an electron from a particular molecule is the ionization energy (or IE)
- The energy must be greater than the IE in order for an ionization detector to be able to detect a particular substance

How does a PID work?



Planar "3D" 2-electrode PID design

- ***Benefits:***
  - ***Rapid response and clearing times***
- ***Limitations:***
  - ***Gap between window and electrodes increases "quenching" effect of water vapor on signal***
  - ***Potential for drawing particulate contaminants into sensor***
  - ***More ionic fragments left behind to be adsorbed onto electrodes and window***
- ***Results:***
  - ***Increased sensitivity to water vapor and humidity***
  - ***Must clean lamp more frequently***

3-electrode PID Design

- ***Benefits:***
  - ***Diffusion design includes "fence electrode" to provide mechanical short circuit between sensing and counter electrodes***
  - ***Electrodes housed in replaceable "stack"***
  - ***Diffusion of molecules into and out of glow zone means less ionic fragments or particulates left behind***
- ***Limitations:***
  - ***Slightly slower response***
  - ***Operation at higher voltage increases vulnerability to EMI / RFI***
- ***Results:***
  - ***Reduced "moisture leakage" response due to humidity***
  - ***Clean lamp less frequently***

Ionization Energy

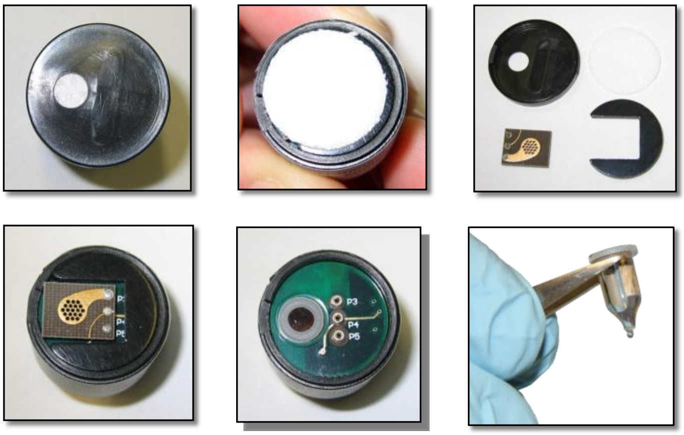
- ***IE determines if the PID can detect the gas***
- ***If the IE of the gas is less than the eV output of the lamp the PID can detectthe gas***
- ***Ionization Energy (IE) measures the bond strength of a gas and does not correlate with the Correction Factor***
- ***Ionization Energies are found in the NIOSH Pocket Guide and many chemical texts***

Ionization energy values

Gas / vapor	*Ionization energy (eV)*
Carbon monoxide	*14.01*
Carbon dioxide	*13.77*
Methane	*12.98*
Water	*12.59*
Oxygen	*12.08*
Chlorine	*11.48*
Hydrogen sulfide	*10.46*
n-Hexane	*10.18*
Ammonia	*10.16*
hexane (mixed isomers)	*10.13*
acetone	*9.69*
benzene	*9.25*
butadiene	*9.07*
toluene	*8.82*

PID Components

- *Detector assembly*
- *Electrodes: sensing, counter and (in some designs) fence*
- *Lamp: most commonly 10.6EV, 11.7eV or 9.8 eV*



PID lamp characteristics

- *Window material and the filler gas determine output characteristics as well as operational life of lamp*

PID lamp characteristics

Nominal lamp photon energies	Primary gas in lamp	Major emission lines		Relative intensity	Window crystal	Crystal transmittance λ range (nm)
		eV	λ (nm)			
11.7 eV	Argon	11.83	104.8	1000	Lithium fluoride (LiF)	105 - 5000
		11.62	106.7	500		
10.6 eV	Krypton	10.64	116.5	200	Magnesium fluoride (MgF_2)	115 - 7000
		10.03	123.6	650		
9.8 eV	Krypton	10.03	123.6	650	Calcium fluoride (CaF_2)	125 - 8000

Critical PID Performance Issues: Effects of Humidity and Contamination

- ***Condensation and contamination on lamp window and sensor surfaces can create surface conduction paths between sensing and counter electrodes***
- ***Buildup of contamination provides nucleation points for condensation, leading to surface currents***
- ***If present, surface currents cause false readings and / or add significant noise that masks intended measurement (sometimes called "moisture leakage")***
- ***PID designs <u>MAY</u> require periodic cleaning of the lamp and detector to minimize the effects of contaminants and humidity condensation on PID readings***

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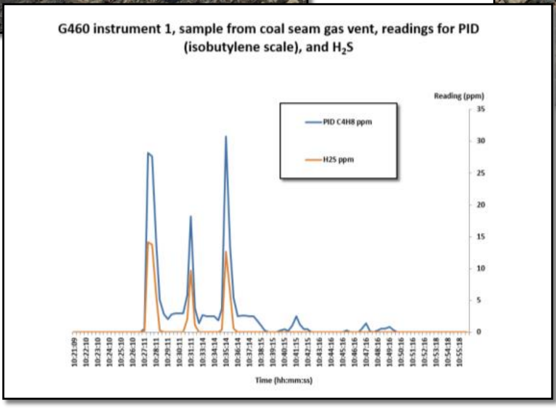
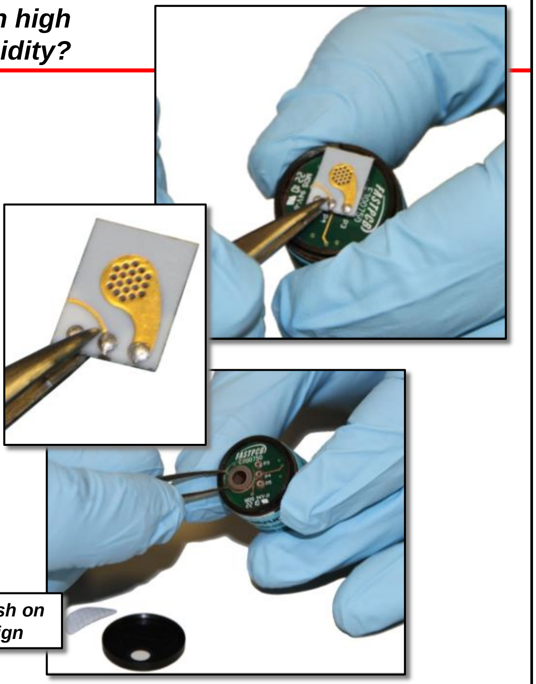
Make sure you understand how to operate your instrument correctly


G460 instrument 1, sample from coal seam gas vent, readings for PID (isobutylene scale), and H_2S

Can PIDs be used in high ambient humidity?

- *It depends on the design of the PID*
- *The greater the gap between the lamp window and the sensing electrode, the greater the effects of humidity and other signal quenching gases (like methane) have on readings*
- *Unless a humidity correction factor is used, some PIDs may display readings 30% to 40% below actual when used in humid conditions*
- *PID designs where the electrode is positioned flush against the window are the least susceptible to signal quenching*



Electrode stack sits flush on window in GfG PID design

What are broad-range sensors?

- *Broad-range sensors (like LEL and PID sensors) are non-specific*
- *Broad-range sensors provide aggregate measurements for all detectable molecules within a specified class, for instance:*
  - *Molecules capable of oxidation by standard LEL sensor*
  - *Molecules capable of ionization by standard PID with 10.6 eV lamp*
- *Cannot distinguish between different contaminants they are able to detect*
- *Provide single total reading for all detectable substances present*
- *PID and LEL readings always relative to gas used to calibrate detector*

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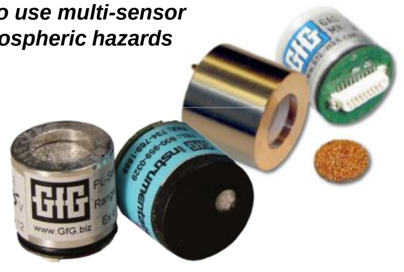
Can a PID be used in place of common substance-specific electrochemical sensors (like those used to measure H_2S)?

- ***For many common toxic gases, substance-specific electrochemical sensors are available to provide highly accurate readings***
- ***When a quantified reading is necessary for a specific contaminant (like CO or H_2S) it is better if feasible to avoid use of a broad-range sensor, and stick with a detection technology that can provide direct, substance-specific readings***

Catalytic (CC) LEL vs. PID Sensors

- ***Catalytic LEL and photoionization detectors are complementary detection techniques***
- ***Catalytic LEL sensors excellent for measurement of methane, propane, and other common combustible gases NOT detectable by PID***
- ***PIDs detect large VOC and hydrocarbon molecules that are undetectable by catalytic sensors***
- ***Best approach to VOC measurement is to use multi-sensor instrument capable of measuring all atmospheric hazards that may be potentially present***



Can I use my PID in place of a traditional LEL sensor?

- ***Photoionization detectors optimized for use at ppm and sub-ppm toxic exposure limit values***
- ***PID linearity may be affected by high LEL range concentrations of gas***
- ***The PID upper range limit can be exceeded***
- ***Gases such as methane and ethane can have a quenching effect, causing lower than actual PID readings***
- ***PID and catalytic LEL sensors work best when used together as complementary detection techniques***

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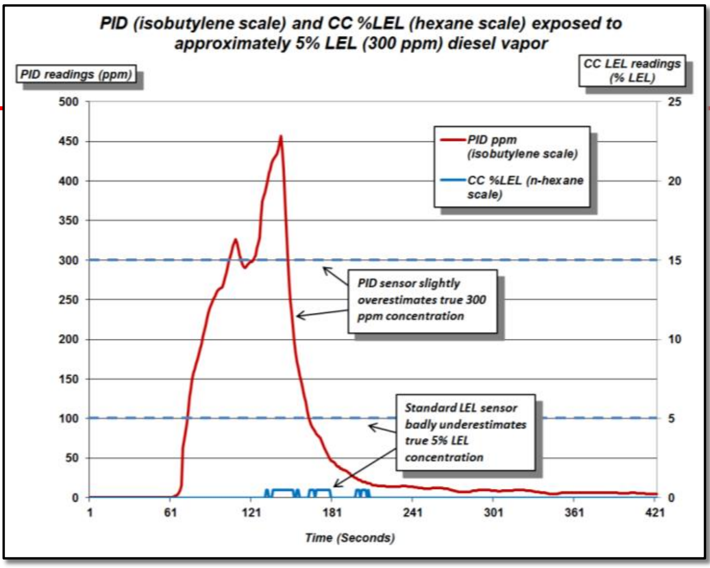
There are strong benefits for including both PID and LEL sensors in the same instrument


PID (isobutylene scale) and CC %LEL (hexane scale) exposed to approximately 5% LEL (300 ppm) diesel vapor

PID sensor slightly overestimates true 300 ppm concentration

Standard LEL sensor badly underestimates true 5% LEL concentration

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PID Correction Factors

- *Correction factors are APPROXIMATE values*
    - *Correction Factor (CF) is measure of sensitivity of PID to specific gas*
    - *CFs do not make PID specific to a chemical, only correct the measurement scale to that chemical*
    - *CFs allow calibration on inexpensive, non-toxic "surrogate" gas (like isobutylene)*
    - *Most manufacturers furnish tables, or built-in library of CFs to correct or normalize readings when contaminant is known*
    - *Instrument able to express readings in parts per million equivalent concentrations for the contaminant measured*

CF measures sensitivity

- *Low CF = high PID sensitivity to a gas*
- *More toxic the gas, more desirable to have low correction factor:*
    - *If Exposure limit is < 10 ppm, CF should be* ≤ 1
- *If chemical less toxic, higher CF may be acceptable*
    - *If Exposure limit is > 10 ppm, CF* ≤ 10
- *When CF > 10 use PIDs as gross leak detectors only*
    - *High correction factor magnifies effects of humidity effects, zero drift, and interfering gases and vapors*

Decision making with a PID

- *Two sensitivities must be understood to make a decision with a PID*
    - *Human Sensitivity: as defined by AGCIH, NIOSH, OSHA or corporate exposure limits*
    - *PID Sensitivity: as defined through testing by the manufacturer of your PID*
    - *ONLY USE A CORRECTION FACTOR FROM THE MANUFACTURER OF YOUR PID!*

Correction Factors (10.6 eV Lamp)

Examples of manufacturer PID correction factors (10.6 eV lamp)

Gas / vapor	RAE	BW	Ion	GfG	IE (eV)
Acetaldehyde	5.50	4.60	4.90	5.40	10.21
Acetone	1.10	0.90	0.70	1.20	9.69
Ammonia	9.70	10.60	8.50	9.40	10.20
Benzene	0.50	0.55	0.50	0.53	9.25
Butadiene	1.00	0.90	0.85	0.69	9.07
Diesel fuel	0.80	0.93	0.75	0.90	n/a
Ethanol	12.00	13.20	8.70	10.00	10.48
Ethylene	10.00	11.00	8.00	10.10	10.52
Gasoline	0.90	0.73	1.10	1.10	n/a
n-Hexane	4.30	4.00	3.30	4.50	10.18
Jet fuel (JP-8)	0.60	0.51	0.70	0.48	n/a
Kerosene	n/a	1.11	0.80	n/a	9.53
Methyl-ethyl-ketone (MEK)	0.90	0.78	0.77	0.90	9.53
Naptha (iso-octane)	1.20	1.20	1.10	1.30	9.82
Styrene	0.40	0.45	0.45	0.40	8.47
Toluene	0.50	0.53	0.51	0.53	8.82
Turpentine	0.40	0.45	0.45	0.45	n/a
Vinyl chloride	2.00	2.19	2.20	1.80	10.00
Xylene (mixed isomers)	0.40	0.50	0.43	0.50	8.50

Can I still use a PID even when I need substance-specific readings?

- ***Broad-range sensors can be calibrated for specific measurable gases, or***
- ***You can choose the correction factor for the desired gas from the on-board library of CF values in the instrument***
- ***Although the sensor will still respond to other measurable gases, readings will be displayed in the correct measurement units and scale***
- ***Alarms should be set at levels which prevent exposure to any of the gases that are potentially present in concentrations that exceed the PEL***

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PID Alarms: Varying Mixtures

- ***The Controlling Compound***
  - ***Every mixture of gases and vapors has a compound that is the most toxic and "controls" the setpoint for the whole mixture***
  - ***Determine that chemical and you can determine a conservative mixture setpoint***
  - ***If we are safe for the "worst" chemical we will be safe for all chemicals***

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PID Alarms:
Varying Mixtures

Chemical Name	*10.6eV CF*	*NIOSH REL Exposure Limit (8-hr. TWA)*
Ethanol	*10.0*	*1000*
Turpentine	*0.45*	*100*
Acetone	*1.2*	*250*

- ***Ethanol "appears" to be the safest compound***
- ***Turpentine "appears" to be the most toxic***
- ***This table only provides half of the decision making equation***

PID Alarms:
Varying Mixtures

- ***Set the PID for the compound with the lowest Exposure Limit (EL) in equivalent units and you are safe for all of the chemicals in the mixture***
- ***Divide the EL in chemical units by CF to get the EL in isobutylene***

$$EL_{Isobutylene} = \frac{EL_{chemical}}{CF_{chemical}}$$

PID Alarms: Varying Mixtures

Chemical name	CF_{iso} (10.6eV)	NIOSH REL (8 hr. TWA)	$EL_{ISO\ (PEL)}$
Ethanol	10.0	1000	100.0
Turpentine	0.45	100	222.3
Acetone	1.2	250	208.4

- *IF you are following the NIOSH REL then ethanol is the "controlling compound" when the exposure limits are expressed in equivalent "Isobutylene Units"*
- *The equivalent EL_{iso} is a calculation that involves a manufacturer specific Correction Factor (CF)*
- *Similar calculations can be done for any PID brand that has a published CF list*

PID Alarms: Varying Mixtures

Chemical name	CF_{iso} (10.6eV)	NIOSH REL (8 hr. TWA)	$EL_{ISO\ (PEL)}$	TLV® (8hr. TWA)	$EL_{ISO\ (TLV)}$
Ethanol	10.0	1000	100.0	1000	100.0
Turpentine	0.45	100	222.3	20	44.5
Acetone	1.2	250	208.4	500	416.7

- *IF you are following the NIOSH REL then ethanol is the "controlling compound" when the exposure limits are expressed in equivalent "Isobutylene Units"*
- *BE CAREFUL: If you are following the TLV the controlling chemical would be turpentine!*

Choosing the best sensor configuration

- ***Multi-sensor instruments can include up to seven channels of real-time measurement***
- ***Available sensors for combustible gas and VOC measurement:***
  - ***CC %LEL***
  - ***IR %LEL***
  - ***IR %Vol***
  - ***Thermal Conductivity (TCD) % vol.***
  - ***Electrochemical toxic***
  - ***PID***

Selection matrix for Sensors for measurement of combustible gas and VOCs

	Able to detect LEL range C1 – C5 hydro-carbon gases (methane, ethane, propane, butane, pentane and natural gas)	Able to detect LEL range C6 – C9 hydro-carbon gases (hexane, heptane, octane, nonane)	Able to accurately detect LEL range heavy fuel vapors (e.g. diesel, jet fuel, kerosene, etc.)	Able to detect heavy fuel vapors in low ppm range (e.g. diesel, jet fuel, kerosene, etc.)	Able to use in low oxygen atmospheres	Vulnerable to sensor poisons (e.g. silicones, phosphine, tetraethyl lead, H2S, etc.)	Able to use for high range combustible gas measurement (100% LEL and higher)	Able to measure H2
Standard Pellistor type LEL sensor	Yes	Yes	No	No	No	Yes	No	Yes
NDIR combustible gas sensor	Yes	Yes	Yes	Yes*	Yes	No	Yes	No
PID (with standard 10.6 eV lamp)	No	Yes**	Yes**	Yes	Yes	No	No	No
Electrochemical H2 sensor	No	No	No	No	Yes	No	No	Yes
Thermal Conductivity Sensor	Yes	Yes	No	No	Yes***	No****	Yes	Yes

Case Study

USCG photo by PA3 Mike Hvozda

- ***Fuel barge explosion and cleanup***
- ***On February 21, 2003, a fuel barge loaded with gasoline exploded at a fuel loading dock on Staten Island, New York***
- ***Two workers were killed and another critically burned***
- ***The explosion was the result of an accident, not terrorism or sabotage***
- ***The barge had unloaded about half its cargo of 4 million gallons of unleaded gasoline when the explosion occurred***

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Case Study

- ***Gasoline was released from the damaged berth area where a section of the aboveground piping ruptured***

USCG photos by PA3 Mike Hvozda

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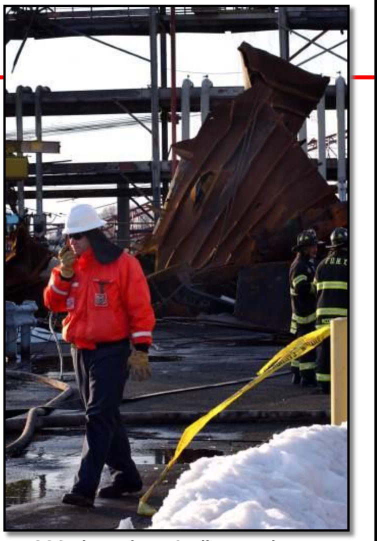
Case Study



USCG photos by PA3 Mike Hvozda

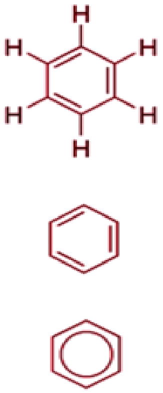
- *As the blaze was at its height, officials used tugs to push a nearby barge loaded with 8 million gallons of gasoline to the other side of the waterway, where they covered it with water and foam to ensure that it did not explode.*

Case Study

- *Once the fire was extinguished and the barges cooled, Marine Chemist and Coast Guard personnel conducted structural inspections*
- *Exposure to toxic VOCs was a primary concern*
- *Chemicals of concern included the remaining gasoline, benzene, total BTEX (benzene, toluene, ethylbenzene, and xylenes) and total polycyclic aromatic hydrocarbons (such as naphthalene)*

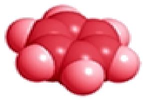
USCG photo by PA3 Mike Hvozda

What about benzene?



- ***Benzene is almost never present all by its by itself***
- ***Benzene is usually minor fraction of total VOC present***
- ***Test for total hydrocarbons (TVOC), especially if the combustible liquid has an established PEL or TLV***

▪ ***Diesel***	***15 ppm***
▪ ***Kerosene***	***30 ppm***
▪ ***Jet Fuel (JP-8)***	***30 ppm***
▪ ***Gasoline***	***300 ppm***



Actual toxicity testing results from gasoline fuel barge #1

Previous Loadings: Cat Feedstock/Crude Oil/Cat Feedstock

SPACE	*% LEL*	*PPM TVOC (iso)*	*PPM Benzene*	*%TVOC from benzene*
No (1) Port Cargo Tank	*0*	*32.8*	*0.8*	*2.44 %*
No (2) Port Cargo Tank	*0*	*38.2*	*0.4*	*1.05%*
No (3) Port Cargo Tank	*0*	*45.5*	*0.4*	*0.88%*
No (4) Port Cargo Tank	*0*	*75.8*	*0.3*	*0.4%*
No (5) Port Cargo Tank	*0*	*64.3*	*0.3*	*0.47%*
No (1) Stbd Cargo Tank	*0*	*34.8*	*0.6*	*1.72%*
No (2) Stbd Cargo Tank	*0*	*44.6*	*0.3*	*0.67 %*
No (3) Stbd Cargo Tank	*0*	*39.6*	*0.2*	*0.51 %*
No (4) Stbd Cargo Tank	*0*	*58.4*	*0.4*	*0.68 %*
No (5) StbdCargoTank	*0*	*64.8*	*0.5*	*0.77%*

TVOC alarm setting based on fractional concentration benzene for Barge #1

- *Worst case (No 1 Port Cargo Tank)*
  - *Solve for desired take action level of 1.0 ppm benzene*
  - *Given "worst case" measured concentration of benzene as fraction of TVOC = .0244*
  - *TVOC threshold alarm = 1.0 ppm ÷ 0.0244 = 40.98 ppm*
  - *Setting TVOC hazardous condition threshold alarm of 41 ppm isobutylene ensures the PEL for benzene of 1.0 PPM is not exceeded: 41 ppm TVOC x .0244 = 1.0004 ppm*

Benzene Exposure Limit	*1.0 PPM*	*0.5 PPM*	*0.1 PPM*
TVOC alarm setting	*41 PPM*	*20.5 PPM*	*4.1 PPM*

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Actual toxicity testing results from gasoline fuel barge #2

Previous Loadings: Natural Gasoline (3X)				
SPACE	***% LEL***	***PPM TVOC (iso)***	***PPM Benzene***	***%TVOC from benzene***
No (1) Port Cargo Tank	*0*	*37.3*	*0.0*	*0 %*
No (2) Port Cargo Tank	*0*	*44.1*	*0.1*	*0.23%*
No (3) Port Cargo Tank	*0*	*53.8*	*0.2*	*0.37 %*
No (4) Port Cargo Tank	*0*	*48.2*	*0.1*	*0.21%*
No (5) Port Cargo Tank	*0*	*68.5*	*0.4*	*0.58 %*
No (1) Stbd Cargo Tank	*0*	*13.2*	*0.0*	*0 %*
No (2) Stbd Cargo Tank	*0*	*29.0*	*0.0*	*0 %*
No (3) Stbd Cargo Tank	*0*	*58.1*	*0.1*	*0.17%*
No (4) Stbd Cargo Tank	*0*	*48.7*	*0.2*	*0.41 %*
No (5) StbdCargoTank	*0*	*63.3*	*0.3*	*0.44%*

TVOC alarm setting based on fractional concentration benzene for Barge #2

- ***Worst case (No 5 Port Cargo Tank)***
  - ***Solve for desired take action level of 1.0 ppm benzene***
  - ***Given "worst case" measured concentration of benzene as fraction of TVOC = .0058***
  - ***TVOC threshold alarm = 1.0 ppm ÷ 0.0058 = 172.4 ppm***
  - ***Setting TVOC hazardous condition threshold alarm of 172.41 ppm isobutylene ensures the PEL for benzene of 1.0 PPM is not exceeded: 172.4 x .0058 = 0.9999 ppm***

Desired Exposure Limit	***1.0 PPM***	***0.5 PPM***	***0.1 PPM***
TVOC alarm setting	***172 PPM***	***86 PPM***	***17.2 PPM***

Questions?

- ***Thank you!***

Portable FTIR Gas Analyzers for Research, EH&S and HAZMAT Applications

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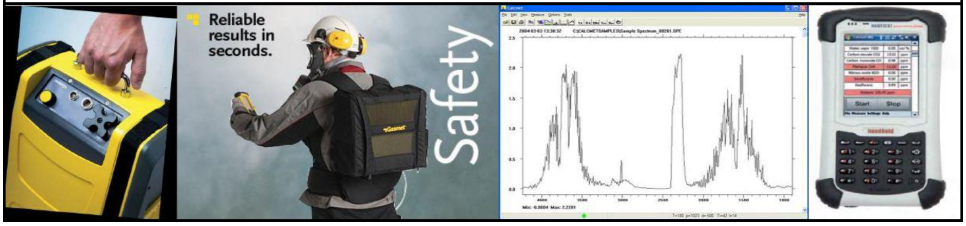
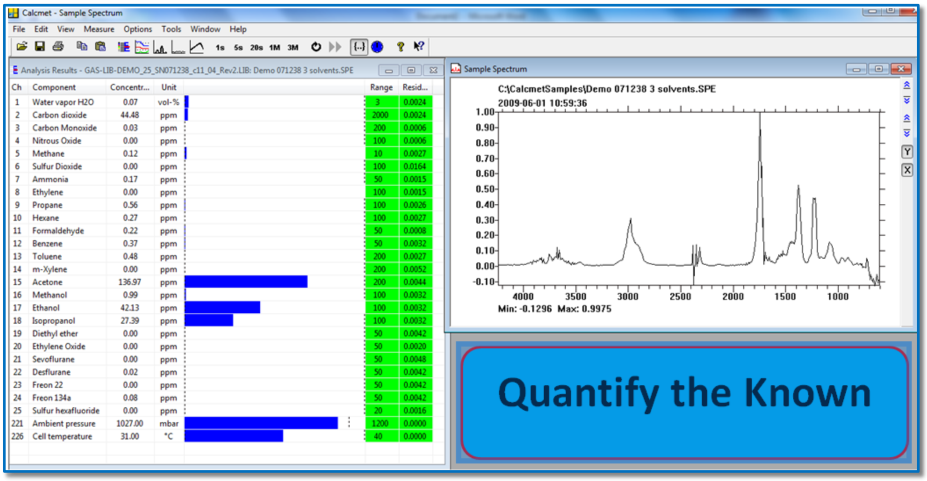
Sales & Technical Support
Gasmet Technologies
Tel : 1-866-685.0050
Jim.cornish@gasmet.com



A. Dual Functionality of FTIR
Protecting employees - Assessing exposures

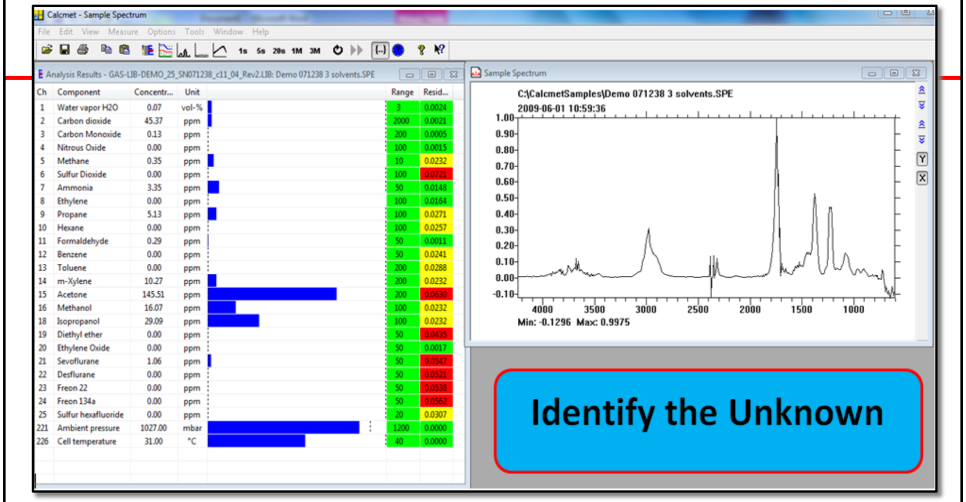


Analysis Results - GAS-LIB-DEMO_25_SN071238_c11_04_Rev2.LIB: Demo 071238 3 solvents.SPE

Ch	Component	Concentr...	Unit	Range	Resid...
1	Water vapor H2O	0.07	vol-%	3	0.0024
2	Carbon dioxide	44.48	ppm	2000	0.0024
3	Carbon Monoxide	0.03	ppm	200	0.0006
4	Nitrous Oxide	0.00	ppm	100	0.0006
5	Methane	0.12	ppm	10	0.0027
6	Sulfur Dioxide	0.00	ppm	100	0.0164
7	Ammonia	0.17	ppm	50	0.0015
8	Ethylene	0.00	ppm	100	0.0015
9	Propane	0.56	ppm	100	0.0026
10	Hexane	0.27	ppm	100	0.0027
11	Formaldehyde	0.22	ppm	50	0.0008
12	Benzene	0.37	ppm	50	0.0032
13	Toluene	0.48	ppm	200	0.0027
14	m-Xylene	0.00	ppm	200	0.0052
15	Acetone	136.97	ppm	200	0.0044
16	Methanol	0.99	ppm	100	0.0032
17	Ethanol	42.13	ppm	100	0.0032
18	Isopropanol	27.39	ppm	100	0.0032
19	Diethyl ether	0.00	ppm	50	0.0042
20	Ethylene Oxide	0.00	ppm	50	0.0020
21	Sevoflurane	0.00	ppm	50	0.0048
22	Desflurane	0.02	ppm	50	0.0042
23	Freon 22	0.00	ppm	50	0.0042
24	Freon 134a	0.08	ppm	50	0.0042
25	Sulfur hexafluoride	0.00	ppm	20	0.0016
221	Ambient pressure	1027.00	mbar	1200	0.0000
226	Cell temperature	31.00	°C	40	0.0000

Protecting Worker Health

B. Dual Functionality of FTIR
Solving air quality problems



Analysis Results - GAS-LIB-DEMO_25_SN071238_c11_04_Rev2.LIB: Demo 071238 3 solvents.SPE

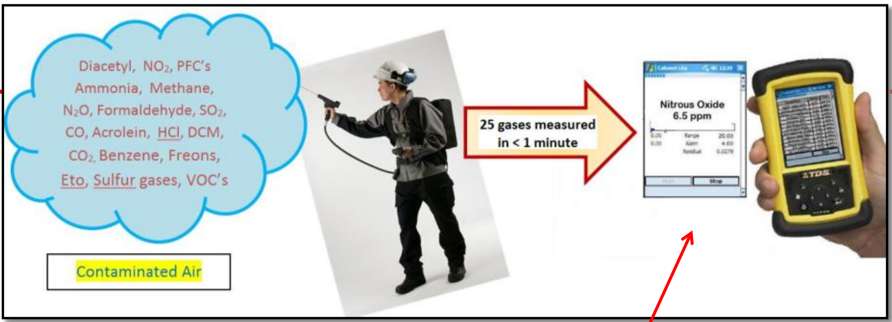
Ch	Component	Concentr...	Unit	Range	Resid...
1	Water vapor H2O	0.07	vol-%	3	0.0024
2	Carbon dioxide	45.37	ppm	2000	0.0021
3	Carbon Monoxide	0.13	ppm	200	0.0005
4	Nitrous Oxide	0.00	ppm	100	0.0015
5	Methane	0.35	ppm	10	0.0232
6	Sulfur Dioxide	0.00	ppm	100	0.0721
7	Ammonia	3.35	ppm	50	0.0148
8	Ethylene	0.00	ppm	100	0.0164
9	Propane	5.13	ppm	100	0.0271
10	Hexane	0.00	ppm	100	0.0257
11	Formaldehyde	0.29	ppm	50	0.0011
12	Benzene	0.00	ppm	50	0.0241
13	Toluene	0.00	ppm	200	0.0288
14	m-Xylene	10.27	ppm	200	0.0232
15	Acetone	145.51	ppm	200	0.0630
16	Methanol	16.07	ppm	100	0.0232
18	Isopropanol	29.09	ppm	100	0.0232
19	Diethyl ether	0.00	ppm	50	0.0435
20	Ethylene Oxide	0.00	ppm	50	0.0017
21	Sevoflurane	1.06	ppm	50	0.0547
22	Desflurane	0.00	ppm	50	0.0521
23	Freon 22	0.00	ppm	50	0.0538
24	Freon 134a	0.00	ppm	50	0.0562
25	Sulfur hexafluoride	0.00	ppm	20	0.0307
221	Ambient pressure	1027.00	mbar	1200	0.0000
226	Cell temperature	31.00	°C	40	0.0000

C:\CalcmetSamples\Demo 071238 3 solvents.SPE
2009-06-01 10:59:36

Min: -0.1296 Max: 0.9975

Identify the Unknown

Understanding the power of FTIR[1] gas analysis


Diacetyl, NO_2, PFC's
Ammonia, Methane,
N_2O, Formaldehyde, SO_2,
CO, Acrolein, HCl, DCM,
CO_2, Benzene, Freons,
Eto, Sulfur gases, VOC's

Contaminated Air

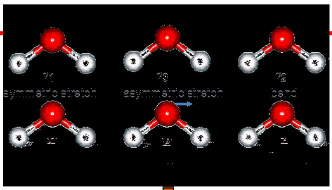
25 gases measured
in < 1 minute

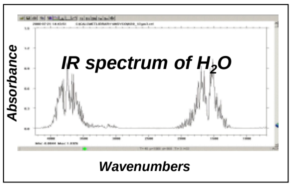
- *FTIR Gas Analysis using a combination of optical light measurement and a mathematical algorithm to measure many gases and their concentrations simultaneously.*

The 25 gases can be chosen from a library of 335 gases. (Reference Library)

[1] *FTIR = Fourier Transform Infrared*

FTIR Measurement Technology





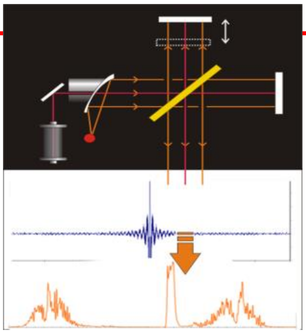
Beer's law: A = ε.b.c

Measure all asymmetric Gas Molecules exceptions

Diatomic homonuclear molecules such as O_2, N_2, H_2, Cl_2, F_2, & the noble gases (He, Ne, Ar..) & "H_2S" is a very weak IR absorber

IR

FTIR



Two Steps –

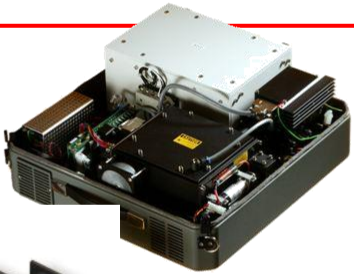
1). Interferometer modulates _ Mirror Moves_ Interferogram

2). Apply mathematics (Fourier Transform) to derive IR Spectrum

IR spectrum measured 10 cycles/sec (10Hz)
Internal calibration with precise laser

Daily Zero calibration, no recalibration required
Fast, extremely accurate measurements

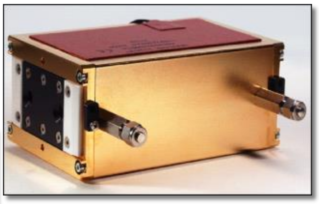
FTIR Gas Analyzer



Interferometer

Compact – Rugged
Fast scanning
Vibration insensitive

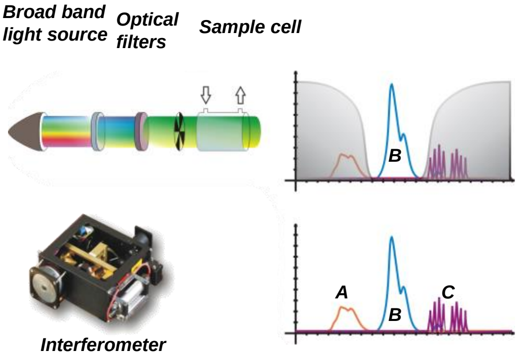
Gas Cell



Corrosion resistant sample cell
Nickel-rhodium-gold plated

Comparing IR Technologies

- *Gas Filter Correlation NDIR (GFC)*
  - ***Measures only separate wavelength bands with gas-filled filters***
  - ***Only one component can be measured with each filter***
  - ***Multiple gases can be measured and spectral interference resolved only with additional filters (typically maximum 6 gases)***
- *Fourier Transform Infrared (FTIR)*
  - ***Spectrometer measures all the IR wavelengths simultaneously and produces a full spectrum.***
  - ***Any number of components (up to 50) can be analysed from single measurement and interferences are automatically resolved***
  - ***Same optical elements used for each measurement, multiple calibration checks are not necessary***


Broad band light source
Optical filters
Sample cell
Interferometer

FTIR Measuring Gases or Solids & Liquids

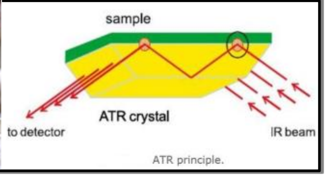
Density of gases ~1000 lower than solids/liquids

Beer's Law : $A= \varepsilon.b.c$
b = long for gases, short for solids & liquids

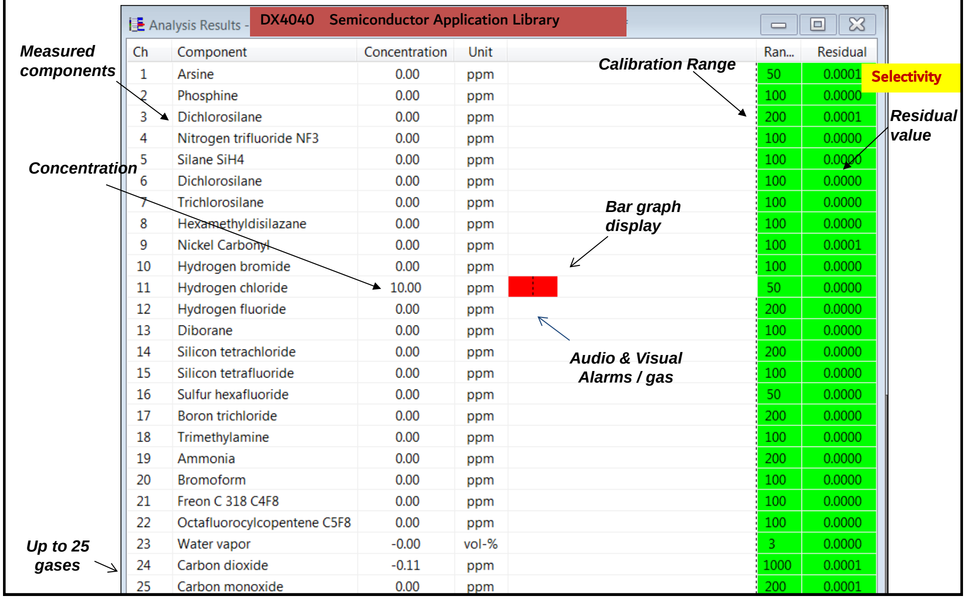
- ***White Cell*** *- Nickel-rhodium-gold plated mirrors & aluminium cell body*
- *Pathlength to 9.8 m multi-pass*
- *Cell windows (ZnSe, immune to water vapour)*
- ***Gas Measurement Range** :*

  Sub-ppm to % levels

***ATR** (Attenuated Total Reflection),*
Solids & Liquids



FTIR provides simultaneous multi-gas readings (25)



Ch	Component	Concentration	Unit		Ran...	Residual
1	Arsine	0.00	ppm		50	0.0001
2	Phosphine	0.00	ppm		100	0.0000
3	Dichlorosilane	0.00	ppm		200	0.0001
4	Nitrogen trifluoride NF3	0.00	ppm		100	0.0000
5	Silane SiH4	0.00	ppm		100	0.0000
6	Dichlorosilane	0.00	ppm		100	0.0000
7	Trichlorosilane	0.00	ppm		100	0.0000
8	Hexamethyldisilazane	0.00	ppm		100	0.0000
9	Nickel Carbonyl	0.00	ppm		100	0.0001
10	Hydrogen bromide	0.00	ppm		100	0.0000
11	Hydrogen chloride	10.00	ppm	🟥	50	0.0000
12	Hydrogen fluoride	0.00	ppm		200	0.0000
13	Diborane	0.00	ppm		100	0.0000
14	Silicon tetrachloride	0.00	ppm		200	0.0000
15	Silicon tetrafluoride	0.00	ppm		100	0.0000
16	Sulfur hexafluoride	0.00	ppm		50	0.0000
17	Boron trichloride	0.00	ppm		200	0.0000
18	Trimethylamine	0.00	ppm		100	0.0000
19	Ammonia	0.00	ppm		200	0.0000
20	Bromoform	0.00	ppm		100	0.0000
21	Freon C 318 C4F8	0.00	ppm		100	0.0000
22	Octafluorocyclopentene C5F8	0.00	ppm		100	0.0000
23	Water vapor	-0.00	vol-%		3	0.0000
24	Carbon dioxide	-0.11	ppm		1000	0.0001
25	Carbon monoxide	0.00	ppm		200	0.0001

Application for Portable FTIR Multi-Gas Analyzers

Applications include :

- ***VOC's in the Workplace***
- ***Contaminated Sites***
- ***Hazmat/Emergency response***
- ***Medical Gases Testing***
- ***Clandestine labs***
- ***Fumigants***
- ***Semiconductor Gases***
- ***Greenhouse Gases (GHG's)***

FTIR _ Sensitivity (mdl's)

1. *Acrolein – (0.13 ppm)*
2. *Acrylonitrile - (0.18 ppm)*
3. *Ammonia - (0.07 ppm)*
4. *Arsine - (0.01 ppm)*
5. *Benzene - (0.07 ppm)*
6. *Boron trichloride – (0.005 ppm)*
7. *Carbon dioxide – (< 10 ppm)*
8. *Carbon monoxide – (0.12 ppm)*
9. *Carbon disulfide - (0.09 ppm)*
10. *Dichloromethane – (0.06 ppm)*
11. *Ethylene oxide - (0.08 ppm)*
12. *Formaldehyde – (0.04 ppm)*
13. *Hydrogen chloride – (0.10 ppm)*
14. *Hydrogen cyanide – (0.17 ppm)*
15. *Hydrogen fluoride – (0.15 ppm)*
16. *Methane - (0.03 ppm)*
17. *Methyl mercaptan – (0.21 ppm)*
18. *Nitrogen dioxide – (0.19 ppm)*
19. *Nitrous oxide – (0.01ppm)*
20. *Phosgene – (0.01 ppm)*
21. *Phosphine – (0.10 ppm)*
22. *Sulfur dioxide – (0.02 ppm)*
23. *Sulfuryl fluoride – (0.02 ppm)*
24. *Toluene – (0.06 ppm)*
25. *Water Vapour*

Sub-ppm / ppb

Gas dependent

Or select from a calibration library to create site specific gas calibration libraries

---

Solving Air Quality Issues

"Assessing Unknown Odors and Chemicals"

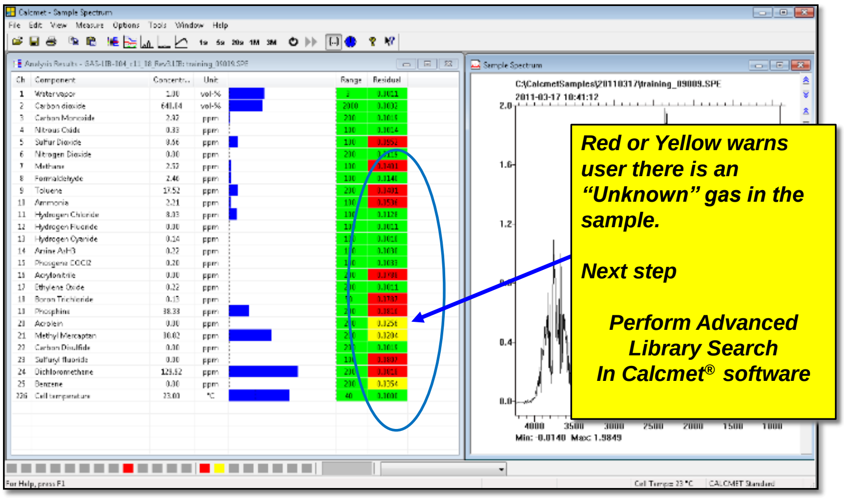
What if the responder has no information on the source of the gas or vapor ?

Time of Response is essential

Utilizing full power of FTIR

Calcmet™ Advanced Library Search

Identification of unknown gases



Ch	Component	Concentr...	Unit
1	Water vapor	1.00	vol-%
2	Carbon dioxide	641.04	vol-%
3	Carbon Monoxide	2.92	ppm
4	Nitrous Oxide	0.33	ppm
5	Sulfur Dioxide	8.56	ppm
6	Nitrogen Dioxide	0.00	ppm
7	Methane	2.52	ppm
8	Formaldehyde	2.46	ppm
9	Toluene	17.52	ppm
10	Ammonia	2.21	ppm
11	Hydrogen Chloride	8.03	ppm
12	Hydrogen Fluoride	0.00	ppm
13	Hydrogen Cyanide	0.14	ppm
14	Arsine AsH3	0.22	ppm
15	Phosgene COCl2	0.20	ppm
16	Acrylonitrile	0.00	ppm
17	Ethylene Oxide	0.22	ppm
18	Boron Trichloride	0.13	ppm
19	Phosphine	38.33	ppm
20	Acrolein	0.00	ppm
21	Methyl Mercaptan	30.02	ppm
22	Carbon Disulfide	0.00	ppm
23	Sulfuryl fluoride	0.00	ppm
24	Dichloromethane	129.52	ppm
25	Benzene	0.00	ppm
226	Cell temperature	23.00	°C

C:\CalcmetSamples\20110317\training_09009.SPE
2011-03-17 10:41:12
Min: -0.0140 Max: 1.9849

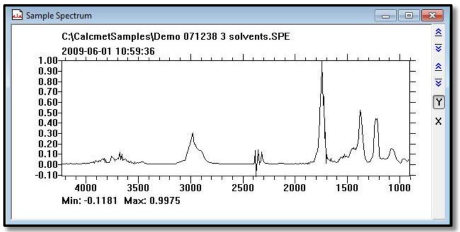
Red or Yellow warns user there is an "Unknown" gas in the sample.

Next step

Perform Advanced Library Search In Calcmet® software

Identifying "Unknown" Gases

The Power and speed of FTIR !

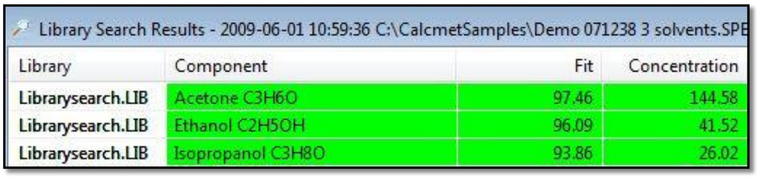


C:\CalcmetSamples\Demo 071238 3 solvents.SPE
2009-06-01 10:59:36
Min: -0.1181 Max: 0.9975

Advanced Library Search

Search Reference Library, over 350+ gases

Search NIST/EPA Library, over 5000 gases



Library Search Results - 2009-06-01 10:59:36 C:\CalcmetSamples\Demo 071238 3 solvents.SPE

Library	Component	Fit	Concentration
Librarysearch.LIB	Acetone C3H6O	97.46	144.58
Librarysearch.LIB	Ethanol C2H5OH	96.09	41.52
Librarysearch.LIB	Isopropanol C3H8O	93.86	26.02

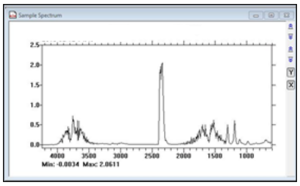
Case Study

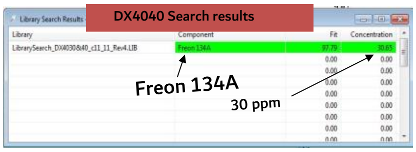
Identify the Unknown

Freon leak goes undetected at Texas University

Analysis Results - GAS-LIB-004_SN112203_c11_11_Rev1.LIB: spe_000392.spe

Ch	Component	Concentration	Unit	Range	Resid...
1	Water vapor	0.62	vol-%	3	0.0004
2	Carbon dioxide	674.13	ppm	2000	0.0014
3	Carbon Monoxide	0.00	ppm	200	0.0015
4	Nitrous Oxide	0.30	ppm	100	0.0008
5	Sulfur Dioxide	0.00	ppm	100	0.4425
6	Nitrogen Dioxide	2.06	ppm	50	0.0022
7	Methane	1.84	ppm	100	0.0103
8	Formaldehyde	0.25	ppm	50	0.0010
9	Toluene	0.00	ppm	200	0.0101
10	Ammonia	2.93	ppm	50	0.0824
11	Hydrogen Chloride	0.00	ppm	50	0.0022
12	Hydrogen Fluoride	0.00	ppm	50	0.0006
13	Hydrogen Cyanide	0.00	ppm	50	0.0005
14	Arsine	0.01	ppm	50	0.0013
15	Phosgene	0.18	ppm	50	0.0020
16	Acrylonitrile	15.67	ppm	50	0.4521
17	Ethylene Oxide	0.15	ppm	50	0.0005
18	Boron Trichloride	0.00	ppm	50	0.4521
19	Phosphine	0.00	ppm	50	0.4671
20	Acrolein	0.00	ppm	50	0.0031
21	Methyl Mercaptan	32.35	ppm	200	0.0059
22	Carbon Disulfide	0.82	ppm	200	0.0009
23	Sulfuryl fluoride	0.00	ppm	50	0.4381
24	Dichloromethane	0.00	ppm	200	0.4495
25	Benzene	0.00	ppm	50	0.0144
226	Cell temperature	28.00	°C	40	0.0000





DX4040 Search results

Library Search Results

Library	Component	Fit	Concentration
LibrarySearch_DX4030&40_c11_11_Rev4.LIB	Freon 134A	97.79	30.65
		0.00	0.00
		0.00	0.00
		0.00	0.00
		0.00	0.00
		0.00	0.00
		0.00	0.00
		0.00	0.00

Freon 134A

30 ppm

Calcmet™ Advanced Library Search

Case Study :

Identify the Unknown

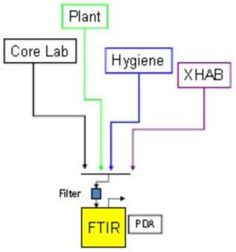
Hospital lab. staff evacuated after chemical leak

***Region 2 South TSRT Coordinator*, was notified of a potential gas or vapor leak in the Human Pathology Laboratory at St. Joseph Hospital, MI.**

"We were advised that the suspicion was increased levels of Formaldehyde. We ran tests in five different work areas within the lab. With the FTIR gas analyzer we were able to simultaneously test for 50 different gases/vapors using quantitative and qualitative analysis. The results of our tests revealed that the substance was Toluene and not Formaldehyde. The levels were well within safe limits of all found substances as well as TWA's [Time Weighted Averages]"

"The FTIR Gas Analyzer performed flawlessly and proved it's capability beyond doubt. The TSRT had a successful training deployment and had many educational benefits from the experience." ***Bob Lovelace _ Region 2 South TSRT Coordinator***

Case Study – NASA



- FTIR used to monitor trace contaminants over 10 day Mission Op. Test
- Oscar trained integrated JSC team on setup, zeroing & downloading data
- An application composed of 20 gases & FTIR zeroed using N_2 gas every time it was relocated.
- Not all the 20 gases in the application sampled were detected
- It was possible to measure dynamic VOC concentrations in each DSH location.

Case Study – NASA

Dynamic Sampling of Cabin VOCs during the Mission Operations Test of the Deep Space Habitat

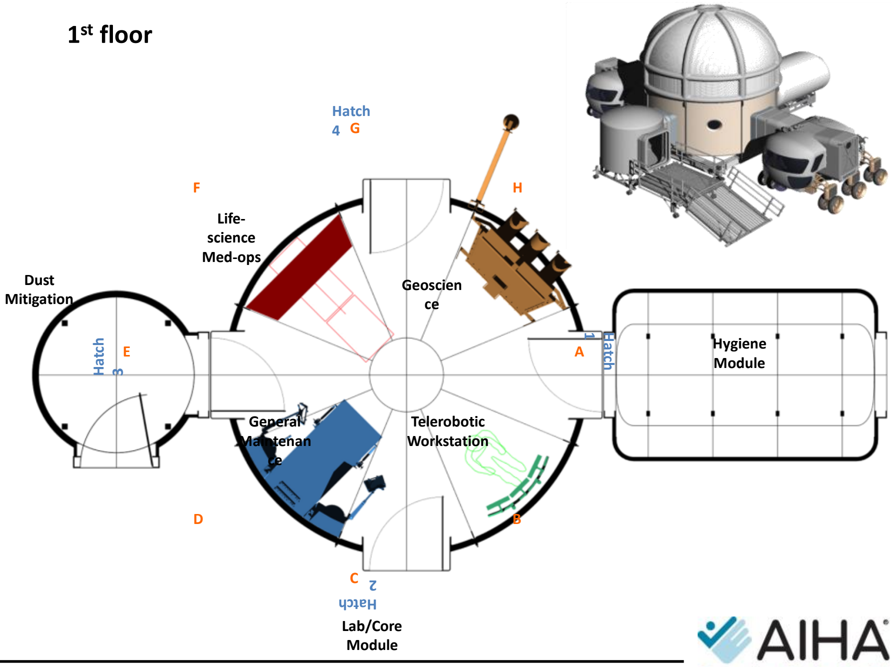
Oscar Monje Research Scientist at KSC

A portable FTIR gas analyzer was used to monitor the atmospheric composition of four modules (lab, Veggie station, hygiene module, and Xhab loft) within the Deep Space Habitat (DSH) during the Mission Operations Test (MOT) conducted at the Johnson Space Center.

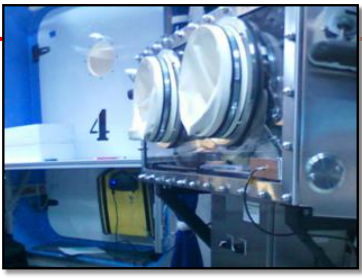
Spacecraft Cabin Air

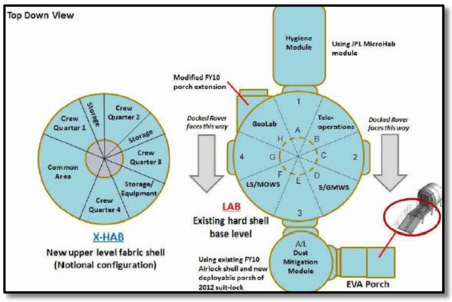
- ***The atmospheric composition inside spacecraft during long duration space missions is dynamic due to changes in the living and working environment of crew members, crew metabolism and payload operations.***
- ***Determines crew health (i.e. prevent accumulation of trace contaminants – NH_3 – irritant, Formaldehyde, health)***
- ***Determines crew comfort (i.e. humidity, temperature)***
- ***A portable FTIR gas analyzer was used to monitor the atmospheric composition within the Deep Space Habitat (DSH) during the Mission Operations Test (MOT) conducted at the Johnson Space Center (JSC).***

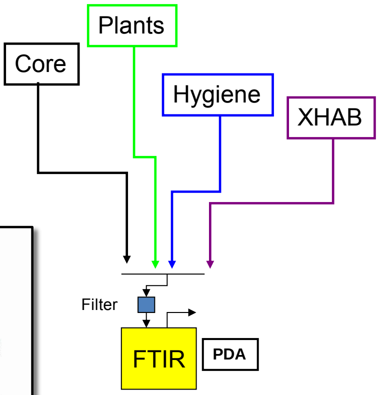
1st floor



Sampling DSH Air

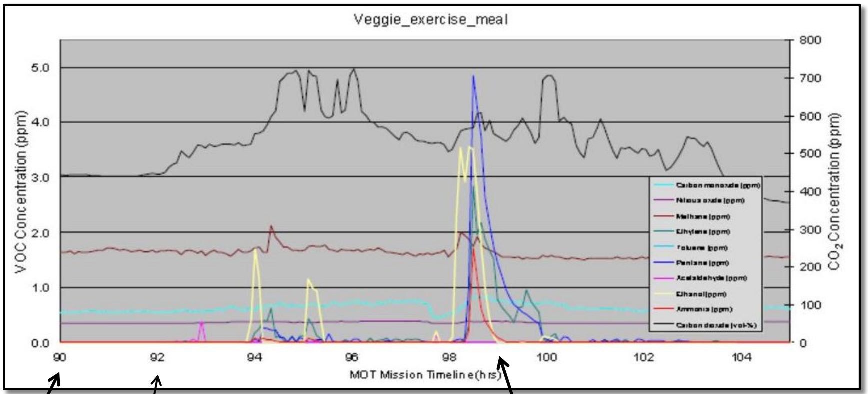






Case Study – NASA

Results & Discussion



Wake

Exercise

Lunch _Prep & eating

----------------------------Crew Activities---------------------------------

Instrument Maintenance

Low Cost of Ownership

Zero gas (Nitrogen, purity 5.0 (99.999%)

Capacity : 552L. Typical usage per zero : 10L
~ 1 year / cylinder based on weekly usage.

Other gas cylinder sizes available. Easy local supply

Particulate Filters

Weekly visual inspection of sample probe filter (change the filter, if necessary).

Anticipate filter change out for each 3 months.
Set of 5 spare filters supplied

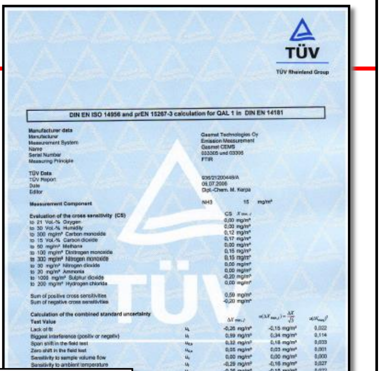
No requirement to send instrument back to manufacturer for annual service

AIHA
Protecting Worker Health

Validation & Certification

FTIR Methodology accepted by leading test organizations including :

- ***NIOSH Method 3800 (Organic & Inorganic gases by extractive FTIR spectrometry)***
- ***USEPA Method 320***
- ***ASTM Method D6348***
- ***TUV & MCERTS 3rd party verification***



TÜV
TÜV Rheinland Group

DIN EN ISO 14956 and prEN 15267-3 calculation for QAL 1 in DIN EN 14181

Manufacturer data	
Manufacturer	Gasmet Technologies Oy
Measurement System	Emission Measurement
Name	Gasmet CEMS
Serial Number	033305 und 03306
Measuring Principle	FTIR
TÜV Data	
TÜV Report	936/21200448/A
Date	09.07.2006
Editor	Dipl.-Chem. M. Karpa
Measurement Component	NH3 15 mg/m³

Evaluation of the cross sensitivity (CS)	CS
to 21 Vol.-% Oxygen	0,00 mg/m³
to 30 Vol.-% Humidity	0,00 mg/m³
to 300 mg/m³ Carbon monoxide	0,12 mg/m³
to 15 Vol.-% Carbon dioxide	0,17 mg/m³
to 50 mg/m³ Methane	0,00 mg/m³
to 100 mg/m³ Distrogen monoxide	0,15 mg/m³
to 300 mg/m³ Nitrogen monoxide	0,15 mg/m³
to 30 mg/m³ Nitrogen dioxide	0,00 mg/m³
to 20 mg/m³ Ammonia	0,00 mg/m³
to 1000 mg/m³ Sulphur dioxide	-0,20 mg/m³
to 200 mg/m³ Hydrogen chloride	0,00 mg/m³
Sum of positive cross sensitivities	0,59 mg/m³
Sum of negative cross sensitivities	-0,20 mg/m³

Calculation of the combined standard uncertainty

quirements keep to QAL 1 of EN 14181

EDGEWOOD
CHEMICAL BIOLOGICAL CENTER

ECBC-TR-690

EVALUATION OF GASMET™ DX-4015 SERIES
FOURIER TRANSFORM INFRARED GAS ANALYZER

Earl Austin
Kenneth T. Hoang

DEPARTMENT OF PROGRAM INTEGRATION

June 2009

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Approved for public release;
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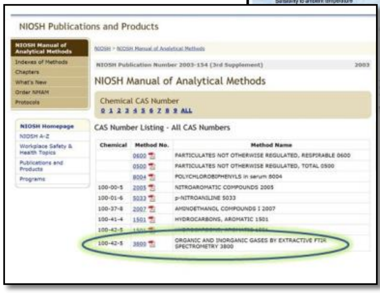
ABERDEEN PROVING GROUND, MD 21010-5424



NIOSH Publications and Products

NIOSH > NIOSH Manual of Analytical Methods

NIOSH Publication Number 2003-154 (3rd Supplement) 2003

NIOSH Manual of Analytical Methods

Chemical CAS Number
0 1 2 3 4 5 6 7 8 9 ALL

CAS Number Listing - All CAS Numbers

Chemical	Method No.	Method Name
	0600	PARTICULATES NOT OTHERWISE REGULATED, RESPIRABLE 0600
	0500	PARTICULATES NOT OTHERWISE REGULATED, TOTAL 0500
	8004	POLYCHLOROBIPHENYLS in serum 8004
100-00-5	2005	NITROAROMATIC COMPOUNDS 2005
100-01-6	5033	p-NITROANILINE 5033
100-37-8	2007	AMINOETHANOL COMPOUNDS I 2007
100-41-4	1501	HYDROCARBONS, AROMATIC 1501
100-42-5	1501	HYDROCARBONS, AROMATIC 1501
100-42-5	3800	ORGANIC AND INORGANIC GASES BY EXTRACTIVE FTIR SPECTROMETRY 3800

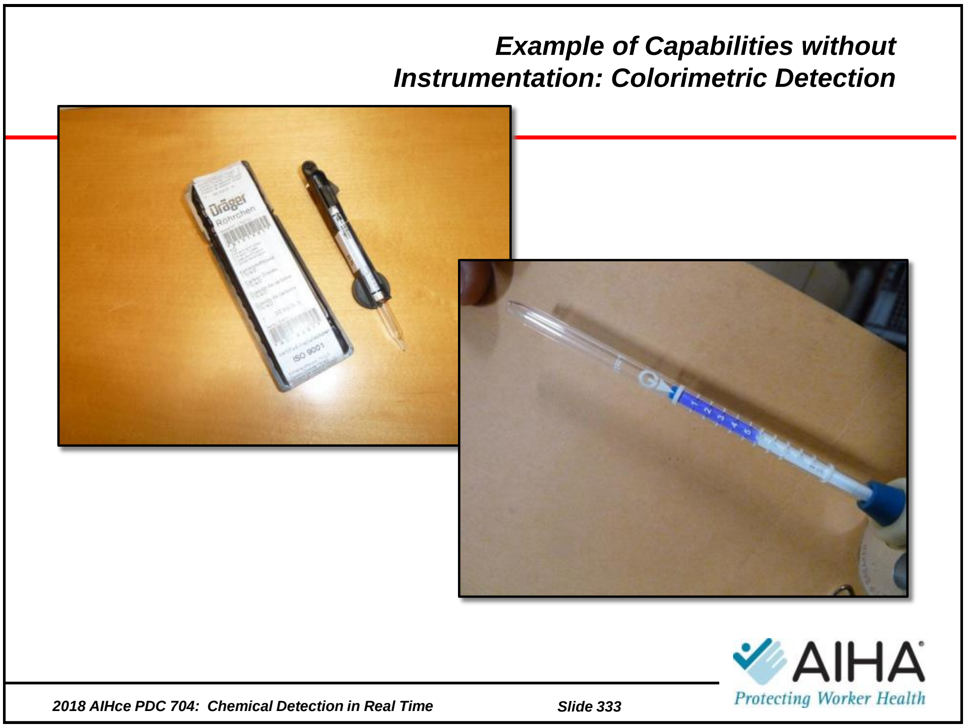
AIHA
Protecting Worker Health

Questions?

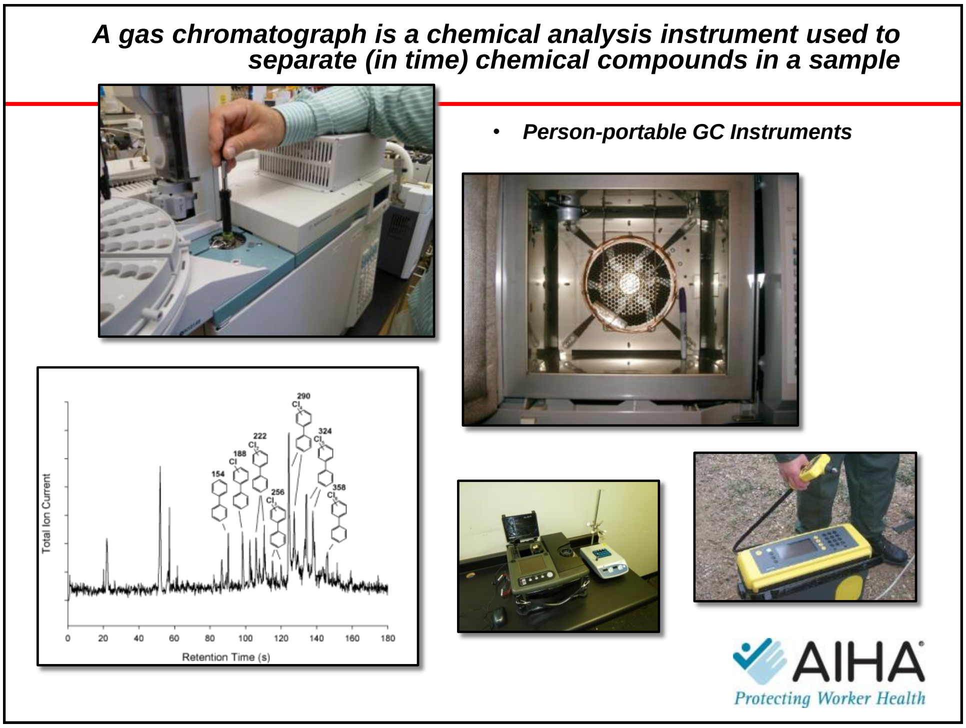
- ***Thank you!***

Portable Gas Chromatography

Phil Smith, PhD, CIH



Example of Capabilities without Instrumentation: Colorimetric Detection



A gas chromatograph is a chemical analysis instrument used to separate (in time) chemical compounds in a sample

- *Person-portable GC Instruments*

Why use GC?

Why use GC?

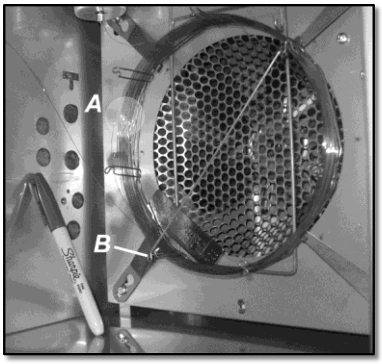
1. ***Provides high-certainty analyte ID based on retention time***
2. ***Area under GC peak is related to analyte concentration***

Arguing against GC use:

1. ***In the past a “full-capability” instrument was large and power-hungry***
2. ***Even modern versions, while smaller and capable of battery operation are still fairly large –require trained operator***
3. ***Sample prep, analysis can take considerable time***

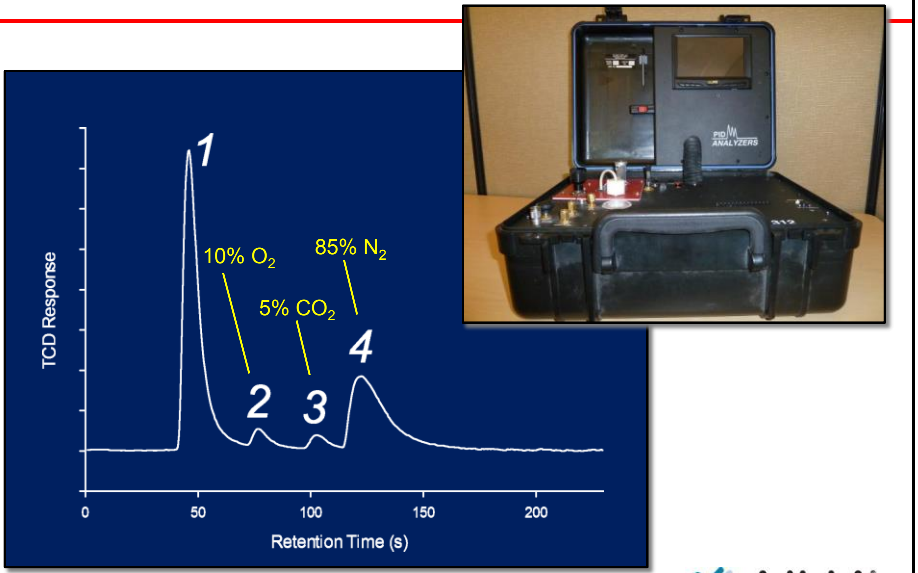
How does it work?

- ***In gas/liquid chromatography, individual chemical components are separated based on differential solubility in a thin liquid film that coats the inside of a capillary column: often 30 m long with 0.25 mm i.d., 0.25 micron film thickness***



- ***Analyte volatility is also an important factor; as this is temperature-dependent, precise control of column temperature is critical***

Adsorptive Stationary Phase, Isothermal Column Temperature

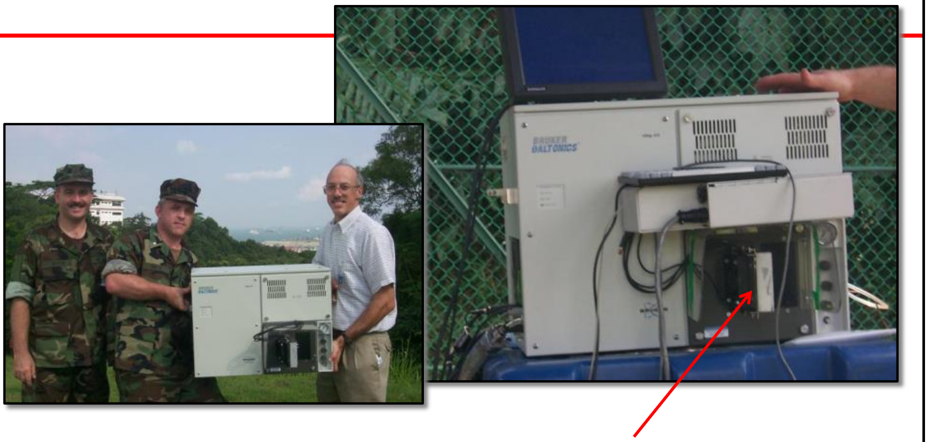


GC Analytes

1. *Organics*
    - *volatile below 350 - 400°C*
    - *Good semi-volatile analytes must be resistant to high temperature degradation and provide rapid transformation to vapor on heating*
2. *Inorganics, metals, salts*
    - *Not good analytes for GC/MS*
3. *Method of sample introduction into instrument must be compatible with sample (many options possible)*

Field GC Systems

Can we speed up analysis and make field-portable systems smaller, and less power intensive?



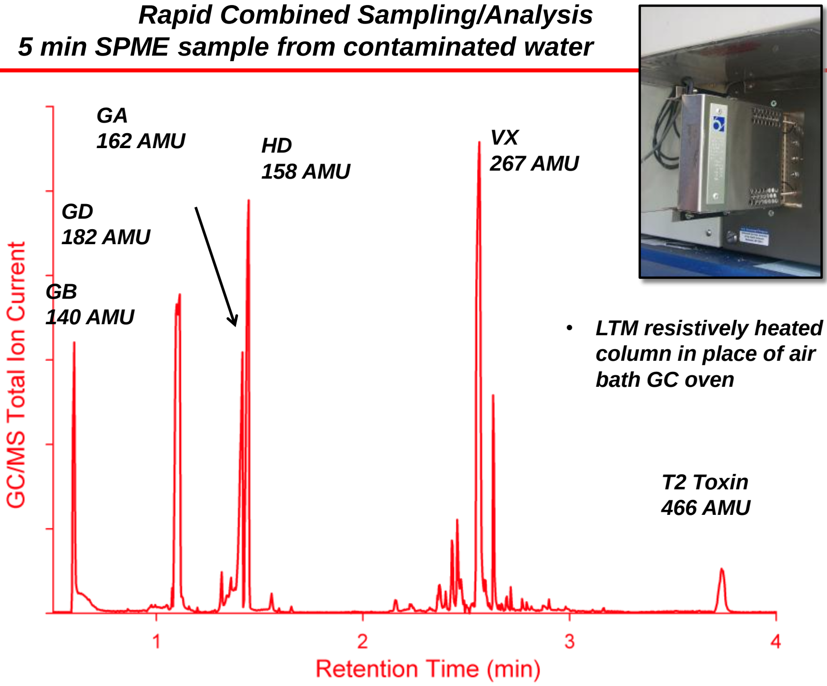
- *Resistively heated LTM GC column (externally mounted)*

Smaller and Faster GC/MS Systems…

- ***Resistively heated GC (fast, small, 100 w power use)***

- ***Air bath oven (slow, large, power hungry)***

Rapid Combined Sampling/Analysis
5 min SPME sample from contaminated water



- ***LTM resistively heated column in place of air bath GC oven***

Portable Mass Spectrometry (Gas Chromatography-Mass Spectrometry)

Phil Smith, PhD, CIH

Gas Chromatography

- ***A gas chromatograph is a chemical analysis instrument for separating chemical compounds in a sample***

Mass Spectrometry

- ***Mass spectrometry measures the mass-to-charge ratio of ions. When molecules of a pure compound are reproducibly fragmented and ionized, the method provides a mass spectrum that can be used to determine the chemical composition of the material. A mass spectrum can be interpreted following predictable rules, and can be searched against a mass spectra database to help identify initially unknown compounds.***

- ***A mass spectrum can be though of as a "fingerprint" for a given chemical.***

What can GC-MS do?

- ***GC-MS can provide "high-certainty" identification of chemical components -even trace-level chemicals in complex mixtures.***

Why use GC-MS?

1. ***"Gold standard" orthogonal data provided***
2. ***Capable of identifying unknown compounds by mass spectrum match***

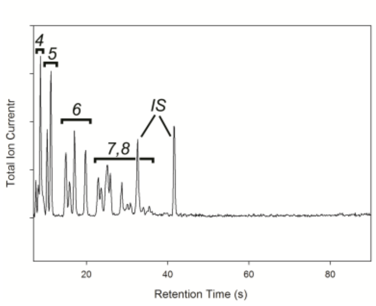
Arguing against GC-MS use:

1. ***Large, power-hungry instrument (until recently)***
2. ***Spectral interpretation can be difficult***
3. ***Sample prep, analysis can take considerable time***

How does it work?

1. ***GC separates individual chemical components (see previous discussion on GC as a stand-alone detection technology)***

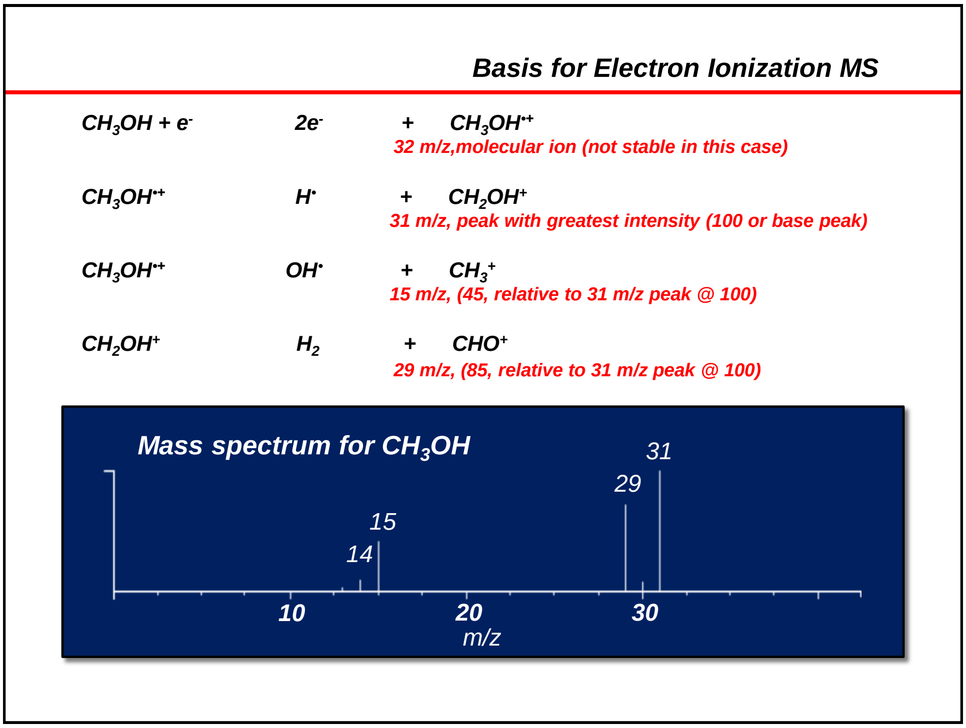
2. ***MS can then identify the (hopefully) pure components***



Data Demonstration…

Show GC-MS data from within GC-MS software, demonstrating concepts of…

1. ***GC peaks***
2. ***Mass spectra***
3. ***Explain concept of MS scanning and data 3-dimensionality***



Basis for Electron Ionization MS

$CH_3OH + e^-$ $2e^-$ + $CH_3OH^{\bullet+}$

32 m/z,molecular ion (not stable in this case)

$CH_3OH^{\bullet+}$ $H^{\bullet}$ + CH_2OH^+

31 m/z, peak with greatest intensity (100 or base peak)

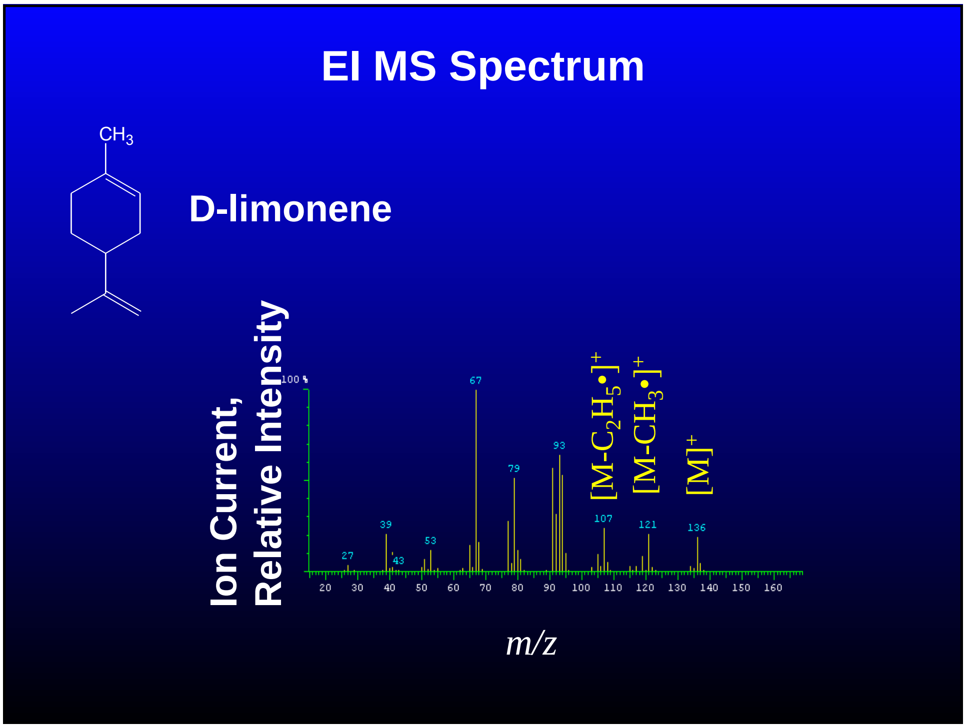
$CH_3OH^{\bullet+}$ $OH^{\bullet}$ + CH_3^+

15 m/z, (45, relative to 31 m/z peak @ 100)

CH_2OH^+ H_2 + CHO^+

29 m/z, (85, relative to 31 m/z peak @ 100)

Mass spectrum for CH_3OH



EI MS Spectrum

D-limonene

Need for Trained GC-MS Operators…

Problems:

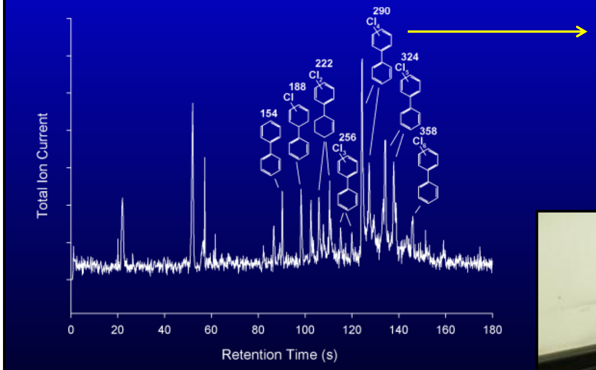
(1) Total reliance on mass spectrum database search can lead to misidentification

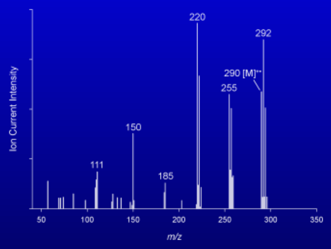
(2) GC-MS instruments are complex and require careful operation and regular maintenance

(3) Steep learning curve –constant practice (use) needed for optimum proficiency

---

Identification of Unexpected Unknowns by GC-MS





GC-MS Field Analysis Case Study

Problem: Initially unknown exposures to volatile organic chemicals among legislative workers handling mail irradiated as a protection against anthrax

Why use GC-MS for this problem?

(1) Complex mixture with many trace components

(2) Initially, composition completely unknown

GC-MS Field Analysis Case Study –Irradiated Mail

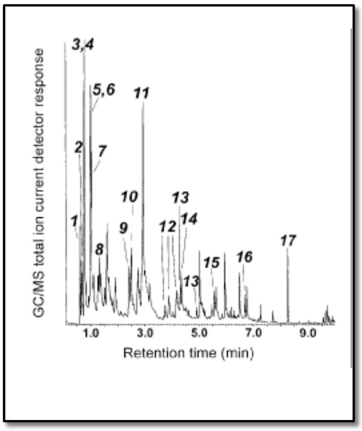
- ***A seemingly simple question: "what's in the sample?"***
- ***Complexities of GC-MS analysis are demonstrated by this project: initial qualitative screen needed first, then different (non-standard) column and sample introduction methods needed to definitively identify a good number of the VOCs present from mail irradiation***
- ***Also, quantitative sampling should not be attempted without first identifying the compounds present***

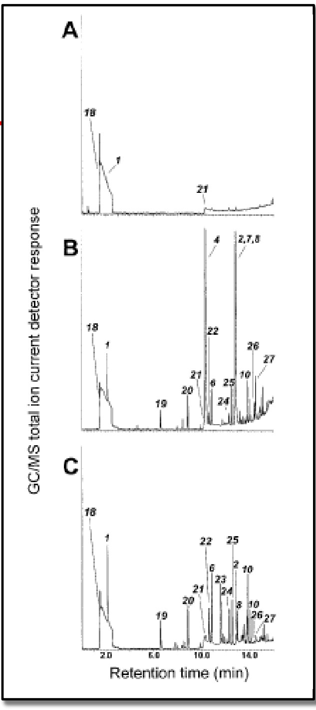
Initial GC-MS Instrumentation Used

Typical GC air bath oven

GC-MS with Mobile Laboratory

- ***Initial screening samples showed rich mix of volatile organic compounds; poor GC resolution meant that different column was needed…***





GC-MS Analyses for Irradiated Mail Project Moved into Laboratory…

Questions?

- ***Thank you!***

Scenario 1

Location: A new-construction manhole that has not yet been connected to an active sewer system

Situation: A worker has entered and exited this manhole numerous times this week. Today, a worker entered the manhole and a few minutes later his supervisor at the surface called to him with no response. When the supervisor looked in the manhole he noticed that the worker was slumped over and not moving.

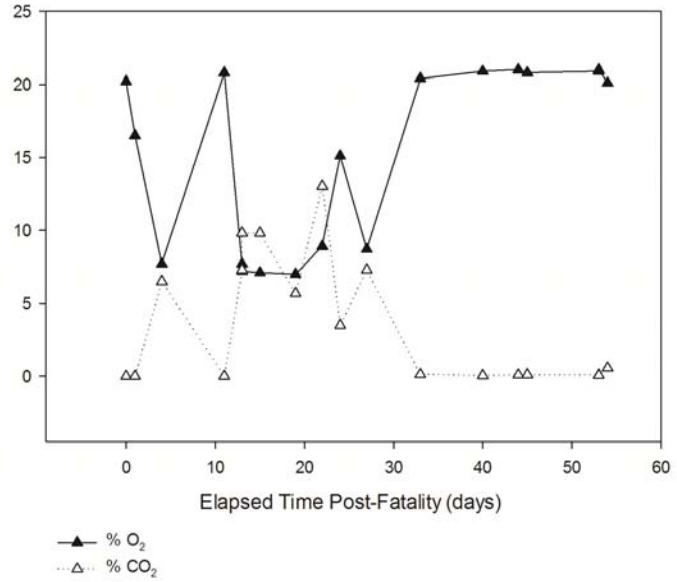
Real-Time Detection Tool Selection:

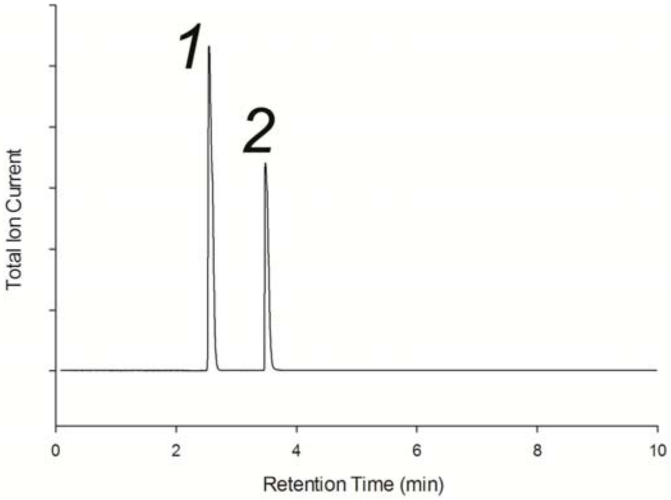
A. What are the possible types of atmospheric hazards and how dangerous is this situation?

B. What types of detection tools should have been used prior to entry?

C. What limitations exist for the detection tools you selected?

D. Describe the training and experience needed to correctly operate the selected detection tools


25
20
15
10
5
0
0
10
20
30
40
50
60
Elapsed Time Post-Fatality (days)
▲ % O_2
△ % CO_2


1
2
Total Ion Current
0
2
4
6
8
10
Retention Time (min)

Below-Ground Fatalities (Partial Listing): No Connection to a Sewer System

State	Year/ Month	Work Process	Fatalities/ Near-Misses	Confined Space Atmosphere
MO	2011/10	Working in new manhole	1/1	lowO_2/high CO_2
NC	2011/06	Working in manhole	2/0	low O_2
TX	2009/04	Fell in manhole/rescue attempt	1/1	low O_2
IL	2007/06	Working in new water vault	2/1	low O_2
LA	2007/08	Grouting in manhole	2/0	low O_2
GA	2006/09	Retrieving laser equipment	1/0	low O_2
TX	2005/07	Testing new storm sewer line	1/0	low O_2
ND	2005/07	Completing new manhole	1/0	–
WI	2005/06	Testing prior to sewer hookup	2/0	–
TN	2004/09	Working in new manhole	2/0	low O_2
MO	2004/08	Grouting in manhole	1/0	low O_2/high CO_2
PA	2004/07	Entry into new manhole	2/0	low O_2
GA	2004/07	Opening valve in water vault	1/1	low O_2/high CO_2
WI	2003/08	Opening valve in water vault	1/0	low O_2/high CO_2
FL	2003/08	Leak repair in new manhole	1/1	–
NC	2003/03	Entry into water vault manhole	1/0	low O_2
TX	2001/12	Checking grade in 24” water pipe	1/0	–
KS	2001/08	Vacuum testing new sewer line	3/0	low O_2/high CO_2
OH	2000/09	Working in new manhole	2/0	low O_2/high CO_2
CA	2000/05	Working in sump manhole	2/0	low O_2

Scenario 2

Location: A manufacturing site where methylene diphenyl diisocyanate (MDI) is stored in a large heated tank.

Situation: A problem developed with the MDI tank heaters over a weekend. The heaters ran continuously and overheated the MDI, leaving a solid mass of material in the tank. A worker entered the tank with a jackhammer to work on the solidified material and spent about 50 minutes inside. He began to feel sick, and the crew broke for lunch. The tank entrant stayed in the air-conditioned vehicle used to drive to Taco Bell while co-workers ordered lunch, but entered to tell them he couldn't hold his head up. He was driven to a hospital, but en route the crew pulled over and an ambulance was called as the tank entrant's condition was worsening. He was admitted to the hospital with methemoglobinemia where he remained for more than 5 weeks. The tank entrant suffered brain damage due to chemical hypoxia (among other maladies).

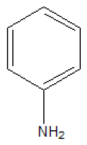
Real-Time Detection Tool Selection:

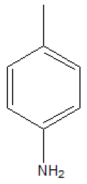
A. What are the possible types of atmospheric hazards and how dangerous is this situation?

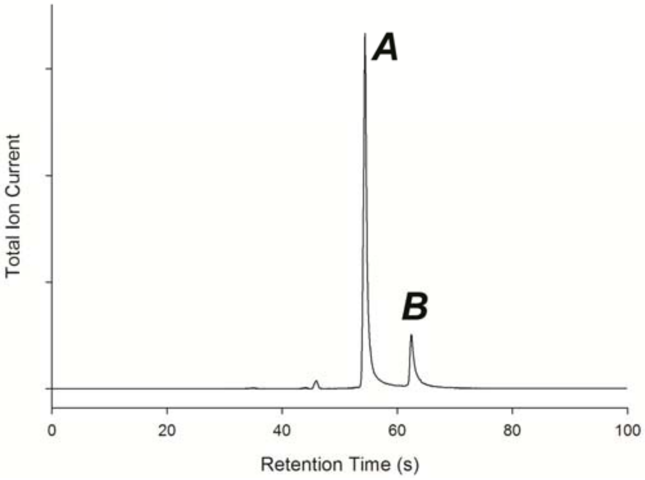
B. What types of detection tools should be used to identify potential airborne stressors?

C. What limitations exist for the detection tools you selected?

D. Describe the training and experience needed to correctly operate the selected detection tools







Person-portable GC-MS (carry-on luggage)

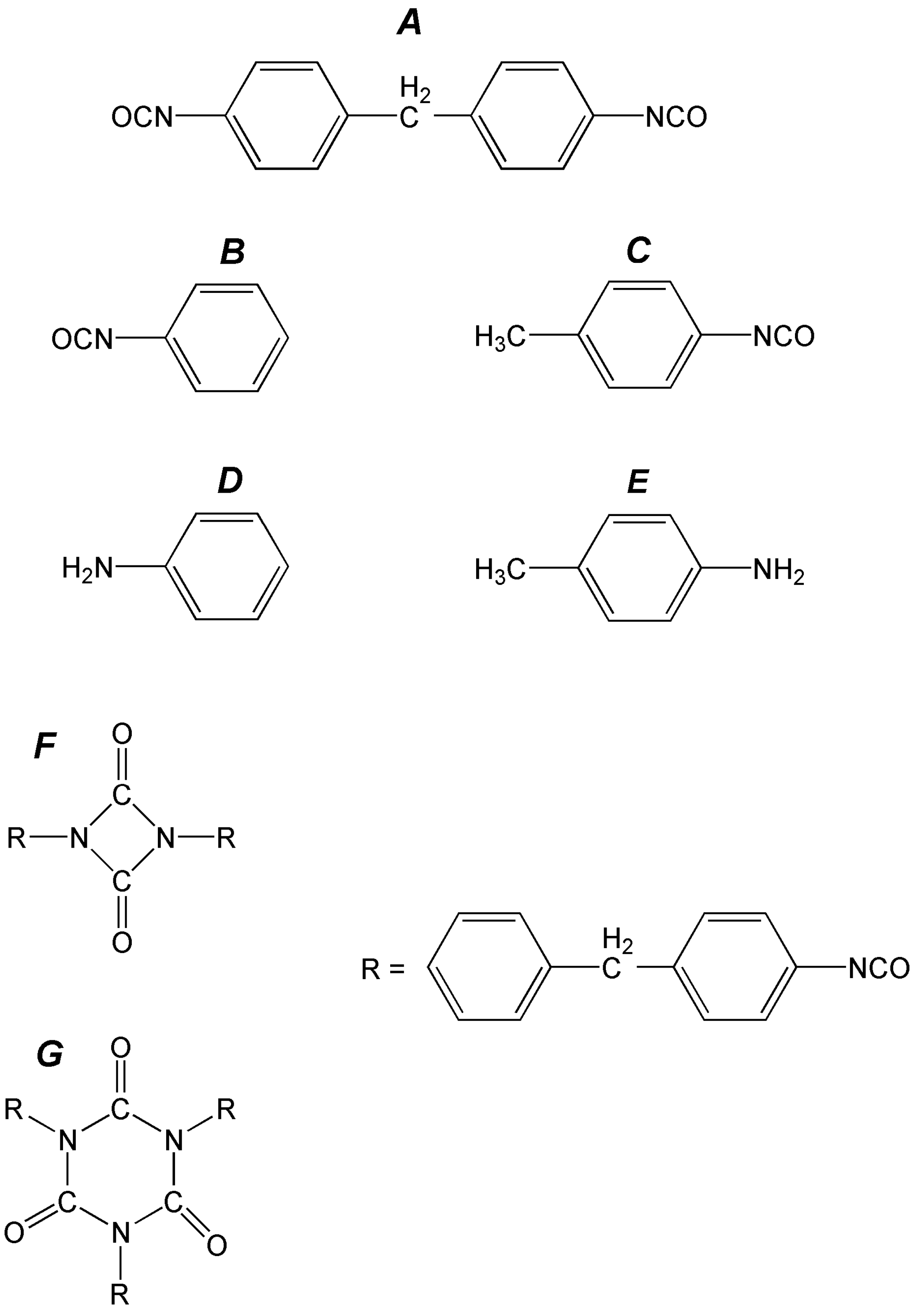


Figure 2. ***A*** MDI, ***B*** phenyl isocyanate, ***C*** p-tolyl isocyanate, ***D*** aniline, ***E*** *p*-toluidine; ***F*** MDI uretidinedione dimer (formation of this compound from MDI is reversible); ***G*** MDI isocyanurate trimer (formation of this compound from MDI is irreversible).

Quantitative laboratory analysis results for 15 minute samples collected from the tank atmosphere through a threaded port (about 2.5 cm diameter) in the MDI tank

Aniline, 62-53-3 (ppm)	*p*-Toluidine, 106-49-0 (ppm)
193.5	44.1
205.9	51.1

Scenario 3

Location: A brewery where large volumes of beer are fermented in chilled vats

Situation: After product is removed from a vat workers empty the remaining material in the vat onto the floor and then clean the floor with a hose to remove the material to a drain nearby. Following this the vat will be ventilated before entry by a cleaning crew. On one occasion a worker who opened a vat to drain the contents was overcome and lost consciousness.

Real-Time Detection Tool Selection:

A. What are the possible types of atmospheric hazards and how dangerous is this situation?

B. What types of detection tools should have been used while draining a vat?

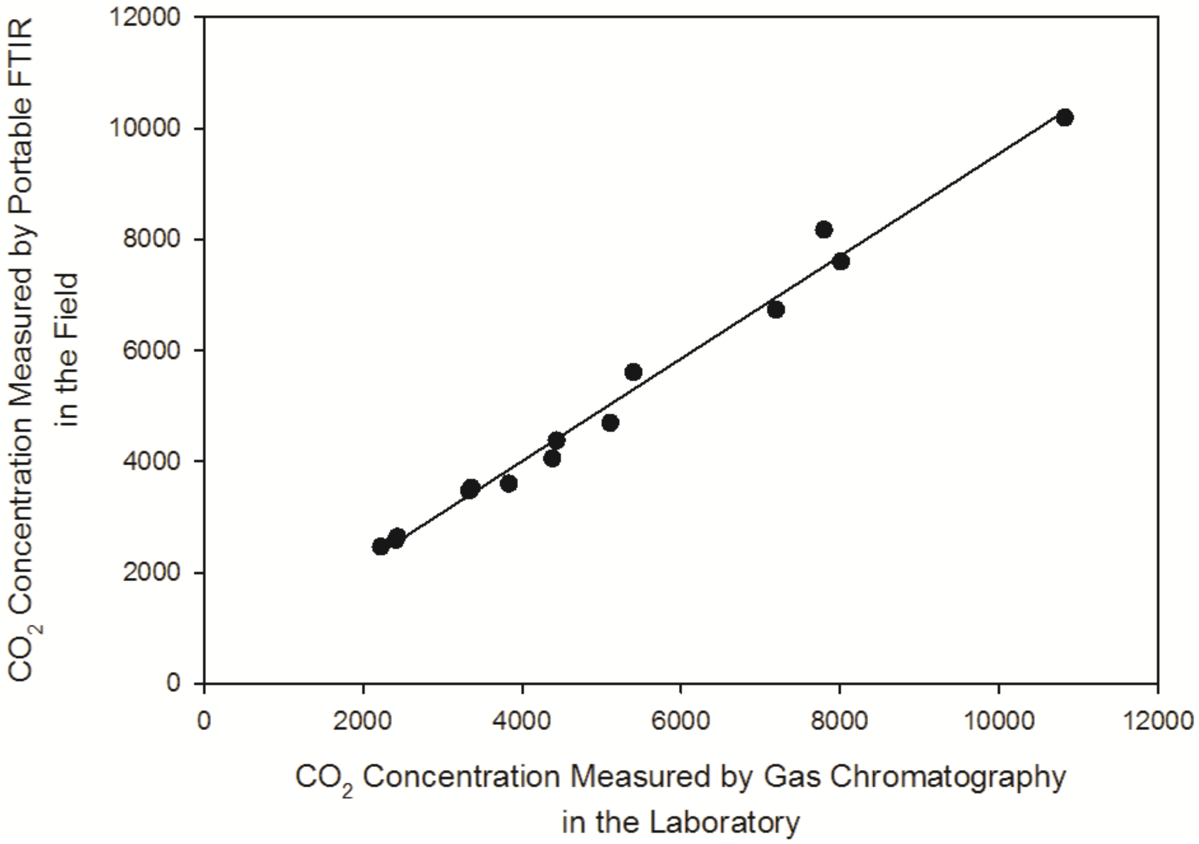
C. What limitations exist for the detection tools you selected?

D. Describe the training and experience needed to correctly operate the selected detection tools

$$CO_2 + N_2H_4 \longrightarrow NH_2NHCOOH$$

Selective NDIR detection of CO_2 ($\lambda \approx 4.3\ \mu m$)

"Other" CO_2 exposure scenarios…



“It must be remembered that when we hold an air sampling device in our hands. We may also hold the life of a fellow human being. They both deserve the best we have to offer.”

J. Brennan Gisclard: *The use of detectors and test kits in industrial hygiene investigations.* The 24th annual meeting, Industrial Hygiene Foundation, Mellon Institute, Pittsburgh, PA, October 28, 1959.

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Nancy Leppink - Branch Chief
International Labour Organization,
(LABADMIN/OSH)
Genève, Switzerland

Ms. Leppink will present worker health issues in a global economy dominated by large multinational corporations with access to labor in lesser developed countries, the impacts of such dependencies on worker well-being and rights, and the occupational health infrastructure needs in developing countries to address these new challenges.

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