

Gas Detector Sensor Technology

Safety equipment and portable instruments - Safety Inc
www.ESafetyInc.com

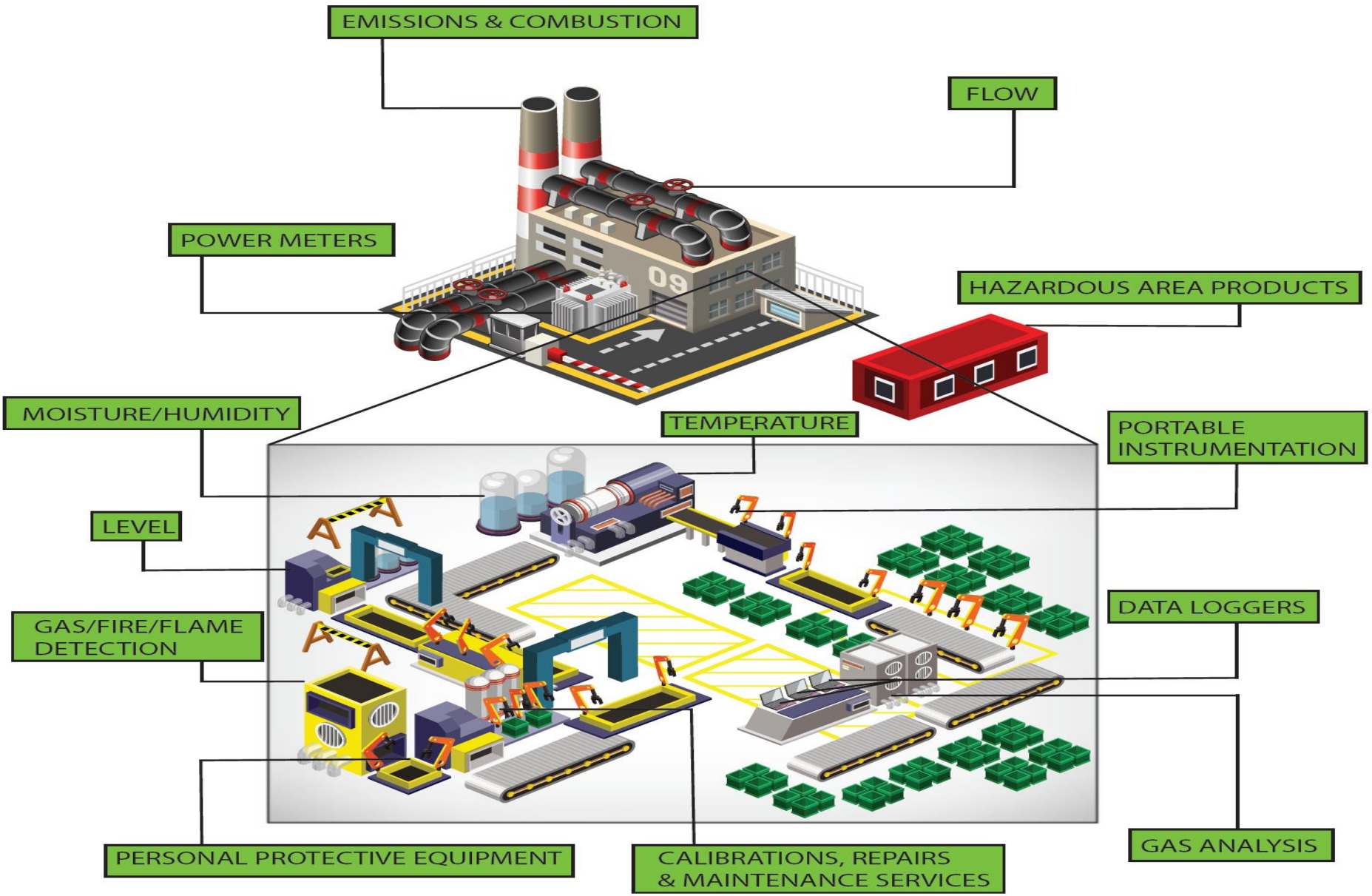
Process Instrumentation

- New England - ***ETA Process Instrumentation*** www.etapii.com
- Upstate NY - ***Martech Controls*** www.martechcontrols.com

Calibration and Repair services - *iFacility Services* www.iFacilityServices.com

Joel Myerson joel@ESafetyInc.com

One Call. One Company.



All your process, facility and safety needs in one place.

SERVICES WE PROVIDE:

- On-site or in our state of the art calibration lab, w/ISO 17025 compliant reporting
- Calibration and repair of portable and fixed instruments
- Respirator maintenance - SCBA, PAPR, airline, breather boxes
- Level A suit testing - to ASTM F 1052 Pressure Test Method
- Fall protection equipment inspection - Competent Person Fall Protection
- Equipment Inspections per ANSI Z359.1-1992 requirements

PRODUCTS CATEGORIES:

On-Line Analyzers - For gases and liquids. Technologies: electrochemical, catalytic, infrared, spectroscopy, spectrometry, chromatography, fourier transform infrared, PID, pH, Conductivity
ORP.

Process Control and Measurement - Flow, pressure, temperature, humidity, moisture, power, level.

Instrumentation - Gas detection, sound, noise, dust, relative humidity, combustion efficiency, Indoor air quality, calibration gases and regulators.

Safety Equipment - Personal protective equipment, fall protection, first aid, spill control

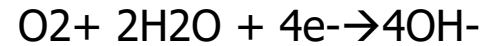
Electrochemical (EC) sensors – For O₂ and Toxics

Important features to review

- Sensor Size – larger size = more electrolyte = longer life. Many fixed sensors are portable sensors in a housing (i.e. same sensor used in both portable and fixed instruments)
- Accuracy and Stability
- Cross Sensitivity – data on interference from other gases
- Detection limits
- Temperature range
- Diagnostics. How do you know when to replace?
- Calibration Interval
- Warranty length
- Warranty provisions – is it pro-rated, or a true replacement warranty?

Principle of Operation – standard 2 electrode electrochemical sensor

Reduction at Cathode:

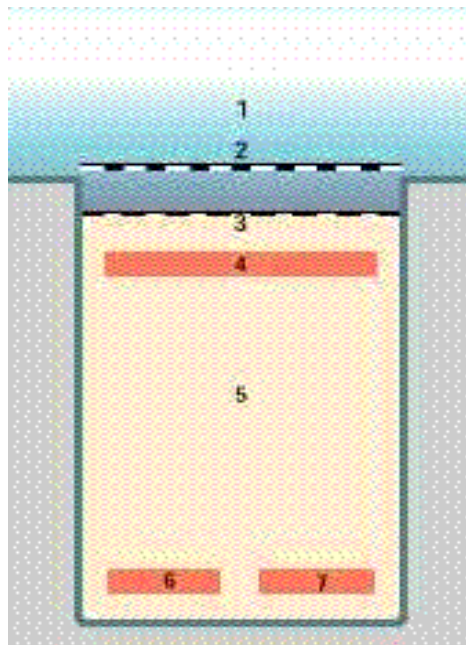


Oxidation at Anode (Pb):



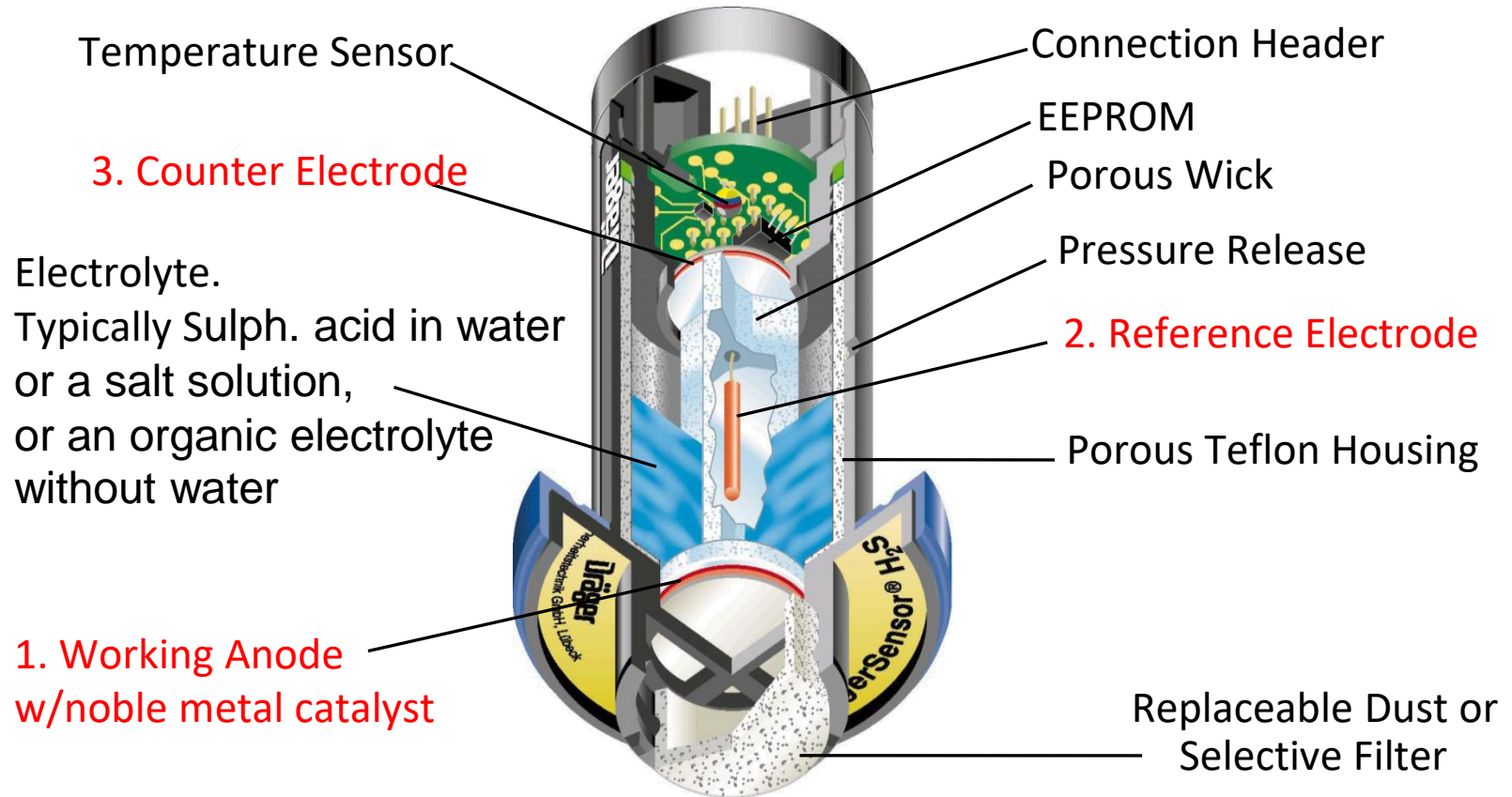
More gas = faster oxidation of the anode, when fully oxidized sensor is used up/dead

Positive cathode and negative anode, each with an electrical contact. Cell is filled with an electrolyte. Sensors work by flowing ions between a cathode and anode through the electrolyte.



1. Gas to be Measured
2. Dust & Mist/Other Filter
3. Diffusion Membrane
4. Measuring Electrode
5. Electrolyte
6. Reference Electrode
7. Anode

3 Electrode EC Sensor



2 Electrode vs 3 Electrode EC Sensor

Oxygen example

- Consumptive 2 Electrode Sensor
 - Two electrode standard electrochemical sensor - **12-18 month life**
 - Oxygen is reduced to hydroxyl ions at the cathode:
 - Cathode reaction $O_2 + 2H_2 \rightarrow O + 4e^- + 4OH$ Hydroxyl
 - Ions oxidize the (lead) anode: $2Pb + 4OH \rightarrow 2PbO + 2H_2O + 4e^-$
 - Overall cell reaction: $2Pb + O_2 \rightarrow 2PbO$
-
- Non-consumptive 3 Electrode Sensor
 - 3-electrode technology – **60-84 month life**
 - $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ at the working electrode, and
 - $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$ at the counter electrode

EC issues

Reasons EC sensors fail or don't perform to spec:

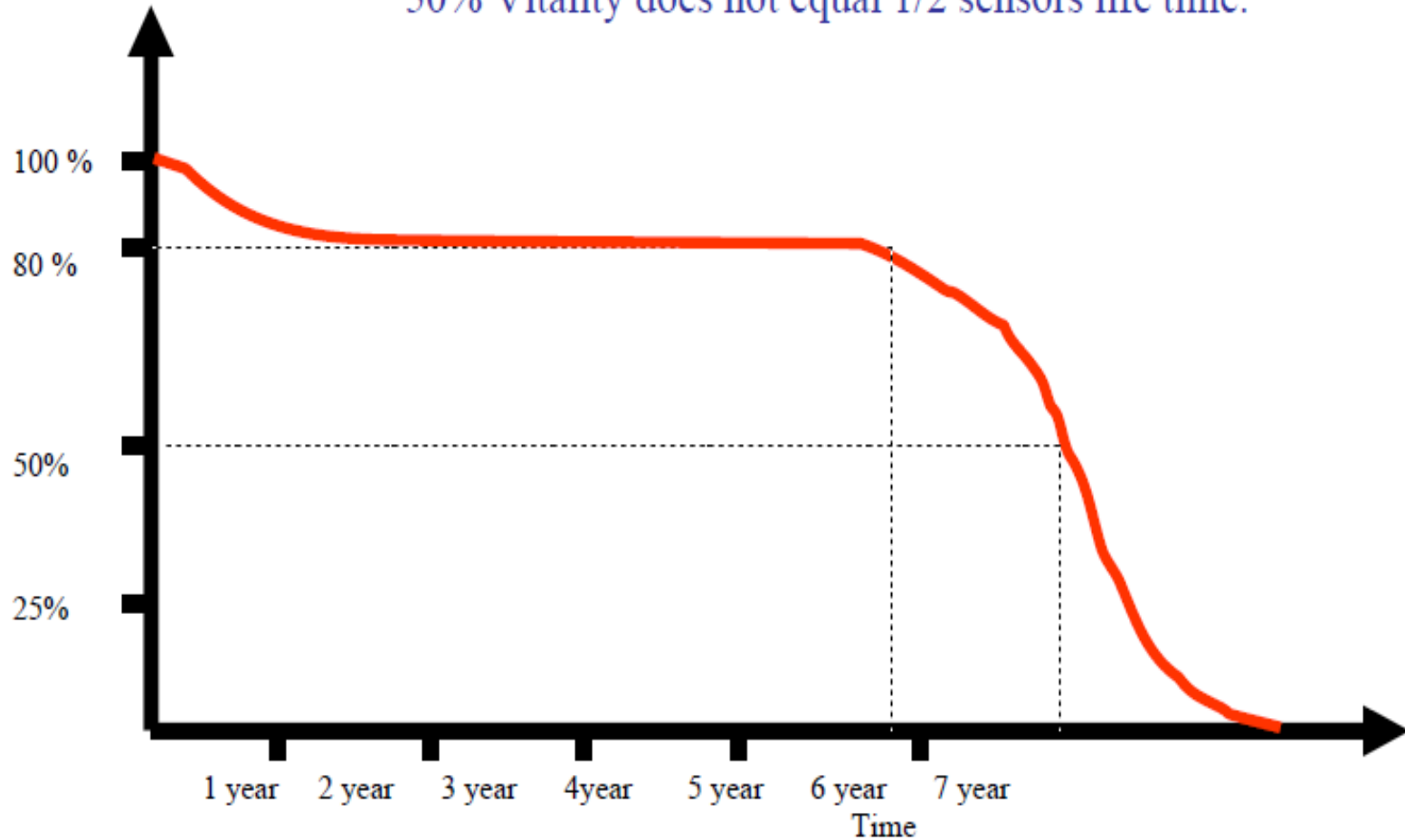
- All of anode is oxidized = sensor is depleted
- Electrolyte poisoned by exposure to contaminants:
- High concentrations of acid gases - H₂S, Cl₂, etc
- Solvents – cross contamination
- Electrolyte leakage
- Desiccation – electrolyte dries out
- Excessive heat and humidity – pay attention to specifications
- Blockage of capillary pore
- Calibration isn't done or isn't done correctly

Typical degradation curve for an EC sensor – pre-failure warning at 25%

Sensor Vitality is not the complete picture when looking at the sensor life.

Sensor Vitality

50% Vitality does not equal 1/2 sensors life time.



Smart sensors – predictive maint.

With the addition of a micro chip in the sensor, a series of self tests are possible such as:

- Electrolyte Level
- Logging of Gas Concentrations over time
- Temperature Real Time for compensation as well as over time
- Sensitivity
- Resistance, etc..
- Any parameter out of check will signal a calibration, warning or fault

True predictive maintenance sensors have the ability to start sending a warning signal 30-60 days before a sensor fails:

- Lower cost of ownership
- Sensors are replaced when they are nearing end of life, not proactively
- Costs associated with down time are avoided
- Sensor replacement can be scheduled, not done as an emergency

Specifications matter!

Look in the manual, not the literature.

Copy of a gas detector manufacturer's manual – Performance/Temp Specifications

Literature

GAS TYPES Combustibles, Oxygen & Toxics

TEMPERATURE TOXICS & OPERATING RANGE 0 to 40°C (32 to +104°F)

**EXTENDED RANGE -20 to +50°C (-4 to +122°F)*

OPERATING RANGE NH₃, CL₂, CLO₂ 0 to +30°C (32 to +86°F)

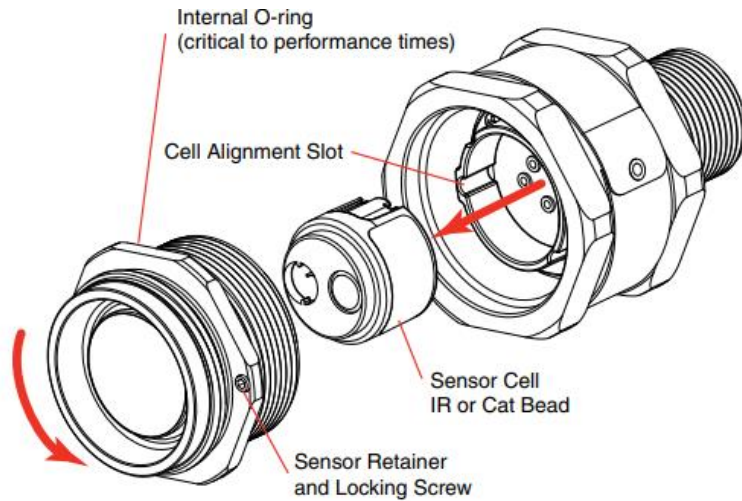
**EXTENDED Range -10 to +40°C (+14 to +104°F)*

Manual

Calibrate within operating range

****Extended Range = The sensor may not meet all of the accuracy parameters listed***

Fixed sensors – portable vs fixed sensors



Catalytic Sensors – measuring for combustion or flammability

- **Lower explosive limit (lel)** - Minimum concentration of a combustible gas or vapor in air which will ignite if a source of ignition is present
- **Upper explosive limit (uel)** - most but not all combustible gases have an upper explosive limit
 - Maximum concentration in air which will support combustion
 - Concentrations which are above the uel are too “rich” to burn
- Flammability range – between LEL and UEL

Oxidation of the coated pellistor

Oxidation leads to energy release

The resulting heat is proportional to the amount of **reactions per time**

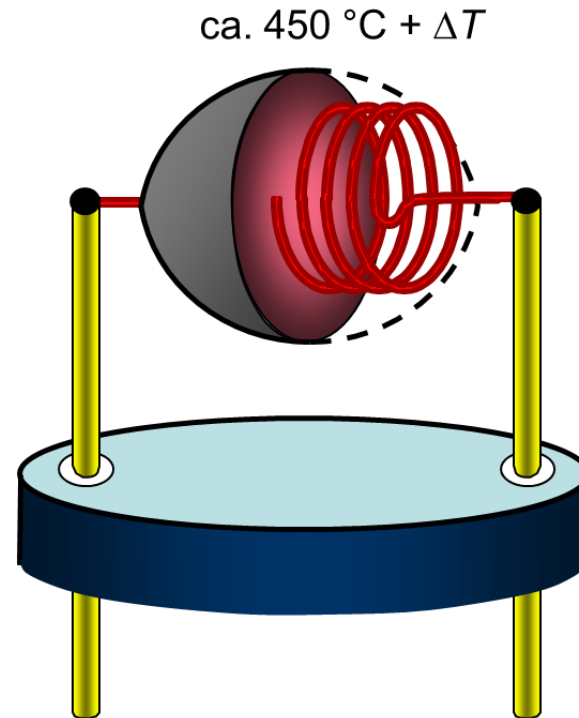
The resulting heat is proportional to the **amount of flammable gas molecules**

The resulting heat leads to a **temperature increase ΔT**

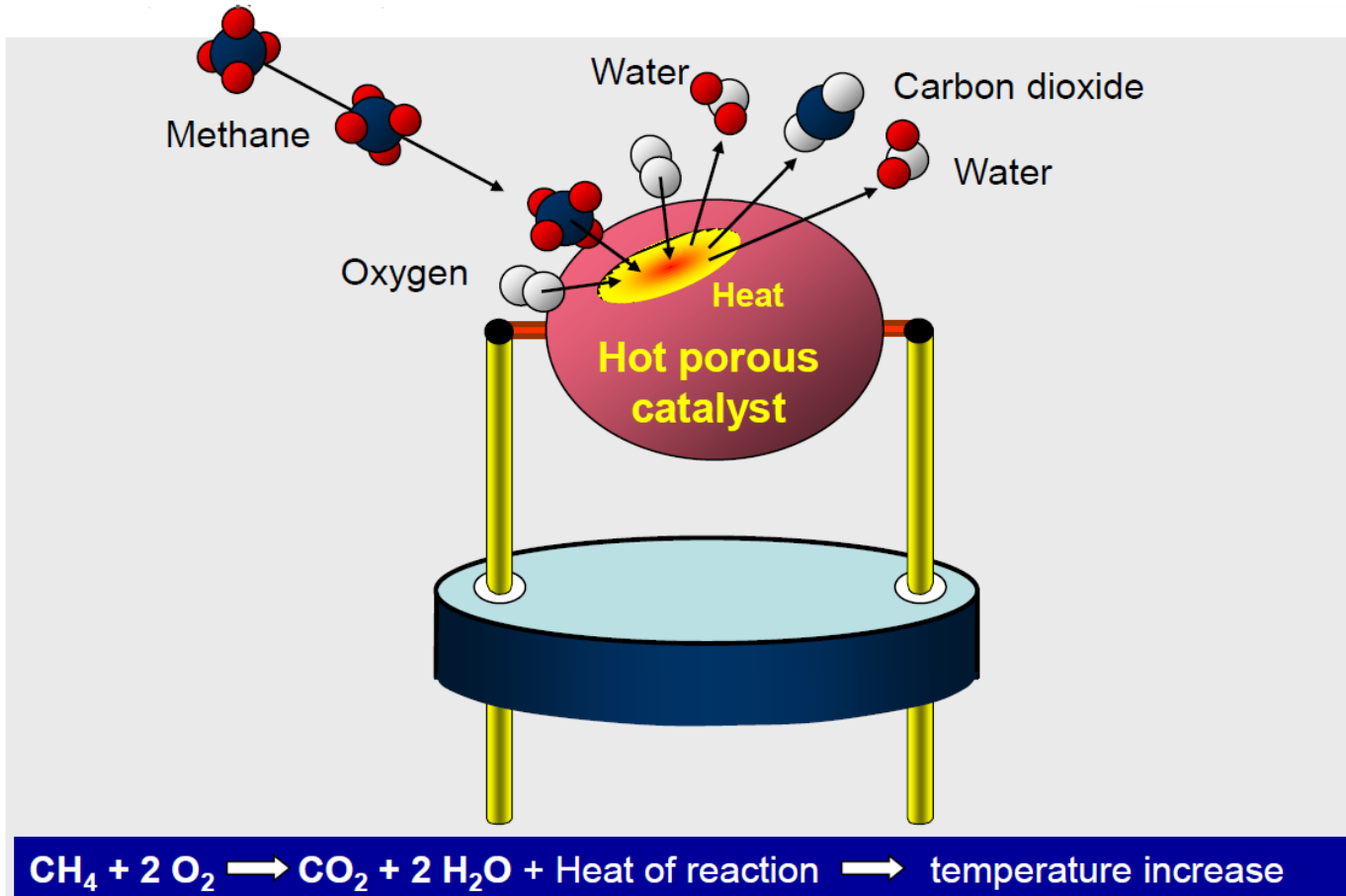
Temperature increase can be measured as **resistance change** of an embedded platinum coil and is proportional to the flammable **gas concentration**.

Pellistor = Pellet + Resistor

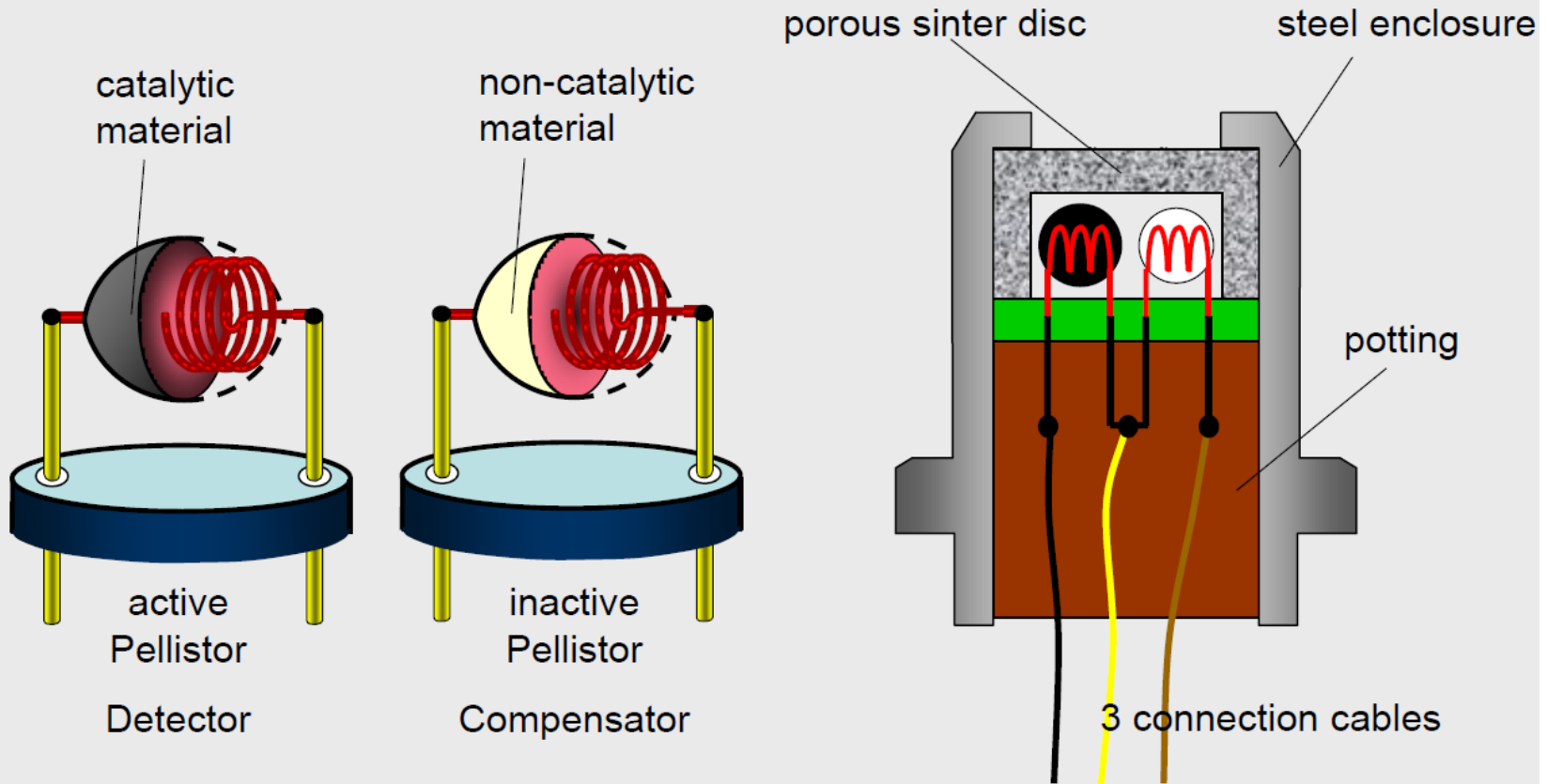
This coil is used for heating (current about 270 mA) *and* for resistance measurement.



Catalytic Bead Sensor



Standard catalytic sensor



If both the detector and compensator change their resistance, it is not a gas but ambient!

Catalytic Bead rules of thumb

2 g/mol	Special	$\text{H}_2 + \text{O}$	\Rightarrow	H_2O	
16 g/mol	Small	$\text{CH}_4 + 2 \text{O}_2$	\Rightarrow	$\text{CO}_2 + 2 \text{H}_2\text{O}$	few reaction steps
		$\text{C}_3\text{H}_8 + 5 \text{O}_2$	\Rightarrow	$3 \text{CO}_2 + 4 \text{H}_2\text{O}$	short reaction time high power - high ΔT
72 g/mol	Medium	$\text{C}_5\text{H}_{12} + 8 \text{O}_2$	\Rightarrow	$5 \text{CO}_2 + 6 \text{H}_2\text{O}$	many reaction steps
		$\text{C}_7\text{H}_{16} + 11 \text{O}_2$	\Rightarrow	$7 \text{CO}_2 + 8 \text{H}_2\text{O}$	long reaction time medium power - medium ΔT
128 g/mol	Large	$\text{C}_9\text{H}_{20} + 14 \text{O}_2$	\Rightarrow	$9 \text{CO}_2 + 10 \text{H}_2\text{O}$	very many reaction steps very long reaction time low power - low ΔT

Rule 1: The greater the molecule the lower the temperature increase

Catalytic Bead rules of thumb

Rule 2: The more molecules the higher the oxidation rate, the higher the temperature increase

Rule 2a: Anything forcing the molecules to move slower will reduce the reaction rate – sensor sensitivity decreases. Example: diffusion rates through sintered discs, filters, contaminated sinter, etc.

Rule 3: Oxygen concentration must be higher than 10-12 %/volume
Need enough oxygen for catalyzing of combustible gas – can't support combustion on the active pellistor without enough O₂.

Rule 4: Catalyst poisoning reduces the reaction rate

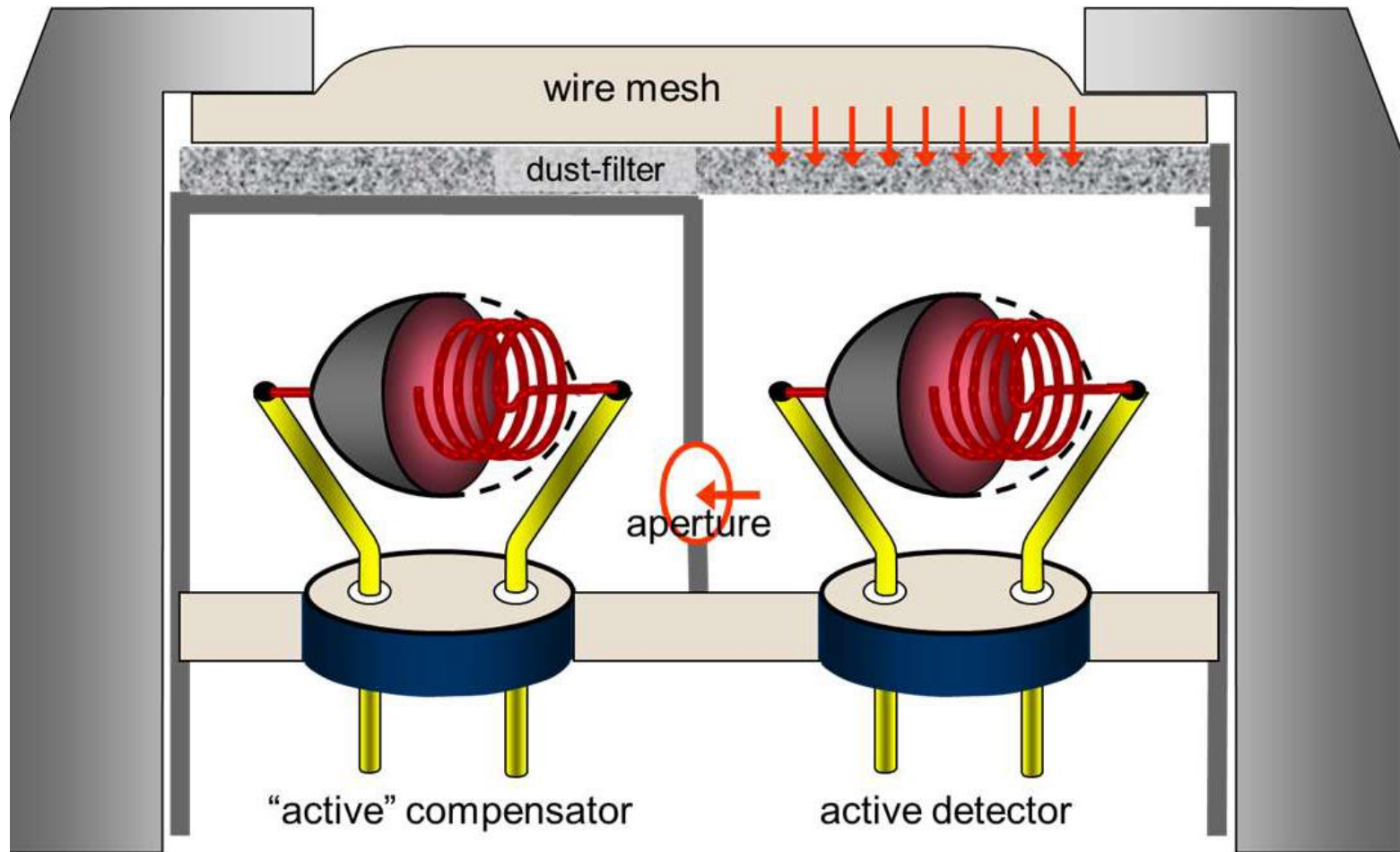
- Oxygen cannot burn on poisoned surfaces.
- Too few reactions produces too little heat

Less reactions per time = less power = less temperature increase.

Issues with single bead catalytic sensors

- Using two different pellistors creates a zero drift/noise issue. Each pellistor degrades at a different rate, changing the reference ratio between the two.
- Require frequent calibration due to above (drift)
- Sintered disk is susceptible to poison and reactive gases.
- Sintered disk delays the response time since molecules have to travel a longer distance to reach the pellistor.
- Sensors typically cannot be used in applications where the physical orientation of the sensor may be variable (i.e. airplanes, ships, etc.)

Two active coated beads



Wire mesh $\frac{1}{4}$ the thickness of sintered disk
= much faster response time



Wire mesh disc

The thickness of the wire mesh disc is only 0.8 mm.

And the diffusion path length is approx. 0.8 mm!



Sinter disc

The thickness of the sinter disc is 3.2 mm.

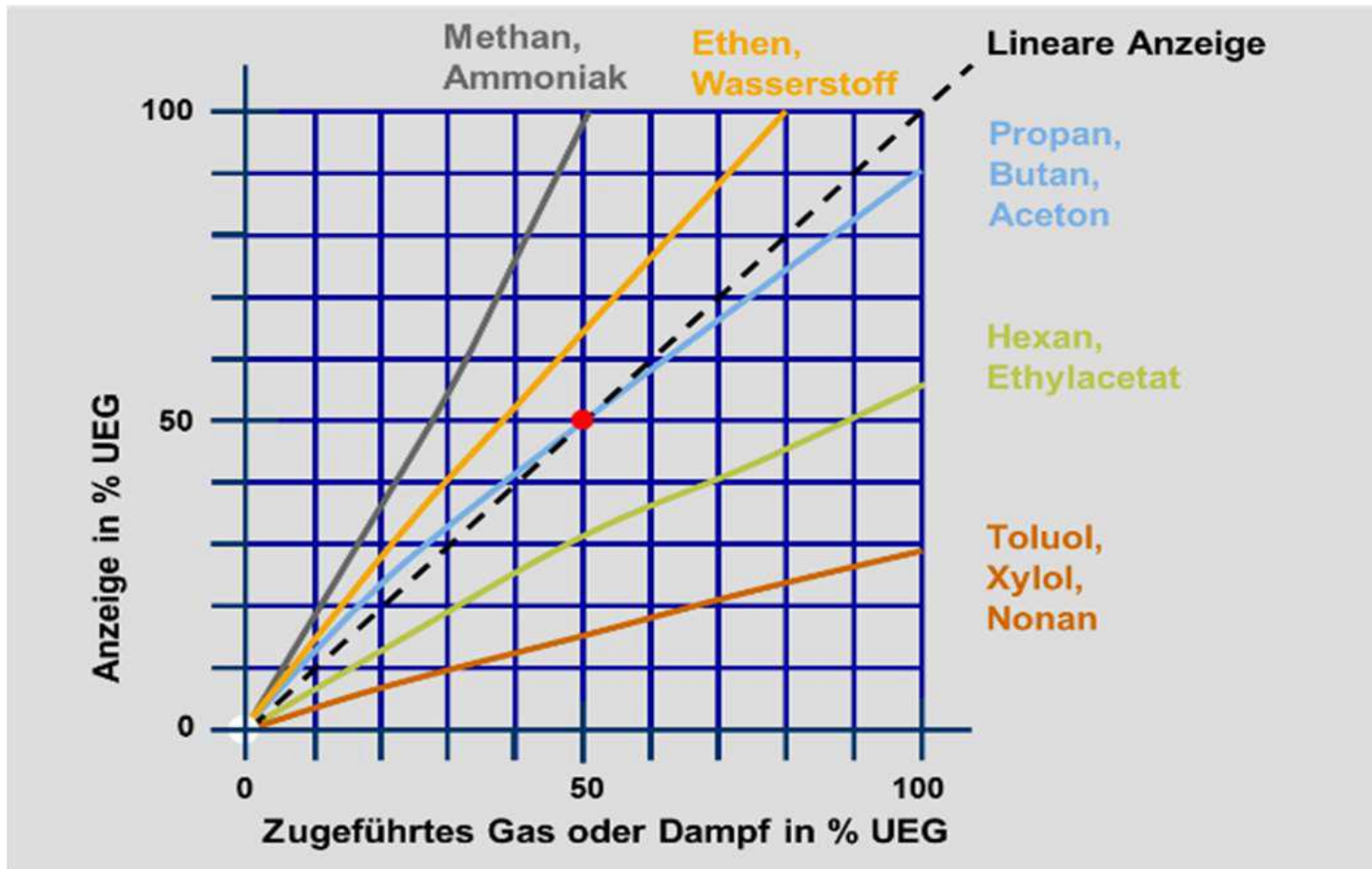
The diffusion path length even greater than 3.2 mm!

Two active bead advantages

- Optimum compensation – both of the sensor's pellistors, and measuring and compensating elements, are part of a Wheatstone bridge and are completely uniform
- Both are active, both degrade at about the same rate
- Faster response times - using a wire mesh disc as the gas entrance and flame arrestor will make the diffusion paths noticeably shorter so that the response times increase
- Independent of orientation
- Improved poison resistance – new ceramics and catalyst

Linear correction factors/multipliers

- cal with methane & apply multiplier



Catalytic advantages and disadvantages

Advantages:

- Low up front cost
- Can measure %LEL H₂
- Small physical footprint

Disadvantages:

- Long term costs
- Finite lifetime
- High frequency of calibration (for standard single active pellistor sensors)
- Should calibrate with measurement gas
- No smarts built into sensor (no calibration curves)
- Potential for pellistors “poisoning” that inhibits the sensor response.

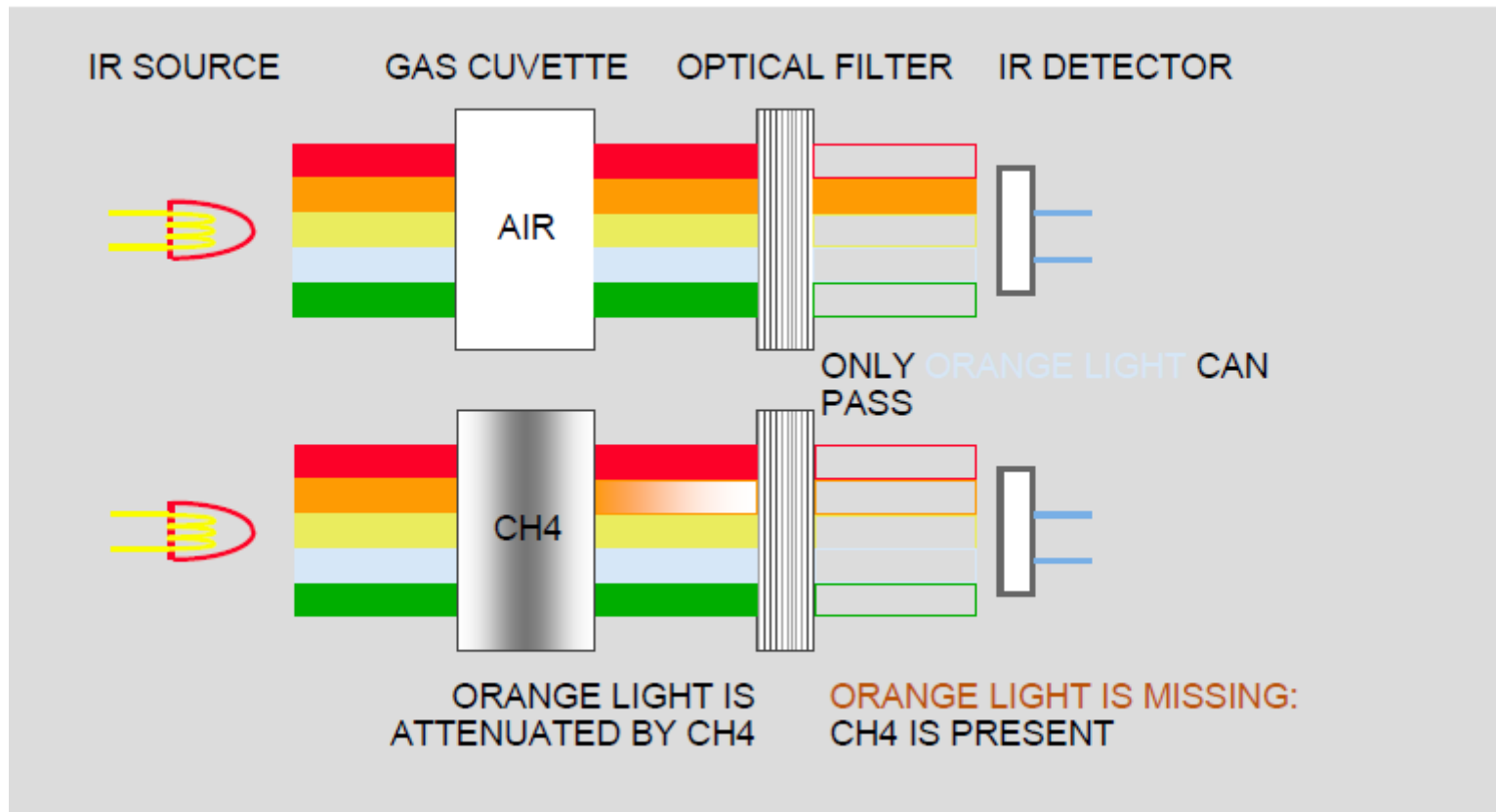
What to look for:

- Long term stability (zero drift)
- Calibration interval requirement
- Position requirement
- Speed of response
- Measure one gas, calibrate with another – for example, calibrate with methane but choose pentane as the target gas

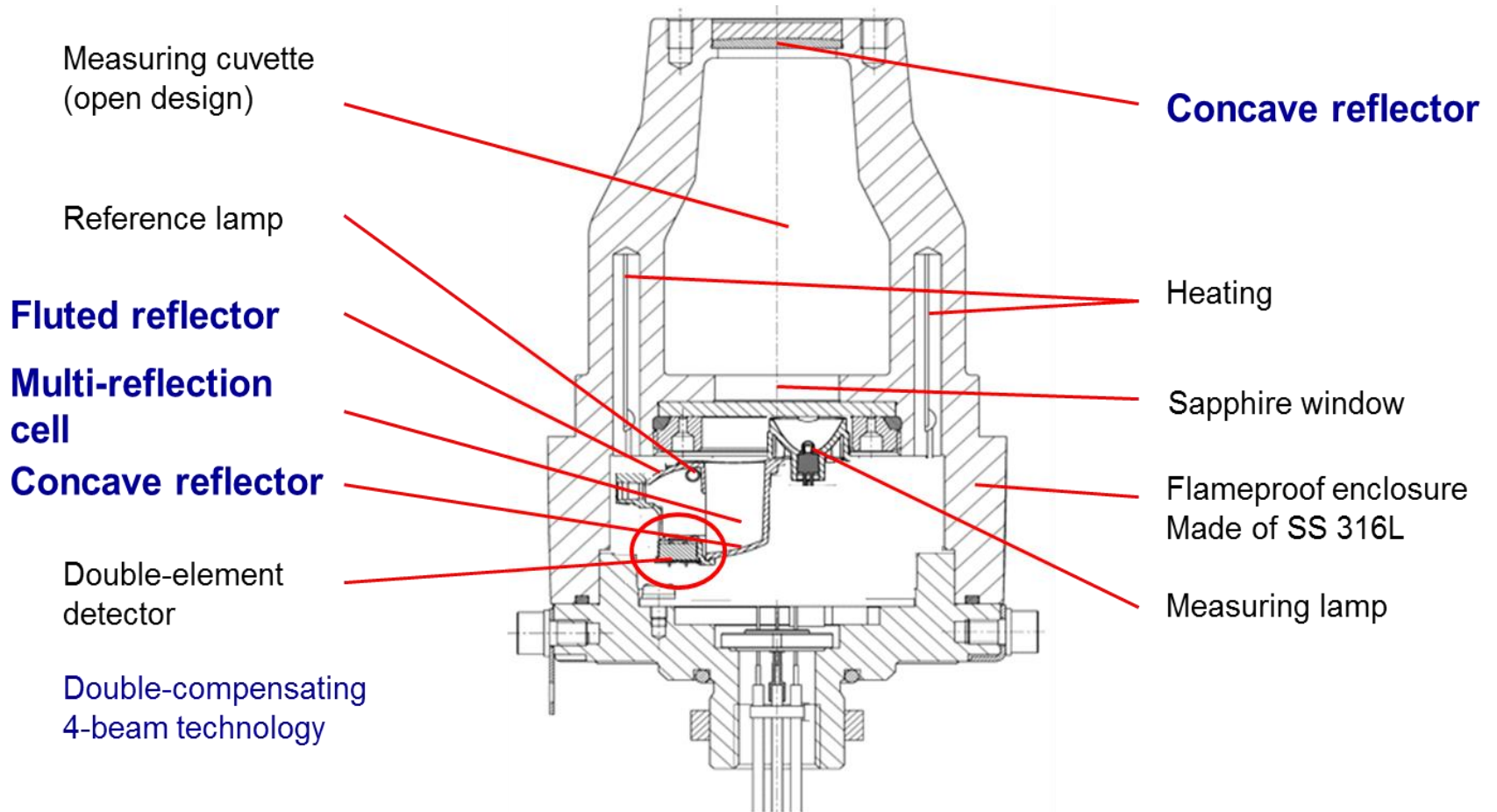
Infrared (IR) sensors for combustibles and organics

- Infrared technology is based on the scientific principle that specific gases absorb infrared light at specific wavelengths.
- Identify and quantify gas volume by measuring infrared light absorption.
- Specific gases can be selectively targeted by narrowly filtering the wavelength of the infrared light introduced, thereby avoiding any infrared absorption by other non-targeted gases that may be present in the sample.
- Higher concentrations of gas will absorb more IR light energy.

Infrared (IR) sensors



Dual Source 4 beam IR Sensor



4 Beam Advantages

- Internal reference lamp provides stability, improved signal:noise and component ageing data
- 4-beam technology for stability and improved signal to noise
- Large pathlength from large sample cell and multiple reflections improves signal, simplifies electronics
- Great diagnostic capability for beam blocks and component near failure
- Great particulate compensation capability.
- 'Optical measuring' cell and 'optical sample conditioning' cell provide optimal signal resolution to the electronics

IR vs. Catalytic

IR-EX Vs. CAT-EX

Infrared

- Operates in environments with Low or No Oxygen concentrations
- Immune to Poisoning and Inhibiting Compounds that affect Cat-Ex
- Measures %LEL, ppm, and %Volume Concentrations of various HC gases
- Different responses to different compounds vs catalytic sensor (specifying)
- Expected useful life well over 5 years regardless of Ex gas exposure

Catalytic

- Requires at least 10 – 12 %Vol Oxygen concentrations to operate properly
- Poisons like H₂S, S- compounds, HFC's, heavy metals affect operation and longevity
- Measures %LEL, and %Volume Concentrations of non-HC gases, including H₂, NH₃, CO
- Different responses to different compounds vs IR sensor (specifying)
- Expected useful life varies according to application and exposure from 2 – 5 years

Infrared advantages and disadvantages

Advantages:

- Extremely stable measurement
- Non consumptive
- Calibration usually not necessary or can be extended.
- Low long term costs
- Can measure %LEL, PPM, %Vol depending on instrument used
- Gas Library – depending on instrument used
- No false zero vs catalytic – i.e. zero reading is all IR light getting to the receiver (100% of light)

Disadvantages:

- Higher initial cost than a catalytic sensor
- Cannot measure H₂

What to look for:

- Gas Library, Measure one gas, calibrate with another.
- Water proof
- Ease of configuring
- Accuracy
- Temp. coefficients
- Dust effects

NIOSH pocket guide

<https://www.cdc.gov/niosh/npg/> - Toluene

- Synonyms & Trade Names Methyl benzene, Methyl benzol, Phenyl methane, Toluol
- CAS No. 108-88-3 RTECS No. XS5250000 DOT ID & Guide 1294 130
- Formula C₆H₅CH₃
- Conversion 1 ppm = 3.77 mg/m³
- IDLH 500 ppm
- NIOSH REL TWA 100 ppm (375 mg/m³) ST 150 ppm (560 mg/m³)
- OSHA PEL TWA 200 ppm C 300 ppm 500 ppm (10-minute maximum peak) See Appendix G
- Physical Description - Colorless liquid with a sweet, pungent, benzene-like odor.
- Molecular Weight 92.1
- Boiling Point 232°F
- Freezing Point -139°F
- Solubility (74°F): 0.07%
- Vapor Pressure :21 mmHg
- Ionization Potential - 8.82 eV
- Specific Gravity - 0.87
- Flash Point - 40°F
- Upper Expositive Limit - 7.1%
- Lower Explosive Limit- 1.1%

Toxic vs Explosive – protection vs combustion

Converting 100 % Vol to ppm

1% = 10,000 ppm

How to convert % LEL to ppm?

Toluene LEL of 1.1% x 10,000 PPM = 11,000 ppm... 20 x the IDLH

GAS	LEL % by vol	% LEL*	PPM**	OSHA exposure limits***
Toluene	1.1%	100% LEL	= 11,000 ppm	IDLH 500 ppm
		10% LEL	= 1,100 ppm	TWA 100 ppm
Xylene	0.9%	100% LEL	= 9,000 ppm	IDLH 900 ppm
		10% LEL	= 900 ppm	TWA 100 ppm
MEK	1.4%	100% LEL	= 14,000 ppm	IDLH 3000
		10% LEL	= 1400 ppm	TWA 300 ppm
Ethylene Glycol	1.8%	100% LEL	= 18,000 ppm	IDLH not specified
		10% LEL	= 1,800 ppm	TWA 50 ppm

N-Hexane curve on Methane Cal

Gas Library Polytron IR Type 334

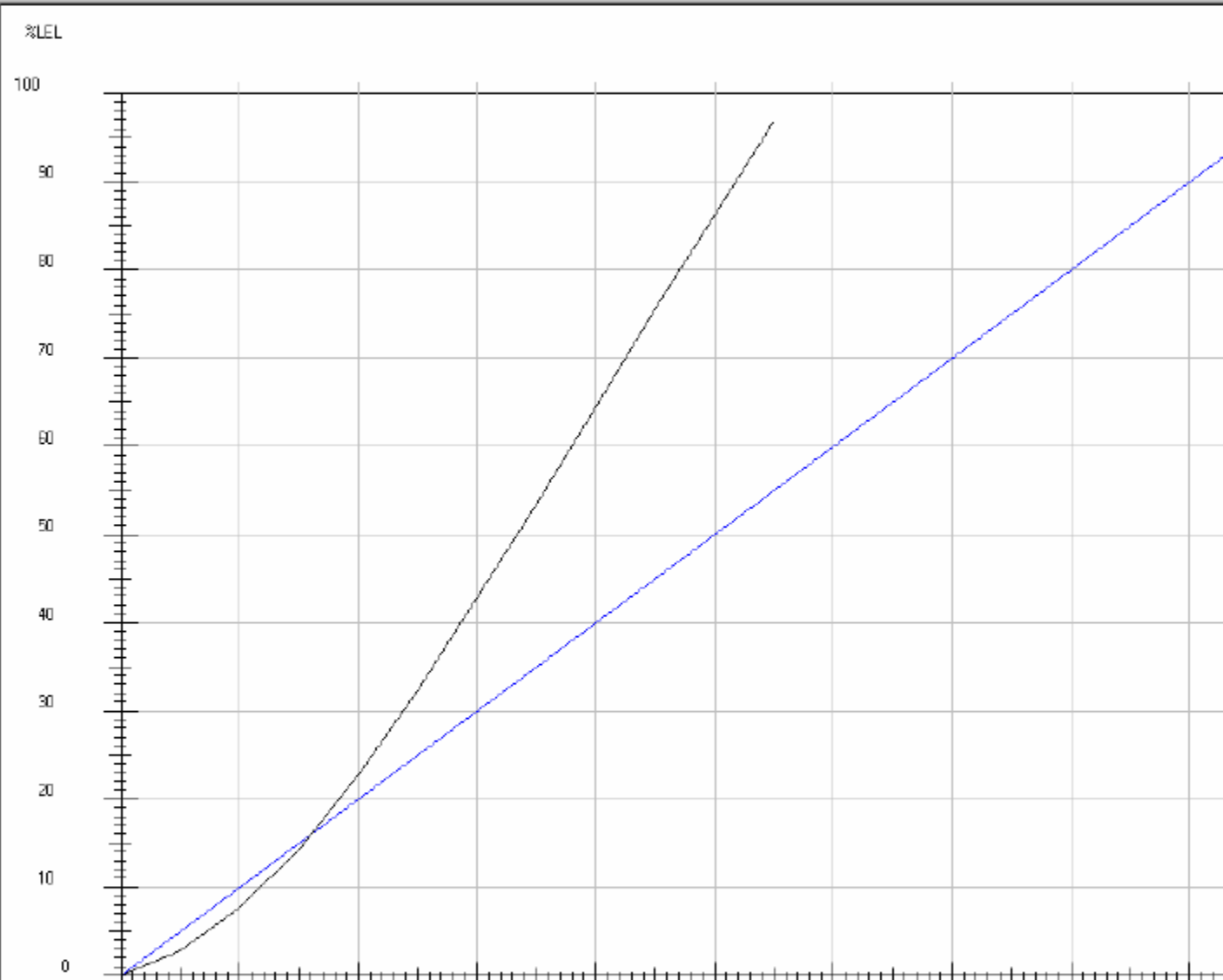
Adjustment
Gas Category: Methane
LEL base: 5.0
USA

Select Substances:

- Methane
- Ethylene
- Propane
- Acetone
- Benzene
- n-Butane
- n-Butanol
- 1,3-Butadiene
- n-Butyl acetate
- n-Butyl acrylate
- 1-Butene
- Cyclopentane
- Dimethyl ether
- 1,4-Dioxane
- Ethanol
- Ethyl acetate
- Ethyl benzene
- Ethylene oxide
- n-Hexane**
- Methyl ethyl ketone

Show Diagram for: Propan

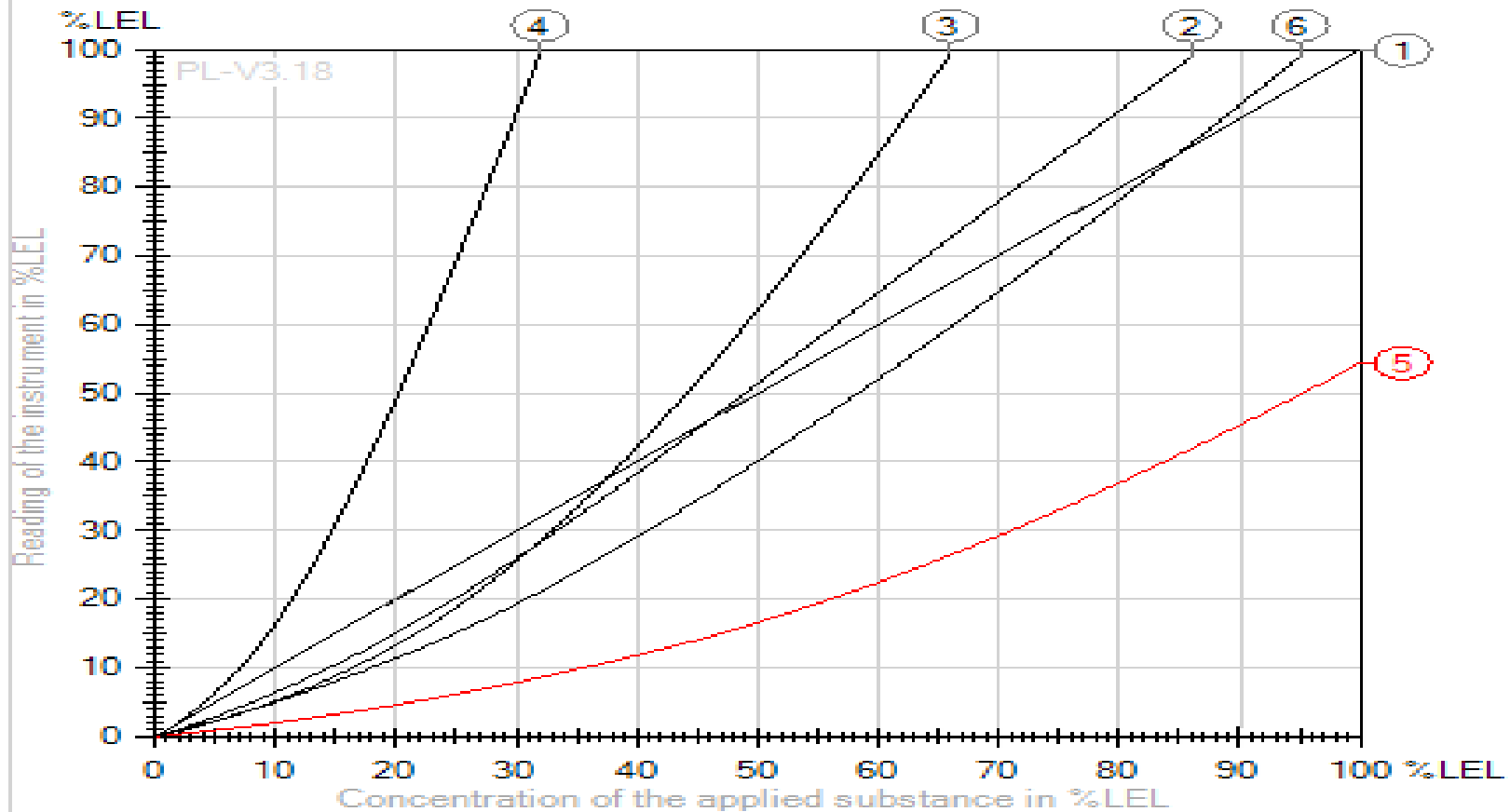
Up Delete
Down New OK



Combustible curves vs multipliers

PIR 7000 type 334 - Cross sensitivities compared to Methane (LEL = 5.00)

NIOSH



- 1: Methane (LEL=5.00)
- 2: n-Decane (LEL=0.80)
- 3: Dimethylamine (LEL=2.80)
- 4: Tetrahydrofuran (LEL=2.00)
- 5: Pentafluoropropane (LEL=3.00)
- 6: Chlorodimethylsilane (LEL=3.00)