Plasmonic sensors for oil and gas

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Hg concerns for oil and gas

- Damage to equipment
  - Liquid metal embrittlement (LME)
  - Amalgamation corrosion
- Occupational exposure

	Hg vapor limits [µg/m^3]
OSHA	
Ceiling	100
NIOSH	
10–hour TWA	50
Ceiling	100
IDLH	10,000
ACGI	
8 – hour TWA	25
WHO	
Public	1

- Environmental release
  - Combustion of fuel gas
  - Disposal of contaminated equipment

LME on aluminum heat exchanger (Carnel 2007)

Plasmonic sensing

- Localized surface plasmon resonance (LSPR): Noble metal nanoparticles exhibit peaks in absorbance that depend on the particles:
  - Shape
  - Size
  - Composition

Figure. Gold nanoparticles of different diameters in solution

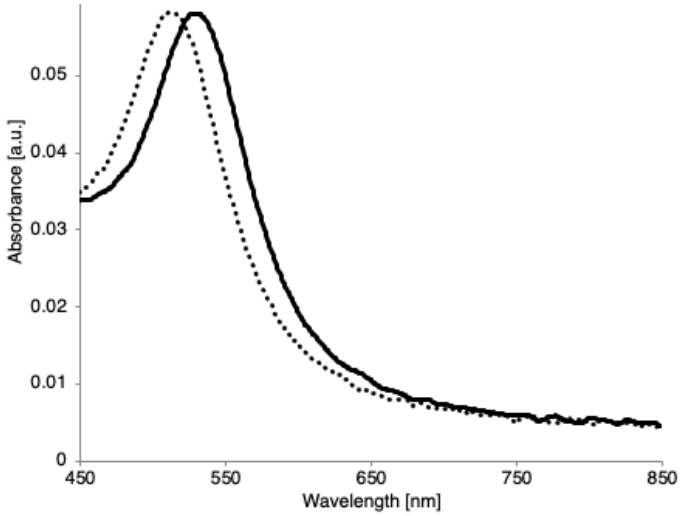


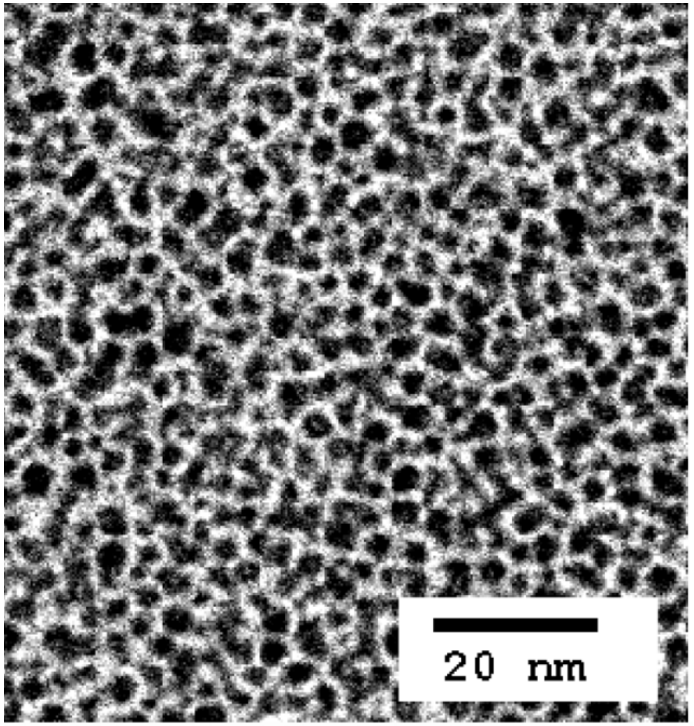
Figure. UV-Vis spectra of gold film pre- (solid) and post- (dashed) amalgamation showing the blue shift in the LSPR peak

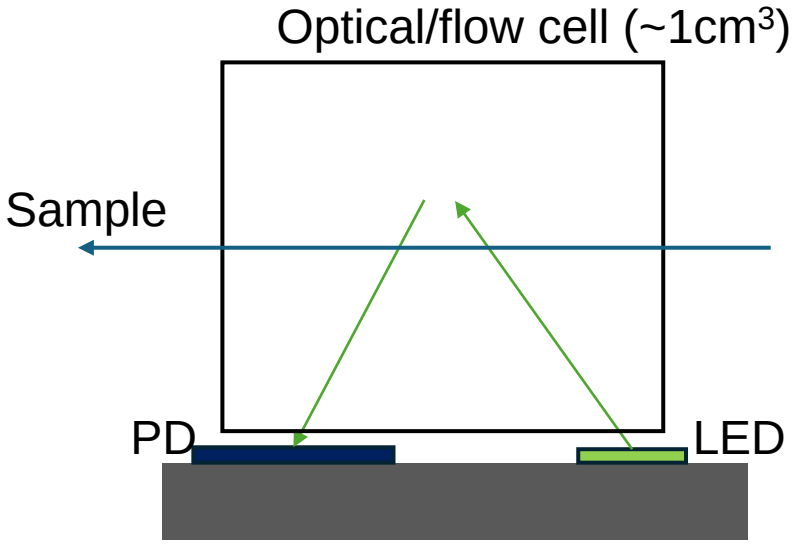
Mie Theory

$$C_{ext} = \frac{24\pi^2 R^3 \varepsilon_m^{3/2}}{\lambda} * \frac{\varepsilon_p''}{\left(\varepsilon_p' + 2\varepsilon_m\right)^2 + \varepsilon_p''^2}$$

Mercury plasmonic signal

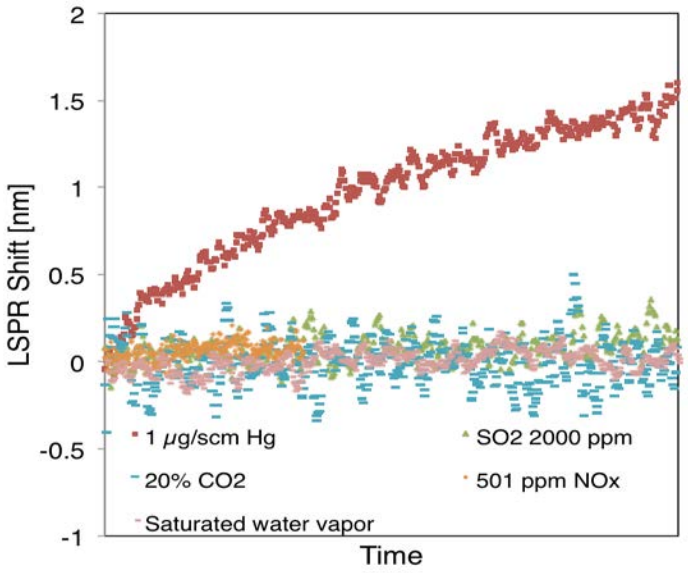
- Nanoparticle are assembled into a submonolayer film
- Plasmonic signal measured in the radiant flux transmitted through the film
- Sensitive optical response to Hg
  - Change in relative radiant flux per picogram per mm^2 of film ~ 5e-5
- Current LOD_{mass} 19 pg (2S)

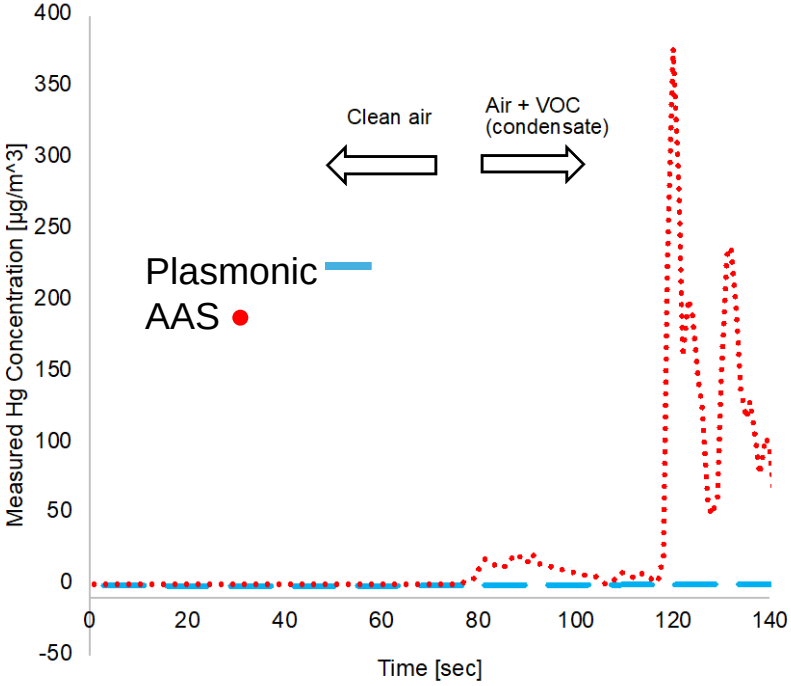


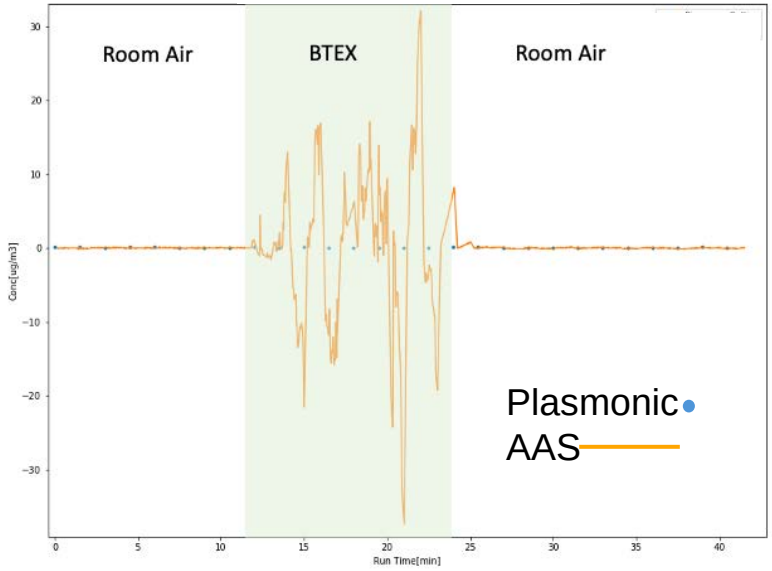


Selectivity

- Selective adsorption/desorption (on/off)
  - Controlled film temperature cycle
  - Cool:Hg on, hot:Hg off
- Not sensitive to BTEX, VOC, SO_2, NO_x, humidity, CO_2





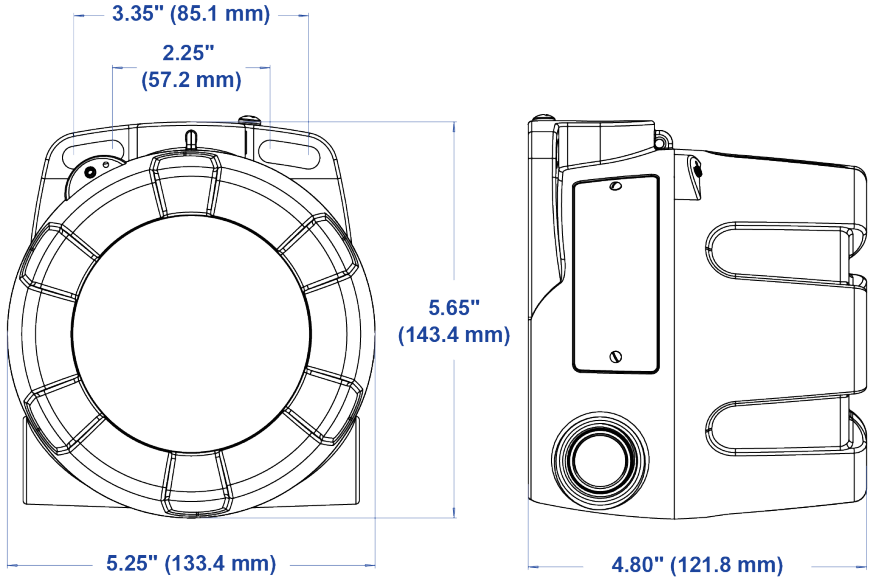


Picoyune Collier

- A mercury analyser for natural gas processing
  - Designed for C1D1 areas
  - Explosion proof
  - Continuous and direct measurements

Ex-Proof enclosure

ATEX	Flameproof protection; II 2GD; Ex db IIC Gb; Ex tb IIIC Db; IP66/IP68; Tamb: -55°C to +85°C
IECEx	Flameproof and dust protection; Ex db IIC Gb; Ex tb IIIC Db; IP66/IP68; Tamb: -55°C to +85°C
CSA	Class I, Division 1, Groups A, B, C, D; Class II, Division 1, Group E, F, G; Class III; Ex db IIC Gb; Ex tb IIIC Db; Class I, Zone 1, AEx db IIC Gb; Zone 21, AEx tb IIIC Db; IP66/IP68/TYPE 4X; Tamb: -55°C to +85°C
UL	Class I, Division 1, Groups A, B, C and D; Class II, Division 1, Groups E, F and G; Class III; Class I, Zone 1, AEx db IIC Gb; Zone 21, AEx tb IIIC Db; Ex tb IIIC Db; IP66/IP68/TYPE 4X; Tamb: -55°C to +85°C
CE	EU and IECEx Attestation of Conformity



Comparison test (2019)

Calibration source

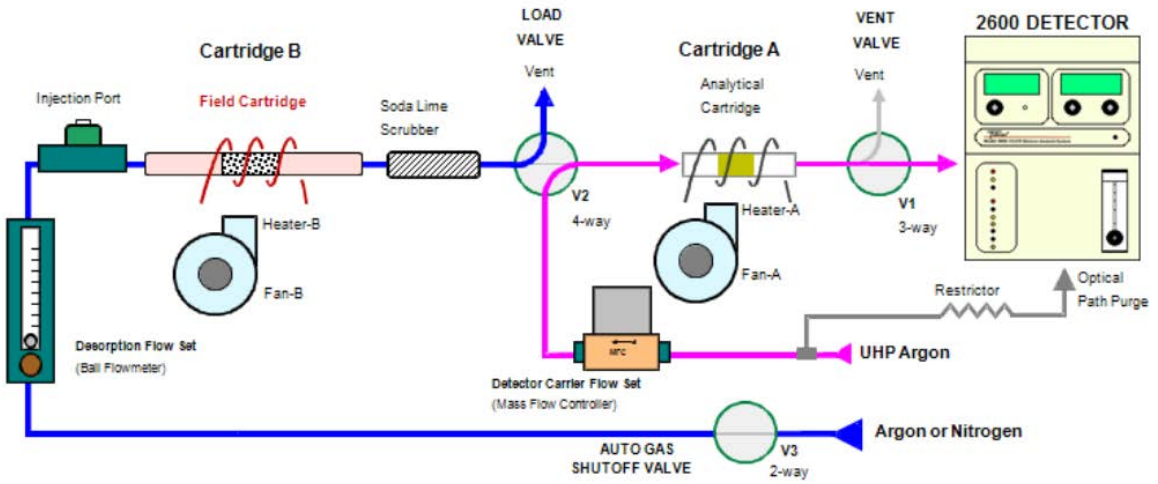
Figure. Photo of test bench 4/8/19

Collier

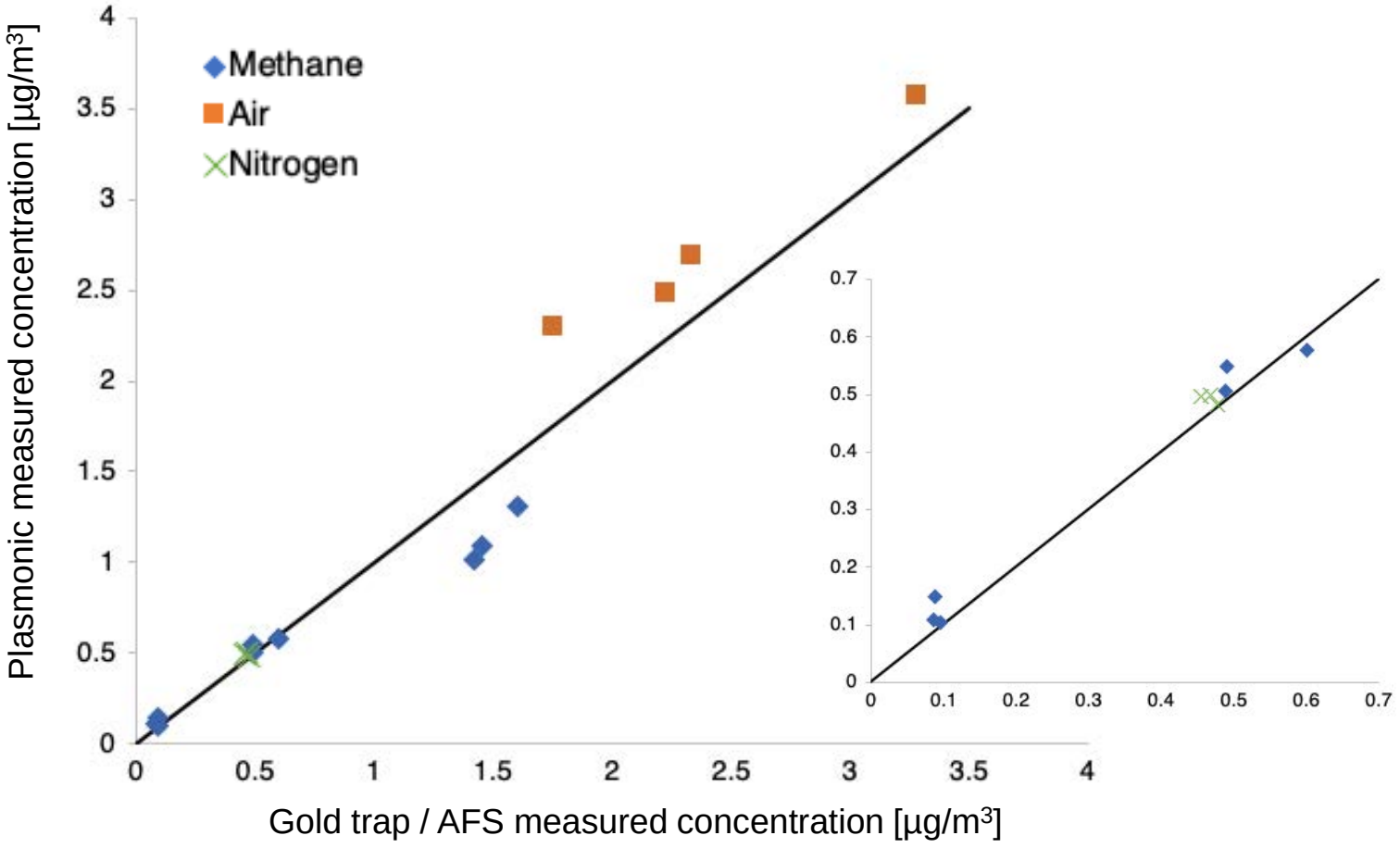
Figure. P&ID of MIG and Collier test bench

PMG's MIG for parallel measurements

- Method is consistent with:
  - GPA 2166 – Techniques for Natural Gas Sampling
  - ASTM D6350 – Standard Test Method for Mercury Sampling and Analysis in Natural Gas by Atomic Fluorescence Spectroscopy
  - ISO 6978 – Natural Gas – Determination of Mercury – Sampling of Mercury by Amalgamation

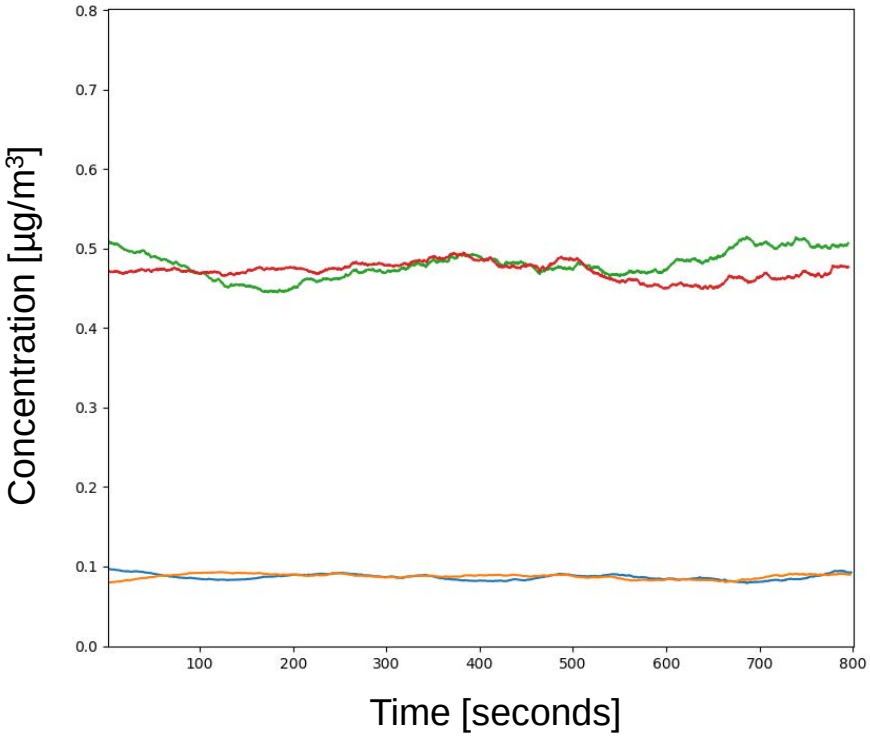


Comparison results



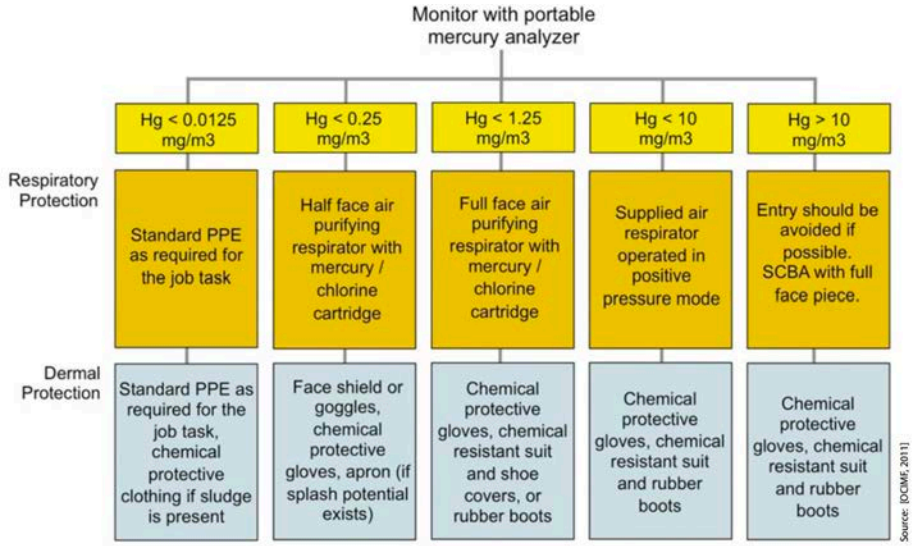
Collier’s continuous measurement

- Traces for 0.1 µg/m^3 (orange and blue) and 0.5µg/m^3 (red and green) in methane (2019)
- Next step is field pilots (2024)



Occupational Hg hazard in Oil and Gas

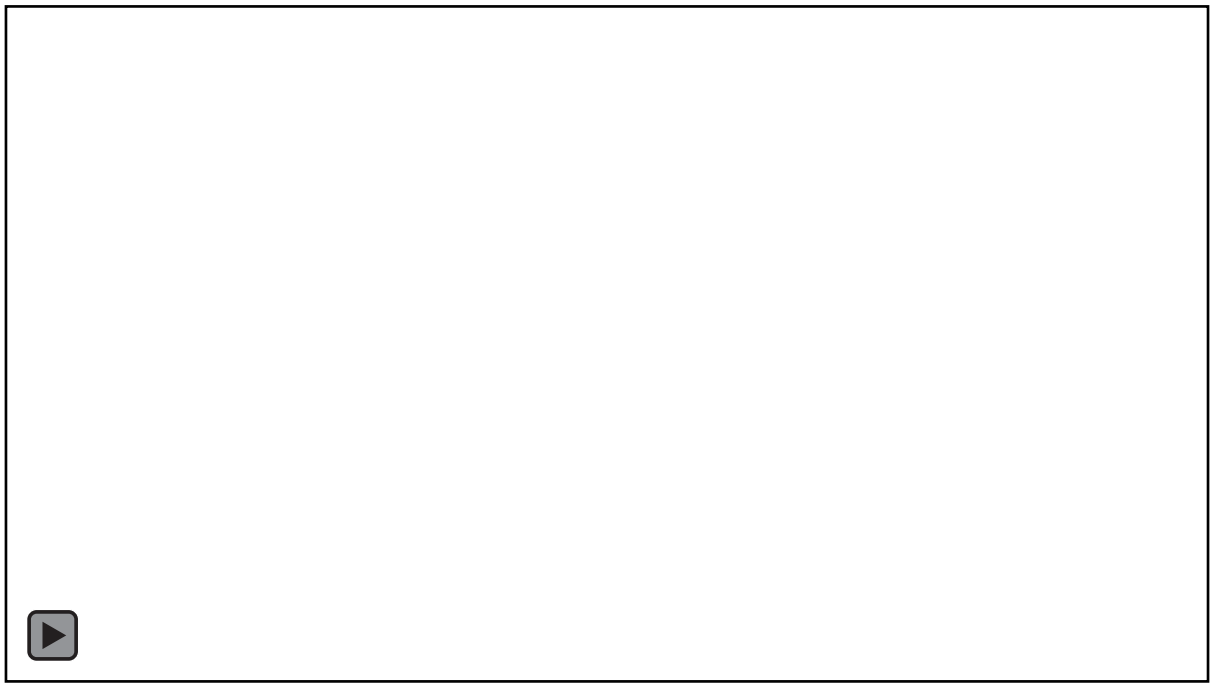
- Up to 20%, of the mercury in oil and gas accumulates in equipment (UNEP, 2022)



Example of action-level matrix for PPE, IPIECA, 2014

Personal monitoring for hot work

- No measurable mercury vapor before hot work
- XRF shows high false negative rates
- Mercury vapor concentrations in the breathing zone well above exposure limits during the hot work.



Thank you

- Other authors
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