Challenges in Managing Mercury in Field Development and Production

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Plasmonic mercury sensors for oil and gas

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Picoyune

Mercury is a potent neurotoxin

- "There is no known safe exposure level for elemental mercury in humans, and effects can be seen even at very low levels." UNEP Minamata Convention Fact Sheet
- Symptoms of occupational exposure have included: irritability, excitability, excessive shyness, insomnia, and tremor.
- Major industrial exposures have caused death and developmental disease (Chisso Coporation and Showa Denko - Japan, Thor Chemicals - South Africa, Dryden Chemicals - Canada).

Minamata, Japan 1950s

Protecting workers from mercury in oil and gas

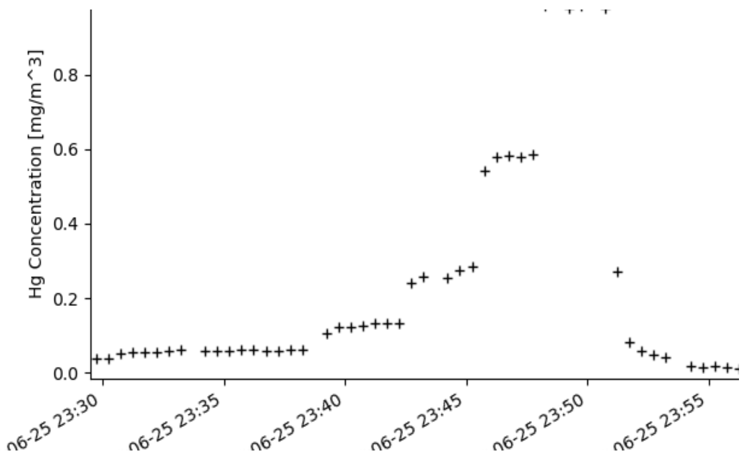
- Mercury is a naturally occurring component of oil and gas.

- Exposures are difficult to predict and have large spatial and temporal variation.
  - ACGIH TLV-TWA: 25 µg/m^3
  - IDLH: 10,000 µg/m^3

- Measure exposure directly and continuously with a personal monitor.

Picoyune MA-1 wearable monitor

- Range: 0 to 20,000 µg/m³
- Weight: 280 grams
- Battery: 16 hours
- Continuous
- Automatic
- Data logging
- Alarms
  - audible and visible



Example data plot

Picoyune MA-1 wearable monitor

Executive Summary

We tested the accuracy and precision of six elemental Hg gas measuring devices, including Picoyune, Jerome 505, sorbent tubes (SKC No. 226-17-1A) using the NIOSH 6009 method, mercury monitor badges (Assay technology, 593 mercury vapor monitor) using the OSHA ID140 method, and two semi-quantitative colorimetric methods (Morphtech, No. 380018 and No. 382005) at both 25 μg m^{-3} and 100 μg m^{-3}. A summary of the test results in provided in the summary Table below. Overall, the mercury sorbent tubes gave the best accuracy and precision, followed by the Picoyune.

Dr. Lowry, Carnegie Melon University

Plasmonic mercury sensing

- Localized surface plasmon resonance (LSPR): Noble metal nanoparticles exhibit peaks in absorbance that depend on the particles shape, size, and composition.

- Mercury vapor quantified by measuring changes in transmitted visible light through plasmonic film

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

Figure. Gold nanoparticles of different diameters in solution

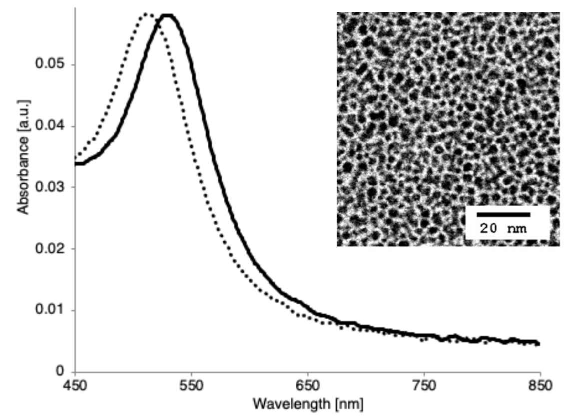
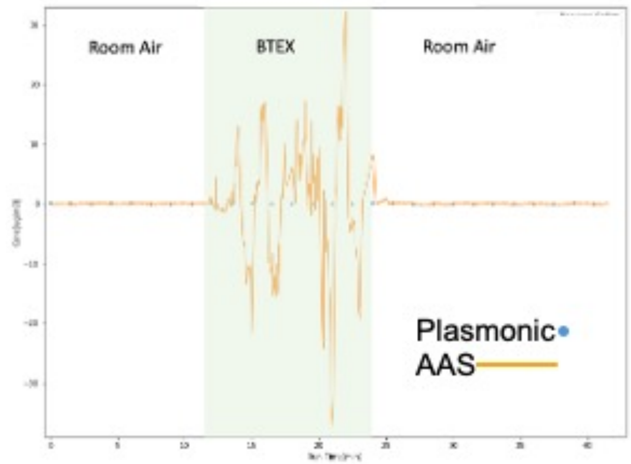
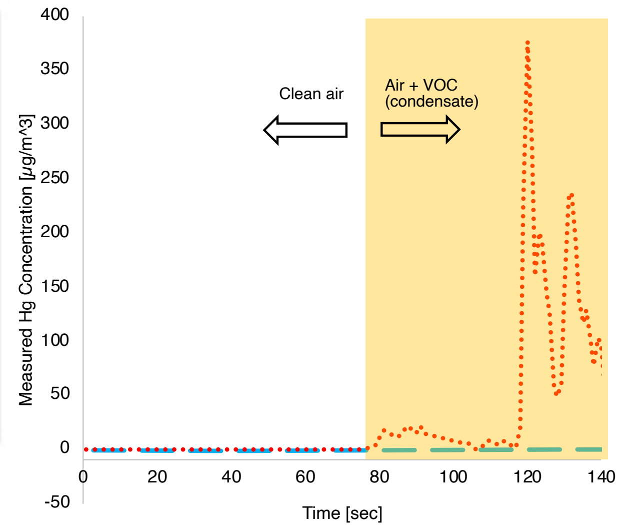


Figure. UV-Vis spectra of gold film pre- (solid) and post- (dashed) amalgamation showing the blue shift in the LSPR peak. (inset gold nanoparticle film TEM image)

No cross sensitivity to hydrocarbon vapors

- Selective adsorption/desorption (on/off)
- Controlled film temperature cycle
- Not sensitive to BTEX, VOC, SO_2, NOx, humidity, CO_2



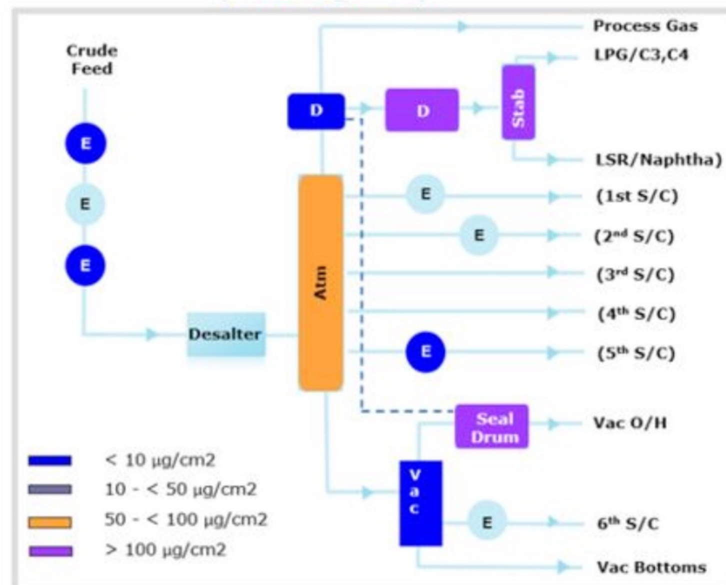


Use cases

- Occupational exposure baseline (hot work and confined space)
- Facility mapping – going from unknown to known – plan ahead – reduce delays
- Downgrading PPE – prevent costs from excess protection level
- Defining contamination/hot zone
- Testing mercury impacted materials, prevent transfer of mercury from the contamination zone
- Real-time continuous exposure tracking
- Breaking containment

Heterogenous accumulation

- Up to 20%, of the mercury in oil and gas accumulates in equipment (UNEP, 2022)
- Mercury in equipment includes:
  - Liquid mercury, readily produces mercury vapor at STP
  - Bound mercury – amalgam, ionic species



Example XRF analysis of surface-bound mercury in crude unit (Alvarado, 2019)

Work generates mercury vapor

- **No measurable mercury vapor before hot work**
- Temporal variation – application of heat vaporizes and converts to Hg(0)
- Spatial heterogeneity – concentrations from a point source drop by the cube of the distance
- XRF shows high false negative rates – Hg under the immediate surface
- Mercury vapor concentrations in the breathing zone well above exposure limits during the hot work.

Field testing, comparison test, 2023

Benefits of downgrading PPE

Monitor with portable mercury analyzer

	Hg < 0.0125 mg/m3	Hg < 0.25 mg/m3	Hg < 1.25 mg/m3	Hg < 10 mg/m3	Hg > 10 mg/m3
Respiratory Protection	Standard PPE as required for the job task	Half face air purifying respirator with mercury / chlorine cartridge	Full face air purifying respirator with mercury / chlorine cartridge	Supplied air respirator operated in positive pressure mode	Entry should be avoided if possible. SCBA with full face piece.
Dermal Protection	Standard PPE as required for the job task, chemical protective clothing if sludge is present	Face shield or goggles, chemical protective gloves, apron (if splash potential exists)	Chemical protective gloves, chemical resistant suit and shoe covers, or rubber boots	Chemical protective gloves, chemical resistant suit and rubber boots	Chemical protective gloves, chemical resistant suit and rubber boots

Source: [OCIMF, 2011]

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

Plasmonic mercury monitoring of natural gas

- Continuous
- Direct
- Automatic calibration
- Small package
- 5 psi, 200 ml/min
- LOD 10 ng/m^3
- 0 to 20,000 $\mu g/m^3$

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

Enclosure ratings

Comparison to reference method

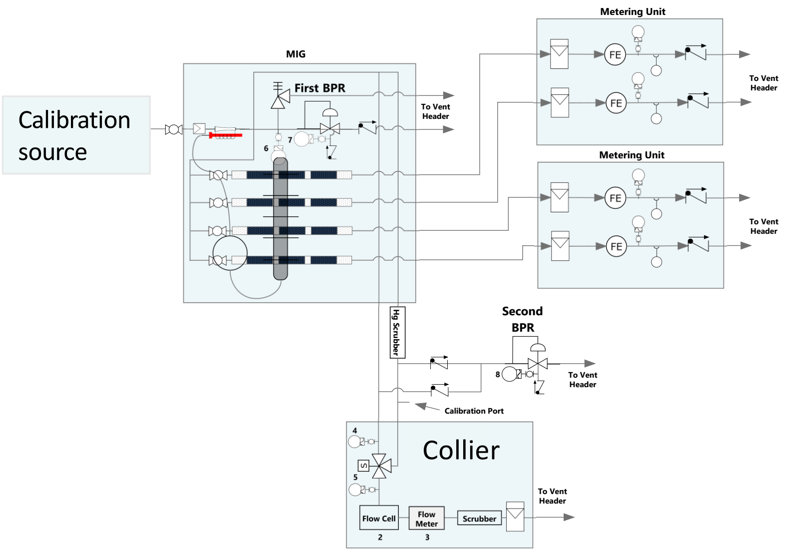
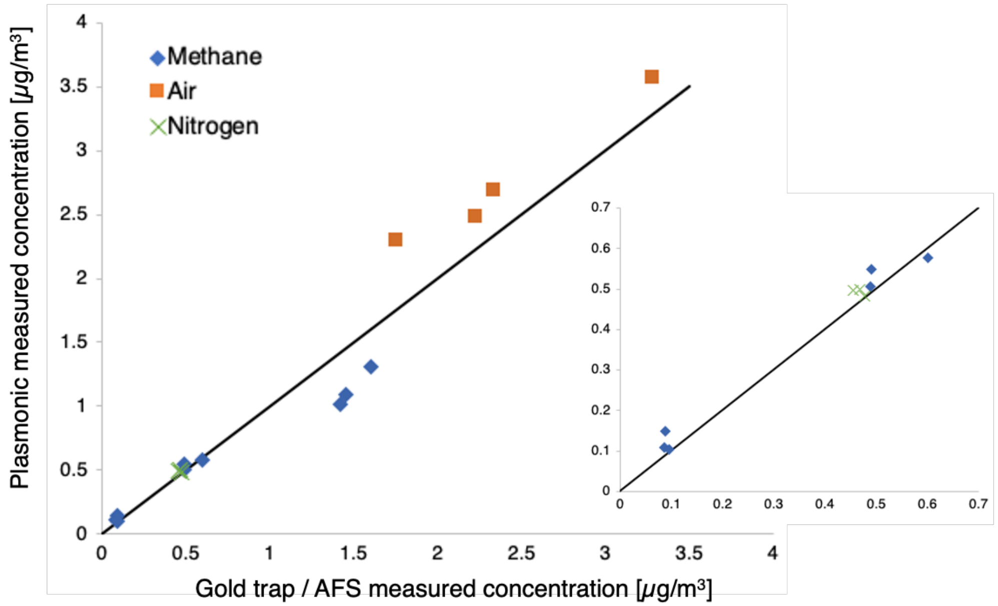


Figure. P&ID of MIG and Collier test bench



Conclusions

- Plasmonic mercury sensing enables new monitoring methods.
- Personal mercury monitors provide real exposure measurements for the highly variable and unpredictable atmospheres in oil and gas.
- Online mercury analysis can be simplified and lower cost by leveraging plasmonic sensors for direct measurement.