Engineering Laser Safety into the Raman Gas Analyzer for Industrial Applications

Michael P. Buric, Steven D. Woodruff, Benjamin T. Chorpening, and Jessica C. Mullen

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Explore Laser safety by example: NETL Raman gas analyzer

- Instrument capabilities / Review of core technology
- Laser beam personnel hazards
- Laser beam ignition hazards
- Flammability and Area Classifications
- Hardware/Instrument safety features
- Software implemented safety features
NETL Raman instrument capabilities

- Measure various gas streams of interest
- Natural gas component analysis (methane, ethane, propane, butane, etc.)
- Homonuclear diatomic measurements ($N_2$, $H_2$, $O_2$)
- Real-time (<1 second) continuous measurement
- Turbine or other dynamic system control
- Replace GC analysis at similar (or lower) cost
- Provide continuous monitoring with little human input
- Operate from 5-800 psig (fuel pipelines, etc.)
- Maintain a high-level of user safety
Review: Waveguide-enhanced Raman

\[ P_s = K L \Omega_0 P_0 \]

\( P_s/P_0 \) is very small! (10^{-13} or less)

L can enhance by 10^3 or more

Free-space configuration (OLD)
(1-lens imaging)

Hollow guide (NEW!)

Notch filter

L2

M

Spectrometer

L1

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Portable unit internal components

- **SPEED:** sub-second response time – faster than GC (minutes), and electrochemical (tens of seconds) – for engine control, process optimization, etc.

- **ACCURACY:** Sub-percent for all species with little cross sensitivity – unlike FIDs and others, differentiate isotopes

- **SIMPLICITY/STABILITY:** Obtains all species (with N\textsubscript{2} H\textsubscript{2} and O\textsubscript{2}) at once with no tunable lasers (i.e. better than TDLAS)

- **SINGLE CALIBRATION:** once during commissioning with pure gasses
Laser personnel hazards

• \(~150\text{mW (maximum), 532nm pump laser}\n  – Class 3b device (Laser Quantum GEM)
  – High power can injure a person
  – Untrained equipment operators use the system
  – Instrument may be opened for service

• **Solution: Interlock for Class 1 operation**
  – Use a laser with interlock input (GEM ok)
  – Interlock the enclosure reliably
  – Use best practices for interlock design
Laser beam containment

- Initial design: single enclosure door, 1 interlock switch. Later design: 2 doors, 2 serial interlock switches
- No removable panels. If present, use a warning label
- Class 1 Laser product label on enclosure exterior
- Maintain internal laser aperture emission labels and beam covers for service personnel (good idea)
- Include a high-quality service manual
- Use a fail-negative design

CLASS 1 LASER PRODUCT
A TOTALLY ENCLOSED LASER SYSTEM CONTAINING A CLASS ____ LASER
Interlock circuitry best practices

• Loss of interlock power disables laser
• Interlock mechanical relay used
• Relay coil is energized when laser is operating
Now that we’re saved from blindness – can we also be safe from EXPLOSION?

• Raman instrument regularly measures natural gas
• Enclosure may reside near a pipeline, gas-well, or natural gas-fired power plant
• Laser beam itself is an ignition hazard
• BUT – we have to use the laser in the sample gas or we don’t have an instrument
Laser ignition safety

• How much power can we use?
• Are there standards to help decide the worst case?
  – NFPA 115: Laser Fire Protection
  – IEC 60079: Explosive atmospheres - Part 28: Protection of equipment and transmission systems using optical radiation
• Determined by flammability or explosivity of mixture
• Remember, a mixture is NOT explosive without O₂
How does an ignition accident occur?

• Flammable or explosive atmosphere
  – See fire triangle
  – $O_2$ must be present

• High radiant energy present – does not necessarily equal high temperature

• Radiant energy required to heat a transparent gas (visible wave) is very large – BUT:

• Target particle or surface (absorber)
  – Small particles can incandesce easily
  – Incandescent particles ignite atmosphere
Some auto-ignition temperatures

- Methane
- Ethane
- Propane
- Butane
- "Heavy" Hydrocarbons
- Hydrogen
Reasonable power limits for explosive mixtures

- NFPA 115: Not much help – guidance for laser construction, not use
- Research (1990’s-2000’s): 50mW lowest igniting CW power
- IEC: very conservative, >35mW is an ignition hazard, ~1.4 safety factor
- All pertain to “explosive environments”, which exist only in the air atmosphere with a leak, not inside the gas-measurement cell
- We can measure fuel at high power, without Oxygen
Anti-ignition procedures

- Measure mixture at 30mW (safe for all mixtures)
- Is the mixture flammable ($O_2 + \text{FUEL}$)?
- If not, measure at higher power
- If so, warn the user, limit the power, divert the flow
## Electrical safety for lasers (NEC)

### Summary of Class I, II, III Hazardous Locations

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<tr>
<th>CLASSES</th>
<th>GROUPS</th>
<th>DIVISIONS</th>
</tr>
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<tr>
<td>I Gases, vapors, and liquids</td>
<td>A: Acetylene</td>
<td>Normally explosive and hazardous</td>
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<td>B: Hydrogen, etc.</td>
<td>Not normally present in an explosive concentration (but may accidentally exist)</td>
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<td>C: Ether, etc.</td>
<td></td>
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<td>D: Hydrocarbons, fuels, solvents, etc.</td>
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<td>II Dusts</td>
<td>E: Metal dusts (conductive,*and explosive)</td>
<td>Ignitable quantities of dust normally are or may be in suspension, or conductive dust may be present</td>
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<tr>
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<td>F: Carbon dusts (some are conductive,*and all are explosive)</td>
<td>Dust not normally suspended in an ignitable concentration (but may accidentally exist). Dust layers are present.</td>
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<td>G: Flour, starch, grain, combustible plastic or chemical dust (explosive)</td>
<td></td>
</tr>
<tr>
<td>III Fibers and flyings</td>
<td>Textiles, wood-working, etc. (easily ignitable, but not likely to be explosive)</td>
<td>Handled or used in manufacturing</td>
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<td>Stored or handled in storage (exclusive of manufacturing)</td>
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</table>
What Area Class is it?

Inside the gas cell: Class 1, div. 1 – can be flammable under normal conditions

Immediately outside the gas cell: Class 1, Div.2 – can be flammable if there is a leak

Outside the instrument: Class 1, Div. 2 – can be flammable if there is a leak

Laser head and power supply area: MUST BE UNCLASSIFIED!

WHAT DO WE DO?
- Lots of “unrated electrical equipment”
- Impossible to find an explosion proof laser
Solution to NEC Classification problem

Instrument enclosure “divider”
- Multiple compartments form a “second seal” (blue line)
- Low pressure windows (<1psi OK) allow light coupling
- Purge and Pressurize!
- Next: use of Type Z purge and pressurization systems
Type Z purge and pressurization

- Compressed air or nitrogen is forced into the enclosure
- Enclosure is “Purged” at startup to remove flammable gasses
- Enclosure is “Pressurized” after the purge to keep flammable gasses OUT.
- Pressurized area is monitored during use
- Monitored area is considered “unclassified” (YEAH!)
- Now we can use any electrical equipment!
Type Z Purge and Pressurization

- Pressure switch for remote monitoring
- Gauge for supply air adjustment (0-150psig)
- Gauge for enclosure pressure (few inches of water) – satisfies local monitoring
- Warning label: “DO NOT OPEN TYPE Z” etc.
- Vents for each enclosure to air
Other notes for Type Z P&P operation

• Seals should be good, but don’t need to be perfect as the “flapper valves” are the first to open @ low-p
• No need for “explosion proof” style threads, etc, under positive internal pressure
• Need an external monitoring point with its own power fed to pressure switches
• Need an external alarm to signal “no pressure” and an external disconnect
• Warning labels!
• Everything external is still C1D2 (air conditioner, lights, switches, etc.)
Other safety features – gas cell
Other safety features – enclosure design

C1D2 Diverter Valve
Explosion safety items

- **Particle contaminants**
  - Filter appreciable particles
  - Filter oils and other liquids

- **Explosive gas streams**
  - Limit power if found to be explosive
  - Divert flow under abnormal circumstances
    - Chemo-luminescence, gas breakdown, etc
Control software with safety features

- Multi-zone temperature monitoring with shutdown
- Diverter valve control
- Flammability determination
Conclusions

• Making a Class 1 laser research-product can be easy!
• Constructing reliable interlock circuits is a breeze.
• New diagnostic tools will likely use more lasers with higher power.
• High powered lasers can be used in hazardous locations IFF the correct procedures are taken!
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Laser-launch conditions

\[ \alpha_{1m} \approx \frac{u_{1m}^2}{K^2 R^3} * Re\left(\frac{1}{2} (v^2 + 1) \frac{1}{\sqrt{v^2 - 1}}\right) \]

\[ \theta_{1m} \approx \frac{u_{1m}}{K \cdot R} \quad K = \frac{2\pi}{\lambda} \]

\( \nu \cong 0.13 + 3.19i \) @ 532nm

\( \Theta_{\text{max}} = 0.52^\circ \)

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Gaussian linear input beam

0.9mm diameter

\( \Theta_{\text{max}} = 0.52^\circ \)

50mm achromat Capillary waveguide

EH\(_{1m}\) TE\(_{1m}\) TM\(_{1m}\)
Plumbing for quick sampling

- Bypass flow determined by upstream tubing and sample rate
- Capillary flow set for max sample-rate
Chemometrics

- Spontaneous Raman is linear with concentration
- Error (~<1%) increases with # of species:
  \[ [G] = [C]^{-1}[M] \]
- [C], the calibration matrix, contains spectra of pure gasses
- Error mostly a result of background subtraction (commercial capillaries)
- Initial calibration only unless more gasses are added
Capillary waveguide improvements

Counts/s in AIR @ ~150mW

Wavelength (nm)

Silica Raman

SNR ~ 90

Laser

Fluorescence

SNR ~ 530!!!

\[ R = \frac{C_{gas}}{\sqrt{C_{noise}}} \]
New Improved Capillaries

- Ag/polymer lined fused-silica
- Wet-chemical Tollens reaction
- NETL-designed deposition system
- Gold waveguides also produced (for 785nm)
- Pre-cleaving for end-facet coating
- Custom testing setup
Current Detection Limits Improved ~5.9X

(1s Integration, 100 mW, 1 m Capillary, OO Spectrometer, computed for binary mixtures)

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Red: Commercial capillary
Blue: NETL Capillary
Industrial high-pressure tests

Industrial automation features: laser fitting, intelligent control of heaters and valves, background subtraction, interlocks, saturation detection
Conclusions

• Raman analysis of gasses can be done very quickly, replacing other equipment
• Sub-percent accuracy, repeatability, and detection limits
• Calculations completed in real-time
• Low-noise NETL capillaries facilitate higher accuracy
• Single calibration sufficient
• High pressure gasses readily measured
Future work

- Test NETL waveguides for H$_2$S resistance
  - Test chamber almost complete
- Continue to improve waveguides and metal coatings
  - Possible ~2-10X signal increase for same laser
  - Possible ~2X noise decrease for same hardware
- Fabricate more GOLD waveguides
  - Process being refined, some waveguides produced
- Assemble prototype #2
  - Most parts are fabricated
- Conduct extended onsite testing (3-12 weeks)
- Control experiment in the Lab Scale Burner facility
- Improve calibration facilities (UHP gases, MFCs, high-accuracy temp. and pressure readouts)
  - Gas delivery system design complete, being fabricated
Recent Publications

- Biedrzycki, Buric, Falk, and Woodruff, (Optical efficiency in metal-lined capillary waveguide Raman sensors”, SPIE Symposium on Defense, Security + Sensing 2011
- Buric, Falk, and Woodruff, “Conversion of a $TEM_{10}$ beam into two nearly Gaussian Beams”, Applied Optics, 2010
Calibrations – critical for calculation
Portable unit internal components

- **SPEED**: One-second response time – faster than GC (minutes), and electrochemical (tens of seconds)
- **ACCURACY**: Sub-percent for all species with little cross sensitivity
- **SIMPLICITY/STABILITY**: Obtains all species at once with no tunable lasers (compare to TDLAS)
Sensor Response Time
Software Improvement – Laser fitting

Circular slit function (fiber bundle)

Gaussian convolution (laser line shape)

Error function for coma correction

Final fit to laser line used to shift spectra

r, c, bet(1-4), off(1-3), Pix#, error  3.95 1.11 0.34 0.66 -0.51-0.75  -250 211 40.02 800.8105
Pipeline contaminant solutions

- **Heavy hydrocarbon condensation**
  - Heat to re-vaporize (>150°C) and filter

- **Compressor oil / liquid droplets**
  - Filter and coalesce
  - New 4-zone heating (vs. 1-zone)
  - Divert flow until cell is hot
First Round Findings and Proposed Solutions

• **Reduce optical background variation**
  – New, low-noise NETL capillaries
  – Improved gas-cell design for stability

• **Protect from pipeline contaminants**
  – Additional filtration and heating (more zones)
  – Diverter valve on input line

• **Reduce software complexities**
  – Automatic features, simplify operation
  – Adjustment for laser frequency drift
  – Minimize species in calculation

• **Improve calibrations (temperature, pressure, etc.)**
  – Ambient or high pressure calibration
New Improved Capillaries
Recent Publications

• SPIE Defense Sensing and Security 2012 - "Field testing the Raman gas composition sensor for gas turbine operation”) with S. Woodruff, J. Mullen, J. Ranalli, B. Chorpening, M. Buric
• Buric, Chen, Falk, and Woodruff, “Multimode metal-lined capillaries for Raman collection and sensing”, JOSA B, 2010
• Buric, Falk, and Woodruff, “Conversion of a TEM$_{10}$ beam into two nearly Gaussian Beams”, Applied Optics, 2010
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Detection Limit (%)

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