Chapter Title:

Instrumentation for Bench- and Large-scale Test Fixtures

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Project working title:

3.C - Laser-Based Instrumentation for Real-Time, In-Situ Measurements of Combustible Gases, Combustion By-Products, & Suppression Concentrations

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Army Research Laboratory (APG, MD)
Working Description:

OPTICAL SPECTROSCOPIC TECHNIQUES FOR ARMY APPLICATIONS

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• joint, effort at ARL (Army Research Laboratory), ATC (Aberdeen Test Center), NIST Using Optical Spectroscopy

• (FY97-02)

• work focussed on needs pertaining to armored vehicles

• field-scale to laboratory scale environment
Talk Outline

- Introduction – Tanks
- Species (Suppressants; Toxic By-products; Fuels; Oxidizers)
- Fast Vibrational/Visible Spectroscopy
- Differential Infrared Rapid Agent Concentration Sensor (DIRRACS)
- Laser Induced Breakdown Spectroscopy for Fire and Explosive Suppressant Measurement
- Diode Laser Spectroscopy for Toxic and Combustible Gas Measurement

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Differential Infrared Rapid Agent Concentration Sensor (DIRRACS)

- Measurement of suppressant concentration
- Previous instrument response time ~ 200 ms (viscosity sensor)
- 1 ms response time
- Infrared absorption
- Insensitivity to vibration

HFC 125

[Graph showing absorbance and % transmitted vs wavelength]
DIRRACS II Schematic
DIRRACS II Instrument
DIRRACS II Test Rig

Transient Application
Recirculating Pool Fire (TARPF) Facility at NIST.
DIRRACS Testing

Time Response < 10 ms
Sensitivity < .005 volume fraction

HFC 125 agent volume fraction versus time for two releases of HFC-125 in the TARPF facility.
Suppressant Gas Measurement: Laser Induced Breakdown Spectroscopy (LIBS)

Plasma Formation
- Multiphoton Absorption --> Ionization
- Absorption of Laser Radiation by Free Electrons, i.e. Inverse Brehmstrahlung
- Electron Collisions --> Ionization --> Heating --> Breakdown
- Typical Gas Temperatures, ca. 20,000 K

Spectrochemical Analysis based on Collection of Emission of Atomic and Molecular Constituents Usually after Plasma Continuum Radiation Decays (2-100 usec).
LIBS Instrumentation

Gated Intensified Camera

Spectrograph

Collimator / Fiber Coupler

Plasma

Analyte Gas Flow

Focusing Lens

1064 nm Pulsed Laser Radiation
LIBS of DMMP

Signal Intensity

Wavelength (nm)

Time Delay (us)

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LIBS of Fire Suppressants

Signal Intensity (arbitrary units) vs. Concentration (ppm)

- FM-200
- Halon-14
- Halon-1301
- HFC-134a

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Toxic and Combustible Gas Measurement: Near Infrared Tunable Diode Laser (TDL) Spectroscopy

HF, O₂, CO, CH₄, HCl, other small molecules

Transmission - no modulation

Transmission - with modulation (note RAM)

Wavelength Modulation Spectroscopy

Demodulated signal (2f)
HF Gas Measurement During Suppressant Testing

![Graph showing HF concentration over time for different suppressants.](image)

Figure 2

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**Oxygen Measurement Using TDL Spectroscopy**

Oxygen Absorption Near 760 nm (b → X, \(^1\Sigma_g^+ \leftrightarrow ^3\Sigma_g^-\))

JP-8 - air fire, inhibition by C\(_3\)F\(_8\), crew compartment test fixture, fire extinguished 150 ms after detection.

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Multiple Species Gas Sensing Using Tunable Diode Lasers (TDL)

Absorption as function of time for each wavelength (i.e., for each gas)
Time Division Multiplexing

Diode laser
Detector
Fiber optic cable

Transmits best at:
780 nm
1310 nm
1550 nm
Detection and Measurement of Middle Distillate Fuel Vapors Using Tunable Diode Lasers

Wavelength (micrometers)

Spectrum of dry air saturated at 294K with vapor from unleaded gasoline, JP-8, DF2. Spectra offset for clarity.
Limitations of TDL Spectroscopy For Measurement of High Molecular Weight Vapors

Absorption features are unstructured.

Can’t use traditional wavelength or frequency modulation techniques to measure big molecules (e.g., middle distillate fuels - JP-8, DF-2, etc.). Unable to scan on and off resonance with single DFB laser.

Develop a near-infrared diode laser-based sensor capable of measuring hydrocarbon fuel vapor concentrations with a time resolution of 10 msec per measurement point; maintain S/N advantages of WMS.
Measurement Technique

- uses laser diode absorption spectroscopy in the near-infrared spectrum (1.3 microns and 1.71 microns)

- Emission intensity from two lasers is varied sinusoidally, with emission from first laser 180 degrees out of phase with emission from second laser.

- Measurement is made in situ.

- Phase sensitive detection is used to measure differential absorption at the two laser emission wavelengths.

- 10 msec response time
Figure 3: The experimental apparatus used to measure vapors from middle distillate fuels.
**Figure 4:** shows the vapor phase absorption spectrum of air saturated by vapor at 294K from JP-8, DF-2, and gasoline between wavelength values of 1.3 and 1.75 micrometers superimposed upon the emission from the optical fiber which carries the mixed wavelength probe beam.
Results: Approach to Lower Explosion Limit (LEL) in a Gasoline Fuel Tank at Room Temperature

Simultaneous measurement of fuel/oxygen concentration (by volume) during displacement of contents (dry air) of a 14 liter vessel by air saturated by gasoline vapor at 294K and 1 atmosphere total pressure. Oxygen sensor courtesy of Oxigraf, Inc.
Results: “Aging” of JP-8 Detected Using Mixed Laser Sensor

Fresh sample

Sample after 5 runs

ppm JP-8 Vapor

Time (s)
For a monochromatic source:

\[ I(\sigma) = I(\nu) \cos 2\pi \nu \sigma \]

For a polychromatic source:

\[ I(\sigma) = \int_{0}^{\infty} I(\nu) \cos 2\pi \nu \sigma \, d\nu \]

\( \sigma \) = mirror position
\( \nu \) = light frequency (cm\(^{-1}\))
\( I(\sigma) \) = intensity at detector
\( I(\nu) \) = source intensity
FT Diode Laser Spectroscopy

IC, QC laser

lens

Analyte region

detector

3.22 μ

3.24 μ

3.26 μ

3.28 μ
FT Diode Laser Spectroscopy

Signal at detector
Laser 1 (100 KHz) at 1.31 μ
Laser 2 (110 KHz) at 1.71 μ

Fourier transform of signal at detector (res. = 100 Hz)
Absorption of laser radiation at 1.71μ as air in 2m cell is displaced by air saturated with gasoline vapor.
Conclusions/Succesess/Failures

- Project greatly enhanced knowledge of fire suppression on board combat vehicles.
- Laser diode systems fielded at ATC/ARL for HF and O$_2$.
- DIRRACS II testing at WPAFB.
- FTLS work continues.
- JP-8 sensor vibration problems
- COF$_2$ formation documented
Conclusions/Successes/Failures (cont.)

- Lasers outside communication bands still very expensive
- Mid-IR RT CW lasers still unreliable
- Narrow BW, broadly tunable, fast light sources still unavailable

Publications

9 open literature, 1 book chapter, 11 Gov’t Tech Reports
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