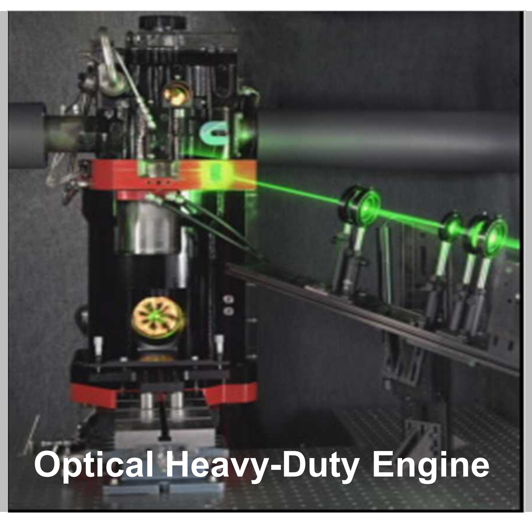
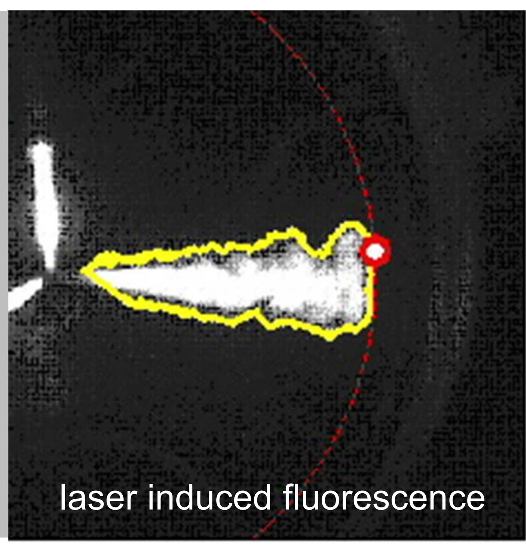
SAND2015-5965D

Tracking Down Fuel Tracers - Fingerprinting electronic, vibrational, and rotational excitation as a means of fuel impurity detection

Ian W. Liu, W. Ethan Eagle, Mark P. B. Musculus
Sandia National Laboratories





Sandia National Laboratories

Exceptional service in the national interest

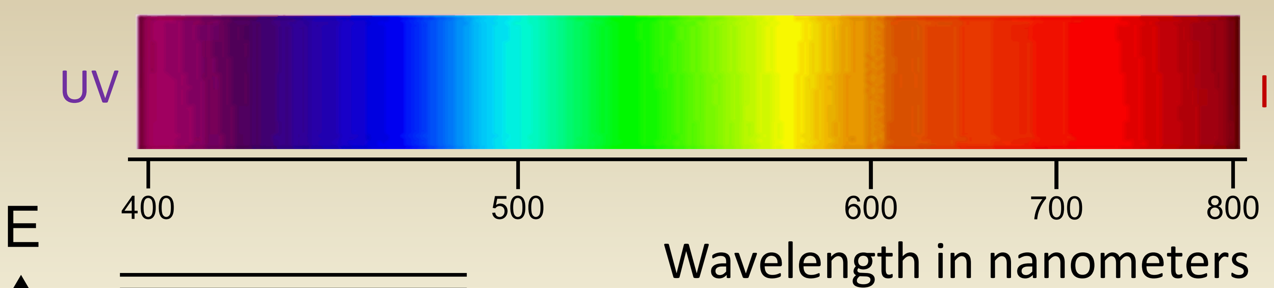
Motivation

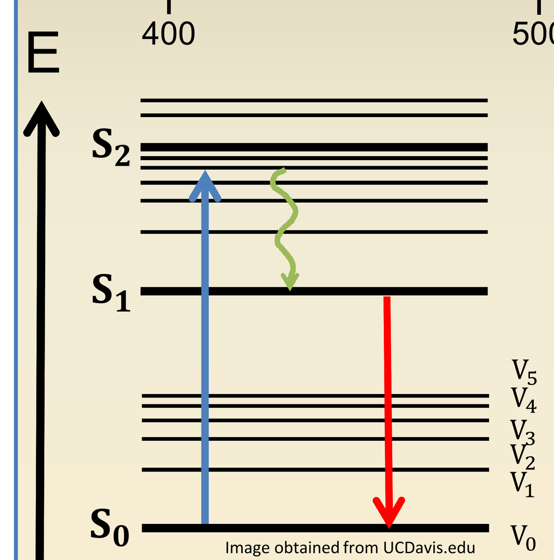
Toluene is a valuable tracer molecule for fuel-spray concentration measurements in our optical engine because it yields a known laser-induced fluorescence (LIF) signal. It works well when mixed with high-purity fuels like n-heptane, which have no LIF signal. We prefer to use a better diesel-fuel surrogate, like **n-dodecane, but it is less pure, and the LIF signal from the impurities is unknown**. To compare our n-dodecane LIF measurements with toluene in n-heptane, e.g. Hartman,[1] we need absorption and fluorescence spectroscopy measurements of our fuel.

Scope and Aims

We use non-fluorescing n-heptane to dilute solutes of interest: bottled n-dodecane (Sigma Aldrich, ≥99.2% purity), "engine" n-dodecane used in the fuel system, and toluene. **We measure the absorption and emission spectra** of each and then use the toluene as a reference to both **calculate the effective toluene concentration** and also attempt to identify the impurities.

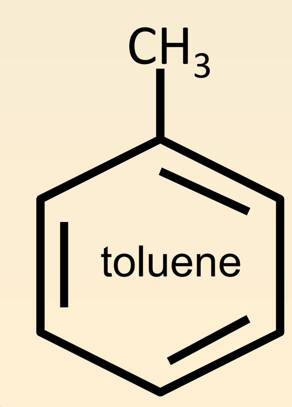
Electromagnetic Spectrum Interactions

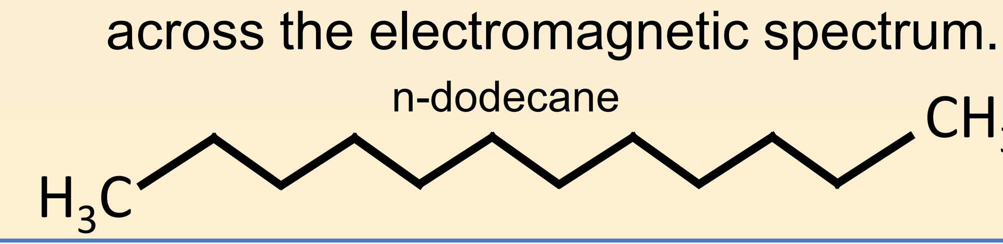




Photons are absorbed at specific wavelengths when electrons jump from ground state (S_0) to a higher energy state (S_1) and are then fluoresced at lower energy, longer wavelengths as they transition back to ground.[2]

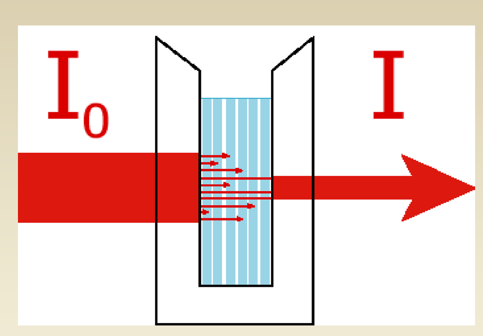
Molecular structures provides a unique pattern of absorbance and fluorescence across the electromagnetic spectrum.





Absorption Spectroscopy

Beer-Lambert Law[3]

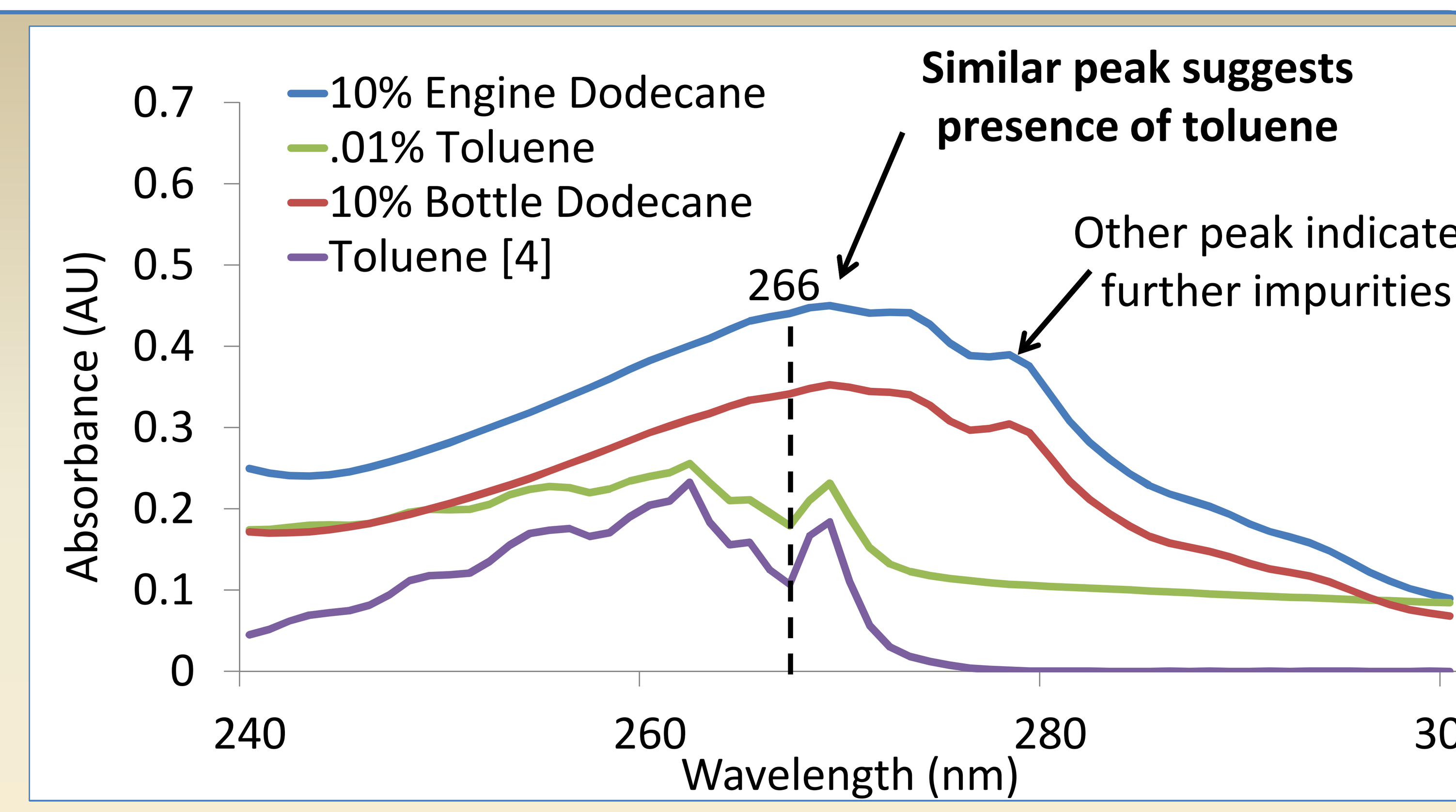


$$\text{Transmittance (T)} = \frac{I}{I_0}$$

$$\text{Absorbance (A)} = -\log_{10}\left(\frac{I}{I_0}\right) = \varepsilon l c \text{ or } A = \sum_{i=0}^{N} \varepsilon_i c_i l$$

Using a sample size of 6, the absorption spectra of three different solutions were obtained using a Hewlett Packard UV-Vis Spectrophotometer placed in rectangular quartz cuvettes averaging 1.4 ml volume with 1cm path length, l.

Solution (in n-heptane)	Mass Conc.
Bottle n-dodecane	10%
Engine n-dodecane	10%
Toluene	0.01%



At our excitation wavelength of 266 nm, we observed absorptions of 0.35, 0.26, and 0.11 for engine n-dodecane, bottle n-dodecane, and toluene respectively.

Absorption at 266 nm

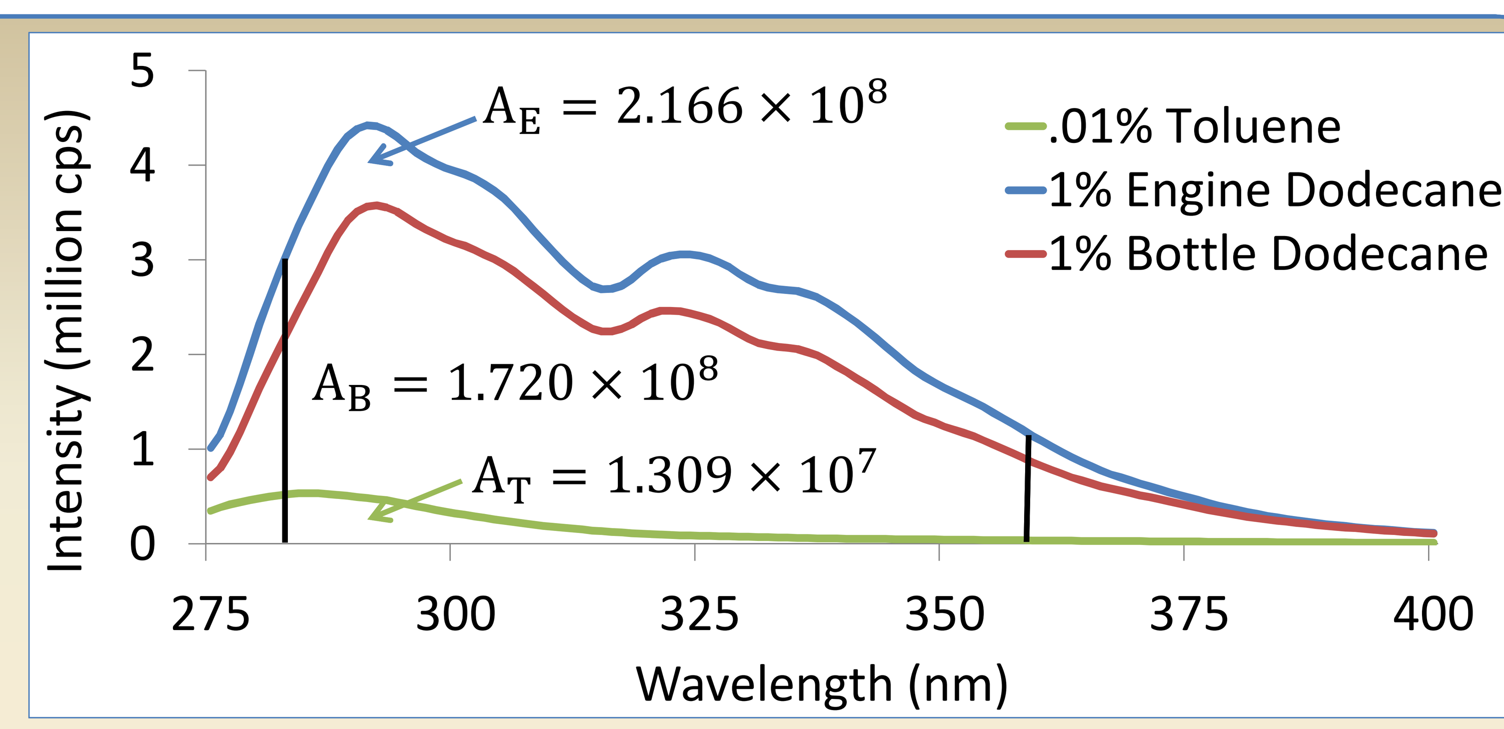
Fuel Type	Mean, as if x% toluene	Std dev of mean
Bottled	0.22	0.07
Engine	**0.30**	**0.07**

Fluorescence Spectroscopy

The three solutions (n=6) were processed with the Horiba FluoroMax-3 at 266nm excitation to produce the fluorescence emission spectra.

Solution (in n-heptane)	Mass Conc (c)
Bottle n-dodecane (A_B)	1%
Engine n-dodecane (A_E)	1%
Toluene (A_T)	0.01%

Knowing the fluorescence is $F = k(1 - 10^{-\varepsilon c l})$, we used the known path length, l, and concentration, c, to fit the resulting spectral emissivity, ε. Then the theoretical fluorescence magnitude of un-diluted n-dodecane is estimated and indexed as if it were instead a solution of toluene / n-heptane.



For the intensified camera filter's detection bandwidth of 285-360nm, we calculated the total detectable fluorescence by the area under each curve.

Fluorescence from 285 to 360nm

Fuel Type	**Mean, as if x% toluene**	Std Dev of mean
Bottled	2.37	0.4
Engine	**2.98**	**0.6**

Future Work

A collaboration with Dr. Darrel Sasaki to make **nuclear magnetic resonance (NMR) measurements** may provide further insight on the identities of our impurities and **further refine our effective percent toluene estimates**. We will seek to further reduce bias introduced due reflection in the absorption measurement to minimize uncertainties in the reported concentrations.

Conclusions

Toluene was a possible impurity present in our fuel, and increased impurity is seen in our fuel system. We demonstrated **equivalent absorbance and fluorescence of our engine's n-dodecane fuel to a 0.30±0.07%. toluene/n-heptane solution and a 2.98±0.6%** toluene/n-heptane solution respectively. This in the low to mid range for toluene/n-heptane mixtures reported in literature.

References

[1] Hartmann, M., I. Gushterova, M. Fikri, C. Schulz, R. Schießl, and U. Maas. "Auto-ignition of Toluene-doped N-heptane and Iso-octane/air Mixtures: High-pressure Shock-tube Experiments and Kinetics Modeling." *Combustion and Flame* 158.1 (2011): 172-78.

[2] Clark, Jim. "Electronic Spectroscopy Basics." *Chemwiki*. UC Davis, n.d. Web. 17 July 2015. <http://chemwiki.ucdavis.edu>.

[3] "Beer's Law." *Beer's Law - Theoretical Principles*. Sheffield Hallam University, n.d. Web. 20 July 2015. <http://teaching.shu.ac.uk>.

[4] Prahl, Scott. "Toluene." *Toluene*. Oregon Laser Medical Center, 05 Mar. 2012. Web. 21 July 2015. <http://omlc.org/spectra/PhotochemCAD/html/090.html>.

Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.
SAND No. 2011-XXXXP

U.S. DEPARTMENT OF ENERGY
NNSA National Nuclear Security Administration