Isotopic Tracing of Fuel Components in Combustion Products

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Outline

- Objectives
- AMS Background
- Results
- Significance
- Future

Objectives

- Determine the propensity of carbon in specific chemical structures to form certain emission products
- Use data to validate combustion modeling
- Exploit measurement capability with other expertise and capabilities at SNL and LLNL

Accelerator Mass Spectrometry (AMS) Measures attomoles of Carbon-14

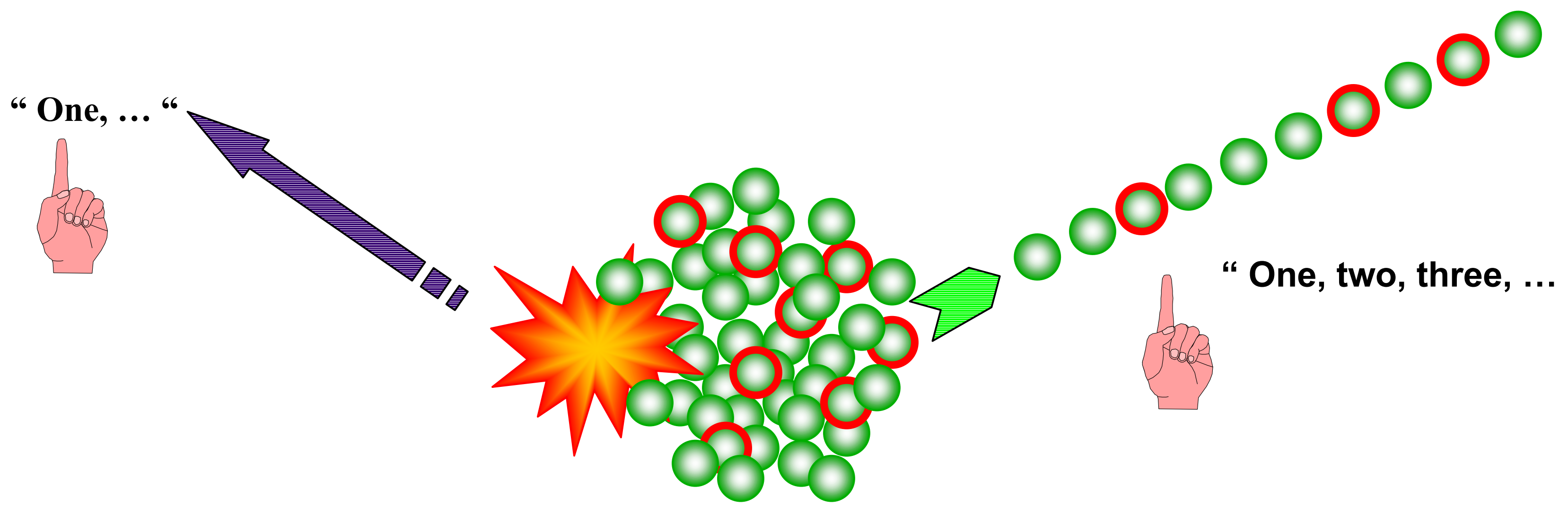
- Cosmic radiation naturally produces ^{14}C in the atmosphere
- All bio-derived fuel components have contemporary ^{14}C label
- Petroleum-derived fuel components are nearly ^{14}C free
- Trace contemporary level (100 amol ^{14}C/ mg C) with no radiation hazard
- Count individual ^{14}C atoms rather than wait for decay

- The Center for AMS at LLNL measures ^{3}H to Pu
- 15,000 ^{14}C samples measured annually with 100 run days

Counting radioactivity is inefficient: mass spectrometry counts ≥1% of isotopes present

Decay Counting

AMS



Sample

$dN / dt = - N / \tau$

$dt = dN / N * \tau$

Counting 0.1% of ^{14}C in a sample

$dt = 0.1\% * \tau = 0.1\% * 8330\ y = 8.3\ y$

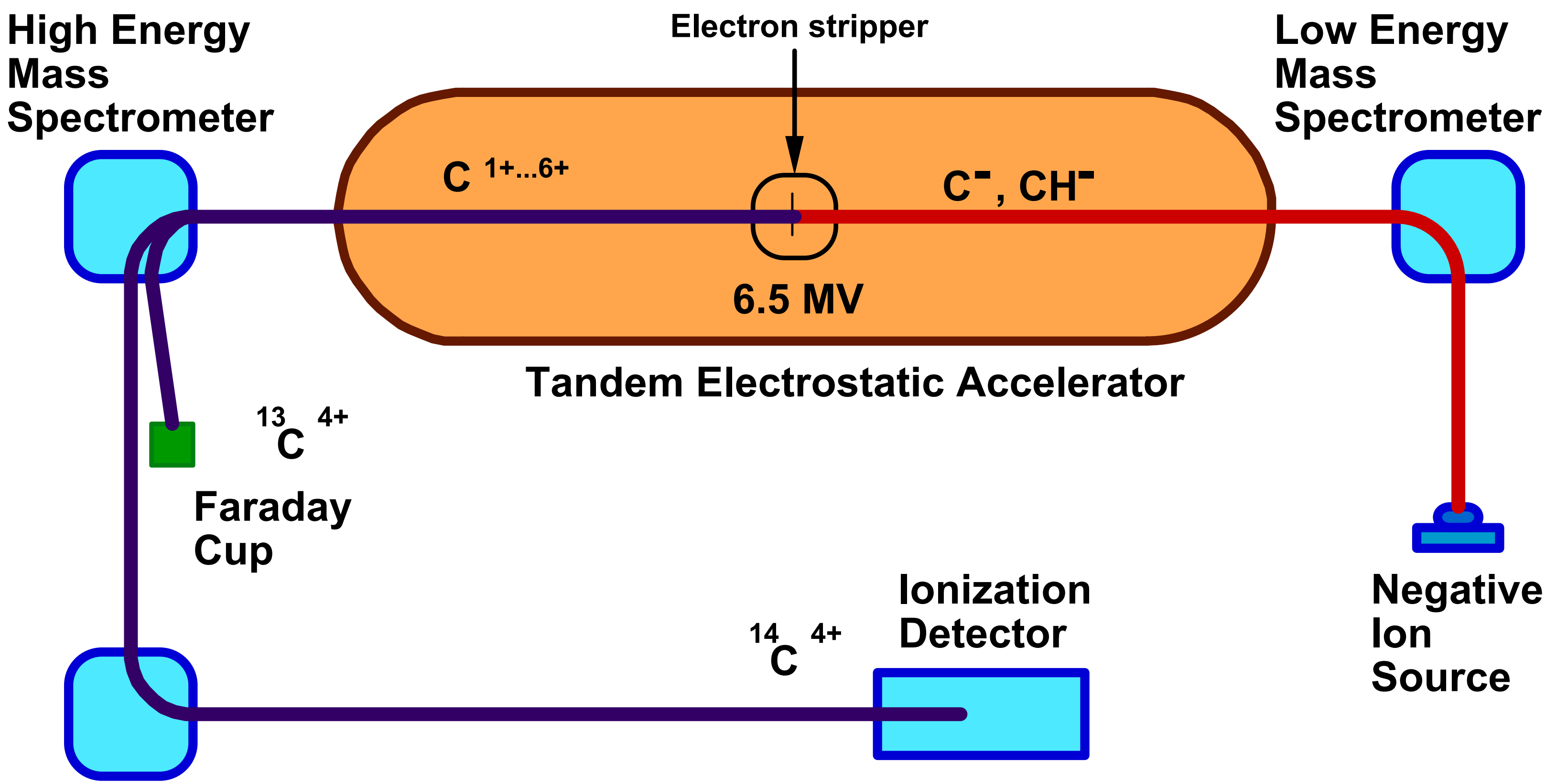
Count atoms, not decays

10,000 ^{14}C can be counted in <30 sec for contemporary sample

Sensitivity is attomole

AMS Uses 2 Fundamental Nuclear Physics Techniques, Both Needing MeV Particle Energies

• Molecular isobar destruction

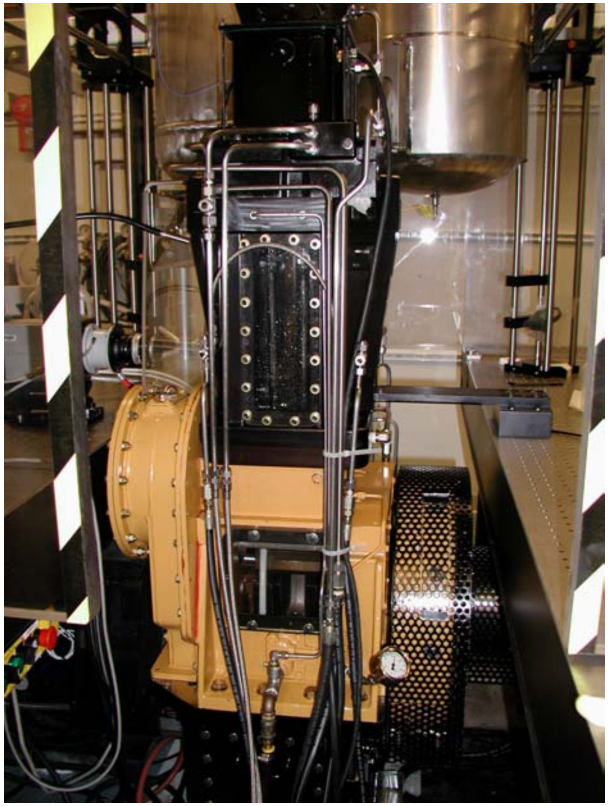


• Nuclear isobar identification

Fuel and Engine

- Create a blend which matches combustion behavior of CN80 reference fuel used at SNL
- High concentration of DBM in blend selected to minimize dilution
- Operate optical engine in skip fire mode

Fuel Component	Volume %
dibutyl maleate	88.0
n-hexadecane	7.0
2-ethylhexyl nitrate	5.0



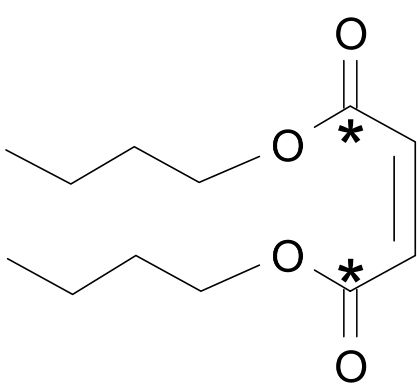
Caterpillar 1.7L, 1 cyl.

CRF, SNL

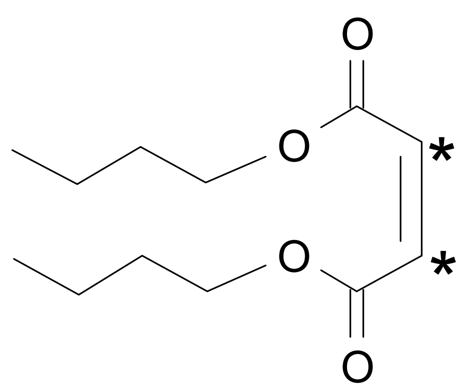
SAE 2002-01-1631

Tracing Flavors of Carbon in Dibutyl Maleate (DBM)

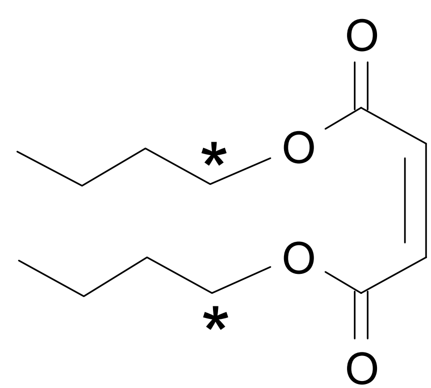
- **Position of carbon within a fuel molecule affects its distribution in combustion products**
- **Nearest neighbors determine molecular fragments produced during combustion**



1,4 maleate



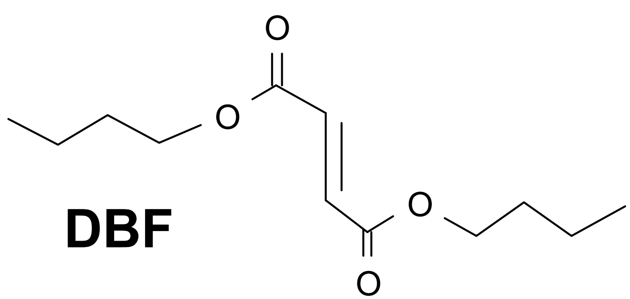
2,3 maleate



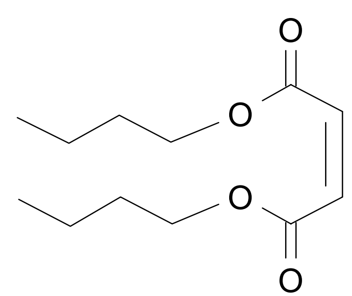
1-butyl

Resolving Impurity Issues with DBM

- **Standard Distillation produced tar-like residue**
  - Apparent polymerization and thermal decomposition
  - Double distillation using distillate also made residue
  - Vacuum distillation failed due to high boiling point
- **No Metal in Filtered Particles Removed from DBM**
  - Ion exchange resin from DBM production
- **Filtrate analyzed by NMR**
  - Evidence of dibutyl fumarate (DBF)



DBF

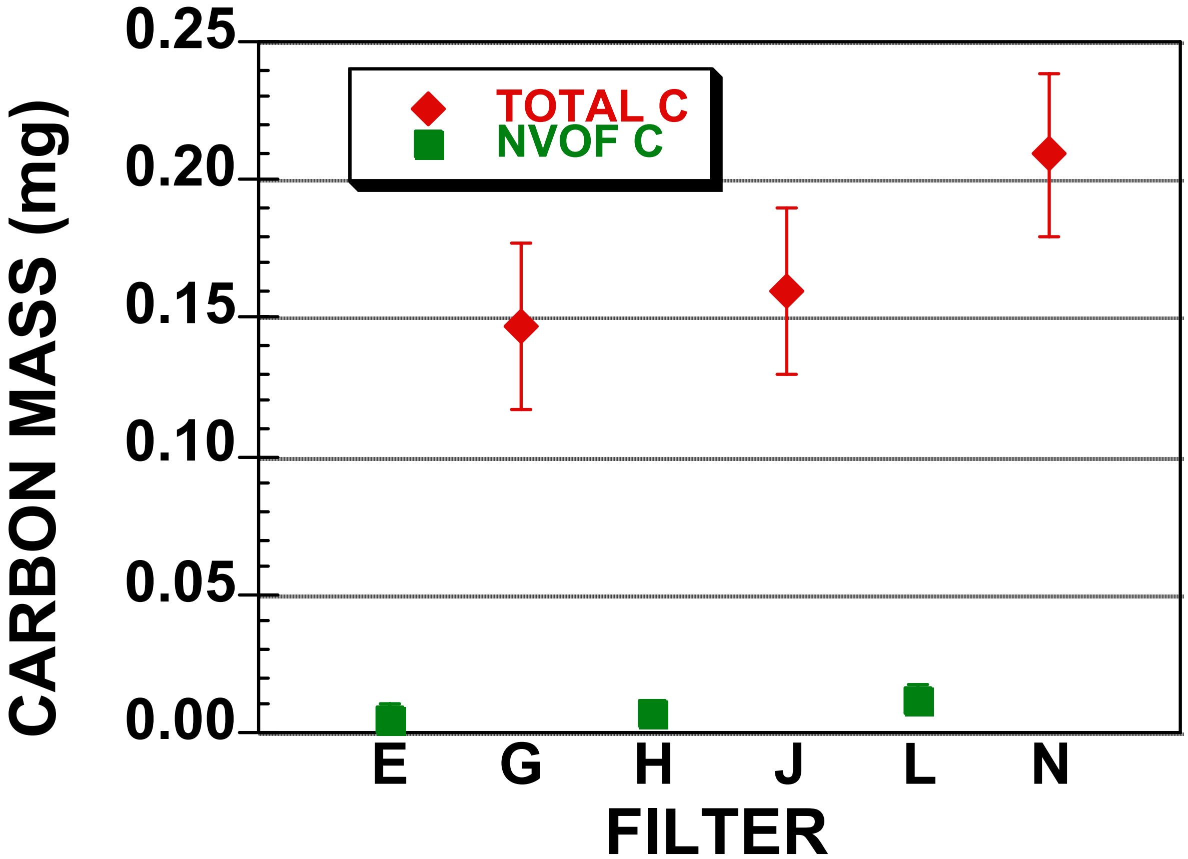


DBM

Coping with Deposited Lubrication Oil

- Require Many Motored Runs to Assess Lube Oil Deposition and Removal Effectiveness
- Sustained Heat Removes Lube Oil
  - 320-340 °C for 2 h removes most oil from motored samples
  - Also removes volatile organic fraction (VOF) of soot
- Solvent Extraction Failed to Remove all Lube Oil
- Switch to more Volatile Lube Oil
- Prevention is the Cure

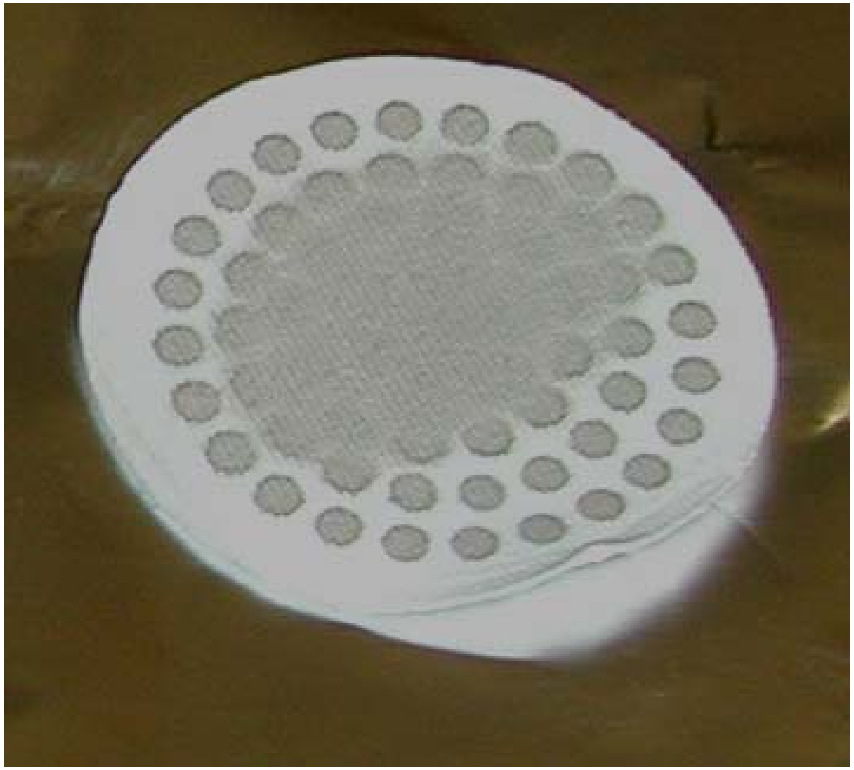
Lube Oil Removal from Motored Carbon Control Filters



Thermal treatment at 320°C for 2 h removes unburned lube oil from motored control filters

Particulate Matter Analysis

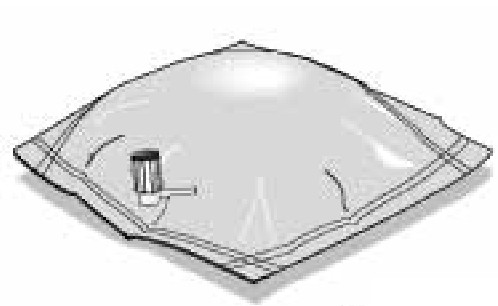
- Collect motored and fired (0.1- 0.5 mg soot) samples on quartz filters
- Treat to remove lube oil and save pair as controls
- Measure carbon mass during AMS sample prep
- Measure ^{14}C content of each sample
- Determine contribution of specific carbon atom in DBM to soot



Volatile organic carbon fraction is susceptible to further catalytic oxidation

Gas Analysis

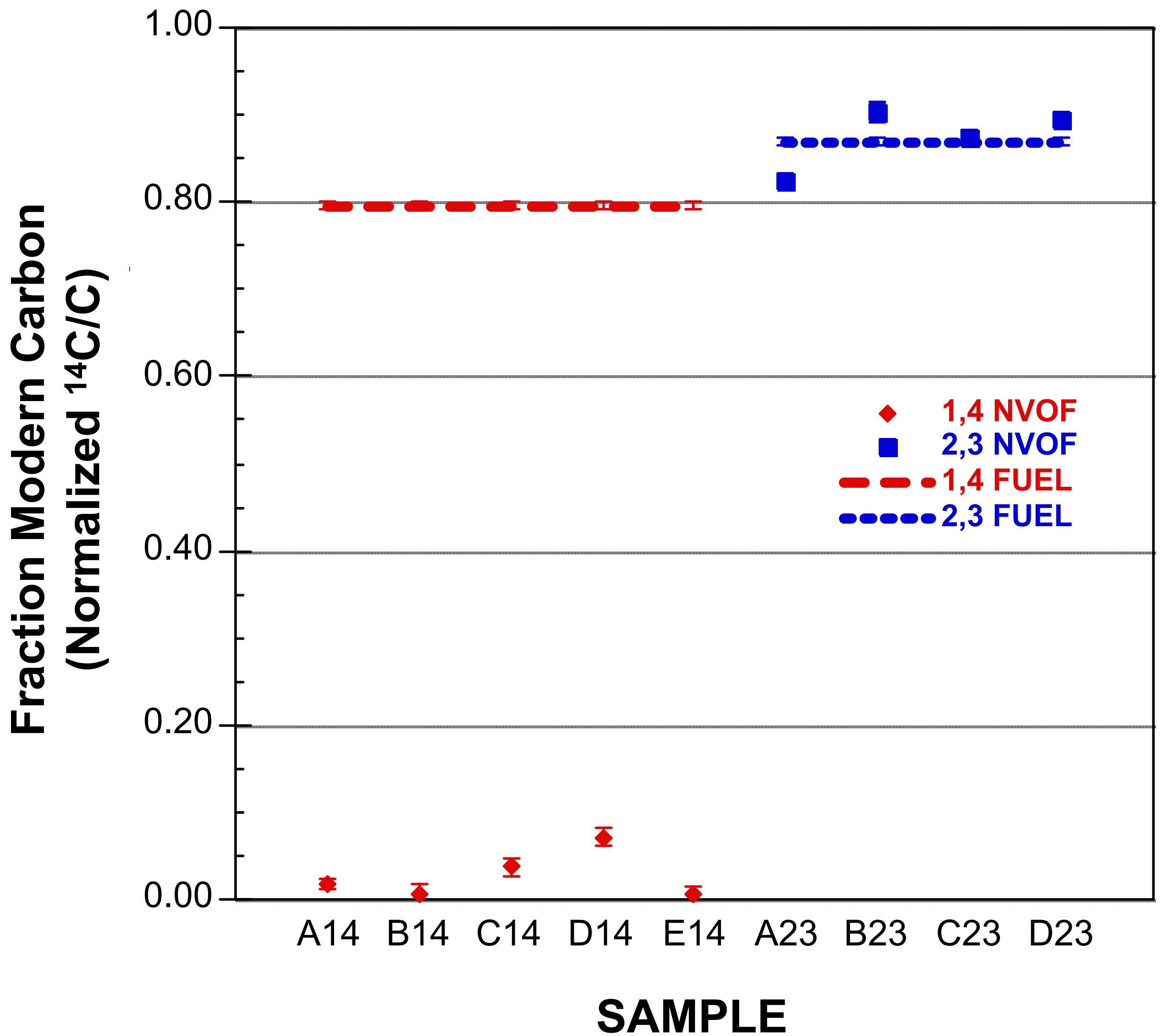
- Collect Combustion Gas Samples in Tedlar Bags
- Cryogenically Separate CO_2 and Convert to AMS Graphite Sample
- Separate other Combustion Gases with Molecular Sieves or Gas Chromatography
  - CO (MS) ✓
  - Unburned hydrocarbons (GC) ✡
  - Small aldehydes (GC or LC) ✡
  - Air toxics (GC) ✡

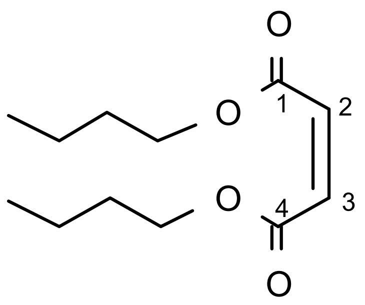


✓ Current Capability

✡ Future Development

Comparison of NVOF soot from [1,4 maleate-^{14}C] and [2,3 maleate-^{14}C] BM88 fuel

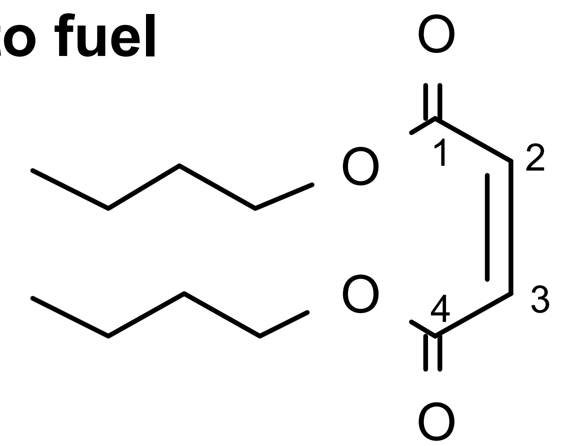




- **2,3 maleate C is slightly more likely to form soot than normal hydrocarbons**
- **1,4 maleate C does not form soot**

Early Results

- PM generated by [1,4 maleate ^{14}C] DBM was essentially ^{14}C free
  - Repeat with gas collection and CO_2 analysis
- Runs with [2,3 maleate ^{14}C] DBM begun
  - PM ^{14}C content same as fuel
  - Gas ^{14}C content comparable to fuel
- Particulate sample size has increased over early runs. Improves AMS sample prep and measurement (heated sampling line)



Converting the Measured Isotope Ratio to a Carbon Contribution

$$R_{sample} = \frac{R_{sample(meas)}}{R_{stand(meas)}} R_{stand}$$

Isotope ratio of the sample (R_{sample}) is calculated from the measured ratio of the sample, an average of measured ratios of standards, and the known ratio of the standard.

Tracer, fuel, additives, background, and unknown contamination all contribute to the ratio of a sample

$$R_{sample} = \frac{{}^{14}C_{tracer} + {}^{14}C_{fuel} + {}^{14}C_{add} + {}^{14}C_{bk} + {}^{14}C_{uk}}{C_{tracer} + C_{fuel} + C_{add} + C_{bk} + C_{uk}}$$

Minimize the Number of Non-Negligible Terms in the Ratio Equation by Prudent Experimental Design

Converting the Measured Isotope Ratio to a Carbon Contribution

$$R_{sample} = \frac{{}^{14}C_{tracer}}{C_{tracer} + C_{fuel} + C_{add}}$$

Background determined and by series of blanks and controls.

$$C_{tracer} = \frac{{}^{14}C_{tracer}}{R_{tracer}}$$

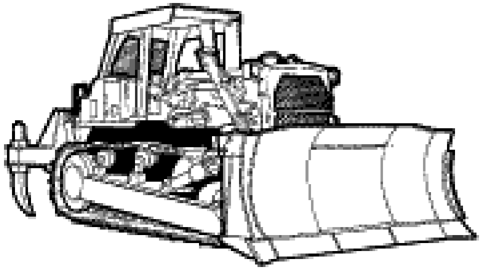
Isotope ratio of the tracer (R_{tracer})is measured. It is the only non-negligible ^{14}C source.

$$F_{tracer} = \frac{C_{tracer}}{C_{sample}}$$

Fraction of carbon due to the tracer (F_{tracer}) is the ratio of trace carbon to sample carbon.

Ongoing Tasks

- Complete Runs of DBM with ^{14}C label in three different positions
- Interpret data and compare to computational predictions
- Improve sample collection & compound separation
- Publish Results (SAE 2002-01-1942, 2002-01-1704), several papers in progress
- Continue to improve schemes to trace variety of oxygenates or other fuel components in particulate and gaseous emissions



Significance to Governments, OEMs, Fuel, Additive, and Catalyst Industries

- Use data for model validation
- Leverage LLNL & SNL unique facilities
- Develop analysis methods suitable for any combustion system
- "Non-radioactive" levels of ^{14}C tracer can be used in any conventional engine lab, dynamometer facility, or open road test

Future Plans

- Use information to design cleaner burning fuels
- Determine combustion fate of carbon from major fuel components (aromatics, alkylated aromatics, cyclo-alkanes, etc.)
- Apply chemical separation and ^{14}C-AMS to assess quality of combustion in new engines (HCCI)
- Selectively label hydrocarbons for use as tracers in investigating mechanisms on catalysts

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