National Renewable Energy Laboratory
*Innovation for Our Energy Future*

# Biodiesel Utilization: Update on Analytical Techniques

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# Key Points of Biodiesel Utilization

- 2007: Energy Independence and Security Act mandates biodiesel production in the United States starting with 500M gallons in 2009, increasing to 1B gallons in 2012[1]
  - Diesel sales are 63B gallons in 2007[2]
- 2008: 700M gallons of biodiesel produced in United States[3]
- October 2008: ASTM adopted Bxx blend specifications
- March 2009: EU added tariff on imported biodiesel[4]
- Therefore, biodiesel *is* being used in the United States

1. http://www.renewableenergyworld.com/rea/partner/stoel-rives-6442/news/article/2008/01/eisa-of-2007-calls-for-additional-production-of-biofuels-51063
2. http://tonto.eia.doe.gov/dnav/pet/pet_cons_821dst_dcu_nus_a.htm
3. http://www.biodiesel.org/resources/faqs/
4. http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2009:067:0022:0049:EN:PDF

# Topics for Discussion

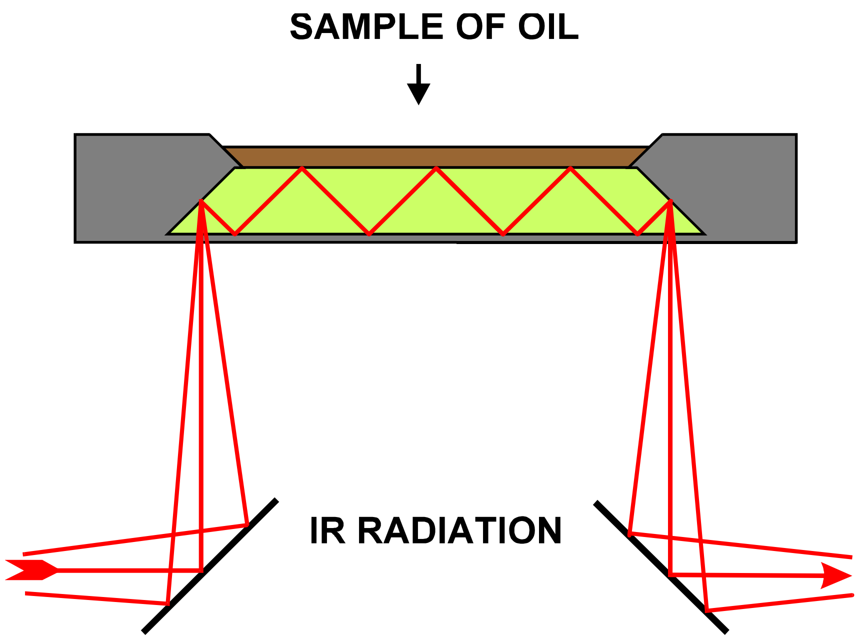
- Biodiesel in lubrication oil
- Cold soak filtration

# Biodiesel in Lubrication Oil

- Biodiesel is less volatile than diesel fuel
  - Possible accumulation in lubrication oil
- Traditional GC methods for fuel dilution don't account for biodiesel (ASTM D3524)
- FTIR/ATR method (D7371) for biodiesel in diesel fuel may be modified to detect biodiesel in lube oil
  - Strong C=O stretch between 1750 $cm^{-1}$ to 1650 $cm^{-1}$
- How does lube oil base stock impact results?

# Benefits of FTIR/ATR

- Horizontal ZnSe 45° multi-bounce ATR cell
- Short path length (10-20 μm) allows measurement of used lubrication oil (soot readily absorbs IR)
- Cell maintains fixed path length over useful life
- Rapid analysis time (~60 seconds) for 32 scans and 4 $cm^{-1}$ resolution



# Engine Durability Tests

- Run diesel engine over durability cycle with advanced emission control systems – NAC and SCR
  - Late cylinder injection and/or fuel injection into exhaust for emission control
- Oil was changed at recommended intervals
  - Collect aliquot for fuel dilution analysis
- Validate FTIR/ATR technique to quantify biodiesel dilution in lube oil
  - PLS model built with fresh oil from project and typical soy-derived biodiesel
    - Base stock character can impact quantitation results

NAC = NOx adsorber catalyst

SCR = selective catalytic reduction

# Engine and Fuel

| | |
|---|---|
| Engine Power | 113 kW at 4,000 rpm |
| Peak Torque | 360 Nm at 2,000 rpm |
| Max. Engine Speed | 4,700 rpm |
| Max. BMEP | 21 bar |
| Cylinder/Firing Order | I-4, 1-3-4-2 |
| Bore to Stroke Ratio | 1.0034 |
| Displacement | 2.15 L |
| Compression Ratio | 18:1 |
| Fuel Injection System | $2^{nd}$ Generation Common Rail |
| | |
| Fuel | Soybean-derived B20 |

Source: SAE 2009-01-1790

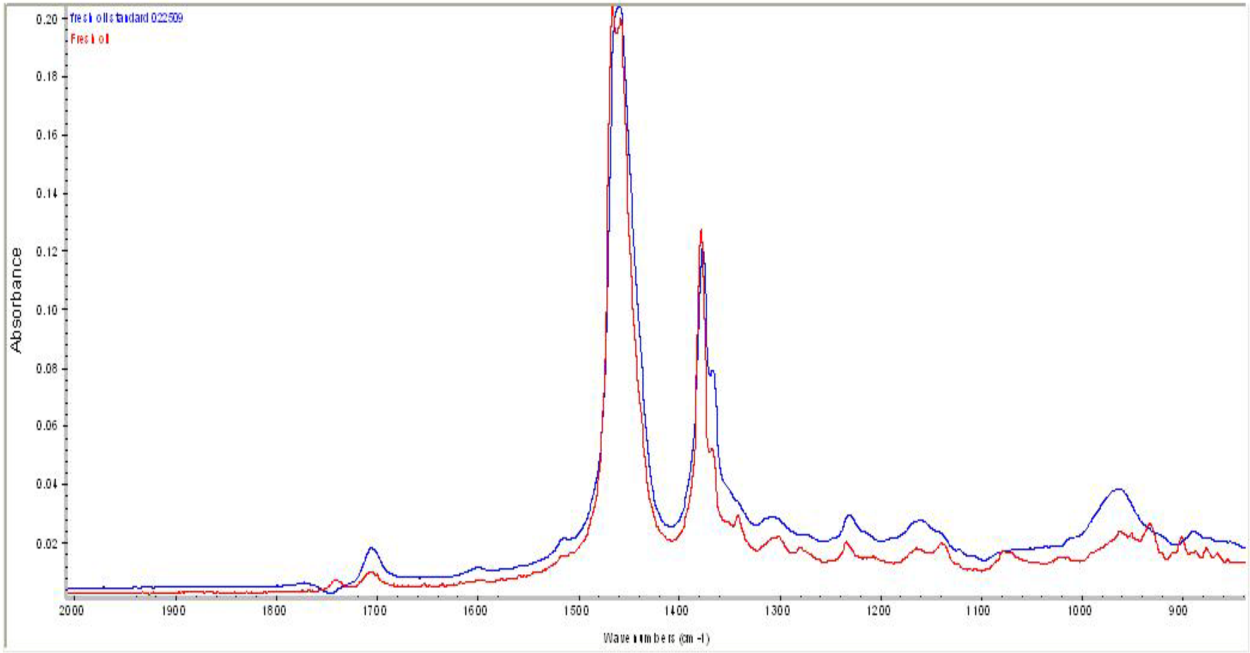
# Emission Control System Parameters

| | | Vol. (L) | Cell Density (cpsi) | PGM Loading (g/ft$^3$) |
|---|---|---|---|---|
| NAC system | DOC | 0.8 | 400 | 150 |
| | DPF | 3.3 | 300 | 60 |
| | NAC | 4.1 | 400 | 120 |
| SCR system | DOC | 1.23 | 400 | 150 |
| | DPF | 4.1 | 300 | 60 |
| | SCR FeZSM-5 | 4.43 | 300 | NA |

Source: SAE 2009-01-1790

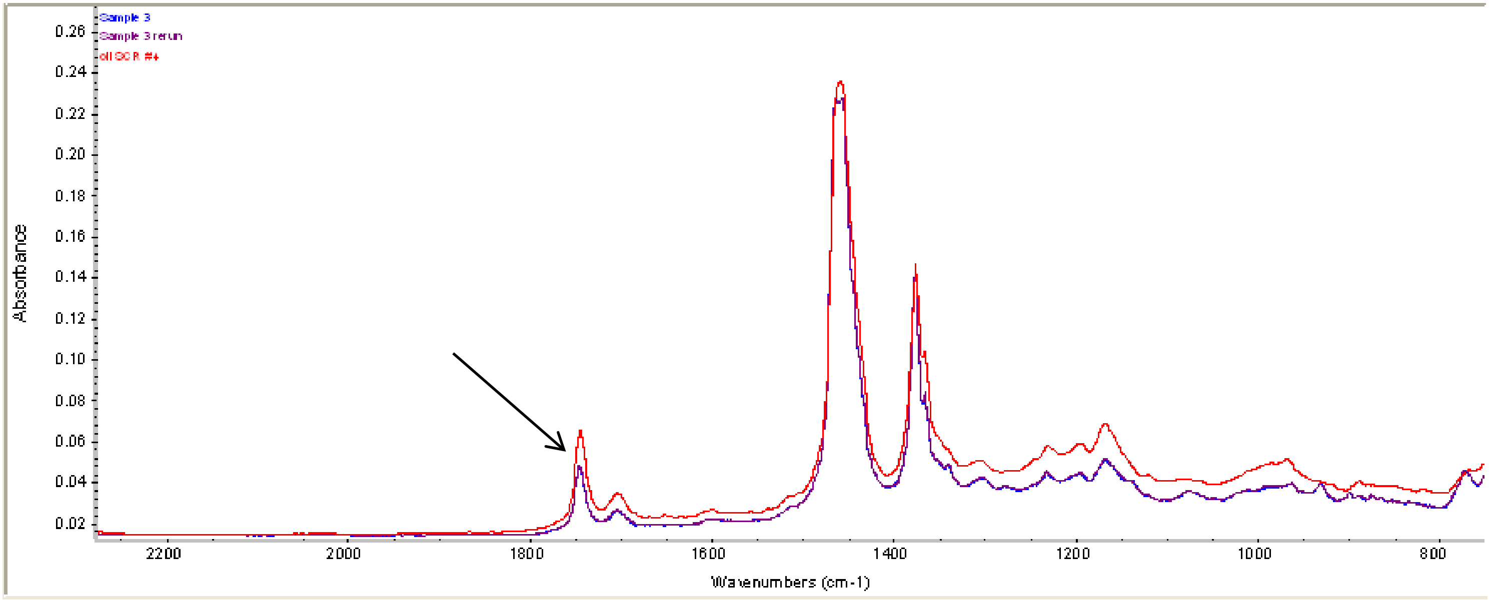
# Differences in Base Oil

- Note the differences between 1800 $cm^{-1}$ and 1700 $cm^{-1}$ (carbonyl stretch ~1750 $cm^{-1}$)
- These differences can lead to over/underreporting of biodiesel dilution



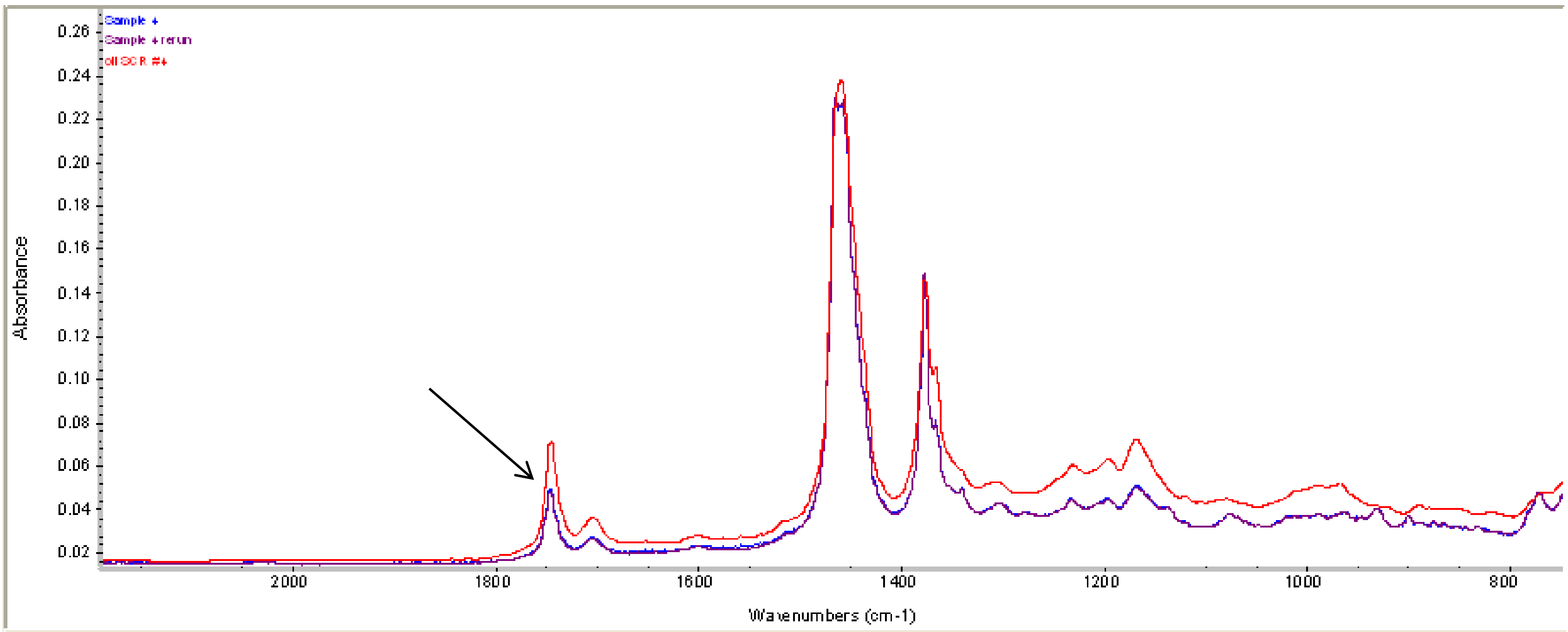
# “Good” vs. “Bad” Calibration Model

- Same sample quantified with parent and unrelated base oil
- Dissimilar base oil leads to underestimation of biodiesel dilution (blue/purple curves)
- Red curve is correct → 6.5 vol% biodiesel



# Another Example

- Valid result (red) is 7.0 vol% dilution; invalid result (blue/purple) is ~50% low



# Results

## NAC

| Sample # | Oil Age (hrs) | System Age (hrs) | Biodiesel (vol%) |
|---|---|---|---|
| 1 | 48 | 48 | 4.7 |
| 2 | 92 | 140 | 6.6 |
| 3 | 65 | 205 | 5.2 |
| 4 | 90 | 295 | 5.7 |
| 5 | 67 | 362 | 5.3 |
| 6 | 65 | 427 | 6.8 |
| 7 | 65 | 492 | 5.9 |
| 8 | 100 | 592 | 8.3 |
| 9 | 158 | 750 | 10.1 |

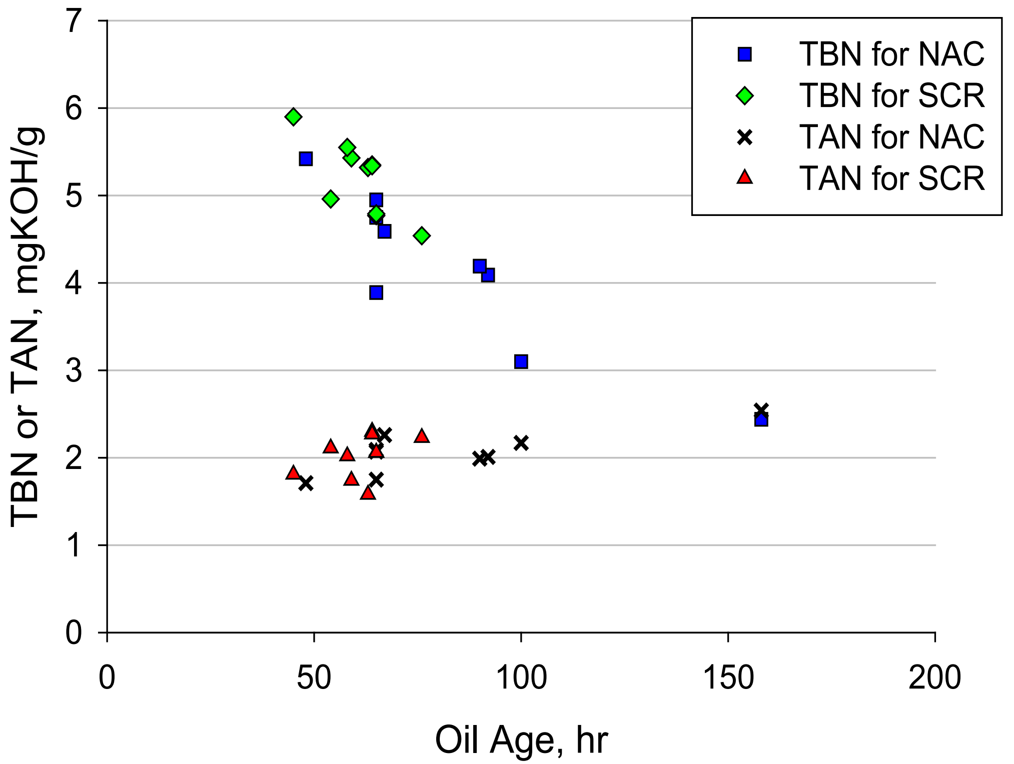
## SCR

| Sample # | Oil Age (hrs) | System Age (hrs) | Biodiesel (vol%) |
|---|---|---|---|
| 1 | 65 | 65 | 8.0 |
| 2 | 76 | 141 | 7.6 |
| 3 | 54 | 195 | 6.5 |
| 4 | 65 | 260 | 7.0 |
| 5 | 59 | 319 | 4.1 |
| 6 | 63 | 382 | 4.7 |
| 7 | 58 | 440 | 4.1 |
| 8 | 64 | 504 | 3.7 |
| 9 | 64 | 568 | 3.6 |
| 10 | 45 | 613 | 3.7 |

Diesel dilution tracks biodiesel dilution, but is typically 50%-67% lower.

# Additional Lubricant Results

- Each oil change represents ~10,000 mi
- TBN decrease is due to normal lubricant aging
- TBN and TAN never cross
  - Lubricant is within normal service interval




TBN = total base number

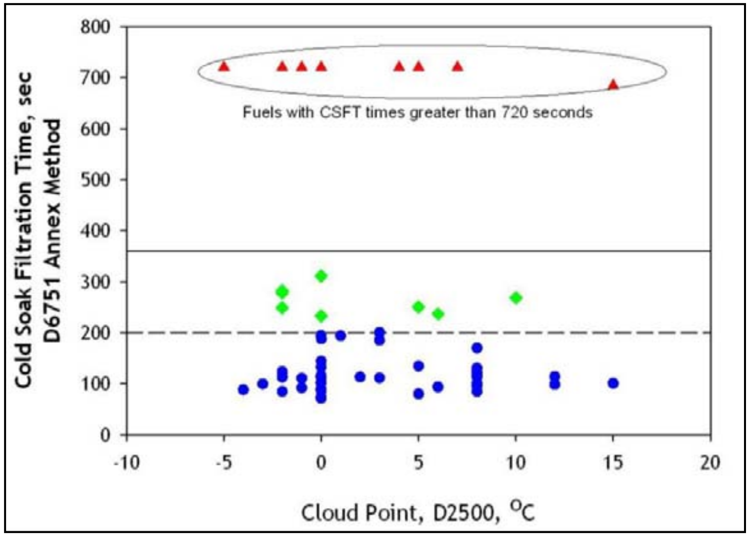
TAN = total acid number

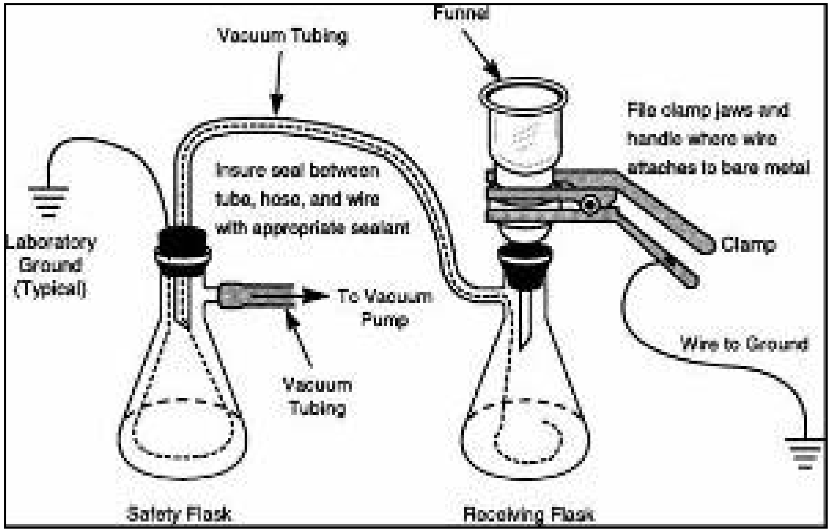
# Wrap-up

- FTIR/ATR is a robust analytical technique to quantify biodiesel dilution in lubrication oil
- It is critical to use the same base oil for calibration that is used in testing
  - Poorly designed model can lead to over/underestimation
- Future research should examine a single technique to quantify biodiesel and diesel in lubrication oil, especially if base stock is unknown

# Cold Soak Filtration Analysis

- Some biodiesel samples exhibit precipitates above the cloud point
  - Cold soak filtration test (CSFT) was adopted as performance specification in ASTM D6751 in October 2008
- CSFT results are bimodal, either passing (<360 second filtration time) or failing (>720 second filtration time)



# CSFT Method

- B100 is chilled to 4.5°C for 16 hours, then warmed and vacuum filtered through 0.7 μm filter; filtration time is reported
- Intent was to make Annex method “official”
- Annex method was used as a starting point to develop ASTM D7501
  - D7501 was published May 2009

# Comparison of CSFT Annex to D7501

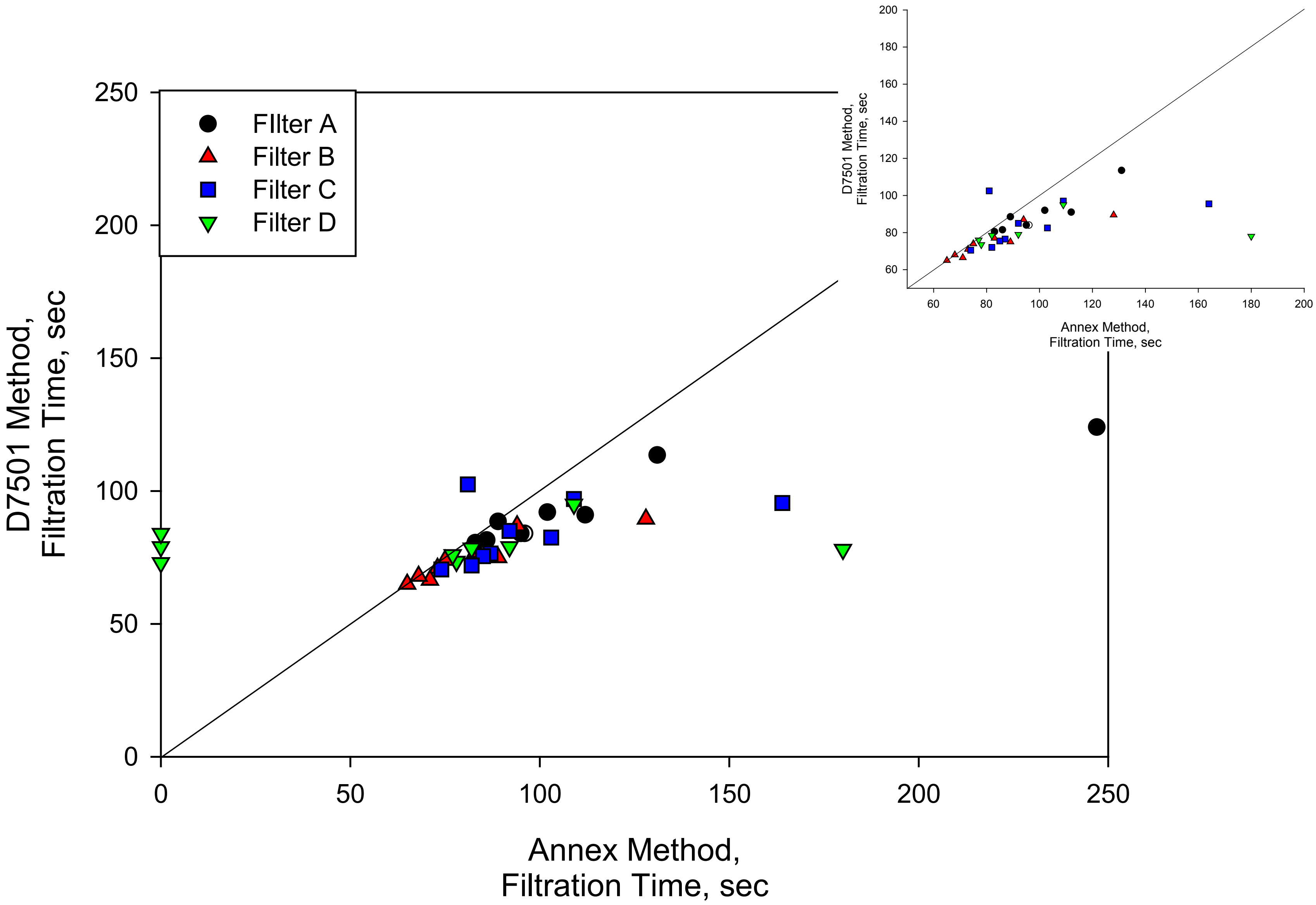
**CSFT Annex**

- Sample can be cooled in lunchroom fridge
- Warm sample on bench top
  - Time to warm may vary greatly
- Filter selection is overly broad

**D7501 CSFT**

- Tighter control of chilling apparatus
- Warm sample in 25°C circulating liquid bath
  - Warm time is specified
- Specific filter brand/type

# Impact of Filter Type on CSFT



# Filter Differences

- Data was validated in a single lab, all data is average of duplicate runs
- For most fuels, differences between filters are nominal
  - Some fuels show significant variability
- Annex method was developed on Filter A
  - Wide variety of filters available led to poor repeatability
  - In round robin testing, specification of filter in D7501 method led to better repeatability
- Annex method has reduced cold weather problems
  - Still no fundamental understanding of the root cause

# Experimental Design to Determine Root Cause of Filter Plugging

- Cause of precipitates and failing filtration times are not well understood
- Potential compounds have similar character as FAME
  - Separation becomes limiting step to analysis
- Goal was to develop high-throughput technique to analyze precipitates inside the biodiesel matrix
- Previous work in lipid-based chemotaxonomic studies of bacteria shows that matrix-assisted laser desorption ionization time-of - flight mass spectrometry (MALDI-TOF MS), with an optimized matrix system, is effective in analyzing diacyl-phosphatidylethanolamines and diacyl-phosphatidylglycerols[1]
- Can biodiesel precipitates be fingerprinted in the same fashion?

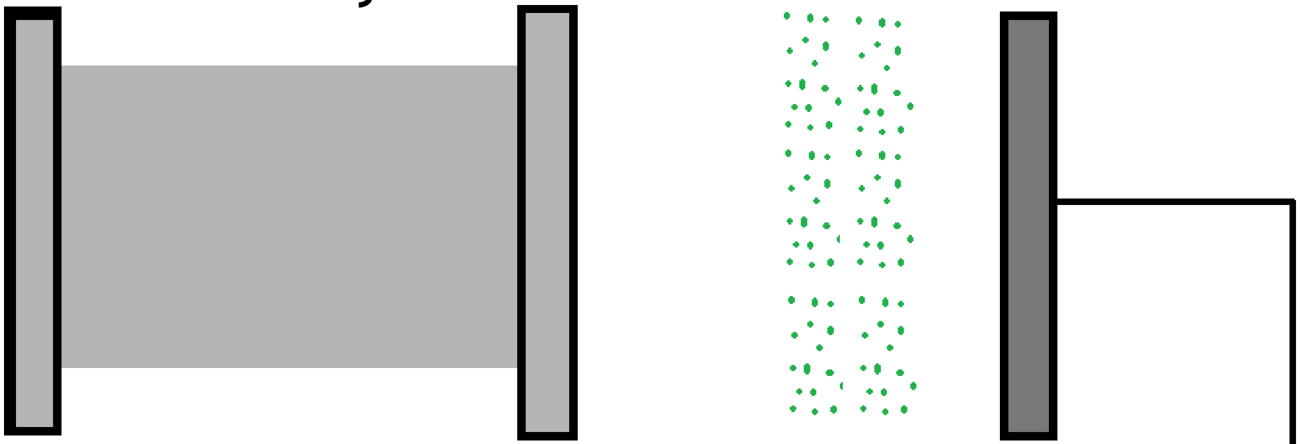
(1) Y. Isahida, A.J. Madonna, J.C. Rees, M.A. Meetani and K.J. Voorhees *Discrimination of Enterobacteriaceae based on Spectral Patterns of Phospholipids using MALDI-TOF/MS Combined with On-Probe Sample Pretreatment*, **Rapid Commun. in Mass Spectrom.**, 2002 16, 1877.

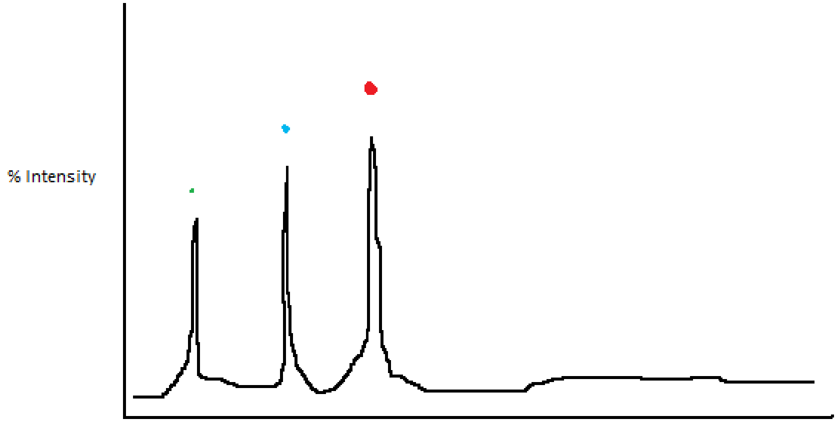
# MALDI-TOF Background

**MALDI**
ionization

**TOF**
Mass analyzer

**Detector**



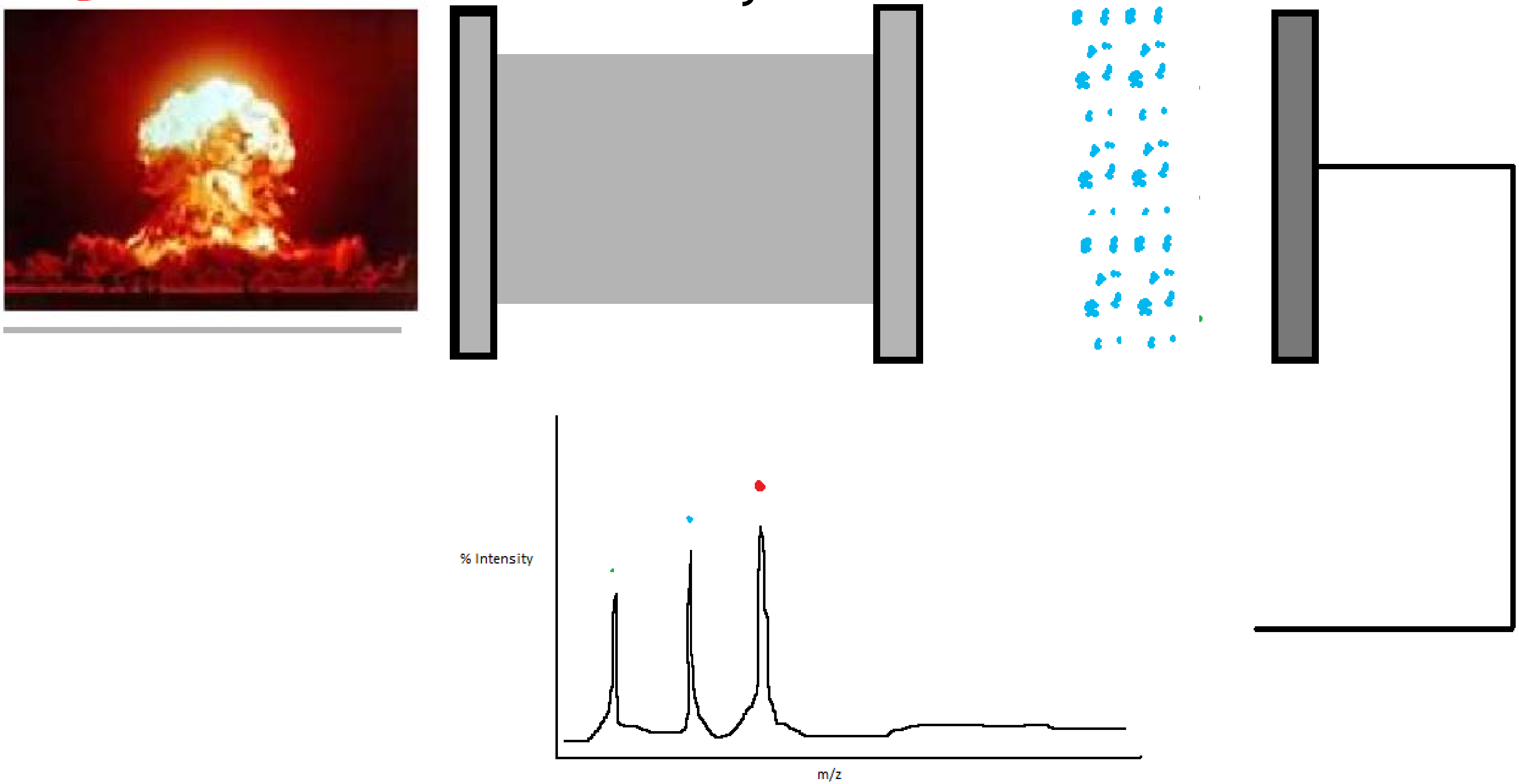


# MALDI-TOF Background

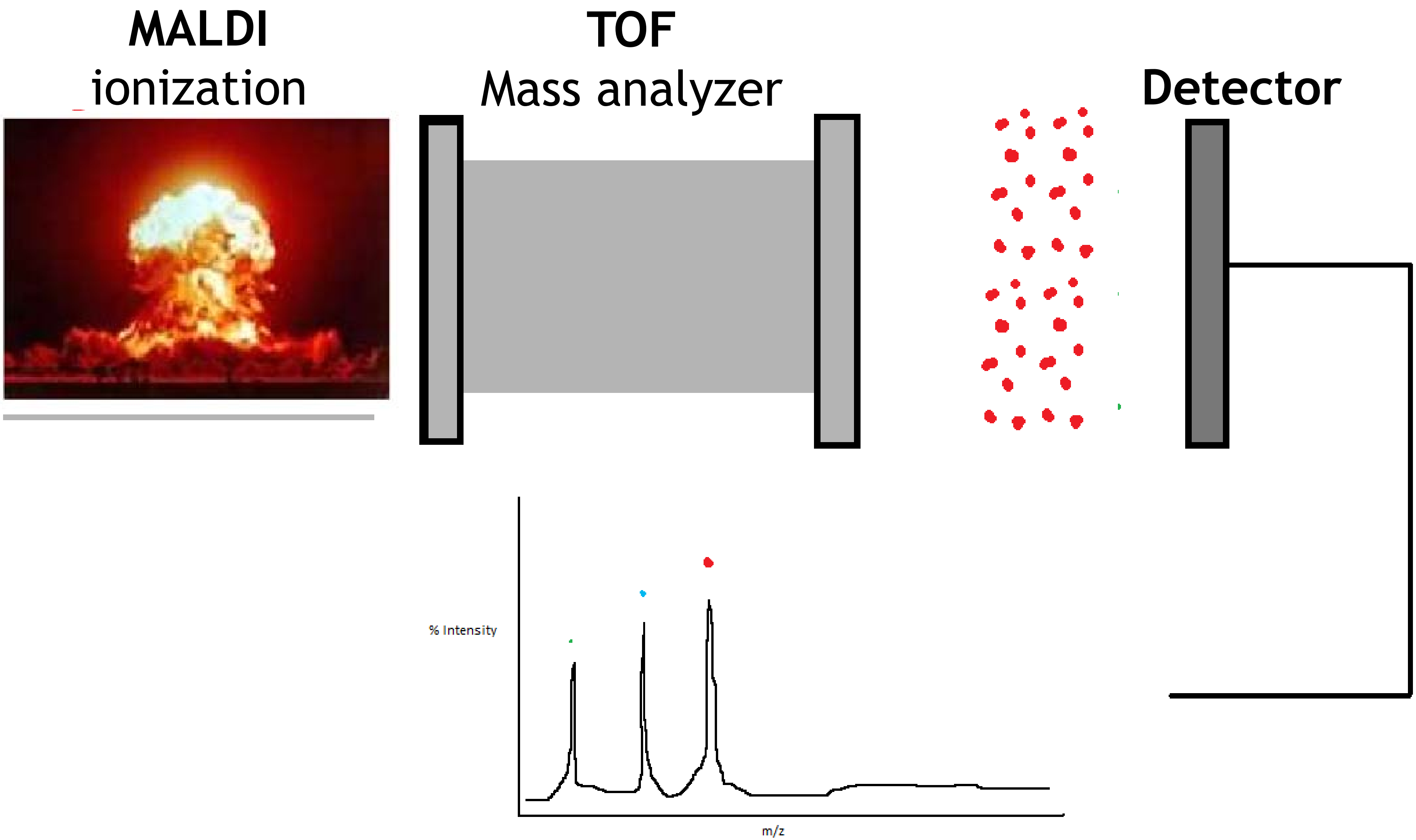
**MALDI** ionization

**TOF** Mass analyzer

**Detector**

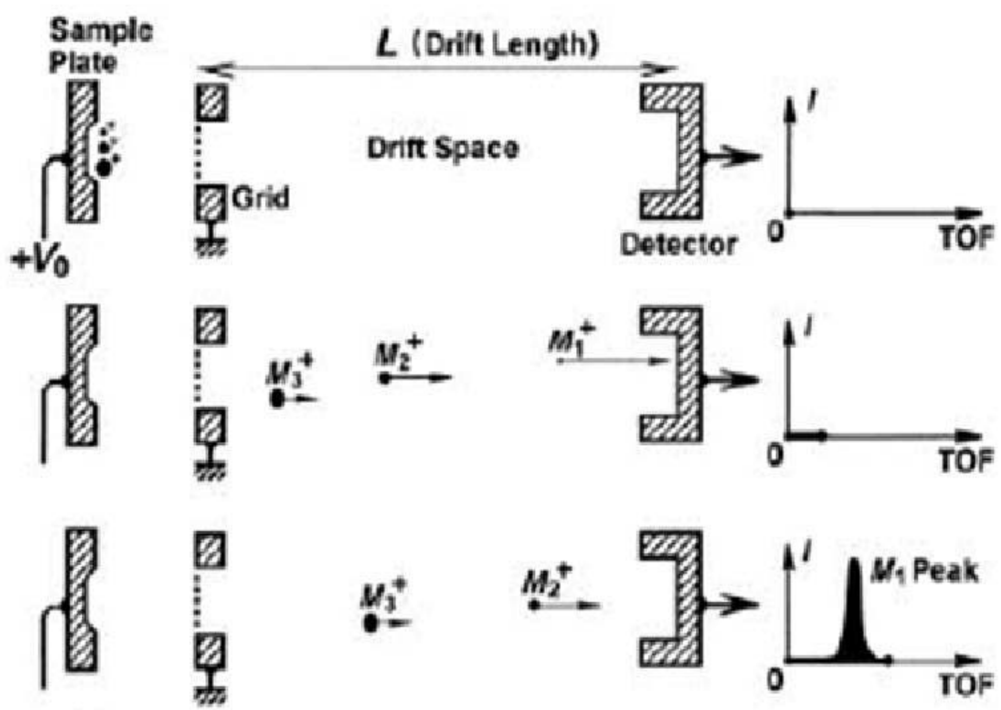


# MALDI-TOF Background



# Mass Analysis TOF

- Ions are analyzed by the amount of time taken to reach detector[1]




• Potential energy assumed to be converted to kinetic:

$$E_p = E_k$$
$$E_p = zV_o$$
$$E_k = 1/2mv^2$$
$$zV_o = 1/2mv^2$$

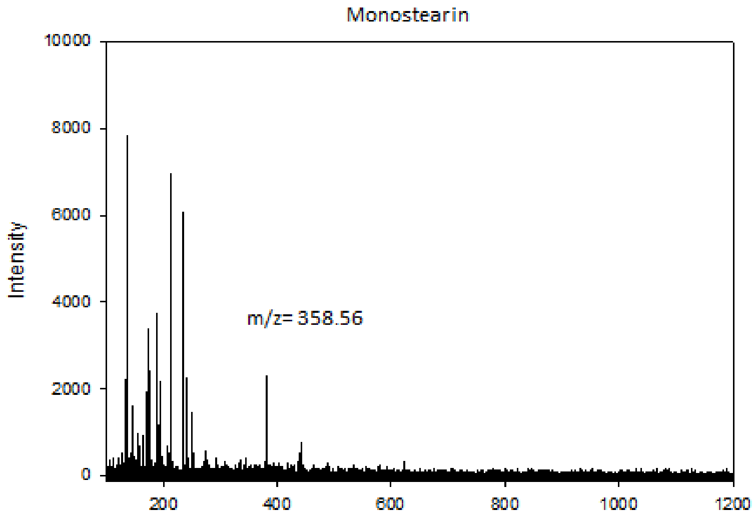
• Ions of lower mass have higher velocity
• Potential can be positive or negative

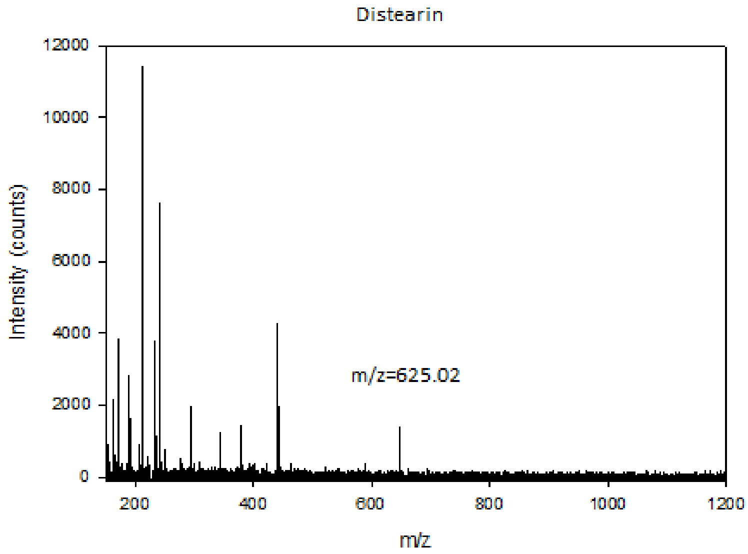

(1) Gross, Jurgen H. *Mass Spectrometry a Textbook*. 1st ed., Springer **2004**, 411-435

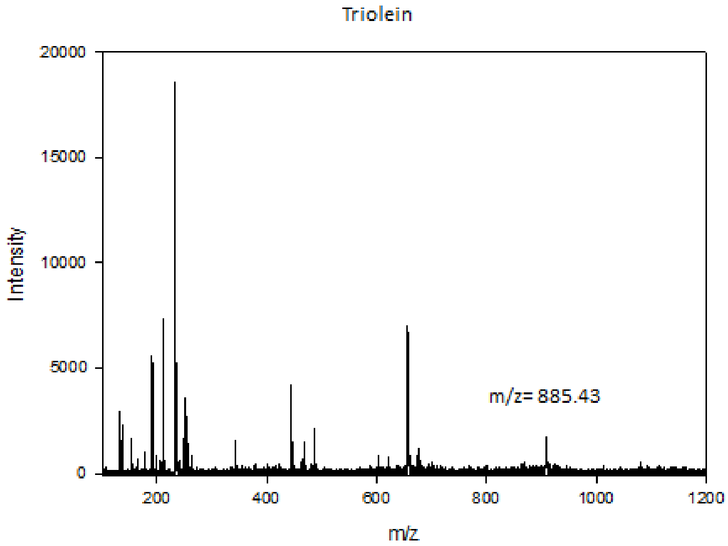
# Methodology

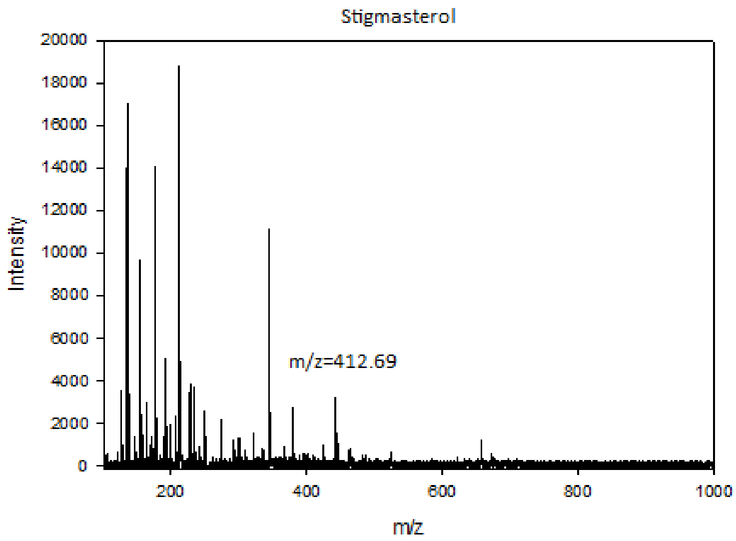
- Take a stepwise approach
- Identify individual trace compounds thought to be present in biodiesel
- Use traditional matrix systems to evaluate pure components
- Test combinations of matrix systems to determine system over the range of components
- Utilize $MS^2$ for positive peak identification

# Single Component Results

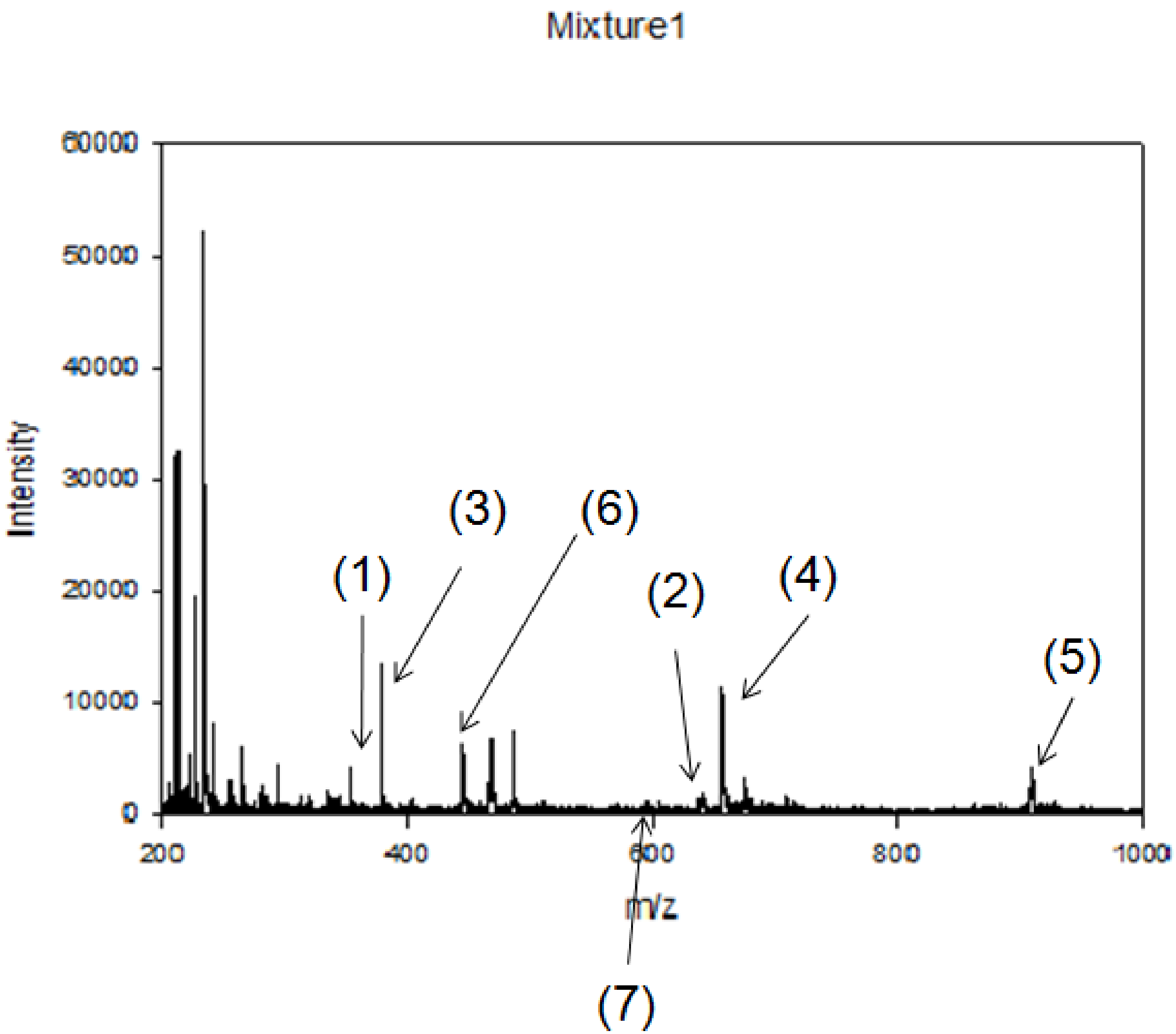


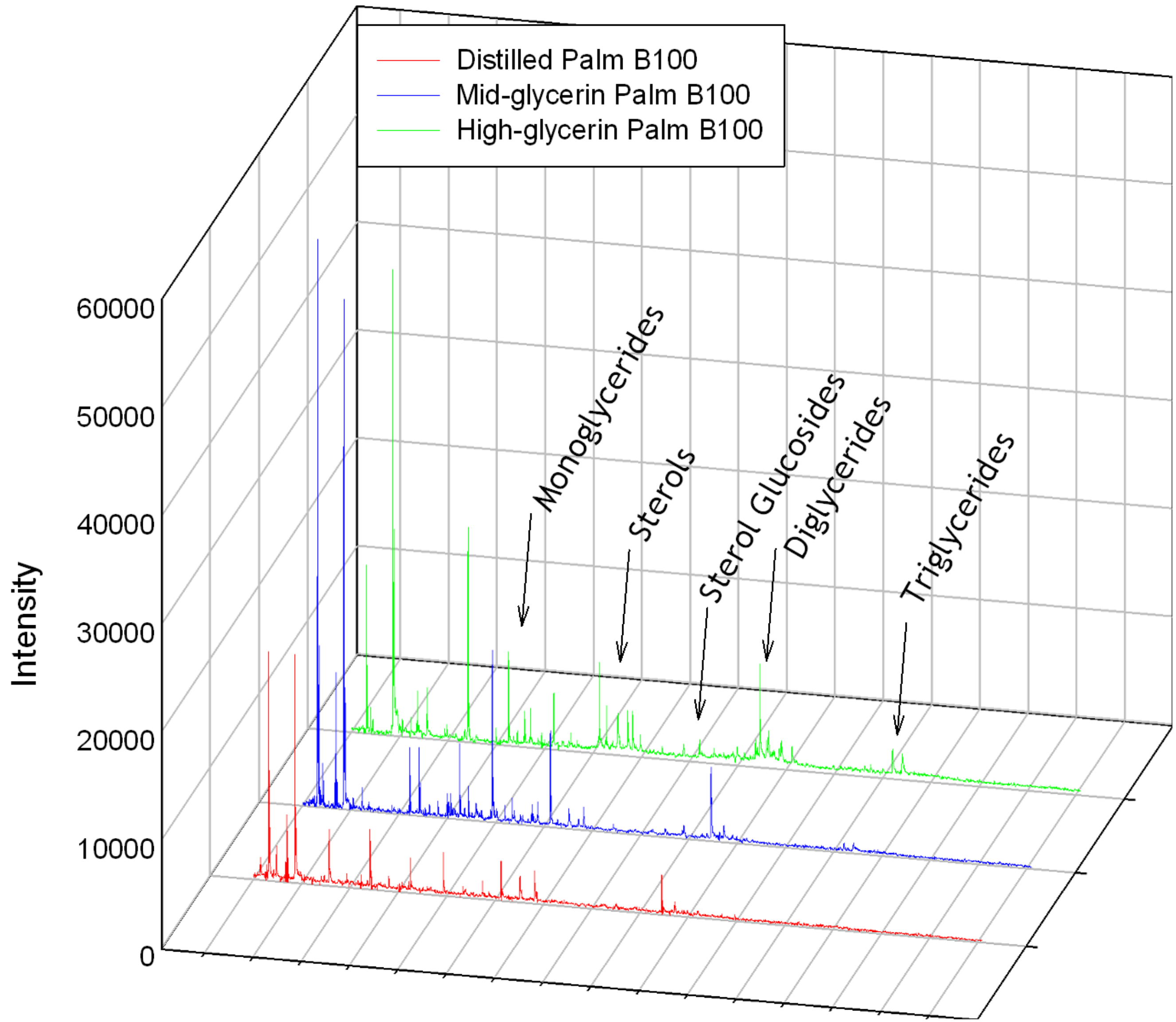



# Complex Mixture Results

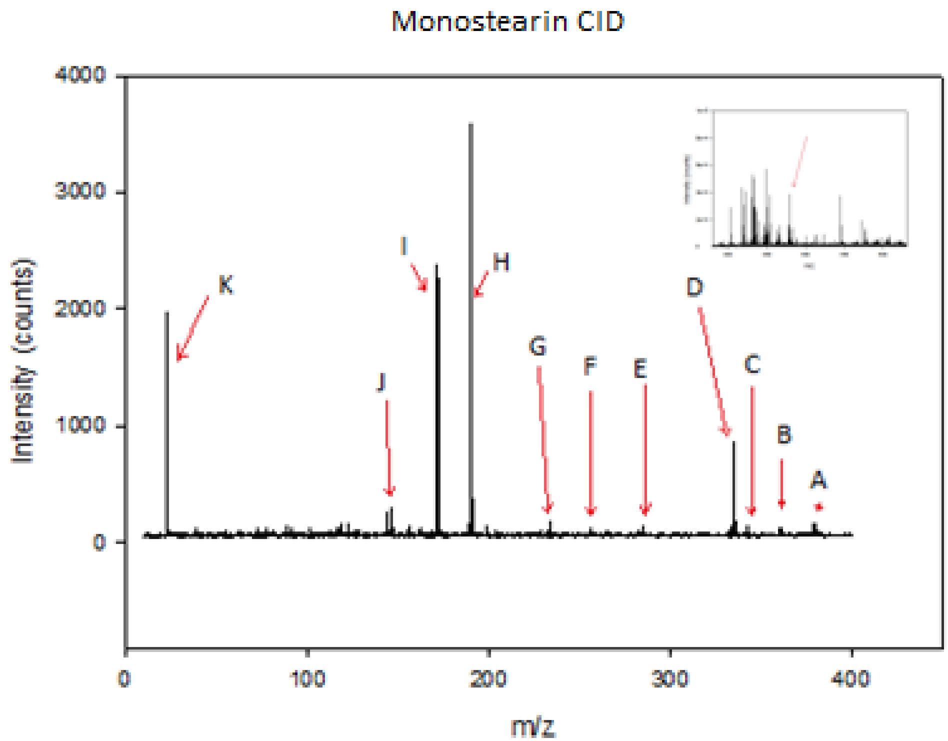



1) [monopalm+Na]+
2) [dilinolein+Na]+
3) [monoolein+Na]+
4) [disterin+Na]+
5) [triolein+Na]+
6) [stigmasterol+Na]+
7) [S.G.+Na]+

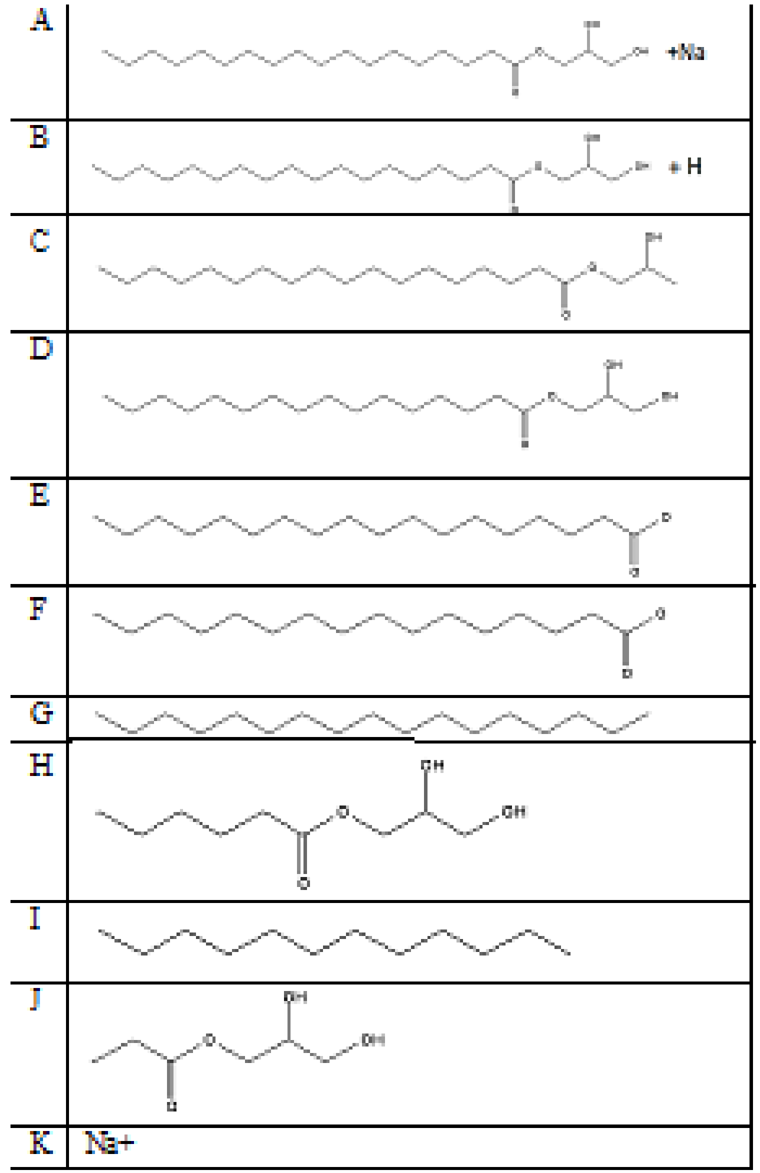
# Comparison of Different Biodiesels



# Results: MS²




Source: Poster to be presented at ASMS Meeting, June 1-3, 2009



# Closing Thoughts

- While biodiesel is mostly FAME, industry is concerned that trace components can impact operability significantly
- To fully understand the utilization of biodiesel, careful attention needs to be paid to the analytical methodology
- Methods need to be shared and compared to ensure that accurate data is gathered for this increasingly complex fuel