

REPORT DOCUMENTATION PAGE

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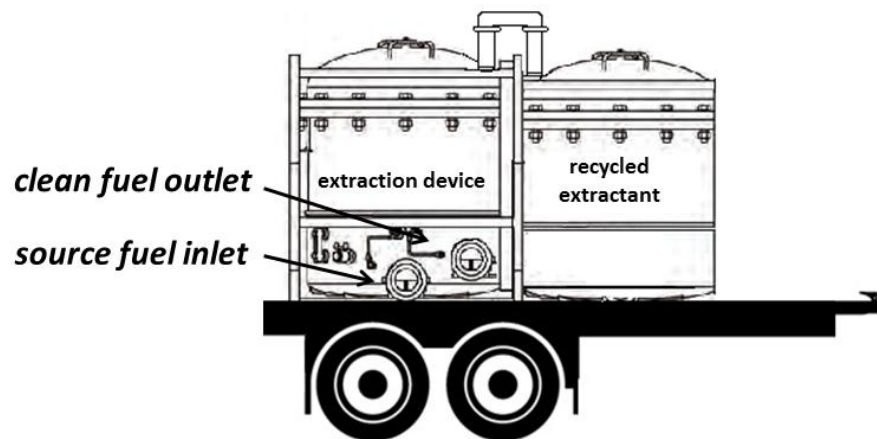
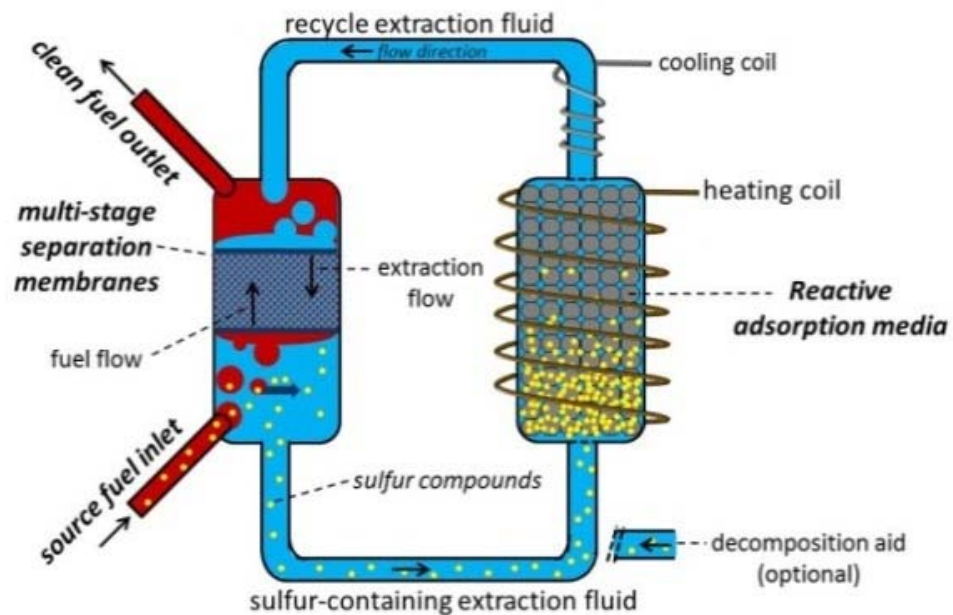
PROJECT SUMMARY: INCREASED FUEL AFFORDABILITY THROUGH DEPLOYABLE REFINING TECHNOLOGY

May 2016

**Joe Mabry, Andrew Guenthner
Applied Materials Group
Propellants Branch (RQRP)
Aerospace Systems Directorate
Air Force Research Laboratory**



Overall Process

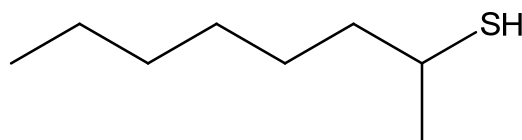




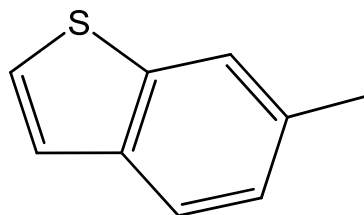
Sulfur in Fuels



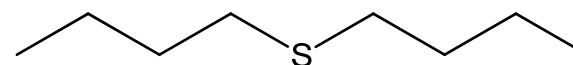
Mercaptans (Thiols)



Thiophenes (and benzothiophenes)



Sulfides

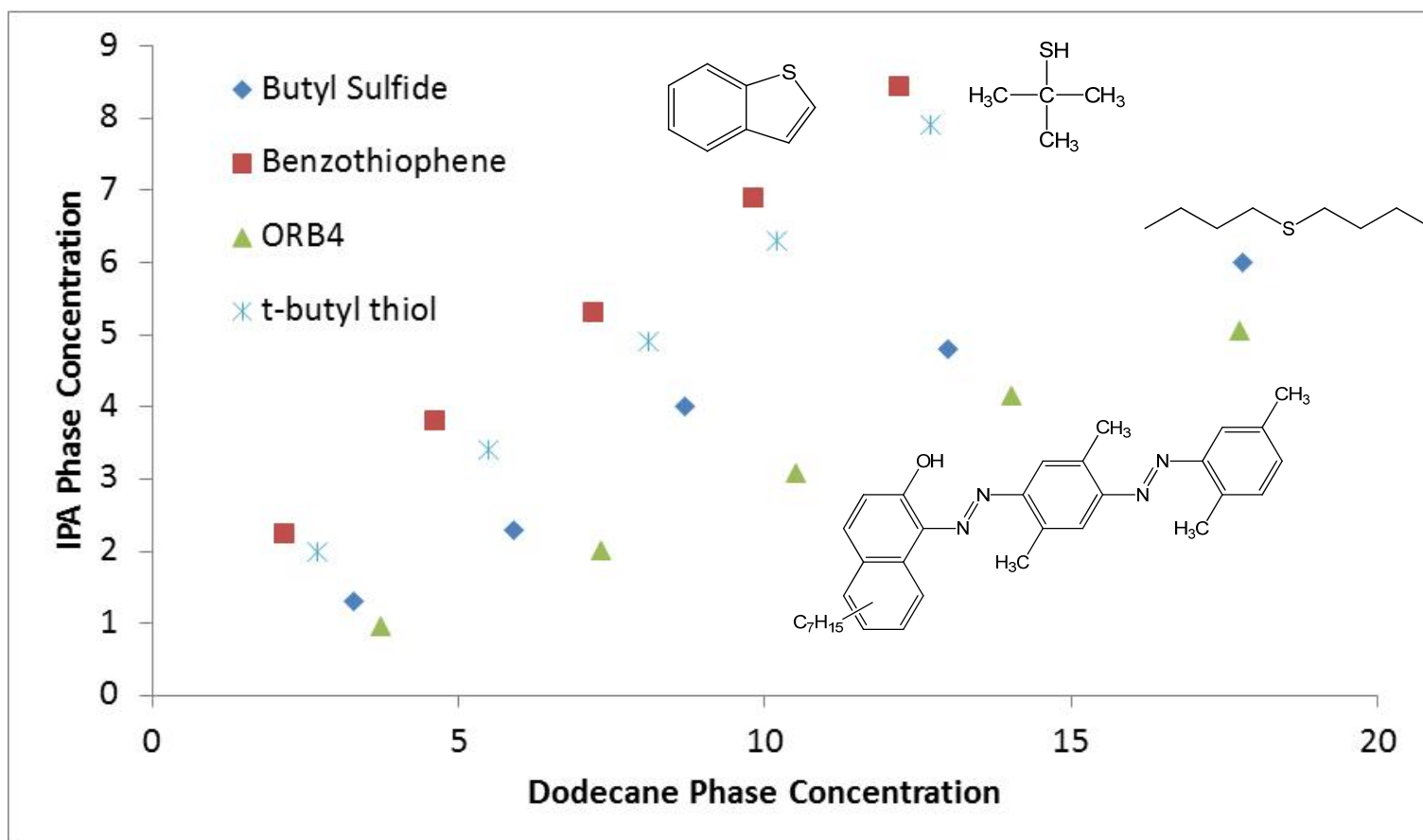


The presence of sulfur in fuels leads to many detrimental effects:

- Coking on rocket engine injector plates
- Deposit formation in hypersonic cooling channels
- Clogging of diesel engine fuel-injectors
- Fouling of automobile catalytic converters
- SO_x emissions
 - Environmental pollution
 - Corrosion issues on military equipment



Extraction Curves

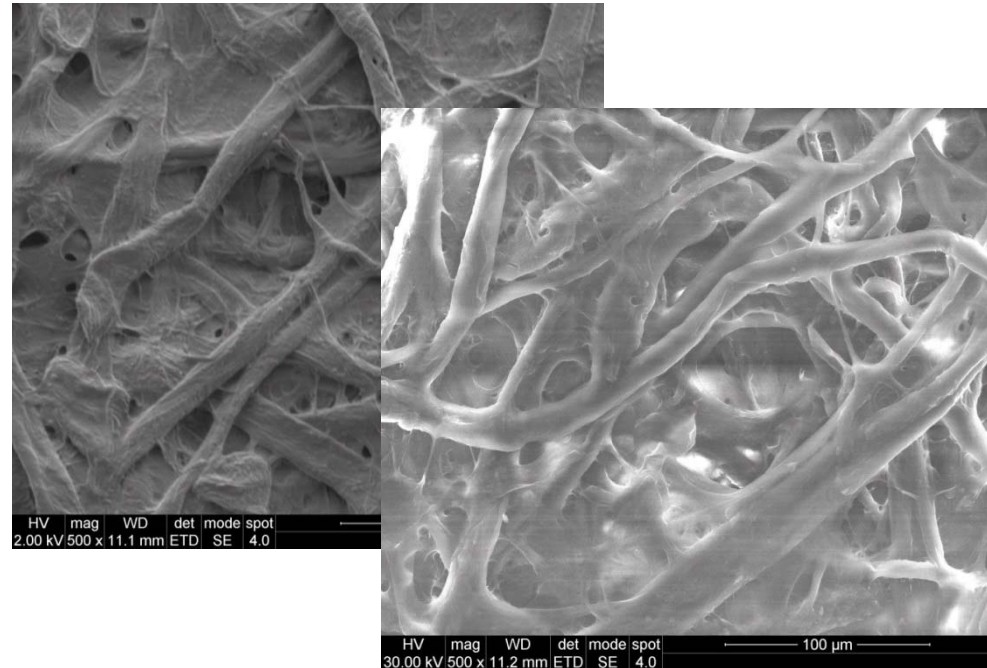
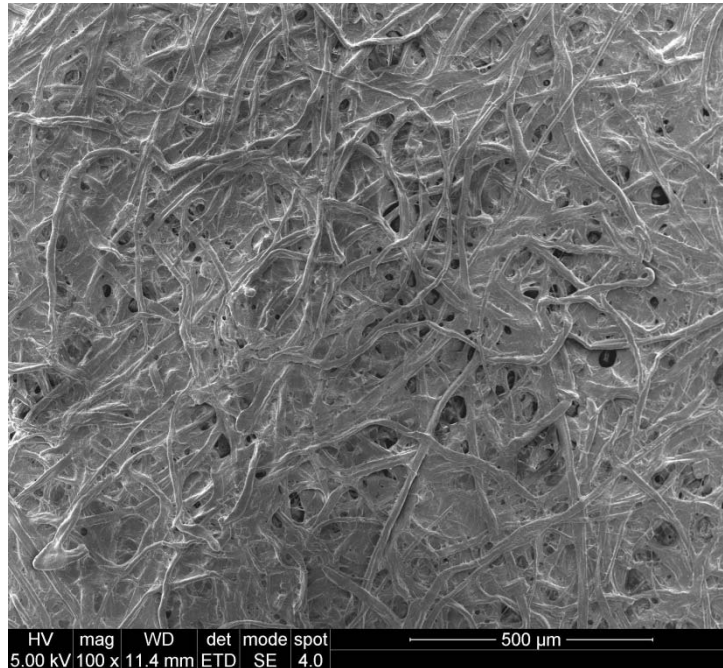


The slope of these lines is the partition coefficient (K). We need $K > \sim 0.1$ for a feasible extraction process.

Equilibrium curve for compounds extracted from dodecane with IPA:water 10:1 v:v ratio



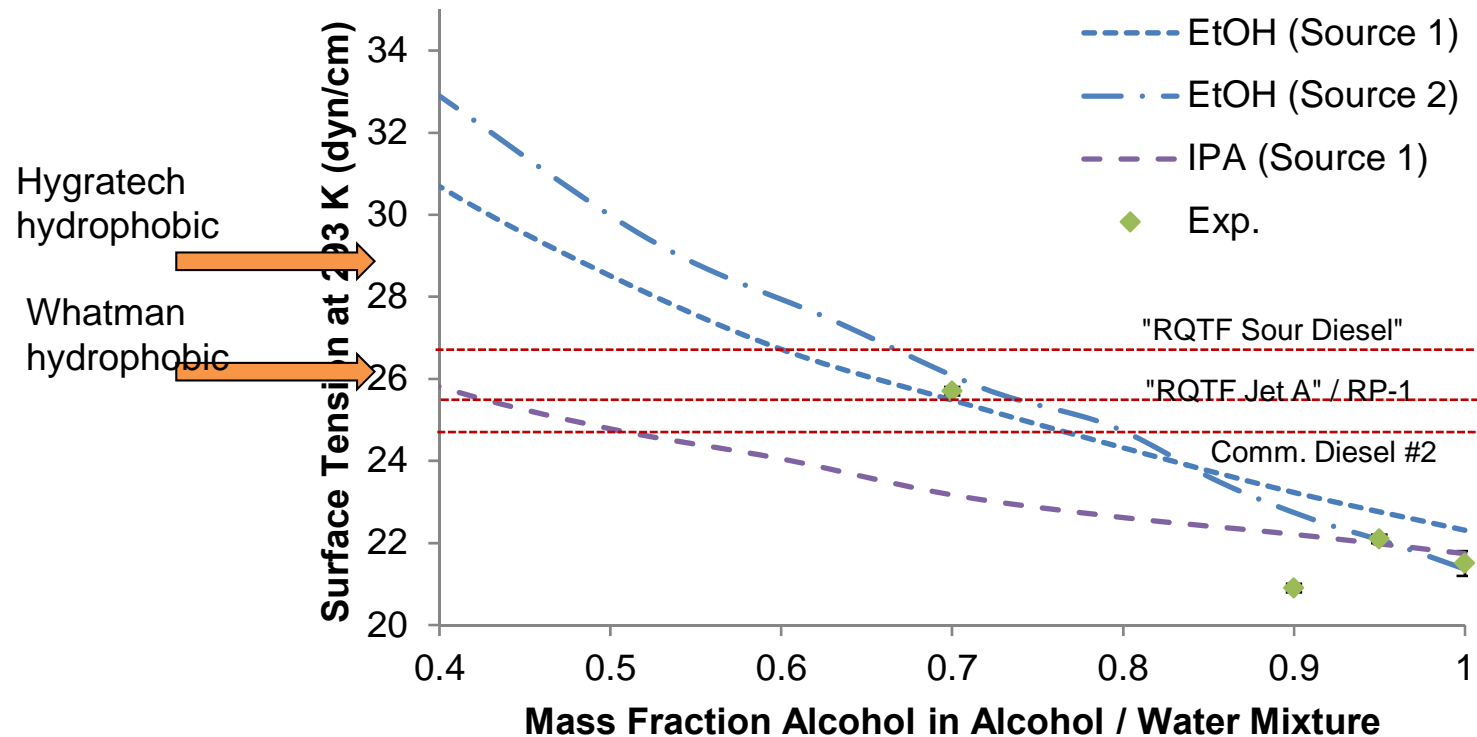
New Hydrophobic Membrane: Whatman Phase Separator Filter



- These surfaces have $\sim 10 \mu\text{m}$ roughness, $\sim 10 \mu\text{m}$ fibers, and $\sim 15 \mu\text{m}$ pores, with a wide range of pore sizes and re-entrant features
- Testing of hydrophilic membranes showed that pore sizes below $\sim 5 \mu\text{m}$ result in high operating pressure drops and mechanical failure at $> \sim 2 \text{ gal} / \text{min} / \text{ft}^2$.
- Current hydrophilic membranes from Hygratech have $\sim 25 \mu\text{m}$ pores, can withstand at least $\sim 5 \text{ gal} / \text{min} / \text{ft}^2$, and have been 100% effective at separation.
- Hygratech hydrophobic membrane appears to have a surface energy near $29 \text{ dyn} / \text{cm}$, whereas the Whatman membrane is $\sim 26 \text{ dyn} / \text{cm}$.



Extraction Media Selection



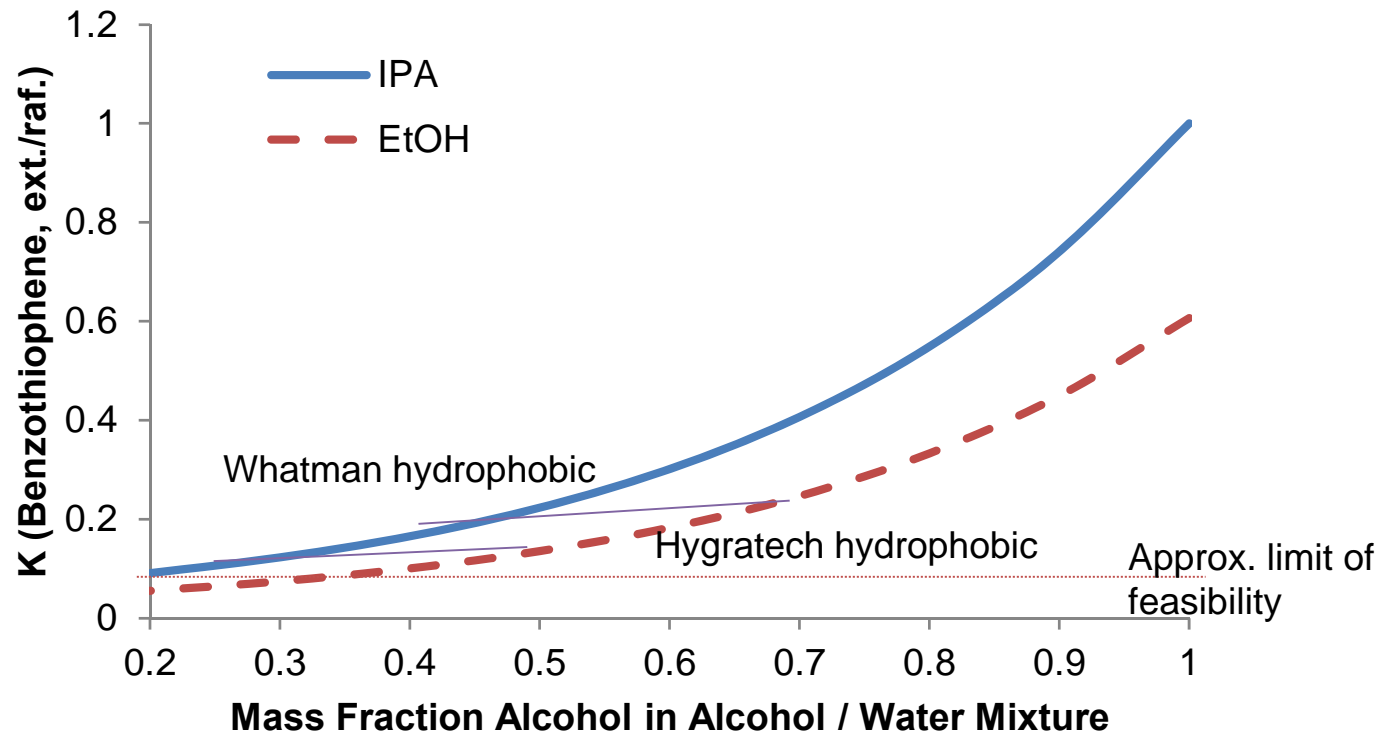
Limiting factor in extraction fluid selection is surface tension (must exceed that of all potential fuels to be utilized) when operating at flow rates high enough that phases do not coalesce within a single stage.

Membrane surface energy must lie between the surface tension of the extraction fluid and that of the fuel to be treated.

Sensitivity of surface tension to composition also plays a key role (smaller is better)



Extraction Media Selection



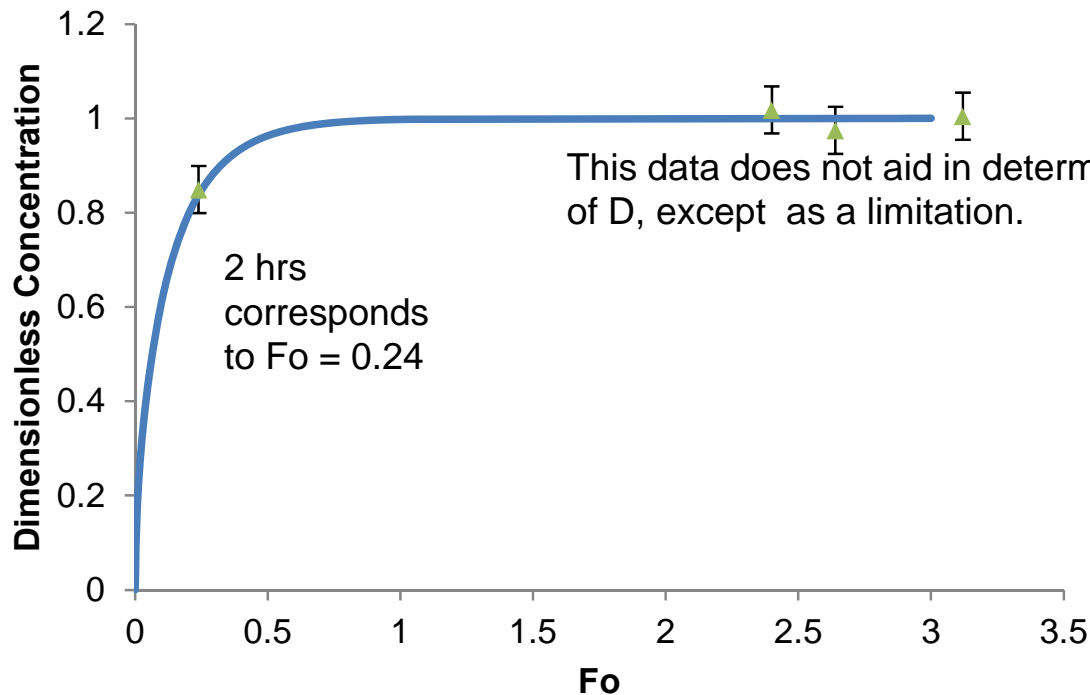
Increased water content results in less efficient extraction (lower K)

Because of surface tension constraints, the design choice falls along the thin lines indicated, not along the horizontal axis

Actual design trade is relatively insensitive to alcohol choice



Diffusion Coefficient Calculations

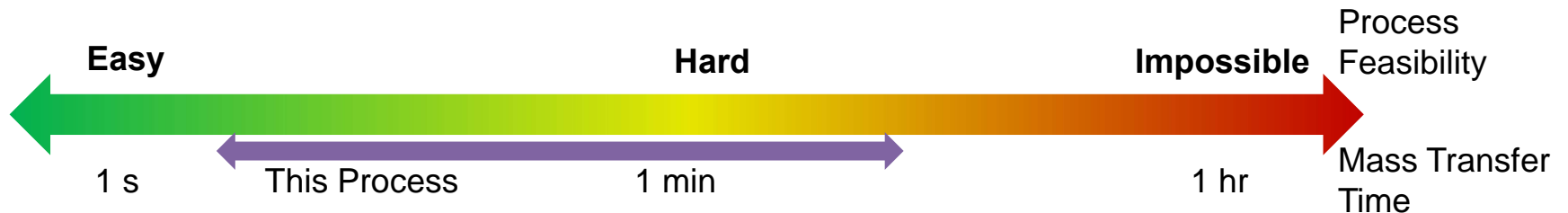


Why Measure?

This is a value we do not control; it is a fundamental constraint on the process

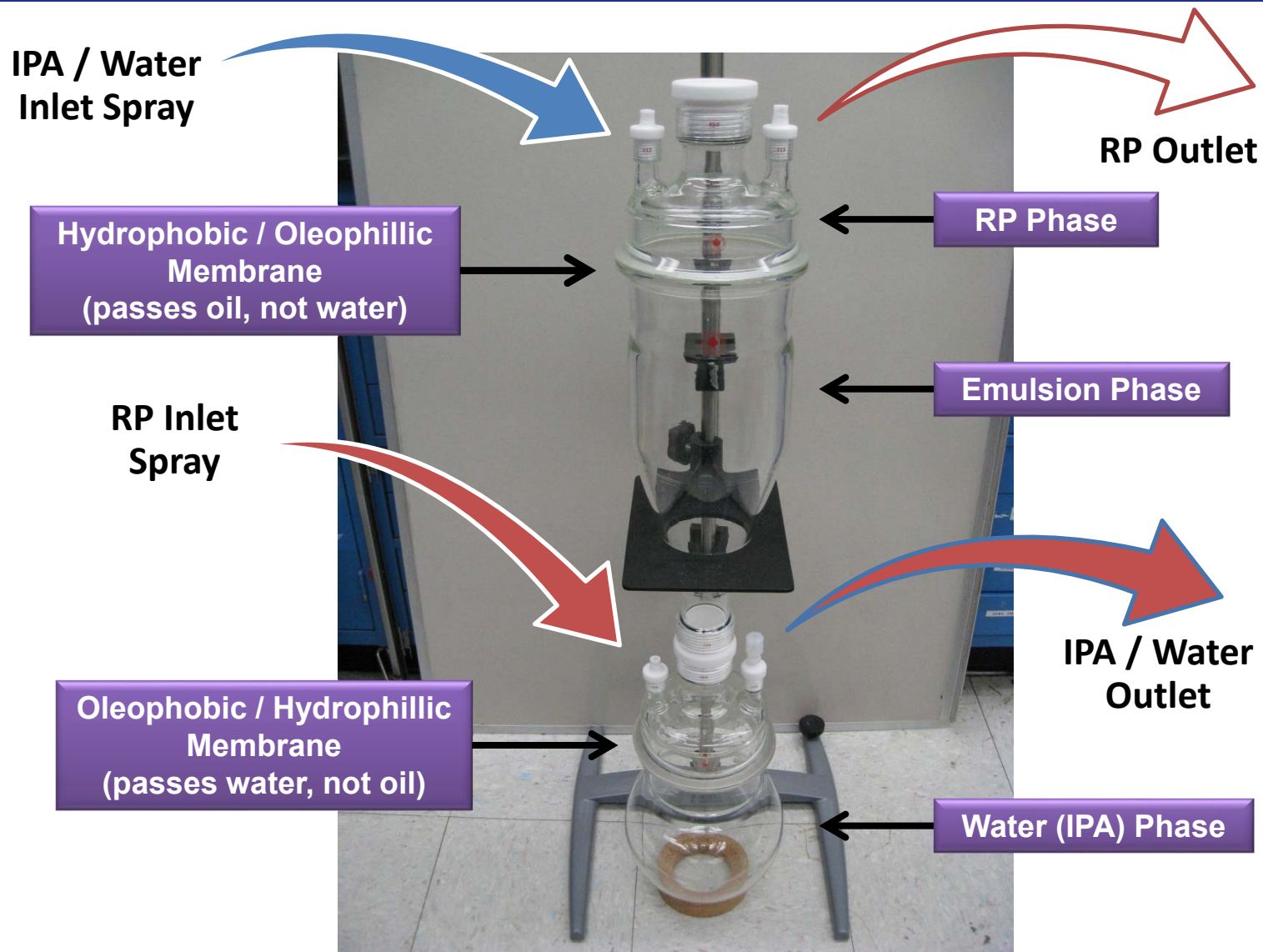
$Fo = D t / L^2$; in this case $L = 0.97\text{cm}$, solving for D yields $3 (\pm 1) \times 10^{-5} \text{ cm}^2 / \text{s}$

This value implies that for ~1 mm droplets, mass transfer will take ~30 s.





Extraction Apparatus





Extraction of Sulfur from RP-1



Sulfur Compounds by GC-SCD (Sulfur Speciation)	Concentration (ppm)
C2 Thiophenes	<0.1
C3-C4 Thiophenes	1.6
C5 Thiophenes	6.3
C6 Thiophenes	6.1
C7 Thiophenes	5.8
C8-C9 Thiophenes	4.9
C10 Thiophenes	1.3
C11 Thiophenes	0.9
C12+ Thiophenes	2.0



Sulfur Compounds by GC-SCD (Sulfur Speciation)	Concentration (ppm)
C2 Thiophenes	0.3
C3-C4 Thiophenes	1.4
C5 Thiophenes	3.7
C6 Thiophenes	3.5
C7 Thiophenes	4.1
C8-C9 Thiophenes	2.9
C10 Thiophenes	0.6
C11 Thiophenes	0.6
C12+ Thiophenes	<0.1

Standard Grade RP-1
(Errors are ± 0.3 ppm)



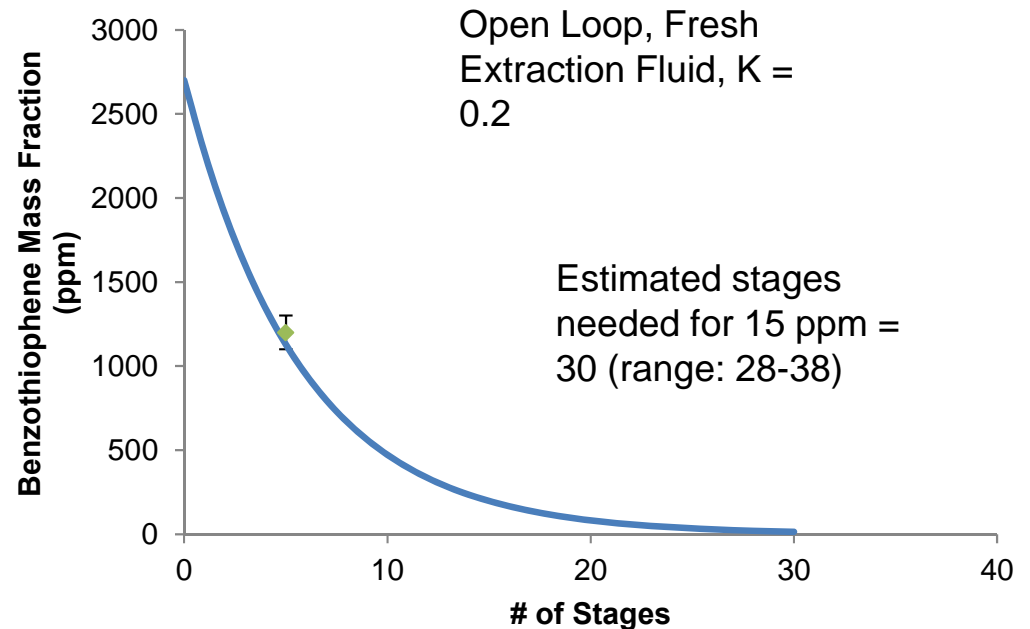
Standard Grade RP-1 after extraction with 10:1 IPA water in extraction apparatus



Extraction of Sulfur from Spiked Diesel #2



Parameter	Value
Input Fuel Source	Diesel #2 procured at Kramer's Junction, CA
Contaminant	Benzothiophene
Initial Contaminant Level	2700 ± 100 ppm
Final Contamination Level	1200 ± 100 ppm
# Stages	5
Expected Extraction Efficiency per Stage	K = 0.2



- Key question = how does extraction curve for other components compare to that of benzothiophene?



Sulfur Chemiluminescence Detector



Sulfur compound (analyte)



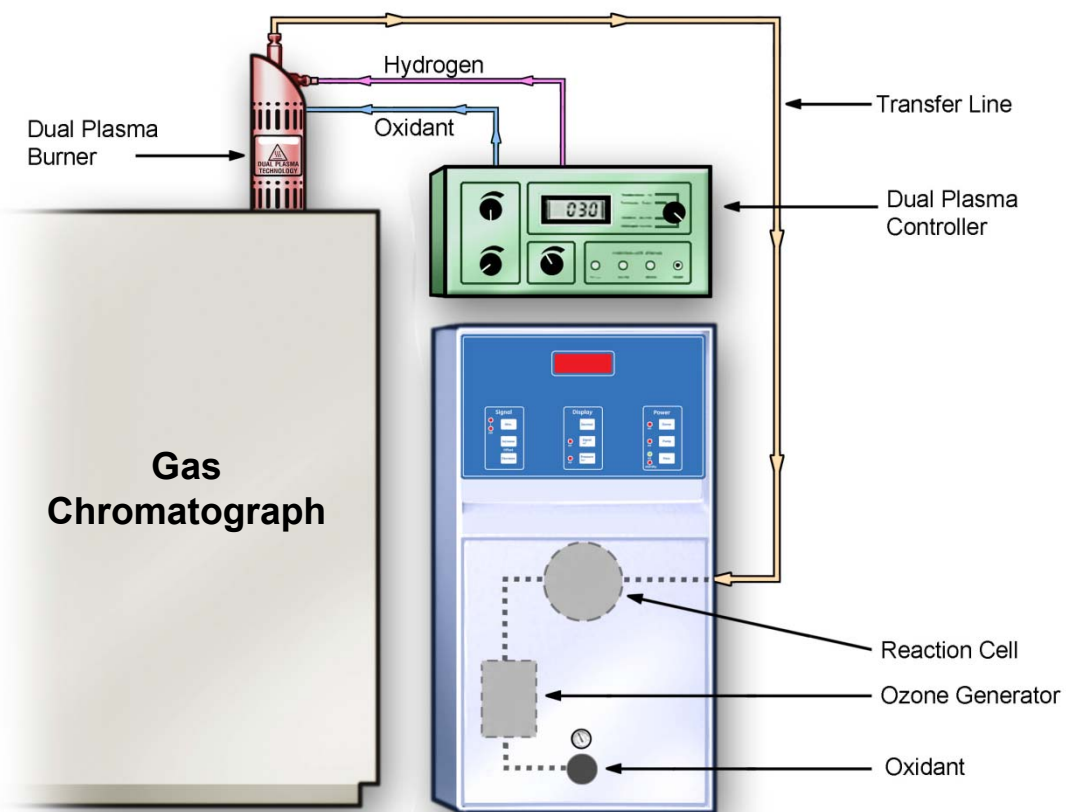
SO + H₂O + other products

SO + O₃



SO₂ + O₂ + hν (<300-400 nm)

The Agilent 355 sulfur chemiluminescence detector (SCD) relies on the detection of light emitted from the reaction of sulfur monoxide (from sulfur-containing analytes) with ozone (produced by the detector) in an internal reaction cell

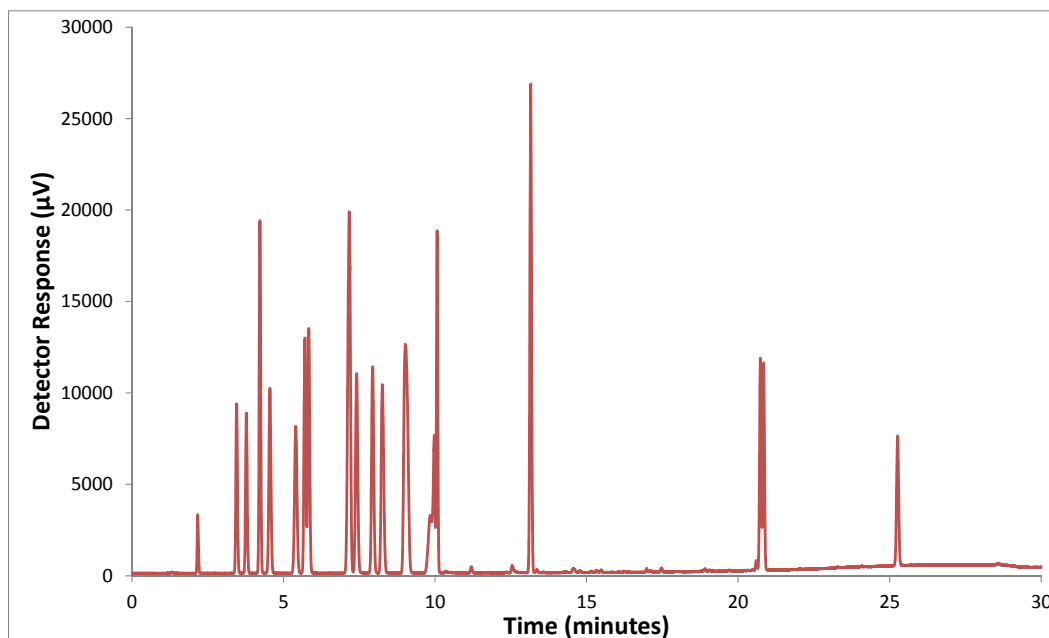




Sulfur Speciation by GC/SCD



Calibration Standard	Retention Time (minutes)
hydrogen sulfide	1.15
carbonyl sulfide	1.35
methyl mercaptan	2.44
ethyl mercaptan	3.99
methyl sulfide	4.37
carbon disulfide	4.84
2-propanethiol	5.24
2-methyl-2-propanethiol	6.17
1-propanethiol	6.50
ethyl methyl sulfide	6.65
1-methyl-1-propanethiol	8.02
thiophene	8.07
2-methyl-1-propanethiol	8.30
diethyl sulfide	8.86
1-butanethiol	9.20
methyl disulfide	9.96
2-methylthiophene	10.93
3-methylthiophene	11.04
diethyl disulfide	14.16
benzothiophene	19.75
5-methylbenzothiophene	21.75
3-methylbenzothiophene	21.85
diphenyl sulfide	26.27

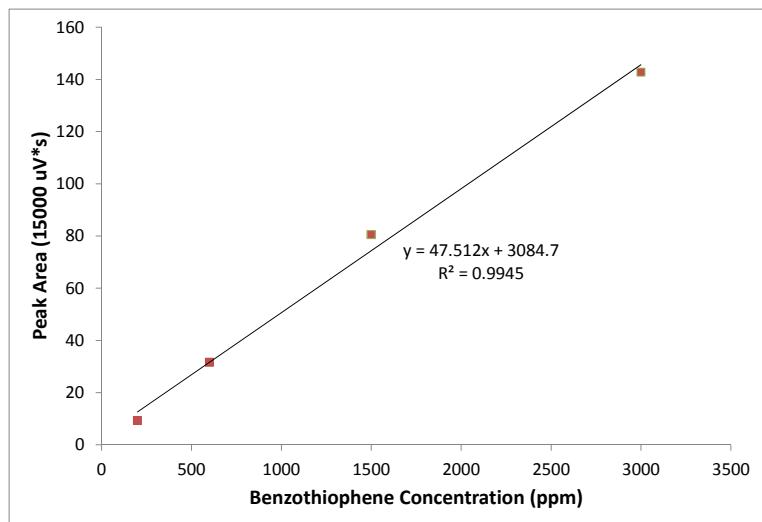


Chromatogram of 8 ppm sulfur standards in toluene
Instrument conditions followed were from ASTM D 5623

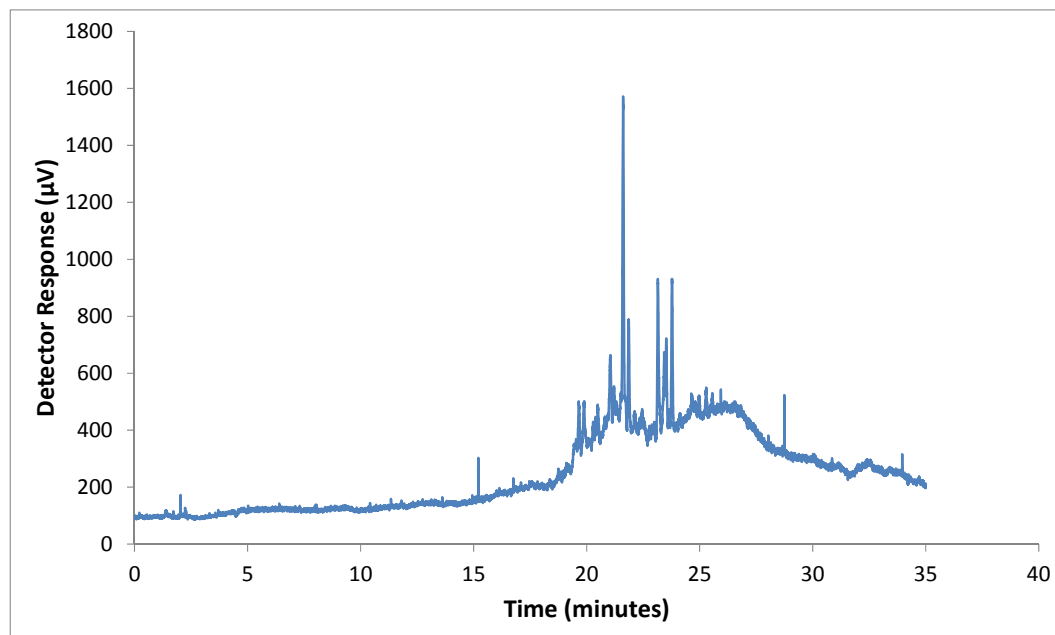
- SCD detector allows for determination of individual sulfur compound concentration (speciation) and total sulfur concentration
- Retention time depends on instrument conditions and molecular weight of sulfur compound



Determination of Sulfur Concentration in RP1 by GC/SCD



Peak area vs concentration of benzothiophene in toluene

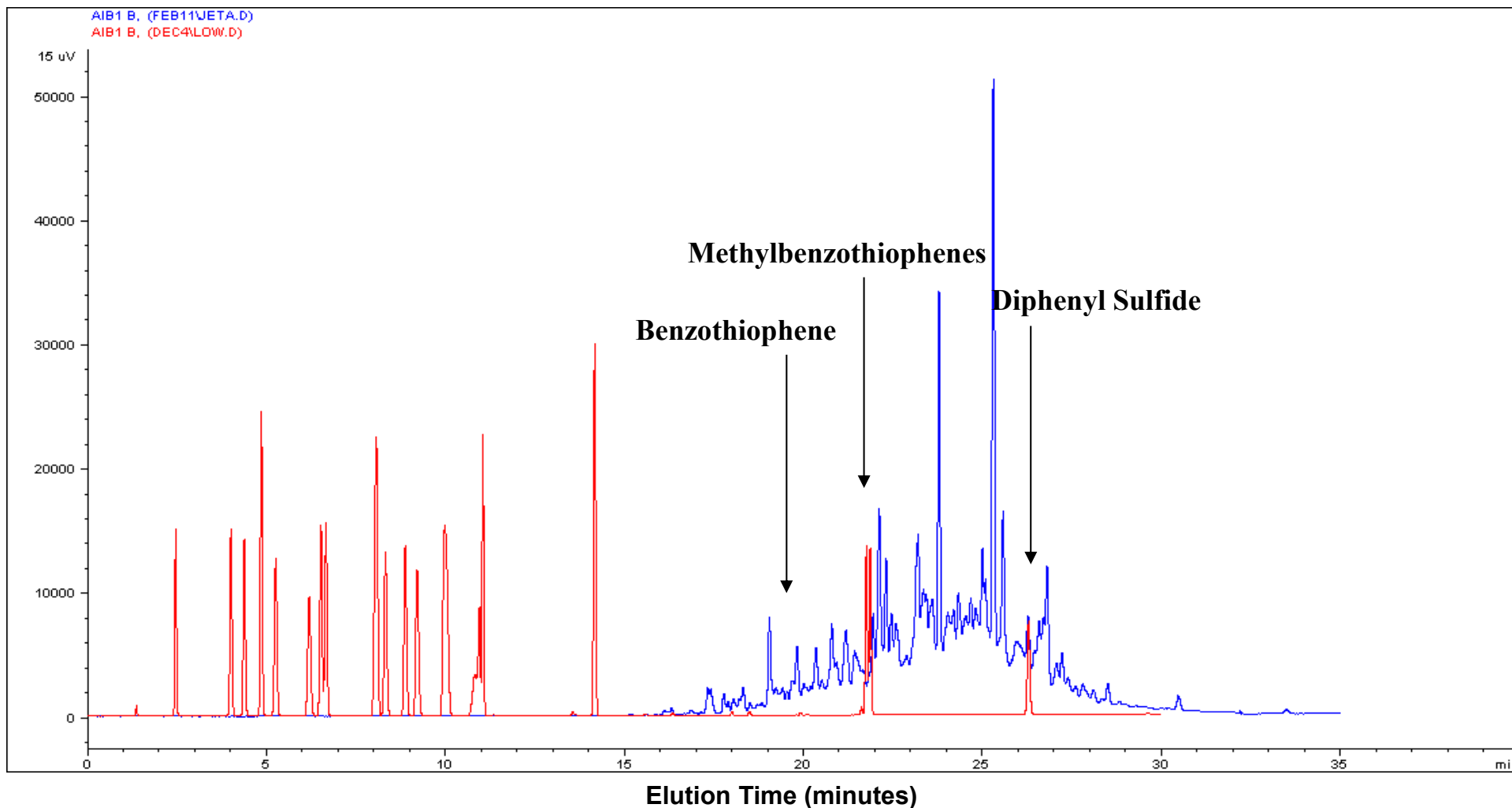


Typical chromatogram of RP1 rocket fuel
Instrument conditions followed were from ASTM D 5623

- SCD allows for a determination of a wide range of concentration, typically from 1 ppm to >3000 ppm for most sulfur compounds
- Typical sulfur compounds present in RP-1 are high molecular weight species such as benzothiophene and methylated isomers resulting in a fairly complex chromatogram



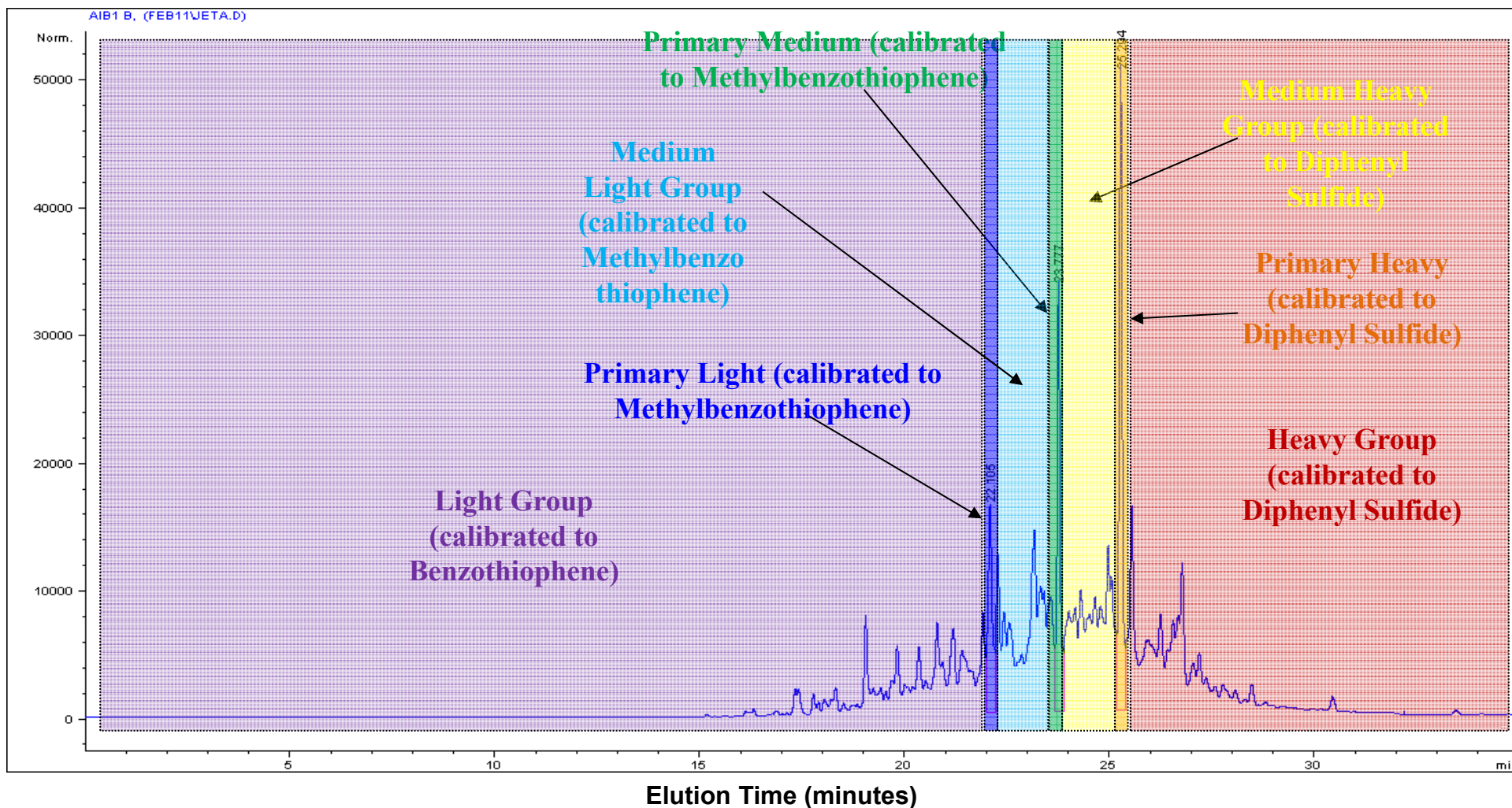
SCD Curve of Jet A with Standards Overlaid



As expected, contaminants in Jet A match elution times for C10-C12 S compounds



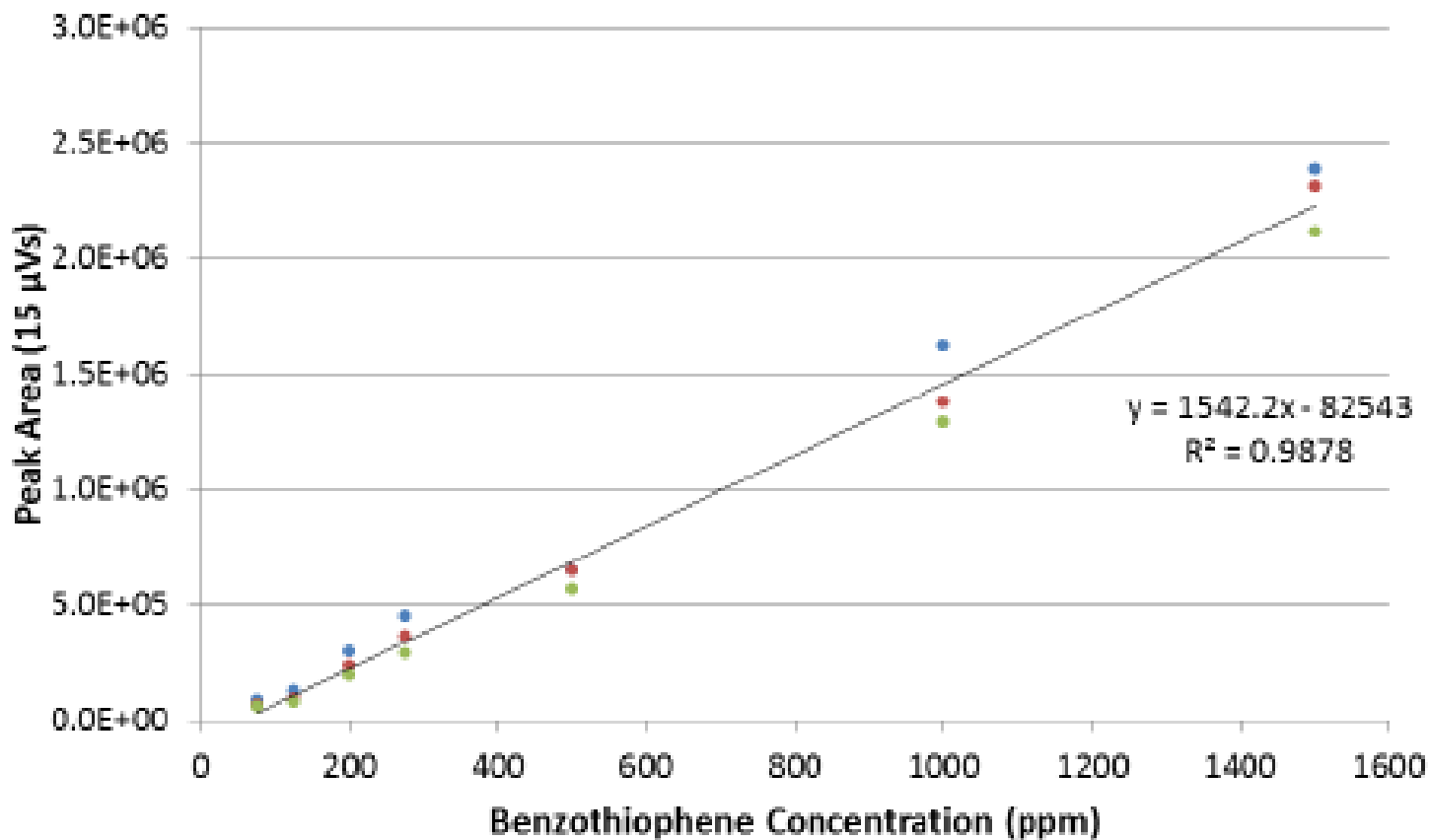
Provisional Speciation Scheme for Jet A



Chromatogram is split into seven regions using the three largest peaks, plus the two intervening and two external regions



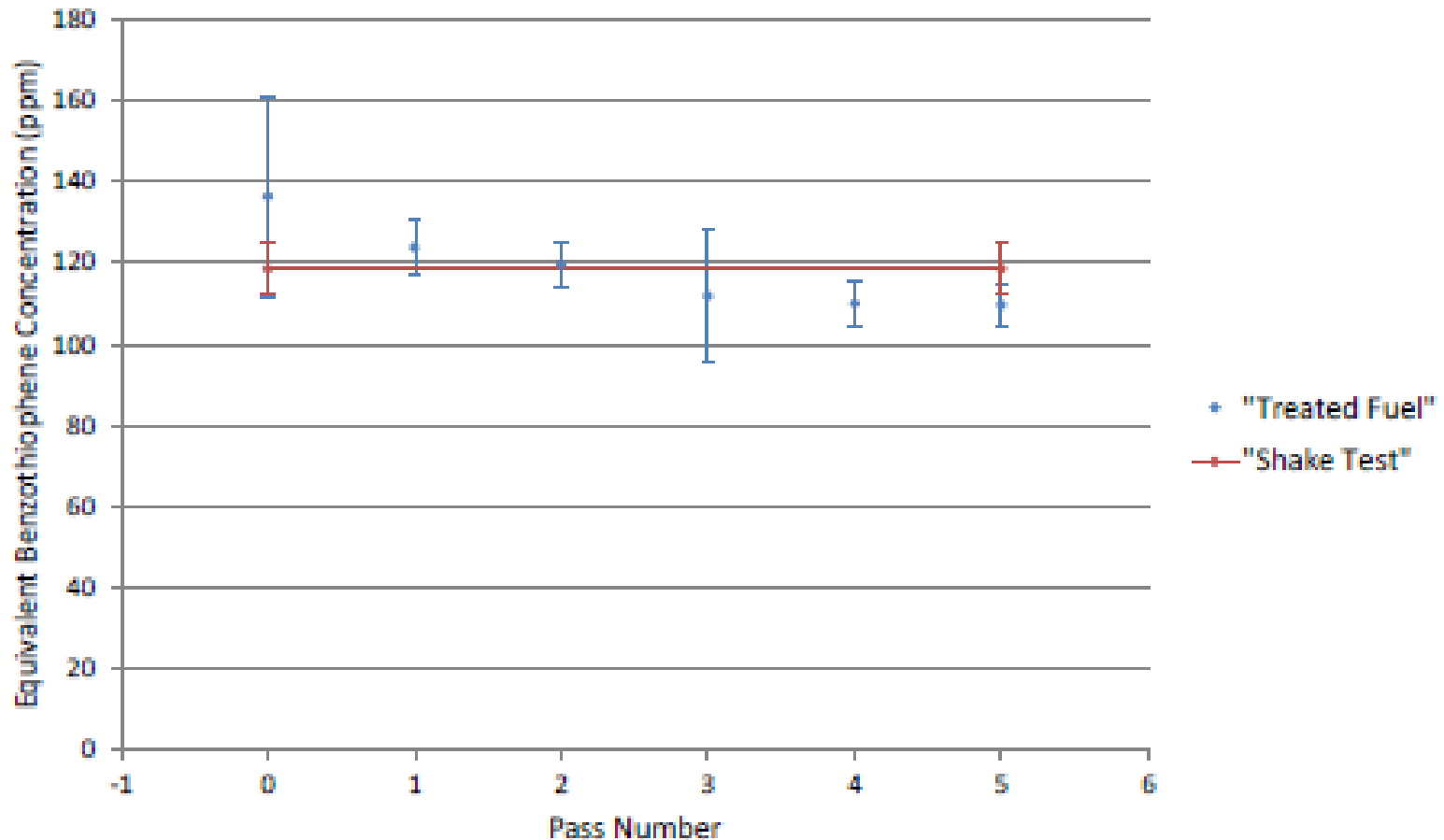
Calibration Curve for Benzothiophene



Although generally linear, some run to run variation is present.



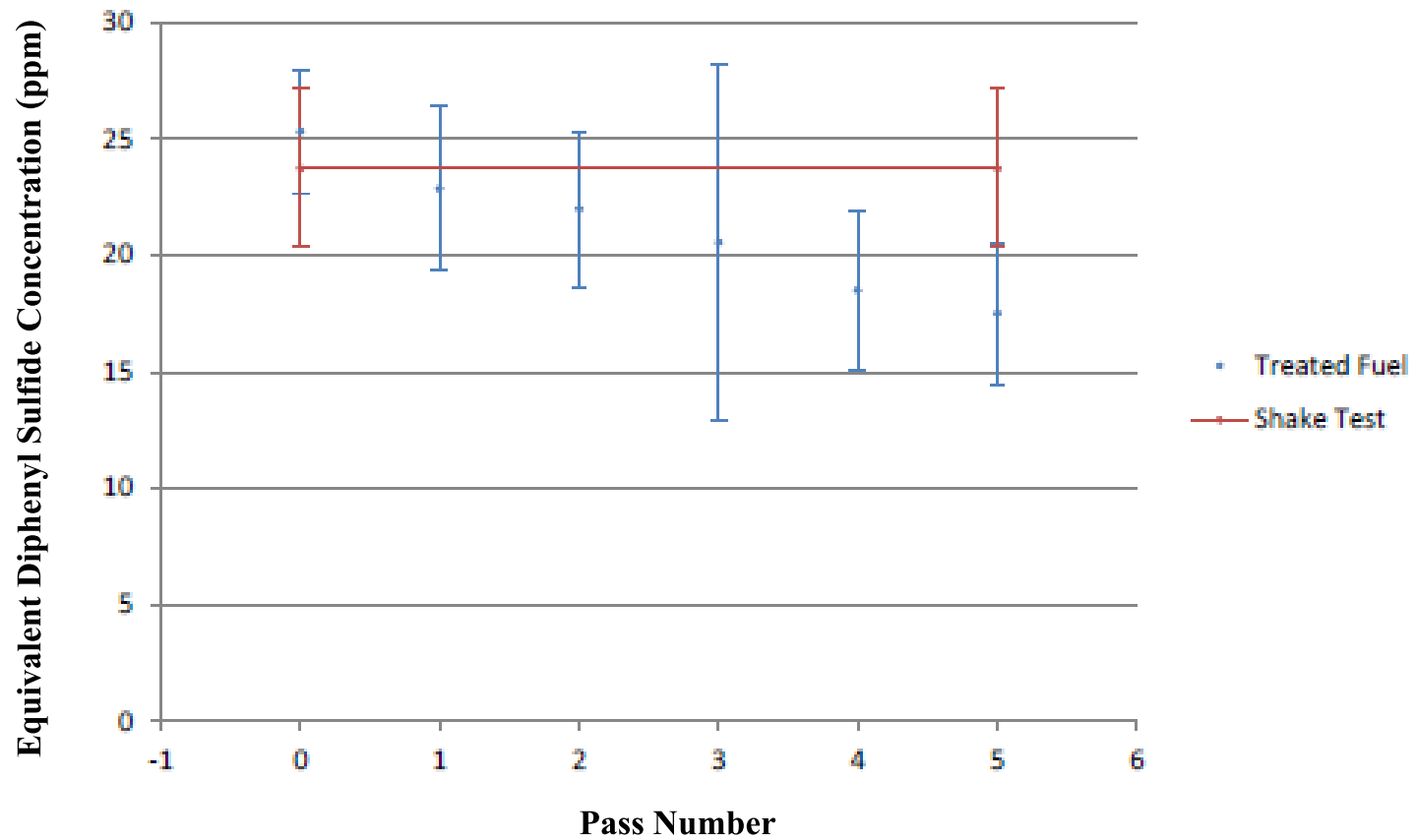
Apparent Concentration Profile of Light Group Contaminants (<22 min)



Extraction efficiency of 10% in first pass is typical of shake tests, but then decreases significantly in later passes, perhaps due to contamination of fuel by extraction fluid.



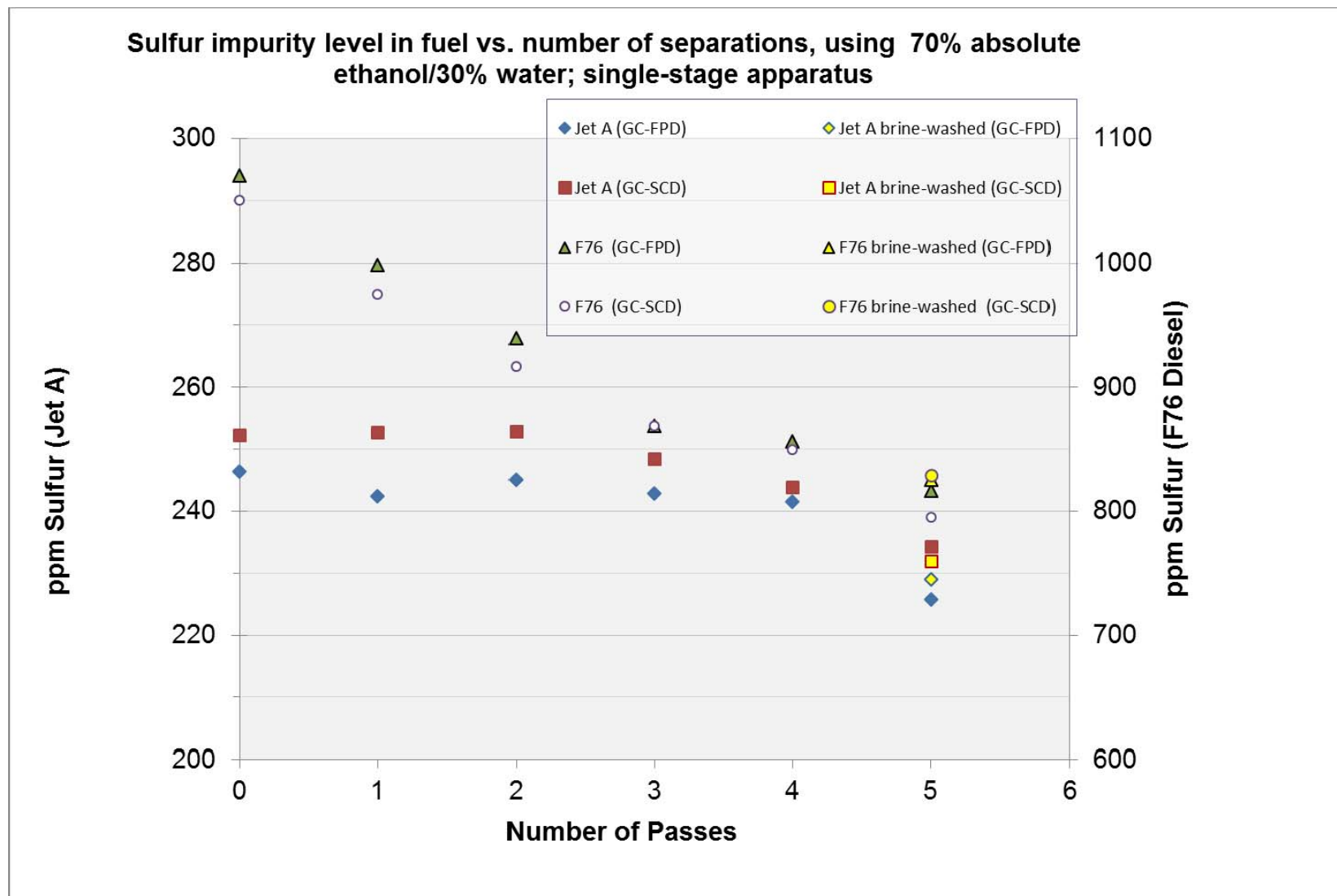
Apparent Concentration Profile of Primary Heavy Contaminant (25 min)



The heavier components appear to be less affected in later stages, with 5-10% extracted per stage.



Analysis of Total Sulfur Concentration





Understanding the Effects of Miscibility on Extraction



Enthalpy of mixing \rightarrow Solubility parameter \rightarrow Molar enthalpy of vaporization \rightarrow Molar volume \rightarrow Dispersive, polar, and H-bonding components

$$\delta^2 = (\Delta H_{\text{vap}} - RT) / V$$

$$\delta^2 = \delta_D^2 + \delta_P^2 + \delta_H^2$$

$$\Delta H_{\text{mix}} = \phi_1 \phi_2 V_{\text{ref}} [(\delta_{D1} - \delta_{D2})^2 + (1/4)(\delta_{P1} - \delta_{P2})^2 + (1/4)(\delta_{H1} - \delta_{H2})^2]$$

Volume fractions

$$K = C_{0,2} / C_{0,1} \leftarrow \text{Partition coefficient}$$

$$RT \ln K = V_0 [(\delta_{D1} - \delta_{D0})^2 + (1/4)(\delta_{P1} - \delta_{P0})^2 + (1/4)(\delta_{H1} - \delta_{H0})^2 - (\delta_{D2} - \delta_{D0})^2 - (1/4)(\delta_{P2} - \delta_{P0})^2 - (1/4)(\delta_{H2} - \delta_{H0})^2] + RT \ln (V_1/V_2)$$

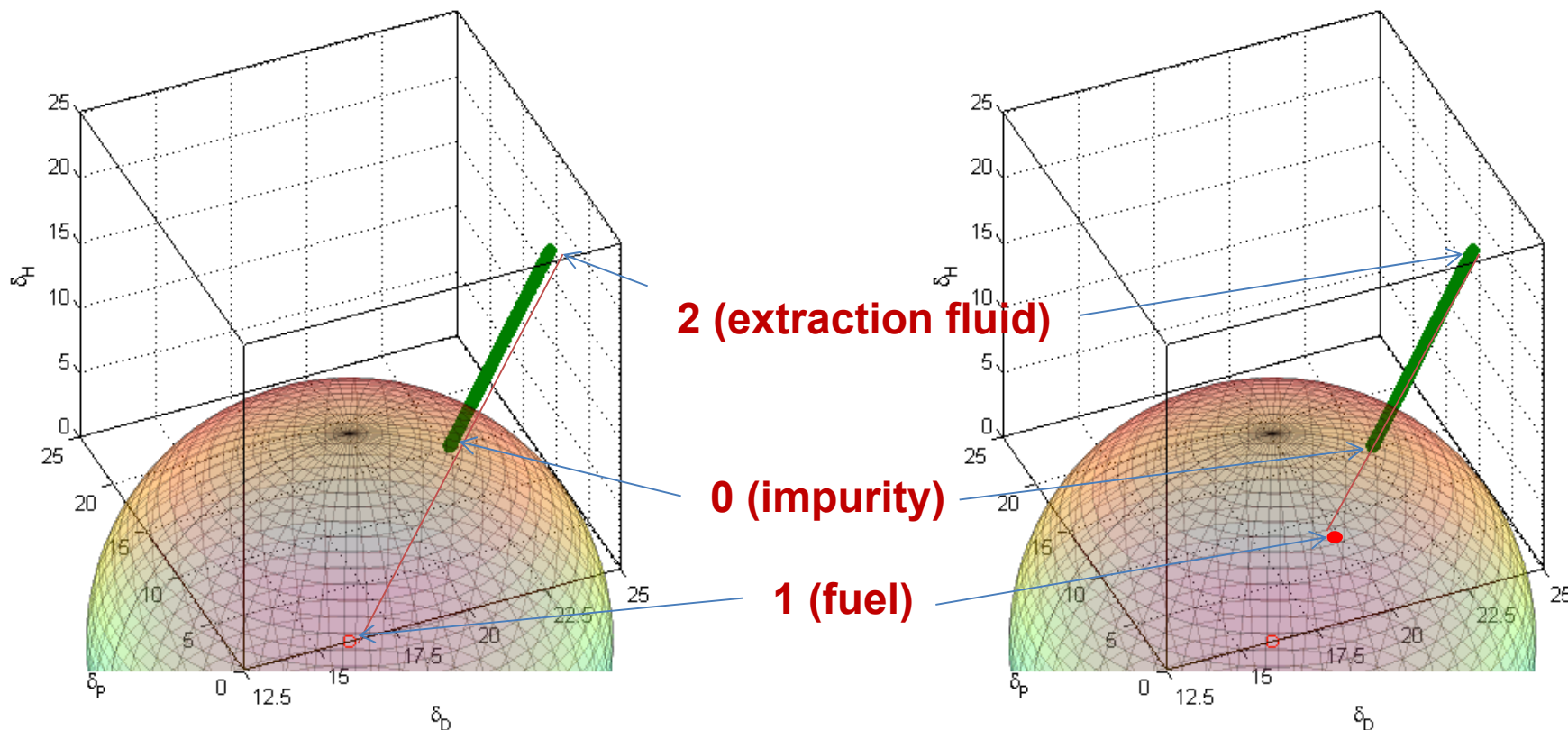
$$RT \ln K = V_0 (D_{1-0}^2 - D_{2-0}^2) + RT \ln (V_1/V_2)$$

D_{i-0} is fixed, so to maximize K , minimize D_{2-0} subject to constraint that 1 and 2 are not miscible (i.e. maximize D_{1-2}).

D_{i-0} is the distance in “solubility parameter space” between liquid i and impurity 0. For reference, phase 1 = fuel, phase 2 = extraction fluid.



Determination of Optimal Extraction Fluid (Graphical)



- Optimal extraction fluid will lie along the line connecting points 1 and 0 in HSP space, but outside the sphere of solubility for 1.
- Extraction efficiency (K) depends on the difference in lengths of the lines connecting points 1-0 and points 2-0.
- When fuel becomes saturated with extraction fluid, its solubility parameters change, shortening the distance 1-0, and lowering K.



Quantitative Predictions: Oil Red B4 in Dodecane / IPA:Water 9:1 (vol)



Case #	Scenario	δ_{D1}	δ_{D1}	δ_{D1}	δ_{D1}	δ_{D1}	δ_{D1}	D_{1-0}^2	D_{2-0}^2	K
1	Baseline	16	0	0	15.8	7.1	16.4	178	148	1000
2	Miscibility	16	1.4	3.7	15.8	7.1	16.4	115	148	0.005
3	Water HSP	16	0	0	15.8	7.1	17.4	178	165	40
4	Dye HSP*	16	0	0	15.8	7.1	16.4	217	189	700

Baseline case assumes no miscibility of dodecane in IPA. Miscibility (case 2) estimates HSP for ~5 vol% IPA in dodecane, based on experience with RP-1.

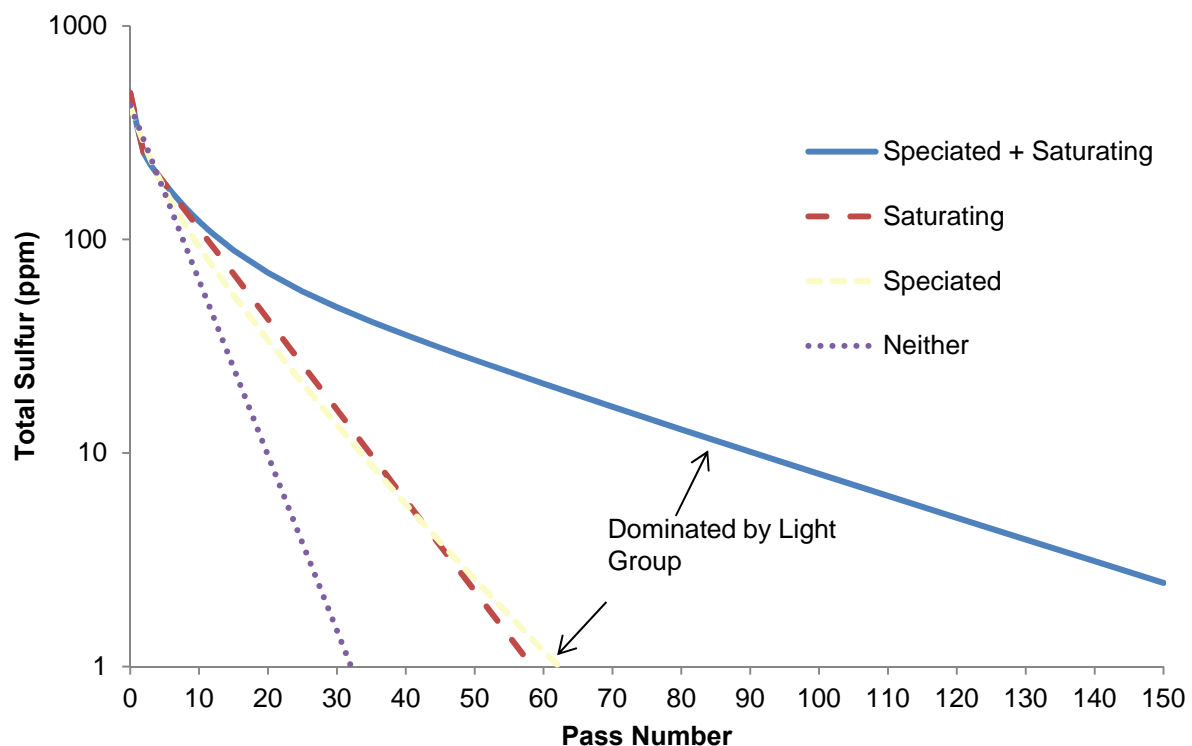
*HSP for Oil Red B4 are $\delta_D = 20.4 \text{ (J/cc)}^{1/2}$
 $\delta_p = 5.0 \text{ (J/cc)}^{1/2}$ $\delta_H = 8.7 \text{ (J/cc)}^{1/2}$ for cases 1, 2, and 3. For case 4, $\delta_D = 21.4 \text{ (J/cc)}^{1/2}$ $\delta_p = 5.0 \text{ (J/cc)}^{1/2}$ $\delta_H = 8.7 \text{ (J/cc)}^{1/2}$

Proper assessment of uncertainties, in particular even slight mutual miscibility, is critical for quantitative predictions of K

HSP for IPA : water mixture is estimated based on either apparent values from miscible solvent / water mixtures (cases 1, 2, and 4) and a slightly higher value based on uncertainty in δ_H for water in mixtures (case 3).



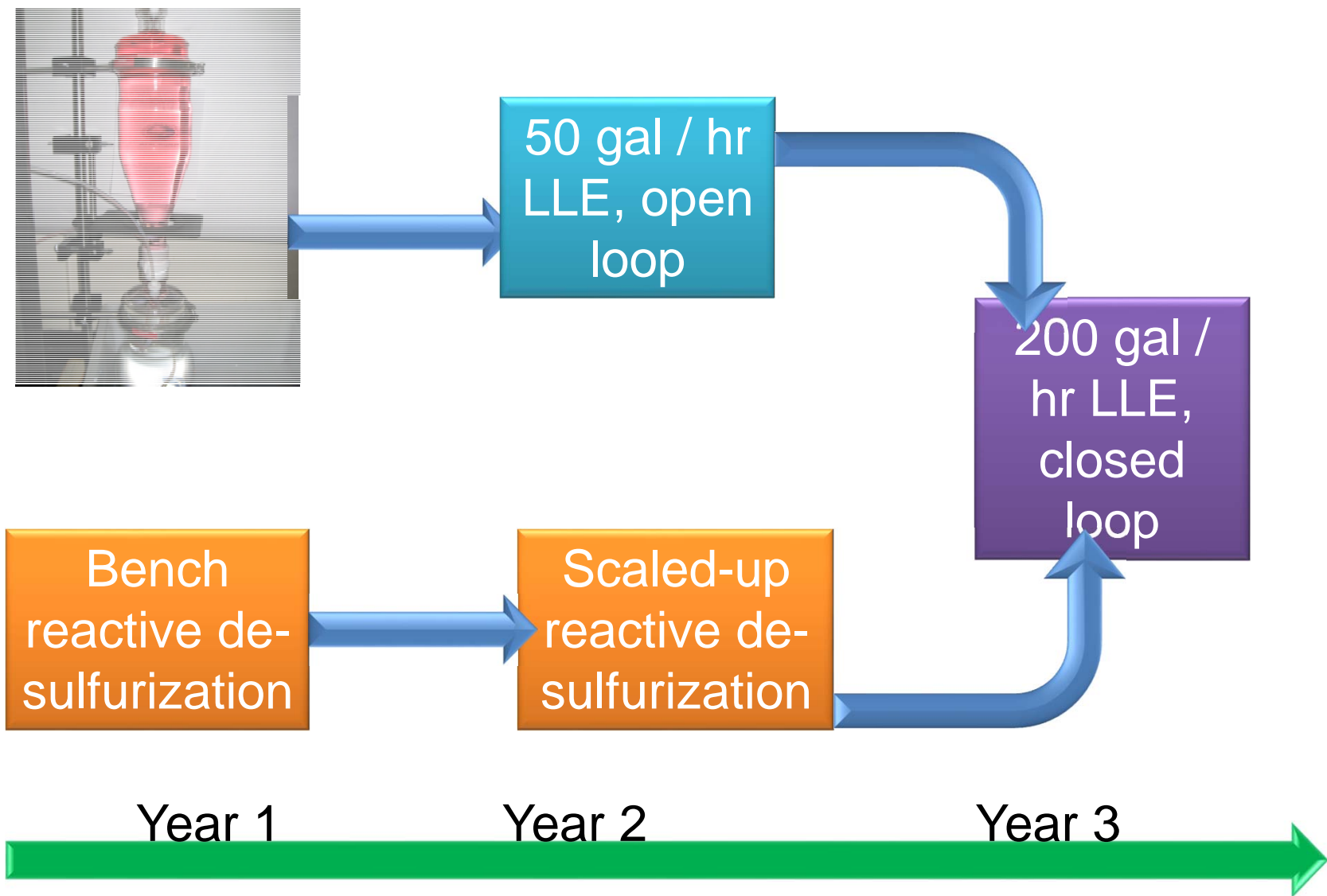
Effects on Speciation and Saturation on Evolution of Total Sulfur Content



Taking speciation and saturation into account results in large changes in the number of predicted passes needed to achieve a given level of sulfur removal.



Process Development Roadmap





Equipment Status



50 gal / hr
LLE, open
loop



Unit 1: **Operational**

Location: EAFB Bldg 8498

Initial Operating Capability: 4 Feb 2016

Current status: Performing several test runs per month.

Current Experiments: Testing of different membrane / disperser configurations and hold-up configurations

Unit 2: **Operational**

Location: WPAFB, Bldg 490 Storage

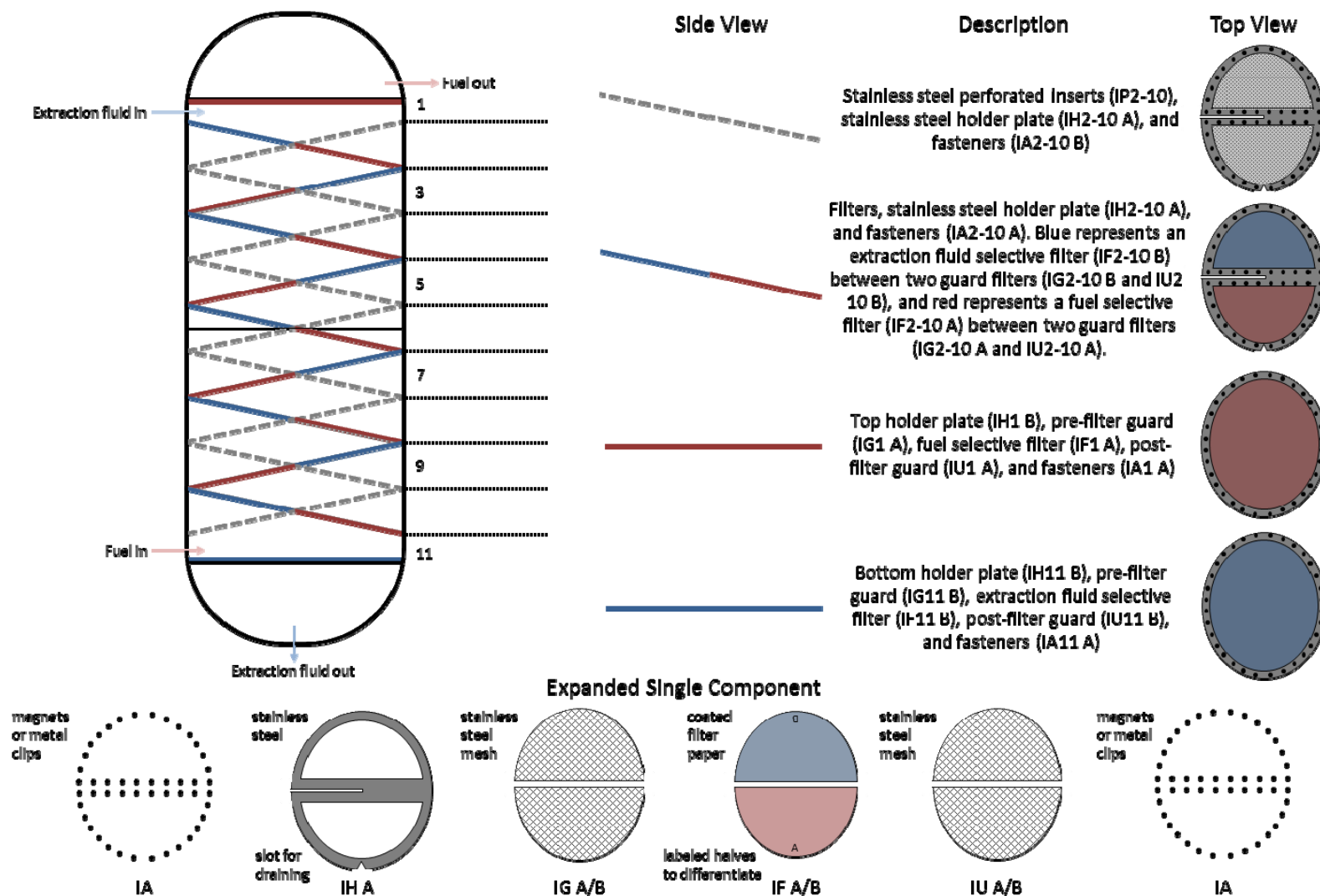
Initial Operating Capability: 20 Jan 2016

Current status: Performing several test runs per month

Current experiments: Testing 2-membrane modified spray column configuration

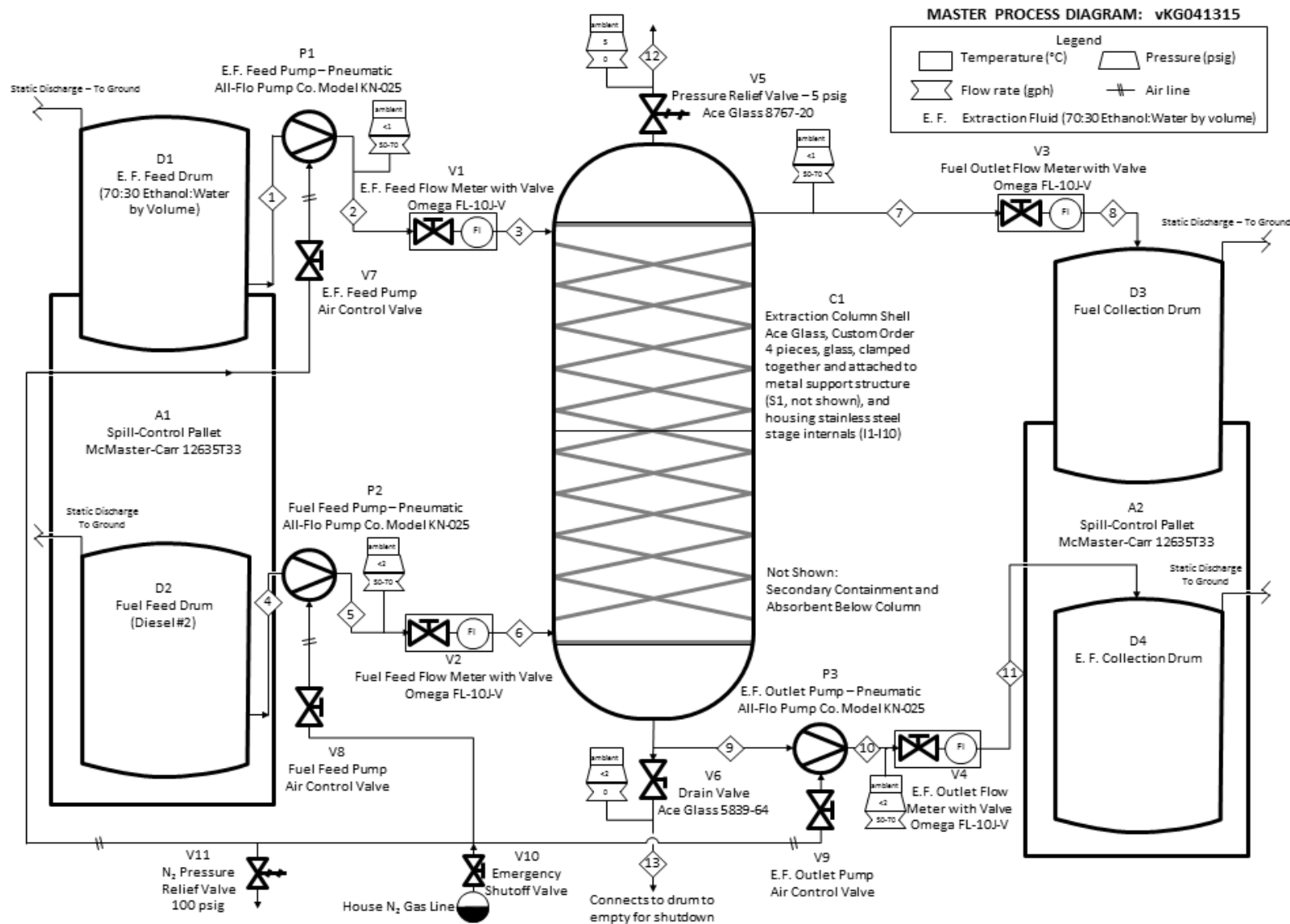


Scale-Up of Liquid/Liquid Extraction





Scale-Up of Liquid/Liquid Extraction



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Future Plans



Finish optimization of configuration using Units 1 and 2

Design and build Unit 3 (200 gph, closed loop system) in a portable container

Refine a 1000-gal batch of Jet A to meet ultra-low sulfur diesel specifications using Unit 3. Perform 40-hr ground engine test using refined fuel.

Retain bench unit and Unit 1 @ Edwards AFB for production of custom-composition batches of rocket fuel for future research; retain Unit 2 @ AFRL/RQ for future fuels research.

Maintain Unit 3 as available for future demonstration activities.



Applied Materials Group / AFRL Edwards AFB



Dr. Jeffrey Alston, Mr. Michael Ford, Dr. Kamran Ghiassi, Mr. Kevin Greeson,
Dr. Andrew Guenthner, Dr. Timothy Haddad, Mr. Madani Kahn, Mr. Jason Lamb,
Mr. Chris Lee, Dr. Joseph Mabry, Mr. Jacob Marcischak, Dr. Joseph Mates,
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