

# Calibration Transfer Between MEMS Based Near-Infrared Spectrometers

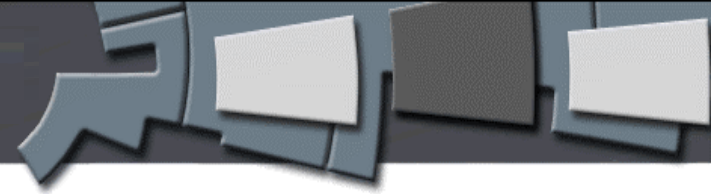
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[www.axsun.com](http://www.axsun.com)

Calibration Transfer - The ability to use calibration models or data developed on one instrument on other instruments with minimal or acceptable performance sacrifice and minimum re-work. (Ideally no sacrifice or re-work...)

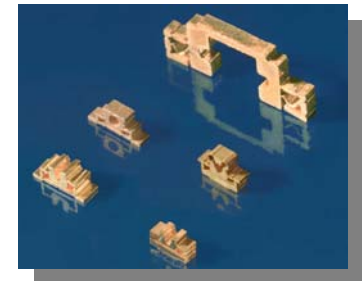
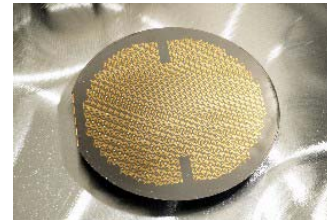
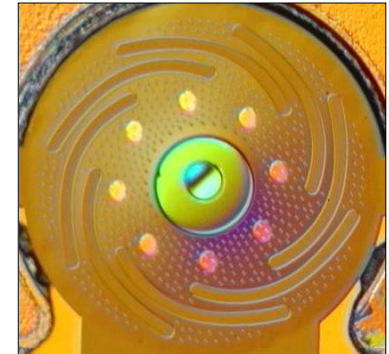
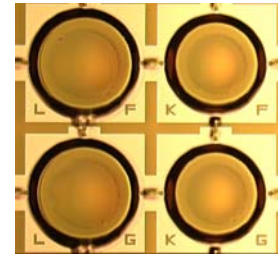
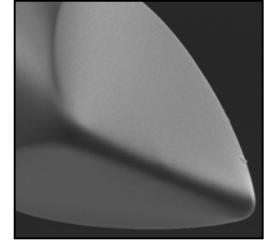
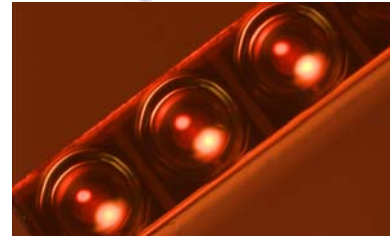
# Calibration Transfer Between MEMS Based Near-Infrared Spectrometers



- Step 1:
  - Develop highly reproducible manufacturing processes and procedures – MEMS = Micro Electro Mechanical System utilizes Semiconductor industry processes.
    - The semiconductor manufacturing processes we employ are highly reproducible
  - Control temperature of detector and critical optics or reduce mechanical impact of thermal effects
- Axsun Spectrometer Elements
  - Pre-dispersive tunable source spectrometer
  - Source
    - Semiconductor gain media
  - Dispersive element
    - MEMS Tunable Fabry-Perot Filter
  - Detector
    - Cooled “large area” PIN Diode
  - Integral point by point, per scan wavelength and amplitude correction
- Advantages of Axsun Design
  - Semiconductor source is much smaller, longer lived, more efficient, and orders of magnitude brighter than a tungsten lamp
  - The MEMS tunable filter is lower cost, faster, smaller, and higher resolution than other choices for dispersion
  - All spectrometers are inherently stable in wavelength and amplitude
  - Very high speeds and SNR achieved in tunable source configuration

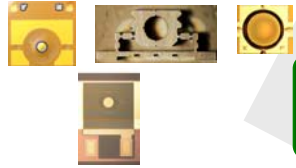
# Optical Toolkit

- The analyzer is fabricated using a complete set of miniature optical components, including
  - Lenses
  - MEMS Tunable Filters
    - Micro Electronic Mechanical Systems
  - Optical mounts
  - Fiber assemblies
  - Optical benches
- Semiconductor manufacturing processes allow for extremely highly reproducible manufacturing.

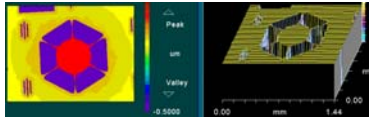


# Automated Volume Manufacturing Processes

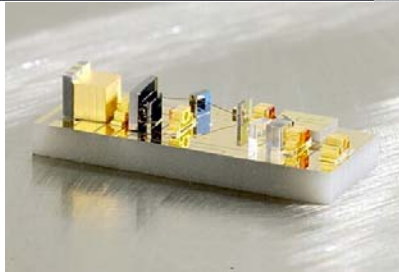
## Micro Optics



Characterize



Pick & Place

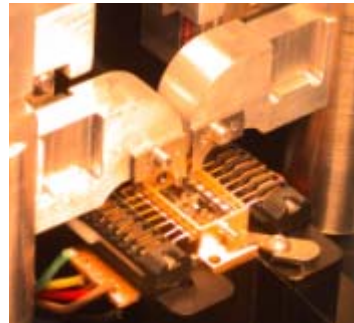


Solder Attach

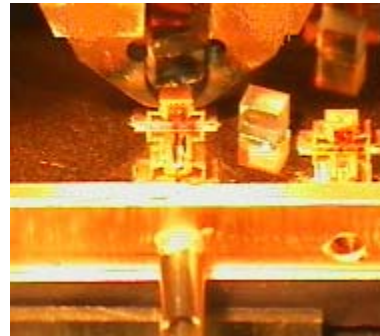


Align

Micro-robotic alignment  
Final alignment capability is  
< 0.1 micron



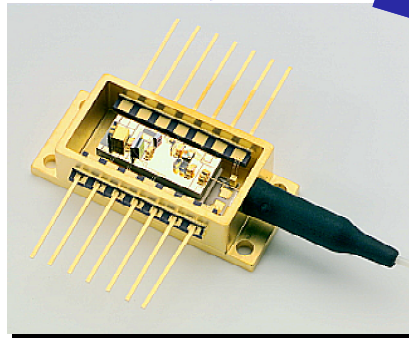
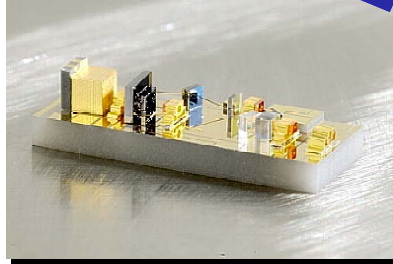
Seal



Test & Sort



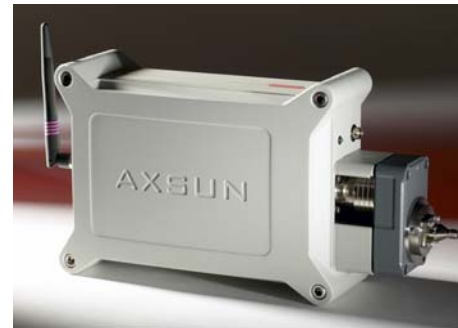
Pick and place



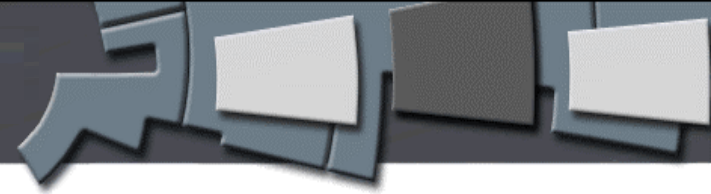
## *Micro-optical instruments*

### *Benefits*

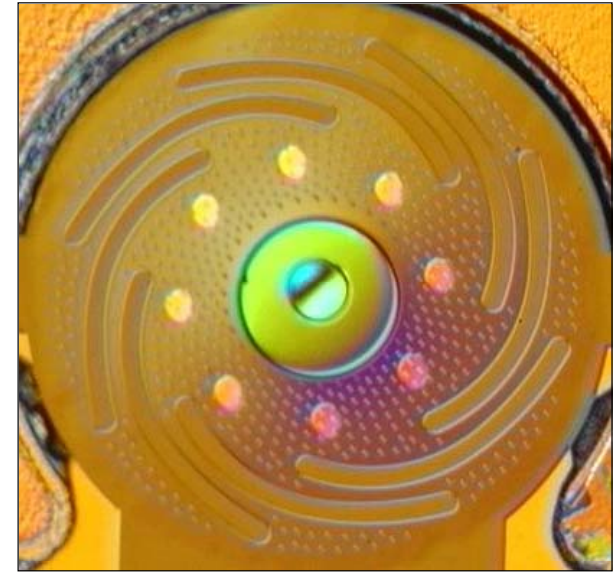
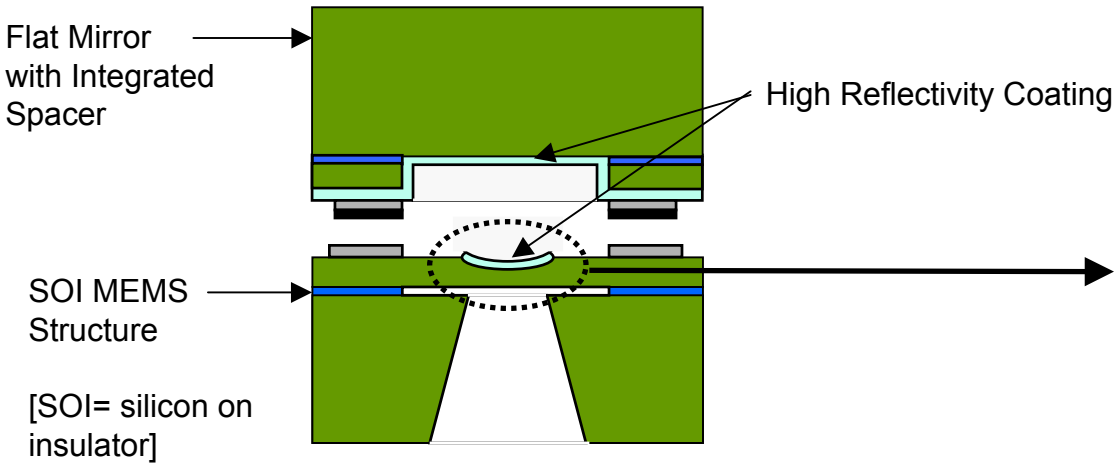
- Mass-produced
- Rugged
- High performance
- Very small
- Low power consumption
- Battery operation



# MEMS Filter Assembly

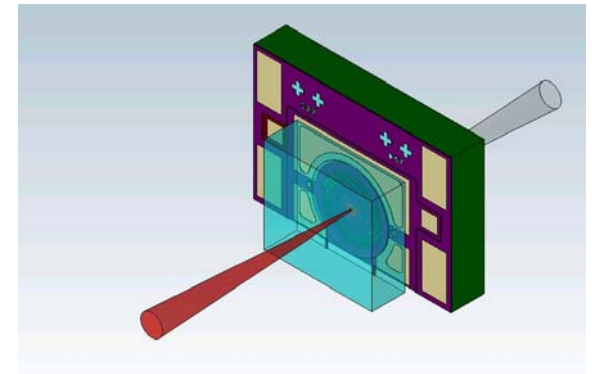


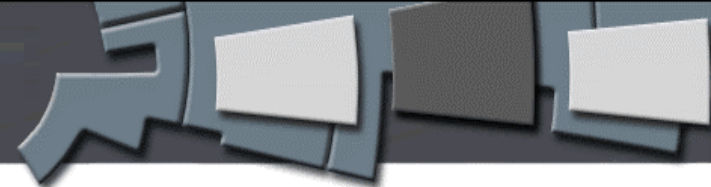
## Fabry-Perot Filter Assembly



~1 mm

- High resolution, broadly tunable filter
  - $4 \text{ cm}^{-1}$  resolution
  - Tuning range of hundreds of nm
  - Scans full range in milliseconds
  - Insensitive to vibration
  - Semiconductor manufacturing process





- Some chemometric models “evolve” over years, becoming very expensive
  - Payback is in replicate analyzers at small incremental cost
- Some analyzers evolve, change or break down
  - Replacement / repaired analyzer may be different
- Lab support of on-line analyzers
  - Often easier to develop calibration models in the laboratory on a bench top scale or in a pilot plant
    - Model development / sampling much easier in lab
    - Lab or pilot plant is often logical starting point for on-line projects
    - Much less expensive
    - Prove out application before investing in capital project
      - (Less chance of career altering change if it doesn’t work out!!!)

# “Calibration” / Method Transfer

- Spectroscopic Matching – How close can the spectrometers be manufactured?
  - Pretty easy to quantify

But there are other factors that effect model transfer and may cloud the issue

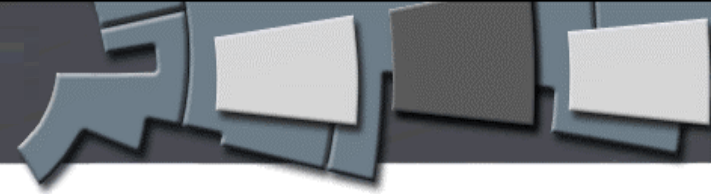
- Product/Process Similarity
  - Is the product really the same, or are there small compositional or morphological differences?
- Sample Conditions during analysis
  - Temperature, Pressure, Flow
  - Sampling point in the process
- Installation issues such as fiber optic specifications, length of cables, reference beam/sample scheme etc.

## Method Transfer

- Same primary method?
  - Moisture by Karl Fisher
  - Vacuum Drying
    - Loss on Drying – Total Volatiles vs Moisture
  - Same Units of measure?
- Plant Bias – Analytical, cultural

*All of these differences tend to get lumped into the “calibration transfer” bin, but must be understood to quantify the success of transfer.*

# Calibration Transfer Key Issues

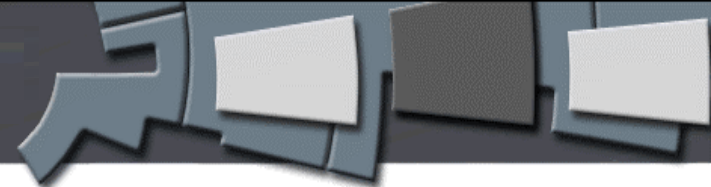


- Signal to Noise
- Photometric Linearity/Reproducibility
- Wavelength Accuracy
- System Resolution / Band Shape

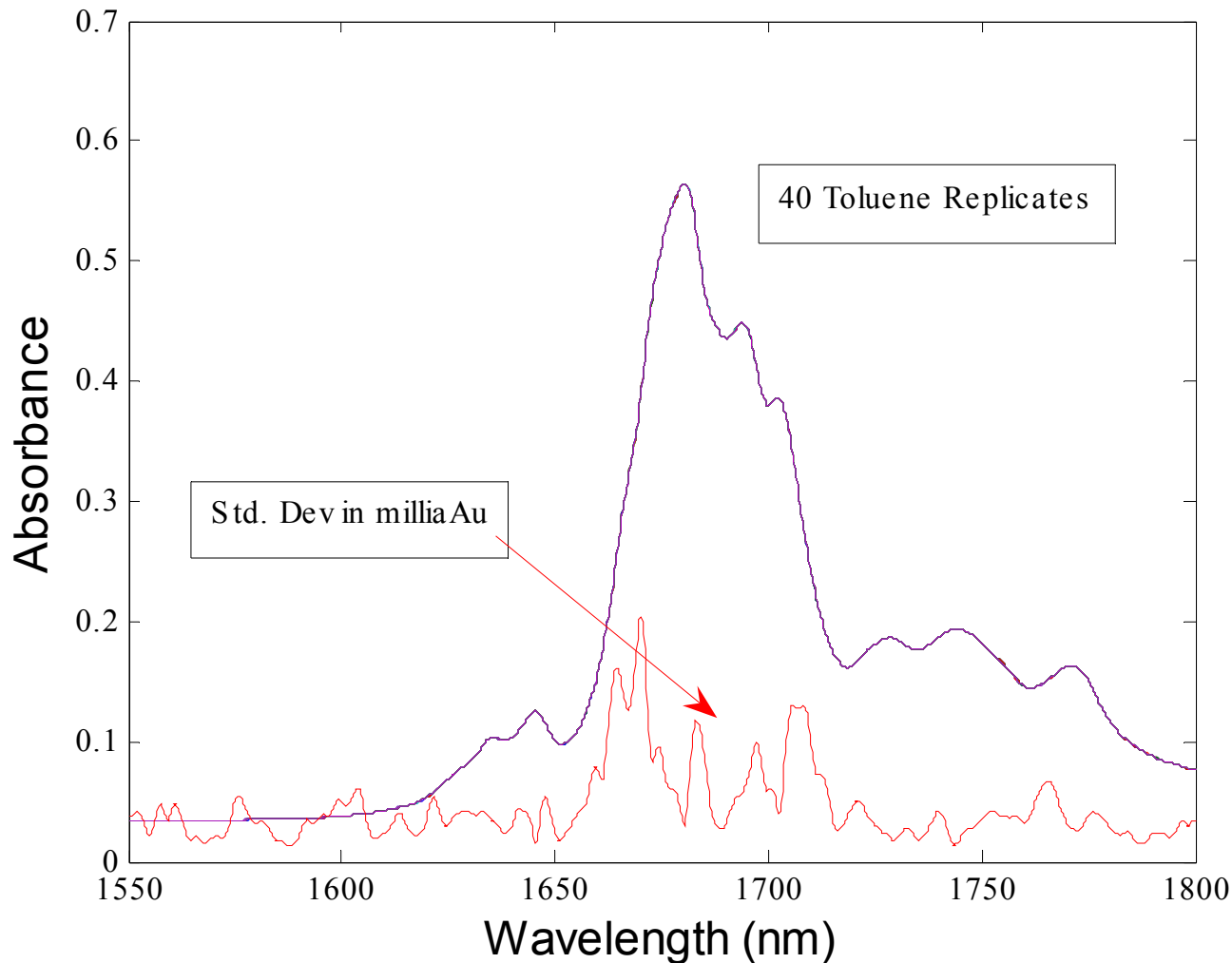
## Required Starting point

- Develop (and meet!) tight manufacturing tolerances for base analyzer performance
  - Resolution, signal to noise, photometric linearity, dynamic range
  - The semiconductor manufacturing processes we employ are highly reproducible
- Control temperature of detector and critical optics or reduce mechanical impact of thermal effects
- Control sampling conditions (temperature etc) if possible if they impact the measurement
- Control or correct for small changes in pathlength

# Spectral repeatability

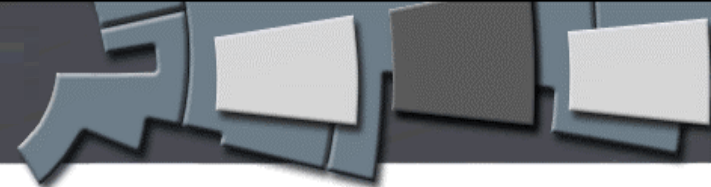


Quantify the base repeatability of the analyzers to be matched,  
insure system repeatability won't limit transfer

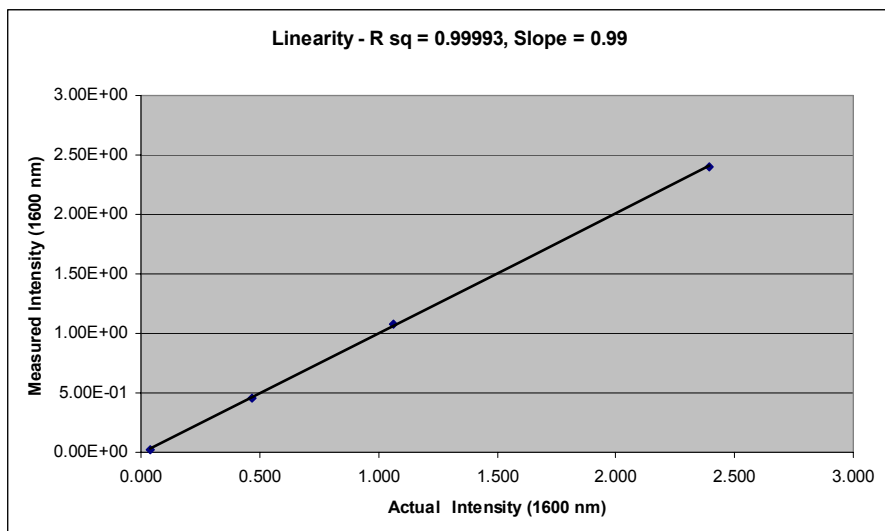


- 16 Scans averaged
- Spectrum collect time = 2 seconds
- 2 nm resolution
- Elapsed time: 20 minutes

# Photometric Linearity using traceable neutral density filters

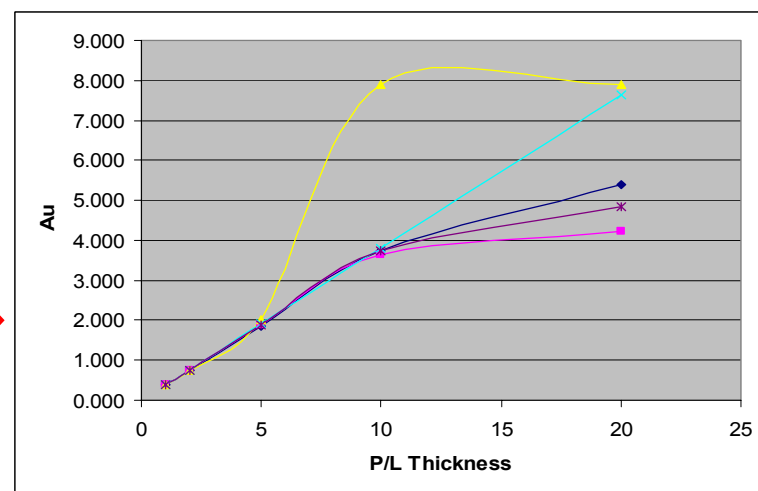


Quantify the base photometric linearity of the analyzers to be matched, insure you're working in a linear range to not limit transfer

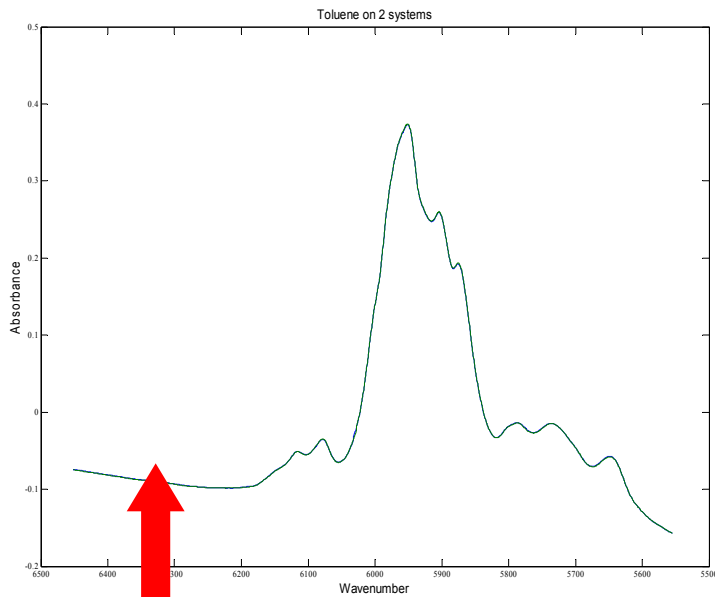
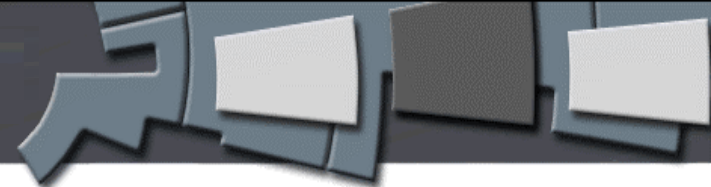


- 16 Scans averaged
- Spectrum collect time = 2 seconds
- 2 nm resolution
- Referenced against air

In this case, the analyzer plotted in yellow is nonlinear > 1.9 AU. This would limit transfer capabilities for highly absorbing data/models

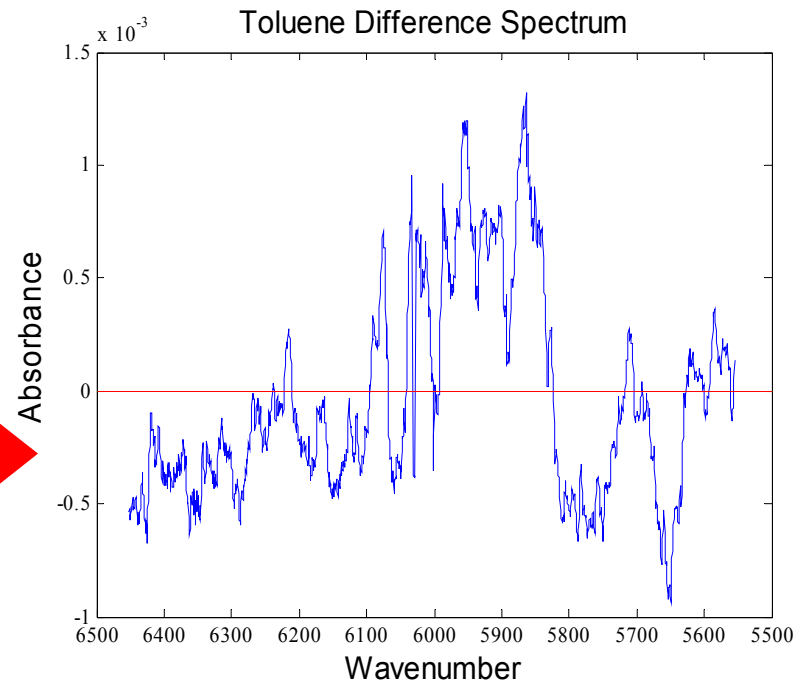


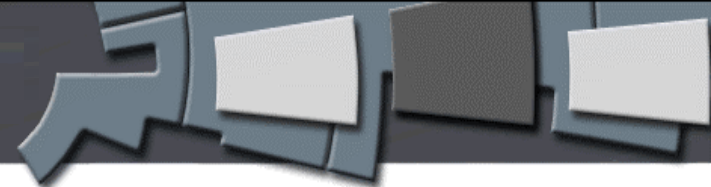
# “Toluene test” using 2 Axsun Microspectrometers



Basic instrument matching is often evaluated using spectral subtraction

- Scan toluene on 2 systems
- Subtract the spectra of instrument 2 from instrument 1
- Maximum specified difference
  - Desired < 2 mAu

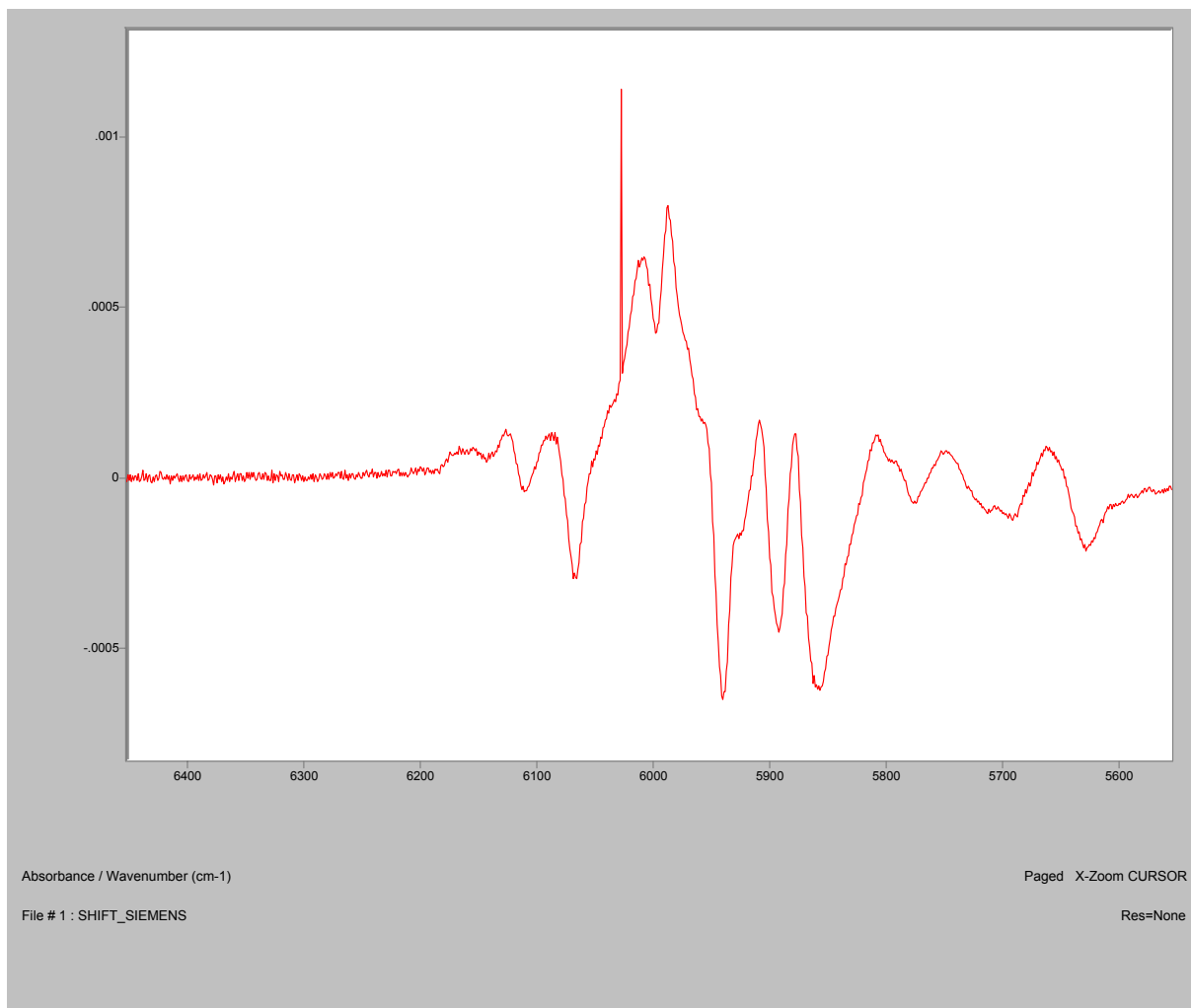




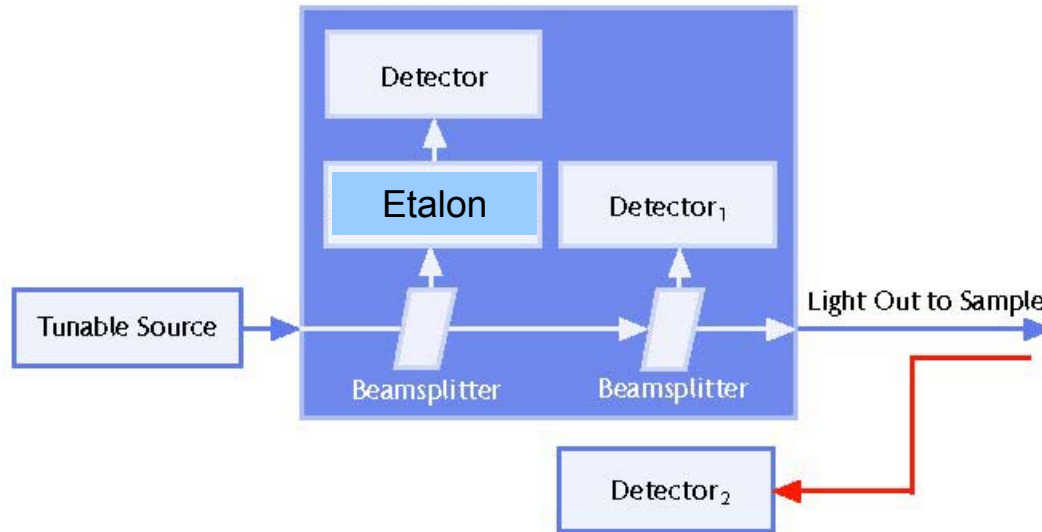
## Toluene Difference Spectrum

Toluene spectrum minus the same toluene spectrum with an Induced frequency Shift of  $0.1 \text{ cm}^{-1}$  results in  $> 1 \text{ mAu}$  difference between original and shifted spectrum

This is enough difference to cause inaccuracy in results

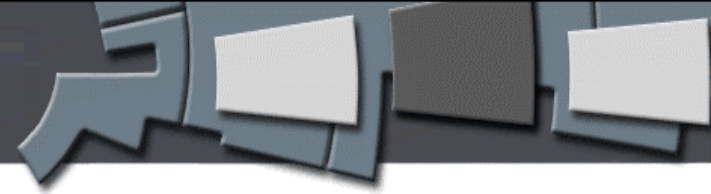


# Axsun Analyzer Standardization

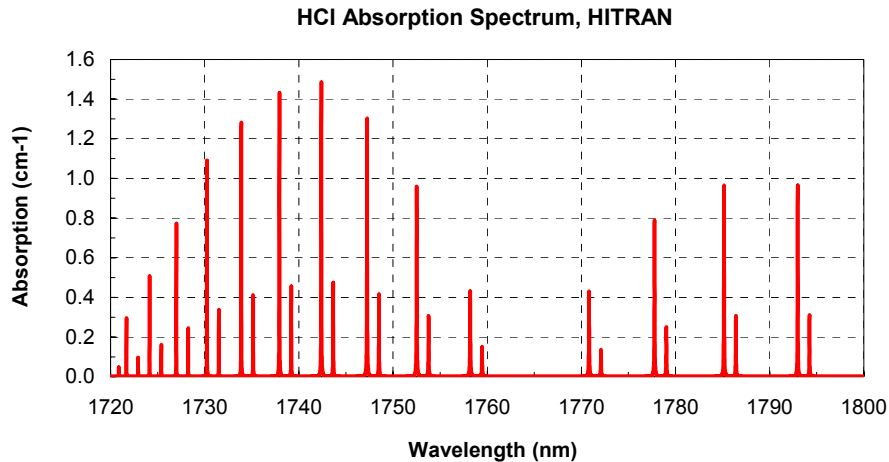


- WARM (Wavelength & Amplitude Reference Module)
  - Ultra stable beamsplitters tap off known quantities of light
  - Absolute wavelength reference provided by an integrated quartz etalon that is temperature controlled to 0.1°C
  - Amplitude reference provided by matched single element photodetectors that divide out responses from every point of a scan

# HCl Gas Absorption Spectrum

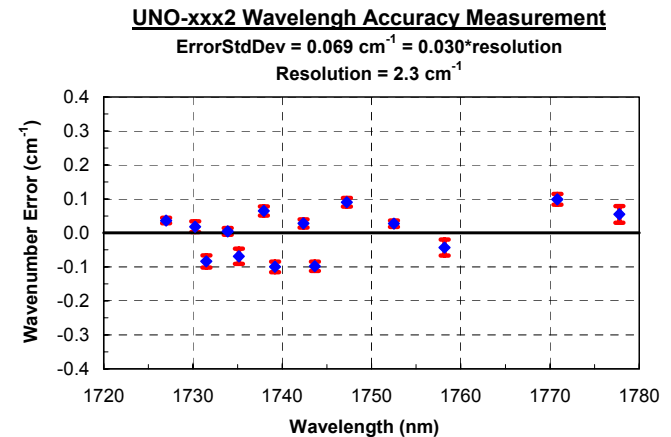


- Use strong gas absorption lines for wavelength standardization and evaluating spectrometer wavelength accuracy
- Compare measured gas line wavelengths with the database reference over multiple repeated spectral scans



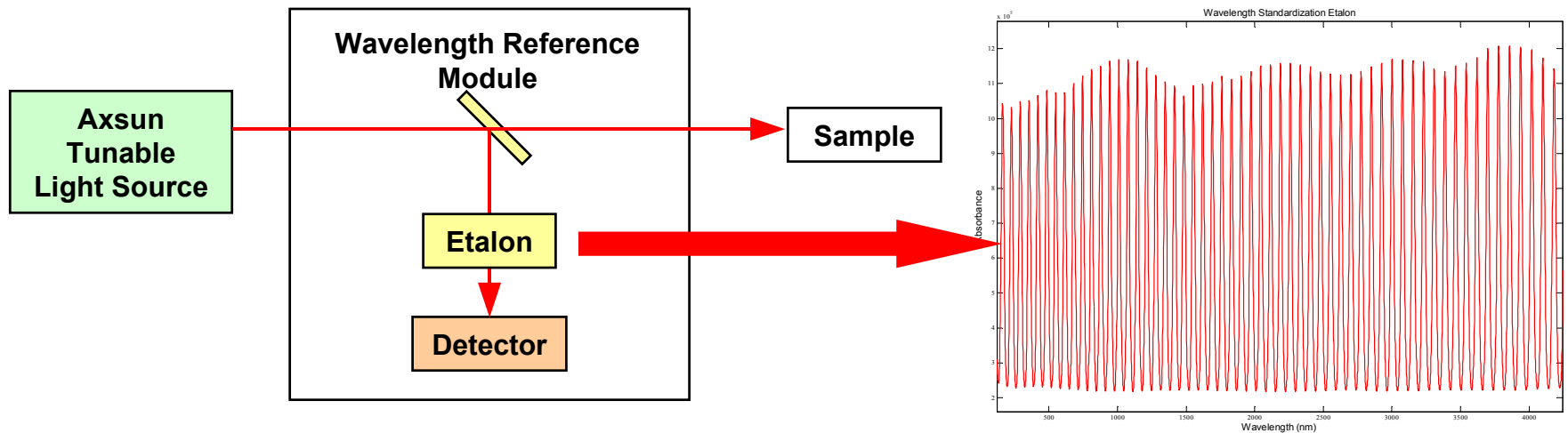
Real-time internal wavelength (and amplitude) referencing allows to attain spectra with high wavelength accuracy and repeatability

<0.1 wavenumber accuracy

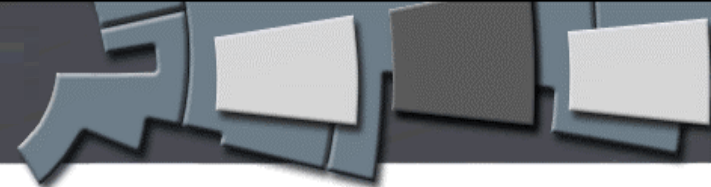


# Wavelength Referencing Scheme

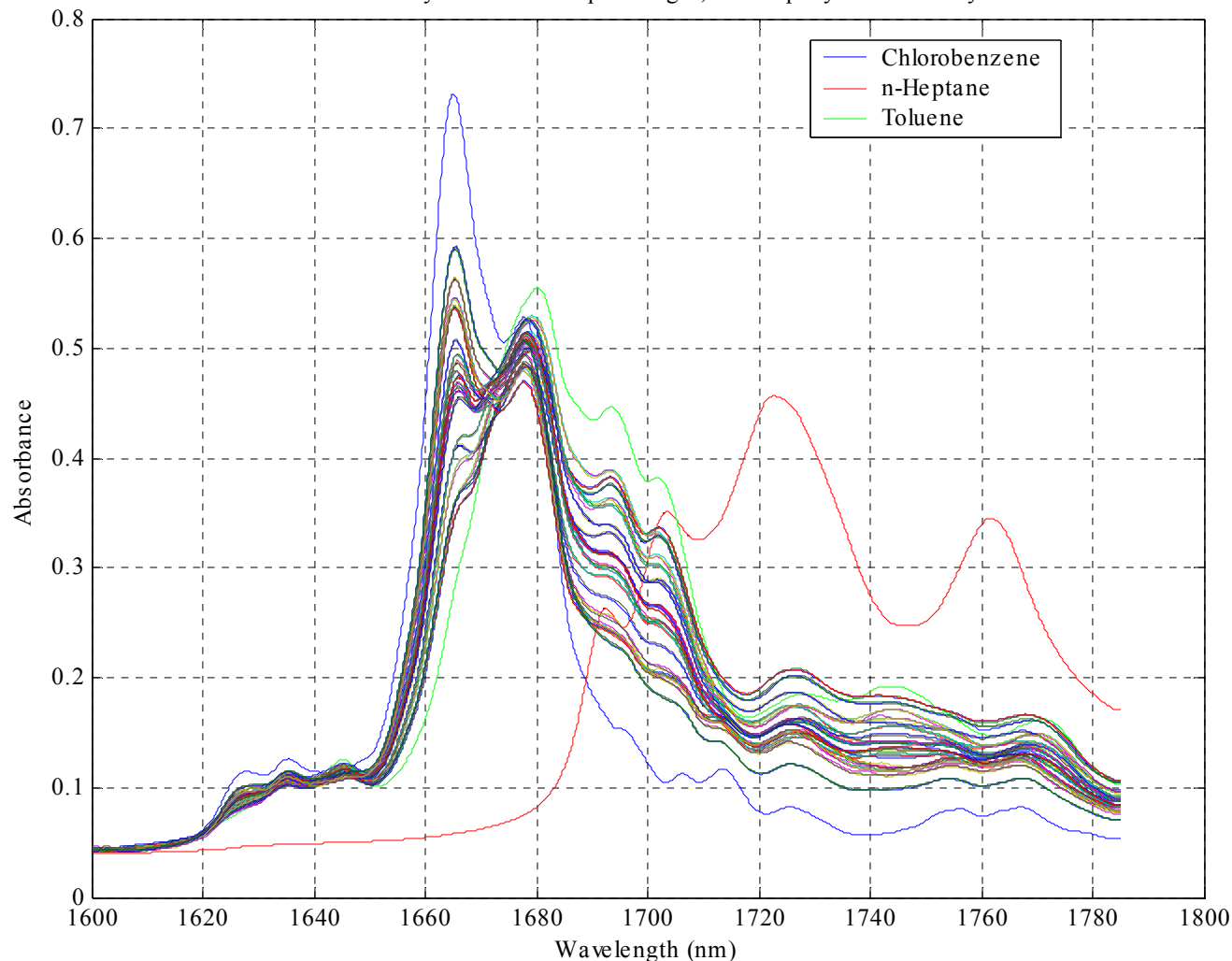
- Wavelength of the light source is scanned linearly with time
- For each wavelength scan an internal reference etalon is measured
- Wavelength for each scan point is given by linear interpolation between wavelengths of the two neighboring etalon peaks



# Calibration Transfer - Quantitative Example



Axsun NIR Analyzer - 0.95mm pathlength, 3 Comp System 3 Analyzers.



Chlorobenzene = 20.74-75.48%

Toluene = 21.59-77.02%

Heptane = 2.07-10.74%

0.95 mm pathlength  
transmission cell

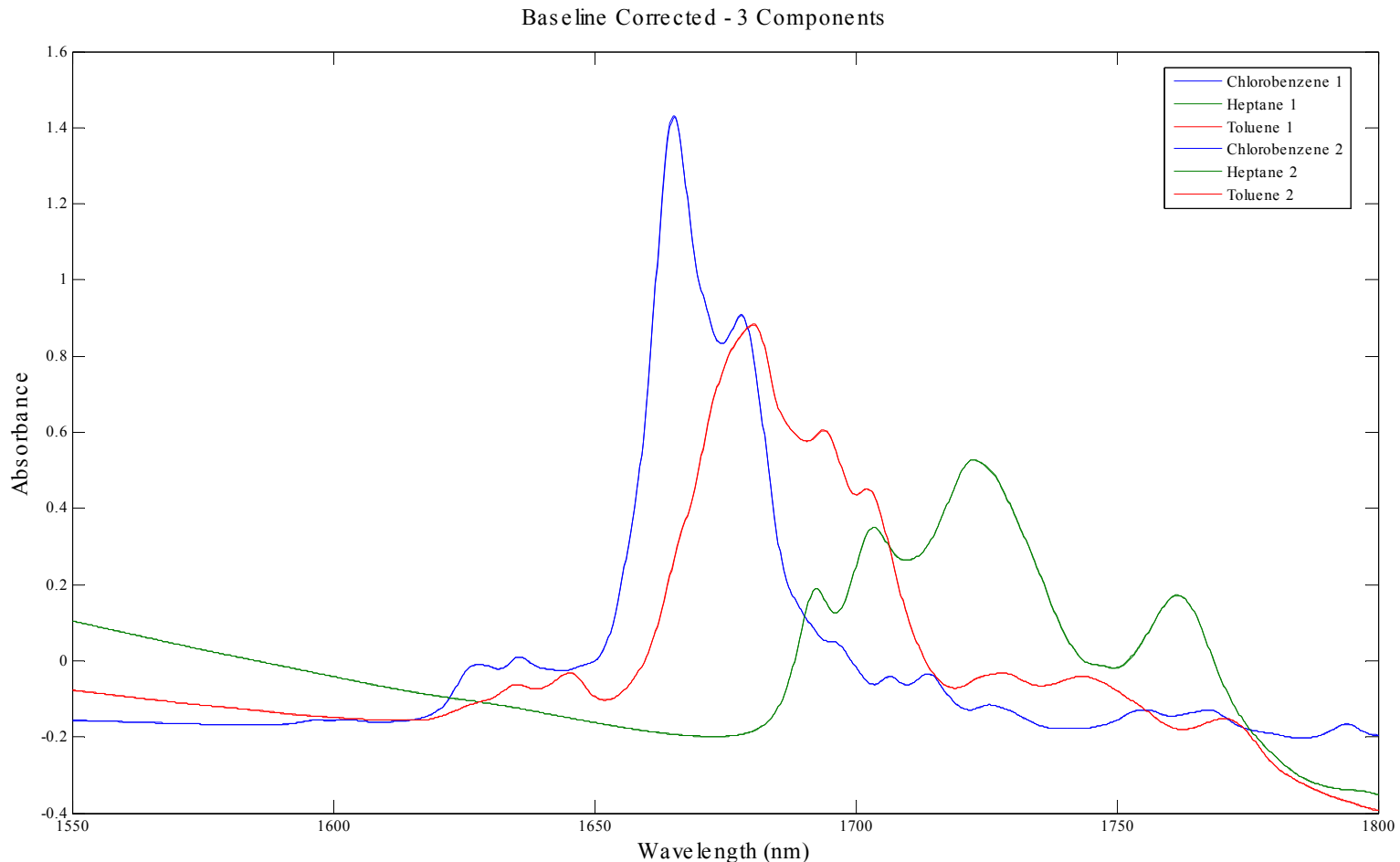
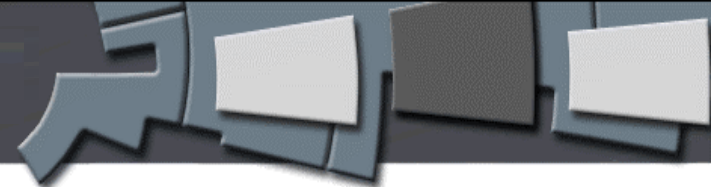
64 scans averaged

Resolution: 2nm

Cal set design based on:  
Wehlburg C. M.; Haaland D. M.; Melgaard D. K, **New Hybrid Algorithm for Transferring Multivariate Quantitative Calibrations of Intra-vendor Near-Infrared Spectrometers,**

[Applied Spectroscopy](#) **1 July 2002, vol. 56, no. 7, pp. 877-886(10)**

# Starting Materials on 2 instruments – Yes, there are really 6 spectra shown

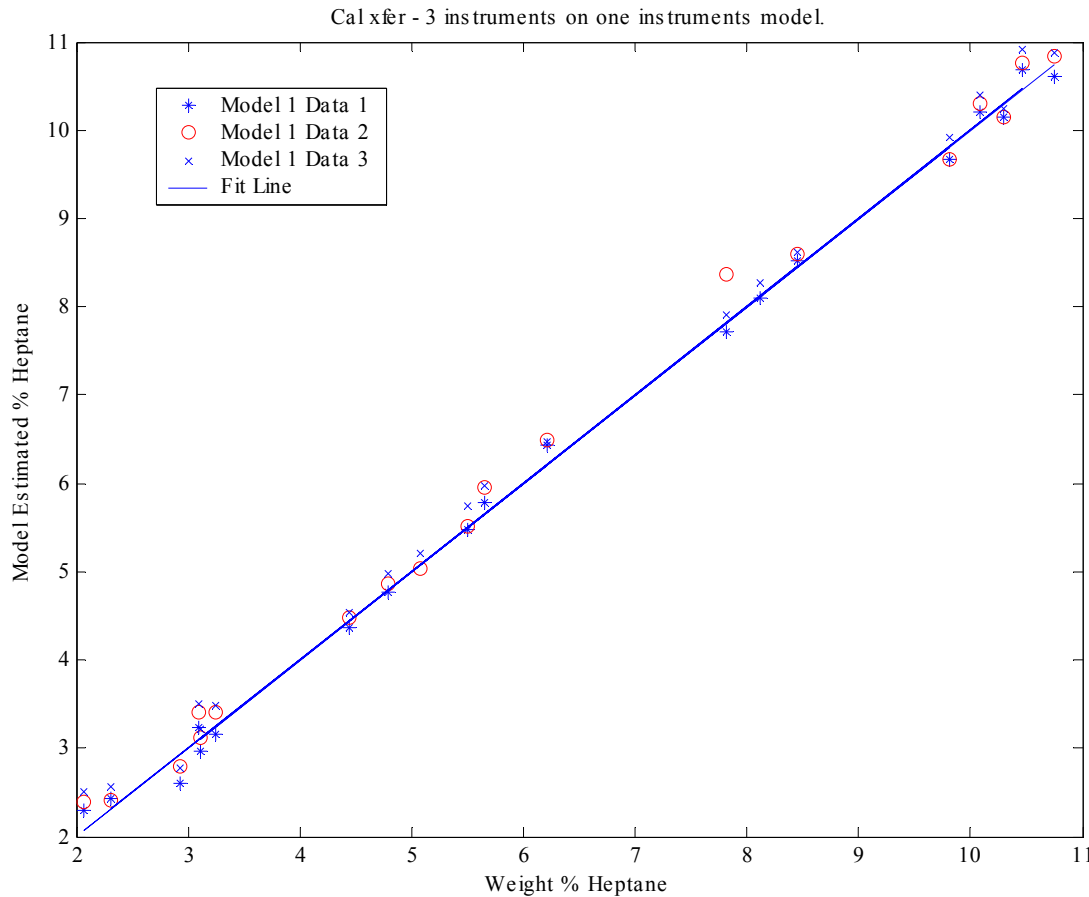


Spectra shown above are “raw” baseline corrected spectra. Only the analyzer standardization function was applied (automatically)

# Transfer study – 3 components

Models for Heptane were developed on each instrument and used to predict the scans from the other instruments.

Raw data pls1 model

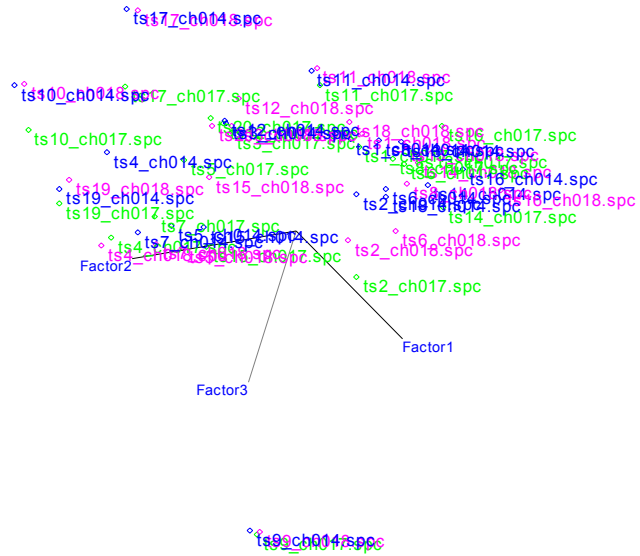
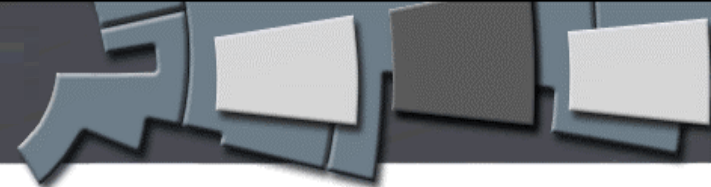


Data	Model	SEP
CH14	CH14	0.2133
CH17	CH14	0.223007
CH18	CH14	0.243117
CH17	CH18	0.16216

Direct Cal  
transfer 3  
Instruments

No Degradation in  
performance across  
instruments!

# 3 Component set – Scores plot

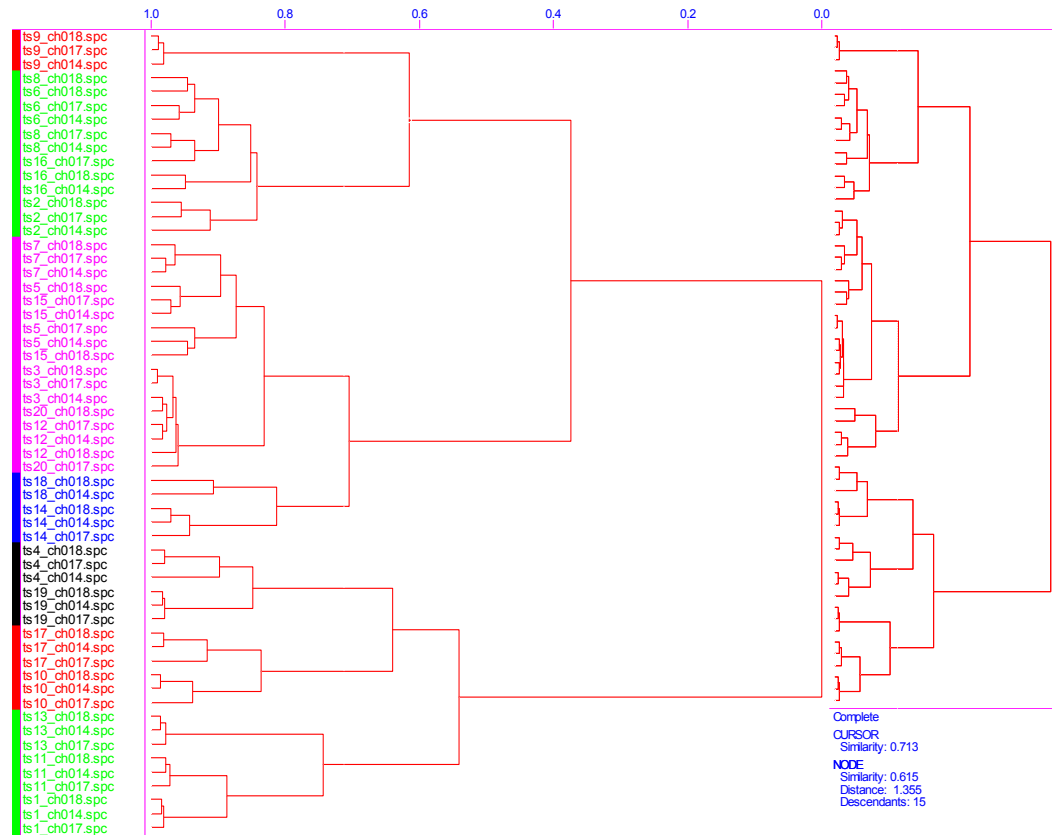


Data from the three instruments  
Instruments appear in different  
colors – No instrument related  
clustering can be seen



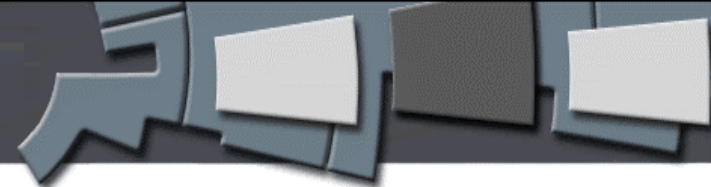
3-Component set on 3 instruments-Note:  
Classes (major branches) correspond to  
concentration not instrument

Dendrogram shows no clustering  
based on instrument



Complete  
CURSOR  
Similarity: 0.713  
NODE  
Similarity: 0.615  
Distance: 1.355  
Descendants: 15

# Calibration transfer – Microspectrometer → Microspectrometer – Generation II



Generation 2 Analyzer

Sys 1 Spectra (20)  
1550-1800nm

1001 pts

PLS model

Generation 2 Analyzer

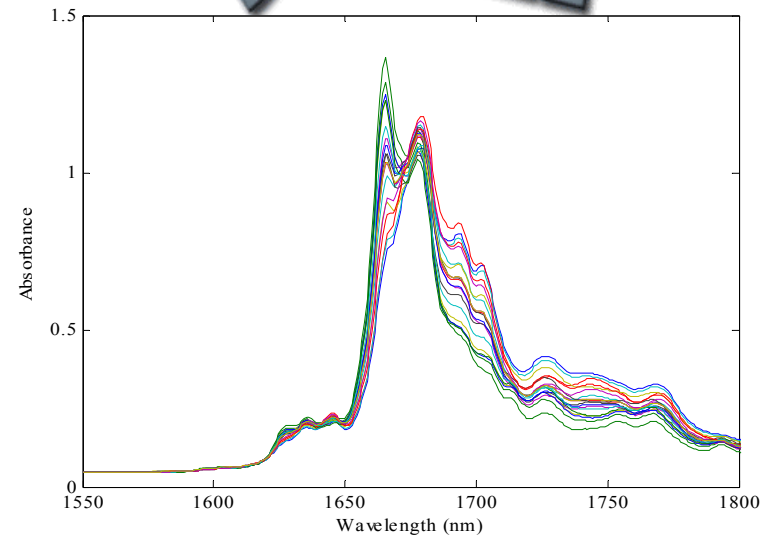
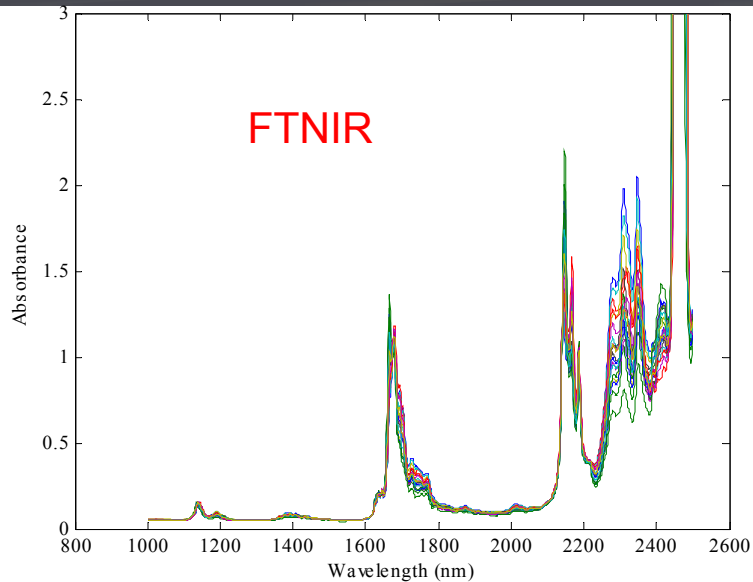
Predict  
Sys 2 Spectra (20)

1001 pts

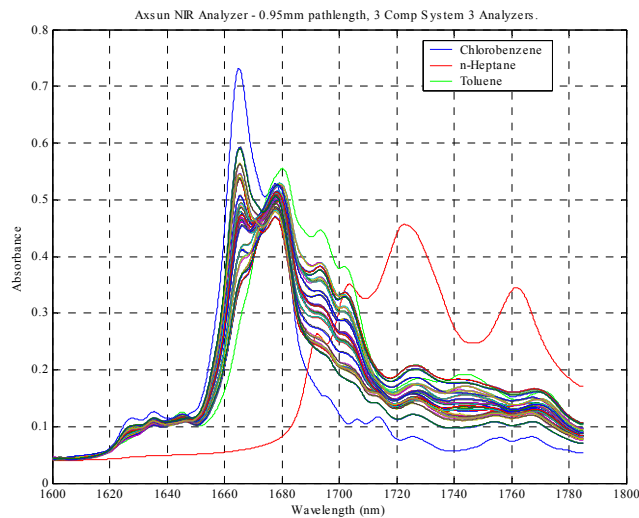
- Heptane
    - Self Predicted model - 3 Factors, 0.10 SEP
    - Predict System 2 0.05 SEP
  - Chlorobenzene
    - Self Predicted model -3 Factor 0.68 SEP
    - Predict System 2 0.43 SEP
  - Toluene
    - Self Predicted model -3 Factor 0.61 SEP
    - Predict System 2 0.49 SEP
- Small Bias obtained for each property.

Data Collection  
2 MM pathlength  
2 nm res.  
64 scans avg.  
7 seconds

# Calibration Transfer from FTNIR analyzer to MEMS system

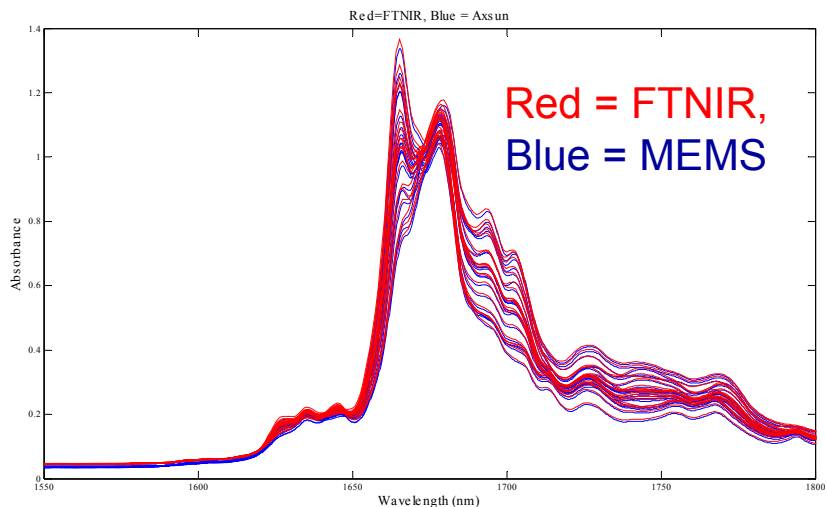
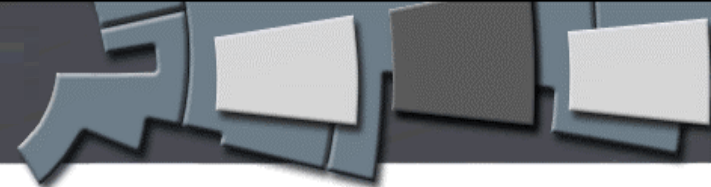


FTNIR – Trimmed to MEMS based wavelength range



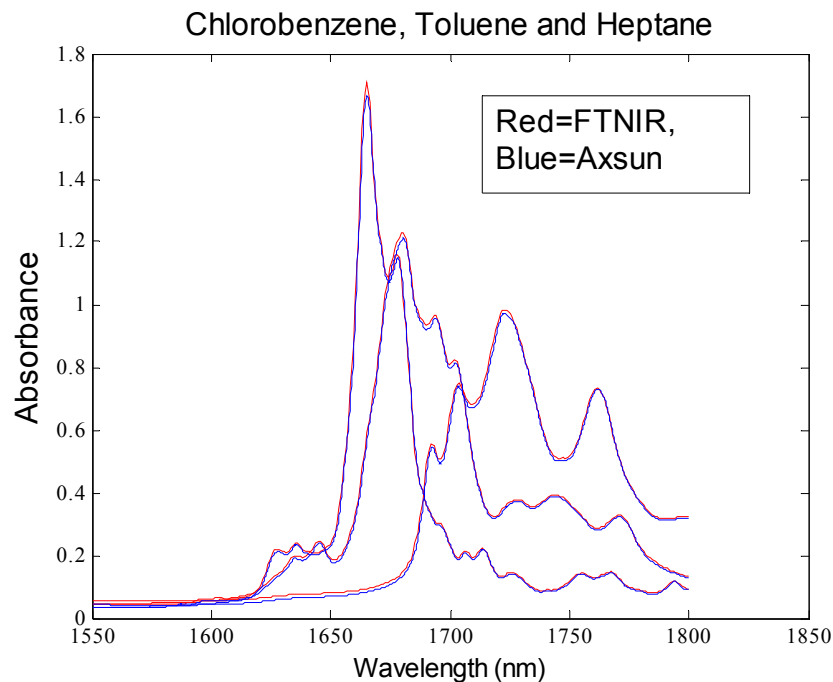
MEMS  
Based  
Instrument

# Calibration Set - FTNIR and Microspectrometer

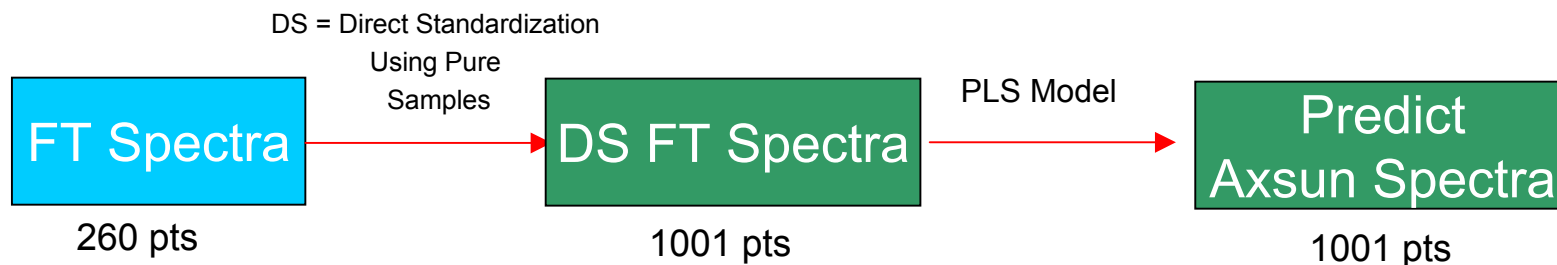
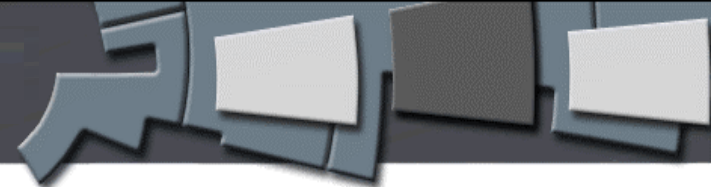


Without doing any transformations, the MEMS based system looks pretty close to the FTNIR system!

Starting Materials  
(Pure)



# Calibration transfer – FT → Microspectrometer



Microspectrometer  
data cross validation

- Heptane
  - FT Transformed model - 4 Factors, 0.14 SEP
  - Predict MEMS NIR – 0.18 SEP
- Chlorobenzene
  - FT Transformed model -1 Factor 0.82 SEP
  - Predict MEMS NIR – 1.2 SEP
- Toluene
  - FT Transformed model -3 Factor 0.67 SEP
  - Predict MEMS NIR – 1.1 SEP
  - Significant Bias obtained for each property
  - Performance Degraded, but may be adequate for some applications

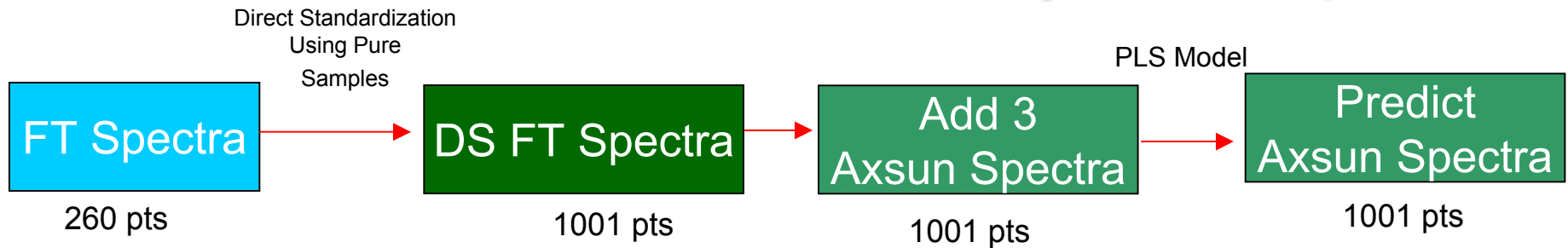
•4 Factors, 0.12 SEP

•2 Factors 0.84%

•4 Factors 0.64%

Direct  
Standardization  
Algorithm from  
Eigenvector  
Research

# FT to Microspectrometer transfer – with inoculation of 3 samples



Microspectrometer  
data cross validation

•4 Factors, 0.12 SEP

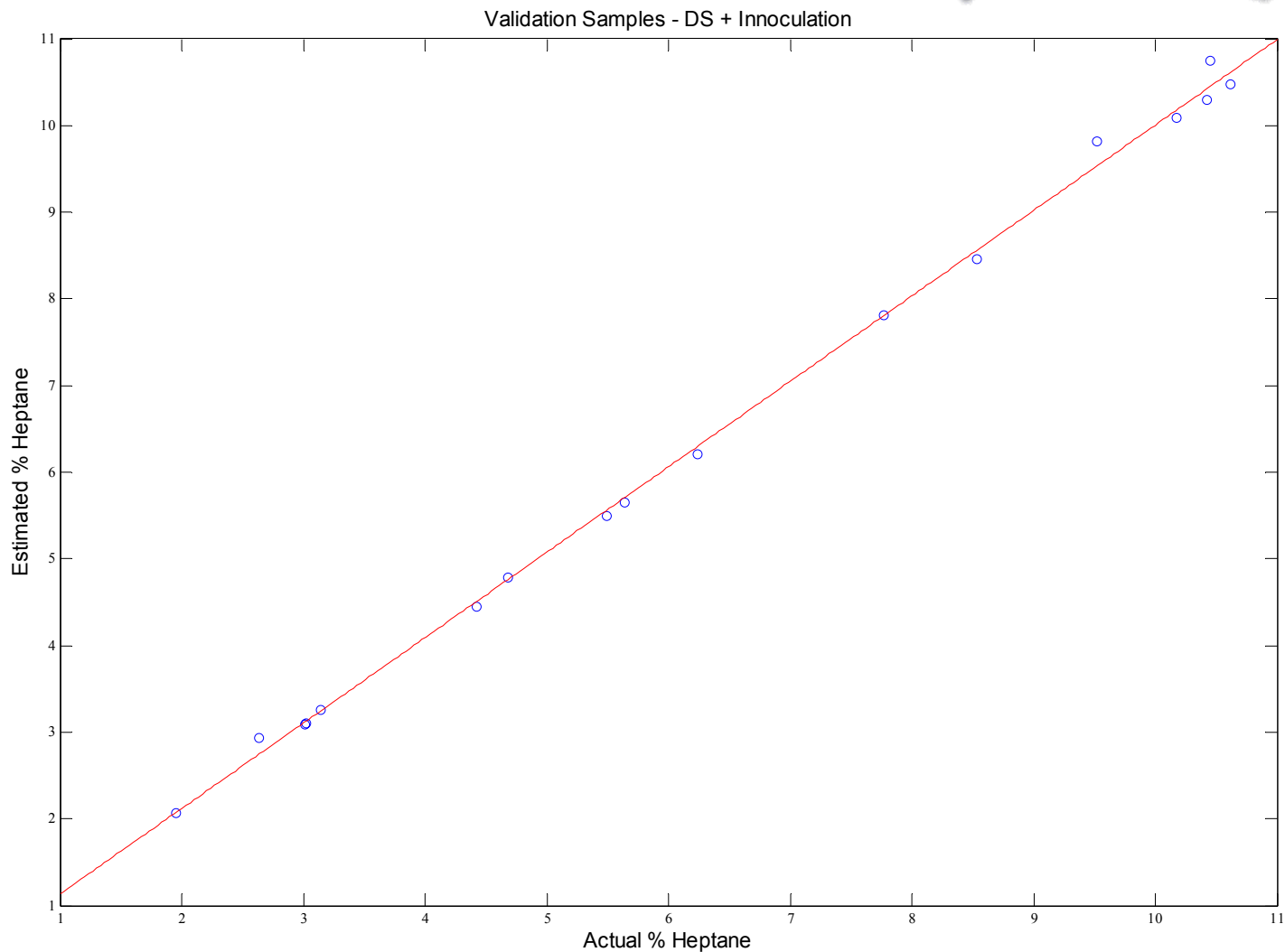
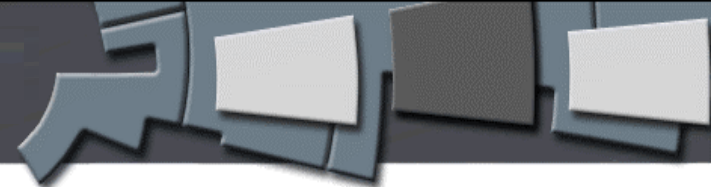
•  
2 Factors 0.84%

•4 Factors 0.64%

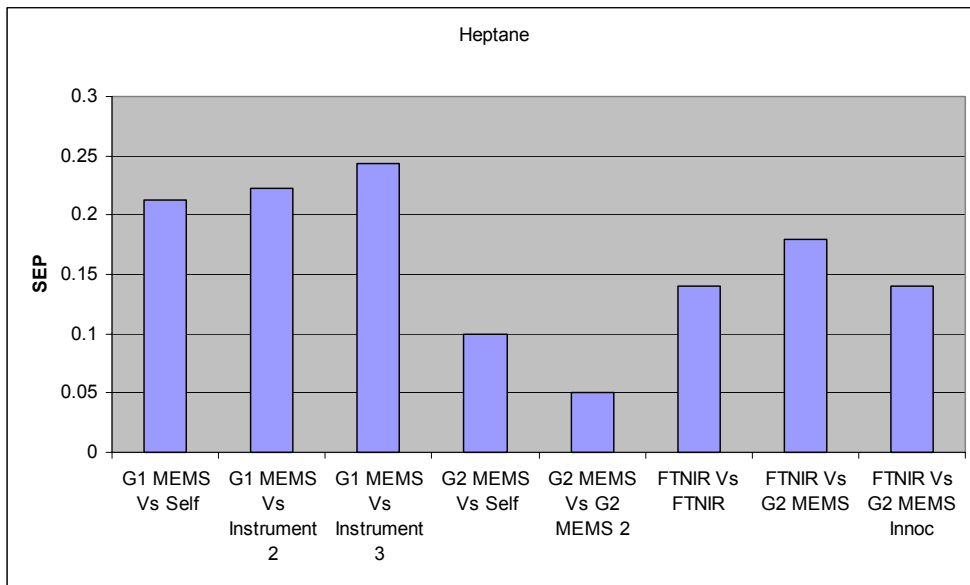
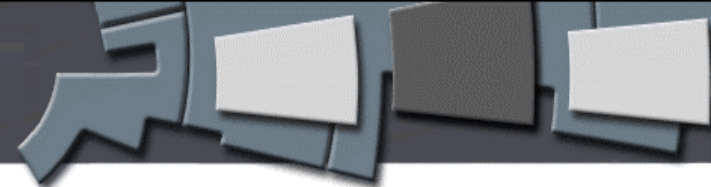
- Heptane
  - FT Transformed model - 4 Factors, 0.13 SEP
  - Predict MEMS NIR – 0.14 SEP (Bias 0.058)
- Chlorobenzene
  - FT Transformed model -2 Factor 0.81 SEP
  - Predict MEMS NIR – 0.72 SEP (Bias 0.7)
- Toluene
  - FT Transformed model -3 Factor 0.77 SEP
  - Predict MEMS NIR – 0.79 SEP (Bias 0.8)

Performance (data from FTNIR + 3 MEMS spectra used to develop model and predict MEMS spectra) approximately matches original performance on MEMS based system (cross validation)!

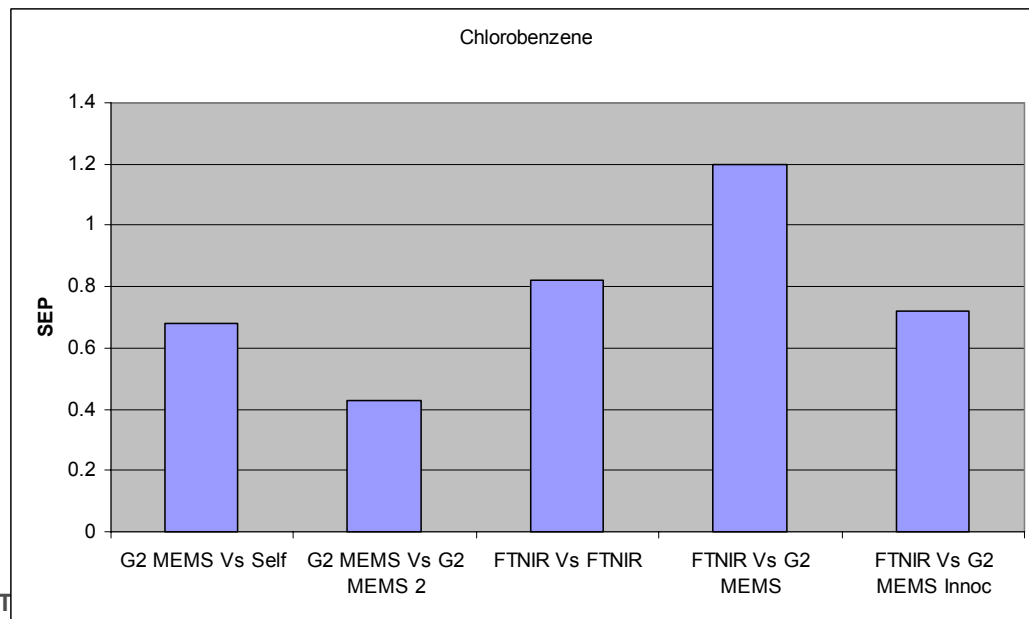
# FT to Microspectrometer transfer – with inoculation of 3 samples



# Transfer Summary



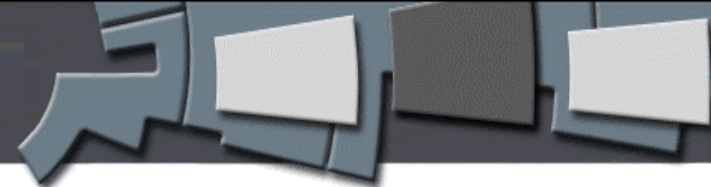
Standard Error of Prediction on Y Axis.  
For Data on one instrument vs itself, the SECV is plotted



# Summary

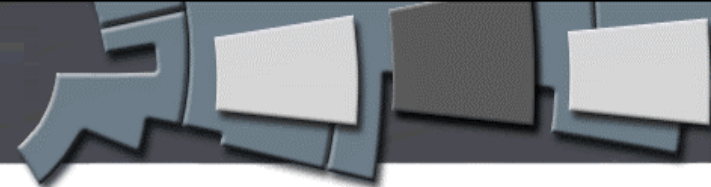
- Success at transferring data between 3 microspectrometers has been demonstrated
  - Direct transfer performed, no instrument/transfer function applied
- Success at transferring data between 2 generation II microspectrometers has been demonstrated
  - Direct transfer performed, no instrument/transfer function applied
- A level of success at transferring FTNIR models to the microspectrometer has been demonstrated – More work in process
  - Optimize FT → Microspectrometer transformation
  - Different transfer algorithms, standards and settings/tolerances

# Conclusions Continued



- Degree of successful transfer is dependant on model complexity
- Degree of effort to successfully transfer models is also dependant on acceptable transfer error tolerances
- Analyzers should be built to exacting (and known and repeatable) specifications
- Temperature control of key optical components minimizes/eliminates thermal artifacts, increasing chance for successful transfer
  - Sample should be treated the same for the parent and child systems
    - Lab sampling and analysis should be consistent or understood
    - Sample temperature – must be evaluated
    - Sample pathlength must be controlled or compensated for
    - Sample conditioning

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