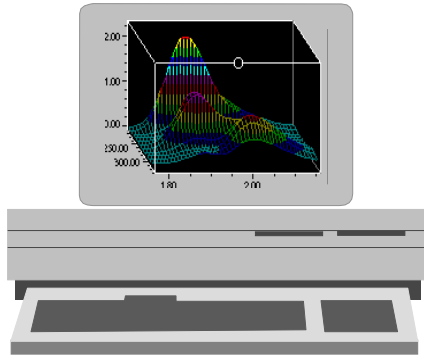
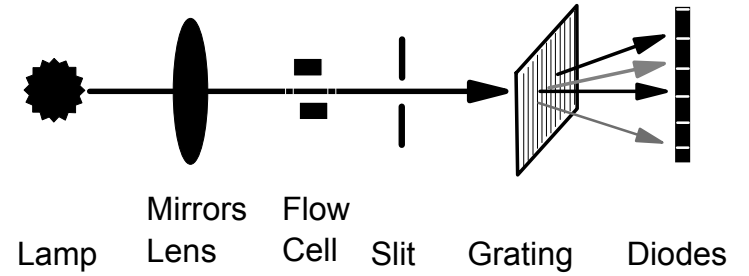


# Photodiode Array

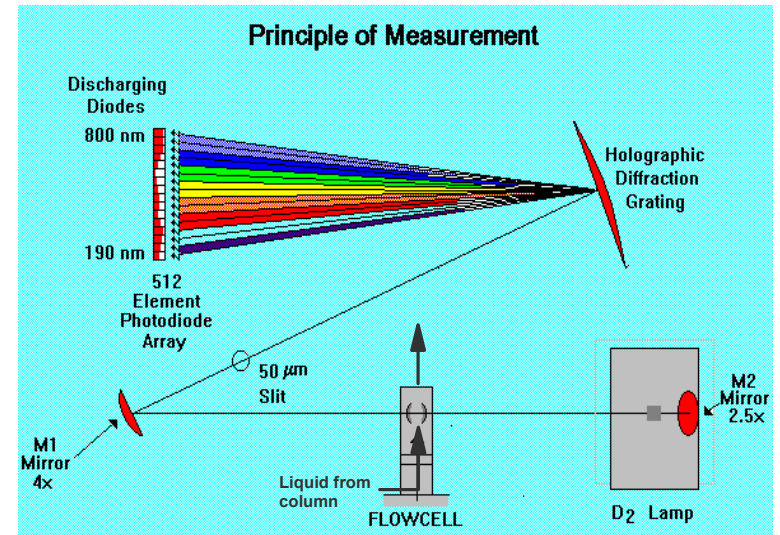
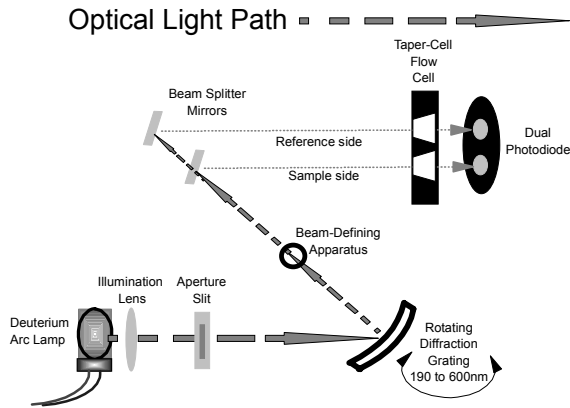


Advanced Detection Technologies  
for Compound Identification

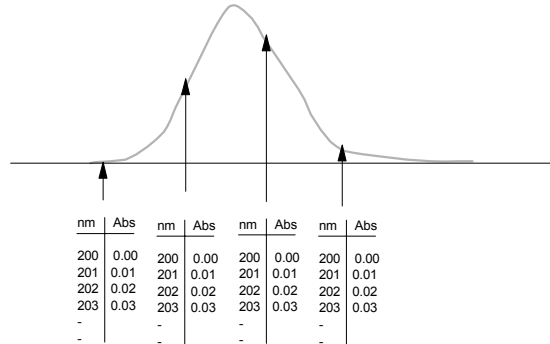
# PDA Optics Diagram



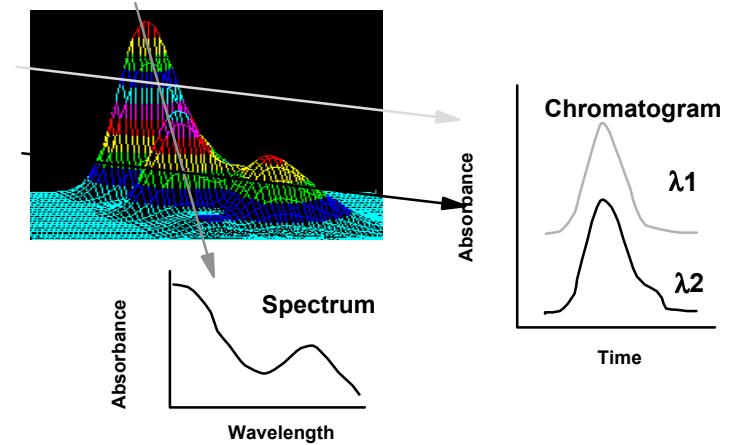
# 486 Detector Optical Bench



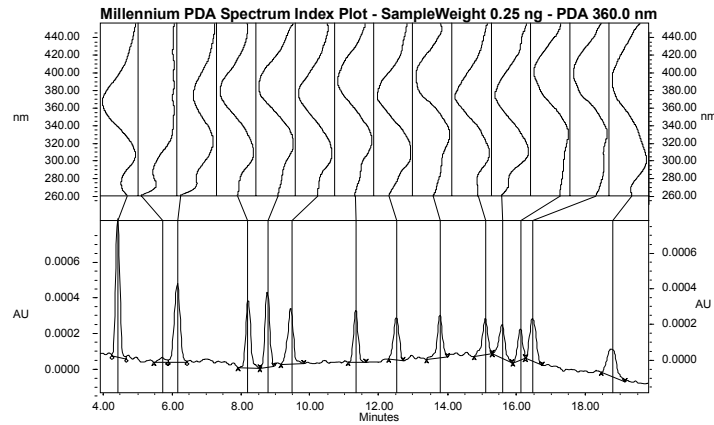
## The Data is 3D



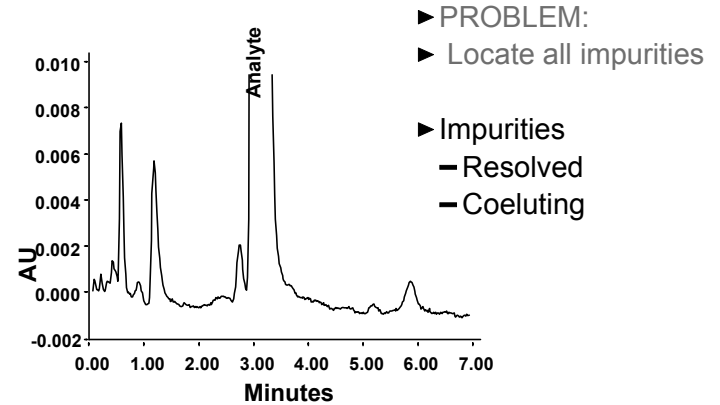
## Extraction of 3D Data



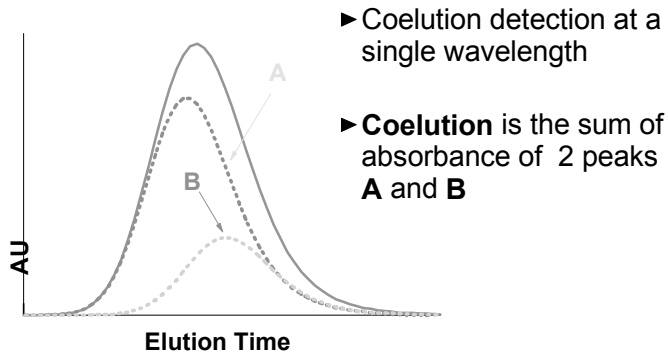
## 996 PDA Spectrum Index Plot DNPH Derivatives 0.25 ng Each Peak



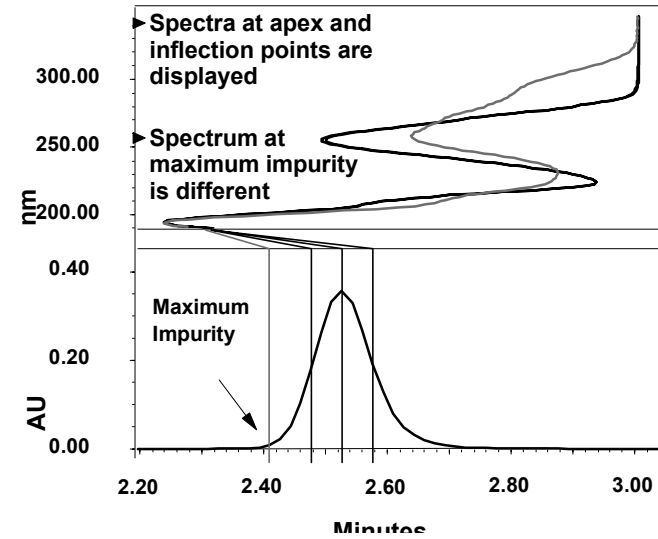
## Major Peak and Minor Peaks



## Coelution of 2 Peaks

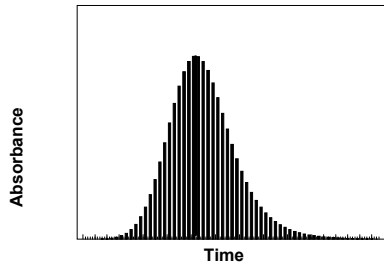


## Spectrum Index Plot



Good quality spectral information is important for:

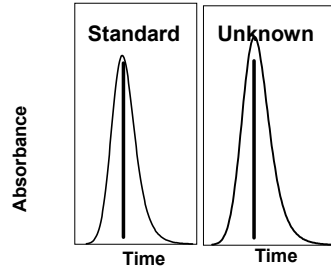
Purity verification



- Peak Purity analyzes all spectra (minimum 15) within a peak
- Apex spectrum is the reference spectrum

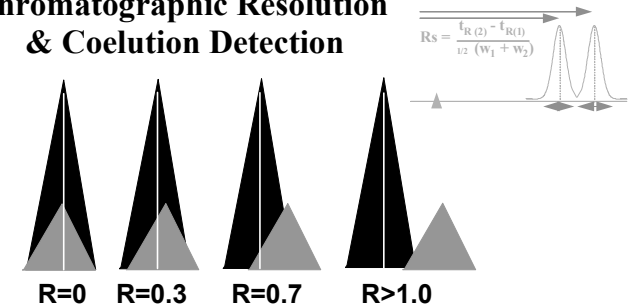
$$\sin \theta_j = \frac{\sqrt{\sum_{i=1}^N (B_{ij} - s_j A_i)^2}}{\sqrt{\sum_{i=1}^N B_{ij}^2}}$$

Library identification



- Matching compares the unknown apex spectrum of the peak with a reference spectrum in a library

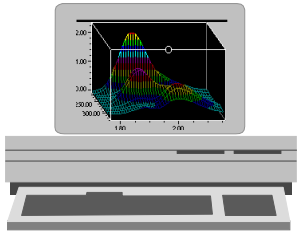
## Chromatographic Resolution & Coelution Detection



- R=0 Purity Angle not effective; Match Angle useful
- R=0.3 to R=0.7 Purity & Match Angle useful
- R>0.7 Match Angle not useful

# Photodiode Array Technology

## Spectral Analyses

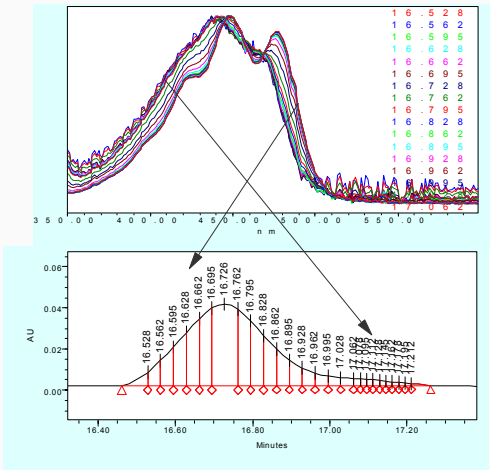


- ▶ Library Matching
  - Compound identification
  - Coelution detection
- ▶ Peak Purity Analysis
  - Peak purity/peak homogeneity
  - Coelution detection

# Importance of Spectral Analyses

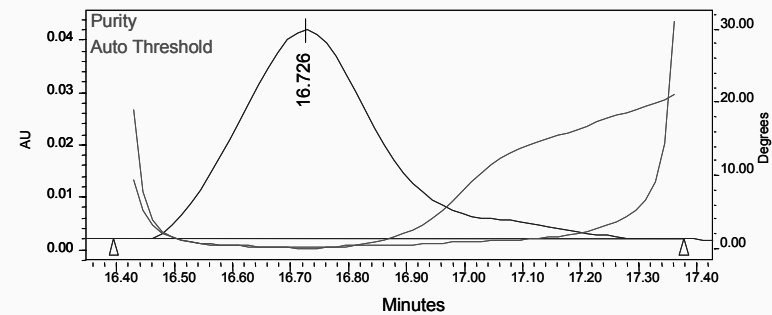
- ▶ Library Matching
  - Compound identification
  - Coelution detection
- ▶ Peak Purity Analysis
  - Peak purity/peak homogeneity
  - Coelution detection

## Spectra Collected from a Peak with Impurity



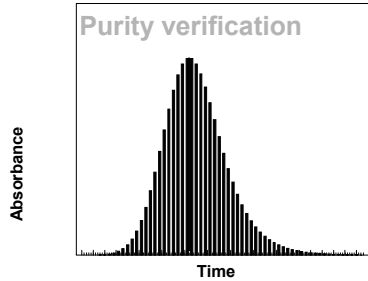
## CAROTENOIDS Purity Plot of Peak 4 - Not Pure

Purity Flag	Maximum Impurity	Purity Threshold	Purity Angle
Yes	17.078	0.404	1.885



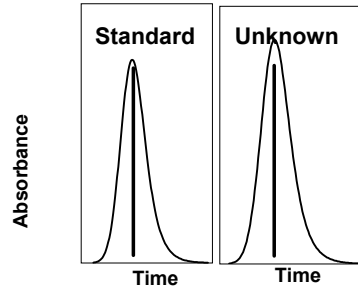
### Comparison between Spectra

$$\sin \theta_j = \frac{\sqrt{\sum_{i=1}^N (B_{ij} - s_j A_i)^2}}{\sqrt{\sum_{i=1}^N B_{ij}^2}}$$



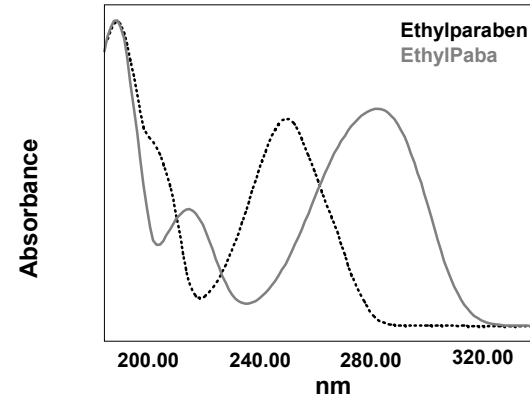
- ▶ Peak Purity analyzes all spectra (minimum 15) within a peak
- ▶ Apex spectrum is the reference spectrum

### Library identification



- ▶ Matching compares the unknown apex spectrum of the peak with a reference spectrum in a library

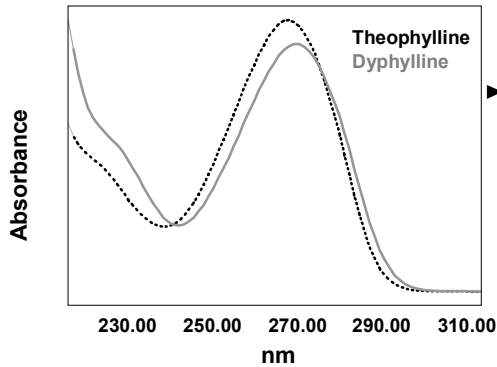
## Spectral Contrast 53 Degrees



- ▶ 53 degrees is a large spectral difference

$$\sin \theta_j = \frac{\sqrt{\sum_{i=1}^N (B_{ij} - s_j A_i)^2}}{\sqrt{\sum_{i=1}^N B_{ij}^2}}$$

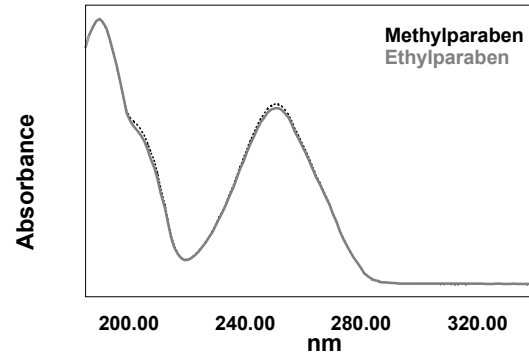
## Spectral Contrast 10 Degrees



- ▶ Similar spectra for structurally related compounds

$$\sin \theta_j = \frac{\sqrt{\sum_{i=1}^N (B_{ij} - s_j A_i)^2}}{\sqrt{\sum_{i=1}^N B_{ij}^2}}$$

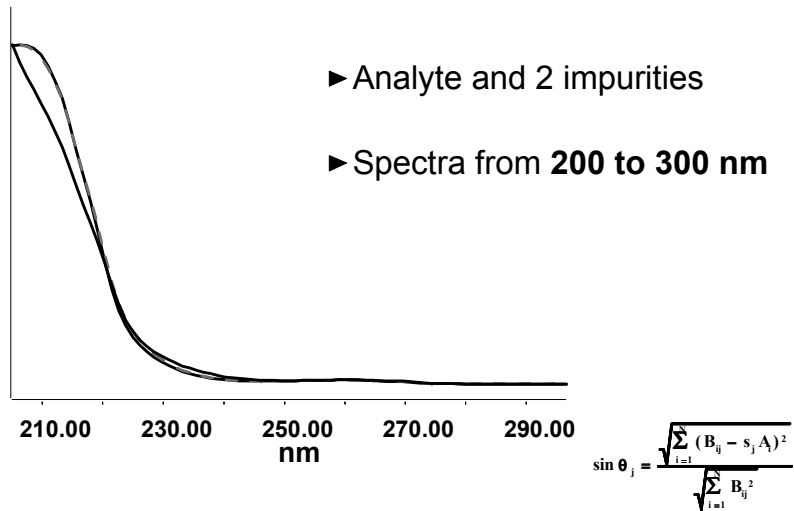
## Spectral Contrast 0.5 Degrees



- ▶ Very similar spectra, CH2 difference
- ▶ Spectral Contrast can differentiate these spectra

$$\sin \theta_j = \frac{\sqrt{\sum_{i=1}^N (B_{ij} - s_j A_i)^2}}{\sqrt{\sum_{i=1}^N B_{ij}^2}}$$

## Very Similar Spectra

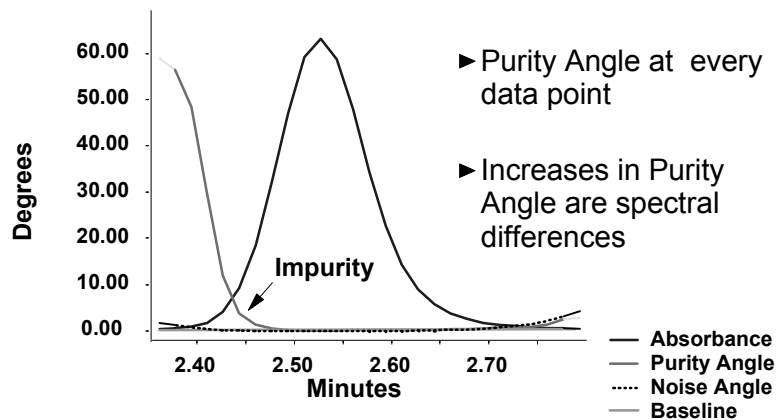


## Interpretation of Peak Purity Plots

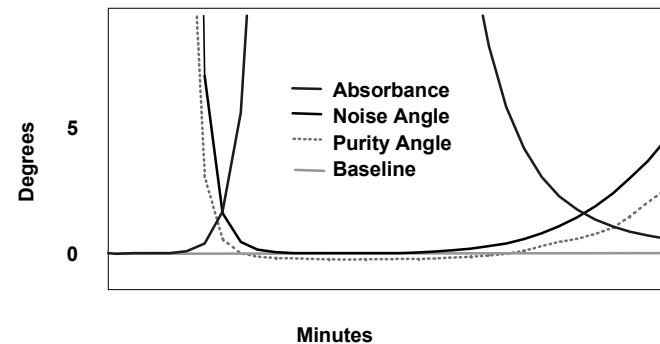
Peak Purity Plots can indicate

- Peak homogeneity
- Spectral homogeneity
- Coeluting impurities
- Spectral differences due to artifacts

## Peak Purity Plot

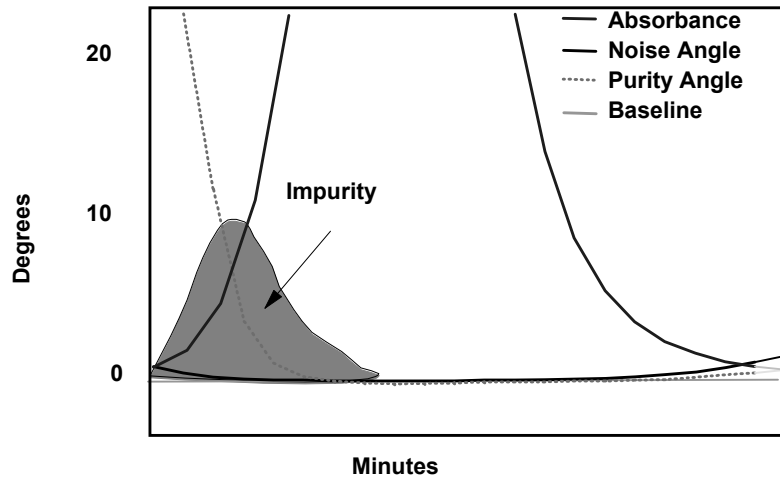


## Purity Plot Chemically Pure Compound



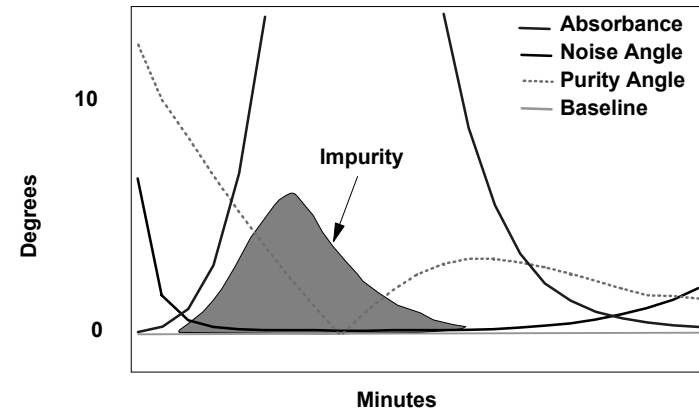
- Purity Angle less than Noise Angle, ideal situation

### Purity Plot: Mixture of 2 Compounds



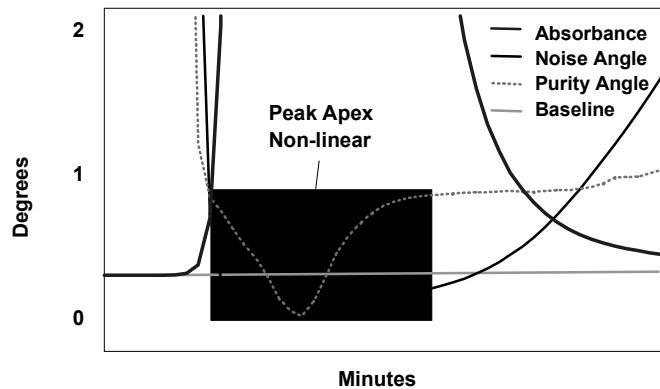
- ▶ Purity Angle is greater than Noise Angle - coelution on the front of the peak

### Purity Plot: Mixture of 2 Compounds



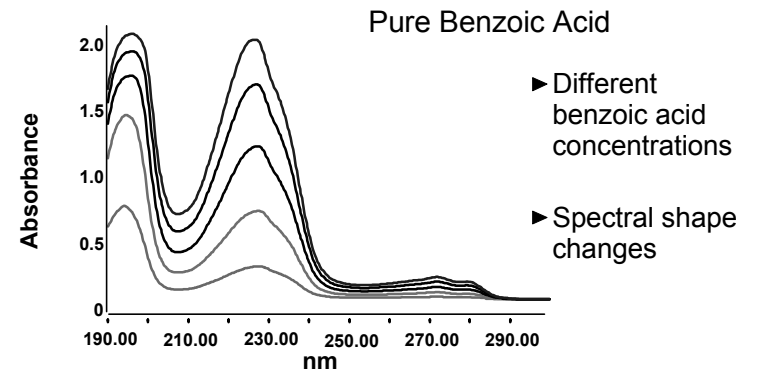
- ▶ Purity Angle is greater than Noise Angle - coelution near the peak apex

### Purity Plot Chemically Pure Compound



- ▶ Purity Angle greater than Noise Angle
- ▶ Absorbance **out of linear range** at some wavelengths

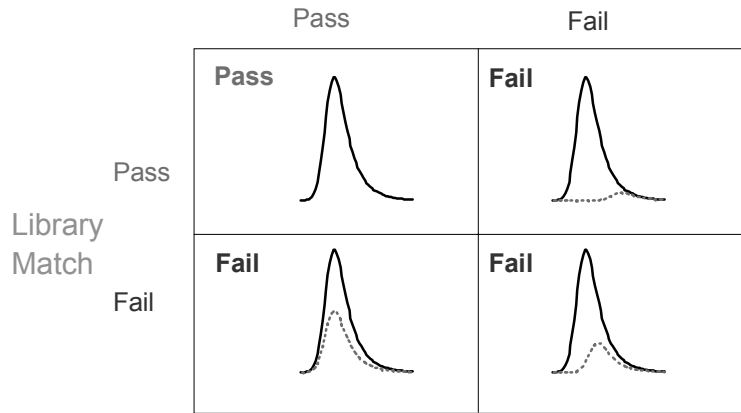
### Effect of Concentration on Spectra



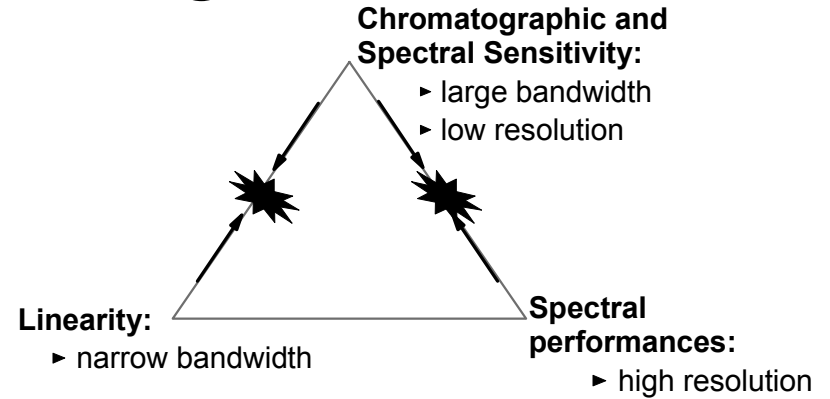
- ▶ Different benzoic acid concentrations
- ▶ Spectral shape changes

# Compound Confirmation

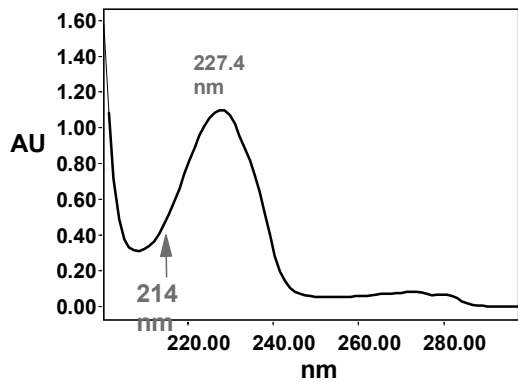
Peak Homogeneity



# Conflicts in Instrument design

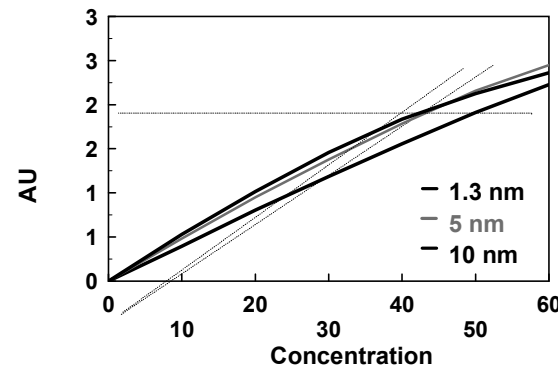


# Benzoic Acid Spectrum



- ▶ 214 nm is on a spectral slope
- ▶ Linearity requires good optical resolution

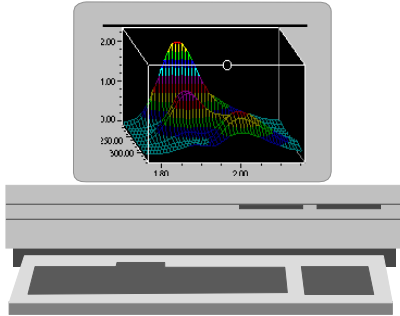
# Effects of Optical Resolution on Linearity



- ▶ 1.3 nm resolution is more linear than 5 or 10 nm
- ▶ Wide bandwidth is non-linear

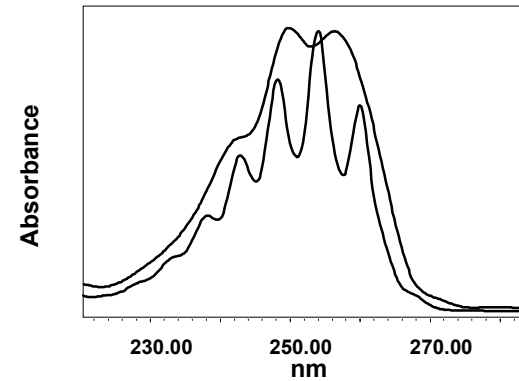
# Photodiode Array Technology

## Optical Performance



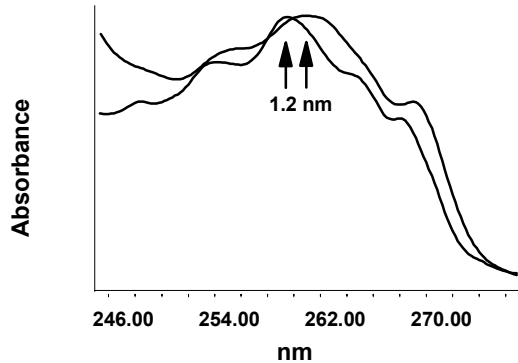
Linearity  
Optical Resolution  
Sensitivity

## Spectral Resolution - 1.2 nm vs. 3.6 nm



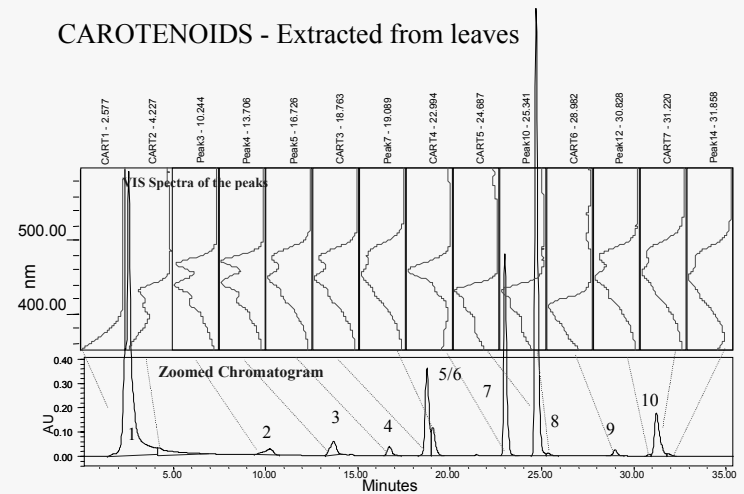
- ▶ Benzene spectra
- ▶ Less resolution at 3.6 nm vs. 1.2 nm
- ▶ UV maxima shifted

## Spectral Fine Structure

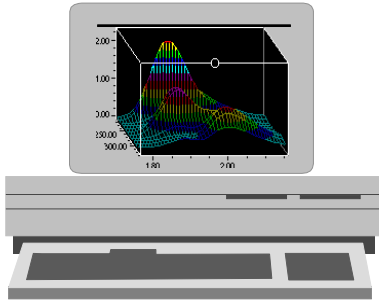


- ▶ Analyte and one impurity spectra from 245 to 275 nm
- ▶ 1.2 nm resolution

## CAROTENOIDS - Extracted from leaves

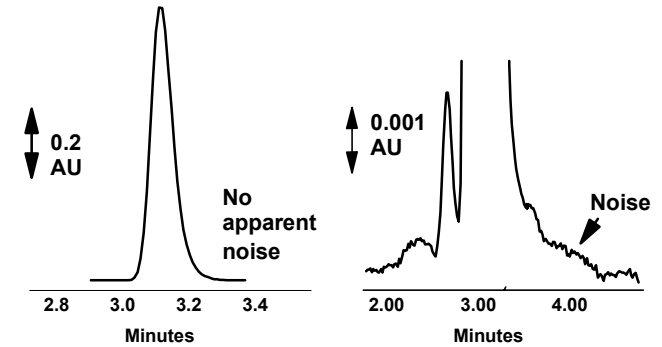


# Photodiode Array Technology Optical Performance

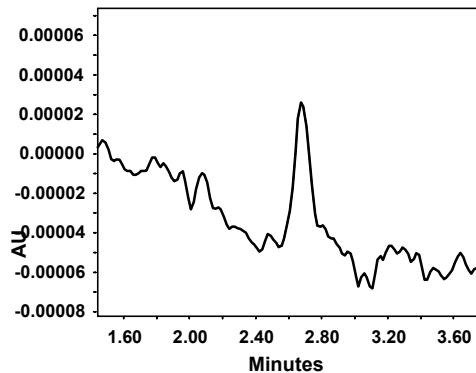


Linearity  
Optical Resolution  
Sensitivity

## Chromatographic Sensitivity Signal-to-Noise Ratio



## High Sensitivity Chromatogram



► **Peak height =  
0.00007 AU  
257 nm  
1 sec filter**

## Benefits of Good Optical Resolution

- **Peak confirmation**
  - Confidence in compound identification
  - Confidence in peak homogeneity with good peak purity analysis
- **Good detector linearity**
  - Quantitation at high and low concentrations
  - Spectral analyses
  - Identification of major and minor compounds