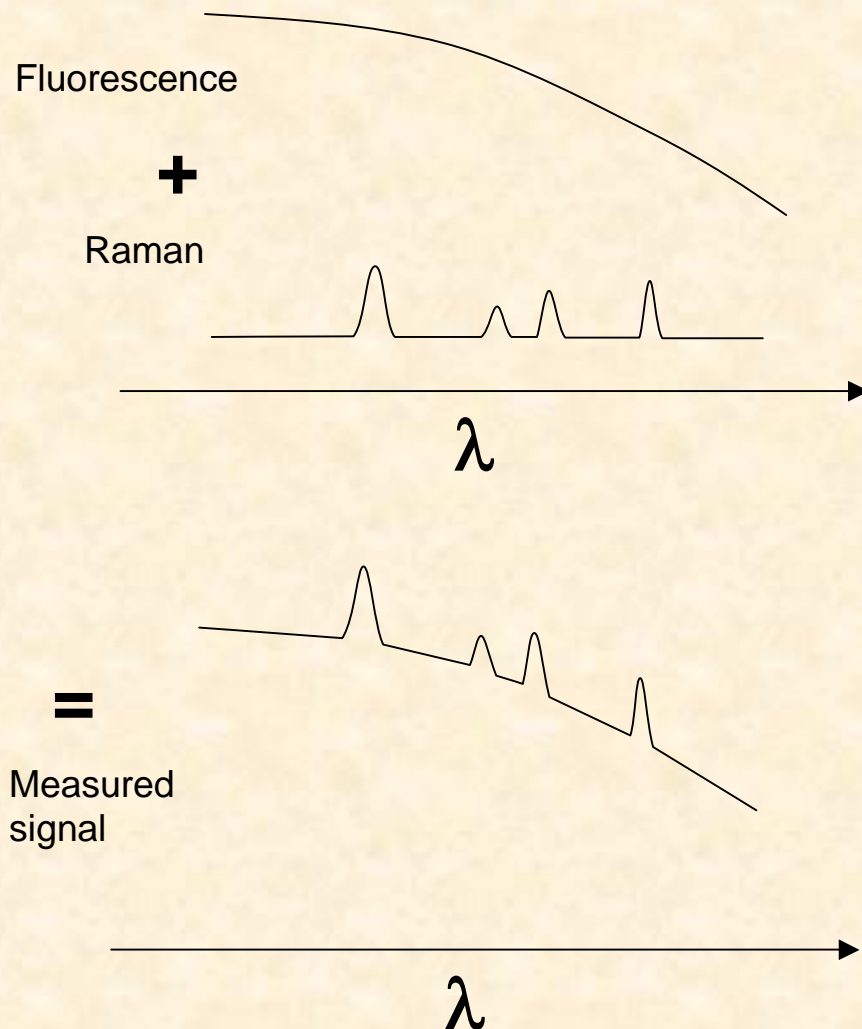


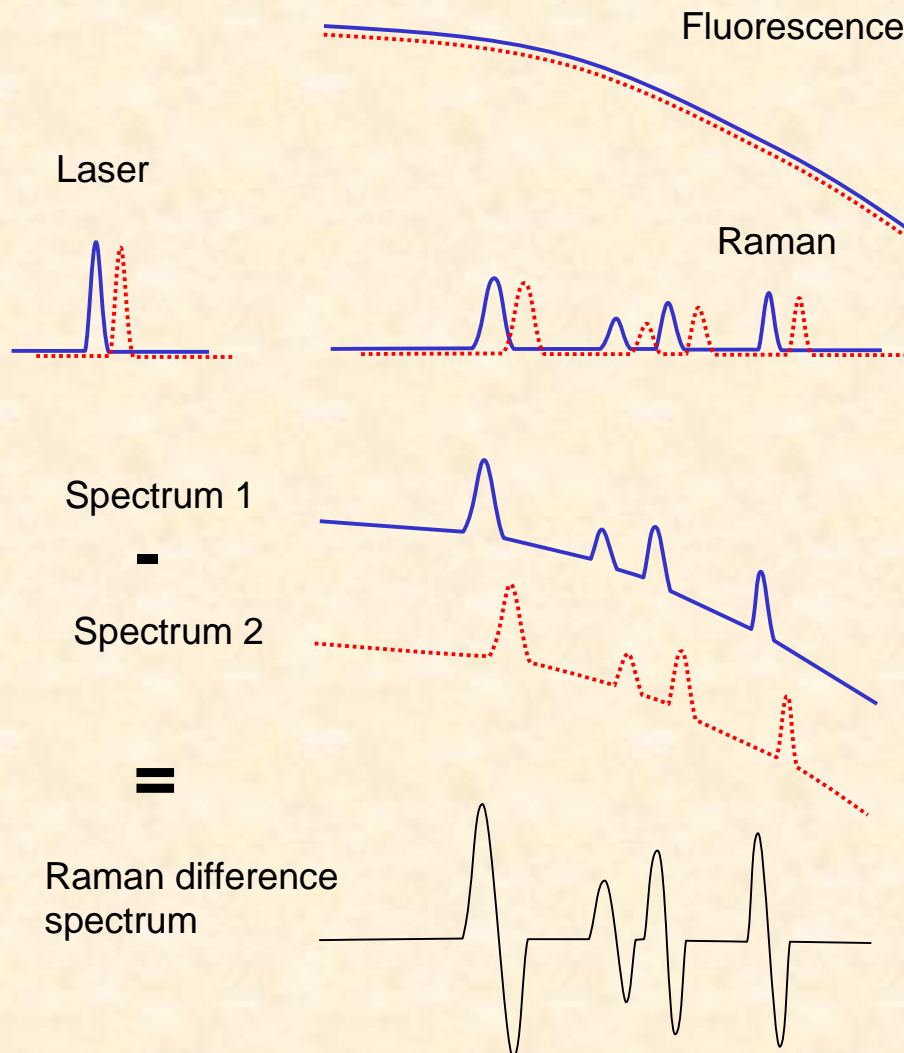
# Review of the SERDS method

# Fluorescence is a problem for Raman measurements



- ❑ Fluorescence often dominates the signal in Raman measurements of real-world samples
- ❑ Presence of the fluorescence complicates Raman measurements and makes them inaccurate or even impossible
- ❑ Quantitative Raman measurements are particularly challenging in presence of the fluorescence
- ❑ Sources of fluorescence are often the contaminants or other minor constituents in the sample
- ❑ Fluorescence often arises in materials as they age (e.g. gasoline, explosives etc.)

# General description of SERDS



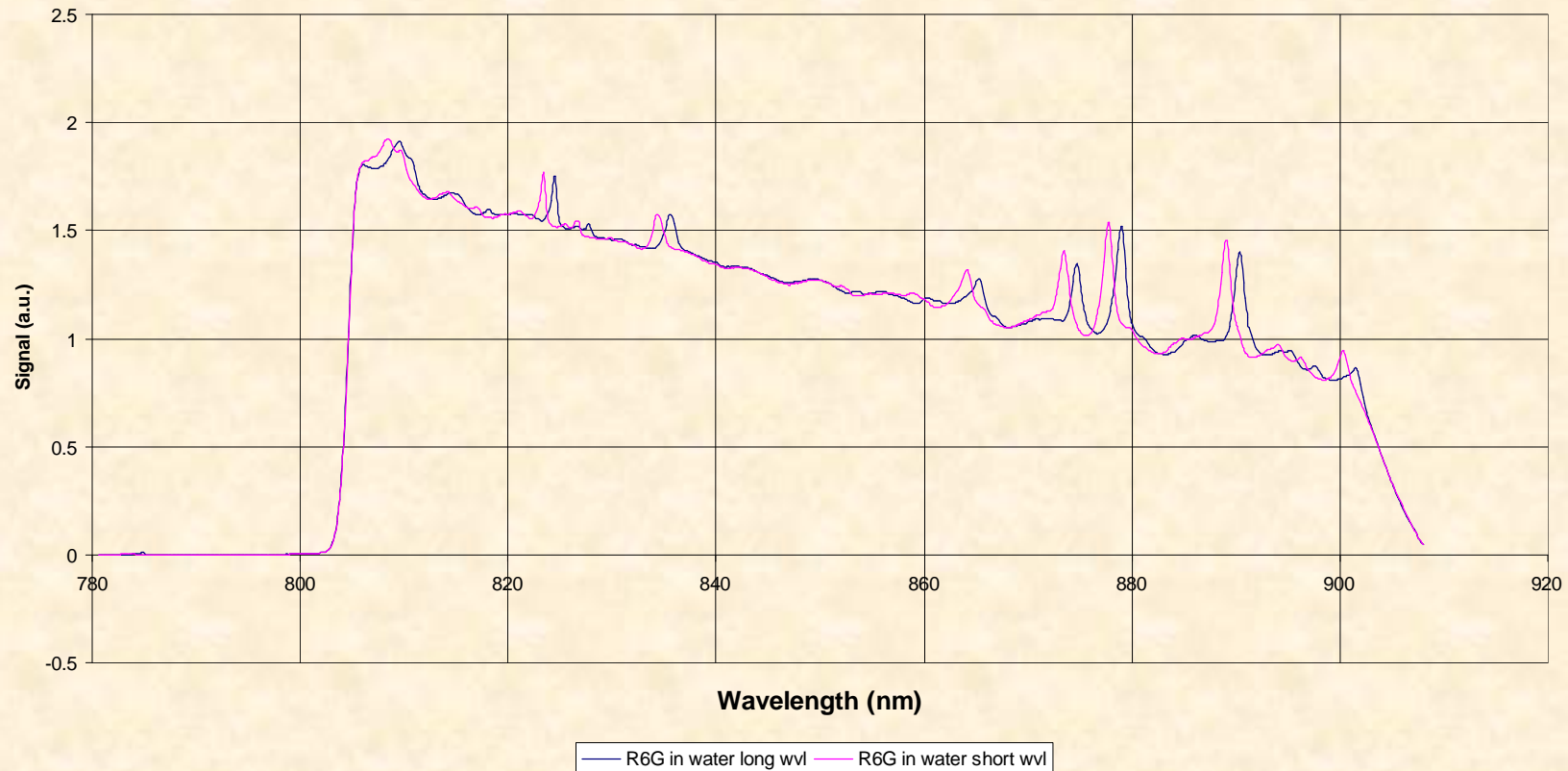
- Both fluorescence and the Raman signal are proportionate to the power of the excitation laser
- Fluorescence spectrum is independent of the wavelength of the excitation laser
- Raman spectrum is shifted from the excitation laser by the frequency of the Stokes shift



- If two spectra are collected in identical conditions using two lasers with slightly different wavelength the fluorescence contribution can be accurately subtracted

# Example: Raman spectra of a strongly fluorescent dye (R6G ) at 785 nm

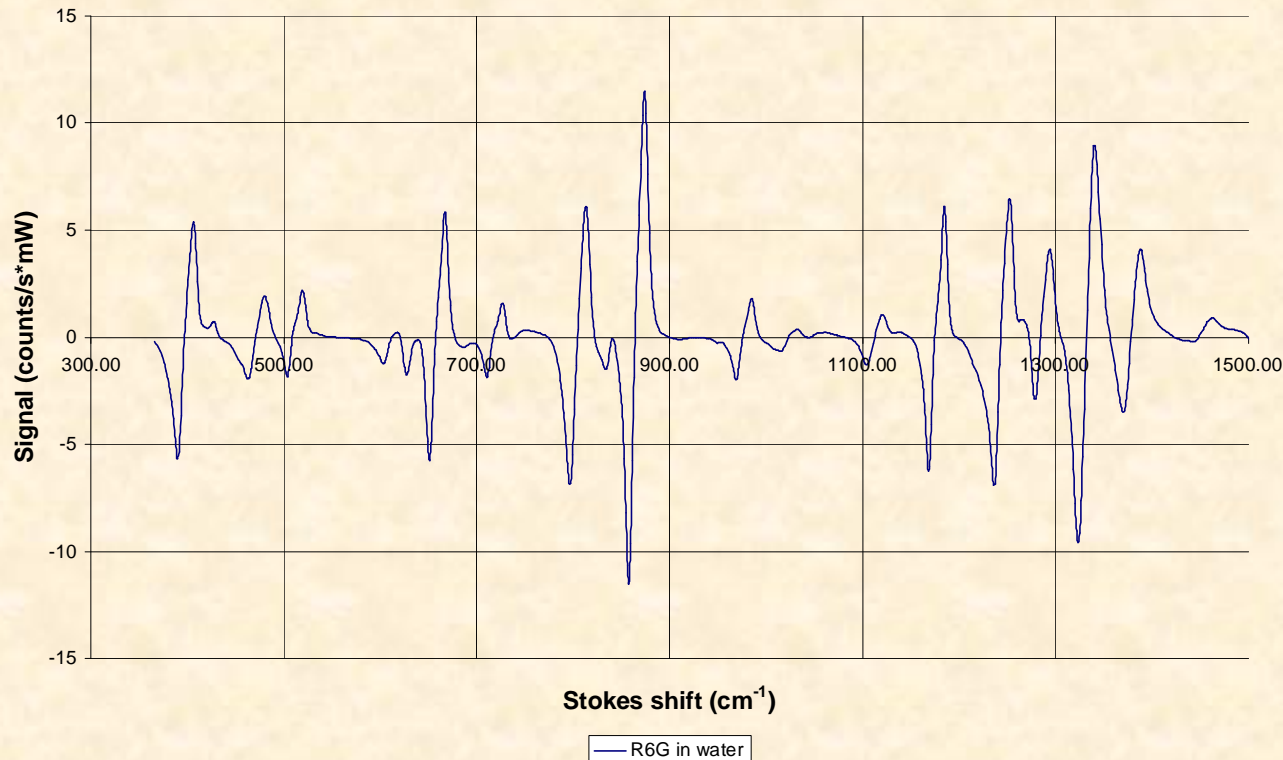
Normalized spectra, not corrected for white light



Numerical filtering is required to analyze spectrum even with this amount of fluorescence

# SERDS spectra: R6G in water

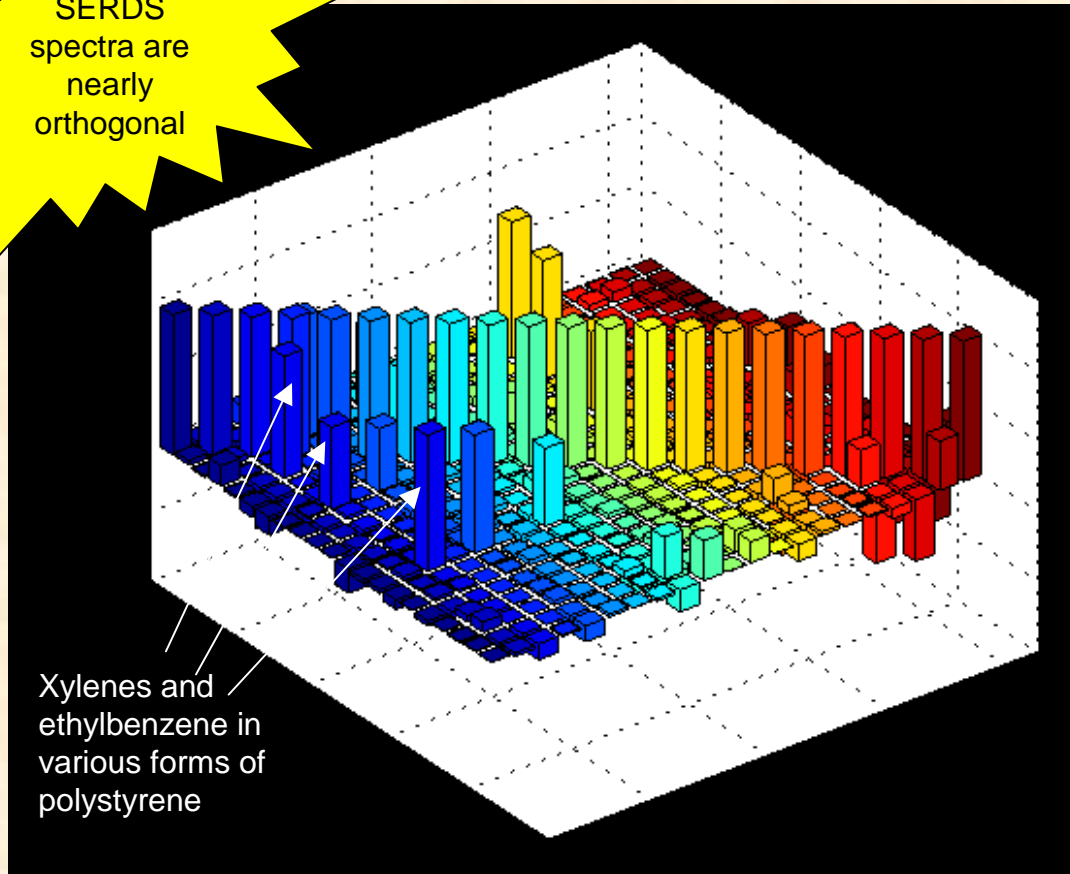
Difference spectra




- SERDS produces very clear and low noise derivative spectrum with no fluorescence remaining
- All required analysis can be performed using derivative spectra (e.g. identification and quantitative Raman)
- No reconstruction of Raman spectrum from its derivative is strictly necessary

# Orthogonality of SERDS spectra

SERDS spectra are nearly orthogonal



- The graph shows dot products of SERDS spectra of various common materials
- Derivative spectra are highly orthogonal to each other
- SERDS spectra orthogonality makes Raman measurements simpler
- The non-orthogonal spectra reflect actual similarity in the molecular structure of the substances (e.g. Styrofoam, transparent polystyrene and xylenes)

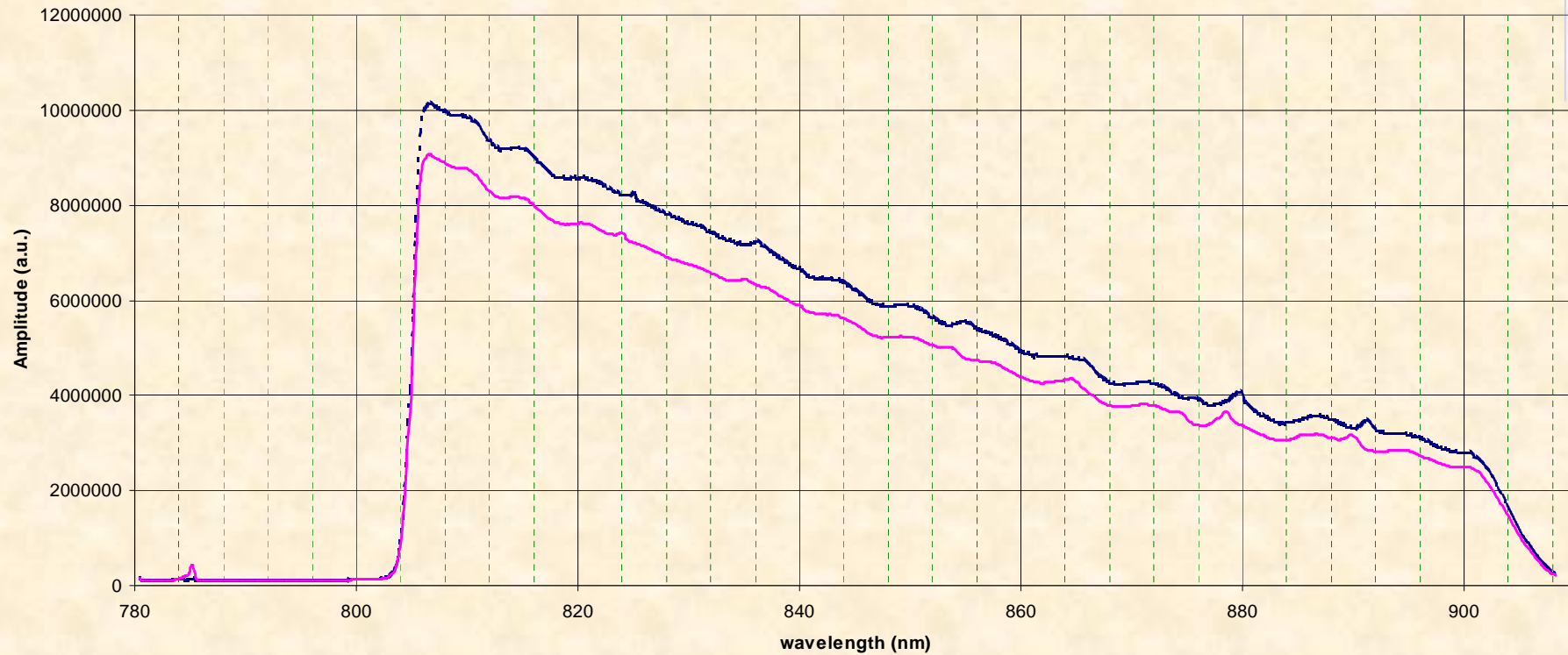


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# Quantitative Raman measurements in presence of strongly fluorescent background

# Raman spectrum of methanol with large amount of R6G dye

Sample 100% methanol & R6G. Uncorrected



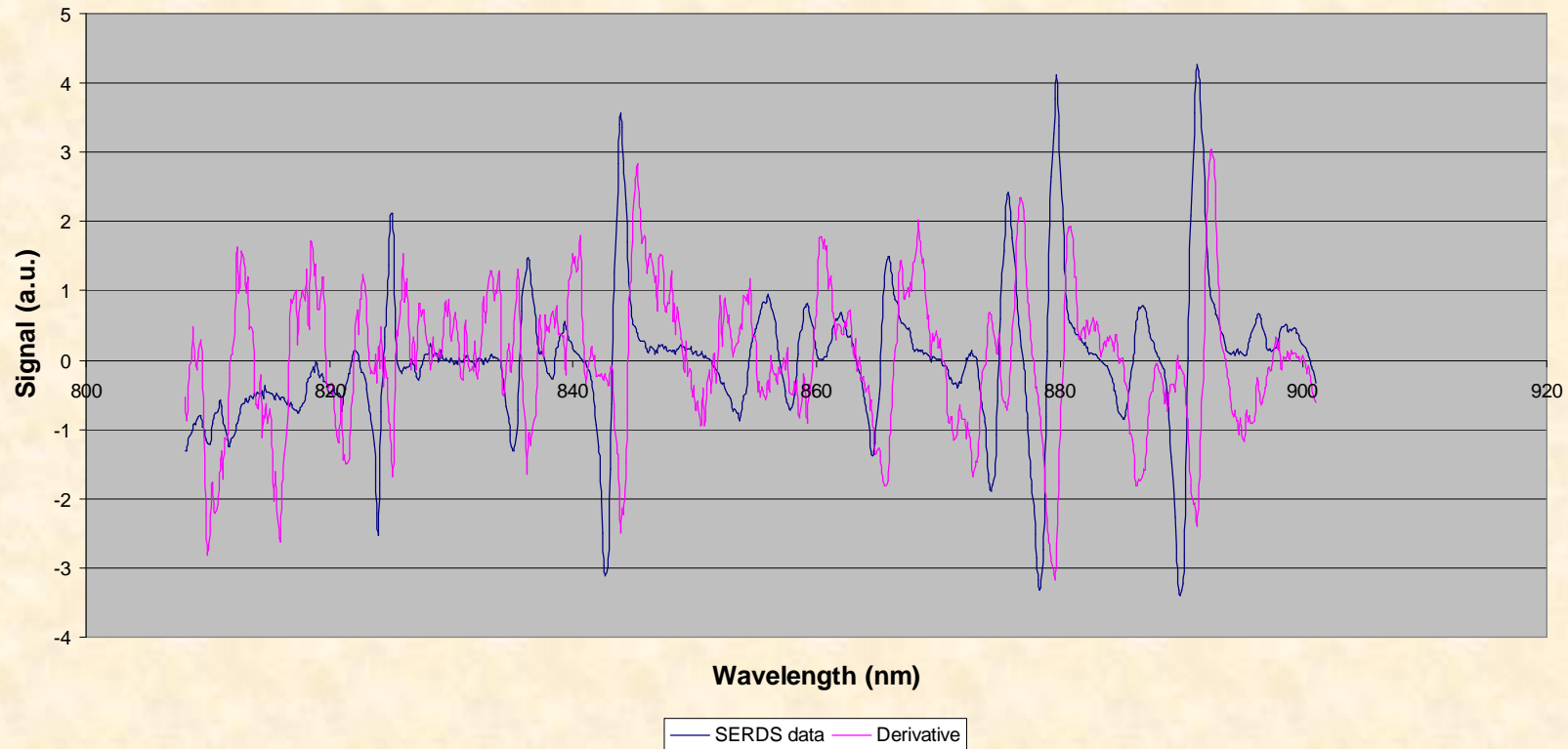
--- 785.7nm      — 784.8nm

- Raman/fluorescence ratio is  $< 1:100$
- Conventional Raman analysis is nearly impossible



# Comparison of SERDS with numerical filtering

SERDS spectrum vs derivative



**SERDS data have much less noise**

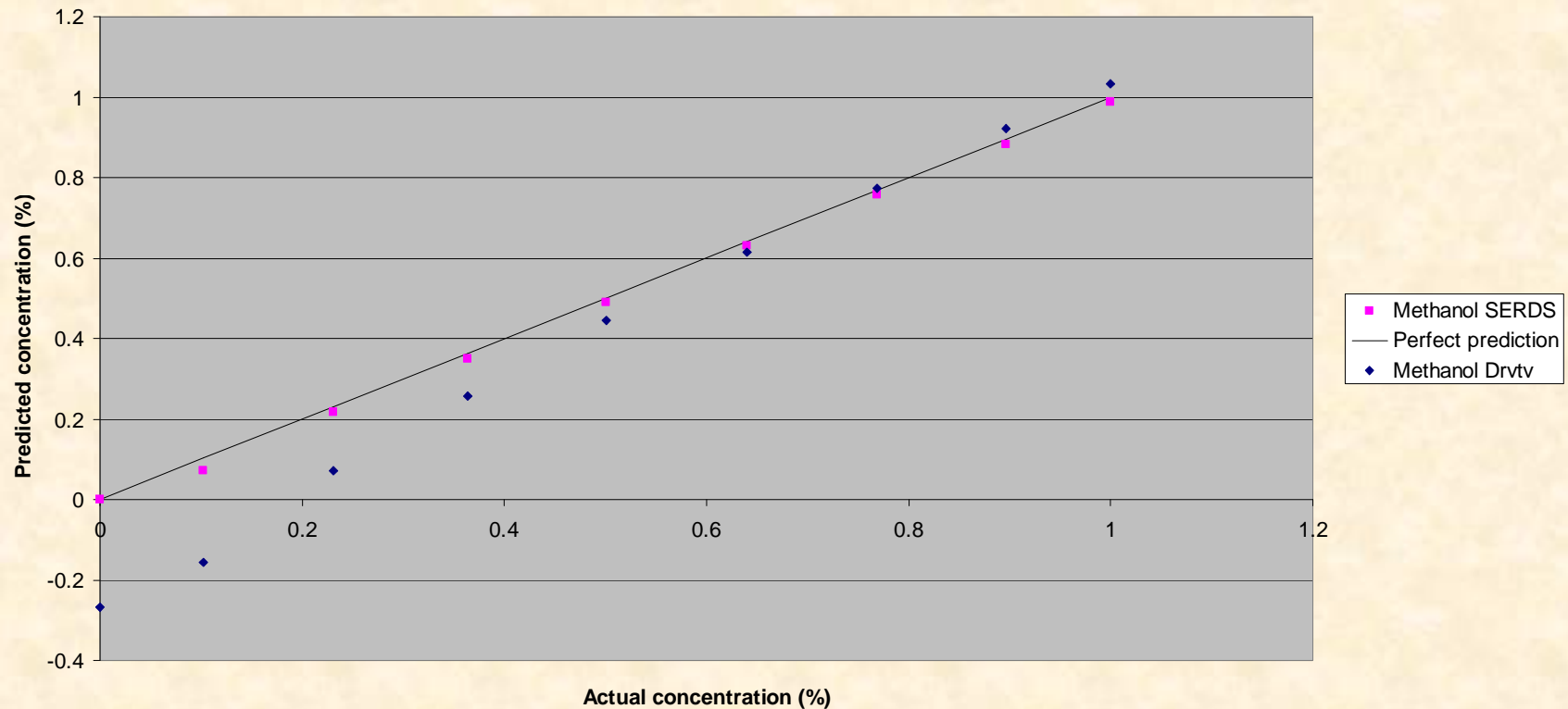
# Measurement methodology

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- ❑ Quantitative information was obtained **without giving the system the *a priori* knowledge of the mixture constituents**
- ❑ Components of the mixtures were recognized using the library SERDS spectra
- ❑ Collected SERDS spectra of the mixtures were then projected into the sub-space of the library spectra of the recognized pure components
- ❑ Predicted concentrations were based on the projection onto the spectra of the pure compounds
- ❑ Similar methodology was employed with derivative spectra

# Prediction of methanol concentration in two-part mixtures with ethanol in presence of R6G

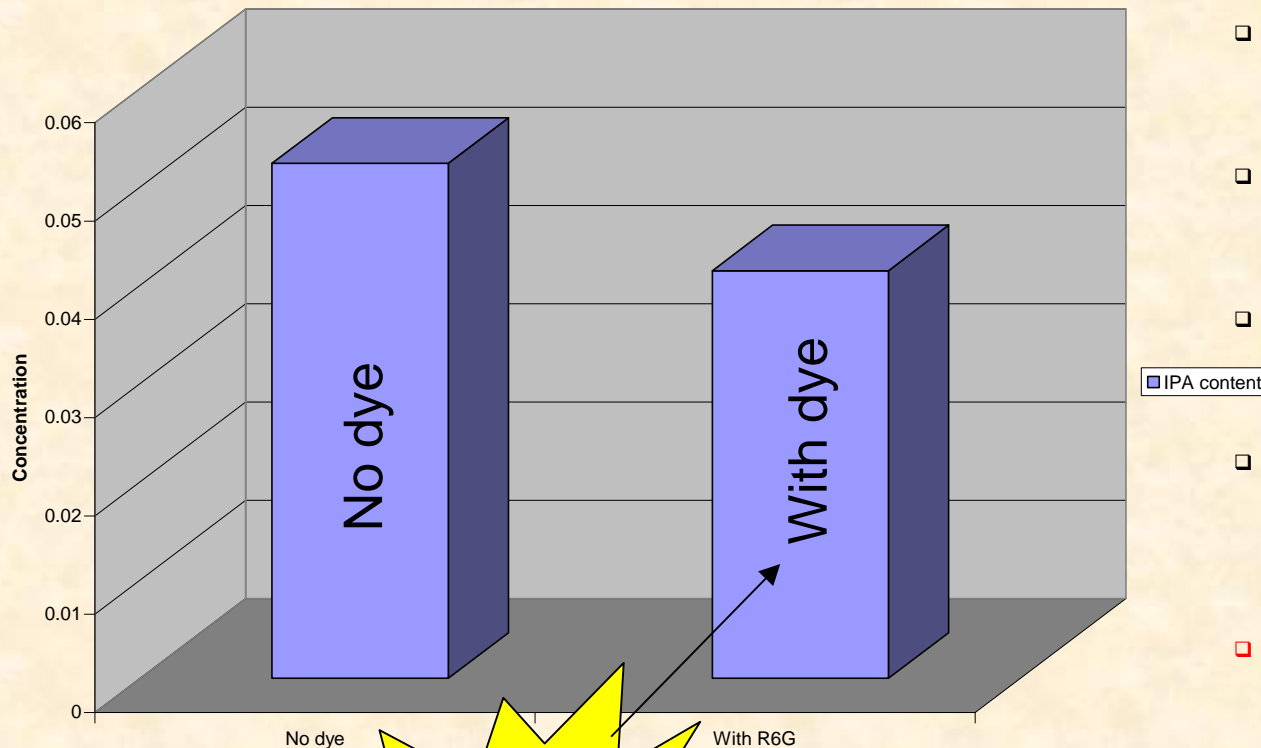
Alcohol concentration prediction with R6G in solution



SERDS has ~ 3x better detection threshold for the minor constituent in the mixture compared with numerical filtering method

# Detection of contamination of ethanol with isopropanol in presence of R6G dye

Predicted concentration of IPA relative to Ethanol in mixtures



Fluorescence is > 100 times stronger than Raman signal!


- Task: detect and quantify ethanol contamination with isopropanol
- IPA concentration measured accurately at ~ 5% level in both cases
- Fluorescence background did not prevent detection of the IPA contamination
- Signal to fluorescence ratio of > 1:100 results in measurement error of only 1% on 5%.
- Numerical derivative calculation method does not detect IPA in this case

# Laser source control: switching

VBG-stabilized Laser Wavelength Stability After Turn-On



Laser wavelength changes by < 5 pm peak-to-peak after laser turn on/ turn off cycle (TEC stays on)



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# Possible Implementations of SERDS Sources

# Different implementation of SERDS sources

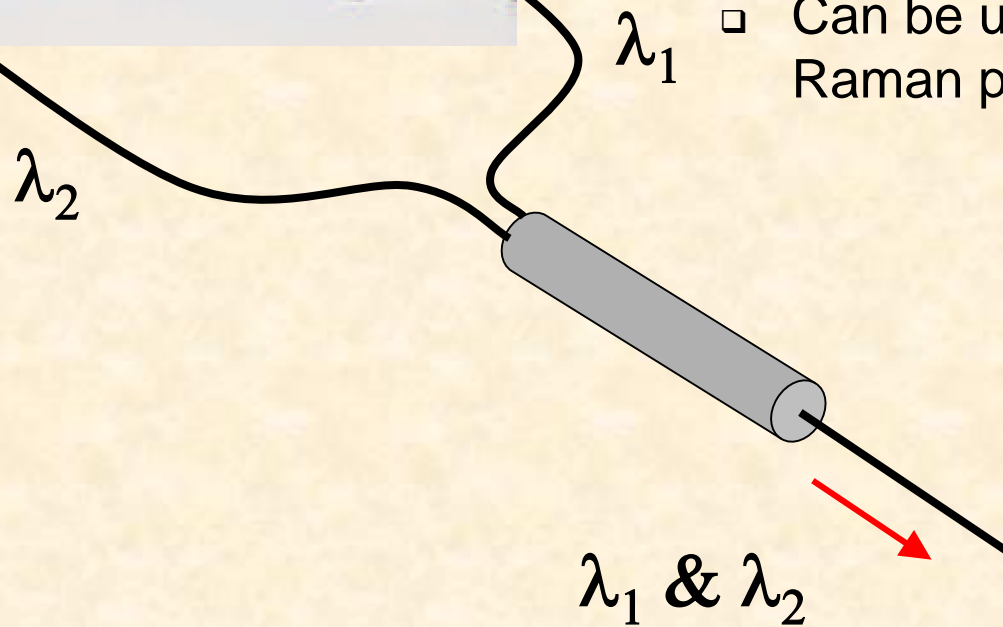
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1. Two separate stand-alone turn-key laser sources (integrated with laser diode driver and temperature controller) combined by an external combiner
2. Free-space collimated output laser combined in a single small housing
3. A butterfly package with fiber-coupled or free-space output housing both laser chips and combined inside the package

# Option 1: two stand-alone turn-key laser sources

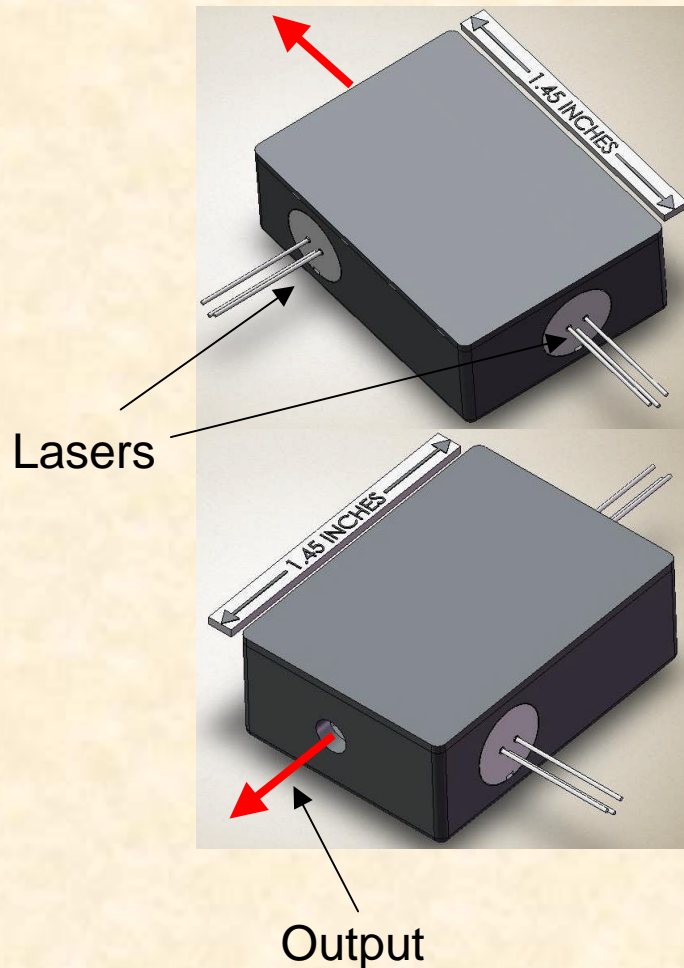


- ❑ Based on the existing PD-LD products
- ❑ Quick to implement, simple to use
- ❑ Can be used with standard Raman probes



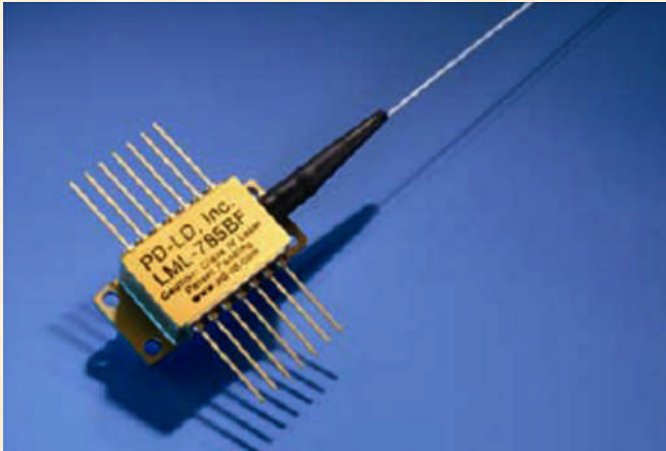


# Option 2: two free-space lasers combined in one housing



- ❑ Both lasers have collimated output
- ❑ The outputs are combined to be collinear and propagate along the same path => they will illuminate exactly the same area on a sample
- ❑ The package can be equipped with a photodiode to monitor the power of the lasers
- ❑ This package has no built-in thermoelectric coolers by default
- ❑ The concept shown here is based on lasers packaged in 9 mm TO cans
- ❑ Smaller diameter 5.6 mm TO cans can be used also for single mode lasers (<150 mW per laser)

# Option 3: two laser diode chips in the same butterfly package



- ❑ Both lasers are combined inside the housing and coupled into the same fiber
- ❑ This package has a built-in thermoelectric cooler that controls both laser chips
- ❑ The package is equipped with a photodiode to monitor the power of the lasers
- ❑ Same size as a single laser
- ❑ Both lasers can be powered individually addressable
- ❑ Can be supplied in a butterfly package or as a turn-key stand-alone laser with all the electronics and drivers

# Summary of SERDS advantages

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- ❑ SERDS method allows accurate and robust Raman measurements even when Raman signal is  $> 100$  times weaker than the fluorescence background
- ❑ SERDS has  $\sim 3x$  better accuracy and detection limit of the numerical filtering methods
- ❑ SERDS analysis can be, and should be performed using the derivative spectra without reconstruction
- ❑ Using fixed wavelength sources, as opposed to tunable laser source, is more advantageous:
  - The wavelength difference is stable and always the same;
  - The sources are simpler to run and control
  - Two-source solution is both cheaper and more robust than a tunable laser source
- ❑ Switching of the laser sources can be done electronically