Quantitative Analysis of CMP Slurry Additives Using Raman Spectroscopy

Presented to: American Vacuum Society - CMP Users Group

Tim Holt (timothy.holt@horiba.com) , Michelle Sestak (michelle.sestak@horiba.com)

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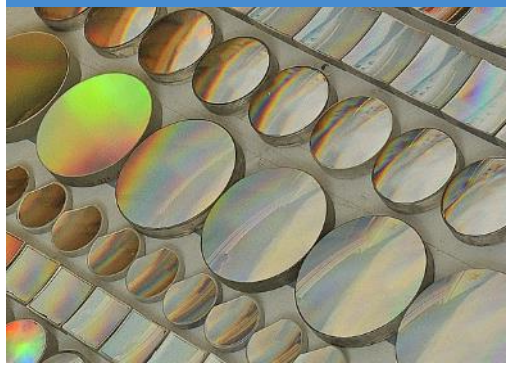
HORIBA Semiconductor

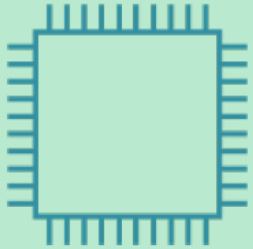
HORIBA's Core Technologies and Applications

Gas Flow Control	Infrared Measurement	Spectroscopic Analysis	Particle-size Analysis	Electrochemistry
				

We invest development resources by focusing on specific analysis and measurement technologies, and then we apply and develop these core technologies to efficiently develop products for five business segments in different markets.

Academia & Research

Mobility

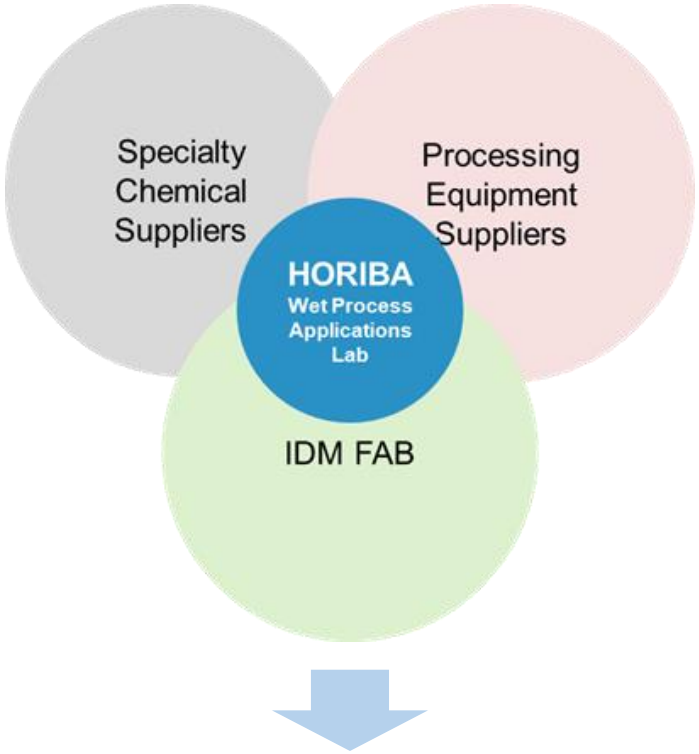


Semiconductor

Environment

Healthcare

Collaboration of HORIBA Semi and Scientific Divisions



HORIBA SEMI & SCIENTIFIC COLLABORATION

Chemical (slurry) suppliers

Tim

Semiconductor

Inline chemical concentration monitor

UV/Vis/NIR → calibration by MVA

Chemical mixtures, mass% of components →

Michelle

Scientific

Materials analysis

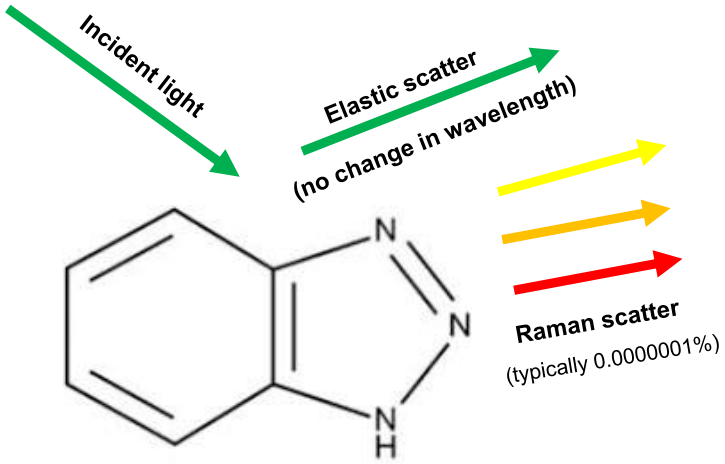
Raman → calibration by MVA

opportunities for Raman; aqueous mixtures

Interpreting Raman Spectral Data: Good for Slurry?

Raman shift:

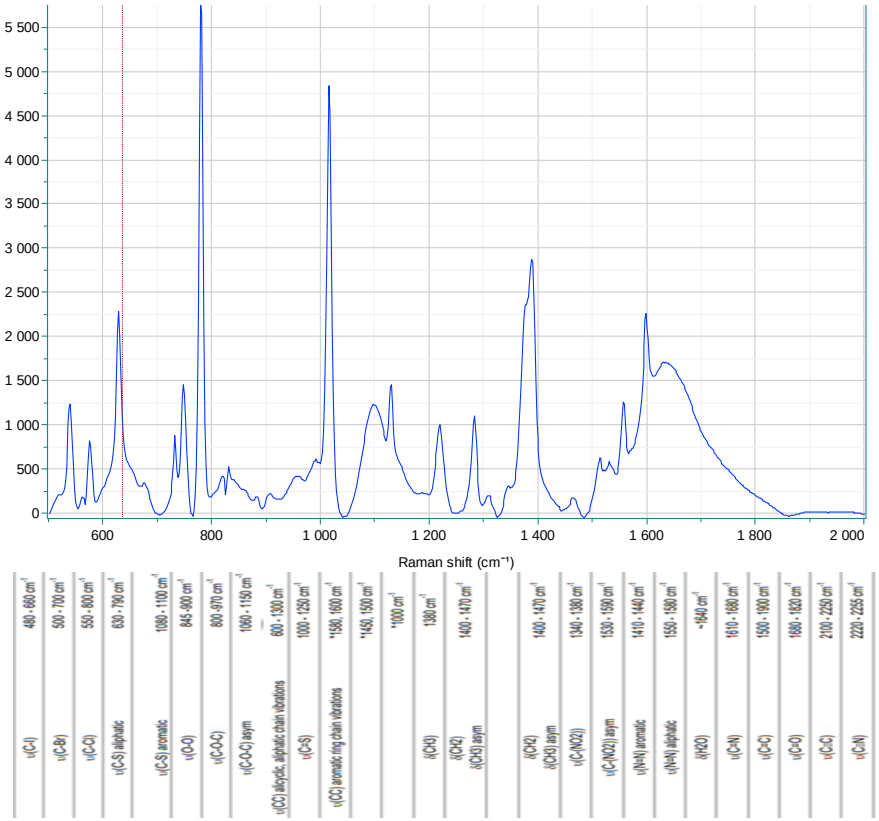
The incident wavelength is changed by the fundamental vibration of the functional group:



- Typically non-destructive
- Chemical structure and identity
- Phase and polymorphism
- Intrinsic stress/strain
- Contamination and impurity
- Fluorescence can be a problem

1. ***Scattered signal, NOT transmission***
2. ***Concentrated vs POU***
   - ***Good for CMP slurry suppliers?***

Functional Group/ Vibration	Region
Lattice vibrations in crystals, LA modes	10 - 200 cm^{-1}
δ(CC) aliphatic chains	250 - 400 cm^{-1}
υ(Se-Se)	290 -330 cm^{-1}
υ(S-S)	430 -550 cm^{-1}
υ(Si-O-Si)	450 -550 cm^{-1}
υ(Xmetal-O)	150-450 cm^{-1}
υ(C-I)	480 - 660 cm^{-1}
υ(C-Br)	500 - 700 cm^{-1}
υ(C-Cl)	550 - 800 cm^{-1}
υ(C-S) aliphatic	630 - 790 cm^{-1}
υ(C-S) aromatic	1080 - 1100 cm^{-1}
υ(O-O)	845 -900 cm^{-1}
υ(C-O-C)	800 -970 cm^{-1}
υ(C-O-C) asym	1060 - 1150 cm^{-1}
υ(CC) alicyclic, aliphatic chain vibrations	600 - 1300 cm^{-1}
υ(C=S)	1000 - 1250 cm^{-1}
υ(CC) aromatic ring chain vibrations	*1580, 1600 cm^{-1}
	*1450, 1500 cm^{-1}
	*1000 cm^{-1}
δ(CH3)	1380 cm^{-1}
δ(CH2) δ(CH3) asym	1400 - 1470 cm^{-1}
δ(CH2) δ(CH3) asym	1400 - 1470 cm^{-1}
υ(C-(NO2))	1340 - 1380 cm^{-1}
υ(C-(NO2)) asym	1530 - 1590 cm^{-1}
υ(N=N) aromatic	1410 - 1440 cm^{-1}
υ(N=N) aliphatic	1550 - 1580 cm^{-1}
δ(H2O)	~1640 cm^{-1}
υ(C=N)	1610 - 1680 cm^{-1}
υ(C=C)	1500 - 1900 cm^{-1}
υ(C=O)	1680 - 1820 cm^{-1}
υ(C≡C)	2100 - 2250 cm^{-1}
υ(C≡N)	2220 - 2255 cm^{-1}
υ(-S-H)	2550 - 2600 cm^{-1}
υ(C–H)	2800 - 3000 cm^{-1}
υ(=(C-H))	3000 - 3100 cm^{-1}
υ(≡(C-H))	3300 cm^{-1}
υ(N-H)	3300 - 3500 cm^{-1}
υ(O-H)	3100 - 3650 cm^{-1}



The resulting spectrum shows the Raman-active fundamental vibrations

Motivation

Establish Raman spectroscopy as a simple alternative to complex, expensive HPLC / IC.

Chromatography (HPLC / IC)

- Excellent limit of detection
- Complex method
- Expert user required
- Digestion/dilution of samples
- High cost consumables

Raman Spectroscopy

- Good Limit of detection
- Simple method
- Non-expert can make measurements
- Direct measurement of samples
- No consumables

Slurry additives are typically measured using chromatographic techniques like ion chromatograph (IC) or High Pressure Liquid Chromatography (HPLC). Raman spectroscopy offers a very simple method capable of detecting slurry additives that offers many benefits over chromatographic techniques.

Chromatographic techniques like IC and HPLC offer very good detection limits and measurement repeatability, but can require significant time and effort to create a method, complex and lengthy sample preparation, and highly skilled operators.

Raman Spectroscopy offers a much simpler approach; direct measurement of slurry with no preparation, configuration options (probe, non-contact, etc.) make measurements very simple,

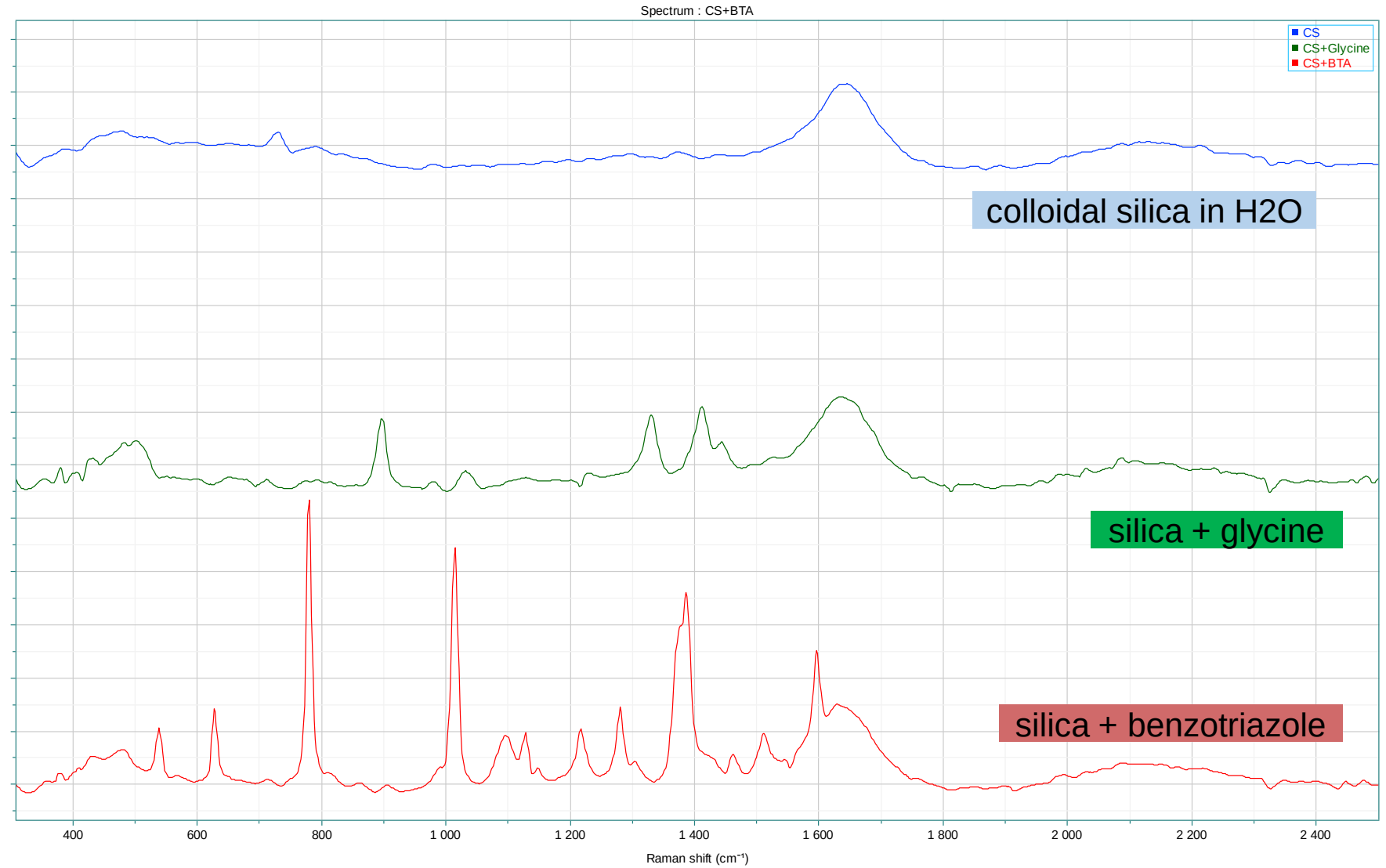
We will establish the capability of Raman spectroscopy to measure the concentrations of typical slurry components.

Colloidal Silica and Common* Additives Feasibility

Feasibility of some typical slurry additives shows good Raman activity

The Raman spectrum of colloidal silica in water is not complicated.

This makes determining the additives in a mixture much simpler.



* Lu, Hai-Sheng & Zeng, Xu & Wang, Jing-Xuan & Chen, Fei & Qu, Xin-Ping. (2012).

The Effect of Glycine and Benzotriazole on Corrosion and Polishing Properties of Cobalt in Acid Slurry.

Journal of the Electrochemical Society. 159. C383-C387. 10.1149/2.036209jes.

Li, Jing & Lu, Xinchun & Ou, Junyu & Cheng, Jie. (2012).

Adsorption Mechanism of Benzotriazole on Copper Surface in CMP Based Slurries Containing Peroxide and Glycine.

Planarization/CMP Technology (ICPT 2012)

Chenqi, Yan & Liu, Yuling & Zhang, Jin & Wang, Chenwei & Zhang, Wenxia & He, Ping & Pan, Guofeng. (2017).

Synergistic Effect of Glycine and BTA on Step Height Reduction Efficiency after Copper CMP in Weakly Alkaline Slurry.

ECS Journal of Solid State Science and Technology. 6. P1-P6. 10.1149/2.0291612jss.

Deshpande, Shwetark & Kuiry, S. & Klimov, Mikhail & Seal, Sudipta. (2005).

Elucidating Cu-glycine and BTA complexations in Cu-CMP using SIMS and XPS.

Electrochemical and Solid State Letters - ELECTROCHEM SOLID STATE LETT. 8. 10.1149/1.1869112.

Choi, Seungchoun & Dornfeld, David & Doyle, Fiona. (2013).

Influence of Copper Ion Concentration on the Kinetics of Formation of a Protective Layer on Copper in an Acidic CMP Solution Containing BTA and Glycine.

Journal of the Electrochemical Society. 160. H653-H658. 10.1149/2.010310jes.

Calibration Options and Sample Matrix

DOE Sample Matrix

Additives commonly found in literature:

- **Colloidal silica @ 0, 1, 2%**
- **Benzotriazole @ 0, 0.2, 0.6 %**
- **Glycine @ 0.5, 1.0, 1.5%**
- **Balance is H2O @ 96 – 100%**

We want to quantify benzotriazole and glycine.

Colloidal silica concentration variable is included to determine any matrix effect or fluorescence.

From these samples we can generate and compare:

- **multivariate calibration model**
- **single peak calibration models**

DOE sample matrix

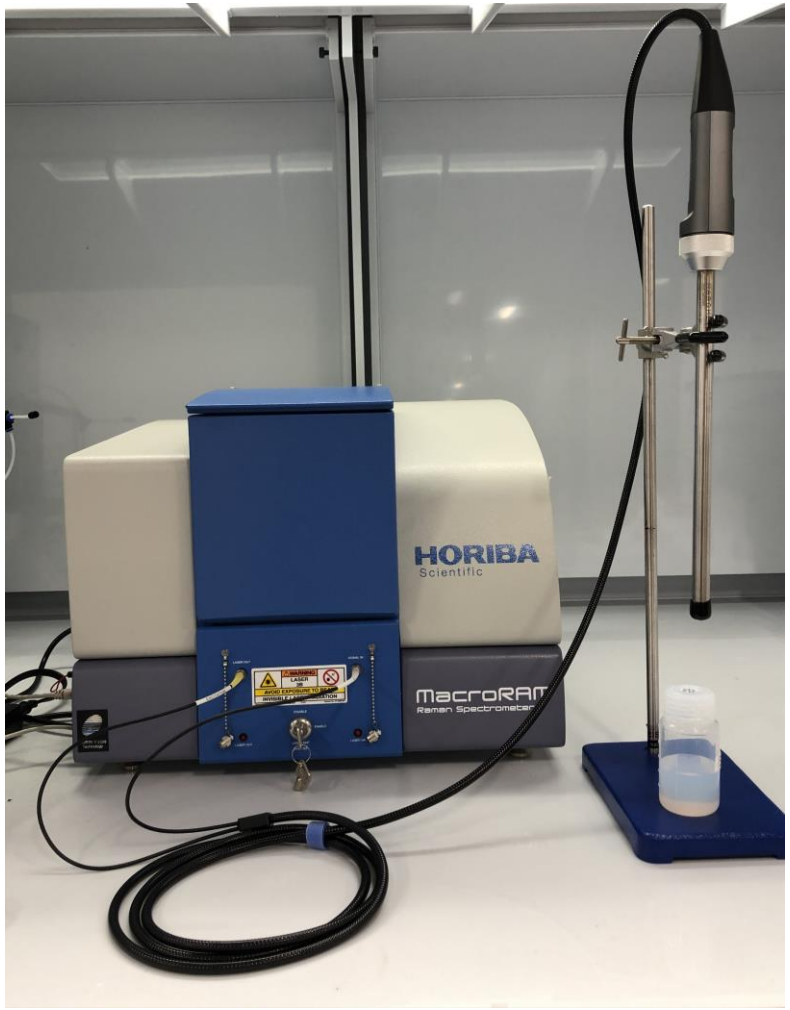
run	silica	benzotriazole	glycine	water
1	0.00%	0.00%	0.00%	100.00%
2	1.01%	0.00%	0.57%	98.42%
3	1.01%	0.00%	1.22%	97.77%
4	1.00%	0.00%	1.74%	97.26%
5	1.00%	0.20%	0.52%	98.28%
6	0.91%	0.18%	1.11%	97.80%
7	1.01%	0.20%	1.71%	97.08%
8	0.99%	0.60%	0.51%	97.90%
9	1.00%	0.60%	1.02%	97.38%
10	1.01%	0.60%	1.52%	96.87%
11	2.00%	0.00%	0.52%	97.48%
12	1.99%	0.00%	1.02%	96.99%
13	1.99%	0.00%	1.49%	96.52%
14	2.00%	0.20%	0.51%	97.28%
15	2.00%	0.20%	1.01%	96.80%
16	2.00%	0.20%	1.53%	96.28%
17	2.11%	0.60%	0.52%	96.77%
18	2.01%	0.60%	1.02%	96.37%
19	1.99%	0.60%	1.49%	95.92%
20	0.00%	0.00%	0.52%	99.48%
21	0.00%	0.00%	1.03%	98.97%
22	0.00%	0.00%	1.51%	98.49%
23	0.00%	0.20%	0.52%	99.28%
24	0.00%	0.20%	1.00%	98.80%
25	0.00%	0.20%	1.50%	98.30%
26	0.00%	0.60%	0.50%	98.90%
27	0.00%	0.60%	1.00%	98.40%
28	0.00%	0.60%	1.48%	97.92%

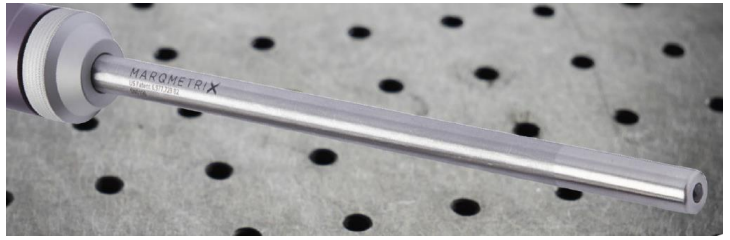
MacroRam Configuration

MacroRam Raman Spectrometer
- 785 nm laser
- Labspec6 software
- MVA EVRi multivariate add-on

+

Marqmetrix Process Ball Probe
Ideal for:
- Corrosive environments
- High pressure
- High temperature





Operating Conditions

Suitable for continuous exposure to dilute and con-centrated acids (hot & cold), bases and most organic solvents including ethanol, THF, ethyl acetate, acetone, DCM, toluene, pentane and acetonitrile
Avoid exposure to aqua regia

Wetted Materials

Probe Body	0.5 in. (12.7mm) OD Hastelloy C-276
Immersion Optics	6.00mm diameter UV-grade sapphire ball
Sealing Materials	Gold

Specifications

Standard Probe Length	11 in. (275mm)
Probe OD (Outside Diameter)	0.5 in. (12.7mm)
Sample Working Distance	TouchRaman (Sample contacts BallProbe lens)
Continuous Operating Temperature Range	-20°C to 300°C
Pressured Design Condition	6,000psi (413 bar)
Compatible Laser Wavelengths	500-1100nm

Other available configurations:
- Cuvette
- Non-contact probe
- Flow cell

Calibration Options

Multi Variate Calibration VS. Single Peak Calibration

DOE sample matrix

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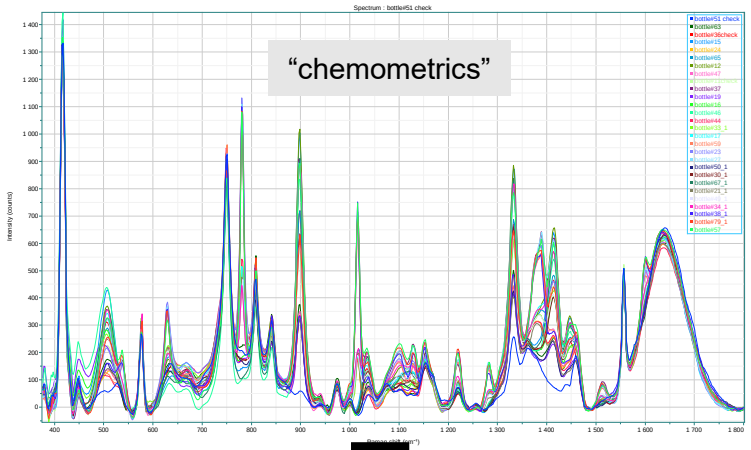
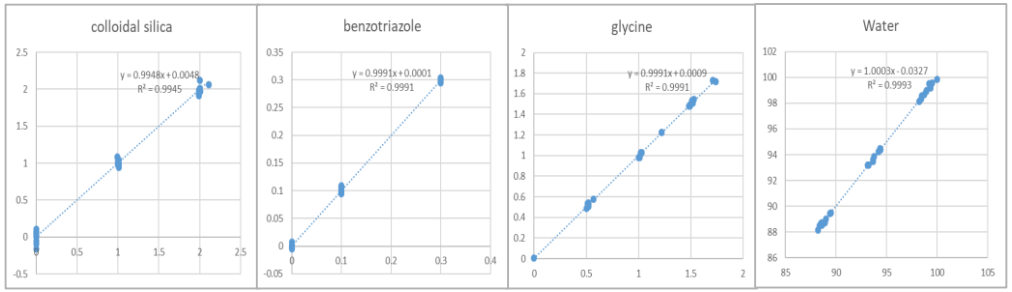
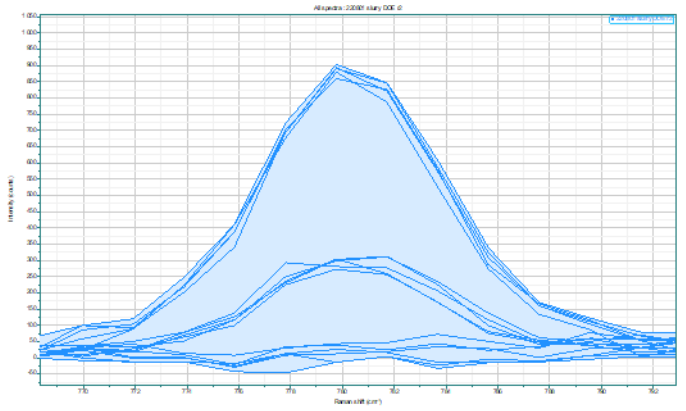
Multivariate calibration can leverage the entire spectral range to analyze multiple components

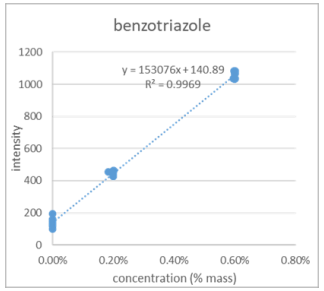




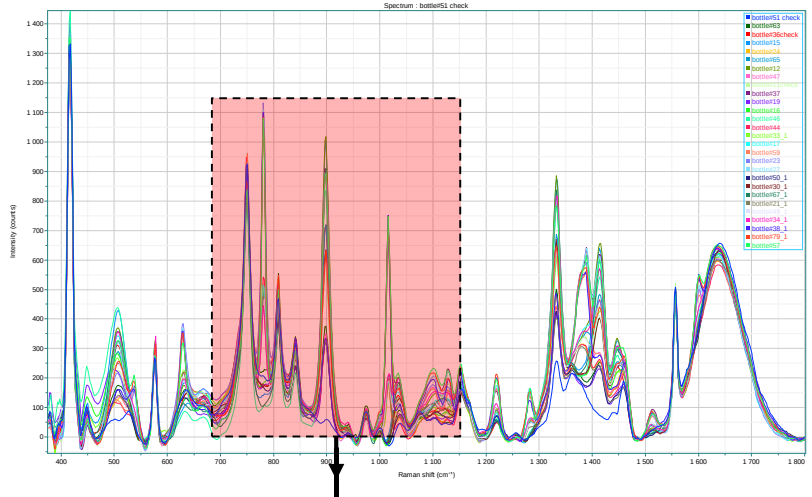
OR

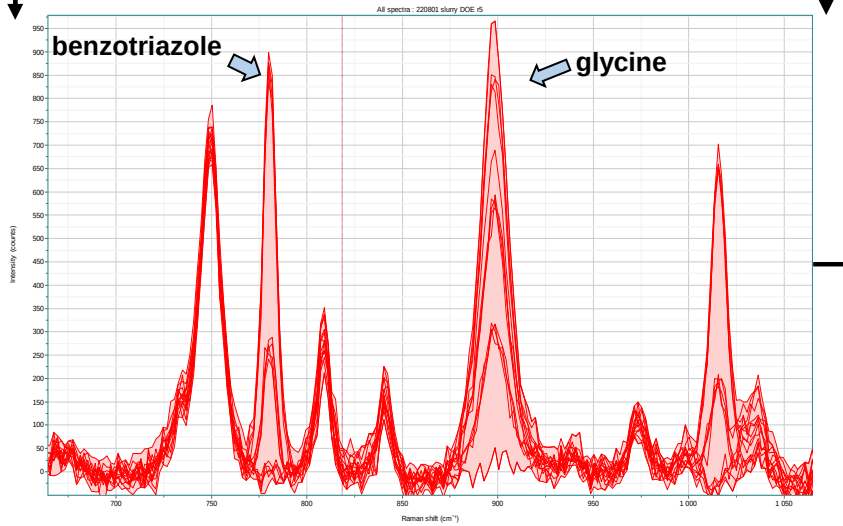
Single peak calibration:
single component for each peak independently

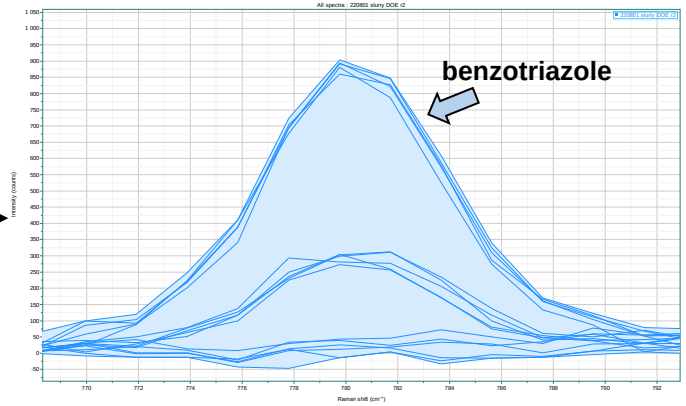


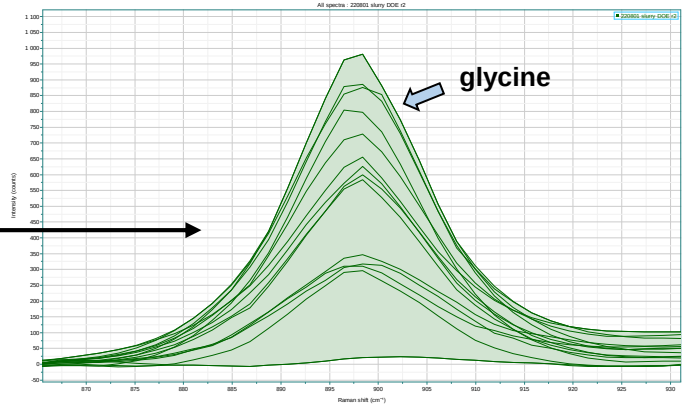


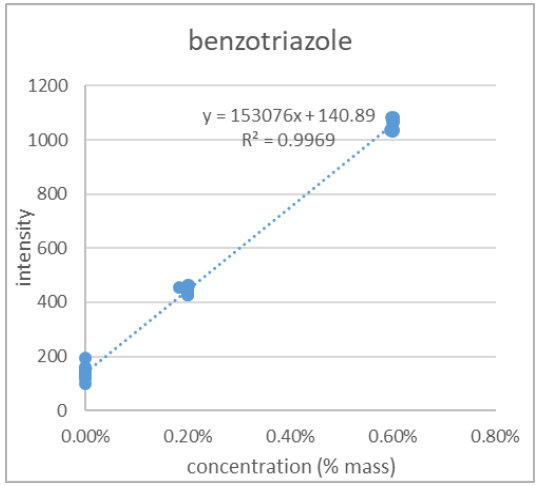
Single Peak Calibration

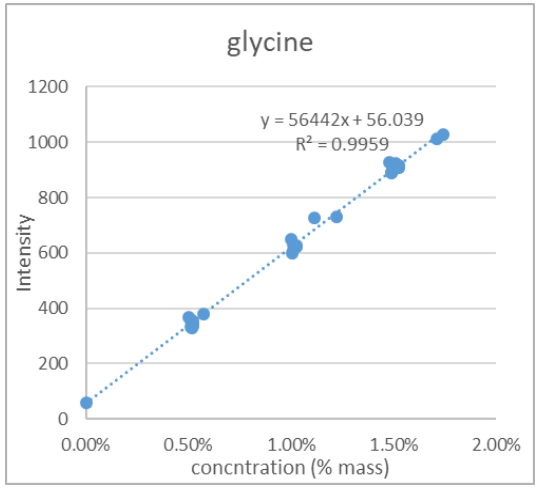




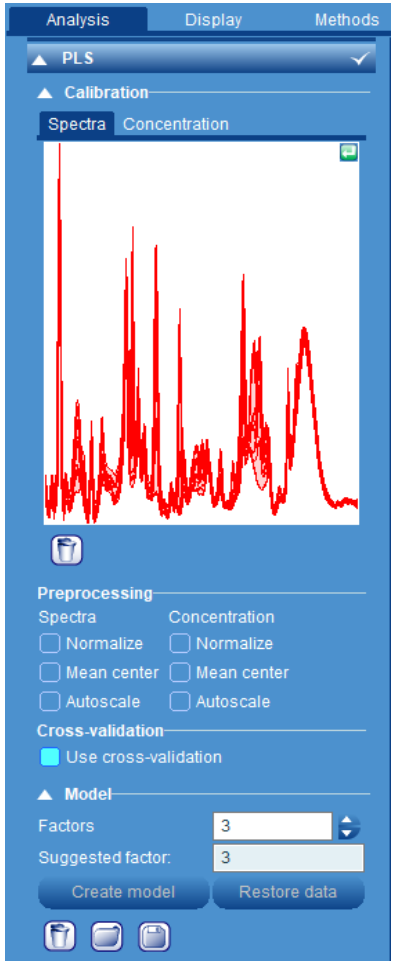








LS6 Software - Multivariate (PLS) Calibration Model



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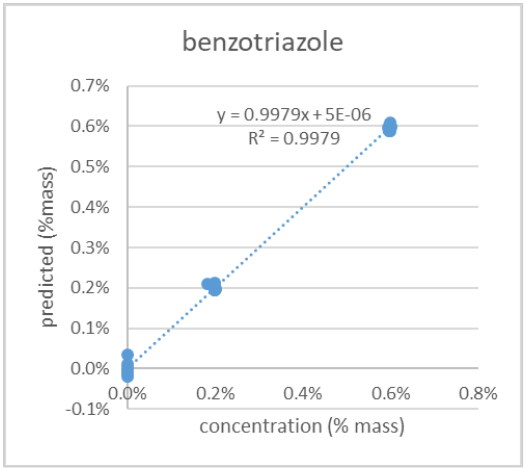
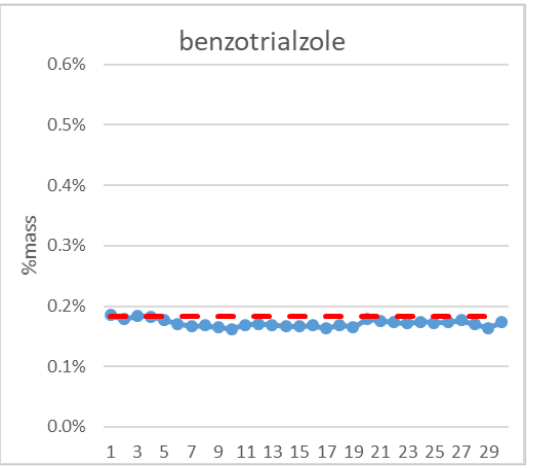
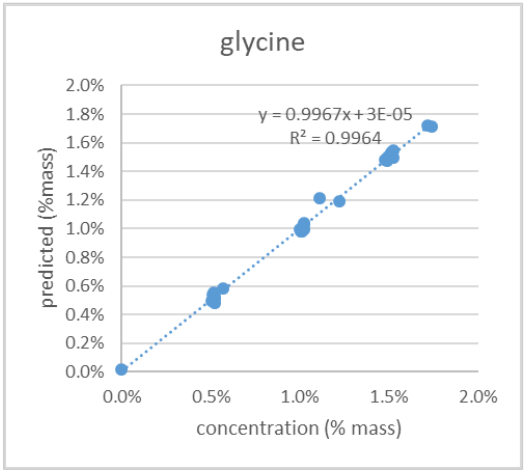
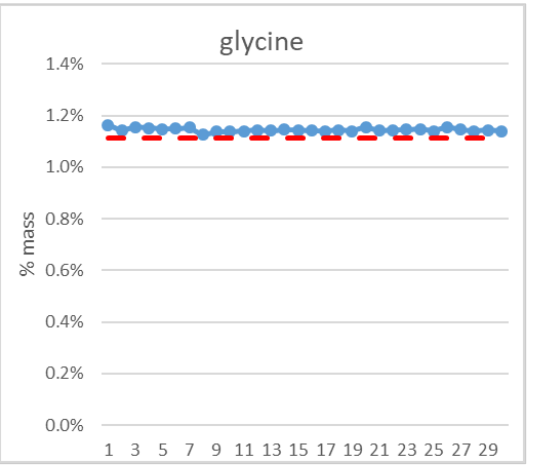
3 create model









1 load spectra

2 load cal DOE

Video instruction for PLS available

4 validate model (linearity)

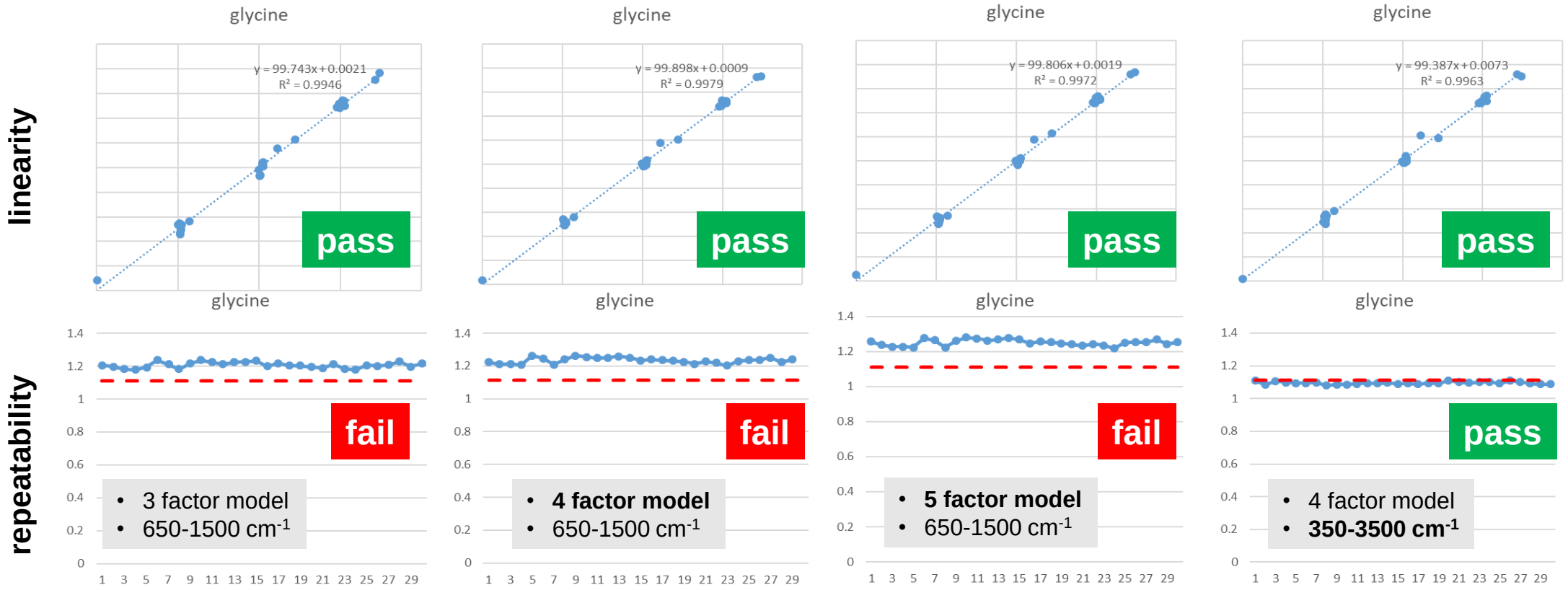
5 apply model (30 run repeatability)

Iterate if necessary

GRR?

Multivariate Iterations

Linearity is easy to model, but some iterations are usually necessary to achieve repeatability.
- # of factors in the model
- Adjustment of the spectral range
- Eigenvector add-on to LabSpec6 (basic PLS modelling) → Eigenvector Solo for advanced PLS modelling

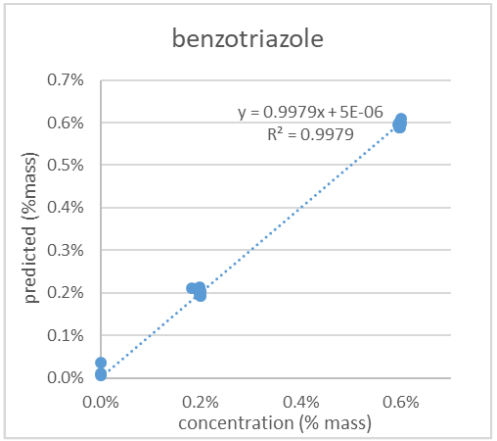


Multivariate vs Single Peak Calibration

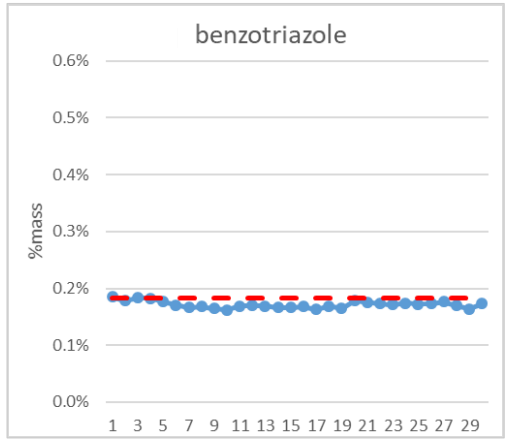
Multivariate Calibration Model:
- ~ full spectrum
- 4 factor PLS model

Single Peak Calibration Model:
- ~780cm^{-1} benzotriazole
- ~900cm^{-1} glycine

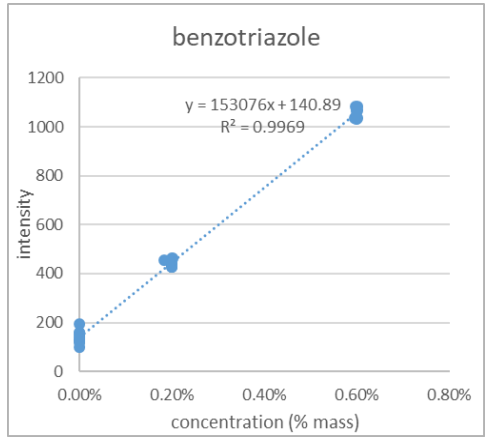
linearity



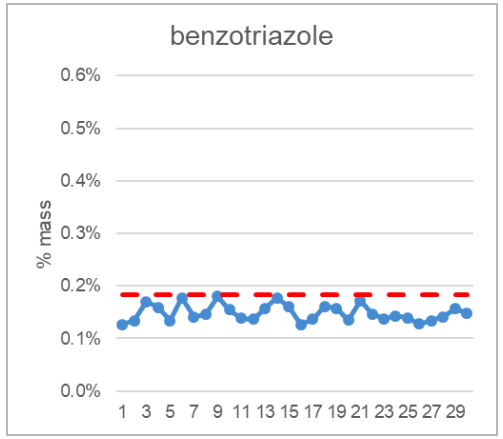
repeatability

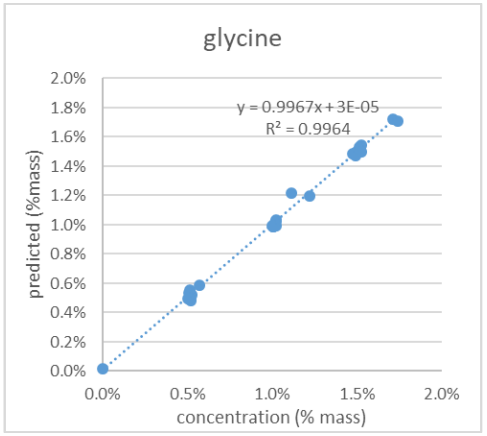


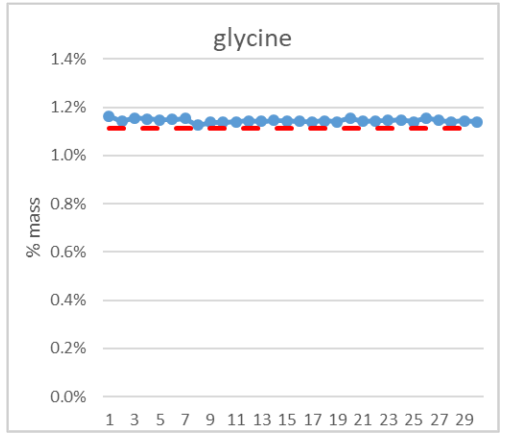
linearity

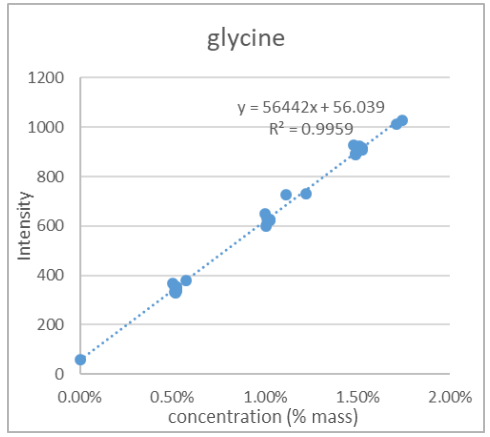


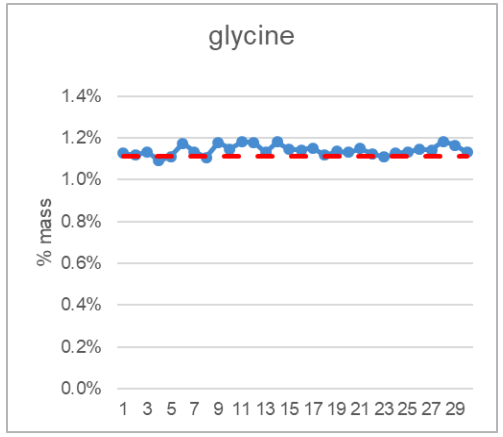
repeatability







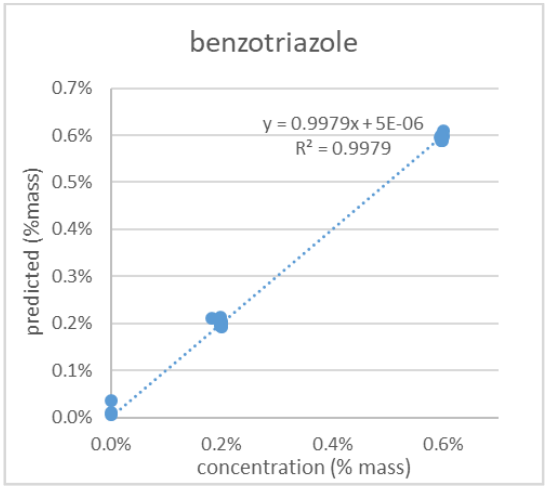


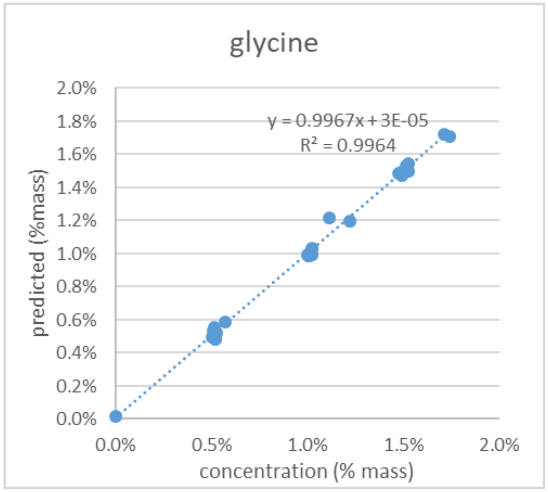


Linearity, Repeatability, Estimating LOD/LOQ

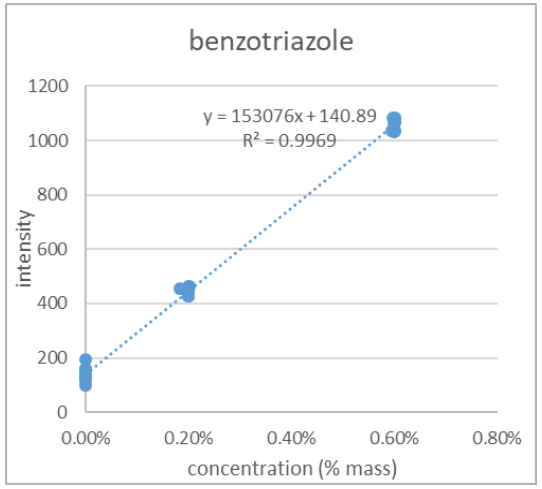
Linearity

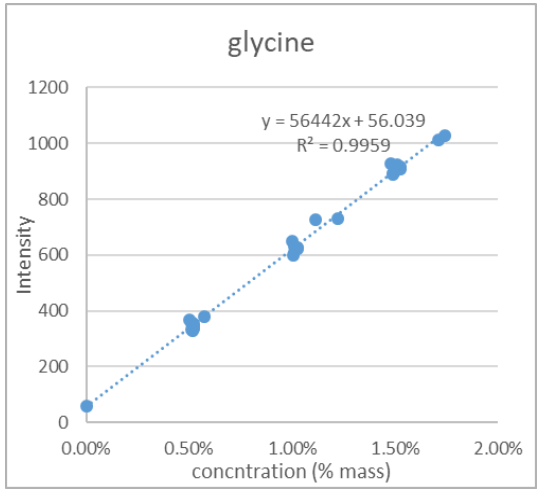
MVA





single peak





Repeatability (n=30)

	MVA		single peak	
	benzotriazole	glycine	benzotriazole	glycine
target	0.18%	1.11%	0.18%	1.11%
avg	0.17%	1.14%	0.15%	1.14%
stdev	0.006%	0.007%	0.016%	0.024%
6*stdev	0.036%	0.043%	0.096%	0.147%

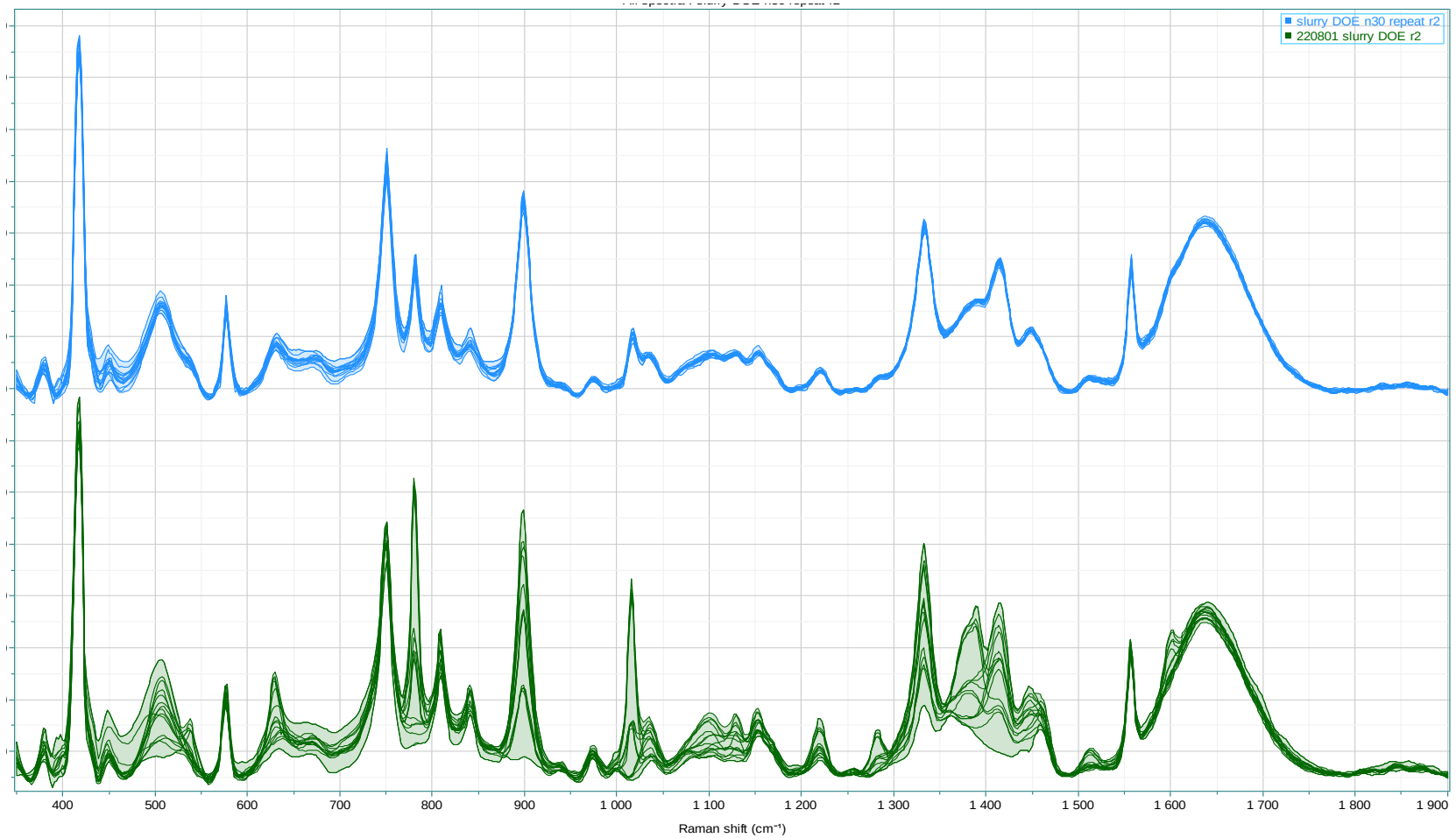
Estimated detection limit for benzotriazole

mass%	"blank" benzotriazole samples				blank values	
run	silica	BTA	glycine	water	MVA	single peak
2	1.01%	0.00%	0.57%	94.40%	-0.004%	0.012%
3	1.01%	0.00%	1.22%	93.75%	-0.015%	-0.003%
4	1.00%	0.00%	1.74%	93.25%	-0.009%	-0.010%
11	2.00%	0.00%	0.52%	89.50%	-0.008%	0.013%
12	1.99%	0.00%	1.02%	89.01%	-0.005%	-0.007%
13	1.99%	0.00%	1.49%	88.54%	0.006%	-0.012%
20	0.00%	0.00%	0.52%	99.48%	-0.018%	0.004%
21	0.00%	0.00%	1.03%	98.97%	-0.007%	-0.015%
22	0.00%	0.00%	1.51%	98.49%	0.011%	-0.027%
				average	-0.005%	-0.005%
				std. dev.	0.009%	0.013%
				LOD	0.022%	0.034%
				LOQ	0.087%	0.125%

LOD = “blank” mean + 3 std. dev.
LOQ = “blank” mean + 10 std. dev.

Troubleshooting and Quality Excursion Support

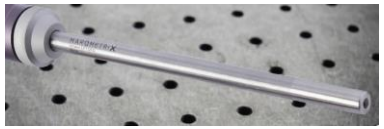
run	silica	benzotriazole	glycine	water
1	0.00%	0.00%	0.00%	100.00%
2	1.01%	0.00%	0.57%	98.42%
3	1.01%	0.00%	1.22%	97.77%
4	1.00%	0.00%	1.74%	97.26%
5	1.00%	0.20%	0.52%	98.28%
6	0.91%	0.18%	1.11%	97.80%
7	1.01%	0.20%	1.71%	97.08%
8	0.99%	0.60%	0.51%	97.90%
9	1.00%	0.60%	1.02%	97.38%
10	1.01%	0.60%	1.52%	96.87%
11	2.00%	0.00%	0.52%	97.48%
12	1.99%	0.00%	1.02%	96.99%
13	1.99%	0.00%	1.49%	96.52%
14	2.00%	0.20%	0.51%	97.28%
15	2.00%	0.20%	1.01%	96.80%
16	2.00%	0.20%	1.53%	96.28%
17	2.11%	0.60%	0.52%	96.77%
18	2.01%	0.60%	1.02%	96.37%
19	1.99%	0.60%	1.49%	95.92%
20	0.00%	0.00%	0.52%	99.48%
21	0.00%	0.00%	1.03%	98.97%
22	0.00%	0.00%	1.51%	98.49%
23	0.00%	0.20%	0.52%	99.28%
24	0.00%	0.20%	1.00%	98.80%
25	0.00%	0.20%	1.50%	98.30%
26	0.00%	0.60%	0.50%	98.90%
27	0.00%	0.60%	1.00%	98.40%
28	0.00%	0.60%	1.48%	97.92%



By using a formulation matrix we see the total “envelope” of variation around the formulation DOE (green) and 30 sample repeatability (blue).
Any new peaks or changes in existing peaks, or in the entire spectrum, can be qualitatively assessed by referencing the DOE.
This can be a very useful reference if there are concerns of contamination, raw material deviation, etc.

Other Raman Products from HORIBA

MacroRAM



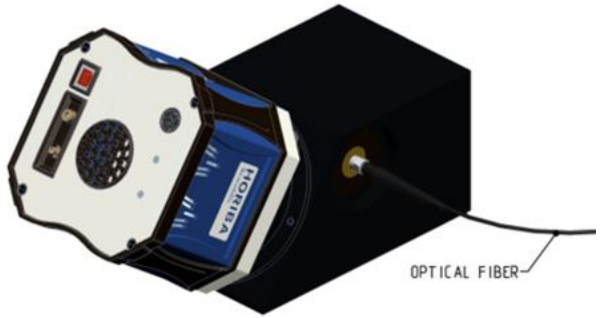
Raman Microscopes

Xplora

LabRAM HR

LabRAM HR

Raman Microscopes +AFM



Customized Raman - OEM