Quantitative Analysis of CMP Slurry Additives Using Raman Spectroscopy

Presented to: American Vacuum Society - CMP Users Group

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December 1st, 2022
HORIBA's Core Technologies and Applications

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.
Collaboration of HORIBA Semi and Scientific Divisions

- Specialty Chemical Suppliers
- Processing Equipment Suppliers
- IDM FAB

HORIBA SEMI & SCIENTIFIC COLLABORATION

- Chemical (slurry) suppliers

 Inline chemical concentration monitor
 UV/Vis/NIR $\rightarrow$ calibration by MVA
 Chemical mixtures, mass% of components $\rightarrow$

- Materials analysis
- Raman $\rightarrow$ calibration by MVA
- opportunities for Raman; aqueous mixtures

- Tim
- Michelle
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?

The resulting spectrum shows the Raman-active fundamental vibrations
Motivation

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

<table>
<thead>
<tr>
<th>Chromatography (HPLC / IC)</th>
<th>Raman Spectroscopy</th>
</tr>
</thead>
<tbody>
<tr>
<td>• Excellent limit of detection</td>
<td>• Good Limit of detection</td>
</tr>
<tr>
<td>• Complex method</td>
<td>• Simple method</td>
</tr>
<tr>
<td>• Expert user required</td>
<td>• Non-expert can make measurements</td>
</tr>
<tr>
<td>• Digestion/dilution of samples</td>
<td>• Direct measurement of samples</td>
</tr>
<tr>
<td>• High cost consumables</td>
<td>• No consumables</td>
</tr>
</tbody>
</table>

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.


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

<table>
<thead>
<tr>
<th>run</th>
<th>silica</th>
<th>benzotriazole</th>
<th>glycine</th>
<th>water</th>
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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 concentrated acids (HCl & HNO3), bases and most organic solvents including ethanol, THF, ethyl acetate, acetonitrile, DCM, toluene, pentane and acetone/MeOH
- Avoid exposure to aqua regia

Wetted Materials
- Probe Body: 0.5 in. (12.7mm) OD, Tefzel PE-275
- Immersion Optics: 6.00mm diameter UV-grade sapphire ball
- Sealing Materials: Gold

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

Specifications
- Standard Probe Length: 11 in. (279mm)
- Probe OD (Outside Diameter): 0.5 in. (12.7mm)
- Sample Working Distance: 0.5 in. (12.7mm)
- Continuous Operating Temperature Range: -20°C to 300°C
- Pressure Design Condition: 6,000psi (413 bar)
- Compatible Laser Wavelengths: 500-1100nm
Calibration Options

Multi Variate Calibration VS. Single Peak Calibration

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</table>

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

Single peak calibration: single component for each peak independently

OR

“chemometrics”
Single Peak Calibration

Raman shift (cm⁻¹) vs. Intensity (counts)

- **Benzotriazole**
  - Equation: \( y = 15307x + 140.89 \)
  - \( R^2 = 0.9969 \)

- **Glycine**
  - Equation: \( y = 56442x + 56.039 \)
  - \( R^2 = 0.9955 \)

Spectrum examples:
- Bottle #51, check
- Bottle #52
- Bottle #36, check
- Bottle #15
- Bottle #24
- Bottle #65
- Bottle #12
- Bottle #47
- Bottle #11, check
- Bottle #37
- Bottle #19
- Bottle #16
- Bottle #46
- Bottle #44
- Bottle #33, 1
- Bottle #17
- Bottle #59
- Bottle #23
- Bottle #27
- Bottle #50, 1
- Bottle #30, 1
- Bottle #67, 1
- Bottle #21, 1
- Bottle #49, 1
- Bottle #34, 1
- Bottle #38, 1
- Bottle #79, 1
- Bottle #57

Single Peak Calibration
LS6 Software - Multivariate (PLS) Calibration Model

1 load spectra

2 load cal DOE

3 create model

4 validate model (linearity)

5 apply model (30 run repeatability)

GRR?

Video instruction for PLS available

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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

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<th>Model</th>
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<th>Spectral Range</th>
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<tr>
<td>5</td>
<td>650-1500 cm(^{-1})</td>
<td>fail</td>
</tr>
<tr>
<td>4</td>
<td>350-3500 cm(^{-1})</td>
<td>pass</td>
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Multivariate vs Single Peak Calibration

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

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

**linearity**
- benzotriazole: \(y = 0.9979x + 5.06\), \(R^2 = 0.9979\)

**repeatability**
- benzotriazole

**linearity**
- glycine: \(y = 0.9967x + 31.05\), \(R^2 = 0.9964\)

**repeatability**
- glycine
Linearity, Repeatability, Estimating LOD/LOQ

MVA

**Linearity**

![Graph showing linearity for benzotriazole](image)

![Graph showing linearity for glycine](image)

**MVA**

\[
\begin{align*}
\text{benzotriazole} & : y = 0.9979x + 56.06, R^2 = 0.9999 \\
\text{glycine} & : y = 0.9976x + 3E-05, R^2 = 0.9964
\end{align*}
\]

**Repeatability (n=30)**

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<th>run</th>
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<table>
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<tr>
<th>mass%</th>
<th>&quot;blank&quot; benzotriazole samples</th>
<th>blank values</th>
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</table>

**Estimated detection limit for benzotriazole**

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

\[
\begin{align*}
\text{LOD} & = \text{"blank" mean} + 3 \times \text{std. dev.} \\
\text{LOQ} & = \text{"blank" mean} + 10 \times \text{std. dev.}
\end{align*}
\]

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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

Raman Microscopes +AFM

LabRAM HR

Customized Raman - OEM
Omoshiro-okashiku
Joy and Fun

THANK YOU

Danke
Gracias
Grazie

Terima kasih
谢谢
Σας ευχαριστώ πάρα πολύ
ขอบคุณครับ
ありがとうございました
Dziękuję
Obrigado
Câm ơn

شكرا
Большое спасибо
감사합니다