Portable, rapid analysis of MEA-Triazine via Raman spectroscopy

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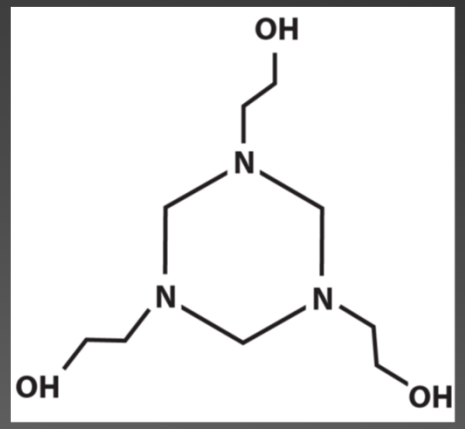
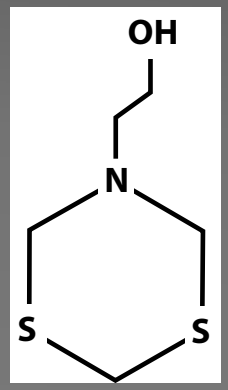
Hydrogen sulfide scavengers

- Used to remove H_2S from oil and gas streams
- Triazine-based materials are popular and convenient
- No field methods to monitor content and analyze the reaction
- Tramp amines downstream



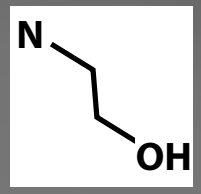
MEA-triazine

+ 2 H_2S



dithiazine

+ 2



ethanolamine

* Hexahydro-1,3,5-tris(hydroxyethyl)-s-triazine

Raman spectroscopy

1920s 

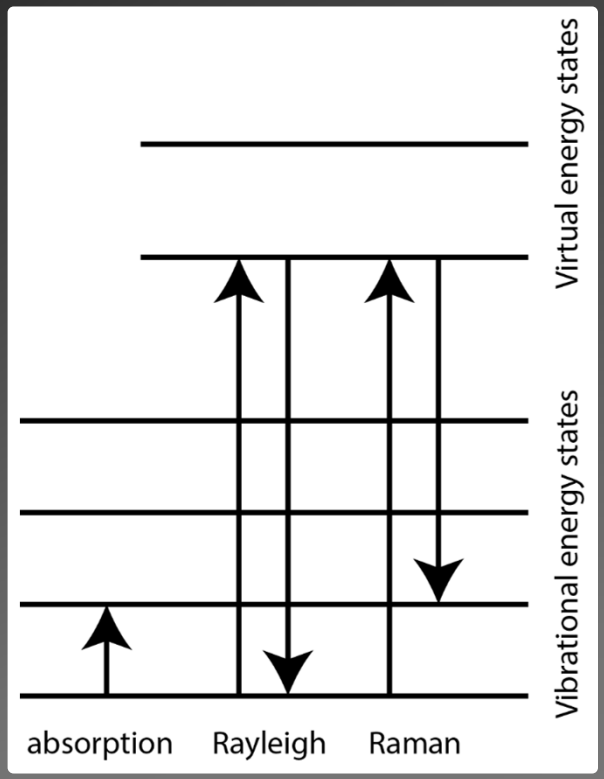
1990s 

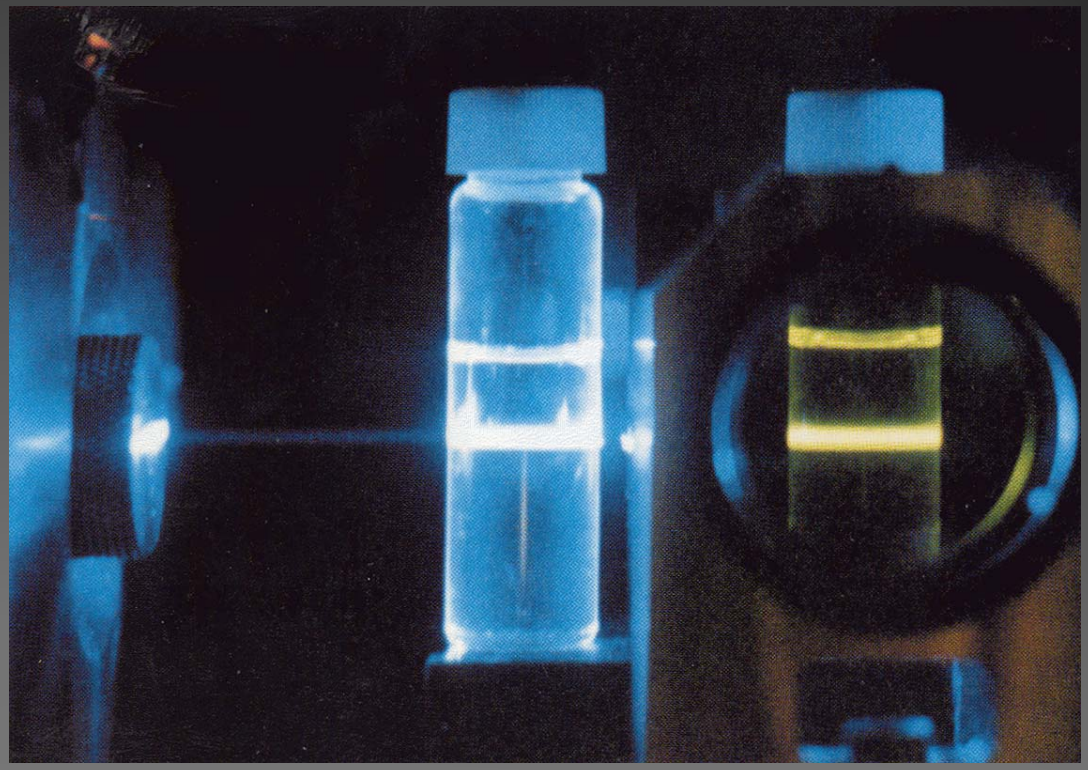
2000s 

is a spectroscopic technique used to observe vibrational, rotational, and other low-frequency modes in a system

commonly used in chemistry to provide a fingerprint by which molecules can be identified

Raman spectroscopy

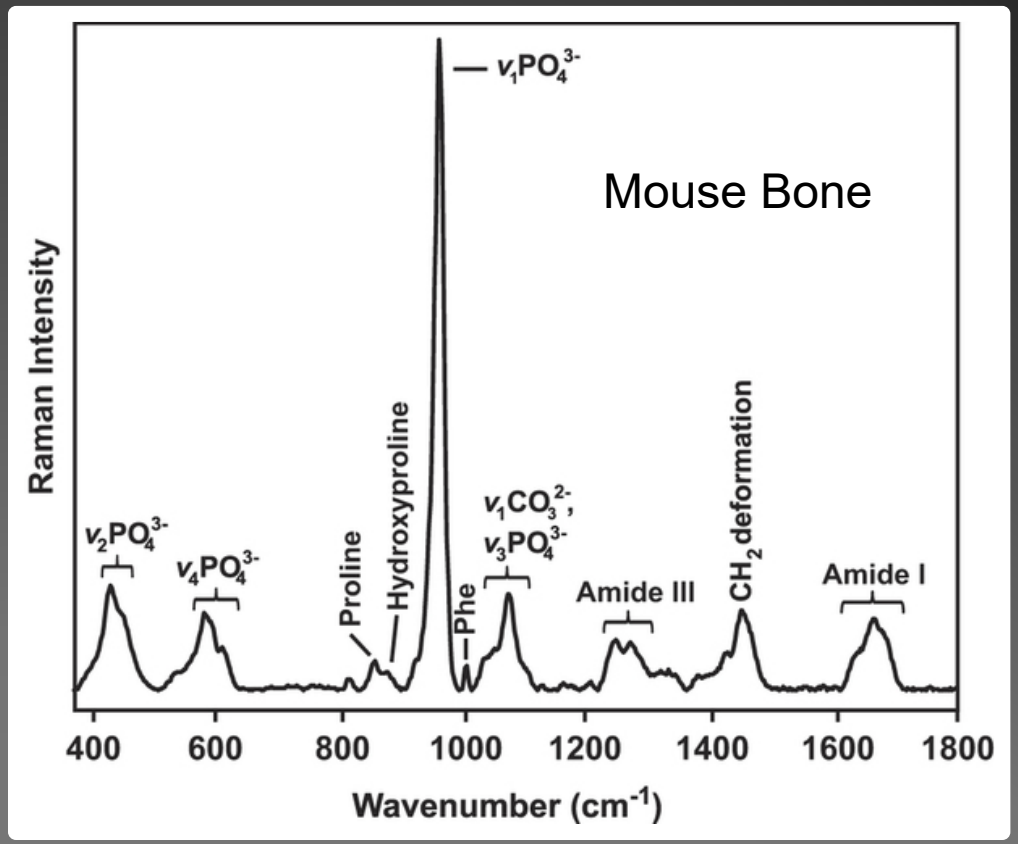




Raman spectroscopy

- Molecular fingerprints / structure
- Works with water
- Completely optical
- Portable
- Commercially available

- **But.. traditionally used for identification not quantification**



Raman vs FTIR

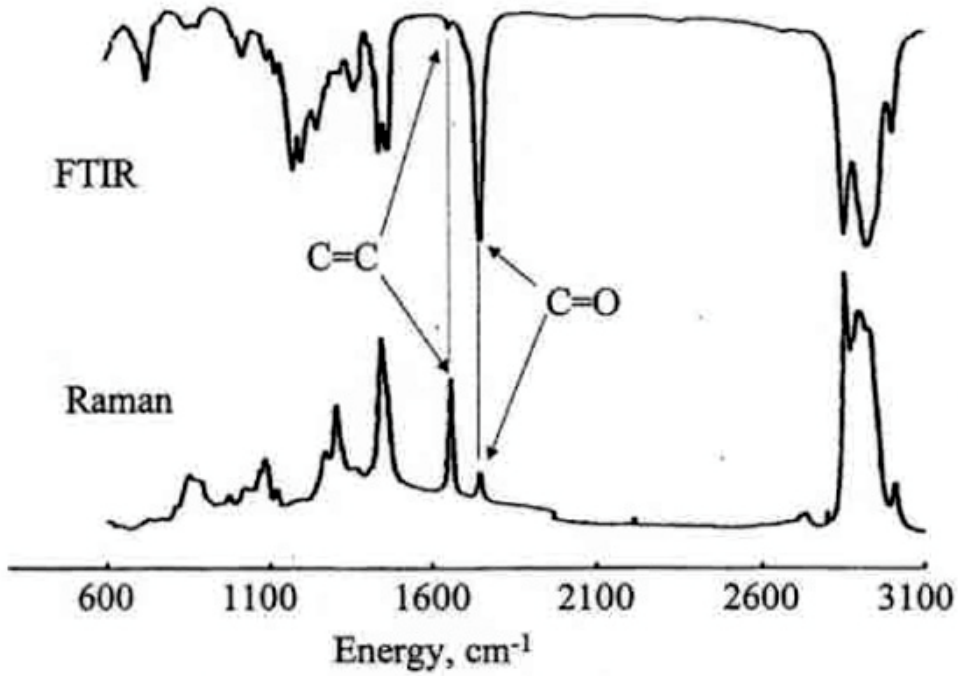


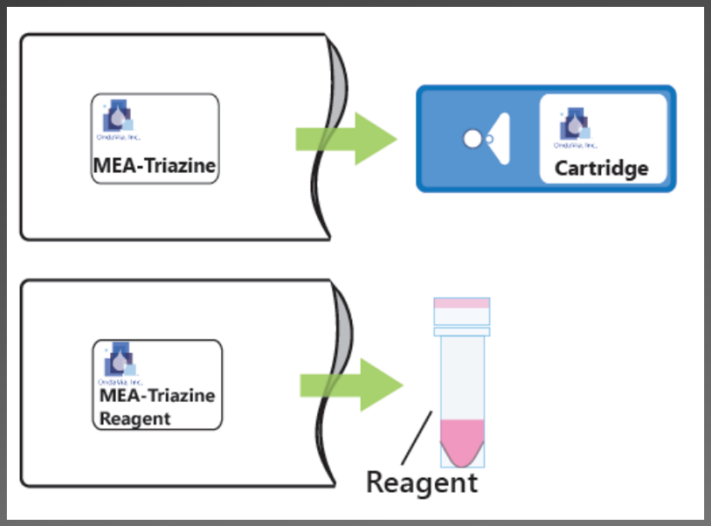
Figure 2.2. FTIR (upper) transmission and Raman scattering (lower) of oleic acid methyl ester.

Experimental setup

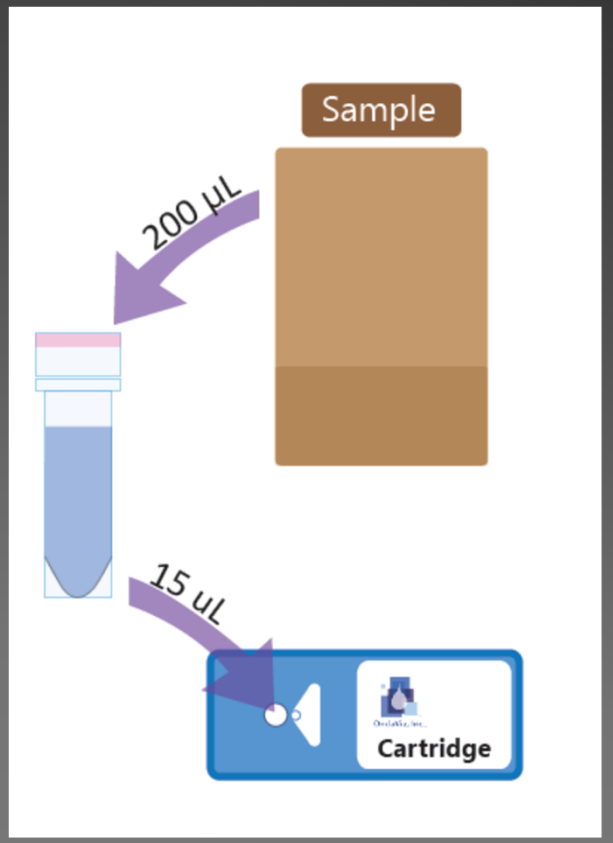
- Spectrometer
  - 785-nm, 60-mW at substrate
  - Cooled (-20°C) detector
  - 200-2000-cm^{-1}, 4-cm^{-1} resolution
  - Weight: 16 lbs
  - Power: 12-V, 2-A

Quantification?

1

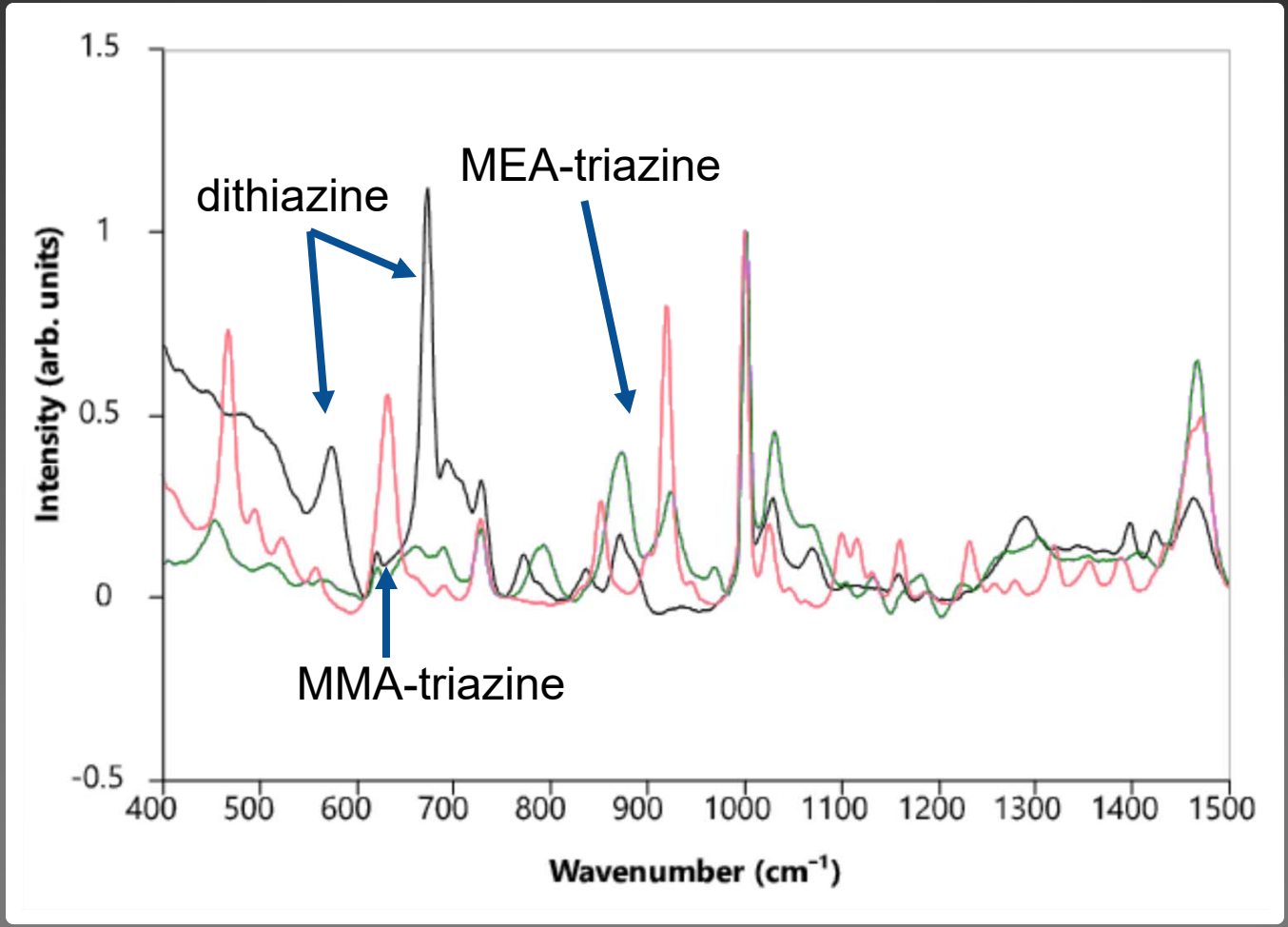


2

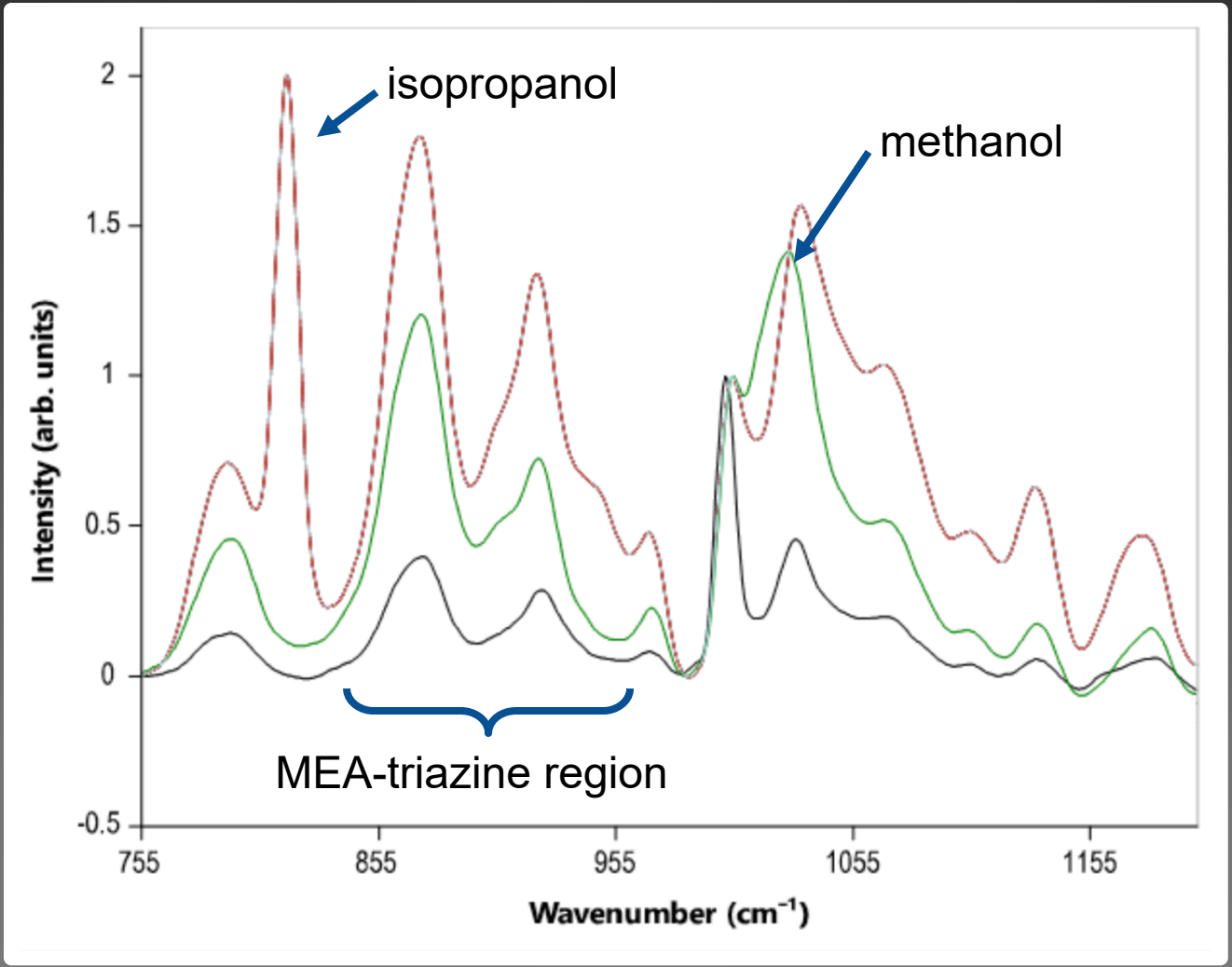


Total Analysis Time: 2 minutes

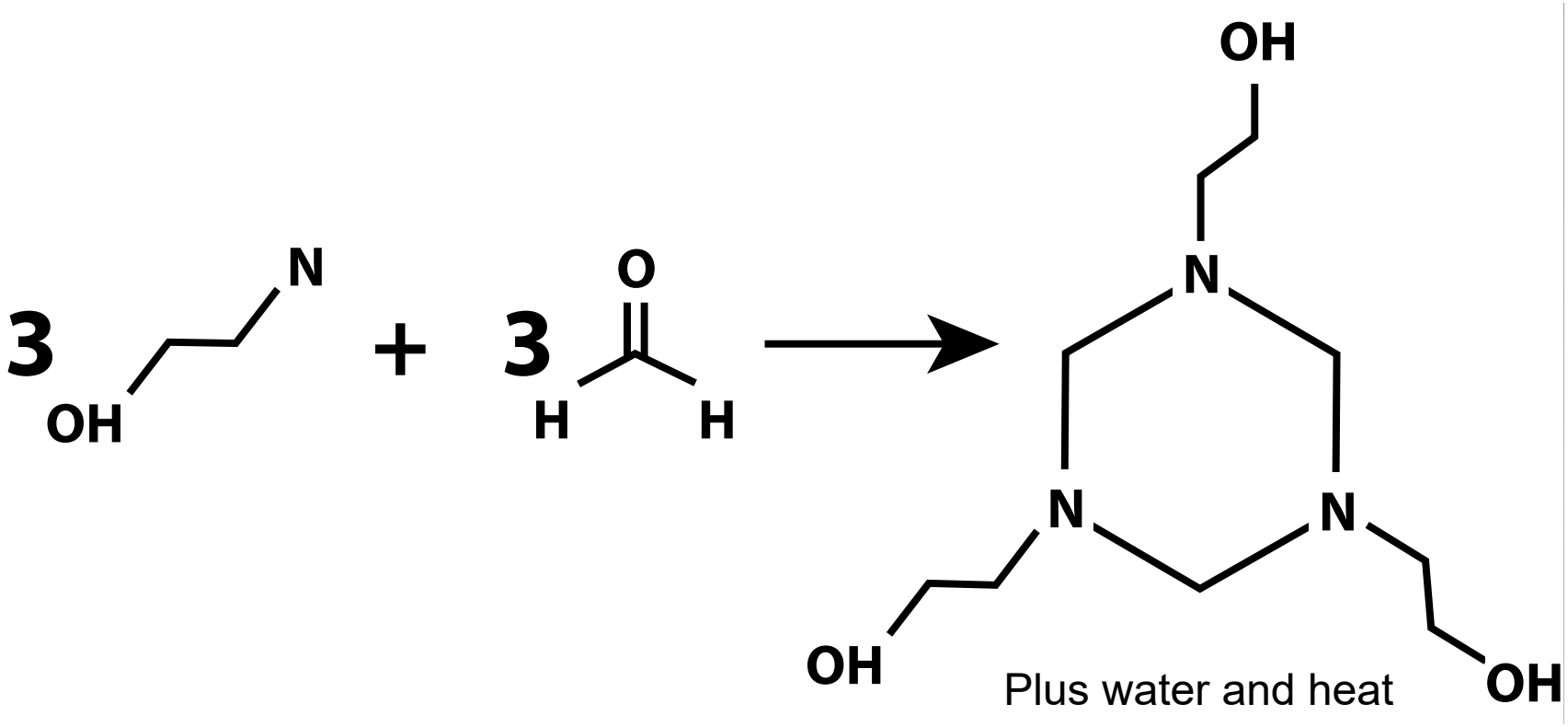
Raman spectra



Common solvents

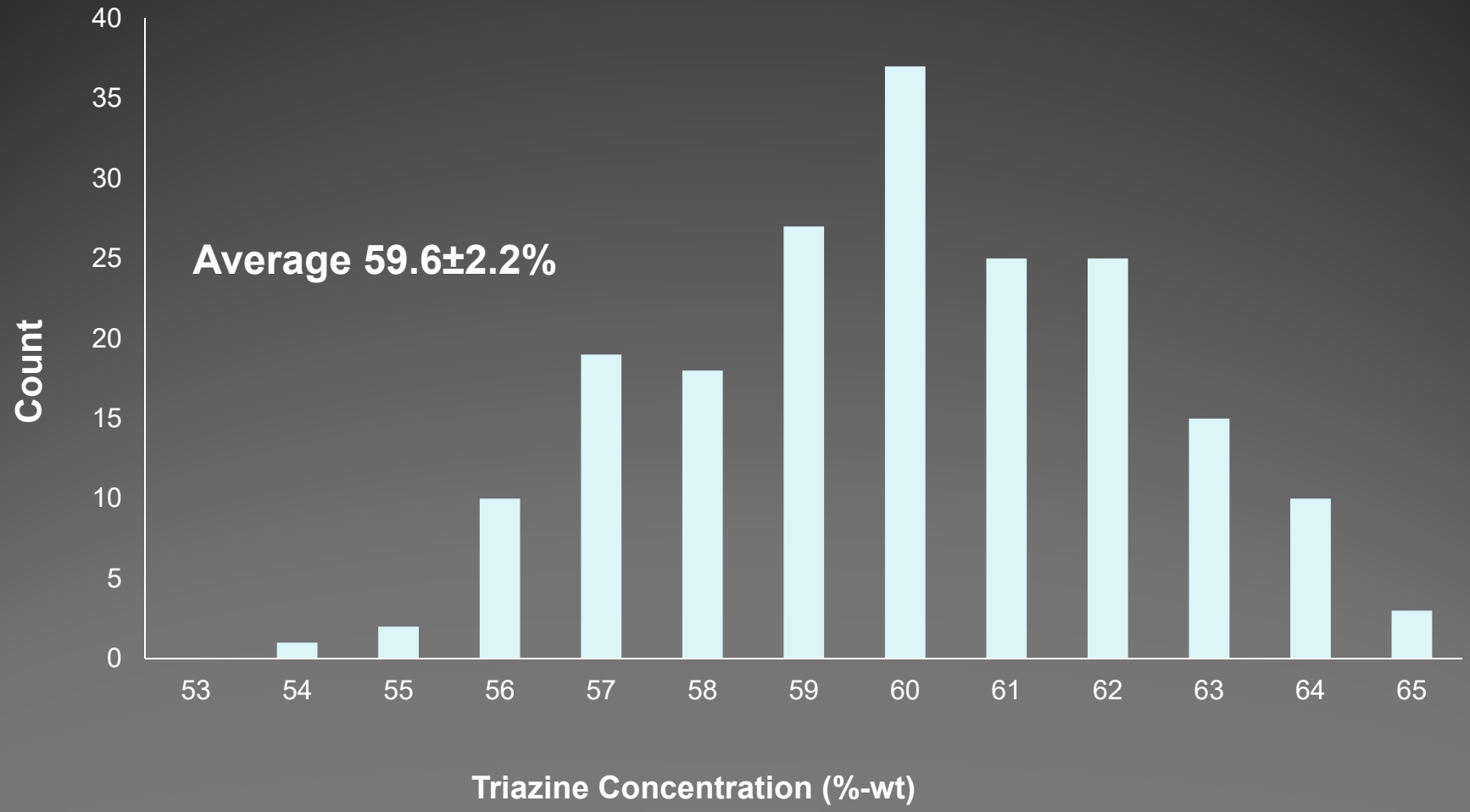


Triazine manufacturing

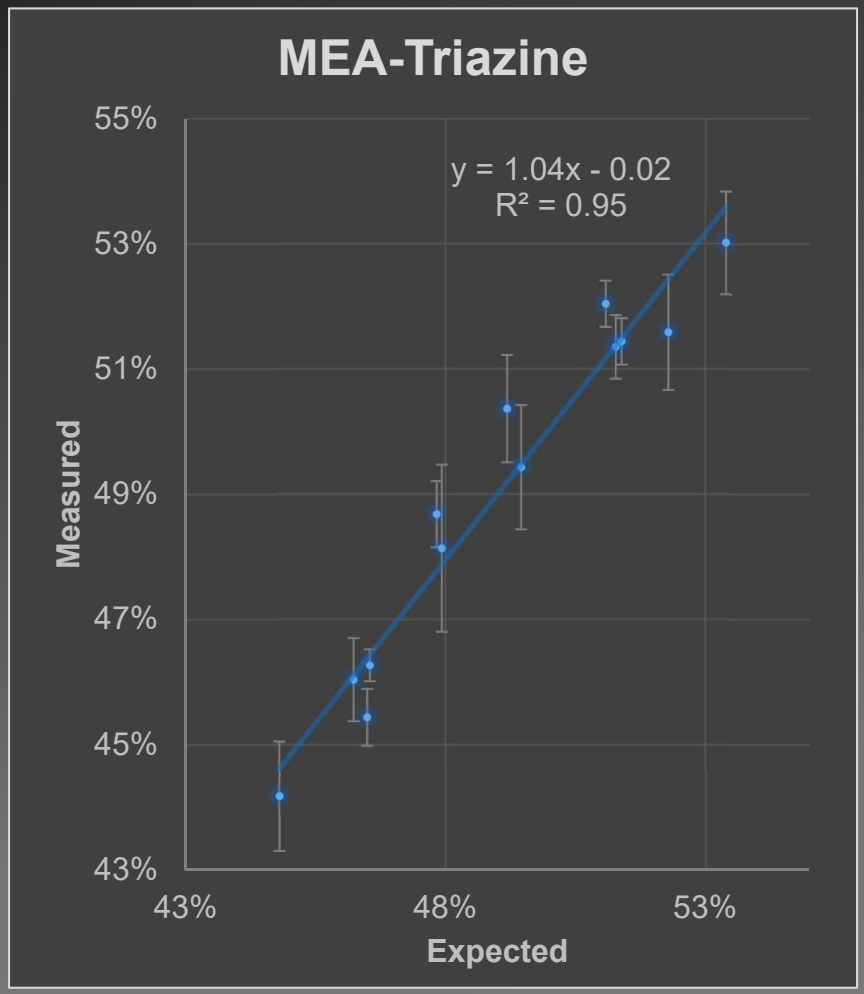


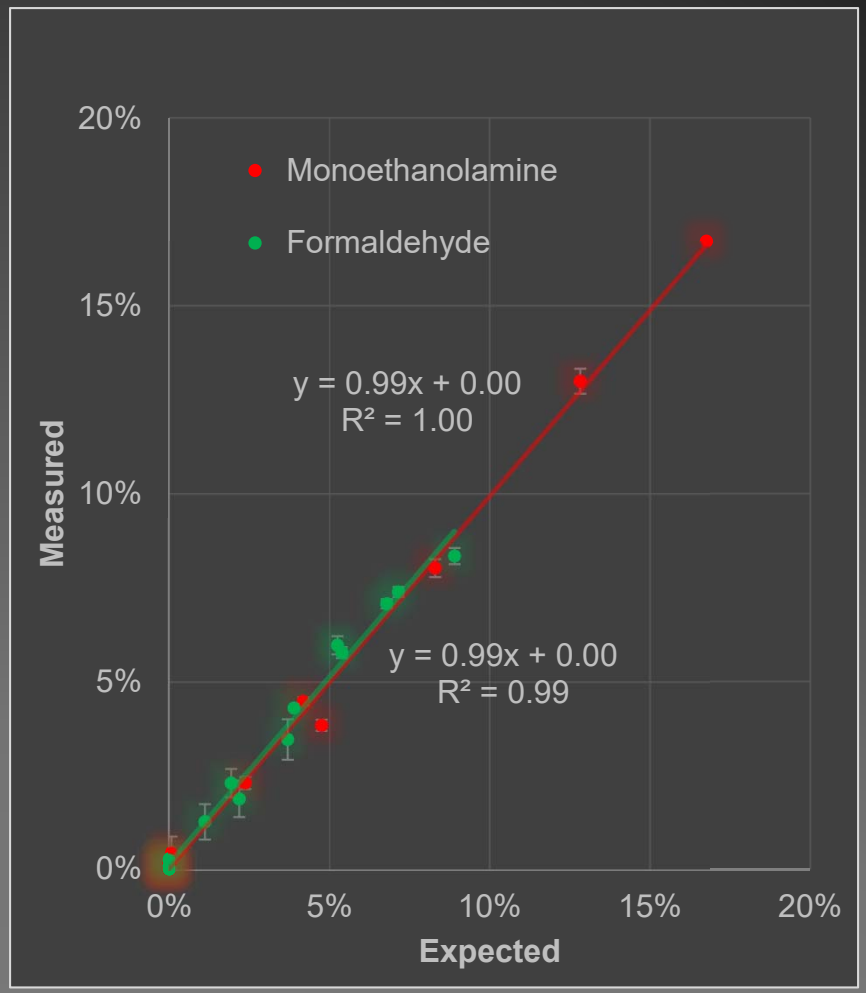
- Typically 60-80% solutions
- But there are many low quality suppliers in the marketplace

Triazine manufacturing QA/QC



Triazine manufacturing QA/QC





MEA-triazine field samples

High dithiazine levels lead to phase separation and less predictable fluid dynamics

- Spent H_2S scavenger
  - Injected at 46% triazine
  - Sampled at multiple points after scavenger injection

Mixer	Triazine (% wt)	Dithiazine (% wt)
#1	42	4
#2	45	17
#3	49	19
#4	51	19

Dithiazine: Raman vs lab

- Spent H_2S scavenger
  - Analysis via Raman spectroscopy
  - Analysis via total sulfur measurement using combustion
- Samples #3a-3c are dilutions of Sample #3

Sample	Combustion (% wt)	OndaVia (% wt)
#1	3	3
#2	6	7
#3	10	10
#4	17	17
#5	24	24
#3a	7	7
#3b	5	4
#3c	2	3

Arbitrary analysis range

Method is ratiometric, only IS to sample ratio matters

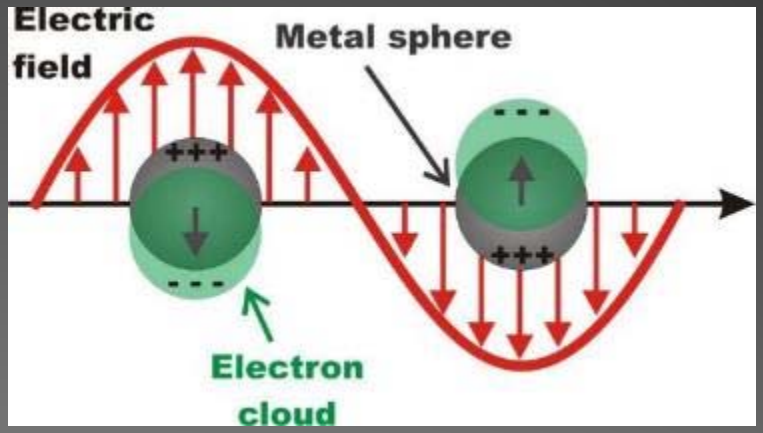
- Reagent contains **100µl** of internal standard plus 800µl water
  - Dithiazine (5-30%)
    - **100µl** sample
  - Triazine (5-45%)
    - **200µl** of sample

- If the user adds 500µl sample to the dithiazine reagent, the results will be 5× high.
  - The 5-30% test becomes 1-6%
- **The triazine 5-45% test can be used directly as a 2.5-15% dithiazine test**

One prep, multiple measurements

Surface enhancement

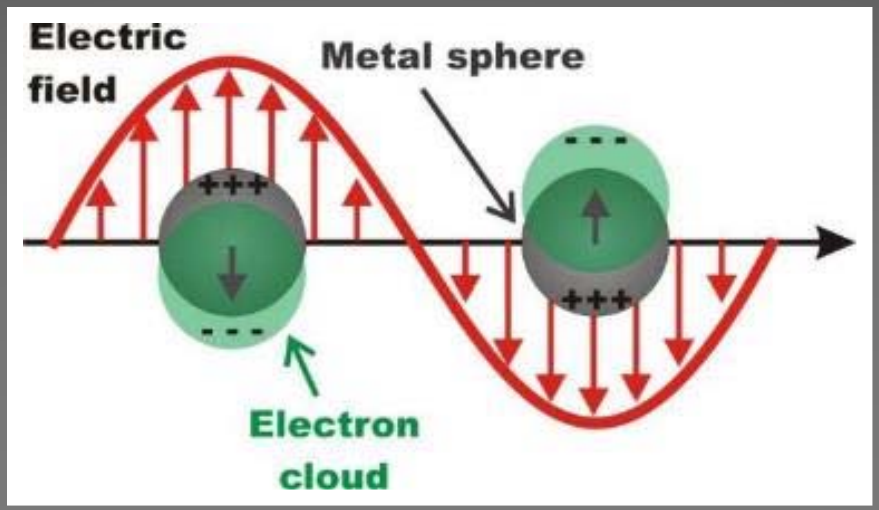
- Normal Raman
  - $\sigma_{NR} \sim 10^{-30}$ cm^2/molecule
  - **1 in 10 million photons**
- LSPR enhancement
- SERS
  - Enhancement factor (EF)
  - EF up to 10^{10}
  - $\sigma_{SERS} = \sigma_{NR} \bullet EF$



$$EF = \frac{I_{SERS} / N_{surf}}{I_{Raman} / N_{vol}}$$

Localized Surface Plasmon Resonance

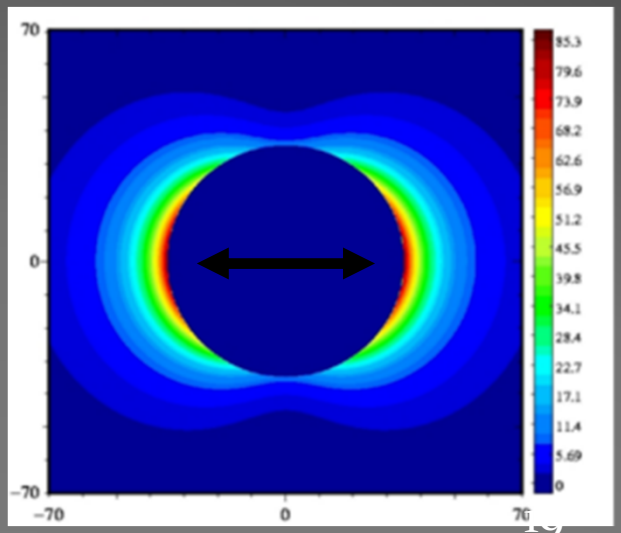
- LSPR is an oscillation of charge (e^-) at metal-dielectric interface
- Two main effects:
  1. Wavelength-specific extinction
  2. Enhanced EM field at surface



Surface-Enhanced Raman Scattering (SERS)

- LSPR causes increased field intensity at surface
- Probe molecules at rough metal surface
  - Increased Raman signal
  - Fluorescence quenching (radiationless decay)
- SERS activity quantified by Enhancement Factor
  - EF range: 1 - 10^{10}

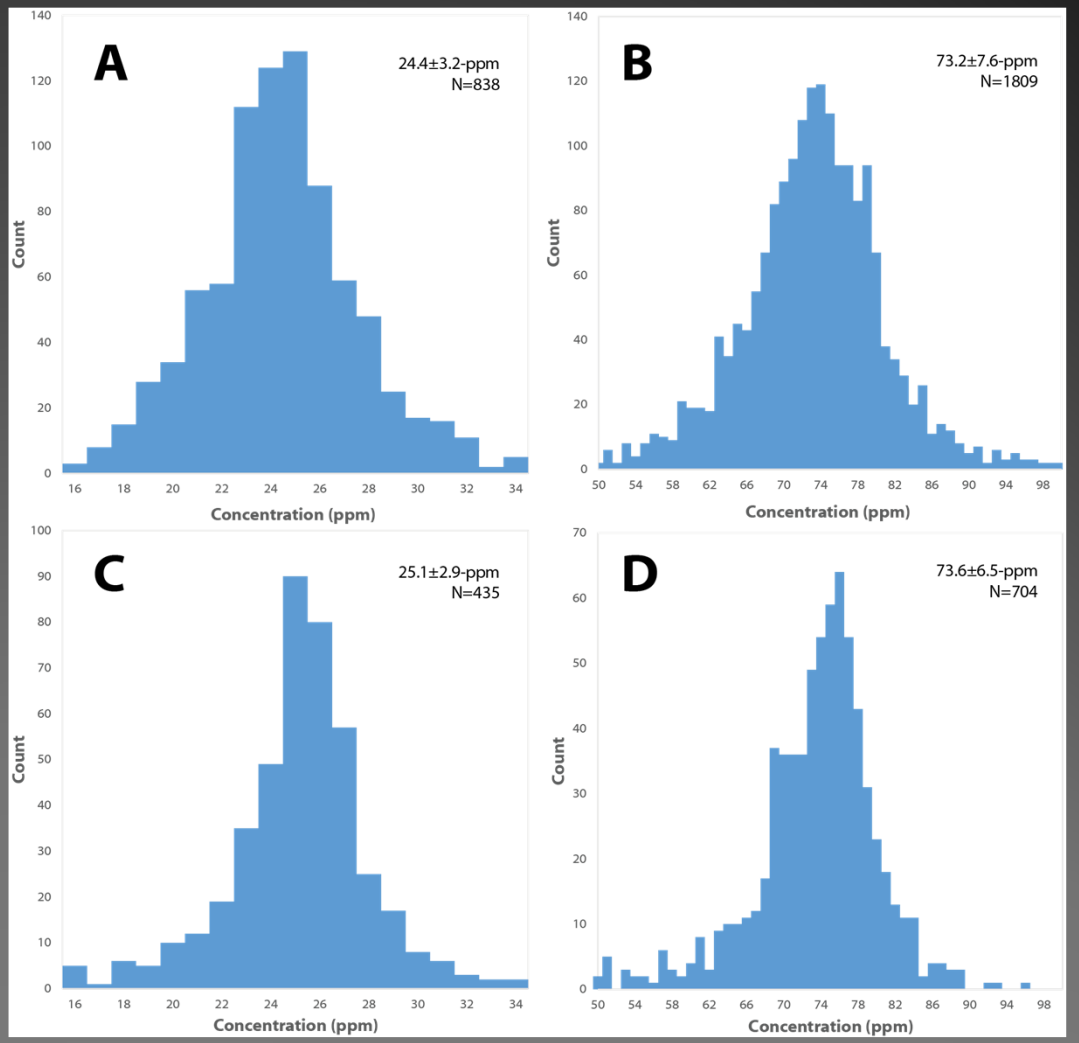
$$EF = \frac{I_{SERS} / N_{surf}}{I_{Raman} / N_{vol}}$$



Trace-level analysis

Combine internal standards with gold nanoparticles for quantitative, trace-level analysis

>2000 data points for ethanolamine (and methylamine) over four years, 25 spectrometers, and one cal curve



H_2S monitoring during drilling

- The H_2S level in the mud can vary due to gas pockets
- Dose scavenger to maximum expected H_2S level?
  - Expensive: wasted chemicals (=money)
  - Risky: what if your expectation is wrong?

- Why not monitor the scavenger concentration?
  - Decrease in scavenger = increase in H_2S

Questions?

Special thanks to…

NATIONAL INSTITUTES OF HEALTH

NSF

USDA

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