

# Be Careful What You Ask For

A Grammatically Challenged Advisory on Analytical Testing Requests

Presented to ***Crude Oil Quality Association***

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WHEN YOU NEED TO BE SURE





# Obvious Problem/Not So Obvious Solution

Heater tubes in a coker are fouling. Analysis of the scrapings off the tubes reveal the presence of a large amount of calcium. The first instinct is to measure the calcium level in the feedstock. But what will that tell you about how to resolve your problem?



## Things to consider

- Analysis of the feedstock will tell you the amount of available calcium.
- Most of the available calcium will be ionic, and therefore water soluble.
- Will the calcium wash out in the desalter?
  - Tendency to form oil-soluble calcium naphthenates is pH dependent
  - What level of pH control exists in the desalter?
  - What is the capacity/efficiency of the desalter?



## Calcium in My Coker Saga (Cont)

- Analyze before and after desalter?
- Special sample prep to mimic ideal pH conditions?
- Wash water adding to problem?
- Hmmmmmmmmmm?



## Silicon/ Silica/ Silicone Silly Misunderstandings

- Most of us know the differences between the three forms of silicon listed above
- ASTM and IP methods are for elemental silicon. Silica ( $\text{SiO}_2$ ) can be calculated by multiplying silicon results by 2.14
- Silicates –  $(\text{Na}_2\text{O})_x(\text{SiO}_2)_y(\text{H}_2\text{O})_z$
- Silicone is a different animal altogether....



## Silicon/ Silica/ Silicates/Silicones

- Silicon, silica, and silicates are usually sourced from sediment normally found in crude oil-natural origins
- During refining they can be flushed from the system at the desalter, but much of the silica will partition to the bottom of the atmospheric tower, then to the bottom of the vacuum tower.
- Silicones are not natural, and usually are added to crude as defoaming agents or as demulsifiers.



## The Skinny on Silicone

- Inherently difficult to quantify
  - Organically bound/Affects different areas of the process than silica
  - Sample prep for silicon/silica will burn off relatively volatile silicone
  - Organic dilutions of oil assumes silica will drop out of solution, and sometimes it does, but fine silica particles can be aspirated into an AA or ICP

## Possible Analytical Approaches

- Filtration to remove inorganic silica, but be mindful of the filter media used. Glass fiber filters are not a good choice..
  
- Entirely different analytical approaches
  - Smith, A. L. *The Analytical Chemistry of Silicones*, John Wiley & Sons, Inc.: New York, 1991.



## Silicones, (Cont'd)

- FTIR (Max absorbance at 1259.82 wavenumbers)
- GC or GC-MS looking for the presence and quantity of siloxane cyclic oligomers that are always associated with polymers
- Gel Permeation Chromatography, Supercritical Fluid Chromatography
- Proton NMR (Chemical shift for SiH is 4.7 ppm). Si29 NMR is possible but detection limits are not as good as with H1 NMR
- WDXRF is possible but sample prep is tedious (as with AA and ICP).



## How Solid are Your Methanol Results?

- Most methanol in crude test results are derived from D7059 or an analogous multi-dimensional GC method.
  - Detection limit is 15 ppm
  - Restricted to samples that are 0.1 v/v % water
  - Reproducibility is about +/- 50% at lower end and about +/- 25% at 50 ppm



## Other Practical Tests for Methanol

- In-line NMR

Basically just an indicator that a slug of ethanol is coming down the pipe

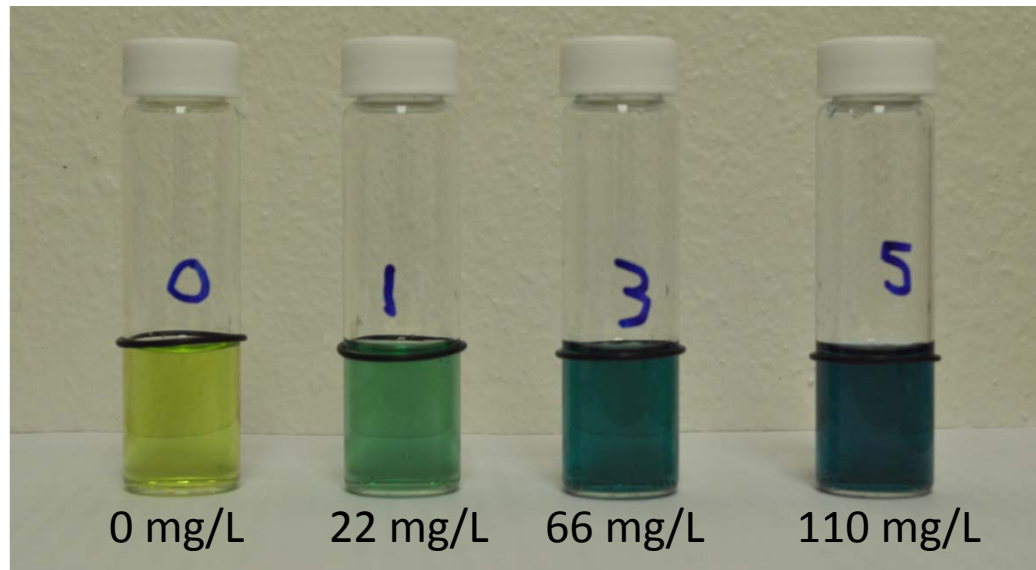
- NIR/FT-NIR

Better precision than the ASTM GC procedure

Detection limits not as good

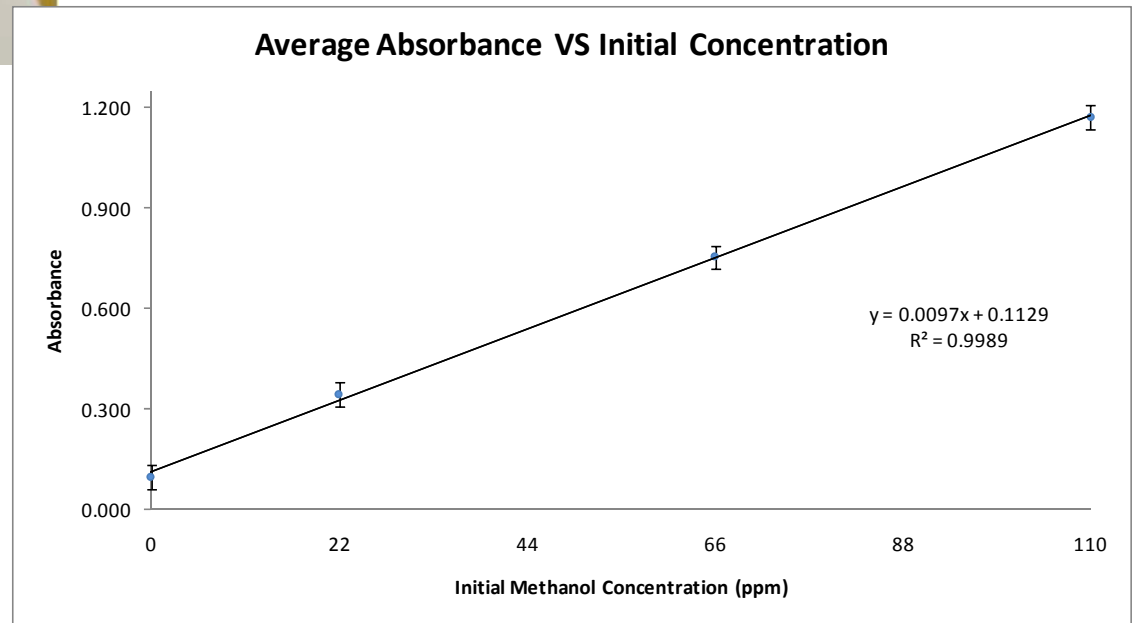
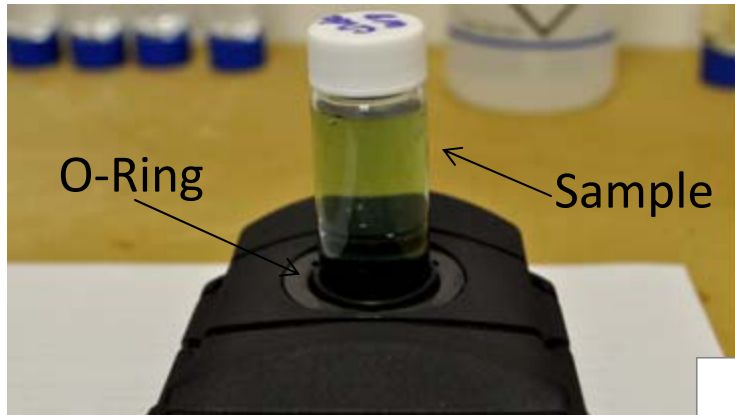
## Methanol in Crude Oil

- Colorimetric field test for methanol content in crude
- 5 mls of sample is extracted with water, oxidized, neutralized, and color is developed



## Methanol in Crude Oil

- Color is read using a portable spectrophotometer





## Summary

Information in and of itself is interesting.

Information in context with your particular analytical challenge is valuable.

Information that is the answer to your specific operational challenge is priceless.