Portable SERS Analysis for Industrial and Environmental Applications

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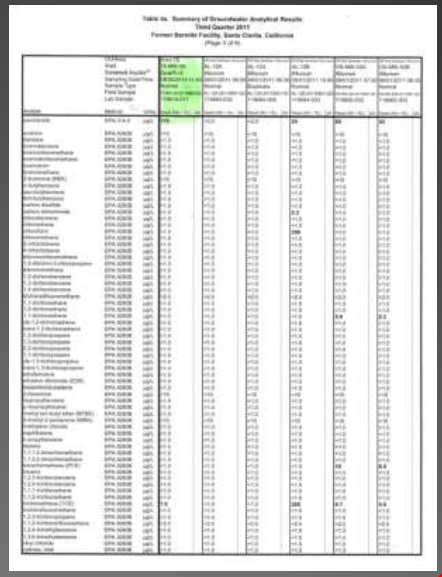
The Question

Can we replace this…

FedEx



…with a portable Raman spectrometer?

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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

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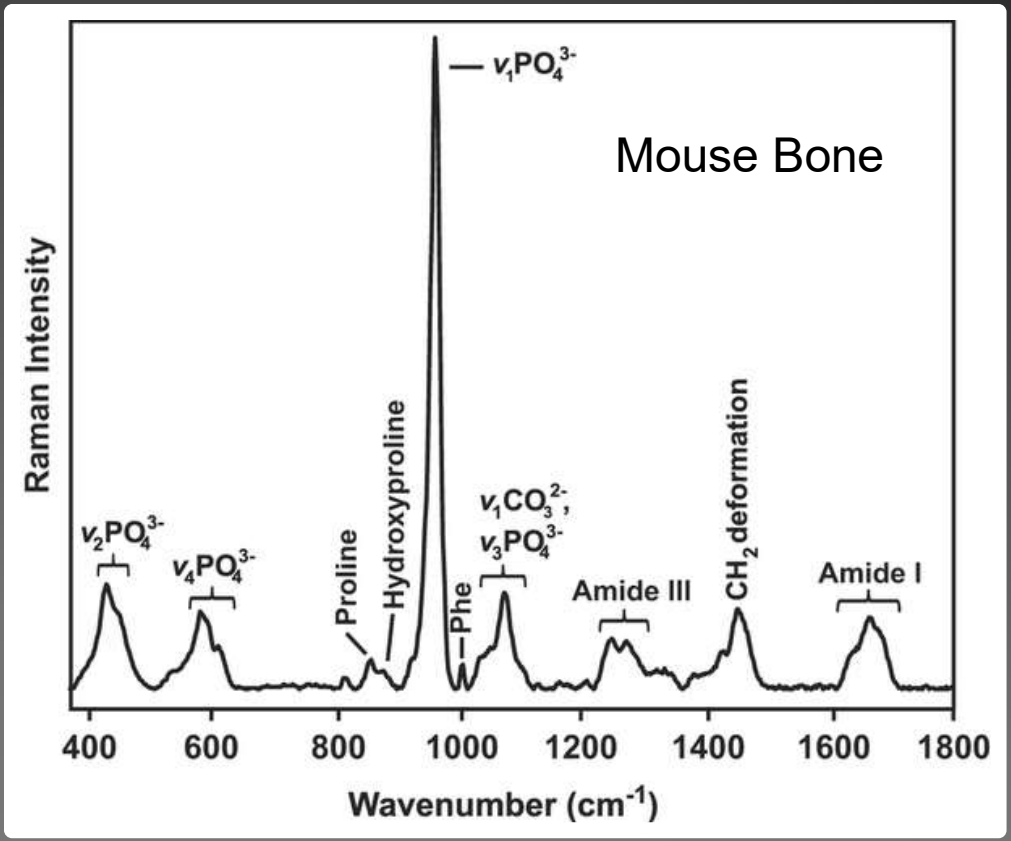
Raman spectroscopy

- Molecular fingerprints / structure
- Works with water
- Completely optical

- Portable
- Commercially available



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Experimental setup

- Spectrometer
  - 785-nm, 60-mW at substrate
  - Cooled (-20°C) detector
  - 200-2000-cm^{-1}, 4-cm^{-1} resolution

- Analyte-specific test kits
  - Colloidal gold nanoparticles
  - Sample holding cartridge

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Quantification of **%-level** hydrogen sulfide scavengers using Raman spectroscopy

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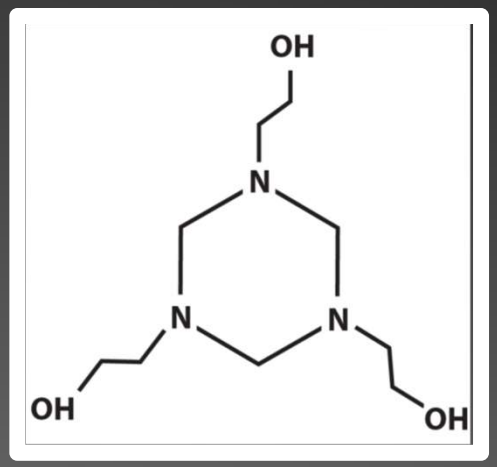
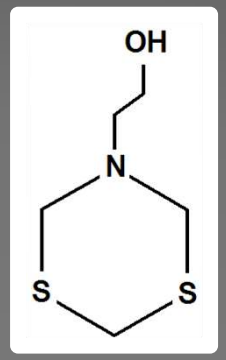
Hydrogen sulfide scavengers

- Used to remove corrosive H_2S from oil and gas streams (sour)
- Triazine-based materials are popular and convenient
- But there exist no field methods to monitor content and analyze the reaction



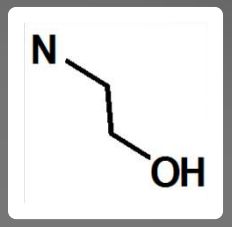
+ 2 H_2S

MEA-triazine



dithiazine

+ 2



ethanolamine

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

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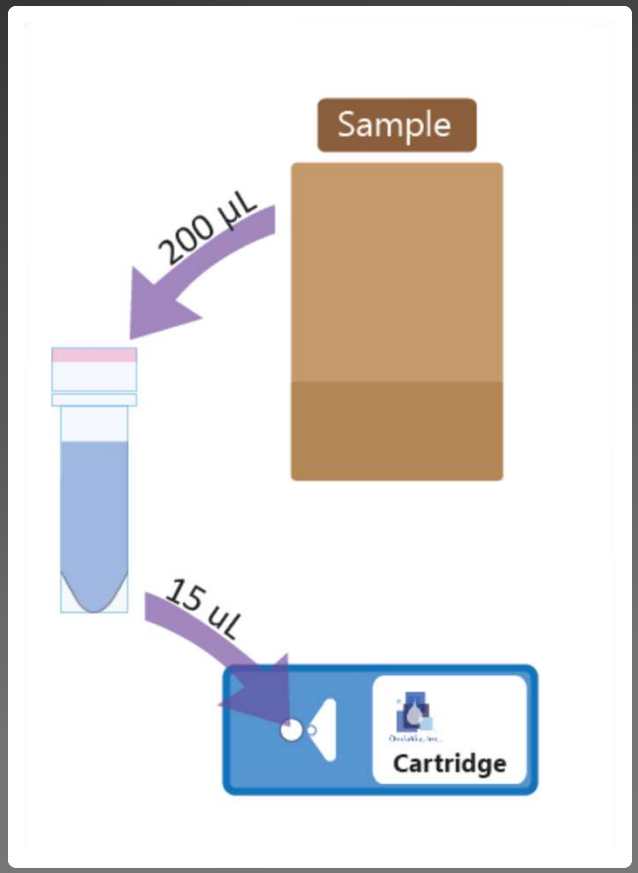
Method



Total Analysis Time: 2 minutes

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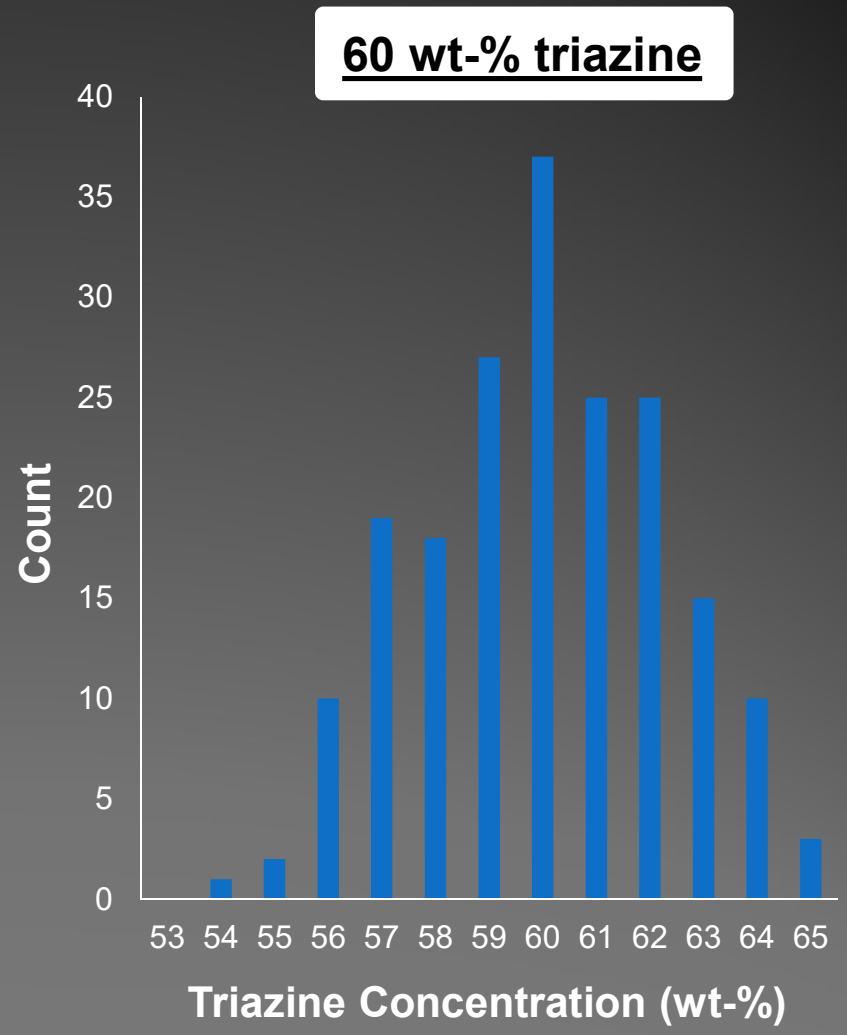
Results

- MEA-triazine manufacturing
  - Typically 60-80% solutions
  - Alternative: UV/vis after four hour derivatization process
- Spent H_2S scavenger

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



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Analysis of **ppm-level** amines in refinery process waters using SERS

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Raman spectroscopy

1920s 

1990s 

2000s 

But not sensitive

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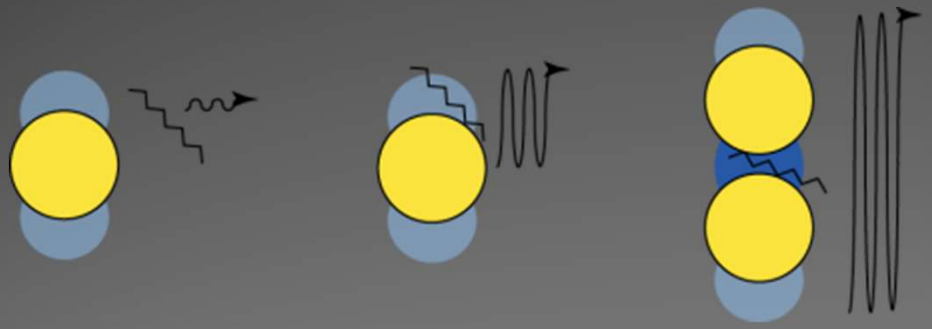
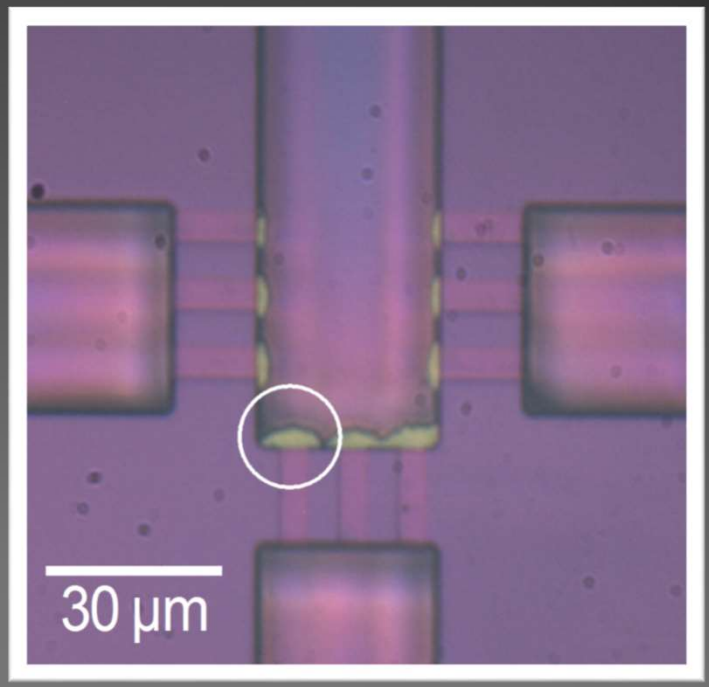
Trace-level detection

Use **Surface-Enhanced Raman Spectroscopy (SERS)** …

Gold nanoparticles enable ppb-level detection





… even though, as one grant reviewer said, “SERS doesn’t work”

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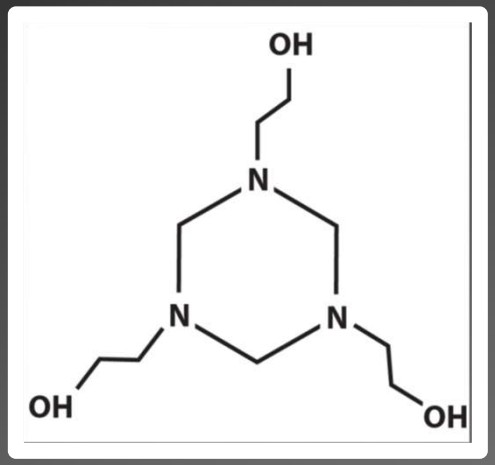
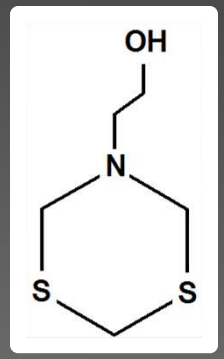
Hydrogen sulfide scavengers



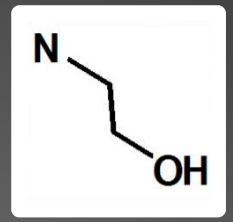
MEA-triazine

+ 2 H_2S



dithiazine

+ 2



ethanolamine

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Amines in refinery process waters

- Residual “tramp amines” from upstream H_2S scavenging processes
  - Leads to heat stable salts that form corrosive deposits
- Process unit “leakage” into waste water streams
  - Costs money due to wasted/lost materials
- Monoethanolamine, methylamine, diethanolamine, methyldiethanolamine

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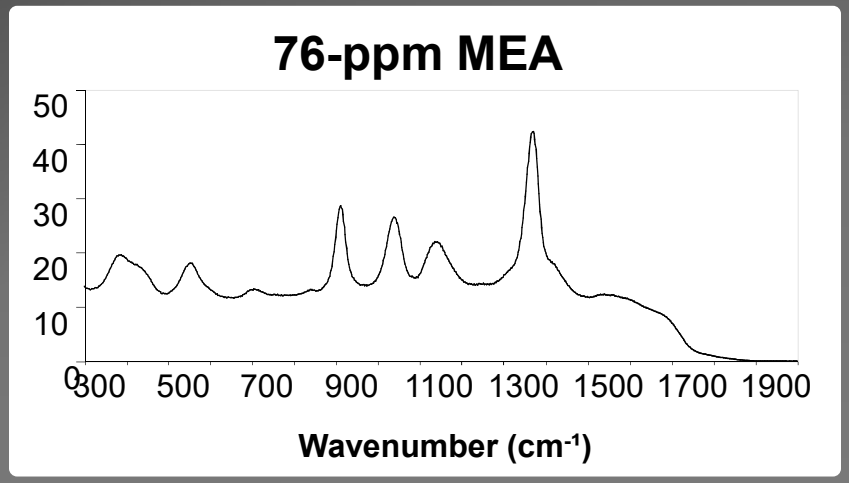
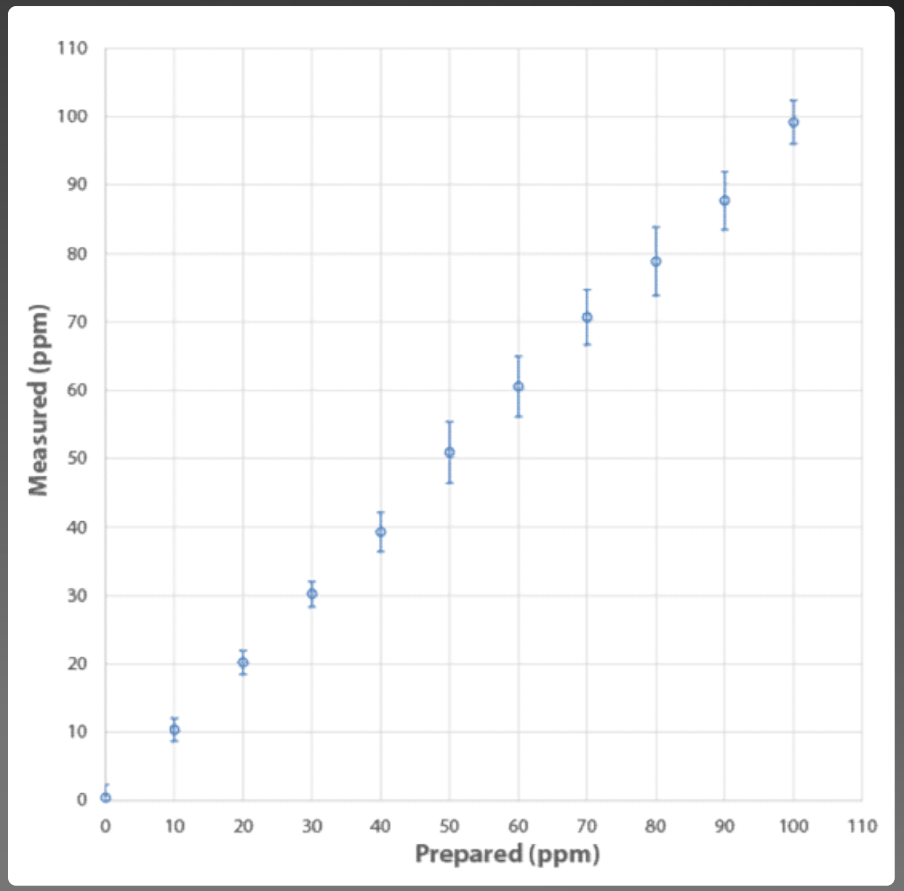
Ethanolamine analysis

- Lab method: IC or GC
- SERS method
  - Adjust sample to pH 12.7
  - Mix with nanoparticles (total 14:1 sample dilution)
  - Take spectrum





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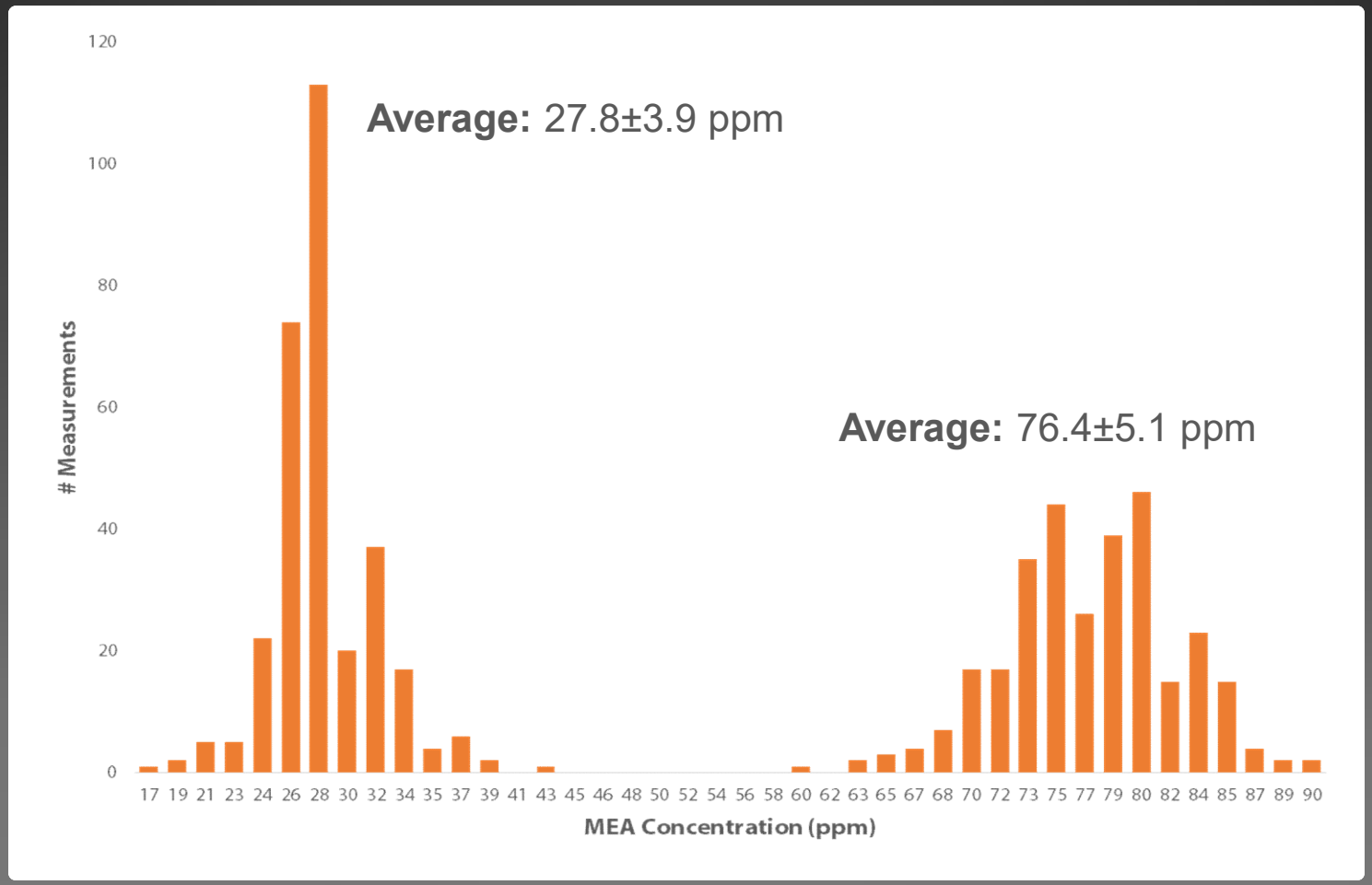
Repeatability



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Amines in sour water

- Samples contain organic acids, salts, and hydrocarbons
- Use solid-phase extraction to remove anionic interferences

Sample	IC (ppm)	OndaVia (ppm)
#1	62	59
#2	38	40
#3	92	96
#4	2	3
#5	1600	1520*

* with 20:1 dilution

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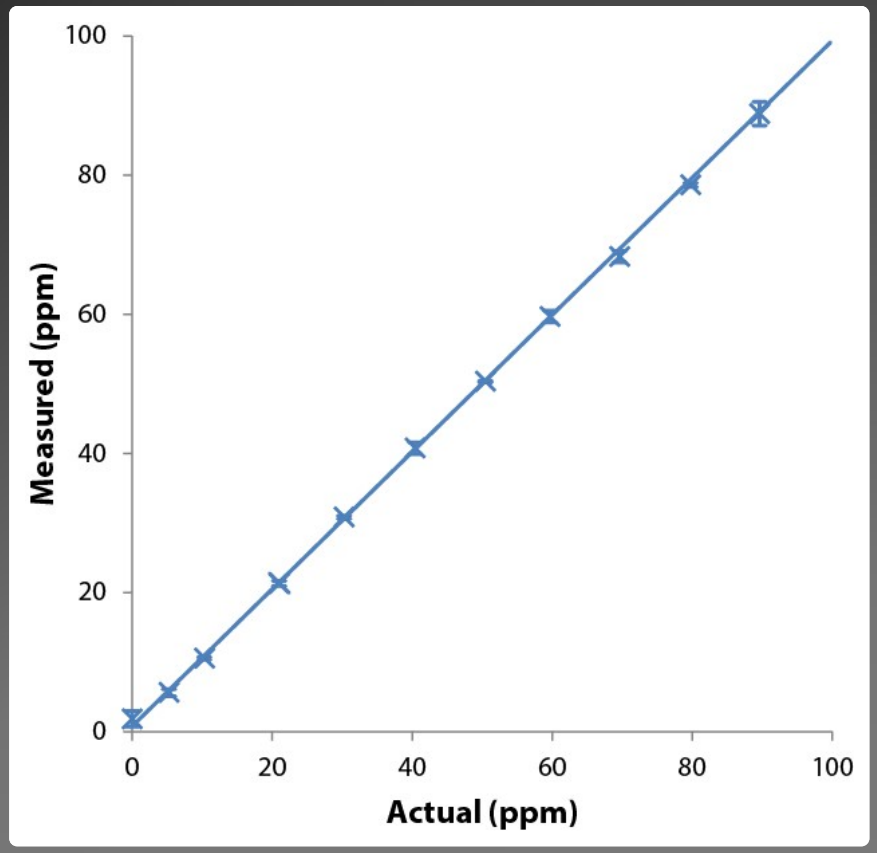
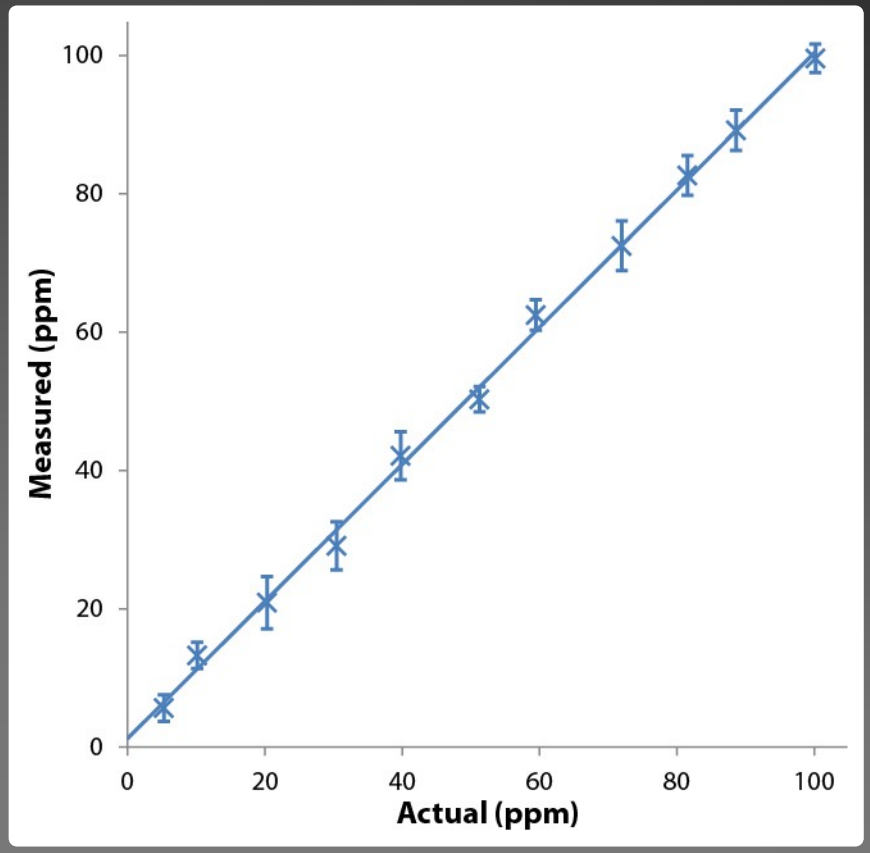
Other amines

Methylamine



Diethanolamine



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Oxyanion quantification and speciation at **ppb-levels**

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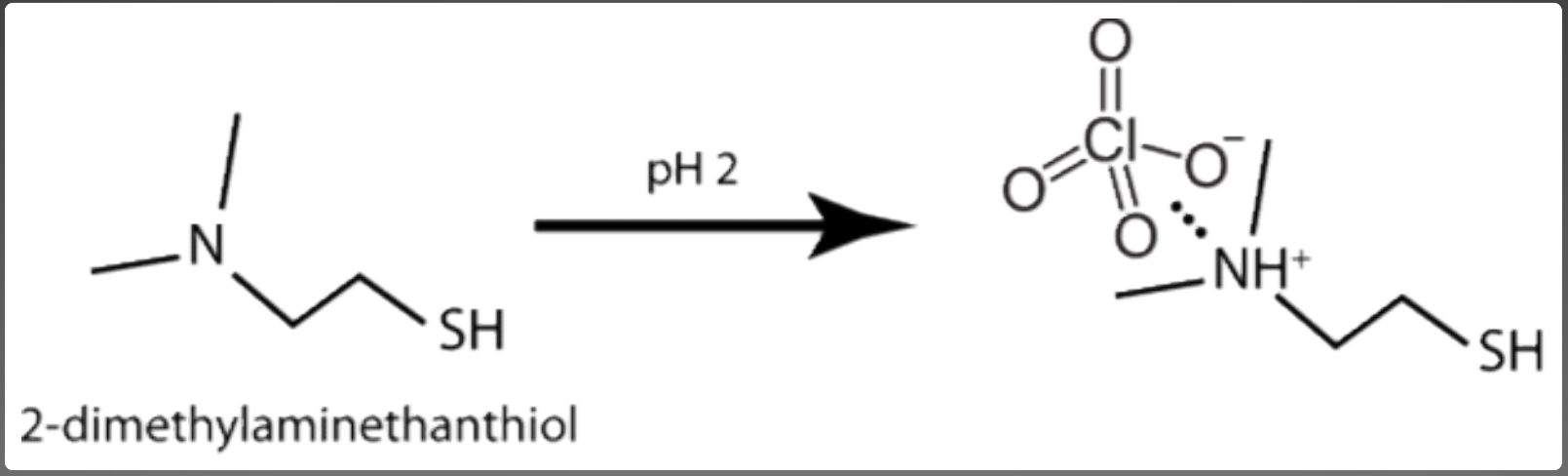
Surface Treatments

If you want to detect ions…

…look to ion chromatography and ion exchange



Gu, Baohua, *et al*. "Raman spectroscopic detection for perchlorate at low concentrations." *Applied Spectroscopy* 58.6 (2004): 741-744.

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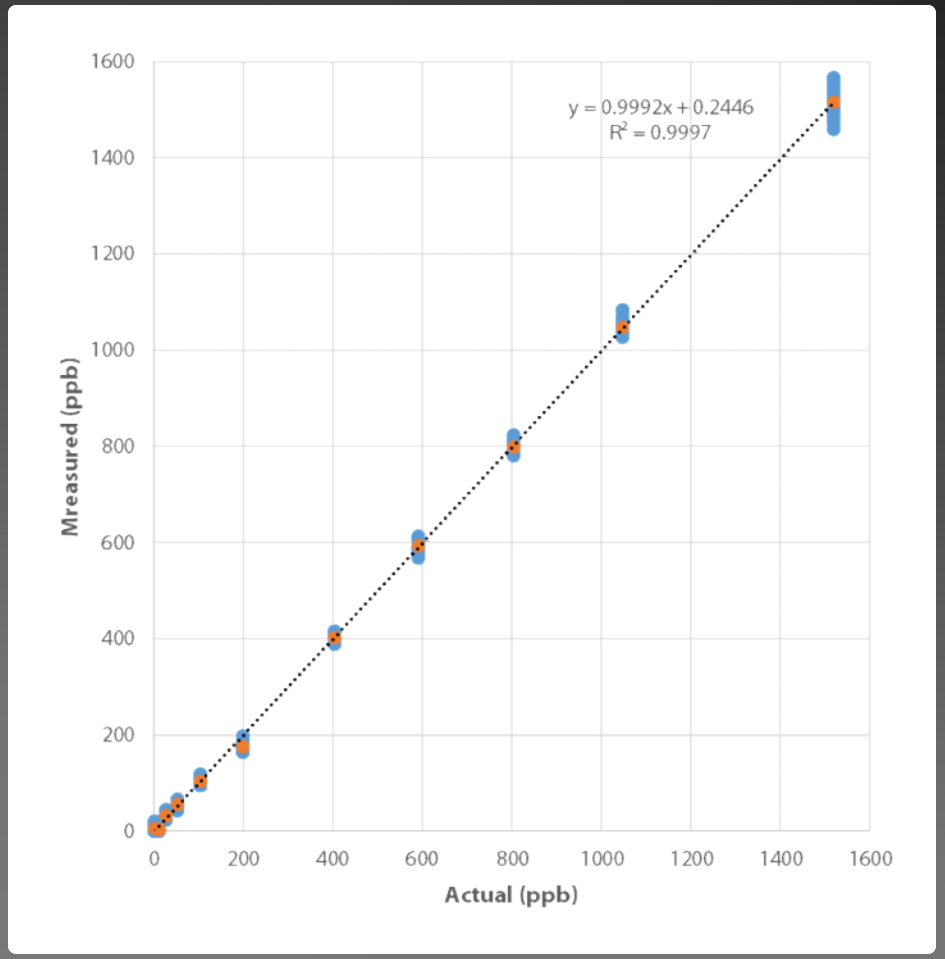
Selenium analysis

- Specific to selenate, Se(VI)
- Applications
  - Refinery waste water
  - Coal-fired power plants / flue-gas desulfurization water
- Detection limit better than 10-ppb



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Selenium speciation

- Se reduced during biological treatment of waste water…
- …so oxidize using bleach to convert all Se(IV) to Se(VI)

Total selenium (ppb)		Selenate (ppb)		Selenite (ppb)	
ICP-MS	*OV*	*ICP-MS*	*OV*	*ICP-MS*	*OV*
101	98	25	29	76	69
114	113	27	29	84	84
78	82	31	39	47	43

Fieldable speciation test:

- First measure Se(VI)
- Oxidize to determine total
- Se(IV) is the difference

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Arsenic analysis

- Exists in natural waters predominantly as arsenite [As(III)] and arsenate [As(V)]
- Regulatory requirement:
  - 10-ppb *total* As in drinking water
  - As(III) is more hazardous that As(V)

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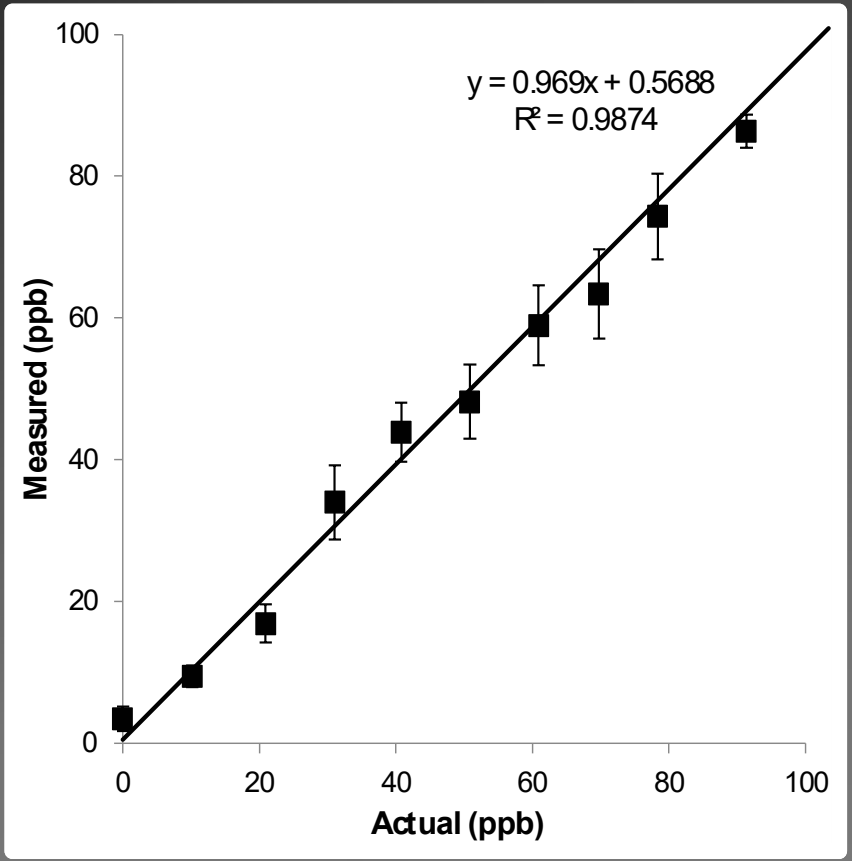
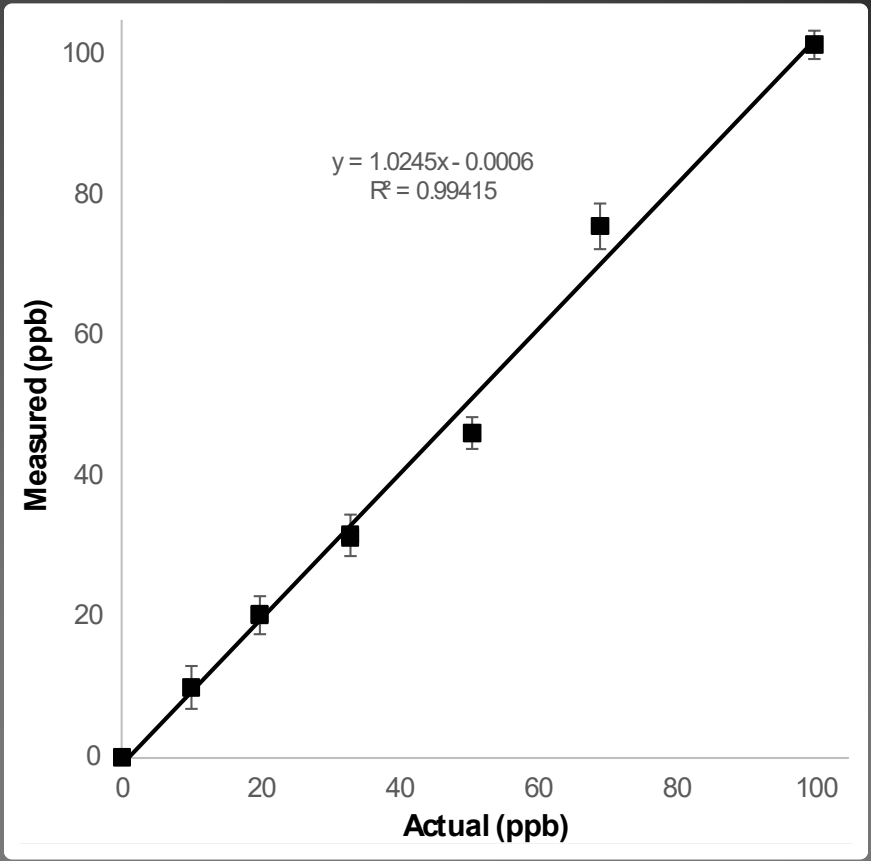
Arsenic speciation

Arsenite [As(III)]



Arsenate [As(V)]



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Lead in drinking water at **ppb levels**

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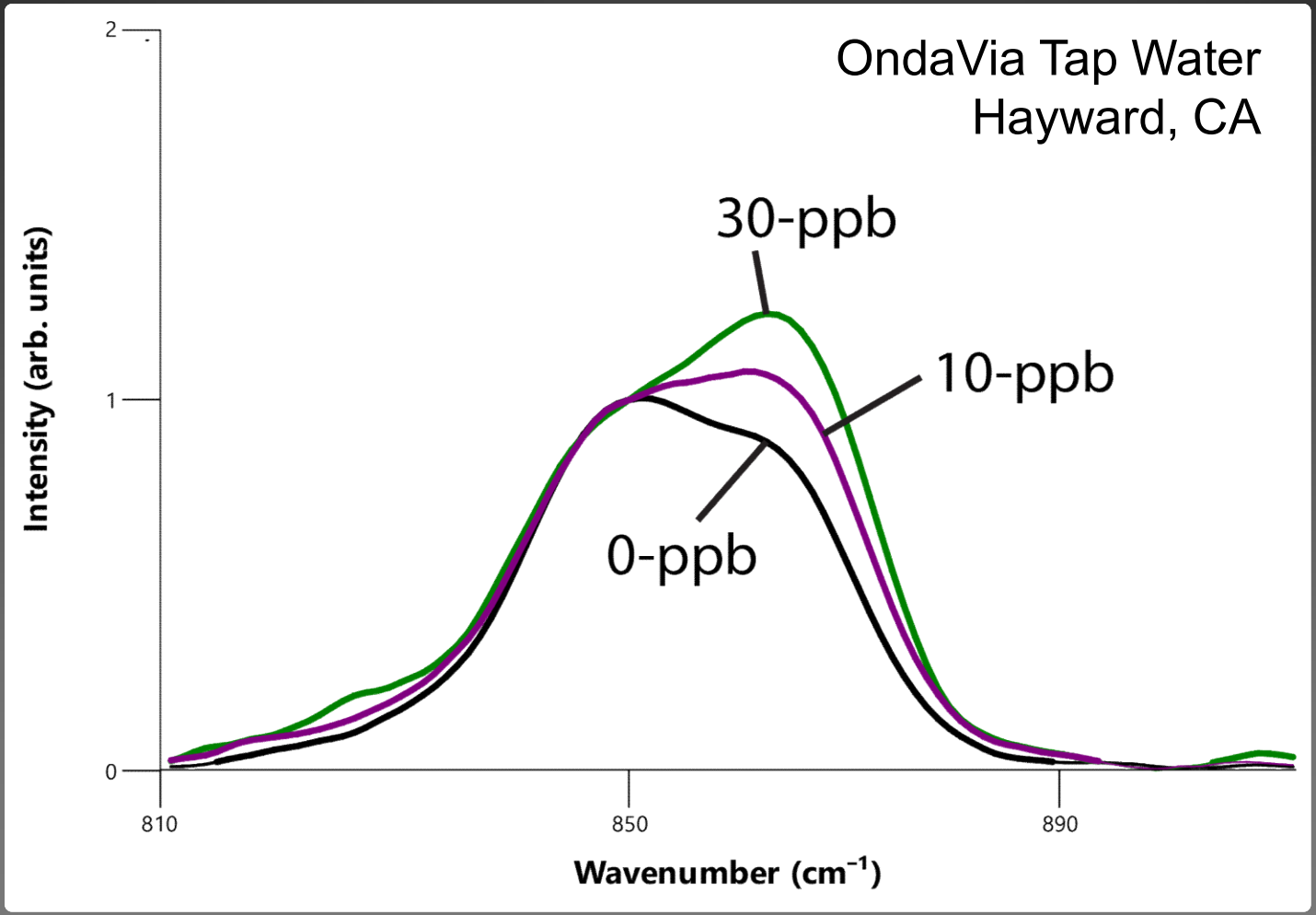
Lead-spiked tap water



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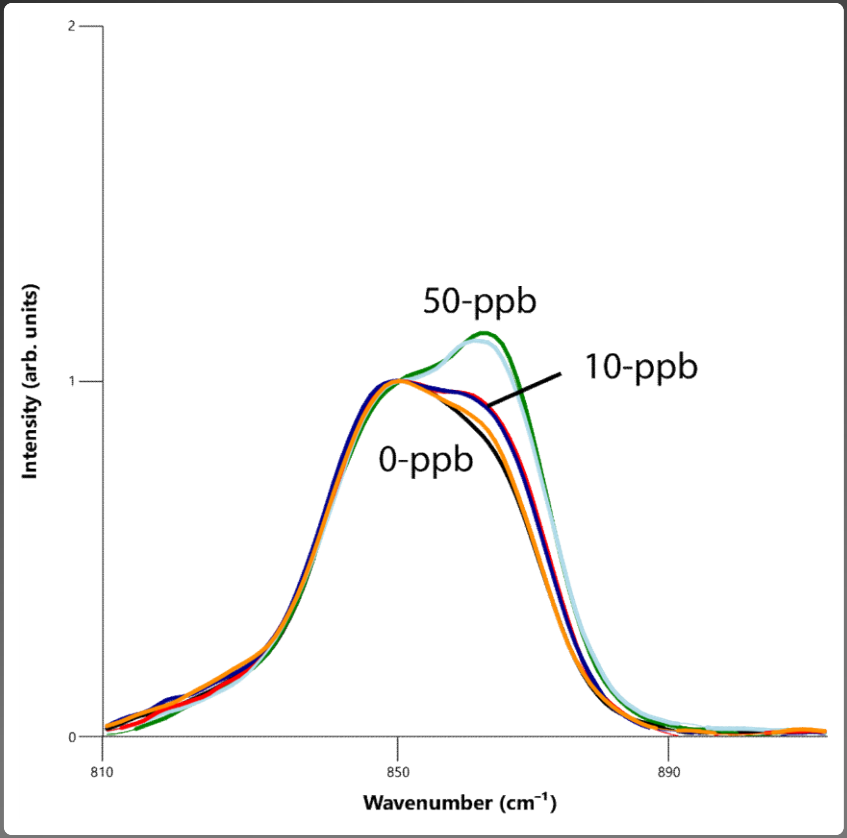
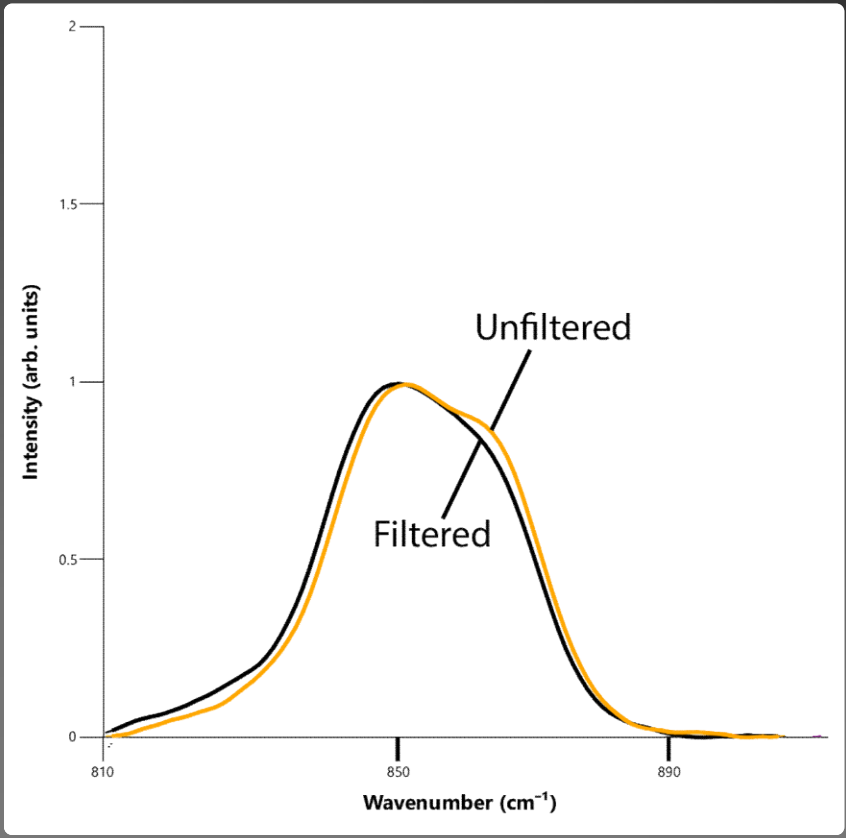
Lead-spiked tap water

Consumer Filter Pitcher



Filtered vs. Unfiltered



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Potential to replace methods

- Simple and easy-to-use
- Fast
- Portable

- Replaces
  - IC (amines, oxyanions, alkaline earths)
  - GC (TCE, BTEX, amines, disinfection by-products)
  - HG-AAS, ICP/MS (metals)

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Questions?

Special thanks to...

NATIONAL INSTITUTES OF HEALTH

NSF

USDA

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