Raman Spectroscopy for Environmental Analysis

Mark C. Peterman

OndaVia, Inc.
Hayward, CA

www.ondavia.com

Raman spectroscopy

1920s 

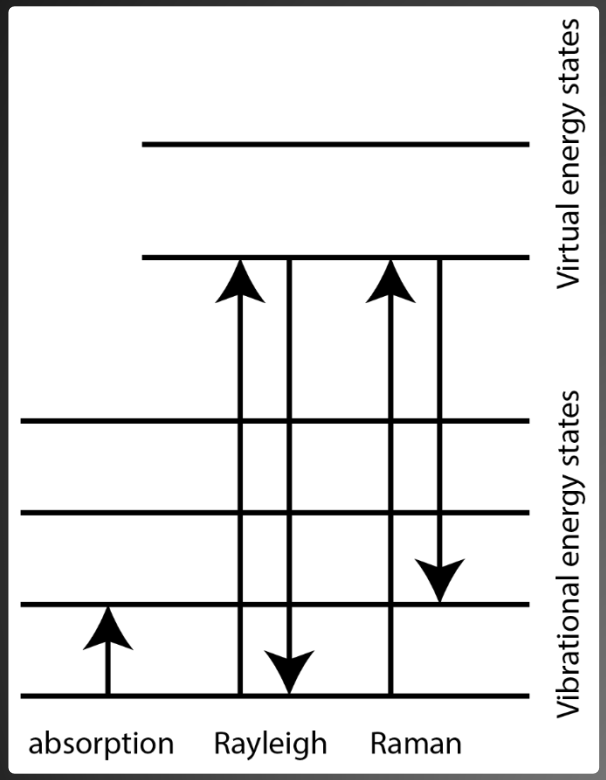
1990s 

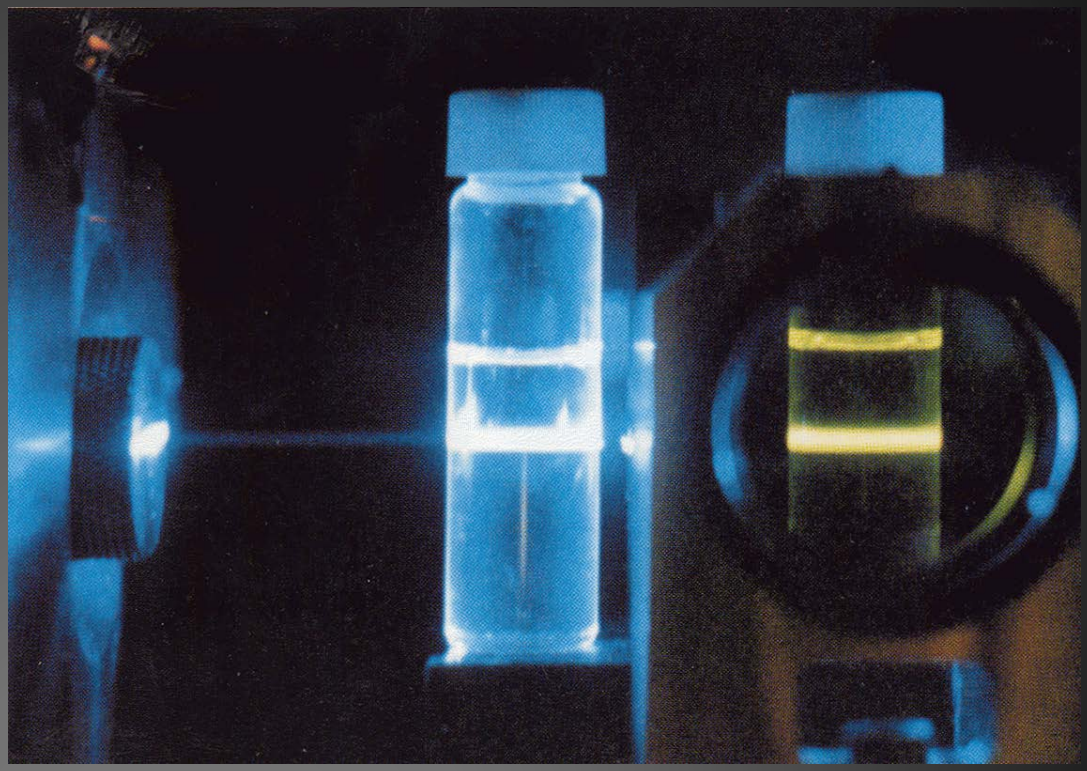
2000s 

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

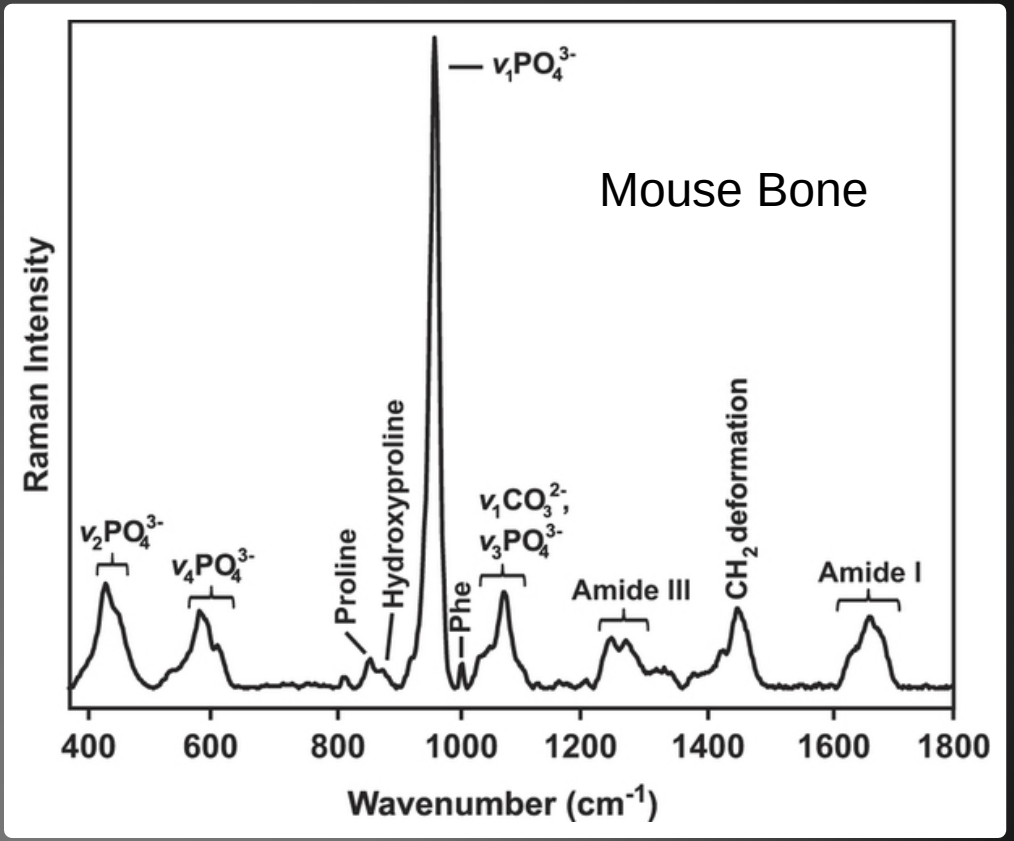




Raman spectroscopy

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

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



Raman vs FTIR

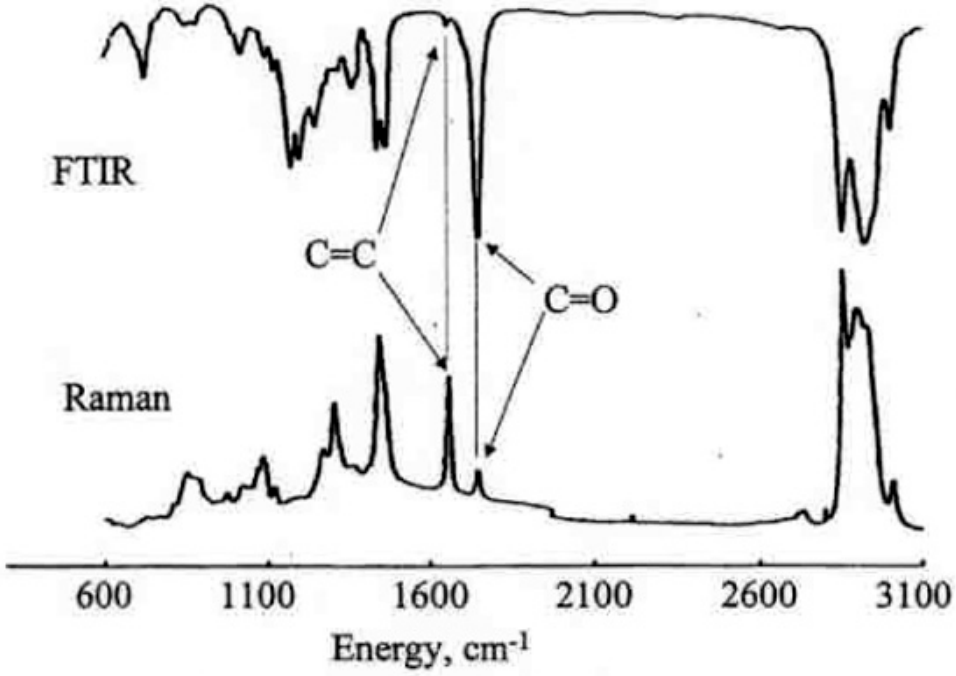


Figure 2.2. FTIR (upper) transmission and Raman scattering (lower) of oleic acid methyl ester.

Spectrometer Options

Benchtop

- Weight: 16 lbs
- Power: 12-V, 2-A

Handheld

- Weight: 2 lbs
- Power: 5-V, 1-A (USB)

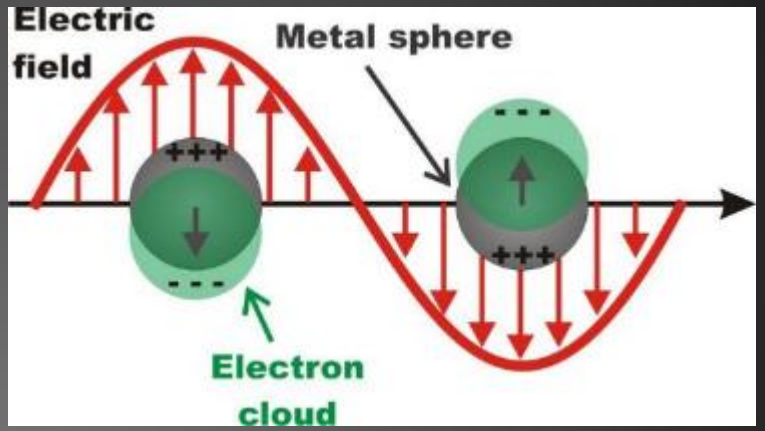
But why not widely used?

Weak signal

Identification, not quantification

Surface Enhancement

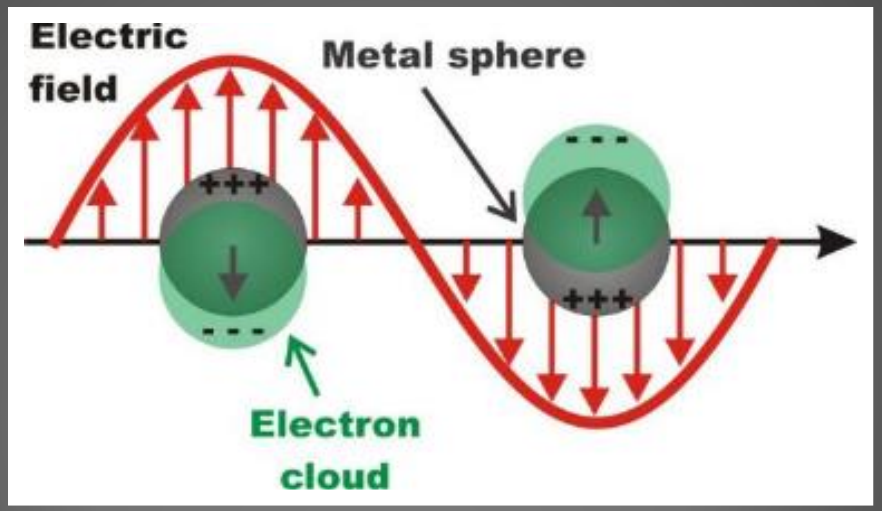
- Normal Raman
  - $\sigma_{NR} \sim 10^{-30}$ cm^2/molecule
  - **1 in 10 million photons**
- LSPR enhancement
- SERS
  - Enhancement factor (EF)
  - EF up to 10^{10}
  - $\sigma_{SERS} = \sigma_{NR} \bullet EF$



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

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

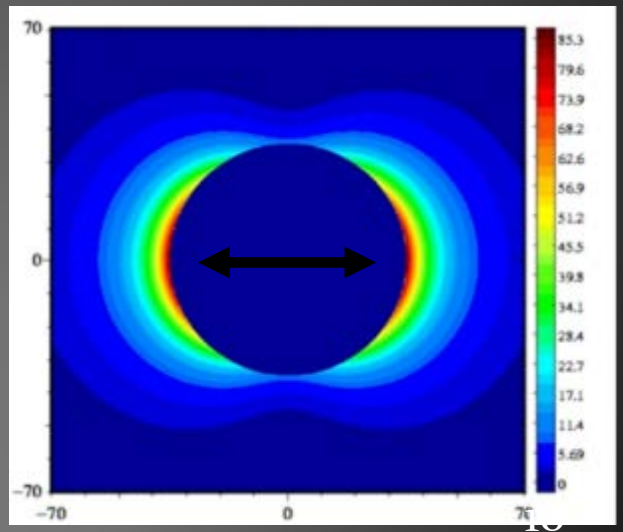


Surface-Enhanced Raman Scattering (SERS)

- LSPR causes increased field intensity at surface
- Increased Raman signal at metal surface (SERS)

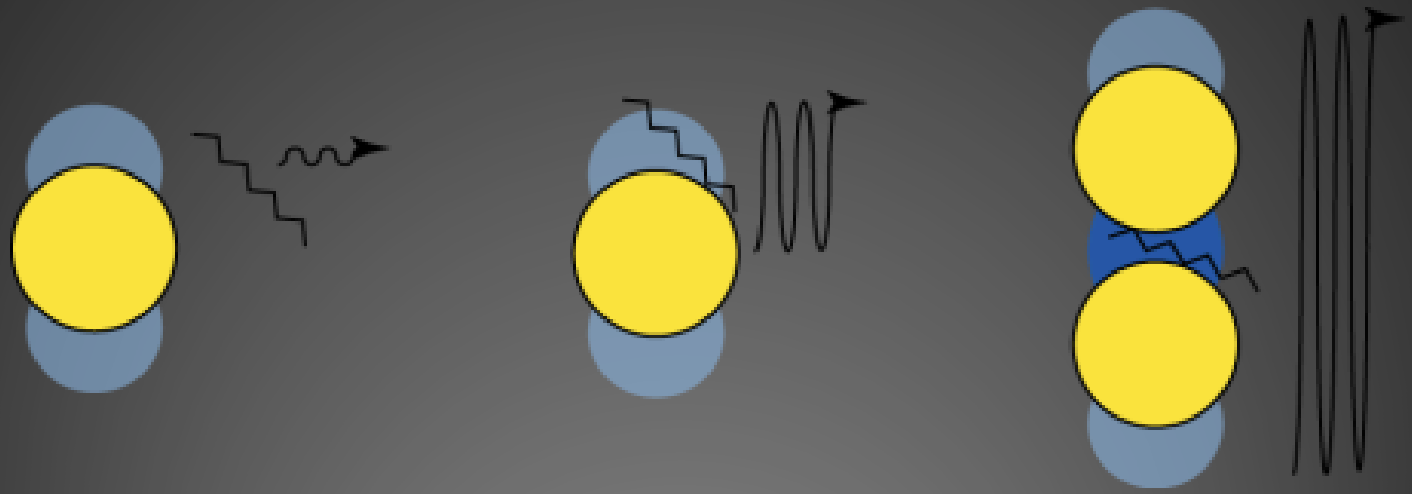
- SERS activity quantified by Enhancement Factor
  - EF range: 1 - 10^{10}

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



Multi-particle effects

Nanoparticles (gold/silver) enable **ppb-level** detection



“Hot Spots”

But still…why not widely used?

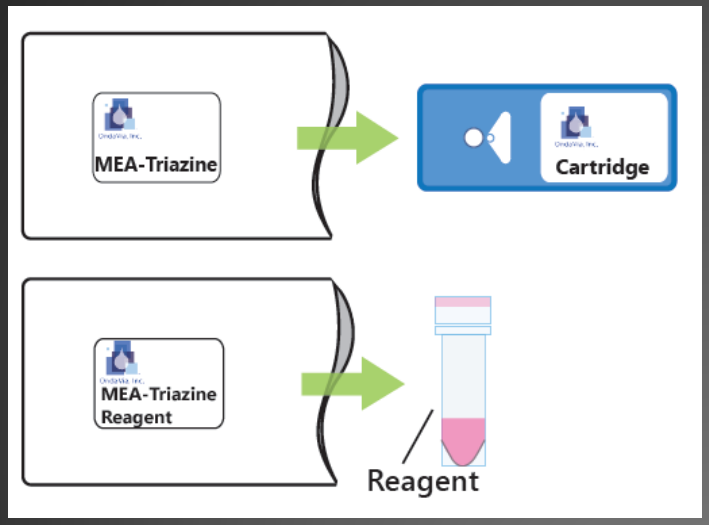
- Achilles' heel: reproducibility
  - Variations in substrate properties
  - Stochastic nanoparticle alignments
- One reviewer: "SERS doesn't work"

OndaVia has made SERS a quantitative, repeatable method using:

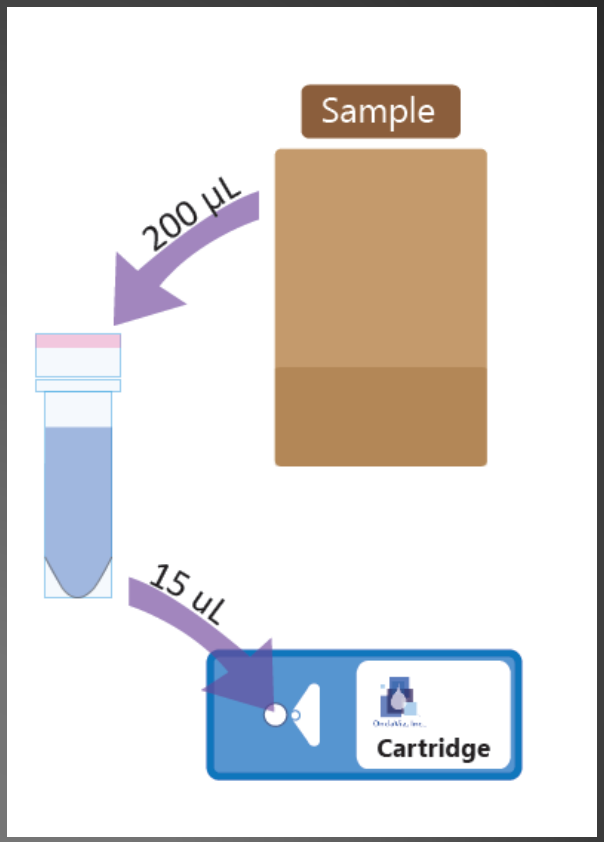
- Internal standards
- Nanoparticle structure
- Surface modifications
- Intelligent software

Quantification

1



2

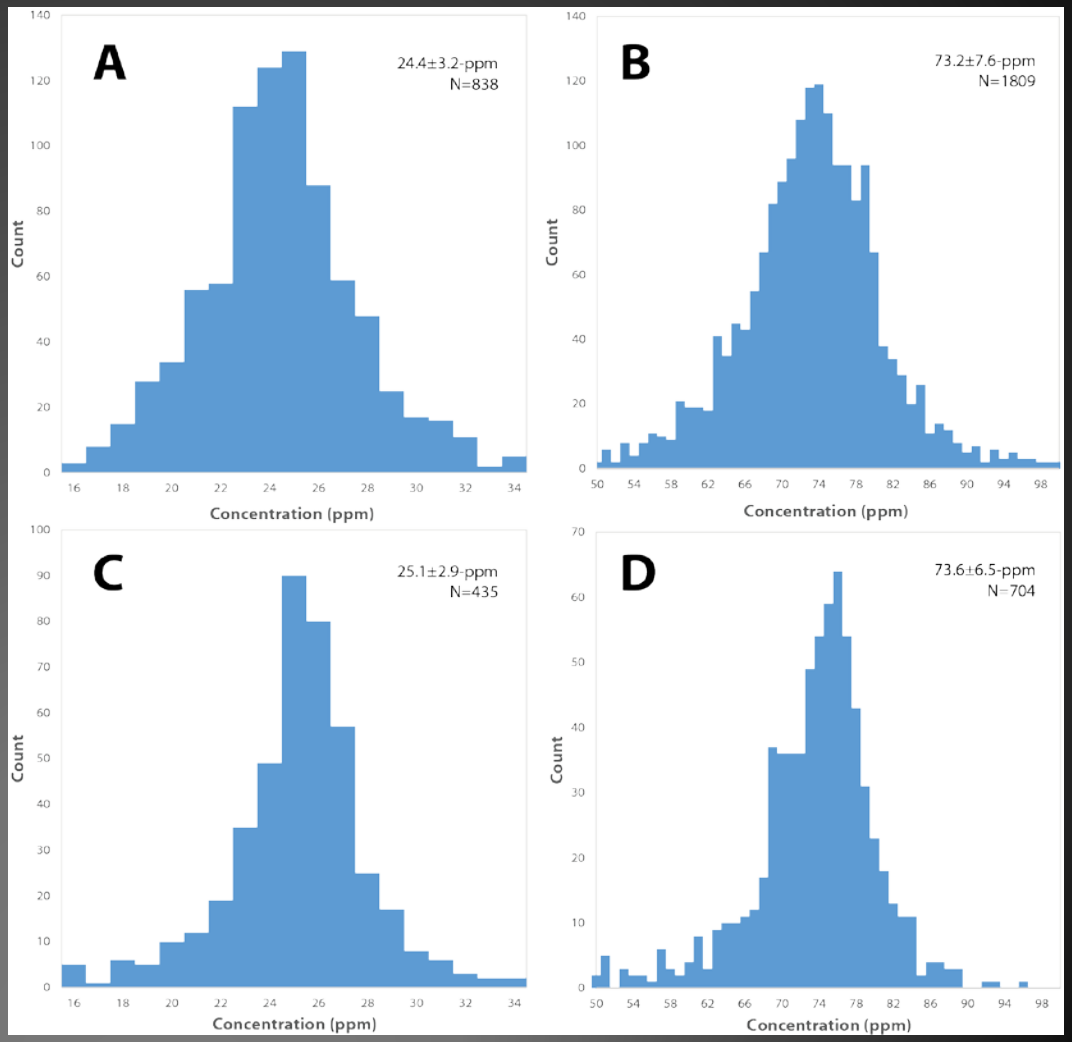


Total Analysis Time: 2 minutes

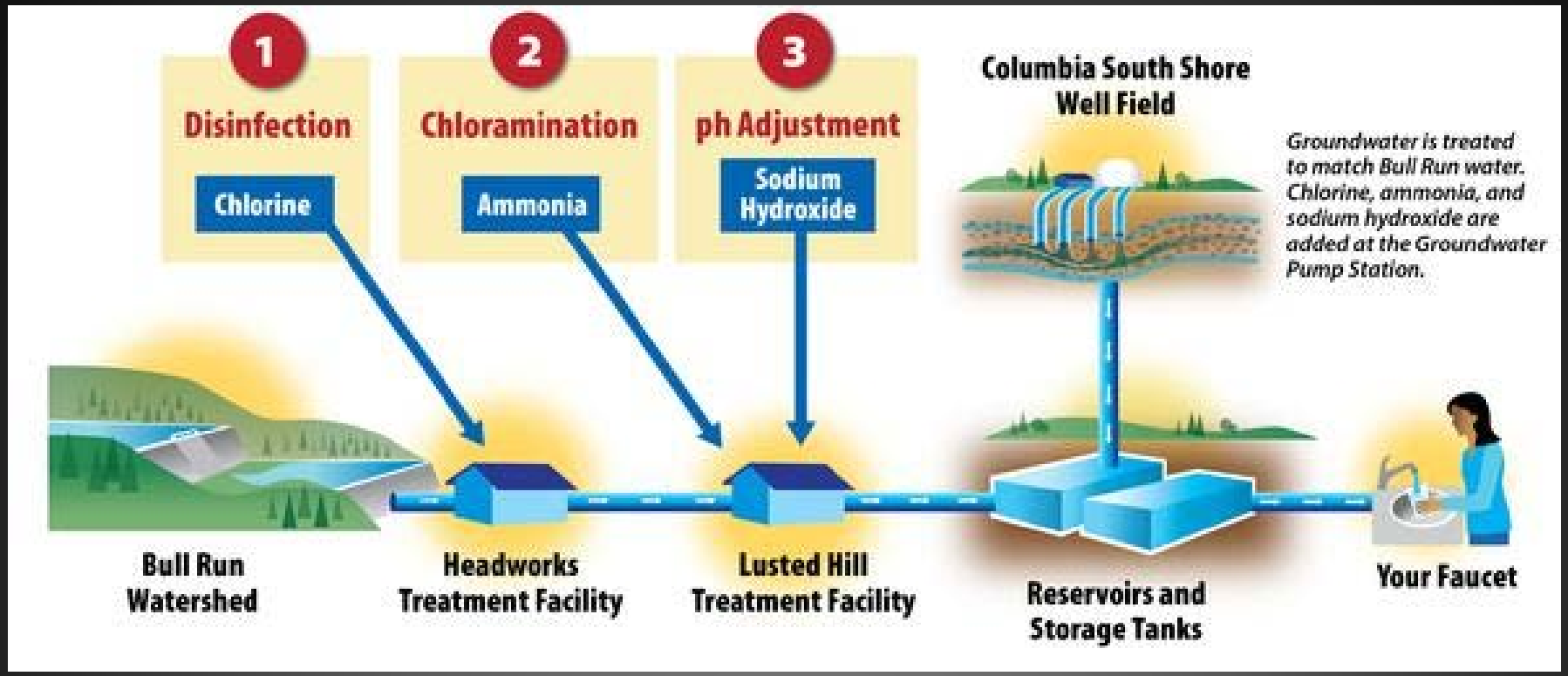
Trace-level analysis

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



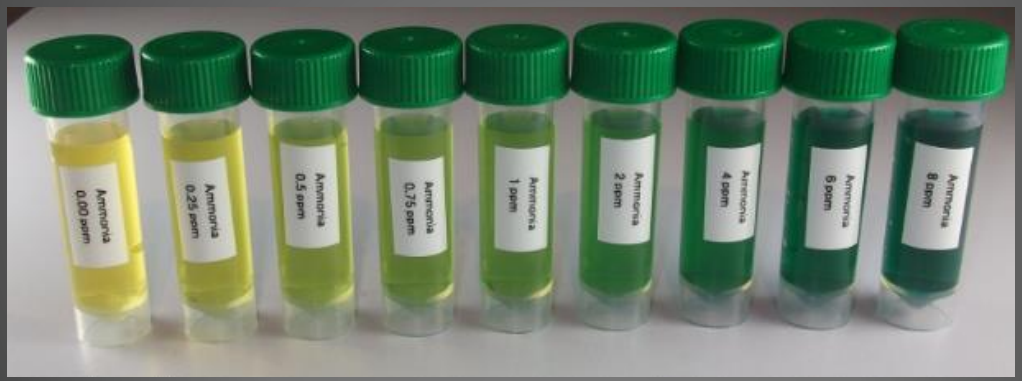
Chloramination for sanitation



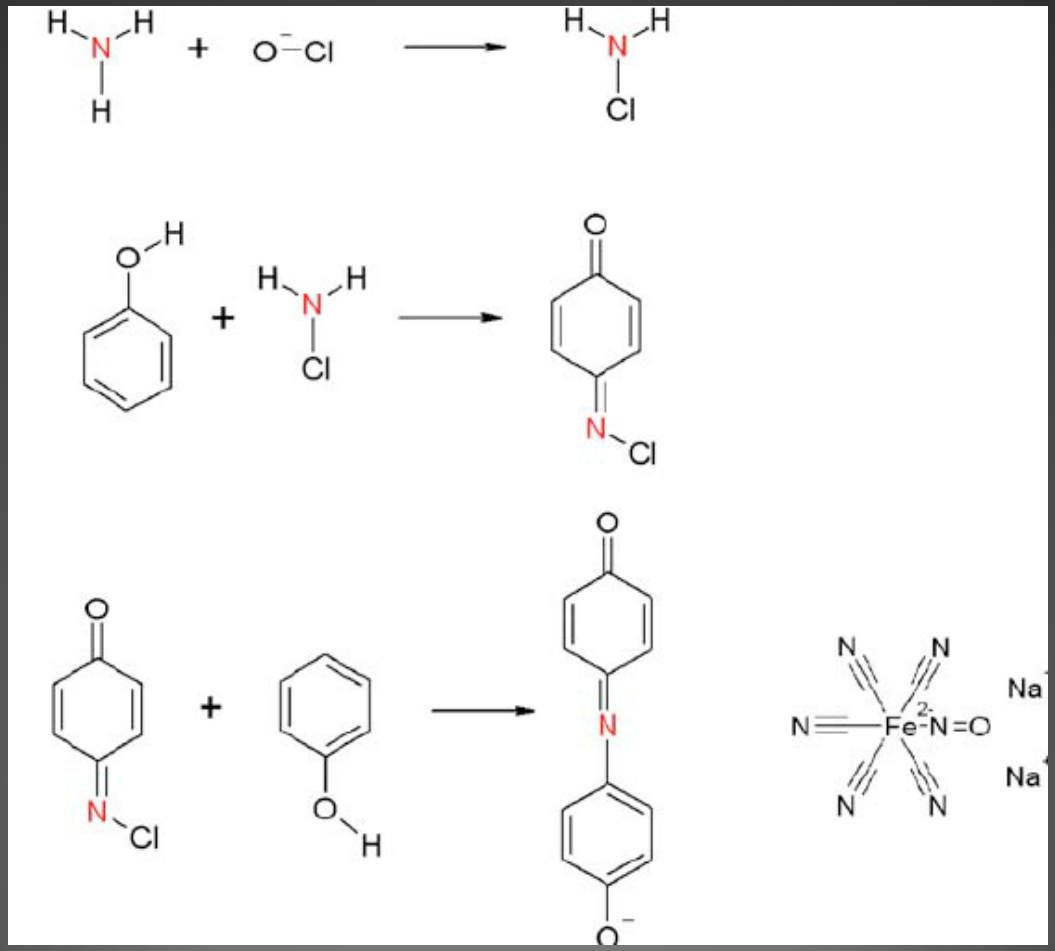
Appearance	Name	Molecular Weight	Preferred pH Value	Biocidating Effect
NH2Cl	Monochloramine	52	> 7	Good
NHCl2	Dichloramine	85	4-7	Tolerable
NCl3	Trichloramine	119	1-3	Average
RNHCl	Organic chloramines	Varies	Unknown	Bad

Pioneering colorimetric SERS

- Most colorimetric dyes have an amine group: affinity with SERS substrate
- SERS, internal standards, and colorimetry:
  - Improve detection limits, accuracy
  - Eliminate sample blanks, interferences
  - Add speciation capability
- Examples:
  - Ammonia, chlorinated solvents, lead, alcohols

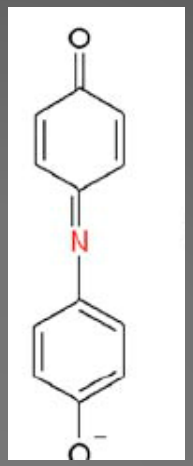


Berthelot reaction



Berthelot reaction

SERS Active!

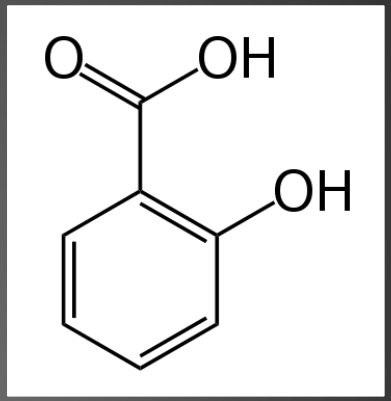


Berthelot reaction

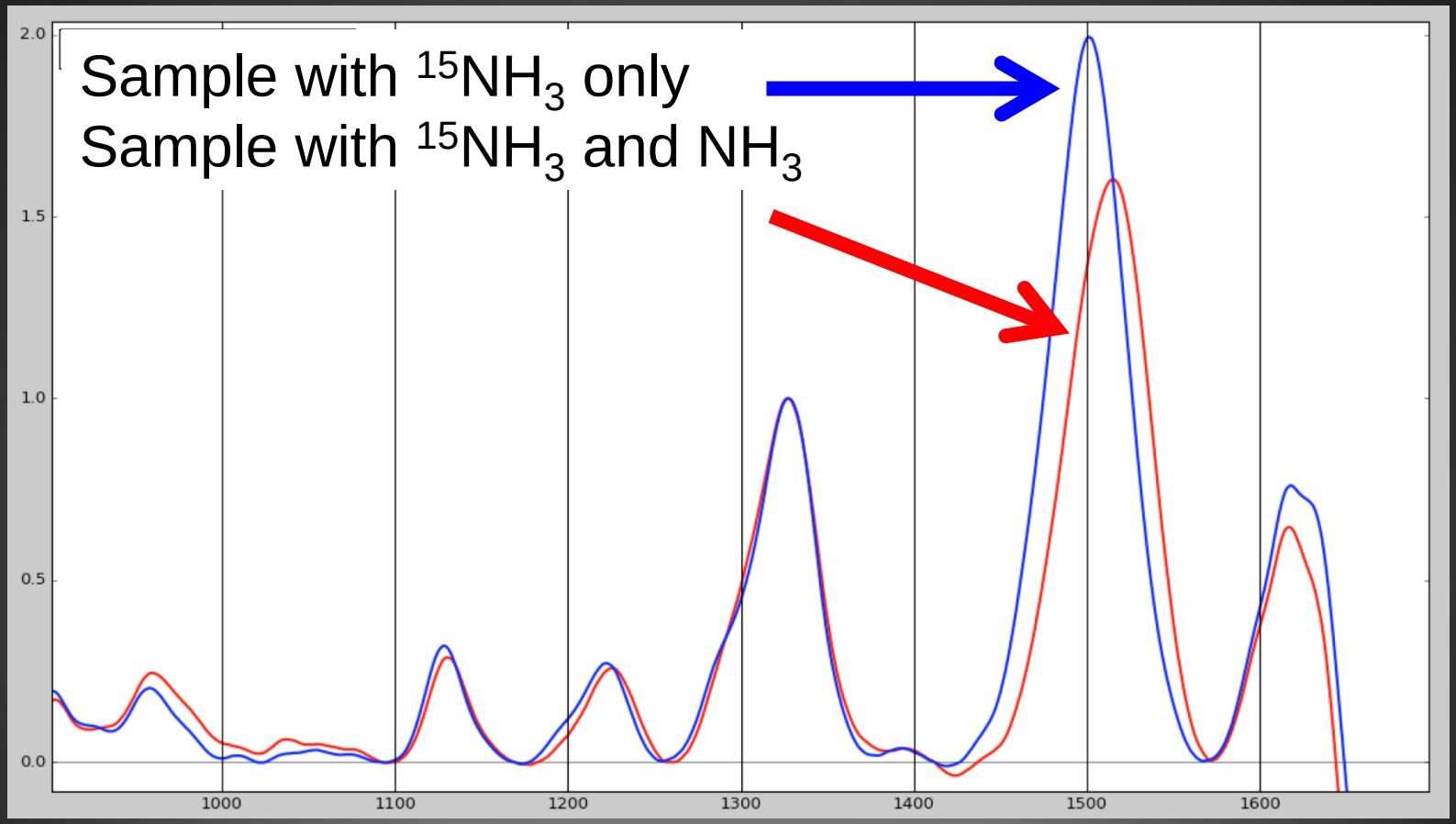
- Add Bleach: Ammonia measurement
- No Bleach: Chloramine measurement

Berthelot dye:

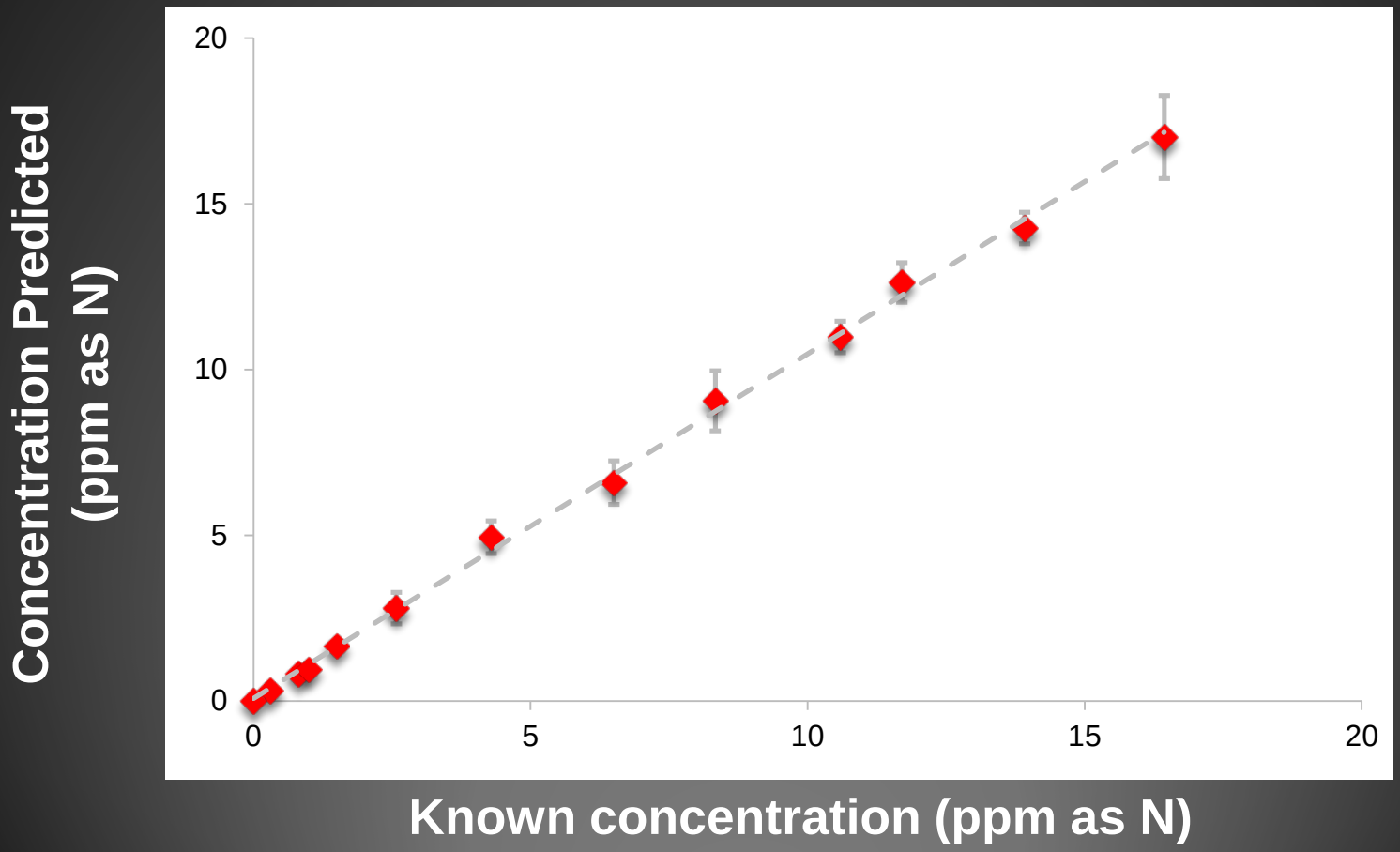
Salicylate instead of phenol



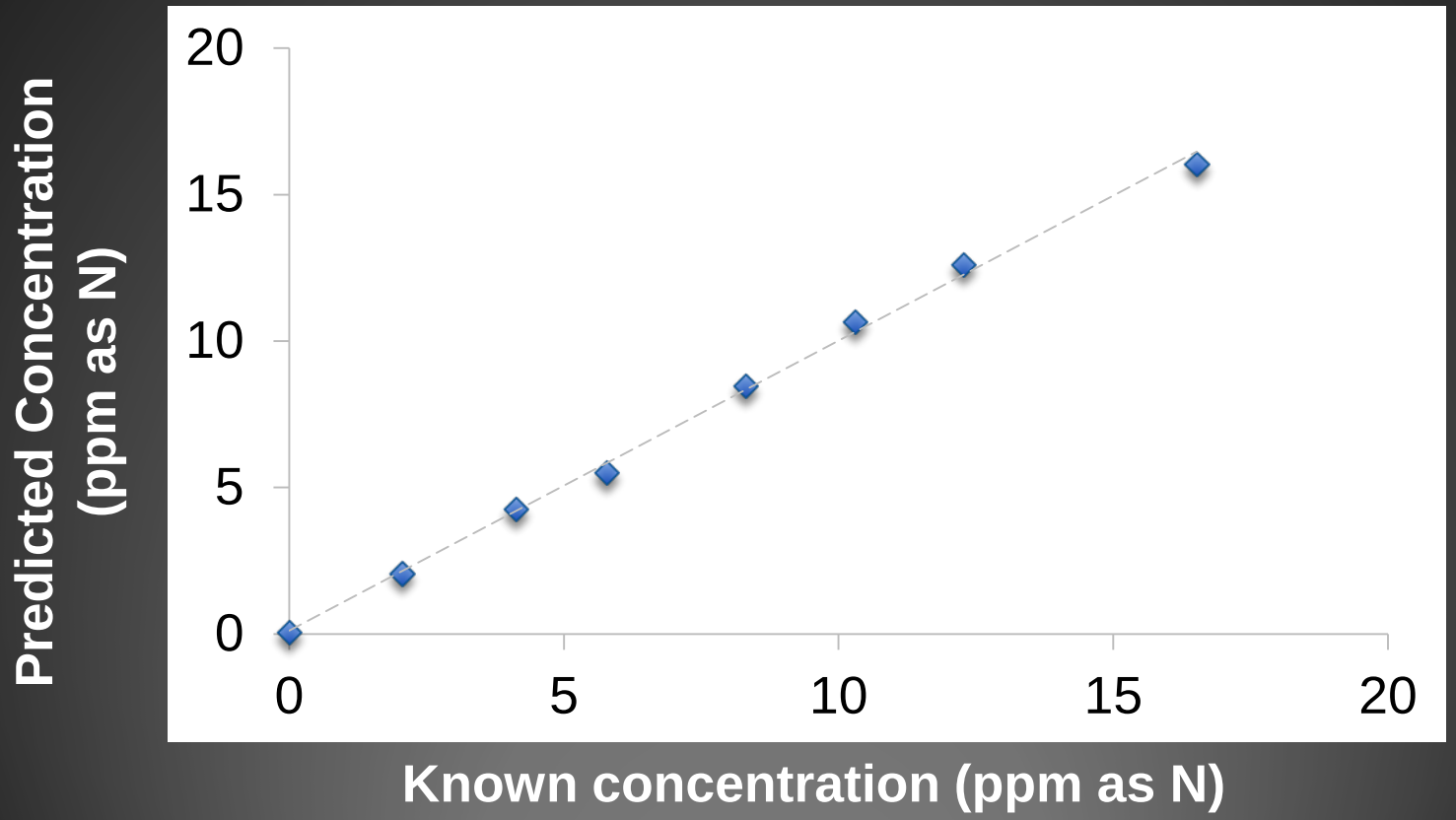
Internal standard: $^{15}NH_3$ => self-calibration



Range of interest 0 – 15-ppm (as N)
Accurate quantification RSD<5%



Quantitative analysis in tap water



Sources of **LEAD** in Drinking Water

Copper Pipe with Lead Solder: Solder made or installed before 1986 contained high lead levels.

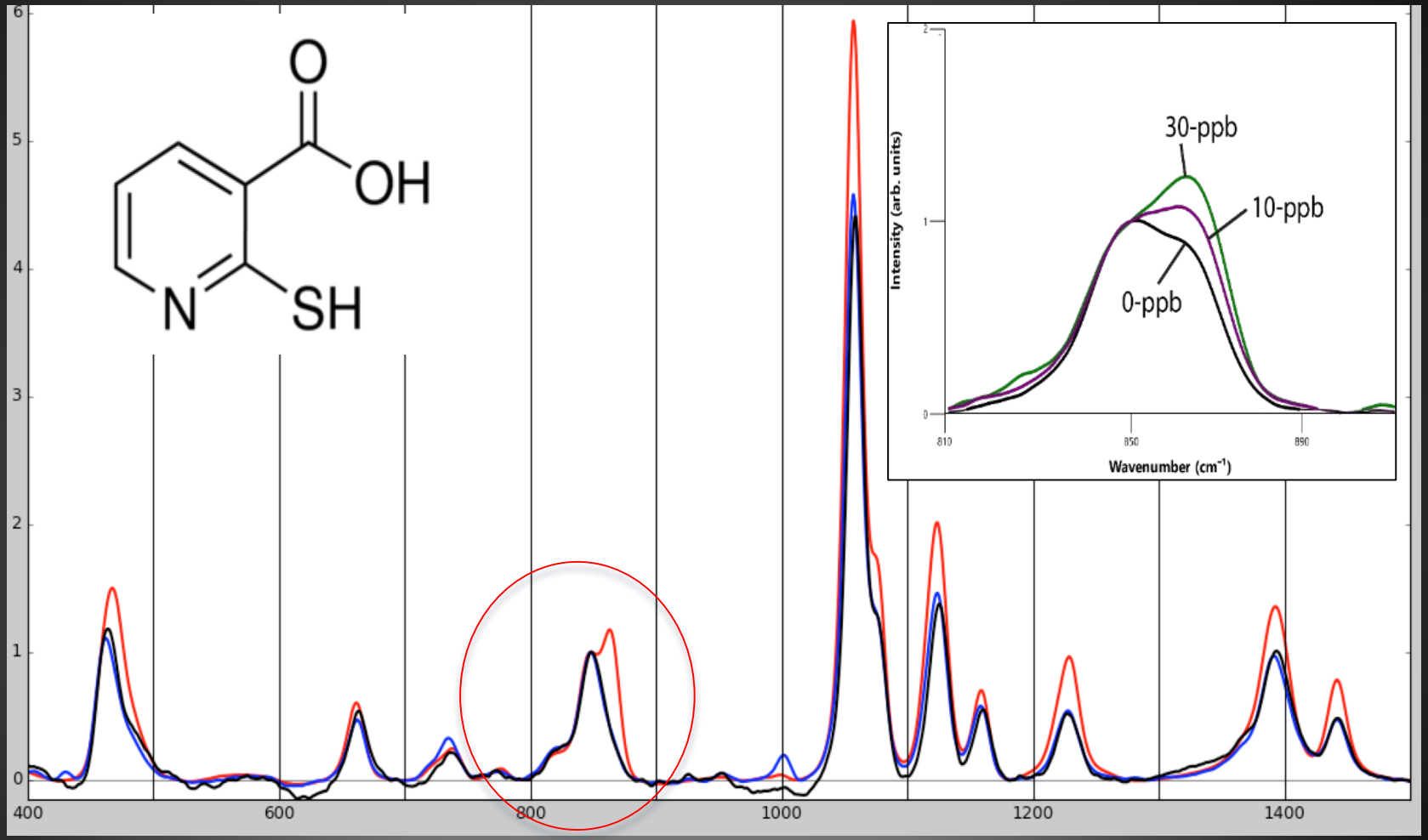
Lead Service Line: The service line is the pipe that runs from the water main to the home's internal plumbing. Lead service lines can be a major source of lead contamination in water.

Faucets: Fixtures inside your home may contain lead.

Galvanized Pipe: Lead particles can attach to the surface of galvanized pipes. Over time, the particles can enter your drinking water, causing elevated lead levels.

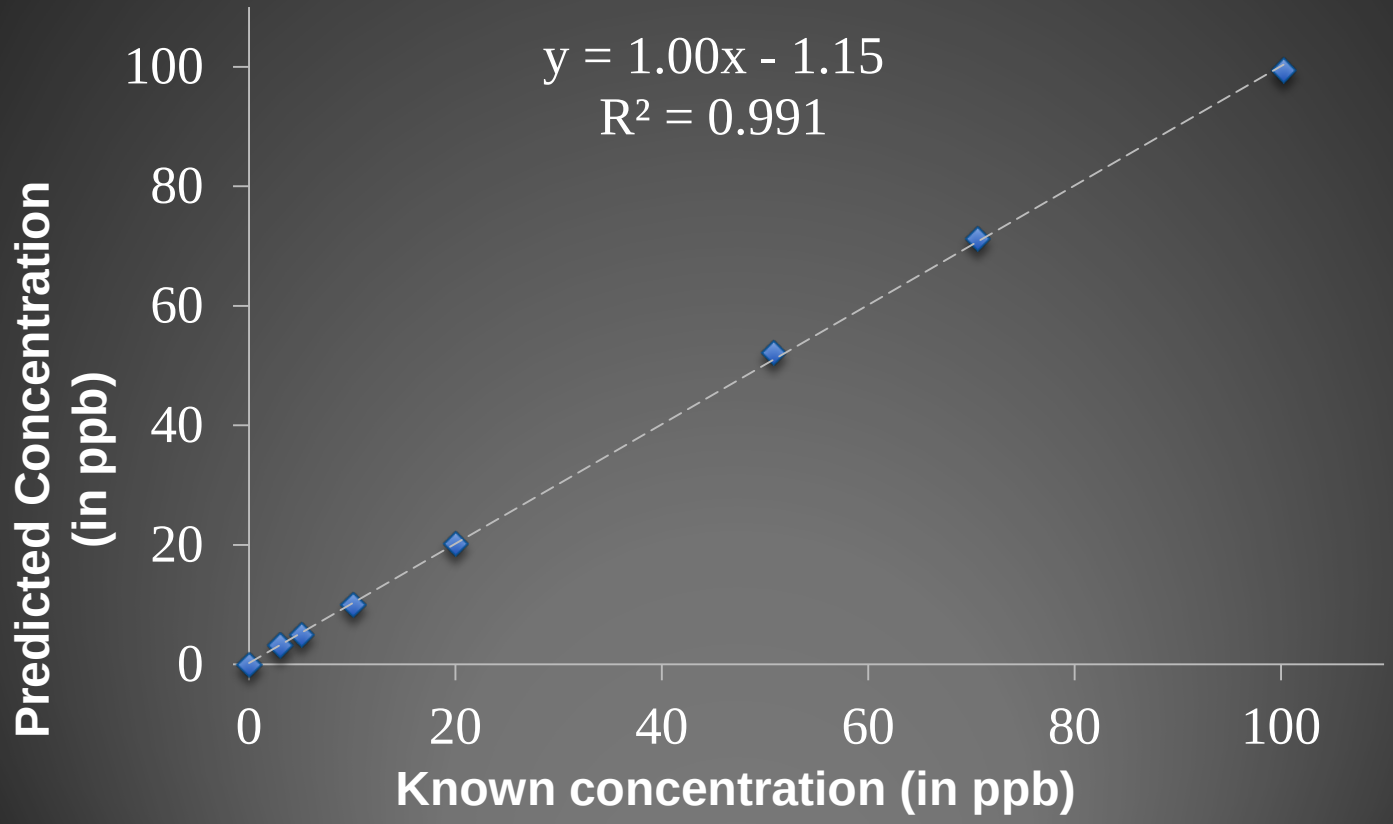
Lead Goose Necks: Goose necks and pigtails are shorter pipes that connect the lead service line to the main.

2-mercaptoisonicotinic acid



Lab standard calibration curve

- Wide dynamic range of interest 0 - 100ppb
- Accurate quantification, repeatable RDS < 2%



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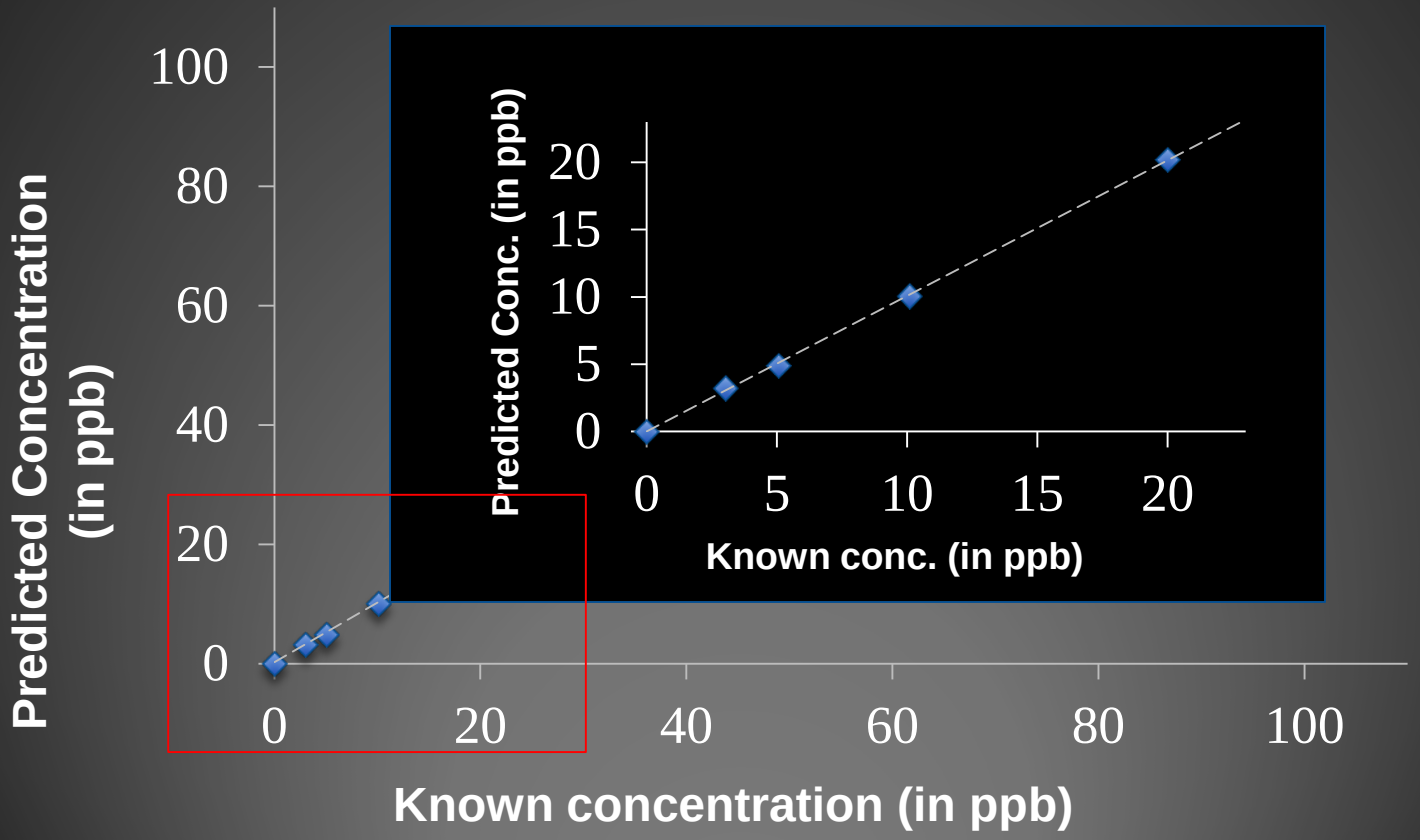
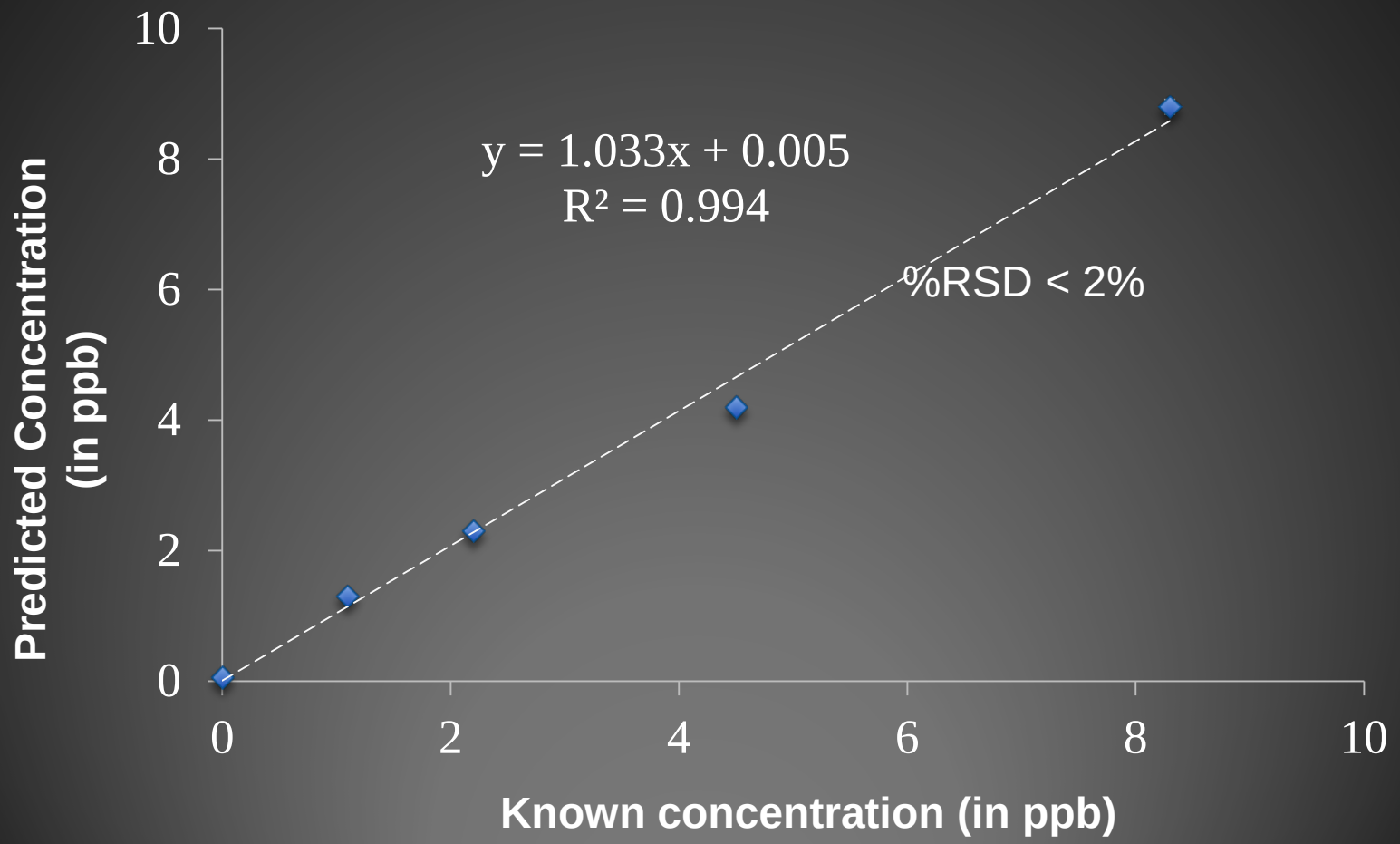
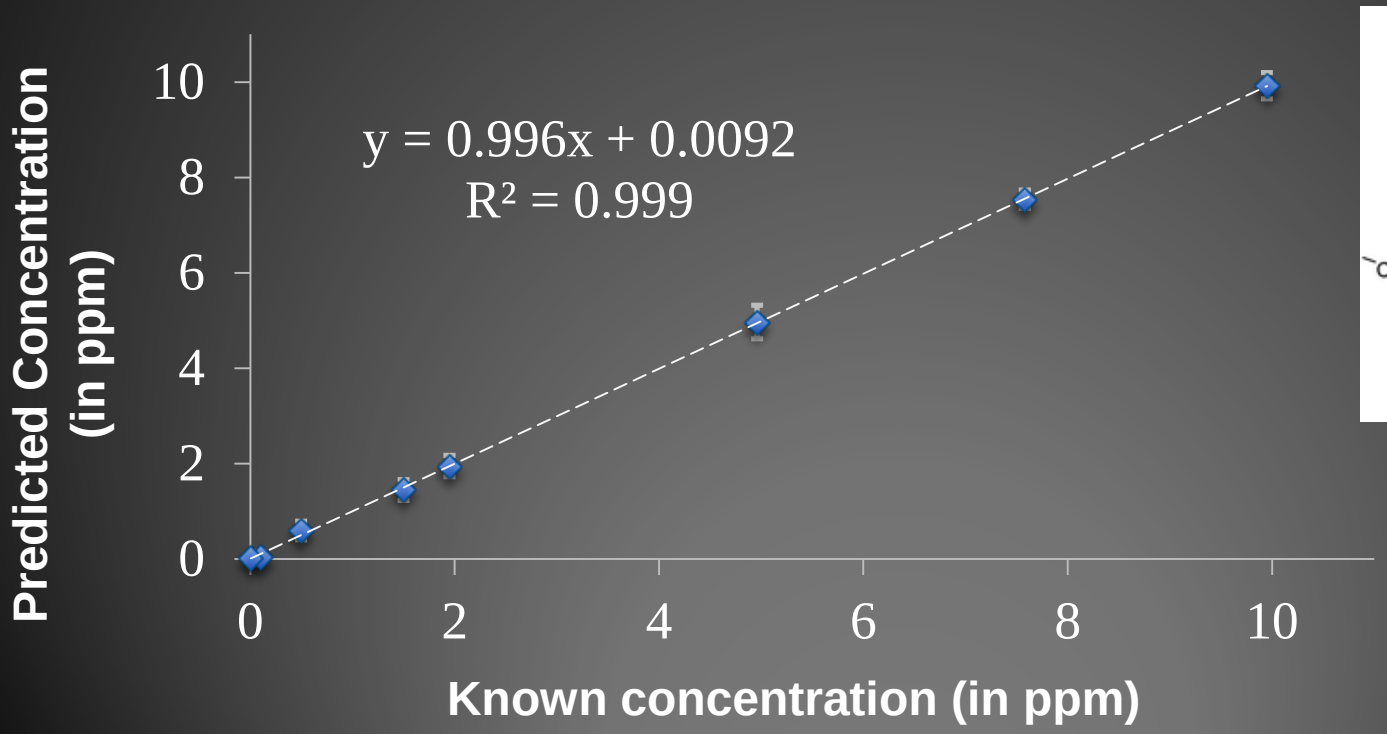


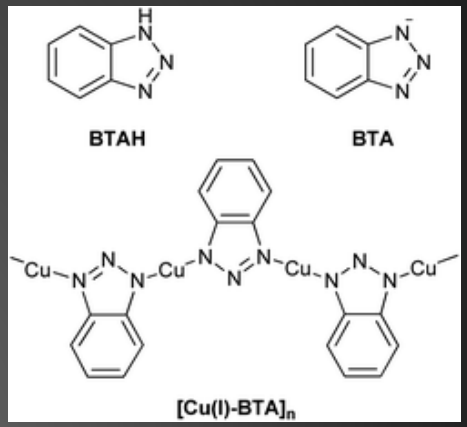
Tap water samples



Lead and copper rule

- Action levels : Pb is 15 ppb and Cu is 1.3 ppm
- Detection strategy: Benzotriazole. Gold Nanoparticles
- Quantification strategy: Standard addition





Flue Gas Desulfurization (FGD)

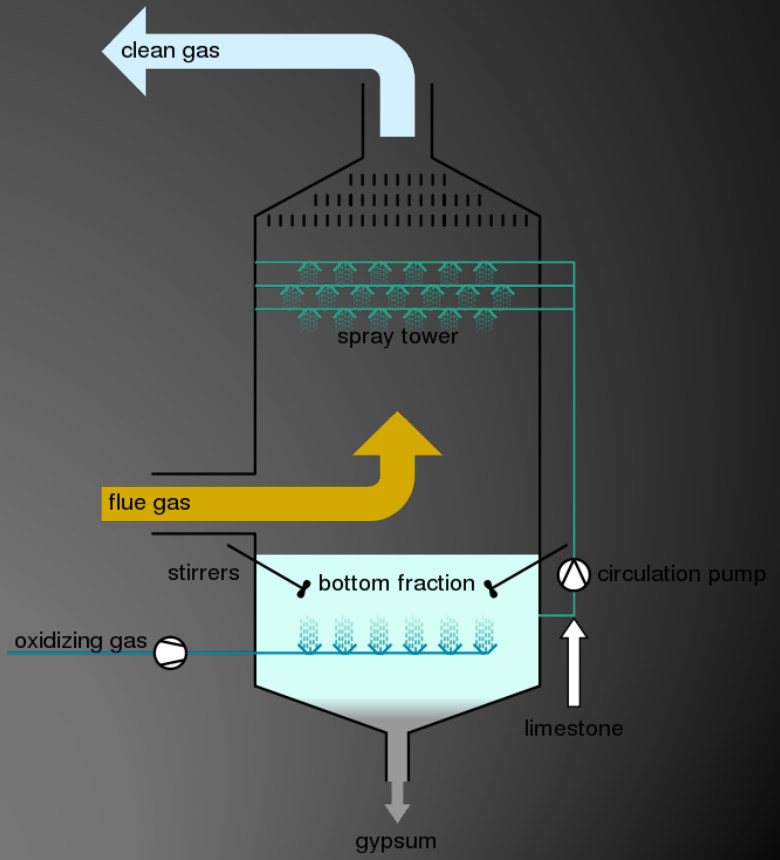
Sulfur content in fossil fuels : **0.4 w% - 0.7 w%**
Burning fossil fuel: emission of sulfur as **SO_2** (~95%) and **SO_3** (~1%)
Regulations on **SO_2** emissions

FGD removes ~90% of the SO

FGD methods :

- Wet scrubbing
- Spray-dry
- Wet sulfuric acid
- SNOX Flue gas desulfurization
- Dry sorbent injection

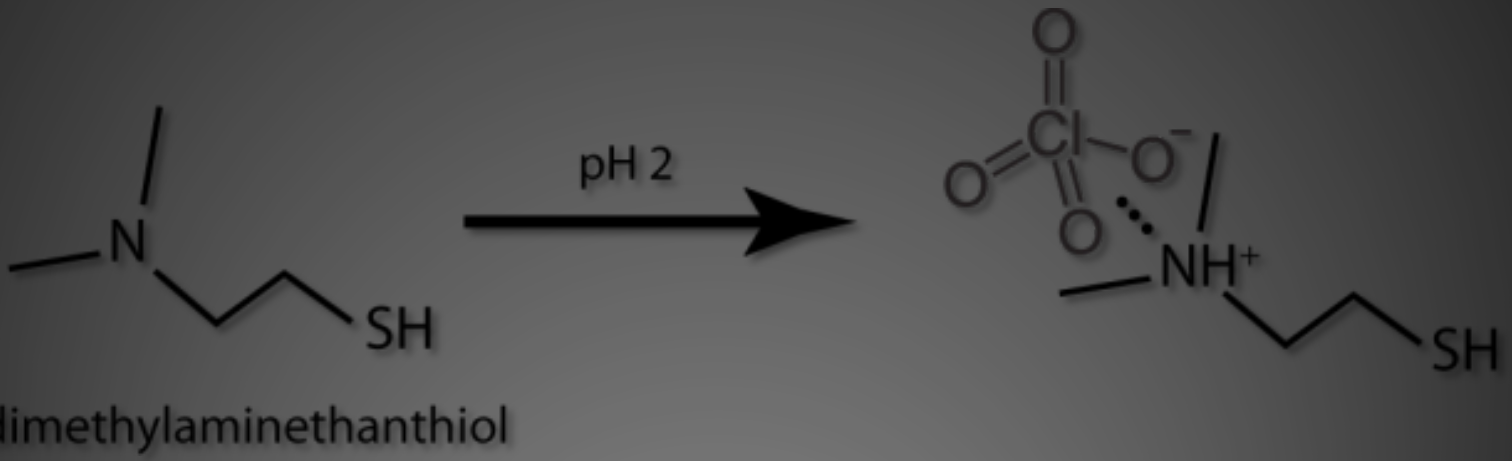
FGD units discharge large levels of **sulfate** and **toxic Selenium** in the wastewater streams



Surface treatments

If you want to detect ions…

…look to ion chromatography and ion exchange

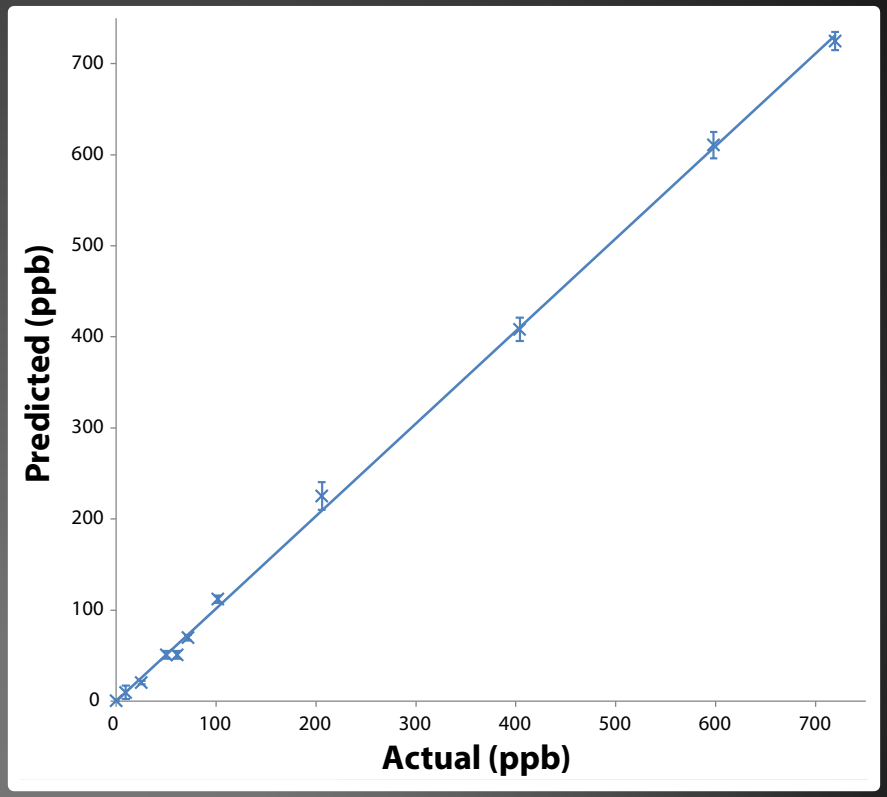


2-dimethylaminethanthiol

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

Selenium analysis

- Regulatory limits (drinking water)
  - 50-ppb, although some States are lower
- Applications
  - Refinery waste water
  - Coal-fired power plants / flue-gas desulfurization water
- Current methods
  - ICP/MS and colorimetry



Selenium speciation

- Test is specific for Se(VI)
- Se reduced during biological treatment of waste water
- Oxidize treated water using bleach and/or H_2O_2 at high pH to convert all Se(IV) to Se(VI)

Facility	ICP/MS (ppb)	OndaVia (ppb)
1 (untreated)	400	405
2 (untreated)	370	420
1 (treated)	55	ND
2 (treated)	160	ND
1 (treated, ox)	--	70
2 (treated, ox)	--	145

Fieldable speciation test:

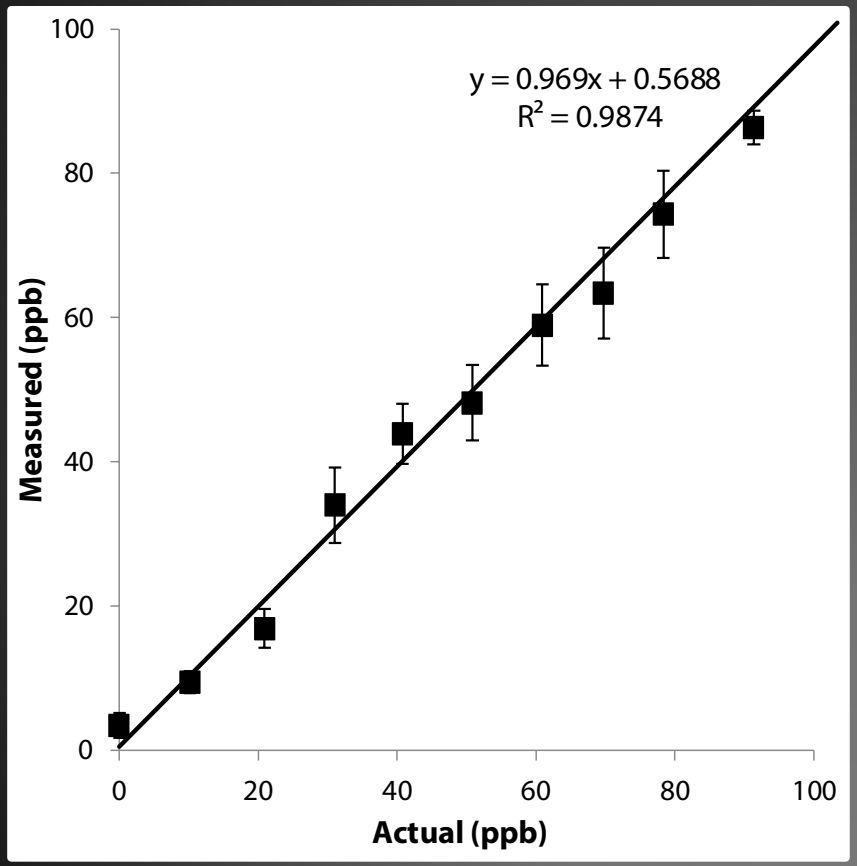
- First measure Se(VI)
- Oxidize to determine total
- Se(IV) is the difference

Arsenic analysis

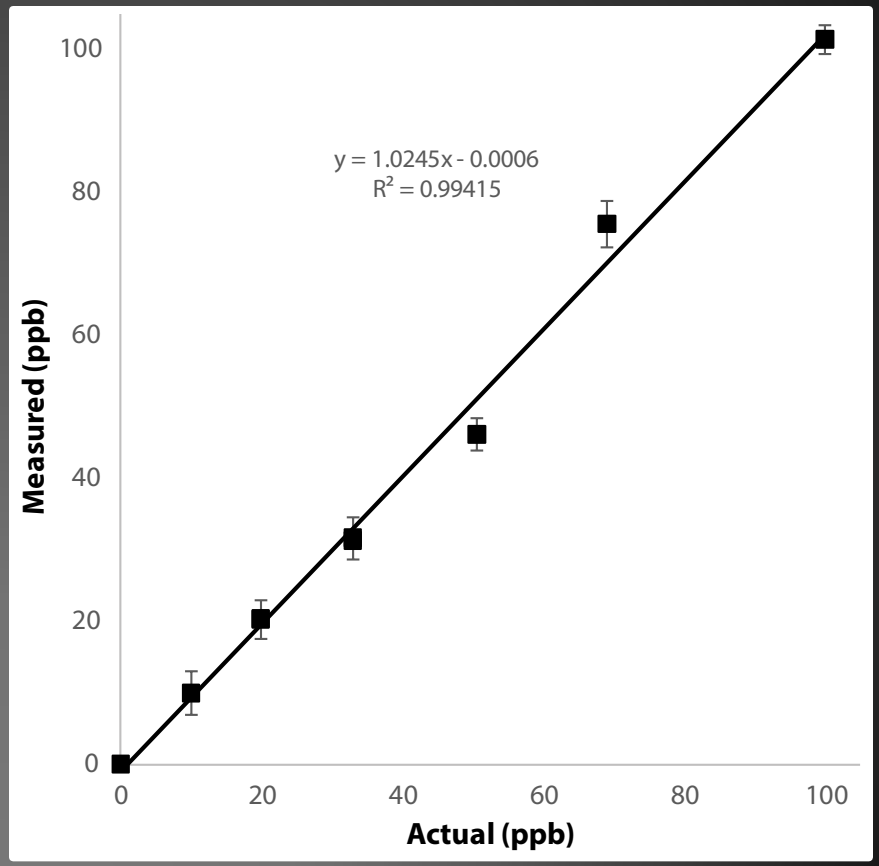
- Arsenic exists in natural waters predominantly as arsenite [As(III)] and arsenate [As(V)]
- Regulatory limit:
  - 10-ppb total As in drinking water
  - *But* As(III) is more hazardous that As(V)
- Current methods:
  - Total via colorimetry, in which arsenic is converted to As(III) and then to arsine gas
  - Speciation via HG-AAS

Arsenic speciation

Arsenite [As(III)]



Arsenate [As(V)]



Summary

- Raman spectroscopy is a powerful tool for analytical chemistry
  - Instruments are portable, easy-to-use
  - And with the right test methods, applicable to environmental analysis
  - Many applications important in California: arsenic, nitrate, hex chrome, perchlorate, to name a few

- Have a project in mind? Drop me a note!

Questions?

Special thanks to…

NATIONAL INSTITUTES OF HEALTH

NSF

USDA

Mark Peterman

peterman@ondavia.com

http://www.ondavia.com