Low-cost, rapid and *in situ* accurate quantification of chloramines and ammonia

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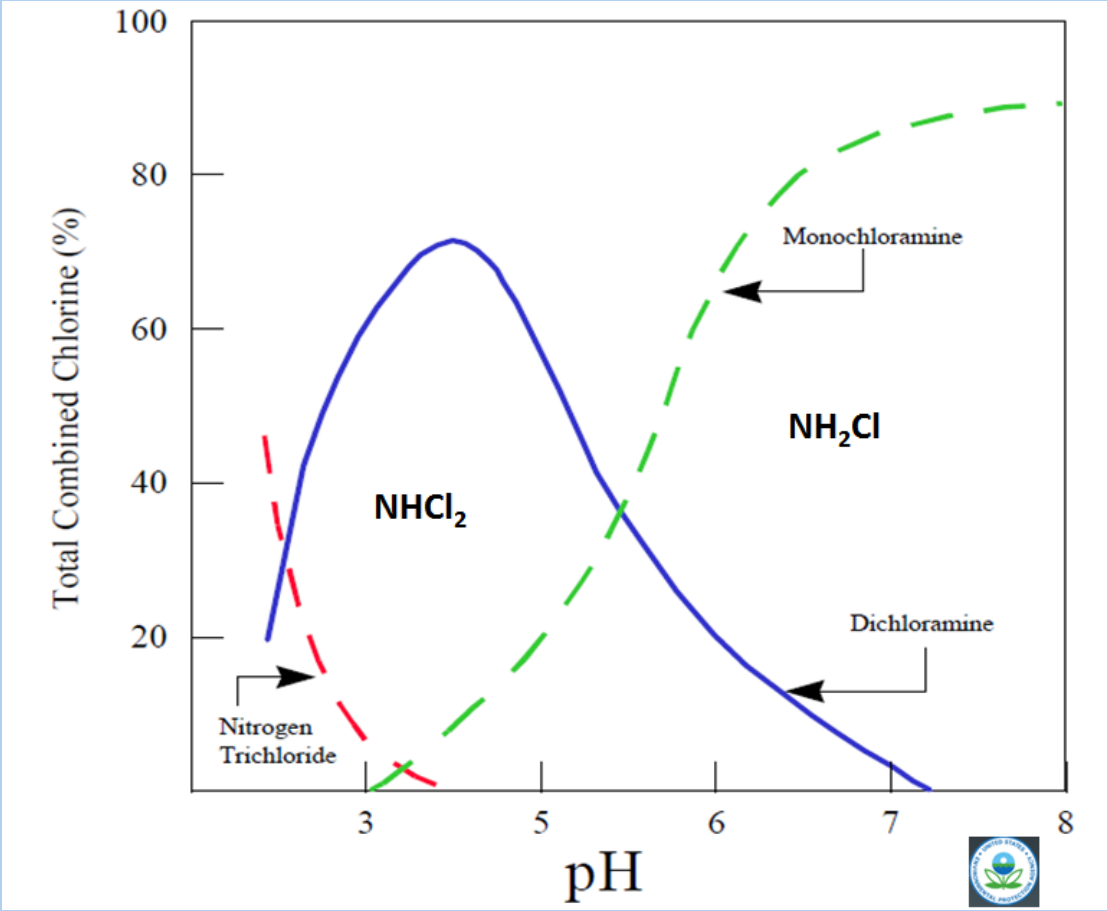
Definitive results. Decisive actions.

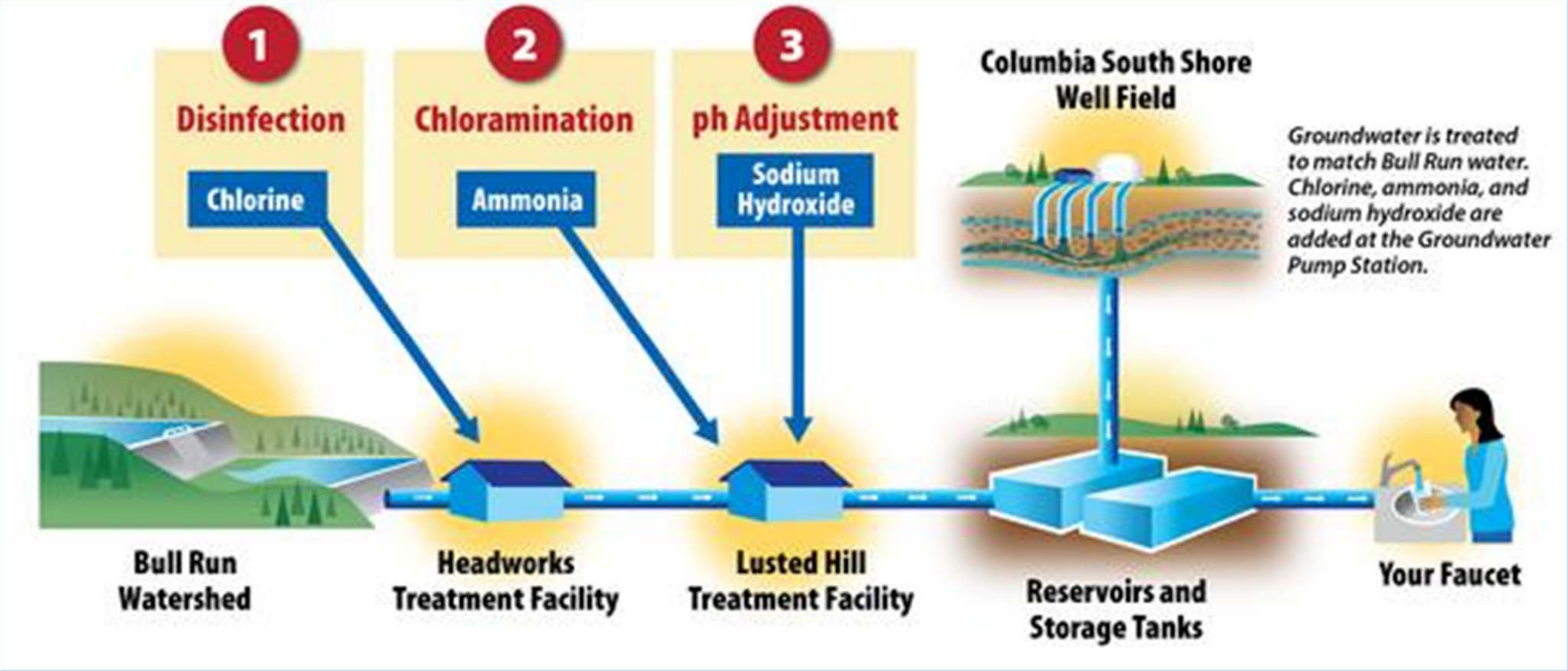
Chlorine + Ammonia



$NH_3 + HOCl \leftrightarrows NH_2Cl + H_2O$	Monochloramine
$NH_2Cl + HOCl \leftrightarrows NHCl_2 + H_2O$	Dichloramine
$NHCl_2 + HOCl \leftrightarrows NCl_3 + H_2O$	Trichloramine or nitrogen trichloride

Rate of formation depends on pH, temperature, time, and initial Cl2 : NH3 ratio

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

Chloramination for sanitation

Inorganic chloramines are **alternate disinfectants to chlorine** that

- Are recognized **as a safer disinfectant**
- forms significantly **lower amount of toxic disinfectant byproducts**
- does not **contribute to taste or odor**
- **more stable in** solution than free residual chlorine

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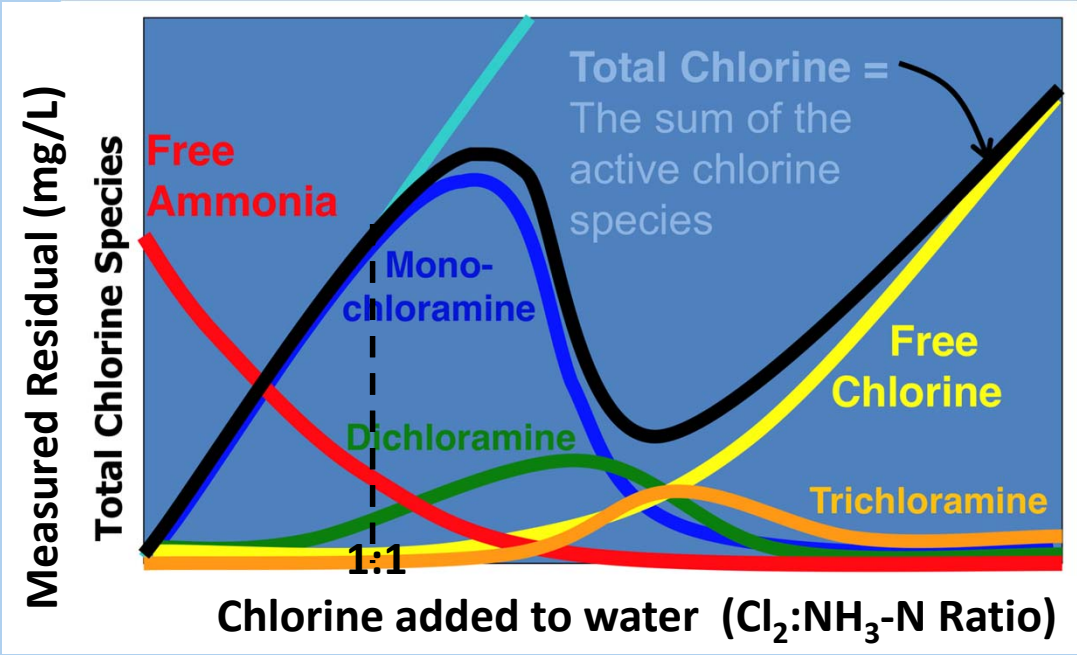
Why optimize

- Control the ratio chlorine : nitrogen
- Avoid nitrification
- Guarantee treatment performance
- Respect EPA guidelines of 4 mg/L for chloramine



=> A method capable of continually, accurately and easily measure chloramine and ammonia is required

Current monitoring procedure

GC/MS :

- Expensive
- Skilled labor required
- Dedicated system and team
- Time consuming
- Not deployable

Colorimetric (EPA method 350.1):
using ferrous diethyl-p-phenylenediamine (DPD) or leucocrystal violet (LCV) dyes:

- Interferences (Ca, Mg, organic amines, color absorbing compound)
- Lower performance than GC
- Speciation is technique dependant

Raman spectroscopy

1920s 

1990s 

2000s 

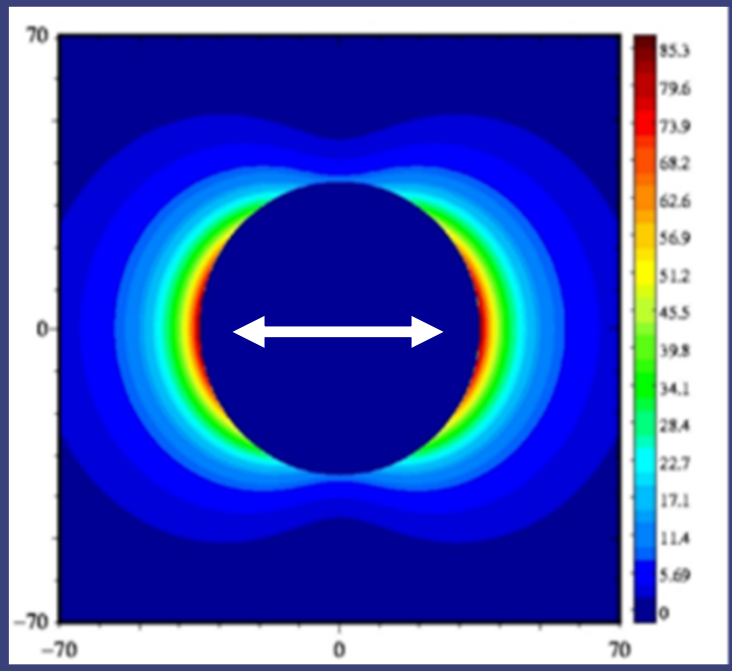
Optical telecomci[cations drove technology needed for portable, in-line, and compact Raman spectroscopy

But Raman is weak

- $\sigma_{NR} \sim 10^{-30}$ cm^2/molecule
- **1 in 10 million photons**

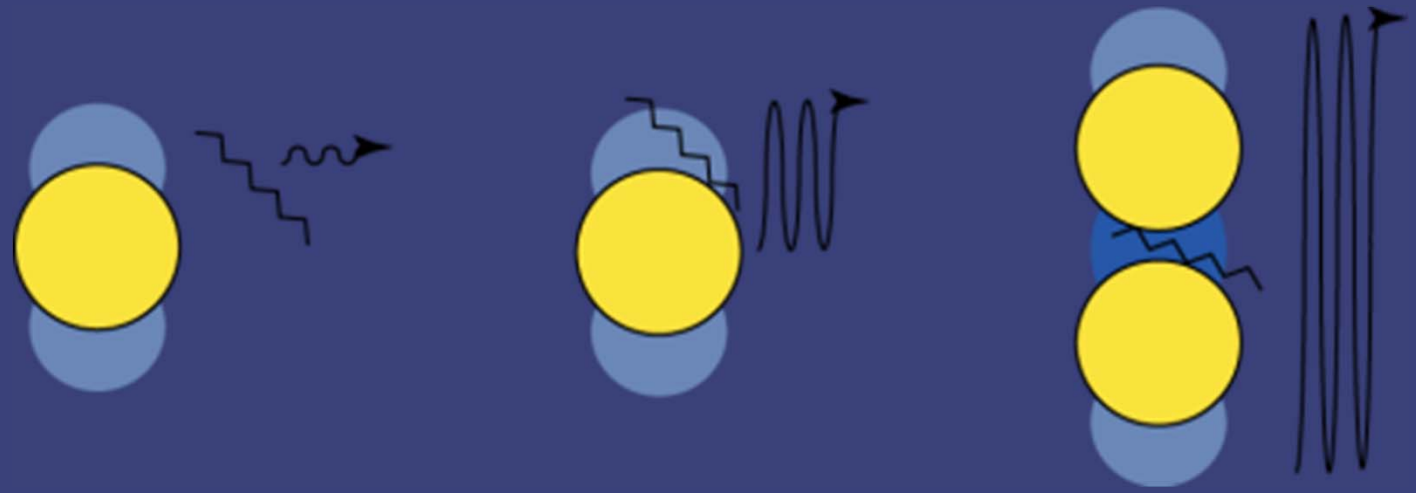
Surface-Enhanced Raman Scattering (SERS)

- At a rough metal surface
  - Increased field intensity
  - Which means increased Raman signal
- SERS activity quantified by Enhancement Factor
  - EF range: 1 - 10^{10}



Multi-particle effects

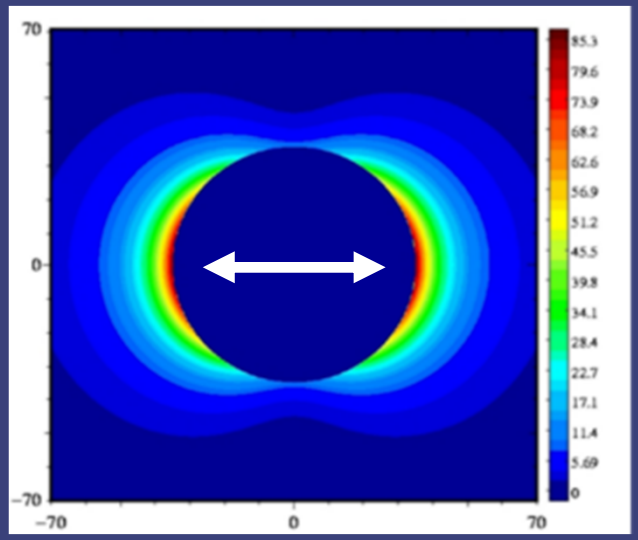
Nanoparticles (gold/silver) enable **ppb-level** detection



"Hot Spots"

Analyte / substrate interaction

- The SERS effect requires an interaction at the surface – within a couple nanometers



- Analyte must
  - Interact with the substrate
  - Interact with a linker molecule
  - Change the properties of another SERS-active molecule
- Gold/Silver nanoparticles: many options to control surface properties

Why not widely used?

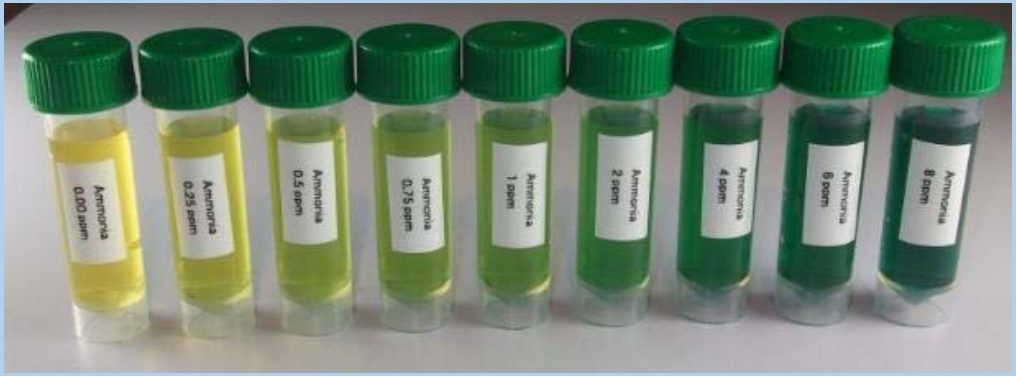
- Achilles' heel: reproducibility
  - Variations in substrate properties
  - Stochastic nanoparticle alignments
- One reviewer: "SERS doesn't work"

OndaVia has made SERS a quantitative, repeatable method using:

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

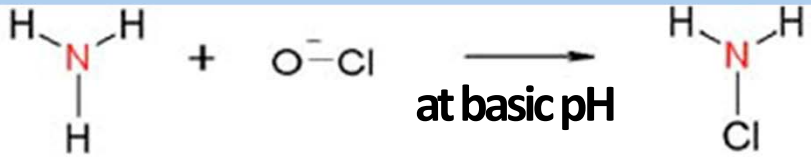
Pioneering colorimetric SERS

- Most colorimetric dyes have an amine group -> affinity with SERS substrate
- SERS coupled with internal standards can be applied to many colorimetric tests:
  - Improve detection limits, accuracy
  - Eliminate sample blanks, interferences
  - Add speciation capability
- Examples:
  - Selenium, ammonia, chlorinated solvents, lead, alcohols



Colorimetric SERS, Berthelot reaction

1-



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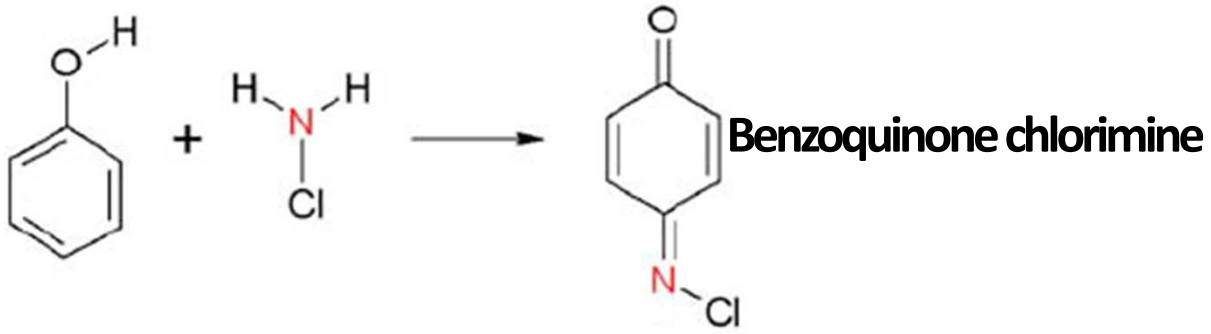

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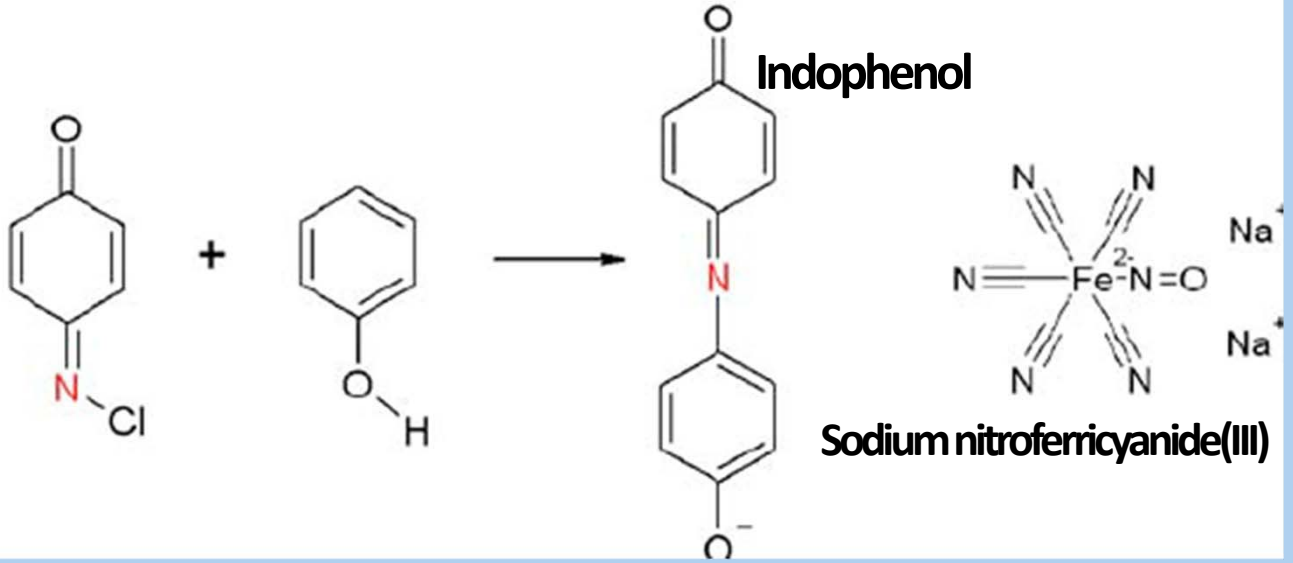
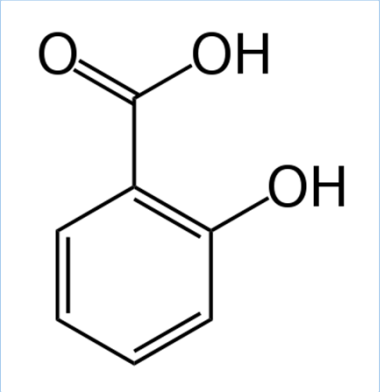


Colorimetric SERS, Berthelot reaction

- Addition of Bleach => Ammonia measurement
- No Bleach => Chloramine measurement

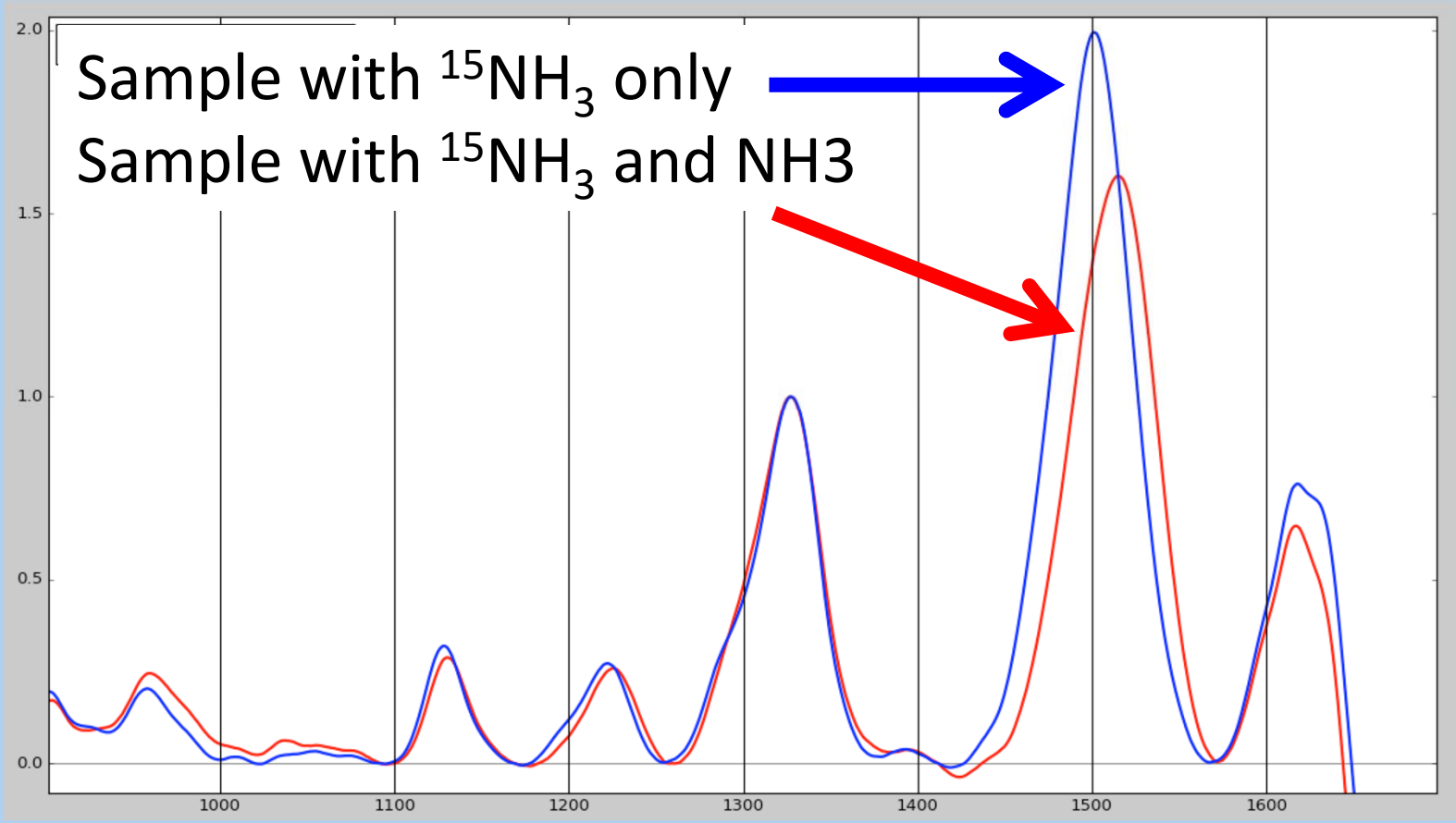
Berthelot dye:

Salicylate instead of phenol
-> Not hazardous



Colorimetric-SERS enables trace-level lab-grade measurement

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



A 15-min standard operating procedure

1. Mix 0.5 ml sample with 0.5 ml I.S.
2. Add 50 ul of reagents (mixture of sodium salicylate, nitroprusside , citrate and base)
3. Add Bleach for Ammonia measurement
4. Heat for 10 min in 70C water bath
5. Mix with Nanoparticles
6. Measure

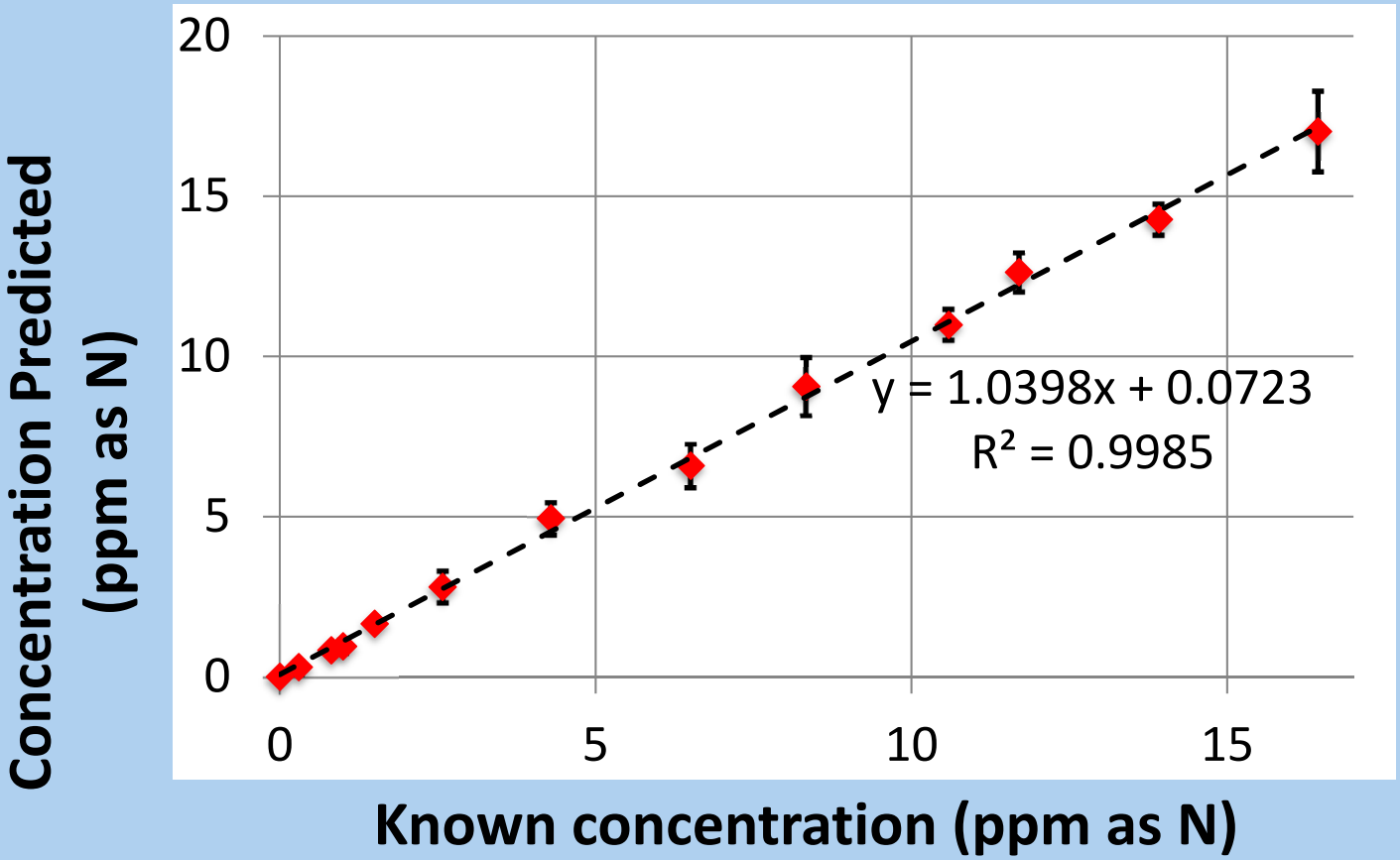
Raman spectrometer equipment

Instrumentation

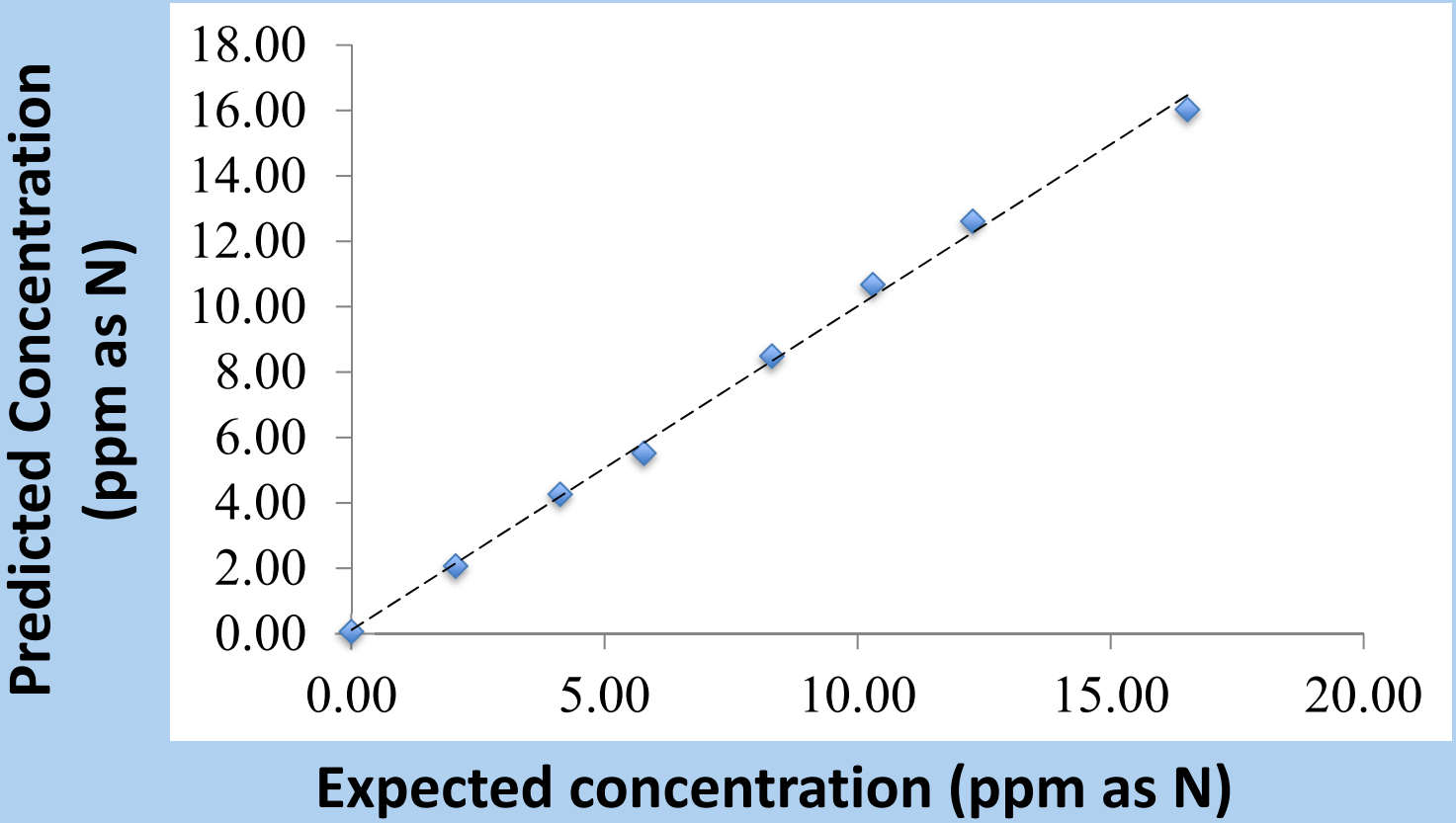
- 785-nm, 60-mW at substrate
- Cooled (-20°C) CCD detector
- 200-2000-cm^{-1}, 4-cm^{-1} resolution

Lab Standard Calibration Curve

- Range of interest 0 - 15ppm (as N)
- Accurate quantification RSD<5%. (Internal standard => self-calibration)



Quantitative analysis in tap water

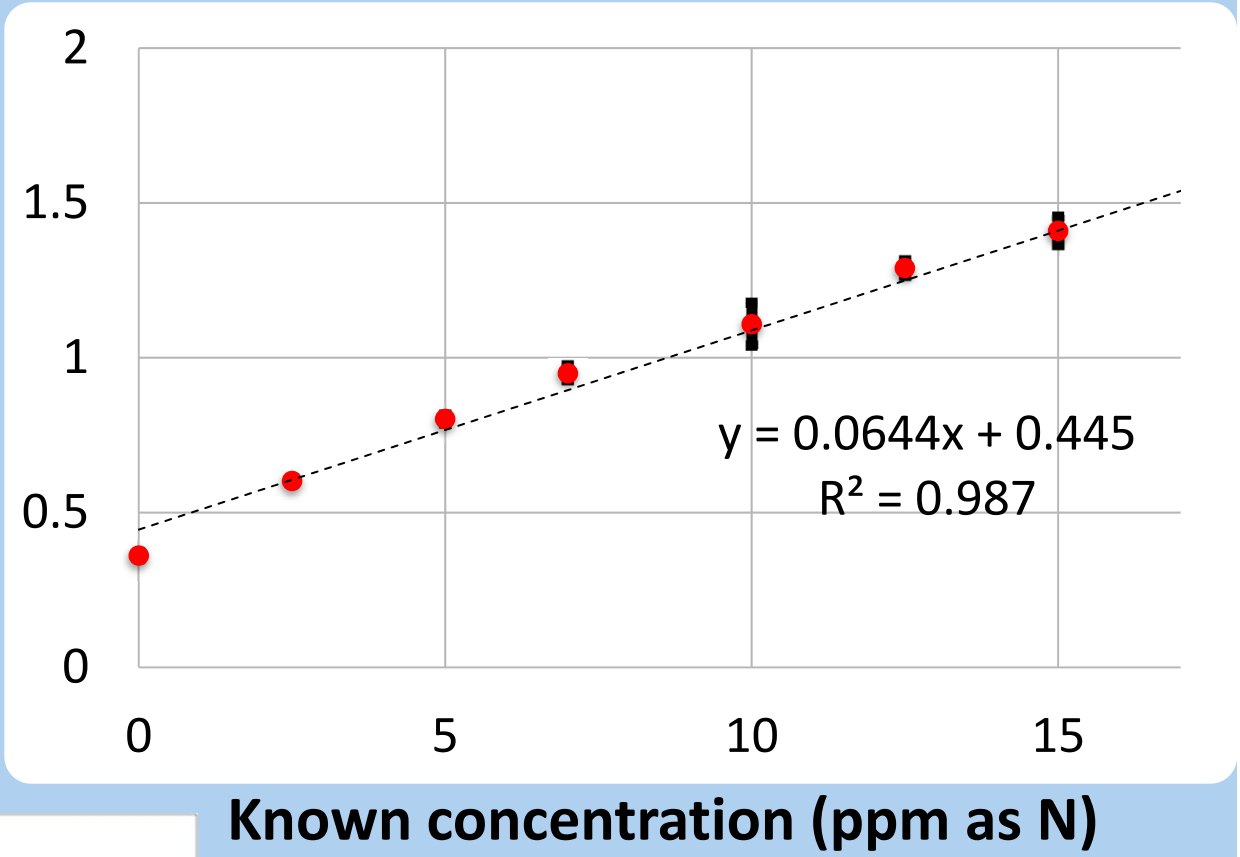


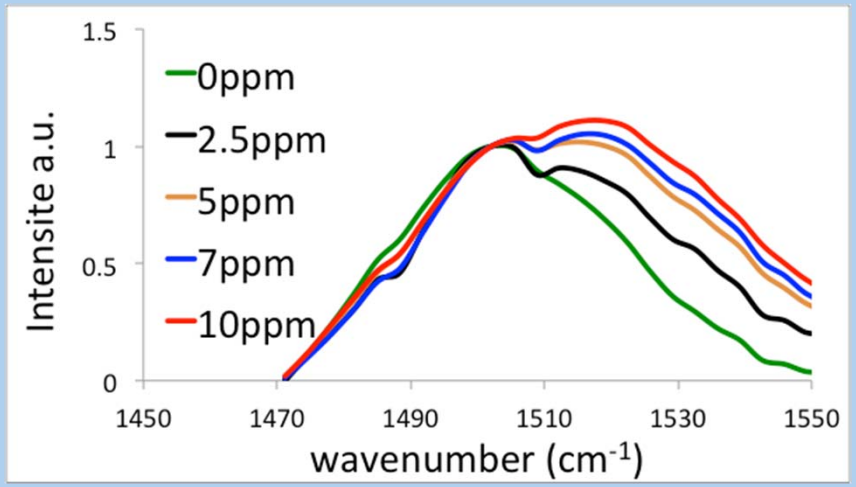
Ultra compact solid state spectrometer

Instrumentation

- 785-nm, 50-mW,

  10 um slit, No temp control
- APS-CMOS Detector
- 200-2000-cm^{-1}, 5-cm^{-1} resolution


Relative intensity at 1530cm-1
2
1.5
1
0.5
0
0
5
10
15
y = 0.0644x + 0.445
R² = 0.987
Known concentration (ppm as N)


Intensite a.u.
1.5
1
0.5
0
0ppm
2.5ppm
5ppm
7ppm
10ppm
1450
1470
1490
1510
1530
1550
wavenumber (cm-1)

Summary & Future Directions

- The successful results obtained in lab settings for standards and field samples demonstrates:
  - No pretreatment necessary
  - Low-cost, rapid and deployable
  - Repeatable accuracies similar to IC
  - Robust to interferents (Ca, Mg, amines)

Next :

- Pilot: looking for users
- Continue to work on the portability of the analysis
- Develop an In-line system
- Measure of Di-Trichloramines (CDC SBIR, chlorine in pool => asthma)

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NSF

USDA

Questions?

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NEMC

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