National Environmental
Monitoring Conference 2018

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Definitive results. Decisive actions.

Surface Enhanced Raman Spectroscopy for Rapid Selenium Monitoring and Speciation, e.g. of Flue Gas Desulfurization Wastewater

Flue Gas Desulfurization (FGD)

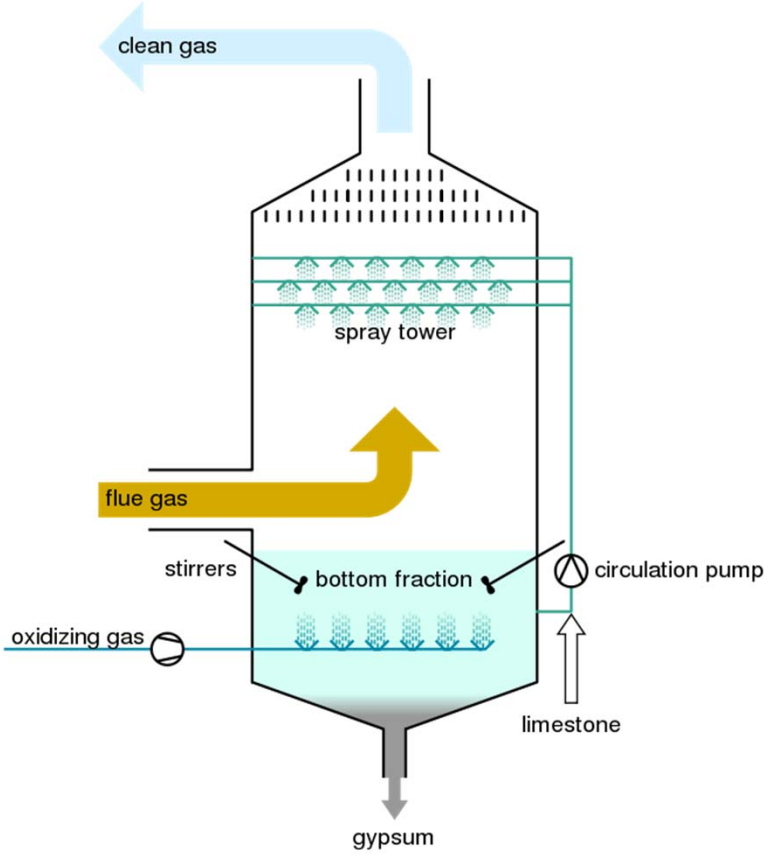
Sulfur content in fossil fuels : **0.4 w% - 0.7 w%**
Burning fossil fuel => emission of sulfur as **SO_2** (~95%) and **SO_3** (~1%)
Regulations on **SO_2** emissions => SO2 needs to be removed from flue gases

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



Schematic design of the absorber of an FGD

Source : https://commons.wikimedia.org/wiki/File:Flue_gas_desulfurization_unit_EN.svg

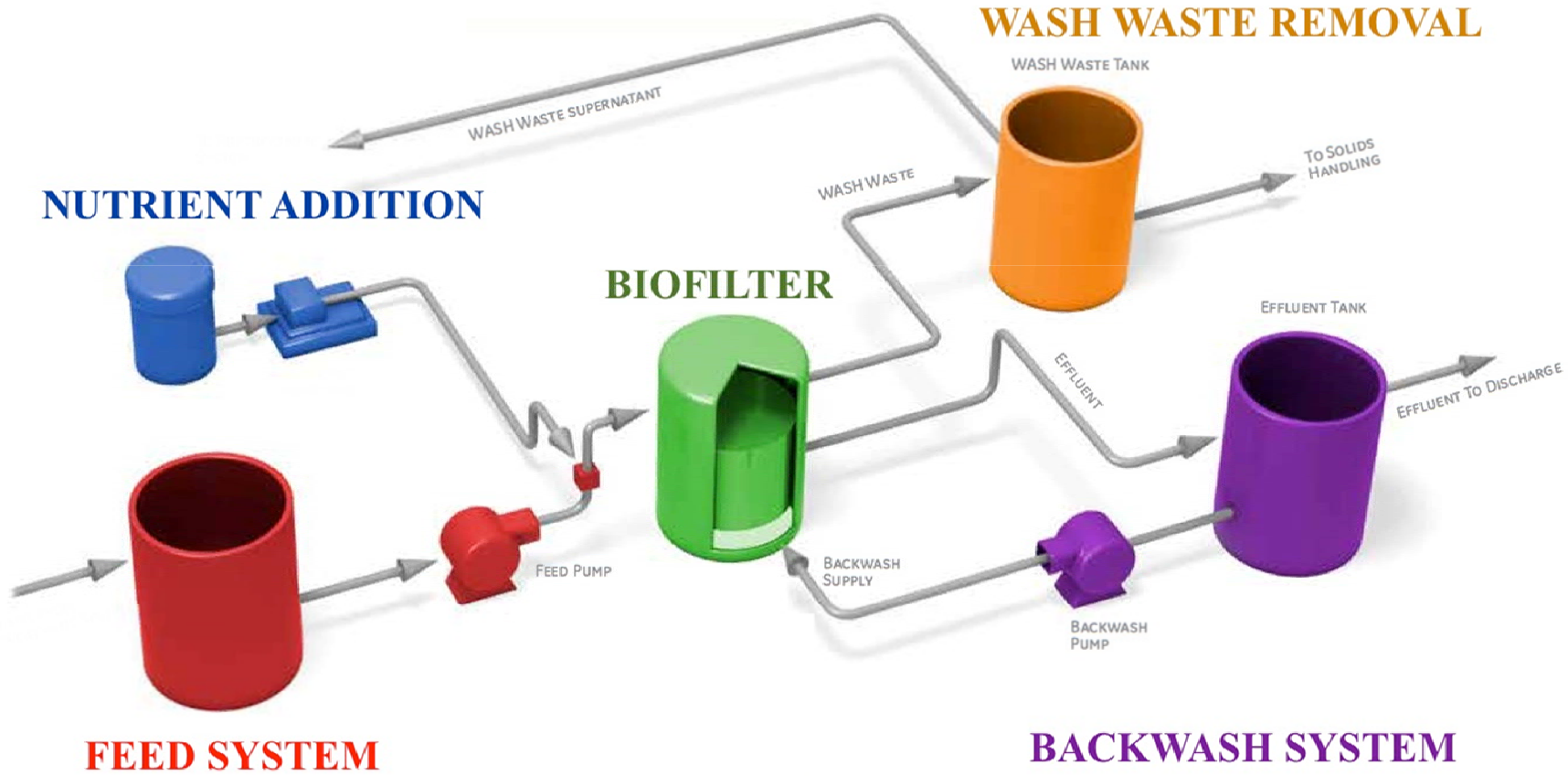
FGD wastewater content

CHEMICAL	CONCENTRATION in PPM
Total Organic Carbon as C	21.9
Al, Mn, Sr, K, F, Na, Br, SiO_2	< 50
Boron as B	128
Nitrate as NO_3	119
Chloride as Cl	4370
Magnesium Total (as Mg)	1030
Magnesium Hardness Total (as $CaCO_3$)	4240
Calcium Total (as Ca)	1660
Calcium Hardness Total (as $CaCO_3$)	4150
Sulfur Total (as SO_4)	2300
Selenium Total as Se	0.9

Adverse effects of Selenium on human health include:
Disruption of endocrine function, impairment of immune system, hepatotoxicity and gastrointestinal disturbances, dermatologic effects, neuro-degeneration

Selenium removal

- Selenium occurs as **selenide (Se II)**, **selenite (Se IV)**, **selenate (Se VI)**
- Regulatory limits (drinking water) : 50-ppb, although some States are lower



Biological Selenium Remediation Unit (source GE ABMET)

Current monitoring procedure

ICP/MS :

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

Colorimetric assay:

- Not quantitative
- No speciation
- Interferences

Raman spectroscopy

1920s 

1990s 

2000s 

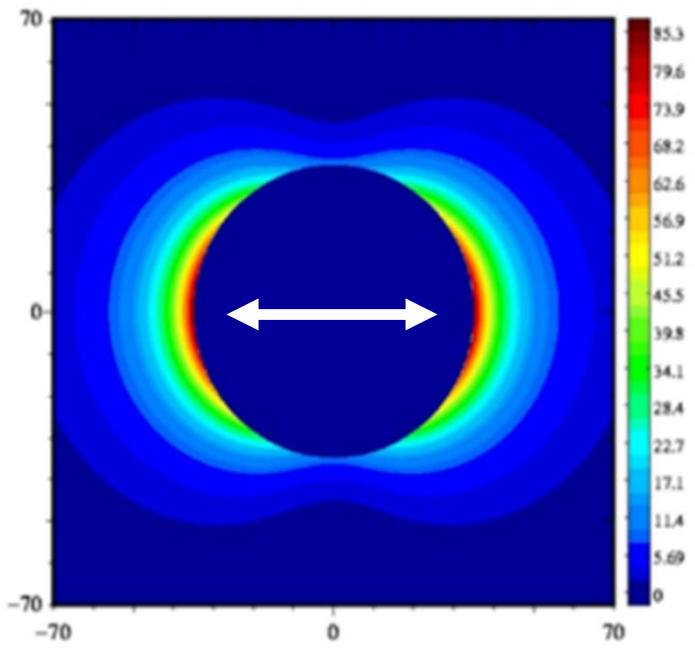
Optical telecommunications drove technology needed for portable, in-line, and compact Raman spectroscopy

But Raman is weak

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

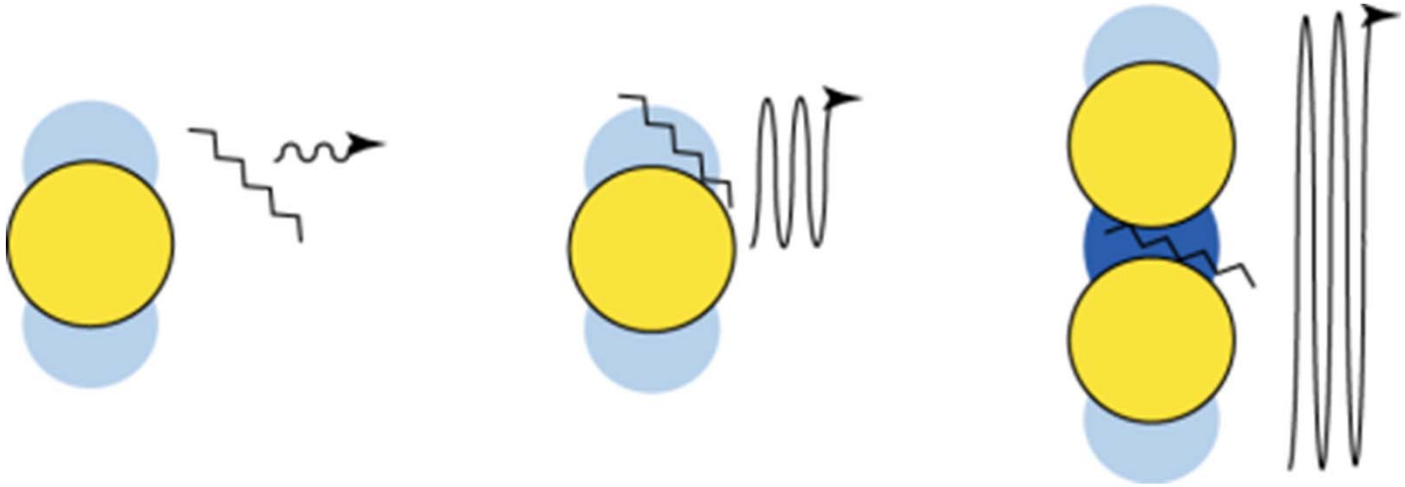
Surface-Enhanced Raman Scattering (SERS)

- 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

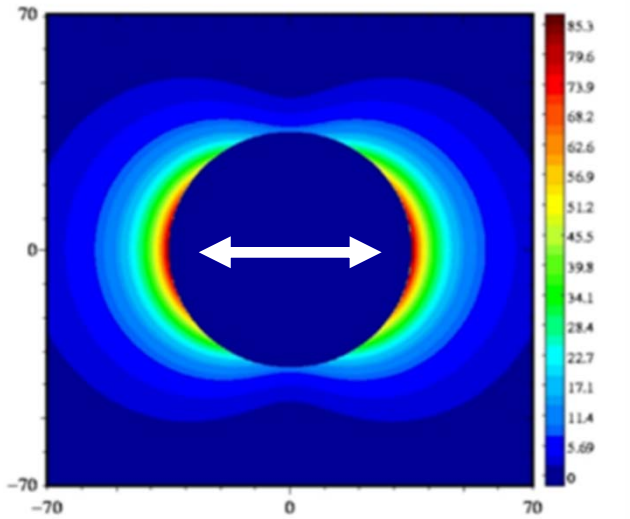
Nanoparticles (gold) enable **ppb-level** detection



"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 nanoparticles: many options to control surface properties

Why not widely used?

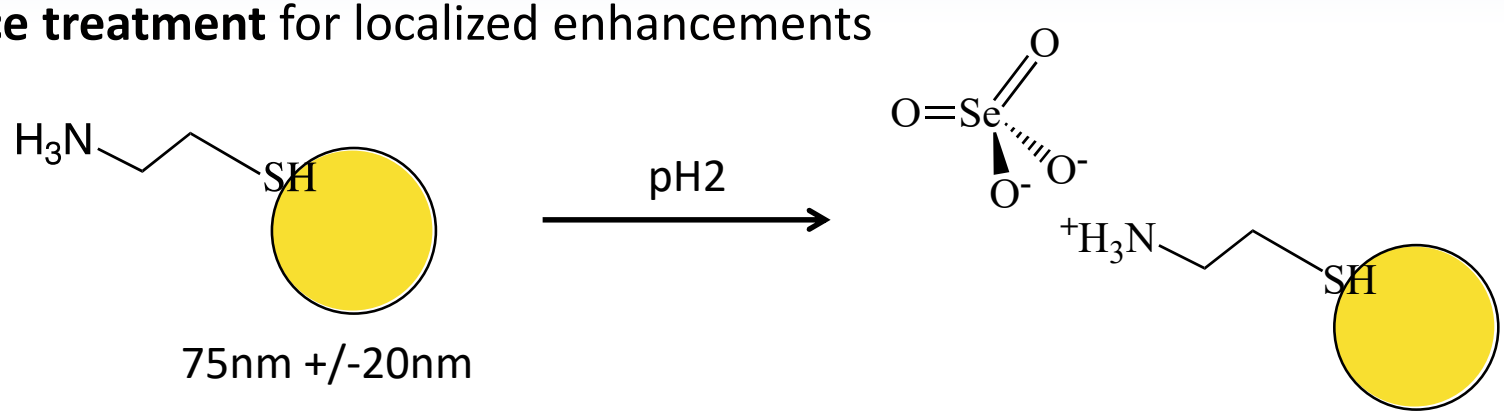
- Achilles' heel: reproducibility
  - Variations in substrate properties
  - Stochastic nanoparticle alignments
- One reviewer: "SERS doesn't work"

OndaVia has made SERS a quantitative, repeatable method using:

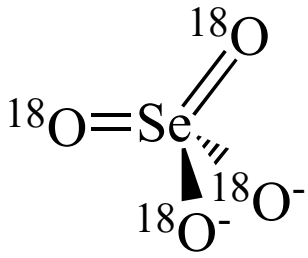
- Internal standards
- Nanoparticle structure
- Surface modifications
- Intelligent software

SERS enables trace-level detection

Surface treatment for localized enhancements



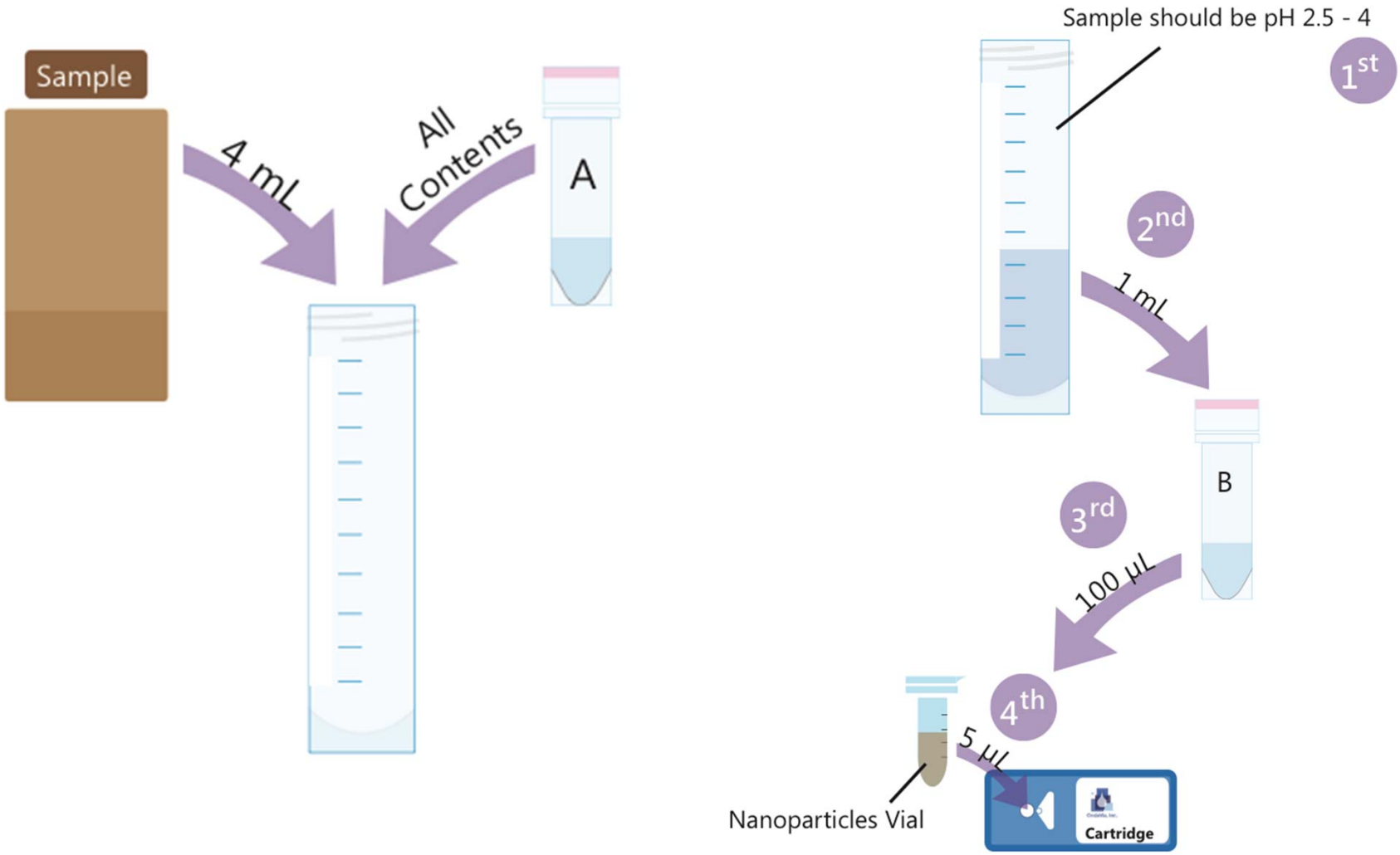
Internal standard: selenium isotoplogue provides self-calibration of the analysis



Instrumentation

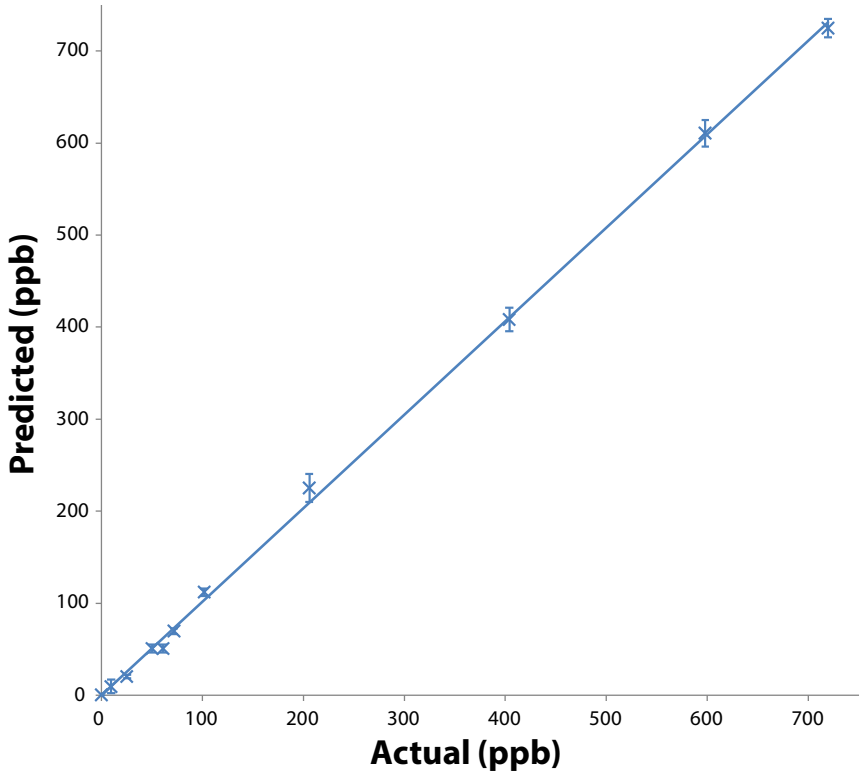
- 785-nm, 60-mW at substrate
- Cooled (-20°C) detector
- 200-2000-cm^{-1}, 4-cm^{-1} resolution

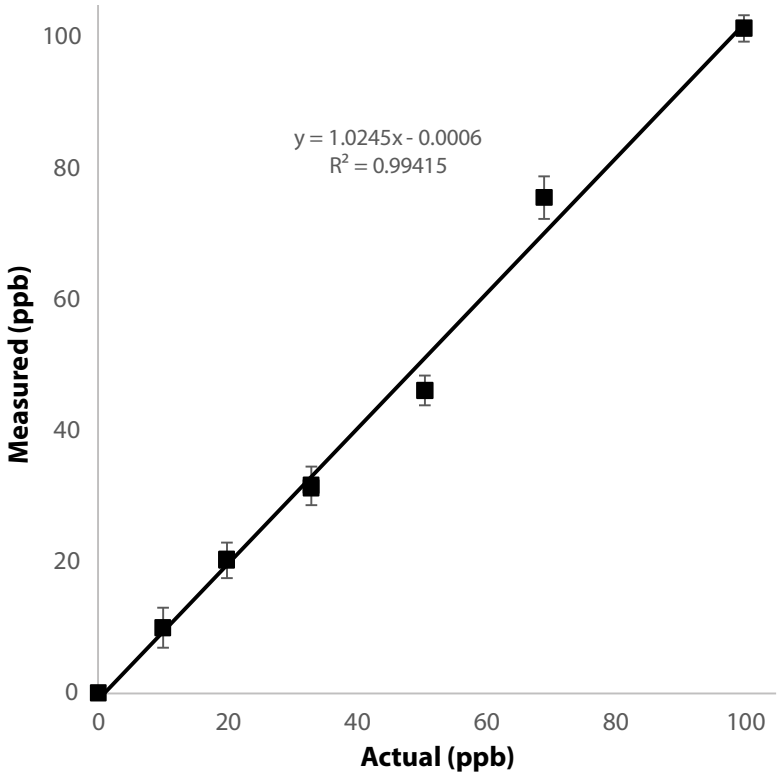
Quantification with SERS



Lab Standard Calibration Curve

- Accurate quantification better than 10%. (Internal standard => self-calibration)
- Significant dynamic range





Selenium speciation

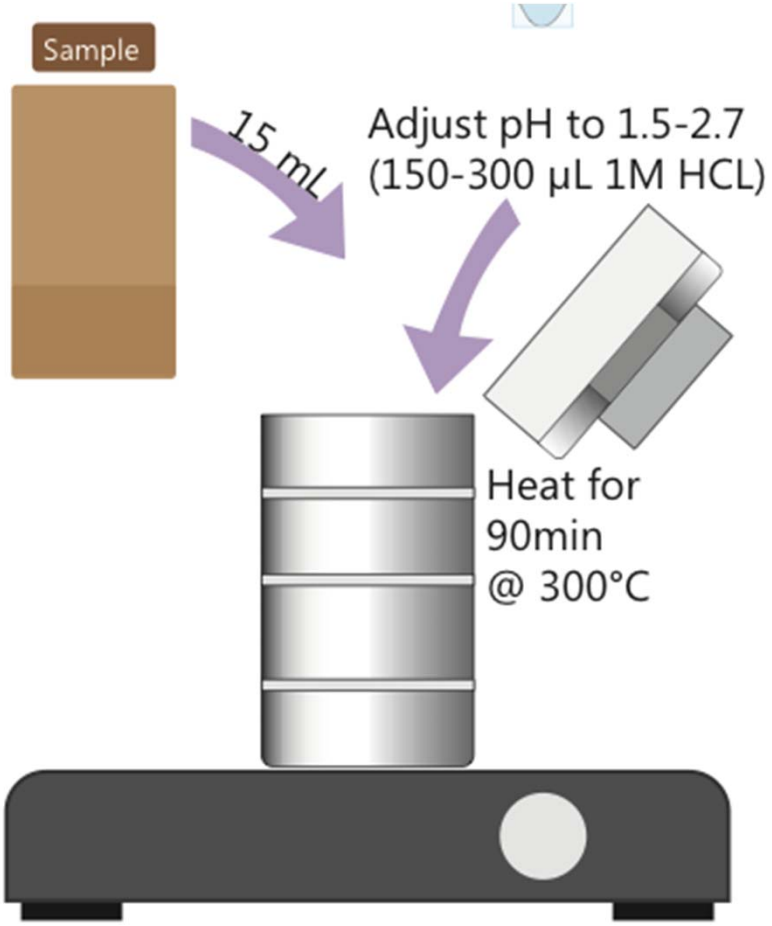
- Test is specific for Se(VI)
- Se reduced during biological treatment of waste water
- Oxidize treated water using bleach and/or H_2O_2 at high pH to convert all Se(IV) to Se(VI)

Fieldable speciation test:

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

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

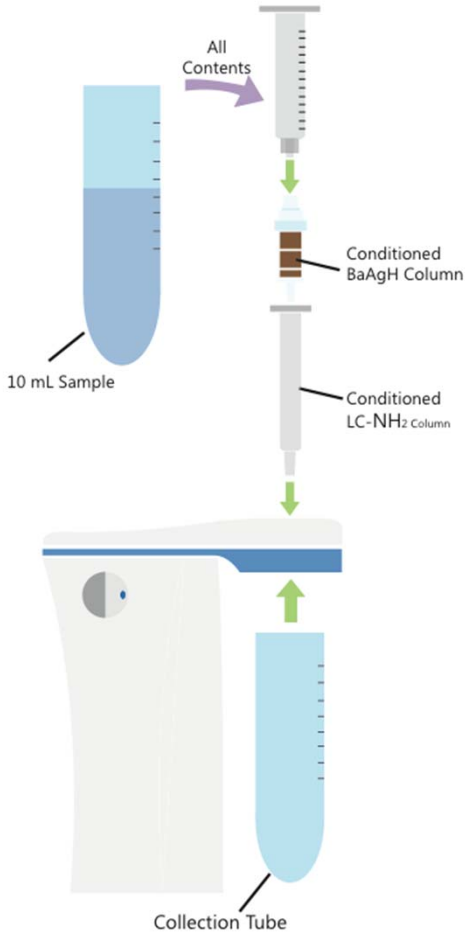
FGD sample pre-processing



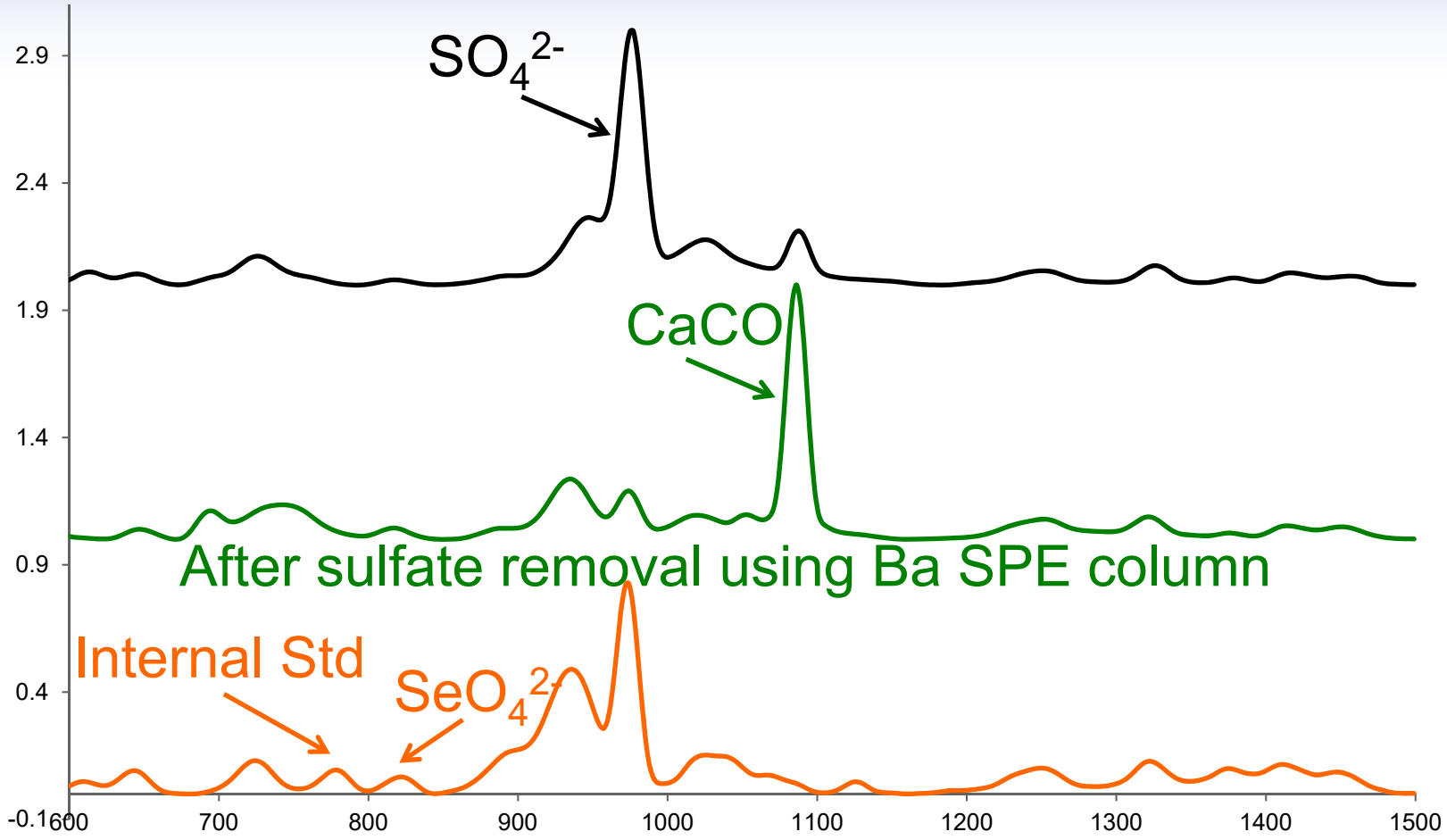
Elimination of the CaCO nanocrystals that formed during the FGD high temperature and pressure process

FGD sample pre-processing

1. Add Internal Standard
2. Oxidation (total Se)
3. Removal of Cl using AgO
4. Removal of SO_4 using standard Ba solid phase extraction (SPE) column
5. Removal of metals with H SPE column
6. 10x concentration step



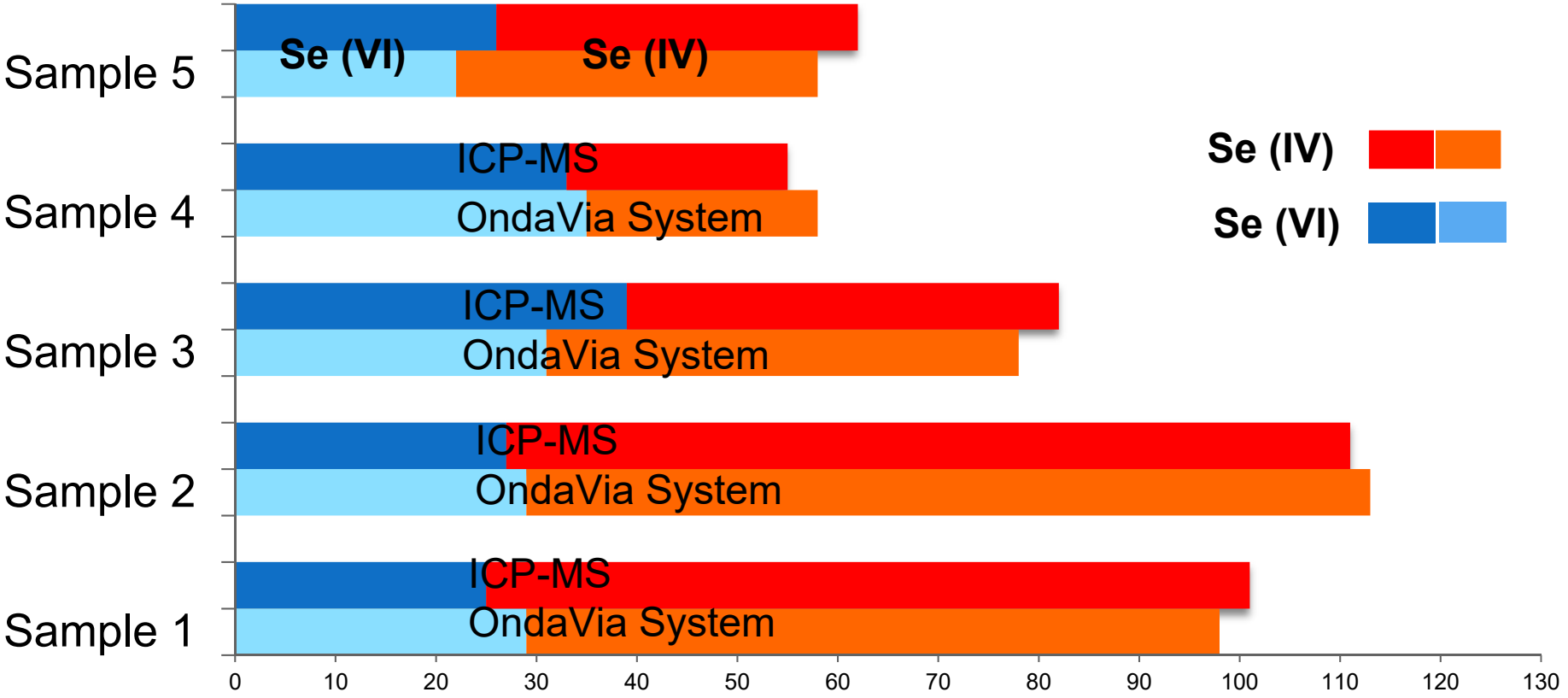
Real-world FGD requires pretreatment



After CaCO digestion in autoclave at 200C

ICP-MS v.s SERS on FGD samples

Selenate (ppb)		Selenite (ppb)	
ICP/MS	*OV*	*ICP/MS*	*OV*
25	29	76	69
27	29	84	84
31	39	47	43
35	33	22	23
22	26	36	36

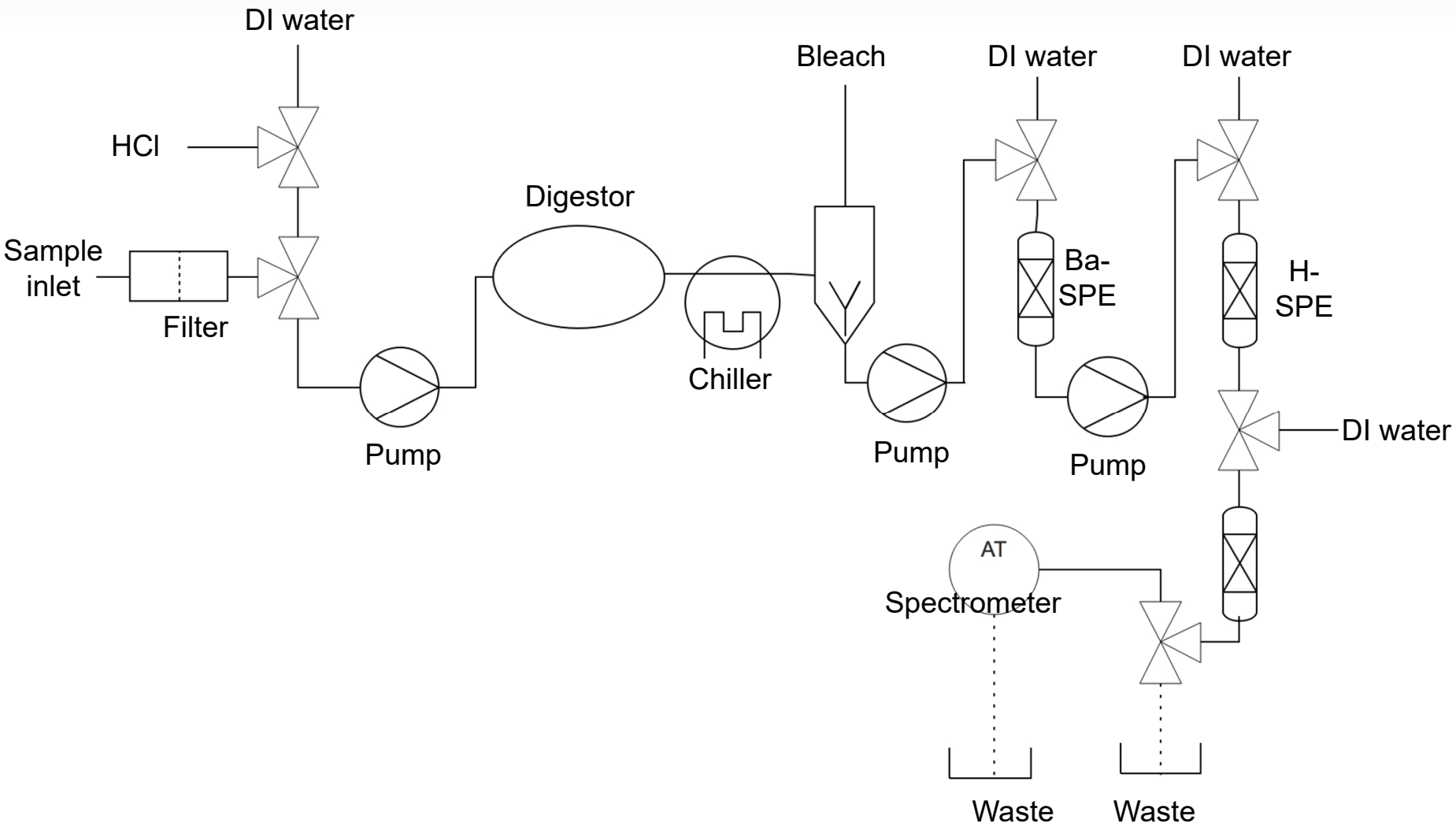


Continuous Monitoring

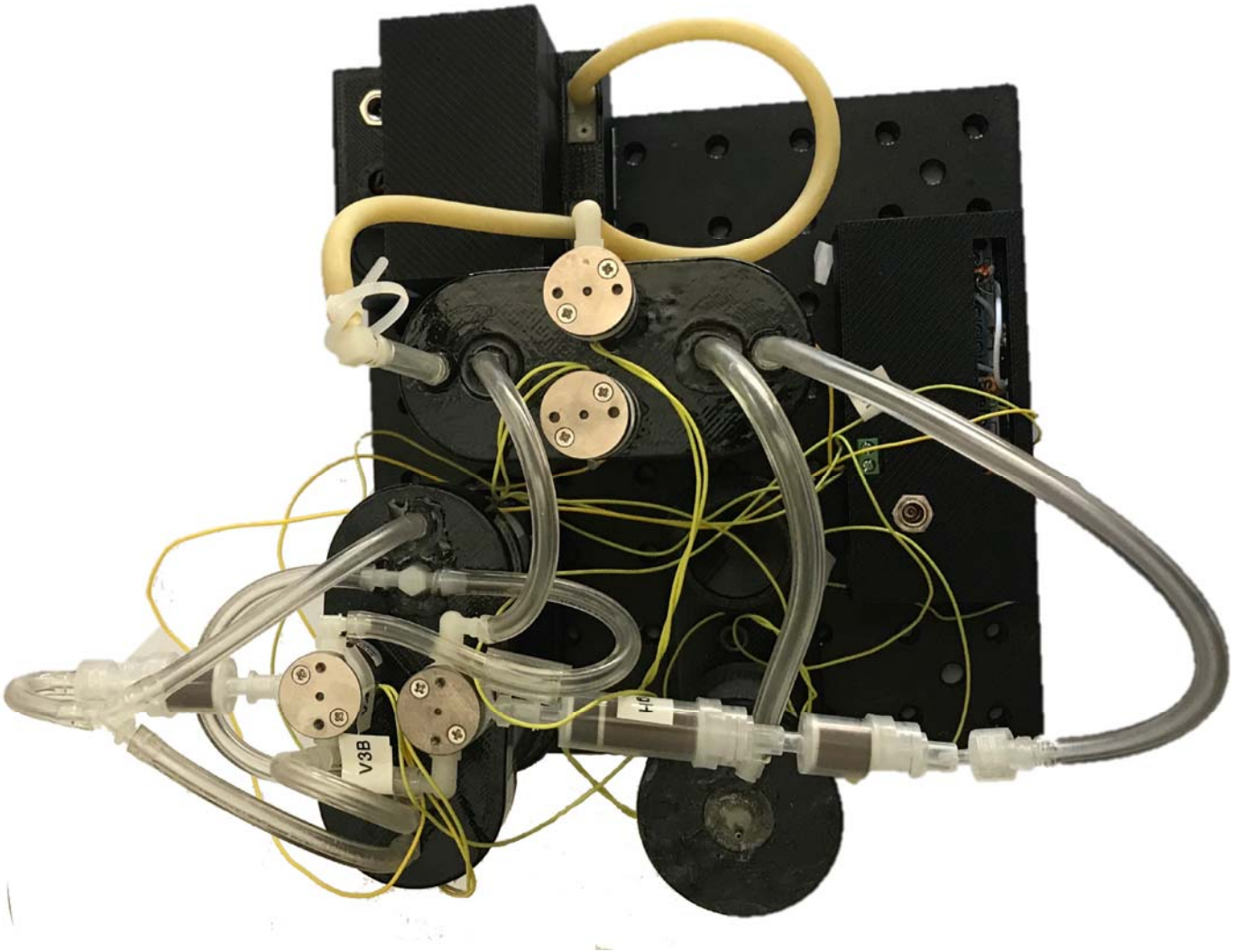
On-line analysis system

- Sample collection and analysis once / hour
- <2 hrs / wk maintenance
- Other potential features
  - Automatic QA/QC (by including a reference standard)
  - Measurement autoscale (with possibly higher consumable use)

Pneumatic schematic



Pneumatic system prototype



Summary & Future Directions

- We've proven that SERS for the detection of Selenium can be quantitative at sub 10-ppb in real-world FGD water
- It is repeatable with accuracies similar to ICP-MS
- It is deployable on-site and automatable (further publications and reports to come)

Next :

- Continuation of the automation
- Measure of multiple analytes simultaneously (e.g. Nitrate/ite)

Special thanks to

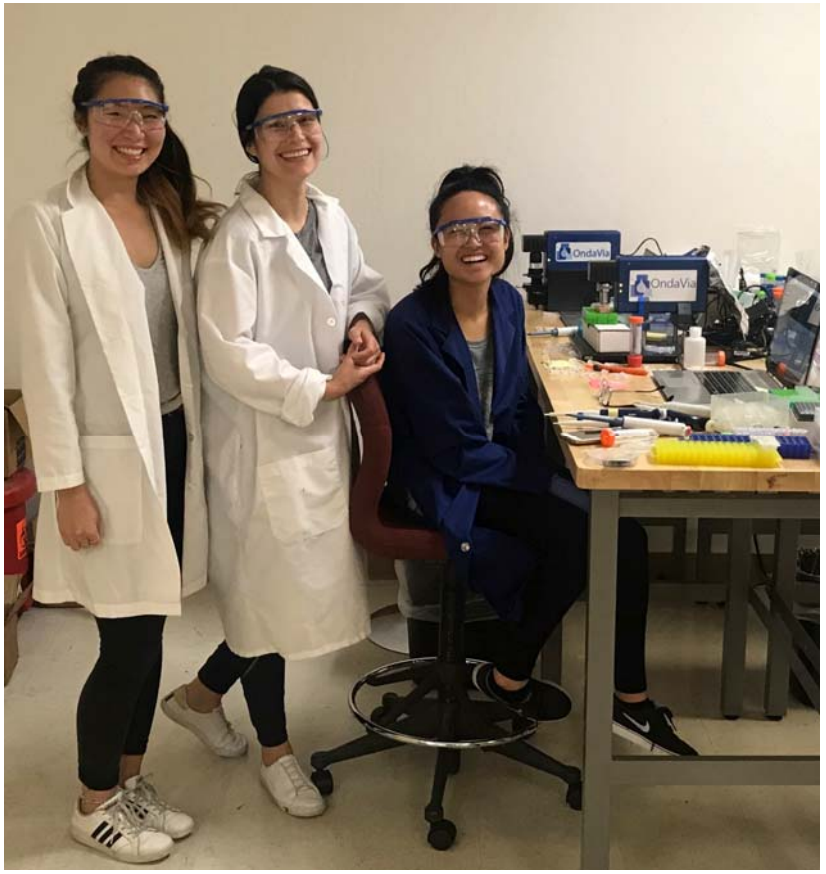
OndaVia, Inc.

Mark Peterman, PhD

Mayra Zaragoza

Melissa Yao

Kristle Cruz Garcia



And to…

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