Applied Speciation

Analysis Research Consulting

Selenium Speciation in Aqueous Matrices and Its Impacts on the Accuracy of Compliance Monitoring Measurements

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Overview of Selenium Speciation

- Significance of Se in the Environment
  - Effects, Sources, Regulations
- Selenium Species in Waters
  - Methods, Common Species, and Often Overlooked Species
- Impact of Se Speciation on the Accuracy of Total Se Measurements
  - Selected Case Studies and Solutions

Why is Selenium Important?

- Se is an essential trace nutrient
- Selenoamino acids → Selenoproteins → Antioxidant enzymes
- Deficiencies in humans have been correlated with hypothyroidism, heart issues, and increased cancer rates
- May provide protection against As and Hg toxicity

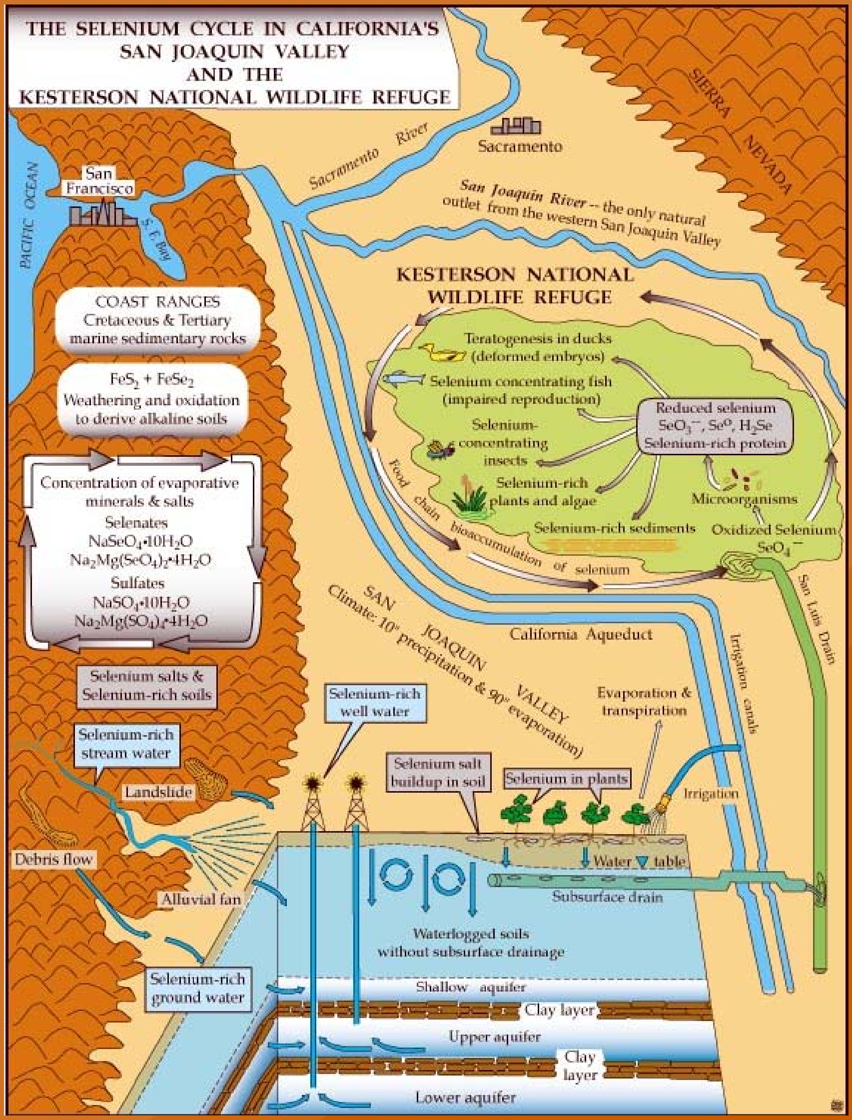
Why is Selenium Important?

- Se is toxic is high concentrations
- Threshold between deficiency and toxicity is low (~1 order of magnitude)
- Effects in wildlife include decreased reproductive success
- Effects in humans include skin/hair changes and neurological symptoms
- Toxic effects mediated by nonspecific substitution of Se for S in proteins

IV	V	VI
6 C	7 N	8 O
14 Si	15 P	16 S
32 Ge	33 As	34 Se

Sources of Selenium

- Naturally occurring in soils
  - CA, SD, WY, CO
- Mining-impacted areas
- Coal Combustion
- FGD wastewater, fly ash
- Oil Refining



Source: USGS

Selenium Regulations

- US Chronic Freshwater Criterion historically has been 5μg/L
  - Based on toxicity to fish observed at Belews Lake, NC in the late 1970s
- USEPA proposed a tissue-based standard in 2004
  - Tissue criterion reflects site-specific chemical and biological factors that can control selenium bioaccumulation
  - Can be converted to water-based criterion using a site-specific bioaccumulation factor
- Many point sources are still regulated based on aqueous concentrations of total Se

Why Speciate Selenium?

- Regulations may be based on total Se concentrations, but the molecular forms present will influence the toxicity, fate and transport, and treatability

- Performance of treatment systems determined by the species of selenium present
  - Iron Co-precipitation
  - Biological Treatment

Selenium Speciation Methods

- Non-chromatographic
  - HG-AAS or HG-AFS

→ Relies on reactive chemistry; can typically only differentiate between inorganic and reduced selenium species

- Chromatographic separation…
  - IC, LC, CE, GC
- …followed by detection
  - ICP-MS, MS/MS

→ Selection of hyphenated method can depend on molecular form of Se

Selenium Speciation Methods

- Ion Chromatography Inductively Coupled Plasma Mass Spectrometry (IC-ICP-MS)
  - Can separate and quantitate ionic forms of selenium
  - Low detection limits (ng/L)
  - Monitor multiple selenium isotopes for confirmation purposes
  - Monitor other elements for identification
  - Quantitation generally is species independent

Common Aqueous Selenium Species

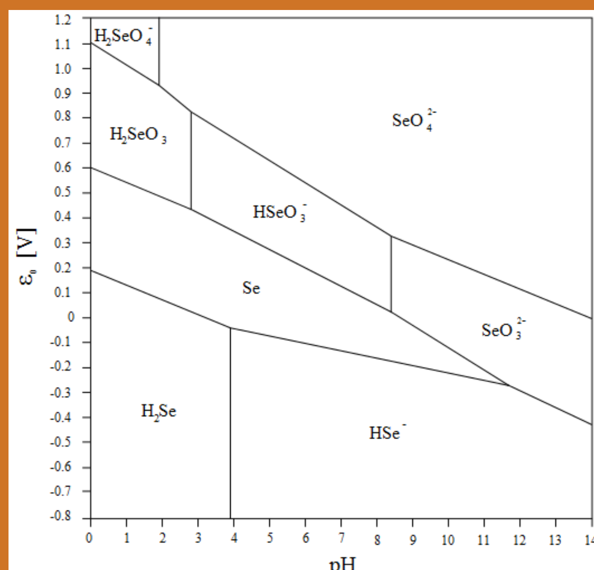
Oxidized

- Selenite – SeO_3^{2-}
- Selenate – SeO_4^{2-}
- Selenocyanate – $SeCN^-$

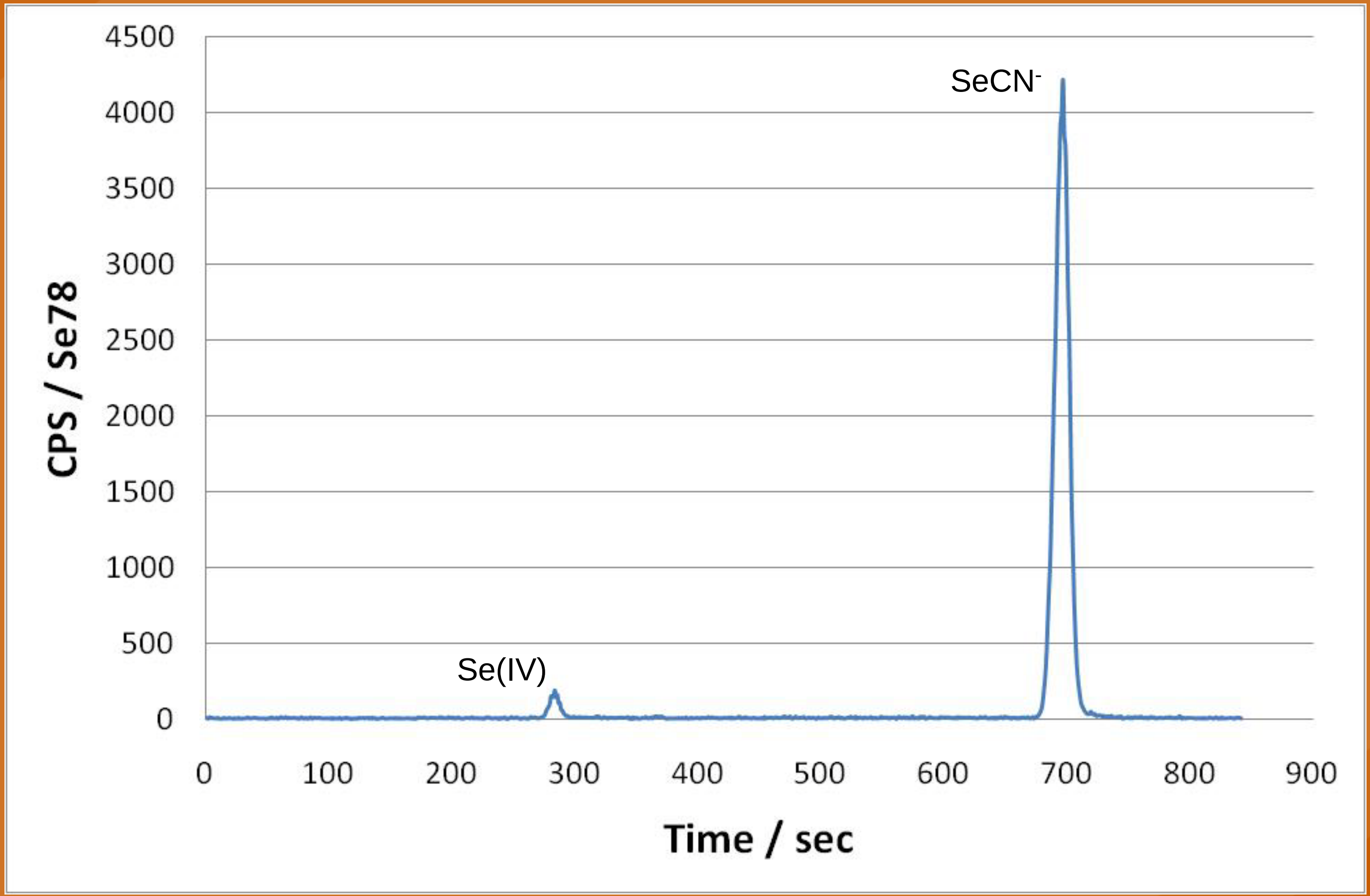
Reduced

Most common aqueous species

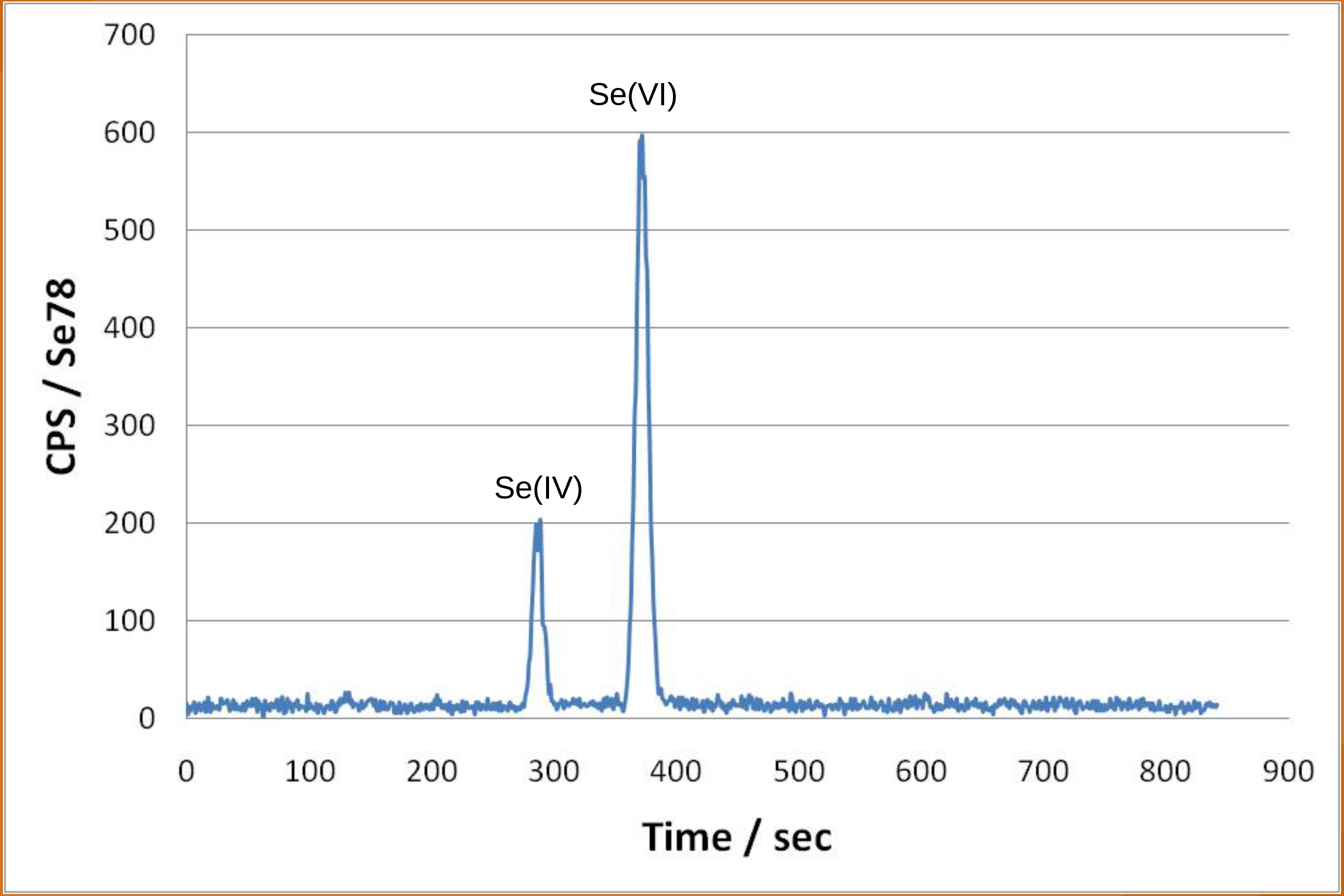
Typically from oil refineries, but also found in some FGD wastewaters; can be biologically generated



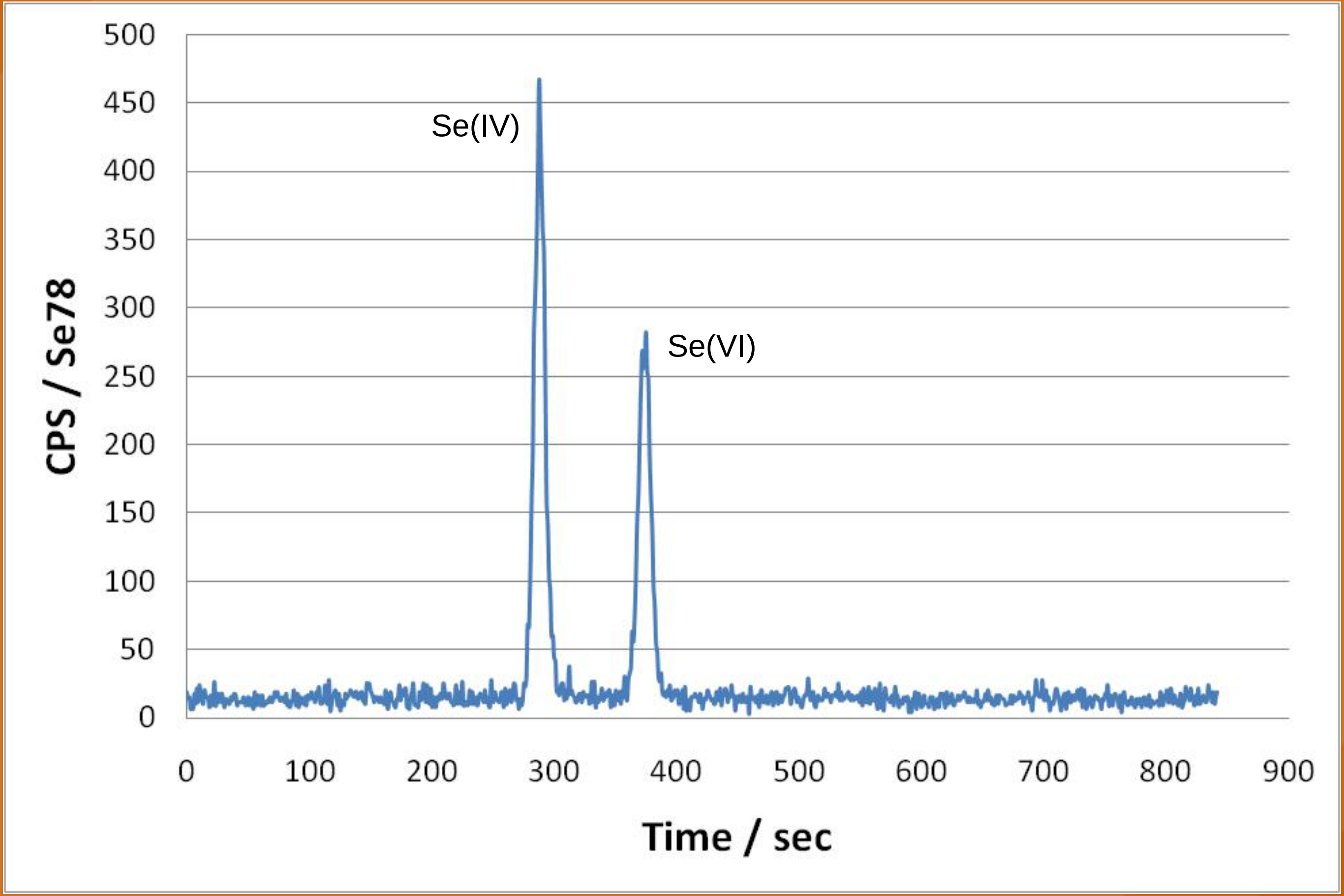
Speciation of a Refinery Wastewater



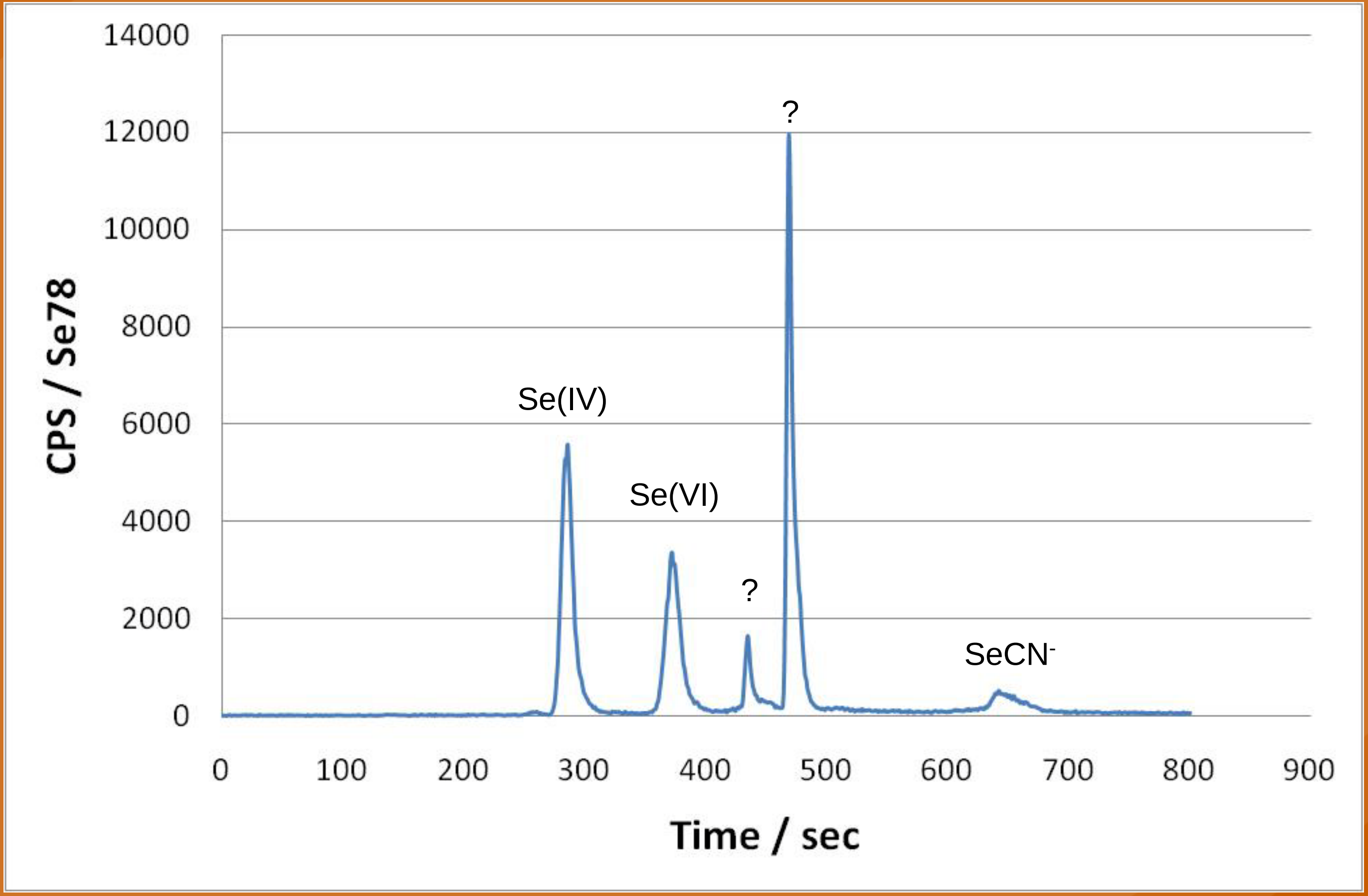
Speciation of a Surface Water



Speciation of a FGD Wastewater



Speciation of a FGD Wastewater



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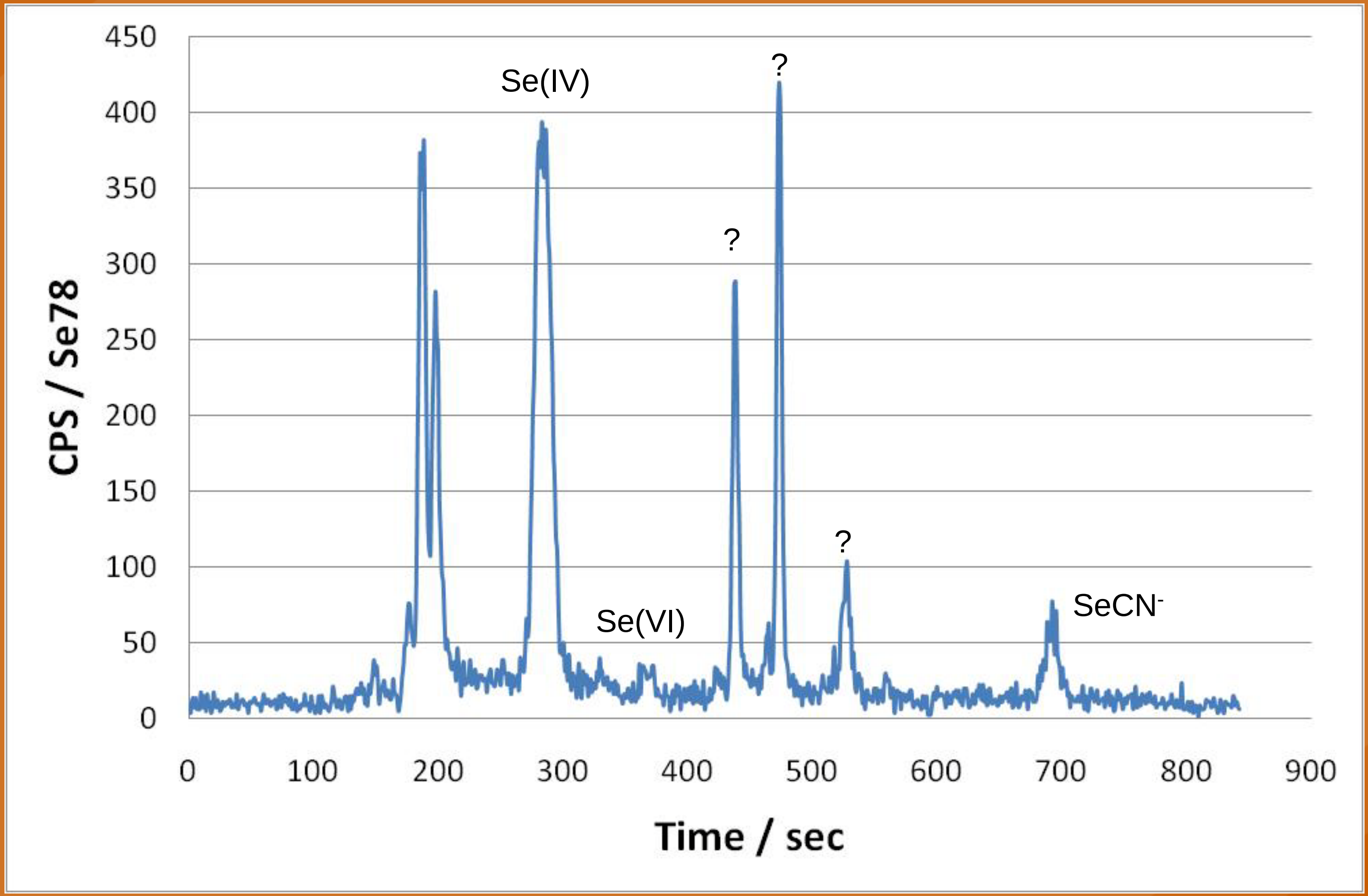
Speciation of a Bioreactor Effluent



What are these unknown species?

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Less Common Selenium Species

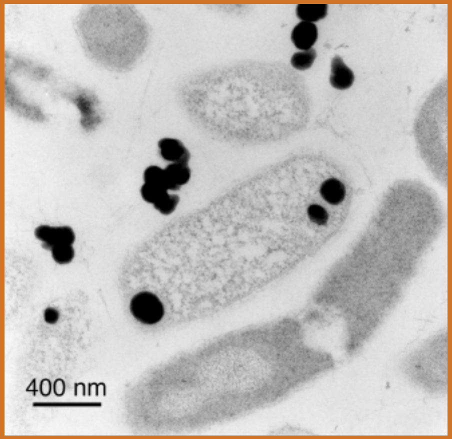
Oxidized

- Selenate – SeO_4^{2-}
- Selenite – SeO_3^{2-}
- Selenocyanate – $SeCN^-$
- Elemental Selenium – Se^0
- Selenosulfate – $SeSO_3^{2-}$
- Dimethylselenide (DMSe) – $(CH_3)_2Se$
- Dimethyldiselenide (DMDSe) – $(CH_3)_2Se_2$
- Other organoselenium species

Reduced

Elemental Selenium

- Can form via reduction of either selenite or selenate by a diverse array of bacteria
- Formation of Se^0 is the basis of many biological and chemical (e.g., iron cementation) treatment systems for selenium
- Can be present in different forms (allotropes) and sizes



Oremland *et al.*, *Appl. Environ. Microbiol.*, **2004**, 70, 52-60.

Elemental Selenium

- Colloidal Se^0 can pass though standard 0.45µm filters
- Colloidal Se^0 does not elute from standard IC columns

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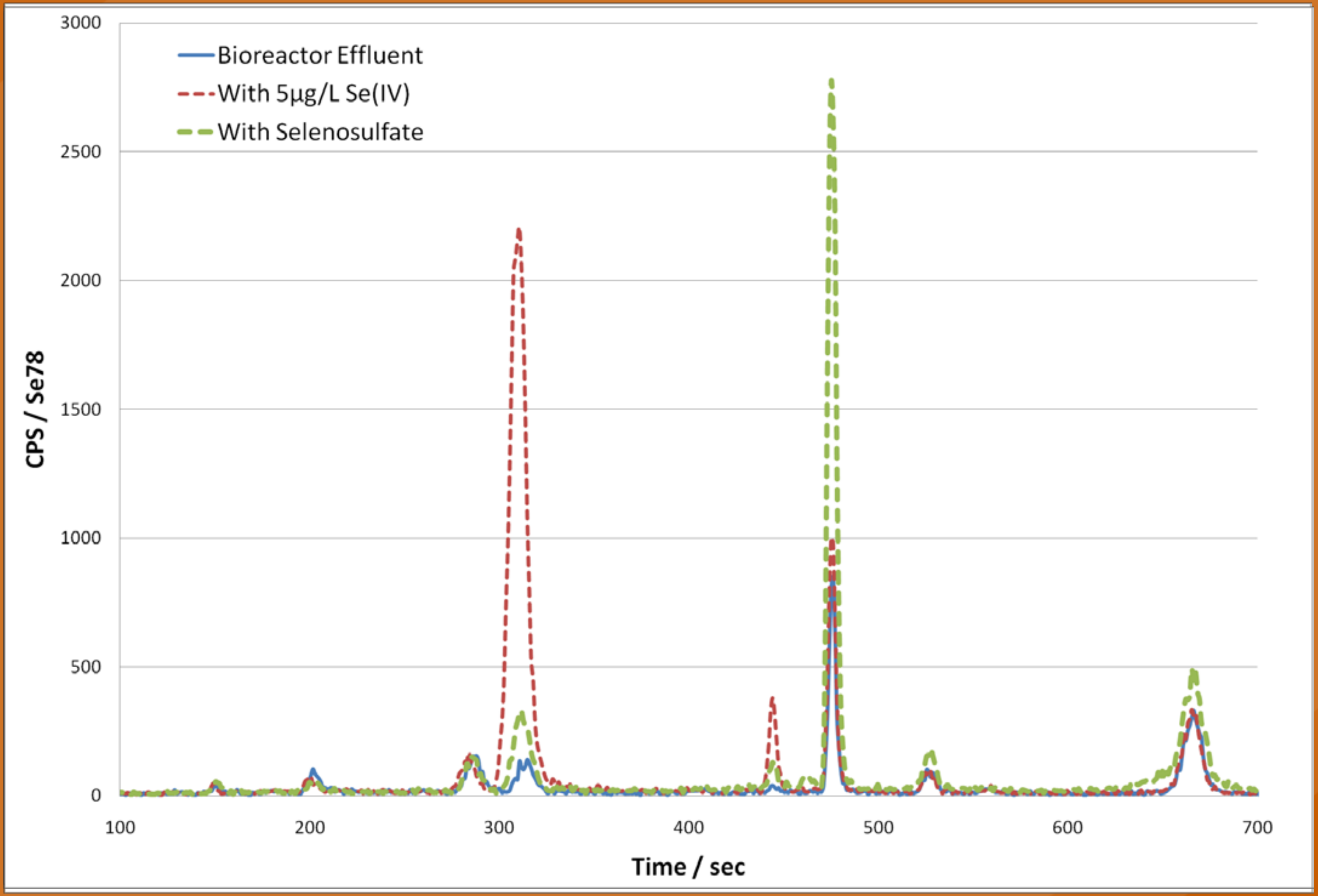
Reduced

Selenosulfate

- Typically found in reducing environments
- Can form via reaction of elemental selenium with sulfite:
  - $Se^0 + SO_3^{2-} \rightarrow SeSO_3^{2-}$
- Found in some FGD wastewaters, esp. natural or inhibited oxidation systems:
  - *e.g.*, $SO_2 + Ca(OH)_2 \rightarrow CaSO_3 + H_2O$

Identification of $SeSO_3^{2-}$ via IC-ICP-MS



Less Common Selenium Species

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Reduced

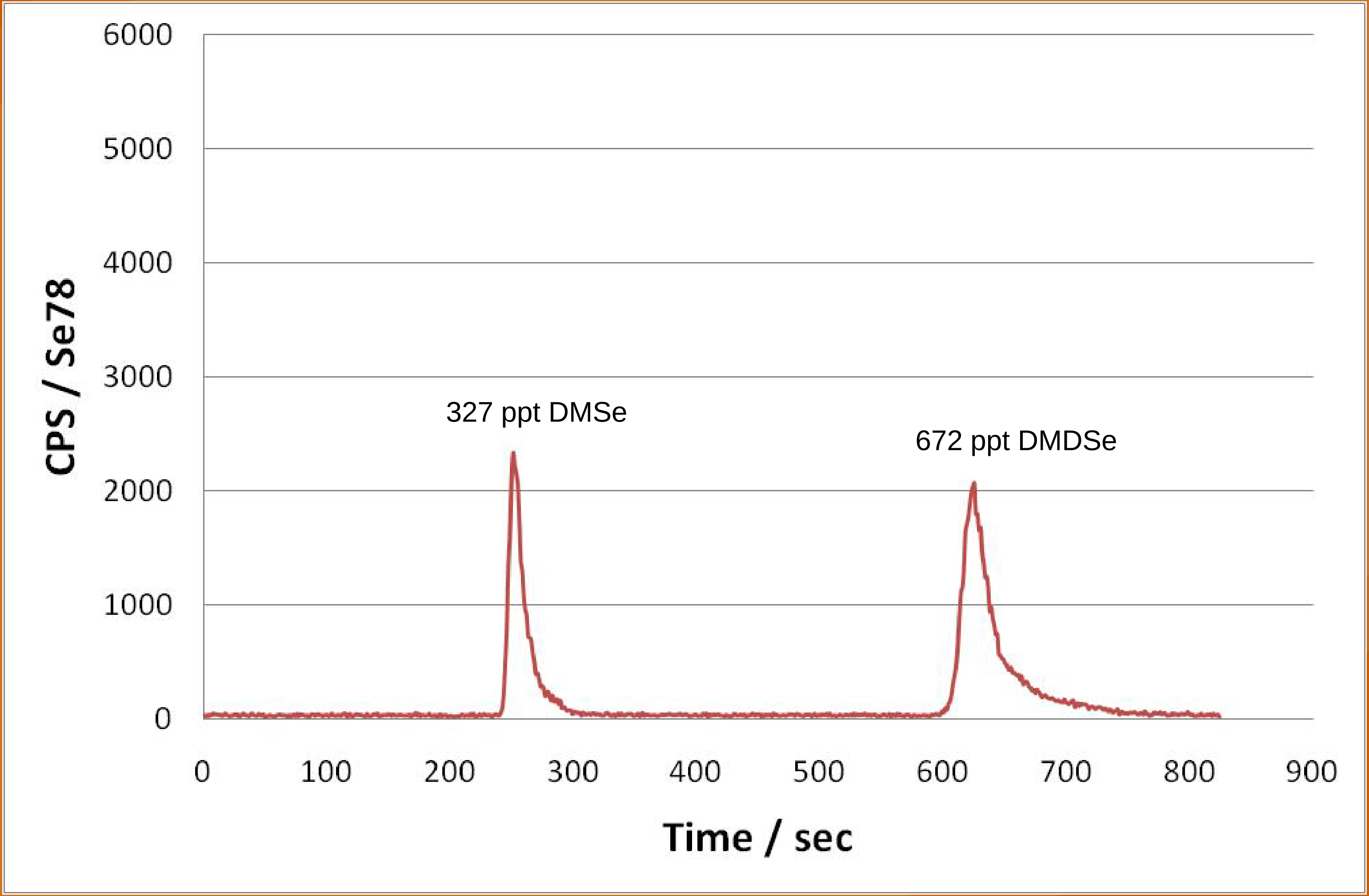
DMSe and DMDSe

- Volatile, less polar selenium species
- Product of biological reduction processes occurring in water and soil/sediment
  - Great Salt Lake, Utah
  - San Joaquin Valley
  - Biological treatment systems
- Do not elute from standard IC columns, so a different analytical method is required

RP-ICP-MS

- Reversed-Phase Inductively Coupled Plasma Mass Spectrometry (RP-ICP-MS)
- Uses a non-polar stationary phase (e.g., C-8 or C-18 modified silica) instead of an anion or cation column for species retention
- Ionic interactions between selenium species and chromatographic column are limited (without mobile phase modifiers)
- Low detection limits (ng/L)
- Can require high concentrations of organic solvents to elute highly retained organic selenium species

RP-ICP-MS of DMSe and DMDSe



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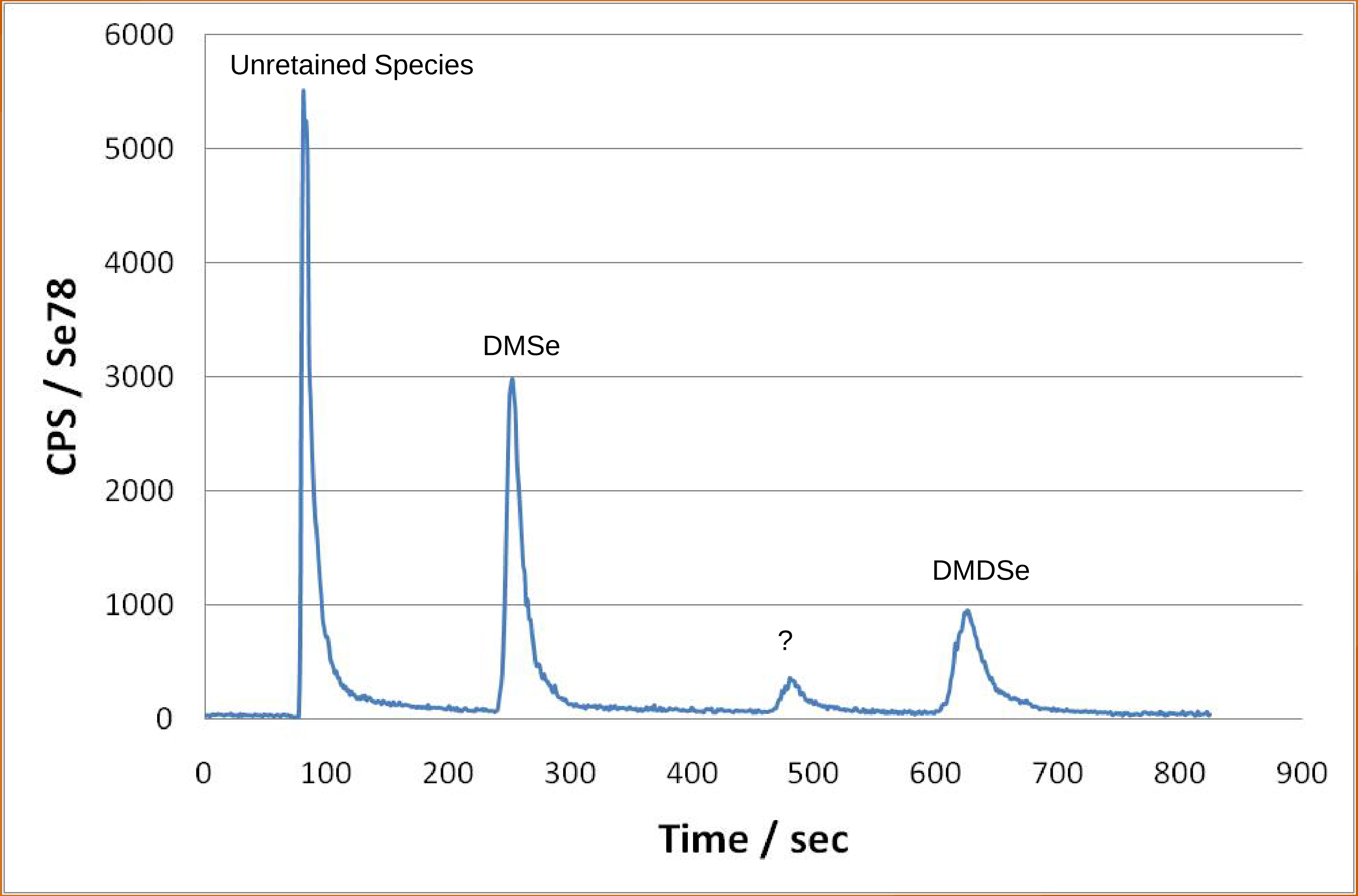
RP-ICP-MS of a Wetland Sample



Promulgated Methods for Selenium Analysis of Aqueous Matrices

- Commonly employed methods include the 200 series, 1638, and the 3000/6000 series
- Samples are to be collected into bottles (typically HDPE)
- Dissolved Se:
  - Samples require filtration followed by preservation to pH < 2
  - Samples *do not* require digestion, unless precipitates form
- Total Se:
  - Samples require preservation to pH < 2
  - Samples require digestion, typically with nitric and hydrochloric acids
  - Aliquot of sample usually is removed from the bottle for digestion

Identification of a Problem with Promulgated Se Methods

- Discrepancy between Se Speciation results and Total/Dissolved Se concentrations
- Dissolved (filtered) Se concentration greater than Total (unfiltered) Se concentration
- Temporally variable Se concentrations

Identification of a Problem – Case 1

- Samples from an oil refinery wastewater treatment plant
- Results:

Sample Type	Se(IV)	Se(VI)	SeCN	∑ Species	Total Se
WW Influent	8.4	44.2	559	611	111
WW Effluent	250	39.4	< 2.0 U	290	340

- Discrepancy between sum of species and total Se concentrations correlated to high $SeCN^-$ concentrations

$SeCN^-$ Decomposition in Acidic Solution

- $SeCN^-$ can decompose to elemental selenium under acidic conditions

- Se^0 can adsorb onto the surface of HDPE bottles
- Aliquoting acidified samples for Total Se analysis can produce biased low Se results!
- Solution: Glass bottles can minimize Se^0 adsorption

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Identification of a Problem – Case 2

- Samples from a WW treatment plant
- Results:

Sample Type	Total Se	Diss Se	Se(IV)	Se(VI)	SeCN	MeSe(IV)	DMSe	DMDSe
Effluent	7.21	37.5	2.98	2.88	< 0.50 U	0.62	1.68	< 0.033 U
Holding Pond	16.4	38.4	9.01	3.55	< 0.50 U	1.54	1.35	< 0.033 U

Sample Type	|Total Se - Diss Se|	Difference / [DMSe]
Effluent	30.3	18.1
Holding Pond	22.0	16.3

- Volatility of DMSe results in increased mass transport to the plasma during nebulization; therefore, ICP-MS not a species-independent method in all cases!

Identification of a Problem – Case 2b

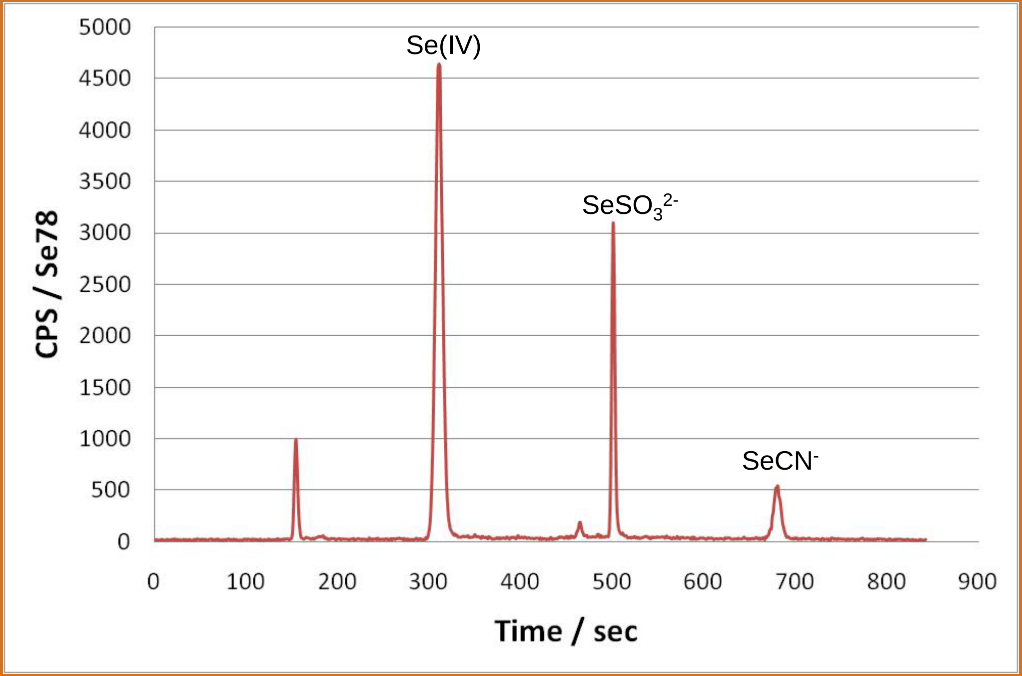
- Samples from a biological treatment system
- Results:

Sample Type	Total Se	Diss Se	Diss Se (Digested)
Influent	153	155	-
Effluent	27.5	185	22.1

- Total Se fractions acidified, digested, then analyzed
- Dissolved Se fractions filtered, acidified, and analyzed without digestion
- Solution to volatility problem: Digestion of dissolved Se fractions

Identification of a Problem – Case 3

- Samples from a biological treatment system
- Results:



Sample Type	Diss Se	Diss Se (+60 Days)
Effluent	52.7	31.4

$SeSO_3^{2-}$ Decomposition in Acidic Solution

- $SeSO_3^{2-}$ can decompose to elemental selenium under acidic conditions, similar to $SeCN^-$

- Elemental Se can adsorb onto bottle walls and therefore be under-represented when samples are aliquoted for digestion

Implications for Regulatory Compliance

- Total and Dissolved Se measurements can be significantly biased depending on the Se species present in a sample and their interactions with the sample matrix, applied preservative, and sample container
  - Volatile Se species can produce a high bias if samples are not first digested
  - Reduced Se species can precipitate from solution and adsorb to container walls when samples are acidified in HDPE bottles, producing a low bias

Implications for Regulatory Compliance

- Generating accurate Se results may require deviation from promulgated methods and/or standard laboratory practices
  - Collection of samples into borosilicate glass instead of HDPE
  - Digestion of both unfiltered and filtered fractions
  - More vigorous digestion procedures (closed-vessel) to fully mineralize all species and prevent losses of volatile species

Final Thoughts

- These issues will likely only increase in the future due to:
  - Increased regulation of the steam electric power industry (Proposed rule due July 2012?)
  - The application of more biological treatment systems
    - Not all treatment systems operate the same
    - Not all system operators know how their treatments work
    - Treatment efficiency and species produced can vary over time
- Generation of accurate data requires appropriate sample collection, preservation, digestion, *and* analysis

Acknowledgements

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