FIA Lab

Fluidics Intelligently Automated

Amperometric CN: The How and Why

FIA Lab

HELLO!

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Outline

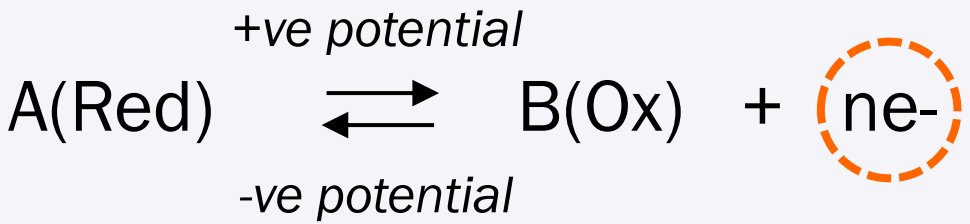
- The How: Fundamentals
  - Principles
  - How to Measure CN
  - How to Use Amp CN
- The Why: Practicals
  - Performance
  - Approved Methods
  - Instrument Considerations
- Conclusions

1

AMPEROMETRIC CN FUNDAMENTALS

Amperometry Principles

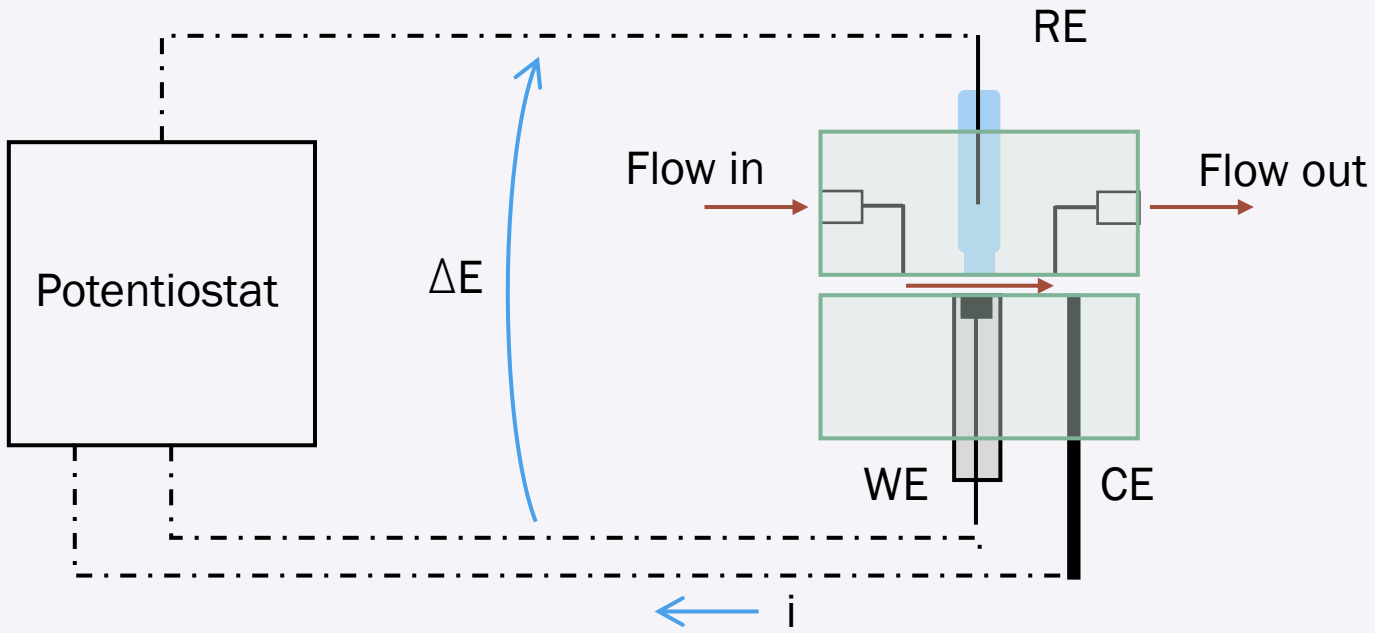
- Amperometry = measurement of electric current
- Needs electrochemical (redox) reaction
  - charge transfer



- OILRIG = Oxidation Is Loss, Reduction Is Gain (of electrons)
- Use a potentiostat to generate & measure current

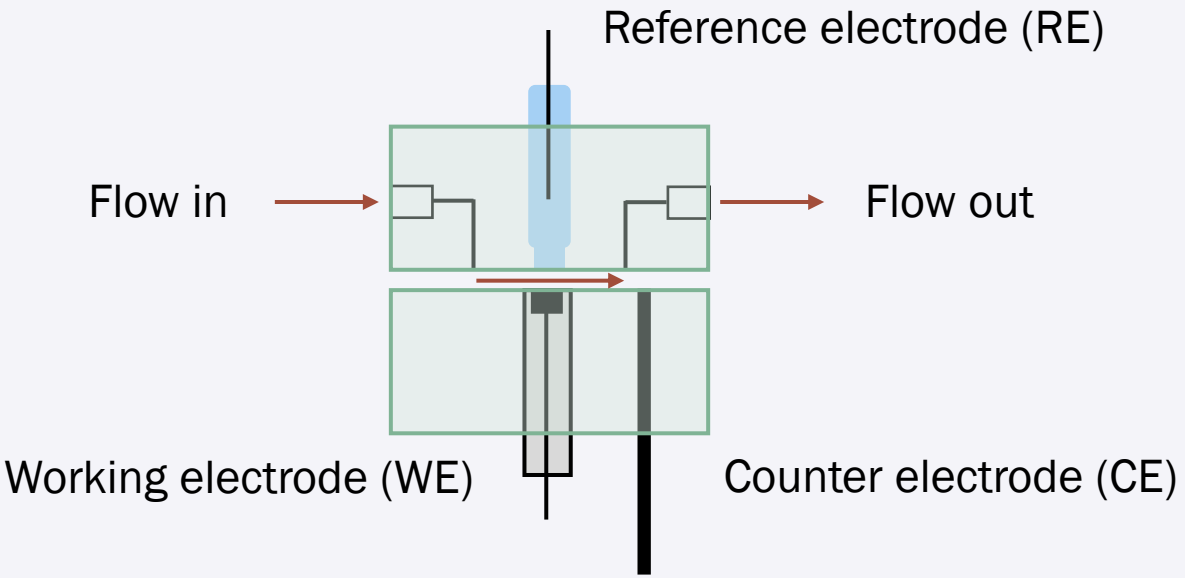
How to Measure CN

- Potentiostat
  - Applies a potential on working electrode (WE) to drive redox reaction
  - Reference electrode (RE) is the reference point for that potential
  - Measures current that flows through WE & counter electrode (CE)

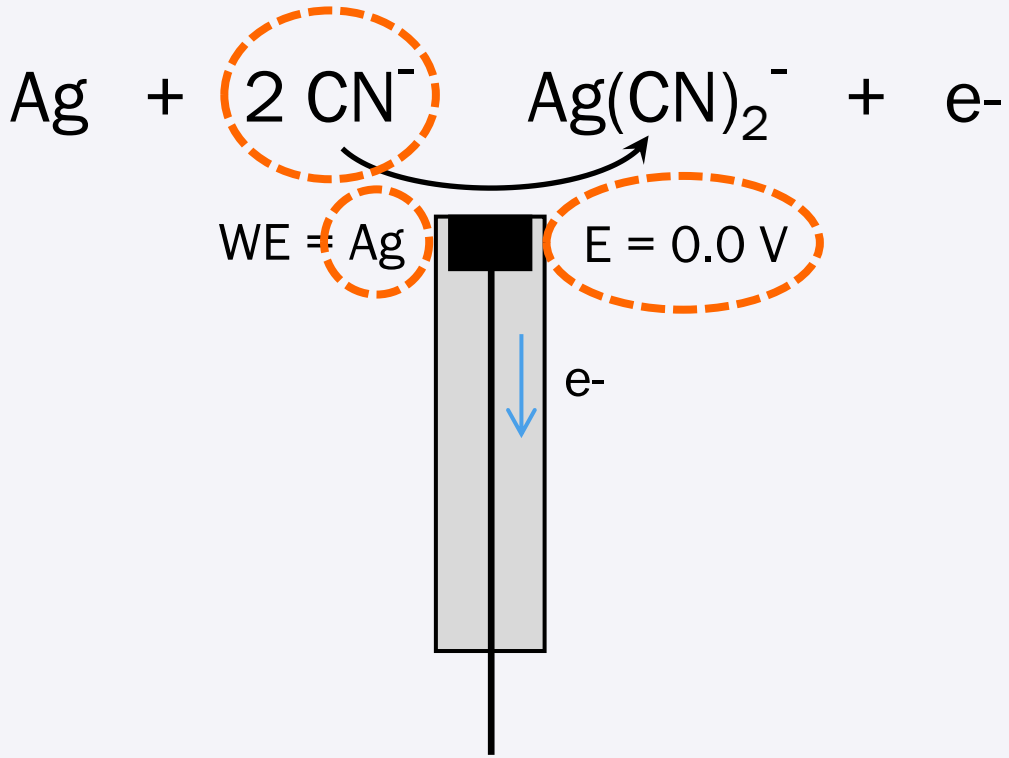


How to Measure CN

- Steady signal requires steadily moving solution
  - Can be implemented on a flow analyzer or using a stirred container
  - Cannot be run manually or on a discrete analyzer

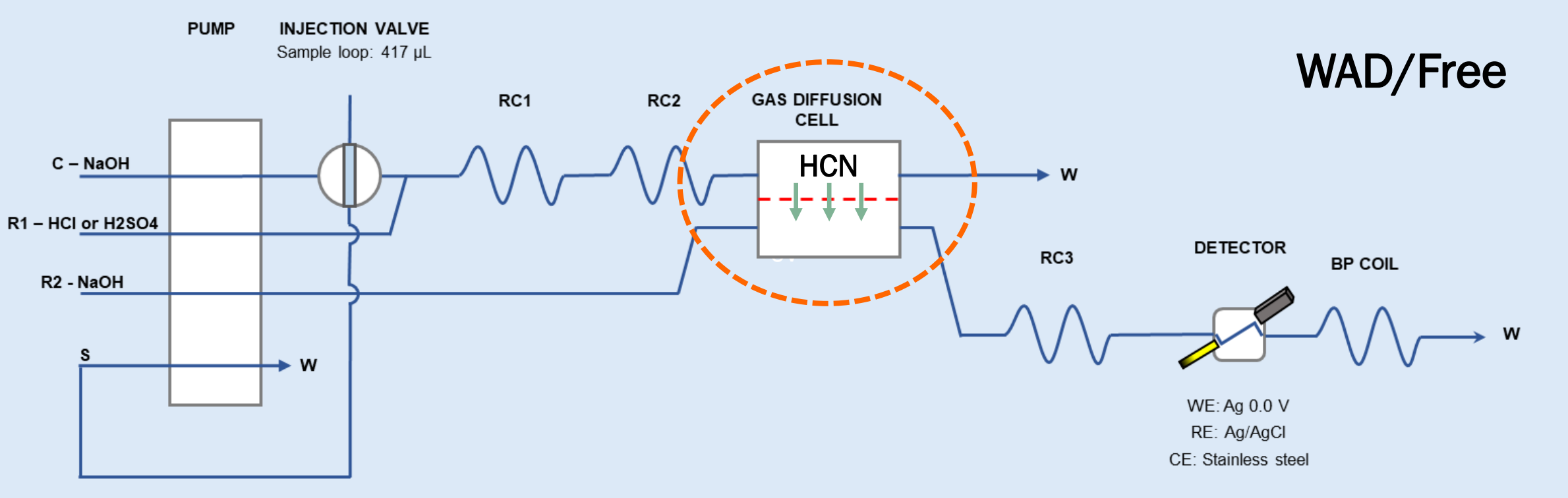


How to Measure CN



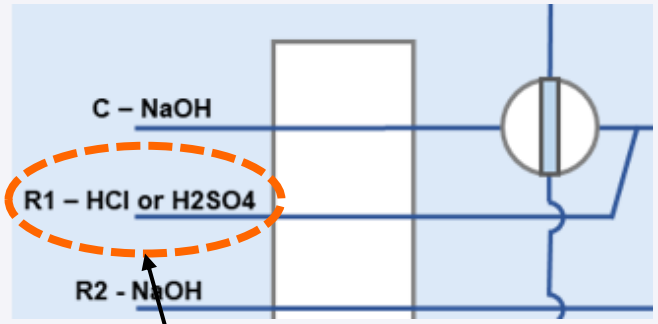
- CN- reacts at Ag electrode, giving rise to a current (flow of e-)

How to Use Amperometric CN?



- All official amp CN methods rely on the concept of gas diffusion

How to Use Amperometric CN?



R1 formulation

CN-Me3 CN- CN-Me2

CN- CN-Me1

CN pool in a sample

Buffer pH 6

Strong acid H_2SO_4, HCl

Ligand cocktail

CN-Me3 HCN CN-Me2

HCN CN-Me1

Free CN

CN-Me3 HCN CN-Me2

HCN HCN + Me1

Available CN by acid dissociation (a.k.a. WAD CN)

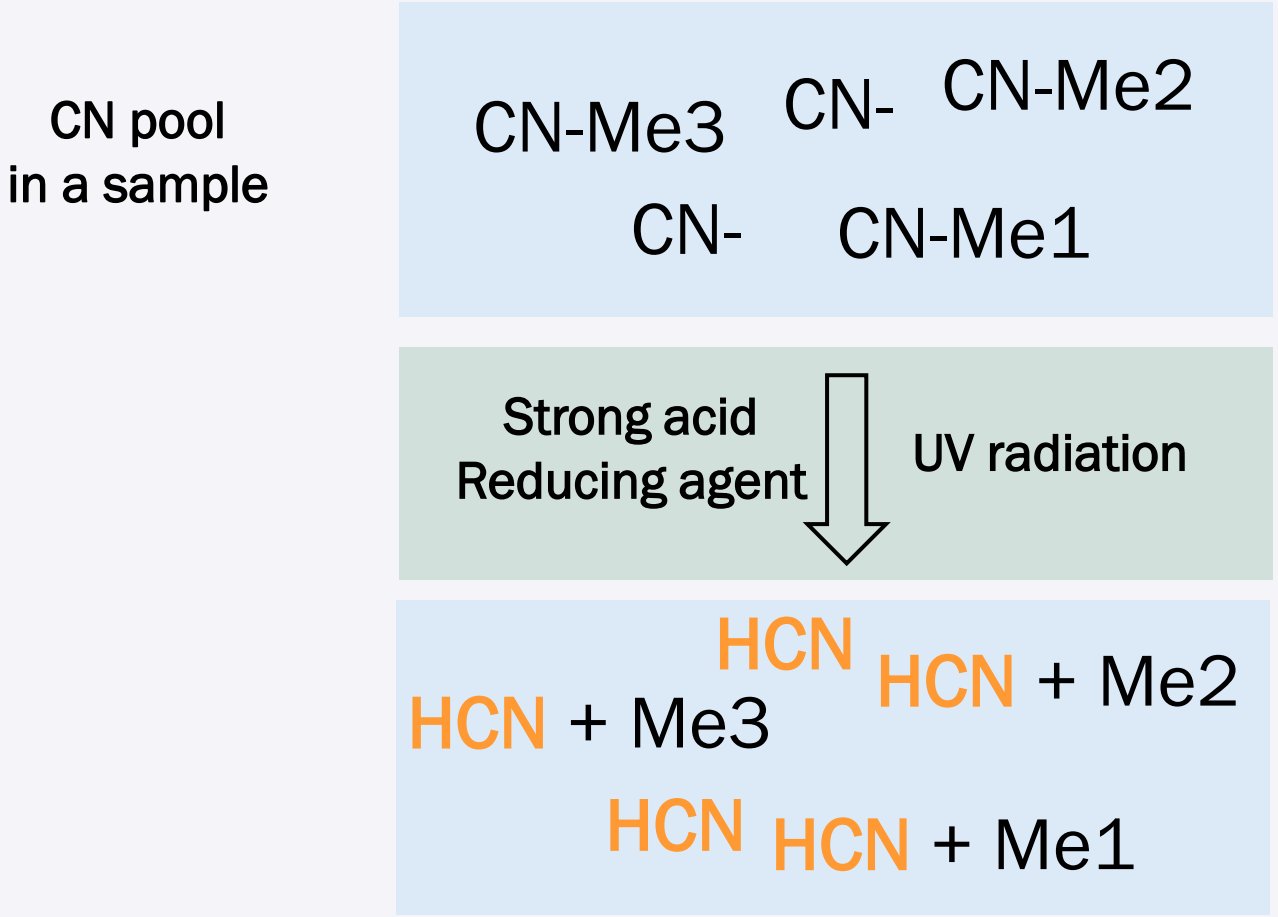
HCN CN-Me2

HCN + Me3-L

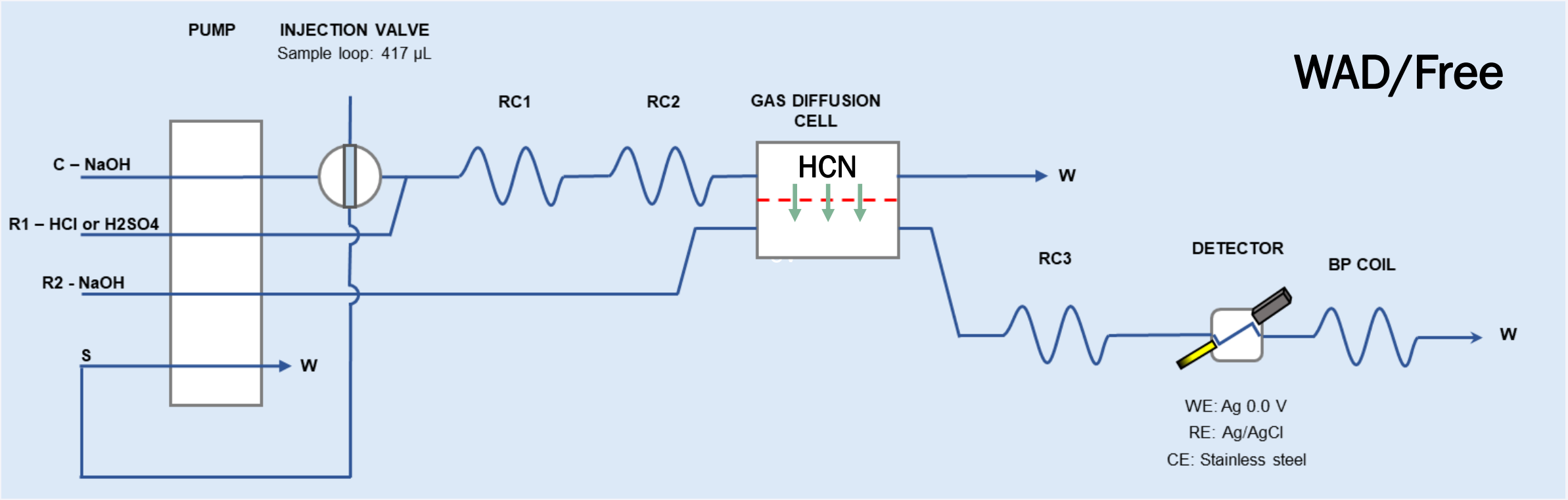
HCN HCN + Me1-L

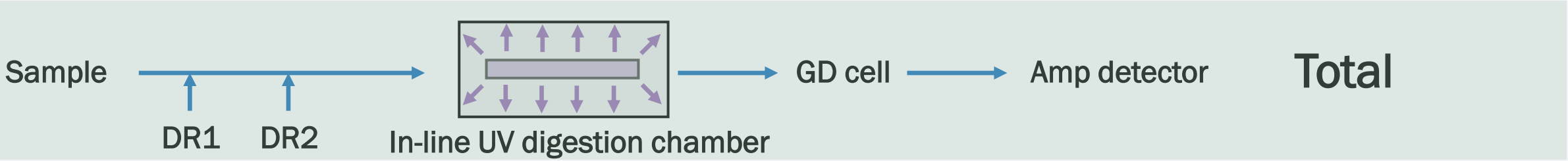
Available CN by ligand displacement (a.k.a. WAD CN)

How to Use Amperometric CN?

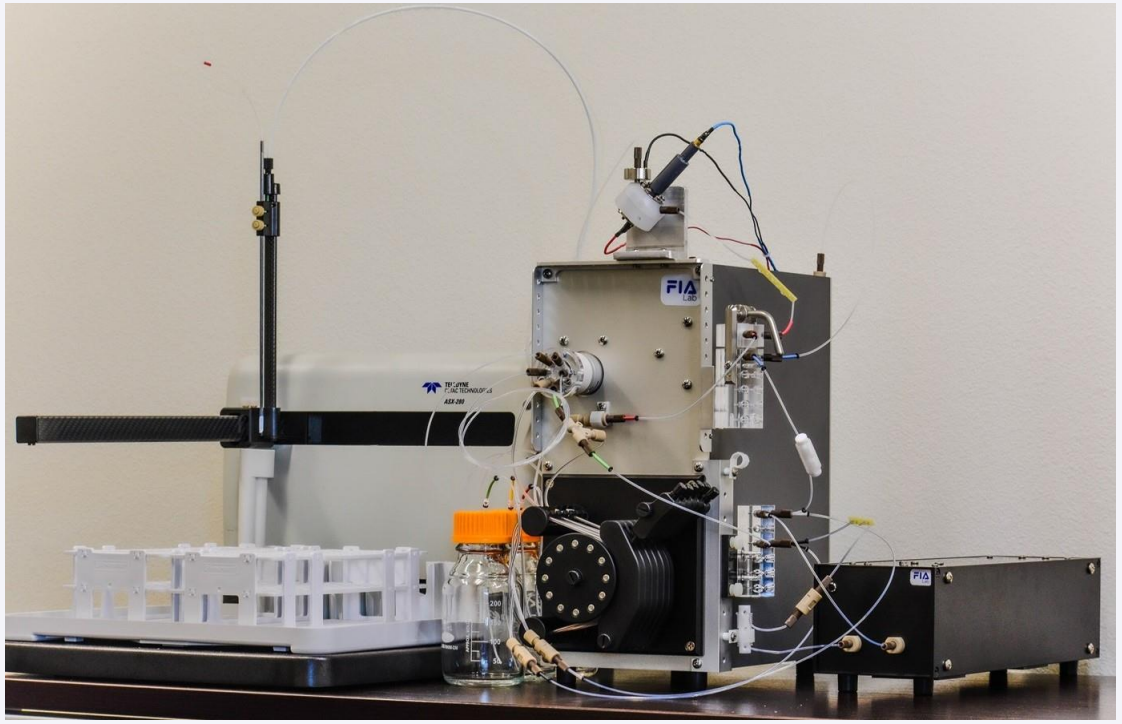


CN by Amperometry

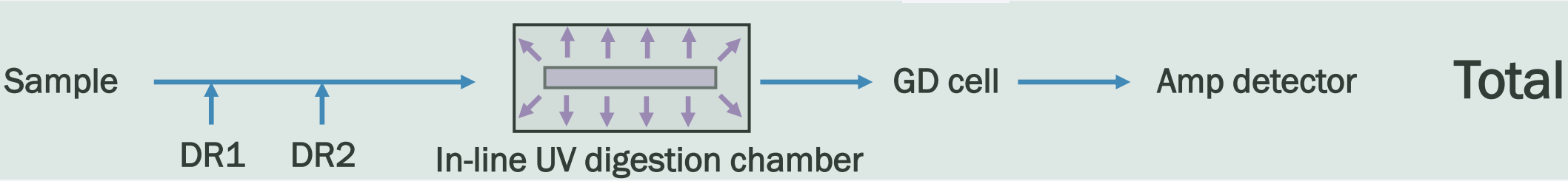


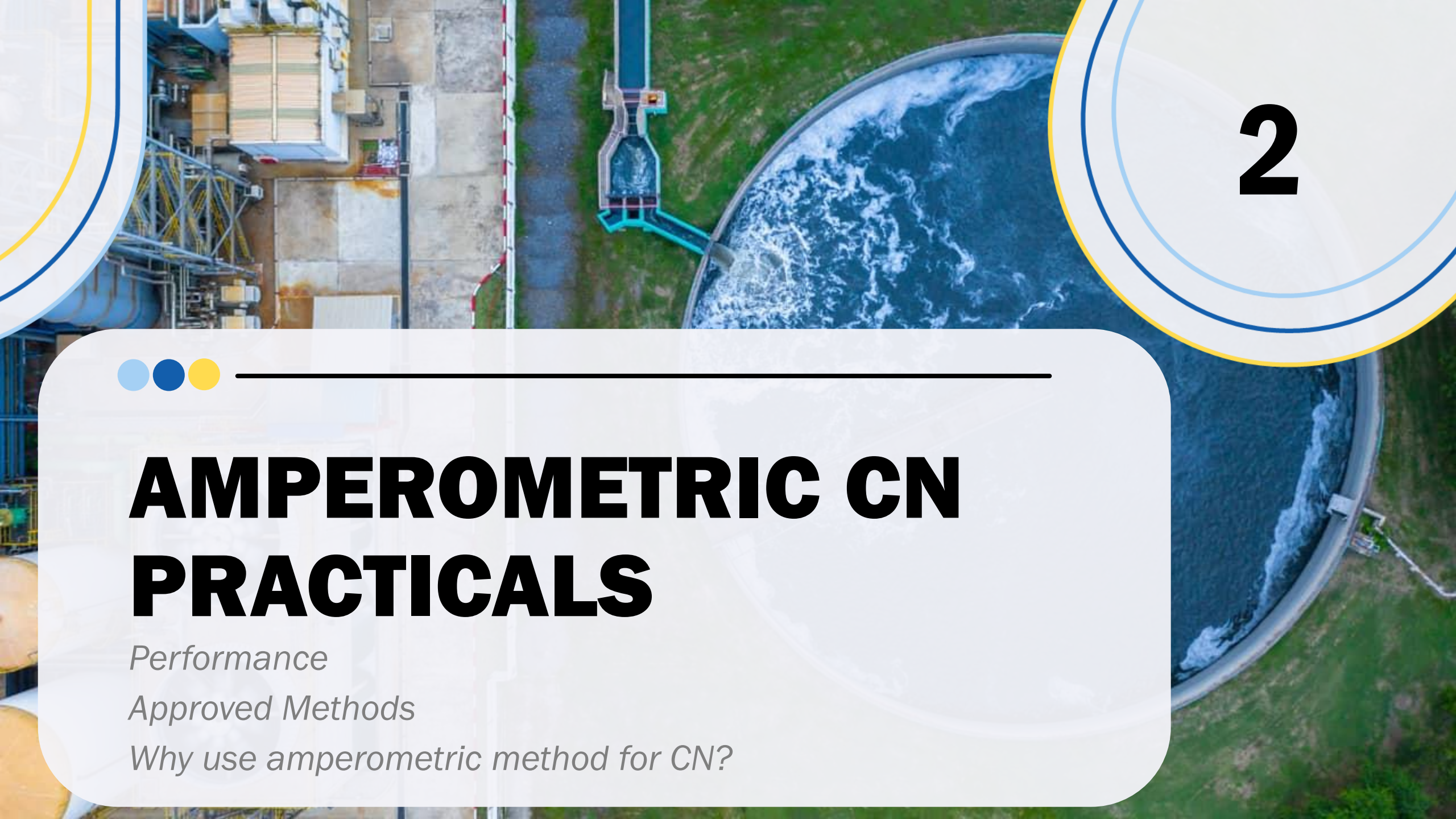


CN by Amperometry



~10”





2

AMPEROMETRIC CN PRACTICALS

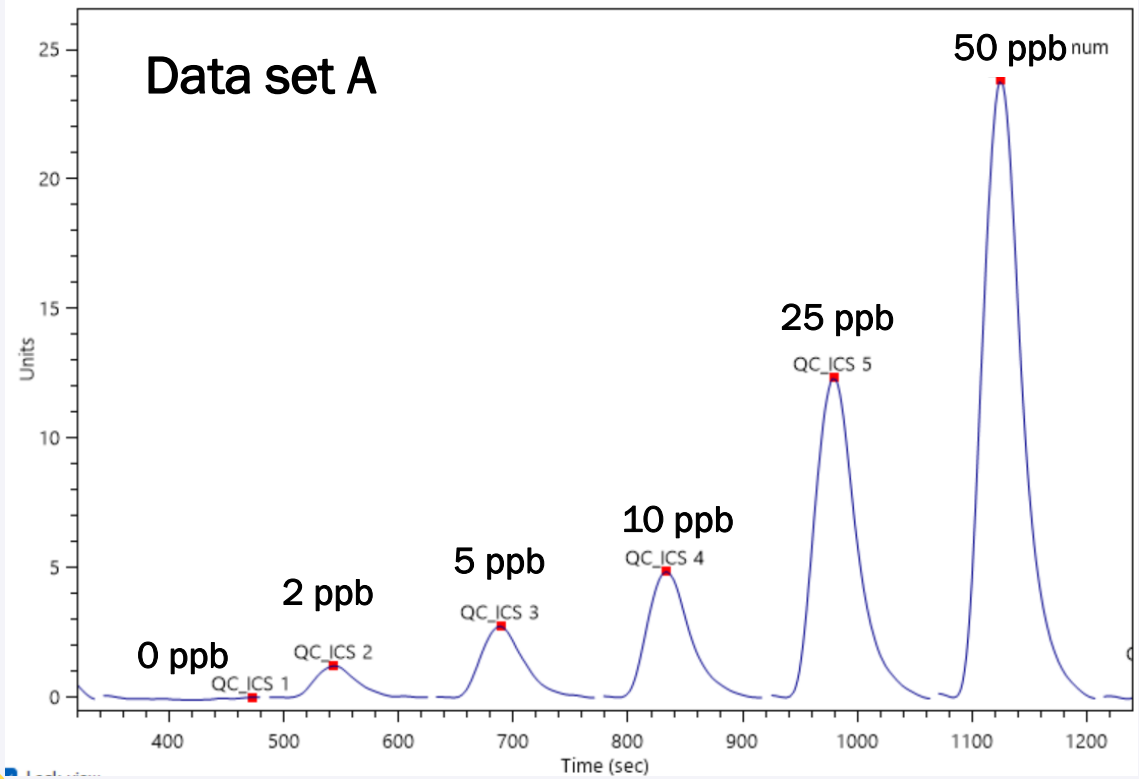
Performance

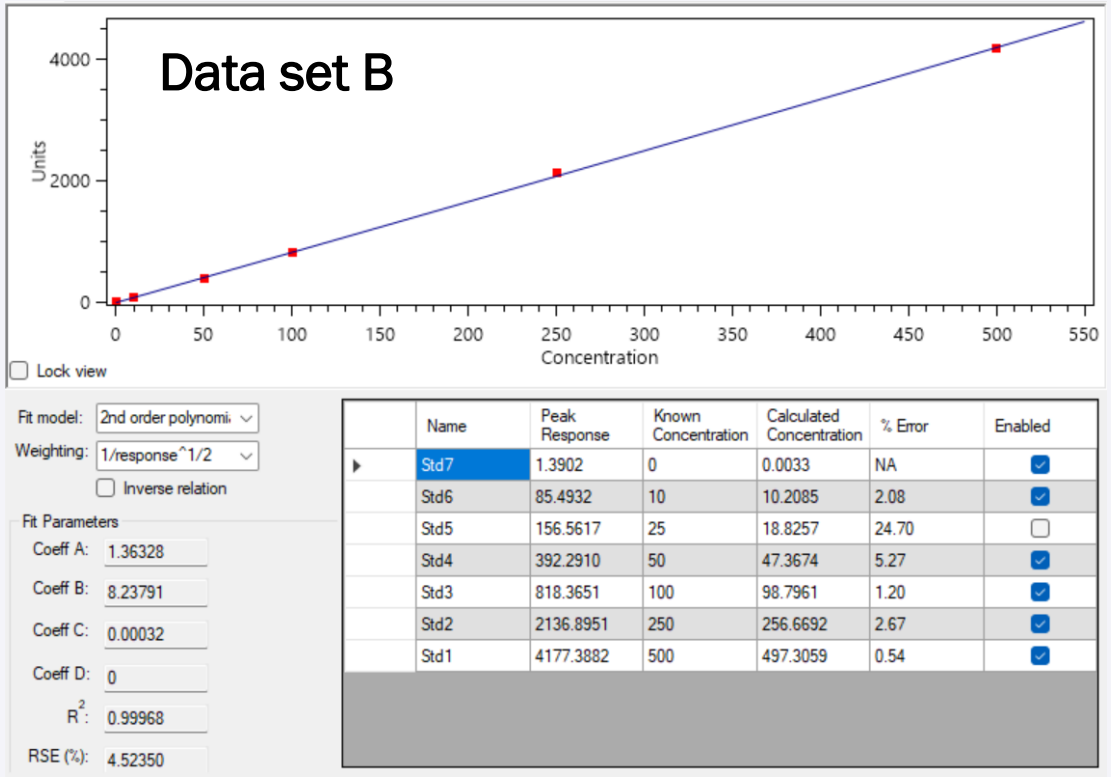
Approved Methods

Why use amperometric method for CN?

Performance

- MDL: ~0.5 ppb (available/free), ~1 ppb (total)
- Range: usually up to 500 ppb, possible to adjust w/ sample loop size
- Throughput: 20-40 samples/h (per ASTM D7511-12)





Name	Peak Response	Known Concentration	Calculated Concentration	% Error	Enabled
Std7	1.3902	0	0.0033	NA	☑
Std6	85.4932	10	10.2085	2.08	☑
Std5	156.5617	25	18.8257	24.70	☐
Std4	392.2910	50	47.3674	5.27	☑
Std3	818.3651	100	98.7961	1.20	☑
Std2	2136.8951	250	256.6692	2.67	☑
Std1	4177.3882	500	497.3059	0.54	☑

Approved Methods

- Many variant methods (* = included in 40 CFR Pt 136/141)

Free	• Free CN (buffer at pH 6): ASTM D7237*[136] ; Uncomplexed CN
WAD	• Available CN (acid dissociable): EPA OIA-1677*[136] ; Ag, Cd, Cu, Zn compl. • Available CN (acid dissociable): ASTM D6888*[136] ; Ag, Cd, Cu, Zn compl.
WAD	• Available CN (ligand displacement): EPA OIA-1677*[136,141] ; + Hg, Ni • Available CN (ligand displacement): ASTM D6888*[136,141] ; + Hg, Ni
Total	• Total CN (following manual distillation): ASTM D7284*[136] ; + Fe, Co, Au • Total CN (in-line digestion): ASTM D7511*[136] ; + Fe, Co, Au

- "WAD" is not always clearly defined for available CN
  - Sometimes used for "acid dissociable".
  - Sometimes used for "ligand displacement".

Why Use Amperometric CN?

- Simplicity
  - No need to deal with toxic chemicals (pyridine, Chloramine T)
  - Reagents simple to prepare, affordable (acid, base)
- Reliability
  - Distillation can result in false positives, UV digestion is less prone to that
- Approved methods available for different CN “classes”
  - Free CN
  - Available (a.k.a. WAD) CN (weak / intermediate CN-metal complexes)
  - Total CN
- Automated removal of sulfide interference

Instrument Considerations

- No two potentiostats are equal
  - Make sure the detector uses a model capable of determining ~1 ppb CN
- Find out whether the method implementations are practical
  - Avoid methods with extreme low throughputs
- Instrument versatility
  - Easy conversion between Free, Available & Total CN setups
    - Get practical versatility with minimized capital investment
- Beware of heat in connection with UV digestion for Total CN
  - Heat can result in false positives (creates CN from SCN, CNO)
  - Some level of false positives are ~50 ppb.

3

CONCLUSIONS

Conclusions

- Amperometry is the measure of electric current created by a redox reaction
- All amp CN use gas diffusion
- Many Benefits of Amperometric CN
  - Practical MDLs, range
  - Ease of reconfiguration
  - Ease of operation
- Eliminates extremely toxic chemicals
- Find an instrument that can analyze all three (Free, WAD, Total)

THANK YOU!

Any questions?

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