FIA Lab

Fluidics Intelligently Automated

Amperometric CN - Principles, Practice & Operational Benefits

A guide to selecting your CN method

Agenda

01 **Amperometric CN - fundamentals**

02 **Amperometric CN - “practicals”**

- Performance
- Method variants: Total CN, Available (WAD) CN, Free CN
- Why use amperometric CN?
- Instrumental considerations

03 **Conclusions and questions**

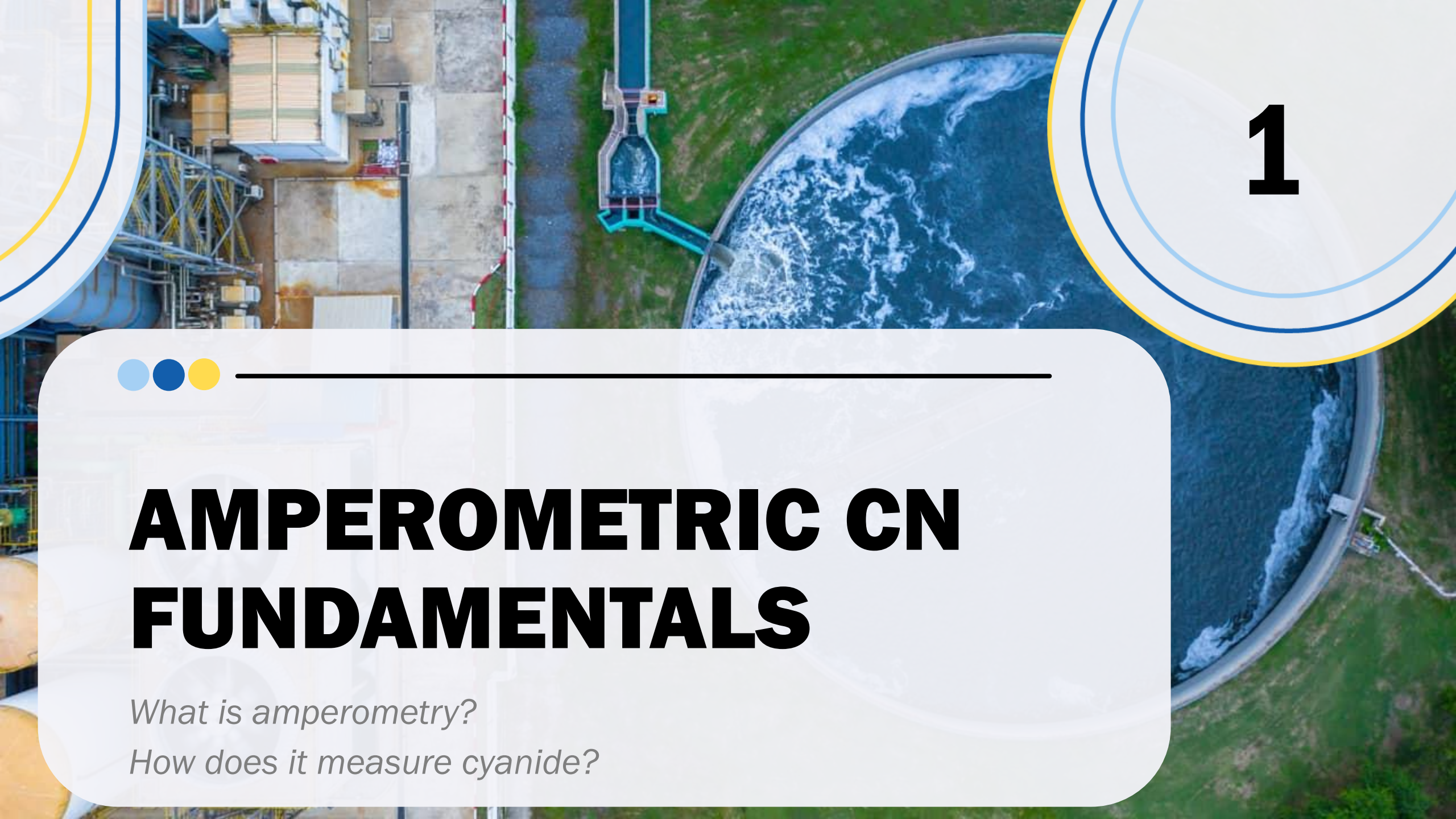
FIA Lab

HELLO!

My name is Ilkka Lahdesmaki

Chief Scientist

You can find me at ilkka@flowinjection.com



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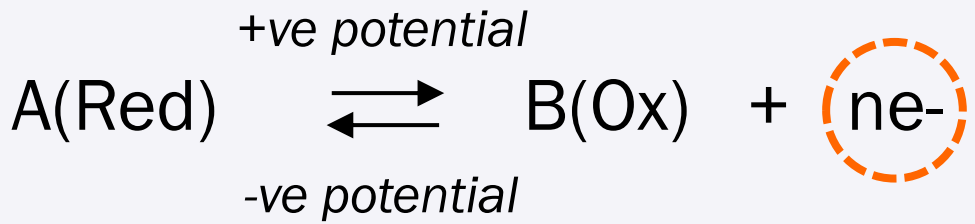
AMPEROMETRIC CN FUNDAMENTALS

What is amperometry?

How does it measure cyanide?

Amperometry Principles

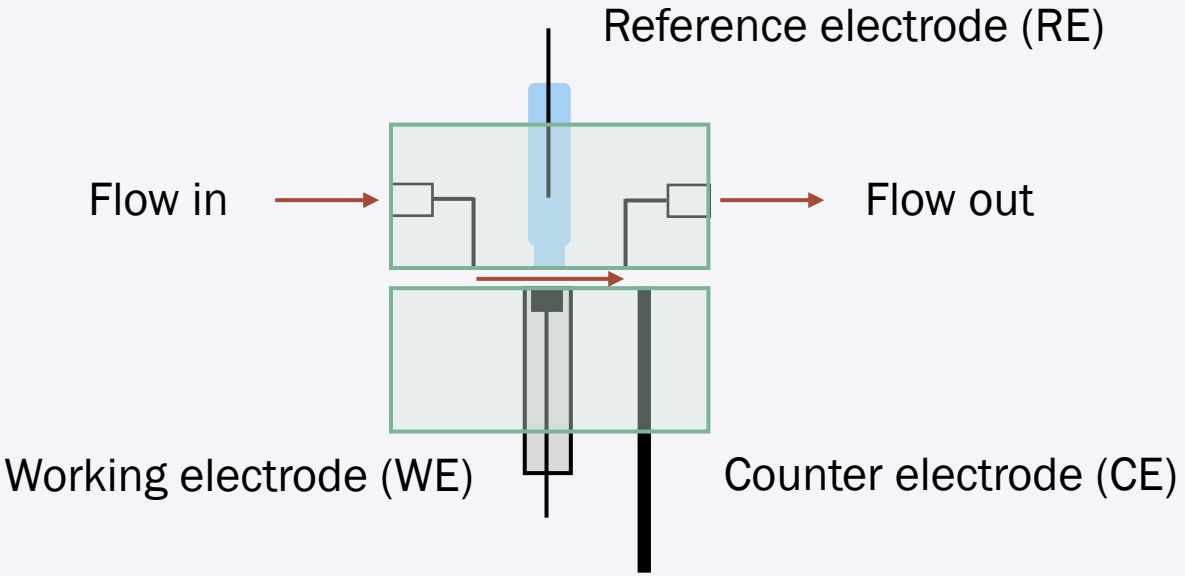
- Amperometry = measurement of electric current
- In chemistry, origin of current = electrochemical (redox) reaction
  - Requires charge transfer



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

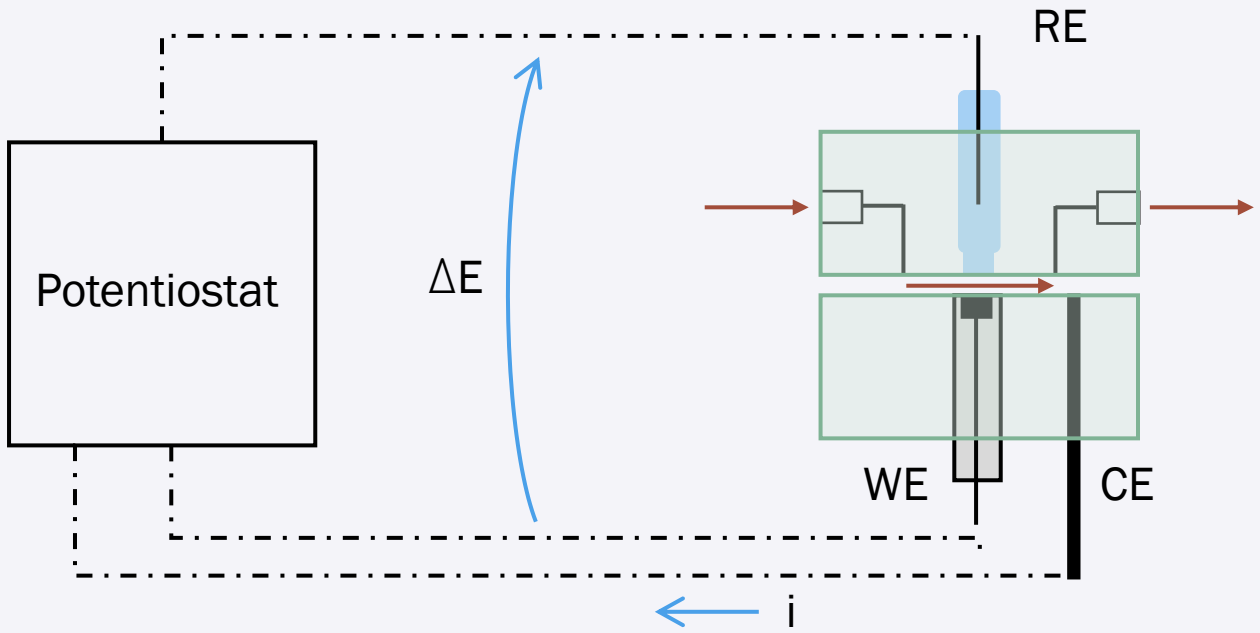
Instrumentation & Methods

- Generation of amperometric signal relies on mass transfer
- 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



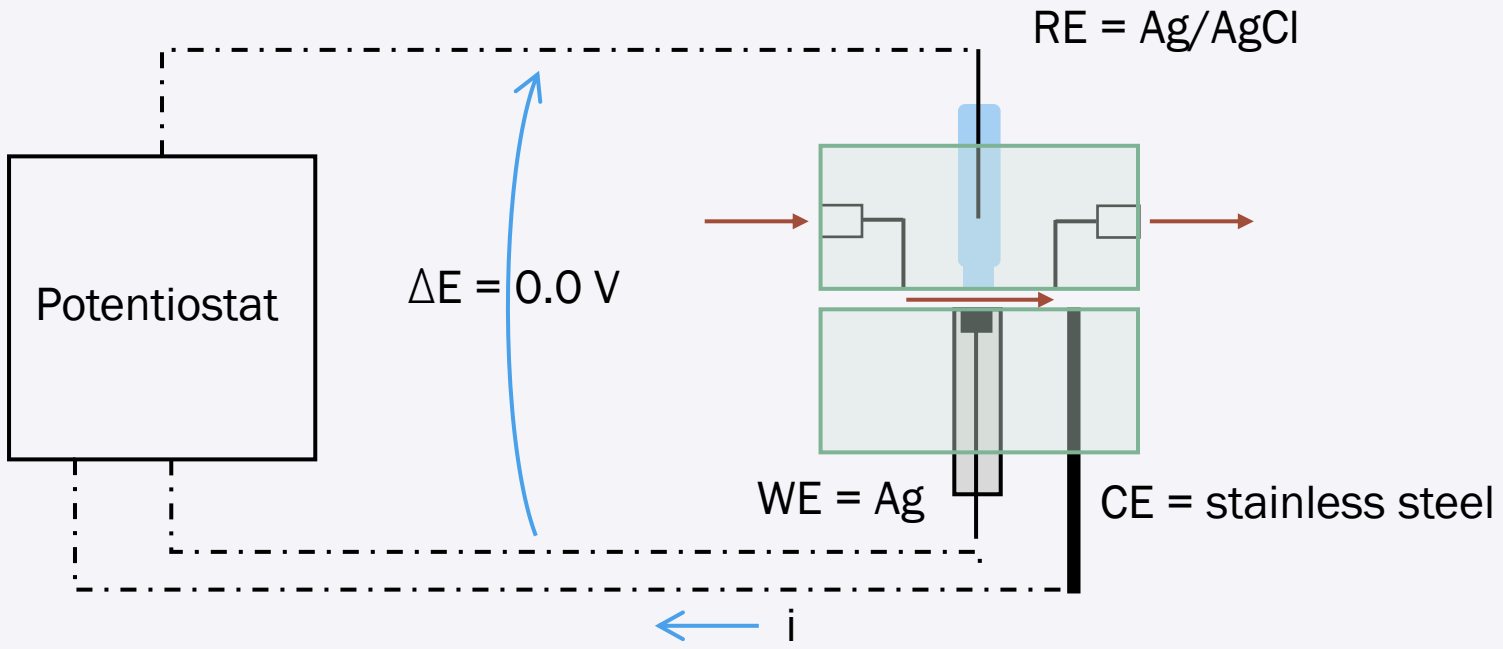
Instrumentation & Methods

- 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)

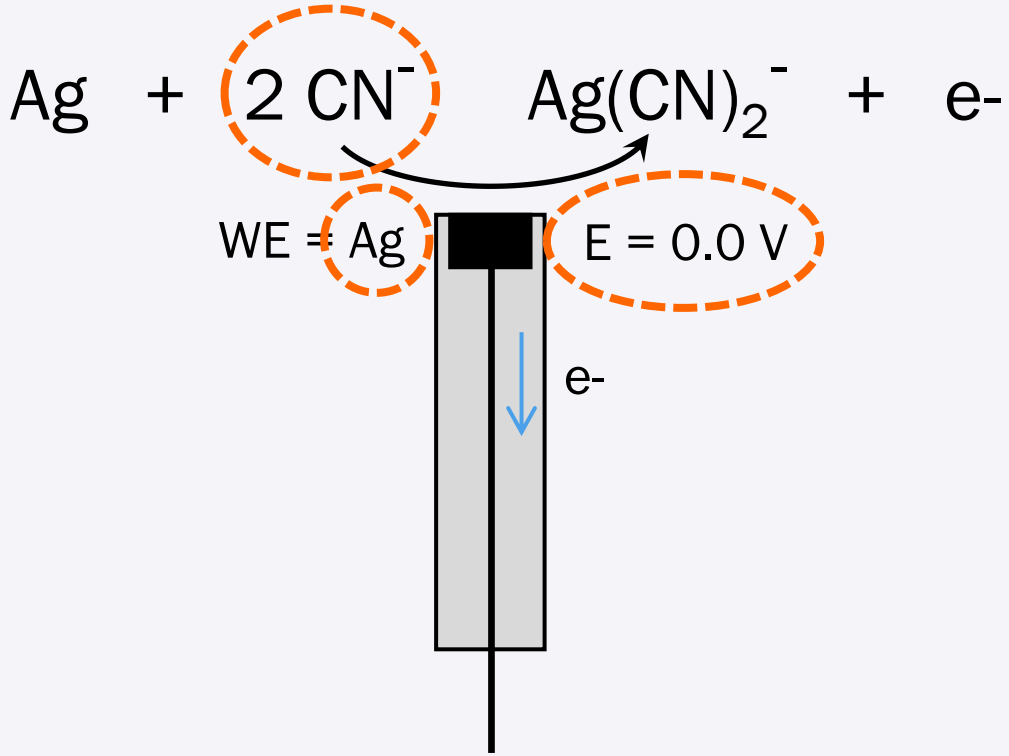


CN by Amperometry

- Detector configuration
  - WE = silver (Ag) electrode
  - RE = Ag/AgCl electrode
  - WE potential = 0.0 V

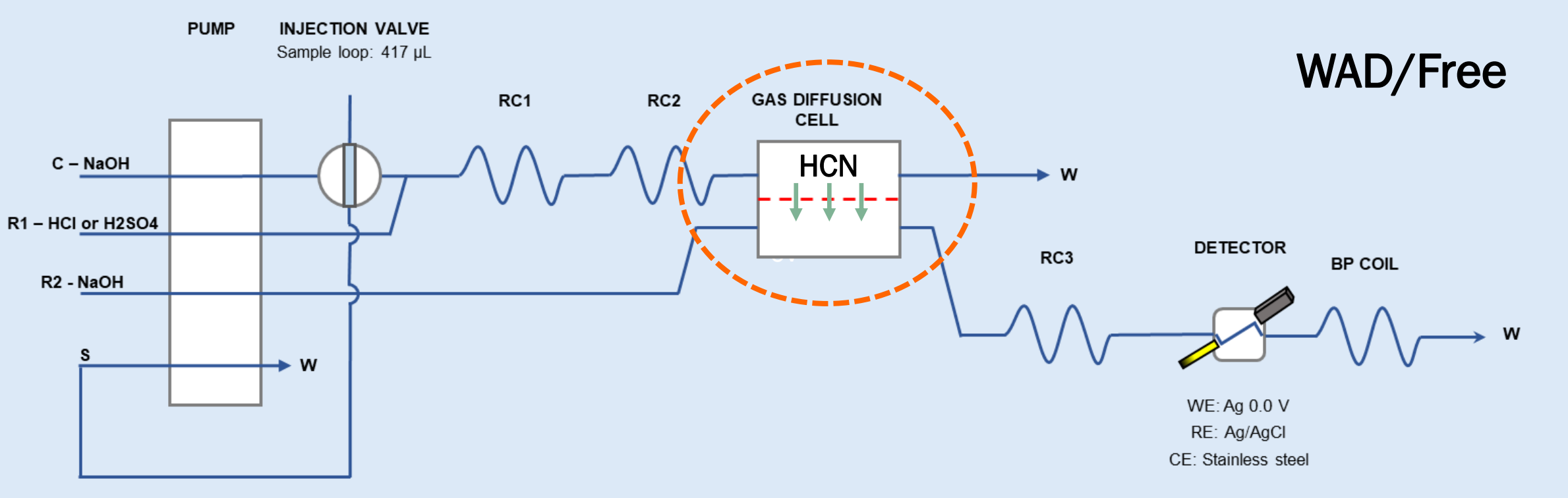


CN by Amperometry

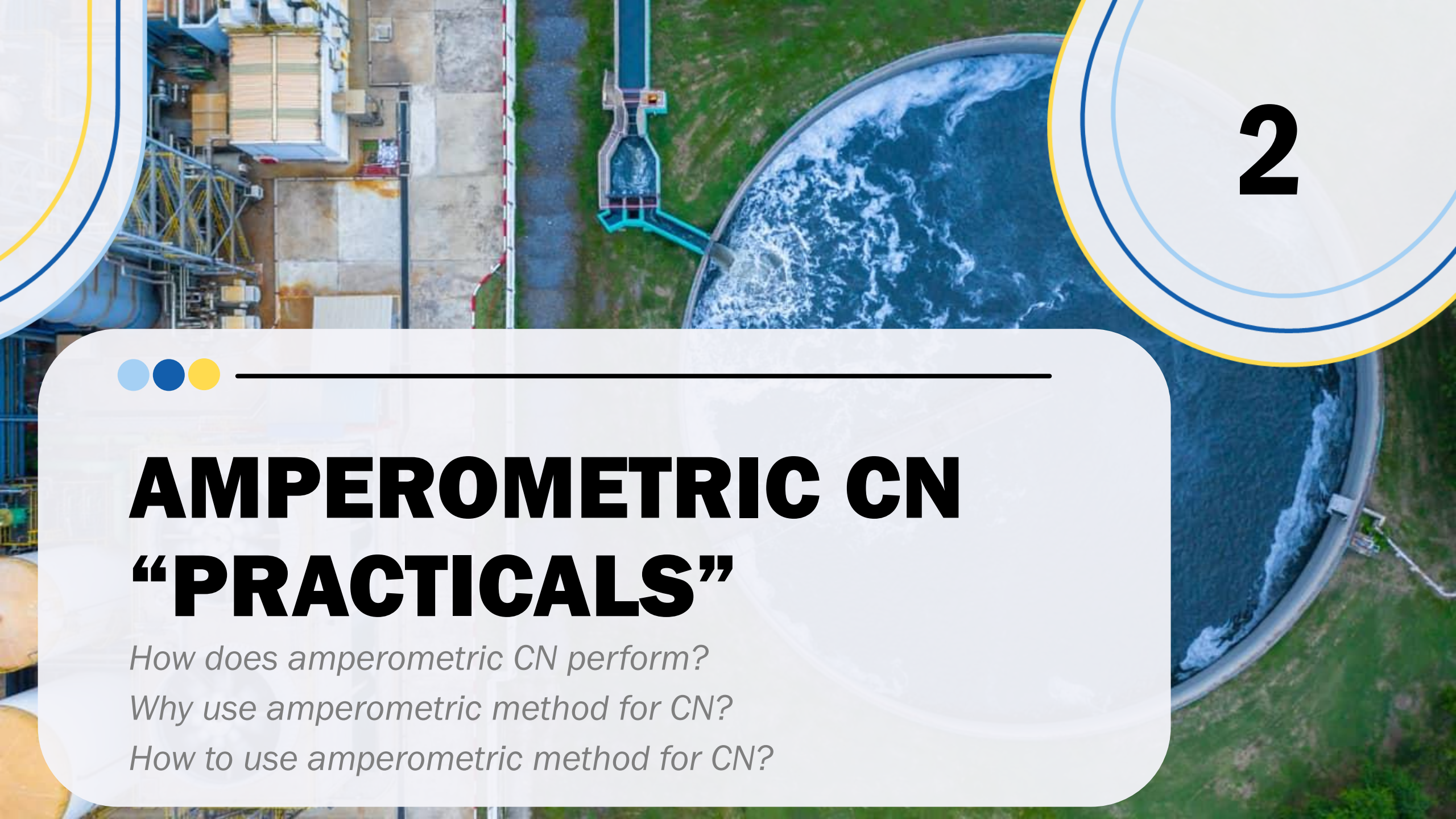


- CN- reacts at Ag electrode, giving rise to a current (flow of e-)

CN by Amperometry



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



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AMPEROMETRIC CN “PRACTICALS”

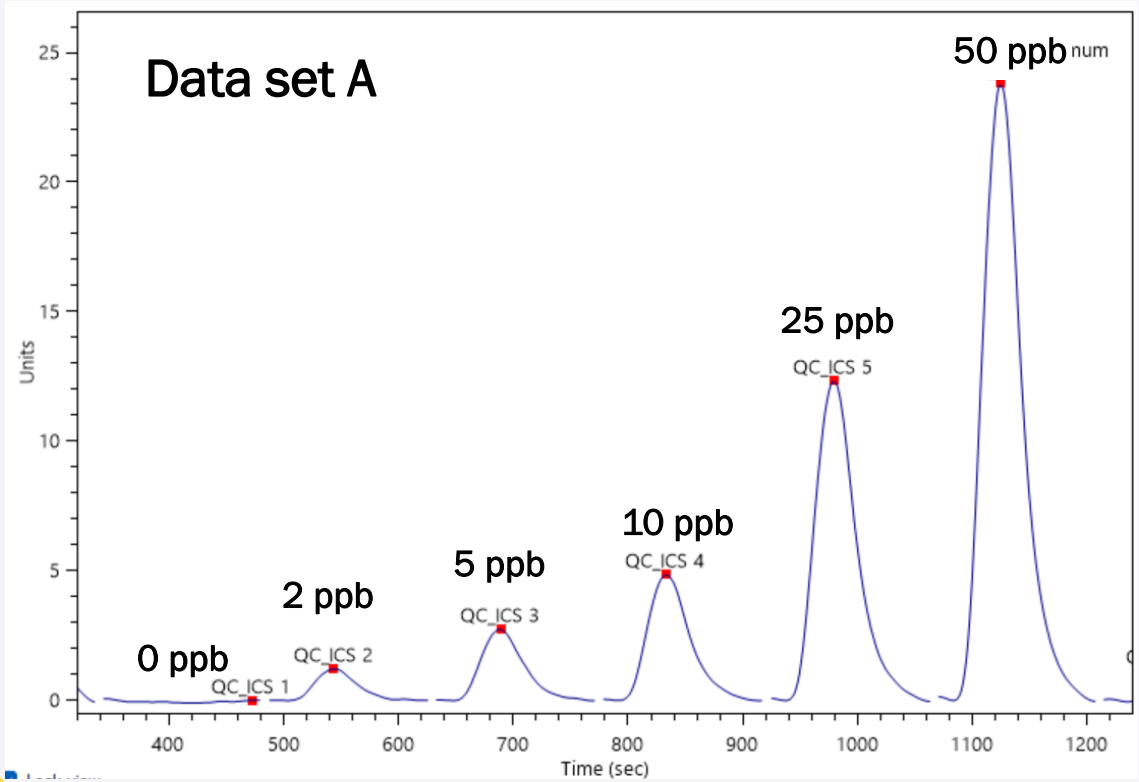
How does amperometric CN perform?

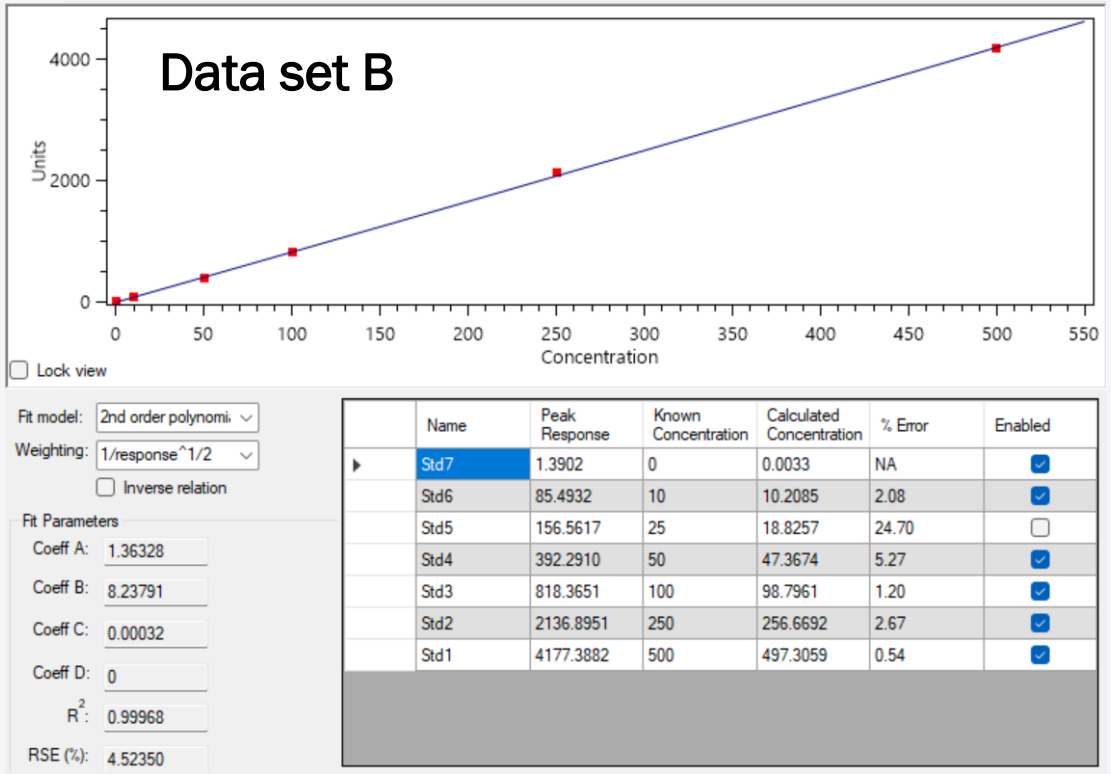
Why use amperometric method for CN?

How to use amperometric method for CN?

Performance

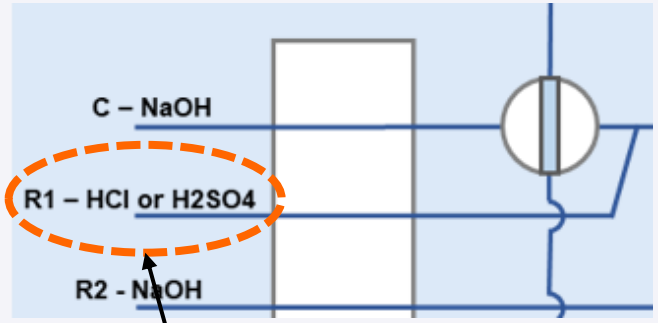
- MDL: ~0.5 ppb (available/free), ~1 ppb (total)
- Range: usually up to 500 ppb, possible to adjust w/ sample loop size
- Throughput: 20-40 samples/h (per ASTM D7511-12)





	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	☑

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 pool
in a sample

CN-Me3 CN- CN-Me2

CN- CN-Me1

Strong acid
Reducing agent

UV radiation

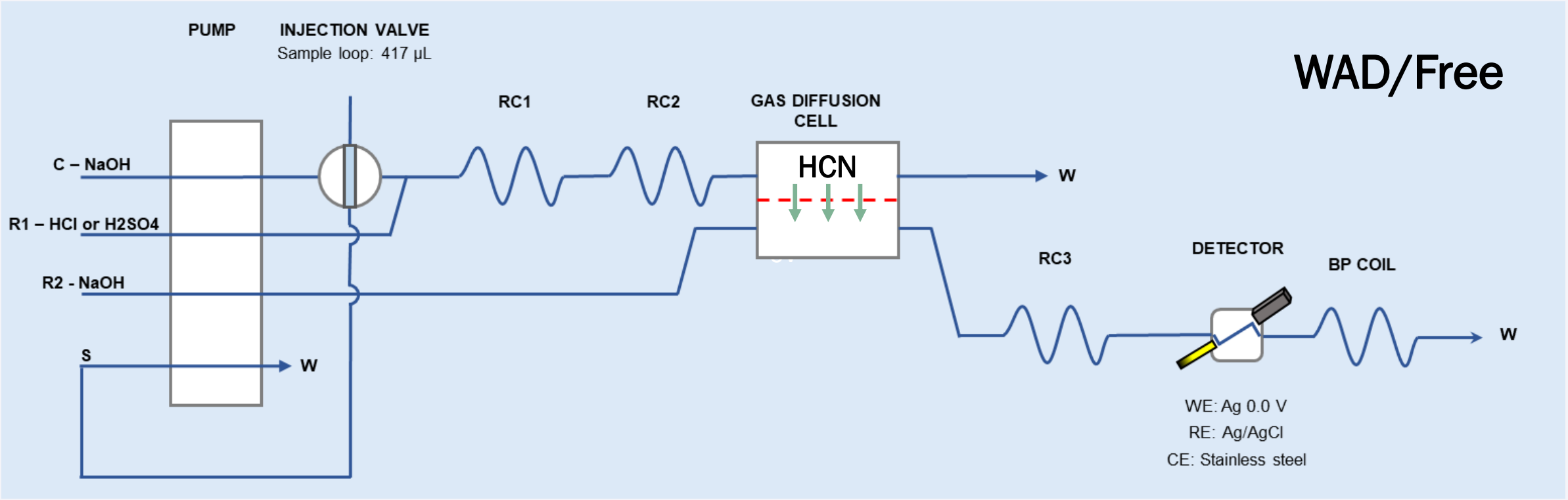
HCN HCN + Me2

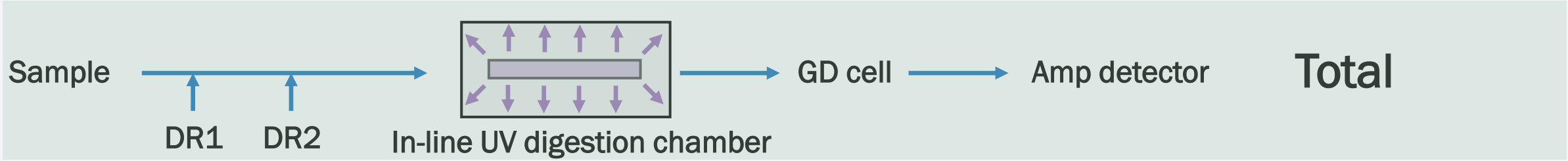
HCN + Me3

HCN HCN + Me1

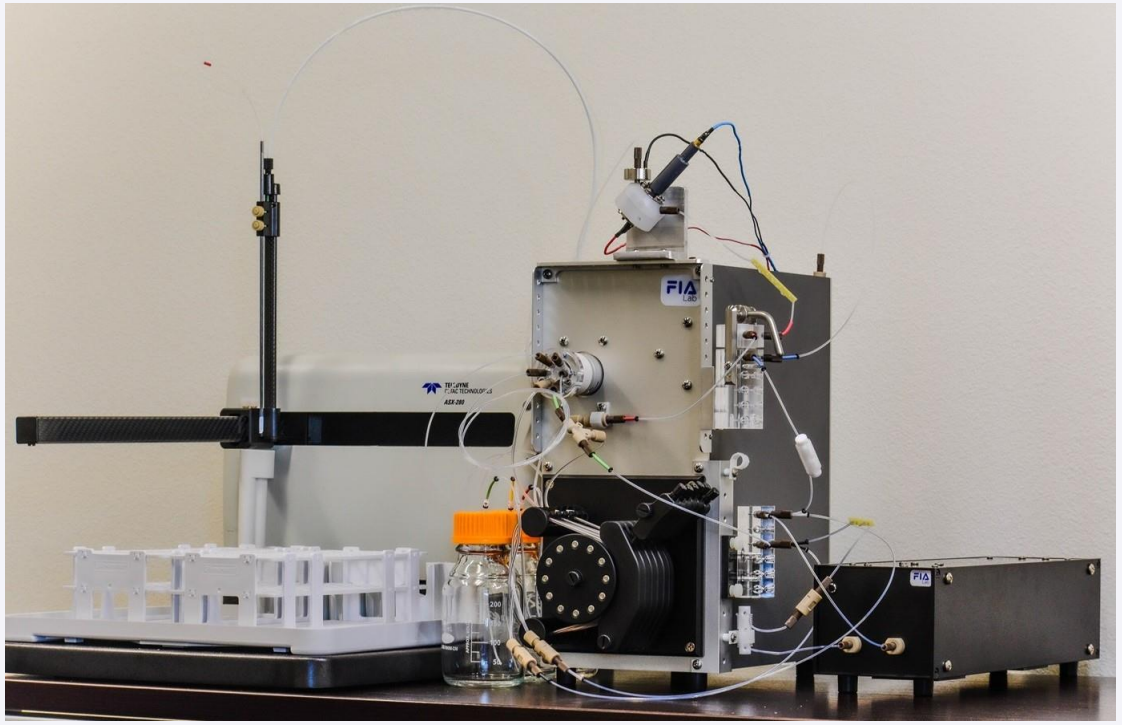
Total CN

CN by Amperometry

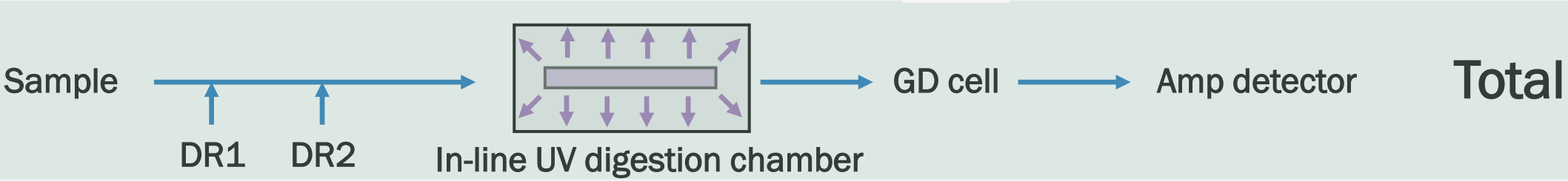




CN by Amperometry



~10”



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

How to use amperometric CN?

- 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".

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 “insane” sample segments, 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 results false positives (creates CN from SCN, CNO)
  - Can test by running ASTM D7511 “challenge matrix”
  - Some level of false positives invariable, “tolerance level” ~50 ppb

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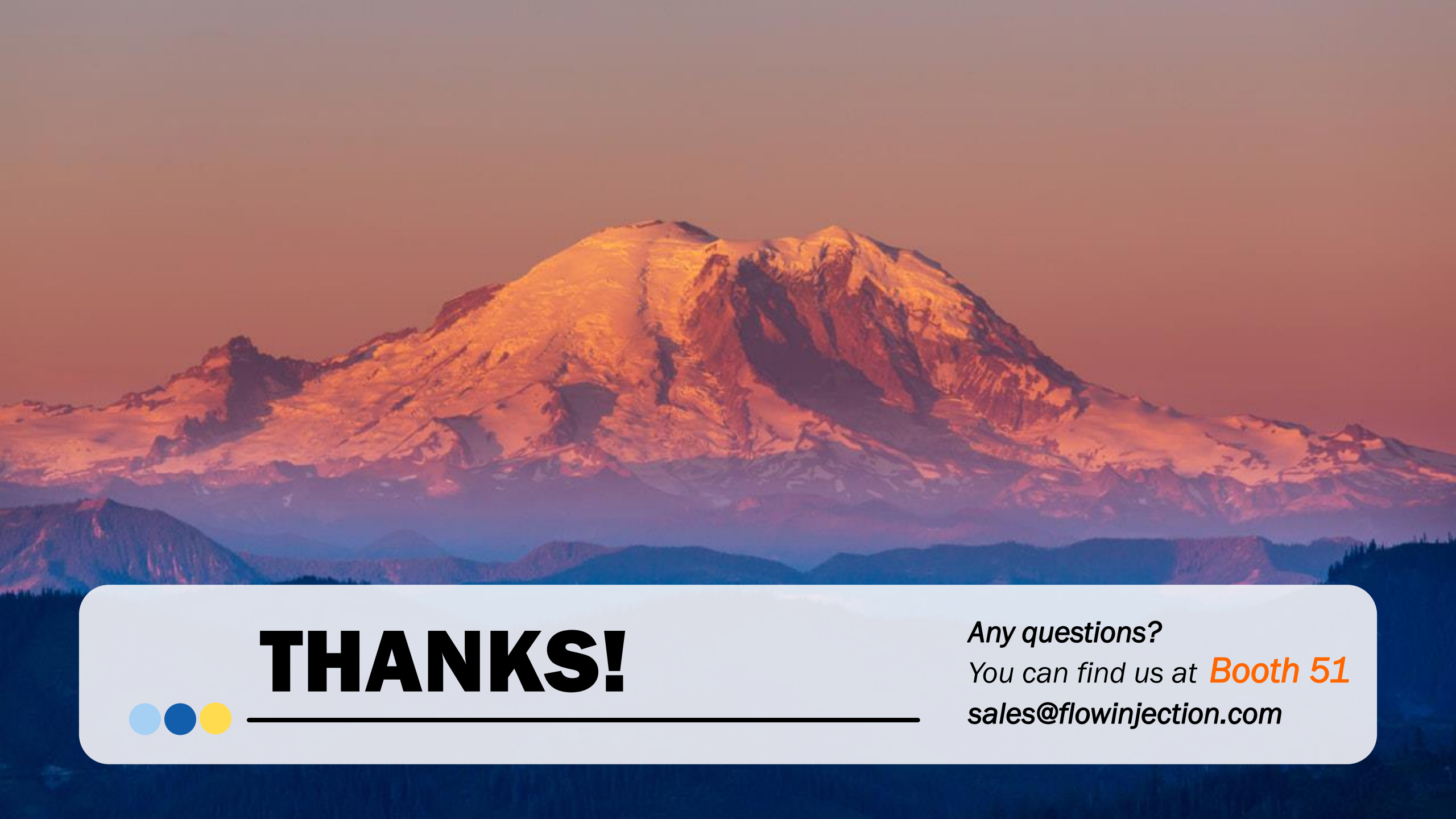
CONCLUSIONS

Conclusions

- Find out what data your customers need
  - Free, WAD, Total CN – or all of the above?
- What kind of sample load are you expecting for each?
  - Determines how many modules you need (1-channel / 2-channel)
- Talk to vendors of amp CN instrumentation
  - Practical MDLs, range
  - Ease of reconfiguration (1-channel used for WAD & Total)
  - Ease of operation
  - Customer support – do their technical staff understand amperometry?
  - If at all possible, talk to a customer reference



THANKS!

Any questions?

You can find us at *Booth 51*

sales@flowinjection.com