Developing A Better Method for Anaerobic Digestion Process Monitoring at a Large Wastewater Treatment Plant

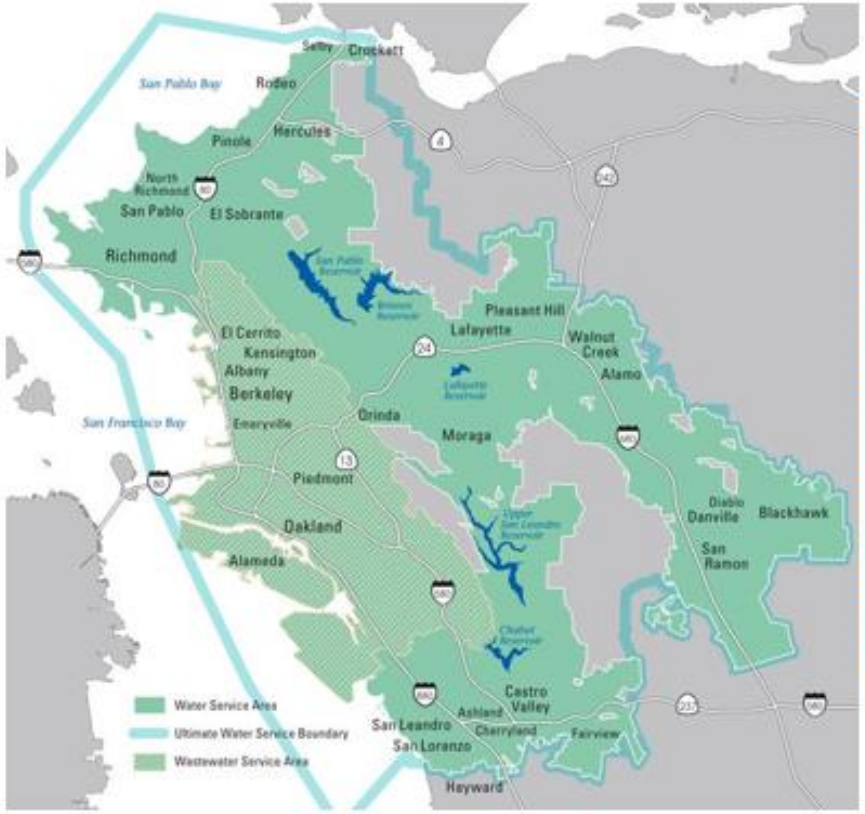
Xin Xu Ph.D.
East Bay Municipal Utility District

8/8/2022

Outlines

- **Background**
  - EBMUD
  - AD Basic chemistry
  - Analytical tools
- **Driver to the new method**
- **Method Validation**
  - Method selection
  - TNI goals
  - Setup
  - Results
- **Method Comparison**
  - Traditional vs new method
- **Indicator for digester monitoring**

EBMUD Laboratory



BY THE NUMBERS

Drinking Water

1.4 Million People

332 Square Mile Area

Wastewater

740 Thousand People

88 Square Mile Area

WATER IS ESSENTIAL SO ARE YOU

AC22 CONFERENCE AND EXPO APRIL 11-14, 2022

CWEA

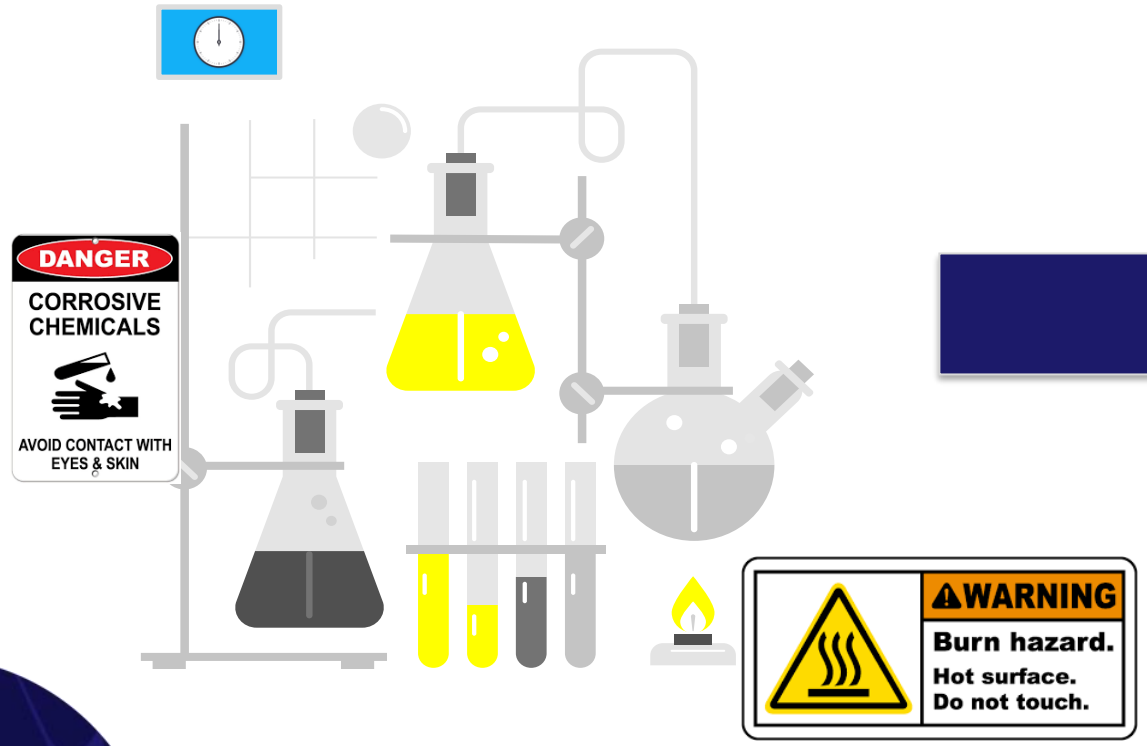
Anaerobic Digesters

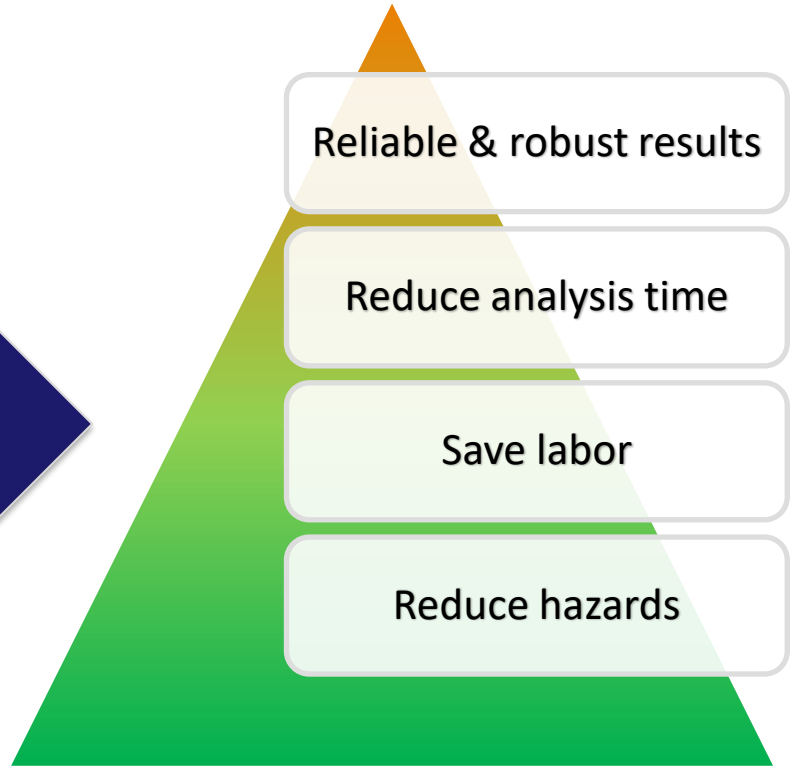
- **11 Digesters (~2 million gallons each) for processing:**
  - Municipal wastewater sludge
  - Trucked high-strength organic waste for Resource Recovery (R2 wastes)
- **Digesters are operated in two stages in series:**
  - 8 X 1st stage digesters at thermophilic temperatures where most reaction occurs
  - 3 X 2nd stage digesters at > 35°C
- **24/7 continuous operation**
- **Lab support on VA analysis**
  - ~ 1200 digester samples/year
  - ~ 1000 hours/year

Drivers to a new method

VA (SM 5560C)

- No VA speciation
- Interference from matrix

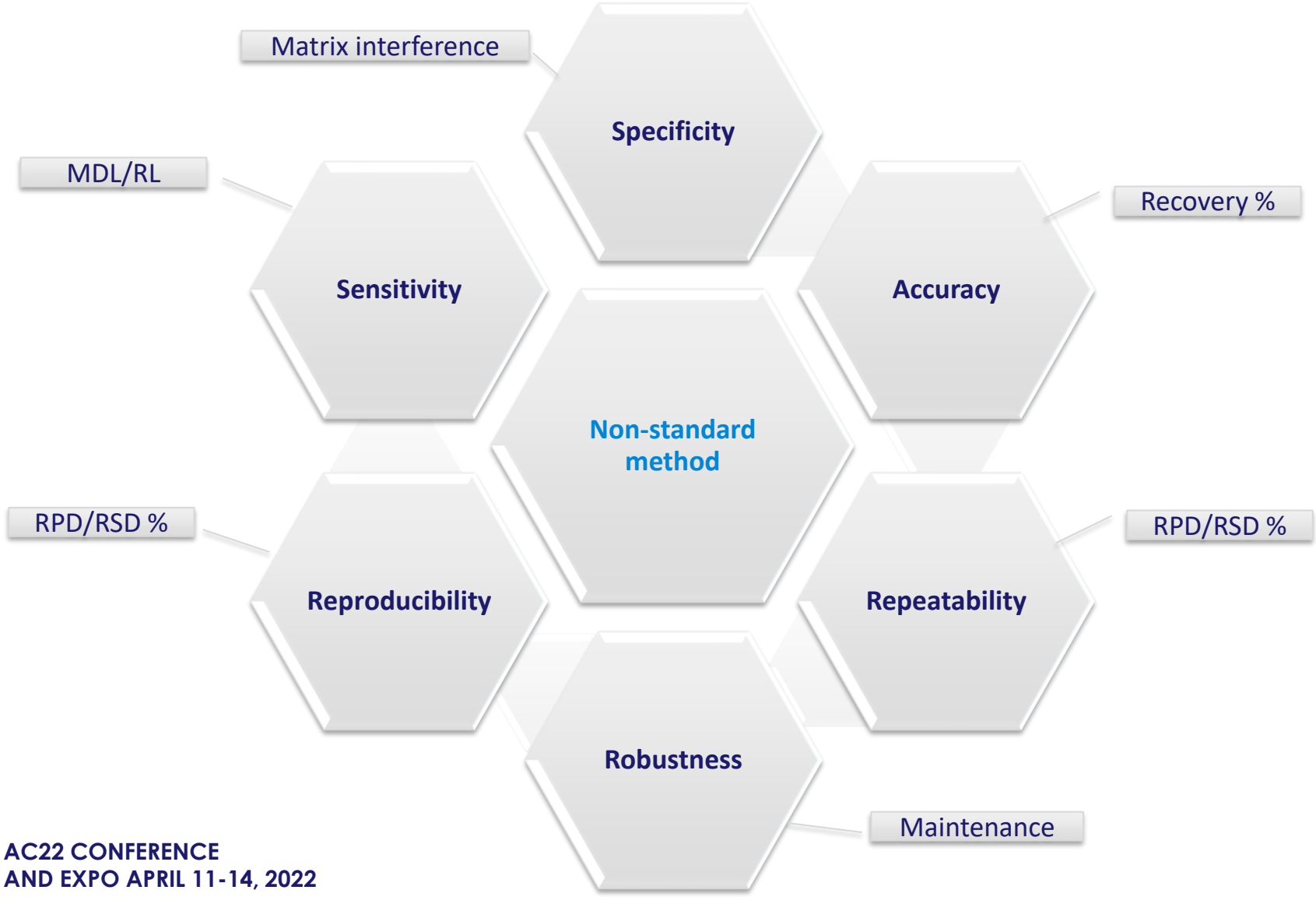




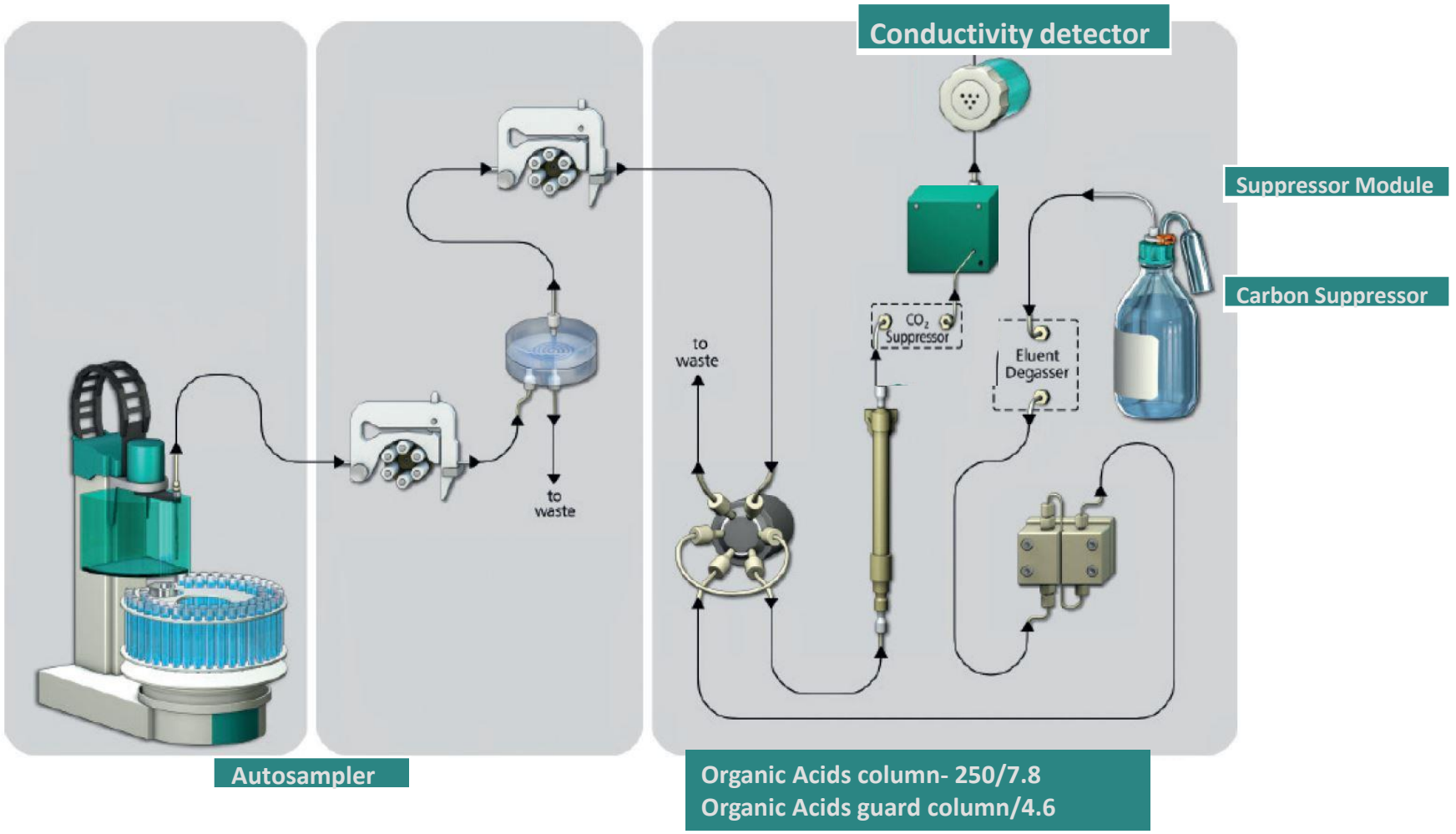
Analytical method selection

Method	Principle	Speciation	Pros and Cons	Reference
Distillation	50mL-250mL distill @ 1 atm	X	• Cumbersome • Azeotropic issue causing poor individual recovery • Conversion factor • Heat and chemical hazards	SOP473 (SM5560C)
Spectrophotometric	Montgomery method	X	• Critical pH control reagent • Less accurate due to various interferences • Cumbersome	Montgomery et al., 1962
GC (Gas chromatography)	1. DI-GC method (DB-WAX column+ FID) 2. GC-MS	√	• Filtration required; negative biases; matrix effect • Sample extraction, DMC or SPE • Limitation and matrix interference	Manni and Caron 1995 Ullah MA 2014 Hayoung Kim 2019
HPLC (High Performance Liquid Chromatography)	cation exchange column selectively separate VFAs according to their respective pKa values.	√	• Special column (Supelcogel 610H, Aminex HPX87H, and ORH 801) • Carbonate interference	Guerrant et al. 1982
IC (Ion Chromatography)	1. Column 2. Suppressor 3. Carbonate removal 4. autosampler+ filtration	√	❖ Separates weakly ionized acids ❖ Elutes strong acid anions ❖ Reduce carbonate interference ❖ Operational ease	Thermo application note Metrohm application note

Followed TNI Method Validation Requirements



IC Setup Scheme



Photos courtesy of Metrohm AG, Application Work AW IC US6-0176-042013

Experiment design of VFA IC Method Validation

Sampling schedule

- 2/1/2022- 3/11/2022 M/W/F, 3/14/2022-3/31/2022 T/Th, total 22 dates

Sample matrix

- 8 digesters/day, 7 from 1st stage, 1 from 2nd stage

Sample preparation

- Centrifugation
- Dilution

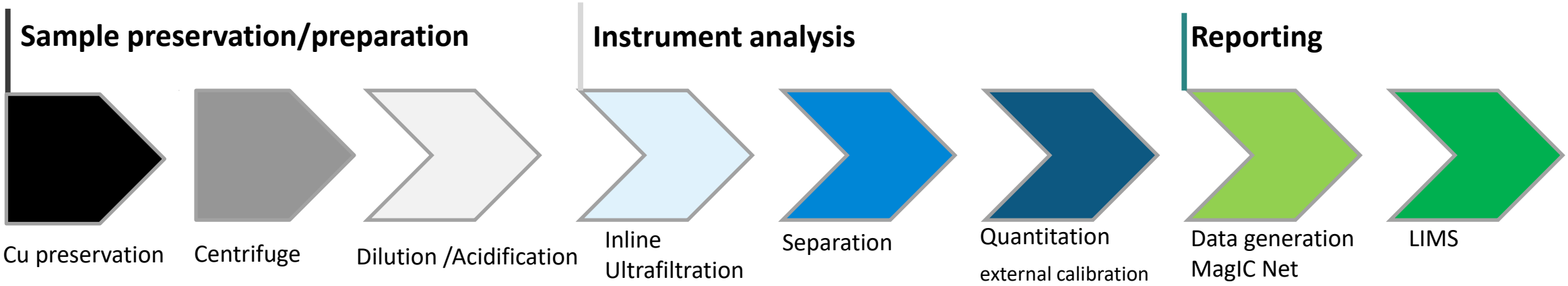
Sample preservation

- Acidification
- Cu preservation

Routine maintenance

- Filter stress test
- Calibration frequence

Analytical Workflow

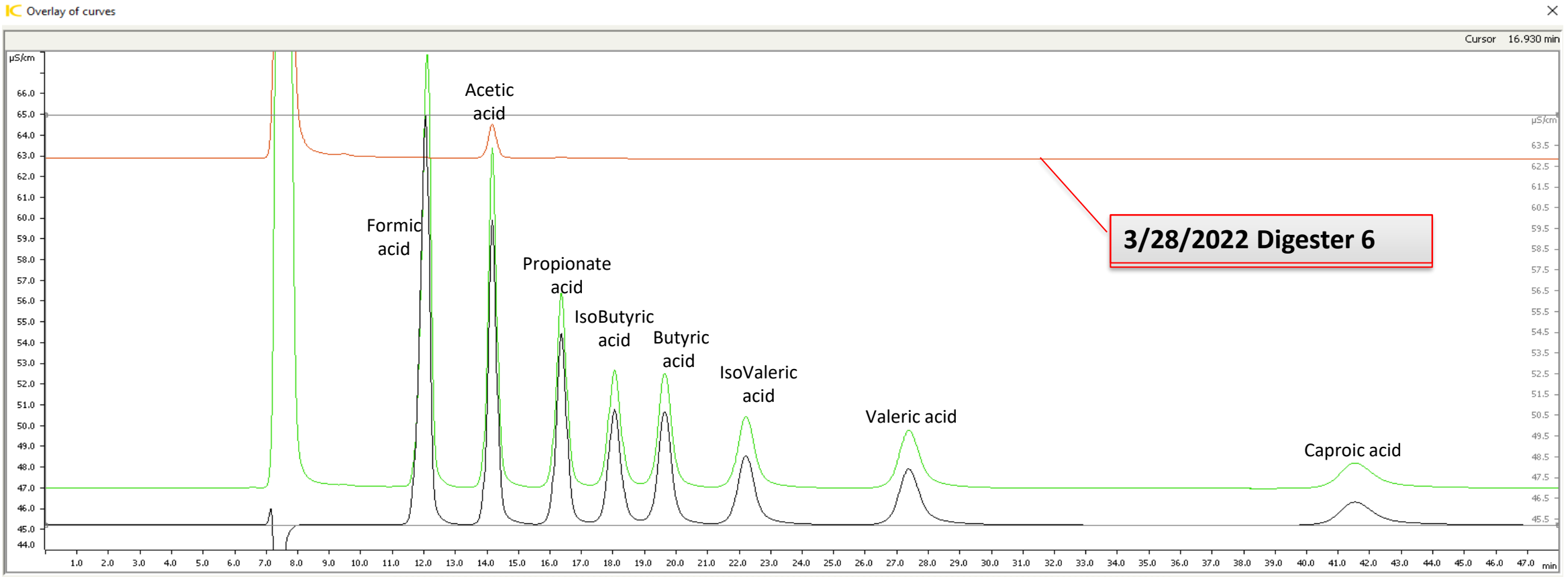


- Cu preservation
- Centrifuge @12,100 rpm for 30 mins
- Dilute by 0.5mM H_2SO_4 10-fold

- Auto filtration 0.2 µm
- Flow @0.5-0.6 ml/min
- Temperature control @32°C
- Pressure <7MPa
- Baseline conductivity: ~40 µs/cm (0.5mM $HClO_4$); ~100 µs/cm (0.5mM H_2SO_4)
- 0.5mM H_2SO_4 for rinsing

- Individual VFA species
- Calculate sum of VFA as HAc

VFA IC Method Performance



	Date	Number	Ident	Sample type	Volume	Dilution	Sample amount	Method	Analysis	Legend	Display
▶ 1	2022-03-28 11:29:56 UTC-7	1	ccv	Sample	50.0	1.0	1.0	Organic Acids 15March2022	Organic Acids		☑
2	2022-03-28 20:54:33 UTC-7	2	C006829-05 UP	Sample	50.0	10.0	1.0	Organic Acids 15March2022	Organic Acids		☑
3	2022-03-28 21:45:54 UTC-7	3	C006829-05MS UP	Sample	50.0	10.0	1.0	Organic Acids 15March2022	Organic Acids		☑

VFA IC Method Performance

	Formic Acid (FA)	Acetic Acid (AA)	Propionate Acid (PA)	IsoButyric Acid (IBA)	Butyric acid (BA)	IsoValeric Acid (IBA)	Valeric Acid (VA)	Caproic Acid (CA)
Typical RT (mins)	11.94	14.19	16.38	18.07	19.67	22.24	27.42	41.63
MDL (mg/L)	0.8	0.2	0.4	0.6	2.3	2	0.6	2.3
RL (mg/L)	2	1	1	2	5	5	2	5
Calibration Range (mg/L)	1- 100				5-100		2-100	5-100

KEY TAKEAWAYS

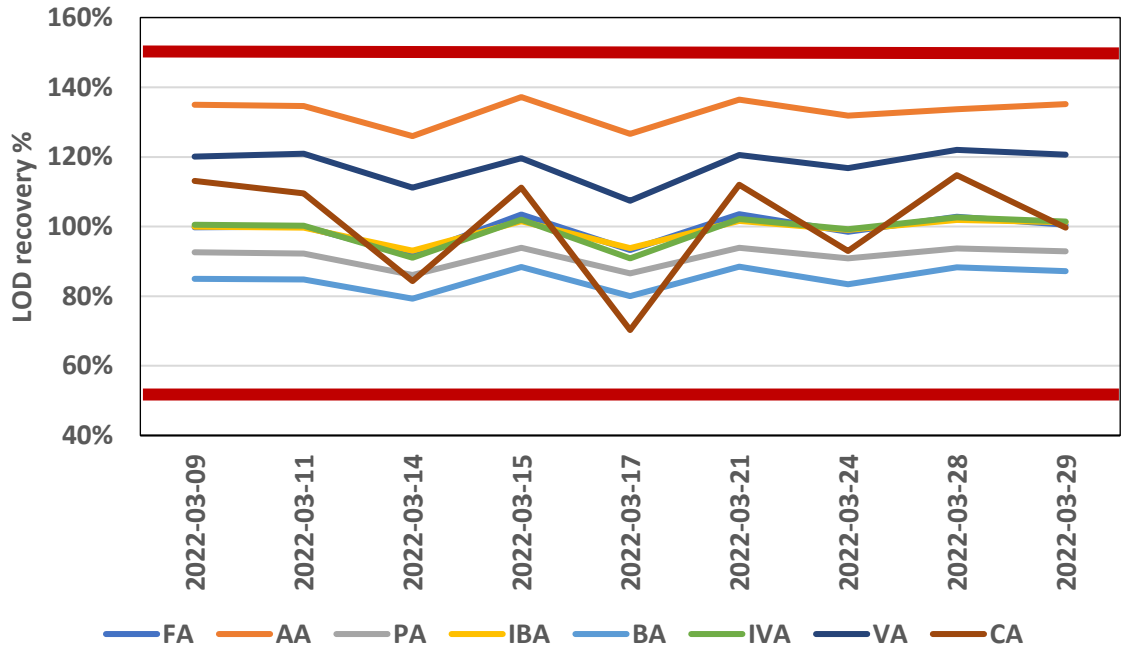
1. Within 50 minutes, all 8 VFAs were separated and analyzed.
   - Can be shortened to ~20 minutes for a typical EBMUD digester sample.
2. Relatively low RLs: 1-5 mg/L.

VFA IC QC Guidelines

QC parameters	Spiked level (mg/L)	Frequency	Criteria	Corrective action
CCV	50	Beginning, at least every 10 samples and at the end of the run	Recovery: 85%-115%	Rerun. If failed, recalibrate.
CCB	-	Right after CCV	< MDL	Rerun after rinse. If failed, troubleshooting e.g. change filters.
QCS	2nd source	1/batch	Recovery: 85%-115%	Rerun. If failed, recalibrate.
MB	-	1/batch, beginning of the batch	< MDL	Rerun fresh prepared QC sample. If failed, apply qualifier to the batch samples.
LCS/LCSD	50	1/batch, before samples	RPD≤20%, Recovery: 80-120%	
LOD	3X MDL	1/batch	Recovery: 50%-150%	
LOQ	@ RL	1/quarter	Recovery: 50%-150%	
MS/MSD	50	1/batch	RPD≤35%, Recovery: 70%-130%	Matrix interference assumed if LCS/LCSD pass.

Sensitivity, Accuracy & Precision

--LOD runs over 1 month



LOD	FA	AA	PA	IBA	BA	IBA	VA	CA
Spiked conc. (mg/L)	2.4	0.6	1.2	1.8	6.9	6.0	1.8	6.9

LOD recovery QC guideline: recovery 50~ 150 %

RSD over 1 month	FA	AA	PA	IBA	BA	IBA	VA	CA
%	4%	4%	3%	3%	4%	5%	5%	15%

KEY TAKEAWAY

VFA IC is an efficient method with high sensitivity, accuracy and precision.

Sample Preservation

Experiment Design — Day 1 — Day 4

Sample ID	Acidification/Dilution	MS/MSD	Cu (3.2 M) preservation
Digester # 2	10-fold by 0.5 mM H_2SO_4	√	√
Digester # 12		X	√

Repeat run all Day 1 prepared samples

Results — Day 1 vs Day 4 — Cu vs no Cu

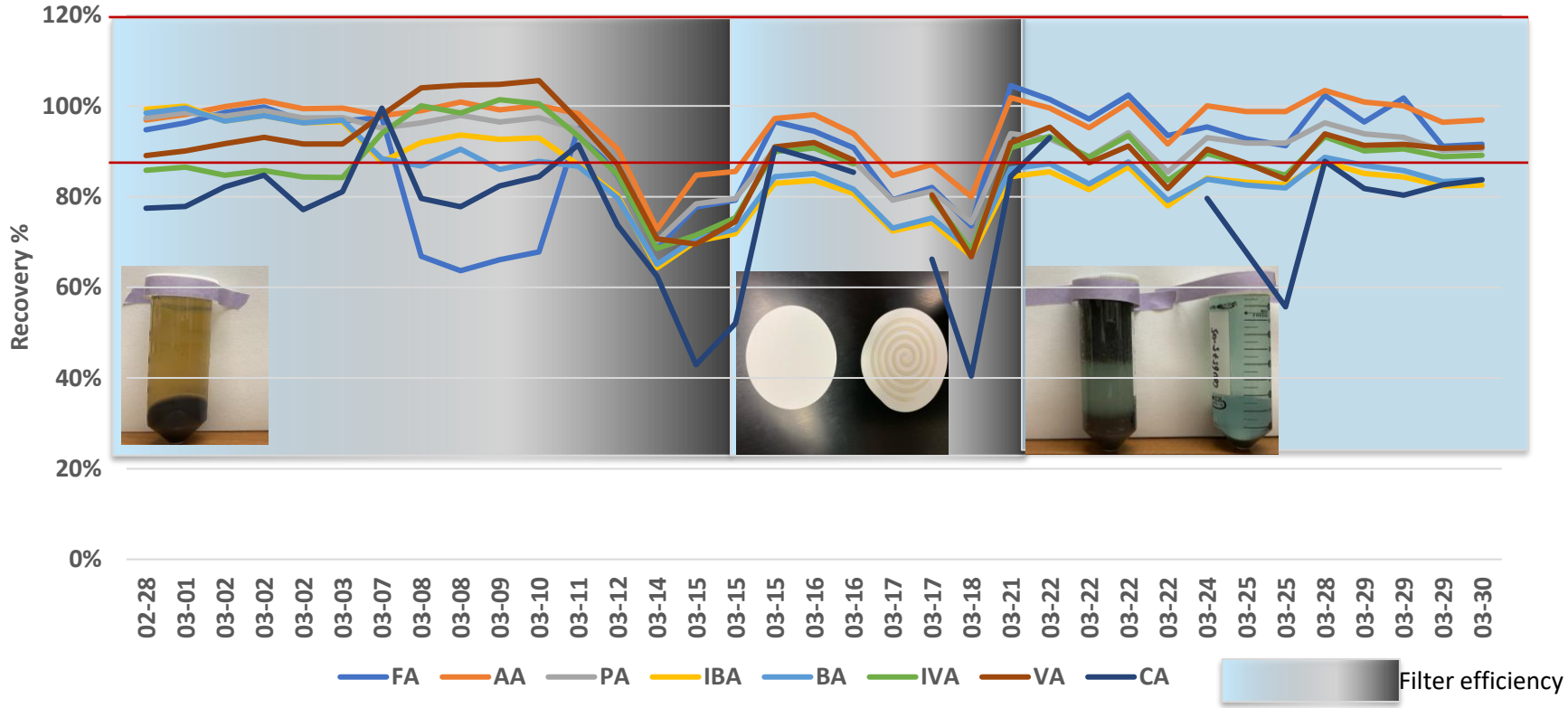
	Day 1 vs Day 4	Cu vs no Cu
α=0.05, F-test and t-test	No significant difference	No significant difference

KEY TAKEAWAYS

1. Centrifuge and acidification can preserve the digester samples at a minimal of 4 days.
2. There is no significant difference between samples w or w/o Cu preservation.

Method Robustness

CCV (50 mg/L) runs over 1 month



KEY TAKEAWAYS

1. Ultrafiltration filter needs change once per week to keep acceptable performance
2. Cu preservation helps suspended solids removal and extends filter usage.

Method Comparison (VFA IC vs VA)

Validation Goals	Parameters	VFA-IC	VA (SM 5560C)
Specificity	Target analytes	8 short chain VFA species	sum
	Matrix Recovery %/RSD %	85±12% (72 runs) for all 8 species, 86±12% (72 runs) for all 4 major species	109.5±62.4% for (22 MS)
Sensitivity	MDL	0.2 mg/L --2.3 mg/L	30 mg/L as HAc
	RL	1 mg/L --5 mg/L	92 mg/L as HAc
Accuracy	2nd source std recovery %	87±11% (21 runs) for all 8 species, 90±12% (21 runs) for all 4 major species	N/A
Repeatability	Recovery± RSD of IDOC/analyst	96.0±3.9% for all 8 species	91.9±1.3%
Reproducibility	Recovery± RSD of all LCS	92±14% (44 runs) for all 8 species, 93±14% (44 runs) for all 4 major species	96.4±4.2% (22 runs)
Robustness	Essential maintenance	Filter change/week	Glassware clean daily
	Operation	• Small volume to prepare and handle • Daily 2-3 hours sample preparation & report • Calibration ~ 1/month	• Larger sample volume • Daily 5-6 hours/ day • Labor intensive • Chemical and heat hazard

VA Distillation efficiency of VFA species

$$mg\ Volatile\ Acids\ as\ Acetic\ Acid/L = \frac{mL\ NaOH \times 0.01 \times 60000 \times 4}{mL\ sample \times 0.30}$$

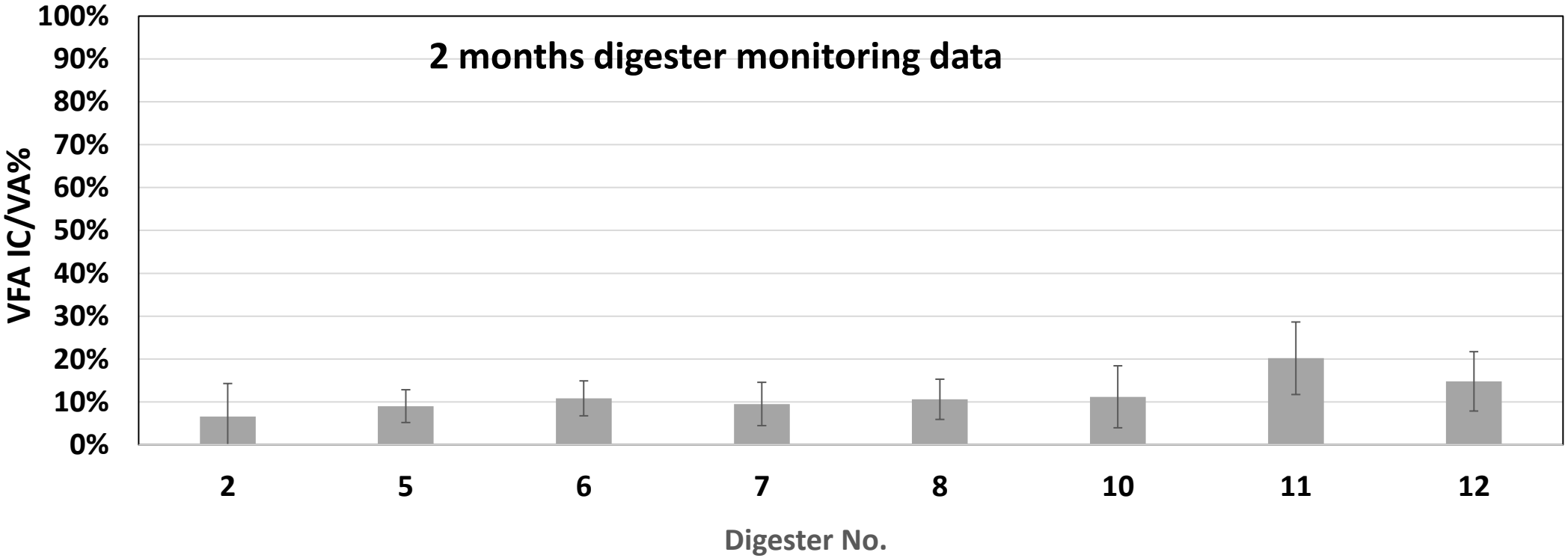
$$f_{\text{based off AA}} = 0.3$$

Initial mass (mg)	VFA	mass in distillate(mg)	Recovery %
10	FA	0.83	8.3%
	AA	2.3	23.0%
	PA	4.49	44.9%
	IBA	5.96	59.6%
	BA	5.85	58.5%
	IVA	5.91	59.1%
	VA	5.71	57.1%
	CA	4.52	45.2%

KEY TAKEAWAYS

1. HAc has about 20-30% recovery.
2. Different VFA species have different distillation recovery rate.

How to compare VFA IC results vs VA(SM5560C)?



KEY TAKEAWAY

Sum of all detected species from VFA IC analysis is about **10-20 %** of VA results.

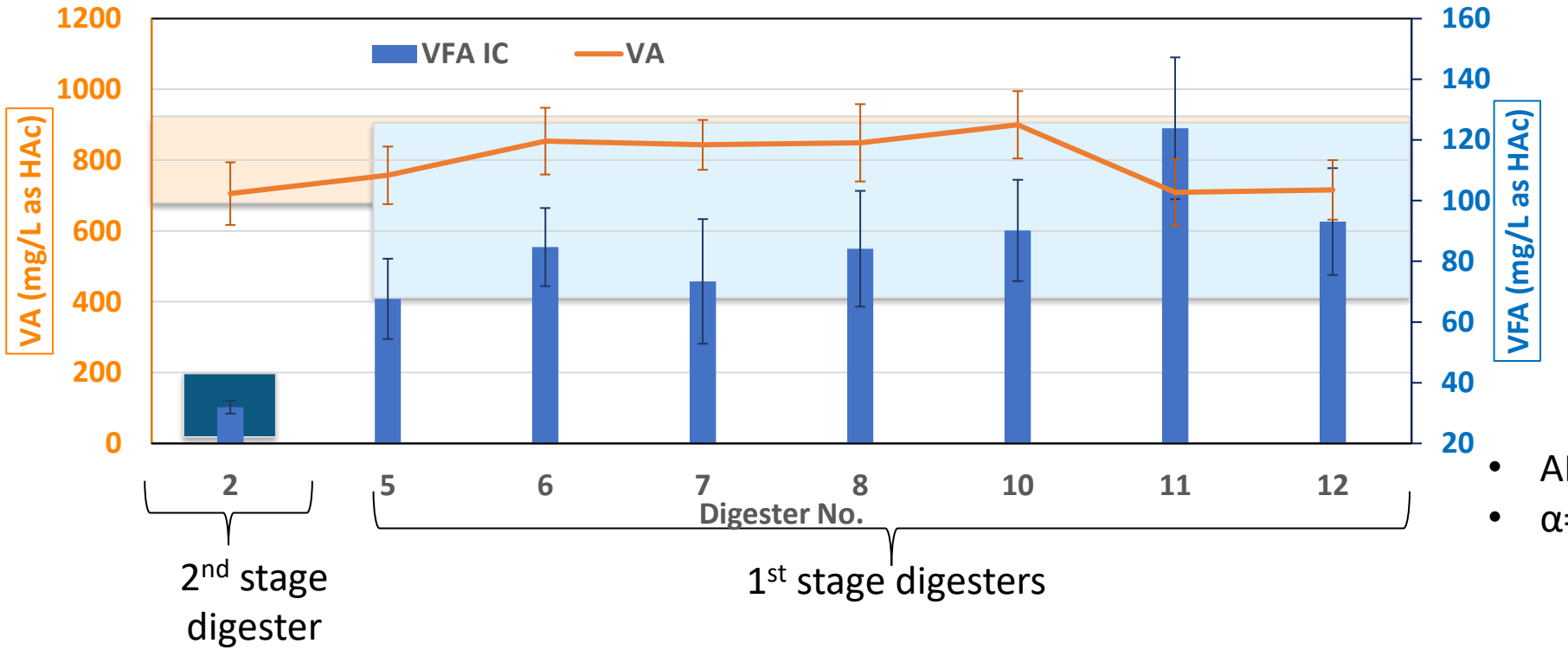
Benefits of the new method for WW Operators in digester monitoring

WATER IS ESSENTIAL SO ARE YOU

AC22 CONFERENCE
AND EXPO APRIL 11-14, 2022

CWEA

Sum of VFA as an indicator



Statistical difference

No statistical difference

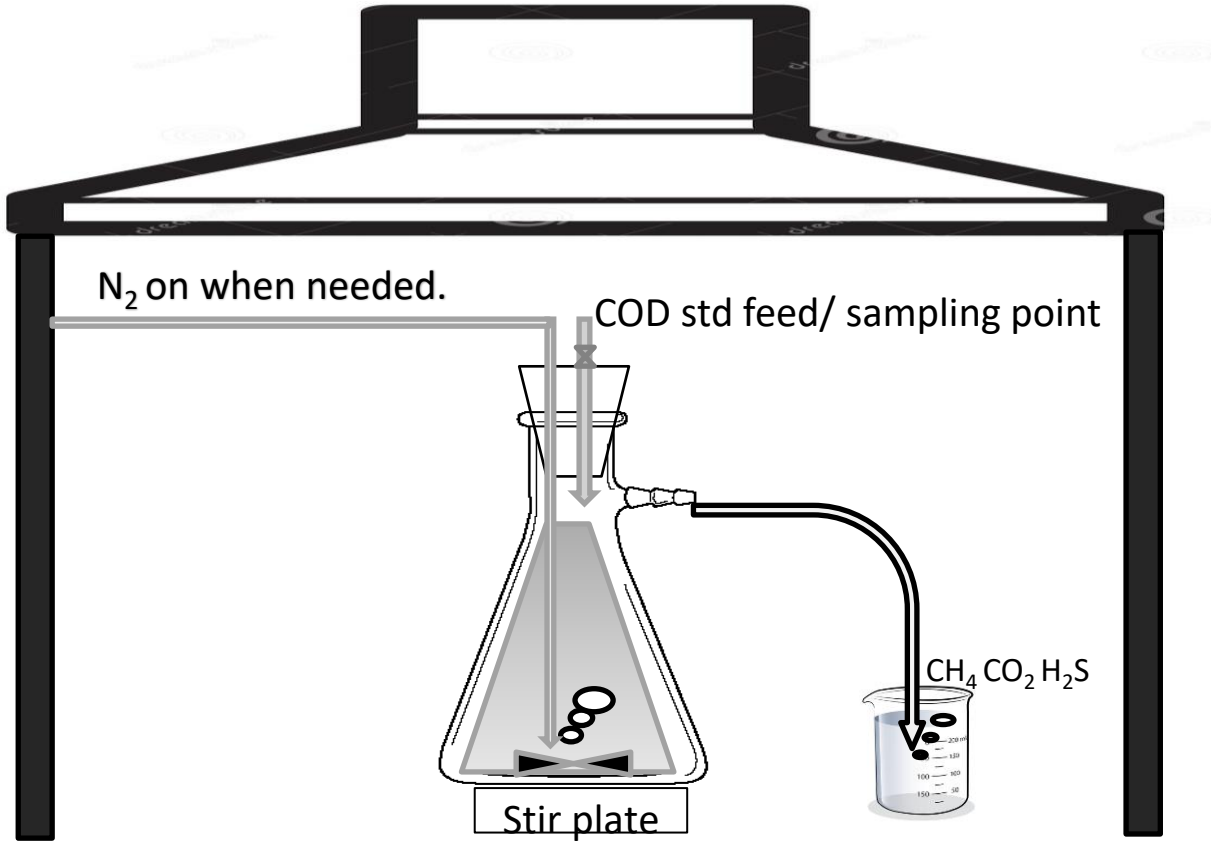
- ANOVA test
- α=0.05 for F-test and t-test

KEY TAKEAWAY

VFA results can differ 1st vs 2nd stage digesters.

Digester stress test design

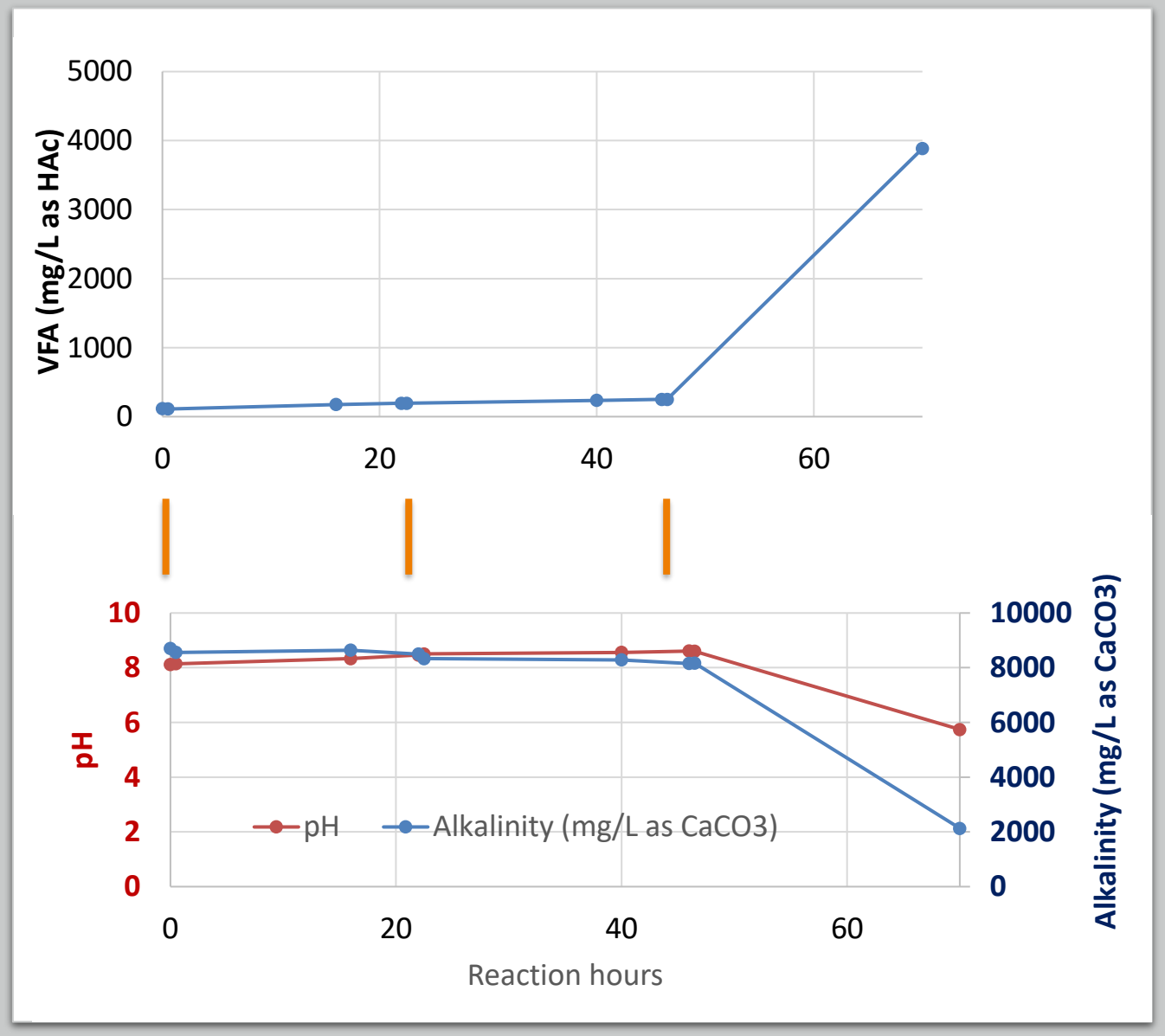
- 4-L sample from Digester No. 12
- Step feed COD (as glucose)
- Anaerobic condition, well mixed
- No temperature control
- Monitoring VFA IC/COD/pH/Alk.



Digester stress

- COD step dosing @ 11-12 g/L

Reaction hours (hr)	VFA/ALK
0	0.014
0.5	0.013
16	0.020
22	0.023
22.5	0.023
40	0.029
46	0.031
46.5	0.031
70	1.826



Indicators for Anaerobic Digesters

Indicator	VA IC	VA	References
VFA/ alkalinity (FOS/TAC)	√	√	B. Palacios-Ruiz H.O, 2008
PA/AA as indicator	√	X	Uri Marchaim, 1993
Individual VFA species, e.g. AA, BA, PP	√	X	Boe, 2006
pH, H_2S, NH_3, COD, VS reduction & chemical compounds etc.	N/A		

$$\frac{VA}{TA} \approx 0.05\sim0.15 \quad \Rightarrow \quad \frac{VFA}{TA} \approx 0.005\sim0.015$$

Summary

VFA IC method meets TNI validation requirements and provides reliable, robust and user-friendly analysis.

Based off 2-month continuous digester monitoring, sample preparation, preservation and routine maintenance are established.

Compared to VA (SM 5560C) method, VFA IC method could offer more accurate and precise VFA species results for better monitoring of digester performance.

Next Steps

- **Quantify deficiency between VA and VFA IC method.**
- **Provide benchmark for digester performance.**
  - VFA/Alkalinity
  - PA/AA ratio (Uri Marchaim, 1993)
  - Individual species concentration (Boe, 2006)
- **Extend analytical scope to other matrix.**

EBMUD team

Q&A

WATER IS
ESSENTIAL
SO ARE
You

Xin Xu

xin.xu@ebmud.com
510-287-1425

CWEA
PROTECTING CALIFORNIA'S MOST CRITICAL RESOURCE