EAST BAY MUNICIPAL UTILITY DISTRICT

Developing A Better Method for Anaerobic Digestion Process Monitoring at a Large Wastewater Treatment Plant - Volatile Fatty Acids by Ion Chromatography with Inline Ultrafiltration

Xin Xu, Research Chemist, EBMUD

Aug. 11, 2021

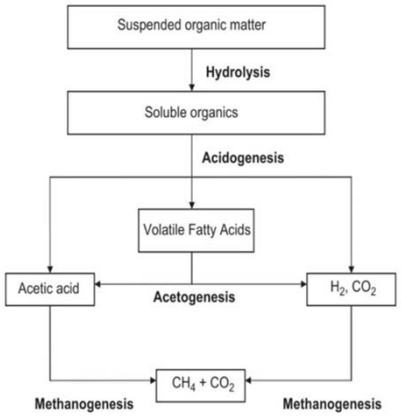
Objectives

- Validate instrumental analysis of target VFAs
- Test new method on various matrices
  - Digester Influent and effluent
  - Blend tank
  - R2
  - Water
  - Other wastewater (landfill leachates, N/DN, activated sludge etc.)
- Method comparison (traditional SM vs. IC method)
- Digester performance monitoring

Background

- Anaerobic digestion process
  - 4 stages
  - Acetic acid, butyric acid, isobutyric acid, isovaleric acid, and propionic acid
  - Inhibition effect
- Main WWTP
  - 2 Blend tanks
  - Two stages thermophilic AD (8+3)
- Denitrification

Subsequent steps in AD process[1]



VA in Digesters[2]

Conc. (mg/L) or ratio	Transfer Sludge (TSL, after 1st stage digesters)	Digested Sludge (DSL, after 2nd stage digesters)
Alk. (mg/L as CaCO3)	8,855	8,945
VA (mg/L as HAc)	491.8	292.1
VA / ALK	0.06	0.03

1. Cited from L. Appels et al. / Progress in Energy and Combustion Science 34 (2008) 755–781

2. Cited from MWWTP master plan 2020

Method comparison

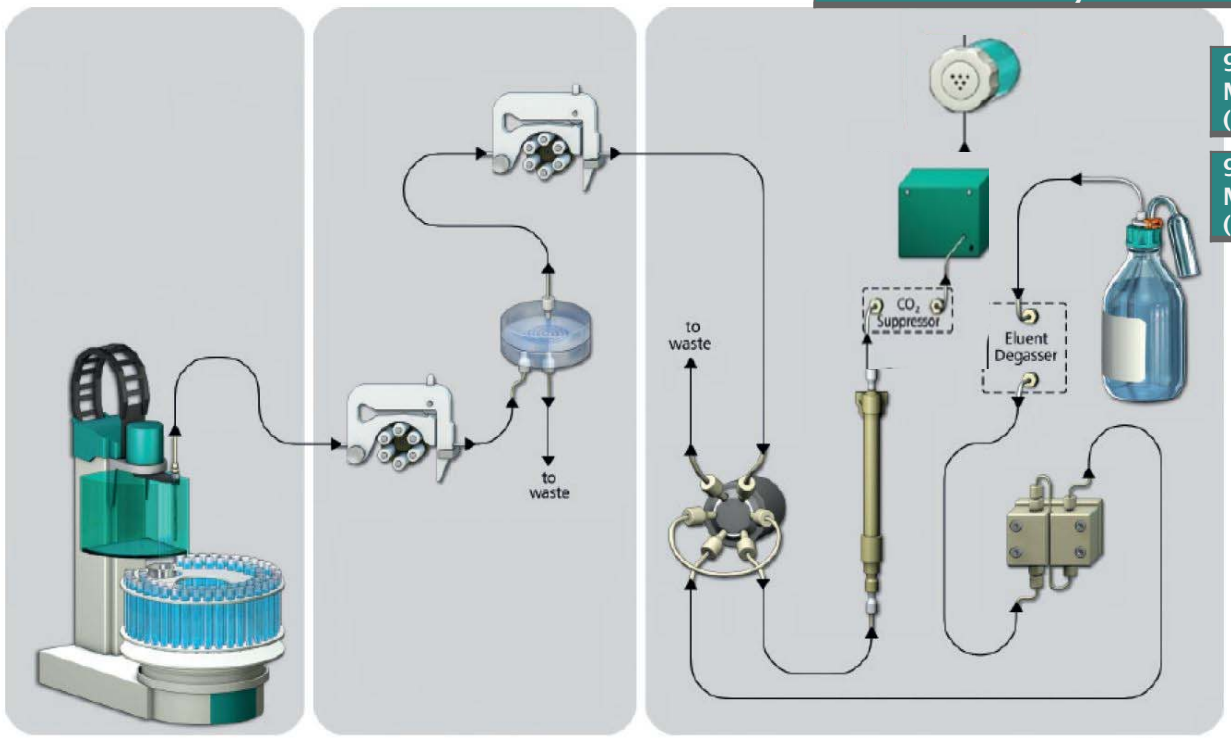
Method	Principle	Speciation	Pros and Cons	Citation
Distillation	50mL-250mL distill @ 1 atm	X	• Cumbersome • Azeotropic issue causing poor individual recovery • Conversion factor • Heat and chemical hazards	SOP473 (SM5560C)
Spectrophotometric	Montgomery method	X	• Critical pH control reagent • Less accurate due to various interferences • Cumbersome	Montgomery et al., 1962
GC	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	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	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

Instrument Selection

Factors to consider		Thermo	Metrohm
Basic performance	Column Autosampler Carbonate removal Suppressor Detector	sulfonated polystyrene/divinylbenzene resin, , particle size 7.5 µm (pH: 0-7) Inline filtration with frit CRD Chemical suppressor Conductivity detector	Polystyrene-divinylbenzene copolymer, particle size 9 µm (pH:0-13) Inline filtration with ultrafiltration system MCS Chemical suppressor Conductivity detector
	Sensitivity Selectivity	8 VFAs @ 0.2-0.8 mg/L; 20-80 mg/L	6 VFAs @ 0.1-50 mg/L willing to customize method
Cost	IC Unit Five yrs cost Consumables Service Long term maintenance	32K 76K Column+ suppressor/yr Need to purchase **Filtration extra 4K/year, manually**	36K 67K Column/2yr Service contract **Automatic filtration and filters are easy to change**
Software/hardware		4K, more training needed	Free and more familiar
Data transfer to LIMS		Need to develop	Upload script ready
Staff experience		limited	significant

Metrohm IC Setup Scheme

850 conductivity detector



930 Compact IC Flex, including Metrohm Carbon Suppressor (MCS)

930 Compact IC Flex, including Metrohm Suppressor Module (MSM)

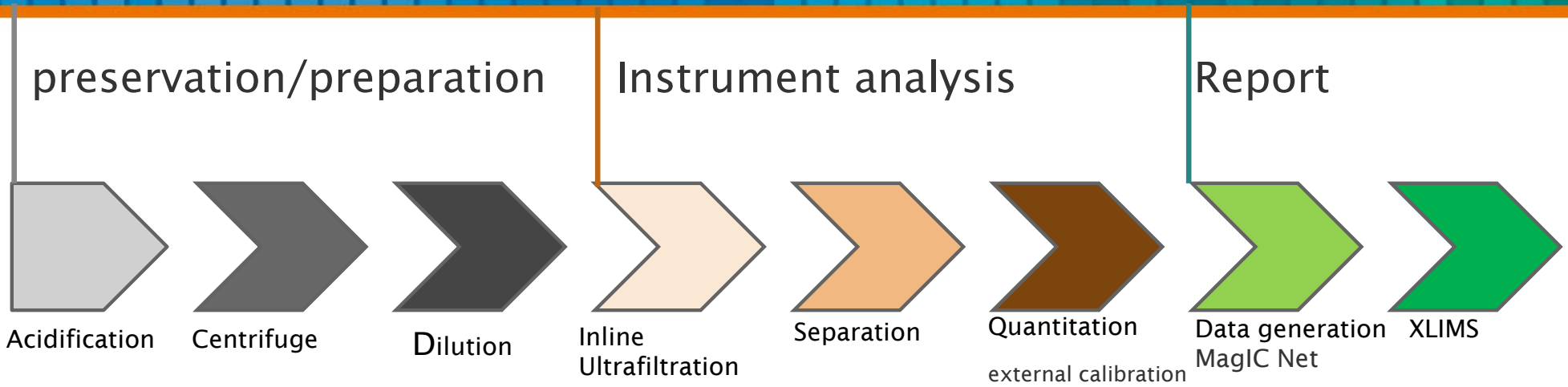
919 IC autosampler plus

Metrosep Organic Acids - 250/7.8
Metrosep Organic Acids Guard/4.6

Method Setup

- Instrument Method
  - Eluent: 0.5mM H_2SO_4 @flow: 0.5 mL/min
  - Regenerate: 0.5mol/L LiCl @flow: 0.5mL/min
  - Injection volume: 50 uL
  - Column temp. 32°C
  - MSM interval 10 mins
- Analytical Method
  - Identify target compounds (speciation by individual acids)
  - Sensitivity (IDL, MDL), Linear Calibration Range (LCR), Limit of Quantification(LOQ)
  - Accuracy & precision: recovery, RSD, RPD.
- Sample preparation
  - Preservation, holding time etc.
  - Rapid handling
- Data report

Analytical Workflow



- 1:1 H_2SO_4 to pH<2
- 50 mL @ for 12,100rpm for10 mins@ 4°C
- Dilute 2-20 times

- Auto filtration 0.2 µm
- Flow @0.5-0.6 ml/min
- Temperature control @32°C
- Pressure <7MPa
- Baseline conductivity: ~100µs/cm

- MagIC process data and generate report
- XLIMS IC script

Identify Target Analytes

Target # (elution order)	VFA	CAS#	RT @0.5 mL/min (mins)	RT @0.6 mL/min (mins)	Calibration Range* (mg/L)
1	Lactic acid	79-33-4	11.6	TBD	TBD
2	Formic Acid	64-18-6	14.8	12.51	2-100
3	**Acetic Acid**	**64-19-7**	**16.9**	**14.21**	**0.5-100**
4	**Propionic Acid**	**79-09-4**	**19.5**	**16.39**	**0.5-100**
5	**Isobutyric Acid**	**79-31-2**	**21.7**	**18.09**	**0.5-100**
6	**Butyric Acid**	**107-92-6**	**23.5**	**19.71**	**1-100**
7	**Isovaleric acid**	**503-74-2**	**26.7**	**22.32**	**2-100**
8	Valeric Acid	109-52-4	32.9	27.50	1-100
9	Caproic Acid	142-62-1	50.0	41.75	5-100

*: Linear regression, weighting 1/x, R^2>0.999

Instrument IDOC

Target #	VFA	spiked conc. (mg/L)	IDOC 1 reading	IDOC 2 reading	IDOC 3 reading	IDOC 4 reading	Ave. (mg/L)	Ave. rec.%	Stdev	RSD%	2nd source check rec. %
2	Formic Acid	50	50.3	50.2	50.4	50.2	50.3	101%	0.08	0.2%	98%
3	Acetic Acid	50	50.3	50.2	50.4	50.0	50.2	100%	0.15	0.3%	94%
4	Propionic Acid	50	50.1	50.0	50.2	49.7	50.0	100%	0.21	0.4%	93%
5	Isobutyric Acid	50	49.9	49.9	50.1	49.8	49.9	100%	0.14	0.3%	94%
6	Butyric Acid	50	50.0	50.1	50.2	49.8	50.0	100%	0.17	0.3%	95%
7	Isovaleric acid	50	50.1	50.0	49.8	49.4	49.8	100%	0.35	0.7%	92%
8	Valeric Acid	50	49.8	49.8	49.5	49.9	49.7	99%	0.17	0.3%	93%
9	Caproic Acid	50	50.1	48.8	48.2	48.1	48.8	98%	0.95	2.0%	75%

Acceptance criteria (request to Metrohm): Accuracy: 80%-120%; Precision (RPD)%≤20%

Instrument Detection Limit (IDL)

Parameter	Formic Acid	Acetic Acid	Propionic Acid	Isobutyric Acid	Butyric Acid	Isovaleric acid	Valeric Acid	Caproic Acid
IDL_{lcs}(mg/L)	0.5	0.1	0.1	0.2	0.6	0.5	0.4	2.0
IDL_{MB}(mg/L)	0.7	0.0	0.1	0.2	0.5	1.0	0.3	4.0
IDL(mg/L)	0.7	0.1	0.1	0.2	0.6	1.0	0.4	4.0
Acceptance Criteria (mg/L)	0.5	1	0.5	--	1	--	--	--

Parameter	Formic Acid	Acetic Acid	Propionic Acid	Isobutyric Acid	Butyric Acid	Isovaleric acid	Valeric Acid	Caproic Acid
RL (mg/L)	2	0.5	0.5	0.5	1	2	1	5
Acceptance Criteria (mg/L)	1	20	1		1			

MDL calculation based on https://www.epa.gov/sites/production/files/2016-12/documents/mdl-procedure_rev2_12-13-2016.pdf

Sample matrix interference

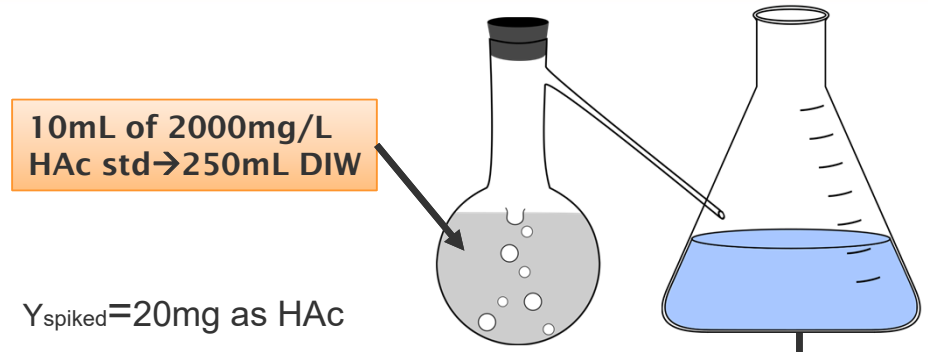
L239937-2 centrifuge @3000 RPM for 30 mins, and then supernatant centrifuge @ 11,000 RPM for 10 mins. Dilute and spiked with 50 mg/L of acetic acid.

Sample	Formic Acid	Acetic Acid	Propionic Acid	Recovery%	RPD%
L239937-2 Supernatant	0.85	54.65	3.79		
L239937-2 MS	0.88	550.44	3.44	99.1%	0.2%
L239937-2 MSD	0.88	549.38	3.42	98.9%	

L240333-5 acidified, centrifuge @3000 RPM for 30 mins, and then supernatant centrifuge @ 11,000 RPM for 10 mins. Dilute and spiked with 50 mg/L of acetic acid.

Sample	Formic Acid	Acetic Acid	Propionic Acid	Recovery%	RPD%
L240333-5 Supernatant	5.25	58.37	4.10		
L240333-5 MS	5.24	462.91	3.85	81%	4.2%
L240333-5 MSD	5.24	482.58	3.83	85%	

Mass Balance Calculation (from IC analysis)



100 mL collected distillate

20 mL discarded distillate

51.26 mg/L as HAc measured by IC

39.85 mg/L as HAc measured by IC

Ycalc.=6 mg as HOAc

Distillation Recovery =30%

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

Impact of distillation on VFAs recovery

Target #	VFAs	Boiling point (°C)	Initial mass (mg)	100 mL distillate*		20 mL discarded distillate*		Total rec. (%)	IC w/o distillation
				Mass (mg)	Rec. %	Mass (mg)	Rec. %		Recovery %
2	Formic Acid	100.8	50	4.26	9%	0.5	1.0%	10%	98%
3	Acetic Acid	117.9		12.36	25%	**	**	25%	94%
4	Propionic Acid	141.2		24.64	49%	**	**	49%	93%
5	Isobutyric Acid	99.5		20.67	41%	**	**	41%	94%
6	Butyric Acid	163.5		27.73	55%	**	**	55%	95%
7	Isovaleric acid	176.5		26.03	52%	**	**	52%	92%
8	Valeric Acid	186		29.09	58%	14.2	28.5%	87%	93%
9	Caproic Acid	205		17.50	35%	19.2	38.3%	73%	75%

*: Data generated from IC run
**: Distillate discarded.

Digester samples (collected on 11/30/20)

Sample ID	Formic Acid (mg/L)	Acetic Acid (mg/L)	Propionic Acid (mg/L)	Valeric Acid (mg/L)	Equal. to HAc(mg/L)	Titration (mg/L as HAc)	ALKALINITY: TOTAL (CaCO3 mg/L)
DIGESTER 12 L239768-8	41.67	48.38	15.48		115.3	900	9700
DIGESTER 11 L239768-7	41.64	54.12	15.56		121.0	610	9700
DIGESTER 10 L239768-6	41.72	63.96	16.06		131.4	1100	9900
DIGESTER 9 L239768-5	42.02	69.57	17.41		138.5	890	9700
DIGESTER 8 L239768-4	42.72	67.18	17.92		137.4	970	9700
DIGESTER 7 L239768-3	46.70	54.79	17.47	63.78	167.4	1100	10000
DIGESTER 5 L239768-2	62.70	56.85	21.52	75.90	200.7	1100	9300
DIGESTER 2 L239768-1	80.89	53.31	28.08	80.21	228.7	1100	10000

Next steps

- Method validation on digester samples followed SOP 194 v1
  - Lactic Acid
  - Sample preservation, storage, sample prep
  - Surrogate - Phenoxyacetic acid
  - IDOC, MDL study, RL
  - Finalize batch QC criteria
- SOP
- For digester samples
  - Parallel study (IC vs. Distillation)
  - Correlation with temperature, pH, Alkalinity, VS, NH_3/NH_4^+
  - Analyze individual VFAs data to predict digester performance

Thank you!

Brian P. Bellefeuille

Artem A. Dyachenko, Jason P. Mitchell, Yun Shang

Melissa Lash

Kamara Vrandecic, Genesis Castellanos, Lauren E. Brougham

References

- https://elibrary.asabe.org/abstract.asp?aid=31977
- https://www.liebertpub.com/doi/abs/10.1089/ees.2017.0190?journalCode=ees
- https://onlinelibrary.wiley.com/doi/epdf/10.1002/elsc.201600095
- New Approach for Determination of Volatile Fatty Acid in Anaerobic Digester Sample ENVIRONMENTAL ENGINEERING SCIENCE, Volume 35, Number 4, 2018
- L. G. M. Gorris, J. M. A. van Deursen, C. van der Drift, and G. D. Vogels, "Inhibition of propionate degradation by acetate in methanogenic fluidized bed reactors," Biotechnology Letters, vol. 11, no. 1, pp. 61–66, 1989.
- L. Appels, J. Baeyens, J. Degrève, and R. Dewil, "Principles and potential of the anaerobic digestion of waste-activated sludge," Progress in Energy and Combustion Science, vol. 34, no. 6, pp. 755–781, 2008.
- K. C. Wijekoon, C. Visvanathan, and A. Abeynayaka, "Effect of organic loading rate on VFA production, organic matter removal and microbial activity of a two-stage thermophilic anaerobic membrane bioreactor," Bioresource Technology, vol. 102, no. 9, pp. 5353–5360, 2011.
- R. Gourdon and P. Vermande, "Effects of propionic acid concentration on anaerobic digestion of pig manure," Biomass, vol. 13, no. 1, pp. 1–12, 1987.

Q&A