



EPA 557 With Approved Modifications To Meet Faster Run Times To Meet Regulatory Requirements

Ali W. Haghani, LCMS Manager
Andy Eaton, PhD, BCES, TDE*



*Technical Director Emeritus

Formation of DBPs



HAA5 Are One Of The Important DBPs With Regulatory Mandates

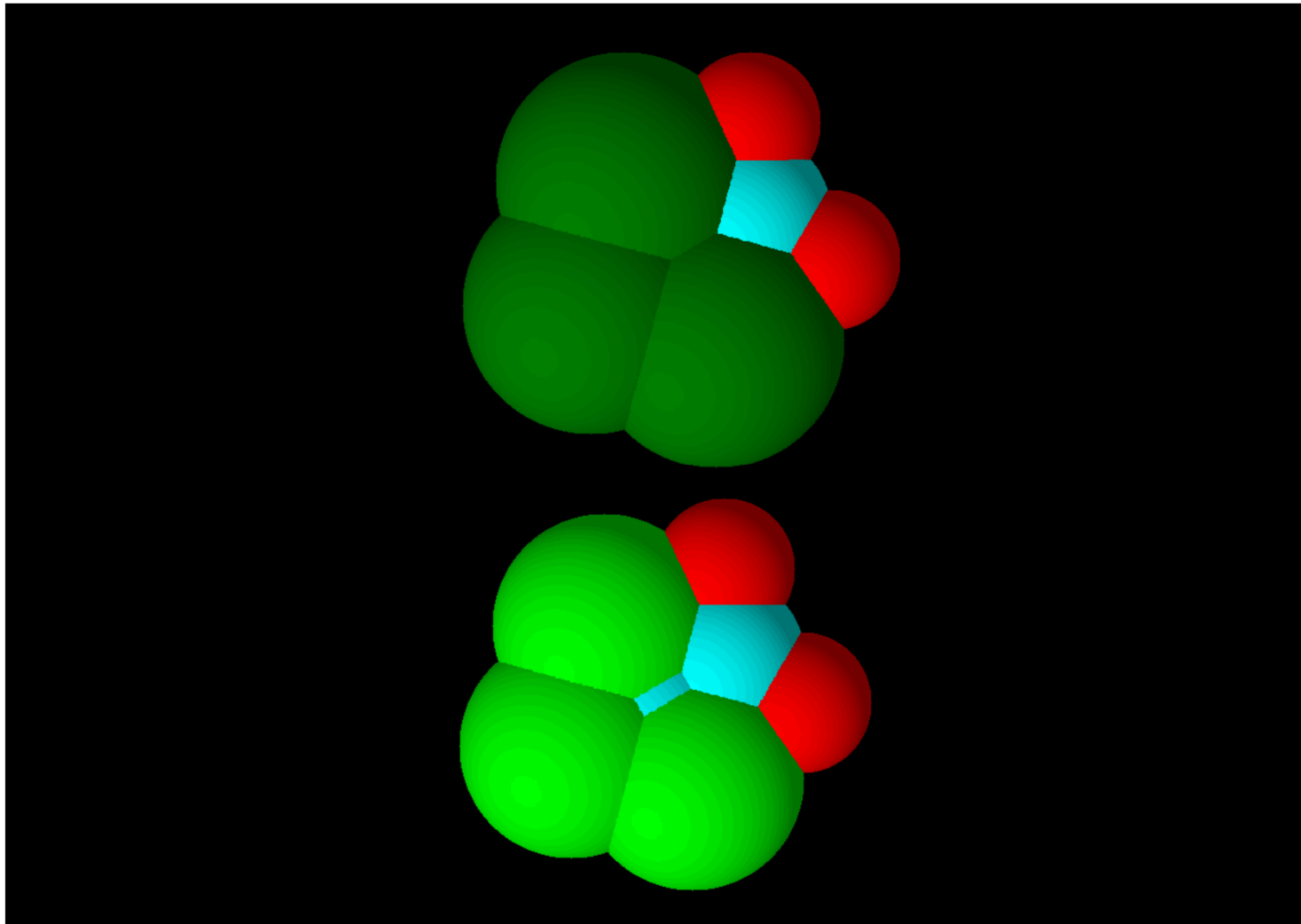


Acid	HAA	Formula		pK _a	logP
Monochloroacetic Acid	MCAA	ClCH ₂ CO ₂ H		2.9	-0.05+/-0.2
Monobromoacetic Acid	MBAA	BrCH ₂ CO ₂ H		2.9	0.51+/-0.25
Dichloroacetic Acid	DCAA	Cl ₂ CHCO ₂ H		1.3	0.54+/-0.29
Bromochloroacetic Acid	BCAA	BrClCHCO ₂ H		1.4	1.14+/-0.32
Dibromoacetic Acid	DBAA	Br ₂ CHCO ₂ H		1.5	1.65+/-0.31
Trichloroacetic Acid	TCAA	Cl ₃ CCO ₂ H		0.6	1.67+/-0.41
Bromodichloroacetic Acid	BDCAA	Cl ₂ ClCCO ₂ H		1.1	2.31+/-0.42
Chlorodibromoacetic Acid	CDBAA	Br ₂ ClCCO ₂ H		1.1	2.86+/-0.42
Tribromoacetic Acid	TBAA	Br ₃ CCO ₂ H		0.7	3.33+/-0.41

HAA5
MCL = 60 ppb
MCLG =
TCAA < 30 ppb
& DCAA 0

Logic is that by controlling HAA5 other DBPs should also fall within control. UCMR4 is currently analyzing for HAA9.

TCAA And TBAA (More Crowded) Making It The Least Stable Of HAA9



Some Time Lines



1854 Cholera outbreak first identified waterborne - London - John Snow
1900- Chlorination best public health improvement.
1970 chloroform DBP#1
1990 EPA 552 HAA Diazomethane GC
1992 EPA 552.1 HAA Acidified Methanol GC
1995 EPA 552.2 HAA Acidified Methanol GC
1996 ICR Stage2 D-DBP rule
1998 SM 6251B HAA Diazomethane GC
1998 Stage1 D-DBP rule
2003 EPA 552.3 HAA Acidified Methanol - TAME GC, to improve HAA3 (Brominated HAA)
2009 EPA 557 HAA9, Bromate, Dalapon, HAA9 IC-MS/MS – new technology
2018 UCMR4 2018-2020, using EPA 552.3 AND EPA 557 FOR HAA9

**1974-1998: Other DBPs followed (~500):
HAA, HAN, haloacetaldehydes, cyanogen chloride, aldehydes, ketoacids, chlorite, bromate, etc**

Current Methodologies for HAA5 and HAA9: GC-ECD Methods



➤ USEPA 552, 552.1, 552.2, and 552.3 and SM 6251B

- Liquid-liquid microextraction, derivatization, and gas chromatography with electron capture detection
- TBAA can be more challenging during extraction process: 552.3>552.2>552 for recoveries for TBAA with changes made per each version
- **Run time 15 minutes per injection, but extraction is cumbersome (but can be batched)**

Current Methodologies for HAA5 and HAA9: IC-MS-MS Methods



➤ USEPA 557 suppressed ion chromatography with MS-MS detection:

- Direct injection method no extraction required
- **Matrix diversion setup**
- No need for liquid-liquid extraction or sample pretreatment
- No need for derivatization
- Also allows bromate in same run
- **Fully automated however >55 minutes run time.**

EPA 557 Setup: IC Conditions



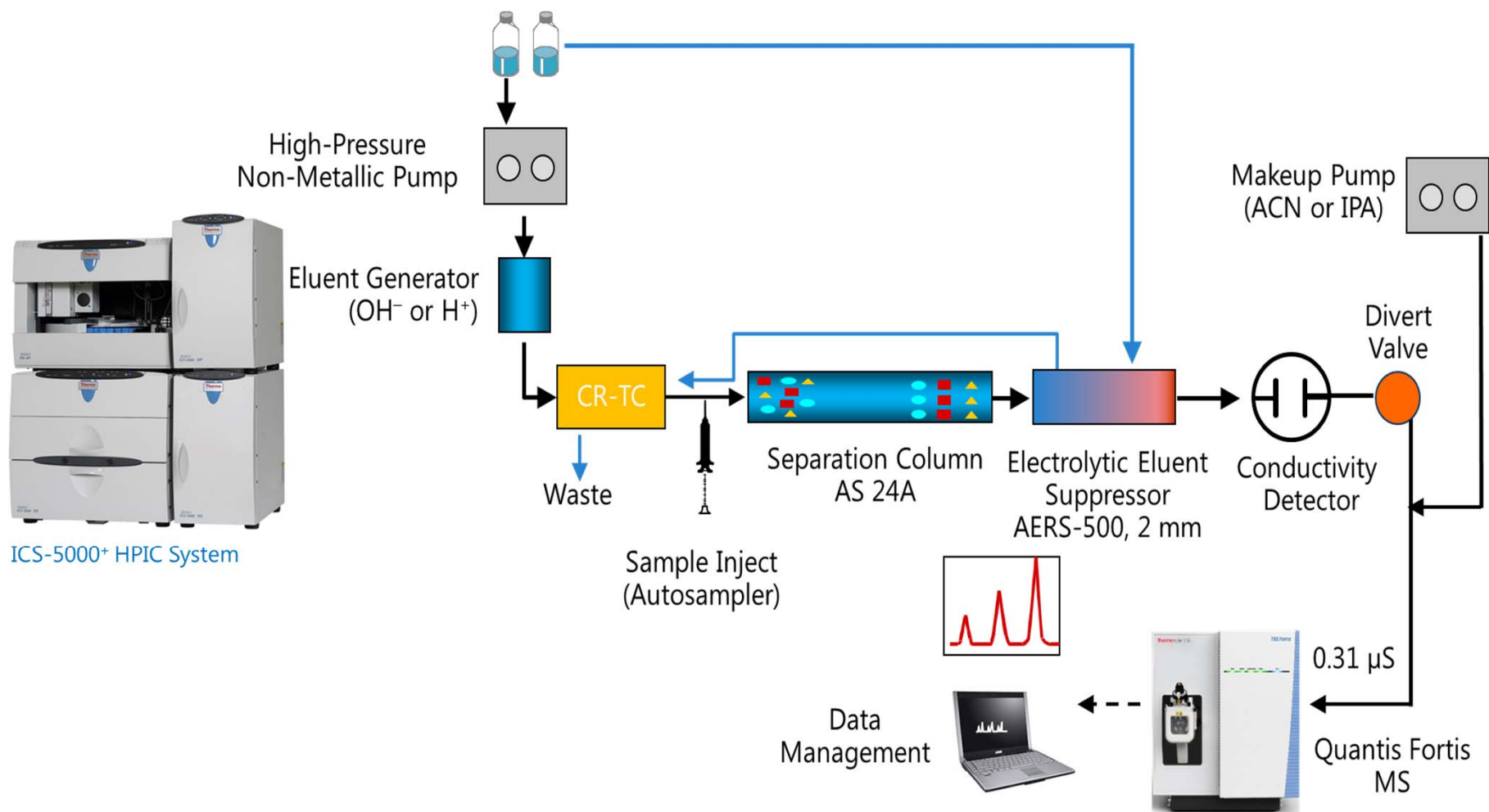
Parameter	Value
▪ Column:	▪ Dionex IonPac AG24 (2 x 50 mm), IonPac AS24 (2 x 250 mm), IonPac AG24A (2 x 50 mm), IonPac AS24A (2 x 250 mm)
▪ Suppressor	▪ Dionex AERS 500 (2 mm)
▪ Column Temperature:	▪ 15 °C
▪ Injection volume:	▪ 50 µL
▪ Flow rate	▪ 0.35 mL/min potassium hydroxide (KOH) gradient, electrolytically generated
▪ Autosampler temperature:	▪ 4 °C

EPA 557 Setup: MS-MS Conditions



Parameter	Value
▪ Ion source polarity	▪ Negative Ion Mode
▪ Spray voltage	▪ 3200 V
▪ Vaporizer gas pressure:	▪ 45 units N2
▪ Auxiliary gas pressure:	▪ 10 units N2
▪ Capillary temperature:	▪ 200 °C
▪ Vaporizer temperature:	▪ 200 °C
▪ Collision gas pressure:	▪ 1.5 mTorr Ar
▪ Ion cycle time	▪ 1 s

IC-MS/MS Configuration.



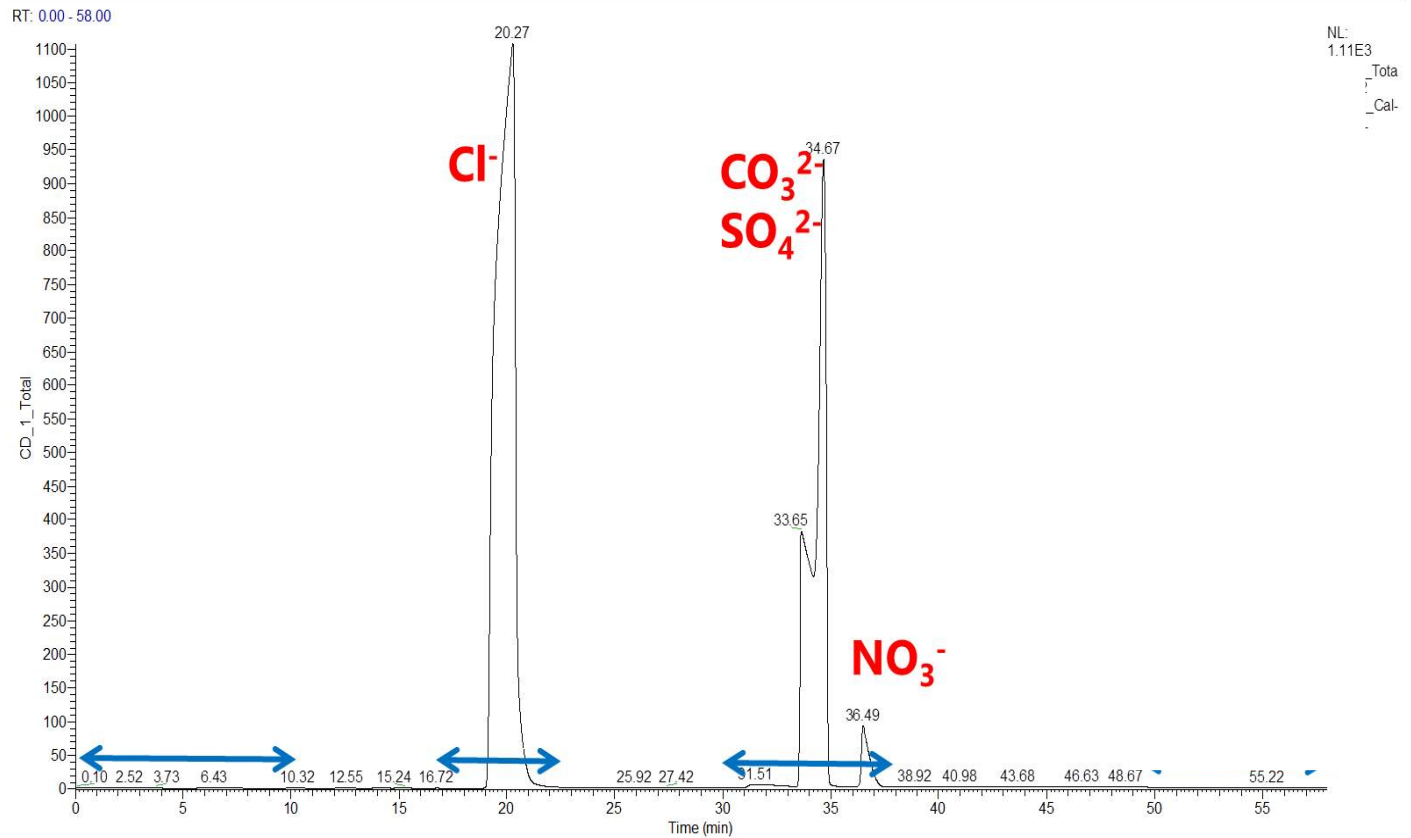
Elimination Of Salts From Matrix – Indicated By Blue Arrows.



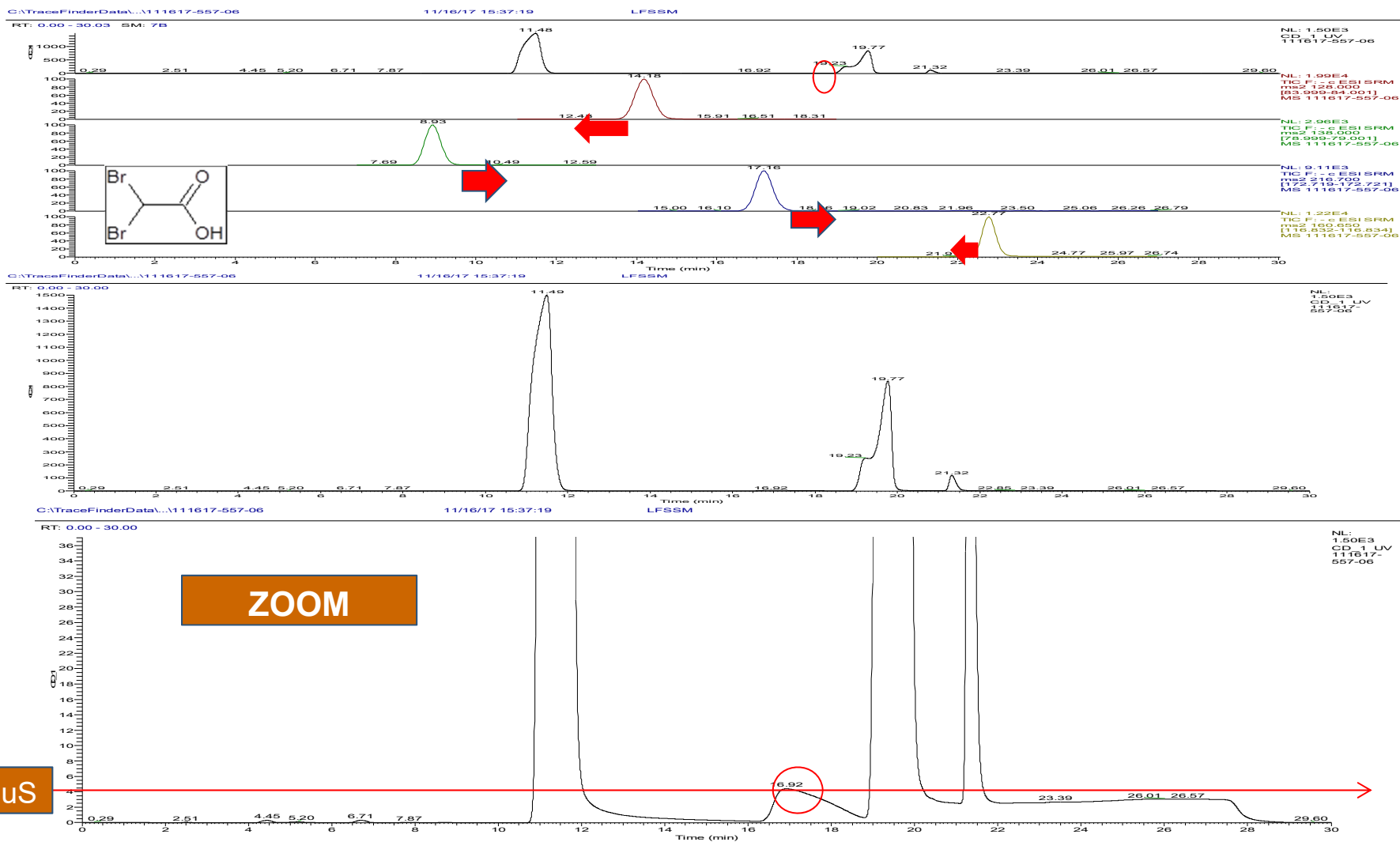
Elimination of Salts



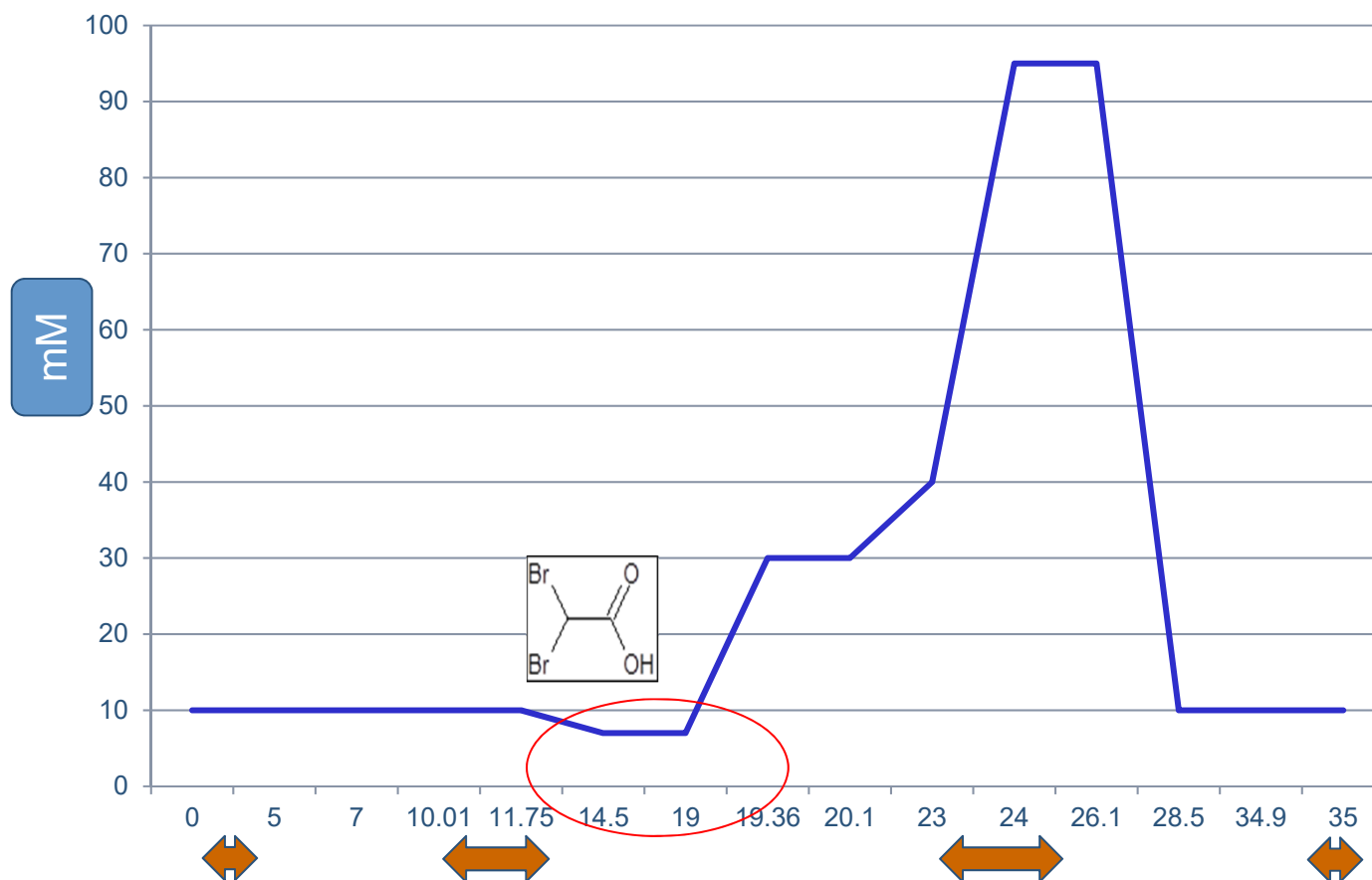
Removes ion suppression



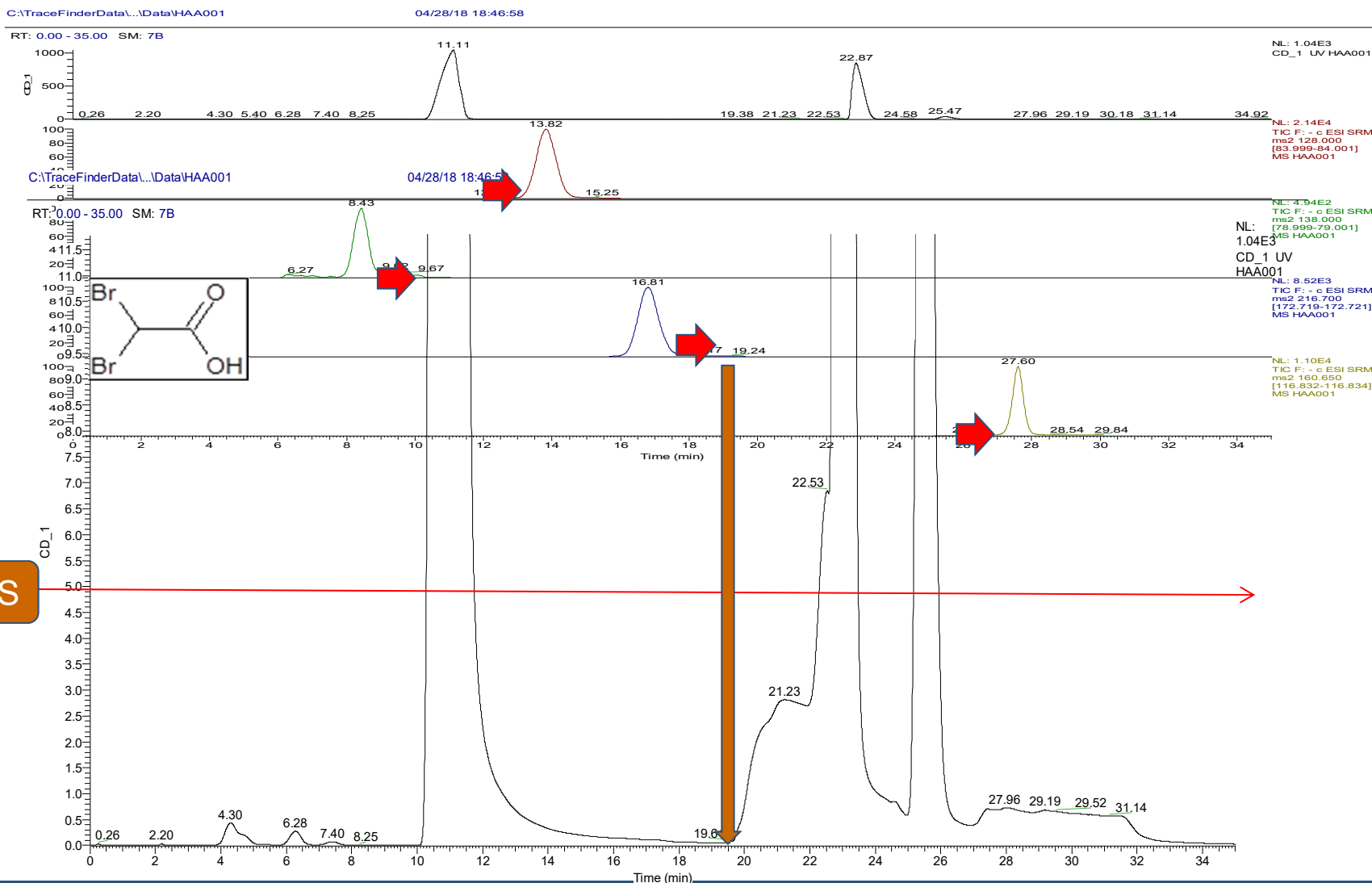
Carbonate and DBAA Challenge



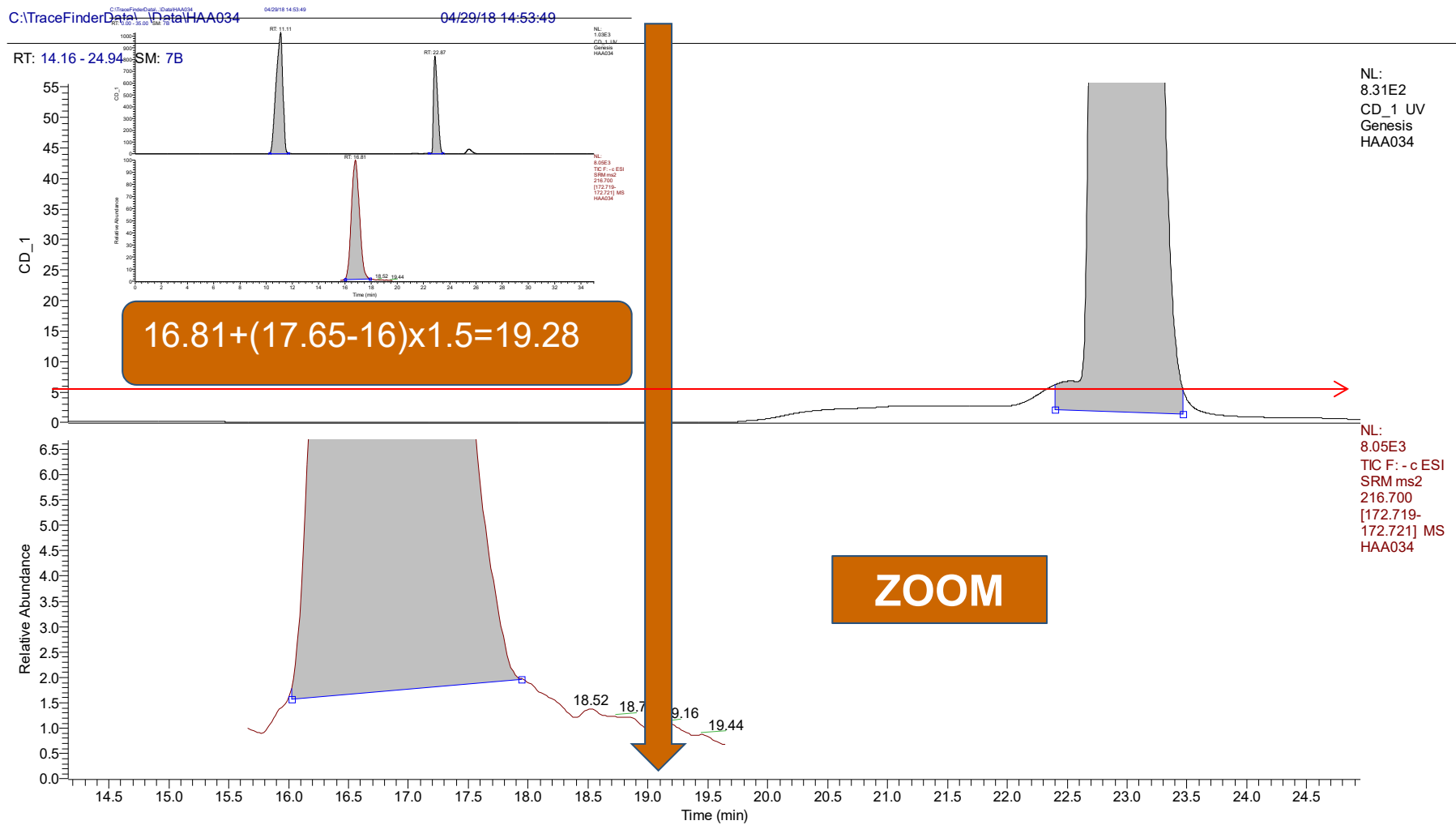
Carbonate And DBAA Separation



Carbonates Eluted 20 Minutes, Shifted 4 Minutes Right, Meeting Divert Valve Criteria



Showing Divert Valve Timing



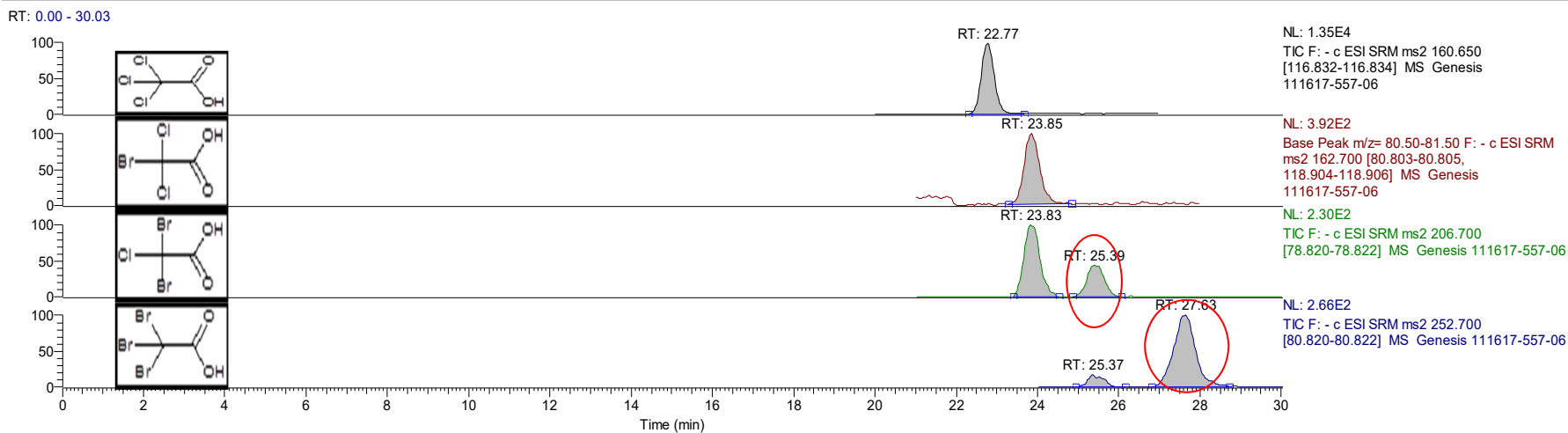
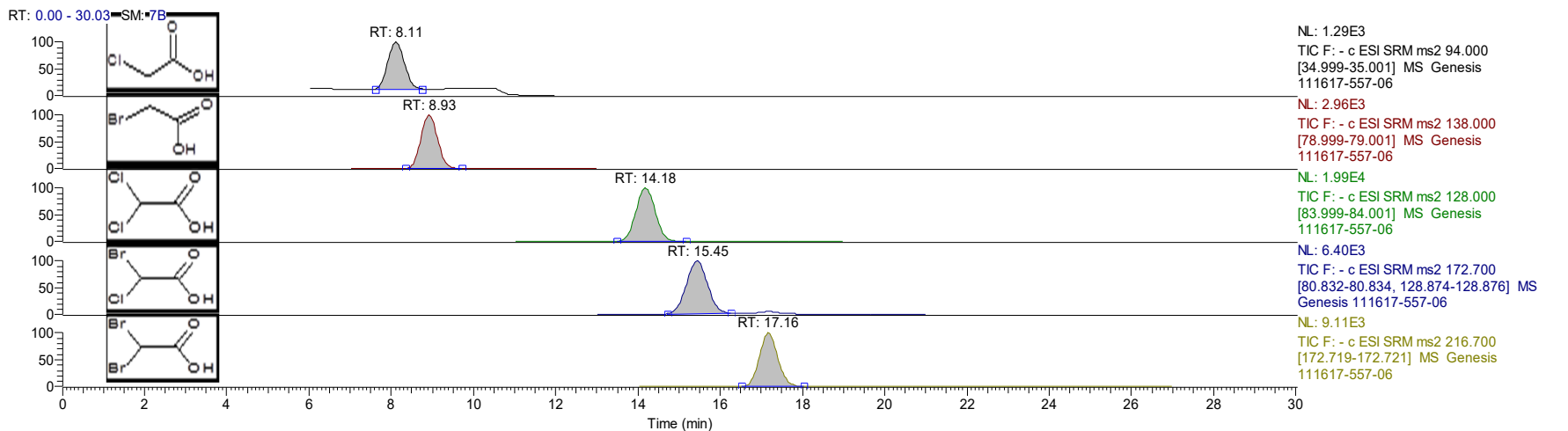
Elution Series With Modified Gradient



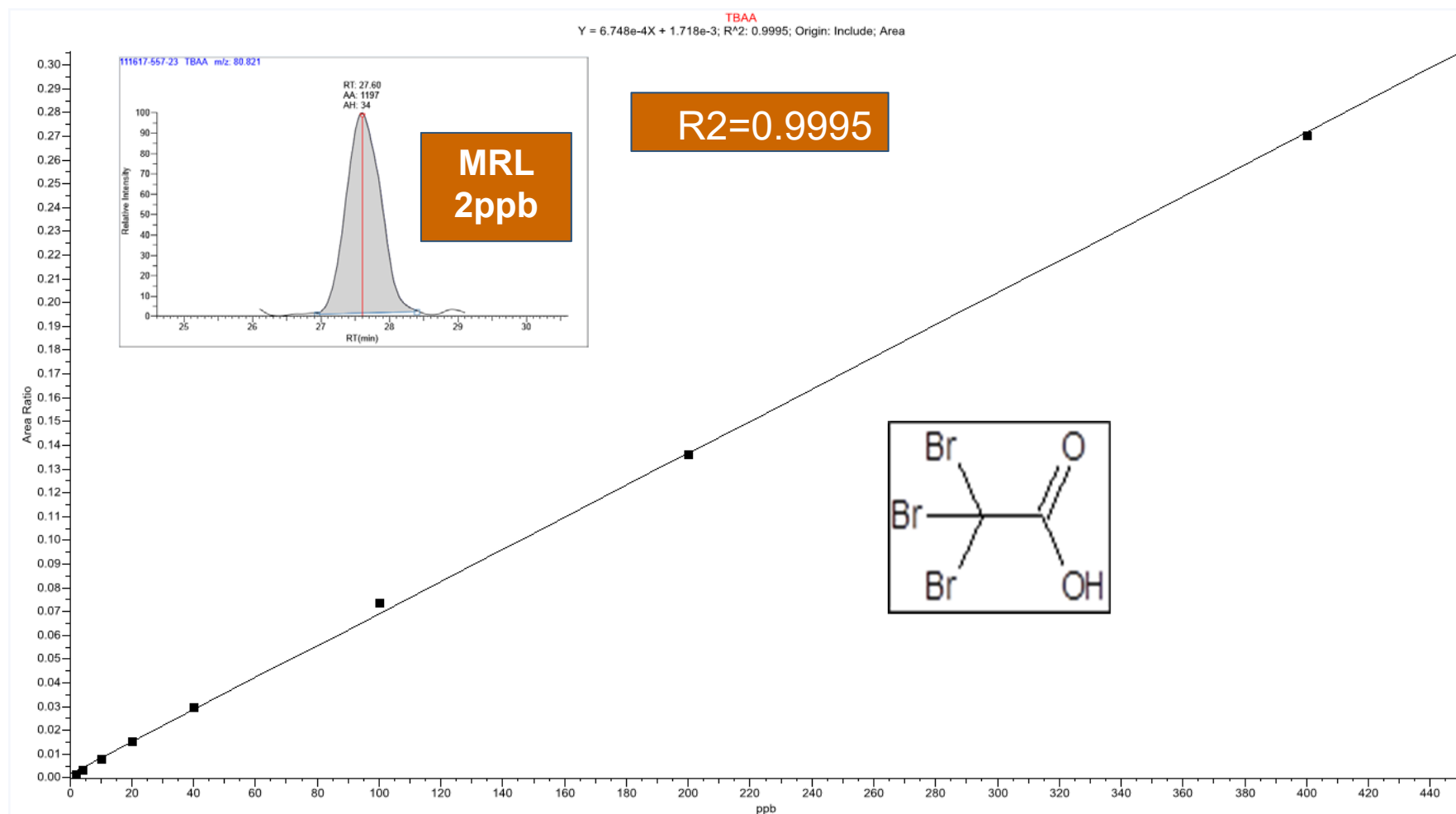
C:\TraceFinderData\...111617-557-06

11/16/17 15:37:19

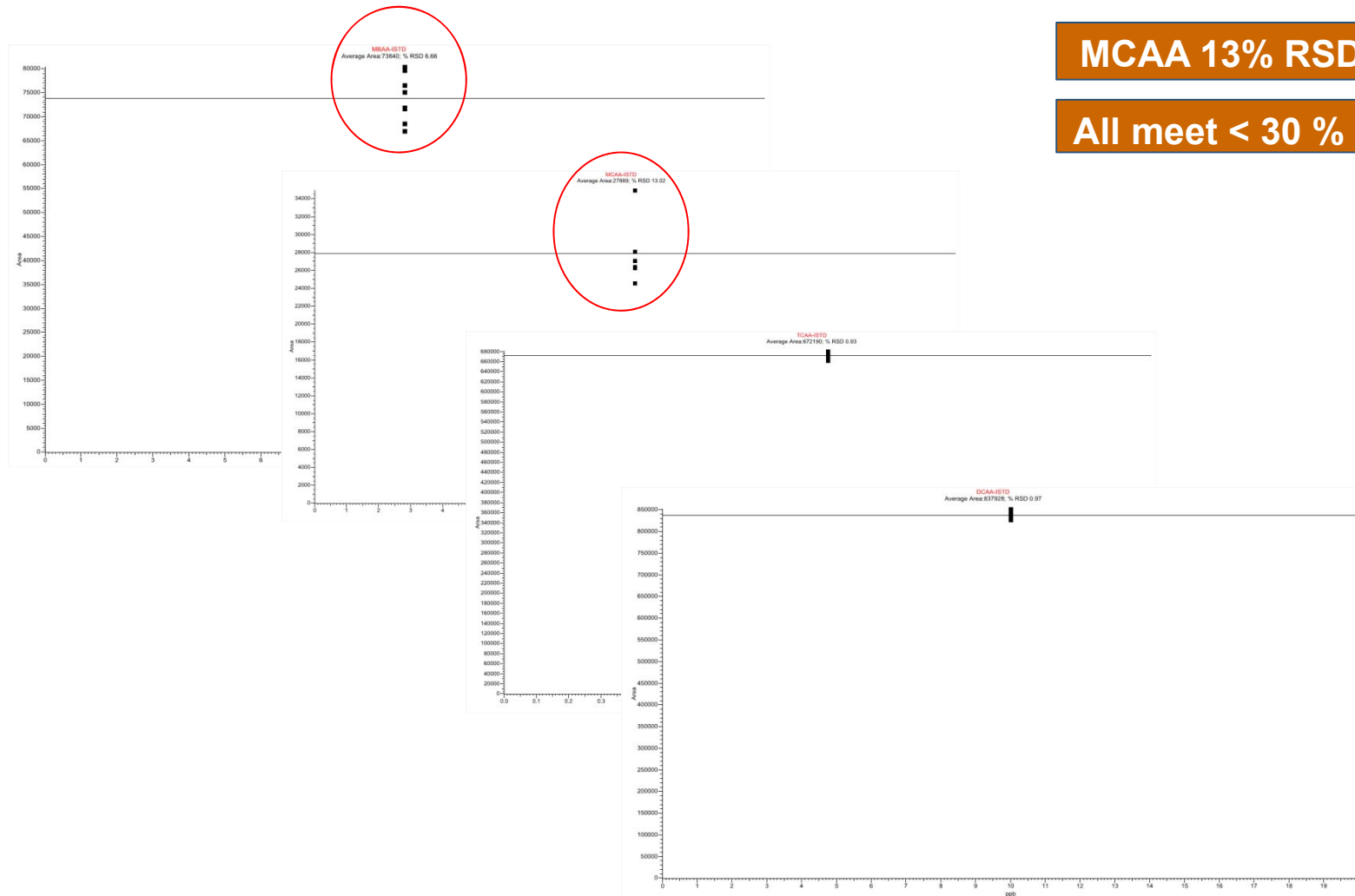
LFSSM



Good Calibration for all HAA9s



Good IS Reproducibility



MCAA 13% RSD

All meet < 30 % RSD

IDOC According to EPA 557



- Demonstration of low system background
- Test for system carryover
- MRL confirmation
- Demonstration of precision and accuracy for LFB and LFSSM

Test for System Carryover



NAME	Highest CAL ppb	R-carry over	MRL	1/3 MRL	limit <1/3 MRL
BCAA	60	0.007	0.3	0.1	Pass
BDCAA	100	N/F	0.5	0.167	Pass
CDBAA	60	0.047	0.3	0.1	Pass
DBAA	60	-0.009	0.3	0.1	Pass
DCAA	40	0.013	0.2	0.067	Pass
MBAA	30	0.1	0.3	0.1	Pass
MCAA	400	0.397	2	0.667	Pass
TBAA	400	-0.239	2	0.667	Pass
TCAA	100	N/F	0.5	0.167	Pass

Demonstration of Low System Background



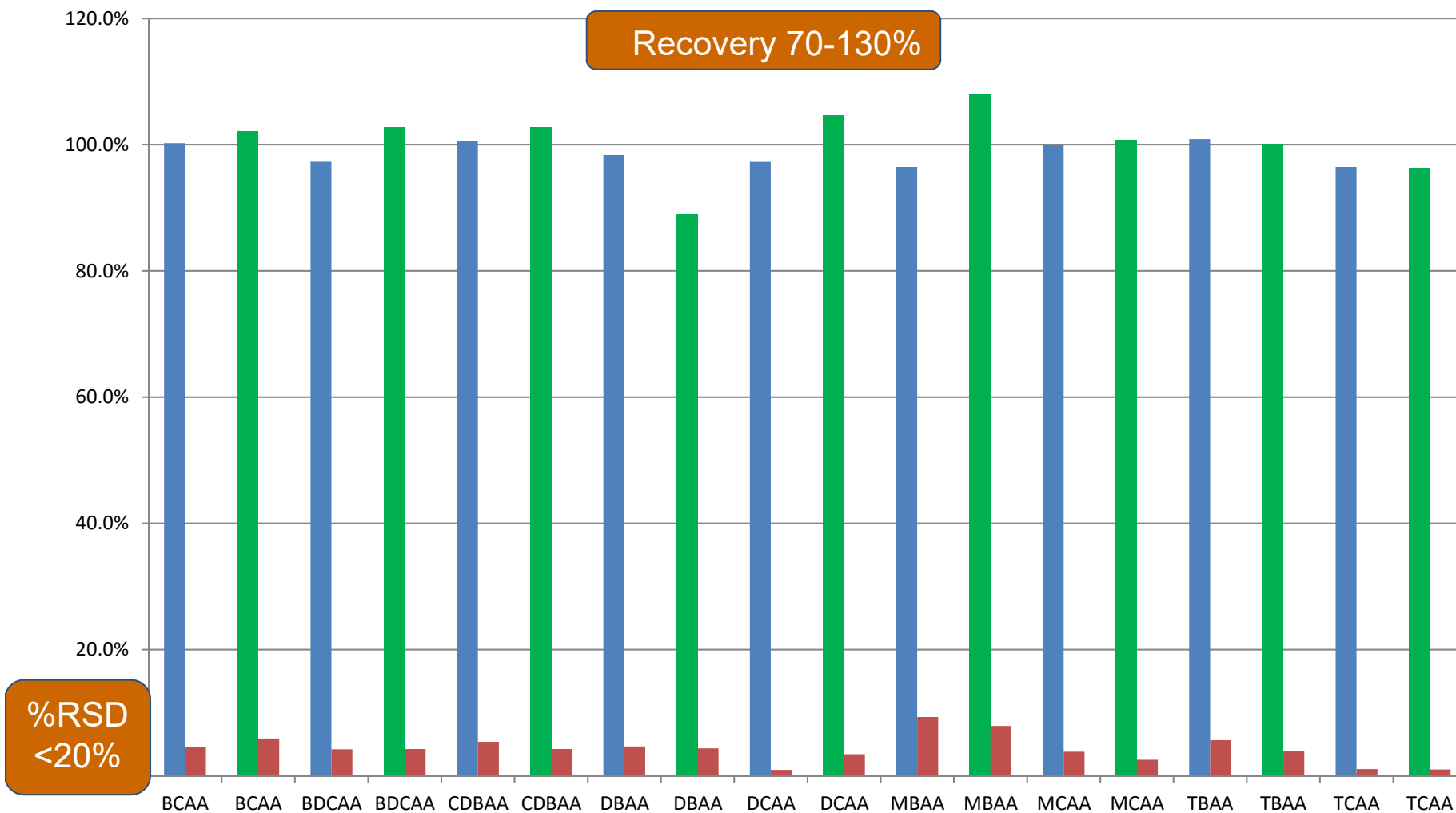
NAME	Method blank ppb	MRL	1/3 MRL	limit <1.3 MRL
BCAA	-0.002	0.3	0.1	Pass
BDCAA	-0.058	0.5	0.167	Pass
CDBAA	0.039	0.3	0.1	Pass
DBAA	-0.003	0.3	0.1	Pass
DCAA	0.011	0.2	0.067	Pass
MBAA	-0.116	0.3	0.1	Pass
MCAA	-0.053	2	0.667	Pass
TBAA	N/F	2	0.667	Pass
TCAA	N/F	0.5	0.167	Pass

MRL Confirmation



Analyte	Actual	Upper HPIR	Lower HPIR	PIR	% Rec.	%RSD
		criteria	criteria			
		≤ 150	≥ 50			
BCAA	0.3	120.3	64.2	Pass	92%	8%
BDCAA	0.5	108.1	72.2	Pass	90%	5%
Bromate	1	106.7	73.0	Pass	90%	5%
CDBAA	0.3	140.3	50.3	Pass	95%	12%
DBAA	0.3	147.1	115.7	Pass	131%	3%
DCAA	0.2	98.6	54.9	Pass	77%	7%
MBAA	0.3	128.4	70.4	Pass	99%	7%
MCAA	2	136.8	57.1	Pass	97%	10%
TBAA	2	102.2	61.2	Pass	82%	6%
TCAA	0.5	126.1	73.5	Pass	100%	7%

Demonstration of Precision and Accuracy for LFB And LFSSM. N=7



Blind Performance Test Result



	PT	True value	%recovery	Limit	PASS/FAIL
	ppb	ppb			
BCAA	2.65	2.26	117%	1.34 - 3.18	pass
BDCAA	3.58	3.72	96.1%	2.21 - 5.23	pass
CDBAA	2.55	2.9	87.8%	1.73 - 4.07	pass
DBAA		NA		NA	
DCAA		NA		NA	
MBAA	2.73	2.21	123%	1.31 - 3.11	pass
MCAA	16.79	13.9	121%	8.27 - 19.5	pass
TBAA	16.53	17.8	92.9%	10.6 - 25.0	pass
TCAA	1.281	1.06	121%	0.631 - 1.49	pass

New Conditions for HAA5 and HAA9:



➤ USEPA 557 suppressed ion chromatography with MS-MS detection:

- Direct injection method no extraction required
- **Matrix diversion setup**
- No need for liquid-liquid extraction or sample pretreatment
- No need for derivatization
- **Fully automated ~30 minutes run time**

Conclusions



- **Demonstrated the analysis of 9 HAAs using IC coupled to MS/MS**
- **Faster method while meeting EPA divert valve criteria**
- **Ion chromatography offers excellent separations, and selectivity for HAAs with advantage of being more rugged for TBAA.**

Any Questions?



Ali Haghani: alihaghani@eurofinsus.com

Andy Eaton: andyeaton@eurofinsus.com

Eurofins Eaton Analytical, LLC

www.eurofinsus.com/eaton