Weck Laboratories

Improved Method for the Detection of Haloacetic Acids in Drinking Water by HPLC-MS/MS

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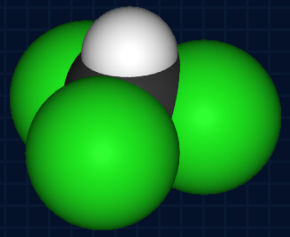
National Environmental Monitoring Conference 2015

Introduction

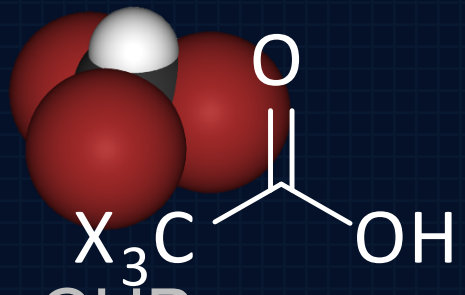
Chlorination disinfection by-products

Disinfection + Humic/fulvic Organics → Disinfection by-products

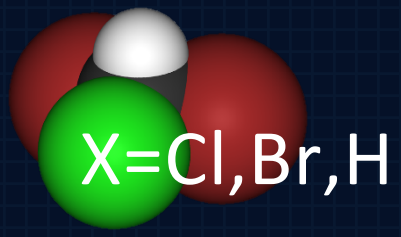
Chlorine
Chloramine
Chlorine dioxide
Ozone
Chlorine agents
Humic acids
Fulvic acids
Trihalomethanes
Haloacetic acids



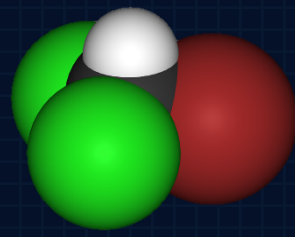
$CHCl_3$



$CHBr_3$

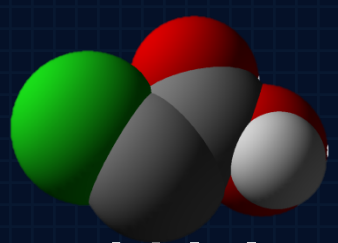
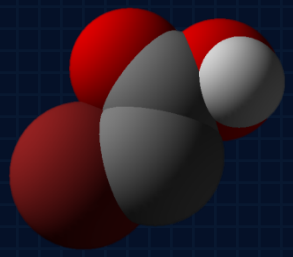
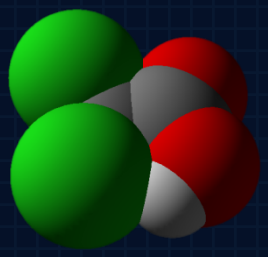
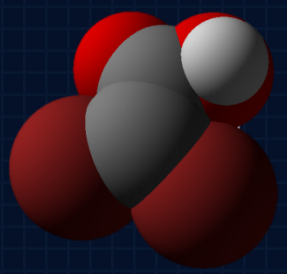
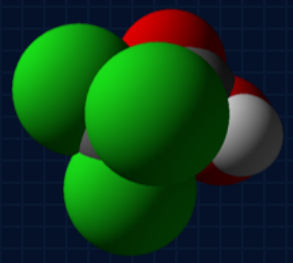


$CHBr_2Cl$



$CHCl_2Br$

Haloacetic acids

HAA5

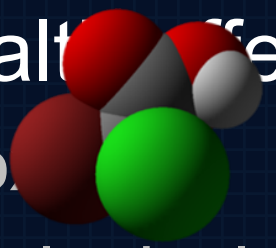
MCAA MBAA DCAA DBAA TCAA

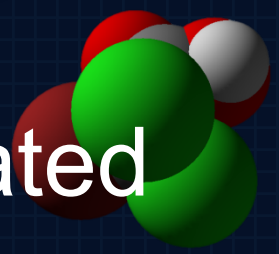
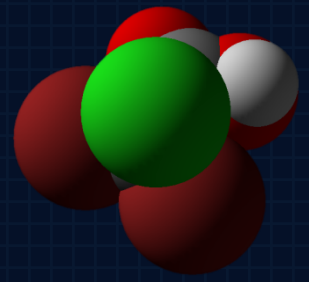
Maximum contaminant level: 60 µg/L total

Health effects

Toxicity

Biological process interference



Regulated

BCAA TBAA BDCAA CDBAA

Existing methodologies

EPA method 552.3

Liqu

Der

X_3C

X=

GC-

Two

1990

METHOD 552

DETERMINATION OF HALOACETIC ACIDS IN DRINKING WATER BY LIQUID-LIQUID EXTRACTION, DERIVATIZATION, AND GAS CHROMATOGRAPHY WITH ELECTRON CAPTURE DETECTION

1992

METHOD 552.1

DETERMINATION OF HALOACETIC ACIDS AND DAL
BY ION-EXCHANGE LIQUID-SOLID EXTRACTION AN
WITH AN ELECTRON CAPTURE D

Revision 1.0

August 1992

Jimmie W. Hodgeson

David Becker (Technology Applicati

ENVIRONMENTAL MONITORING SYSTEM
OFFICE OF RESEARCH AND DEVEL
U.S. ENVIRONMENTAL PROTECTIO
CINCINNATI, OHIO 45268

552.1-1

1995

METHOD 552.2

DETERMINATION OF HALOACETIC ACIDS AND DALAPON IN DRINKING WATER BY LIQUID-LIQUID EXTRACTION, DERIVATIZATION AND GAS CHROMATOGRAPHY WITH ELECTRON CAPTURE DETECTION

J.W. Hodge
Method 552

J.W. Hodge

D.J. Munch
Method 552

2003

METHOD 552.3 DETERMINATION OF HALOACETIC ACIDS AND DALAPON IN DRINKING WATER BY LIQUID-LIQUID MICROEXTRACTION, DERIVATIZATION, AND GAS CHROMATOGRAPHY WITH ELECTRON CAPTURE DETECTION

EPA 815-B-03-002

Revision 1.0

July 2003

M. M. Domino and B.V. Pepich (Shaw Environmental and Infrastructure, Inc.)
D.J. Munch and P.S. Fair (US EPA, Office of Ground Water and Drinking Water)
Y. Xie (Penn State University)

D.J. Munch, J.W. Munch (US EPA, Office of Ground Water and Drinking Water) and A. M. Pawlecki-Vonderheide (ICI) Method 552.2, Revision 1.0 (1995)

J.W. Hodgeson (USEPA), D. Becker (Technology Applications, Inc.) Method 552.1, (1992)

J.W. Hodgeson (USEPA), J. Collins and R. E. Barth (Technology Applications, Inc.) Method 552.0, (1990)

TECHNICAL SUPPORT CENTER
OFFICE OF GROUND WATER AND DRINKING WATER
U. S. ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OHIO 45268

552.3-1

EPA method 552.3 drawbacks

Sample preparation time required

5 hours

Liquid-liquid extraction

Derivatization

Extract transfer

20 hours total

Other drawbacks

Analysis time required

15 hours

Derivatization step

Target confirmation

EPA method 557

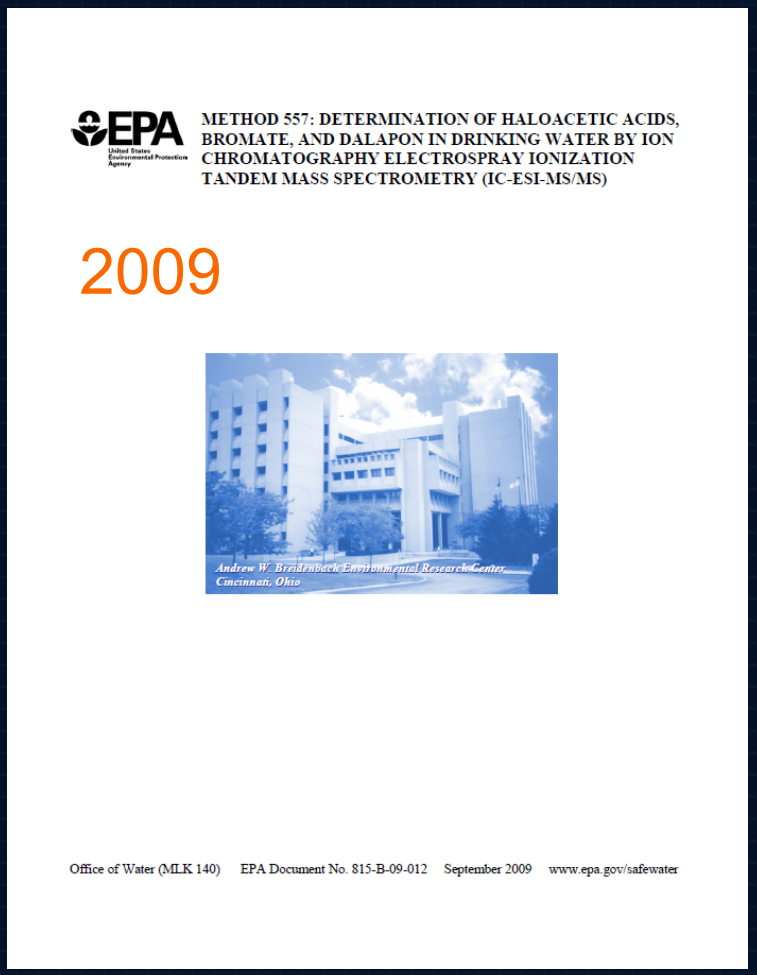
IC-ESI-MS/MS

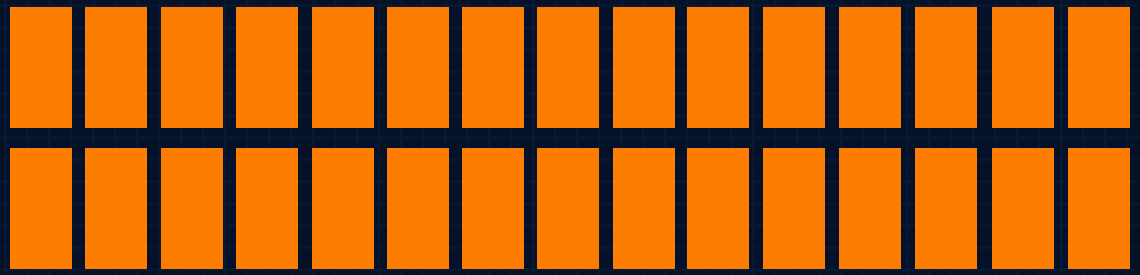
Benefits

- Direct injection
- MS specificity
- Isotopically enriched IS

Drawbacks

- Ion chromatography
- Very long run times





30 hours total

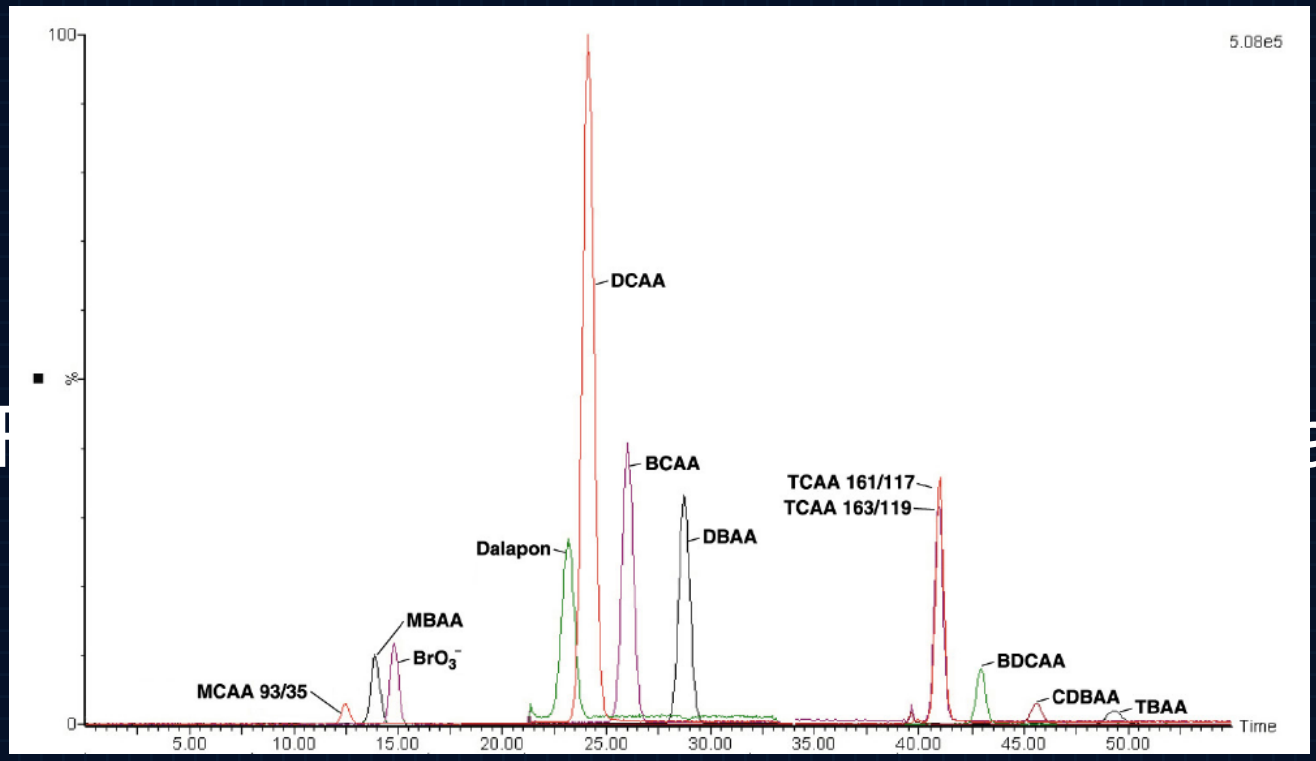
Our approach

Method goals

- Adapt EPA 557
  - Simplify technique
  - Handle high ionic strength matrix
    - Separate matrix from targets
  - Shorter analysis times

Simplify the chromatography

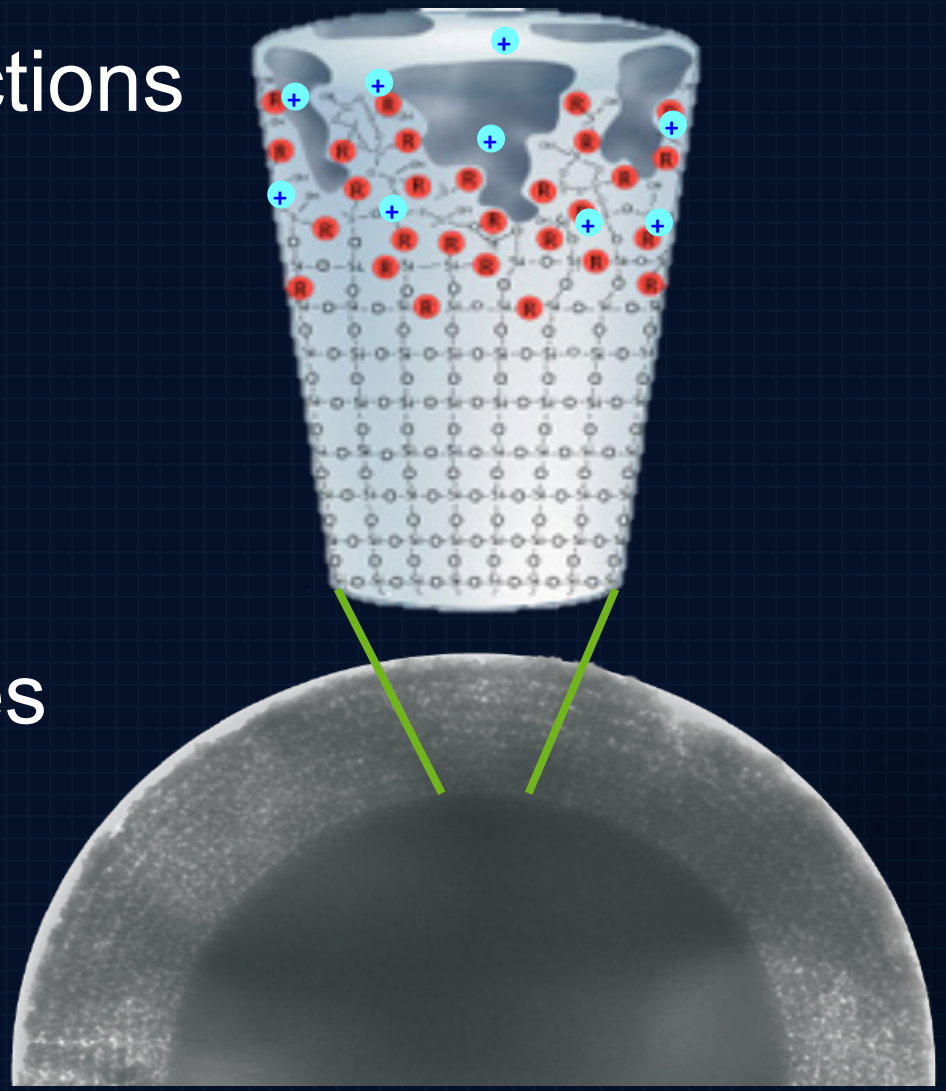
Ion chromatography



aphy

Phenomoenex Kinetex EVO C18

Secondary interactions



Core-shell particles

Chromatography

Column: Phenomenex Kinetex EVO C18

100 x 2.1 2.6 µm

Mobile phase: A: Water with formic acid

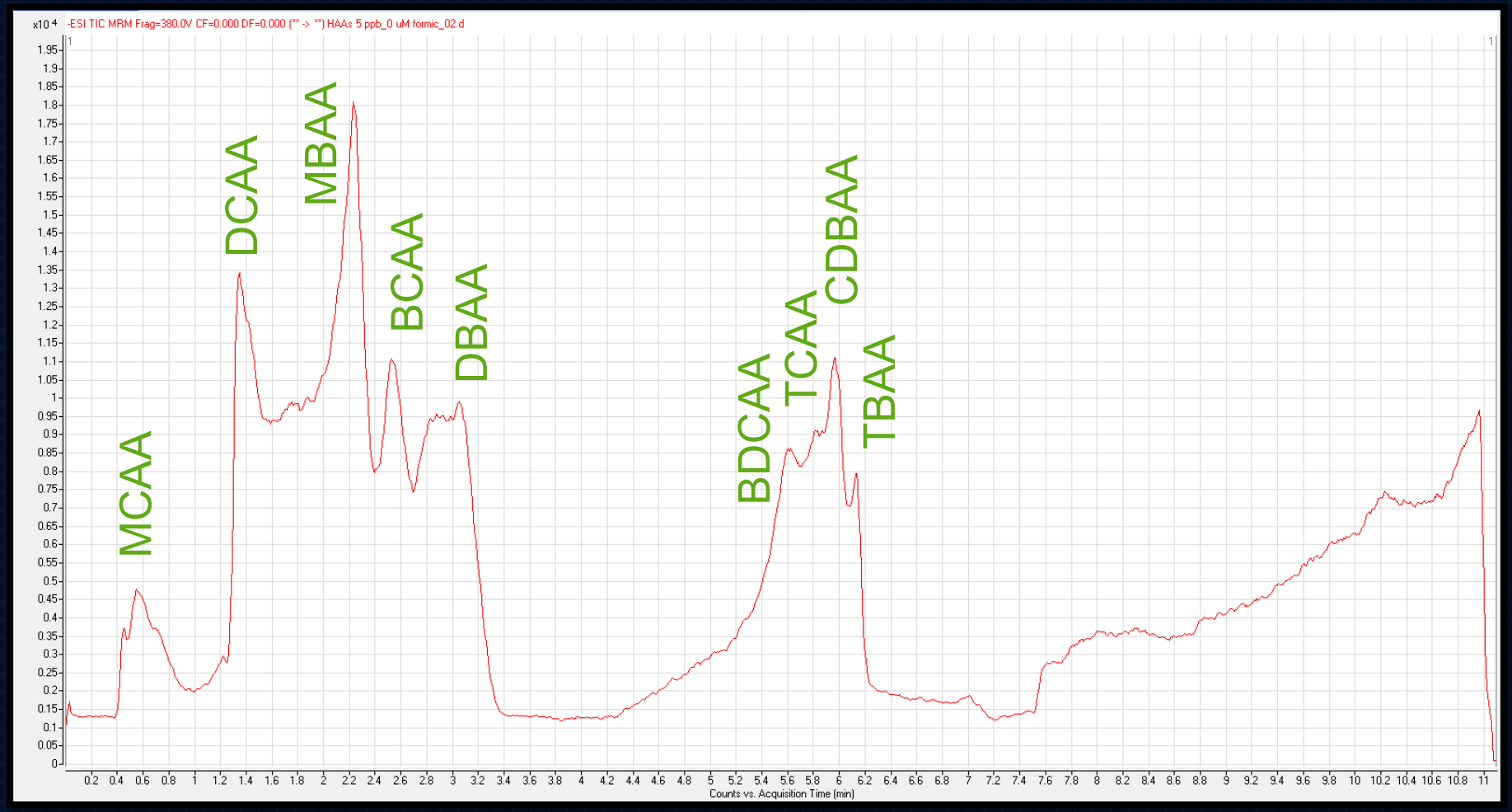
B: Methanol with formic acid

Flow Rate: 0.500 mL/min

Gradient:

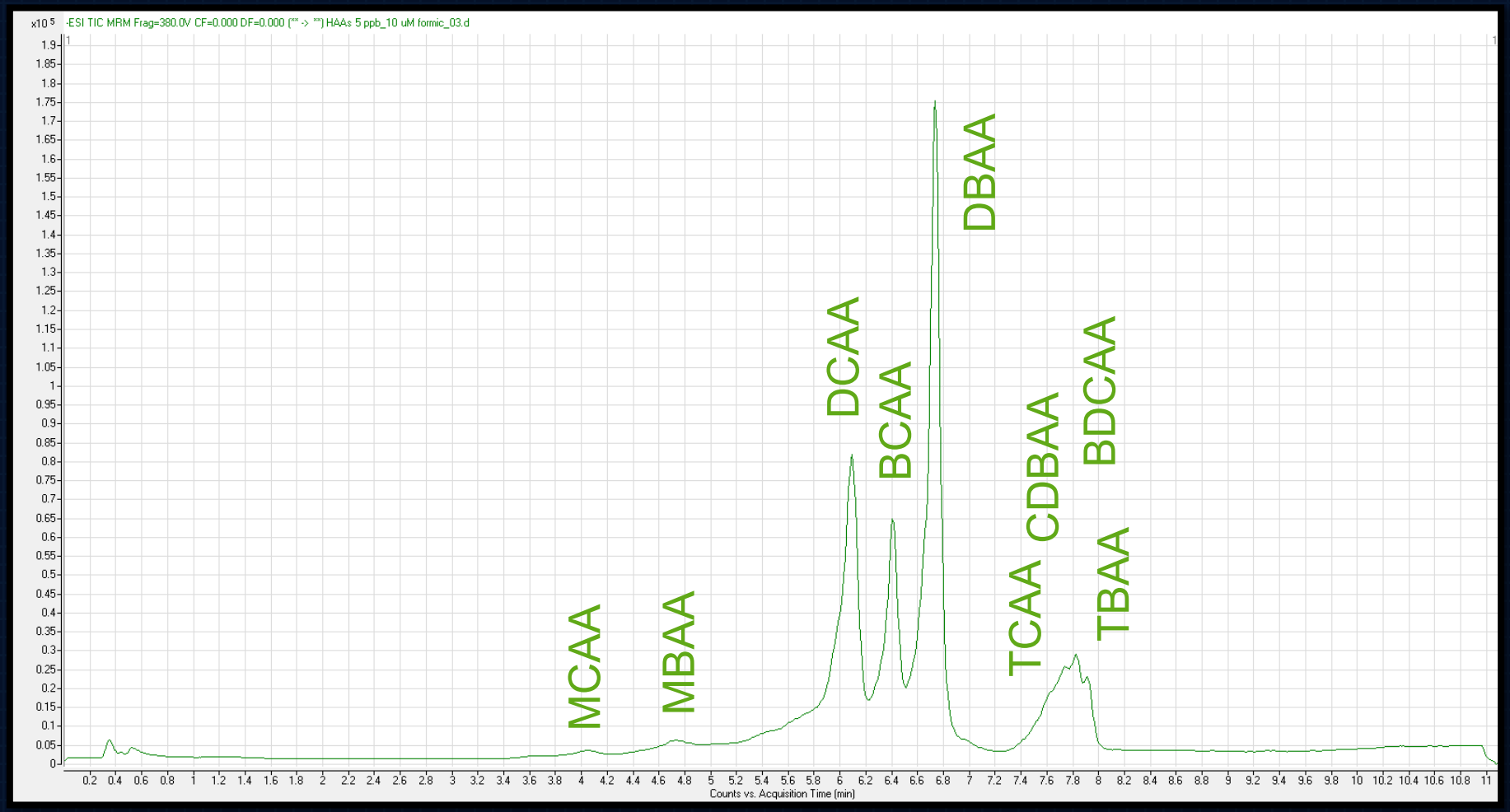
Time	%B
3	1
8	100
11	100

0 µM formic acid



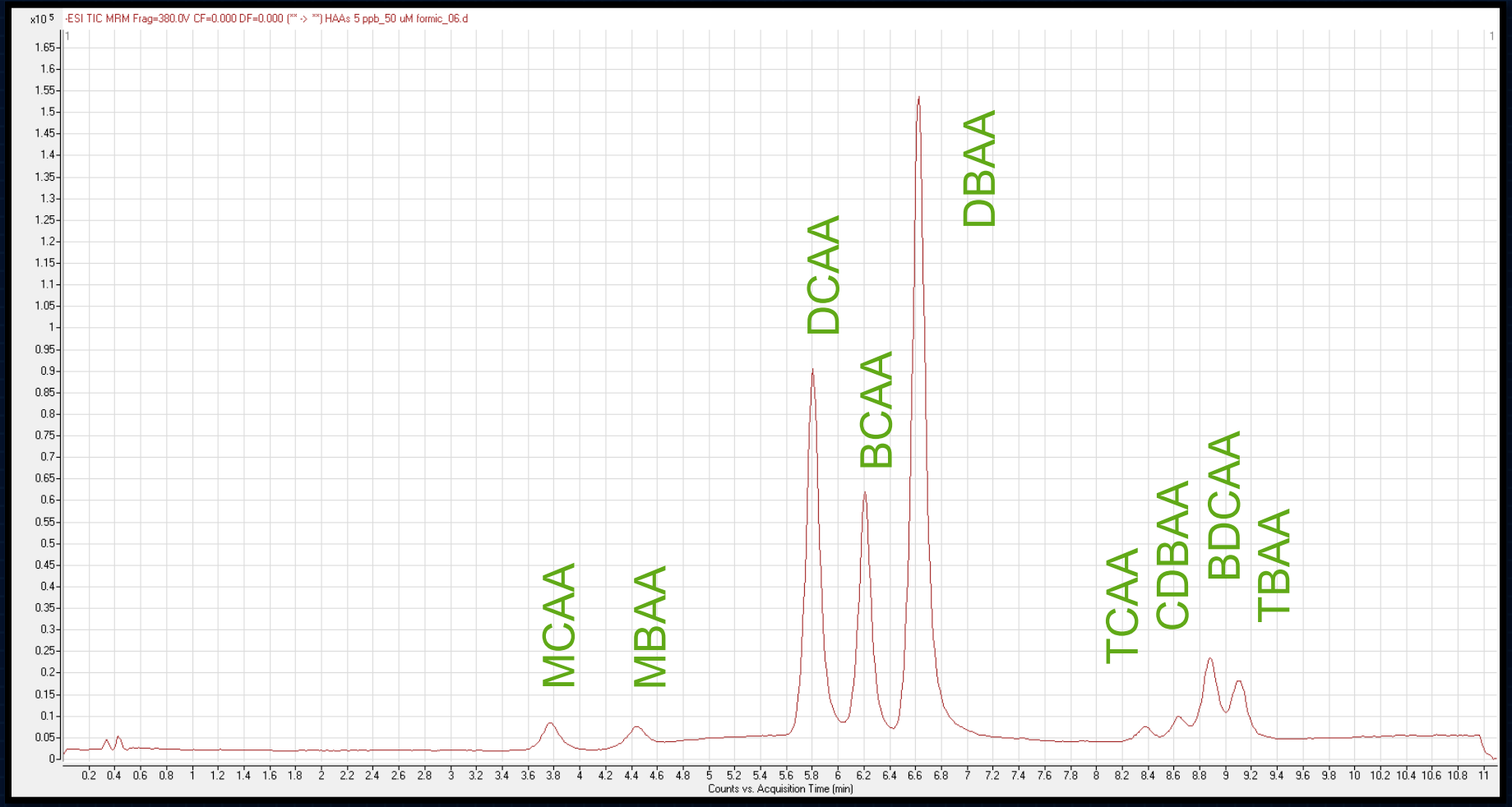
MCAA K'=0.3

10 µM formic acid



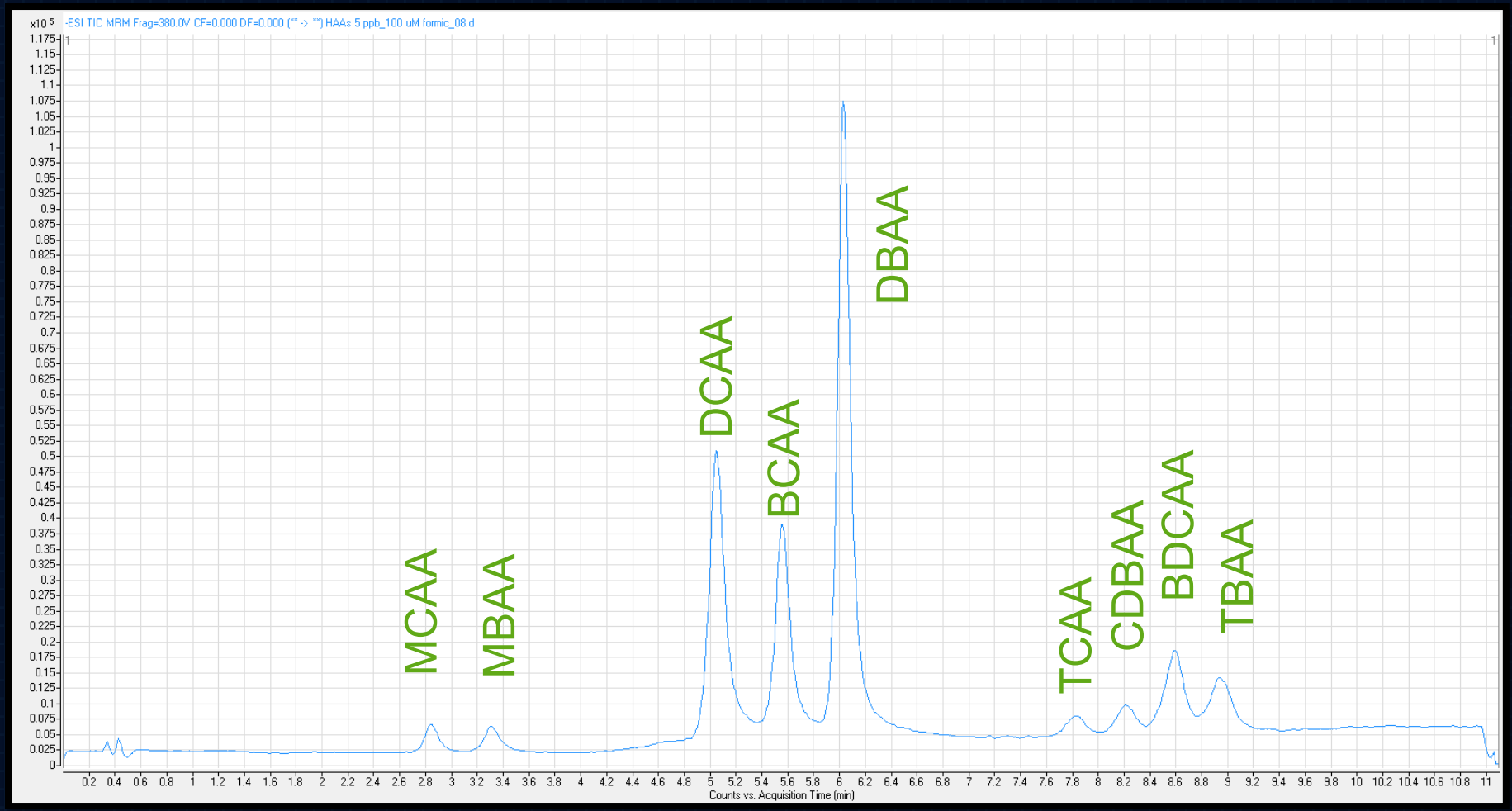
MCAA K'=11.2

50 µM formic acid



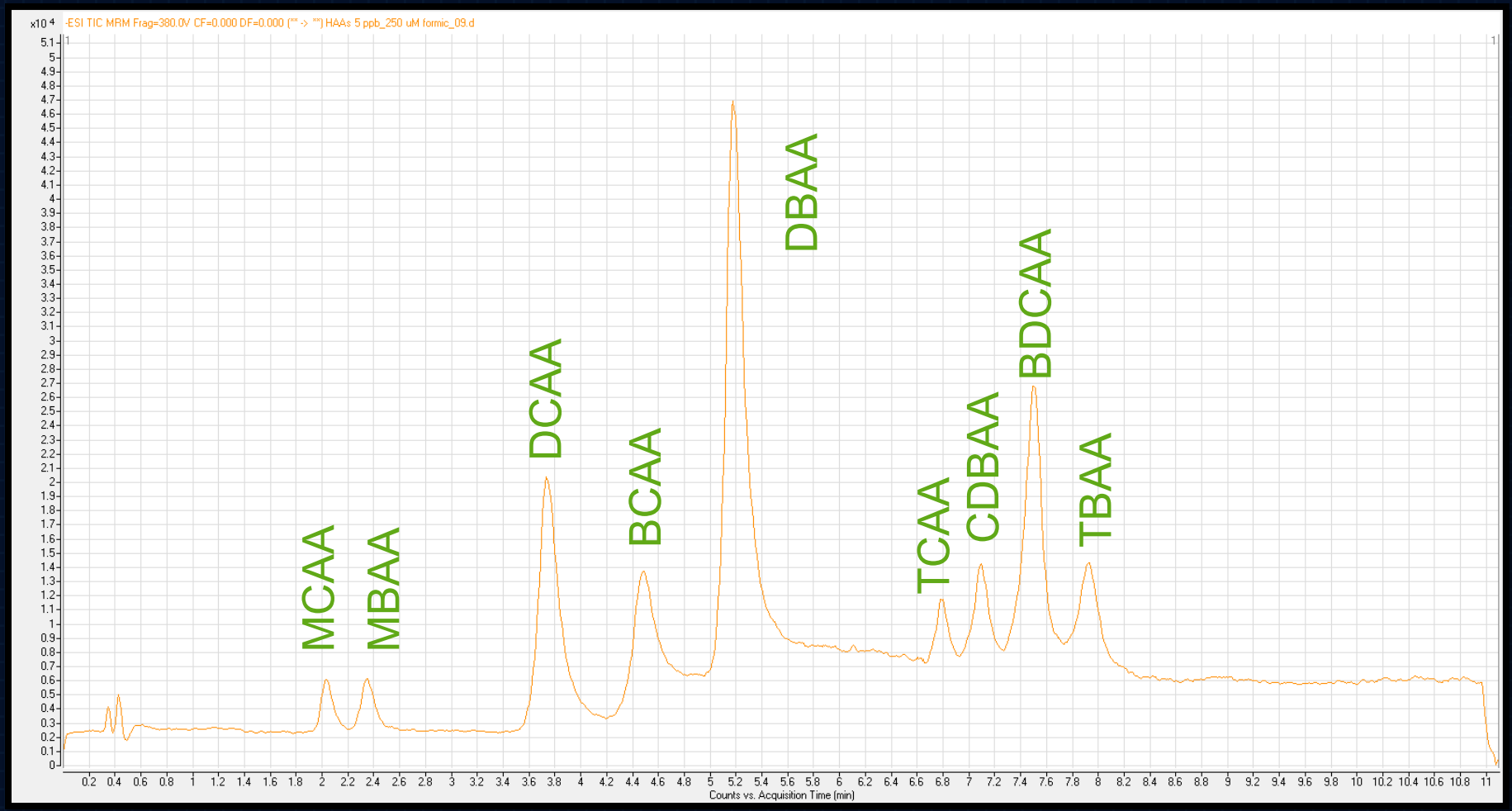
MCAA K'=10.5

100 µM formic acid



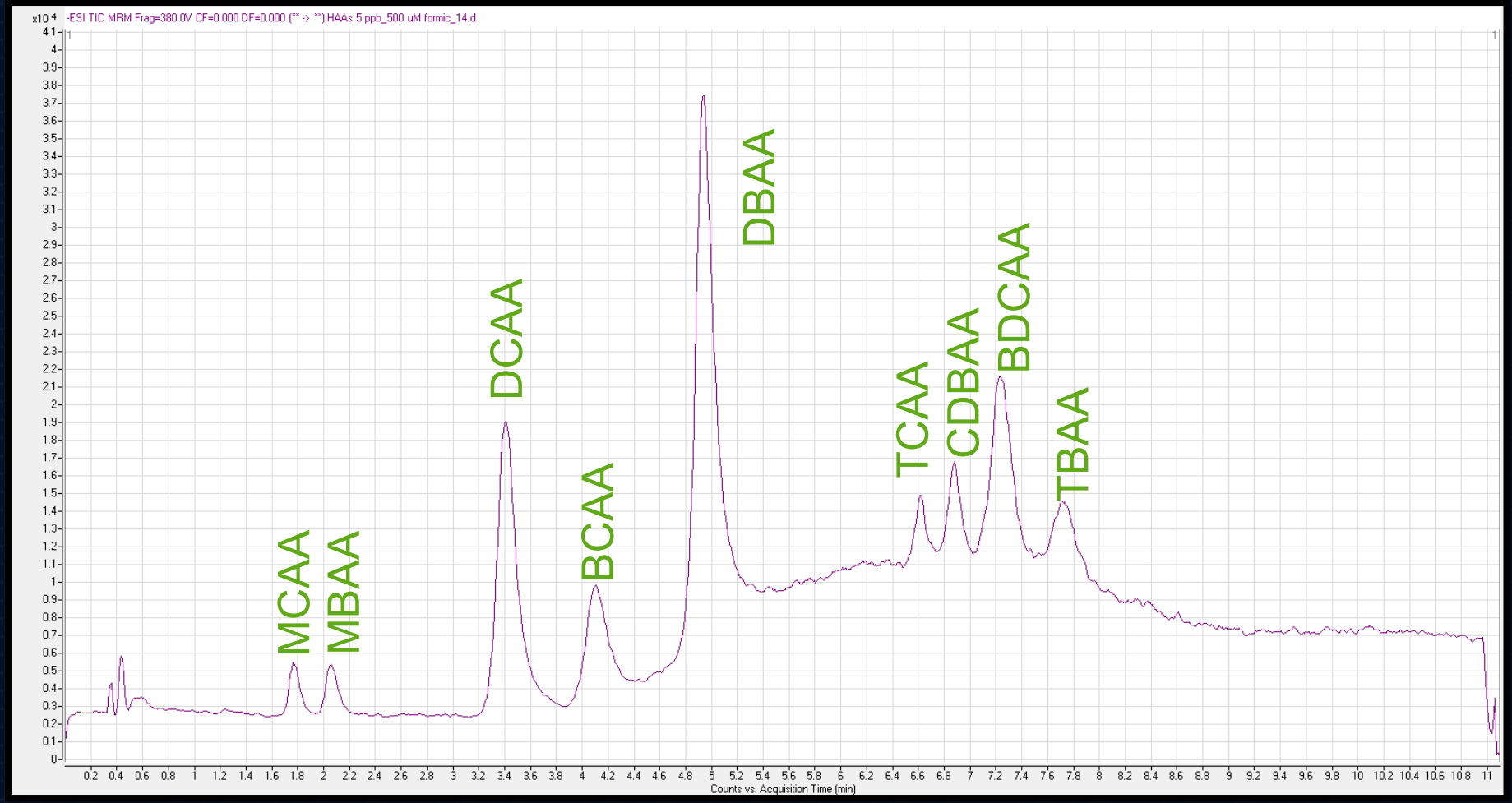
MCAA K'=7.6

250 µM formic acid



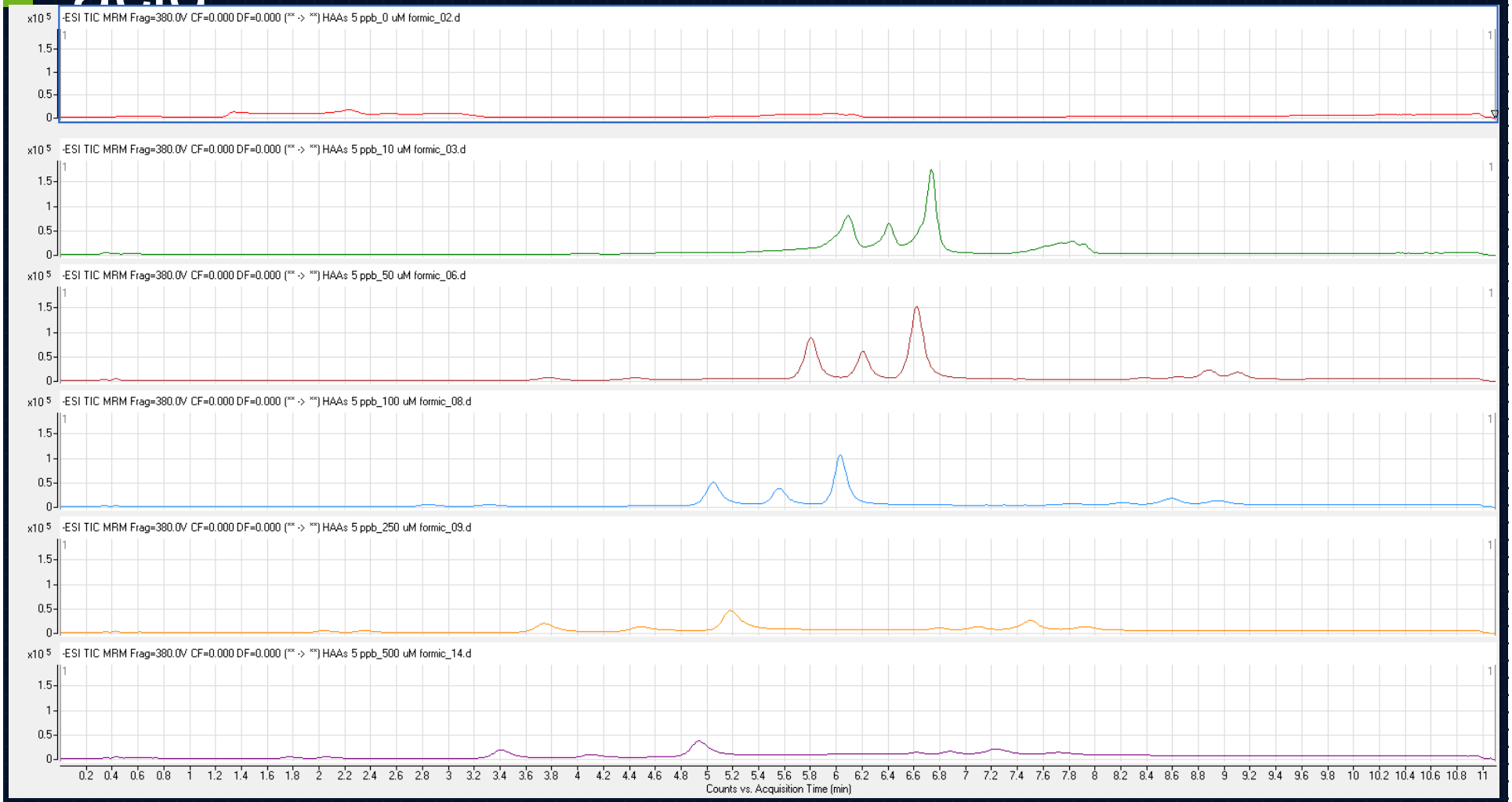
MCAA K'=5.2

500 µM formic acid

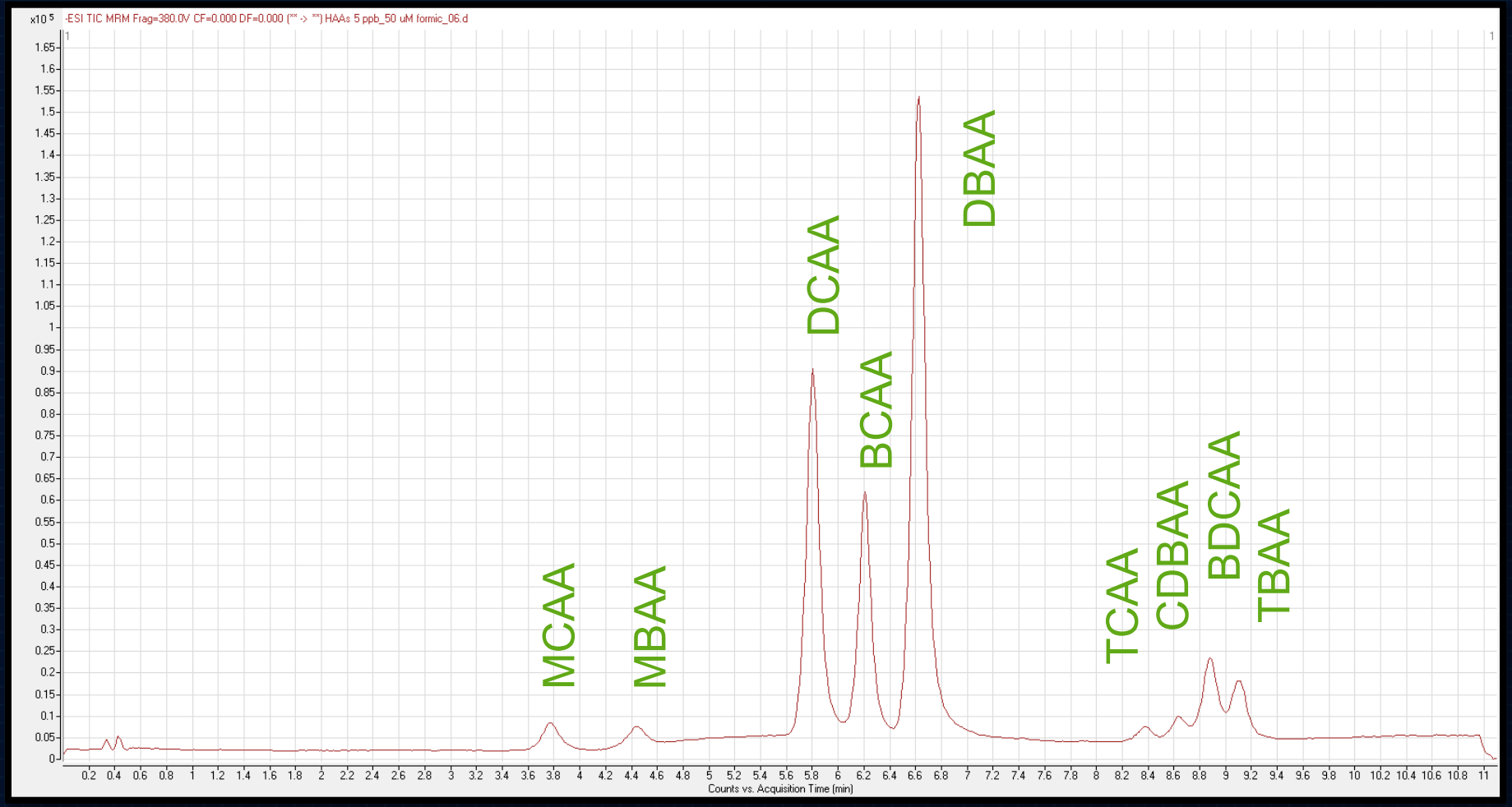


MCAA K'=4.4

Increasing concentration of acid



50 µM formic acid



MCAA K'=10.5

Matrix effects

10 ppb in synthetic matrix:

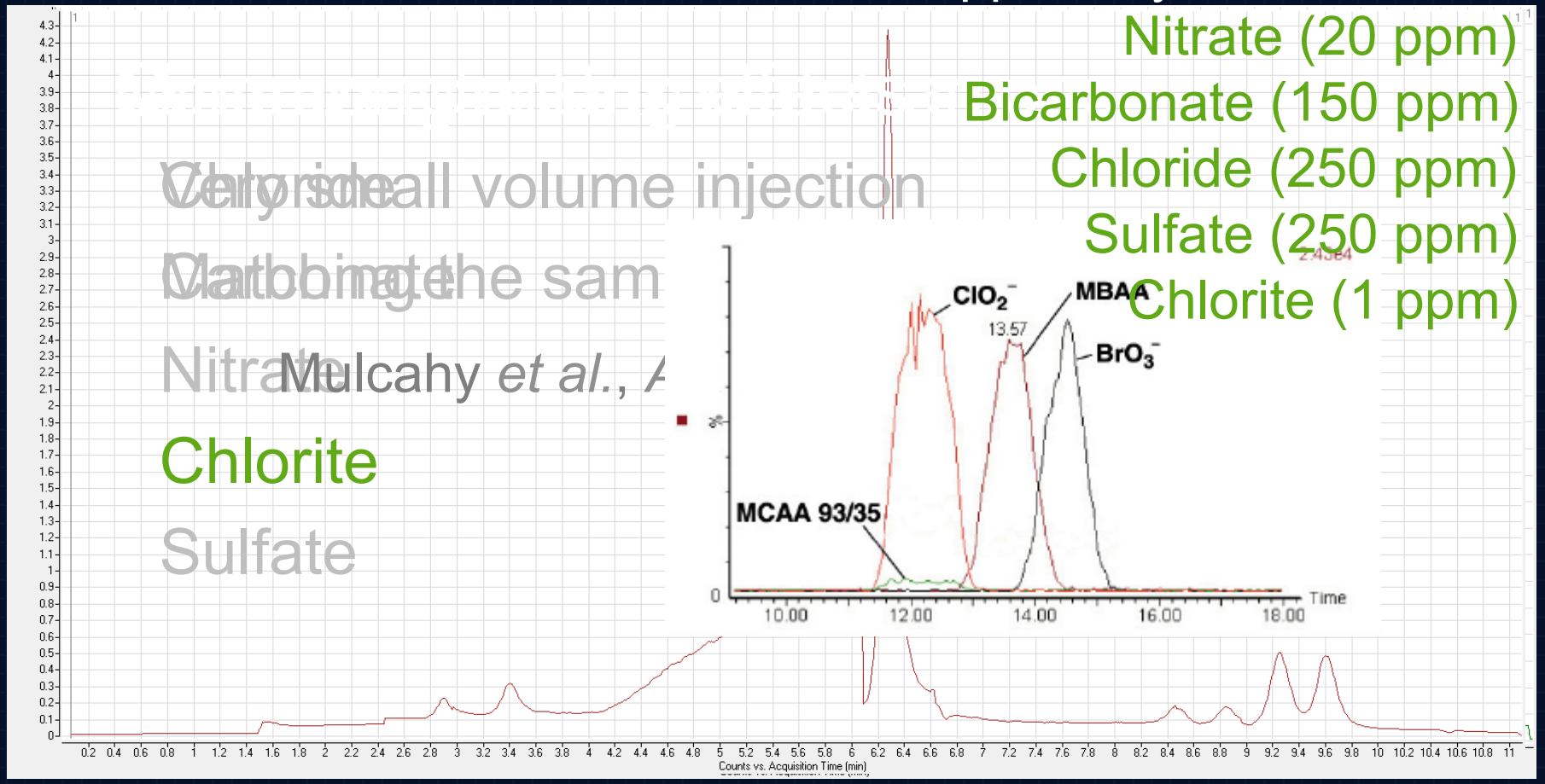
Nitrate (20 ppm)

Bicarbonate (150 ppm)

Chloride (250 ppm)

Sulfate (250 ppm)

Chlorite (1 ppm)



10 uL injection, adjusted to pH 3

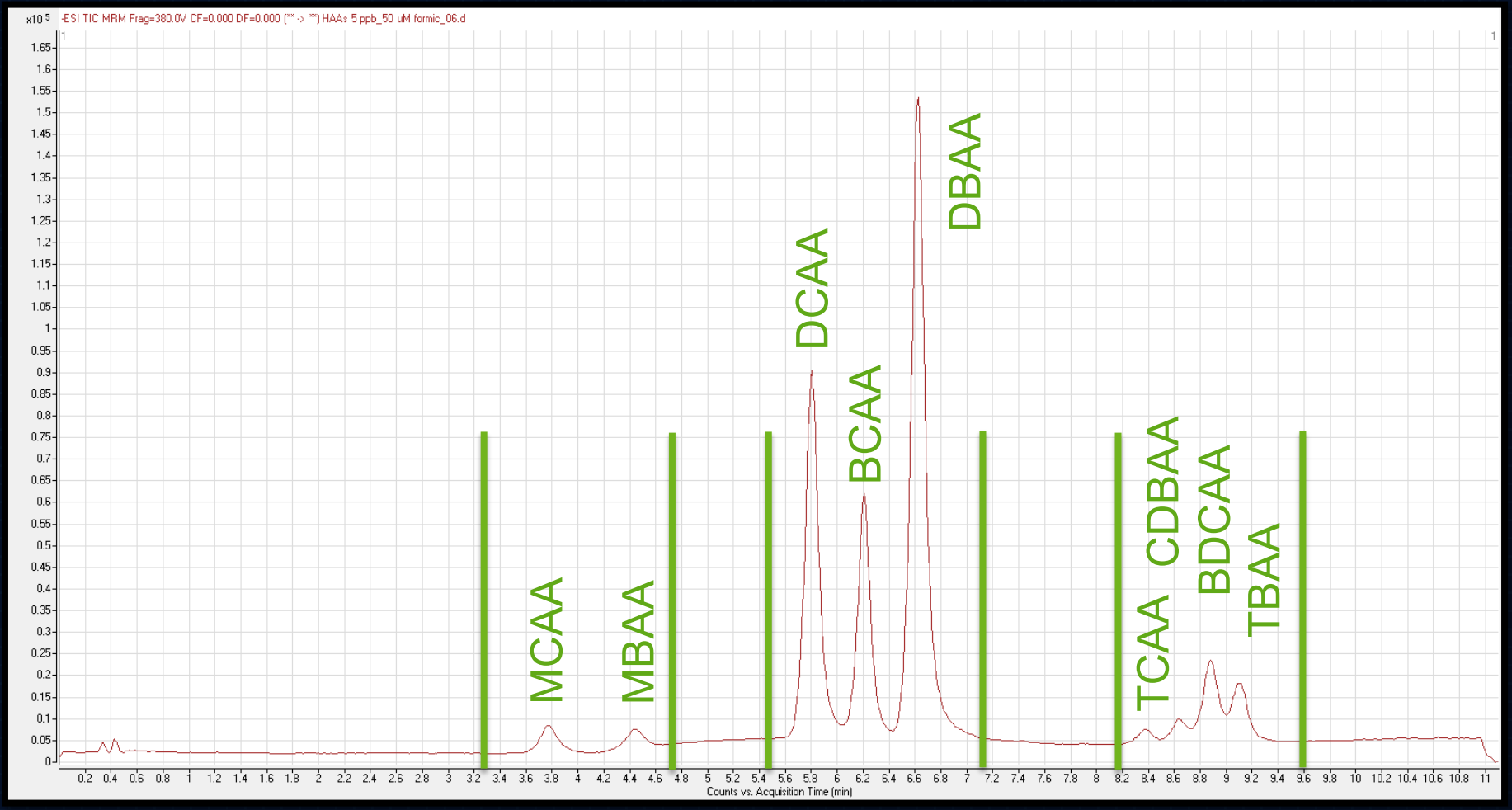
Agilent 6495 QQQ

Column: Phenomenex Kinetex EVO C18

DCAA-2-^{13}C

TCAA-2-^{13}C

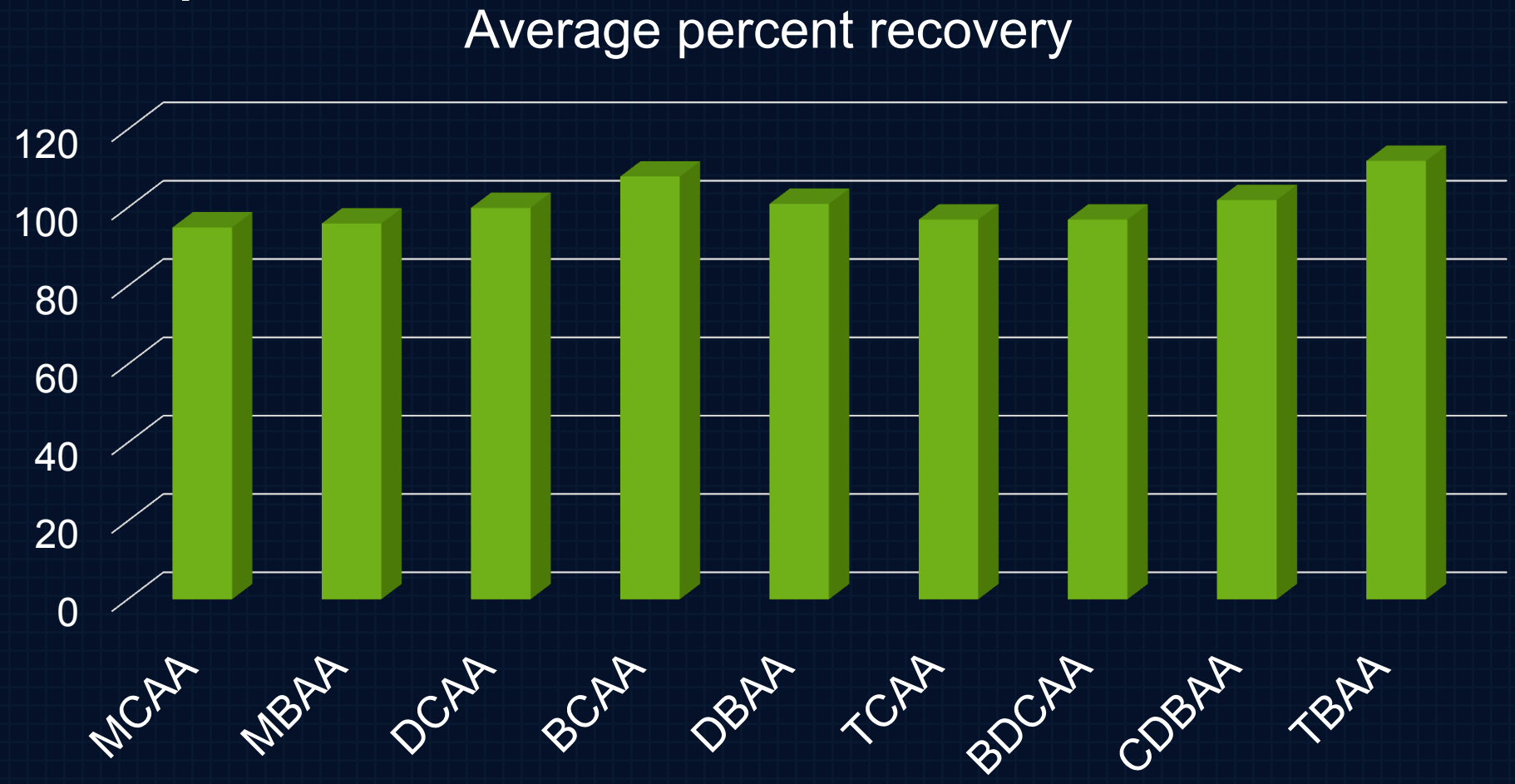
Final method



Detection limits

Target	557M MDL (µg/L)	557M RL (µg/L)	552.2 RL (µg/L)
MCAA	0.25	1	2
MBAA	0.07	0.5	1
DCAA	0.05	0.5	1
BCAA	0.03	0.5	1
DBAA	0.06	0.5	1
TCAA	0.09	0.5	1
BDCAA	0.07	0.5	1
CDBAA	0.1	0.5	1

Comparison with EPA 552.2 in real samples

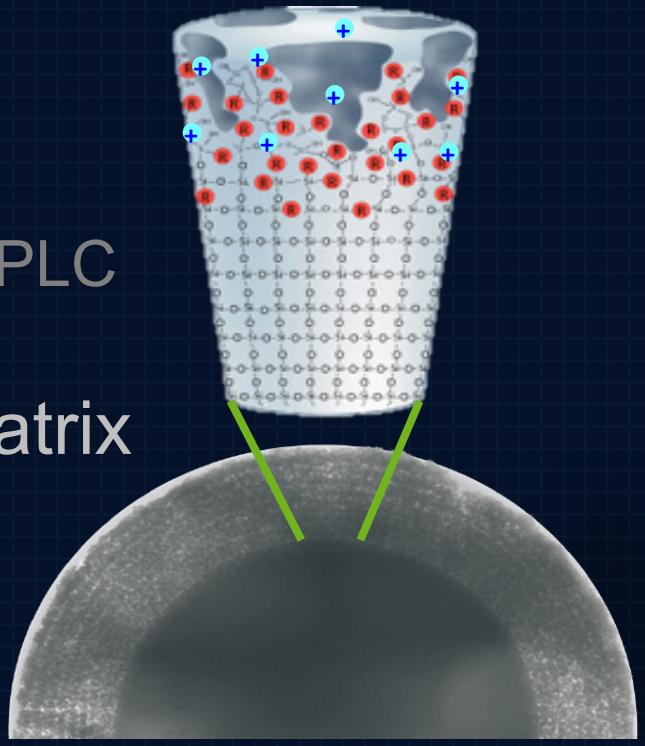


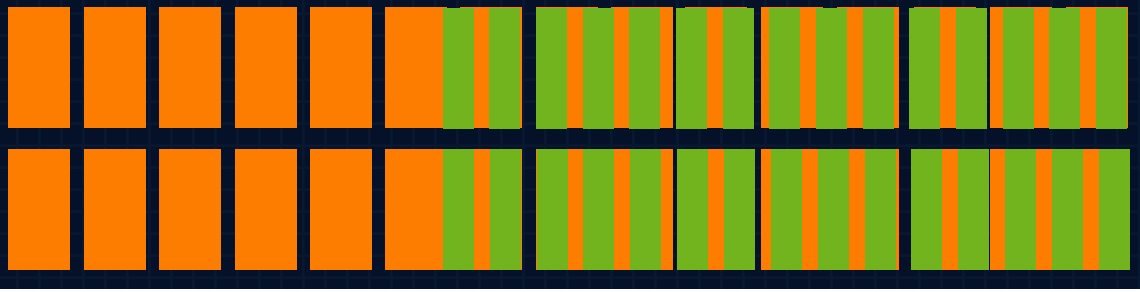
n = 72

Method goals

Adapt EPA 557

- Simplify technique
  - Conventional reversed-phase HPLC
- Handle high ionic strength matrix
  - Separate matrix from targets
  - Small injection volume
- Shorter analysis time
  - 15 minutes injection to injection





30 hours total

7.5 hours total

Acknowledgements

Phenomenex

Sean Orlowicz

Allen Misa

Weck Laboratories

Questions?

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