Weck Laboratories

Nitrosamines in drinking water by direct-inject LC-MS/MS

Agustin Pierri, PhD

NEMC 2017
Washington DC

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EPA method 521 by direct-inject LC-MS/MS

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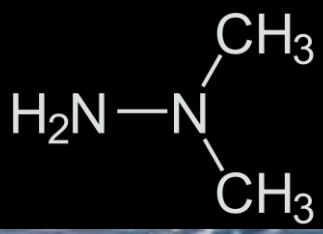
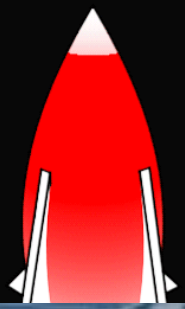
Background

Nitrosamines

Synthesis of UDMH





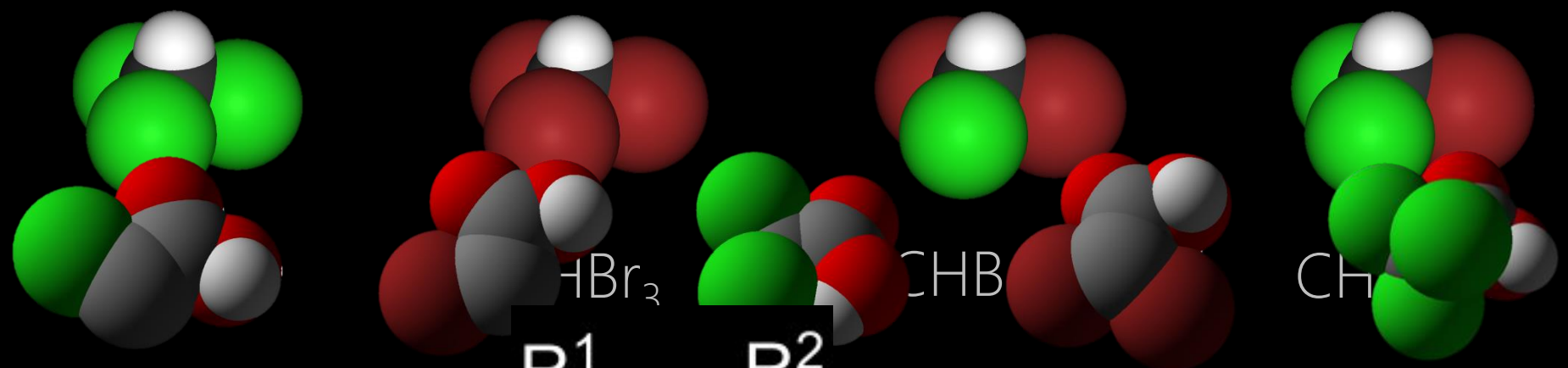
From fo

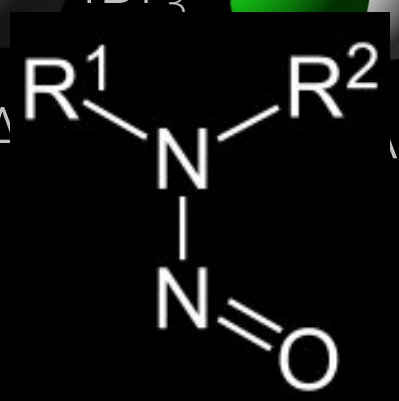
From water treatment

Chlorination disinfection by-products

Disinfection agents + Organics → Nitrosamines

Chlorine
Chloramine

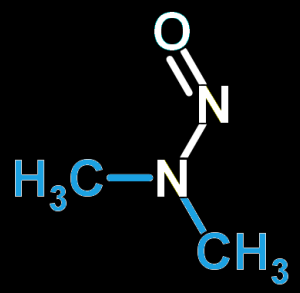




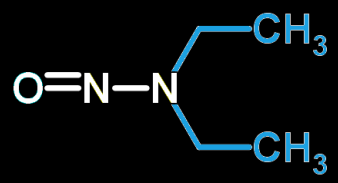
R=Me,Et,Pr,Bu,
Ph,Pyr,Mor,Pip

Nitrosamines

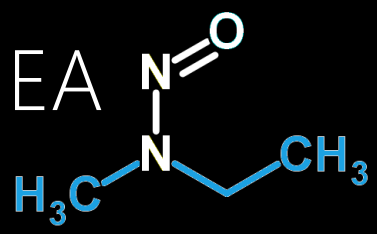
NDMA



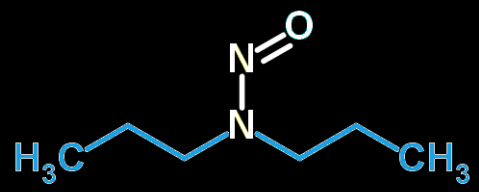
NDEA



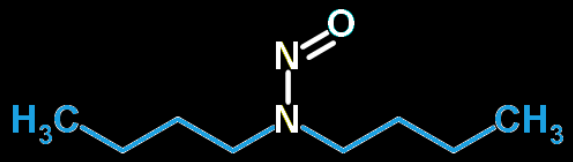
NMEA



NDPA



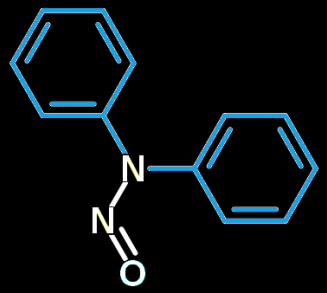
NDBA



NPYR

NPIP

NMOR



NDPhA

Existing method

EPA method 521

UCMR 2

Offline SPE

- Coconut charcoal

GC-MS/MS

- Chemical ionization
- MRL: 2 ng/L

2004

EPA Document #: EPA/600/R-05/054

METHOD 521 DETERMINATION OF NITROSAMINES IN DRINKING WATER BY SOLID PHASE EXTRACTION AND CAPILLARY COLUMN GAS CHROMATOGRAPHY WITH LARGE VOLUME INJECTION AND CHEMICAL IONIZATION TANDEM MASS SPECTROMETRY (MS/MS)

Version 1.0

September, 2004

J.W. Munch
M.V. Bassett

NATIONAL EXPOSURE RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OHIO 45268

Offline SPE

Sample prep:

- 500 mL → 0.5
- Condition
- Load
- Elute
- Evaporate
- Transfer

Extract Analysis:

12.5 hours total

4 hours total

16.5 hours total

Direct inject LC/MS

Method goals

Adapt the offline SPE GC-MS/MS method to direct-inject LC-MS/MS

- ☐ No sample prep
- ☐ Handle typical DW matrix
- ☐ Shorten the total analysis time
- ☐ Minimize sample volume needed
- ☐ Maintain method 521 perfomance

Maximize sensitivity

Agilent 6495 QQQ

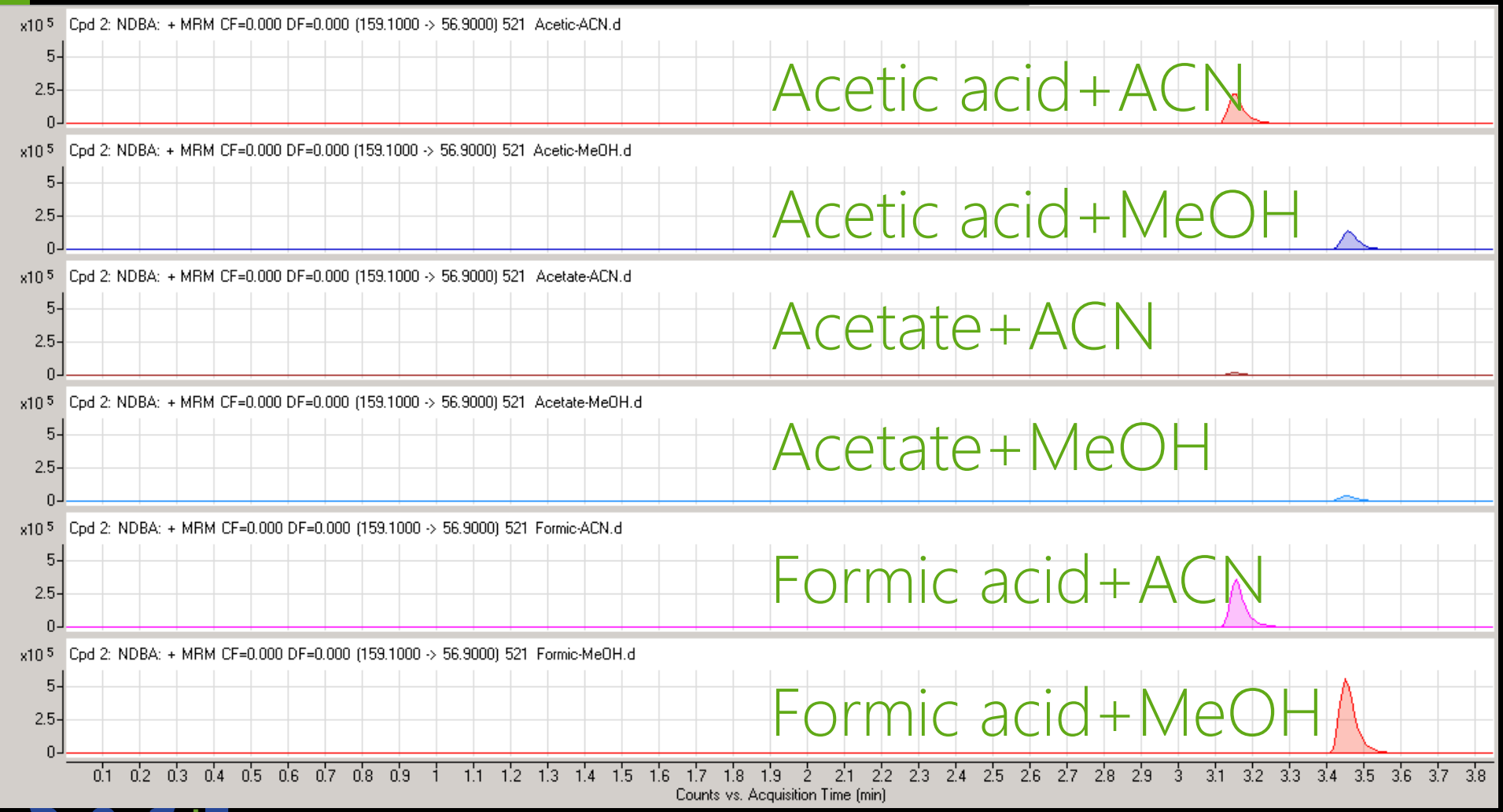
Instrument background

NDMA suppression

Before passivation

Mobile phase modifiers

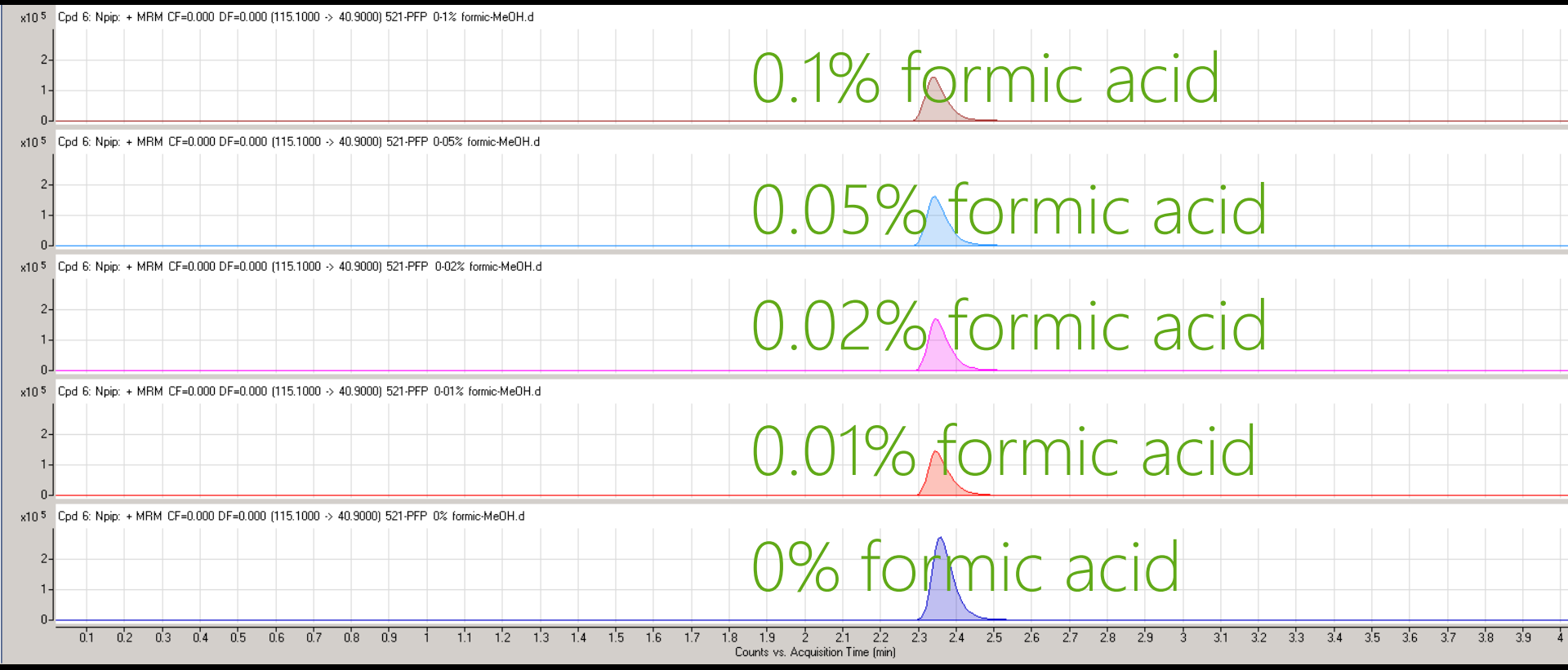
NDBA



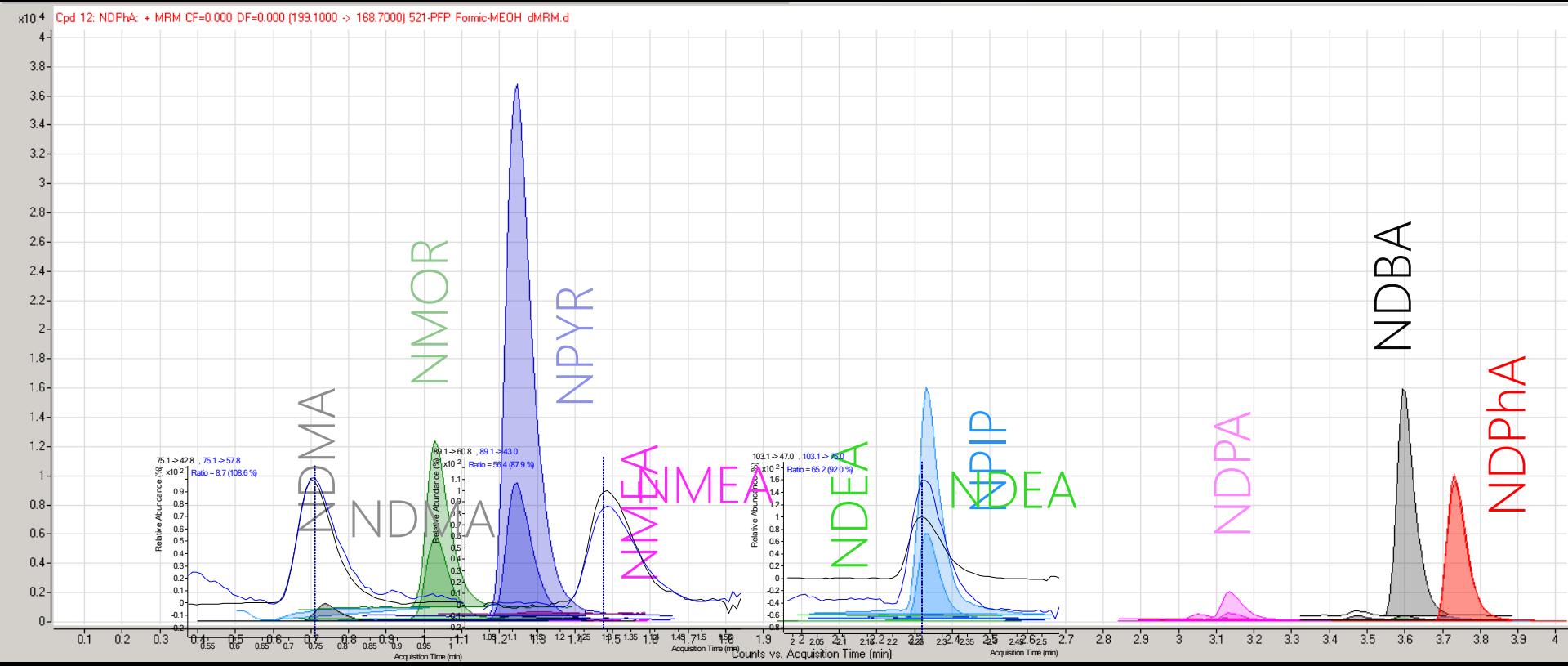
NDMA

Acid concentration

NDMA NPIP



Direct-inject at MRL (2 ng/L)



NDMA-d_6 NDEA-d_{10} NDPA-d_{14}

Chromatographic conditions

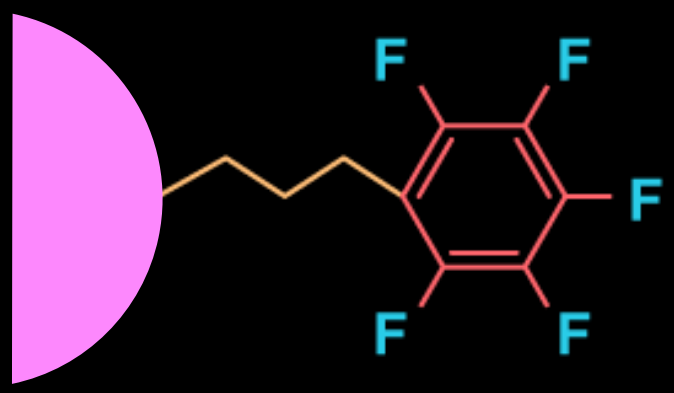
Column: Poroshell 120 PFP 50 x 2.1 mm, 2.7 µm

Injection volume: 100 µL

Mobile phase: A: Water with 0.05% formic acid

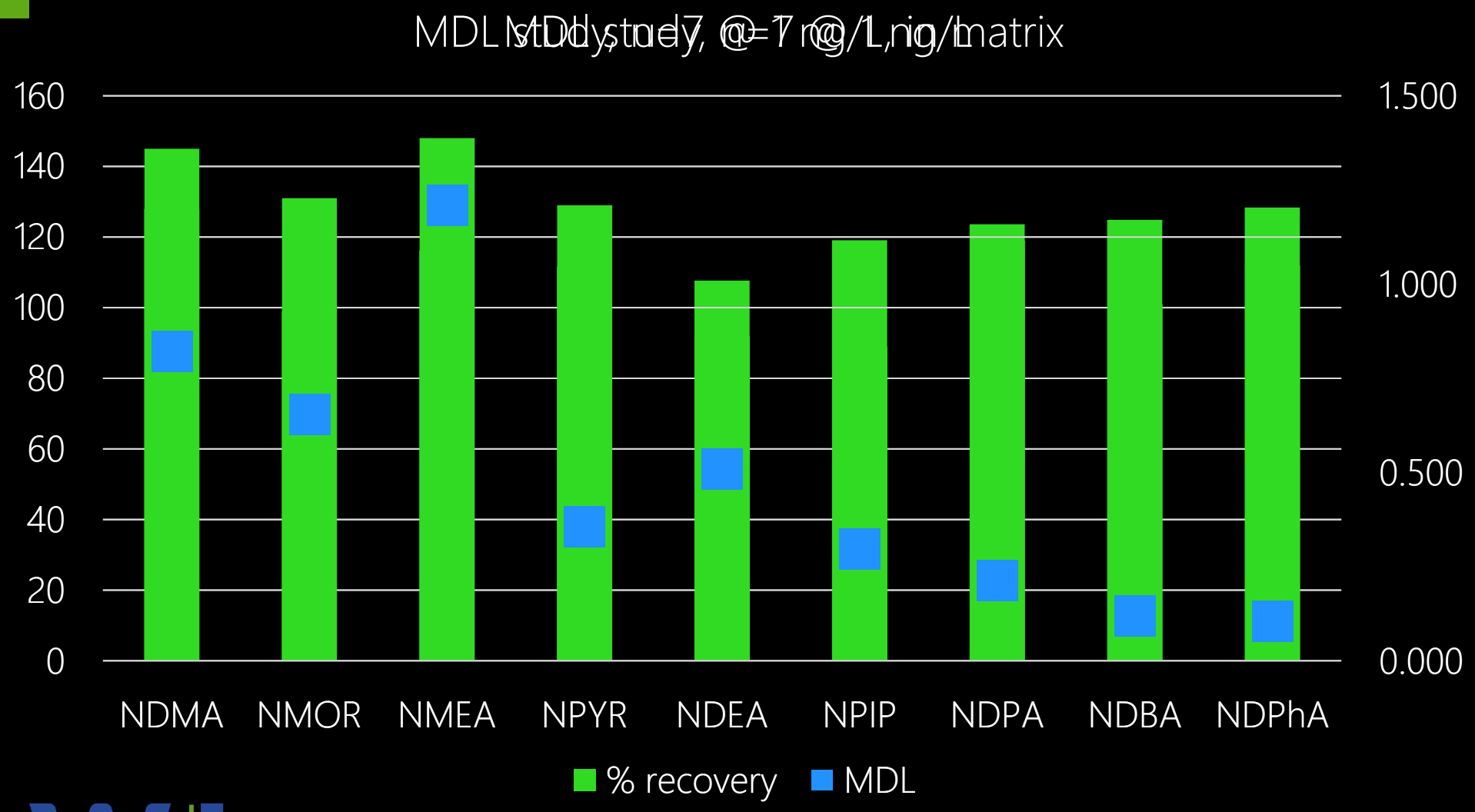
B: 100% methanol

Flow rate: 0.650 mL/min

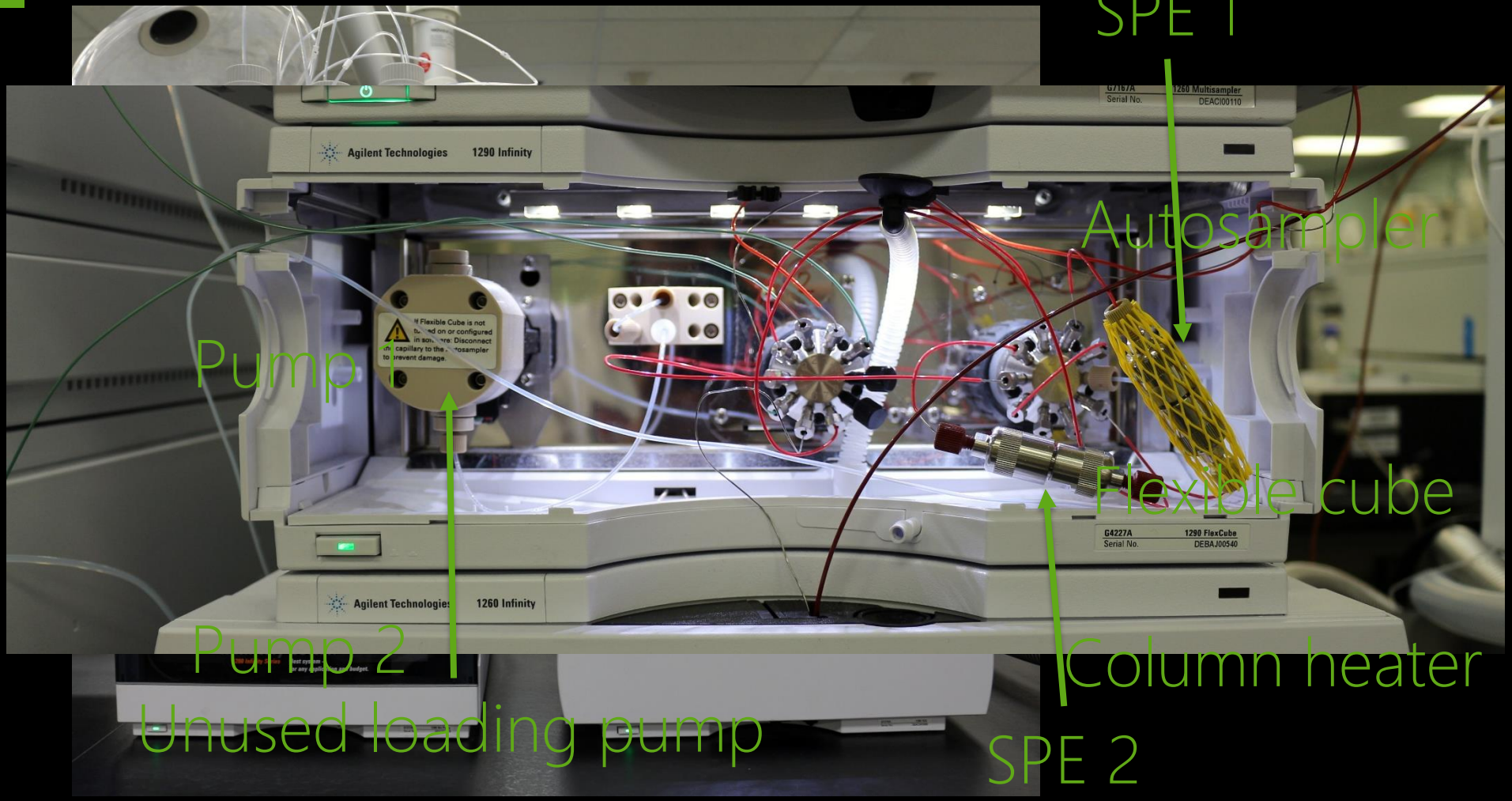


Time	%B
0.0	3
1	3
4.0	100
4.5	100

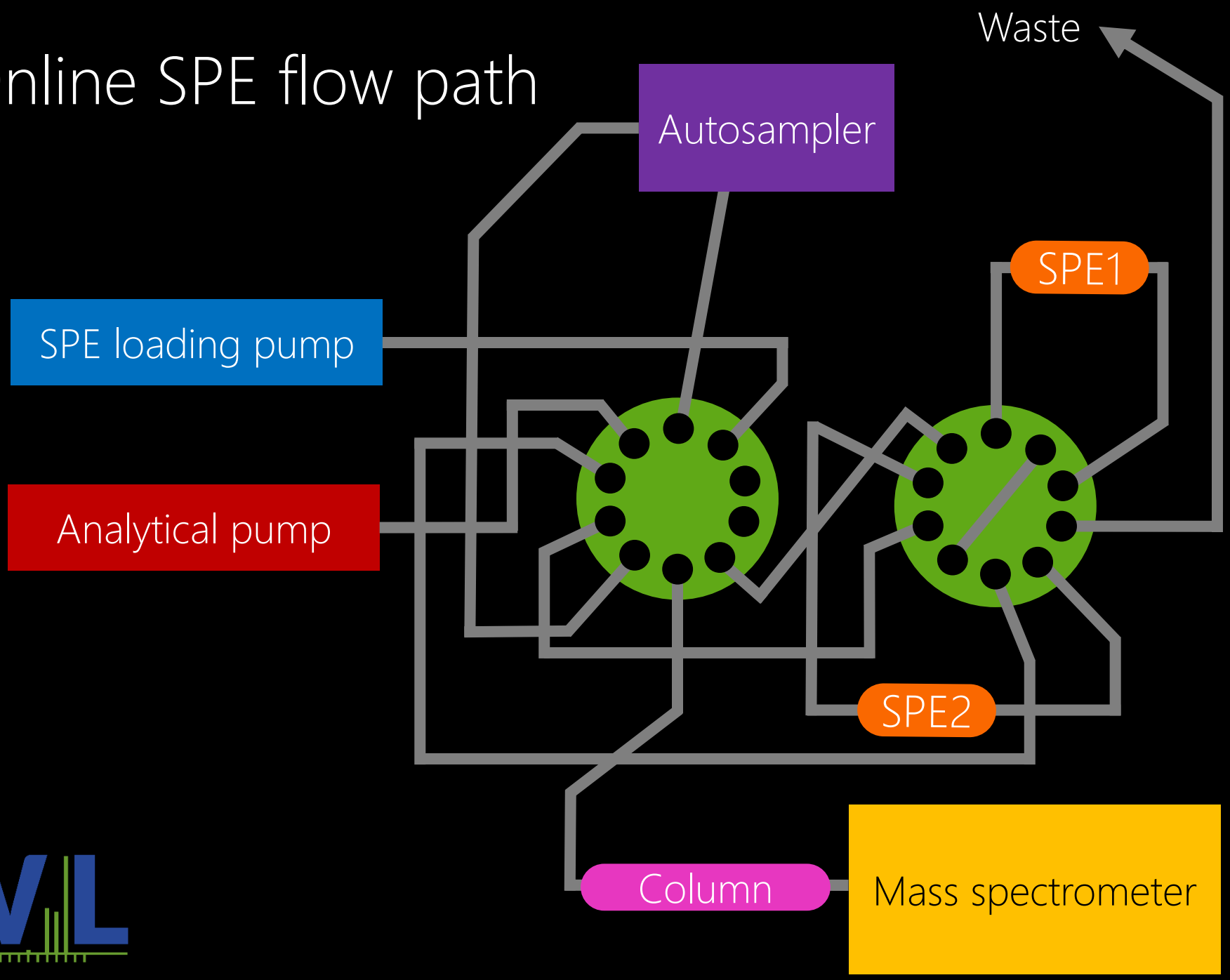
MDL study


MDL study, n=7 @ 1 ng/L in matrix
160
140
120
100
80
60
40
20
0
1.500
1.000
0.500
0.000
NDMA
NMOR
NMEA
NPYR
NDEA
NPIP
NDPA
NDBA
NDPhA
% recovery
MDL

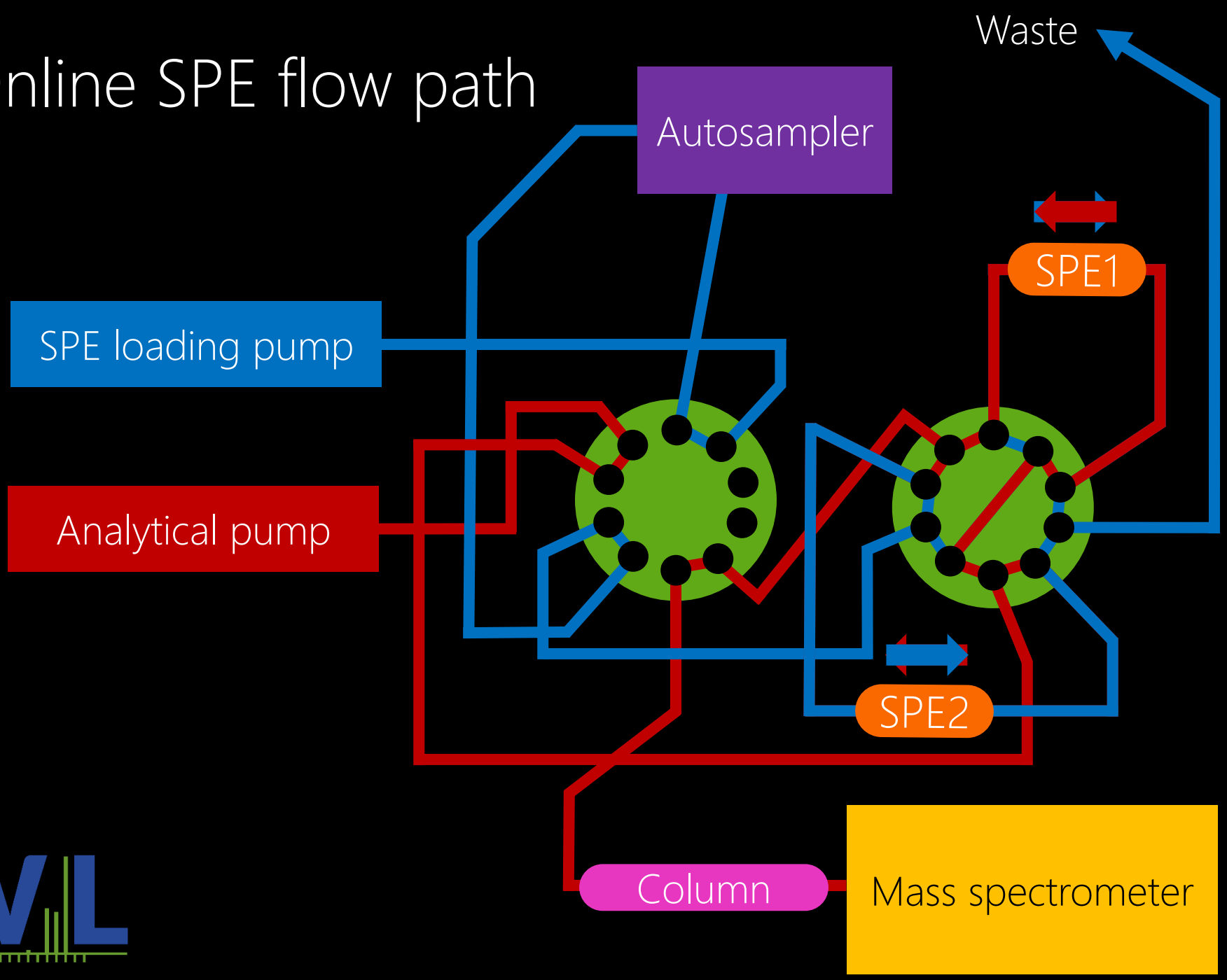
Online SPE hardware



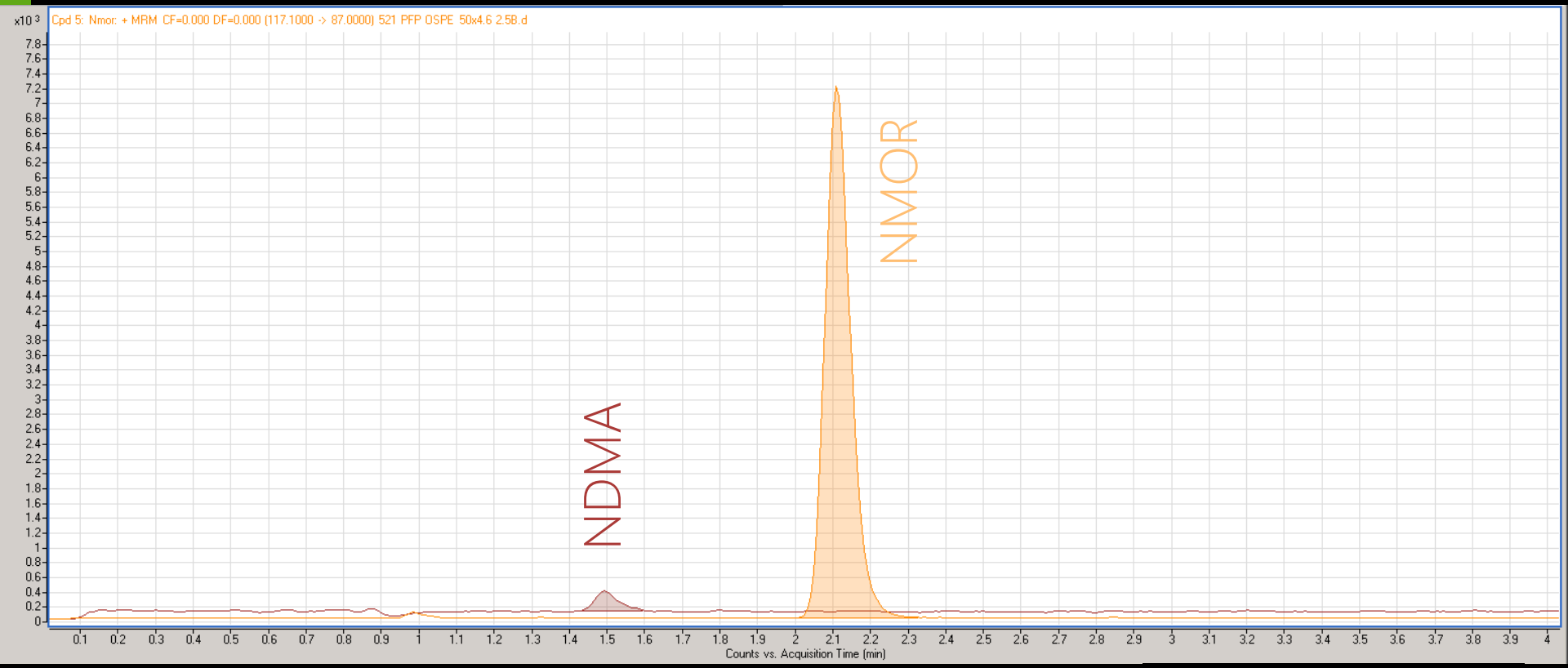
Online SPE flow path



Online SPE flow path

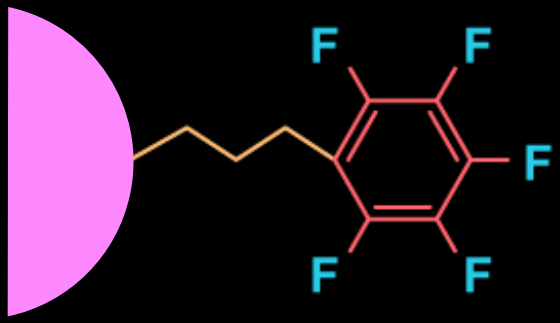


Online SPE breakthrough

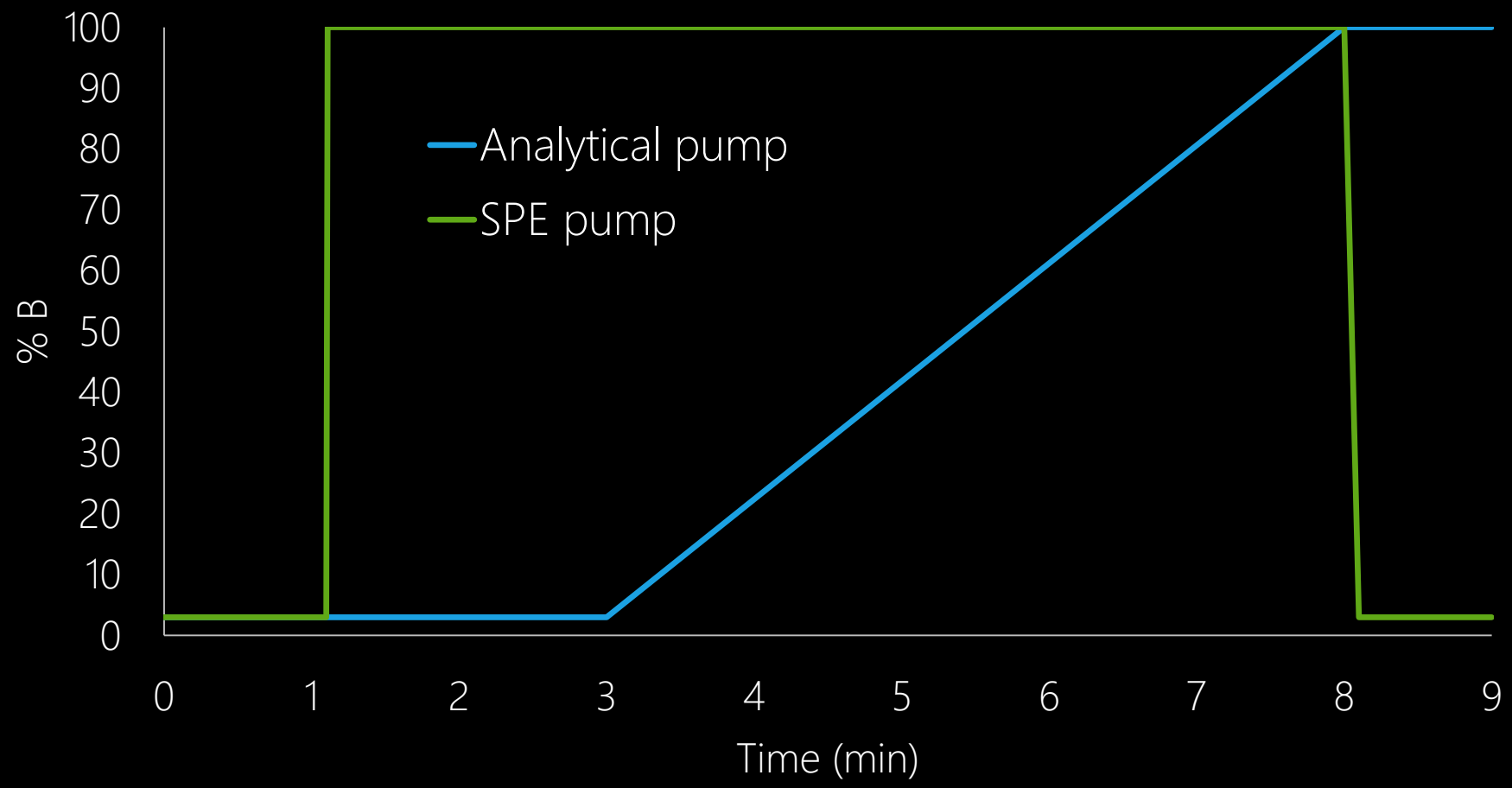


NDMA RT 1.5 min at 0.8 mL/min

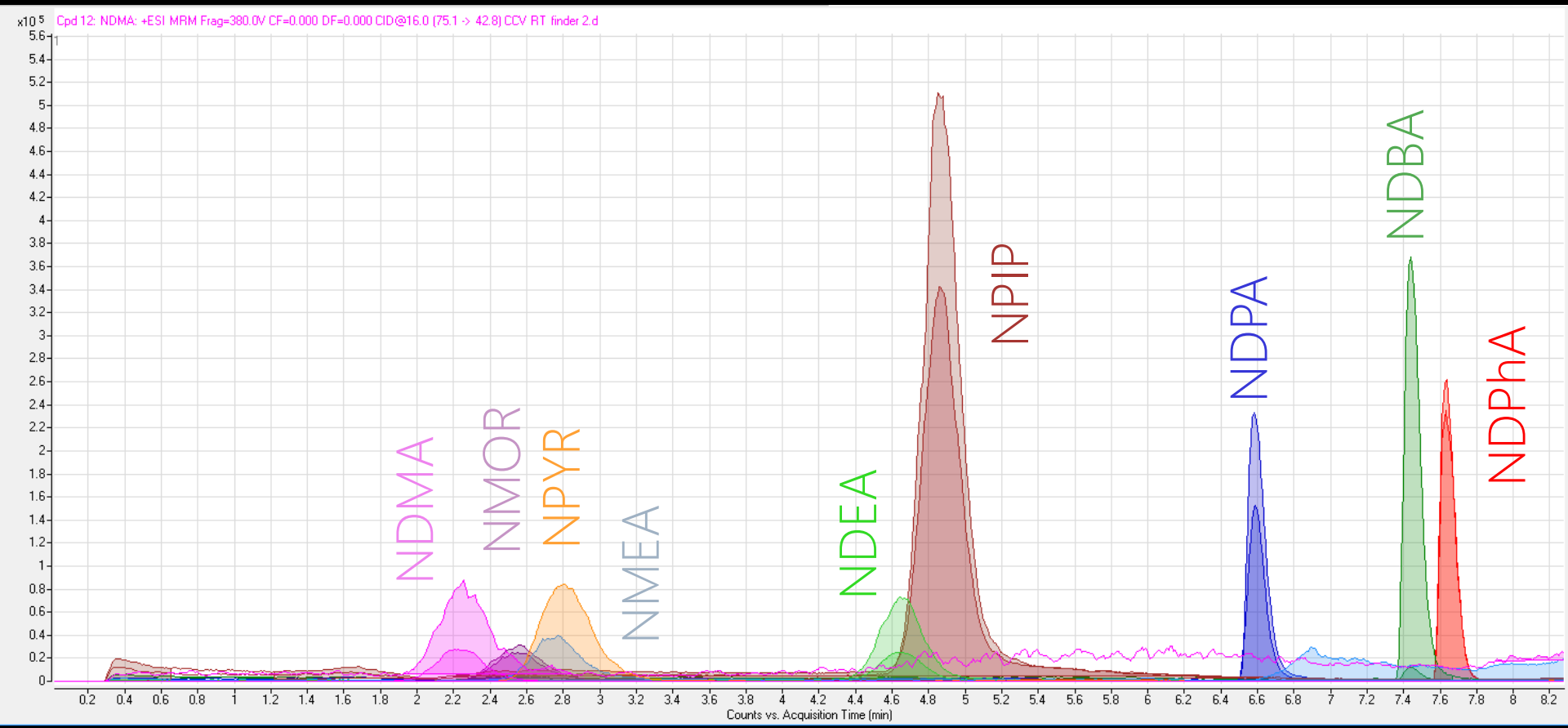
50 x 4.6 mm, 5 µm Pursuit PFP



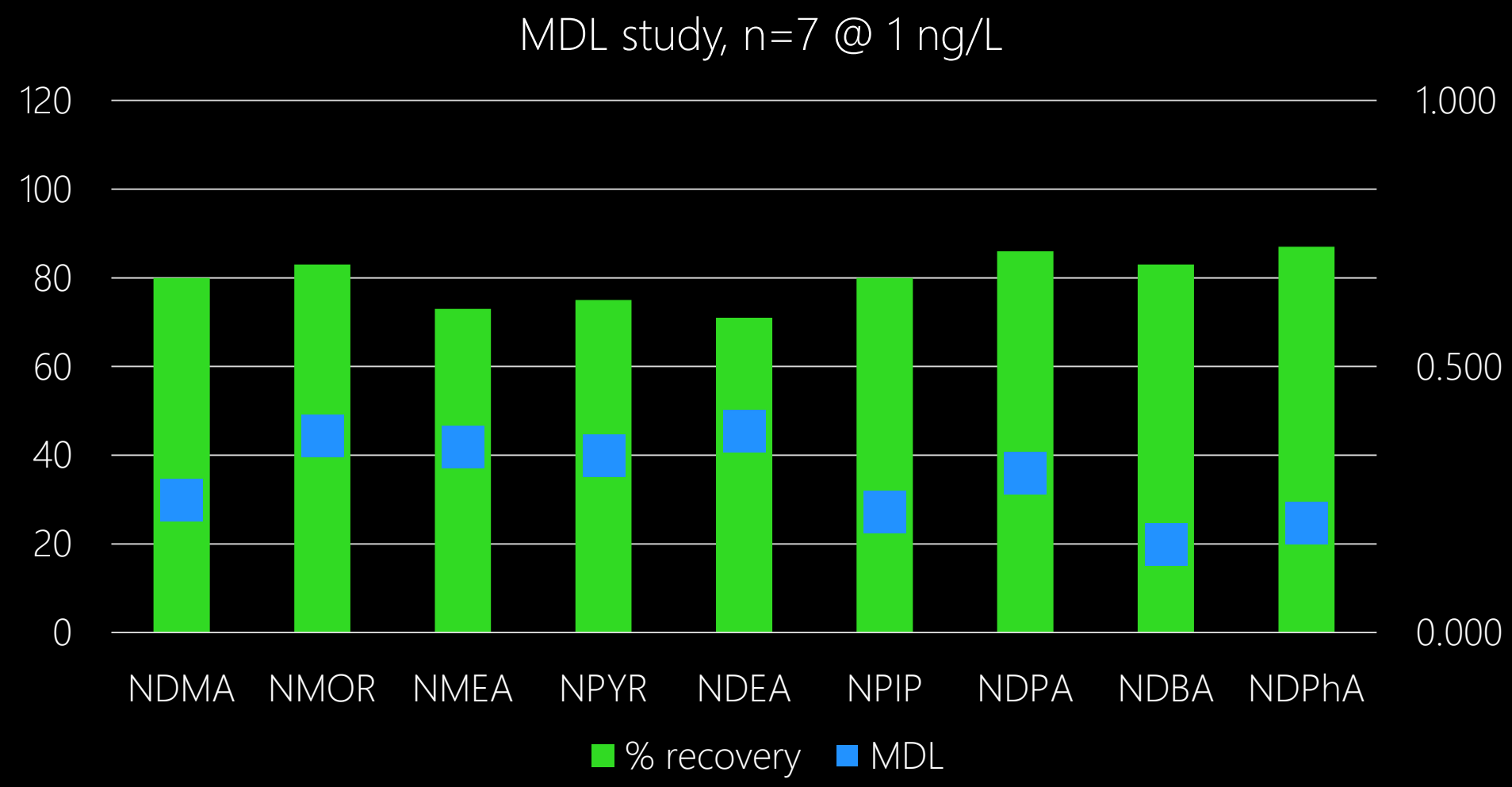
Online SPE pump profiles



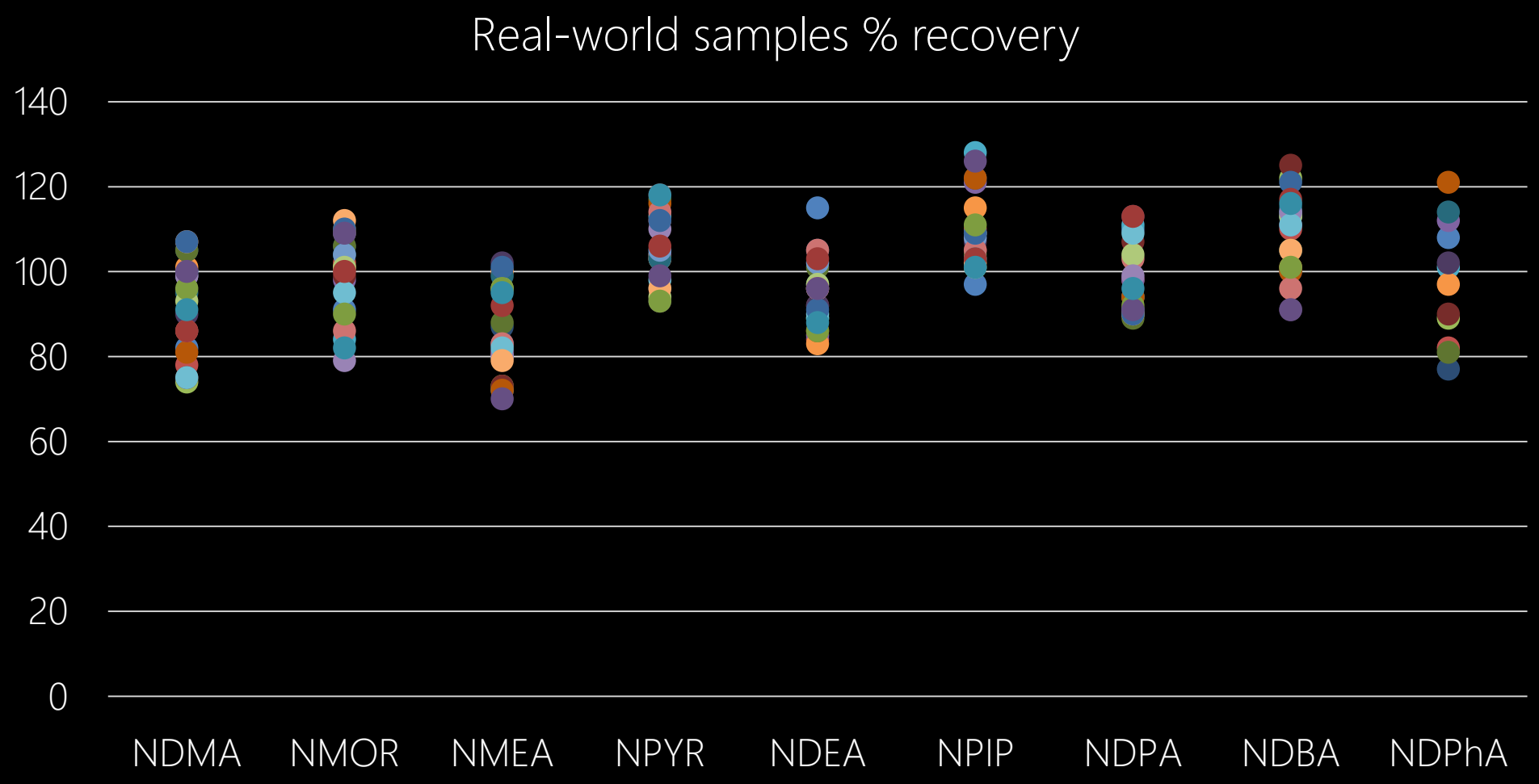
Online SPE at 5 ng/L



MDL study—online SPE



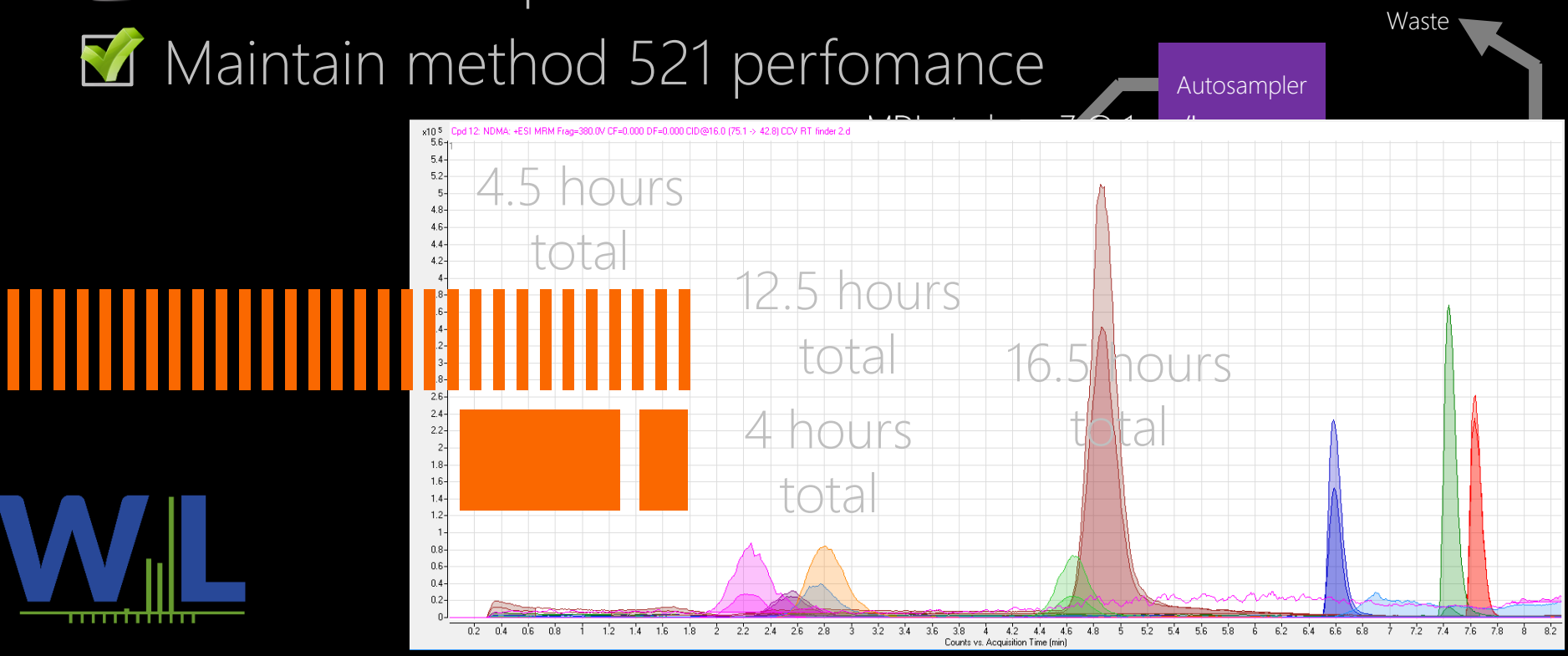
Real-world sample comparison



n=80

Method goals

- ☑ No sample prep
- ☑ Handle typical DW matrix
- ☑ Shorten the total analysis time
- ☑ Minimize sample volume needed
- ☑ Maintain method 521 perfomance



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Questions?

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