A Fast GC/MS/MS MRM Method for Semivolatiles that Meets EPA 8720D/E Requirements

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Introduction: Scope of EPA method 8270E

Semivolatiles in many types of solid waste matrices, soils, air sampling media and water samples

Listed in EPA's Selected Analytical Methods for Environmental Remediation and Recovery (SAM)

Historically a single quad method, method 8270 - now as 8270E - allows use of the triple quad mass spectrometer

- Expect increased selectivity and sensitivity over the single quad
- Possibility to speed up analysis

Introduction: Goal

Achieve widest calibration range in a single, 10-minute run using MRM

- Goal: 0.02 – 160 ppm

Considerations for calibration:

- Low compound %RSDs are indicative of how long the continuing calibration will last

- An extended maintenance interval would lead to increased productivity and a lower cost of operation

Introduction: Experimental plan

Analyze extracts of real samples to evaluate the method

- Compare dynamic MRM (dMRM) and scan mode
- Demonstrate that batch review is facilitated by using MRM
- Expect to observe improved detection

Experimental details: Samples

Calibration standards and ISTDs were purchased from AccuStandard

- 77 target analytes
- 6 ISTDs

Extracted field samples were provided by Weck Labs

- Water: LLE (950 mL → 0.95 mL)

- Landfill leachate: High solid content – treated as soil
  (Method 3545: 2.28 g to 20 mL)

Experimental details: Instrument parameters

Parameter	Value
Injection volume	1 µL
Inlet	Split/splitless 280 °C; Split 20:1
Inlet liner	Agilent Ultra Inert universal low pressure drop single-taper liner with wool
Column temperature program	40 °C, 35 °C/min to 320 °C (hold 2 min)
Column	J&W DB-5ms UI 20 m × 0.18 mm × 0.18 µm column
Retention time locking	Locked to acenaphthene-d10 @ 4.58 min
Carrier gas and flow rate	Helium at 1.2 mL/min, constant flow
MS parameters	
Transfer line temperature	320 °C
Ion source temperature	300 °C
Modes	Dynamic MRM and Scan
Tune	etune

Agilent 7890B GC/ 7000D MS/MS

Optimize sample load and maximize linearity

Split ratio:

- adjusted to meet isomer resolution requirements

Detector gain:

- set to maximize linearity - critical to achieve the widest calibration range and run the analysis in only one injection
- Maximum peak height in BPC of the high 160 ppm standard did not exceed 6×10^7 counts in height

Initial Calibration

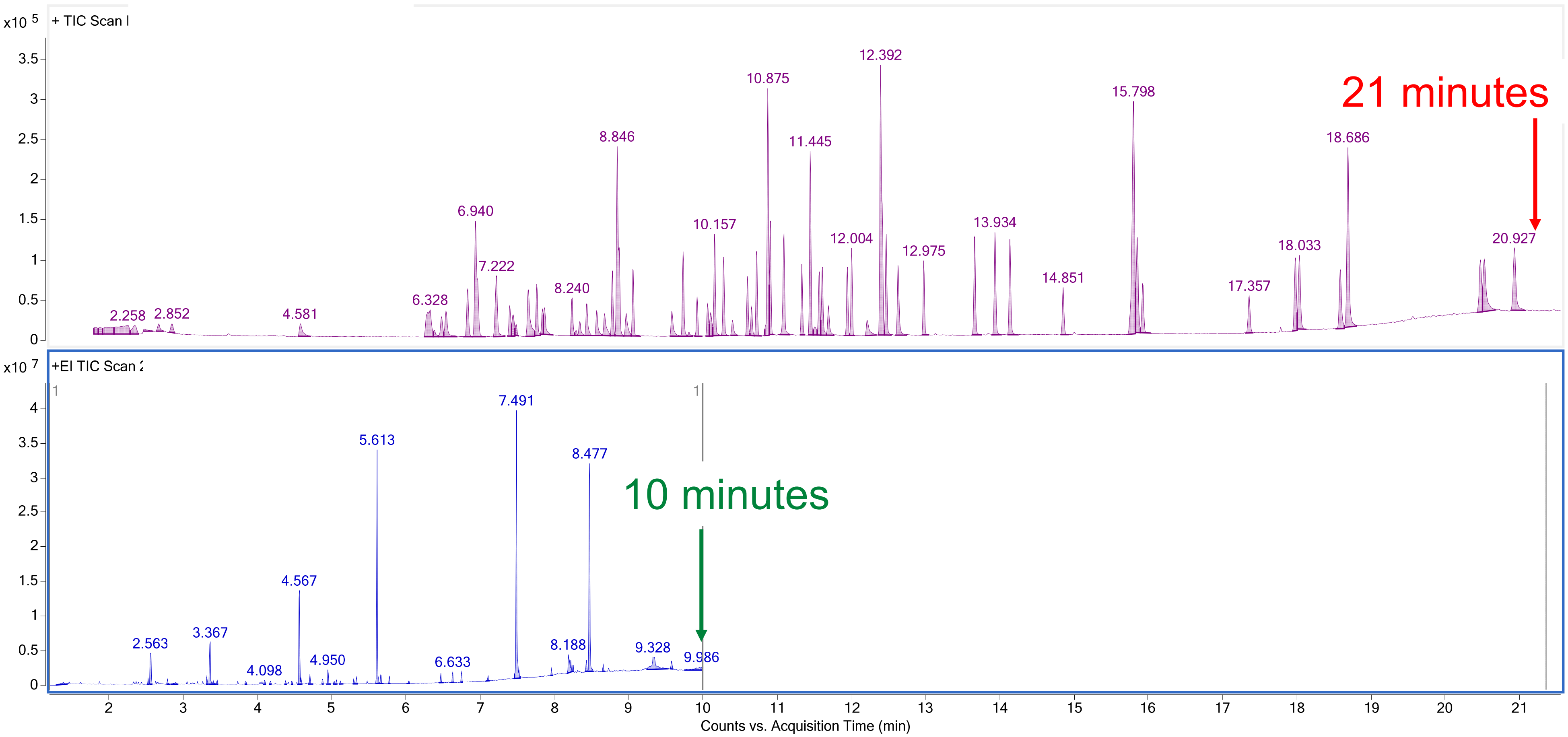
Prepared eleven calibration levels from 0.02 -160 ppm

Add ISTDs for concentration of 20 ppm

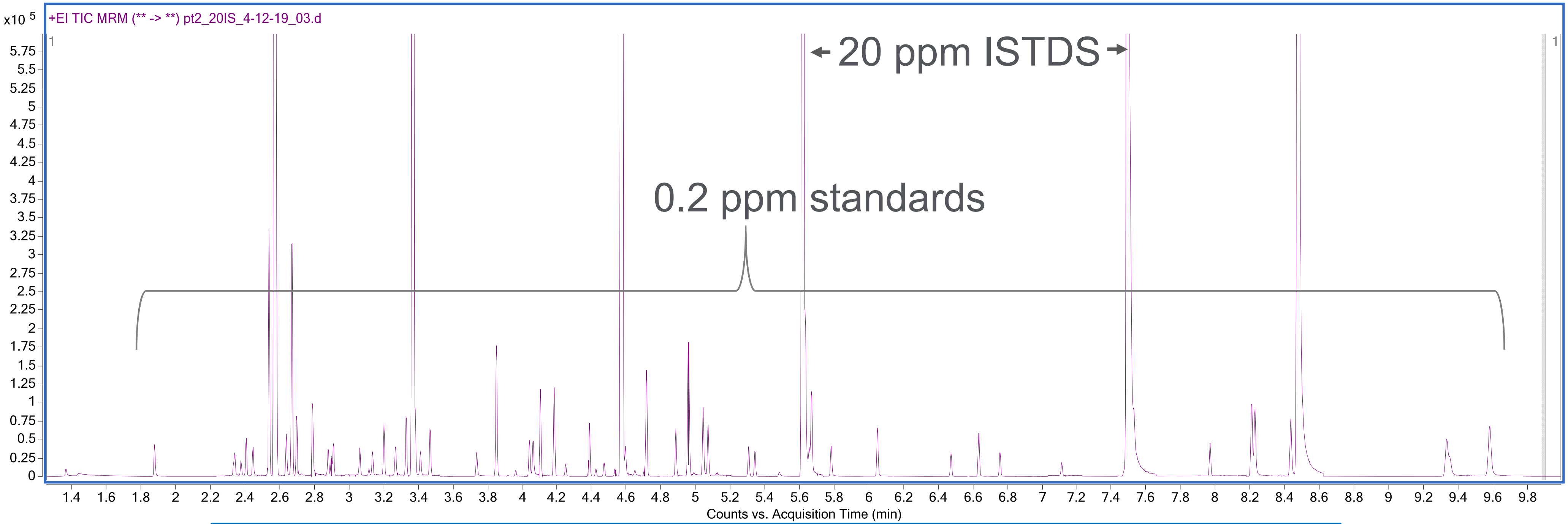
Data points for each compound at the low and high ends of the calibration range were removed to meet published calibration criteria

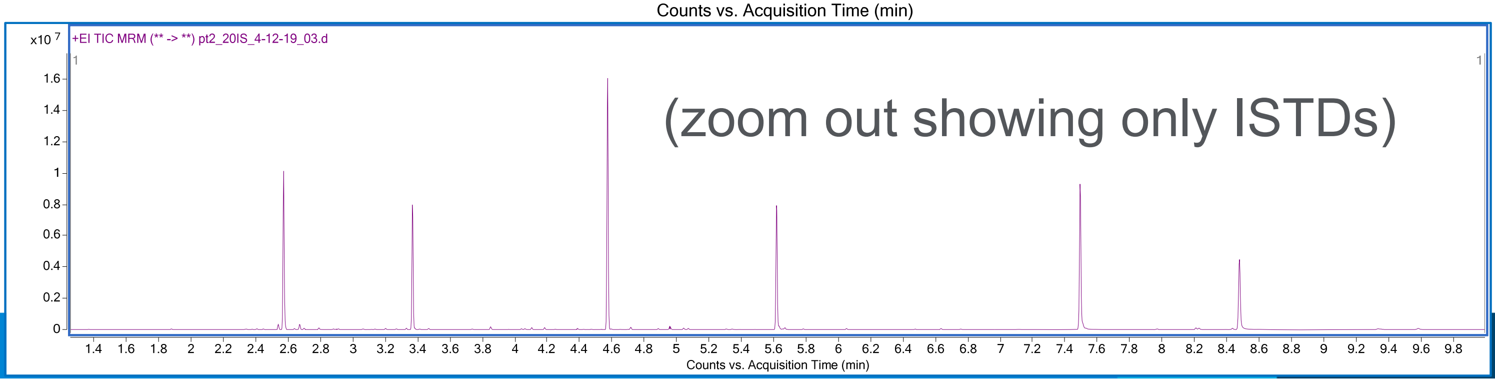
Results using dMRM are presented

Comparison of GC/MS scan and GC-MS/MS MRM methods



MRM TIC for 77 standards and 6 ISTDs – 10 minute run





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Initial Calibration results: 0.02 – 160 ppm

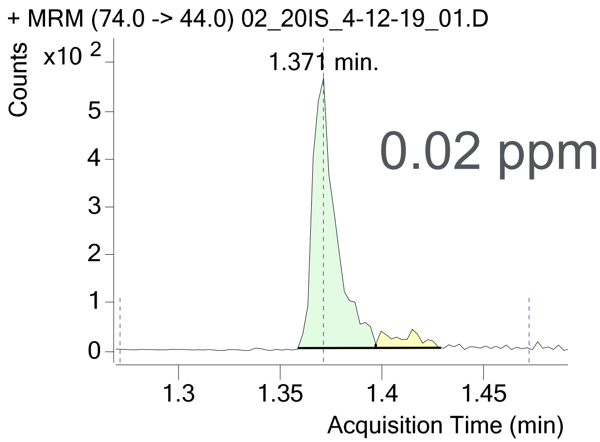
60 out of 77 compounds passed average RF %RSD criteria (< 20%)

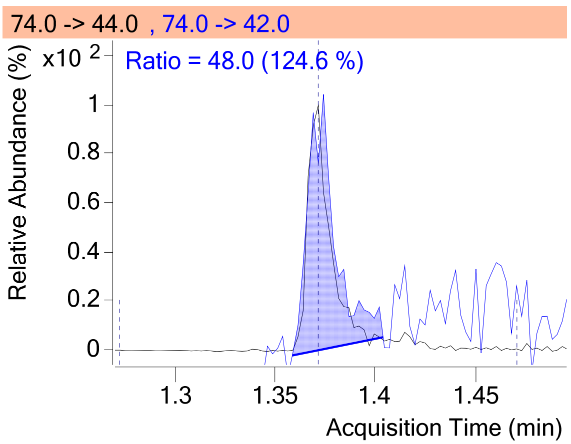
Curve fit used for 16 compounds: 4 linear, 12 quadratic (1 failed)

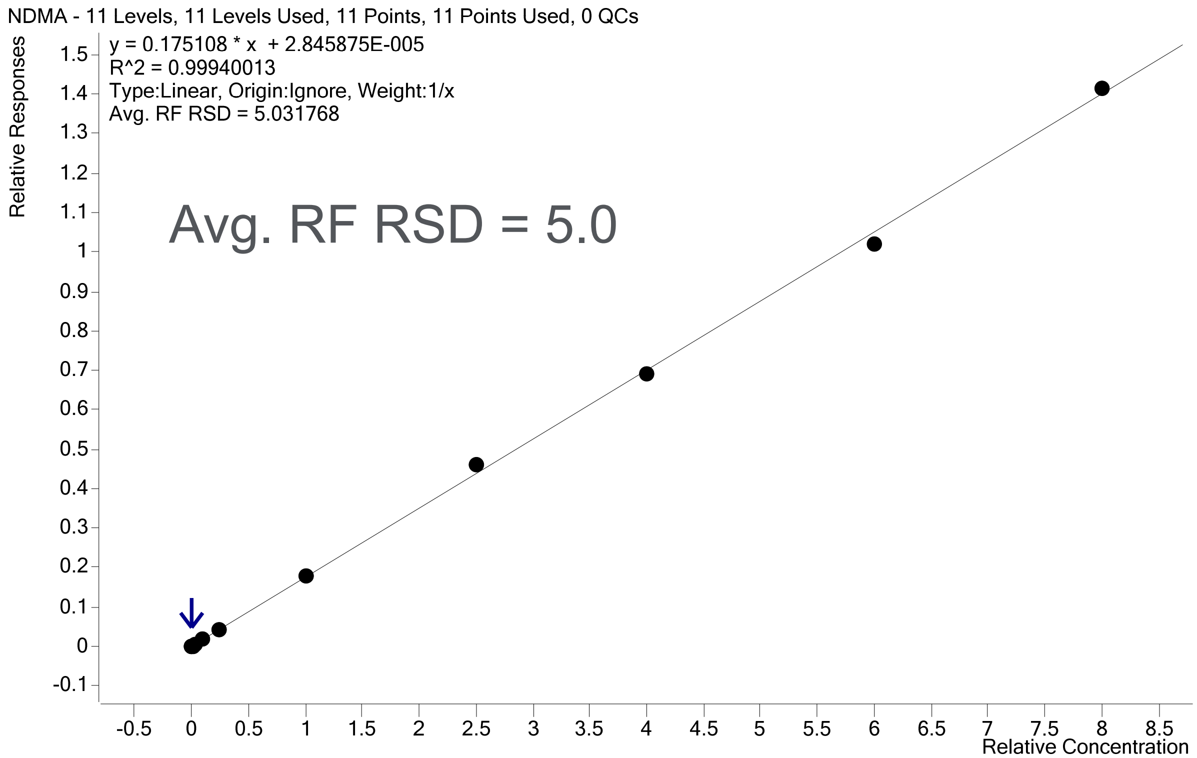
Average of the average RF %RSD (for all compounds) = 13.8%
- Max = 47% (benzoic acid)
- Min = 3.6% (Bis[2-chloroethyl] ether)

56 of 77 compounds had a full calibration range of 0.02 – 160 ppm

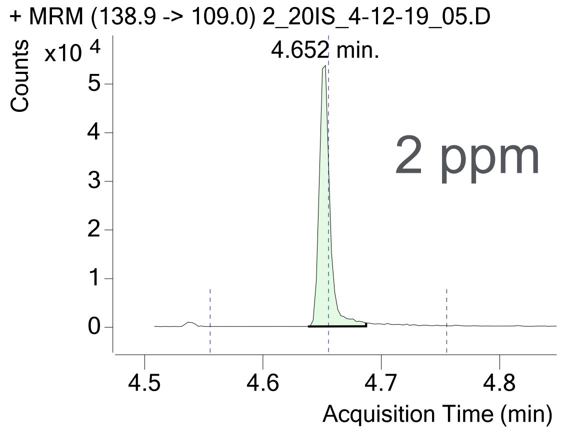
Initial Calibration results: NDMA (0.02 – 160 ppm)

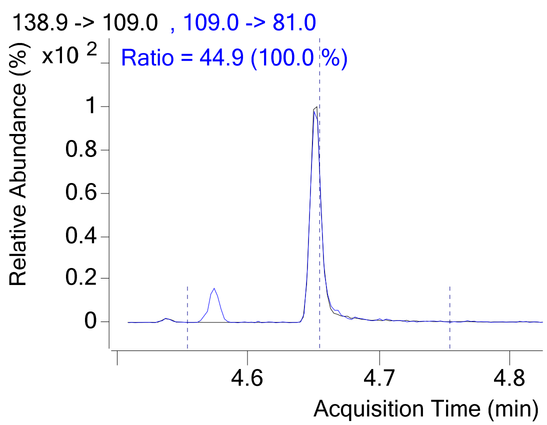


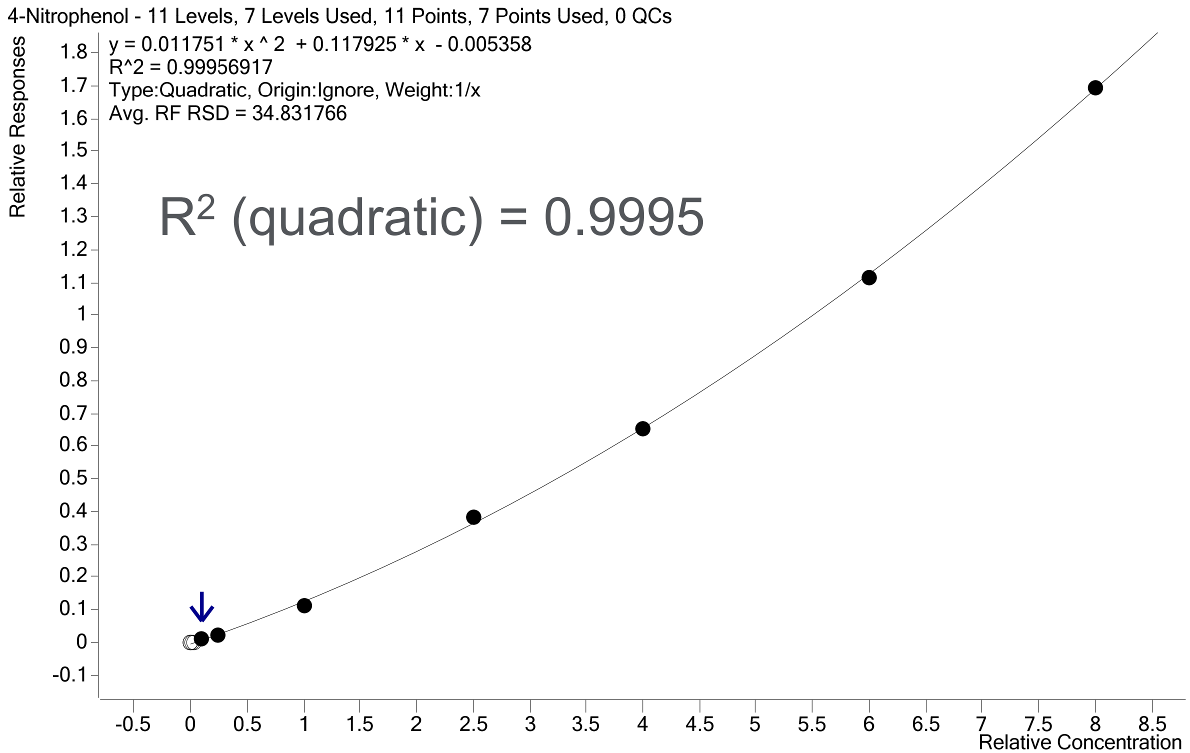




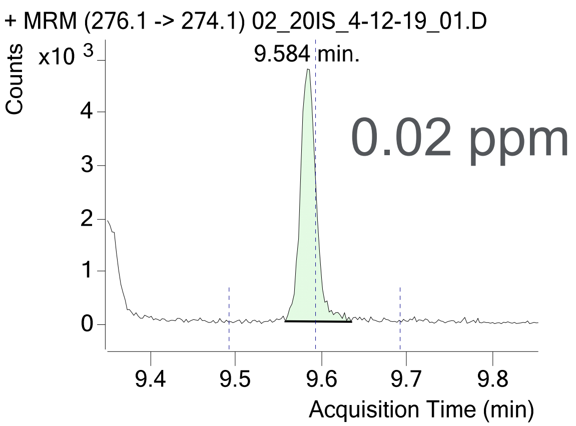
Initial Calibration results: 4-Nitrophenol (2 – 160 ppm)

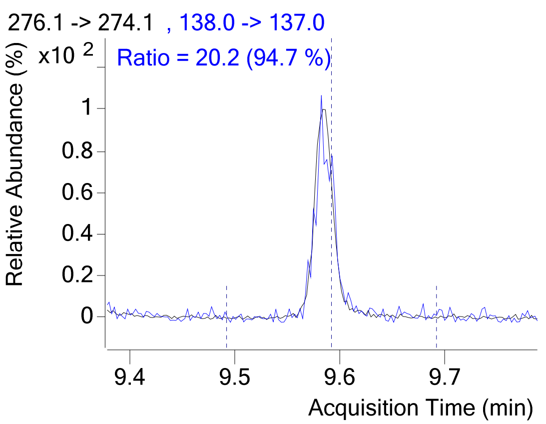


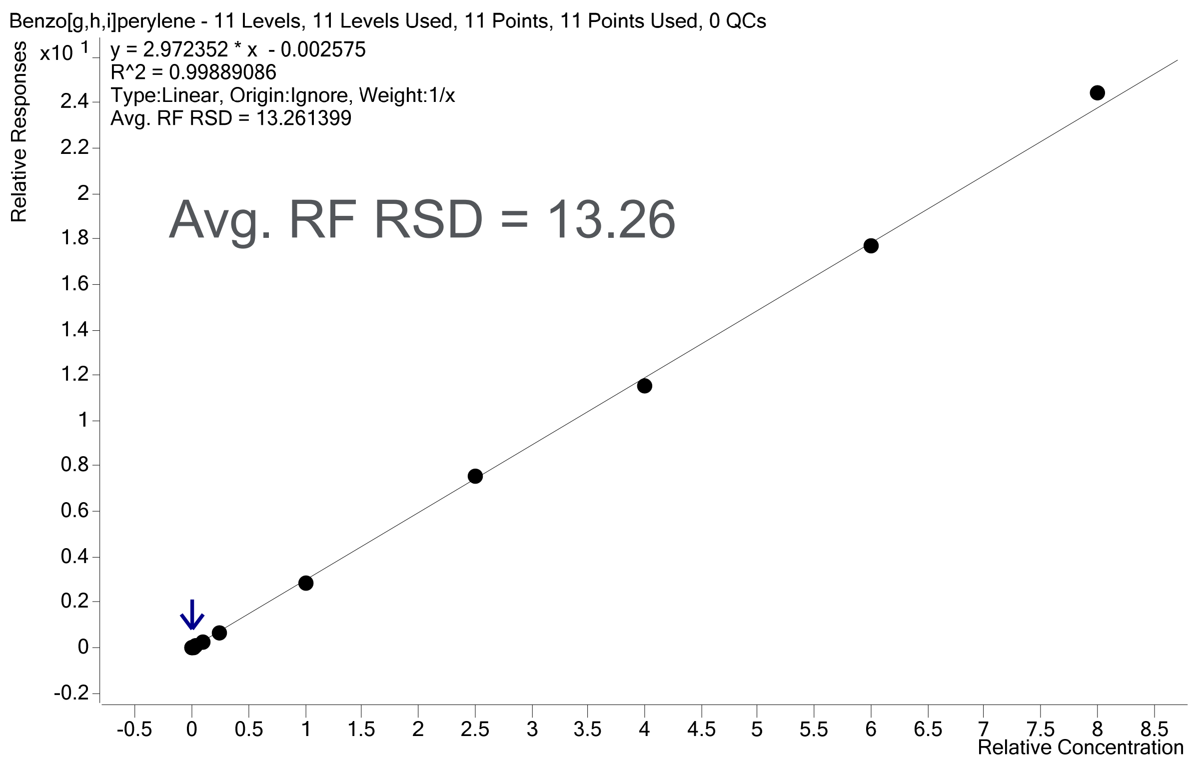




Initial Calibration results: Benzo[g,h,i]perylene (0.02 – 160 ppm)

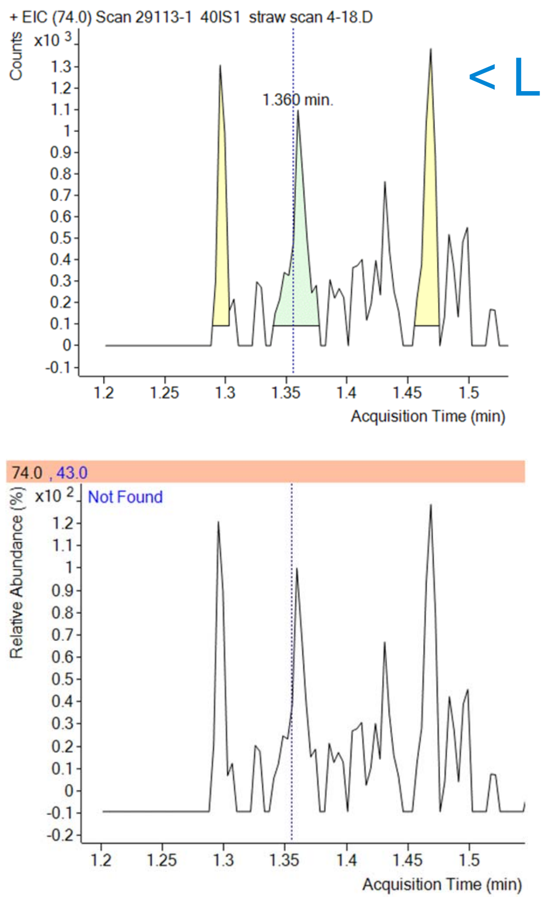






Field water sample: NDMA

Scan EIC



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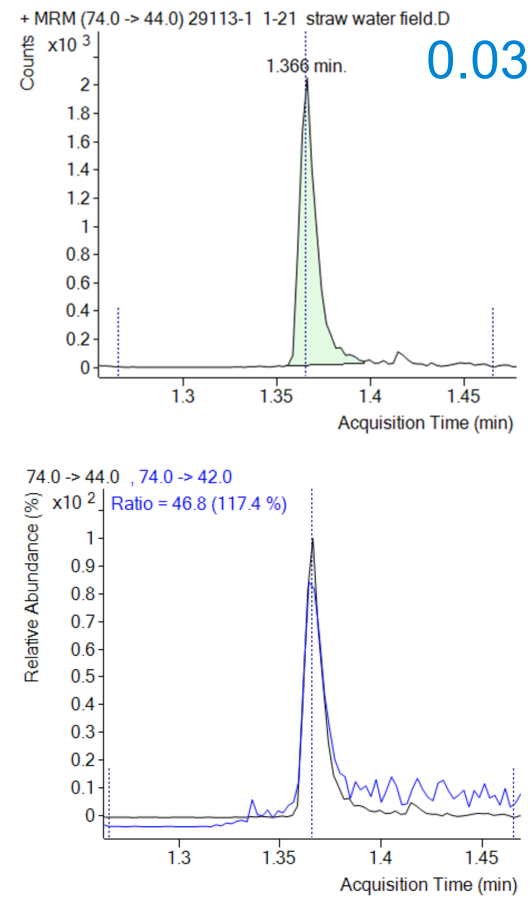
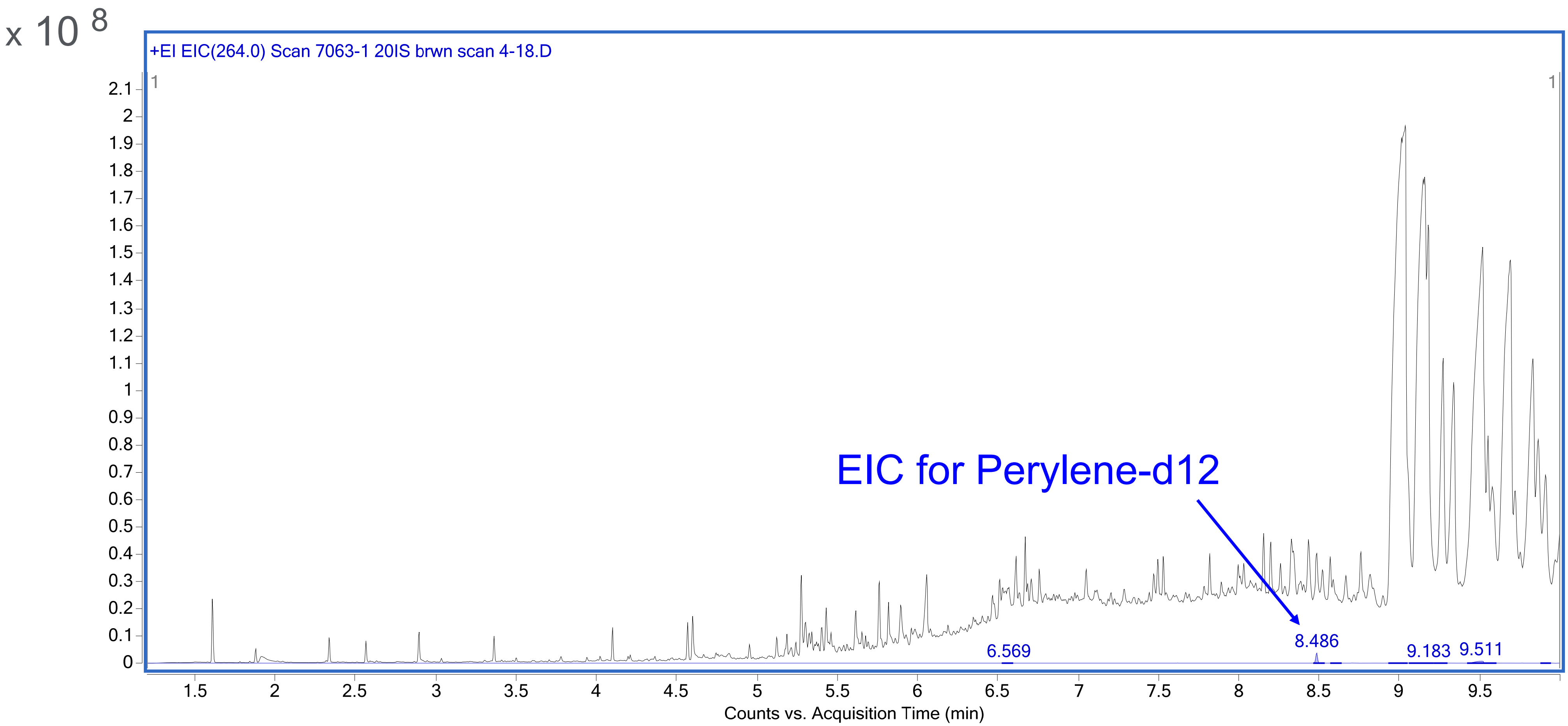
dMRM



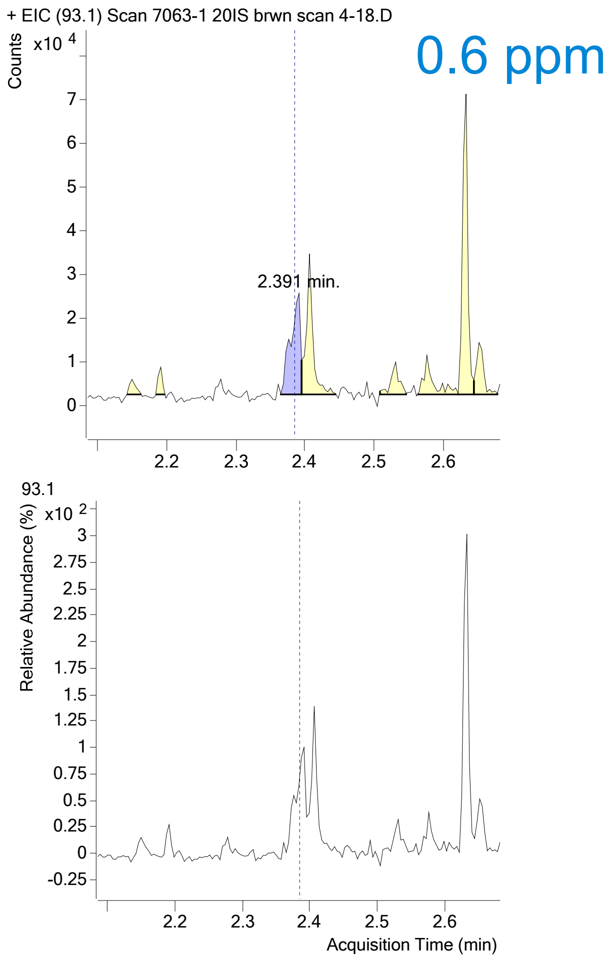
0.03 ppm

Landfill leachate sample: TIC in scan mode

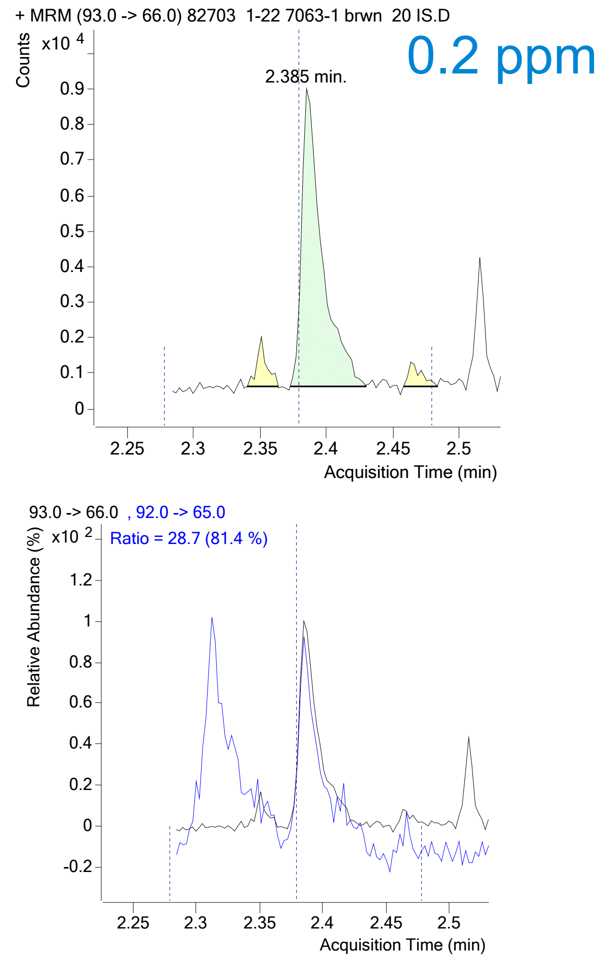


Landfill leachate sample: Aniline

Scan EIC

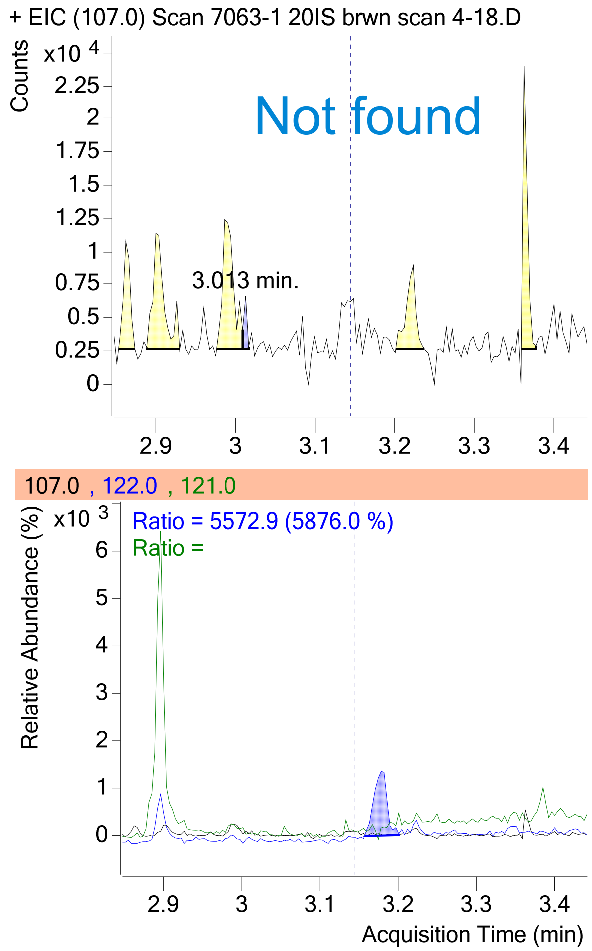


dMRM

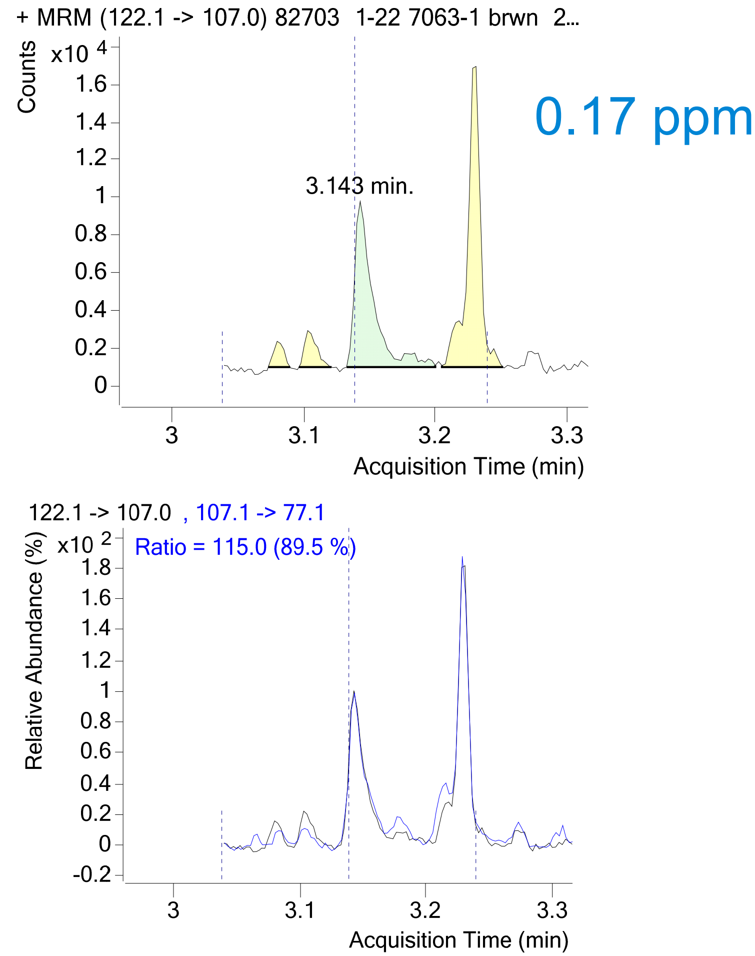


Landfill leachate sample: 2,4-dimethylphenol

Scan EIC

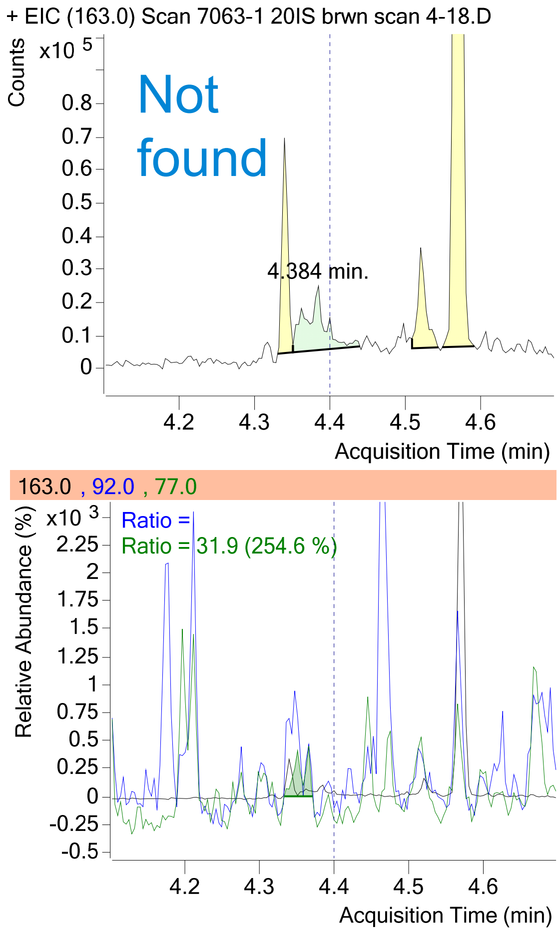


dMRM

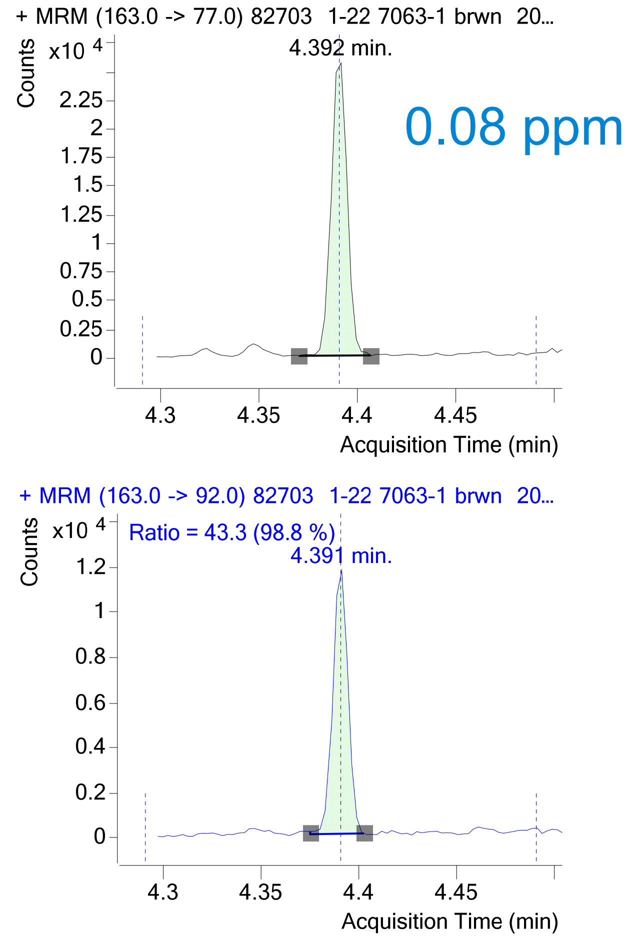


Landfill leachate sample: Dimethyl phthalate

Scan EIC

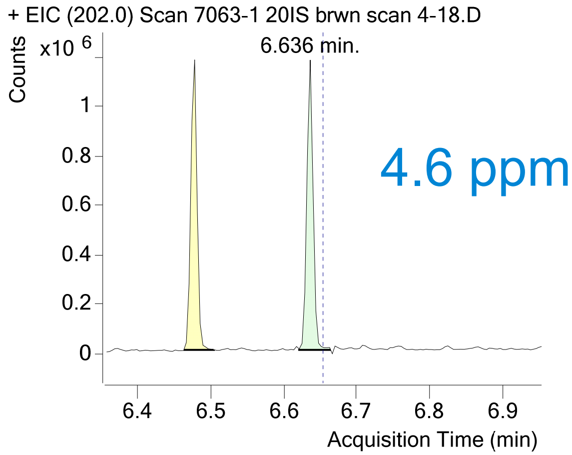


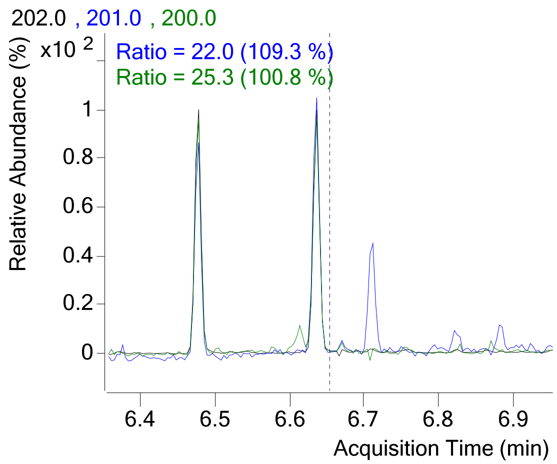
dMRM



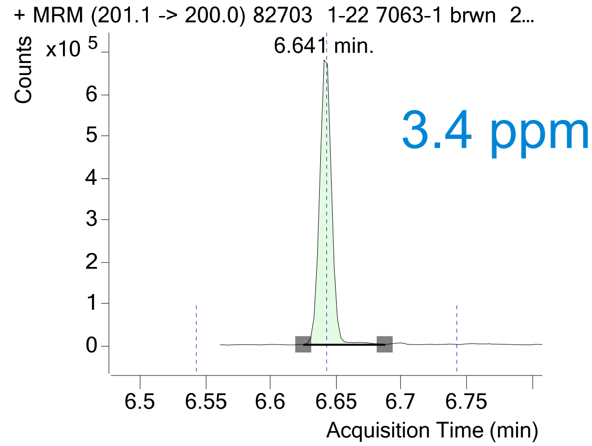
Landfill leachate sample: Pyrene

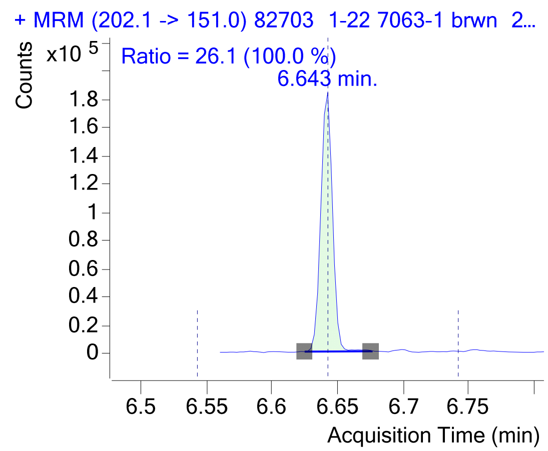
Scan EIC





dMRM





Conclusions

A 10-minute method for EPA 8270 has been developed using dMRM mode

Calibration range of 0.02 – 160 ppm can be met

More target compounds were found using dMRM as opposed to scan mode

Batch review was easier with the improved sensitivity and selectivity of MRM

The level of sensitivity may allow for extracting or injecting less sample if desired (calibrate from 0.2 ppm)

Acknowledgement

The authors would like to thank Agustin Pierri of Weck Labs, Inc. for samples and his contributions to this work.

Initial Calibration results: 0.02 – 160 ppm

Name	Avg. RF RSD	CF R2
NDMA	5.0	0.9994
Pyridine	8.6	0.9979
2-Fluorophenol	5.0	0.9979
Phenol-d6	8.7	0.9967
Phenol	7.9	0.9983
Aniline	5.0	0.9987
Bis(2-chloroethyl) ether	3.6	0.9990
2-Chlorophenol	9.8	0.9969
1,3-Dichlorobenzene	6.4	0.9978
1,4-Dichlorobenzene-d4	4.9	
1,4-Dichlorobenzene	7.9	0.9976
Benzyl alcohol	11.6	0.9942
1,2-Dichlorobenzene	6.2	0.9979
2-Methylphenol (o-Cresol)	10.1	0.9983
Bis(2-chloro-1-methylethyl) ether	4.0	0.9994
4-Methylphenol (p-Cresol)	13.7	0.9964
N-Nitrosodi-n-propylamine	13.7	0.9955
Hexachloroethane	4.4	0.9995
Nitrobenzene-d5	15.5	0.9943
Nitrobenzene	8.7	0.9984
Isophorone	7.5	0.9991
2-Nitrophenol	19.1	0.9916
2,4-Dimethylphenol	14.0	0.9951
Bis(2-chloroethoxy)methane	4.9	0.9991
Benzoic acid	47.2	0.9996
2,4-Dichlorophenol	16.8	0.9954
1,2,4-Trichlorobenzene	7.6	0.9977

Name	Avg. RF RSD	CF R2
Naphthalene-d8	5.0	
Naphthalene	6.3	0.9979
4-Chloroaniline	7.0	0.9992
Hexachlorobutadiene	5.5	0.9978
4-Chloro-3-methylphenol	16.9	0.9932
2-Methylnaphthalene	9.9	0.9942
Hexachlorocyclopentadiene	16.8	0.9948
2,4,5-Trichlorophenol	15.4	0.9891
2,4,6-Trichlorophenol	19.7	0.9989
2-Fluorobiphenyl	9.2	0.9953
Chloronaphthalene, 2-	7.3	0.9961
2-Nitroaniline	26.1	0.9994
Dimethyl phthalate	9.6	0.9982
2,6-Dinitrotoluene	21.7	0.9933
Acenaphthylene	4.9	0.9995
3-Nitroaniline	27.2	0.9995
Acenaphthene-d10	6.2	
Acenaphthene	5.9	0.9991
2,4-Dinitrophenol	35.5	0.9998
4-Nitrophenol	34.8	0.9996
2,4-Dinitrotoluene	29.7	0.9997
Dibenzofuran	11.5	0.9903
Diethyl phthalate	17.2	0.9962
Fluorene	8.1	0.9905
4-Chlorophenyl phenyl ether	6.6	0.9954
4-Nitroaniline	27.8	0.9995
DNOC	32.7	0.9999

Name	Avg. RF RSD	CF R2
N-Nitrosodiphenylamine	11.9	0.9991
Azobenzene	12.9	0.9989
2,4,6-Tribromophenol	24.0	0.9916
4-Bromophenyl phenyl ether	6.0	0.9992
Hexachlorobenzene	7.1	0.9979
Pentachlorophenol	26.8	0.9997
Phenanthrene-d10	6.4	
Phenanthrene	8.6	0.9963
Anthracene	5.8	0.9991
Carbazole	12.1	0.9990
Dibutyl phthalate	26.0	0.9972
Fluoranthene	10.7	0.9988
Pyrene	6.6	0.9977
p-Terphenyl-d14	8.7	0.9967
Benzyl butyl phthalate	30.8	1.0000
3,3'-Dichlorobenzidine	29.3	0.9993
Chrysene-d12	13.7	
Benz[a]anthracene	10.0	0.9957
Chrysene	6.2	0.9984
Bis(2-ethylhexyl) phthalate	36.7	0.9993
Di-n-octyl phthalate	20.0	0.9788
Benzo[b]fluoranthene	11.0	0.9988
Benzo[k]fluoranthene	14.8	0.9971
Benzo[a]pyrene	16.6	0.9991
Perylene-d12	20.6	
Benzo[g,h,i]perylene	13.3	0.9989
Indeno[1,2,3-cd]pyrene	13.3	0.9989
Dibenz[a,h]anthracene	20.7	0.9951

8270 initial calibration criteria

- ✓ Avg RF %RSD ≤ 20 (preferred as default)
- ✓ If not, linear curve fit ($R^2 \geq 0.990$)
- ✓ If not, then quadratic fit
  - 6 points needed for a curve fit
  - Accuracy for lowest point needs to be ±30%