Poster Reprint

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# Fast Semivolatiles Method by GC/MS/MS that Meets EPA 8720D/E Requirements

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## Introduction

A wide calibration range of 0.02 – 160 ppm was achieved in a single, 10-minute MRM analysis for EPA 8270D/E compounds. Low compound %RSDs were achieved, which are indicative of how long the continuing calibration will last. An extended maintenance interval results, leading to increased productivity and a lower cost of operation.

Real field samples were analyzed by a 7000D GC/TQ using Dynamic MRM (dMRM) and in scan mode to compare results. Use of dMRM lowers detection limits and facilitates sample batch review when compared with scan analysis.

A new direct insertion device for GC/MS, which contains a very short GC column and is mounted on either a 5975 or 5977 GC/MSD, was evaluated for quick sample screening as this may expedite the laboratory workflow by identifying high-level analytes and matrix prior to the extraction process.

## Experimental

### 8270 initial calibration criteria

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

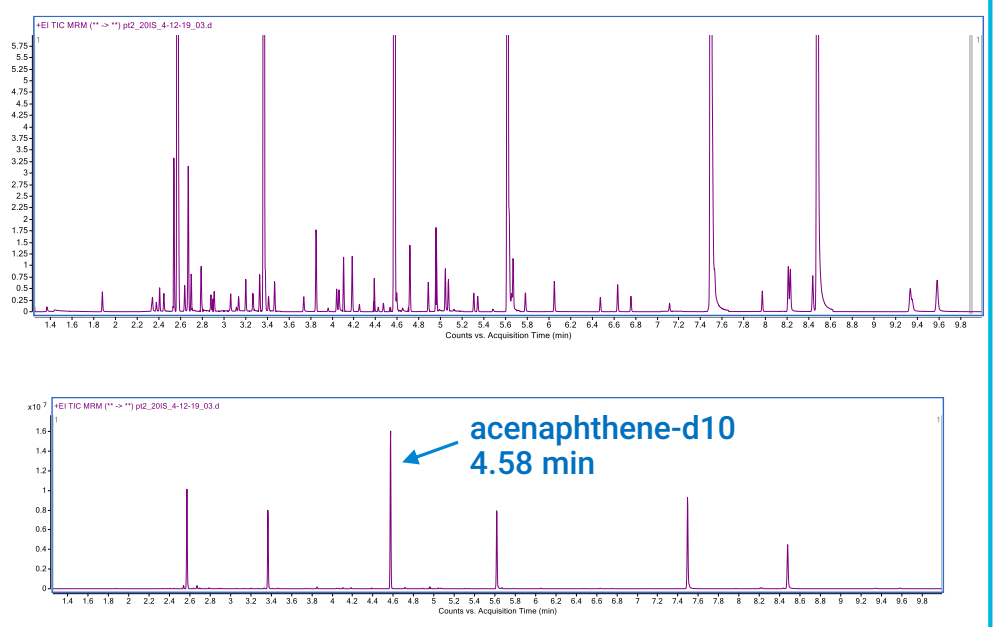
### Instrument conditions

The 7890B/7000D was autotuned. The GC column was a 20m x 180µm x 0.18 µm 5% phenyl (polysiloxane) which was connected to a SSL inlet. Injection was 1 µL using a 1:20 split into an Ultra Inert low pressure drop split liner with wool. Flow was set to 1.2 mL/min and the method was retention time locked to acenaphthene-d10 at 4.58 minutes. The instrument was operated in dMRM mode. Batches were also run in scan mode to compare chromatography.

The split ratio was adjusted to meet isomer resolution requirements and avoid wide peaks with rounded tops. Detector gain was adjusted to maximize linearity, which is critical to achieving the widest calibration range. Therefore, no peak in the BPC of the high 160ppm standard exceeded 6 x $10^7$ counts in height.

## Experimental, cont.

### 10-minute analysis of 77 standards and 6 ISTDs



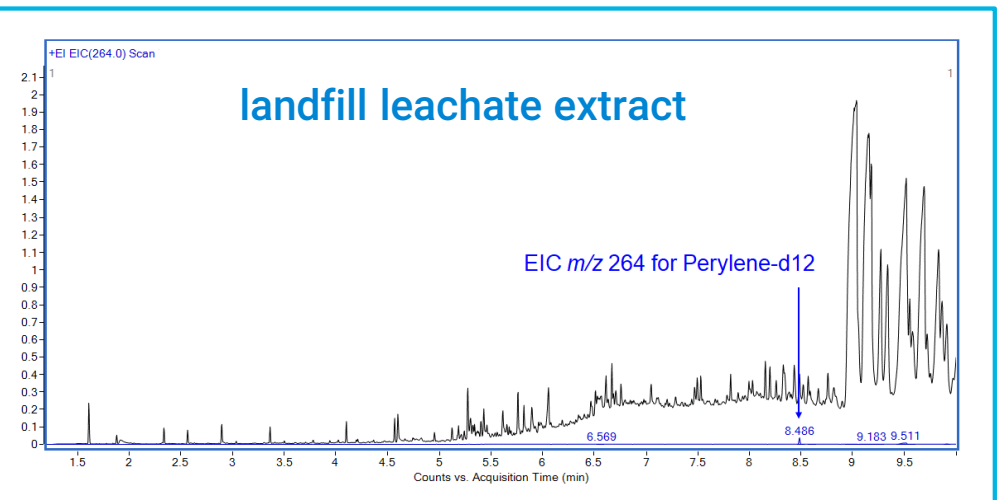

Top: Zoom of MRM TIC showing 77 targets at the 0.2 ppm level. Bottom: Zoom out showing all six ISTDs (refer to initial calibration table for ISTDs)

### Calibration

Eleven levels ranging from 0.02 -160 ppm were prepared and 20 ppm ISTD was added. Results were analyzed using MassHunter Quantitative Analysis software. Data points for each compound at the low and high ends of the calibration range could be deleted to meet calibration criteria. Results by dMRM are presented.

## Results

### A complex field sample in scan mode




ISTD perylene-d12 in landfill leachate extract. The EIC trace in blue is overlaid with the complex scan TIC trace shown in black. Analysis of highly complex samples such as this was improved in terms of detection and relative ease of batch review by using dMRM. Field sample results in both dMRM and scan modes are compared later on this poster.

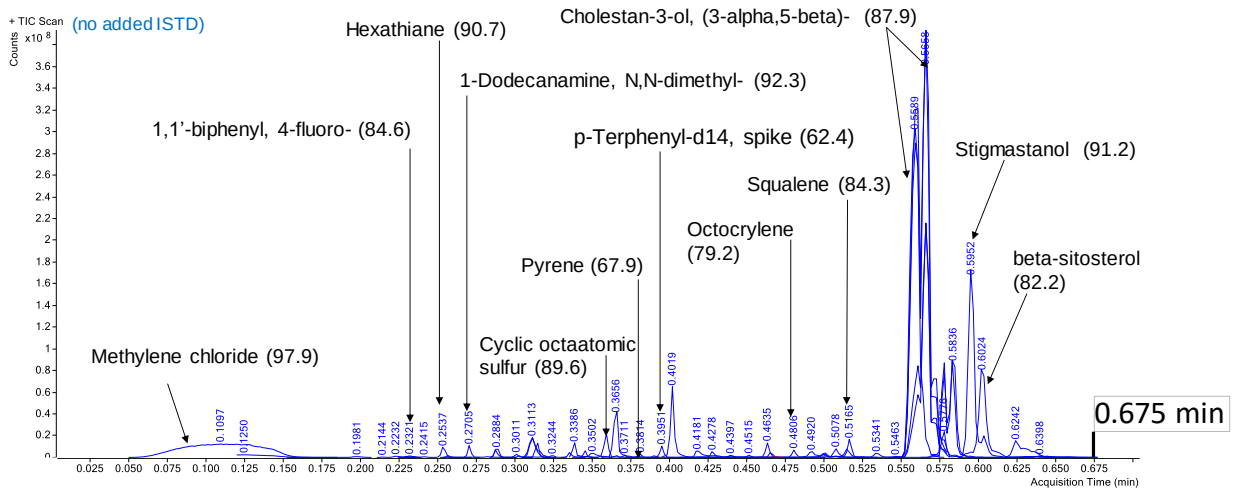
## Initial calibration over the range of 0.02 – 160 ppm

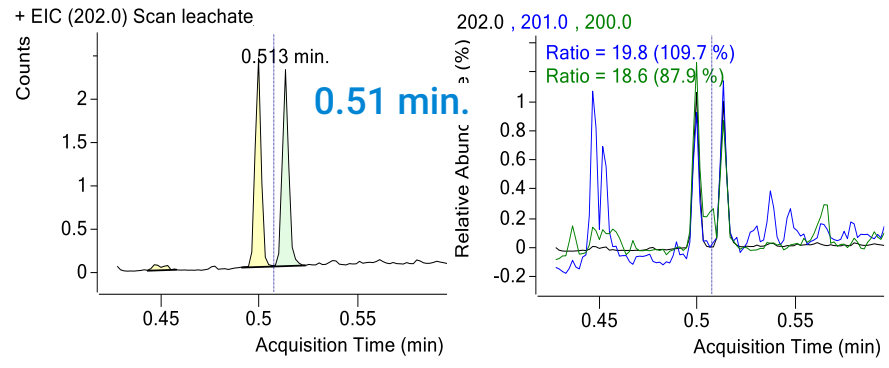
| Name | RT | Avg. RF RSD | CF R2 | Curve Fit |
|---|---|---|---|---|
| NDMA | 1.364 | 5.0 | 0.9994 | Linear |
| Pyridine | 1.389 | 8.6 | 0.9979 | Linear |
| 2-Fluorophenol | 1.877 | 5.0 | 0.9979 | Linear |
| Phenol-d6 | 2.336 | 8.7 | 0.9967 | Linear |
| Phenol | 2.344 | 7.9 | 0.9983 | Linear |
| Aniline | 2.379 | 5.0 | 0.9987 | Linear |
| Bis(2-chloroethyl) ether | 2.409 | 3.6 | 0.9990 | Linear |
| 2-Chlorophenol | 2.447 | 9.8 | 0.9969 | Linear |
| 1,3-Dichlorobenzene | 2.538 | 6.4 | 0.9978 | Linear |
| 1,4-Dichlorobenzene-d4 | 2.571 | 4.9 | | Linear |
| 1,4-Dichlorobenzene | 2.581 | 7.9 | 0.9976 | Linear |
| Benzyl alcohol | 2.641 | 11.6 | 0.9942 | Linear |
| 1,2-Dichlorobenzene | 2.672 | 6.2 | 0.9979 | Linear |
| 2-Methylphenol (o-Cresol) | 2.700 | 10.1 | 0.9983 | Linear |
| Bis(2-chloro-1-methylethyl) ether | 2.728 | 4.0 | 0.9994 | Linear |
| 4-Methylphenol (p-Cresol) | 2.794 | 13.7 | 0.9964 | Linear |
| N-Nitrosodi-n-propylamine | 2.806 | 13.7 | 0.9955 | Linear |
| Hexachloroethane | 2.880 | 4.4 | 0.9995 | Linear |
| Nitrobenzene-d5 | 2.901 | 15.5 | 0.9943 | Linear |
| Nitrobenzene | 2.913 | 8.7 | 0.9984 | Linear |
| Isophorone | 3.065 | 7.5 | 0.9991 | Linear |
| 2-Nitrophenol | 3.115 | 19.1 | 0.9916 | Linear |
| 2,4-Dimethylphenol (2,4-Xylenol) | 3.136 | 14.0 | 0.9951 | Linear |
| Bis(2-chloroethoxy)methane | 3.204 | 4.9 | 0.9991 | Linear |
| Benzoic acid | 3.216 | 47.2 | 0.9996 | Quadratic |
| 2,4-Dichlorophenol | 3.269 | 16.8 | 0.9954 | Linear |
| 1,2,4-Trichlorobenzene | 3.329 | 7.6 | 0.9977 | Linear |
| Naphthalene-d8 | 3.368 | 5.0 | | Linear |
| Naphthalene | 3.383 | 6.3 | 0.9979 | Linear |
| 4-Chloroaniline | 3.413 | 7.0 | 0.9992 | Linear |
| Hexachlorobutadiene | 3.467 | 5.5 | 0.9978 | Linear |
| 4-Chloro-3-methylphenol | 3.737 | 16.9 | 0.9932 | Linear |
| 2-Methylnaphthalene | 3.853 | 9.9 | 0.9942 | Linear |
| Hexachlorocyclopentadiene | 3.962 | 16.8 | 0.9948 | Linear |
| 2,4,5-Trichlorophenol | 4.057 | 15.4 | 0.9891 | Linear |
| 2,4,6-Trichlorophenol | 4.065 | 19.7 | 0.9989 | Linear |
| 2-Fluorobiphenyl | 4.107 | 9.2 | 0.9953 | Linear |
| Chloronaphthalene, 2- | 4.187 | 7.3 | 0.9961 | Linear |
| 2-Nitroaniline | 4.254 | 26.1 | 0.9994 | Quadratic |
| Dimethyl phthalate | 4.391 | 9.6 | 0.9982 | Linear |
| 2,6-Dinitrotoluene | 4.428 | 21.7 | 0.9933 | Linear |

| Name | RT | Avg. RF RSD | CF R2 | Curve Fit |
|---|---|---|---|---|
| Acenaphthylene | 4.475 | 4.9 | 0.9995 | Linear |
| 3-Nitroaniline | 4.54 | 27.2 | 0.9995 | Quadratic |
| Acenaphthene-d10 | 4.575 | 6.2 | | Linear |
| Acenaphthene | 4.597 | 5.9 | 0.9991 | Linear |
| 2,4-Dinitrophenol | 4.619 | 35.5 | 0.9998 | Quadratic |
| 4-Nitrophenol | 4.654 | 34.8 | 0.9996 | Quadratic |
| 2,4-Dinitrotoluene | 4.707 | 29.7 | 0.9997 | Quadratic |
| Dibenzofuran | 4.719 | 11.5 | 0.9903 | Linear |
| Diethyl phthalate | 4.89 | 17.2 | 0.9962 | Linear |
| Fluorene | 4.959 | 8.1 | 0.9905 | Linear |
| 4-Chlorophenyl phenyl ether | 4.965 | 6.6 | 0.9954 | Linear |
| 4-Nitroaniline | 4.97 | 27.8 | 0.9995 | Quadratic |
| DNOC (2-Methyl-4,6-dinitrophenol) | 4.99 | 32.7 | 0.9999 | Quadratic |
| N-Nitrosodiphenylamine | 5.046 | 11.9 | 0.9991 | Linear |
| Azobenzene | 5.076 | 12.9 | 0.9989 | Linear |
| 2,4,6-Tribromophenol | 5.125 | 24.0 | 0.9916 | Linear |
| 4-Bromophenyl phenyl ether | 5.308 | 6.0 | 0.9992 | Linear |
| Hexachlorobenzene | 5.344 | 7.1 | 0.9979 | Linear |
| Pentachlorophenol | 5.483 | 26.8 | 0.9997 | Quadratic |
| Phenanthrene-d10 | 5.617 | 6.4 | | Linear |
| Phenanthrene | 5.635 | 8.6 | 0.9963 | Linear |
| Anthracene | 5.67 | 5.8 | 0.9991 | Linear |
| Carbazole | 5.784 | 12.1 | 0.9990 | Linear |
| Dibutyl phthalate | 6.049 | 26.0 | 0.9972 | Linear |
| Fluoranthene | 6.477 | 10.7 | 0.9988 | Linear |
| Pyrene | 6.636 | 6.6 | 0.9977 | Linear |
| p-Terphenyl-d14 | 6.757 | 8.7 | 0.9967 | Linear |
| Benzyl butyl phthalate | 7.115 | 30.8 | 1.0000 | Quadratic |
| 3,3'-Dichlorobenzidine | 7.474 | 29.3 | 0.9993 | Quadratic |
| Chrysene-d12 | 7.495 | 13.7 | | Linear |
| Benz[a]anthracene | 7.509 | 10.0 | 0.9957 | Linear |
| Chrysene | 7.514 | 6.2 | 0.9984 | Linear |
| Bis(2-ethylhexyl) phthalate | 7.532 | 36.7 | 0.9993 | Quadratic |
| Di-n-octyl phthalate | 7.972 | 20.0 | 0.9788 | Linear |
| Benzo[b]fluoranthene | 8.213 | 11.0 | 0.9988 | Linear |
| Benzo[k]fluoranthene | 8.233 | 14.8 | 0.9971 | Linear |
| Benzo[a]pyrene | 8.44 | 16.6 | 0.9991 | Linear |
| Perylene-d12 | 8.48 | 20.6 | | Linear |
| Benzo[g,h,i]perylene | 9.593 | 13.3 | 0.9989 | Linear |
| Indeno[1,2,3-cd]pyrene | 9.593 | 13.3 | 0.9989 | Linear |
| Dibenz[a,h]anthracene | 9.595 | 20.7 | 0.9951 | Linear |

In the table above, ISTDs are highlighted in orange, 69 compounds that passed RSD criteria are in green and 15 that passed by regression analysis are in blue. Benzidine did not pass. Two compounds had an acceptable range of 5 -160 ppm, six each had a range of 2-160 ppm or 0.5 -160 ppm, two were at 0.2 – 160 ppm and two at 0.02 – 120 ppm. The majority of compounds, 57 in number, passed calibration from 0.02 -160 ppm. One method covered the entire range.

## New technology: A GCMS direct insertion device screens samples - even unprepped - in 60-90 seconds



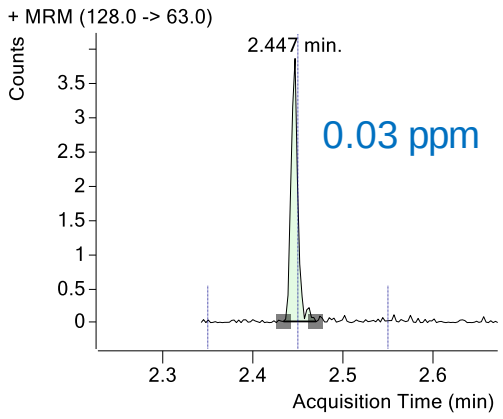

**Pyrene screened in landfill leachate**

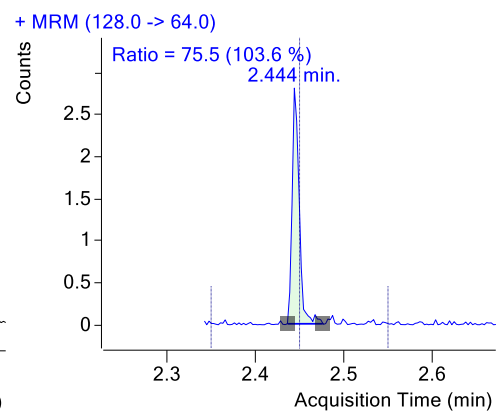
The QuickProbe utilizes a short column with open inlet and was mounted on the GC of a 5977 GC-MSD. Sampling was done using solid glass probes. Unknowns Analysis software was used to search deconvoluted components of landfill leachate extract against the NIST library (left). Targeted screening in MassHunter Quant shows that pyrene is present (right). The concentration of pyrene was determined to be 3 ppm by dMRM analysis.

## Improved detection for field samples using Dynamic MRM

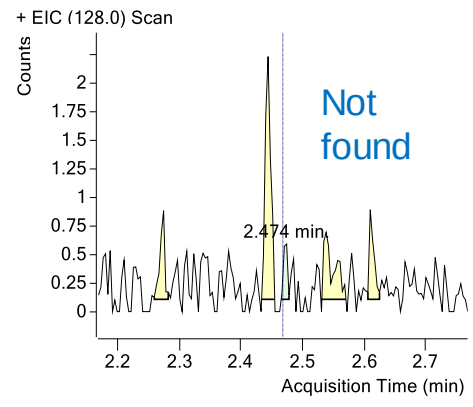
### Field water

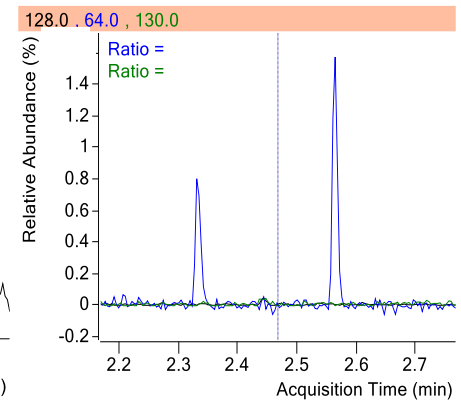
#### dMRM results



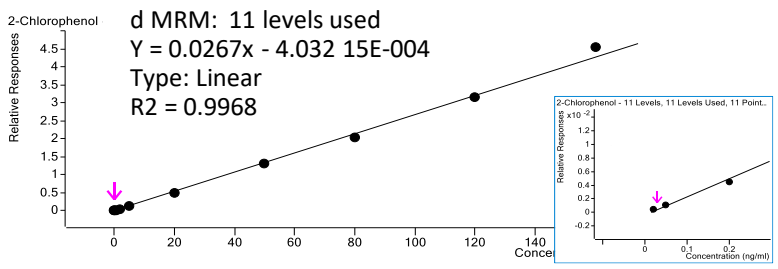




#### Scan results



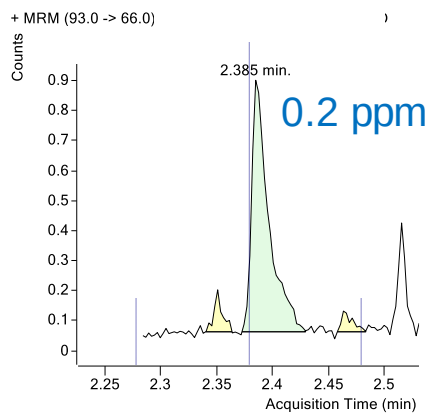



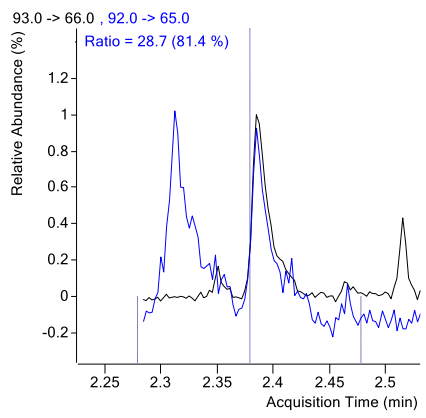

#### 2-chlorophenol




### Landfill leachate

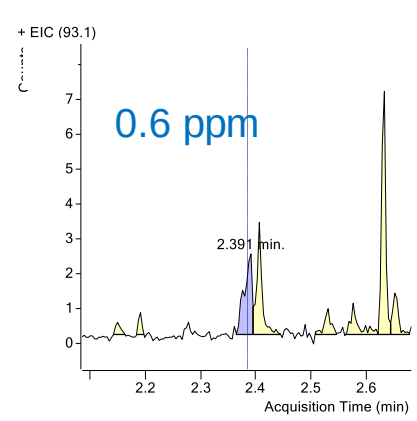
#### dMRM results

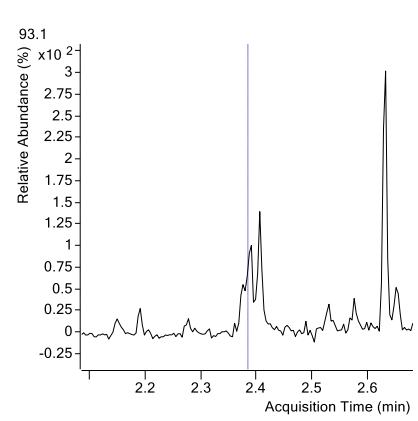


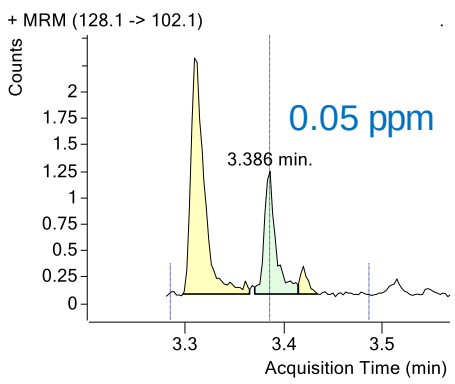



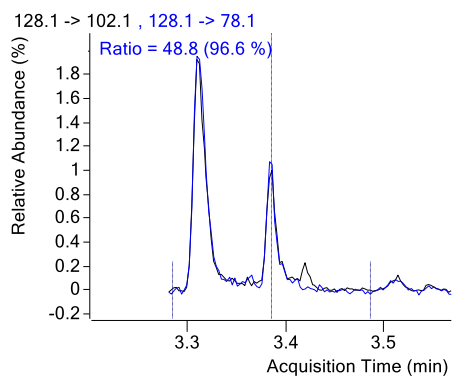

#### aniline

#### Scan results

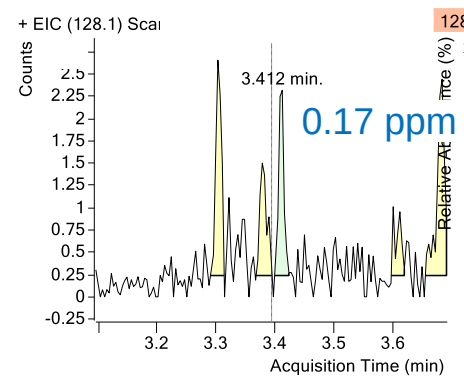


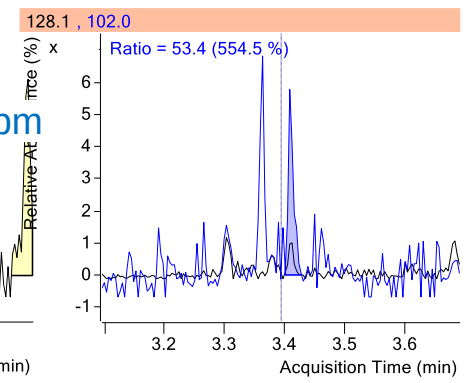




#### naphthalene




Chromatograms for field samples that were analyzed by both dMRM (left) and scan (right). More targets were detected using dMRM vs. scan. Batch review may be facilitated due to the improved chromatography with dMRM.

## Conclusions

A 10-minute method for EPA 8270 has been developed using dMRM mode. More target compounds were found in real samples using dMRM as opposed to scan mode, and batch review was made easier due to the increased selectivity.

A 60-90 second sample pre-screen using a direct insertion device for GC/MS can expedite laboratory workflow.

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