EPA 8270D Optimized for Modern Instrumentation

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Agilent

The goal of EPA 8270 re-optimization

8270 criteria were initially developed on specific instrument platforms

- rigorous due to diverse mix of target compound classes and wide calibration range

The goal of re-optimization was to achieve the widest calibration range in just one injection

- using standard column dimensions and specified upper limit

EPA 8270 initial calibration considerations

Initial calibration results are indicative of how long the continuing calibration will last

- a lower %RSD during initial calibration is indicative that the calibration will last longer
- decreased cost of operation results from less frequent intervention by the operator

Splitless sample injection often results in overloaded column capacity and manual integration is often required

- at calibration levels approaching 160 ppm and with a 0.25 µm column film thickness to avoid long run times

Many practitioners have adopted a “ramped flow” approach

- reduces the effective amount injected

Batch review: initial calibration 0.05 – 160 ppm (10 levels)

Calibration points were deleted from each end of range to meet one of the required EPA 8270D criteria:

1. Avg RF %RSD ≤ 20 (usually most desirable)
2. If not, linear curve fit R2 ≥ 0.990 (usually desired to be minimal)
3. If not, quadratic fit (meets method criteria)

6 points needed for a curve fit

Accuracy for lowest point needs to be within ±30%

Systems used for 8270 study

All systems: 30m x 250 µm x 0.25 µm DB-UI 8270D column

7890 - Inert Plus 5977 MSD	3, 6 mm lens (3 Units)	
7890 - Inert Plus 5977 MSD	9 mm lens (4 Units)	Also with 0.50 µm film (2 Units)
Intuvo GC - Inert 5977 MSD	6 mm lens	

7890 – Inert Plus 5977 MSD 9 mm lens, with online H_2

Conditions tested

Tunes: DFTPP, Atune

Extractor lens diameters : 3 (standard), 6, and 9 mm

Inlet parameters: Pulsed splitless, Pulsed split, “ramped flow” *

Coated (deactivated) or uncoated SSL

*technical splitless injection but with brief initial flow ramp and Purge ON, which effectively reduces the amount of loaded sample. Mimics about a 6:1 split.

Conditions tested

GC Liners: Agilent dual taper no wool (5190-3315)

split liner, low pressure drop, LPD (5190-2295)

single taper Glass Wool UI (5190-2293)

Other manufacturer splitless ST Glass Wool

Conditions tested

Constant Flow at 1.2 mL/min was used throughout (Retention Time Locked)

Temperatures held constant: Inlet, transfer line, source (300°C) and quadrupole (150°C)

Oven ramps were consistent

A note about GC liners with Ultra Inert SSL inlets

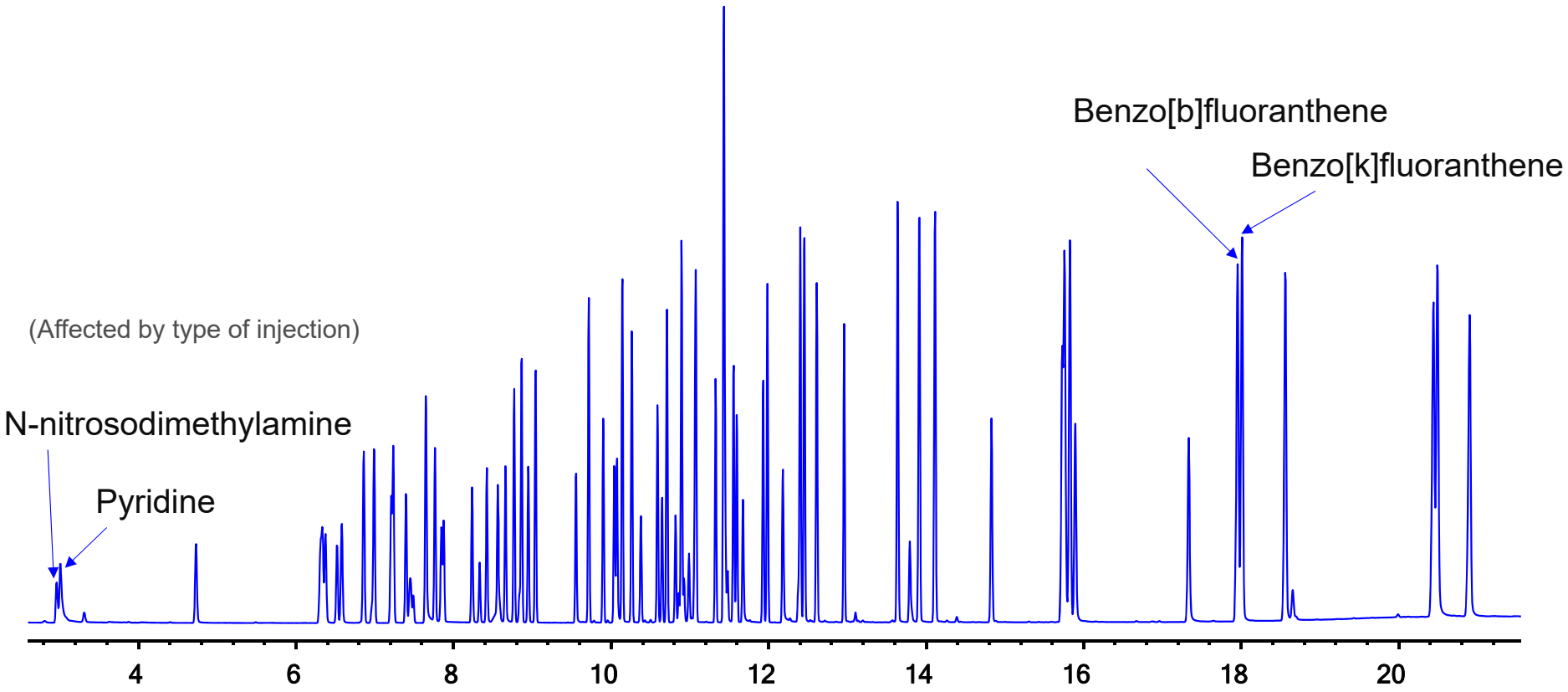
UI Universal Low Pressure Drop (LPD) Liner 5190-2295

We found this LPD 2295 liner to work better, especially in UI coated inlets. This liner has the smaller OD of a split liner and is not so tight a fit.

Compounds in calibration standards

Phenols	Nitros	Nitrosos	PAHs	Misc
Phenol, 2-fluoro-	Nitrobenzene-D5	N-Nitrosodimethylamine	Naphthalene	1,3-dichlorobenzene
Phenol-d6-	nitrobenzene	N-Nitrosodipropylamine	2-methylnaphthalene	1,4-dichlorobenzene
Phenol	2-nitrophenol	N-Nitrosodiphenylamine	2-fluorobiphenyl	Benzyl alcohol
2-chlorophenol	2- nitroaniline		2-chloronaphthalene	1,2-dichlorobenzene
2 methylphenol	2,6-dinitrotoluene	**Phthalates**	Acenaphthylene	Hexachloroethane
p-Cresol	3-Nitroaniline	Dimethyl phthalate	Acenaphthene	Isophorone
2,4- Dimethylphenol	2,4-dinitrophenol	Diethyl Phthalate	Fluorene	1,2,4-trichlorobenzene
2,4-dichlorophenol	4-nitrophenol	Dibutyl phthalate	Phenanthrene	Hexachlorobutadiene
4-chloro-3-methylphenol	2,4-dinitrotoluene	Benzyl butyl phthalate	Anthracene	Hexachlorocyclopentadien
2,4,5-trichlorophenol	4-Nitroaniline	Bis(2-ethylhexyl) phthalate	Fluoranthene	Azobenzene
2,4,6-trichlorophenol		Di-n-octyl phthalate	Pyrene	Hexachlorobenzene
2-methyl-4,6-dinitrophenol	**Acids**		p-Terphenyl-d14	
2,4,6-tribromophenol	Benzoic acid		Benz[a]anthracene	
Pentachlorophenol			Chrysene	
			Benzo[b]fluoranthene	
Bases	**Ethers**	**ISTDs**	Benzo[k]fluoranthene	
benzidine	Bis(2-chloroethyl) ether	1,4-Dichlorobenzene-D4	Benzo[a]pyrene	
Pyridine	Bis(2-chloro-1-methylethyl) ether	Naphthalene-D8	Indeno[1,2,3-cd]pyrene	
Aniline	bis(2-chloroethoxy)-methane	Acenaphthene-D10	Dibenz[a,h]anthracene	
4-Chloroaniline	4 chlorophenylphenyl ether	Phenanthrene-D10	Benzo(g,h,i)perylene	
Carbazole	4 bromophenylphenyl ether	Chrysene-D12		
3,3'-Dichlorobenzidine	Dibenzofuran	Perylene-D12		

77 Compounds and 6 ISTDs



TIC: 50ppm_NewMix_0.D\data.ms

Instrument optimization – fit the range to a specific system

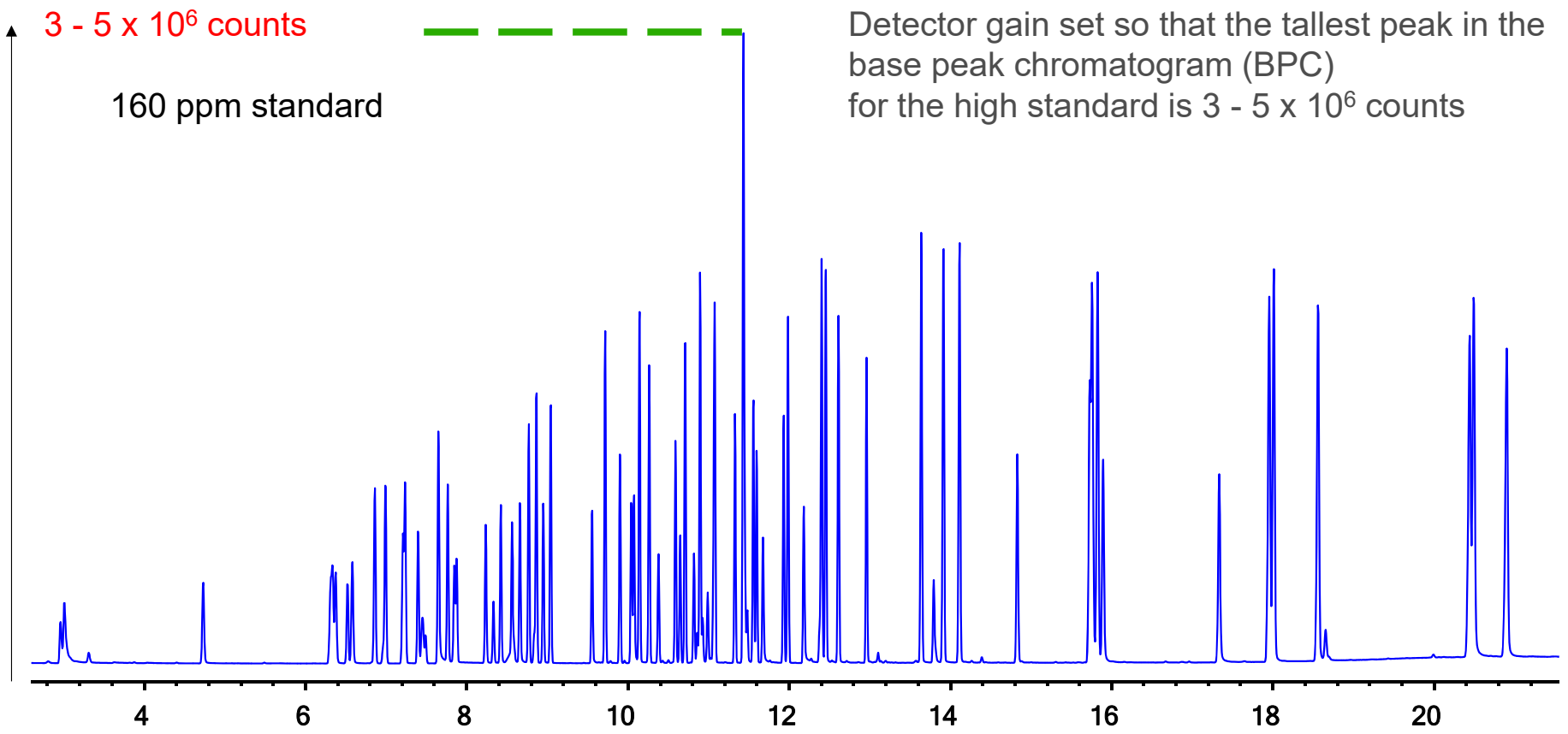
1. Inject the highest calibration standard, at a low gain setting (e.g., 1), adjust the split ratio (or ramped flow)

   - check performance of low responders
   - look for overloaded peak shapes
   - ensure that the separation of benzo[b] and benzo[k] fluoranthene isomers meets requirements (>50%)

2. Properly set the gain factor so that the BPC tallest peak is 3-5 x 10^6 counts (SQ) or 10^7 (TQ)

   - Avoid detector saturation

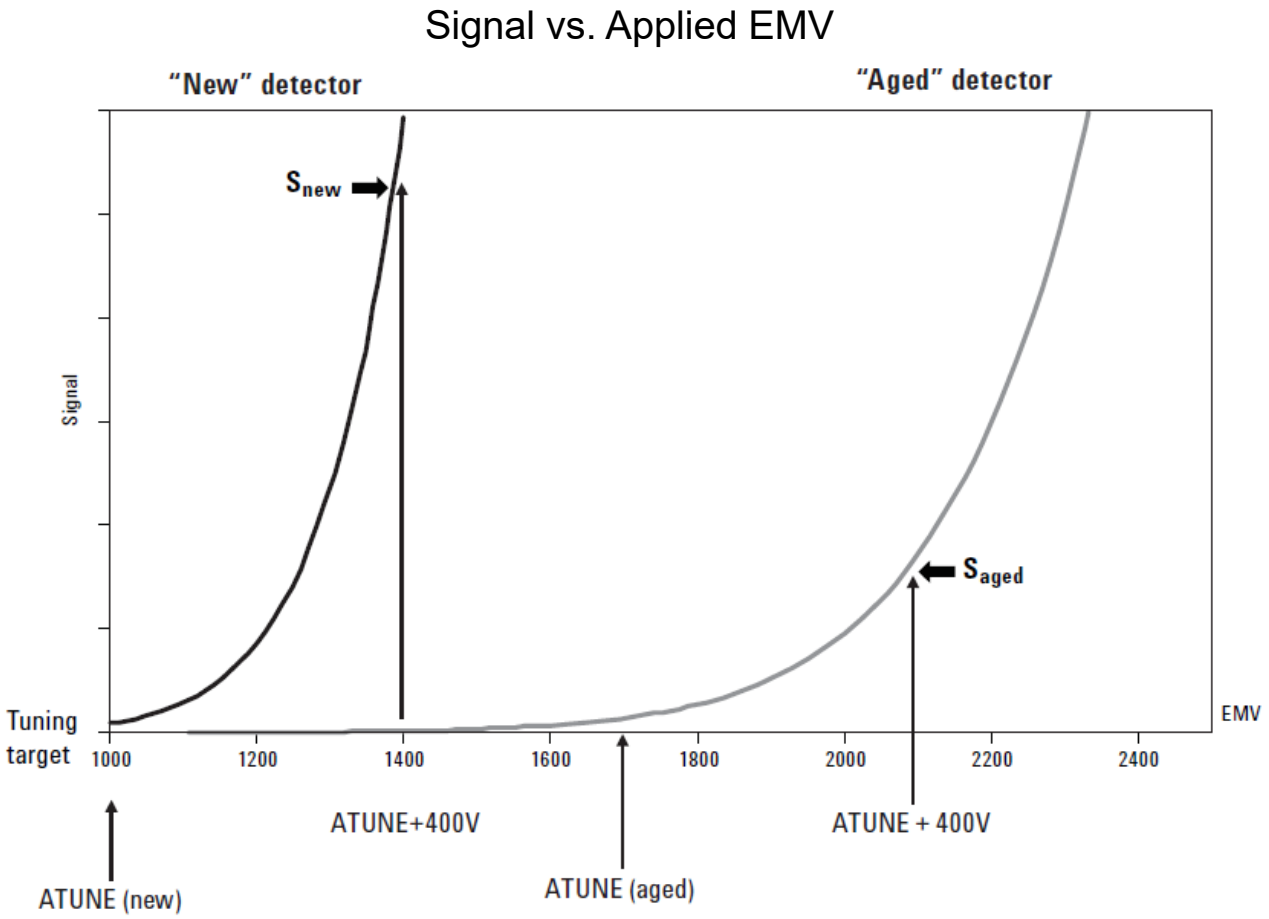
Instrument optimization – fit the range to a specific system



Detector gain set so that the tallest peak in the base peak chromatogram (BPC) for the high standard is 3 - 5 x 10^6 counts

TIC: 50ppm_NewMix_0.D\data.ms

Why is gain factor important? The detector ages over time



Analysis of individual batches

Data points for each compound were deleted in some cases to meet method criteria (lower, upper end of range)

Results were entered into a spreadsheet columns (for each batch)

- average %RSD for the entire 77-compound list
- number of compounds that met average RF %RSD criteria
- those that required a linear curve fit

Initial calibration batch review showing tracking of exceptions

0.05 – 160 ppm (10 points)

Avg RF %RSD: green if passes (≤ 20%)

Blue if linear fit

Pulsed split 3:1 Inst 1, LPD liner, 9mm Analyst 1 Atune

All curve fits are LINEAR unless there is an Exception

Calibration is 0.05 - 160 ppm, 10 Levels = 0.05, 0.2, 0.5, 2, 5, 20, 50, 80, 120, 160 (4 ppm IS constant)

				Exceptions			
Name	RT	Avg. RF RSD	CF R2	Cal Range	# points	Curve fit	pts deleted
N-Nitrosodimethylamine	3.010	25.4	1.000				
Pyridine	3.052	9.8	1.000				
Phenol, 2-fluoro-	4.764	13.6	1.000				
Phenol-d6-	6.347	14.2	1.000				
Phenol	6.374	11.7	0.999				
Aniline	6.411	7.7	0.993				
Bis(2-chloroethyl) ether	6.561	2.8	1.000				
2-chlorophenol	6.615	12.4	1.000				

Exceptions – range, # points deleted, etc.

Summary of all batches spreadsheet - sorted for best results

Excerpt, ranked by lowest average %RSD:

System	Inlet	Lens	Injection	Liner	Tune	Pass	Chemist	77 Cmpds	# Cmpds	# Cmpds	# Cmpds	CAL	# Cmpds	# Points	Presumptive		Compounds that are
	Coat.	diam.	Type		Type	DFTPP		Avg %RSD	< 20% RSD	Linear	Quadr	Range	Deleted	Deleted	Cal Range		Exceptions
System 2	C	9	RF	LPD	A	Y	a	10.2	73	3	1	0.05-160	14	24	**0.2**	**160**	7
System 2	C	9	3:1 PSP	LPD	A	Y	a	11.2	69	7	1	0.05-160	9	13	**0.2**	**160**	4
System 3	C	9	RF	LPD	D	Y	b	11.3	70	6	1	0.05 - 160	34	51	**0.5**	**160**	6
System 2	C	6	RF	Split	A	Y	a	11.5	66	10	1	0.05 - 160	18	31	**0.5**	**160**	5

- number of compounds that required point deletion to meet acceptability criteria
- total number of data points deleted for all compounds (to meet criteria)
- presumptive working calibration range for each compound

  - useful range when the number of exceptions was < 8 of 77 compounds, or 10% of the target list

- number of compound exceptions to that range (acceptable, but outside the working range)

Improved sensitivity for low responding compounds with 9mm lens

MDL ratios were calculated for easy comparison (3 vs. 6mm and 3 vs. 9 mm)

On the table on the next slide:

Higher ratios (>1) show that the MDL is lower (better sensitivity) using a larger diameter lens

- MDL Criterion: “MDL” is the amount (pg) required to achieve S/N ≥ 5
  - MH Quant – noise regions manually selected
  - peak-to-peak

Improved sensitivity for low responding compounds with 9mm lens

	r.t.	MDL ratio 3mm/6mm	MDL ratio 3mm/9mm		r.t.	MDL ratio 3mm/6mm	MDL ratio 3mm/9mm
Acenaphthene	10.904	0.2	0.3	Phenol-d6-	6.337	0.8	0.8
Diethyl Phthalate	11.327	0.3	0.7	Fluorene	11.439	0.8	0.5
Phenol, 2-fluoro-	4.764	0.4	0.2	2,4,6-tribromophenol	11.685	0.9	1.0
4 chlorophenylphenyl ether	11.445	0.4	0.2	2-methylnaphthalene	9.733	0.9	0.7
bis(2-chloroethoxy)-methane	8.578	0.4	0.3	Benz[a]anthracene	15.777	1.0	0.7
Di-n-octyl phthalate	17.344	0.4	0.6	Benzo[b]fluoranthene	17.975	1.0	0.9
Hexachlorobutadiene	9.054	0.5	0.5	1,2-dichlorobenzene	7.267	1.0	0.4
Chrysene	15.841	0.5	0.4	4 bromophenylphenyl ether	11.942	1.0	0.8
Carbazole	12.621	0.6	0.7	N-Nitrosodipropylamine	7.668	1.0	0.7
2-fluorobiphenyl	10.156	0.6	0.5	1,3-dichlorobenzene	6.893	1.0	0.4
Dimethyl phthalate	10.594	0.6	0.9	1,2,4-trichlorobenzene	8.786	1.0	0.3
Phenanthrene	12.413	0.6	0.3	Benzo[k]fluoranthene	18.029	1.0	1.0
Naphthalene	8.883	0.6	0.8	Bis(2-ethylhexyl) phthalate	15.9	1.1	1.3
Dibenzofuran	11.086	0.6	0.4	1,4-dichlorobenzene	7.027	1.1	0.4
2-chloronaphthalene	10.279	0.7	0.9	Benzo(g,h,i)perylene	20.923	1.1	0.5
Fluoranthene	13.648	0.7	1.0	2,4-dinitrophenol	10.937	1.1	1.5
Hexachlorobenzene	11.99	0.7	0.3	Pyrene	13.926	1.2	1.6
Hexachloroethane	7.792	0.7	0.5	Benzyl butyl phthalate	14.841	1.2	1.2
4-Chloroaniline	8.968	0.7	0.5	3-Nitroaniline	10.83	1.2	1.0
Bis(2-chloro-1-methylethyl) ether	7.471	0.8	0.3	2,4-dichlorophenol	8.674	1.2	0.6

	r.t.	MDL ratio 3mm/6mm	MDL ratio 3mm/9mm		r.t.	MDL ratio 3mm/6mm	MDL ratio 3mm/9mm
p-Terphenyl-d14	14.124	1.2	0.7	Pentachlorophenol	12.188	1.9	2.6
Acenaphthylene	10.723	1.3	0.8	2,4,6-trichlorophenol	10.086	1.9	1.3
Anthracene	12.461	1.3	0.9	2,4,5-trichlorophenol	10.054	2.0	1.5
Pyridine	3.069	1.3	0.6	Benzoic acid	8.519	2.1	7.2
3,3'-Dichlorobenzidine	15.745	1.3	1.3	2-nitrophenol,	8.353	2.3	2.5
Hexachlorocyclopentadiene	9.915	1.3	0.7	2-methyl-4,6-dinitrophenol	11.487	2.3	5.3
4-chloro-3-methylphenol	9.567	1.4	1.7	4-Nitroaniline	11.455	2.3	2.1
Benzyl alcohol	7.235	1.4	0.3	2- nitroaniline	10.391	2.4	0.8
2-chlorophenol	6.615	1.4	1.3	Nitrobenzene -D5	7.872	2.4	0.8
Isophorone	8.251	1.5	1.1	Bis(2-chloroethyl) ether	6.556	2.5	1.2
p-Cresol	7.663	1.5	0.7	Aniline	6.412	2.9	1.0
N-Nitrosodimethylamine	3.015	1.6	1.0	Benzo[a]pyrene	18.58	3.0	1.3
N-Nitrosodiphenylamine	11.562	1.7	1.2	benzidine	13.809	3.1	4.9
2,4-dinitrotoluene	11.07	1.7	2.2	nitrobenzene	7.898	3.3	2.4
Phenol	6.363	1.7	1.0	Dibenz[a,h]anthracene	20.511	3.3	3.6
Azobenzene	11.605	1.8	1.9	2,6-dinitrotoluene	10.658	3.8	2.1
Dibutyl phthalate	12.964	1.8	1.2	2 methylphenol	7.417	3.9	0.7
Indeno[1,2,3-cd]pyrene	20.457	1.8	1.5	4-nitrophenol	10.995	4.4	2.4
2,4- Dimethylphenol	8.439	1.9	0.8				

- MDL ratios, small vs. large diameter lens: MDL is defined as the number of pg required to achieve S/N ≥ 5 (p2p)
- Ratios > 1 show that the MDL is lower (better sensitivity) using a larger diameter lens
- Many of the highest responders are seen in the top left of the table:
- These are compounds for which sensitivity is much less of an issue and many have a ratio < 1
- ✓ Many challenging compounds (yellow) improved the most with a 9mm diameter lens (circled in red)

Low responding compounds

Improved sensitivity for low responding compounds with 9mm lens

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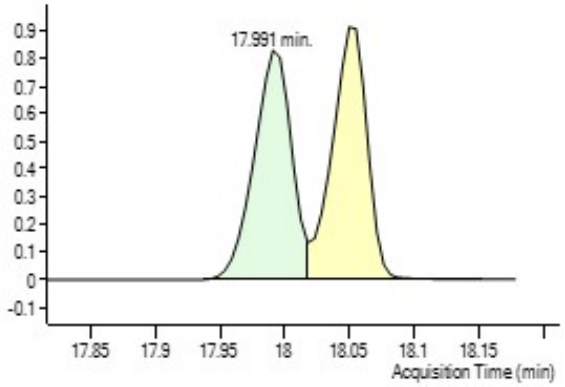
Sensitivity is better or equal using a 6 mm vs. a 3 mm lens (53 of 77 compounds)

9 mm lens vs. 3 mm: 34 of 77 compounds show better or equal sensitivity

Low responding compounds

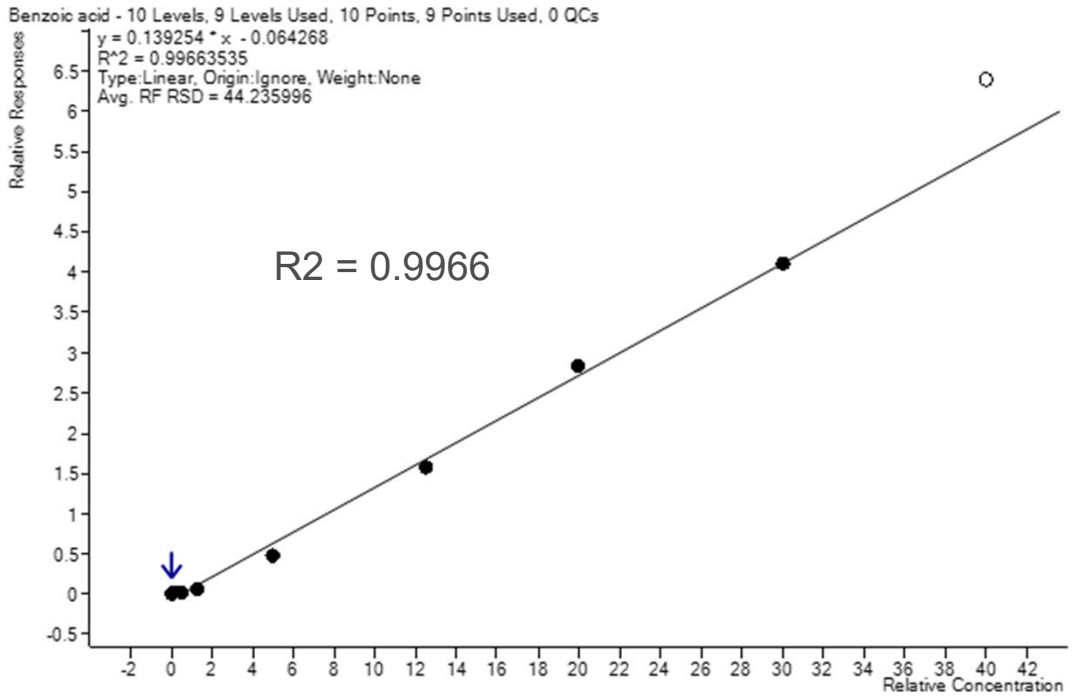
Sufficient peak resolution for benzo [b and k] fluoranthene using a 9mm lens



50 ppm, 1:3 split, LPD liner, 9 mm lens (17 ng injected)

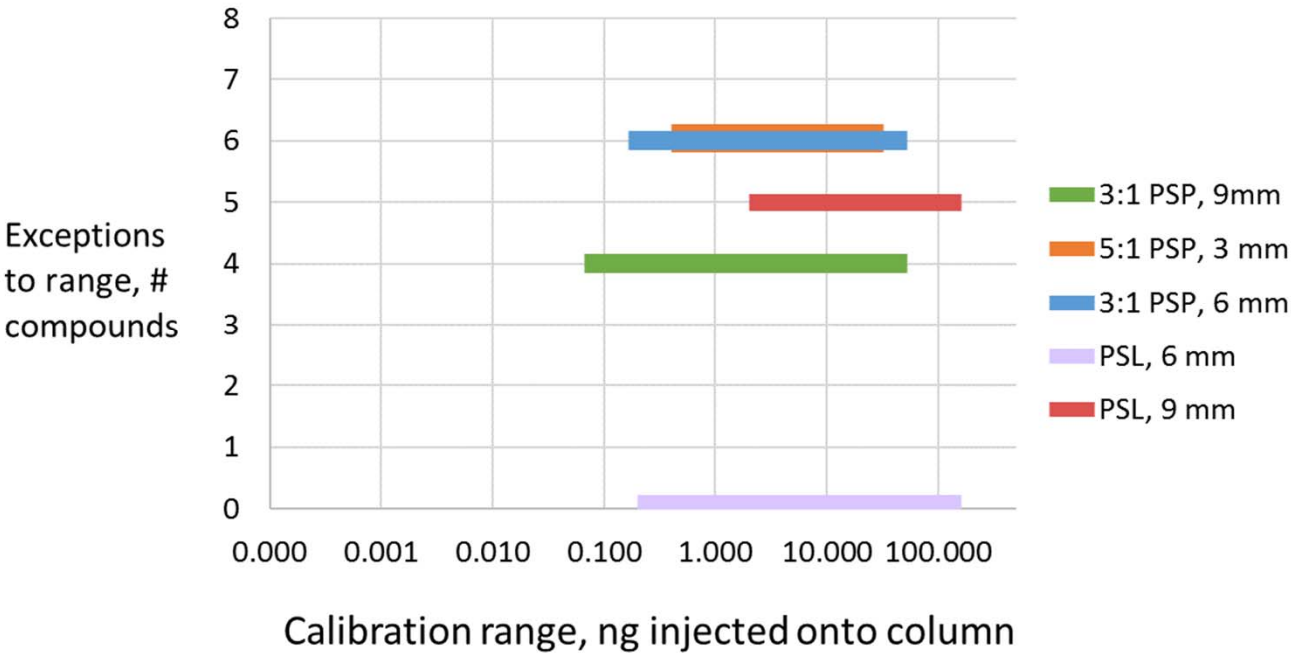
From 8270D: Sufficient resolution is achieved if the height of the valley between two isomer peaks is less than 50% of the average of the two peak heights (at the mid-point concentration level)

Calibration curve for benzoic acid using a 9mm lens



Calibration results for the challenging compound benzoic acid (0.05 – 120 ppm)

Wide calibration range in one injection



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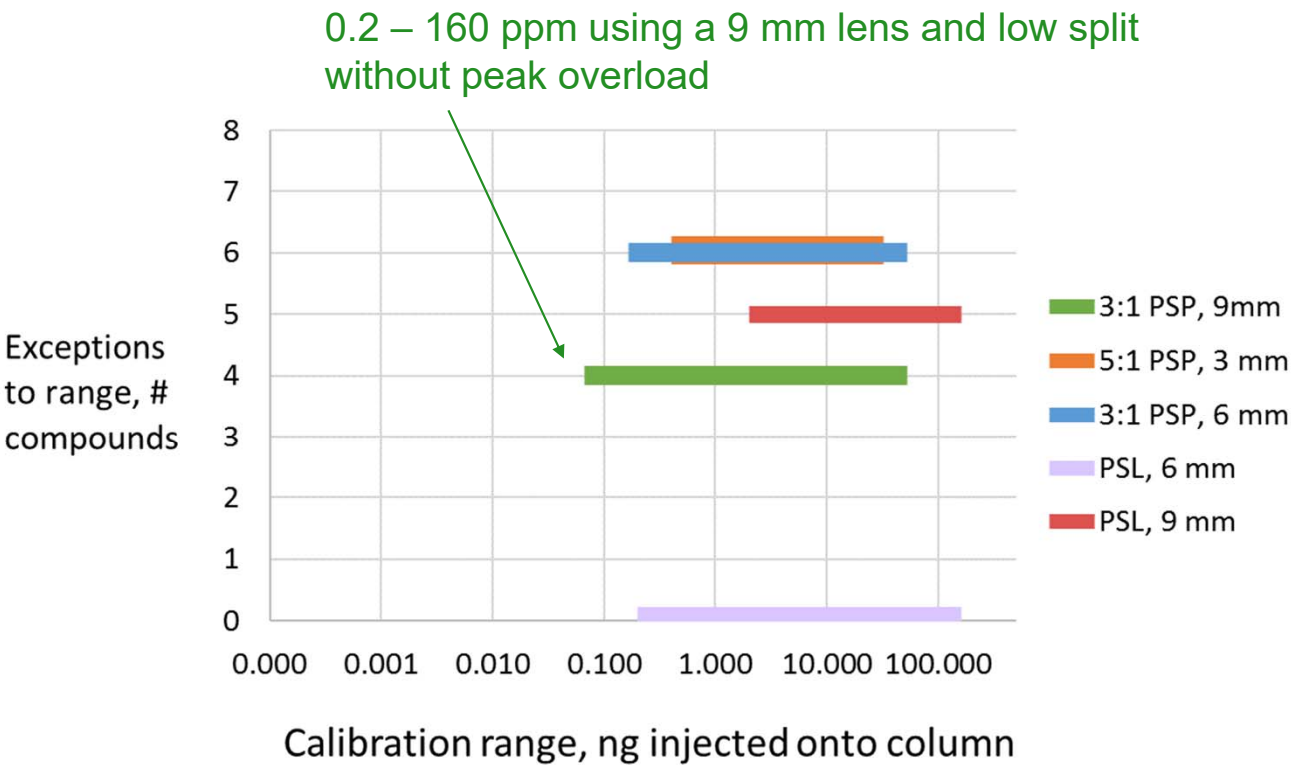

Maximum number of compounds passing criteria and lowest %RSD

(conditions, in order of significance)

- ✓ ion source temperature ≥ 300°C
- ✓ 9mm ion source drawout lens diameter
- ✓ PSP, pulsed split injection - best peak shape, widest calibration range
- ✓ Ultra Inert LPD split liner with wool  Also, the single taper Ultra Inert with glass wool
- ✓ either DFTPP tune or Autotune

Summary of recommended conditions

Injection type	Pulsed split (PSP)	Adjust to avoid peak overload Meet peak resolution criteria
GC liner	Low pressure drop split (LPD)	Best peak shape
column dimensions	30m x 0.25 mm x 0.25 µm DB - UI 8270D	Optimize peak separation
ion source draw out lens diameter	9 mm	Wide calibration range Improves sensitivity for active compounds

Thank you very much