EPA 8270D Re-Optimized for State-of-the-Art Instrumentation Extends Continuing Calibration

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Calibration criteria for 8270D were initially developed on specific instrument platforms and are rigorous due to the diverse mix of target compound classes and the desired wide calibration range. At calibration levels approaching 160 ppm, and using a 0.25 µm column film thickness to avoid long run times, splitless sample injection results in overloaded column capacity and manual integration is often required. Many practitioners have thus adopted a "ramped flow" approach, which reduces the amount injected. In contrast, pulsed split injection, which is allowed by 8270D, was found in this study to be the optimal injection method and is simply configured within the control SW. The goal was to achieve the widest calibration range in just one injection. Initial calibration results are indicative of how long the continuing calibration will last and, thus, the length of time that samples may be analyzed without intervention by the operator, lowering the cost of operation.

**Introduction**

**Experimental**

8270D initial calibration criteria

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

Optimizing each system prior to analysis

Optimizing the amount of sample introduced and detector gain leads to the widest dynamic range: The split ratio (or ramped flow*) was adjusted to meet isomer resolution requirements and avoid wide peaks with rounded tops. The detector gain was adjusted to maximize linearity, which is critical to the analysis.

*Splitless, ramped initial column flow, inlet purge on at approximately 0.5 minutes; reduces column loading.

Optimization results were evaluated for acceptability according to method requirements

- Data points for each compound at the low and high ends of the calibration range (0.05 and 160 ppm, respectively) could be deleted to meet method criteria
- Results were entered into a spreadsheet as the average %RSD for the entire 77-compound list, the number of compounds that met average RF %RSD criteria and those that required a linear curve fit

Determined working calibration range

The working range for a given set of conditions was defined as the useful concentration range when the number of exceptions to that range was ≤ 7 of 77 compounds (~10% of the list). The results spreadsheet could be re-sorted in various ways to better visualize the effects of each variable. Variables that produced the maximum number of compounds passing criteria are listed in the following box.

**7890B/5977B MSD Inert Plus**

- Four Agilent gas chromatographs, SSL inlet
- 30m x 250µm x 0.25µm DB-UI 8270D column (p/n 122-9732)

Ten calibration levels were prepared from 0.05 to 160 ppm using a 77-compound mix and six ISTDs. ISTD concentration was at the mid-point.

**Variables tested**

- Pulsed splitless (PSL), pulsed split (PSP) injection; less conventional "ramped flow" approach
- Liners: Agilent dual taper (p/n 5190-3315); Ultra Inert low pressure drop (LPD) split liner with wool (p/n 5190-2295); single taper Ultra Inert with glass wool (p/n 5190-2293); high performing, non-Agilent
- DFTPP, Autotune
- Ion source draw out lens diameter: 3 mm (standard), 6 mm, and 9 mm
- Source temperature

**Analysis of data sets and results spreadsheet**

- Calibration results were evaluated for acceptability according to method requirements
- Data points for each compound at the low and high ends of the calibration range (0.05 and 160 ppm, respectively) could be deleted to meet method criteria
- Results were entered into a spreadsheet as the average %RSD for the entire 77-compound list, the number of compounds that met average RF %RSD criteria and those that required a linear curve fit
- Tracked were the number of compounds that required point deletion to meet acceptability criteria, the total number of data points deleted for all compounds to meet criteria, the presumptive working range, and the number of exceptions to that range (acceptable, but outside the working range).
Variable that produced the maximum number of compounds passing criteria and lowest %RSD

(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

This study was aimed at reaching the broadest calibration range possible. Alternate approaches may be taken to increase overall method sensitivity, such as limiting the range, in which case lower MDLs easily may be achieved.

After the initial calibration step, continuing calibration checks are required every 12 hours in regulated laboratories. Lower %RSD values, as the average for all 77 compounds, are indicative of a longer lasting calibration and are desirable.

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 (Optimize peak separation)
- Ion source draw out lens diameter: 9 mm (Wide calibration range; Improves sensitivity for active compounds)

8270D allows for split injection, which improves method performance when compared to splitless, pulsed splitless and ramped flow techniques. Further enhancement in performance is achieved by the use of a GC liner that is optimized for split injection (p/n 5190-2295).

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

50 ppm, 1:3 split, LPD liner, 9mm 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)
Improved sensitivity for low responding compounds with 9mm lens

<table>
<thead>
<tr>
<th>Compounds</th>
<th>MDL ratio r.t.</th>
<th>3mm/6mm</th>
<th>3mm/9mm</th>
<th>3mm/6mm</th>
<th>3mm/9mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acenaphthene</td>
<td>10.904</td>
<td>0.2</td>
<td>0.3</td>
<td>6.337</td>
<td>0.8</td>
</tr>
<tr>
<td>Diethyl Phthalate</td>
<td>11.327</td>
<td>0.3</td>
<td>0.7</td>
<td>11.439</td>
<td>0.8</td>
</tr>
<tr>
<td>Phenol, 2-fluoro-</td>
<td>4.764</td>
<td>0.4</td>
<td>0.2</td>
<td>2,4,6-tribromophenol</td>
<td>11.685</td>
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<tr>
<td>4-chlorophenylphenyl ether</td>
<td>11.445</td>
<td>0.4</td>
<td>0.2</td>
<td>2-methylphenanthrene</td>
<td>9.733</td>
</tr>
<tr>
<td>bis(2-chloroethoxy)methane</td>
<td>8.578</td>
<td>0.4</td>
<td>0.3</td>
<td>15.777</td>
<td>1.0</td>
</tr>
<tr>
<td>Di-n-octyl phthalate</td>
<td>17.344</td>
<td>0.4</td>
<td>0.6</td>
<td>Benzo[a]fluoranthene</td>
<td>17.975</td>
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<tr>
<td>Hexachlorobutadiene</td>
<td>9.054</td>
<td>0.5</td>
<td>0.5</td>
<td>1,2-dichlorobenzene</td>
<td>7.267</td>
</tr>
<tr>
<td>Chrysene</td>
<td>15.841</td>
<td>0.5</td>
<td>0.4</td>
<td>4 bromophenylphenyl ether</td>
<td>11.942</td>
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<tr>
<td>Carbazole</td>
<td>12.621</td>
<td>0.6</td>
<td>0.7</td>
<td>N,Nitrosodipropylamine</td>
<td>7.688</td>
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<tr>
<td>2-fluorobiphenyl</td>
<td>10.156</td>
<td>0.6</td>
<td>0.5</td>
<td>1,3-dichlorobenzene</td>
<td>6.893</td>
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<tr>
<td>Dimethyl phthalate</td>
<td>10.594</td>
<td>0.6</td>
<td>0.9</td>
<td>1,2,4-trichlorobenzene</td>
<td>8.786</td>
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<tr>
<td>Phenanthrene</td>
<td>12.413</td>
<td>0.6</td>
<td>0.3</td>
<td>Benzo[k]fluoranthene</td>
<td>18.029</td>
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<tr>
<td>Naphthalene</td>
<td>8.883</td>
<td>0.6</td>
<td>0.8</td>
<td>Bis(2-ethylhexyl) phthalate</td>
<td>15.9</td>
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<tr>
<td>Dibenzo-furan</td>
<td>11.086</td>
<td>0.6</td>
<td>0.4</td>
<td>1,4-dichlorobenzene</td>
<td>7.027</td>
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<td>2-chloronaphthalene</td>
<td>10.279</td>
<td>0.7</td>
<td>0.9</td>
<td>Benzo[g]fluorene</td>
<td>20.923</td>
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<tr>
<td>Fluorantherene</td>
<td>13.648</td>
<td>0.7</td>
<td>1.0</td>
<td>2,4-dinitrophenol</td>
<td>10.937</td>
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<tr>
<td>Hexachlorobenzene</td>
<td>11.99</td>
<td>0.7</td>
<td>0.3</td>
<td>Pyrene</td>
<td>13.926</td>
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<td>Hexachloroethane</td>
<td>7.972</td>
<td>0.7</td>
<td>0.5</td>
<td>Benzo butyl phthalate</td>
<td>14.841</td>
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<tr>
<td>4-Chloroaniline</td>
<td>8.968</td>
<td>0.7</td>
<td>0.5</td>
<td>3-Nitroaniline</td>
<td>10.83</td>
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<tr>
<td>Bis(2-chloro-1-methylethyl)ether</td>
<td>7.471</td>
<td>0.8</td>
<td>0.3</td>
<td>2,4-dichlorophenol</td>
<td>8.674</td>
</tr>
</tbody>
</table>

- **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)

**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**

**Conclusions**

EPA 8270D, which is a regulated, legacy method that is currently used throughout the environmental industry, has been rigorously tested on multiple systems and re-optimized for state-of-the-art instrumentation. Standard column dimensions allowed for the best separation for 77 compounds. Properly adjusted sample amounts (column loading) achieved through a fully supportable pulsed split injection, choice of GC liner, detector gain setting and ion source draw out lend diameter combine to greatly enhance method performance and reduce the need for manual integration. Calibration using one injection for a broad range and low method %RSDs translate to extended continuing calibration and greater laboratory productivity. Lowering the MDLs even further is possible by narrowing and lowering the calibration range, in which case column overloading is avoided.

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