

EPA 8270 Re-optimized for Widest Calibration Range on the 5977 Inert Plus GC/MSD

Authors

Melissa Churley,
Mike Szelewski, and
Bruce Quimby
Agilent Technologies, Inc.

Introduction

The methodology described within United States EPA Method 8270 for the analysis of semivolatile organic compounds by GC/MS is applicable to other regions worldwide. The method presents several analytical challenges due to the requirement for simultaneous measurement of diverse classes of compounds over a wide concentration range. The 5977A and B Inert Plus GC/MSD meet the performance requirements of Method 8270D/E over a working range of 0.2–160 ppm using a single injection (one calibration). Initial calibration results are indicative of how long the continuing calibration will last and, thus, the length of time samples may be analyzed without intervention by the operator, which lowers the cost of operation. A wider calibration range and low compound %RSDs were achieved with this method.

Method

The Agilent 7890B GC coupled to an Agilent 5977A or B Inert Plus GC/MSD was equipped with a SSL inlet, low pressure-drop (LPD) GC inlet liner (p/n 5190-2295), and a 30 m × 0.25 mm, 0.25 μm 5 % phenyl (polysiloxane) column for best separation (p/n DB-UI 8270D). The ion source was equipped with a 9 mm diameter draw out lens (p/n G3870-20449). Other sets of conditions evaluated included the use of the single taper glass wool (STGW) UI liner (p/n 5190-2293), and the standard 3 mm and 6 mm draw out lenses. Atune was evaluated using the DFTPP criteria set forth by the USEPA EPA (8270D and E). The injection volume was 1 μL in pulsed split mode. Ten calibration levels were prepared from 0.05 to 160 ppm using a 77-compound mix and six ISTDs. ISTD concentration was at the midpoint. Agilent MassHunter Workstation software was used for data acquisition and processing.

System optimization

Optimizing the amount of sample introduced and the detector gain leads to the widest dynamic range. Using the highest-level calibration standard (160 ppm), the split ratio was adjusted to meet benzo[b and k]fluoranthene isomer resolution requirements and avoid wide peaks with rounded tops; this ratio was generally under 1:10. Detector gain was adjusted to maximize linearity, which is critical to the analysis. For the MSD, gain was set so that the tallest peak in the base peak chromatogram (BPC) for the highest-level calibration standard used was in the range of 3–5 × 10⁶ counts.

Passing criteria

A multipoint calibration was run, and the relative response factor was determined for each component at each calibration level. The mean response factor was then calculated across the average relative response factors for the calibration curve of each compound, along with its relative standard deviation (RSD). Passing criteria are that the average response factor %RSD must be ≤20 (preferred as default passing criteria); if not, R² ≥0.990 is required for a linear curve fit; finally, a quadratic fit may be used. Accuracy for the lowest data point must be ±30 %, and six points are needed when a curve fit is used.

Calibration results

Calibration results obtained on several instruments on different days were evaluated for acceptability. Data points for each compound at the low and high ends of the calibration range (0.05 and 160 ppm, respectively) were deleted to meet method criteria. The practical working range and the number of compound exceptions to that range (acceptable, but at a range narrower than the working range) were determined. The practical range of the method was defined as the useful concentration range when the number of compound exceptions is <10 % of the of compounds in the target list (Table 1).

Table 1. Average RF %RSD and practical working range.

| Number of compounds with average RF %RSD <20 | Average RF %RSD for 77 compounds (average of three batches) | Practical working range (ppm) | Number of calibration batches |
|--|---|-------------------------------|-------------------------------|
| 66 | 12 | 0.2–160 | 3 |

Table 1 shows results for a method that used a 1:3 split, the LPD liner, and a 9 mm diameter draw out lens. Values are averages based on results from three initial calibration batches. Compounds that passed the average RF %RSD criteria were 66 out of 77. A linear fit was used for 10 compounds, on average. The exception was benzidine, which usually required a quadratic fit and did not always pass the criteria under this set of conditions. The average RF %RSD for the list of 77 compounds in each batch was calculated, and the average of this value was 12 % (including benzidine) over the three calibration batches. Results were similar when using the single taper glass wool (STGW) UI liner. However, use of the 9 mm diameter draw out lens versus the 3 or 6 mm was clearly advantageous in terms of recovery of the most challenging classes of compounds, and led to the widest overall calibration range for the analysis.

The practical, working range of the analysis is 0.2–160 ppm when the number of compound exceptions to this range is maintained at six or less, which is a rigorous approach. However, the overall range can be as wide as 0.05–160 ppm, if up to 10 exceptions are present. Compounds with narrower analysis ranges, such as benzoic acid and benzidine, are generally known to be the most challenging in terms of GC technology.

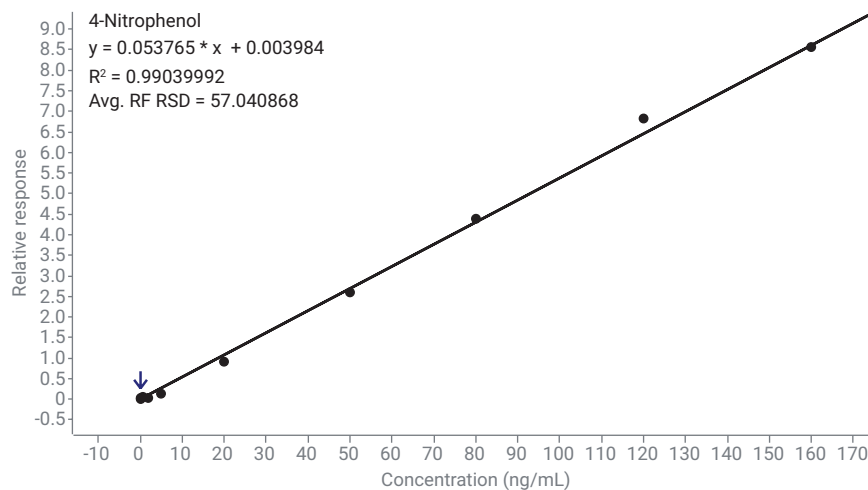


Figure 1. Example calibration results for the challenging compound 4-nitrophenol. The acceptable analysis range is 0.05–160 ppm ($R^2 = 0.9904$; linear fit) using a 1:3 split, the LPD liner, and 9 mm diameter draw out lens.

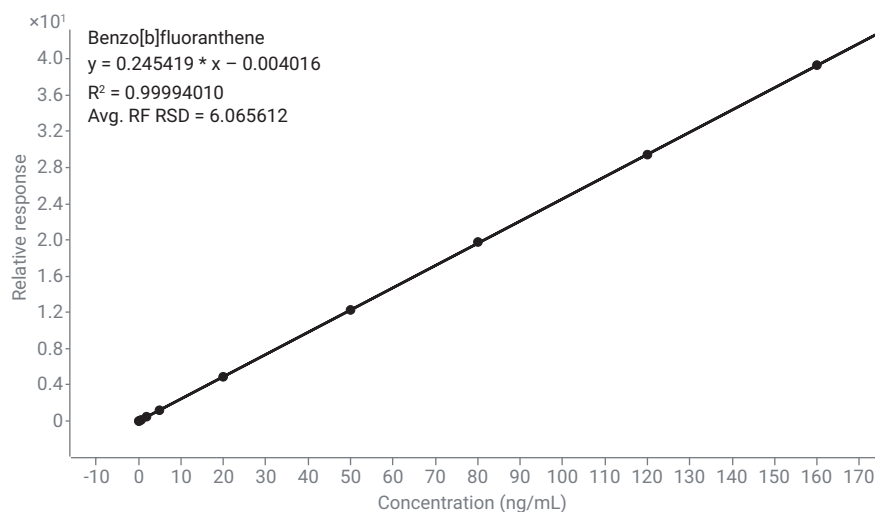


Figure 2. Example calibration results for benzo[b]fluoranthene. The acceptable analysis range is 0.05–160 ppm (Avg RF %RSD = 6.1; $R^2 = 0.9999$; linear fit) using the same conditions described in Figure 1.

Conclusion

EPA 8270D is a regulated, legacy method currently used throughout the environmental industry, and has been re-optimized for state-of-the-art instrumentation. Standard column dimensions enabled the best separation for 77 compounds. Properly adjusted sample amounts achieved through a fully supportable pulsed split injection, choice of GC liner, detector gain setting, and ion source draw out lens diameter combine to greatly enhance method performance and reduce the need for manual integration. Calibrating using one injection for the entire range and low method %RSDs translate to extended continuing calibration and greater laboratory productivity.

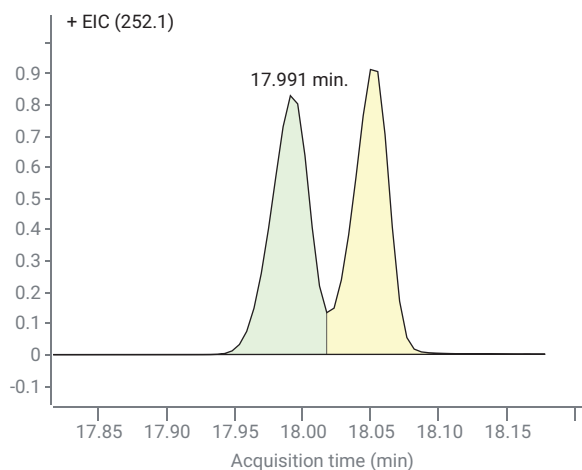


Figure 3. Benzo[b and k]fluoranthene isomer resolution at 50 ppm (midpoint). Split is 1:3 (17 ng injected), LPD liner, and 9 mm diameter draw out lens. Sufficient resolution is achieved if the height of the valley between two isomer peaks is less than 50 % of the average of the two peak heights at the midpoint concentration level (8270D).

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