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Research Report: D02-1816

Relative Bias Assessment of D5769 as an Alternative to D3606 for Determination of Benzene in Gasoline

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Summary

This study was conducted to establish that ASTM D5769 meets EPA requirements[1] for use as an alternative method to determine the volume percent of benzene in gasoline. The study was based on robust means and robust standard deviations of measurements from 106 fuels distributed between January, 2006 and October, 2014 by the Reformulated Gasoline program of the ASTM Proficiency Testing Program (Interlaboratory Crosscheck Program). It applied the statistical procedures of D6708, *Standard Practice for Statistical Assessment and Improvement of Expected Agreement Between Two Test Methods that Purport to Measure the Same Property of a Material*.

This evaluation meets the requirements of D6708, with a recommended bias adjustment and no observed sample-specific biases.

The principal findings and conclusions of the study are as follows:

- Benzene concentrations of 106 fuels were determined by multiple labs by both methods. Benzene concentrations ranged from 0% to 2.47% by volume as measured by non-outlying labs using D3606. Robust mean concentrations ranged from 0.06% to 2.17% by D3606.

- The reproducibilities of the two methods as determined from these data are 46% and less than 1% smaller, respectively, than the reproducibilities for benzene published in the active versions of the standards as of this writing: D5769-10 and D3606-10.

- The data meet the requirements of D6708, in that they displayed adequate variation among concentrations of the fuels, sufficient correlation between the methods, and adequate randomness of the weighted residuals.

- A constant bias was observed between the methods. The correction equation was calculated as

$$C_{Adjusted} = C_{D5769} + 0.01.$$

- The variability of residuals was consistent with that expected due only to measurement error: there were no discernable sample-specific biases. The between-methods reproducibility – the root mean square of the reproducibilities of the two methods – for these data averaged 16% smaller than the reproducibility of D3606-10.

These conclusions, when taken together, affirm that the evaluation meets the requirements of D6708, with passing category A3.

[1] 40 C.F.R. § 80.47.

This report specifies the data analyzed, describes all steps of the analysis, and presents the results from each step. The report is supported with a number of graphics which are integrated into the text. Supporting tables are found in an appendix.

Statistical Report

The Data

API obtained from ASTM the raw results provided by Proficiency Test Program (PTP) participants. These data included measurements of the volume percent benzene (by either of the two methods) on 123 fuels distributed by ASTM's Reformulated Gasoline (RFG) and Motor Gasoline Programs. RFG samples are distributed monthly and 106 fuels were distributed between January, 2006 (RFG0601) and October, 2014 (RFG1410). Motor Gasoline is distributed three times yearly, and 17 fuels were distributed between April, 2009 and October, 2014. Results were provided with labs identified by codes. To preserve laboratory anonymity, the codes were not consistent from one month to the next – it was not possible to track an individual lab's results over time. All results submitted were provided for every fuel sample, including those results that had been identified and excluded as outliers after the first pass of the robust routine. The robust means and standard deviations as calculated from the second pass of the robust routine were not provided. They are available from the monthly reports, but were recomputed as a part of this data analysis and verified by spot checking against the reports.

Following verbal instructions from EPA staff, fuels measured by fewer than 16 non-outlying labs by either method were excluded from this study. None of the seventeen fuels from the Motor Gasoline program were measured by 16 or more labs, so all were excluded. None of the 106 fuels from the RFG program were excluded. Among these remaining fuels, the benzene concentrations ranged from 0% to 2.47% by volume, as measured by D3606 and from 0.05% to 2.50% by volume as determined by D5769.

The robust means and standard deviations, numbers of participating labs, and numbers of non-outliers for each of the monthly distributions are displayed in Table 1 in the appendix. Tables 3 and 4 contain the complete set of data, by individual result. Results preceded with asterisks were identified as outliers by ASTM.

Precisions and Calculated Standard Errors

Paralleling the regression procedures of D6300, the logarithms of the robust standard deviations were regressed against the logarithms of the robust means, in order to determine the best fitting model for standard deviation (and thus reproducibility) as a function of benzene concentration. The forms considered were

$s = K(C + B_0)$, equivalently $R = 2.77K(C + B_0)$, the *linear* form,

or

$s = KC^B$, equivalently $R = 2.77KC^B$, the *power* form.