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Committee D02 on Petroleum Products and Lubricants
Subcommittee D02.04 on Hydrocarbon Analysis

Research Report RR #D02-1446

Inter-Laboratory Study to Establish Precision Statements for ASTM D6379, Standard Test Method for Determination of Aromatic Hydrocarbon Types in Aviation Fuels and Petroleum Distillates—High Performance Liquid Chromatography Method with Refractive Index Detection

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DETERMINATION OF AROMATIC HYDROCARBON TYPES IN AVIATION FUELS BY HIGH PERFORMANCE LIQUID CHROMATOGRAPHY

Dear Colleague,

Thank you for agreeing to participate in this round robin study organised on behalf of the Institute of Petroleum. The proposed test method uses high performance liquid chromatography with refractive index detection to quantify mono-aromatic and di-aromatic compounds in aviation fuels and other petroleum products in the 50° - 300°C boiling range. A copy of the method is enclosed with this letter. Please read through it carefully and contact the undersigned if you have any comments or queries regarding the method. Those laboratories performing the IP391/90 test method (Determination of Aromatic Hydrocarbon Types in Diesel Fuels) will already be familiar with the method protocol. Ten kerosene samples selected from the recent ASTM D1840 round robin will be despatched under separate cover.

The main difference between this method and IP391/90 is the use of a high resolution column set to effect a separation between the various di-aromatic hydrocarbons (naphthalenes, biphenyls and fluorenes). In our laboratory we employ two 15cm x 0.46cm Spherisorb 3µm NH_2 cartridge columns connected in series. Other stationary phases, column dimensions and particle sizes may be suitable. The improved separation allows naphthalenes to be quantified as a subset of the total di-aromatic fraction. Data are reported on a m/m basis (IP391/90 reports on a v/v basis) although it is still possible to determine v/v if required.

IMPORTANT: Do not despair if you do not have a sufficiently high resolution column set to perform the test method as written. Follow the instructions using a conventional column (typically this would be a single 250 x 4.6 mm ID 5µm amino or a 150 x 4.6 mm ID 3µm amino column) and report the data as mono-, di- and total aromatics only (i.e. do not attempt to quantify the naphthalenes as a subset of the di-aromatics). An example chromatogram on a 'low resolution' column is appended to this letter. For your information, the main reason for developing a method to determine naphthalenes (rather than total di-aromatics) was to offer an alternative to ASTM D1840. In spite of its method title, however, ASTM D1840 actually measures di-aromatic content, though not as accurately as this HPLC method or the recent version of ASTM D5186. It may be more appropriate therefore to re-write this HPLC method

for the determination of mono-, di- and total aromatics only. Your data, whether on a high resolution or a low resolution column set, is therefore critical to the success of the round robin.

Round Robin Details

1. Analyse each sample in duplicate. This means:

(i) Same operator
(ii) Same instrumentation/laboratory
(iii) Each sample solution should be freshly prepared (i.e. duplicate analyses should **not** be performed on the **same** sample solution).

It is not necessary however to prepare fresh calibration solutions before repeating the duplicate analyses. The reason for this is that the calibration solutions have a long shelf life if stored correctly; in real situations therefore a laboratory performing duplicate analyses on a sample will always use the same calibration standards. The round robin exercise should mimic as closely as possible what happens in the real world!! For the same reason it is permissable to analyse the duplicates in the same batch as the original analyses, i.e. there is no need to have an artificial delay of, say, one week between the first analysis and the duplicate analysis. It is recommended however that you should perform the analysis on all the samples first before repeating the analyses (on fresh solutions) to obtain duplicate results.

2. The order of analysis should be randomly chosen, i.e. do not analyse the samples in alphabetical order (A through K).

3. Report data on the calibration standards, i.e. concentrations and peak areas for each standard solution. Remember, the standard concentrations should be close to, but not necessarily exactly, the concentrations given in Table 1. The calibration plots should be linear with an intercept close to zero. Note that if the intercept is non-zero then this can have an adverse effect on the accuracy of the method for samples containing low levels of naphthalenes (di-aromatics). One option would be to force the regression lines (calibration plots) through zero; I can evaluate this option if you provide peak area data for calibration standards and samples.

4. Report original (Run 1) and duplicate (Run 2) peak areas for each sample along with calculated mono-, di- and total aromatic contents.

5. Report any deviations from the written test procedure.

6. Supply chromatograms for each sample if possible. Please indicate the integration baseline and cut points on each chromatogram. Note there is no need to send the duplicate chromatograms unless there was a problem with the analysis.

7. Send all data/chromatograms to:

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