SCREENING PROCEDURE FOR DETERMINATION OF OXYGENATES, AROMATICS, BENZENE, OLEFINS AND DISTILLATION TEMPERATURES IN GASOLINE, AND POLYCYCLIC AND TOTAL AROMATIC HYDROCARBONS, BIODIESEL CONTENT AND CETANE NUMBER IN DIESEL FUEL BY INFRARED SPECTROSCOPY

SOP MV-FUELS-133
Version 4.1
Effective Date: December 1, 2019

Fuels Analysis and Methods Evaluation Section
Chemical Analysis and Emissions Research Branch
Mobile Source Laboratory Division

1 Introduction

1.1 This standard operating procedure (SOP) is used to give screen results to Enforcement Division for several regulated parameters in fuel. In gasoline the following parameters are screened: oxygenates, aromatics, benzene, olefins, and distillation temperatures. In diesel the following parameters are screened: total aromatics hydrocarbons, polycyclic aromatic hydrocarbons, biodiesel content, and cetane number.

1.2 This method is not based on any one American Society for Testing and Materials (ASTM) method.

1.3 The instruments measure a sample's infrared (IR) absorbances at fixed individual wavelengths or across a wide spectrum. Using calibration data calculated from a large set of samples with known properties, the absorbances are used to generate approximate values for fuel properties. The results from the screening instruments are never data-for-record, but are used by Enforcement Division to select samples to be analyzed by regulatory methods when resources are not available to analyze all the samples. Generally, samples with the highest readings are analyzed by regulatory methods.

2 Summary of Method

2.1 Gasoline and diesel samples are collected and brought to the laboratory by Enforcement Division. Samples are kept at ambient temperature or allowed to come to ambient temperature.

3 Interferences and Limitations

3.1 The primary limitations of this procedure are interference with spectral peaks of other chemical compounds (for chemical analytes) and the presence of similar in the library of similar fuels (for distillation temperatures and cetane number.) As long as the fuel samples analyzed are similar to those in the calibration set, this interference is minimized.

4 Equipment, Apparatus, Reagents, and Forms

4.1 IR screening instrument equipped with internal sample pump.

4.2 Computer (any type) for writing the instrument's output to a printer or text file.

5 Procedure

5.1 Make sure the instrument has been turned on for a sufficient amount of time

before analyzing samples.

5.2 Clear the instrument's results log.

5.3 If necessary, empty the instrument's waste bottle.

5.4 Connect the system's sample inlet to the sample.

5.5 Set the sample type on the instrument and input the sample ID.

5.6 Start the analysis and visually confirm that liquid is dripping into the waste bottle while the pump is operating (there may be a 5-10 second delay before sample begins flowing.)

5.7 If no sample is flowing after 15 seconds, abort the run and check the connection between the sample and instrument. If sample flow cannot be obtained in two tries, check the instrument's filter and clean it if necessary. For systems with a pressurized sampling system, transfer the sample into a new can.

5.8 Repeat steps 5.4 – 5.7 for each sample.

5.9 Transfer the results log to a flash drive, using a computer if necessary. The results log is exported in the form of a text file.

5.10 A results spreadsheet is created from the text file. See section 8 below for calculation instructions.

5.11 Clean the instrument if recommended by the manufacturer with pentane or isooctane. The data log should not be cleared until the following day. This allows for reexportation of the data in case of any problems.

6 Safety Precautions

6.1 Standard laboratory safety procedures and equipment should be used in performing this method. For example, safety glasses and gloves should be worn. Sandals and open-toed shoes should not be worn. All standard and sample preparation should be done in the fume hood. Gasoline and diesel contain compounds known to be toxic and carcinogenic. These instruments should be operated in a fume hood or outdoors.

7 Calibration

7.1 The instruments are supplied by the manufacturer with a library of calibration data. New samples can be added to this library using built-in functions or via an

external computer with software provided by the manufacturer. Samples which have been analyzed by the designated test methods are periodically added to the instruments' calibration libraries to improve the agreement between the screening and designated results.

8 Calculation of Results

8.1 A results spreadsheet is created from the text file. The instrument output is edited to report only the regulated fuel parameters.

8.2 For gasoline, the regulated parameters are MTBE, ethanol, oxygen, aromatics, benzene, olefins, T50, and T90.

8.2.1 The screening instruments may erroneously report low levels of various oxygenates, such as DIPE and butanol. As a result, the calculated oxygen concentration will often be incorrect. The chemist must place the following formula into each cell for oxygen concentration:

= 0.1815*a + 0.3478*b

where a is the cell containing MTBE concentration (if greater than 0.9%) and b is the cell containing ethanol concentration (if greater than 0.9%.) If the MTBE and/or the ethanol concentration is equal to or less than 0.9%, its value is not used in the oxygen concentration calculation.

8.2.2 If any oxygenate other than ethanol is reported by the instrument at a level higher than 0.9 wt%, notify the inspection coordinator.

8.3 For diesel, the regulated parameters are cetane number, aromatic wt%, aromatic vol%, and PAH wt%.

8.3.1 Aromatic vol% is not calculated by the instrument. The operator must manually add a column to the spreadsheet with the following formula:

vol% = 0.916*a + 1.33

where a is the cell containing aromatic wt% concentration.

8.3.2 Biodiesel content (as FAME and/or FAEE) is reported on the spreadsheet, although it is not a regulated parameter.

8.4 The spreadsheet is printed out, with one copy going to the inspection coordinator and one copy saved by FAMES for Quality Control (QC) report use. No electronic archiving is performed.

9 Quality Control and Assurance

9.1 Standard Reference Material - No suitable Standard Reference Material (SRM) has yet been found for this method.

9.2 Control Standard Analysis – a quality control sample is run at the beginning and end of each analysis day. The samples (one gasoline and one diesel) must be kept well-sealed to minimize evaporation.

9.3 Quality Control Charts - A quality control chart shows the results of all quality control sample runs and will be maintained on the Mobile Laboratory. Deviations from the mean of more than 10% (20% for olefins; 15 degrees for T50 and T90) indicate a potential problem which must be addressed.

9.4 Limits of Detection - The limits of detection (LOD) are similar to those from the regulatory methods since the data for the calibrations are using the regulatory methods. Exact LODs have not been determined.

10 References

10.1 Instrument and software manuals.

11 Revision History

11.1 Version 3.0

Significant changes:

Extensive changes, including the replacement of the Midac FOx FTIR by the Petrospec Cetane 2000 and GS1000 instruments.

Replicate analysis was replaced by control standards.

Control standards are now practical due to the small amount of sample consumed.

Replicate analysis is no longer necessary due to different pump function.

11.2 Revision 3.1

Significant changes:

QC tolerance for olefins increased to +/- 15%. The olefin measurements on the

QC material have proven to be less stable than the measurements of the other parameters. The reasons are unclear. Olefins are poor infrared absorbers, and sample stability may be an issue as well. Repeated investigations have not shown any malfunction in the instrument.

11.3 Revision 3.2

Significant changes:

All references to the Cetane 2000 were updated to reflect the purchase of the TD-PPA analyzer. FAMES content (biodiesel) is now recorded on the spreadsheet.

11.4 Revision 3.3

Significant changes:

The oxygen calculation was updated to eliminate the use of oxygenate concentrations below 1.0%. This change was made in consultation with Enforcement Division.

11.5 Revision 3.4 Effective Date: July 1, 1014

Significant changes:

Section 1.3 was updated to reflect the new instrument.

Section 1.1 was updated to add FAME content to the parameters measured.

11.6 Version 4.0 Effective date: May 1, 2017

Significant changes:

All references to brands and brand-specific instructions were removed. The QC criterion for olefins was updated to reflect current practice.

11.7 Version 4.1 Effective date: December 1, 2019

SOP format updated for ADA compliance