

**California Environmental Protection Agency**



**Air Resources Board**

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

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SOP NO. MLD 133 - SCREENING PROCEDURE FOR DETERMINATION OF OXYGENATES, AROMATICS, BENZENE, OLEFINS AND DISTILLATION TEMPERATURES IN GASOLINE, AND POLYCYCLIC AND TOTAL AROMATIC HYDROCARBONS AND CETANE NUMBER IN DIESEL FUEL BY FOURIER TRANSFORM INFRA-RED SPECTROSCOPY

## Introduction

- 1.1 The Monitoring and Laboratory Division uses this SOP to give screen results to Enforcement Division for several 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, and cetane number.
  - 1.2 This method is not based on any one ASTM method.
  - 1.3 The Petrospec GS1000 and Cetane 2000 are fuel screening tools utilized by FAMES. The instruments measure a sample's infrared (IR) absorbances at fixed individual wavelengths. 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 determine representative 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. Samples are introduced by screwing the standard one liter aluminum bottles onto the instrument's sample port.
- ## 3 Interferences and Limitations
- 3.1 The known interference or limitation to this procedure is interference with spectral peaks of other chemical compounds. As long as gasoline samples analyzed are similar to those in the calibration and validation, this interference is minimized.

- 4 Equipment, Apparatus, Reagents, and Forms
  - 4.1 Petrospec GS1000 and Cetane 2000 with internal sample pump.
  - 4.2 Computer (any type) for writing the instrument's output to a printer or text file.
  - 4.3 Proprietary software supplied by Petrospec is used to update the calibration sets (PC with Microsoft Windows 95 or later required)
  
- 5 Procedure
  - 5.1 Make sure the instrument has been turned on for a minimum of 30 minutes to warm up. The instrument will not allow samples to be analyzed until is has warmed up.
  - 5.2 Clear the instrument's log by pressing "3" and confirming.
  - 5.3 If necessary, empty the instrument's waste bottle.
  - 5.4 Screw the metal sample can onto the instrument's sample port tightly. Begin the sample analysis by pressing "1."
  - 5.5 (GS1000 only) Press "exit" when prompted for the gasoline's expected octane number.
  - 5.6 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.)
    - 5.6.1 If no sample is flowing after 15 seconds, abort the run by pressing "exit", unscrew the sample can, and try again. If sample flow cannot be obtained in three tries, transfer the sample into a different can and discard the original can.
  - 5.7 The instrument will beep when the analysis is done. Press "enter" to cycle through the test results. Press "exit" at the end of the sample results. Press "yes" when asked if data is to be logged. Enter the sample ID and press "enter" to log the data.
  - 5.8 Repeat steps 5.4 – 5.7 for each sample.

5.9 Attach a serial cable from the back of the instrument to the computer. Use the export function from the instrument menu and appropriate software (i.e. Hyper Terminal) to send the results log to the computer as an ASCII text file.

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

5.11 No cleaning of the instrument is required. However, 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 software provided by Petrospec. 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 GS1000 often erroneously reports 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 and b is the cell containing ethanol concentration.

8.2.2 If any oxygenate other than MTBE or 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:

$$= 0.916*a + 1.33$$

where a is the cell containing aromatic wt% concentration.

8.4 The spreadsheet is printed out, with one copy going to the inspection coordinator and one copy saved by FAMES for 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% (15% 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

This SOP was begun on 2/25/00 and completed on 8/18/00. SOP was revised and upgraded on 10/10/01.

Version 3.0 – 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.

Version 3.1 – 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.