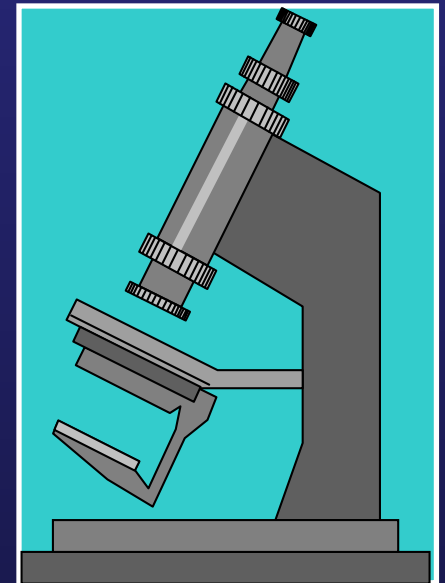
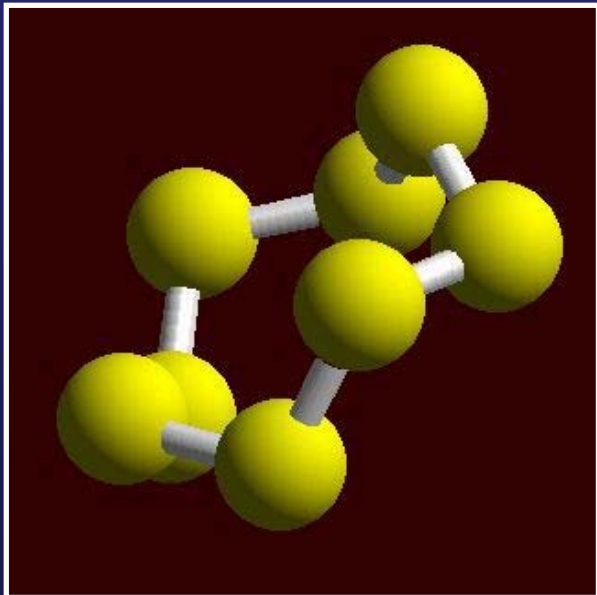


HD 2007 Rule

Diesel Fuel Sulfur Testing and Sampling Methods and Requirements

US EPA Office of Transportation and Air Quality

November 20, 2002



Diesel Fuel Test Methods and Testing Requirements

- Designated method is the method that EPA utilizes in its own laboratory to determine compliance with a given standard
- Alternative methods are allowed provided they are correlated to the designated method
- No requirement for refiners/importers to test every batch of diesel fuel
- However, the sulfur standard will be enforced at all points in the distribution system
- Test results may be used for affirmative defense in the event of a violation



Designated and Alternative Test Methods for Diesel Fuel

- For 15 ppm sulfur diesel fuel:
 - designated test method—ASTM D 6428-99
 - alternative test methods—
 - ASTM D 5453-00
 - ASTM D 3120-96
 - ASTM D 2622-98 as modified
- For 500 ppm sulfur diesel fuel:
 - designated test method—ASTM D 2622-98
 - alternative test methods—
 - ASTM D 5453-00
 - ASTM D 6428-99
 - ASTM D 4294-83 (updated to the current version)



Diesel Fuel Sampling Methods

- Manual Sampling — ASTM D 4057-95
- Automatic Sampling — ASTM D 4177-95
- Automatic Sampling from Pipelines / In-line Blending — ASTM D 4177-95
- Effective June 1, 2001
- Same methods are used for low sulfur gasoline



Overview of ASTM's Round Robin Test Results



EPA Method Issues

- Precision
 - Standard Deviation of Group of Repeat Measurements on the Same Material
- Limit of Quantification (LOQ)
 - Sensitivity
- Accuracy
 - Interferences
- Cost



ASTM Statistics

- Repeatability
 - 95% CL for Back to Back Repeat Measurements
 - Surrogate for Precision
- Reproducibility
 - 95% CL for Duplicate Measurements Made of the Same Material in Different Laboratories
 - Surrogate for Accuracy



Recent Sulfur Round Robin Diesel Results

- Included Several Methods and Instruments
- Repeatability Results
 - One Instrument Value of 0.39 ppm, Several Others near 1 ppm.
 - Generally Encouraging
- Reproducibility Results
 - Not as Good, No Results below 6 ppm



Interpretation of Repeatability

- Best Estimate of Precision
- Method Precision is Inherent Property
 - Moderate Influence by Operator Technique
 - Because Measurements are All Made on the Same Sample, Other Influences Like Interferences Have Little Effect.
- Can be Expressed as Precision, SD is Roughly Half of the Repeatability.



Interpretation of Reproducibility

- Inter-Lab Correlation
- Reported Values are a Function of:
 - Precision
 - Quality of Written Document
 - Experience of Operator
 - Availability of Standards
 - Availability and Quality of Blanks
 - Uncorrected Interference



Round Robin Observations

- No Observed Bias Between Methods
 - No Problems with Accuracy
- Instruments with Good Precision are Available
- While There is Room for Improvement, The LOQ Seems Adequate for 15 ppm Diesel Regulation
- Instrument Cost is Consistent with Expectations



Draft Test Method Plan



Potential Test Method Amendment – Performance Criteria Approach

- Intend to follow Agency standard guidelines for performance based testing
- Conveys “what” needs to be accomplished but not prescriptively “how” to do it
- Under this approach, there would be no designated method but we would notify industry on what method we will use
- Allows for greater flexibility in instrument selection and encourages the development and use of better instrumentation



Potential Test Method Amendment – Performance Criteria Approach (cont)

- Based on specified precision and accuracy criteria from existing approved methods (i.e., from the round robin results)
- Possible for measuring properties with gravimetric standards
- Could also require QA/QC records documenting initial and continuing demonstration of method performance
- Allows everyone to know that they are measuring accurately within the repeatability of the instrument



Potential Performance Criteria

- Proposed precision and accuracy values which would allow multiple commercially available instruments
- Recommend ongoing measurement to ensure that no shift in precision or accuracy has occurred
- Data must be retained for audit purposes



Precision & Accuracy Demonstration

- How method could be qualified for use:
 - Precision:
 - 10-30 tests over 1 week
 - Using any commercially available diesel fuel subject to the 15 ppm sulfur standard
 - Current premise is that these precision samples could be run at any point in the day after any routine checks are completed
 - Accuracy:
 - 10-20 tests over 1 week
 - Using any commercially acceptable gravimetric sulfur standard
 - Samples could be run in the same sets as the precision samples, if desired
- Objective is to make this effort consistent with the normal start up procedure of a test method



Terminology

- **Precision and Accuracy**

- Precision deals with the consistency of a set of measurements. Can the method get close to the same answer each time in repeat measurements on the same material.
- Accuracy is concerned with whether the average of a large number of measurements is very close to the “true value” of what’s being measured.

- **Repeatability and Reproducibility (both precision measures)**

- Repeatability, as used by ASTM, is a measure of the consistency with which the same instrument in the same laboratory run by the same operator can get a similar answer on back-to-back tests.
- Reproducibility is an interlaboratory precision measure. It looks at the dispersion in a set of tests on the same material using the same method, but in different labs and run by different operators.



Terminology (continued)

- **Gravimetric standard.** This is a calibration material that is made by adding a carefully weighed or measured amount of the substance of interest to a known quantity of other materials to give a known concentration.
- **Matrix effect.** This is where a measurement method gets different answers for the concentration of the substance of interest depending on the composition of the “other materials” to which that substance was added. Some methods are able to mostly ignore such matrix differences, while others are said to be “matrix-sensitive”.



Terminology (continued)

- **Statistical Quality Control (SQC).** A set of practices designed to monitor and document the quality of ongoing measurement work and alert the analyst to problems before they result in unacceptable quality levels (control charts, etc.)
- **Round Robin.** These are test programs, frequently organized and administered by ASTM, in which the same set of materials (gasolines, diesel fuels, etc.) are sent simultaneously to many different laboratories that are all operating a particular test method. These programs may be conducted for a variety of purposes, but one very important role is to establish the precision of the method in question—both repeatability (intralab), and reproducibility (interlab).

