HORIBA Scientific

Corporation

HORIBA Instruments, Inc.

Gulf Coast Conference 2016 Presentation

Measuring Sulfur in Tier III Gasoline

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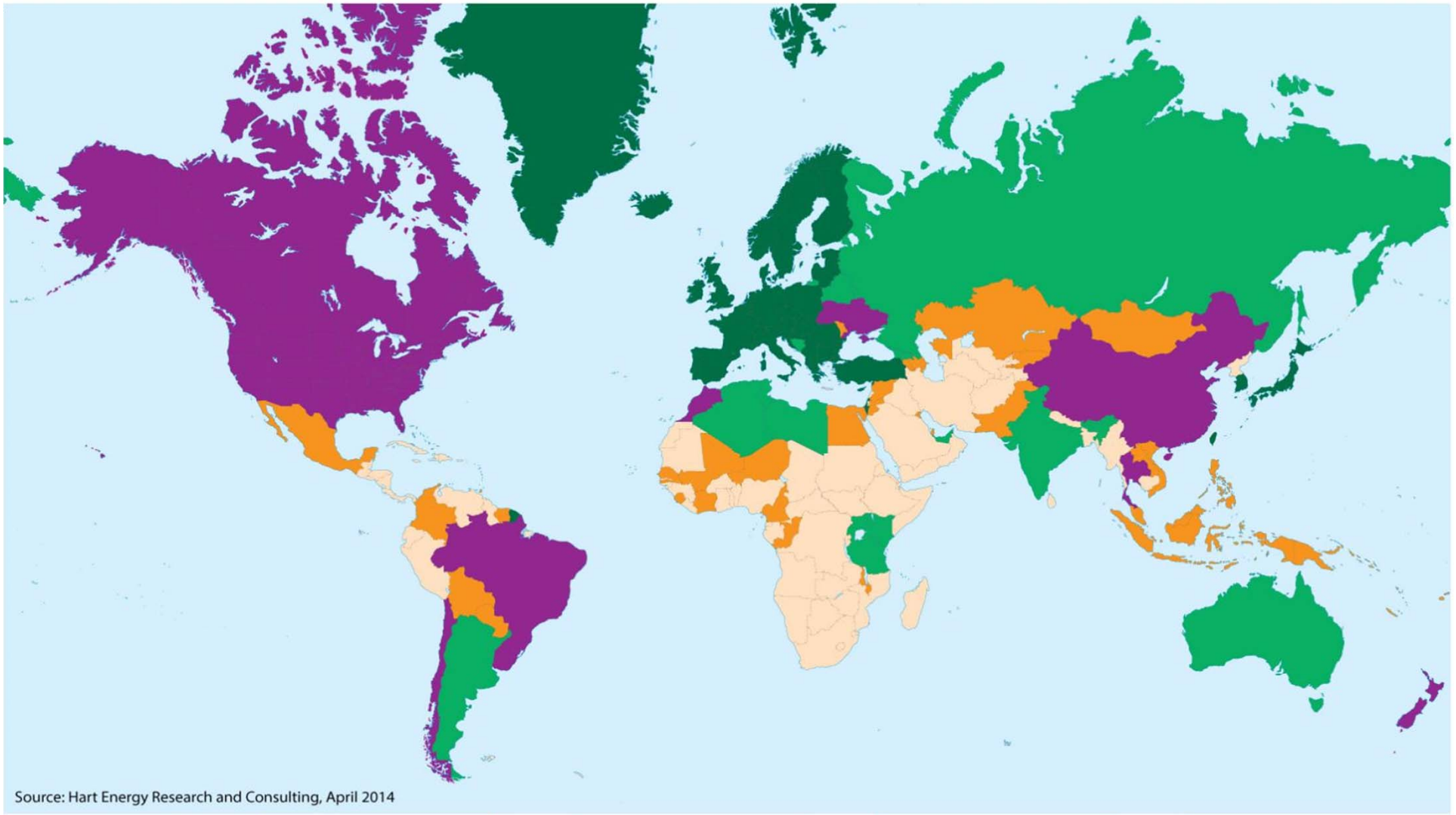
Room 611
2:20PM

The Way Forward

Maximum Gasoline Sulfur Limit



Countries may apply lower limits for different grades, regions/cities, or based on average content.
Detailed information on limits and regulations can be found at www.ifqc.org

Tier 3 Overview and Opportunities

- Federal Register / Vol. 79, No. 81
- 40 CFR Parts 79, 80, 85, 86, 600, 1036, 1037, 1039, 1042, 1048, 1054, 1065, and1066
- Control of Air Pollution From Motor Vehicles: Tier 3 Motor Vehicle Emission and Fuel Standards

U.S. EPA Tier 3 Goals and Status

- **Control of Air Pollution From Motor Vehicles:**
- **Tier 3 Motor Vehicle Emissions**
  - More stringent vehicle emissions standards
- **Fuel Standards**
  - Reduce sulfur in gasoline beginning in 2017
    - Now averaging in the 30 mg/kg S range
    - Future 8-11 mg/kg S, or less
  - Ethanol content
    - Newly defined Specification Fuel has 10 volume %
    - Future – 15 volume % **?**
- **California, Europe and Japan currently have gasoline specifications similar to Tier 3**
- **Final rule Published April 28, 2014**

Tier 3 Impact – 1)

- EPA recognized approving methods through rulemaking is a barrier for innovative analytical test methods.
  - EPA decided to incorporate the PBMS approach

- Consistent with the Agency's Performance Based Measurement System ("PBMS"), **EPA proposes not to require the use of specific, prescribed analytic methods.**

- The PBMS approach is intended to be more flexible and cost-effective for the regulated community; it is also intended to encourage innovation in analytical technology and improved data quality.

- EPA is not precluding the use of any method, whether it constitutes a voluntary consensus standard or not, as long as it meets the performance criteria specified.

Tier 3 Impact – 2)

- **Once fully implemented, this rule will:**
  - (1) Requires individual laboratories to demonstrate adequate measurement quality
  - (2) allow laboratories to choose methods that meet their own needs, provided they can **meet prescribed criteria** rather than specific methods
  - (3) requires all laboratories making regulatory measurements to establish and maintain a statistical quality control program

- **Qualification process intent** - demonstrate the facility's capability with the test method they choose.
  - Each instrument or operator is not required to qualify
  - Labs may have multiple qualified instruments using a method

Tier 3 Impact – 3)

- PBMS is based upon an established performance criteria for accuracy and precision.

- Laboratories demonstrate that a particular analytical test method is acceptable for demonstrating compliance.
  - **Precision** - The degree of agreement in a set of measurements performed on the same property of identical test material.
  - **Accuracy** – The closeness between an observed value from a test measurement and an accepted reference value (ARV).
  - **QC Program** - require all labs making regulatory measurements to establish / maintain a statistical quality control (SQC) program.

- **Beginning January 1, 2016, sulfur in gasoline must be determined** by a test method approved under **§ 80.47 - Performance-based Test Method Approach.**

- **EPA predicts -750 labs subject to info collection.**

Tier 3 Definitions

- ***Absolute fuel parameter -*** **a fuel parameter for which a gravimetric standard is practical to construct and use. Sulfur content of gasoline or diesel fuel are examples.**
- ***Method-defined fuel parameter -*** **a fuel parameter for which an EPA-prescribed primary test method or designated method defines the regulatory standard. Examples include Reid vapor pressure (RVP) and distillation parameters.**
- ***Correlation equation (For method-defined fuel parameters)*** **- a correction equation as determined by ASTM standard practice D6708. This standard practice determines whether the comparison between the alternative test method and the designated test method is a null result (No Bias). If the comparison is not null (Bias Found), then the standard practice provides for a correlation equation (Correction Factor) that predicts designated test method results.**

Tier 3 Sulfur PBMS Tests and SQC (1
Absolute fuel parameter

- **(b)(1) Sulfur repeatability - (r)**
- **Maximum allowable standard deviation computed from a minimum 20 results made over 20 days**
  - **7 or fewer tests per week**
  - **2 or fewer tests per day**
- **STDEV ≤ 1.5 * (r / 2.77)**
  - **"r" equals the repeatability of D7039–07**
    - **Chosen because it had biggest r of alternate methods**
- **Example: A 10 mg/kg sulfur gasoline sample:**
  - **maximum allowable standard deviation of 20 gasoline tests**

    ≤ 1.5*(1.76 mg/kg / 2.77) = 0.95 mg/kg
- **20 Diesel low (5-15 mg/kg S) – *Max STDEV = 0.72***

Tier 3 Sulfur PBMS Tests and SQC (2
Absolute fuel parameter

- (b)(2) **Sulfur accuracy**

- Average of at least 10 continuous tests performed on a commercially available gravimetric sulfur standard
  - In the range of 1–10 ppm shall not differ from the ARV of the standard by more than **0.71 ppm sulfur**; ***(Diesel – 0.54)***
  - In the range of 10–20 ppm shall not differ from the ARV of the standard by more than **1.00 ppm sulfur**;

- In applying the accuracy tests individual test results shall be compensated for any known chemical interferences.

- (The test method specified at § 80.46(a)(1) (D2622) and in use prior to May 30, 2014 is exempt from the repeatability and accuracy requirements of paragraphs (b)(1) and (2) of this section.) ? Still must do QC.

Tier 3 Sulfur PBMS Tests and SQC (3

- ***(SQC) Requirements for Absolute (defined) Fuel Parameters - Follows ASTM practice D6299***
- **(1) *Accuracy SQC***
  - ***Mandatory at-least quarterly testing each instrument with* gravimetric reference material or check standard**
  - **Pre-treat and assess results from the check standard testing after at least 15 testing occasions (D 6299 section 8.2)**
  - **Mandatory "MR' and "I" charts**
  - **Root cause investigation triggers, "back-to-back results greater than standard error of the ARV in the consensus-named fuel**
- **(2) Precision SQC**
  - **QC samples either once a week or every 20 tests**
  - **Mandatory "MR' and "I" charts**
  - **Root cause investigation triggers, Maintain records five years.**
- **(3) Validation of new QC material**
  - **I-Procedure or Q- Procedure, then verified 3 times per year**

Performance Based Measurements System (PBMS) General Requirements

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- Generally developed along the lines of ULSD in 2006
  - Included some improvements and additions
- Requires accuracy and repeatability data same as ULSD
  - Same tests as ULSD
- Testing covers two ranges
  - 5-10 PPM and 10-20 PPM
- Data retention is now at the customer location for five years
  - Previously submitted to EPA using required spread sheets
- Spreadsheet will be up on EPA website shortly
  - Provides immediate PASS/FAIL result
- Added Quality Control Charting as a specific requirement
  - Monitoring of Precision and Accuracy are required
- Entire procedure is spelled out in CFR Part 80 several sections
  - Legalistically written

Example of Tier III Accuracy Testing

5.0 mg/kg S	
Test #	**Result**
1	5.1
2	5.3
3	5.7
4	5.4
5	5.5
6	5.2
7	4.9
8	4.8
9	4.6
10	4.8
Mean	**5.12**
Δ COA	**0.12**
	PASS

15.0 mg/kg S	
Test #	**Result**
1	15.5
2	15.7
3	15.9
4	15.8
5	16.1
6	15.9
7	15.5
8	15.8
9	15.9
10	16
Mean	**15.81**
Δ COA	**0.81**
	PASS

MESA-7220 Tier 3 Testing Results for Accuracy @ 5.0 and 15.0 mg/kg Sulfur

Example of Tier III Repeatability Testing

MESA-7220 Testing Repeatability

Results @ 10.0 mg/kg S

10.0 mg/kg S			
Test #	Result	Test #	Result
1	9.1	12	9.4
2	10.7	13	9.7
3	9.9	14	9
4	9.1	15	10.6
5	9.9	16	9.3
6	10.4	17	10.5
7	9.7	18	9.9
8	9.7	19	9.7
9	9.3	20	10.4
10	9.4	**Mean**	**9.8**
11	10.9	**STDEV**	**0.58**
PASS			

MESA-7220 Testing Repeatability

Results @ 6.0 mg/kg S

10.0 mg/kg S			
Test #	Result	Test #	Result
1	5.8	12	6.3
2	6.7	13	5.9
3	6.6	14	5
4	6.4	15	5.9
5	6.5	16	5.3
6	4.8	17	5.9
7	5.9	18	6.6
8	6	19	5.9
9	6.3	20	5.8
10	6.5	**Mean**	**6**
11	6.1	**STDEV**	**0.52**
PASS			

MESA-7220 Tier III Testing Results for Repeatability at 6.0 and 10.0 mg/kg Sulfur

Acceptable Quality Control Charting for Precision (repeatability)

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Every facility shall conduct tests on every instrument with a quality control material and construct and maintain an "I" chart and a "MR" chart as defined in ASTM D6299 either once per week or once per every 20 production tests, whichever is more frequent.

Run Rule Strategy - Any one of the following occurrences shall be interpreted as a strong signal that a change in state of the measurement system has likely occurred:

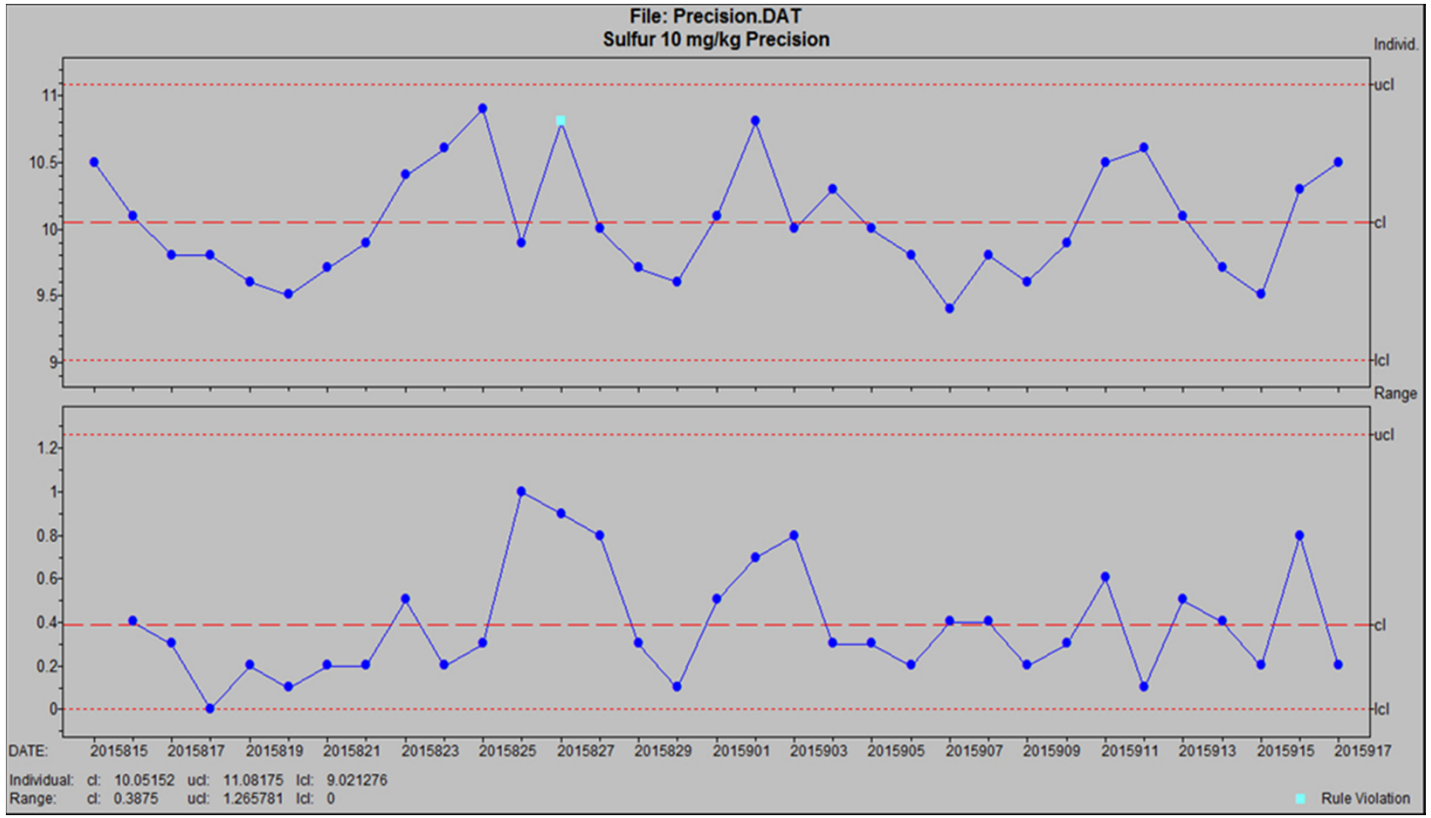
(1) Two out of three consecutive results on the I chart that are more than 2σR′ from the center line in the same direction.

(2) Five consecutive results on the I chart that are more than 1σR′ from the centerline in the same direction.

(3) Nine or more points in a row above or below the centerline on the I chart.

(4) Seven points in a row steadily increasing or decreasing.

Typical MESA-7220 Precision SQC Data



Acceptable Quality Control Charting for Accuracy

For each instrument used, testing of a **reference material or certified check standard** at least 3 times a year is required. The facility must construct “MR” and “I” charts with control lines as described in ASTM D6299. The following accuracy control charts track a daily check standard testing scheme.

Run Rule Strategy - Any one of the following occurrences shall be interpreted as a strong signal that a change in state of the measurement system has likely occurred:

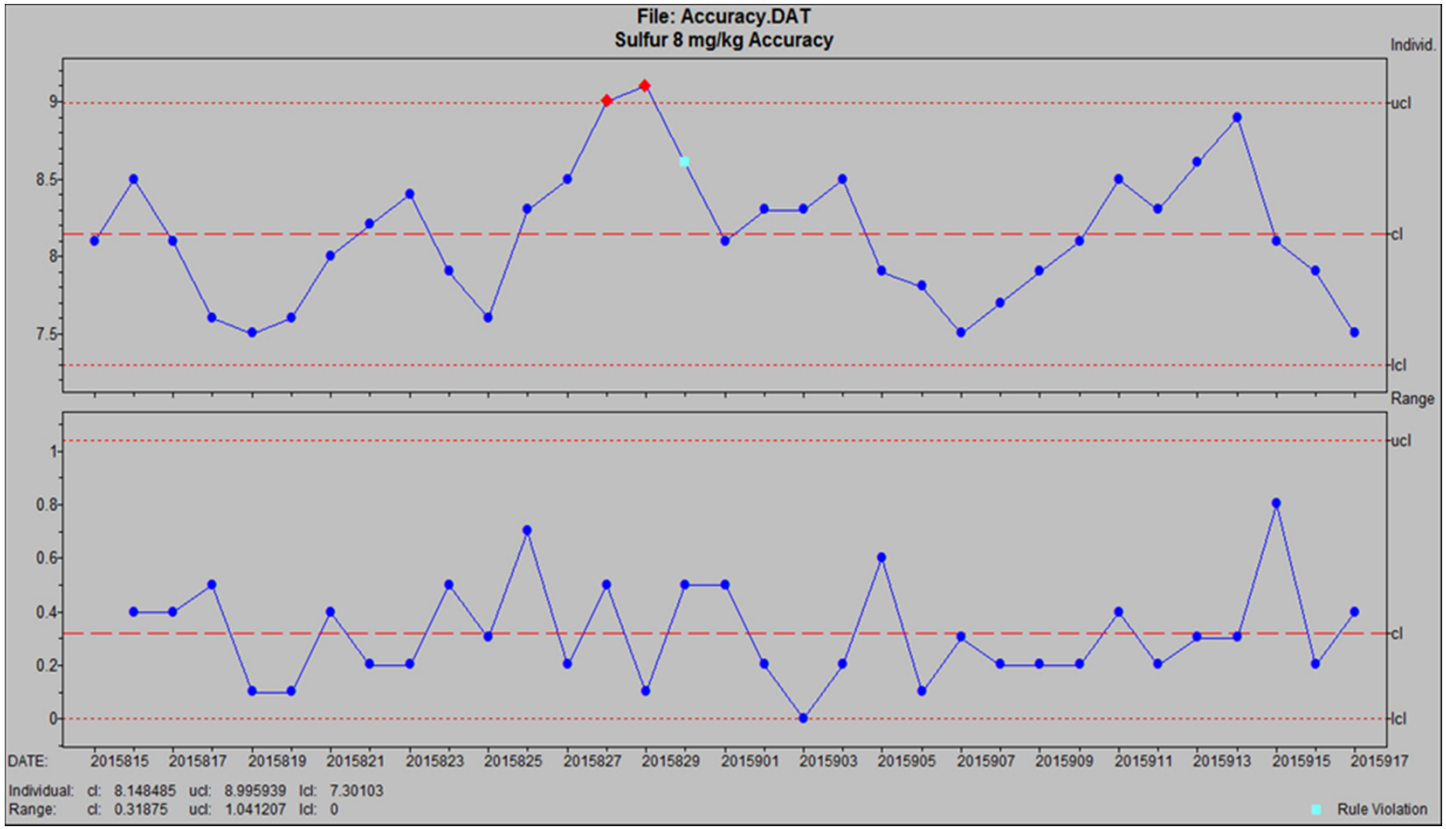
(1) Two out of three consecutive results on the I chart that are more than 2σR′ from the center line in the same direction.

(2) Five consecutive results on the I chart that are more than 1σR′ from the centerline in the same direction.

(3) Nine or more points in a row above or below the centerline on the I chart.

(4) Seven points in a row steadily increasing or decreasing.

Typical MESA-7220 Accuracy SQC Data



The Path to Qualification

- Determine tentative technology to be employed
- Select a protocol for your own testing
- Obtain samples for testing
- Record data from sample testing
- Download the data into EPA spreadsheet
- Print out the results of the project
- Prepare to implement SQC protocol

D7220 Tier 2 & Tier 3 Testing Kits

Item				
SEPA-T2-KIT-500	SEPA-T2-O2-KIT-500	SEPA-T3-KIT-500	SEPA-T3-O2-KIT-500	

Contains:

1. SEPA-T(X)-Set of customer Choice - Complete Test Set,
2. Pertinent excerpts from Congressional Federal Register,
3. Plain Language Descriptions of Required Testing
4. Pass/Fail Calculations with Worked Examples.
5. An overview of EPA/D6299 SQA requirements

- For EPA Sulfur in Gasoline Test Method Qualification

Thank you

Omoshiro-okashiku

Joy and Fun

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감사합니다

Cảm ơn

ありがとうございました

Dziękuję

धन्यवाद

Grazie

Merci

谢谢

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ขอบคุณครับ

Obrigado

Σας ευχαριστούμε

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Tack ska ni ha

Большое спасибо

Danke