The Importance of Reference Materials in Verifying Crude Oil Quality

Vishal Patel, ASI Standards
Introduction

• ASI Standards has been producing quality reference standards for the petroleum, petrochemical and polymers industry for 25 years

• Our mission is to provide reliable, quality reference standards to our customers and to be on the forefront in the development of innovative solutions based on customer feedback and industry standards
Purpose of this Presentation

• To show the importance of using carefully-designed, standard-based calibrations to improve analytical results in your laboratory.
  • Sample Preparation
  • Standard test method requirements
  • Provide traceability to SRMs

• Discuss the quality control procedures used to ensure proper validation and certification of calibration standards.
Analytical Measurement System

- A collection of one or more components or subsystems, such as samplers, instrumentation, calibration materials, data handlers, or printouts that is used to determine a quantitative value of a specific property for an unknown sample in accordance with a test method.
Sample Variation
Importance of Standards

Sample Preparation
• Matrix matching
  • C/H ratio
  • Density
  • Particle Size
• Preparation
  • Oils, Light & Heavy
  • Pellets
  • Pressed Pellets
  • Plastic Discs
Importance of Standards

Matrix Matching

• Sulfur in Gasoline, Crude Oil, etc;
  • To correct for C/H ratio like Ethanol in Gasoline and Diesel.
• Multi-elements in Lube Oil, Crude Oil, etc;
  • Account for Oxygen’s impact on analysis of Ca, P and S.
• Account for interfering elements
Importance of Standards

*Required by standard test methods (ASTM, ISO, etc.)*

- D4294 : Sulfur in Petroleum Products by EDXRF
  - Certified Dibutyl Sulfide (DBS) in Oil

- D3230 : Salts in Crude Oil by Electrometric Method
  - Common chlorides like Ca, Mg, Na

- D5708 : Ni, V, Fe in Crude Oil by ICP-AES

- D8056 : Guide for Elemental Analysis of Crude Oil
Importance of Standards

**Required by other specifications**

- WTI Quality Specifications
  - Current: Sulfur, Gravity, Viscosity, RVP, Sediment/Water, Pour Point
  - 2019 adds: C residue, TAN, Ni < 8 ppm, V < 15 ppm, Sim Dist.

- ISO 17025: Competence of testing and calibration laboratories

- ISO 17034: Competence of reference material producers
Procedure for Preparing and Certifying Standards

- Establish representative calibrations on WDXRF instruments.
- Establish representative calibrations on combustion analysis analyzer.
- Establish traceability to NIST or other SRM’s whenever available and appropriate.
  - Use the calibration curve to analyze the SRM and a control sample (check standard).
  - When assaying a prepared set of standards, analyze the control sample at the same time for verification of the curve.
Procedure for Preparing and Certifying Standards (cont.)

- Preparation and assay of standards.
  - Certify all starting reagents
    - Acceptance of COA of purchased reagents
    - Certify other reagents by WDXRF and/or ICP

- Gravimetrically prepare the standards.

- Assay the standards using the appropriate x-ray calibration curve.

- Analyze the control standard for verification and traceability.
Sulfur in Crude Oil COA

Sulfur in Crude Oil
Calibration Standards

Expiration Date: May 20, 2020

Product Code: SCO7-L-100
Lot Number: 052118HM

<table>
<thead>
<tr>
<th>Standard Number</th>
<th>Lot Number</th>
<th>Concentration wt%</th>
<th>Expanded Degree of Uncertainty</th>
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<td>3</td>
<td>052118HM-3</td>
<td>0.500</td>
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Standard deviation (2-Sigma): 3% (Relative)

Approximate Matrix Viscosity @ 40°C: 3.67 cSt
Density @ 20°C: 0.8634 g/mL

These standards were checked by x-ray fluorescence spectrometry, (XRF) method ASTM D2622, and are traceable to NIST SRM 2723b (sulfur in diesel fuel oil), NIST SRM # 1616a (sulfur in kerosene), NIST SRM # 2717a (sulfur in residual fuel oil), NIST SRM 2721 (sulfur in crude oil) or NIST SRM # 1624d (sulfur in diesel fuel oil).
Sulfur in Crude Oil Curve

$y = 1.0093x - 0.0056$

$R^2 = 0.9998$
LOE23

• 8 elements - Ba, Ca, Cl, Cu, Mg, P, S, Zn
• 23 standards in the set
• P 0-0.15 wt.%
• S 0-0.75 wt.%
• Other elements similarly randomized over a range of 0-0.75 wt.%
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<th>Lot No.</th>
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<th>Ca</th>
<th>Cl</th>
<th>Cu</th>
<th>Mg</th>
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* THE 3.0% RELATIVE UNCERTAINTY IS BASED ON ERRORS FROM THE ASSAY ANALYSIS AND WEIGHING OF RAW MATERIALS AT A 95 % CONFIDENCE LEVEL OR (k = 2).
LOE23 Phosphorus Curve

\[ R^2 = 0.9991 \]
LOE23 Zinc Curve

Gravimetric (Wt%) vs. Analysis

Zn
- Zn
- control
- Linear (Zn)

$R^2 = 0.9982$
### Total Acid Number COA

**ASTM D664**  
**Total Acid Number**  
**Check Standards**

<table>
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<th>Standard Number</th>
<th>Lot Number</th>
<th>Acid Number</th>
<th>Expanded Degree of Uncertainty</th>
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<td>081216EJ-2</td>
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<td>0.05</td>
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**Product Code:** TAN2  
**Lot Number:** 081216EJ

These standards were checked by ASTM D664. The titrant used to assay the above gravimetric certified value is traceable to NIST SRM 84L (potassium hydrogen phthalate).

**Expiration Date:**  
August 12, 2018
Uncertainty

• We use the error propagation method of calculating uncertainty
• Estimated accumulation of errors from assay analysis and weighing of raw materials at a 95% confidence interval or (k=2).
• \[ u = \sqrt{A^2 + (WE1)^2 + (WE)^2} \]
  Where A = Assay error
  WE1 = Weighing error, First dilution
  WE2 = Weighing error, Second dilution

ASI Standards
Control Charting

• Risk Tolerance (Sometimes decided for you…Thanks EPA!)
• Controls are tested by XRF and combustion to ensure the validity of the calibration.
  • Sulfur in Mineral Oil
    • Low level @ 15 mg/kg
    • Medium level @ 400 mg/kg
• Nitrogen and Sulfur in Isooctane 0-5 mg/kg
  • Low @ 0.25 mg/kg (250 ppb)
  • High @ 2.5 mg/kg
  • Be sure that calibration units match check standard units!
• MR-I individual and moving range chart
ASTM D6299 Compliance

- Generation of MR and I charts and associated limits
- Q procedure for new or short-run materials
- Q/Q plots for normality visualization
- Anderson Darling Statistics
- GESD Outliers
- EWMA trend generation
- F and T-testing for mean and variance
ASTM D6299 Compliance
ASI Standards & Services

• Quality, Customization and Flexibility
  – Products and Experience for many different applications
  – Willing to work with the customer every step of the way to find a solution for their specific application

• Education and Insight
  – Keeping up with ASTM, EPA, and the latest quality control trends
  – Attend industry meetings and shows, always available on email
    – sales@asistandards.com
Any Questions?