National Institute of Standards & Technology

Certificate of Analysis

Standard Reference Material® 2721

Crude Oil (Light-Sour)

This Standard Reference Material (SRM) is a commercial crude oil intended for use in the evaluation of methods and the calibration of instruments used in the determination of total sulfur, mercury, and water in crude oil or materials of a similar matrix. The light-sour Texas crude oil used for this SRM was passed through a 10 µm filter and blended before being ampouled. A unit of SRM 2721 consists of five amber ampoules, each containing approximately 10 mL of crude oil.

Certified Values: The certified values for sulfur and mercury content are provided in Table 1. A NIST certified value is a value for which NIST has the highest confidence in its accuracy in that all known or suspected sources of bias have been investigated or accounted for by NIST. The certified value for sulfur content is based on analyses by isotope dilution thermal ionization mass spectrometry (ID-TIMS) [1]. Homogeneity testing was performed using X-ray fluorescence spectrometry. The certified value for mercury is based on analysis by cold vapor isotope dilution inductively coupled plasma mass spectrometry (CV-ID-ICP-MS) [2,13]. The uncertainty in each certified value is expressed as an expanded uncertainty, $U = ku_c$, calculated according to the method in the ISO/JCGM and NIST Guides [3]. The quantity u_c represents, at the level of one standard deviation, the combined effects of measurement variability. The quantity k is the coverage factor used to obtain an expanded uncertainty with an approximate confidence interval of 95 %. The value of the coverage factors for sulfur and mercury are $k = 2.45$ and $k = 2.01$, derived from the Student's t-value with 6 and 10 degrees of freedom, respectively. The measurand is the total mass fraction of the constituent listed. The certified values are metrologically traceable to the SI unit of grams per 100 grams and nanograms per kilogram, respectively.

Table 1. Certified Values (mass fraction)

Sulfur:	1.5832 %	±	0.0044 %
Mercury:	41.7 ng/kg	±	5.7 ng/kg

Reference Values: Two reference values for water are given in Table 2. The water reference value is based on the ASTM-Method water value corrected for interferences. The ASTM-Method reference value for water is based on coulometric and volumetric Karl Fischer method determinations using the ASTM methods [4,5] and does not include the correction for the interferences measured by NIST [Appendix and reference 6]. The uncertainty for each reference value for water is expressed as an expanded uncertainty, $U = ku_c$, calculated according to the methods in ISO and NIST Guides [3]. A NIST reference value is a non-certified value that is the best estimate of the true value; however, the value does not meet NIST criteria for certification and is provided with an associated uncertainty that may not include all sources of uncertainty [7]. The value of the coverage factor is $k = 2$ and is derived from the Student's t-value with 60 degrees of freedom and a confidence level of 95 %. The measurand is water concentration as determined by the methods indicated [4,5]. Metrological traceability is to the SI units of milligram per kilogram.

Table 2. Reference Values (mass fraction)

Water:	134 mg/kg	±	18 mg/kg
ASTM-Method Water:	941 mg/kg	±	16 mg/kg

Expiration of Certification: The certification of **SRM 2721** is valid, within the measurement uncertainty specified, until **31 December 2018**, provided the SRM is handled in accordance with instructions given in this certificate (see "Instructions for Use"). This certification is nullified if the SRM is damaged, contaminated, or otherwise modified.

Maintenance of Certification: NIST will monitor this SRM over the period of its certification. If substantive technical changes occur that affect the certification before the expiration of certification, NIST will notify the purchaser. Registration (see attached sheet) will facilitate notification.

Carlos A. Gonzalez, Chief
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Gaithersburg, MD 20899
Certificate Issue Date: 12 March 2014
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Robert L. Watters, Jr., Director
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Overall direction and coordination of the technical measurements leading to certification of this SRM were performed by J.D. Fassett and S.A. Margolis of the NIST Chemical Sciences Division.

Analytical measurements were performed by W.R. Kelly, S.E. Long, J.L. Mann, S.A. Margolis, A.F. Marlow, J.R. Sieber, and R.D. Vocke of the NIST Chemical Sciences Division.

Overall direction and coordination of the statistical consultation for this SRM were provided by C.R. Hagwood of the NIST Statistical Engineering Division. Additional statistical consultation was provided by W.F. Guthrie of the NIST Statistical Engineering Division.

Support aspects involved in the issuance of this SRM were coordinated through the NIST Office of Reference Materials.

Information Values: The information values reported in Table 3 are noncertified values with no uncertainty assessed. They are provided as supplemental information to characterize the matrix. Information Values cannot be used to establish metrological traceability.

The crude oil for this SRM was donated by the Yates Field Unit operated by Marathon Oil Company, Iraan, TX.[1]

INSTRUCTIONS FOR USE

Each SRM ampoule should only be opened for the minimum time required to dispense the material and should be used in a well-ventilated area, away from sources of heat, open flames, and strong oxidizing materials. For sulfur measurements, once an ampoule is opened, the material must be used within a period of 5 h to avoid a significant change in the sulfur content. To relate analytical determinations to the certified value in this Certificate of Analysis, a minimum sample mass of 150 mg should be used. The unopened ampoules should be stored under normal laboratory conditions away from direct sunlight. For water measurements by the Karl Fischer method, once the ampoule is opened the sample must be removed immediately and assayed. Information regarding the measurement of the non-aqueous substances that interfere with the coulometric Karl Fischer method by reacting with iodine is provided in the appendix to the certificate.

Analytical Methods for Water Measurement: The ASTM-Method reference value for water is based on coulometric and volumetric Karl Fischer determinations using ASTM Standard D 4928-00 and D 4377-00 for water. The first reference value for water listed in Table 2 is the combined value of measurements made by the coulometric [4] and volumetric [5] Karl Fischer methods corrected for interferences [6].

The water reference value is more accurate than the ASTM-Method value because a variety of volatile and non-volatile substances, such as sulfides, are present in crude oils and represent interferences that react with iodine to inflate the measurement of water by the Karl Fischer method. A coulometric method was developed for determining the amount of these interfering compounds using a sulfur dioxide (SO_2) free solution that is similar in composition to the Karl Fischer anode reagent [6]. The results of this NIST determination indicate that the content of interferences in this SRM is 807 mg/kg ± 45 mg/kg of water equivalents. Approximately 20 % of the materials that interfere with the Karl Fischer measurement of water volatilize within 15 min after the ampoule is opened and then the amount of interfering materials remains stable for a minimum of 2 h. The combined content of water and interferences is 941 mg/kg ± 16 mg/kg of oil.

Measurements of water in SRM 2721 were also made in an interlaboratory comparison exercise using the coulometric Karl Fischer Method, ASTM Standard D 4928-00 [4]. The results of the interlaboratory exercise (817 mg/kg ± 120 mg/kg) confirmed the NIST measurements for water (plus interferences). However, these measurements were not used in assigning the reference value because the uncertainty of these measurements is significantly higher than that of the NIST measurements.

[1]Certain commercial equipment, instruments or materials are identified in this certificate to adequately specify the experimental procedure. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

SUPPLEMENTAL INFORMATION

Information Values: The information values given in Table 3 are based on results provided by a commercial laboratory using ASTM methods. They are given as additional information on the matrix only.

Table 3. Information Values

Measurement		ASTM Standard Used	Result
Flash Point, PMCC		D 93 (A)-00 [8]	< 21 °C (70 °F)
API Gravity	@ 60 °F	D 4052-96 [9]	29.3 API
Kinematic Viscosity	@ 100 °C	D 445-97 [10]	16.63 10^{-6} m^2/s (16.63 cSt)
	@ 100 °C	D 2161-93 [11]	83.9 SUS
Carbon		D 5291-96 [12]	84.6 %
Hydrogen		D 5291-96 [12]	11.8 %

REFERENCES

[1] Kelly, W.R.; Paulsen, P.J.; Murphy, K.E.; Vocke, R.D., Jr.; Chen, L.-T.; *Determination of Sulfur in Fossil Fuels by Isotope Dilution Thermal Ionization Mass Spectrometry*; Anal. Chem., Vol. 66, pp. 2505–2513 (1994).

[2] Long, S.; Kelly, W.R.; *Determination of Mercury in Coal by Isotope Dilution Cold-Vapor Generation Inductively Coupled Plasma Mass Spectrometry*; Anal. Chem., Vol. 74, pp. 1477–1483 (2002).

[3] JCGM 100:2008; *Evaluation of Measurement Data — Guide to the Expression of Uncertainty in Measurement* (GUM 1995 with Minor Corrections); Joint Committee for Guides in Metrology (2008); available at http://www.bipm.org/utils/common/documents/jcgm/JCGM_100_2008_E.pdf (accessed Feb 2014); see also Taylor, B.N.; Kuyatt, C.E.; *Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results*; NIST Technical Note 1297, U.S. Government Printing Office: Washington, DC (1994); available at http://physics.nist.gov/Pubs/guidelines/TN1297/tn1297s.pdf (accessed Feb 2014).

[4] ASTM D 4928-00; *Standard Test Methods for Water in Crude Oils By Coulometric Karl Fischer Titration*; Annu. Book ASTM Stand., Vol. 5.03: West Conshohocken, PA, pp. 1–5 (2001).

[5] ASTM D 4377-00; *Standard Test Method for Water in Crude Oils By Potentiometric Karl Fischer Titration*; Annu. Book ASTM Stand., Vol. 5.02: West Conshohocken, PA, pp. 883–888 (2001).

[6] Margolis, S.A.; Paulsen, J.; Park, E.; *A Novel Method for Determining Substances that Interfere with the Measurement of Water in Oils and Other Chemicals by the Karl Fischer Method*; Anal. Bioanal. Chem. (submitted).

[7] May, W.; Parris, R.; Beck, C.; Fassett, J.; Greenberg, R.; Guenther, F.; Kramer, G.; Wise, S.; Gills, T.; Colbert, J.; Gettings, R.; MacDonald, B.; *Definitions of Terms and Modes Used at NIST for Value-Assignment of Reference Materials for Chemical Measurements*; NIST Special Publication 260-136, U.S. Government Printing Office: Washington, DC (2000); available at http://www.nist.gov/srm/publications.cfm (accessed Feb 2014).

[8] ASTM D 93 (A)-00; *Test Method for Flash Point by Pensky-Martens Closed Cup Test*; Annu. Book ASTM Stand., Vol. 05.01: West Conshohocken, PA, pp. 52–66 (1999).

[9] ASTM D 4052-96; *Test Method for Density and Relative Density of Liquids by Digital Density Meter*; Annu. Book ASTM Stand., Vol. 05.02: West Conshohocken, PA, pp. 683–686 (1998).

[10] ASTM D 445-97; *Test Method of Kinematic Viscosity of Transparent and Opaque Liquids* (*and the Calculation of Dynamic Viscosity*); Annu. Book ASTM Stand., Vol. 10.03: West Conshohocken, PA, pp. 184–192 (1999).

[11] ASTM D 2161-93; *Practice for the Conversion of Kinematic Viscosity to Saybolt Universal Viscosity or to Saybolt Furol Viscosity*; Annu. Book ASTM Stand., Vol. 05.01: West Conshohocken, PA, pp. 704–728 (1999).

[12] ASTM D 5291-96; *Test Methods for Instrumental Determination of Carbon, Hydrogen, and Nitrogen in Petroleum Products and Lubricants*; Annu. Book ASTM Stand., Vol. 05.03: West Conshohocken, PA, pp. 236–240 (2001).

[13] Kelly, W.R.; Long, S.E.; Mann, J.L.; *Determination of Mercury in SRM Crude Oils and Refined Products by Isotope Dilution Cold Vapor ICP-MS Using Closed System Combustion*; Anal. Bioanal. Chem. abstract available at http://link.springer.de/link/service/journals/00216/contents/03/01952/ (2003) (accessed Feb 2014).

Certificate Revision History: 12 March 2014 (Extension of the expiration date; editorial changes) 25 February 2008 (Update of expiration date and editorial changes); 01 July 2003 (Certified Hg value and uncertainty updated; Reference 13 added); 01 July 2002 (Original certificate).

Users of this SRM should ensure that the Certificate of Analysis in their possession is current. This can be accomplished by contacting the SRM Program: telephone (301) 975-2200; fax (301) 948-3730; e-mail srminfo@nist.gov; or via the Internet at http://www.nist.gov/srm.

APPENDIX

Measurement of the Non-Aqueous Substances That Interfere With the Coulometric Karl Fischer Method by Reacting With Iodine

Compounds that rapidly reduce I_2, oxidize I^-, or add I_2 to double bonds can compromise the accuracy of the measurement of water by the Karl Fischer reaction. These include such strong reducing agents as stannous salts, thiosulfate, mercaptans, sulfite, and ascorbic acid; oxidizing agents such as chlorine and dichromate; and compounds that add I_2 across an unsaturated bond. These rapid interfering or side reactions can be titrated independently by using a reagent that is similar to the Karl Fischer reagent but lacks the sulfur dioxide and is thus incapable of reacting with water. A number of these types of compounds, which have not been specifically identified, are present in relatively large amounts in some crude oils. This is particularly the case for SRM 2721. Summarized below is a method NIST has developed for measuring the interfering substances using a Metrohm 756 coulometer (Brinkmann Instrument Co., Westbury, NY) with a diaphragm cell in the Karl Fischer mode [6].

A sulfur dioxide-free coulometric reagent solvent was prepared, consisting of 1.4 mol/L imidazole, 0.2 mol/L potassium iodide, 0.5 mol/L trichloroacetic acid, and 40 μmol/L sodium thiosulfate in methanol. This solution was allowed to stand for at least 12 h. The reagent was then added to both the anode, which contained 30 % vol. xylene to increase the solubility of the oils, and the cathode compartments. If over titration was observed, then a small amount of thiosulfate was added to eliminate over titration (approximately 0.4 mL of 0.1 mol/L sodium thiosulfate). The instrument was then calibrated with thiosulfate and the samples were analyzed for the amount of interference present. Two reference values are reported for water in this certificate. The ASTM-Method water value represents the total Karl Fischer reacting material and includes the interferences. The water value represents the ASTM-Method water value corrected for the interferences.