National Institute of Standards & Technology

Certificate of Analysis

Standard Reference Material® 2722

Crude Oil (Heavy-Sweet)

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 heavy-sweet Texas crude oil used for this SRM was passed through a 10 μm filter and blended before being ampouled. A unit of SRM 2722 consists of five amber ampoules, each containing approximately 10 mL of crude oil.

Certified Value: 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]. The uncertainty in each certified value is expressed as an expanded uncertainty, $U = ku_c$, calculated according to the method in the ISO Guide [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 $k = 2.57$ and $k = 2.26$, derived from the Student's t-value with 6 and 9 degrees of freedom, respectively.

Table 1. Certified Values (mass fraction)

Sulfur:	0.21037 %	±	0.00084 %
Mercury:	144 ng/kg	±	34 ng/kg

Reference Value: 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 the ISO Guide [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 %.

Table 2. Reference Values (mass fraction)

Water:	99 mg/kg	±	6 mg/kg
ASTM-Method Water:	104 mg/kg	±	6 mg/kg

Expiration of Certification: The certification of this SRM is valid until **31 December 2008**, within the uncertainty specified, provided the SRM is handled and stored in accordance with the instructions given in the certificate (see Instructions for Use). However, the certification will be nullified if the SRM is damaged, contaminated, or otherwise modified.

The support aspects involved in the preparation, certification, and issuance of this SRM were coordinated through the NIST Standard Reference Materials Group by B.S. MacDonald.

Willie E. May, Chief
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Certificate Issue Date: 01 July 2002

The 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 Analytical Chemistry 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 Analytical Chemistry Division.

The overall direction and coordination of the statistical consultation for this SRM was 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.

Information Values: The information values reported in Table 3 are non-certified values with no uncertainty assessed. They are provided as supplemental information to characterize the crude oil matrix.

The crude oil for this SRM was taken from a Rufugio, TX, oil field and donated by Koch Industries, Inc., of Wichita, KS.[1]

Maintenance of SRM Certification: This material is considered to be stable during the period of certification. NIST will monitor this material and will report any significant changes in certification to the purchaser. Return of the attached registration card will facilitate notification.

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 very small (5 mg/kg ± 2 mg/kg of water equivalents). The combined content of water and interferences is 108 mg/kg ± 6 mg/kg of oil.

Measurements of water in SRM 2722 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 (108 mg/kg ± 34 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, instrumentation, or materials are identified in this certificate to specify adequately the experimental procedure. Such identification does not imply recommendation or endorsement by the NIST, 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]	23.7 API
Kinematic Viscosity	@ 100 °C	D 445-97 [10]	9.499 10^{-6} m^2/s (9.499 cSt)
	@ 100 °C	D 2161-93 [11]	57.1 SUS
Carbon		D 5291-96 [12]	85.9 %
Hydrogen		D 5291-96 [12]	11.9 %

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 by Coal by Isotope Dilution Cold-Vapor Generation Inductively Coupled Plasma Mass Spectrometry*; Anal. Chem. (in press).

[3] *Guide to the Expression of Uncertainty in Measurement*; ISBN 92-67-10188-9, lst Ed. ISO, Geneva, Switzerland, (1993); 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/).

[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).

[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).

Users of this SRM should ensure that the certificate in their possession is current. This can be accomplished by contacting the SRM Program at: telephone (301) 975-6776; fax (301) 926-4751; e-mail srminfo@nist.gov; or via the Internet 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 2722. Summarized below is a method NIST has developed for measuring the interfering substances using a Metrohm 756 coulometer (Brinkmann Instrument Co., Westbury, NY)[2] 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.

[2]Certain commercial equipment, instrumentation, or materials are identified in this certificate to specify adequately the experimental procedure. Such identification does not imply recommendation or endorsement by the NIST, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.