National Institute of Standards & Technology

Certificate of Analysis

Standard Reference Material® 2296

Reformulated Gasoline (13 % ETBE)

This Standard Reference Material (SRM) is intended primarily for use in the calibration of instruments and the evaluation of methods used for the determination of total sulfur, benzene, toluene, and ethyl tert-butyl ether (ETBE) in reformulated gasoline or similar matrices. A unit of SRM 2296 consists of a set of two 20 mL ampoules containing a synthetic gasoline blend of 25 organic compounds.

Certified Mass Fraction Values: Certified mass fraction values and associated 95 % confidence intervals are given 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 taken into account [1].

Reference Mass Fraction Values: Reference mass fraction values and associated 95 % confidence intervals are given in Table 2. A NIST reference value is a noncertified value that is an estimate of the true value. However, the value does not meet the NIST criteria for certification and is provided with an associated uncertainty that may reflect only measurement precision, may not include all sources of uncertainty, or may reflect a lack of sufficient statistical agreement among multiple analytical methods [1].

Expiration of Certification: The certification of **SRM 2296** is valid, within the measurement uncertainty specified, until **31 December 2022**, provided that the SRM is handled and stored in accordance with the instructions given in this certificate. (See "Instructions for Storage and Use.") However, the certification is nullified if the SRM is damaged, contaminated, or otherwise modified.

Maintenance of SRM 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 this certificate, NIST will notify the purchaser. Registration (see attached sheet) will facilitate notification.

The overall direction and coordination of technical measurements leading to certification were performed by G.W. Kramer and F.R. Guenther of the NIST Analytical Chemistry Division.

Analytical measurements required for certification of this SRM were performed by S.N. Chesler, S.J. Choquette, F.R. Guenther, T.L. Green, W.R. Kelly, J.L. Mann, S.A. Margolis, L.C. Sander, and R.D. Vocke, Jr. of the NIST Analytical Chemistry Division. Data analysis was performed by D.L. Duewer of the NIST Analytical Chemistry Division.

Support aspects involved in the issuance of this SRM were coordinated through the NIST Measurement Services Division.

Stephen A. Wise, Chief
Analytical Chemistry Division

Gaithersburg, MD 20899
Certificate Issue Date: 18 September 2012
Certification Revision History on Last Page

Robert L. Watters, Jr., Chief
Measurement Services Division

NOTICE AND WARNING TO USERS

Consult the Material Safety Data Sheet for details on safe handling before use. Ensure local exhaust or adequate ventilation in storage and laboratory facilities meet published gasoline exposure limits. Prevent contact with heat, sparks, or open flame. Those handling gasoline should wear appropriate clothing and gloves to prevent skin contact with this material and appropriate safety goggles to prevent eye contact.

Protect ampoules from physical damage. The unscored, thick-walled ampoules of this SRM must be opened with care and attention. Score the ampoule completely around the neck with a sharp triangular file or other scoring tool. Wrap the body of the ampoule in a thick cotton towel or use leather gloves while snapping the neck from the body of the ampoule.

INSTRUCTIONS FOR STORAGE AND USE

Storage: Sealed ampoules, as received, should be stored in the dark at temperatures between 10 °C to 30 °C away from incompatible materials (see "Notice and Warning to Users"). Ampoules should be opened as described above.

Use: Aliquots for analysis (minimum sample size of 1 g) should be withdrawn at 20 °C to 25 °C and used immediately after opening the ampoules. Samples must be processed without delay for the certified values to be valid within the stated confidence intervals.

SOURCE AND PREPARATION

This SRM was prepared by Spectrum Quality Standards, Inc. at their facilities in Houston, TX[(1)]. All chemicals used in the preparation of this material were obtained from commercial sources. The synthetic gasoline base was prepared from twenty-one reagent-grade saturate, olefinic, and aromatic stock materials. A typical gas chromatogram of the reformulated gasoline base is shown in Figure 1. Three reagent-grade thionate stock materials were mixed with HPLC-grade ETBE. Known masses of synthetic gasoline base, thionate/ETBE mixture, and ETBE were combined, mixed, and chilled in a pressurized vessel. The solution was dispensed into 20 mL glass ampoules; the ampoules were cooled to –30 °C and flame sealed.

Homogeneity Assessment: The homogeneity of SRM 2296 was assessed at NIST at a 1 g sample size.

Value Assignment: The mass fraction (mass constituent/total mass) of sulfur is based on isotope-dilution thermal ionization mass spectrometry [2]. The mass fraction of benzene and the mass fraction of ETBE are based upon split-injection, flame-ionization detection gas chromatographic (GC-FID) analysis coupled with gravimetry. The mass fraction of toluene is based upon reverse-phase liquid chromatography, GC-FID analysis, and gravimetry. The reference value of water is based on coulometric Karl Fischer titration. The major aromatic and olefinic constituents of the synthetic base gasoline were determined using GC-FID after a rigorous evaluation of the purity of the constituent stock materials by gas chromatography-mass spectrometry (GC/MS). The reference values of the organic components of this SRM have been deduced from the GC-FID measurements of the base gasoline composition combined with the known mass of the various components of the mixture. The aromatic, olefinic, and saturate composite reference values are the sum of all constituents identified as belonging to each of these groupings. The reference value of the total organic oxygen composite is the sum of the oxygen mass fraction of all identified organic oxygenates.

The 95 % confidence interval for each certified and reference value has been assigned on the basis of analytical judgment [3,4]. It incorporates estimates of analytical precision, known biases among methods of differing analytical reliability, reliability estimates for the mass-spectrometric identification of impurities, and allowance for apparent heterogeneity among the ampoules. The certified mass fraction of each component is expected to lie within the specified interval with a 95 % level of confidence. The reference values do not meet NIST criteria for certification and the uncertainty associated with each reference value may not include all sources of uncertainty.

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

Table 1. Certified Mass Fraction Values for Selected Constituents of SRM 2296

Constituent	CAS Registry Number	Mass Fraction (g/g)	95 % Analytical Confidence Interval (g/g)
Total sulfur		40.0×10^{-6}	$(39.6 \text{ to } 40.4) \times 10^{-6}$
Benzene	71-43-2	1.01×10^{-2}	$(1.00 \text{ to } 1.02) \times 10^{-2}$
Toluene	108-88-3	8.02×10^{-2}	$(7.92 \text{ to } 8.11) \times 10^{-2}$
ETBE	637-92-3	13.02×10^{-2}	$(12.87 \text{ to } 13.17) \times 10^{-2}$

Table 2. Reference Mass Fraction Values for Selected SRM 2296 Constituents

Constituent	CAS Registry Number	Mass Fraction ($\times 10^{-2}$) (g/g)	95 % Analytical Confidence Interval ($\times 10^{-2}$) (g/g)
1,2,4,5-Tetramethylbenzene	95-93-2	0.98	0.96 to 1.03
Naphthalene	91-20-3	1.17	1.15 to 1.19
Ethylbenzene	100-41-4	1.99	1.98 to 2.01
1,3,5-Trimethylbenzene	108-67-8	2.01	1.99 to 2.04
o-Xylene	95-47-6	2.01	1.99 to 2.05
1,2,4-Trimethylbenzene	95-63-6	2.05	2.02 to 2.08
m-Xylene and *p*-xylene	108-38-3 106-42-3	5.98	5.96 to 6.02
Total identified aromatics		25.38	25.27 to 25.56
1-Pentene	109-67-1	0.75	0.73 to 0.78
2,3-Dimethyl-2-butene	563-79-1	1.61	1.59 to 1.64
1-Heptene	592-76-7	1.63	1.60 to 1.66
Total identified olefins		4.14	4.12 to 4.18
n-Pentane	109-66-0	3.63	3.62 to 3.64
n-Hexane	110-54-3	3.77	3.76 to 3.78
n-Decane	124-18-5	4.21	4.20 to 4.22
n-Heptane	142-82-5	7.92	7.91 to 7.93
2,4-Dimethylpentane	108-08-7	8.05	8.04 to 8.06
n-Octane	111-65-9	8.13	8.12 to 8.14
Cyclohexane	110-82-7	9.01	9.00 to 9.02
2,2,4-Trimethylpentane	540-84-1	12.02	12.01 to 12.03
Total identified saturates		57.10	57.05 to 57.14
Thiophene	110-02-1	0.0031	0.0030 to 0.0032
Benzo[*b*]thiophene	95-15-8	0.0069	0.0068 to 0.0070
3-Methylthiophene	616-44-4	0.0036	0.0035 to 0.0037
Water	7732-18-5	0.018	0.017 to 0.019
Total oxygen from identified organic oxygenates		2.06	2.01 to 2.08

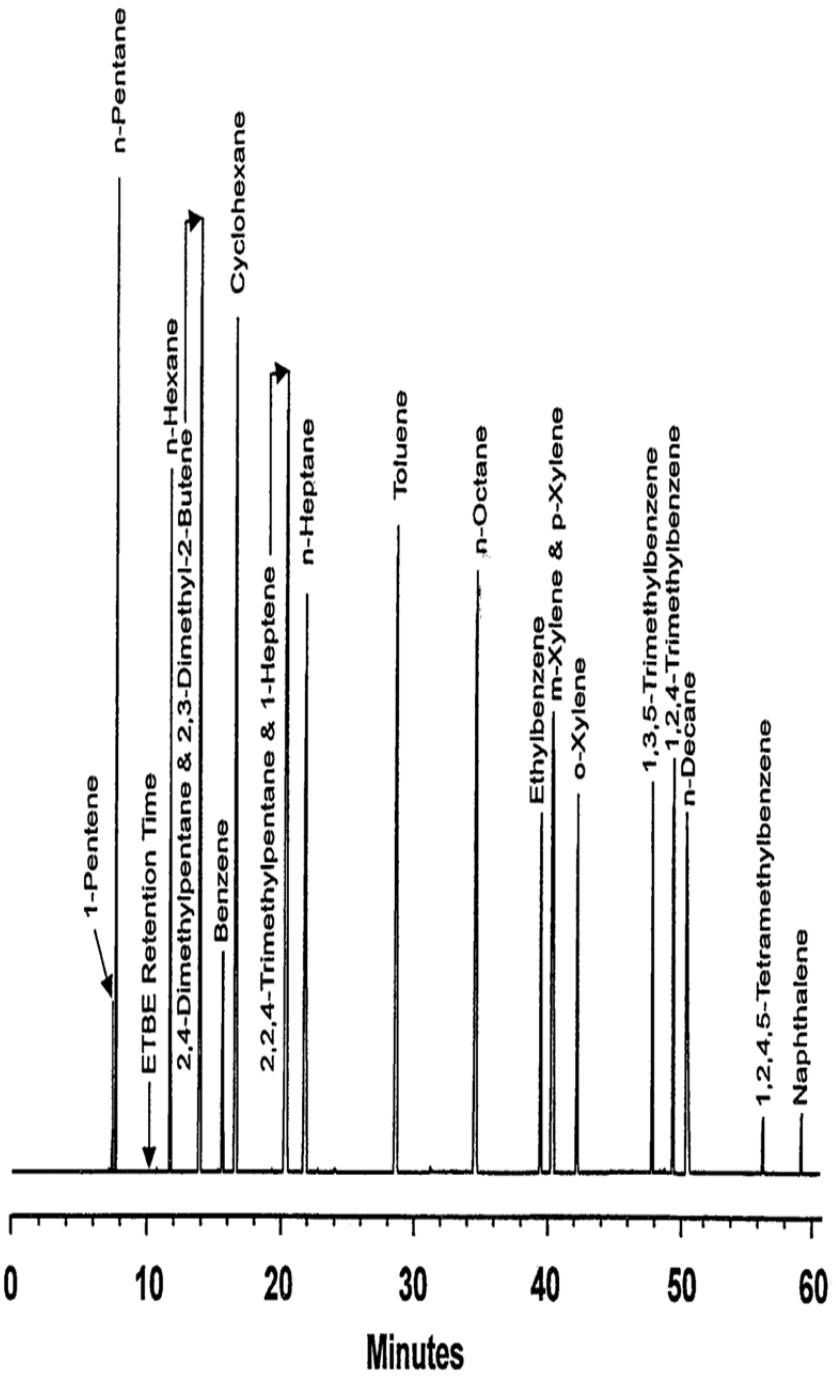

Figure 1. Chromatogram of reformulated gasoline base. Conditions: 100 m methylpolysiloxane column; injector temperature 200 °C; split ratio 200:1; initial temperature 35 °C, hold 10 min, programming rate 4 °C per min to 200 °C, final hold 10 min; detector temperature 280 °C. Except for *m*-xylene and *p*-xylene, the components unresolved by the conditions used to obtain the chromatogram in Figure 1 may be separated using the following: 30 m (6 % cyanopropyl) methylpolysiloxane column; injector temperature 200 °C; split ratio 200:1 initial temperature 30 °C, initial hold 5 min, programming rate 25 °C per min to 200 °C, final hold 0.2 min; detector temperature 280 °C.

REFERENCES

[1] 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 Sep 2012).

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

[3] JCGM 100:2008; *Evaluation of Measurement Data — Guide to the Expression of Uncertainty in Measurement* (ISO GUM 1995 with Minor Corrections); Joint Committee for Guides in Metrology (JCGM) (2008); available at http://www.bipm.org/utils/common/documents/jcgm/JCGM_100_2008_E.pdf (accessed Sep 2012); 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://www.nist.gov/pml/pubs/index.cfm (accessed Sep 2012).

[4] JCGM 101:2008; *Evaluation of measurement data – Supplement 1 to the Guide to the Expression of Uncertainty in Measurement – Propagation of Distributions Using a Monte Carlo Method*; Joint Committee for Guides in Metrology (JCGM) (2008); available at http://www.bipm.org/utils/common/documents/jcgm/JCGM_101_2008_E.pdf (accessed Sep 2012).

Certificate Revision History: 18 September 2012 (Extension of certification period; editorial changes); 05 January 2007 (Corrected reference values for 3-methylthiophene and benzo[b]thiophene); 22 February 2006 (Editorial changes); 04 January 2006 (Editorial changes); 30 December 2005 (Extension of certification period); 10 March 1998 (Original certificate date).

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.