National Institute of Standards & Technology

Certificate of Analysis

Standard Reference Material® 2037

Solvent Red 24 Diesel Fuel Dye

This Standard Reference Material (SRM) is intended for the verification and calibration of spectrophotometers used to measure the concentration of Solvent Red dyes employed as colorants to mark "off-road" diesel fuel. SRM 2037 is certified for the purity of the Solvent Red 24 Dye ($C_{24}H_{20}N_4O$, molecular mass 380.45) and for the second-derivative-based molecular absorption coefficients (extinction coefficients) of solutions of Solvent Red 24 Dye in *p*-xylene and in 97:3 (v:v) kerosene:*p*-xylene. Each unit of SRM 2037 consists of an amber 30 mL (1 oz), screw-capped bottle containing approximately 100 mg of solid Solvent Red 24 Dye.

Certified Values: A NIST certified value is a value for which NIST has the highest confidence in its accuracy and that all known or suspected sources of bias have been investigated or accounted for by NIST [1]. The certified mass fraction (purity) of the Solvent Red 24 dye is given in Table 1. The certified second-derivative-based molecular absorption coefficients, defined as ΔD2 / bc, which corresponds to an absorption coefficient based on second derivative absorbance spectra, where ΔD2 is the difference between the local maximum and local minimum second derivative absorbance values at the wavelengths given in Table 2, b is the pathlength and c is the concentration, for solutions of SRM 2037 at a 95 % uncertainty interval (at 22.5 °C ± 0.5 °C) are listed in Table 2.

Table 1. Mass Fraction (Purity) of Solvent Red 24 Dye

Constituent	Mass Fraction (%)	95 % Uncertainty Interval
Solvent Red 24 Dye	98.0	92.3 % to 100 %

Table 2. Second-Derivative-Based Molecular Absorption Coefficients for Solutions of Solvent Red 24 Dye

Solvent	Wavelength of Second Derivative Maximum (nm)	Wavelength of Second Derivative Minimum (nm)	Second-Derivative-Based Absorption Coefficients ($L\ g^{-1}cm^{-1}$)	($L\ mol^{-1}cm^{-1}$)
p-Xylene	534	557	0.088 ± 0.005	33 ± 2
Kerosene:*p*-Xylene	531	555	0.101 ± 0.006	39 ± 3

Expiration of Certification: The certification of this SRM is valid until **31 October 2014**, within the measurement uncertainties specified, provided the SRM is handled and stored in accordance with the instructions given here (see "Instructions for Use").

Maintenance of SRM Certification: NIST will monitor this SRM over the period of its certification. If substantive 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 of the NIST Analytical Chemistry Division.

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Production and certification of SRM 2037 were performed by P.C. DeRose, B. Coxon, and G.W. Kramer of the NIST Analytical Chemistry Division with assistance from D.L. Duewer, M.B. Satterfield, D.M. Bunk, M.J. Welch, E. White V, S.A. Margolis, J.R. Sieber, B.J. Porter, and M.M. Schantz of the NIST Analytical Chemistry Division.

Statistical consultation was provided by H–k. Liu of the NIST Statistical Engineering Division.

Packaging of SRM 2037 was coordinated through the NIST Standard Reference Materials Program by M.P. Cronise of the NIST Measurement Services Division.

The support aspects involved in the issuance of this SRM were coordinated through the NIST Standard Reference Materials Program by B.S. MacDonald of the NIST Measurement Services Division.

Reference Values: 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 associated uncertainty that may reflect only measurement precision and may not include all sources of uncertainty [1]. Reference values for the molecular absorption coefficient for solutions of SRM 2037 at a 95 % uncertainty interval (at 22.5 °C ± 0.5 °C) are listed in Table 3.

Table 3. Molecular Absorption Coefficients for Solutions of Solvent Red 24 Dye

Solvent	Wavelength	Molecular Absorption Coefficients	
	(nm)	(L $g^{-1}cm^{-1}$)	(L $mol^{-1}cm^{-1}$)
p-Xylene	520.5	87.4 ± 5.7	33 200 ± 2 200
Kerosene:*p*-Xylene	515.3	87.9 ± 5.7	33 400 ± 2 200

Information Values: A NIST information value is considered to be a value that will be of interest and use to the SRM user, but insufficient information is available to assess adequately the uncertainty associated with the value or only a limited number of analyses were performed [1]. A NIST information value is provided for information purposes only. Information values for the temperature coefficients of the second-derivative-based coefficients and the temperature coefficients of the absorption coefficients are listed in Table 4.

Table 4. Temperature Coefficients of the Second-Derivative-Based Coefficients and Temperature Coefficients of the Absorption Coefficients

Solvent	Temperature Range (ºC)	Temperature Coefficients of the Second-Derivative-Based Coefficients (% per ºC)	Temperature Coefficients of the Absorption Coefficients (% per ºC)
p-Xylene	19 to 37	–1.2	–0.22
Kerosene:*p*-Xylene	19 to 37	–1.1	–0.25

INSTRUCTIONS FOR USE

CAUTION: Solvent Red 24 has been designated a possible mutagen and is a common biological colorant for staining lipids and fatty substances in cells and tissues. Proper hand and eye protection should always be used when handling this SRM. The material and its solutions are intensely red and nearly invisible amounts of the solid dye can stain clothing, equipment, etc. if handled improperly. Any unused material should be discarded properly (see the Material Safety Data Sheet (MSDS) accompanying the SRM.

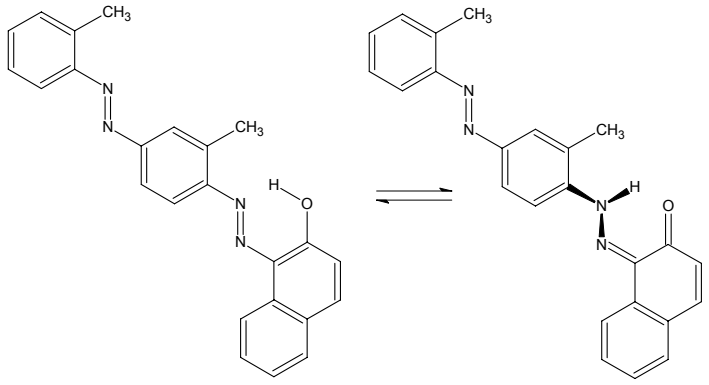
This material is not hydroscopic under the normal conditions of storage as described above and can be used without preliminary drying.

This material is not easily dissolved in aliphatic hydrocarbons (e.g., kerosene or diesel fuel). To facilitate preparation of such solutions, dissolution of a weighed amount of the solid dye in a small amount of an aromatic hydrocarbon (e.g., toluene or xylene in which it is more soluble) followed by dilution with the aliphatic material is suggested.

Software routines for calculating second derivative spectra often contain magnitude scaling factors [4–6]. Furthermore, the type and amount of spectral smoothing used when determining the second derivatives can affect

the result calculations [4–8]. The user is urged to thoroughly understand the calculations being utilized in the method employed. Consultation with the instrument vendor may be necessary if the algorithms are not fully documented.

Source of Material:. The Solvent Red 24 dye was obtained from Aldrich Chemical Company (Milwaukee, WI): Sudan IV, Certified, P/N 19810-2, Lot 05716ER and purified by Regis Technologies, Inc. (Morton Grove, IL): Lot No. P144-61-1.[1] Figure 1 shows both the azo-phenol (1a) and quinone-hydrazone (1b) structures of Solvent Red 24 dye. Spectral evidence suggests that structure 1b predominates; however, the distribution of tautomers depends on the solvent and temperature. Steric factors argue for the *E*-configurations about the nitrogen double bounds, but ^{1}H NMR evidence suggests that a *Z* configuration can exist for the simple azo substructure.



1a 1b

Figure 1. Tautomeric Structures of Solvent Red 24 Dye

Determination of Solvent Red 24 Dye Purity: Table 5 summarizes the Solvent Red 24 dye purity and impurity determinations on the material used for SRM 2037.

Table 5. Summary of Solvent Red 24 Dye Purity and Impurity Determinations and Associated Uncertainties

Constituent	Technique	Mass Fraction (%)	Uncertainty (U_{95})
Solvent Red 24 Dye	^{1}H NMR[(a)] & HPLC[(b)]	97.95	92.26 to 100
Orange OT Dye	^{1}H NMR[(a)] & HPLC[(b)]	0.44	± 0.13
Chloroform	^{1}H NMR[(a)]	0.30	± 0.04
Other Solvent Red Type Dyes	HPLC[(b)]	0.07	± 0.01
Water	Karl Fisher Titration	0.05	± 0.03
Total Organics	CHON Analysis[(c)]	99.96	± 0.26

(a) 500 MHz Proton Nuclear Magnetic Resonance Spectroscopy
(b) High Performance Liquid Chromatography and High Performance Liquid Chromatography-Mass Spectrometry, both normal and reversed phase
(c) Elemental analyses carried out by Atlantic Microlab, Inc.[1] (Norcross, GA) and Galbraith Laboratories, Inc. (Knoxville, TN).

Assignment of Uncertainties: Except for the Solvent Red 24 purity determination, standard uncertainty components equivalent to the estimated standard deviation for a normal distribution were assigned for measurement repeatabilities and were combined with balance accuracy uncertainties and estimated instrument method uncertainties using the root-sum-of-squares method. An expansion factor of $k = 2$ was applied such that the

[1]Certain commercial equipment, instruments, or materials are identified in this certificate in order to specify adequately 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.

expanded uncertainties given in this certificate express an interval within which the true value is expected to fall with a level of confidence of approximately 95 % [2]. The uncertainty of the purity of the Solvent Red 24 was handled differently because for any material the upper limit for purity is 100 %. Accordingly, a Baysian approach was used that distributes the calculated combined uncertainty density uniformly across the constrained mass fraction range to give an unsymmetrical interval bounded by 100 % within which the true value is expected to fall with a level of confidence of approximately 95 % [3].

SRM Stability: NIST has monitored the stability of solutions of prototype materials similar to SRM 2037 for over 36 months. Within the error of the measurements, the absorbance spectrum of the prototype solutions did not change, providing the solutions were stored in the dark. Exposure of solutions of Solvent Red 24 and similar dyes to sunlight or other sources of ultraviolet light causes slow fading of the red color and a decrease in the molecular absorption coefficient due to photochemical decomposition of the dye itself. No specific photostability studies have been carried out on the solid dye, but given the solution results, it seems prudent to store the SRM in its original amber container in the dark. SRM 2037, if stored tightly re-capped, in the dark between 15 °C and 30 °C, will likely maintain its original optical properties for the duration of its certification period and perhaps beyond that. NIST will validate this conclusion by periodic monitoring of the stability over the time the lifetime of the SRM.

REFERENCES

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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.