

California Environmental Protection Agency



Air Resources Board

PROCEDURE FOR DETERMINATION OF EQUIVALENT SOLVENT RED 26 DYE CONCENTRATION IN DIESEL FUELS

Standard Operating Procedure No. MLD 140

Revision No. 1.3

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1 Introduction

This document describes a method of determining the concentration of dye Solvent Red 164 in commercially available diesel and burner fuels using visible spectroscopy. Solvent Red 26 is the standard against which the concentration of Solvent Red 164 is measured.

- 1.1 The concentration ranges specified for the calibration standards are established in response to Internal Revenue Service regulations governing the addition of dyes to tax exempt diesel fuels. Current regulations state that an amount of red dye spectrally equivalent to 3.9 pounds per thousand barrels (11.1 mg/L) of Solvent Red 26 shall be added into tax exempt diesel fuels.
- 1.2 This method is based on ASTM D6258-98.

2 Method Summary

The diesel samples are transferred into a cuvette and the visible absorbance spectra is measured over a specified wavelength range. The spectra are then analyzed using derivative analysis methodology in order to minimize interferences caused by variations in the color and composition of the fuel samples. The equivalent Solvent Red 26 concentrations are determined against the appropriate calibration curve prepared by measuring a series of standard Solvent Red 26 solutions of known concentrations.

3 Interferences and Limitations

Diesel fuels naturally range in color from water white to nearly black. These variations in absorbance in principle would cause interferences as long as an undyed sample is not available to be measured for background correction. The differences of the second derivative spectra are proportional to concentrations of the Red Dye, but are unaffected by background absorbance up to the second order. Therefore, by measuring the differences of the second derivative spectra, the effect of such interferences is minimized. However, when the color of the diesel fuel sample is too black, even this derivative method is not going to make the interferences negligible. In this case, there is a possibility that there is no violation even if the analysis shows otherwise.

4 Instrumentation and Apparatus

- 4.1 Varian Cary 100 Conc UV-Visible Spectrophotometer, which is equipped with automated scanning, background correction and electronic data storage capabilities, and the ability to automatically record absorbance or transmittance of solutions in the spectral region from 400 to 800 nanometers (nm) with a spectral slit width of 1 nm or less.

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- 4.2 Sample cells (cuvettes), one or more fused silica or glass cells have sample path length of 10 mm.
- 4.3 Analytical balance, 0.1 mg sensitivity.
- 4.4 Pipettes/volumetric syringes, 1.00 to 5.00 milliliters (mLs).
- 4.5 Volumetric flasks, 100 mL and 250 mL.

5 Reagents and Materials

- 5.1 Solvent Red 26, 1-[[2,5-dimethyl-4-[(2-methylphenyl)azo]phenyl]azo]-2-naphthol, CAS number 4477-79-6, Dry powder with certified purity, and maximum absorbance at 512 ± 20 nm.
- 5.2 Kerosene, 1-K, water-white, conforming to ASTM Specification D 3699, and having a maximum absorbance against air of 0.08 over the wavelength range of 450 to 750 nm (10 mm cell, 120 nm/min scan rate, spectral slit width 1.0 nm).
- 5.3 Xylene, mixed, ACS Reagent grade.

6 Safety Precautions

- 6.1 Standard laboratory safety procedures and equipment should be used in performing this method. For example, safety glasses and gloves should be worn. All standard and sample preparation should be done in the fume hood. Diesel fuel contains compounds known to be toxic and carcinogenic.

7 Samples

- 7.1 A minimum of 100 mL of the diesel fuel sample is required.
- 7.2 Refer to ASTM D 4057 for proper sampling techniques. Since red dye is known to decompose slowly under direct sunlight, precautions must be taken to shield the samples prior to analysis.

8 Procedure

- 8.1 Preparation of stock standard Solvent Red 26 Dye solution:
 - 8.1.1 Weigh approximately 0.0750 g of the dye standard to the nearest 0.1 mg on an analytical balance. Quantitatively transfer the dye to a 250 mL volumetric flask, and dilute to mark with xylene. Thoroughly mix the solution.
 - 8.1.2 The exact concentration of the red dye in the stock standard is calculated using the following equation:

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$$C = \frac{(M) (P) (1000)}{0.250},$$

where:

C = concentration of active dye ingredient in the stock standard in mg/L,

M = mass of the dye standard weighed in grams and

P = purity of the dye standard.

8.1.3 Store the stock standard in tightly capped/sealed brown glass bottles and store in a dark, locked cabinet at room temperature when not in use to prevent decomposition of the dye. Refrigeration is not necessary.

8.2 Preparation of working calibration standards:

8.2.1 Pipet stock standard of volumes specified below into separate 100 mL volumetric flasks and dilute to mark with kerosene.

Volume of Stock Standard	Approximate concentration of Working Standards
0.0 mL	0 mg/L
1.0 mL	3 mg/L
2.0 mL	6 mg/L
3.0 mL	9 mg/L
4.0 mL	12 mg/L
5.0 mL	15 mg/L

8.2.2 The exact concentration of the red dye in each working standard is calculated using the following equation:

$$C_s = \frac{(V) (C)}{100},$$

where:

C_S = concentration of each working standard in mg/L,

V = volume of stock standard in mL and

C = concentration of active dye ingredient in the stock standard in mg/L.

8.2.3 Store the working calibration standards in tightly capped/sealed brown glass bottles with the stock standard when not in use.

8.3 Turn on the spectrophotometer at least one hour before use.

8.4 Using a clean 10 mm cuvette, scan each of the working standards against air (empty reference sample compartment) from 450 to 750 nm, recording the absorbance for each solution using a scan rate of 120 nm/min, a maximum data recording interval of 0.11 nm and a maximum spectral slit width of 1.0 nm. An example of the Red Dye 26 spectrum is shown in Figure 1 on the next page.

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- 8.5 Using derivative analysis software, calculate and plot the second derivative spectra for each standard over the range of scan. Use appropriate software settings to avoid magnification of instrument noise and ensure a smooth second derivative curve.
- 8.6 On the second derivative curve, measure the local maximum at 538 ± 20 nm and local minimum at 561 ± 20 nm (Figure 2). Note: the positions and relative heights of the maximum and the minimum can vary. Obviously this method is only valid when it is absolutely clear which maximum and which minimum correspond to the Red Dye absorption in the region.
- 8.7 Repeat the same procedure from section 8.4 to 8.6 for each sample, including runs for quality control and repeatability (see section 10).

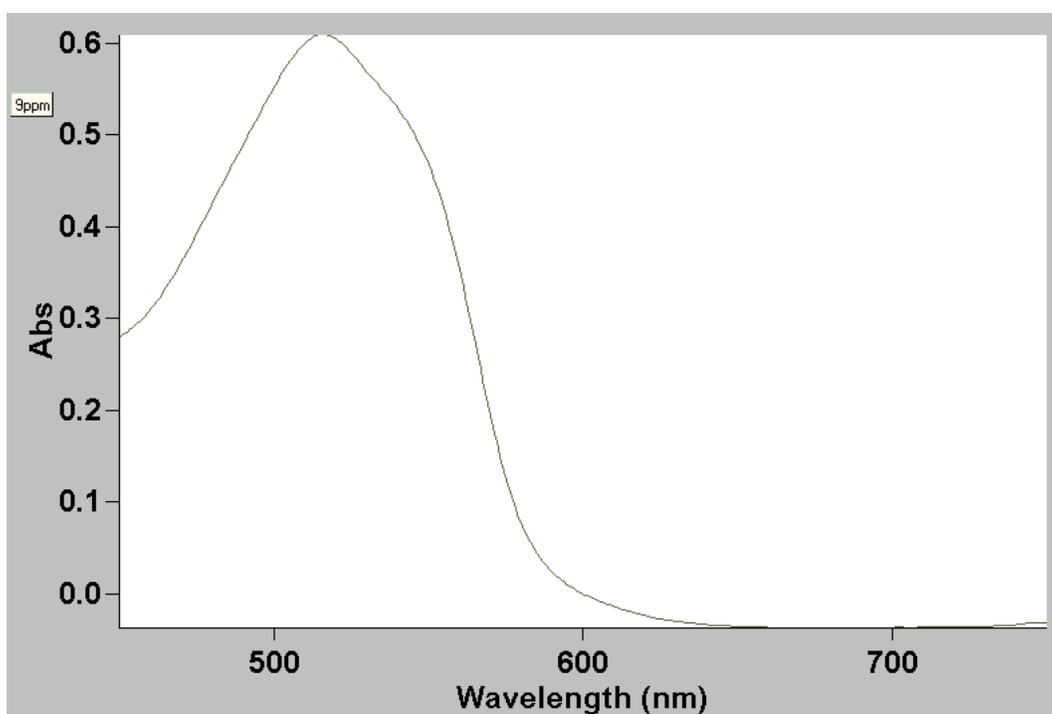


Figure 1: an example spectrum of 9 ppm Red Dye 26 between 450 nm and 750 nm.

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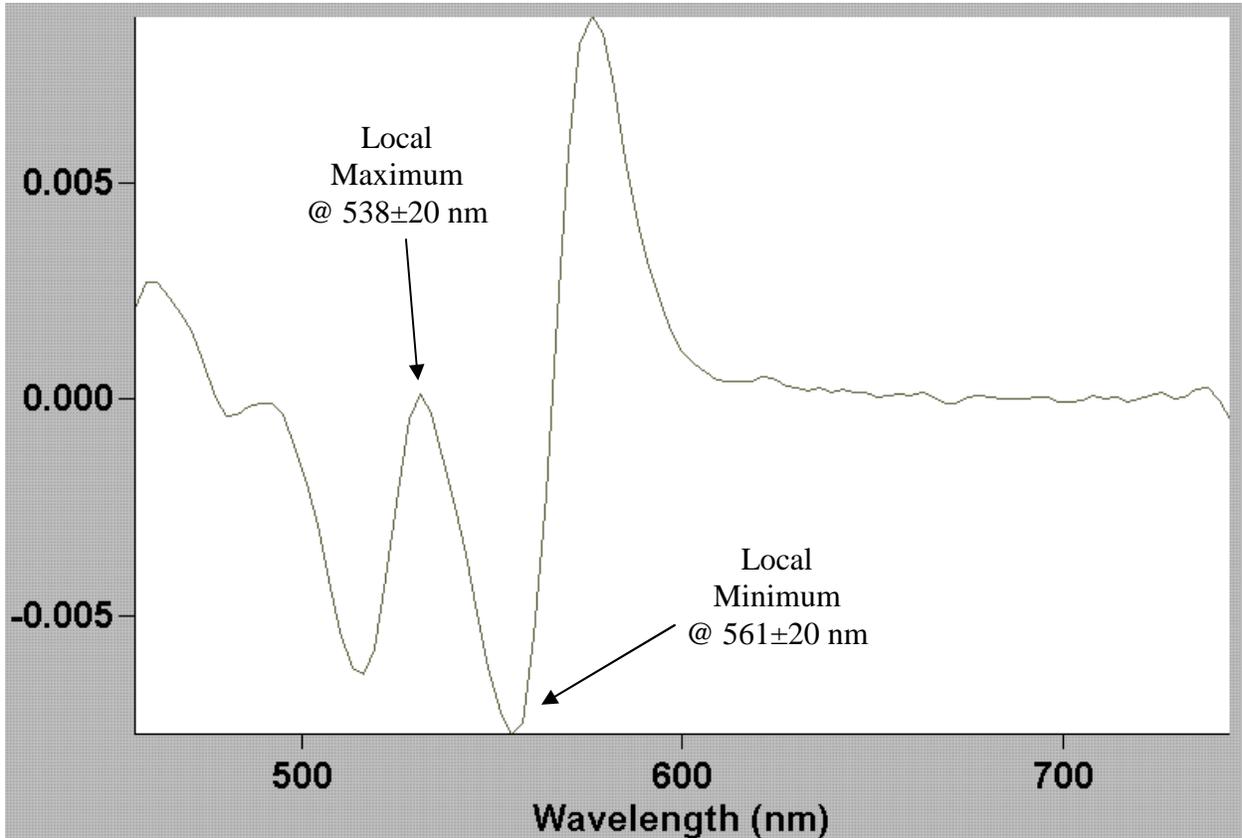


Figure 2: measure the local maximum at 538 ± 20 nm and local minimum at 561 ± 20 nm on the second derivative curve of a Red Dye absorption spectrum.

9 Calculations

- 9.1 Prepare a calibration curve, plotting the amplitude difference for each working calibration standard on the y axis versus the dye concentration on the x axis.
- 9.2 Determine the concentration of dye in the sample by comparing the amplitude difference measured in section 8.6 for the sample against the calibration curve. Computer systems/software having appropriate multi-point calibration program capabilities may be used instead of a manual interpolation from calibration curves.
- 9.3 Report dye concentration in the sample to one decimal place, for example, 11.1 mg/L. Report concentrations greater than 15.0 mg/L as ">15.0 mg/L".
- 9.4 If the diesel fuel visually is very black instead of red, note that on the report. In this case, the results from this method may not be reliable.

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10 Quality Control (QC)

10.1 A QC standard is analyzed at the beginning and end of each set of samples. Determine the Red Dye concentration of the standard the same way as other samples. The concentration of the QC standard is between 3 mg/L and 15 mg/L.

10.2 In each day when analyses are performed, repeat the analysis of at least one sample. If the two results differ by more than the repeatability, it is considered a QC failure and all sample results for the set from this instrument must be invalidated. The source of the problem has to be eliminated and then the samples have to be reanalyzed. It is recommended to pick a sample concentration higher than 2 mg/L for this test. The repeatability of this method is determined by the ASTM as

$$\text{Repeatability (r)} = 0.1847 (x)^{0.5},$$

where:

x = mean dye concentration (mg/L) of two results from the same laboratory.

10.3 Record the values of concentration of the quality control standard obtained from calculations in an Excel spreadsheet. QC results must agree with historical values of the same QC sample to within two standard deviations to pass and for the results to be valid. If QC measurements exceed two standard deviations, a warning is given; the QC sample has to be rerun immediately. If two consecutive warnings are recorded or if a QC measurement exceeds three standard deviations, it is considered a QC failure and all results for the day from the spectrophotometer must be invalidated. In this case, find out the problem and repeat the analyses after the problem is solved. Use a new QC standard if the current one is no longer usable (Refer to Table 1 on page 9 as an example).

10.4 When it is time for a new QC standard, the new QC should have an equivalent concentration between 3 mg/L and 15 mg/L. Measure the new QC standard as an unknown on at least two different days, twice per day to have a minimum of four data points for the initial average concentration and calculation of the ASTM repeatability (r). QC results must be within (r) to pass until 20 "good" data points are accumulated for section 10.3 to be applied.

10.5 The r^2 correlation coefficient of the linear regression of the calibration curve has to be better than 0.995 for the results to be valid. Make sure the instrument is warmed up for at least one hour. Repeat the measurement(s) or preparation of the working standards if this criterion is not met.

11 Reference

ASTM D6258-98

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12 Revision History

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|------|----------------------|--|
| 12.1 | Revision No. 1.2 | Effective date: November 14, 2005 |
| 12.2 | Revision No. 1.1 | Effective date: August 3, 2006 |
| | Significant changes: | Added section 10.4 to cover the transfer to a new QC standard. |

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Red Dye Control Chart

QC Requirements:

PASS < 2 SD off mean
 WARNING >= 2 SD off mean
 FAILURE > 3 SD off mean

Instrument - Varian 100 Conc UV-Vis Spectrophotometer

Control Standard - Exxon 6549

Date	No.	2.08	0.26	12.70	Status
		Value(v)	v-m = Deviation	v-m/SD = # of SD off	
1/28/2004	1	12.8	0.10	0.40	PASS
	2	12.6	-0.10	-0.36	PASS
3/2/2004	3	12.8	0.10	0.40	PASS
	4	12.4	-0.30	-1.12	PASS
3/18/2004	5	12.7	0.00	0.02	PASS
	6	12.2	-0.50	-1.88	PASS
5/3/2004	7	12.8	0.10	0.40	PASS
	8	12.2	-0.50	-1.88	PASS
5/18/2004	9	13.2	0.50	1.91	PASS
	10	12.9	0.20	0.78	PASS
7/7/2004	11	12.6	-0.10	-0.36	PASS
	12	12.4	-0.30	-1.12	PASS
7/22/2004	13	12.8	0.10	0.40	PASS
	14	12.8	0.10	0.40	PASS
8/19/2004	15	12.6	-0.10	-0.36	PASS
	16	12.5	-0.20	-0.74	PASS
11/30/2004	17	13.0	0.30	1.16	PASS
	18	12.9	0.20	0.78	PASS
3/8/2005	19	13.1	0.40	1.54	PASS
	20	12.6	-0.10	-0.36	PASS
4/27/2005	21	12.7	0.00	0.02	PASS
	22	12.6	-0.10	-0.36	PASS
6/1/2005	23	12.7	0.00	0.02	PASS
	24	12.7	0.00	0.02	PASS
6/30/2005	25	12.6	-0.10	-0.36	PASS
	26	12.7	0.00	0.02	PASS
8/2/2005	27	12.8	0.10	0.40	PASS
	28	13.0	0.30	1.16	PASS
10/18/2005	29	12.9	0.20	0.78	PASS
	30	13.0	0.30	1.16	PASS
11/18/2005	31	13.0	0.29	1.12	PASS
	32	12.8	0.07	0.28	PASS

Table 1: a real example of the quality control spreadsheet.