



Standard Practices for Uniformity of Traffic Paint Vehicle Solids by Spectroscopy and Gas Chromatography¹

This standard is issued under the fixed designation D 2743; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 These practices provide general information on the instrumental techniques available for detecting adulteration or nonuniformity of the chemical nature of the vehicle solids in purchased lots of traffic paints by means of the individual or combined use of infrared and ultraviolet spectroscopy and gas chromatography. The procedures given are applicable when traffic paint is selected and purchased on the basis of prequalification laboratory or road performance tests, or both, and a *reference sample* of the original paint so evaluated and selected is retained and compared with test samples representative of subsequent purchased and delivered lots of such paint and which are required to be the same as the original reference sample.

1.2 Although not specifically provided for in these practices, the methods given may also be applied, with appropriate modification, to evaluating the acceptability of traffic paints that have been purchased on the basis of composition specifications. In such cases, application is limited to the vehicle solids as before, as well as the availability of a suitable standard or range of standards representative of the vehicle solids that are acceptable and with which samples of subsequent delivered lots will be compared.

1.3 The techniques provided are wholly adequate for detecting gross adulteration of the vehicle solids where completely different drying oils, resins, or polymers, or combinations of these have been substituted for those originally contained in the reference sample. In cases of lesser adulteration or modification, these methods have been found adequate for detecting vehicle solids, adulterations, or modifications as low as 5 weight % of the vehicle solids.

1.4 These techniques have been developed on the basis of cooperative work with alkyd, chlorinated rubber-alkyd, and poly(vinyl toluene) type paints involving the detection of nonuniformity when such extraneous materials as rosin, fish

oil, hydrocarbon resin, and chlorinated paraffin have been added. The procedures given may be, but are not necessarily completely applicable to all other types of vehicle solids or extraneous additions, or both.

1.5 The methods provided appear in the following order:

Method A—Infrared Spectral Analysis of Total Vehicle Solids	Section 10-12
Method B—Infrared Spectral Analysis of Unsaponifiable Matter from Vehicle Solids	13-15
Method C—Gas Chromatographic Analysis of Oils and Oil Acids Separated from Vehicle Solids	16-18
Method D—Ultraviolet Spectral Analysis of Total Vehicle Solids	19, 20, and 21

1.6 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 ASTM Standards:²

- D 1259 Test Methods for Nonvolatile Content of Resin Solutions
- D 1397 Test Method for Unsaponifiable Matter in Alkyd Resins and Resin Solutions
- D 2245 Test Method for Identification of Oils and Oil Acids in Solvent-Reducible Paints
- D 2372 Practice for Separation of Vehicle from Solvent-Reducible Paints
- D 2621 Test Method for Infrared Identification of Vehicle Solids from Solvent-Reducible Paints
- E 105 Practice for Probability Sampling of Materials
- E 131 Terminology Relating to Molecular Spectroscopy

3. Terminology

3.1 For definitions of terms and symbols, refer to Terminology E 131.

¹ These practices are under jurisdiction of ASTM Committee D01 on Paint and Related Coatings, Materials, and Applications and are the direct responsibility of Subcommittee D01.44 on Traffic Coatings.

Current edition approved June 1, 2004. Published June 2004. Originally approved in 1968. Last previous edition approved in 1998 as D 2743 – 68 (1998)

² For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

4. Summary of Methods

4.1 Each of the methods given requires both a reference and a test sample of traffic paint and a preliminary separation and removal of the pigment component in each.

4.2 *Method A* involves infrared spectral analysis of cast films of the total vehicle solids to detect spectral differences between the reference and test samples caused by gross or minor adulteration of the test sample.

4.3 *Method B* involves infrared spectral analysis of cast films of the unsaponifiable matter that has been separated from the vehicle solids in order to detect spectral differences between the reference and test samples caused by lesser adulterations of an unsaponifiable nature and which was not readily evident when using Method A.

4.4 *Method C* involves gas chromatographic analysis of prepared methyl esters of the separated fatty acids obtained from the vehicle solids in order to detect chromatographic differences between the reference and test samples caused by either gross or lesser adulteration of the drying oil fraction with extraneous drying oils which may not have been readily evident by the use of Methods A and B.

4.5 *Method D* involves quantitative ultraviolet spectral analysis of the total vehicle solids dissolved in a nonaromatic spectral grade solvent to give precise concentrations in order to detect ultraviolet spectral absorbance differences between the reference and test samples caused by minor or sophisticated adulterations of the vehicle solids and which may not be readily detected by Method A. Method D is to be used as an alternative to Methods B and C.

5. Selection of Test Methods and Significance and Use

5.1 All of the methods provided involve comparisons between the spectra or chromatograms of the reference and test samples to determine if they show significant differences. It is not possible at this time to establish quantitative limits as a guide to whether a spectral or chromatographic difference is truly significant. Certainly the presence or absence of a moderate or strong peak in the test sample which is not evident in the reference is significant. A persistent difference in the ratios of two peaks of one spectrum as compared to the reference sample is significant. On the whole, some judgment must be exercised in this respect and it is advisable to refer to published data on infrared or gas chromatography in order to establish, where feasible, the possible overall nature of the adulterant or its functional group which might be causing the comparison spectra to differ.

5.2 *Method A* is rapid and the most convenient of the procedures given. It should be utilized first in order to detect nonuniformity of the test sample. Significant spectral differences from that of the reference sample can be taken as an indication of adulteration and in such cases the use of the other methods is not necessary. As a general rule, Method A is sufficient to detect gross or major adulteration of the vehicle solids. However, where Method A shows no significant spectral differences, it cannot be assumed that the test sample is completely acceptable since changes in the type of drying oil, polyol, and certain dibasic acids in alkyd resins, addition of certain aliphatic or nonfunctional hydrocarbon resins, and

many minor adulterations may not always show characteristic infrared spectral differences. Therefore, in such cases it is best to proceed to additional tests as given in Methods B and C or else alternatively directly to Method D.

5.3 *Method B* is useful in detecting adulterations that are unsaponifiable or else have an unsaponifiable component that has escaped detection in Method A only because the adulterant may have been small in amount and therefore its strong spectral peaks may have been masked over by the rest of the vehicle solids. Some care should be taken in interpreting spectral differences in Method B to avoid an erroneous conclusion that the test sample is unacceptable because its spectrum is different. Apparent but unreal differences can occur as a result of incomplete saponification, failure to remove all saponifiable material, and varying degrees of contamination of the unsaponifiable fraction with sterols, etc., present in the vehicle solids. After it has thus been firmly established that a real spectral difference does exist, further tests are unnecessary, except that it is wise to resort again to the published literature on infrared to attempt to identify the possible nature of the adulterant. Where Methods A and B indicate acceptability of the test sample, it is still not always possible to rule out adulteration caused by changes or modifications in the saponifiable portion, that is, the type of fatty acid, dibasic acids, and polyol. In such cases, it is best to continue on to Method C for determination of the oil acids, and to other gas chromatographic methods for the polyol and dibasic acids when such equipment is available.

5.4 *Method C* is extremely sensitive in detecting adulterations and changes that have been made in the oil or fatty acid portion of the vehicle solids. It can, for example, detect whether linseed, coconut, oiticica, etc., has been substituted for soya oil and vice versa, or whether fish or tall oil has partially or wholly replaced some other drying oil, etc. Consequently, when the results of Methods A and B suggest that the test sample is acceptable and where a drying oil component is known to be present, Method C should be used additionally for more complete assurance of product uniformity. Where the results from Method C along with those from Methods A and B indicate product uniformity, it is a fairly safe assumption that the product has not been significantly altered.

5.5 *Method D* is intended as an alternative to Methods B and C and where the results from Method A indicate apparent product acceptability. Method D, by the use of quantitative ultraviolet spectral absorbance data, is an extremely sensitive procedure for the detection of complete or even partial adulteration of the test sample. However, considerable caution must be exercised in the preliminary pre-drying of the vehicle solids since it is at this stage that the components are extremely sensitive to oxidative changes. Even minor oxidative changes can seriously affect the absorbance data obtained in ultraviolet spectral analysis and may give an impression that the two samples being compared are different when in fact they are the same. When these considerations are provided for, and the comparison spectra are identical in Method D as well as in Method A, then it can be assumed that the sample is acceptable. Significant differences in the spectra from Method D would

indicate nonuniformity of the product even though Method A may fail to reveal such nonuniformity.

6. Reference Sample

6.1 The reference sample of traffic paint should be at least 250 mL and should be truly representative of the initial paint found acceptable in pre-qualification laboratory or field service tests, or both, and which paint is subsequently specified for purchase.

6.2 In cases where paint is purchased on the basis of formulation specifications and it is desired to utilize these procedures to detect adulteration in delivered lots of paint, reference samples may be synthetically prepared to represent the extremes of the range that will be permitted in the formulation.

7. Test Sample

7.1 The test samples of the traffic paint should be at least 250 mL and should be representative of each delivered lot of paint that was specified for purchase and which is intended to be the same as the initial reference paint used in the pre-qualifications acceptance tests from which a reference sample was retained.

8. Sampling Reference and Test Samples

8.1 Test and reference samples of the traffic paint should be obtained in accordance with Practice E 105.

9. Preparation of Samples

9.1 Separate the vehicle from the pigment by centrifuging the paint in accordance with Practice D 2372. Transfer and preserve the vehicle in a well-stoppered amber bottle.

METHOD A—INFRARED SPECTRAL ANALYSIS OF TOTAL VEHICLE SOLIDS

10. Apparatus

10.1 *Infrared Spectrophotometer*, recording double-beam, and accessory equipment as described in Test Method D 2621.

11. Procedure

11.1 Obtain the infrared spectra of a cast film of the vehicle solids of both the test and reference samples by utilizing the procedure referred to in 10.1. In all cases, however, the spectral intensity of both samples should be well matched (by adjusting the film thickness) to within 5 % transmission of each other at the strongest peak, and the transmission of this peak shall be between 5 and 15 %. It is also desirable to obtain additional spectra on thicker films or else ordinate scale expansion if available, to bring out spectral differences in the weak to moderate peak areas. Here again, the same degree of care should be taken as above to match the film thickness and thereby the overall spectral intensities of the two samples. If desired, an aid in comparison is to run the test sample against the reference sample in the reference beam in order to show significant differences by means of a single differential spectrum. Considerable caution is required in the use and interpretation of differential spectra as well as proper adjustments of gain, speed, and slit programs.

12. Interpretation of Results

12.1 Compare the companion spectra from the test and reference samples for identity by visual inspection preferably over a light box. Note particularly the presence of an extraneous peak or peaks in one which is (are) not in the other. Also note the ratio of intensities of two adjacent or pairs of peaks on one spectra and determine whether this ratio is similar on the comparison spectra. Any significant difference should be considered as an indication of lack of uniformity between the reference and test samples. Attempt to ascribe this difference to some extraneous component or formulation difference between the comparison samples by referring to available infrared literature and published spectra. Where it is evident that the comparison spectra are significantly different, no further tests are necessary. When the spectra are identical, proceed to Methods B and C or alternatively to Method D for a fuller evaluation of possible minor or more sophisticated adulteration.

METHOD B—INFRARED SPECTRAL ANALYSIS OF UNSAPONIFIABLE MATTER FROM VEHICLE SOLIDS

13. Apparatus

13.1 Same as in 10.1.

14. Procedure

14.1 Treat a portion of the separated vehicle from both the sample and reference paints so as to obtain an ether solution of the unsaponifiable matter in accordance with Test Method D 1397. Take care to ensure rigorous quantitative separations and similar handling and exposure of the comparison samples. Determine the percentage of unsaponifiable matter. Obtain infrared spectra of cast films of the dried unsaponifiable matter in a manner similar to that described in 11.1.

15. Interpretation of Results

15.1 Compare the percentages of unsaponifiable matter. Compare the spectra and interpret the results in a similar manner as in 12.1. Care should be taken to avoid an erroneous conclusion that the materials are different when in fact they are the same. Such a misinterpretation could be caused by incomplete removal of oil acids and varying degrees of sterol contamination, solvent residues, etc. If it is firmly established that the companion samples are truly different, then further tests are unnecessary. If, on the other hand, the spectra and unsaponifiable contents are identical and the results from Method A were similar, then proceed to Method C to determine adulteration of the oil fraction or by oils if such is present or suspected of being present.

METHOD C—GAS CHROMATOGRAPHIC ANALYSIS OF OILS AND OIL ACIDS SEPARATED FROM VEHICLE SOLIDS

16. Apparatus and Reagents

16.1 Same as in Test Method D 2245.

17. Procedure

17.1 Proceed as in Test Method D 2245 utilizing a portion of the vehicles separated from both the test and reference samples.

18. Interpretation of Results

18.1 Compare the two recorded chromatograms and the calculated percentages of individual fatty acids for similarity. Note particularly the absence or presence of extraneous peaks in one and not the other as well as the percentages of individual fatty acids and polymers in one sample as compared to the other. Any significant difference should be taken as an indication of test sample adulteration or lack of uniformity.

METHOD D—ULTRAVIOLET SPECTRAL ANALYSIS OF TOTAL VEHICLE SOLIDS

19. Apparatus

19.1 *Spectrophotometer*, recording double-beam, suitable for use in the ultraviolet region of the electromagnetic spectrum from 190 to 350 nm.

20. Procedure

20.1 On a portion of the previously separated vehicles of the test and reference samples, determine the nonvolatile content by means of Test Methods D 1259. On the basis of this determination, quantitatively weigh out, by difference, from the stoppered bottles of the total vehicle, samples to yield 0.2 ± 0.0005 g of vehicle solids and place in a 100-mL beaker. Take care to avoid weighing errors caused by evaporation of solvent in the stoppered bottle during the weighing process.

20.2 Evaporate the volatile material by placing the beaker over an even heat source maintained at 60 to 65°C and under a constant blanket of dry, inert gas, preferably nitrogen, fed through a bell jar in which the beaker is placed. The bell jar should also be fitted with a stoppered separatory funnel with its delivery tube directly over the beaker. Evaporate until all the solvent is completely removed but avoid excessive exposure to these conditions much beyond this point. With the inert gas flow uninterrupted, transfer about 25 to 30 mL of spectral grade cyclohexane to the beaker through the assembled separatory funnel. Remove the beaker and immediately stir to dissolve all the solid material in the solvent. Quantitatively transfer to a 50-mL volumetric flask and fill to mark with additional spectral solvent. This yields a 0.4 % stock solution (wt/vol) of the vehicle solids in solution. If solution is not complete, try gentle warming or else start over using another suitable spectral grade nonaromatic solvent with an ultraviolet cut-off point at least as low as 220 or 230 nm.

20.3 With appropriate calibrated pipets or hypodermic syringes, volumetric flask, and the same lot of solvent used before, prepare several dilute quantitative solutions from aliquots of each stock solution that will enable quantitative measurements of all peak heights in the subsequent ultraviolet analysis (Note 1). In all cases, a specific quantitative dilution of

the reference sample should be matched by exactly the same dilution of the test sample. For each such matched dilution, use the exact same pipet for the test sample as was used for the reference sample to avoid dilution errors of comparison samples.

NOTE 1—The concentrations and numbers of dilute solutions necessary to obtain all the spectral peaks characteristic of a material will vary with the type of vehicle solids under examination. Generally, three dilutions of each stock solution to yield 0.03, 0.01, and 0.005 % solutions should suffice.

20.4 Within 24 h, and after making certain that the dilute solution is perfectly clear and without sediment and insolubles, record the ultraviolet absorbance spectrum of the dilute solution using a 1-cm stoppered quartz cell against the solvent blank in a reference cell. Obtain all absorbance peaks for each material that may occur between 200 and 300 nm. By appropriate use of the various dilutions of each sample, the spectral peaks should be made to fall between 0.3 and 0.8 absorbance unit. In all cases, record the exact absorbance value for each of the peaks for both test and reference samples. For each peak at a specific wavelength, the concentrations used for both the test and reference samples should be identical. It is wise to prepare several replicate standard stock and dilute solutions for each concentration independently of each other in order to obtain an idea of the range in each peak absorbance of the standard sample that might be expected in this procedure, especially as a result of the preliminary removal of original solvent by heating and its possible oxidative effects.

21. Interpretation of Results


21.1 Compare the nature and shape of the ultraviolet absorption curves obtained for both the test and reference samples. Any significant difference is an indication of adulteration or nonuniformity. Also compare the absorbance value of each peak given by the test sample with that given by the comparison reference sample. Any significant difference should be an indication of adulteration or nonuniformity. It is difficult to fix precise criteria for spectral differences that apply to all materials. As a general guide, the following criteria may be useful for evaluating comparable absorbance peaks. Comparison peaks should be within 0.05 absorbance units when occurring between 220 and 350 nm, and within 0.08 at lower wavelengths.

22. Report

22.1 Indicate uniformity or lack of uniformity of the vehicle solids of the test sample with respect to the reference sample and the method or methods (A, B, C, and D) used for this judgment. If possible, attempt to report the nature of possible adulterant(s) present or the cause of the nonuniformity.

23. Keywords

23.1 gas chromatography; spectroscopy; traffic paint; uniformity of paint vehicle

 **D 2743 – 68 (2004)**

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