



Designation: D8321 – 22

Standard Practice for Development and Validation of Multivariate Analyses for Use in Predicting Properties of Petroleum Products, Liquid Fuels, and Lubricants based on Spectroscopic Measurements¹

This standard is issued under the fixed designation D8321; 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 This practice covers a guide for the multivariate calibration of infrared (IR) spectrophotometers and Raman spectrometers used in determining the physical, chemical, and performance properties of petroleum products, liquid fuels including biofuels, and lubricants. This practice is applicable to analyses conducted in the near infrared (NIR) spectral region (roughly 780 nm to 2500 nm) through the mid infrared (MIR) spectral region (roughly 4000 cm^{-1} to 400 cm^{-1}). For Raman analyses, this practice is generally applied to Stokes shifted bands that occur roughly 400 cm^{-1} to 4000 cm^{-1} below the frequency of the excitation.

NOTE 1—While the practice described herein deals specifically with mid-infrared, near-infrared, and Raman analysis, much of the mathematical and procedural detail contained herein is also applicable for multivariate quantitative analysis done using other forms of spectroscopy. The user is cautioned that typical and best practices for multivariate quantitative analysis using other forms of spectroscopy may differ from the practice described herein for mid-infrared, near-infrared, and Raman spectroscopies.

1.2 Procedures for collecting and treating data for developing IR and Raman calibrations are outlined. Definitions, terms, and calibration techniques are described. The calibration establishes a multivariate correlation between the spectral features and the properties to be predicted. This correlation is herein referred to as the multivariate model. Criteria for validating the performance of the multivariate model are described. The properties against which a multivariate model is calibrated and validated are measured by Primary Test Methods (PTMs) and the results of the PTM measurement are herein referred to as Primary Test Method Results (PTMR). The analysis of the spectra using the multivariate model produces a Predicted Primary Test Method Result (PPTMR).

1.3 The implementation of this practice requires that the IR spectrophotometer or Raman spectrometer has been installed in compliance with the manufacturer's specifications. In addition, it assumes that, at the time of calibration, validation, and analysis, the analyzer is operating at the conditions specified by the manufacturer. The practice includes instrument performance tests which define the instrument performance at the time of calibration, and which qualify the instrument by demonstrating comparable performance during validation and analysis.

1.4 This practice covers techniques that are routinely applied for online, at-line, and laboratory quantitative analysis. The practice outlined covers the general cases for liquids and solids that are single phase homogeneous samples when presented to the analyzers. Online application is limited by sample viscosity and the ability to introduce sample to the analyzer. All techniques covered require the use of a computer for data collection and analysis.

1.5 This practice is most typically applied when the spectra and the PTMR against which the analysis is calibrated are measured on the same sample. However, for some applications, spectra may be measured on a basestock and the PTMR may be measured on the same basestock after constant level addition.

1.5.1 Biofuel applications will typically fall into three categories.

1.5.1.1 The spectra and the PTM both measure the finished biofuel blend.

1.5.1.2 The spectra are measured on a petroleum derived blendstock, and the PTM measures the same blendstock after a constant level addition with the biocomponent.

1.5.1.3 The spectra and PTM both measured the petroleum derived blendstock, and the PPTMRs from the multivariate model are used as inputs into a second model which predicts the results obtained when the PTM is applied to the analysis of the finished blended product. The practice described herein only applies to the first of these two models.

¹ This practice is under the jurisdiction of ASTM Committee D02 on Petroleum Products, Liquid Fuels, and Lubricants and is the direct responsibility of Subcommittee D02.25 on Performance Assessment and Validation of Process Stream Analyzer Systems.

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*A Summary of Changes section appears at the end of this standard

1.6 This practice includes a checklist in [Annex A2](#) against which multivariate calibrations can be examined to determine if they conform to the requirements defined herein.

1.7 For some multivariate spectroscopic analyses, interferences and matrix effects are sufficiently small that it is possible to calibrate using mixtures that contain substantially fewer chemical components than the samples that will ultimately be analyzed. While these surrogate methods generally make use of the multivariate mathematics described herein, they do not conform to procedures described herein, specifically with respect to the handling of outliers. Surrogate methods may indicate that they make use of the mathematics described herein, but they should not claim to follow the procedures described herein. Test Methods [D5845](#) and [D6277](#) are examples of surrogate methods.

1.8 *Disclaimer of Liability as to Patented Inventions*—Neither ASTM International nor an ASTM committee shall be responsible for identifying all patents under which a license is required in using this document. ASTM International takes no position respecting the validity of any patent rights asserted in connection with any item mentioned in this standard. Users of this standard are expressly advised that determination of the validity of any such patent rights, and the risk of infringement of such rights, are entirely their own responsibility.

1.9 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.10 *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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

1.11 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 ASTM Standards:²

- [D1265](#) Practice for Sampling Liquefied Petroleum (LP) Gases, Manual Method
- [D1319](#) Test Method for Hydrocarbon Types in Liquid Petroleum Products by Fluorescent Indicator Adsorption
- [D2699](#) Test Method for Research Octane Number of Spark-Ignition Engine Fuel
- [D3764](#) Practice for Validation of the Performance of Process Stream Analyzer Systems
- [D4057](#) Practice for Manual Sampling of Petroleum and Petroleum Products
- [D4177](#) Practice for Automatic Sampling of Petroleum and Petroleum Products

- [D4175](#) Terminology Relating to Petroleum Products, Liquid Fuels, and Lubricants
- [D4307](#) Practice for Preparation of Liquid Blends for Use as Analytical Standards
- [D5769](#) Test Method for Determination of Benzene, Toluene, and Total Aromatics in Finished Gasolines by Gas Chromatography/Mass Spectrometry
- [D5842](#) Practice for Sampling and Handling of Fuels for Volatility Measurement
- [D5845](#) Test Method for Determination of MTBE, ETBE, TAME, DIPE, Methanol, Ethanol and *tert*-Butanol in Gasoline by Infrared Spectroscopy
- [D6122](#) Practice for Validation of the Performance of Multivariate Online, At-Line, Field and Laboratory Infrared Spectrophotometer, and Raman Spectrometer Based Analyzer Systems
- [D6277](#) Test Method for Determination of Benzene in Spark-Ignition Engine Fuels Using Mid Infrared Spectroscopy
- [D6299](#) Practice for Applying Statistical Quality Assurance and Control Charting Techniques to Evaluate Analytical Measurement System Performance
- [D6792](#) Practice for Quality Management Systems in Petroleum Products, Liquid Fuels, and Lubricants Testing Laboratories
- [D7278](#) Guide for Prediction of Analyzer Sample System Lag Times
- [D7453](#) Practice for Sampling of Petroleum Products for Analysis by Process Stream Analyzers and for Process Stream Analyzer System Validation
- [D7717](#) Practice for Preparing Volumetric Blends of Denatured Fuel Ethanol and Gasoline Blendstocks for Laboratory Analysis
- [D7915](#) Practice for Application of Generalized Extreme Studentized Deviate (GESD) Technique to Simultaneously Identify Multiple Outliers in a Data Set
- [D8009](#) Practice for Manual Piston Cylinder Sampling for Volatile Crude Oils, Condensates, and Liquid Petroleum Products
- [D8340](#) Practice for Performance-Based Qualification of Spectroscopic Analyzer Systems
- [E131](#) Terminology Relating to Molecular Spectroscopy
- [E456](#) Terminology Relating to Quality and Statistics
- [E1655](#) Practices for Infrared Multivariate Quantitative Analysis
- [E1866](#) Guide for Establishing Spectrophotometer Performance Tests
- [E2056](#) Practice for Qualifying Spectrometers and Spectrophotometers for Use in Multivariate Analyses, Calibrated Using Surrogate Mixtures

3. Terminology

3.1 For terminology related to molecular spectroscopic methods, refer to Terminology [E131](#). For terminology relating to quality and statistics, refer to Terminology [E456](#). For terminology relating to petroleum products, liquid fuels and lubricants, refer to Terminology [D4175](#).

3.2 Definitions:

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.