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.

Designation: D8321 – 21

Standard Practice for Development and Validation of Multivariate Analyses for Use in Predicting Properties of Petroleum Products, Liquid Fuels, and Lubricants based on Spectroscopic Measurements[1]

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 40 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 additivation.

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 additivation 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.

Current edition approved May 1, 2021. Published July 2021. Originally approved in 2020. Last previous edition approved in 2020 as D8321 – 20. DOI: 10.1520/D8321-21.

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

Copyright © ASTM International, 100 Barr Harbor Drive, PO Box C700, West Conshohocken, PA 19428-2959. United States