APPLICATION NOTE

Infrared Spectroscopy

Determination of Benzene in Gasoline by ASTM® D6277 with Spectrum Two

Introduction

Benzene has long been used as an anti-knock agent in gasoline. However, as it is a well known carcinogen and pollutant, regulations are in place in many countries to limit its concentration in gasoline to levels of 1% or less.

IR spectroscopy is an ideal method for quantifying benzene at the concentration levels required, and there are several standard methods for this measurement, all of which utilize the distinctive C–H out-of-plane deformation band at around 673 cm^{-1}. While this band is characteristic of benzene, toluene and xylenes have some weak absorption at this frequency that can interfere with the results if high concentrations are present. EN 238[1] and ASTM® D4053[2] employ a single-wavelength calibration for benzene, with ASTM® D4053 including a correction for toluene. A more recent standard, ASTM® D6277[3] employs a partial least squares (PLS) calibration with a set of calibration standards designed to account for interferences by substituted benzenes, providing accurate results regardless of the aromatic content of the fuel.

The Spectrum Two™ FT-IR spectrometer combines excellent performance, stability and ruggedness with a compact footprint, and is ideal for quantitative applications demanding low detection limits. Benzene in Gasoline ASTM® D6277 FT-IR Application Pack contains everything needed to implement ASTM® D6277 including starter calibrations that can be validated on your system or used as templates for recalibration. This note describes the calibration and qualification of the system according to the ASTM® specifications.

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Figure 1. The Spectrum Two FT-IR spectrometer and Benzene in Gasoline ASTM® D6277 Application Pack.

Materials and methods

Isooctane, benzene, toluene and *o-*, *m-*, *p*-xylenes were obtained from SigmaAldrich® in spectroscopic grade.

Calibration and validation standard sets A (0–1.5 %m/m benzene) and B (1–6 %m/m) were prepared gravimetrically as described in ASTM® D6277. Mass concentrations were converted to volume concentrations by measuring the densities of the pure components and assuming the standards show ideal mixture behavior. Due to the difference in density between the aromatic compounds and isooctane, and the significant concentrations of toluene and xylenes, it is essential to carry out the calibration with respect to volume concentration.

***Table 1.* Summary of the calibration and validation sets.**

	Conc. range (%v/v)	No. of standards
Calibration set A	0–1.27	35
Validation set A	0–1.39	25
Calibration set B	0.71–5.32	25
Validation set B	0.86–4.61	26

Spectra were measured using a PerkinElmer® Spectrum Two FT-IR spectrometer equipped with a 0.025 mm-pathlength liquid cell having KBr windows. The spectral resolution was 4 cm^{-1} and an accumulation time of <30 s was used.

The PLS models were calibrated using PerkinElmer Quant+ software and following the parameters specified by ASTM® D6277.

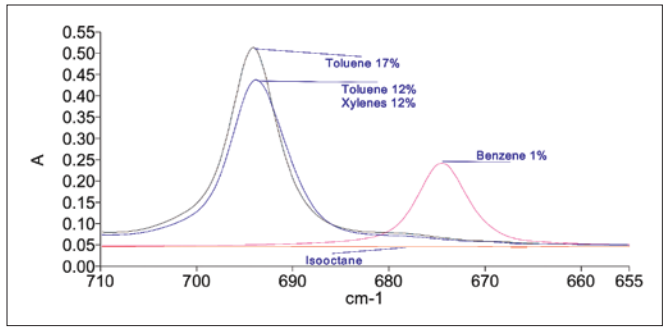

Figure 2. Spectra of benzene, toluene and mixed xylene solutions in isooctane. Isooctane itself has negligible absorption in this region.

Results and discussion

Spectra of the various components in the calibration standards are shown in Figure 2, showing the interference with the benzene peak caused by high concentrations of substituted benzenes. Single-wavelength methods would be affected by this overlap, but because it is built into the calibration set for the PLS model used in ASTM® D6277, this method is not affected.

The results of the independent validations are given in Table 2 and Figure 3, showing excellent linearity and precision. For both calibrations the validation SEP is well below the repeatability value quoted in ASTM® D6277 for the midpoint of the concentration ranges.

***Table 2.* Results of the PLS calibrations.**

	Range A (0–1.3 %v/v)	Range B (0.8–5.3 %v/v)
Calibration SEP (%v/v)	0.015	0.051
Validation SEP (%v/v)	0.016	0.078

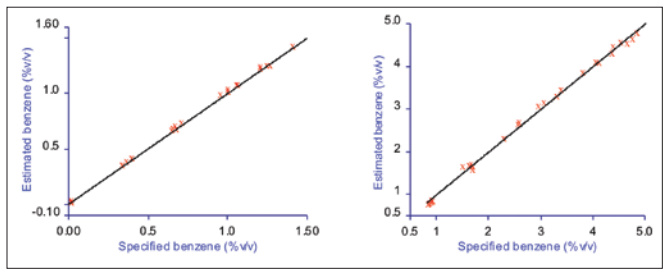

Figure 3. Independent validation results for benzene. Left: calibration range A (SEP = 0.016 %v/v); right: calibration range B (SEP = 0.078 %v/v).

ASTM® D6277 specifies that an instrument is qualified to perform the analysis if the F-ratio between the SEP for the validation samples and the pooled SEP from the initial ASTM® round-robin study is below a critical value. In this example, coincidentally, the F-ratio is 1.0, comfortably below the threshold of 1.39, so the instrument is successfully qualified.

Conclusions

Performance of the analyzer was found to be comfortably better than required by ASTM® D6277, with an SEP below 0.02 %v/v obtained for the more relevant low-concentration calibration range. The system is straightforward to use, with clear on-screen instructions and automatic detection of the appropriate concentration range to use.

Ordering information

To order a complete system to perform this analysis, select your Spectrum Two model and then add the Benzene in Gasoline ASTM® D6277 FT-IR Application Pack, which includes the software, sampling accessories and documentation needed to perform the analysis.

Additional application packs are available for biodiesel (FAME) blend analysis, determination of oil and grease in water samples, and condition monitoring for in-service lubricants.

L1608012	Benzene in Gasoline ASTM® D6277 FT-IR Application Pack
L1608010	Biodiesel EN14078 FT-IR Analysis Pack
L1608006	Environmental Hydrocarbons ASTM® D7066 FT-IR Analysis Pack
L1608009	In-service Lubricants FT-IR Analysis Pack

See www.perkinelmer.com/energy for more information about PerkinElmer's comprehensive range of offerings for fuels and lubricants analysis.

References

1. EN 238, 1996. Liquid petroleum products – Petrol – Determination of the benzene content by infrared spectrometry. European Committee for Standardization.
2. ASTM® D4053-04, 2009. Standard Test Method for Benzene in Motor and Aviation Gasoline by Infrared Spectroscopy. ASTM® International.
3. ASTM® D6277-07, 2007. Standard Test Method for Determination of Benzene in Spark-Ignition Engine Fuels Using Mid Infrared Spectroscopy. ASTM® International.

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