



Standard Test Method for Determination of Benzene in Spark-Ignition Engine Fuels Using Mid Infrared Spectroscopy¹

This standard is issued under the fixed designation D 6277; 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 test method covers the determination of the percentage of benzene in spark-ignition engine fuels. It is applicable to concentrations from 0.1 to 5 volume %.

1.2 SI units of measurement are preferred and used throughout this standard.

1.3 *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:

- D 1298 Test Method for Density, Relative Density (Specific Gravity), or API Gravity of Crude Petroleum and Liquid Petroleum Products by Hydrometer Method²
- D 4052 Test Method for Density and Relative Density of Liquids by Digital Density Meter³
- D 4057 Practice for Manual Sampling of Petroleum and Petroleum Products³
- D 4177 Practice for Automatic Sampling of Petroleum and Petroleum Products³
- D 4307 Practice for Preparation of Liquid Blends for Use as Analytical Standards³
- D 5769 Test Method for Determination of Benzene, Toluene, and Total Aromatics in Finished Gasolines by Gas Chromatography/Mass Spectrometry⁴
- D 5842 Practice for Sampling and Handling of Fuels for Volatility Measurements⁴

D 5854 Practice for Mixing and Handling of Liquid Samples of Petroleum and Petroleum Products⁴

E 168 Practices for General Techniques of Infrared Quantitative Analysis⁵

E 1655 Practices for Infrared Multivariate Quantitative Analysis⁵

E 2056 Practice for Qualifying Spectrometers and Spectrophotometers for Use in Multivariate Analyses, Calibrated Using Surrogate Mixtures⁵

3. Terminology

3.1 Definitions:

3.1.1 *multivariate calibration*—a process for creating a calibration model in which multivariate mathematics is applied to correlate the absorbances measured for a set of calibration samples to reference component concentrations or property values for the set of samples.

3.1.1.1 *Discussion*—The resultant multivariate calibration model is applied to the analysis of spectra of unknown samples to provide an estimate of the component concentration or property values for the unknown sample.

3.1.1.2 *Discussion*—Included in the multivariate calibration algorithms are Partial Least Squares, Multilinear Regression, and Classical Least Squares Peak Fitting.

3.1.2 *oxygenate*—an oxygen-containing organic compound which may be used as a fuel or fuel supplement, for example, various alcohols and ethers.

4. Summary of Test Method

4.1 A sample of spark-ignition engine fuel is introduced into a liquid sample cell. A beam of infrared light is imaged through the sample onto a detector, and the detector response is determined. Wavelengths of the spectrum, that correlate highly with benzene or interferences, are selected for analysis using selective bandpass filters or by mathematically selecting areas of the whole spectrum. A multivariate mathematical analysis

¹ This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.04.0F on Absorption Spectroscopic Methods.

Current edition approved Aug. 10, 2001. Published October 2001. Originally published as D 6277 – 98. Last previous edition D 6277 – 99.

² *Annual Book of ASTM Standards*, Vol. 05.01.

³ *Annual Book of ASTM Standards*, Vol. 05.02.

⁴ *Annual Book of ASTM Standards*, Vol. 05.03.

⁵ *Annual Book of ASTM Standards*, Vol. 03.06.

converts the detector response for the selected areas of the spectrum of an unknown to a concentration of benzene.

5. Significance and Use

5.1 Benzene is a compound that endangers health, and the concentration is limited by environmental protection agencies to produce a less toxic gasoline.

5.2 This test method is fast, simple to run, and inexpensive.

5.3 This test method is applicable for quality control in the production and distribution of spark-ignition engine fuels.

6. Interferences

6.1 The primary spectral interferences are toluene and other monosubstituted aromatics. In addition, oxygenates can interfere with measurements made with filter apparatus. Proper choice of the apparatus, proper design of a calibration matrix, and proper utilization of multivariate calibration techniques can minimize these interferences.

7. Apparatus

7.1 *Mid-IR Spectrometric Analyzer (of one of the following types):*

7.1.1 *Filter-based Mid-IR Test Apparatus*—The type of apparatus suitable for use in this test method minimally employs an IR source, an infrared transmission cell or a liquid attenuated total internal reflection cell, wavelength discriminating filters, a chopper wheel, a detector, an A-D converter, a microprocessor, and a method to introduce the sample. The frequencies and bandwidths of the filters are specified in Table 1.

7.1.2 *Fourier Transform Mid-IR Spectrometer*—The type of apparatus suitable for use in this test method employs an IR source, an infrared transmission cell or a liquid attenuated total internal reflection cell, a scanning interferometer, a detector, an A-D converter, a microprocessor, and a method to introduce the sample. The following performance specifications (through the ATR cell) must be met:

scan range	4000 to 600 cm ⁻¹
resolution	4 cm ⁻¹
S/N at 674 cm ⁻¹	>300:1 RMS

The signal to noise level will be established by taking a single beam spectrum using air or nitrogen as the reference and declaring that spectrum as the background. The background single beam spectrum obtained can be the average of multiple FTIR scans, but the total collection time shall not exceed 60 s. If interference from water vapor or carbon dioxide is a problem, the instrument shall be purged with dry air or

TABLE 1 Specification for Filters Used in Filter-based Mid-IR Test

Center Wavenumber (± 0.15 % of wavenumber)	Bandwidth (in wavelength units) (full width at half height)
673 cm ⁻¹	1 % of λ _c
729 cm ⁻¹	1 % of λ _c
769 cm ⁻¹	1 % of λ _c
1205 cm ⁻¹	1 % of λ _c
1054 cm ⁻¹	1 % of λ _c
1188 cm ⁻¹	1 % of λ _c
1117 cm ⁻¹	1 % of λ _c

nitrogen. A subsequent single beam spectrum shall be taken under the same conditions and ratioed to the background spectrum. The RMS noise of the ratioed spectra, the 100 % line, shall not exceed 0.3 % transmittance in the region from 700 to 664 cm⁻¹.

7.2 *Absorption Cell*— The absorption cell can be either transmission or attenuated total reflectance.

7.2.1 *Transmission Cells*, shall have windows of potassium bromide, zinc selenide, or other material having a significant transmission from 712 cm⁻¹ to 660 cm⁻¹. The cell path length of the transmission cell shall be 0.025 (± 0.005) mm. The use of a wedged transmission cell with the same nominal path length is acceptable.

7.2.2 *Attenuated Total Reflectance (ATR) Cells*, shall have the following specifications:

ATR element material	ZnSe
beam condensing optics	conical, non-focussing optics integral to cell body
element configuration	circular cross section with coaxial conical ends
cone half angle	60°
element length	1.55 in.
element diameter	0.125 in.
angle of incidence at sample interface	53.8°
maximum range of incidence angles	± 1.5°
standard absorbance (1428 cm ⁻¹ band of acetone)	0.38 ± 0.02 AU
material of construction	316 stainless steel
seals	Chemraz or Kalraz o-rings

8. Reagents and Materials (see Note 1)

8.1 *Standards for Calibration, Qualification, and Quality Control Check Standards*—Use of chemicals of at least 99 % purity, where available, for quality control checks is required when preparing samples. (**Warning**—These materials are flammable and may be harmful if ingested or inhaled.)

- 8.1.1 *tert*-Amyl methyl ether, TAME [994-05-8].
- 8.1.2 Benzene [1076-43-3].
- 8.1.3 *tert*-Butyl ethyl ether, ETBE [637-92-3].
- 8.1.4 *tert*-Butyl methyl ether, MTBE [1634-04-4].
- 8.1.5 1,3 Dimethylbenzene (*m*-xylene).
- 8.1.6 Ethanol [64-17-5].
- 8.1.7 Ethylbenzene [100-41-4].
- 8.1.8 3-Ethyltoluene [620-14-4].
- 8.1.9 Heavy aromatic/reformate petroleum stream (high boiling cut: IPB of 150 ± 5° C and EP of 245 ± 8° C) certified to contain less than 0.025 % benzene (an absorbance of less than 0.03 at 675 cm⁻¹ using a 0.2 mm cell and a baseline between approximately 680 cm⁻¹ and 670 cm⁻¹) [64741-68-0].
- 8.1.10 Hexane (an absorbance versus water of less than 0.1 at 250 nm using a 1cm cell) [110-54-3].
- 8.1.11 2,2,4-Trimethylpentane (*isooctane*) [540-84-1].
- 8.1.12 Pentane (an absorbance versus water of less than 0.1 at 250 nm using a 1 cm cell) [109-66-0].
- 8.1.13 Propylbenzene [103-65-1].
- 8.1.14 Toluene [108-88-3].
- 8.1.15 1,3,5-Trimethylbenzene (*mesitylene*) [108-67-8].
- 8.1.16 *m*-Xylene [108-38-3].

NOTE 1—Only some of the reagents are required in each calibration or qualification procedure.

9. Sampling and Sample Handling

9.1 General Requirements:

9.1.1 The sensitivity of the measurement of benzene to the loss of benzene or other components through evaporation and the resulting changes in composition is such that the utmost precaution and the most meticulous care in the drawing and handling of samples is required.

9.1.2 Fuel samples to be analyzed by the test method shall be sampled using procedures outlined in Practices D 4057, D 4177, or D 5842, where appropriate. Do not use the “Sampling by Water Displacement.” With some alcohol containing samples, the alcohol will dissolve in the water phase.

9.1.3 Protect samples from excessive temperatures prior to testing. This can be accomplished by storage in an appropriate ice bath or refrigerator at 0 to 5°C.

9.1.4 Do not test samples stored in leaky containers. Discard and obtain a new sample if leaks are detected.

9.2 Sample Handling During Analysis:

9.2.1 When analyzing samples by the mid infrared apparatus, the sample must be between a temperature of 15 to 38°C. Equilibrate all samples to the temperature of the laboratory (15 to 38°C) prior to analysis by this test method.

9.2.2 After analysis, if the sample is to be saved, reseal the container and store the sample in an ice bath or a refrigerator at 0 to 5°C.

10. Calibration and Qualification of the Apparatus

10.1 Before use, the instrument must be calibrated according to the procedure described in **Annex A1**. This calibration can be performed by the instrument manufacturer prior to delivery of the instrument to the end user. If, after maintenance, the instrument calibration is repeated, the qualification procedure must also be repeated.

10.2 Before use, the instrument must be qualified according to the procedure described in **Annex A1**. The qualification need only be carried out when the instrument is initially put into operation, recalibrated, or repaired.

11. Quality Control Checks

11.1 Confirm the calibration of the instrument each day it is used by measuring the benzene concentration using the procedure outlined in Section 12 on at least one quality control sample of known benzene content. The preparation of known benzene concentration is described in 11.1.1 and 11.1.2.

11.1.1 Standard(s) of known benzene concentration shall be made up by mass according to **A1.1** and converted to volume % using the measured density as outlined in Section 13. At least one standard shall be made up at 1.2 (\pm 0.2) mass % benzene, that is, nominally 1.0 volume %. Additional standards may also be prepared and used for quality control checks.

11.1.2 Standard(s) should be prepared in sufficient volume to allow for a minimum of 30 quality control measurements to be made on one batch of material. Package or store, or both, quality control samples to ensure that all analyses of quality control samples from a given lot are performed on essentially identical material.

11.2 If the benzene volume % value estimated for the quality control sample prepared at 1.2 mass % benzene differs

from the known value by more than 0.12 volume %, then the measurement system is out-of-control and cannot be used to estimate benzene concentrations until the cause of the out-of-control behavior is identified and corrected.

11.3 If correction of out-of-control behavior requires repair to the instrument or recalibration of the instrument, the qualification of instrument performance described in **A1.3** shall be performed before the system is used to measure benzene content on samples.

12. Procedure

12.1 Equilibrate the samples to between 15 and 38°C before analysis.

12.2 Clean the sample cell. If a separate baseline using the empty cell is required, and if residual fuel is in the sample cell, remove the fuel by flushing the cell and inlet-outlet lines with enough pentane to ensure complete washing. Evaporate the residual pentane with either dry air or nitrogen.

12.3 If needed, obtain a baseline spectrum in the manner established by the manufacturer of the equipment.

12.4 Prior to the analysis of unknown test samples, establish that the equipment is running properly by collecting the spectrum of the quality control standard(s), by analyzing the spectrum with the calibration model, and by comparing the estimated benzene concentration to the known value for the QC standard(s). Introduce enough standard to the cell to ensure that the cell is washed a minimum of three times with the standard solution.

12.5 Introduce the unknown fuel sample in the manner established by the manufacturer. Introduce enough of the fuel sample to the cell to ensure the cell is washed a minimum of three times with the fuel.

12.6 Obtain the spectral response of the fuel sample.

12.6.1 If a filter based mid IR instrument is used, acquire the absorbance for the fuel sample at the wavelengths corresponding to the specified filters.

12.6.2 If an FTIR is used, acquire the digitized spectral data for the fuel sample over the frequency region from 4000 cm^{-1} to 600 cm^{-1} .

12.7 Determine the benzene concentration (volume %) according to the appropriate calibration equation developed in **Annex A1**.

12.7.1 For filter based mid IR instruments, apply the calibration equation determined in **A1.2.4** to convert the absorbances at each of the wavelengths to the benzene concentration expressed in volume %.

12.7.2 For FTIR instruments using a PLS calibration, determine the benzene concentration using the calibration models developed in **A1.2.5** by following the steps outlined as follows.

12.7.2.1 Baseline correct the spectrum using a linear baseline fit to absorbances measured between 712 and 658 cm^{-1} .

12.7.2.2 Estimate the benzene concentration in the fuel sample by applying the low calibration (see **A1.2.5.1**) to the baseline corrected spectrum in the region of 712 to 664 cm^{-1} .

12.7.2.3 If the estimated benzene concentration (determined in **12.7.2.2**) is equal to or less than 1.30 volume %, determine the benzene concentration by applying the low calibration (see **A1.2.5.2**) to the baseline corrected spectrum in the region of 712 to 664 cm^{-1} .

12.7.2.4 If the estimated benzene concentration (determined in 12.7.2.2) is greater than 1.30 volume %, estimate the benzene concentration by applying the high calibration (see A1.2.5.3) to the baseline corrected spectrum in the region of 712 to 664 cm^{-1} .

12.7.2.5 If the value estimated by application of the high calibration (determined in 12.7.2.4) is less than or equal to 1.30 volume %, report the value determined by the low calibration (even if the value is greater than 1.30 volume %). For estimated values greater than 1.30 volume % (determined in 12.7.2.4), report the value obtained.

12.7.3 For FTIR instruments using a classical least squares peak fitting calibration, fit the absorption spectrum in the region of 710 through 660 cm^{-1} using a classical least squares fit (k-matrix method). The fit matrix must include the *derived* spectra of toluene, 1,3-dimethylbenzene, 3-ethyltoluene, 1,3,5-trimethylbenzene, ethylbenzene, and propylbenzene (as determined in A1.2.6.1).

12.7.3.1 To eliminate spectral overlaps, subtract the *derived* spectra of toluene, 1,3-dimethylbenzene, 3-ethyltoluene, 1,3,5-trimethylbenzene, ethylbenzene and propylbenzene, multiplied by the coefficients that resulted from the classical least squares fit to the absorption spectrum. In this way, a *residual* benzene peak is obtained.

12.7.3.2 Fit the *residual* benzene peak with a Lorentzian line shape function (as defined in A1.2.6.4) with a linear background in the region of 691 through 660 cm^{-1} and determine the peak height of the *residual* benzene peak.

12.7.3.3 Determine the benzene concentration expressed in mass % in the fuel sample by applying the calibration (see A1.2.6) using the peak height of the *residual* benzene peak determined in 12.7.3.2.

12.7.3.4 Determine the density of the fuel sample by Test Method D 1298 or Test Method D 4052.

12.7.3.5 Convert the determined mass % to volume % for the sample using the equation in Section 13.

13. Calculation

13.1 *Conversion to Volume % of Benzene*—To convert the calibration and qualification standards to volume % use Eq 1.

$$V_b = M_b (D_f / 0.8844) \quad (1)$$

where:

V_b = benzene volume %,

M_b = benzene mass %, and

D_f = relative density at 15.56°C of the calibration or qualification standard being tested as determined by Practice D 1298 or Test Method D 4052.

14. Report

14.1 Report the following information:

14.1.1 Filter instruments (Test Method D 6277a).

14.1.1.1 Volume % benzene by Test Method D 6277a, to the nearest 0.01%.

14.1.2 FTIR instruments with PLS calibration (Test Method D 6277b).

14.1.2.1 Volume % benzene by Test Method D 6277b, to the nearest 0.01%.

TABLE 2 Repeatabilities as a Function of Concentration

Benzene Concentration (volume %)	Filter Instruments	FTIR with PLS Calibration	FTIR with CLS Calibration
0.1	0.02	0.02	0.05
0.3	0.03	0.03	0.06
0.5	0.03	0.04	0.07
0.7	0.04	0.05	0.08
0.9	0.05	0.06	0.09
1.1	0.05	0.07	0.09
1.3	0.06	0.08	0.10
1.5	0.06	0.09	0.11
1.8	0.07	0.11	0.12
4	0.18	0.14	0.18

TABLE 3 Reproducibilities as a Function of Concentration

Benzene Concentration (volume %)	Filter Instruments	FTIR with PLS Calibration	FTIR with CLS Calibration
0.1	0.12	0.03	0.10
0.3	0.12	0.06	0.11
0.5	0.13	0.08	0.11
0.7	0.13	0.10	0.12
0.9	0.13	0.13	0.13
1.1	0.13	0.15	0.13
1.3	0.14	0.18	0.14
1.5	0.14	0.20	0.15
1.8	0.14	0.23	0.15
4	0.59	0.47	0.23

14.1.3 FTIR instruments with CLS calibration (Test Method D 6277c).

14.1.3.1 Volume % benzene by Test Method D 6277c, to the nearest 0.1%.

15. Precision and Bias

15.1 Interlaboratory tests of each of the procedures (filter instruments, FTIR instruments with PLS calibration, and FTIR instruments with CLS calibration) were carried out using twenty samples that covered the range from 0 to 1.8 volume % and at least six laboratories for each of the procedures. An additional sample containing approximately 4 volume % benzene was also included in the interlaboratory results. The precision of the test method as obtained by statistical examination of interlaboratory results⁶ is summarized in Table 2 and Table 3 and is as follows:

15.2 *Repeatability for Filter Based Mid IR Instruments*—For benzene concentrations between 0.1 and 1.8 volume %, the difference between successive test results obtained by the same operator with the same apparatus under constant operating conditions on identical test samples would, in the long run, and in the normal and correct operation of the test method, exceed the following values only in one case in twenty:

$$r = 0.021 + 0.027 X \quad (2)$$

where X is the benzene concentration determined. For the one sample at approximately 4 volume % benzene, the difference between successive test results, obtained by the same operator with the same apparatus under constant operating conditions on identical test samples would, in the long run, and

⁶ Available from ASTM Headquarters. Request RR: D02-1431.

in the normal and correct operation of the test method, exceed 0.18 only in one case in twenty.

15.3 Repeatability for FTIR Instruments Using PLS Calibration Instruments—For benzene concentrations between 0.1 and 1.8 volume %, the difference between successive test results obtained by the same operator with the same apparatus under constant operating conditions on identical test samples would, in the long run, and in the normal and correct operation of the test method, exceed the following values only in one case in twenty.

$$r = 0.013 + .052 X \quad (3)$$

where X is the benzene concentration determined. For the one sample at approximately 4 volume % benzene, the difference between successive test results obtained by the same operator with the same apparatus under constant operating conditions on identical test samples would, in the long run, and in the normal and correct operation of the test method, exceed 0.14 only in one case in twenty.

15.4 Repeatability for FTIR Instruments Using a Classical Least Squares Calibration—For benzene concentrations between 0.1 and 1.8 volume %, the difference between successive test results obtained by the same operator with the same apparatus under constant operating conditions on identical test samples would, in the long run, and in the normal and correct operation of the test method, exceed the following values only in one case in twenty.

$$r = 0.047 + 0.043 X \quad (4)$$

where X is the benzene concentration determined. For the one sample at approximately 4 volume % benzene, the difference between successive test results obtained by the same operator with the same apparatus under constant operating conditions on identical test samples would, in the long run, and in the normal and correct operation of the test method, exceed 0.18 only in one case in twenty.

15.5 Reproducibility for Filter Based Mid IR Instruments—For benzene concentrations between 0.1 and 1.8 volume %, the difference between two single and independent results, obtained by different operators working in different laboratories on identical test samples would, in the long run, and in the normal and correct operation of the test method, exceed the following values only in one case in twenty:

$$R = 0.121 + .012 X \quad (5)$$

where X is the benzene concentration determined. For the one sample at approximately 4 volume % benzene, the difference between two single and independent results, obtained by different operators working in different laboratories on identical test samples would, in the long run, and in the normal and correct operation of the test method, exceed 0.59 only in one case in twenty.

15.6 Reproducibility for FTIR Instruments Using a PLS Calibration Instrument—For benzene concentrations between

0.1 and 1.8 volume %, the difference between two single and independent results obtained by different operators working in different laboratories on identical test samples would, in the long run, and in the normal and correct operation of the test method, exceed the following values only in one case in twenty:

$$R = 0.022 + 0.118 X \quad (6)$$

where X is the benzene concentration determined. For the one sample at approximately 4 volume % benzene, the difference between two single and independent results obtained by different operators working in different laboratories on identical test samples would, in the long run, and in the normal and correct operation of the test method, exceed 0.47 only in one case in twenty.

15.7 Reproducibility for FTIR Instruments Using a Classical Least Squares Calibration Instrument—For benzene concentrations between 0.1 to 1.8 volume %, the difference between two single and independent results obtained by different operators working in different laboratories on identical test samples would, in the long run, and in the normal and correct operation of the test method, exceed the following values only in one case in twenty.

$$R = 0.099 + .031 X \quad (7)$$

where X is the benzene concentration determined. For the one sample at approximately 4 volume % benzene, the difference between two single and independent results obtained by different operators working in different laboratories on identical test samples would, in the long run, and in the normal and correct operation of the test method, exceed 0.23 only in one case in twenty.

15.8 Bias—Since there were no suitable reference materials included in the interlaboratory test program, no statement of bias is being made. However, the samples of the test program were shared with an interlaboratory study of Test Method D 5769 and small biases (see **Note 2**) relative to that test method were observed. The relative biases were not the same for all procedures, nor were they the same for all samples within each procedure. Because such sample biases are not correctable, users wishing to use this test method to substitute for Test Method D 5769, or conversely, are cautioned to consider the specific source or sources of subject fuels and to assure, through periodic comparative testing, that any differences are consistent and manageable.

NOTE 2—The average bias, relative to Test Method D 5769, was -0.06 volume % for the FTIR procedures and +0.06 for the filter procedure. After accounting for the averages, the fuel-specific differences exceeded 0.1 volume % for only one fuel on one procedure (out of 62 combinations).

16. Keywords

16.1 aromatics; benzene; infrared spectroscopy; spark-ignition engine fuel

(Mandatory Information)
A1. CALIBRATION AND QUALIFICATION OF THE APPARATUS

A1.1 *Calibration Matrix*—Calibration standards shall be prepared in accordance with Practice D 4307 or appropriately scaled for larger blends and Practices D 5842 and D 5854, where appropriate. Whenever possible, use chemicals of at least 99 % purity. To minimize the evaporation of light components, chill all chemicals and fuels used to prepare standards.

A1.1.1 *Calibration Matrix for Filter Based Mid IR Instruments*—Prepare the set of calibration standards as defined in **Table A1.1**.

TABLE A1.1 Filter Based Mid IR Instrument Calibration Sample Set (mass %)

Sample	Benzene	Toluene	Xylenes	Hvy. Ref. ^A	MTBE	EtOH	TAME	ETBE	Isooctane	C ₅ C ₆ ^B
1	0.00	2.50	12.5	5.00	0.00	00.0	20.0	0.00	30.0	30.0
2	0.00	2.50	25.0	2.50	0.00	0.00	0.00	0.00	35.0	35.0
3	0.00	5.00	7.50	10.0	1.00	0.00	2.50	15.0	25.0	34.0
4	0.00	12.5	12.5	3.00	20.0	0.00	2.50	0.00	25.0	24.5
5	0.00	20.0	10.0	1.00	0.00	10.00	0.00	0.00	25.0	34.0
6	0.00	25.0	7.50	2.50	0.00	0.00	0.00	0.00	40.0	25.0
7	0.00	25.0	2.50	7.50	0.00	4.00	0.00	0.00	20.0	41.0
8	0.25	0.00	10.0	5.00	0.00	0.00	0.00	20.00	25.0	39.75
9	0.25	2.50	6.00	2.50	0.00	0.00	0.00	0.00	35.0	53.75
10	0.25	4.75	15.0	1.00	0.00	7.50	0.00	0.00	25.0	46.50
11	0.25	10.0	0.00	10.0	15.00	0.00	0.00	0.00	30.0	34.75
12	0.25	14.0	7.50	3.00	0.00	5.00	0.00	0.00	30.0	40.25
13	0.50	2.50	12.5	5.00	5.00	0.00	5.00	5.00	20.0	44.5
14	0.50	5.00	10.0	2.00	0.00	0.00	0.00	0.00	30.0	42.5
15	0.50	6.00	7.50	7.50	0.00	0.00	20.0	0.00	25.0	33.5
16	0.50	10.0	15.0	2.50	0.00	12.5	0.00	0.00	25.0	34.5
17	0.50	12.5	4.00	7.50	0.00	0.00	0.00	20.0	20.0	35.5
18	0.50	25.0	10.0	1.00	0.00	0.00	0.00	0.00	25.0	38.5
19	0.75	5.00	25.0	1.00	0.00	0.00	0.00	0.00	30.0	38.25
20	0.75	10.0	10.0	5.00	0.00	0.00	0.00	0.00	30.0	44.25
21	0.75	12.5	0.00	10.0	0.00	5.00	0.00	0.00	35.0	36.75
22	0.75	12.5	12.5	1.00	0.00	0.00	0.00	0.00	30.0	43.25
23	0.75	25.0	20.0	10.0	0.00	0.00	0.00	0.00	14.25	30.0
24	1.00	15.00	25.0	1.00	7.50	0.00	15.0	2.50	10.0	23.0
25	1.00	5.00	7.50	10.0	0.00	2.00	0.00	0.00	35.0	39.5
26	1.00	7.50	10.0	7.50	20.00	0.00	0.00	0.00	20.0	34.0
27	1.00	10.0	10.0	5.00	0.00	10.0	0.00	0.00	30.0	34.0
28	1.00	15.0	2.00	2.5	15.0	0.00	2.50	7.50	20.0	37.0
29	1.00	25.0	20.0	0.00	0.00	0.00	0.00	0.00	25.0	29.0
30	1.50	5.00	15.0	5.00	5.00	0.00	10.00	5.00	20.0	33.5
31	1.50	15.0	15.0	1.00	0.00	0.00	5.00	20.0	20.0	22.5
32	1.50	15.0	15.0	1.00	0.00	0.00	0.00	0.00	30.0	37.5
33	1.50	10.0	5.00	7.50	0.00	7.50	0.00	2.50	25.0	41.0
34	1.50	25.0	10.0	0.00	0.00	0.00	0.00	0.00	25.0	38.5
35	2.00	5.00	7.50	2.50	7.50	0.00	2.50	2.00	30.0	41.0
36	2.00	5.00	20.0	0.00	0.00	0.00	0.00	0.00	30.0	43.0
37	2.00	12.5	12.5	5.00	0.00	8.00	0.00	0.00	25.00	35.0
38	2.00	25.0	5.00	3.00	20.00	0.00	0.00	0.00	20.0	25.0
39	2.00	25.0	20.0	0.00	0.00	0.00	0.00	0.00	20.0	33.0
40	2.50	0.00	15.0	2.50	0.00	0.00	15.0	0.00	25.0	40.0
41	2.50	5.00	5.00	10.0	15.0	0.00	0.00	0.00	25.0	37.5
42	2.50	15.0	0.00	7.50	0.00	10.0	0.00	0.00	30.0	35.0
43	2.50	10.0	15.0	2.5	0.00	0.00	0.00	15.0	25.0	30.0
44	2.50	20.0	20.0	3.00	0.00	0.00	0.00	0.00	25.0	29.5
45	3.00	5.00	25.0	5.00	0.00	0.00	7.50	7.50	20.0	27.0
46	3.00	10.0	15.0	5.00	0.00	7.50	0.00	7.50	20.0	32.0
47	3.00	15.0	5.00	2.00	2.50	0.00	10.0	2.50	25.0	35.0
48	3.00	20.0	20.0	5.00	0.00	0.00	0.00	0.00	25.0	27.0
49	3.00	25.0	10.0	2.00	0.00	0.00	0.00	0.00	30.0	30.0
50	4.00	0.00	20.0	2.50	0.00	5.00	0.00	0.00	25.0	43.5
51	4.00	2.50	5.00	10.0	5.00	0.00	5.00	5.00	25.0	38.5
52	4.00	15.0	2.50	5.00	2.00	10.0	2.00	0.00	20.0	39.5
53	4.00	20.0	15.0	2.00	0.00	0.00	0.00	0.00	25.0	34.0
54	4.00	25.0	20.0	1.00	0.00	0.00	0.00	0.00	25.0	25.0