

**United States
Environmental Protection Agency
Office of Transportation and Air Quality
National Vehicle and Fuel Emissions Laboratory
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**Determination of Benzene
in Gasoline Method**

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1. Scope

This procedure measures benzene in gasoline samples that may contain ethanol and/or other oxygenated compounds. The method is applicable to measuring benzene in gasoline samples in the range of 0.01 to 5.00 % volume/volume (v/v). Samples containing more than this amount may be diluted to fall within the range.

2. Summary of Method

F-118 is a back-flush gas chromatograph analysis for benzene in gasoline using packed columns and a thermal conductivity detector

3. Significance

Gasoline samples, containing between 0.01 % (v/v) and 5.00 % (v/v) benzene and up to 12% (v/v) ethanol can be checked for the presence of a compliable concentration of benzene. Oxygenates other than ethanol have not been found to interfere with this benzene analysis and are not restricted in quantity.

4. Applicable Documents

- 4.1 "Code of Federal Regulations," Title 40, Part 80, Section 46
- 4.2 Quality Assurance Management Staff, "Calculation of Precision, Bias, and Method Detection Limit for Chemical and Physical Measurements," U.S. EPA, March 30, 1984
- 4.3 American Society for Testing and Materials (ASTM) D 3606-92: "Standard Test Method for Determination of Benzene and Toluene in Finished Motor and Aviation Gasoline by Gas Chromatography," and modifications as presented in Question and Answer document dated November 1994
- 4.4 "Hewlett-Packard 5890A Instrument Manual"
- 4.5 "Hewlett-Packard Chemstation Manual"
- 4.6 Wasson – "ECE Instrumentation Manual"
- 4.7 Environmental Protection Agency (EPA) Engineering Operation Division (EOD) "TP109, Chain of Custody Procedure"

5. Definitions

5.1 Independent Standard:

National Institute of Standards and Technology (NIST) standards are not available for this analysis, so an independent standard is prepared by a different analyst using a different lot number of benzene from that used to produce the calibration standards. Production is otherwise identical to production of calibration standards.

5.2 Control fluid:

California Phase II test fuel drawn from the National Vehicle and Fuel Emissions Laboratory (NVFEL) underground storage tanks is used as a control fluid. The concentration of benzene in each batch of this fluid is measured against calibration standards for consistency.

5.3 Calibration standard:

Calibration standards are made from the purest compounds available, diluted in benzene-free blank stock to the desired concentrations. They are used for the purpose of calibrating the instrument.

5.4 Check standard:

Check standards are prepared in exactly the same manner as calibration standards, and may be identical to the calibration standards except that they are used to check the calibration after it has been established.

5.5 Internal standard:

The internal standard is sec-butanol. It is added to each sample to be analyzed to allow for compensation of sample injection quantity variation and other sampling factors during analysis.

5.6 Blank stock:

The blank stock is a mixture of 10% (v/v) benzene-free ethanol in benzene-free iso-octane. It is used as a diluent in standards and for reagent blanks

5.7 Reagent blank:

A reagent blank is a sample prepared by the analyst that contains only blank stock and internal standard. It is used to verify that the blank stock and internal standard contain no benzene and that benzene is not introduced through the normal preparation of standards.

6.0 Interferences and/or Limitations

The purity of chemicals used as standards is not absolute. Some correction may be necessary to prevent offsets.

Because of the dependence of the density of reference materials on temperature, the preparation of standards and samples must be done with all materials at lab temperature using Class A glassware.

If an unknown sample is found to be above 5.0% (v/v) benzene, it must be volumetrically diluted to fall within the specified range of 1.0% to 5.0% (v/v) benzene. Samples found to contain ethanol should be diluted with blank stock. Samples containing no ethanol should be diluted with iso-octane. The diluent in either case must be analyzed prior to dilution to verify that it contains no detectable quantity of benzene. All dilutions must be done with Class-A volumetric glassware.

If the dilute analysis is satisfactory, calculate the concentration of benzene in the undiluted sample as follows:

$$B = B_b * [(V_s + V_o) / V_s]$$

where:

B_b = concentration of benzene in the diluted sample

V_s = Volume of the original sample

V_o = Volume of the diluent

This calculation must be shown on the instrument-generated sample analysis report for the diluted sample.

7. Safety

7.1. Gasoline, benzene, and oxygenated compounds are extremely flammable and may be toxic when exposure is over a prolonged period. Benzene is a known carcinogen. Persons performing this procedure must be familiar with the chemicals and hazards involved.

7.1.1 Dilutions must be performed in well-ventilated areas, preferably in a fume hood, away from open flames and sparks.

7.1.2 For fires or spills, specific instructions are available from the supervisor and/or Safety Officer.

- 7.1.3 Prior to performing the analysis, the analyst must read and comprehend the Material Safety Data Sheets (MSDS) for materials used in this analysis. The MSDS will recommend personal protection equipment and practices to follow when using particular substances.
- 7.2 Gas cylinders must be properly secured and handled with extreme caution because of the high volumes contained and the high pressures at which they are contained.

8. Apparatus

- 8.1 Gas chromatograph (GC) equipped with a backflush valve and a thermal-conductivity detector (TCD).

Equipment Used: Hewlett-Packard 5890-A equipped with the following columns, in order:

5' X 1/8" Methyl Silicone on Chromasorb (10% OV101 on Chrom PAW 80/100)

5' X 1/8" TCEP on Chromasorb (20% TCEP on Chrom PAW 80/100)

15' X 1/8" Carbowax 1540 (15%) on Chromasorb W (e.g. Wasson-ECE K16)

- 8.2 Computer system for controlling the analysis and collecting data.

Equipment Used: MICRON with Hewlett-Packard Chemstation software

9. Reagents and Materials

- 9.1 2-milliliter (mL) sample vials or vials suitable for the autosampler with aluminum crimp caps and lined rubber septa
- 9.2 30-mL vials for calibration standards and samples
- 9.3 Class A glass pipets and volumetric flasks (various sizes) for preparation of calibration standards, check standards, analytical samples, and control fluid samples
- 9.4 GC injection syringe, 5-microliter (μL) volume, or autosampler with same.
- 9.5 Reagent grade or better ethanol, benzene, toluene and sec-butanol.

- 9.6 Benzene free iso-octane used as solvent to prepare standards.
- 9.7 Helium; ultra pure grade (used as GC carrier gas).
- 9.8 Compressed nitrogen or air for valve operation.

10. Sampling

Sampling is done by agents in the field.

11. Calibration

Determine if an instrument calibration is required. The following are guidelines for this determination:

If the instrument has not been previously used for this analysis.

If the current calibrations are lost or damaged.

If the instrument has been reconfigured or repaired.

If the check standards or control fluids are outside the acceptance criteria and it is determined that the instrument calibration is at fault.

- 11.1 Prepare the calibration standards. Calibration standards are created by appropriate dilution of chemicals used as standards. The highest purity chemicals available are diluted using Class A glassware to achieve a range of concentrations encompassing the range of analysis desired.
- 11.2 The following represents one dilution scheme for preparing a set of calibration standards. Other dilution schemes may be used, provided they are consistent with the range and concentration coverage presented here. Enforcement analysis covers the range of 0.05%(v/v) to 5.00%(v/v) benzene with seven concentrations.
- 11.3 The high-concentration standard is made by volumetrically diluting 10 mL benzene, 20 mL ethanol, and 40 mL toluene to 200 mL with iso-octane. Toluene and ethanol are added volumetrically to provide reference peaks.

- 11.4 Subsequent standards are prepared by dilution of this mixture with calibration blank stock. The following dilution scheme is typically employed:

Volume of Intermediate (mL)	Flask Volume (mL)	Benzene Concentration (% V/V)	Toluene Concentration (% V/V)
50	100	2.50	10.0
25	100	1.25	5.0
15	100	0.75	3.0
7	100	0.35	1.4
3	100	0.15	0.6
1	100	0.05	0.2

- 11.5 Prepare the calibration standards for GC calibration.
- 11.5.1 Pipet 25 mL of standard into a 30-mL vial and add 1 mL of sec-butanol internal standard.
- 11.5.2 Mix each standard and fill an autosampler vial with it using a disposable pipet.
- 11.5.3 Label each vial with the benzene concentration and load it into the autosampler.
- 11.6 Check the instrument setup for the calibration run.
- 11.6.1 The calibration fit should be selected as linear, forced through the origin.
- 11.6.2 Verify that the retention time window has been set properly. The typical value is $\pm 5\%$ (this is the Chemstation default).
- 11.6.3 Check recent analyses for ethanol, benzene, sec-butanol, and toluene retention times and edit the correct value for each into the Chemstation calibration table if necessary. Refer to the Chemstation instruction manual for details of this operation.
- 11.6.4 The instrument should be calibrated with a range of standards that will encompass the likely concentration of the samples.
- 11.6.5 Initiate the calibration analysis according to the HP Chemstation Manual.
- 11.6.6 Following the completion of a calibration analysis, check the calibration curve to ensure that all points are on the line. If not this must be investigated. Analysis cannot proceed until the cause is resolved.

- 11.6.7 If the calibration is satisfactory, analyze the calibration standards and the independent standard.
- 11.6.8 If the difference between the result of these analyses and the named concentration of the standards exceeds the larger of 5.0% of the named concentration of the standard or 0.05% absolute, investigation, correction and successful reanalysis are required before proceeding.
- 11.7 If the analysis of the standards are satisfactory, add 1 mL of internal standard to the control fluid and analyze it. The result of this analysis should be within the standard deviation of the most recent analyses of this compound.
- If it is not within these limits, the calibration is considered suspect and the cause of the discrepancy must be resolved before the calibration can be accepted or samples analyzed.
- 11.8 If the data from this analysis appear satisfactory, the calibration must be saved within the data system.
- 11.9 The naming convention for saving a calibration is a prefix BXZ plus a date, written as a month and day, were X is the year. For example, if a calibration were completed on the twenty-ninth day of December in the year 2001, it would be named "B1Z12-29".
- 11.10 After saving the calibration, a plot of the calibration should be printed, along with a list of the calibration parameters. This printout should be saved, along with the results of the independent standard analysis and the "Chromatograph Calibration Curve Evaluation Report".

12 Analytical Procedure

- 12.1 Pipet 25 mL of each sample into individual 30-mL disposable vials.
- 12.2 Pipet 1 mL of sec-butanol internal standard into each container.
- 12.3 Seal each container and mix the contents.
- 12.4 Using a disposable pipet, fill each autosampler vial with sample. Close each vial according to the manufacturer's instructions and label it with the sample number.

- 12.5 Create a sequence file for the Chemstation per the Chemstation instruction manual. Arrange the standards and test samples in the autosampler as described in the table below, and then input the sample and standard IDs into the data system.

Control fluid
Check standard
Reagent blank
Control fluid
Samples (10)
Duplicate sample
Control Fluid
Samples (10)
Duplicate sample
Control Fluid
Etc.

A minimum of one check standard and one reagent blank are used for each analysis session. The analytical session always begins and ends with the control fluid sample.

- 12.6 Operate the autosampler per the manufacturer's instructions to initiate the analysis.
- 12.7 At the completion of each analysis, the HP Chemstation will produce an output report showing the chromatogram and calculated concentrations. Review the individual GC reports to verify that all retention times are within the retention time window by verifying that each peak of interest is identified.
- 12.8 Ensure that the difference between the reported concentration of the check standard and its nominal concentration is less than the larger of 0.06% absolute or 3% of point. If it is not within this limit, discard the vial and replace it with a fresh one. If a fresh vial is out of specification, investigate the cause; it may be necessary to make new standards and recalibrate.
- 12.9 If all acceptance criteria are met, the analyst transfers the sample results to the sample data base.
- 12.10 Discard the contents of the sample vials into an approved disposal container.

13. Calculations

- 13.1 The instrument calculates the concentration of each sample based on the active calibration curve and the benzene response with reference to the internal standard response.
- 13.2 Upon completion of each discrete analysis, a summary report is generated by the GC data system (see Attachment). The operator must verify that the identity and label on the chromatogram match the sample identification number from the vial.

- 13.3 The analyst reviews the individual reports to verify peak recognition, internal standard consistency, baseline stability, accuracy of the standard and control fluid measurements, and peak morphology. For this analysis, peaks should be reasonably symmetrical with no obvious splitting, flat tops, or baseline aberrations. Excessive trailing is an indication of column decay or other instrument problems.
- 13.4 Analysis results for diluted samples are corrected in the data base, per the formula in (), to reflect their undiluted concentration by multiplying by the dilution factor.
- 13.5 The analyst reviews the results of the analyses of samples, control fluids, check standard, duplicate samples, and independent standard for conformance to acceptance criteria.

14. Performance Criteria

- 14.1 The ethanol, benzene, sec-butanol, and toluene GC retention times for the check standard and control fluid analyses must be within the recognition time window of the current calibration, as evidenced by instrument peak identification.
- 14.2 The composite points of the calibration curve must not differ from the curve by more than 0.06% absolute or 3.0% of point.
- 14.3 If a new calibration curve is generated, then the difference between the result of the analysis of the independent standard and the named concentration of that standard must not exceed the larger of 5.0% of the named concentration of that standard or 0.05% absolute.
- 14.4 The difference between the reported concentration of the check standard and its nominal concentration must be less than the larger of 0.06% absolute or 3% of point.
- Failure to meet this criterion requires investigation and corrective action. Samples analyzed since the last successful duplicate analysis must be reanalyzed.
- 14.5 The baseline of any analysis run must not contain any noise greater than the threshold level for the lowest calibrated point and have no discernible drift. Individual peaks should not display any excessive tailing or other aberrant morphology.
- 14.6 The "Fuels Field Inspection" forms must be initialed by the analyst to signify they have been checked for compliance with the acceptance criteria.
- 14.7 The blank stock analyzed as part of the calibration and used for dilutions must have no detectable amount of benzene.