

§ 80.415

40 CFR Ch. I (7-1-00 Edition)

including use of any forms that may be specified by the Administrator; and

(2) Be signed by the president or owner of the foreign refiner company, or by that person's immediate designee, and shall contain the following declaration:

I hereby certify: (1) that I have actual authority to sign on behalf of and to bind [insert name of foreign refiner] with regard to all statements contained herein; (2) that I am aware that the information contained herein is being certified, or submitted to the United States Environmental Protection Agency, under the requirements of 40 CFR, Part 80, subpart H, and that the information is material for determining compliance under these regulations; and (3) that I have read and understand the information being certified or submitted, and this information is true, complete and correct to the best of my knowledge and belief after I have taken reasonable and appropriate steps to verify the accuracy thereof.

I affirm that I have read and understand the provisions of 40 CFR Part 80, subpart H, including 40 CFR 80.410 [insert name of foreign refiner]. Pursuant to Clean Air Act section 113(c) and Title 18, United States Code, section 1001, the penalty for furnishing false, incomplete or misleading information in this certification or submission is a fine of up to \$10,000, and/or imprisonment for up to five years.

ATTEST ENGAGEMENTS

§ 80.415 What are the attest engagement requirements for gasoline sulfur compliance applicable to refiners and importers?

In addition to the requirements for attest engagements that apply to refiners and importers under §§ 80.125 through 80.130, and § 80.410, the attest engagements for importers and refiners must include the following procedures and requirements each year.

(a) *Baseline.* (1) Obtain the EPA sulfur baseline approval letter for the refinery to determine the refinery's applicable sulfur baseline and baseline volume under §§ 80.250 or 80.295.

(2) If the year being reviewed is 2004 through 2006 (2007 for refineries with small refiner status) and the refinery or importer produced or imported any GPA gasoline under § 80.216 or the refiner has approved status for a small refinery:

(i) Obtain the refinery's annual sulfur reports for 2000 through 2003; and

(ii) Determine whether the annual average sulfur level for any year credits were generated for 2000 through 2003 was less than the baseline level under paragraph (a)(1) of this section.

(3) If the annual average sulfur content for any year credits were created for 2000 through 2003 was less than the baseline level under paragraph (a)(1) of this section, report as a finding the lowest annual sulfur level as the new baseline value. For GPA gasoline add 30 ppm to obtain the GPA standard, not to exceed 150 ppm.

(4) If the refinery being reviewed is a small refinery and the annual volume under paragraph (b)(2) of this section is greater than the baseline volume, calculate the applicable standard in accordance with § 80.240(c).

(5) Obtain a written representation from the company representative stating the sulfur value that the company used as its baseline and agree that number to paragraphs (a)(1) through (a)(4) of this section and to the reports to EPA.

(b) *EPA reports.* (1) Obtain and read a copy of the refinery's or importer's annual sulfur reports filed with EPA for the year.

(2) Agree the yearly volume of gasoline reported to EPA in the sulfur reports with the inventory reconciliation analysis under § 80.128.

(3) For the years 2004 through 2006, calculate the annual volume and average sulfur level for gasoline classified as GPA gasoline under §§ 80.216 and 80.219, and calculate the annual volume and average sulfur level for gasoline not classified as GPA gasoline, and agree these values with the values reported to EPA.

(4) Except as provided in paragraph (b)(3) of this section, calculate the annual average sulfur level for all gasoline and agree that value with the value reported to EPA.

(5) Obtain and read a copy of the refinery's or importer's sulfur credit report.

(c) *Credit generation before 2004.* In the case of a refinery that only generates credits during 2000 through 2003:

(1) Obtain a written representation from the company representative stating the refinery produces gasoline from crude oil.

Environmental Protection Agency

§ 80.415

(2) Compute and report as a finding the sulfur baseline from paragraph (a) of this section multiplied by 0.9.

(3) Obtain the annual average sulfur level from paragraph (b)(4) of this section.

(4) If the sulfur value under paragraph (c)(3) of this section is less than the sulfur value under paragraph (c)(2) of this section, compute and report as a finding the difference between the annual average sulfur level and the refinery's sulfur baseline from paragraph (a) of this section.

(5) Compute and report as a finding the total number of sulfur credits generated by multiplying the value in paragraph (c)(4) of this section by the volume of gasoline in paragraph (b)(2) of this section, and agree this value with the value reported to EPA.

(d) *Credit generation in 2004 and thereafter.* The following procedures shall be completed for a refinery or importer that generates credits in 2004 and thereafter:

(1) Obtain the annual average sulfur level for gasoline not classified as GPA from paragraph (b)(3) of this section.

(2) If the sulfur value under paragraph (d)(1) of this section is less than 30 ppm, compute and report as a finding the difference between the sulfur level under paragraph (d)(1) of this section and 30 ppm.

(3) Compute and report as a finding the total number of sulfur credits generated by multiplying the value calculated in paragraph (d)(2) of this section by the volume of gasoline not classified as GPA in paragraph (b)(3) of this section, and agree this number with the number reported to EPA.

(4) Obtain the annual average sulfur level for gasoline classified as GPA from paragraph (b)(3) of this section.

(5) If the sulfur value under paragraph (d)(4) of this section is less than the applicable level under § 80.310, compute and report as a finding the difference between the sulfur level under paragraph (d)(4) of this section and the appropriate level in § 80.310 .

(6) Compute and report as a finding the total number of sulfur credits generated by multiplying the value calculated in paragraph (d)(5) of this section by the volume of gasoline classified as GPA in paragraph (b)(3) of this

section, and agree this number with the number reported to EPA.

(7) If the refinery has an approved status as a small refinery, obtain the annual average sulfur level for gasoline from paragraph (b)(4) of this section.

(8) If the sulfur value under paragraph (d)(7) of this section is less than the applicable standard under § 80.240, compute and report as a finding the difference between the sulfur level under paragraph (d)(7) of this section and the appropriate standard under § 80.240.

(9) Compute and report as a finding the total number of sulfur credits generated by multiplying the value calculated in paragraph (d)(8) of this section by the volume of gasoline in paragraph (b)(4) of this section, and agree this number with the number reported to EPA.

(e) *Credit purchases and sales.* The following attest procedures shall be completed for a refinery or importer that is a transferor or transferee of credits during an averaging period:

(1) Obtain contracts or other documents for all credits transferred to another refinery or importer during the year being reviewed; compute and report as a finding the number and year of creation of credits represented in these documents as being transferred away; and agree with the report to EPA.

(2) Obtain contracts or other documents for all credits received during the year being reviewed; compute and report as a finding the number and year of creation of credits represented in these documents as being received; and agree with the report to EPA.

(f) *Credits required for non-GPA gasoline.* The following attest procedures shall be completed for refineries and importers in 2005 and thereafter (2004 and thereafter for refineries having standards under § 80.240):

(1) Obtain the annual average sulfur level for gasoline not classified as GPA from paragraph (b)(3) of this section.

(2) If the value in paragraph (f)(1) of this section is greater than 30 ppm (or greater than the small refinery standard), compute and report as a finding the difference between 30 ppm (or the standard under § 80.240) and the value in paragraph (f)(1) of this section.

(3) Compute and report as a finding the total sulfur credits required by multiplying the value in paragraph (f)(2) of this section times the volume of gasoline not classified as GPA in paragraph (b)(3) of this section, and agree with the report to EPA.

(4) Obtain the refiner's or importer's representation as to the portion of the deficit under paragraph (f)(3) of this section that was resolved with credits, the portion that was resolved with allotments in 2005 only or that was carried forward as a deficit under § 80.205, and agree with the report to EPA (refineries subject to standards under § 80.240 cannot carry deficits forward).

(g) *Credits required for GPA gasoline.* The following attest procedures shall be completed in 2004 through 2006 for a refinery or importer that produces gasoline subject to the geographic phase-in area standards under § 80.216:

(1) Obtain the annual average sulfur level for the refinery's or importer's GPA gasoline from paragraph (b)(3) of this section.

(2) If the value in paragraph (g)(1) of this section is greater than the refinery's or importer's baseline plus 30 ppm under § 80.216, as determined in paragraph (a) of this section or 150 ppm, whichever is less, compute and report as a finding the difference between the annual average sulfur level and the baseline level plus 30 ppm, or 150 ppm, whichever is less.

(3) Compute and report as a finding the total sulfur credits and/or allotments required by multiplying the value in paragraph (g)(2) of this section times the volume of GPA gasoline from paragraph (b)(3) of this section.

(4) Obtain the refiner's or importer's representation as to the portion of the deficit under paragraph (g)(3) of this section that was resolved with credits, or the portion that was resolved with allotments in 2004 or 2005 only (compliance deficits for GPA gasoline cannot be carried forward).

(h) *Credit expiration.* The following attest procedures shall be completed for a refinery or importer that possesses credits during an averaging period:

(1) Obtain a list of all credits in the refiner's or importer's possession at any time during the year being re-

viewed, identified by the year of creation of the credits.

(2) If the year being reviewed is 2006 and thereafter, except in the case of gasoline produced for use in the GPA and gasoline produced by small refiners, determine whether any credits identified in paragraph (h)(1) of this section or Type A sulfur allotments created under paragraph (i) of this section and converted to credits were created before 2004, and if so, report as a finding this number of expired credits.

(3) If the year being reviewed is 2008 and thereafter, determine whether any credits identified in paragraph (h)(1) of this section or Type B sulfur allotments created under paragraph (i) of this section and converted to credits were created more than 5 years before the year being reviewed, and if so, report as a finding this number of expired credits (for example, unused credits created during the 2004 averaging period expire at the end of the 2009 averaging period).

(i) *Optional credit and allotment generation in 2003.* The following requirements apply to any refinery that generates credits and allotments in 2003 under § 80.275(a):

(1) Obtain a written representation from the company representative stating the refinery produces gasoline from crude oil.

(2) Obtain the refinery baseline value from paragraph (b)(1) of this section, the annual volume from paragraph (b)(2) of this section and the annual average sulfur level from paragraph (b)(4) of this section.

(3) Based on the annual sulfur level and refinery baseline, determine which equation under § 80.275(a)(2) applies.

(4) Using the applicable equations under § 80.275(a)(2), recalculate the sulfur allotments, by type, and credits and report as a finding.

(j) *Credit reconciliation.* The following attest procedures shall be completed each year credits were in the refiner's or importer's possession at any time during the year:

(1) Obtain the credits remaining or the credit deficit from the previous year from the refiner's or importer's report to EPA for the previous year.

Environmental Protection Agency

§ 80.415

(2) Compute and report as a finding the net credits remaining at the conclusion of the year being reviewed by totaling:

(i) Credits remaining from the previous year; plus

(ii) Credits generated under paragraphs (c), (d) and (i) of this section; plus

(iii) Allotments generated under paragraph (i) of this section which are converted to credits; plus

(iv) Credits purchased under paragraph (e) of this section; minus

(v) Credits sold under paragraph (e) of this section; minus

(vi) Credits used under paragraphs (f) and (g) of this section; minus

(vii) Credits expiring under paragraph (h) of this section; minus

(viii) Credit deficit from the previous year.

(3) Agree the credits remaining or the credit deficit at the conclusion of the year being reviewed with the report to EPA.

(4) If the refinery or importer had a credit deficit for both the previous year and the year being reviewed, report this fact as a finding.

(k) *Sulfur allotments in 2004 and 2005.* The following requirements apply to any refinery or importer that is subject to corporate pool average standards under § 80.195:

(1) *Corporate pool average.* (i) Obtain the annual average sulfur level for the refiner or importer from the sulfur report filed with EPA for all gasoline subject to corporate pool standards (all gasoline produced and imported, except that if 50% or greater of the gasoline volume was GPA gasoline the refiner or importer is not subject to the corporate pool average).

(ii) Compute and report as a finding the company's gasoline volume subject to corporate pool standards and average sulfur level for gasoline subject to corporate pool standards, and agree with the values reported to EPA.

(2) *Allotment generation.* (i) For 2004, if the corporate pool average is less than 120 ppm, compute and report as a finding the number and type of sulfur allotments generated in accordance with the applicable provisions under § 80.275(b).

(ii) For 2005, if the corporate pool average is less than 90 ppm, compute and report as a finding the number and type of sulfur allotments generated in accordance with the applicable provisions under § 80.275(b).

(iii) If the refiner or importer produced and imported 50% or more of its gasoline for GPA use in 2004 or 2005, no allotments can be generated in that year.

(3) *Allotment purchases and sales.* (i) Obtain contracts or other documents for all allotments transferred to another company during the year being reviewed; compute and report as a finding the number of allotments represented in these documents as being transferred away; and agree with the report to EPA.

(ii) Obtain contracts or other documents for all allotments received during the year being reviewed; compute and report as a finding the number of allotments represented in these documents as being received; and agree with the report to EPA.

(4) *Allotments required.* (i) For 2004, if the corporate pool average is greater than 120 ppm, compute and report as a finding the number of allotments required by multiplying the amount the corporate pool average is above 120 ppm times the corporate pool volume, and agree with the report to EPA.

(ii) For 2005, if the corporate pool average is greater than 90 ppm, compute and report as a finding the number of allotments required by multiplying the amount the corporate pool average is above 90 ppm times the corporate pool volume, and agree with the report to EPA.

(iii) Obtain the number of allotments used to meet standards for GPA gasoline determined in paragraph (g) of this section.

(5) *Allotment reconciliation.* (i) Compute and report as a finding the net allotments remaining at the conclusion of the year being reviewed by totaling allotments:

(A) Generated under paragraphs (i)(4) and (k)(2) of this section; plus

(B) Purchased under paragraph (k)(3) of this section; minus

(C) Sold under paragraph (k)(3) of this section; minus

(D) Used under paragraph (k)(4) of this section for demonstrating compliance with the corporate pool average.

(ii) Report as a finding any allotments generated in 2003 or 2004 that are used to meet the corporate pool standards in 2005 that were not reduced to 50% of their original value.

(iii) If the company's net allotments remaining are less than zero, report this fact as a finding.

APPENDIX A TO PART 80—TEST FOR THE DETERMINATION OF PHOSPHORUS IN GASOLINE

1. Scope.

1.1 This method was developed for the determination of phosphorus generally present as pentavalent phosphate esters or salts, or both, in gasoline. This method is applicable for the determination of phosphorus in the range from 0.0008 to 0.15 g P/U.S. gal, or 0.2 to 49 mg P/liter.

2. Applicable documents.

2.1 ASTM Standards:

D 1100 Specification for Filter Paper for Use in Chemical Analysis.

3. Summary of method.

3.1 Organic matter in the sample is decomposed by ignition in the presence of zinc oxide. The residue is dissolved in sulfuric acid and reacted with ammonium molybdate and hydrazine sulfate. The absorbance of the "Molybdenum Blue" complex is proportional to the phosphorus concentration in the sample and is read at approximately 820 nm in a 5-cm cell.

4. Apparatus.

4.1 Buret, 10-ml capacity, 0.05-ml subdivisions.

4.2 Constant-Temperature Bath, equipped to hold several 100-ml volumetric flasks submerged to the mark. Bath must have a large enough reservoir or heat capacity to keep the temperature at 180 to 190 °F (82.2 to 87.8 °C) during the entire period of sample heating.

NOTE 1: If the temperature of the hot water bath drops below 180 °F (82.2 °C) the color development may not be complete.

4.3 Cooling Bath, equipped to hold several 100-ml volumetric flasks submerged to the mark in ice water.

4.4 Filter Paper, for quantitative analysis, Class G for fine precipitates as defined in Specification D 1100.

4.5 Ignition Dish—Coors porcelain evaporating dish, glazed inside and outside,

with pourout (size no. 00A, diameter 75 mm, capacity 70 ml).

4.6 Spectrophotometer, equipped with a tungsten lamp, a red-sensitive phototube capable of operating at 830 nm and with absorption cells that have a 5-cm light path.

4.7 Thermometer, range 50 to 220 °F (10 to 105 °C).

4.8 Volumetric Flask, 100-ml with ground-glass stopper.

4.9 Volumetric Flask, 1000-ml with ground-glass stopper.

4.10 Syringe, Luer-Lok, 10-ml equipped with 5-cm. 22-gage needle.

5. Reagents.

5.1 Purity of Reagents—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Purity of Water—Unless otherwise indicated, references to water shall be understood to mean distilled water or water of equal purity.

5.3 Ammonium Molybdate Solution—Using graduated cylinders for measurement add slowly (Note 2), with continuous stirring, 225 ml of concentrated sulfuric acid to 500 ml of water contained in a beaker placed in a bath of cold water. Cool to room temperature and add 20 g of ammonium molybdate tetrahydrate ((NH₄)₆ Mo₇ O₂₄·4H₂O). Stir until solution is complete and transfer to a 1000-ml flask. Dilute to the mark with water.

NOTE 2: Wear a face shield, rubber gloves, and a rubber apron when adding concentrated sulfuric acid to water.

5.4 Hydrazine Sulfate Solution—Dissolve 1.5 of hydrazine sulfate (H₂NNH₂·H₂SO₄) in 1 litre of water, measured with a graduated cylinder.

NOTE 3: This solution is not stable. Keep it tightly stoppered and in the dark. Prepare a fresh solution after 3 weeks.

5.5 Molybdate-Hydrazine Reagent—Pipet 25 ml of ammonium molybdate solution into a 100-ml volumetric flask containing approximately 50 ml of water, add by pipet 10 ml of N₂NNH₂·H₂SO₄ solution, and dilute to 100 ml with water.

NOTE 4: This reagent is unstable and should be used within about 4 h. Prepare it immediately before use. Each determination (including the blank) uses 50 ml.

5.6 Phosphorus, Standard Solution (10.0 µg P/ml)—Pipet 10 ml of stock standard phosphorus solution into a 1000-ml volumetric flask and dilute to the mark with water.

5.7 Phosphorus, Stock Standard Solution (1.00 mg P/ml)—Dry approximately 5 g of potassium dihydrogen phosphate (KH₂PO₄) in an oven at 221 to 230 °F (105 to 110 °C) for 3 h. Dissolve 4.393±0.002 g of the reagent in 150 ml, measured with a graduated cylinder, of H₂SO₄(1+10) contained in a 1000-ml volumetric flask. Dilute with water to the mark.

5.8 Sulfuric Acid (1+10)—Using graduated cylinders for measurement add slowly (Note 2), with continuous stirring, 100-ml of concentrated sulfuric acid (H₂SO₄, sp gr 1.84) to 1 litre of water contained in a beaker placed in a bath of cold water.

5.9 Zinc Oxide.

NOTE 5: High-bulk density zinc oxide may cause spattering. Density of approximately 0.5 g/cm³ has been found satisfactory.

6. Calibration.

6.1 Transfer by buret, or a volumetric transfer pipet, 0.0, 0.5, 1.0, 1.5, 2.0, 3.0, 3.5, and 4.0 ml of phosphorus standard solution into 100-ml volumetric flasks.

6.2 Pipet 10 ml of H₂SO₄ (1+10) into each flask. Mix immediately by swirling.

6.3 Prepare the molybdate-hydrazine solution. Prepare sufficient volume of reagent based on the number of samples being analyzed.

6.4 Pipet 50 ml of the molybdate-hydrazine solution to each volumetric flask. Mix immediately by swirling.

6.5 Dilute to 100 ml with water.

6.6 Mix well and place in the constant-temperature bath so that the contents of the flask are submerged below the level of the bath. Maintain bath temperature at 180 to 190 °F (82.2 to 87.8 °C) for 25 min (Note 1).

6.7 Transfer the flask to the cooling bath and cool the contents rapidly to room temperature. Do not allow the samples to cool more than 5 °F (2.8 °C) below room temperature.

NOTE 6: Place a chemically clean thermometer in one of the flasks to check the temperature.

6.8 After cooling the flasks to room temperature, remove them from the cooling water bath and allow them to stand for 10 min. at room temperature.

6.9 Using the 2.0-ml phosphorus standard in a 5-cm cell, determine the wavelength near 820 nm that gives maximum absorbance. The wavelength giving maximum absorbance should not exceed 830 nm.

6.9.1 Using a red-sensitive phototube and 5-cm cells, adjust the spectrophotometer to zero absorbance at the wavelength of maximum absorbance using distilled water in both cells. Use the wavelength of maximum

absorbance in the determination of calibration readings and future sample readings.

6.9.2 The use of 1-cm cells for the higher concentrations is permissible.

6.10 Measure the absorbance of each calibration sample including the blank (0.0 ml phosphorus standard) at the wavelength of maximum absorbance with distilled water in the reference cell.

NOTE 7: Great care must be taken to avoid possible contamination. If the absorbance of the blank exceeds 0.04 (for 5-cm cell), check for source of contamination. It is suggested that the results be disregarded and the test be rerun with fresh reagents and clean glassware.

6.11 Correct the absorbance of each standard solution by subtracting the absorbance of the blank (0 ml phosphorus standard).

6.12 Prepare a calibration curve by plotting the corrected absorbance of each standard solution against micrograms of phosphorus. One millilitre of phosphorus standard solution provides 10 µg of phosphorus.

7. Sampling.

7.1 Selection of the size of the sample to be tested depends on the expected concentration of phosphorus in the sample. If a concentration of phosphorus is suspected to be less than 0.0038 g/gal (1.0 mg/litre), it will be necessary to use 10 ml of sample.

NOTE 8: Two grams of zinc oxide cannot absorb this volume of gasoline. Therefore the 10-ml sample is ignited in aliquots of 2 ml in the presence of 2 g of zinc oxide.

7.2 The following table serves as a guide for selecting sample size:

Phosphorus, milligrams per liter	Equivalent, grams per gallon	Sample size, milliliter
2.5 to 40	0.01 to 0.15	1.00
1.3 to 20	0.005 to 0.075	2.00
0.9 to 13	0.0037 to 0.05	3.00
1 or less	0.0038 or less	10.00

8. Procedure.

8.1 Transfer 2±0.2 g of zinc oxide into a conical pile in a clean, dry, unetched ignition dish.

NOTE 9: In order to obtain satisfactory accuracy with the small amounts of phosphorus involved, it is necessary to take extensive precautions in handling. The usual precautions of cleanliness, careful manipulation, and avoidance of contamination should be scrupulously observed; also, all glassware should be cleaned before use, with cleaning acid or by some procedure that does not involve use of commercial detergents. These compounds often contain alkali phosphates

which are strongly adsorbed by glass surfaces and are not removed by ordinary rinsing. It is desirable to segregate a special stock of glassware for use only in the determination of phosphorus.

8.2 Make a deep depression in the center of the zinc oxide pile with a stirring rod.

8.3 Pipet the gasoline sample (Note 10) (see 7.2 for suggested sample volume) into the depression in the zinc oxide. Record the temperature of the fuel if the phosphorus content is required at 60 °F (15.6 °C) and make correction as directed in 9.2.

NOTE 10: For the 10-ml sample use multiple additions and a syringe. Hold the tip of the needle at approximately $\frac{2}{3}$ of the depth of the zinc oxide layer and slowly deliver 2 ml of the sample: fast sample delivery may give low results. Give sufficient time for the gasoline to be absorbed by the zinc oxide. Follow step 8.6. Cool the dish to room temperature. Repeat steps 8.3 and 8.6 until all the sample has been burned. Safety—cool the ignition dish before adding the additional aliquots of gasoline to avoid a flash fire.

8.4 Cover the sample with a small amount of fresh zinc oxide from reagent bottle (use the tip of a small spatula to deliver approximately 0.2 g). Tap the sides of the ignition dish to pack the zinc oxide.

8.5 Prepare the blank, using the same amount of zinc oxide in an ignition dish.

8.6 Ignite the gasoline, using the flame from a bunsen burner. Allow the gasoline to burn to extinction (NOTE 10).

8.7 Place the ignition dishes containing the sample and blank in a hot muffle furnace set at a temperature of 1150 to 1300 °F (621 to 704 °C) for 10 min. Remove and cool the ignition dishes. When cool gently tap the sides of the dish to loosen the zinc oxide. Again place the dishes in the muffle furnace for 5 min. Remove and cool the ignition dishes to room temperature. The above treatment is usually sufficient to burn the carbon. If the carbon is not completely burned off place the dish into the oven for further 5-min. periods.

NOTE 11: Step 8.7 may also be accomplished by heating the ignition dish with a Meker burner gradually increasing the intensity of heat until the carbon from the sides of the dish has been burned, then cool to room temperature.

8.8 Pipet 25 ml of H₂SO₄ (1+10) to each ignition dish. While pipeting, carefully wash all traces of zinc oxide from the sides of the ignition dish.

8.9 Cover the ignition dish with a borosilicate watch glass and warm the ignition dish on a hot plate until the zinc oxide is completely dissolved.

8.10 Transfer the solution through filter paper to a 100-ml volumetric flask. Rinse the watch glass and the dish several times with

distilled water (do not exceed 25 ml) and transfer the washings through the filter paper to the volumetric flask.

8.11 Prepare the molybdate-hydrazine solution.

8.12 Add 50 ml of the molybdate-hydrazine solution by pipet to each 100-ml volumetric flask. Mix immediately by swirling.

8.13 Dilute to 100 ml with water and mix well. Remove stoppers from flasks after mixing.

8.14 Place the 100-ml flasks in the constant-temperature bath for 25 min. so that the contents of the flasks are below the liquid level of the bath. The temperature of the bath should be 180 to 190 °F (82.2 to 87.8 °C) (NOTE 1).

8.15 Transfer the 100-ml flasks to the cooling bath and cool the contents rapidly to room temperature (NOTE 6).

8.16 Allow the samples to stand at room temperature before measuring the absorbance.

NOTE 12: The color developed is stable for at least 4 h.

8.17 Set the spectrophotometer to the wavelength of maximum absorbance as determined in 6.9. Adjust the spectrophotometer to zero absorbance, using distilled water in both cells.

8.18 Measure the absorbance of the samples at the wavelength of maximum absorbance with distilled water in the reference cell.

8.19 Subtract the absorbance of the blank from the absorbance of each sample (NOTE 7).

8.20 Determine the micrograms of phosphorus in the sample, using the calibration curve from 6.12 and the corrected absorbance.

9. Calculations.

9.1 Calculate the milligrams of phosphorus per litre of sample as follows:

$$P, \text{ mg/litre} = P/V$$

where:

P = micrograms of phosphorus read from calibration curve, and
V = millilitres of gasoline sample.

To convert to grams of phosphorus per U.S. gallon of sample, multiply mg P/litre by 0.0038.

9.2 If the gasoline sample was taken at a temperature other than 60 °F (15.6 °C) make the following temperature correction:

$$\text{mg P/litre at } 15.6 \text{ }^\circ\text{C} = [\text{mg P/litre at } t] \\ [1 + 0.001(t - 15.6)]$$

where:

t = observed temperature of the gasoline, °C.

9.3 Concentrations below 2.5 mg/litre or 0.01 g/gal should be reported to the nearest 0.01 mg/litre or 0.0001 g/U.S. gal.

9.3.1 For higher concentrations, report results to the nearest 1 mg P/litre or 0.005 g P/U.S. gal.

10. Precision.

10.1 The following criteria should be used for judging the acceptability of results (95 percent confidence):

10.2 Repeatability—Duplicate results by the same operator should be considered suspect if they differ by more than the following amounts:

g P/U.S. gal (mg. P/litre)	Repeatability
0.0008 to 0.005 (0.2 to 1.3) ..	0.0002 g P/U.S. gal (0.05 mg P/litre).
0.005 to 0.15 (1.3 to 40)	7% of the mean.

10.3 Reproducibility—The results submitted by each of two laboratories should not be considered suspect unless they differ by more than the following amounts:

g P/U.S. gal (mg. P/litre)	Reproducibility
0.0008 to 0.005 (0.2 to 1.3) ..	0.0005 g P/U.S. gal (0.13 mg P/litre).
0.005 to 0.15 (1.3 to 40)	13% of the mean.

[39 FR 24891, July 8, 1974; 39 FR 25653, July 12, 1974]

APPENDIX B TO PART 80—TEST METHODS FOR LEAD IN GASOLINE

METHOD 1—STANDARD METHOD TEST FOR LEAD IN GASOLINE BY ATOMIC ABSORPTION SPECTROMETRY

1. Scope.

1.1. This method covers the determination of the total lead content of gasoline. The procedure's calibration range is 0.010 to 0.10 gram of lead/U.S. gal. Samples above this level should be diluted to fall within this range or a higher level calibration standard curve must be prepared. The higher level curve must be shown to be linear and measurement of lead at these levels must be shown to be accurate by the analysis of control samples at a higher level of alkyl lead content. The method compensates for variations in gasoline composition and is independent of lead alkyl type.

2. Summary of method.

2.1 The gasoline sample is diluted with methyl isobutyl ketone and the alkyl lead compounds are stabilized by reaction with iodine and a quarternary ammonium salt. The lead content of the sample is determined by atomic absorption flame spectrometry at 2833 Å, using standards prepared from reagent grade lead chloride. By the use of this treatment, all alkyl lead compounds give identical response.

3. Apparatus.

3.1 Atomic Absorption Spectrometer, capable of scale expansion and nebulizer adjustment, and equipped with a slot burner and premix chamber for use with an air-acetylene flame.

3.2 Volumetric Flasks, 50-ml, 100-ml, 250-ml, and one litre sizes.

3.3 Pipets, 2-ml, 5-ml, 10-ml, 20-ml, and 50-ml sizes.

3.4 Micropipet, 100- μ l, Eppendorf type or equivalent.

4. Reagents.

4.1 Purity of Reagents—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

4.2 Purity of Water—Unless otherwise indicated, references to water shall be understood to mean distilled water or water of equal purity.

4.3 Aliquat 336 (tricapryl methyl ammonium chloride).

4.4 Aliquat 336/MIBK Solution (10 percent v/v)—Dissolve and dilute 100 ml (88.0 g) of Aliquat 336 with MIBK to one liter.

4.5 Aliquat 336/MIBK Solution (1 percent v/v)—Dissolve and dilute 10 ml (8.8 g) of Aliquat 336 with MIBK to one liter.

4.6 Iodine Solution—Dissolve and dilute 3.0 g iodine crystals with Toluene to 100 ml.

4.7 Lead Chloride.

4.8 Lead-Sterile Gasoline—Gasoline containing less than 0.005 g Pb/gal.

4.9 Lead, Standard Solution (5.0 g Pb/gal)—Dissolve 0.4433 g of lead chloride (PbCl_2) previously dried at 105 °C for 3 h in about 200 ml of 10 percent Aliquat 336/MIBK solution in a 250-ml volumetric flask. Dilute to the mark with the 10 percent Aliquat solution, mix, and store in a brown bottle having a polyethylene-lined cap. This solution contains 1,321 μ g Pb/ml, which is equivalent to 5.0 g Pb/gal.

4.10 Lead, Standard Solution (1.0 g Pb/gal)—By means of a pipet, accurately transfer 50.0 ml of the 5.0 g Pb/gal solution to a 250-ml volumetric flask, dilute to volume with 1 percent Aliquat/MIBK solution. Store in a brown bottle having a polyethylene-lined cap.

4.11 Lead, Standard Solutions (0.02, 0.05, and 0.10 g Pb/gal)—Transfer accurately by means of pipets 2.0, 5.0, and 10.0 ml of the 1.0-g Pb/gal solution to 100-ml volumetric flasks; add 5.0 ml of 1 percent Aliquat 336 solution to each flask; dilute to the mark with MIBK.

Mix well and store in bottles having polyethylene-lined caps.

4.12 Methyl Isobutyl Ketone (MIBK). (4-methyl-2-pentanone).

5. Calibration.

5.1 Preparation of Working Standards—Prepare three working standards and a blank using the 0.02, 0.05, and 0.10-g Pb/gal standard lead solutions described in 4.11.

5.1.1 To each of four 50-ml volumetric flasks containing 30 ml of MIBK, add 5.0 ml of low lead standard solution and 5.0 ml of lead-free gasoline. In the case of the blank, add only 5.0 ml of lead-free gasoline.

5.1.2 Add immediately 0.1 ml of iodine/toluene solution by means of the 100- μ l Eppendorf pipet. Mix well.¹

5.1.3 Add 5 ml of 1 percent Aliquat 336 solution and mix.

5.1.4 Dilute to volume with MIBK and mix well.

5.2 Preparation of Instrument—Optimize the atomic absorption equipment for lead at 2833 Å. Using the reagent blank, adjust the gas mixture and the sample aspiration rate to obtain an oxidizing flame.

5.2.1 Aspirate the 0.1-g Pb/gal working standard and adjust the burner position to give maximum response. Some instruments require the use of scale expansion to produce a reading of 0.150 to 0.170 for this standard.

5.2.2 Aspirate the reagent blank to zero the instrument and check the absorbances of the three working standards for linearity.

6. Procedure.

6.1 To a 50 ml volumetric flask containing 30 ml MIBK, add 5.0 ml of gasoline sample and mix.²

6.1.1 Add 0.10 ml (100 μ l) of iodine/toluene solution and allow the mixture to react about 1 minute.³

6.1.2 Add 5.0 ml of 1 percent Aliquot 336/MIBK solution and mix.

6.1.3 Dilute to volume with MIBK and mix.

6.2 Aspirate the samples and working standards and record the absorbance values with frequent checks of the zero.

6.3 Any sample resulting in a peak greater than 0.05 g Pb/gal will be run in duplicate. Samples registering greater than 0.10 g Pb/gal should be diluted with iso-octane or unleaded fuel to fall within the calibration range or a higher level calibration standard curve must be prepared. The higher level curve must be shown to be linear and measurement of lead at these levels must be shown to be accurate by the analysis of con-

trol samples at a higher level of alkyl lead content.

7. Calculations.

7.1 Plot the absorbance values versus concentration represented by the working standards and read the concentrations of the samples from the graph.

8. Precision.

8.1 The following criteria should be used for judging the acceptability of results (95 percent confidence):

8.1.1 Repeatability—Duplicate results by the same operator should be considered suspect if they differ by more than 0.005 g/gal.

8.1.2 Reproducibility—The results submitted by each of two laboratories should not be considered suspect unless the two results differ by more than 0.01 g/gal.

METHOD 2—AUTOMATED METHOD TEST FOR LEAD IN GASOLINE BY ATOMIC ABSORPTION SPECTROMETRY

1. Scope and application.

1.1 This method covers the determination of the total lead content of gasoline. The procedure's calibration range is 0.010 to 0.10 gram of lead/U.S. gal. Samples above this level should be diluted to fall within this range or a higher level calibration standard curve must be prepared. The higher level curve must be shown to be linear and measurement of lead at these levels must be shown to be accurate by the analysis of control samples at a higher level of alkyl lead content. The method compensates for variations in gasoline composition and is independent of lead alkyl type.

1.2 This method may be used as an alternative to the Standard Method set forth above.

1.3 Where trade names or specific products are noted in the method, equivalent apparatus and chemical reagents may be used. Mention of trade names or specific products is for the assistance of the user and does not constitute endorsement by the U.S. Environmental Protection Agency.

2. Summary of method.

2.1 The gasoline sample is diluted with methyl isobutyl ketone (MIBK) and the alkyl lead compounds are stabilized by reacting with iodine and a quaternary ammonium salt. An automated system is used to perform the diluting and the chemical reactions and feed the products to the atomic absorption spectrometer with an air-acetylene flame.

2.2 The dilution of the gasoline with MIBK compensates for severe non-atomic absorption, scatter from unburned carbon containing species and matrix effects caused in

¹EPA practice will be to mix well by shaking vigorously for approximately one minute.

²The gasoline should be allowed to come to room temperature (25 °C).

³See footnote 1 of section 5.1.2.

part by the burning characteristics of gasoline.

2.3 The *in-situ* reaction of alkyl lead in gasoline with iodine eliminates the problem of variations in response due to different alkyl types by leveling the response of all alkyl lead compounds.

2.4 The addition of the quarternary ammonium salt improves response and increases the stability of the alkyl iodide complex.

3. Sample handling and preservation.

3.1 Samples should be collected and stored in containers which will protect them from changes in the lead content of the gasoline such as from loss of volatile fractions of the gasoline by evaporation or leaching of the lead into the container or cap.

3.2 If samples have been refrigerated they should be brought to room temperature prior to analysis.

4. Apparatus.

4.1 AutoAnalyzer system consisting of:

4.1.1 Sampler 20/hr cam, 30/hr cam.

4.1.2 Proportioning pump.

4.1.3 Lead in gas manifold.

4.1.4 Disposable test tubes.

4.1.5 Two 2-liter and one 0.5 liter Erlenmeyer solvent displacement flasks. Alternatively, high pressure liquid chromatography (HPLC) or syringe pumps may be used.

4.2 Atomic Absorption Spectroscopy (AAS) Detector System consisting of:

4.2.1 Atomic absorption spectrometer.

4.2.2 10" strip chart recorder.

4.2.3 Lead hollow cathode lamp or electrodeless discharge lamp (EDL).

5. Reagents.

5.1 Aliquat 336/MIBK solution (10% v/v): Dissolve and dilute 100 ml (88.0 g) of Aliquat 336 (Aldrich Chemical Co., Milwaukee, Wisconsin) with MIBK (Burdick & Jackson Lab., Inc., Muskegon, Michigan) to one liter.

5.2 Aliquat 336/iso-octane solution (1% v/v): Dissolve and dilute 10 ml (8.8 g) of Aliquat 336 (reagent 5.1) with iso-octane to one liter.

5.3 Iodine solution (3% w/v): Dissolve and dilute 3.0 g iodine crystals (American Chemical Society) with toluene (Burdick & Jackson Lab., Inc., Muskegon, Michigan) to 100 ml.

5.4 Iodine working solution (0.24% w/v): Dilute 8 ml of reagent 5.3 to 100 ml with toluene.

5.5 Methyl isobutyl ketone (MIBK) (4-methyl-2-pentanone).

5.6 Certified unleaded gasoline (Phillips Chemical Co., Borger, Texas) or iso-octane (Burdick & Jackson Lab, Inc., Muskegon, Michigan).

6. Calibration standards.

6.1 Stock 5.0 g Pb/gal Standard:

Dissolve 0.4433 gram of lead chloride ($PbCl_2$) previously dried at 105 °C for 3 hours in 200 ml of 10% v/v Aliquat 336/MIBK solution (reagent 5.1) in a 250 ml volumetric flask. Dilute to volume with reagent 5.1 and store in an amber bottle.

6.2 Intermediate 1.0 g Pb/gal Standard:

Pipet 50 ml of the 5.0 g Pb/gal standard into a 250 ml volumetric flask and dilute to volume with a 1% v/v Aliquat 336/iso-octane solution (reagent 5.2). Store in an amber bottle.

6.3 Working 0.02, 0.05, 0.10 g Pb/gal Standards:

Pipet 2.0, 5.0, and 10.0 ml of the 1.0 g Pb/gal solution to 100 ml volumetric flasks. Add 5 ml of a 1% Aliquat 336/iso-octane solution to each flask. Dilute to volume with iso-octane. These solutions contain 0.02, 0.05, and 0.10 g Pb/gal in a 0.05% Aliquat 336/iso-octane solution.

7. AAS Instrumental conditions.

7.1 Lead hollow cathode lamp.

7.2 Wavelength: 283.3 nm.

7.3 Slit: 4 (0.7mm).

7.4 Range: UV.

7.5 Fuel: Acetylene (approx. 20 ml/min at 8 psi).

7.6 Oxidant: Air (approx. 65 ml/min at 31 psi).

7.7 Nebulizer: 5.2 ml/min.

7.8 Chart speed: 10 in/hr.

8. Procedures.

8.1 AAS start-up.

8.1.1 Assure that instrumental conditions have been optimized and aligned according to Section 7 and the instrument has had substantial time for warm-up.

8.2 Auto Analyzer start-up [see figure 1].

8.2.1 Check all pump tubing and replace as necessary. Iodine tubing should be changed daily. All pump tubing should be replaced after one week of use. Place the platen on the pump.

8.2.2 Withdraw any water from the sample wash cup and fill with certified unleaded gasoline (reagent 5.6).

8.2.3 Fill the 2-liter MIBK dilution displacement Erlenmeyer flask (reagent 5.5) and the 0.5 liter Aliquat 336/MIBK 1% v/v (reagent 5.2) displacement flask and place the rubber stopper glass tubing assemblies in their respective flasks.

8.2.4 Fill a 2-liter Erlenmeyer flask with distilled water. The water will be used to displace the solvents. Therefore, place the appropriate lines in this flask. This procedure is not relevant if syringe pumps are used.

8.2.5 Fill the final debubbler reverse displacement 2-liter Erlenmeyer flask with distilled water and place the rubber stopper glass tubing assembly in the flask.

Pt. 80, App. B

40 CFR Ch. I (7-1-00 Edition)

8.2.6 Place the appropriate lines for the iodine reagent (reagent 5.4) and the wash solution (reagent 5.6) in their respective bottles.

8.2.7 Start the pump and connect the aspiration line from the manifold to the AAS.

8.2.8 Some initial checks to assure that the reagents are being added are:

- a. A good uniform bubble pattern.
- b. Yellow color evident due to iodine in the system.

c. No surging in any tubing.

8.3 Calibration.

8.3.1 Turn the chart drive on and obtain a steady baseline.

8.3.2 Load standards and samples into sample tray.

8.3.3 Start the sampler and run the standards (Note: first check the sample probe positioning with an empty test tube).

8.3.4 Check the linearity of calibration standards response and slope by running a least squares fit. Check these results against previously obtained results. They should agree within 10%.

8.3.5 If the above is in control then start the sample analysis.

8.4 Sample Analysis.

8.4.1 To minimize gasoline vapor in the laboratory, load the sample tray about 5-10 test tubes ahead of the sampler.

8.4.2 Record the sample number on the strip chart corresponding to the appropriate peak.

8.4.3 Every ten samples run the high calibration standard and a previously analyzed sample (duplicate). Also let the sampler skip to check the baseline.

8.4.4 After an acceptable peak (within the calibration range) is obtained, pour the excess sample from the test tube into the waste gasoline can.

8.4.5 Any sample resulting in a peak greater than 0.05 g Pb/gal will be run in duplicate. Samples registering greater than 0.10 g Pb/gal should be diluted with iso-octane or unleaded fuel to fall within the calibration range or a higher level calibration standard curve must be prepared. The higher level curve must be shown to be linear and measurement of lead at these levels must be shown to be accurate by the analysis of control samples at a higher level of alkyl lead content.

8.5 Shut Down.

8.5.1 Replace the solvent displacement flask with flasks filled with distilled water. Also place all other lines in a beaker of distilled water. Rinse the system with distilled water for 15 minutes.

8.5.2 Withdraw the gasoline from the wash cup and fill with water.

8.5.3 Dispose of all solvent waste in waste glass bottles.

8.5.4 Turn the AAS off after extinguishing the flame. Also turn the recorder and pump off. Remove the platen and release the pump tubing.

8.5.5 Shut the acetylene off at the tank and bleed the line.

9. Quality control.

9.1 Precision.

9.1.1 All duplicate results should be considered suspect if they differ by more than 0.005 g Pb/gal.

9.2 Accuracy.

9.2.1 All quality control standard checks should agree within 10% of the nominal value of the standard.

9.2.2 All spikes should agree within 10% of the known addition.

10. Past quality control data.

10.1 Precision.

10.1.1 Duplicate analysis for 156 samples in a single laboratory has resulted in an average difference of 0.00011 g Pb/gal with a standard deviation of 0.0023.

10.1.2 Replicate analysis in a single laboratory (greater than 5 determinations) of samples at concentrations of 0.010, 0.048, and 0.085 g Pb/gal resulted in relative standard deviations of 4.2%, 3.5%, and 3.3% respectively.

10.2 Accuracy.

10.2.1 The analysis of National Bureau of Standards (NBS) lead in reference fuel of known concentrations in a single laboratory has resulted in found values deviating from the true value for 11 determinations of 0.0322 g Pb/gal by an average of 0.56% with a standard deviation of 6.8%, for 15 determinations of 0.0519 g Pb/gal by an average of -1.1% with a standard deviation of 5.8%, and for 7 determinations of 0.0725 g Pb/gal by an average of 3.5% with a standard deviation of 4.8%.

10.2.2 Twenty-three analyses of blind reference samples in a single laboratory (U.S. EPA, RTP, N.C.) have resulted in found values differing from the true value by an average of -0.0009 g Pb/gal with a standard deviation of 0.004.

10.2.3 In a single laboratory, the average percent recovery of 108 spikes made to samples was 101% with a standard deviation of 5.6%.

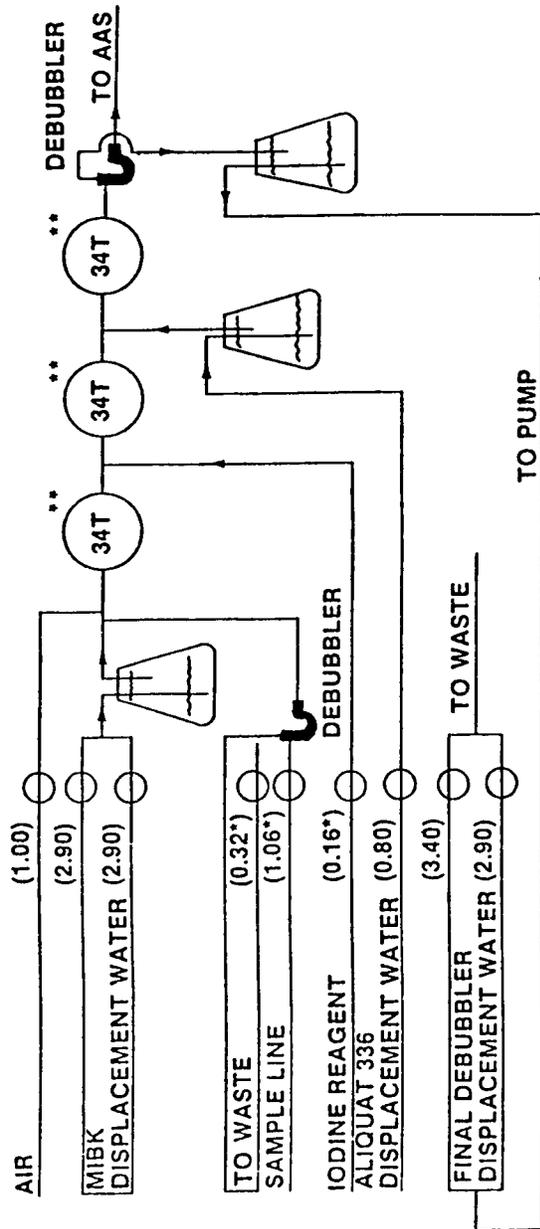


Figure 1

Flow Diagram for the Automated System. (*: Solvaflex pump tubing, **: Technicon part no. 157-0225) Numbers in parentheses refer to the flow rate (ml/min.).

METHOD 3—TEST FOR LEAD IN GASOLINE BY X-RAY SPECTROMETRY

1. Scope and application.

1.1 This method covers the determination of the total lead content of gasoline. The procedure's calibration range is 0.010 to 5.0 grams of lead/U.S. gallon. Samples above this level should be diluted to fall within the range of 0.05 to 5.0 grams of lead/U.S. gallon. The method compensates for variations in gasoline composition and is independent of lead alkyl type.

1.2 This method may be used as an alternative to Method 1—Standard Method Test for Lead in Gasoline by Atomic Absorption Spectrometry, or to Method 2—Automated Method Test for Lead in Gasoline by Atomic Absorption Spectrometry.

1.3 Where trade names or specific products are noted in the method, equivalent apparatus and chemical reagents may be used. Mention of trade names or specific products is for the assistance of the user and does not constitute endorsement by the U.S. Environmental Protection Agency.

2. Summary of method.

2.1 A portion of the gasoline sample is placed in an appropriate holder and loaded into an X-ray spectrometer. The ratio of the net X-ray intensity of the lead L alpha radiation to the net intensity of the incoherently scattered tungsten L alpha radiation is measured. The lead content is determined by reference to a linear calibration equation which relates the lead content to the measured ratio.

2.2 The incoherently scattered tungsten radiation is used to compensate for variations in gasoline samples.

3. Sample handling and preservation.

3.1 Samples should be collected and stored in containers which will protect them from changes in the lead content of the gasoline, such as loss of volatile fractions of the gasoline by evaporation or leaching of the lead into the container or cap.

3.2 If samples have been refrigerated they should be brought to room temperature prior to analysis.

3.3 Gasoline is extremely flammable and should be handled cautiously and with adequate ventilation. The vapors are harmful if inhaled and prolonged breathing of vapors should be avoided. Skin contact should be minimized. See precautionary statements in Annex A1.3.

4. Apparatus.

4.1 X-ray Spectrometer, capable of exciting and measuring the fluorescence lines mentioned in 2.1 and of being operated under the following instrumental conditions or others giving equivalent results: a tungsten

target tube operated at 50 kV, a lithium fluoride analyzing crystal, an air or helium optical path and a proportional or scintillation detector.

4.2 Some manufacturers of X-ray Spectrometer units no longer allow use of air as the beam path medium because the X-ray beam produces ozone, which may degrade seals and electronics. In addition, use of the equipment with liquid gasoline in close proximity to the hot X-ray tube could pose flammability problems with any machine in case of a rupture of the sample container. Therefore, use of the helium alternative is recommended.

5. Reagents.

5.1 Isooctane. Isooctane is flammable and the vapors may be harmful. See precautions in Annex A1.1.

5.2 Lead standard solution, in isooctane, toluene or a mixture of these two solvents, containing approximately 5 gm Pb/U.S. gallon may be prepared from a lead-in-oil concentrate such as those prepared by Conostan (Conoco, Inc., Ponca City, Oklahoma). Isooctane and toluene are flammable and the vapors may be harmful. See precautionary statements in Annex A1.1 and A1.2.

6. Calibration.

6.1 Make exact dilutions with isooctane of the lead standard solution to give solutions with concentrations of 0.01, 0.05, 0.10, 0.50, 1.0, 3.0 and 5.0 g Pb/U.S. gallon. If a more limited range is desired as required for linearity, such range shall be covered by at least five standard solutions approximately equally spaced and this range shall not be exceeded by any of the samples. Place each of the standard solutions in a sample cell using techniques consistent with good operating practice for the spectrometer employed. Insert the sample in the spectrometer and allow the spectrometer atmosphere to reach equilibrium (if appropriate). Measure the intensity of the lead L alpha peak at 1.175 angstroms, the Compton scatter peak of the tungsten L alpha line at 1.500 angstroms and the background at 1.211 angstroms. Each measured intensity should exceed 200,000 counts or the time of measurement should be at least 30 seconds. The relative standard deviation of each measurement, based on counting statistics, should be one percent or less. The Compton scatter peak given above is for 90° instrument geometry and should be changed for other geometries. The Compton scatter peak (in angstroms) is found at the wavelength of the tungsten L alpha line plus 0.024 (1-cos phi), where phi is the angle between the incident radiation and the take-off collimator.

6.2 For Each of the standards, as well as for an isooctane blank, determine the net lead intensity by subtracting the corrected

background from the gross intensity. Determine the corrected background by multiplying the intensity of the background at 1.211 angstroms by the following ratio obtained on an isoctane blank:

$$\frac{\text{Background at 1.175 angstroms}}{\text{Background at 1.211 angstroms}}$$

$$R = \frac{\text{Lead L alpha-background}}{\text{Incoherent tungsten L alpha-corrected background}}$$

6.4 Obtain a linear calibration curve by performing a least squares fit of the corrected lead intensity ratios to the standard concentrations.

7. Procedure.

7.1 Prepare a calibration curve as described in 6. Since the scattered tungsten radiation serves as an internal standard, the calibration curve should serve for at least several days. Each day the suitability of the calibration curve should be checked by analyzing several National Bureau of Standards (NBS) lead-in-reference-fuel standards or other suitable standards.

7.2 Determine the corrected lead intensity ratio for a sample in the same manner as was done for the standards. The samples should be brought to room temperature before analysis.

7.3 Determine the lead concentration of the sample from the calibration curve. If the sample concentration is greater than 5.0 g Pb/U.S. gallon or the range calibrated for in 6.1, the sample should be diluted so that the result is within the calibration span of the instrument.

7.4 Quality control standards, such as NBS standard reference materials, should be analyzed at least once every testing session.

7.5 For each group of ten samples, a spiked sample should be prepared by adding a known amount of lead to a sample. This known addition should be at least 0.05 g Pb/U.S. gallon, at least 50% of the measured lead content of the unspiked sample, and not more than 200% of the measured lead content of the unspiked sample (unless the minimum addition of 0.05 g Pb/U.S. gallon exceeds 200%). Both the spiked and unspiked samples should be analyzed.

8. Quality control.

8.1 The difference between duplicates should not exceed 0.005 g Pb/U.S. gallon or a relative difference of 6%.

6.3 Determine the corrected lead intensity ratio, which is the net lead intensity corrected for matrix effects by division by the net incoherently scattered tungsten radiation. The net scattered intensity is calculated by subtracting the background intensity at 1.211 angstroms from the gross intensity of the incoherently scattered tungsten L alpha peak. The equation for the corrected lead intensity ratio follows:

8.2 All quality control standard check samples should agree within 10% of the nominal value of the standard.

8.3 All spiked samples should have a percent recovery of 100% ±10%. The percent recovery, P, is calculated as follows:

$$P = 100 \times (A-B)/K$$

where

A = the analytical result from the spiked sample, B = the analytical result from the unspiked sample, and K = the known addition.

8.4 The difference between independent analyses of the same sample in different laboratories should not exceed 0.01 g Pb/U.S. gallon or a relative difference of 12%.

9. Past quality control data.

9.1 Duplicate analysis for 26 samples in the range of 0.01 to 0.10 g Pb/U.S. gallon resulted in an average relative difference of 5.2% with a standard deviation of 5.4%. Duplicate analysis of 14 samples in the range 0.1 to 0.5 g Pb/U.S. gallon resulted in an average relative difference of 2.3% with a standard deviation of 2.0. Duplicate analysis of 47 samples in the range of 0.5 to 5 g Pb/U.S. gallon resulted in an average relative difference of 2.1% with a standard deviation of 1.8%.

9.2 The average percent recovery for 23 spikes made to samples in the 0.0 to 0.1 g Pb/U.S. gallon range was 103% with a standard deviation of 3.2%. For 42 spikes made to samples in the 0.1 to 5.0 g Pb/U.S. gallon range, the average percent recovery was 102% with a standard deviation of 4.2%.

9.3 The analysis of National Bureau of Standards lead-in-reference-fuel standards of known concentrations in a single laboratory has resulted in found values deviating from the true value for 14 determinations of 0.0490 g Pb/U.S. gallon by an average of 2.8% with a standard deviation of 6.4%, for 11 determinations of 0.065 g Pb/U.S. gallon by an average of 4.4% with a standard deviation of 2.9%, and for 15 determinations of 1.994 g Pb/U.S. gallon by an average of 0.3% with a standard deviation of 1.3%.

9.4 Eighteen analyses of reference samples (U.S. EPA, Research Triangle Park, NC) have resulted in found values differing from the true value by an average of 0.0004 g Pb/U.S. gallon with a standard deviation of 0.004 g Pb/U.S. gallon.

ANNEX

A1. Precautionary Statements

A1.1 ISOCTANE

Danger—Extremely flammable. Vapors harmful if inhaled.
Vapor may cause flash fire.
Keep away from heat, sparks, and open flame.
Vapors are heavier than air and may gather in low places, resulting in explosion hazard.
Keep container closed.
Use adequate ventilation.
Avoid buildup of vapors.
Avoid prolonged breathing of vapor or spray mist.
Avoid prolonged or repeated skin contact.

A1.2 TOLUENE

Warning—Flammable. Vapor harmful.
Keep away from heat, sparks, and open flame.
Keep container closed.
Use with adequate ventilation.
Avoid breathing of vapor or spray mist.
Avoid prolonged or repeated contact with skin.

A1.3 GASOLINE

Danger—Extremely flammable. Vapors harmful if inhaled.
Vapor may cause flash fire.
Keep away from heat, sparks, and open flame.
Vapors are heavier than air and may gather in low places, resulting in explosion hazard.
Keep container closed.
Use adequate ventilation.
Avoid buildup of vapors.
Avoid prolonged breathing of vapor or spray mist.
Avoid prolonged or repeated skin contact.

[39 FR 24891, July 8, 1974; 39 FR 25653, July 12, 1974; 39 FR 26287, July 18, 1974, as amended at 47 FR 765, Jan. 7, 1982; 52 FR 259, Jan. 5, 1987; 56 FR 13768, Apr. 4, 1991]

APPENDIX C TO PART 80 [RESERVED]

APPENDIX D TO PART 80—SAMPLING PROCEDURES FOR FUEL VOLATILITY

1. Scope.

1.1 This method covers procedures for obtaining representative samples of gasoline for the purpose of testing for compliance

with the Reid vapor pressure (RVP) standards set forth in §80.27.

2. Summary of method.

2.1 It is necessary that the samples be truly representative of the gasoline in question. The precautions required to ensure the representative character of the samples are numerous and depend upon the tank, carrier, container or line from which the sample is being obtained, the type and cleanliness of the sample container, and the sampling procedure that is to be used. A summary of the sampling procedures and their application is presented in Table 1. Each procedure is suitable for sampling a material under definite storage, transportation, or container conditions. The basic principle of each procedure is to obtain a sample in such manner and from such locations in the tank or other container that the sample will be truly representative of the gasoline.

3. Description of terms.

3.1 *Average sample* is one that consists of proportionate parts from all sections of the container.

3.2 *All-levels sample* is one obtained by submerging a stoppered beaker or bottle to a point as near as possible to the draw-off level, then opening the sampler and raising it at a rate such that it is 70-85% full as it emerges from the liquid. An all-levels sample is not necessarily an average sample because the tank volume may not be proportional to the depth and because the operator may not be able to raise the sampler at the variable rate required for proportionate filling. The rate of filling is proportional to the square root of the depth of immersion.

3.3 *Running sample* is one obtained by lowering an unstoppered beaker or bottle from the top of the gasoline to the level of the bottom of the outlet connection or swing line, and returning it to the top of the gasoline at a uniform rate of speed such that the beaker or bottle is 70-85% full when withdrawn from the gasoline.

3.4 *Spot sample* is one obtained at some specific location in the tank by means of a thief bottle, or beaker.

3.5 *Top sample* is a spot sample obtained 6 inches (150 mm) below the top surface of the liquid (Figure 1).

3.6 *Upper sample* is a spot sample taken at the mid-point of the upper third of the tank contents (Figure 1).

3.7 *Middle sample* is a spot sample obtained from the middle of the tank contents (Figure 1).

3.8 *Lower sample* is a spot sample obtained at the level of the fixed tank outlet or the swing line outlet (Figure 1).

3.9 *Clearance sample* is a spot sample taken 4 inches (100 mm) below the level of the tank outlet (Figure 1).

3.10 *Bottom sample* is one obtained from the material on the bottom surface of the tank, container, or line at its lowest point.

3.11 *Drain sample* is one obtained from the draw-off or discharge valve. Occasionally, a drain sample may be the same as a bottom sample, as in the case of a tank car.

3.12 *Continuous sample* is one obtained from a pipeline in such manner as to give a representative average of a moving stream.

3.13 *Mixed sample* is one obtained after mixing or vigorously stirring the contents of the original container, and then pouring out or drawing off the quantity desired.

3.14 *Nozzle sample* is one obtained from a gasoline pump nozzle which dispenses gasoline from a storage tank at a retail outlet or a wholesale purchaser-consumer facility.

4. Sample containers.

4.1 Sample containers may be clear or brown glass bottles, or cans. The clear glass bottle is advantageous because it may be examined visually for cleanliness, and also allows visual inspection of the sample for free water or solid impurities. The brown glass bottle affords some protection from light. Cans with the seams soldered on the exterior surface with a flux of rosin in a suitable solvent are preferred because such a flux is easily removed with gasoline, whereas many others are very difficult to remove. If such cans are not available, other cans made with a welded construction that are not affected by, and that do not affect, the gasoline being sampled are acceptable.

4.2 *Container closure.* Closure devices may be used as long as they meet the following test: The quality of closures and containers must be determined by the particular laboratory or company doing the testing through the analysis of at least six sample pairs of gasoline and gasoline-oxygenate blends. The six sample pairs must include at least one pair of ethanol at 10 percent and one pair of MTBE at 15 percent. The second half of the pair must be analyzed in a period of no less than 90 days after the first. The data obtained must meet the following criteria and should be made available to the EPA upon request;

n = number of pairs

d = duplicate bottle's-initial bottle's vapor pressure

t = student t statistic; the double sided 95% confidence interval for $n-1$ degrees of freedom

$\Sigma d/n \pm (2)^{1/2} * t * ((\Sigma d^2 - (\Sigma d)^2/n)/(n-1))^{1/2} \leq 0.38$ psi

4.2.1 Screw caps must be protected by material that will not affect petroleum or petroleum products. A phenolic screw cap with a teflon coated liner may be used, since it has met the requirements of the above performance test upon EPA analysis.

4.3 *Cleaning procedure.* The method of cleaning all sample containers must be consistent with the residual materials in the container and must produce sample containers that are clean and free of water, dirt, lint, washing compounds, naphtha or other solvents, soldering fluxes, and acids, corrosion, rust, and oil. New sample containers should be inspected and cleaned if necessary. Dry either the container by passing a current of clean, warm air through the container or by allowing it to air dry in a clean area at room temperature. When dry, stopper or cap the container immediately.

5. Sampling apparatus.

5.1 Sampling apparatus is described in detail under each of the specific sampling procedures. Clean, dry, and free all sampling apparatus from any substance that might contaminate the material, using the procedure described in 4.3.

6. Time and place of sampling.

6.1 When loading or discharging gasoline, take samples from both shipping and receiving tanks, and from the pipeline if required.

6.2 *Ship or barge tanks.* Sample each product after the vessel is loaded or just before unloading.

6.3 *Tank cars.* Sample the product after the car is loaded or just before unloading.

NOTE: When taking samples from tanks suspected of containing flammable atmospheres, precautions should be taken to guard against ignitions due to static electricity. No object or material should be lowered into or suspended in a compartment of a tank which is being filled. A recommended waiting period of no less than five minutes after cessation of pumping will generally permit a substantial relaxation of the electrostatic charge for small volume vessels such as tank cars and tank trucks; under certain conditions a longer period may be deemed advisable. A recommended waiting period of no less than 30 minutes will generally permit a substantial relaxation of the electrostatic charge for large volume vessels such as storage tanks or ship tanks; under certain conditions a longer period may be deemed advisable.

7. Obtaining samples.

7.1 Directions for sampling cannot be made explicit enough to cover all cases. Extreme care and good judgment are necessary to ensure samples that represent the general character and average condition of the material. Clean hands are important. Clean gloves may be worn but only when absolutely necessary, such as in cold weather, or when handling materials at high temperature, or for reasons of safety. Select wiping cloths so that lint is not introduced, contaminating samples.

7.2 As many petroleum vapors are toxic and flammable, avoid breathing them or igniting them from an open flame or a spark produced by static. Follow all safety precautions specific to the material being sampled.

7.3 When sampling relatively volatile products (more than 2 pounds (0.14 kgf/cm²) RVP), the sampling apparatus shall be filled and allowed to drain before drawing the sample. If the sample is to be transferred to another container, this container shall also be rinsed with some of the volatile product and then drained. When the actual sample is emptied into this container, the sampling apparatus should be upended into the opening of the sample container and remain in this position until the contents have been transferred so that no unsaturated air will be entrained in the transfer of the sample.

8. Handling samples.

8.1 *Volatile samples.* It is necessary to protect all volatile samples of gasoline from evaporation. Transfer the product from the sampling apparatus to the sample container immediately. Keep the container closed except when the material is being transferred. After delivery to the laboratory, volatile samples should be cooled before the container is opened.

8.2 *Container outage.* Never completely fill a sample container, but allow adequate room for expansion, taking into consideration the temperature of the liquid at the time of filling and the probable maximum temperature to which the filled container may be subjected.

9. Shipping samples.

9.1 To prevent loss of liquid and vapors during shipment, and to protect against moisture and dust, cover the stoppers of glass bottles with plastic caps that have been swelled in water, wiped dry, placed over the tops of the stoppered bottles, and allowed to shrink tightly in place. The caps of metal containers must be screwed down tightly and checked for leakage. Postal and express office regulations applying to the shipment of flammable liquids must be observed.

10. Labeling sample containers.

10.1 Label the container immediately after a sample is obtained. Use waterproof and oilproof ink, or a pencil hard enough to dent the tag, since soft pencil and ordinary ink markings are subject to obliteration from moisture, oil smearing and handling. An indelible identification symbol, such as a bar code, may be used in lieu of a manually addressed label. The label shall reference the following information:

10.1.1 Date and time (the period elapsed during continuous sampling);

10.1.2 Name of the sample;

10.1.3 Name or number and owner of the vessel, car, or container;

10.1.4—Brand and grade of material; and

10.1.5—Reference symbol or identification number.

11. Sampling procedures.

11.1 The standard sampling procedures described in this method are summarized in Table 1. Alternative sampling procedures may be used if a mutually satisfactory agreement has been reached by the party(ies) involved and EPA and such agreement has been put in writing and signed by authorized officials.

11.2 *Bottle or beaker sampling.* The bottle or beaker sampling procedure is applicable for sampling liquids of 16 pounds (1.12 kgf/cm²) RVP or less in tank cars, tank trucks, shore tanks, ship tanks, and barge tanks.

11.2.1 *Apparatus.* A suitable sampling bottle or beaker as shown in figure 2 is required. Recommended diameter of opening in the bottle or beaker is 3/4 inch (19 mm).

11.2.2 Procedure.

11.2.2.1 *All-levels sample.* Lower the weighted, stoppered bottle or beaker as near as possible to the draw-off level, pull out the stopper with a sharp jerk of the cord or chain and raise the bottle at a uniform rate so that it is 70-85% full as it emerges from the liquid.

11.2.2.2 *Running sample.* Lower the unstoppered bottle or beaker as near as possible to the level of the bottom of the outlet connection or swing line and then raise the bottle or beaker to the top of the gasoline at a uniform rate of speed such that it is 70-85% full when withdrawn from the gasoline.

11.2.2.3 *Upper, middle, and lower samples.* Lower the weighted, stoppered bottle to the proper depths (Figure 1) as follows:

Upper sample	middle of upper third of the tank contents
Middle sample	middle of the tank contents
Lower sample	level of the fixed tank outlet or the swing-line outlet

At the selected level pull out the stopper with a sharp jerk of the cord or chain and allow the bottle or beaker to fill completely, as evidenced by the cessation of air bubbles. When full, raise the bottle or beaker, pour off a small amount, and stopper immediately.

11.2.2.4 *Top sample.* Obtain this sample (Figure 1) in the same manner as specified in 11.2.2.3 but at six inches (150 mm) below the top surface of the tank contents.

11.2.2.5 *Handling.* Stopper and label bottle samples immediately after taking them, and deliver to the laboratory in the original sampling bottles.

11.3 *Tap sampling.* The tap sampling procedure is applicable for sampling liquids of

twenty-six pounds (1.83 kgf/cm²) RVP or less in tanks which are equipped with suitable sampling taps or lines. This procedure is recommended for volatile stocks in tanks of the breather and balloon roof type, spheroids, etc. (Samples may be taken from the drain cocks of gage glasses, if the tank is not equipped with sampling taps.) The assembly for tap sampling is shown in figure 3.

11.3.1 Apparatus.

11.3.1.1 *Tank taps.* The tank should be equipped with at least three sampling taps placed equidistant throughout the tank height and extending at least three feet (0.9 meter) inside the tank shell. A standard ¼ inch pipe with suitable valve is satisfactory.

11.3.1.2 *Tube.* A delivery tube that will not contaminate the product being sampled and long enough to reach to the bottom of the sample container is required to allow submerged filling.

11.3.1.3 *Sample containers.* Use clean, dry glass bottles of convenient size and strength or metal containers to receive the samples.

11.3.2 *Procedure.* Before a sample is drawn, flush the tap (or gage glass drain cock) and line until they are purged completely. Connect the clean delivery tube to the tap. Draw upper, middle, or lower samples directly from the respective taps after the flushing operation. Stopper and label the sample container immediately after filling, and deliver it to the laboratory.

11.4 *Continuous sampling.* The continuous sampling procedure is applicable for sampling liquids of 16 pounds (1.12 kgf/cm²) RVP or less and semiliquids in pipelines, filling lines, and transfer lines. The continuous sampling may be done manually or by using automatic devices.

11.4.1 Apparatus.

11.4.1.1 *Sampling probe.* The function of the sampling probe is to withdraw from the flow stream a portion that will be representative of the entire stream. The apparatus assembly for continuous sampling is shown in figure 4. Probe designs that are commonly used are as follows:

11.4.1.1.1 A tube extending to the center of the line and beveled at a 45 degree angle facing upstream (Figure 4(a)).

11.4.1.1.2 A long-radius forged elbow or pipe bend extending to the center line of the pipe and facing upstream. The end of the probe should be reamed to give a sharp entrance edge (Figure 4(b)).

11.4.1.1.3 A closed-end tube with a round orifice spaced near the closed end which should be positioned in such a way that the orifice is in the center of the pipeline and is facing the stream as shown in figure 4(c)).

11.4.1.2 *Probe location.* Since the fluid to be sampled may not in all cases be homogeneous, the location, the position and the size of the sampling probe should be such as to minimize stratification or dropping out of heavier particles within the tube or the dis-

placement of the product within the tube as a result of variation in gravity of the flowing stream. The sampling probe should be located preferably in a vertical run of pipe and as near as practicable to the point where the product passes to the receiver. The probe should always be in a horizontal position.

11.4.1.2.1 The sampling lines should be as short as practicable and should be cleared before any samples are taken.

11.4.1.2.2 Where adequate flowing velocity is not available, a suitable device for mixing the fluid flow to ensure a homogeneous mixture at all rates of flow and to eliminate stratification should be installed upstream of the sampling tap. Some effective devices for obtaining a homogeneous mixture are as follows: Reduction in pipe size; a series of baffles; orifice or perforated plate; and a combination of any of these methods.

11.4.1.2.3 The design or sizing of these devices is optional with the user, as long as the flow past the sampling point is homogeneous and stratification is eliminated.

11.4.1.3 To control the rate at which the sample is withdrawn, the probe or probes should be fitted with valves or plug cocks.

11.4.1.4 Automatic sampling devices that meet the standards set out in 11.4.1.5 may be used in obtaining samples of gasoline. The quality of sample collected must be of sufficient size for analysis, and its composition should be identical with the composition of the batch flowing in the line while the sample is being taken. An automatic sampler installation necessarily includes not only the automatic sampling device that extracts the samples from the line, but also a suitable probe, connecting lines, auxiliary equipment, and a container in which the sample is collected. Automatic samplers may be classified as follows:

11.4.1.4.1 Continuous sampler, time cycle (nonproportional) type. A sampler designed and operated in such a manner that it transfers equal increments of liquid from the pipeline to the sample container at a uniform rate of one or more increments per minute is a continuous sampler.

11.4.1.4.2 Continuous sampler, flow-responsive (proportional) type. A sampler that is designed and operated in such a manner that it will automatically adjust the quantity of sample in proportion to the rate of flow is a flow-responsive (proportional) sampler. Adjustment of the quantity of sample may be made either by varying the frequency of transferring equal increments of sample to the sample container, or by varying the volume of the increments while maintaining a constant frequency of transferring the increments to the sample container. The apparatus assembly for continuous sampling is shown in figure 4.

11.4.1.4.3 *Intermittent sampler.* A sampler that is designed and operated in such a manner that it transfers equal increments of liquid from a pipeline to the sample container at a uniform rate of less than one increment per minute is an intermittent sampler.

11.4.1.5 *Standards of installation.* Automatic sampler installations should meet all safety requirements in the plant or area where used, and should comply with American National Standard Code for Pressure Piping, and other applicable codes (ANSI B31.1). The sampler should be so installed as to provide ample access space for inspection and maintenance.

11.4.1.5.1 Small lines connecting various elements of the installation should be so arranged that complete purging of the automatic sampler and of all lines can be accomplished effectively. All fluid remaining in the sampler and the lines from the preceding sampling cycle should be purged immediately before the start of any given sampling operation.

11.4.1.5.2 In those cases where the sampler design is such that complete purging of the sampling lines and the sampler is not possible, a small pump should be installed in order to circulate a continuous stream from the sampling tube past or through the sampler and back into the line. The automatic sampler should then withdraw the sample from the sidestream through the shortest possible connection.

11.4.1.5.3 Under certain conditions, there may be a tendency for water and heavy particles to drop out in the discharge line from the sampling device and appear in the sample container during some subsequent sampling period. To circumvent this possibility, the discharge pipe from the sampling device should be free of pockets or enlarged pipe areas, and preferably should be pitched downward to the sample container.

11.4.1.5.4 To ensure clean, free-flowing lines, piping should be designed for periodic cleaning.

11.4.1.6 *Field calibration.* Composite samples obtained from the automatic sampler installation should be verified for quantity performance in a manner that meets with the approval of all parties concerned (including EPA), at least once a month and more often if conditions warrant. In the case of time-cycle samplers, deviations in quantity of the sample taken should not exceed \pm five percent for any given setting. In the case of flow-responsive samplers, the deviation in quantity of sample taken per 1,000 barrels of flowing stream should not exceed \pm five percent. For the purpose of field-calibrating an installation, the composite sample obtained from the automatic sampler under test should be verified for quality by comparing on the basis of physical and chemical properties, with either a properly secured continuous nonautomatic sample or tank sample.

The tank sample should be taken under the following conditions:

11.4.1.6.1 The batch pumped during the test interval should be diverted into a clean tank and a sample taken within one hour after cessation of pumping.

11.4.1.6.2 If the sampling of the delivery tank is to be delayed beyond one hour, then the tank selected must be equipped with an adequate mixing means. For valid comparison, the sampling of the delivery tank must be completed within eight hours after cessation of pumping, even though the tank is equipped with a motor-driven mixer.

11.4.1.6.3 When making a normal full-tank delivery from a tank, a properly secured sample may be used to check the results of the sampler if the parties (including EPA) mutually agree to this procedure.

11.4.1.7 *Receiver.* The receiver must be a clean, dry container of convenient size to receive the sample. All connections from the sample probe to the sample container must be free of leaks. Two types of containers may be used, depending upon service requirements.

11.4.1.7.1 *Atmospheric container.* The atmospheric container shall be constructed in such a way that it retards evaporation loss and protects the sample from extraneous material such as rain, snow, dust, and trash. The construction should allow cleaning, interior inspection, and complete mixing of the sample prior to removal. The container should be provided with a suitable vent.

11.4.1.7.2 *Closed container.* The closed container shall be constructed in such a manner that it prevents evaporation loss. The construction must allow cleaning, interior inspection and complete mixing of the sample prior to removal. The container should be equipped with a pressure-relief valve.

11.4.2 *Procedure.*

11.4.2.1 *Nonautomatic sample.* Adjust the valve or plug cock from the sampling probe so that a steady stream is drawn from the probe. Whenever possible, the rate of sample withdrawal should be such that the velocity of liquid flowing through the probe is approximately equal to the average linear velocity of the stream flowing through the pipeline. Measure and record the rate of sample withdrawal as gallons per hour. Divert the sample stream to the sampling container continuously or intermittently to provide a quantity of sample that will be of sufficient size for analysis.

11.4.2.2 *Automatic sampling.* Purge the sampler and the sampling lines immediately before the start of a sampling operation. If the sample design is such that complete purging is not possible, circulate a continuous stream from the probe past or through the sampler and back into the line. Withdraw the sample from the side stream through the automatic sampler using the shortest possible connections. Adjust the

sampler to deliver not less than one and not more than 40 gallons (151 liters) of sample during the desired sampling period. For time-cycle samplers, record the rate at which sample increments were taken per minute. For flow-responsive samplers, record the proportion of sample to total stream. Label the samples and deliver them to the laboratory in the containers in which they were collected.

11.5 *Nozzle sampling.* The nozzle sampling procedure is applicable for sampling gasoline from a retail outlet or wholesale purchaser-consumer facility storage tank.

11.5.1 *Apparatus.* Sample containers conforming with section 4.1 should be used. A spacer, if appropriate (figure 6), and a nozzle extension device similar to that shown in figures 7, 7a, or 7b shall be used when nozzle sampling. The nozzle extension device does not need to be identical to that shown in figures 7, 7a, or 7b but it should be a device that will bottom fill the container with a minimum amount of vapor loss.

11.5.2 *Retail sampling procedure*

11.5.2.1 If a nozzle extension as found in figure 7 or 7a is used, 3 gallons of gasoline should first be dispensed from the pump nozzle to purge the pump hose and nozzle. Then a small amount of product should be dispensed through the nozzle extension into the sample container to rinse the sample container. A pump nozzle spacer (figure 6) may be used if the pump is a vapor recovery type. Rinse the sample container and discard the waste product into an appropriate container. Insert the nozzle extension (figure 7 or 7a) into the sample container and insert the pump nozzle into the extension with slot over the air bleed hole (when using figure 7). Fill the sample container slowly through the nozzle extension to 70-85 percent full (figure 8). Remove the nozzle extension. Cap the sample container at once. Check for leaks. Discard the sample container and re-sample if leak occurs. If the sample container is leak tight, label the container and deliver it to the laboratory.

11.5.2.2 If a nozzle extension as found in figure 7b is used, 3 gallons of gasoline should first be dispensed from the pump nozzle to purge the pump hose and nozzle. Then screw a dry and dirt free 4 oz sample bottle container onto the bottle filling fixture. Insert the nozzle into the nozzle extension. Insert the discharge end of the modified nozzle extension into a gasoline safety can or into the filler neck of a vehicle. Obtain the sample by pumping at least 0.2 gallon through the sampler. Remove the sample bottle from the fixture. The sample must be 70-85 percent full. Cap the sample container at once. Check for leaks. Discard the sample container and re-sample if a leak occurs. If the sample container is leak tight, label the container and deliver it to the laboratory.

12. *Special Precautions and Instructions.*

12.1 *Precautions.* Vapor pressures are extremely sensitive to evaporation losses and to slight changes in composition. When obtaining, storing, or handling samples, observe the necessary precautions to ensure samples representative of the product and satisfactory for RVP tests. Official samples should be taken by, or under the immediate supervision of, a person of judgment, skill, and sampling experience. Never prepare composite samples for this test. Make certain that containers which are to be shipped by common carrier conform to applicable Interstate Commerce Commission, State, and local regulations. When flushing or purging lines or containers, observe the pertinent regulations and precautions against fire, explosion, and other hazards.

12.2 *Sample containers.* For nozzle sampling, use containers of not less than 4 ounces (118 ml) nor more than two gallons (7.6 liters) capacity, of sufficient strength to withstand the pressure to which they may be subjected, and of a type that will permit replacement of the cap or stopper with suitable connections for the transfer of the sample to the gasoline chamber of the vapor pressure testing apparatus. For running or all-level sampling procedures, use containers of not less than one quart (0.9 liter) nor more than two gallons (7.6 liters) capacity. Open-type containers have a single opening which permits sampling by immersion. Closed-type containers have two openings, one in each end (or the equivalent thereof), fitted with valves suitable for sampling by purging.

12.3 *Transfer connections.* The transfer connection for the open-type container consists of an air tube and a liquid delivery tube assembled in a cap or stopper. The air tube extends to the bottom of the container. One end of the liquid delivery tube is flush with the inside face of the cap or stopper and the tube is long enough to reach the bottom of the gasoline chamber while the sample is being transferred to the chamber. The transfer connection for the closed-type container consists of a single tube with a connection suitable for attaching it to one of the openings of the sample container. The tube is long enough to reach the bottom of the gasoline chamber while the sample is being transferred.

12.4 *Sampling open tanks.* Use clean containers of the open type when sampling open tanks and tank cars. An all-levels or a running sample obtained by the bottle procedure described in 11.2 is recommended. When the question exists of stratification of the contents of the tank, it is recommended that either a running or all-levels sample be taken along with upper, middle, and lower spot sampling. Before taking the sample, flush the container by immersing it in the product

to be sampled. Then obtain the sample immediately. The sample must be 70-85 percent full. Close the container promptly and confirm it is not leaking. Label the container and deliver it to the laboratory.

12.5. *Sampling closed tanks.* Containers of the closed type may be used to obtain samples from closed or pressure tanks. Obtain the sample using the purging procedure described in 12.6.

12.6. *Purging procedure.* Connect the inlet valve of the closed-type container to the tank sampling tap or valve. Throttle the outlet valve of the container so that the pressure in it will be approximately equal to that in the container being sampled. Allow a volume of product equal to at least twice that of the container to flow through the sampling system. Then close all valves, the outlet valve first, the inlet valve of the container second, and the tank sampling valve last, and disconnect the container immediately. Withdraw enough of the contents so

that the sample container will be 70-80 percent full. If the vapor pressure of the product is not high enough to force liquid from the container, open both the upper and lower valves slightly to remove the excess. Promptly seal and label the container, and deliver it to the laboratory.

TABLE 1—SUMMARY OF GASOLINE SAMPLING PROCEDURES AND APPLICABILITY

Type of container	Procedure	Paragraph
Storage tanks, ship and barge tanks, tank cars, tank trucks.	Bottle sampling.	11.2
Storage tanks with taps	Tap sampling..	11.3
Pipes and lines	Continuous line sampling.	11.4
Retail outlet and whole-sale purchaser-consumer facility storage tanks.	Nozzle sampling.	11.5

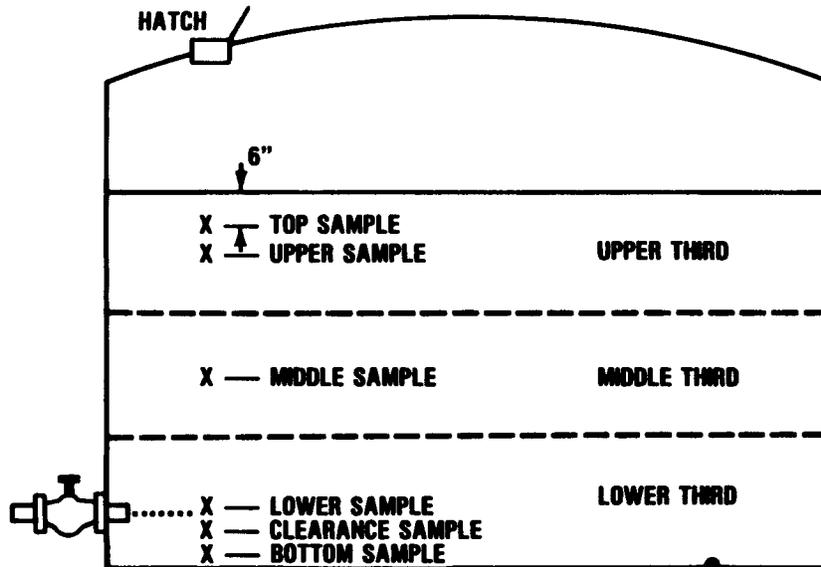
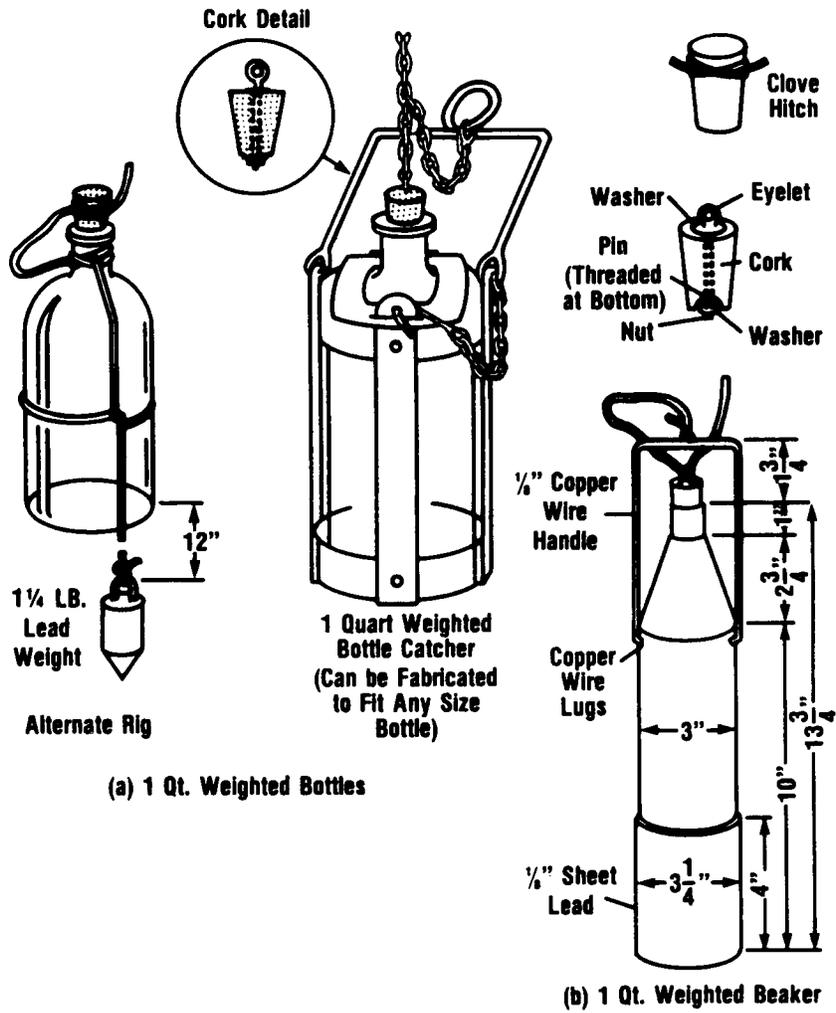


Figure 1. Sampling Depths



METRIC EQUIVALENTS

in.	1/8	1	1 1/4	2 1/4	3 1/4	4	10	12	13 3/4
mm	3	25	45	70	83	102	250	300	350

Figure 2. Assembly for Bottle Sampling

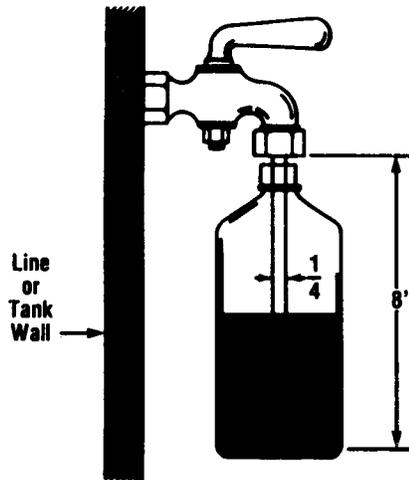
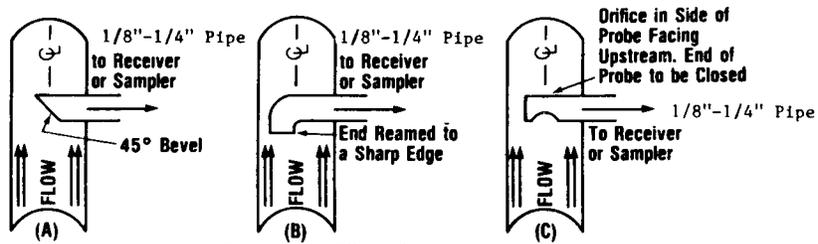


Figure 3. Assembly for Tap Sampling



Note: Probe may be fitted with valves or plug cocks.
Probe should be disposed horizontally.

PROBES FOR CONTINUOUS SAMPLING



TYPICAL ASSEMBLY FOR LINE SAMPLING

Figure 4. Probes for Continuous Sampling

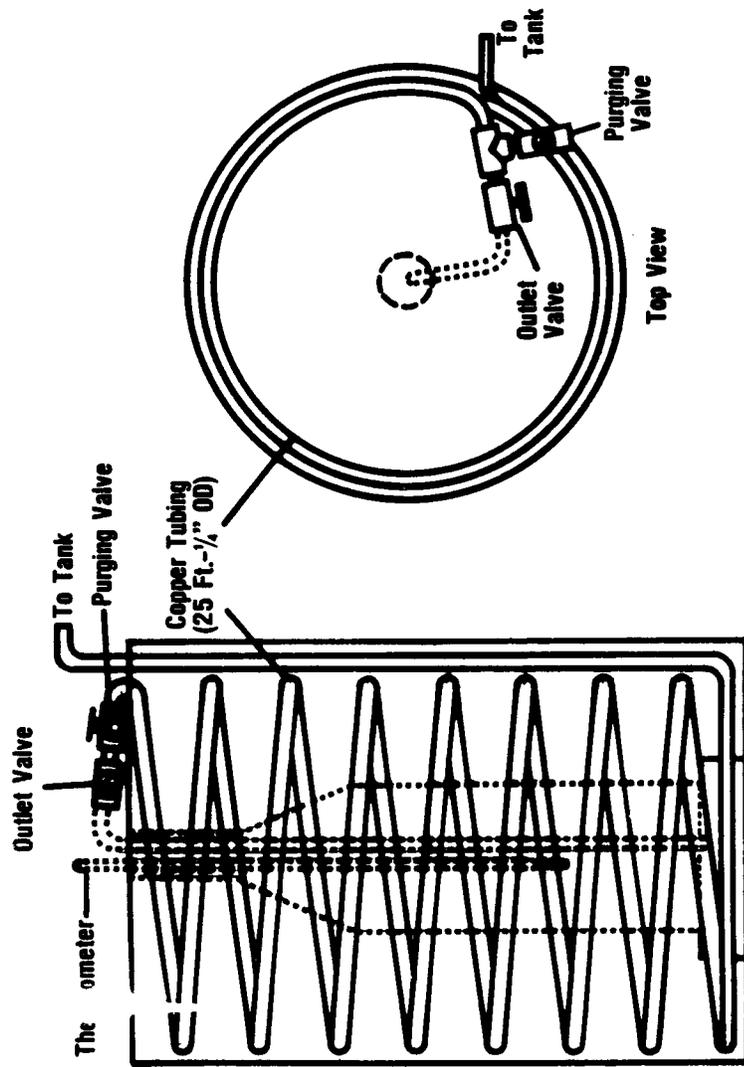
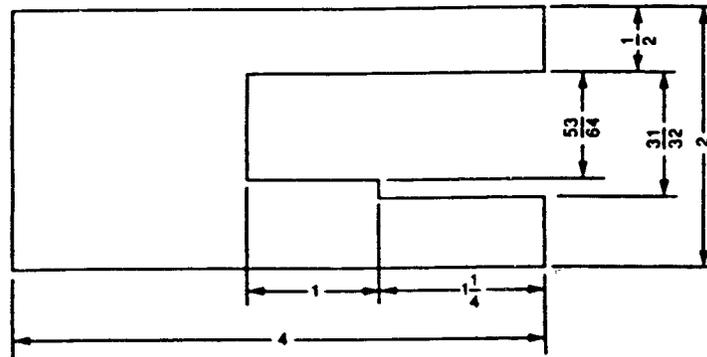
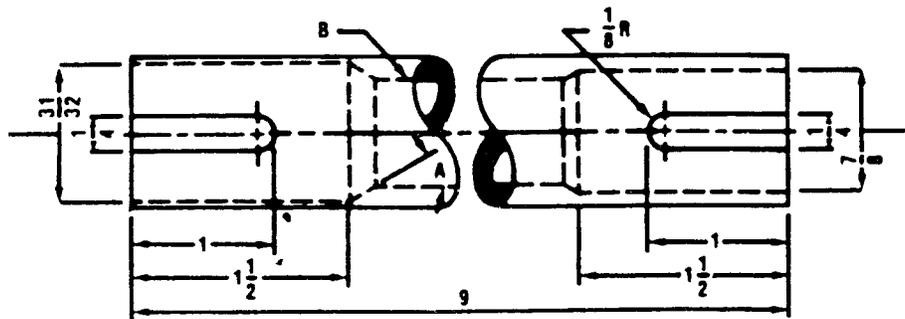


Figure 5. Cooling Bath for Reid Vapor Pressure Sampling



Make from 1/4 Inch flat stock (recommend non-ferrous material)
 All dimensions in inches
 Scale: 1inch = 1 inch
 Break all edges and corners

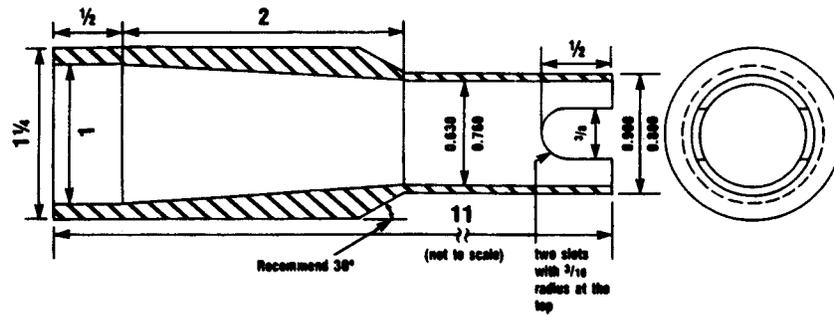
Figure 6. Spacer for Nozzle Sampling



Use 1/2 in. Schedule 80 Black Iron Pipe
 All dimensions in inches
 All tolerances $\pm 1/32$

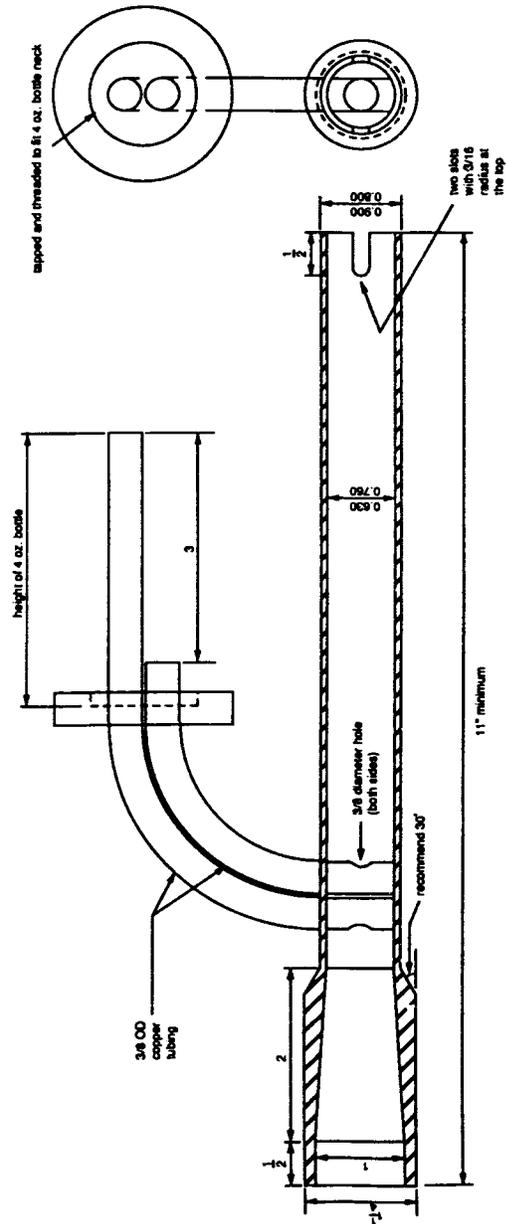
A—Recommend 30°
 B—Inside Diameter Schedule 80 Black Iron Pipe

Figure 7. Nozzle Extension for Nozzle Sampling



All Dimensions in inches (full scale except as noted)
 All decimal dimensions represent minimum and maximum
 Tolerance for all other dimensions is $\pm 1/32$ "
 Made of non-ferrous material, uneffected by gasoline

Figure 7a. Nozzle Extension for Nozzle Sampling
 (Compatible with narrow neck sample containers)



All dimensions in inches
 All decimal dimensions represent minimum and maximum
 Tolerance for all other dimensions is $\pm 1/32$ "
 Made of non-ferrous material, unaffected by gasoline
 Scale: 0.700 inch = 1 inch

Figure 7b. Nozzle Extension for Nozzle Sampling with 4 ounce bottle

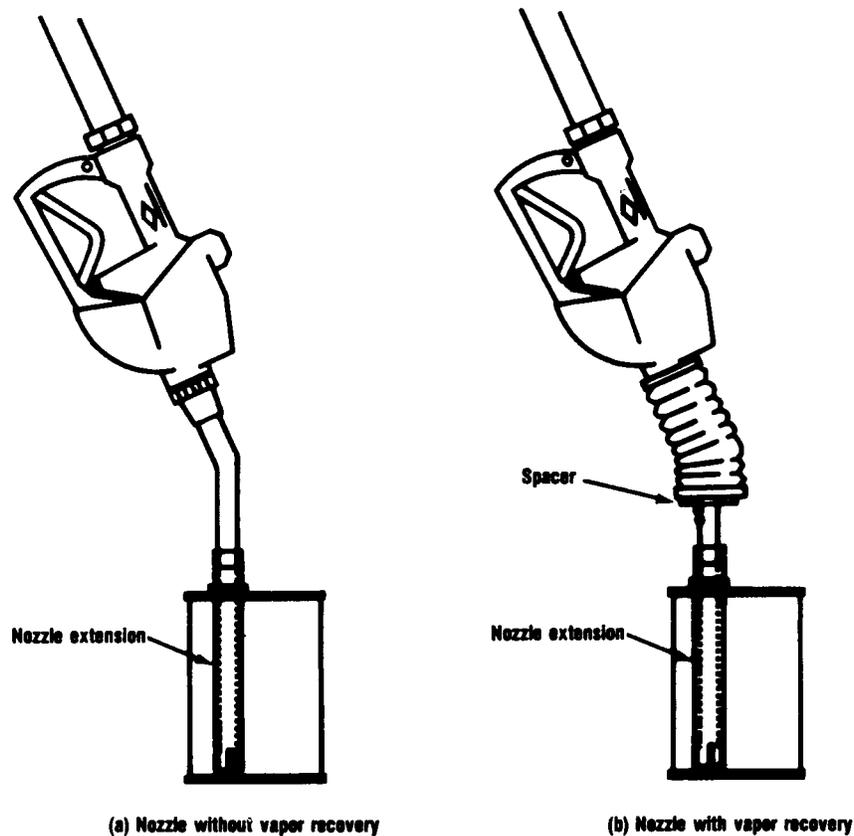


Figure 8. Assembly for Nozzle Sampling

[54 FR 11886, Mar. 22, 1989; 54 FR 27017, June 27, 1989, as amended at 55 FR 25835, June 25, 1990; 58 FR 14485, Mar. 17, 1993; 58 FR 19152, Apr. 12, 1993]

APPENDIX E TO PART 80—TEST FOR DETERMINING REID VAPOR PRESSURE (RVP) OF GASOLINE AND GASOLINE-OXYGENATE BLENDS

METHOD 3—EVACUATED CHAMBER METHOD

1. Scope.

1.1 This method covers the determination of the absolute pressure, measured against a vacuum of a gasoline or gasoline-oxygenate blend sample saturated with air at 32–40 °F (0–4.5 °C). The absolute (measured) pressure is observed with a system volume ratio of 1 part sample and 4 parts evacuated space at 100 °F (37.8 °C).

1.2 The values stated in pounds per square inch absolute are standard.

2. Summary of method.

2.1 A known volume of air-saturated fuel at 32–40 °F is introduced into an evacuated, thermostatically controlled test chamber, the internal volume of which is or becomes five times that of the total test specimen introduced into the test chamber. After the injection the test specimen is allowed to reach thermal equilibrium at the test temperature, 100 °F (37.8 °C). The resulting pressure increase is measured with an absolute pressure measuring device whose volume is included in the total of the test chamber volume. The

measured pressure is the sum of the partial pressures of the sample and the dissolved air.

2.2 The total measured pressure is converted to Reid vapor pressure by use of a correlation equation (see Section 9).

3. Apparatus.

3.1 The apparatus shall employ a thermostatically controlled test chamber which is capable of maintaining a vapor-to-liquid ratio between 3.95 and 4.05 to 1.00.

3.2 The pressure measurement device shall have a minimum operation range from 0 to 15 psia (0 to 103 kPa) with a minimum resolution of 0.05 psia (0.34 kPa). The pressure measurement device shall include any necessary electronic and readout devices to display the resulting reading.

3.3 The test chamber shall be maintained at $100 \pm 0.2^\circ\text{F}$ ($37.8 \pm 0.1^\circ\text{C}$) for the duration of the test except for the time period after sample injection when the sample is coming to equilibrium with test temperature of $100 \pm 0.2^\circ\text{F}$ ($37.8 \pm 0.1^\circ\text{C}$).

3.4 A thermometer that meets the specification ASTM 18 F (18 C) or a platinum resistance thermometer shall be used for measuring the temperature of the test chamber. The minimum resolution for the temperature measurement device is 0.2°F (0.1°C) and an accuracy of $\pm 0.2^\circ\text{F}$ ($\pm 0.1^\circ\text{C}$).

3.5 The vapor pressure apparatus shall have a provision for the introduction of the test specimen into the evacuated or to be evacuated test chamber and for the cleaning or purging of the chamber following the test.

3.6 If a vacuum pump is used, it must be capable of reducing the pressure in the test chamber to less than 0.01 psia (0.07 kPa). If the apparatus uses a piston to induce a vacuum in the sample chamber the residual pressure shall be no greater than 0.01 psia (0.07 kPa) upon full expansion of the test chamber devoid of any material at $100 \pm 0.2^\circ\text{F}$ ($37.8 \pm 0.1^\circ\text{C}$).

3.7 Ice water or air bath for chilling the sample to a temperature between $32\text{--}40^\circ\text{F}$ ($0\text{--}4.5^\circ\text{C}$).

3.8 Mercury barometer, 0 to 17.4 psia (0 to 120 kPa) range.

3.9 McLeod vacuum gauge, to cover at least the range of 0 to 5 mm Hg (0 to 0.67 kPa). Calibration of the McLeod gauge is checked as in accordance with Annex A6 of ASTM test Method D 2892-84, (Standard test method for distillation of Crude Petroleum (15-Theoretical Plate Column)). ASTM D-2892-84 is incorporated by reference. This incorporation by reference was approved by the Director of the Federal Register in accordance with 5 U.S.C 552(a) and 1 CFR part 51. Copies may be obtained from the American Society for Testing and Materials, 1916 Race St., Philadelphia, PA 19103. Copies may be inspected at the U.S. Environmental Protection Agency, Air Docket Section, room M-1500, 401 M Street, SW., Washington, DC

20460 or at the Office of the Federal Register, 800 North Capitol Street, NW., Washington, DC.

4. Reagents and materials.

4.1 *Quality control standards.* Use chemicals of at least 99% purity for quality control standards. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the committee on Analytical Reagents of the American Chemical Society where such specifications are available (see section 7.3). Specifications for analytical reagents may be obtained from the American Chemical Society, 1155 16th Street, NW., Washington, DC 20036.

4.1.1 2,2,4-trimethylpentane

4.1.2 2,2-dimethylbutane

4.1.3 3-methylpentane

4.1.4 n-pentane

4.1.5 acetone

4.2 n-pentane (commercial grade-95% pure)

5. Handling of samples.

5.1 The sensitivity of vapor pressure measurements to losses through evaporation and the resulting change in composition is such as to require the utmost precaution in the handling of samples. The provisions of this section apply to all samples for vapor pressure determinations.

5.2 Sample in accordance with 40 CFR part 80, appendix D.

5.3 Sample container size. The minimum size of the sample container from which the vapor pressure sample is taken is 4 ounces (118 ml). It will be 70 to 85% filled with sample.

5.4 *Precautions.*

5.4.1 Determine vapor pressure as the first test on a sample. Multiple analyses may be performed, but must be evaluated given the stated precision for the size of the sample container, and the order in which they were run in relation to the initial analysis.

5.4.2 Protect samples from excessive heat prior to testing.

5.4.3 Leaking samples should be replaced if possible. Analysis results from leaking sample containers must be marked as such.

5.4.4 Samples that have separated into two phases should be replaced if possible. Analysis results from samples that have phase separated must be marked as such.

5.4.5 Sample handling temperature. In all cases, cool the sample to a temperature of $32\text{--}40^\circ\text{F}$ ($0\text{--}4.5^\circ\text{C}$) before the container is opened. To ensure sufficient time to reach this temperature, directly measure the temperature of a similar liquid at a similar initial temperature in a like container placed in the cooling bath at the same time as the sample.

6. Preparation for test.

6.1 *Verification of sample container filling.* With the sample at a temperature of 32–40 °F (0–4.5 °C), take the container from the cooling bath, wipe dry with an absorbent material, unseal it, and examine its ullage. The sample content, as determined by use of a suitable gauge, should be equal to 70 to 85 volume % of the container capacity.

6.1.1 Analysis results from samples that contain less than 70 volume % of the container capacity must be marked as such.

6.1.2 If the container is more than 85 volume % full, pour out enough sample to bring the container contents within the 70 to 85 volume % range. Under no circumstance may any sample poured out be returned to the container.

6.2 Air saturation of the sample in the sample container. With the sample at a temperature of 32–40 °F (0–4.5 °C), take the container from the cooling bath, wipe dry with an absorbent material, unseal it momentarily, taking care to prevent water entry, re-seal it, and shake it vigorously. Return it to the bath for a minimum of 2 minutes. Repeat the air introduction procedure twice, for a total of three air introductions to completely saturate the sample.

6.3 Prepare the instrument for operation in accordance with the manufacturer's instructions.

6.3.1 *Instruments with vacuum pumps.* Clean and dry the test chamber as required to obtain a sealed test chamber pressure of less than 0.01 psi (0.07 kPa) for 1 minute. If the pressure exceeds this value check for and resolve in the following order; residual sample or cleaning solvent, sample chamber leaks, and transducer calibration.

6.3.2 *Instruments without vacuum pumps.* The sample purges the sample chamber through a series of rinses before the analysis occurs. Errors due to leaks in the plunger, piston seals, or carryover from previous samples or standards may give erratic results (see Note of section 6.3.2). The operator must run a quality control standard for at least one in twenty analyses or once a day to determine if there is carryover from previous analyses or if leaks are occurring.

NOTE: When using a self cleaning apparatus some residual product may be carried over into subsequent analyses. Carryover effect should be investigated when conducting sequential analyses of dissimilar materials, especially calibration standards. Inaccuracies caused by carryover effect should be resolved using testing procedures designed to minimize such interferences.

6.4 If a syringe is used for the physical introduction of the sample specimen, it must be either clean and dry before it is used or it may be rinsed out at least three times with the sample. When cleaning the syringe, the rinse may not be returned to the sample con-

tainer. The syringe must be capable of obtaining, upon filling with the sample charge, a quantity of sample that has an entrained gas volume of less than 3% of the necessary sample volume.

7. Calibration.

7.1 Pressure measurement device.

7.1.1 Check the calibration of the pressure measurement device daily or until the stability of the device is documented as having less than or equal to 0.03 psi (0.2 kPa) drift per unit of the appropriate calibration period. When calibration is necessary, follow the procedures in sections 7.1.2 through 7.1.4.

7.1.2 Connect a properly calibrated McLeod gauge to the vacuum source line to the test chamber. Apply vacuum to the test chamber. When the McLeod gauge registers a pressure less than 0.8 mm Hg (0.1 kPa) adjust the pressure measurement device's zero control to match to within ± 0.01 psi (0.07 kPa) of the McLeod Gauge.

7.1.3 Open the test chamber to the atmosphere and observe the pressure measurement device's reading. Adjust the pressure measurement devices span control to within ± 0.01 psi (0.07 kPa) of a temperature and latitude adjusted mercury barometer.

7.1.4 Repeat steps 7.1.2 and 7.1.3 until the instrument zero and barometer readings read correctly without further adjustments.

7.2 *Thermometer.* Check the calibration of the ASTM 18 F (18 C) thermometer or the platinum resistance thermometer used to monitor the test chamber at least every six months in accordance ASTM E1-86, (Standard Specification for ASTM Thermometers). ASTM E1-86 is incorporated by reference. This incorporation by reference was approved by the Director of the Federal Register in accordance with 5 U.S.C. 552(a) and 1 CFR part 51. Copies may be obtained from the American Society for Testing and Materials, 1916 Race St., Philadelphia, PA 19103. Copies may be inspected at the U.S. Environmental Protection Agency, Air Docket Section, room M-1500, 401 M Street, SW., Washington, DC 20460 or at the Office of the Federal Register, 800 North Capitol Street, NW., Washington, DC. Check the reading of the thermometer against a National Institute of Standards and Technology traceable thermometer.

7.3 *Quality assurance.* The instrument's performance must be checked at least once per day using a quality control standard listed in section 4.1. In the case of the non-vacuum pump instruments the frequency is stated in section 6.3.2. The standards must be chilled to the same temperature, have the same ullage, and saturated with air in the same manner as the samples. Record total measured pressure and compare against the following reference values:

Compound	Lower control limit	Upper control limit
2,2,4-trimethylpentane	2.39 psia (16.5 kpa)	3.03 psi (20.9 kpa)
3-methylpentane	6.86 psia (47.3 kpa)	7.26 psi (50.1 kpa)
acetone	7.97 psia (55.0 kpa)	8.12 psi (56.0 kpa)
2,2-dimethylbutane	10.64 psia (73.4 kpa)	10.93 psi (75.4 kpa)
n-pentane	16.20 psia (111.7 kpa)	16.40 psi (113.1 kpa)

If the observed pressure does not fall between the reference values, check the instrument for leaks and its calibration (Section 7).

7.3.1 Other compounds, gasolines, and gasoline blends may be used as control standards as long as these materials have been statistically evaluated for their mean total measured pressure using an instrument that conforms to this procedure.

7.3.2 The control limits can be calculated with the following formula:

MEAN MEASURED PRESSURE

$$\bar{x} = \frac{\sum x_i}{n}$$

Standard Deviation

$$s_{x_i} = \frac{\sum x_i^2 - (\sum x_i)^2 / n}{(n-1)}^{0.5}$$

Upper Control Limit (UCL)

$$UCL = \bar{x} + (t_{n-1,0.975}) * (S_x)$$

Lower Control Limit (LCL)

$$LCL = \bar{x} - (t_{n-1,0.975}) * (S_x)$$

where:

x_i is the individual analyses of the control standard, n is the number of analyses (for a new instrument or a new control standard this should be at least ten analyses); $(t_{n-1,0.975})$ is the two-tailed student t statistic for $n-1$ degrees of freedom for 95% of the expected data from the analysis of the standard.

8. Procedure.

8.1 Remove the sample from the cooling bath or refrigerator, dry the exterior of the container with absorbent material, unseal, and insert the transfer tube, syringe, or transfer connection (see section 6). Draw an aliquot (minimize gas bubbles) of sample into a gas tight syringe or transfer the sample using tubing or transfer connection and deliver this test specimen to the test chamber as rapidly as possible. The total time between opening the chilled sample container

and inserting/securing the syringe or transfer connection into the sealed test chamber shall not exceed one minute.

8.2 Follow the manufacturer's instructions for injection of the test specimen into the test chamber, and for the operation of the instrument to obtain a total measured vapor pressure result for the test specimen.

8.3 Set the instrument to read the test results in terms of total measured pressure. If the instrument is capable of calculating a Reid Vapor Pressure equivalent value ensure that only the parameters in section 9.2 are used.

9. Calculation and record of result.

9.1 Note the total measured vapor pressure reading for the instrument to the nearest 0.01 psi (0.07 kPa). For instruments which do not automatically display a stable pressure value, manually note the pressure indicator reading every minute to the nearest 0.01 psi (0.07 kPa). When three successive readings agree to within 0.01 psia (0.07 kPa) note the final result to the nearest 0.01 psia (0.07 kPa).

9.2 Using the following correlation equation, calculate the Reid Vapor Pressure (RVP) that is equivalent to the total measured vapor pressure obtained from the instrument, in order to compare the vapor pressure standards set out in 40 CFR 80.27. Ensure that the instrument reading in this equation corresponds to the total measured pressure and has not been corrected by an automatically programmed correction factor.

$$RVP \text{ psi} = (0.956 * X) - 0.347$$

$$RVP \text{ kPa} = (0.956 * X) - 2.39$$

where:

X = total measured vapor pressure in psi or kPa

9.3 Record the RVP to the nearest 0.01 psi (0.07 kPa) as the official test result.

9.4 EPA will use the above method as the official vapor pressure test method. EPA will recognize correlations from regulated parties if the correlations are established directly with EPA's test laboratory. Any test method may be used for defense as long as adequate correlation is demonstrated to this method (i.e., any vapor pressure defense test method could be used if adequate correlation exists directly to this method, which can then be converted to Reid Vapor Pressure by use of

the EPA Grabner correlation equation in section 9.2 of this method).

[58 FR 14488, Mar. 17, 1993]

APPENDIX F TO PART 80—TEST FOR DETERMINING THE QUANTITY OF ALCOHOL IN GASOLINE

METHOD 1—WATER EXTRACTION METHOD

1. *Scope.*

This test method covers the determination of the type and amount of alcohols in gasoline.

2. *Summary of method.*

Gasoline samples are extracted with water prior to analysis on a gas chromatograph (GC). The extraction eliminates hydrocarbon interference during chromatography. A known quantity of isopropanol is added to the fuel prior to extraction to act as an internal standard.

3. *Sample description.*

3.1 Sample in accordance with 40 CFR part 80, appendix D.

3.2 At least 100 ml. of gasoline suspected of containing ethanol and/or methanol are required.

4. *Apparatus.*

4.1 Gas chromatograph—A gas chromatograph equipped with a flame ionization detector.

4.2 Column—A gas chromatograph column, glass, 1800 by 6.35 cm. outside diameter, packed with Chromosorb 102.

4.3 Recorder—A 1-mv recorder with a 1 second full scale response and a chart speed of 10 mm. per minute (0.4 inches per minute).

4.4 Syringe (100 ul.) for adding the internal standard.

4.5 Pipet.

4.6 Injection syringe (10 ul.).

4.7 Extraction syringe (1-5 ml.) with 3-inch needle.

4.8 250 ml. (½ pint) glass sample bottles with screw caps or equivalent.

4.9 Calibration standard solutions extracted from gasoline containing known quantities of alcohols.

4.10 Reference standard solutions extracted from gasoline containing known quantities of alcohols.

4.11 Distilled water.

4.12 Reagent grade isopropanol.

4.13 Rubber gloves.

4.14 I.D. tags.

5. *Precautions.*

NOTE 1: Gasoline and alcohols are extremely flammable and may be toxic over prolonged exposure. Methanol is particularly hazardous. Persons performing this proce-

dures must be familiar with the chemicals involved and all precautions applicable to each.

5.1 Extractions and dilutions must be performed in well-ventilated areas, preferably under a fume hood, away from open flames and sparks.

5.2 Rubber gloves must be worn during the handling of gasoline and alcohols.

5.3 Avoid breathing fumes from gasoline and alcohols, particularly methanol.

5.4 Gas cylinders must be properly secured and the hydrogen FID fuel must be segregated from the compressed air (oxidizer) tank.

6. *Visual inspection.*

6.1 Ensure that the samples do not contain sediment or separated phases prior to extraction.

6.2 Ensure adequate quantities of GC supply gases to maintain a run.

7. *Test article preparation.*

7.1 Gas chromatography—Use carrier gas, flow rates, detector and injection temperatures and column as specified in the GC manufacturer's specifications.

7.2 Sample extraction, preparation and analysis.

7.2.1 Label two 6 ml. vials with the sample identification number supplied with the original sample. The estimated percent alcohol from any screening tests must also be included on the label.

7.2.2 Pipet 4 ml.±0.01 ml. of sample into one of the vials. Label as vial #1.

7.2.3 Measure 100 ul. (0.1 ml.)±0.5 ul. of isopropanol into vial #1.

NOTE: This adds an internal standard to the sample which is required for accurate analysis.

7.2.4 Add 1 ml.±0.2 ml. of distilled water to the gasoline sample in vial #1 and shake for 10 seconds.

7.2.5 Allow the mixture to separate into two phases (at least 5 minutes).

7.2.6 Carefully draw off the aqueous (lower) phase using a 5 ml. syringe and long needle.

NOTE: Be careful not to allow any of the gasoline phase to get into the needle. Leave a small amount (approximately 0.2 ml.) of the aqueous phase in the vial.

7.2.7 Transfer the aqueous phase into the other 6 ml. vial (vial #2).

7.2.8 Repeat steps 7.2.4 to 7.2.6 two more times.

7.2.9 Fill vial #2 (the aqueous phase) to 4 ml.±0.05 ml. with distilled water.

7.2.10 Retain the remaining original gasoline sample (not the gasoline phase).

7.2.11 Discard the extracted gasoline phase in vial #1 in an appropriate manner.

7.2.12 Perform a second extraction on one sample in every 20. This sample is to be labeled with the sample number and as a duplicate and run as a normal sample.

7.2.13 Transfer approximately 2 ml. of the aqueous solution to vials compatible with the autosampler. Tag the vial with the sample number.

7.2.14 Perform analysis of the sample according to the GC manufacturer's specifications.

7.3 Standards.

7.3.1 Calibration standard solutions (made in gasoline).

7.3.1.1 Reagent grade or better alcohols (including undenatured ethanol) are to be diluted with regular unleaded gasoline. The isopropanol internal standard is to be added during extraction of the alcohols. Newly acquired stocks of reagent grade alcohols shall be diluted to 10% with hydrocarbon-free water and analyzed for contamination by GC before use.

7.3.1.2 Required calibration standards (% by volume in gasoline):

Alcohol	Range (percent)	Standard (MIN)
Methanol	0.5-12	5
Ethanol	0.5-11	5

The standards should be as equally spaced within the range as possible and may contain more than one alcohol.

NOTE: Level #1 must contain all of the alcohols.

8. Quality control provisions.

8.1 Alcohol(s) in water solution may be used to characterize the GC. The resulting characterization always reflects the absolute sensitivity of the instrument to each alcohol.

8.2 Calibration standards are made by extraction of known alcohol(s) in gasoline blends. These standards account for inaccuracies caused by incomplete extraction of alcohols.

$$C_i = \frac{W_{is} \times A_i \times F_i}{W_i \times A_{is}} \times 100 = \text{weight \% component } i$$

where:

- A_i = peak area component i,
- A_{is} = peak area of internal standard,
- W_i = weight of sample,
- W_{is} = weight of internal standard, and
- F_i = response factor for component i.

10. REPORT.

10.1 Report results to the nearest 0.1%.

curacies caused by incomplete extraction of alcohols.

8.3 The addition of isopropanol as an internal standard reduces errors caused by variations in injection volumes, and further reduces inaccuracies caused by incomplete extraction of alcohols.

8.4 Sufficient sample should be retained to permit reanalysis.

8.5 Running averages of reference standards data must not exceed 0.75% of applicable limits or investigation should be started for the cause of such variation.

9. Calculations.

9.1 Calculate purity of component as follows:

$$P_i = \frac{A_i}{\sum A} \text{ expressed as a decimal fraction, that is } 0.999$$

where:

- P_i = purity of component i,
- A_i = area of response of component i, and
- ΣA = total area response of all components.

9.2 Calculate response factors as follows:

$$F_i = \frac{A_{is} \times W_i \times P_i}{A_i \times W_{is} \times P_{is}}$$

where:

- F_i = response factor for component of interest i,
- A_i = area response for component of interest i,
- A_{is} = area response of internal standard,
- W_i = weight of component of interest i (be sure to consider all sources),
- W_{is} = weight of internal standard,
- P_i = purity of component of interest i as determined in 9.1 expressed as a decimal, and
- P_{is} = purity of internal standards as determined in 9.1 expressed as a decimal.

9.3 Calculate the percent alcohols as follows:

11. PRECISION AND ACCURACY.

11.1 Precision—The precision of this test method has not been determined.

11.2 Accuracy—The accuracy of this test method has not been determined.

METHOD 2—TEST METHOD FOR DETERMINATION OF C₁ TO C₄ ALCOHOLS AND MTBE IN GASOLINE BY GAS CHROMATOGRAPHY*1. Scope.*

1.1 This test method covers a procedure for determination of methanol, ethanol, isopropanol, n-propanol, isobutanol, sec-butanol, tert-butanol, n-butanol, and methyl tertiary butyl ether (MTBE) in gasoline by gas chromatography.

1.2 Individual alcohols and MTBE are determined from 0.1 to 10 volume %. Any sample found to contain greater than 10 volume % of an alcohol or MTBE shall be diluted to concentrations within these limits.

1.3 SI (metric) units of measurement are preferred and used throughout this standard. Alternative units, in common usage, are also provided to improve the clarity and aid the user of this test method.

1.4 This standard may involve hazardous materials, operations, and equipment. This standard does not purport to address all of the safety problems 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 4307 Practice for Preparation of Liquid Blends for Use as Analytical Standards¹

D 4626 Practice for Calculation of Gas Chromatographic Response Factors¹

E 260 Practice for Packed Column Gas Chromatographic Procedures²

E 355 Practice for Gas Chromatography Terms and Relationships²

2.2 EPA Regulations:

40 CFR Part 80 Appendix D

3. Descriptions of terms specific to this standard.

3.1 MTBE—methyl tertiary butyl ether.

3.2 Low volume connector—a special union for connecting two lengths of tubing 1.6 mm inside diameter and smaller. Sometimes this is referred to as a zero dead volume union.

3.3 Oxygenates—used to designate fuel blending components containing oxygen, either in the form of alcohol or ether.

3.4 Split ratio—a term used in gas chromatography using capillary columns. The split ratio is the ratio of the total flow of the carrier gas to the sample inlet versus the flow of carrier gas to the capillary column. Typical values range from 10:1 to 500:1 depending upon the amount of sample injected and the type of capillary column used.

¹Annual Book of ASTM Standards, Vol. 05.03.

²Annual Book of ASTM Standards, Vol. 14.01.

3.5 WCOT—abbreviation for a type of capillary column used in gas chromatography that is wall-coated open tubular. This type of column is prepared by coating the inside of the capillary with a thin film of stationary phase.

3.6 TCEP—1,2,3,-tris-2-cyanoethoxypropane—a gas chromatographic liquid phase.

4. Summary of test method.

4.1 An internal standard, tertiary amyl alcohol, is added to the sample which is then introduced into a gas chromatograph equipped with two columns and a column switching valve. The sample first passes onto a polar TCEP column which elutes lighter hydrocarbons to vent and retains the oxygenated and heavier hydrocarbons. After methylcyclopentane, but before MTBE elutes from the polar column, the valve is switched to backflush the oxygenates onto a WCOT non-polar column. The alcohols and MTBE elute from the non-polar column in boiling point order, before elution of any major hydrocarbon constituents. After benzene elutes from the non-polar column, the column switching valve is switched back to its original position to backflush the heavy hydrocarbons. The eluted components are detected by a flame ionization or thermal conductivity detector. The detector response, proportional to the component concentration, is recorded; the peak areas are measured; and the concentration of each component is calculated with reference to the internal standard.

5. Significance and use.

5.1 Alcohols and other oxygenates may be added to gasoline to increase the octane number. Type and concentration of various oxygenates are specified and regulated to ensure acceptable commercial gasoline quality. Drivability, vapor pressure, phase separation, and evaporative emissions are some of the concerns associated with oxygenated fuels.

5.2 This test method is applicable to both quality control in the production of gasoline and for the determination of deliberate or extraneous oxygenate additions or contamination.

*6. Apparatus.**6.1 Chromatograph:*

6.1.1 A gas chromatographic instrument which can be operated at the conditions given in Table 1, and having a column switching and backflushing system equivalent to Fig. 1. Carrier gas flow controllers shall be capable of precise control where the required flow rates are low (Table 1). Pressure control devices and gages shall be capable of precise control for the typical pressures required.

TABLE 1—CHROMATOGRAPHIC OPERATING CONDITIONS

Temperatures		Flows, mL/min		Other parameters: Carrier gas, helium	
Column oven, °C	60	To injector	75	Sample size, µL	3
Injector, °C	200	Column	5	Split ratio	15:1
Detector—TCD, °C	200	Auxiliary	3	Backflush, min	0.2–0.3
FID, °C	250	Makeup	18	Valve reset time, min	8–10
Valve, °C	60			Total analysis time, min	18–20

6.1.2 Detector—A thermal conductivity detector or flame ionization detector may be used. The system shall have sufficient sensitivity and stability to obtain a recorded deflection of at least 2 mm at a signal-to-noise ratio of at least 5 to 1 for 0.005 volume % concentration of an oxygenate.

6.1.3 Switching and backflushing valve—A valve, to be located within the gas chromatographic column oven, capable of performing the functions described in Section 11. and illustrated in Fig. 1. The valve shall be of low volume design and not contribute significantly to chromatographic deterioration.

6.1.3.1 Valco Model No. CM-VSV-10-HT, 1.6-mm (1/16-in.) fittings. This particular valve was used in the majority of the analyses used for the development of Section 15.

6.1.3.2 Valco Model No. C10W, 0.8-mm (1/32-in.) fittings. This valve is recommended for use with columns of 0.32-mm inside diameter and smaller.

6.1.4 Although not mandatory, an automatic valve switching device is strongly recommended to ensure repeatable switching times. Such a device should be synchronized with injection and data collection times. If no such device is available, a stopwatch, started at the time of injection, should be used to indicate the proper valve switching time.

6.1.5 Injection system—The chromatograph should be equipped with a splitting-type inlet device. Split injection is necessary to maintain the actual chromatographed sample size within the limits of column and detector optimum efficiency and linearity.

6.1.6 Sample introduction—Any system capable of introducing a representative sample into the split inlet device. Microlitre syringes, automatic syringe injectors, and liquid sampling valves have been used successfully.

6.2 Data presentation or calculation, or both:

6.2.1 Recorder—A recording potentiometer or equivalent with a full-scale deflection of 5 mV or less. Full-scale response time should be 1 s or less with sufficient sensitivity and stability to meet the requirements of 6.1.2.

6.2.2 Integrator or computer—Devices capable of meeting the requirements of 6.1.2, and providing graphic and digital presentation of the chromatographic data, are recommended for use. Means shall be provided

for determining the detector response. Peak heights or areas can be measured by computer, electronic integration or manual techniques.

6.3 Columns, two as follows:

6.3.1 Polar column—This column performs a pre-separation of the oxygenates from volatile hydrocarbons in the same boiling point range. The oxygenates and remaining hydrocarbons are backflushed onto the non-polar column in section 6.3.2. Any column with equivalent or better chromatographic efficiency and selectivity to that described in 6.3.1.1 can be used. The column shall perform at the same temperature as required for the column in 6.3.2.

6.3.1.1 TCEP micro-packed column, 560 mm (22 in.) by 1.6-mm (1/16-in.) outside diameter by 0.38-mm (0.015-in.) inside diameter stainless steel tube packed with 0.14 to 0.15g of 20% (mass/mass) TCEP on 80/100 mesh Chromosorb P(AW). This column was used in the (ASTM) cooperative study to provide the Precision and Bias data referred to in Section 15.

6.3.2 Non-polar (analytical) column—Any column with equivalent or better chromatographic efficiency and selectivity to that described in 6.3.2.1 and illustrated in Fig. 2 can be used.

6.3.2.1 WCOT methyl silicone column, 30m (1181 in.) long by 0.53 mm (0.021-in.) inside diameter fused silica WCOT column with a 2.6-µm film thickness of cross-linked methyl siloxane. This column was used in the (ASTM) cooperative study to provide the Precision and Bias data referred to in Section 15.

7. Reagents and materials.

7.1 Carrier gas—Carrier gas appropriate to the type of detector used. Helium has been used successfully. The minimum purity of the carrier gas used must be 99.95 mol %.

7.2 Standards for calibration and identification—Standards of all components to be analyzed and the internal standard are required for establishing identification by retention as well as calibration for quantitative measurements. These materials shall be of known purity and free of the other components to be analyzed.

NOTE 1. Warning—These materials are flammable and may be harmful or fatal if ingested or inhaled.

7.3 Preparation of calibration blends—For best results, these components must be added to a stock gasoline or petroleum naphtha, free of oxygenates (Warning—See Note 2). Refer to Test Method D 4307 for preparation of liquid blends. The preparation of several different blends, at different concentration levels covering the scope of the method, is recommended. These will be used to establish the linearity of the component response.

NOTE 2. Warning—Extremely flammable. Vapors harmful if inhaled.

7.4 Methylene chloride—Used for column preparation. Reagent grade, free of non-volatile residue.

NOTE 3. Warning—Harmful if inhaled. High concentrations may cause unconsciousness or death.

8. Preparation of column packings.

8.1 TCEP column packing:

8.1.1 Any satisfactory method, used in the practice of the art that will produce a column capable of retaining the C₁ to C₄ alcohols and MTBE from components of the same boiling point range in a gasoline sample. The following procedure has been used successfully.

8.1.2 Completely dissolve 10 g of TCEP in 100 mL of methylene chloride. Next add 40 g of 80/100 mesh Chromosorb P(AW) to the TCEP solution. Quickly transfer this mixture to a drying dish, in a fume hood, without scraping any of the residual packing from the sides of the container. Constantly, but gently, stir the packing until all of the solvent has evaporated. This column packing can be used immediately to prepare the TCEP column.

9. Preparation of micro-packed TCEP column.

9.1 Wash a straight 560 mm length of 1.6-mm outside diameter (0.38-mm inside diameter) stainless steel tubing with methanol and dry with compressed nitrogen.

9.2 Insert 6 to 12 strands of silvered wire, a small mesh screen or stainless steel frit inside one end of the tube. Slowly add 0.14 to 0.15 g of packing material to the column and gently vibrate to settle the packing inside the column. When strands of wire are used to retain the packing material inside the column, leave 6.0 mm (0.25 in.) of space at the top of the column.

9.3 Column conditioning—Both the TCEP and WCOT columns are to be briefly conditioned before use. Connect the columns to the valve (see 11.1) in the chromatographic oven. Adjust the carrier gas flows as in 11.3 and place the valve in the RESET position. After several minutes, increase the column oven temperature to 120 °C and maintain these conditions for 5 to 10 min. Cool the columns below 60 °C before shutting off the carrier flow.

10. Sampling.

10.1 Gasoline samples to be analyzed by this test method shall be sampled in accordance with 40 CFR part 80, appendix D.

11. Preparation of apparatus and establishment of conditions.

11.1 Assembly—Connect the WCOT column to the valve system using low volume connectors and narrow bore tubing. It is important to minimize the volume of the chromatographic system that comes in contact with the sample, otherwise peak broadening will occur.

11.2 Adjust the operating conditions to those listed in Table 1, but do not turn on the detector circuits. Check the system for leaks before proceeding further.

11.3 Flow rate adjustment.

11.3.1 Attach a flow measuring device to the column vent with the valve in the RESET position and adjust the pressure to the injection port to give 5.0 mL/min flow (14 psig). Soap bubble flow meters are suitable.

11.3.2 Attach a flow measuring device to the split injector vent and adjust flow from the split vent using the A flow controller to give a flow of 70 mL/min. Recheck the column vent flow set in 11.3.1 and adjust if necessary.

11.3.3 Switch the valve to the BACKFLUSH position and adjust the variable restrictor to give the same column vent flow set in 11.3.1. This is necessary to minimize flow changes when the valve is switched.

11.3.4 Switch the valve to the inject position RESET and adjust the B flow controller to give a flow of 3.0 to 3.2 mL/min at the detector exit. When required for the particular instrumentation used, add makeup flow or TCD switching flow to give a total of 21 mL/min at the detector exit.

11.4 When a thermal conductivity detector is used, turn on the filament current and allow the detector to equilibrate. When a flame ionization detector is used, set the hydrogen and air flows and ignite the flame.

11.5 Determine the Time of Backflush—The time to backflush will vary slightly for each column system and must be determined experimentally as follows. The start time of the integrator and valve timer must be synchronized with the injection to accurately reproduce the backflush time.

11.5.1 Initially assume a valve BACKFLUSH time of 0.23 min. With the valve RESET, inject 3 µL of a blend containing at least 0.5% or greater oxygenates (7.3), and simultaneously begin timing the analysis. At 0.23 min., rotate the valve to the BACKFLUSH position and leave it there until the complete elution of benzene is realized. Note this time as the RESET time, which is the time at which the valve is returned to the RESET position. When all of the remaining hydrocarbons are backflushed

the signal will return to a stable baseline and the system is ready for another analysis. The chromatogram should appear similar to that illustrated in Fig. 2.

11.5.2 It is necessary to optimize the valve BACKFLUSH time by analyzing a standard blend containing oxygenates. The correct BACKFLUSH time is determined experimentally by using valve switching times between 0.2 and 0.3 min. When the valve is switched too soon, C₅ and lighter hydrocarbons are backflushed and are co-eluted in the C₄ alcohol section of the chromatogram. When the valve BACKFLUSH is switched too late, part or all of the MTBE component is vented resulting in an incorrect MTBE measurement. Chromatograms resulting from incorrect valve times are shown in Figs. 3 and 4.

12. Calibration and standardization.

12.1 Identification—Determine the retention time of each component by injecting small amounts either separately or in known mixtures or by comparing the relative retention times with those in Table 2.

12.2 Standardization—The area under each peak in the chromatogram is considered a quantitative measure of the corresponding compound. Measure the peak area of each oxygenate and of the internal standard by either manual methods or electronic integrator. Calculate the relative volume response factor of each oxygenate, relative to the internal standard, according to Test Method D 4626.

TABLE 2—RETENTION CHARACTERISTICS FOR TCEP/WCOT COLUMN SET CONDITIONS AS IN TABLE 1

Component	Retention time, min	Relative retention time (tert-amyl alcohol = 1.00)
Methanol	3.21	0.44
Ethanol	3.58	0.50
Isopropanol	3.95	0.56
tert-Butanol	4.31	0.61
n-Propanol	4.75	0.68
MTBE	5.29	0.76
sec-Butanol	5.63	0.82
Isobutanol	6.33	0.93
n-Butanol	7.55	1.10
Benzene	7.88	1.17

13. Procedure.

13.1 Preparation of sample—Precisely add a quantity of the internal standard to an accurately measured quantity of sample. Concentrations of 1 to 5 volume percent have been used successfully.

13.2 Chromatographic analysis—Introduce a representative aliquot of the sample, containing internal standard, into the chromatograph using the same technique as used for the calibration analyses. An injection

volume of 3 µL with a 15:1 split ratio has been used successfully.

13.3 Interpretation of chromatogram—Compare the results of sample analyses to those of calibration analyses to determine identification of oxygenates present.

14. Calculation.

14.1 After identifying the various oxygenates, measure the area of each oxygenate peak and that of the internal standard. Calculate the volume percent of each oxygenate as follows:

$$V_j = \frac{V_s \times PA_j \times 100}{PA_s \times S_j \times V_G}$$

where:

- V_j = volume percent of oxygenate to be determined,
- V_s = volume of internal standard (tert-amyl alcohol) added,
- V_G = volume of gasoline sample taken,
- PA_j = peak area of the oxygenate to be determined,
- PA_s = peak area of the internal standard (tert-amyl alcohol), and
- S_j = relative volume response factor of each component (relative to the internal standard).

14.2 Report the volume of each oxygenate. If the volume percent exceeds 10%, dilute the sample to a concentration lower than 10% and repeat the procedures in sections 13 and 14.

15. Precision and bias.

15.1 Precision—The precision of this test method as determined by statistical examination of the interlaboratory test results is as follows:

15.1.1 Repeatability—The difference between successive results obtained by the same operator with the same apparatus under constant operating conditions on identical test materials would, in the long run, in the normal and correct operation of the test method exceed the following values only in one case in twenty (see Table 3).

- Methanol 0.086 × (V+0.070).
- Ethanol 0.083 × (V+0.000).
- Isopropanol 0.052 × (V+0.150).
- n-Propanol 0.040 × (V+0.026).
- Isobutanol 0.064 × (V+0.086).
- sec-Butanol 0.014 × √ V
- tert-Butanol 0.052 × (V+0.388)
- n-Butanol 0.043 × (V+0.020)
- MTBE 0.104 × (V+0.028)

where V is the mean volume percent.

Environmental Protection Agency

Pt. 80, App. F

15.1.2 Reproducibility—The difference between two single and independent results obtained by different operators working in different laboratories on identical material would, in the long run, exceed the following values only in one case in twenty (see Table 3).

Methanol $0.361 \times (V+0.070)$
 Ethanol $0.373 \times (V+0.000)$
 Isopropanol $0.214 \times (V+0.150)$
 Isobutanol $0.179 \times (V+0.086)$
 sec-Butanol $0.277 \times \sqrt{V}$
 tert-Butanol $0.178 \times (V+0.388)$

n-Propanol $0.163 \times (V+0.026)$.

n-Butanol $0.415 \times (V+0.020)$

MTBE $0.244 \times (V+0.028)$

where
 V is the mean volume percent.

15.2 Bias—Since there is no accepted reference material suitable for determining bias for the procedure in the test method, bias cannot be determined.

TABLE 3—PRECISION INTERVALS—DETERMINED FROM COOPERATIVE STUDY DATA SUMMARIZED IN SECTION 15

Components	Volume percent							
	0.20	0.50	1.00	2.00	3.00	4.00	5.00	6.00
Repeatability								
Methanol	0.02	0.05	0.09	0.18	0.26	0.35	0.44	0.52
Ethanol	0.02	0.04	0.08	0.17	0.25	0.33	0.42	0.50
Isopropanol	0.02	0.03	0.06	0.11	0.16	0.22	0.27	0.32
n-Propanol	0.01	0.02	0.04	0.08	0.12	0.16	0.20	0.24
tert-Butanol	0.03	0.05	0.07	0.12	0.18	0.23	0.28	0.33
sec-Butanol	0.01	0.01	0.01	0.02	0.02	0.03	0.03	0.03
Isobutanol	0.02	0.04	0.07	0.13	0.20	0.26	0.33	0.39
n-Butanol	0.01	0.02	0.04	0.09	0.13	0.17	0.22	0.26
MTBE	0.02	0.05	0.11	0.21	0.31	0.42	0.52	0.63
Reproducibility								
Methanol	0.10	0.21	0.39	0.75	1.11	1.47	1.83	2.19
Ethanol	0.07	0.19	0.37	0.75	1.12	1.49	1.87	2.24
Isopropanol	0.07	0.14	0.25	0.46	0.67	0.89	1.10	1.32
n-Propanol	0.04	0.09	0.17	0.33	0.49	0.66	0.82	0.98
tert-Butanol	0.10	0.16	0.25	0.43	0.60	0.78	0.96	1.14
sec-Butanol	0.12	0.20	0.28	0.39	0.48	0.55	0.62	0.68
Isobutanol	0.05	0.10	0.19	0.37	0.55	0.73	0.91	1.09
n-Butanol	0.09	0.22	0.42	0.84	1.25	1.67	2.08	2.50
MTBE	0.05	0.12	0.23	0.45	0.68	0.90	1.13	1.35

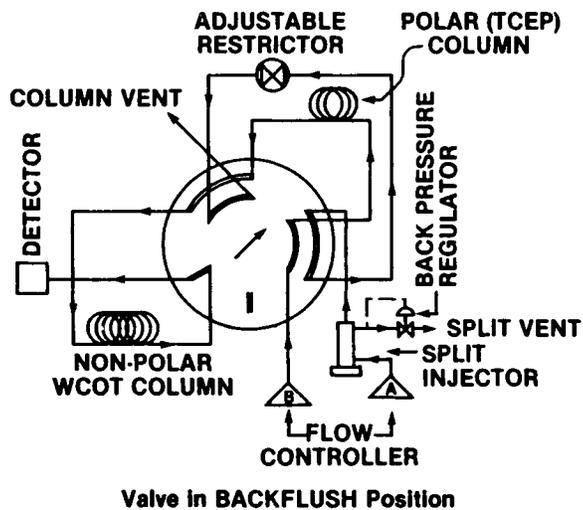
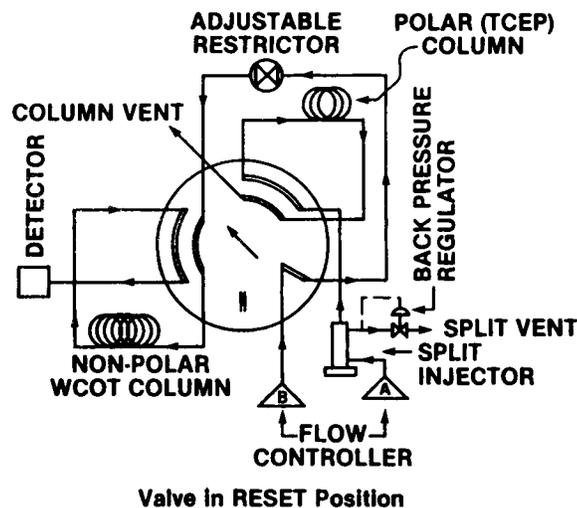


FIG. 1 Analysis of Oxygenates in Gasoline Schematic of Chromatographic System

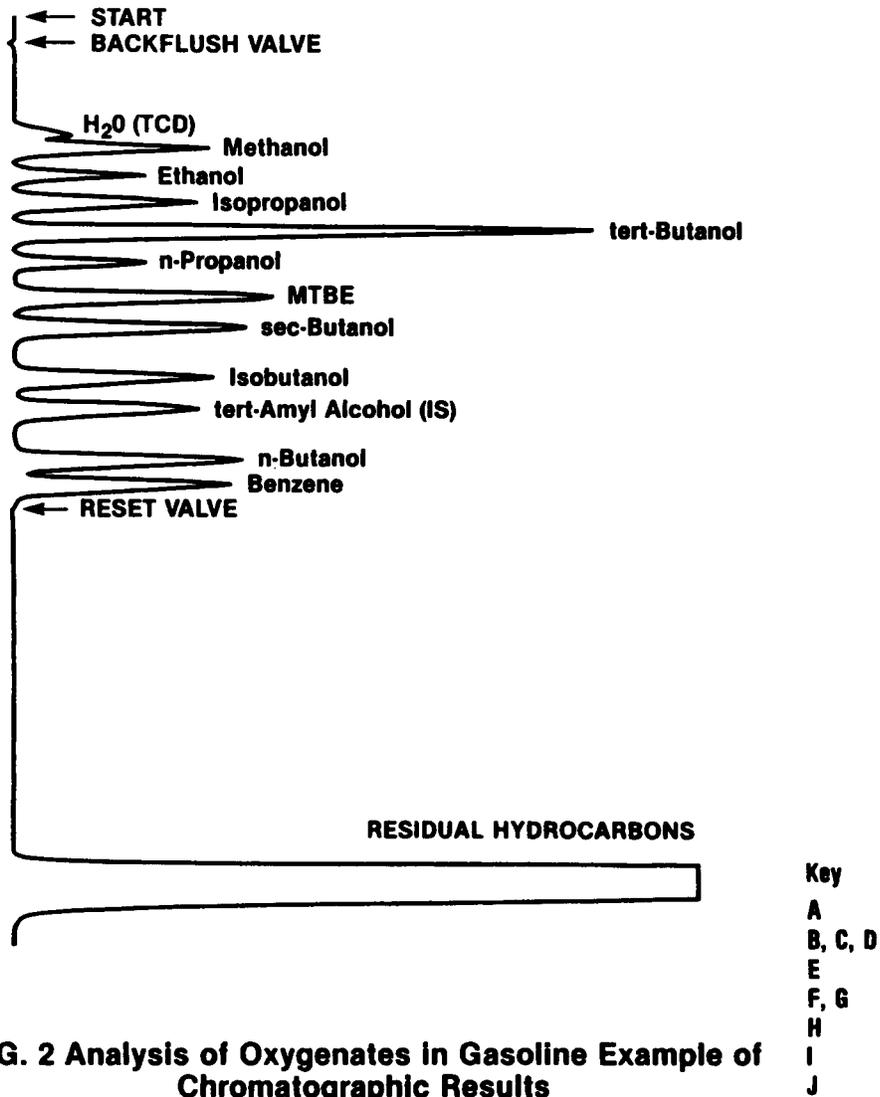


FIG. 2 Analysis of Oxygenates in Gasoline Example of Chromatographic Results

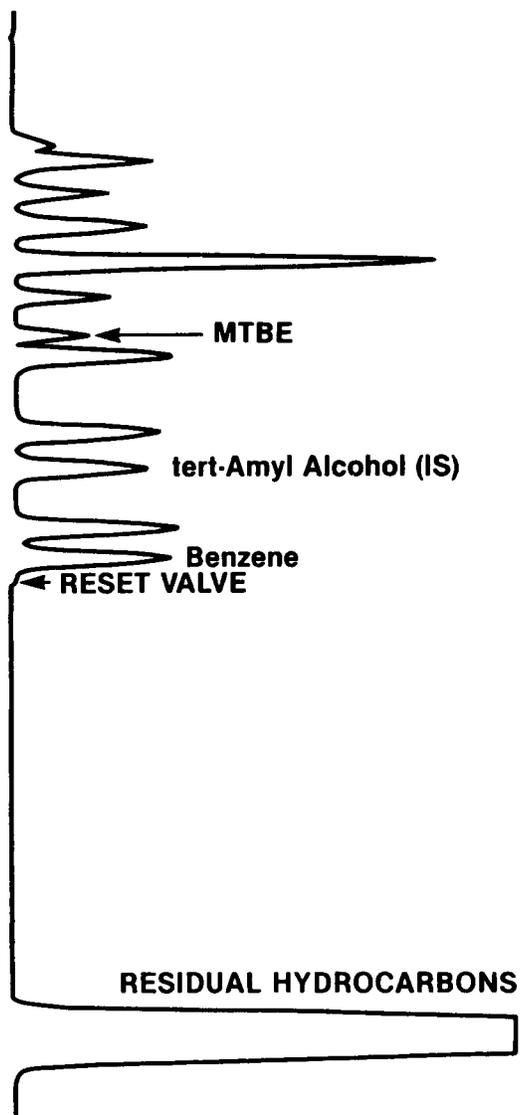


FIG. 3 Analysis of Oxygenates in Gasoline Example Chromatogram Showing Loss of MTBE Due to Venting with Light Hydrocarbons by Late Backflush Time

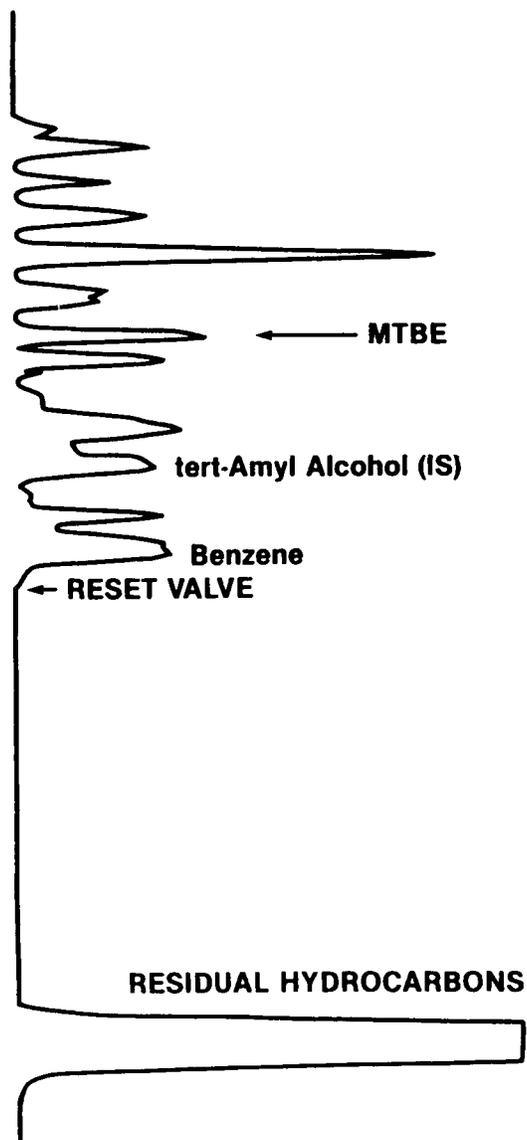


FIG. 4 Analysis of Oxygenates in Gasoline Example Chromatogram Showing Presence of Interferences Caused by Early Backflush Time

[54 FR 11903, Mar. 22, 1989]

APPENDIX G TO PART 80—SAMPLING PROCEDURES FOR DIESEL FUEL

1. Scope

1.1 This method covers procedures for obtaining representative samples of diesel fuel for the purpose of testing for compliance with the cetane index and sulfur percentage standards set forth in §80.29.

2. Summary of Method

2.1 It is necessary that the samples be truly representative of the diesel fuel in question. The precautions required to ensure the representative character of the samples are numerous and depend upon the tank, carrier, container or line from which the sample is being obtained, the type and cleanliness of the sample container, and the sampling procedures that are to be used. A summary of the sampling procedures and their application is presented in Table 1. Each procedure is suitable for sampling a material under definite storage, transportation, or container conditions. The basic principle of each procedure is to obtain a sample in such manner and from such locations in the tank or other container that the sample will be truly representative of the diesel fuel.

3. Description of Terms

3.1 *Average sample* is one that consists of proportionate parts from all sections of the container.

3.2 *All-levels sample* is one obtained by submerging a stoppered beaker or bottle to a point as near as possible to the draw-off level, then opening the sampler and raising it at a rate such that it is about $\frac{3}{4}$ full (maximum 85 percent) as it emerges from the liquid. An all-levels sample is not necessarily an average sample because the tank volume may not be proportional to the depth and because the operator may not be able to raise the sampler at the variable rate required for proportionate filling. The rate of filling is proportional to the square root of the depth of immersion.

3.3 *Running sample* is one obtained by lowering an unstoppered beaker or bottle from the top of the gasoline to the level of the bottom of the outlet connection or swing line, and returning it to the top of the top of the diesel fuel at a uniform rate of speed such that the beaker or bottle is about $\frac{3}{4}$ full when withdrawn from the diesel fuel.

3.4 *Spot sample* is one obtained at some specific location in the tank by means of a thief bottle, or beaker.

3.5 *Top sample* is a spot sample obtained 6 inches (150 mm) below the top surface of the liquid (Figure 1 of appendix D).

3.6 *Upper sample* is a spot sample taken at the mid-point of the upper third of the tank contents (Figure 1 of appendix D).

3.7 *Middle sample* is a spot sample obtained from the middle of the tank contents (Figure 1 of appendix D).

3.8 *Lower sample* is a spot sample obtained at the level of the fixed tank outlet or the swing line outlet (Figure 1 of appendix D).

3.9 *Clearance sample* is a spot sample taken 4 inches (100 mm) below the level of the tank outlet (Figure 1 of appendix D).

3.10 *Bottom sample* is a spot sample obtained from the material on the bottom surface of the tank, container, or line at its lowest point.

3.11 *Drain sample* is a tap sample obtained from the draw-off or discharge valve. Occasionally, a drain sample may be the same as a bottom sample, as in the case of a tank car.

3.12 *Continuous sample* is one obtained from a pipeline in such manner as to give a representative average of a moving stream.

3.13 *Nozzle sample* is one obtained from a diesel pump nozzle which dispenses diesel fuel from a storage tank at a retail outlet or a wholesale purchaser-consumer facility.

4. Sample Containers

4.1 Sample containers may be clear or brown glass bottles, or cans. The clear glass bottle is advantageous because it may be examined visually for cleanliness, and also allows visual inspection of the sample for free water or solid impurities. The brown glass bottle affords some protection from light. Cans with the seams soldered on the exterior surface with a flux of rosin in a suitable solvent are preferred because such a flux is easily removed with diesel fuel, whereas many others are very difficult to remove. If such cans are not available, other cans made with a welded construction that are not affected by, and that do not affect, the diesel fuel being sampled are acceptable.

4.2 Container closure. Cork or glass stoppers, or screw caps of plastic or metal may be used for glass bottles; screw caps only shall be used for cans to provide a vapor-tight closure seal. Corks must be of good quality, clean and free from holes and loose bits of cork. Never use rubber stoppers. Contact of the sample with the cork may be prevented by wrapping tin or aluminum foil around the cork before forcing it into the bottle.

Glass stoppers must be a perfect fit. Screw caps must be protected by a cork disk faced with tin or aluminum foil, or other material that will not affect petroleum or petroleum products. In addition, a phenolic cap with a teflon coated liner may be used.

4.3 Cleaning procedure. The method of cleaning all sample containers must be consistent with the residual materials in the container and must produce sample containers that are clean and free of water, dirt, lint, washing compounds, naphtha, or other

solvents, soldering fluxes or acids, corrosion, rust, and oil.

New sample containers should be inspected and cleaned if necessary. Dry the container by either passing a current of clean, warm air through the container or by allowing it to air dry in a clean area at room temperature. When dry, stopper or cap the container immediately.

5. Sampling Apparatus

5.1 Sampling apparatus is described in detail under each of the specific sampling procedures. Clean, dry, and free all sampling apparatus from any substance that might contaminate the material, using the procedure described in 4.3.

6. Time and Place of Sampling

6.1 When loading or discharging diesel fuel, take samples from both shipping and receiving tanks, and from the pipeline if required.

6.2 Ship or barge tanks. Sample each product after the vessel is loaded or just before unloading.

6.3 Tank cars. Sample the product after the car is loaded or just before unloading.

NOTE: When taking samples from tanks suspected of containing flammable atmospheres, precautions should be taken to guard against ignitions due to static electricity. Metal or conductive objects, such as gage tapes, sample containers, and thermometers, should not be lowered into or suspended in a compartment or tank which is being filled or immediately after cessation of pumping. A waiting period of approximately one minute will generally permit a substantial relaxation of the electrostatic charge; under certain conditions a longer period may be deemed advisable.

7. Obtaining Samples

7.1 Directions for sampling cannot be made explicit enough to cover all cases. Extreme care and good judgment are necessary to ensure samples that represent the general character and average condition of the material. Clean hands are important. Clean gloves may be worn but only when absolutely necessary, such as in cold weather, or when handling materials at high temperature, or for reasons of safety. Select wiping cloths so that lint is not introduced, contaminating samples.

7.2 As many petroleum vapors are toxic and flammable, avoid breathing them or igniting them from an open flame or a spark produced by static. Follow all safety precautions specific to the material being sampled.

8. Handling Samples

8.1 Container outage. Never completely fill a sample container, but allow adequate

room for expansion, taking into consideration the temperature of the liquid at the time of filling and the probable maximum temperature to which the filled container may be subjected.

9. Shipping Samples

9.1 To prevent loss of liquid during shipment, and to protect against moisture and dust, cover with suitable vapor tight caps. The caps of all containers must be screwed down tightly and checked for leakage. Postal and express office regulations applying to the shipment of flammable liquids must be observed.

10. Labeling Sample Containers

10.1 Label the container immediately after a sample is obtained. Use waterproof and oilproof ink or a pencil hard enough to dent the tag, since soft pencil and ordinary ink markings are subject to obliteration from moisture, oil smearing and handling. An indelible identification symbol, such as a bar code, may be used in lieu of a manually addressed label. The label shall reference the following information:

- 10.1.1 Date and time (the period elapsed during continuous sampling);
- 10.1.2 Name of the sample;
- 10.1.3 Name or number and owner of the vessel, car, or container;
- 10.1.4 Brand and grade of material; and
- 10.1.5 Reference symbol or identification number.

11. Sampling procedures

11.1 The standard sampling procedures described in this method are summarized in Table 1. Alternative sampling procedures may be used if a mutually satisfactory agreement has been reached by the party(ies) involved and EPA and such agreement has been put in writing and signed by authorized officials.

TABLE 1—SUMMARY OF DIESEL FUEL SAMPLING PROCEDURES AND APPLICABILITY

Type of container	Procedure	Paragraph
Storage tanks, ship and barge tanks, tank cars, tank trucks.	Bottle sampling	11.2
Storage tanks with taps ..	Tap sampling	11.3
Pipe and lines	Continuous line sampling.	11.4
Retail outlet and wholesale purchaser-consumer facility storage tanks.	Nozzle sampling ...	11.5

11.2 Bottle or beaker sampling. The bottle or beaker sampling procedure is applicable for sampling liquids of 16 pounds (1.12 kgf/cm²) RVP or less in tank cars, tank trucks, shore tanks, ship tanks, and barge tanks.

11.2.1 Apparatus. A suitable sampling bottle or beaker as shown in figure 2 of appendix D is required.

11.2.2 Procedure.

11.2.2.1 All-levels sample. Lower the weighted, stoppered bottle or beaker as near as possible to the draw-off level, pull out the stopper with a sharp jerk of the cord or chain and raise the bottle at a uniform rate so that it is about $\frac{3}{4}$ full as it emerges from the liquid.

11.2.2.2 Running sample. Lower the unstoppered bottles or beaker as near as possible to the level of the bottom of the outlet connection or swing line and then raise the bottle or beaker to the top of the gasoline at a uniform rate of speed such that it is about $\frac{3}{4}$ full when withdrawn from the diesel fuel.

11.2.2.3 Upper, middle, and lower samples. Lower the weighted, stoppered bottle to the proper depths (Figure 1 of appendix D) as follows:

Upper sample ..	middle of upper third of the tank contents
Middle sample ..	middle of the tank contents
Lower sample ..	level of the fixed tank outlet or the swing-line outlet

At the selected level pull out the stopper with a sharp jerk of the cord or chain and allow the bottle or beaker to fill completely, as evidenced by the cessation of air bubbles. When full, raise the bottle or beaker, pour off a small amount, and stopper immediately.

11.2.2.4 Top sample. Obtain this sample (Figure 1 of appendix D) in the same manner as specified in 11.2.2.3 but at six inches (150 mm) below the top surface of the tank contents.

11.2.2.5 Handling. Stopper and label bottle samples immediately after taking them, and deliver to the laboratory in the original sampling bottles.

11.3 Tap sampling. The tap sampling procedure is applicable for sampling liquids of twenty-six pounds (1.83 kgf/cm²) RVP or less in tanks which are equipped with suitable sampling taps or lines. The assembly for tap sampling is shown in figure 3 of appendix D.

11.3.1 Apparatus

11.3.1.1 Tank taps. The tank should be equipped with at least three sampling taps placed equidistant throughout the tank height and extending at least three feet (0.9 meter) inside the tank shell. A standard $\frac{1}{4}$ inch pipe with suitable valve is satisfactory.

11.3.1.2 Tube. A delivery tube that will not contaminate the product being sampled and long enough to reach to the bottom of the sample container is required to allow submerged filling.

11.3.1.3 Sample containers. Use clean, dry glass bottles of convenient size and strength or metal containers to receive the samples.

11.3.2 Procedure

11.3.2.1 Before a sample is drawn, flush the tap (or gage glass drain cock) and line until they are purged completely. Connect the clean delivery tube to the tap. Draw upper, middle, or lower samples directly from the respective taps after the flushing operation. Stopper and label the sample container immediately after filling, and deliver it to the laboratory.

11.4 Continuous sampling. The continuous sampling procedure is applicable for sampling liquids of 16 pounds (1.12 kgf/cm²) RVP or less and semiliquids in pipelines, filling lines, and transfer lines. The continuous sampling may be done manually or by using automatic devices.

11.4.1 Apparatus

11.4.1.1 Sampling probe. The function of the sampling probe is to withdraw from the flow stream a portion that will be representative of the entire stream. The apparatus assembly for continuous sampling is shown in figure 4 of appendix D. Probe designs that are commonly used are as follows:

11.4.1.1.1 A tube extending to the center of the line and beveled at a 45 degree angle facing upstream (Figure 4(a) of appendix D).

11.4.1.1.2 A long-radius forged elbow or pipe bend extending to the center line of the pipe and facing upstream. The end of the probe should be reamed to give a sharp entrance edge (Figure 4(b) of appendix D).

11.4.1.1.3 A closed-end tube with a round orifice spaced near the closed end which should be positioned in such a way that the orifice is in the center of the pipeline and is facing the stream as shown in figure 4(c) of appendix D.

11.4.1.2 Probe location. Since the fluid to be sampled may not in all cases be homogeneous, the location, the position and the size of the sampling probe should be such as to minimize stratification or dropping out of heavier particles within the tube or the displacement of the product within the tube as a result of variation in gravity of the flowing stream. The sampling probe should be located preferably in a vertical run of pipe and as near as practicable to the point where the product passes to the receiver. The probe should always be in a horizontal position.

11.4.1.2.1 The sampling lines should be as short as practicable and should be cleared before any samples are taken.

11.4.1.2.2 Where adequate flowing velocity is not available, a suitable device for mixing the fluid flow to ensure a homogeneous mixture at all rates of flow and to eliminate stratification should be installed upstream of the sampling tap. Some effective devices for obtaining a homogeneous mixture are as follows: Reduction in pipe size; a series of baffles; orifice or perforated plate; and a combination of any of these methods.

11.4.1.2.3 The design or sizing of these devices is optional with the user, as long as the

flow past the sampling point is homogeneous and stratification is eliminated.

11.4.1.3 To control the rate at which the sample is withdrawn, the probe or probes should be fitted with valves or plug cocks.

11.4.1.4 Automatic sampling devices that meet the standards set out in 11.4.1.5 may be used in obtaining samples of diesel fuel. The quality of sample collected must be of sufficient size for analysis, and its composition should be identical with the composition of the batch flowing in the line while the sample is being taken. An automatic sampler installation necessarily includes not only the automatic sampling device that extracts the samples from the line, but also a suitable probe, connecting lines, auxiliary equipment, and a container in which the sample is collected. Automatic samplers may be classified as follows:

11.4.1.4.1 Continuous sampler, time cycle (nonproportional) type. A sampler designed and operated in such a manner that it transfers equal increments of liquid from the pipeline to the sample container at a uniform rate of one or more increments per minute is a continuous sampler.

11.4.1.4.2 Continuous sampler, flow-responsive (proportional) type. A sampler that is designed and operated in such a manner that it will automatically adjust the quantity of sample in proportion to the rate of flow is a flow-responsive (proportional) sampler. Adjustment of the quantity of sample may be made either by varying the frequency of transferring equal increments of sample to the sample container, or by varying the volume of the increments while maintaining a constant frequency of transferring the increments to the sample container. The apparatus assembly for continuous sampling is shown in figure 4 of appendix D.

11.4.1.4.3 Intermittent sampler. A sampler that is designed and operated in such a manner that it transfers equal increments of liquid from a pipeline to the sample container at a uniform rate of less than one increment per minute is an intermittent sampler.

11.4.1.5 Standards of installation. Automatic sampler installations should meet all safety requirements in the plant or area where used, and should comply with American National Standard Code for Pressure Piping, and other applicable codes (ANSI B31.1). The sampler should be so installed as to provide ample access space for inspection and maintenance.

11.4.1.5.1 Small lines connecting various elements of the installation should be so arranged that complete purging of the automatic sampler and of all lines can be accomplished effectively. All fluid remaining in the sampler and the lines from the preceding sampling cycle should be purged immediately before the start of any given sampling operation.

11.4.1.5.2 In those cases where the sampler design is such that complete purging of the sampling lines and the sampler is not possible, a small pump should be installed in order to circulate a continuous stream from the sampling tube past or through the sampler and back into the line. The automatic sampler should then withdraw the sample from the sidestream through the shortest possible connection.

11.4.1.5.3 Under certain conditions, there may be a tendency for water and heavy particles to drop out in the discharge line from the sampling device and appear in the sample container during some subsequent sampling period. To circumvent this possibility, the discharge pipe from the sampling device should be free of pockets or enlarged pipe areas, and preferably should be pitched downward to the sample container.

11.4.1.5 To ensure clean, free-flowing lines, piping should be designed for periodic cleaning.

11.4.1.6 Field calibration. Composite samples obtained from the automatic sampler installation should be verified for quantity performance in a manner that meets with the approval of all parties concerned (including EPA), at least once a month and more often if conditions warrant. In the case of time-cycle samplers, deviations in quantity of the sample taken should not exceed \pm five percent for any given setting. In the case of flow-responsive samplers, the deviation in quantity of sample taken per 1,000 barrels of flowing stream should not exceed \pm 5 percent. For the purpose of field-calibrating an installation, the composite sample obtained from the automatic sampler under test should be verified for quality by comparing on the basis of physical and chemical properties, with either a properly secured continuous nonautomatic sample or tank sample. The tank sample should be taken under the following conditions:

11.4.1.6.1 The batch pumped during the test interval should be diverted into a clean tank and a sample taken within one hour after cessation of pumping.

11.4.1.6.2 If the sampling of the delivery tank is to be delayed beyond one hour, then the tank selected must be equipped with an adequate mixing means. For valid comparison, the sampling of the delivery tank must be completed within eight hours after cessation of pumping, even though the tank is equipped with a motor-driven mixer.

11.4.1.6.3 When making a normal full-tank delivery from a tank, a properly secured sample may be used to check the results of the sampler if the parties (including EPA) mutually agree to this procedure.

11.4.1.7 Receiver. The receiver must be a clean, dry container of convenient size to receive the sample. All connections from the sample probe to the sample container must be free of leaks. Two types of container may

be used, depending upon service requirements.

11.4.1.7.1 Atmospheric container. The atmospheric container shall be constructed in such a way that it retards evaporation loss and protects the sample from extraneous material such as rain, snow, dust, and trash. The construction should allow cleaning, interior inspection, and complete mixing of the sample prior to removal. The container should be provided with a suitable vent.

11.4.1.7.2 Closed container. The closed container shall be constructed in such a manner that it prevents evaporation loss. The construction must allow cleaning, interior inspection and complete mixing of the sample prior to removal. The container should be equipped with a pressure-relief valve.

11.4.2 Procedure.

11.4.2.1 Nonautomatic sample. Adjust the valve or plug cock from the sampling probe so that a steady stream is drawn from the probe. Whenever possible, the rate of sample withdrawal should be such that the velocity of liquid flowing through the probe is approximately equal to the average linear velocity of the stream flowing through the pipeline. Measure and record the rate of sample withdrawal as gallons per hour. Divert the sample stream to the sampling container continuously or intermittently to provide a quantity of sample that will be of sufficient size for analysis.

11.4.2.2 Automatic sampling. Purge the sampler and the sampling lines immediately before the start of a sampling operation. If the sample design is such that complete purging is not possible, circulate a continuous stream from the probe past or through the sampler and back into the line. Withdraw the sample from the side stream through the automatic sampler using the shortest possible connections. Adjust the sampler to deliver not less than one and not more than 40 gallons (151 liters) of sample during the desired sampling period. For time-cycle samplers, record the rate at which sample increments were taken per minute. For flow-responsive samplers, record the proportion of sample to total stream. Label the samples and deliver them to the laboratory in the containers in which they were collected.

11.5 Nozzle sampling. The nozzle sampling procedure is applicable for sampling diesel fuel from a retail outlet or wholesale purchaser-consumer facility storage tank.

11.5.1 Apparatus. Sample containers conforming with 4.1 should be used. A spacer, if appropriate (Figure 6 of appendix D), and a nozzle extension device similar to that shown in figures 7 or 7a of appendix D shall be used when nozzle sampling. The nozzle extension device does not need to be identical to that shown in figure 7 or 7a of appendix D but it should be a device that will bottom fill the container.

11.5.2 Procedure. Immediately after diesel fuel has been delivered from the pump and the pump has been reset, deliver a small amount of product into the sample container. Rinse sample container and dump product into waste container. Insert nozzle extension (Figure 7 or 7a of appendix D) into sample container and insert pump nozzle into extension with slot over air bleed hole. Fill slowly through nozzle extension to 70-80 percent full (Figure 8 of appendix D). Remove nozzle extension. Cap sample container at once. Check for leaks.

12. Special Precautions and Instructions.

12.1 Precautions. Official samples should be taken by, or under the immediate supervision of, a person of judgment, skill, and sampling experience. Never prepare composite samples for this test. Make certain that containers which are to be shipped by common carrier conform to applicable Interstate Commerce Commission, State, and local regulations. When flushing or purging lines or containers, observe the pertinent regulations and precautions against fire, explosion, and other hazards.

12.2 Sample containers. Use containers of not less than one quart (0.9 liter) nor more than two gallons (7.6 liters) capacity, of sufficient strength to withstand the pressure to which they may be subjected. Open-type containers have a single opening which permits sampling by immersion. Closed-type containers have two openings, one in each end (or the equivalent thereof), fitted with valves suitable for sampling by water displacement or by purging.

12.3 Transfer connections. The transfer connection for the open-type container consists of an air tube and a liquid delivery tube assembled in a cap or stopper. The air tube extends to the bottom of the container. One end of the liquid delivery tube is long enough to reach the bottom of the diesel fuel chamber while the sample is being transferred to the chamber. The transfer connection for the closed-type container consists of a single tube with a connection suitable for attaching it to one of the openings of the sample container. The tube is long enough to reach the bottom of the diesel chamber while the sample is being transferred.

12.4 Sampling open tanks. Use clean containers of the open type when sampling open tanks and tank cars. An all-level sample obtained by the bottle procedure described in 11.2 is recommended. Before taking the sample, flush the container by immersing it in the product to be sampled. Then obtain the sample immediately. Pour off enough so that the container will be 70-80 percent full and close it promptly. Label the container and deliver it to the laboratory.

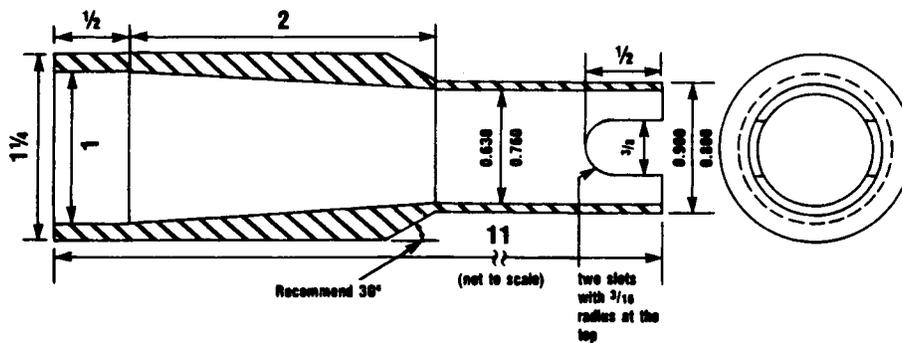
12.5 Sampling closed tanks. Containers of either the open or closed type may be used to obtain samples from closed or pressure

tanks. If the closed type is used, obtain the sample using the water displacement procedure described in 12.8 or the purging procedure described in 12.9. The water displacement procedure is preferable because the flow of product involved in the purging procedure may be hazardous.

12.6 Water displacement procedure. Completely fill the closed-type container with water and close the valves. While permitting a small amount of product to flow through the fittings, connect the top or inlet valve of the container to the tank sampling tap or valve. Then open all valves on the inlet side of the container. Open the bottom or outlet valve slightly to allow the water to be displaced slowly by the sample entering the container. Regulate the flow so that there is no appreciable change in pressure within the container. Close the outlet valve as soon as diesel fuel discharges from the outlet; then in succession close the inlet valve and the sampling valve on the tank. Disconnect the container and withdraw enough of the contents so that it will be 70-80 percent full. If the vapor pressure of the product is not high

enough to force liquid from the container, open both the upper and lower valves slightly to remove the excess. Promptly seal and label the container, and deliver it to the laboratory.

12.7 Purging procedure. Connect the inlet valve of the closed-type container to the tank sampling tap or valve. Throttle the outlet valve of the container so that the pressure in it will be approximately equal to that in the container being sampled. Allow a volume of product equal to at least twice that of the container to flow through the sampling system. Then close all valves, the outlet valve first, the inlet valve of the container second, and the tank sampling valve last, and disconnect the container immediately. Withdraw enough of the contents so that the sample container will be 70-80 percent full. If the vapor pressure of the product is not high enough to force liquid from the container, open both the upper and lower valves slightly to remove the excess. Promptly seal and label the container, and deliver it to the laboratory.



All Dimensions in inches (full scale except as noted)
All decimal dimensions represent minimum and maximum
Tolerance for all other dimensions is $\pm 1/32$ "
Made of non-ferrous material, uneffected by gasoline

Figure 7a. Nozzle Extension for Nozzle Sampling
(Compatible with narrow neck sample containers)

[55 FR 34140, Aug. 21, 1990]