Appendix C to AHRI Standard 700-2014
(formerly Appendix C to AHRI Standard 700-2012)

2008 Appendix C for

Analytical Procedures For AHRI Standard 700-2014 – Normative

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FOREWORD

The intent of this normative appendix is to establish definitive test procedures for determining the quality of new, reclaimed and/or repackaged refrigerants for use in new and existing equipment within the scope of AHRI.

These test methods are established as referee test methods. If alternate test methods are employed, the user must be able to demonstrate that the results of these procedures are equivalent to the specified referee test methods (see Section 7 of each test method for information concerning the sensitivity, precision and accuracy of that test method).

Note:

This Appendix supersedes Appendix C-1999 to ARI Standard 700.

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PART 1

DETERMINATION OF ACIDITY IN NEW AND RECLAIMED REFRIGERANTS BY TITRATION

Section C1-1. Purpose

The purpose of this test method is to determine the amount of acidity in new and reclaimed refrigerants.

Section C1-2. Scope

This test method is for use with low, medium and high pressure fluorocarbon refrigerants.

Section C1-3. Definitions

Definitions for this part are identical to those of ARI Standards 700 and 740.

Section C1-4. Principle

A known quantity of a liquid refrigerant sample is added to, or bubbled through, an extraction solvent that is a mixture of toluene, isopropanol and water to which bromothymol blue indicator has been added. The acidity imparted to the extraction solvent by the sample quantity is titrated with standardized potassium hydroxide to the indicator endpoint. The acidity is reported in ppm as HCl.

Section C1-5. Applicability

This method is applicable to the routine quantitative determination of acidity in low, medium and high pressure refrigerants.

Section C1-6. Limitations and Interferences

None of the refrigerants tested interfere with the acidity determination. The test must be performed quickly after the indicator solution is brought to its blue/green end point to avoid interferences from atmospheric carbon dioxide.

Section C1-7. Sensitivity, Precision and Accuracy

7.1 *Sensitivity*. The sensitivity of the acidity test using 50 g of sample in 100 g of extraction solvent is 0.1 ppm. Care must be taken in sample handling and in avoiding cross contamination when performing this test.

7.2 *Precision.* (Data is not available)

7.3 *Accuracy.* (Data is not available)

Section C1-8. Special Apparatus and Reagents

1. Capillary tubing 1/16 inch x 0.007 inch tetrafluoroethylene
2. Top loading balance, 1000 g with 0.1 g resolution
3. 100 mL stainless steel double-ended, 1/4 inch FNPT cylinder (1800 psig)
4. Two 1/4 inch stainless steel valves with MNPT fittings
5. Two 1/4 inch FNPT x 1/4 inch flare fittings
6. 1/16 inch x 1/4 inch stainless steel tube compression fitting reducing union
7. 1/4 inch compression x 1/4 inch flare AN female adaptor
8. 1/4 inch x 1/4 inch copper flare connector
9. 1/4 inch inlet MNPT x 1/4 inch outlet FNPT pressure relief valve (350 to 400) psig
10. 250 mL Erlenmeyer flask
11. Bromothymol blue sodium salt endpoint indicator
12. Reagent grade isopropanol
13. Reagent grade toluene
14. 0.1 N Potassium hydroxide in methanol
15. 0.1 N Sulfuric acid
16. Absolute methanol (Anhydrous, reagent grade)
17. Stir plate/stir bar
18. Glass distilled water
19. Buret (10 mL with 0.05 mL graduation)

Section C1-9. Procedure

9.1 *Capillary Tubing Connector*. Take 1/16 inch x 0.007 inch tetrafluoroethylene tubing and "swage" on a 1/16 inch nut and ferrule. Connect this to a 1/16 inch x 1/4 inch compression fitting reducing union and then connect it to the 1/4 inch compression fitting x 1/4 inch flare adaptor. The 1/4 inch flare adaptor can then be connected to the 1/4 inch flare fitting on the cylinder assembly just before each acidity determination.

9.2 *Cylinder Assembly*. The cylinder assembly is used as the sampling apparatus for each acidity determination. Before assembly, all pipe fittings must be taped with tetrafluoroethylene to ensure a proper seal at each joint.

Attach the pressure relief valve to the 100 mL stainless steel cylinder. Attach one of the 1/4 inch MNPT x 1/4 inch MNPT stainless steel valves to the pressure relief valve. Connect a 1/4 inch FNPT x 1/4 inch flare fitting to the 1/4 inch MNPT valve. To the other side of the 100 mL cylinder, attach another 1/4 inch

MNPT x 1/4 inch MNPT valve. Sampling should occur from the side of the 100 mL cylinder that does not have the pressure relief valve.

9.3 *Reagent Preparation.*

9.3.1 *0.01 N KOH Solution.* Pipet 100 mL of 0.1 N KOH solution into a 1000 mL volumetric flask. Dilute to the mark with absolute methanol and mix thoroughly.

9.3.2 *0.01 N Sulfuric Acid Solution.* Pipet 100 mL of 0.1 N sulfuric acid solution into a 1000 mL volumetric flask. Dilute to the mark with distilled water and mix thoroughly.

9.3.3 *Extraction Solvent.* Add 495 mL of toluene to 495 mL of isopropanol. Add 10 mL of water to the toluene/isopropanol solution and mix thoroughly.

9.3.4 *Bromothymol Blue Indicator Solution.* Dissolve 1 g of bromothymol blue sodium salt in 100 mL of methanol. Mix thoroughly and store in a dropper bottle.

9.4 *Sample Analysis.*

9.4.1 Thoroughly clean the 100 mL stainless steel cylinder, the valve, the capillary tube, the copper connector and the 250 mL Erlenmeyer flask before initiating testing. Oven heat all of the components to 110°C [230°F] and pull a vacuum.

9.4.2 Weigh the cylinder assembly to the nearest 0.1 g and designate this weight as "X."

9.4.3 Attach the 1/4 inch copper fitting to the vapor valve of the sample cylinder and to the cylinder assembly. Open the vapor valve; loosen the connector and quickly tighten the fitting. This will purge the 1/4 inch connector of air.

9.4.4 Invert the sample cylinder with the attached cylinder assembly. Open the sample cylinder valve and then the cylinder assembly valve. Allow the refrigerant to be introduced into the cylinder assembly until 50 g to 75 g of refrigerant is sampled.

9.4.5 Close the cylinder assembly valve and set the sample cylinder upright. Close the sample cylinder valve, loosen the 1/4 inch connector and remove the cylinder assembly.

9.4.6 Reweigh the cylinder assembly with the refrigerant and designate this value as "Y." The weight of the refrigerant is given by Y-X = grams of refrigerant sampled. (Value for X is in 9.4.2 above).

Note: For the low pressure refrigerants, weigh the sample cylinder before sampling and then add the refrigerant directly to the extraction solvent. Reweigh the sample cylinder and subtract the initial weight from the final weight to obtain the total weight of the refrigerant sampled.

9.4.7 Add 100 mL of the prepared extraction solvent to a 250 mL Erlenmeyer flask. Add a clean magnetic stirring bar. Add 6 drops of the indicator solution to the extraction solvent and initiate moderate stirring.

9.4.8 If the extraction solvent/indicator solution is yellow, add 0.01 N potassium hydroxide through the buret until a just noticeable difference of blue/green is seen in the extraction solvent. Half drops from the buret may be necessary to achieve the real end point.

9.4.9 If the extraction solvent/indicator solution is green or blue, add 0.01 N sulfuric acid through the buret dropwise until the solution is yellow and then proceed as in 9.4.8 immediately above.

9.4.10 Attach the cleaned capillary connector to the cylinder assembly containing the refrigerant sample and slowly introduce the entire sample into the extraction solvent/indicator solution by gradually opening the cylinder valve until it is fully open. The cylinder assembly should be clamped to a ring stand throughout the procedure.

9.4.11 Add all of the refrigerant sample to the extraction solvent. If the color of the solution is green or blue, the result is reported as "non-detect." If the solution is yellow, record the buret volume to the nearest 0.01 mL (designate this value as V_1) and add 0.01 N KOH dropwise until the green endpoint is reached. Record the final buret volume to the nearest 0.01 mL (designate this value as V_2).

Final volume (designate this value as V_f) of 0.01 N KOH added:

$$V_f = V_2 - V_1 \qquad \text{C1.1}$$

9.4.12 Calculation of total acidity expressed in ppm as HCl is given by:

$$\text{ppm as HCI} = \frac{V_f \cdot \text{normality KOH} \cdot 36{,}500}{\text{refrigerant weight sampled}} \qquad \text{C1.2}$$

Note: The value 36,500 is the equivalent weight of HCl (36.5×10^3).

PART 2

DETERMINATION OF WATER IN NEW AND RECLAIMED REFRIGERANTS BY KARL FISCHER COULOMETRIC TITRATION

Section C2-1. Purpose

The purpose of this test method is to determine moisture in new and reclaimed refrigerants by the Karl Fischer coulometric titration method.

Section C2-2. Scope

This test method is for use with low, medium and high pressure refrigerants.

Section C2-3. Definitions

Definitions for this part are identical to those of ARI Standards 700 and 740.

Section C2-4. Principle

Karl Fischer (KF) titrimetry is based upon the redox reaction of water, iodine and sulfur dioxide:

$$H_2O + I_2 + SO_2 \rightarrow 2HI + SO_3 \qquad \text{C2.1}$$

The solvent is typically a mixture of methanol and a weak organic base (imidazole, pyridine, etc.) with the base serving to neutralize the reaction products. In coulometric KF titrimetry, iodine is generated at the anode in direct proportion to the amount of water introduced, and the end point is detected bi-amperametrically as the first appearance of excess free I_2. The added refrigerant eventually evaporates; hence, the solvent can be used repeatedly until either the SO_2 or the base solution is consumed.

Section C2-5. Applicability

This method is applicable to the routine quantitative determination of small amounts of water in low, medium, and high pressure refrigerants.

Section C2-6. Limitations and Interferences

None of the refrigerants tested interfere with the titration. Oxidizing agents such as $Mn0_4$, $Cr_2O_7^{-2}$, H_20_2, Fe (III), Cu (II) and reducing agents such as S^{-2}, thiosulphates and Sn (II) will interfere. Also, certain compounds such as basic oxides and salts of weak acids ($NaHC0_3$, for example) can form water with the KF reagent. None of these interferences are normally present in new or reclaimed refrigerants.

Section C2-7. Sensitivity, Precision and Accuracy

7.1 *Sensitivity*. The sensitivity of the analyzer in this method using a 10 g sample is 1 ppm. Extreme care must be used in sample handling in order to achieve this sensitivity.

7.2 *Precision and Accuracy.* The mean of the analysis ($\overline{X}$), standard deviation (σ) and 95% confidence limits (CL) established for the single operator precision of this method are shown in Table C2-1.

The data in Table C2-1 were calculated from 17 replicate analyses of one sample (approximately 10 g) performed by one analyst over a period of two days.

The samples in Table C2-2 were tested for total percent recovery. They were prepared by analyzing R-12 and R-22 to 4.8 ppm and 7.1 ppm, respectively, and then contaminating the refrigerants with known amounts of water. Both samples were then mixed for a period of 24 hours before analyzing. Results are shown in Table C2-2.

The total percent recovery for each sample was 99.3% for R-12 and 99.7% recovery for R-22.

Section C2-8. Special Apparatus and Reagents

1. KF coulometric titrator system (contains a drying tube for venting refrigerant, anode and cathode solutions, septum, and water vaporizer)

2. Drierite, 20-40 mesh

3. Desiccator, containing Drierite

4. Refrigerant sample cylinder, e.g. 50 mL, 500 mL, 1000 mL stainless steel double ended 1/4 inch FNPT cylinders (1800 psig), steel cylinder, 2.2 lb, single 9 gauge valve, 3/8 inch pipeneck, disposable can, 17 oz, or other suitable cylinder

5. Stainless steel integral bonnet non-rotating stem valve, 1/4 inch MNPT x 1/4 inch FNPT

6. Brass screwed-bonnet needle valve, 1/4 inch MNPT

7. Male Luer lock 10-32 standard thread needle connector, Cut threads back 1/8 inch (threads are too long as received)

8. Needle, 19 gage Luer lock, 4-1/2 inch length

9. 1/4 inch compression fitting to 1/4 inch AN female flare adaptor

10. Quick Seal Flare Cap, No. NFT5-4, 1/4 inch tubular seal gasket

11. Sample Injection Needle and Valve Attachment (see Figure C2-1). Remove the inner gasket-then drill and tap for a 10/32 inch standard thread through the center of the flare cap. Coat the threads with epoxy-then screw the needle connector (item No. 7) into the hole until snug, then allow the epoxy to set overnight. The needle is attached to the connector and the assembly then screwed onto the needle valve AN female flare adapter

12. Syringe, 10 mL, gas tight

13. Syringe needle, 19 gage-4 inch (deflected point)

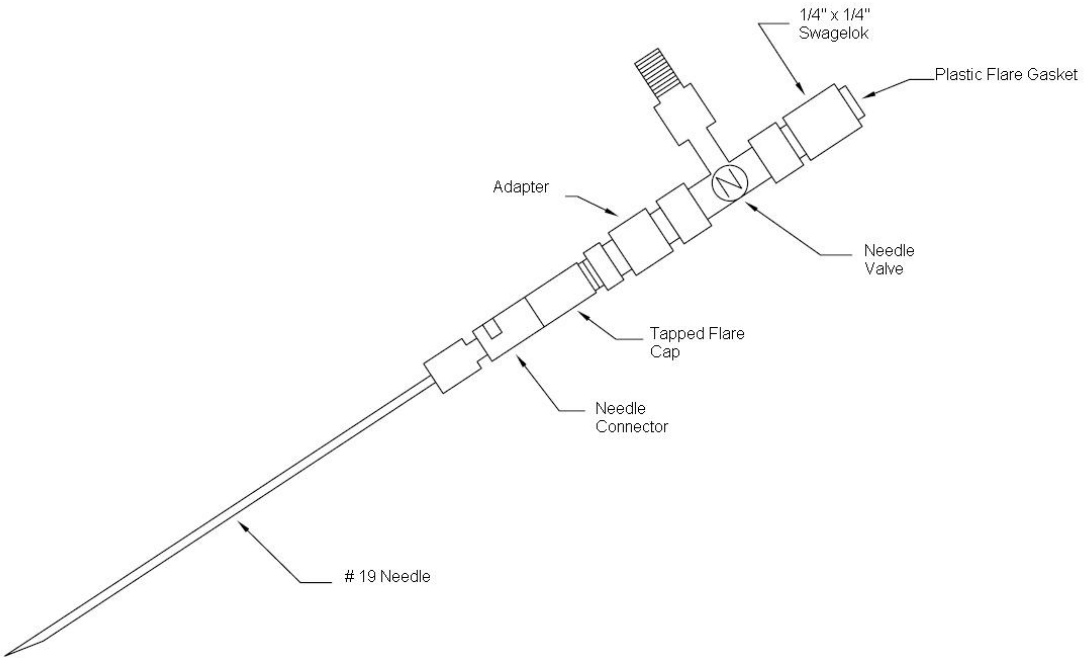


Figure C2-1. Needle Attachment Assembly for Cylinder Sampling

Section C2-9. Procedure

9.1 *Verification.* Verify that the instrument is operating accurately by injecting quantified moisture standard prior to sample testing.

9.2 *Sample Analysis.*

Note: To minimize contamination from moisture, the sample should be introduced directly from the refrigerant sample cylinder into the coulometric titrator, i.e., avoid a secondary container transfer, whenever possible. Also, the effects of moisture contamination and phase distribution will be minimized if the sample container is 60% to 80% liquid filled with refrigerant. If the sample is a very high pressure refrigerant, cool the cylinder to approximately 14 K [25.0°F] below critical temperature (T_C) of the refrigerant and allow 30 minutes for equilibrium to be established before starting the analysis.

9.2.1 Refer to the instruction manual for moisture analyzer installation and operation. Instrument sensitivity should be set at 0.10 and a new septum should be attached.

9.2.2 Turn-on the analyzer and magnetic stirrer and wait until the background current (µg H_2O per second) has reached a low, steady level. It may be necessary to "shake" the titration vessel to contact (wash down) any water mist on the upper inside walls with the anode solution. Optimum levels are below 0.10 microgram of water per second (normally 0.02 to 0.05).

Note: If after 15 minutes a low (< 0.1 µg per second) background current is not obtained or if the cathode solution turns a dark reddish brown color, turn off the moisture meter and, using a small funnel, renew both anode and cathode solutions. Also, should a negative background reading persist (free I_2 in the anode solution), introduce a drop of R-113 or methanol-water wetting solution into the vessel to eliminate the free I_2 via reaction with water and produce a positive background. This wetting solution can be made by adding a small amount of water (typically less than 500 ppm) to methanol or R-113.

9.2.3 Using a heat gun, dry-off the valve threaded end of the sample cylinder valve that contains a pressure relief valve (350 psi to 400 psi) and cylinder stem valve (1/4 inch MNPT x 1/4 inch FNPT).

9.2.4 Remove the Needle/Needle Valve attachment (see Figure C2-1) from the oven or desiccator and immediately attach to the sample cylinder valve.

9.2.5 Open the refrigerant sample cylinder valve, then slowly open the needle valve and purge a small amount of sample liquid phase to flush the air from the needle (1 second to 2 second purge). Close both valves.

9.2.6 Using a heat gun (high position), carefully dry the needle for 20 seconds to 30 seconds.

9.2.7 Weigh the refrigerant sample cylinder plus attachment on a top loader balance (nearest 0.1 g) and record on a work sheet.

9.2.8 Using a clamp (or clamps) and weighted ring stand, invert and position the sample cylinder such that the needle punctures the septum and is immersed to the hub of the needle. The needle should be submerged about one inch below the KF solution surface.
Note: The background current will rise after inserting the needle, then return back to the normal low valve.

9.2.9 At this juncture it is assumed that the instrument has been turned on, preset for a 5 minute titration start delay, verified, and that the background current is at a low (0.02 µg to 0.05 µg) value.

Notes:

1. Do not initiate the titration unless and until the background current has stabilized at a low µg value.

2. The coulometric titrator background signal (given as µg H_2O per second) is subtracted from the analyzed result and represents the background moisture presumably accumulated during the time taken to introduce and to titrate the sample. The background value subtracted is the final value read just before sample addition begins. An artificially elevated background value will result in an erroneously low result (i.e. negatively biased). Hence, it is important that the background value be as small (but correct) as possible. Often, it is necessary to physically "swirl" the titration cell as to rinse moisture accumulated on the inner walls into the KF solution. This operation normally speeds up the process of reaching a low background signal.

9.2.10 Ensure that the desiccant tube is clear of obstructions.

9.2.11 Enter the gross cylinder weight (W_1) from 9.2.7 into the moisture meter, if applicable, or record the initial weight of the cylinder to the nearest 0.1 g on a worksheet.

9.2.12 If applicable, remove any prior number displayed for the second weight.

9.2.13 When the moisture meter is stable (maintains a low background current), initiate a run, slowly open the needle valve and introduce sample at a moderate rate such that no foaming is observed on the KF solution surface. Add at a rate such that 15 g to 20 g of the sample is added over an approximate 10 minute period. Use the sample addition count down (delay) if available.

9.2.14 Normally, a 20 g sample is desirable for best accuracy. Observe the cell potential reading or microgram reading. If during sample addition this number climbs rapidly to a comparatively

large value (range: 200 to 300), this means the sample contains high moisture, and a smaller than normal sample size (5 g to 10 g) is sufficient. .

9.2.15 After the proper sample size has been added, initiate the titration, or after the count down (delay) period ends the coulometer will begin the titration.

Note: If the sample contains high moisture, the rate of titration may never exceed the rate of H_2O addition and the titration must be terminated (closing off the needle valve) before too much sample is added. Conversely, if the sample added is small (4 g to 5 g) and the moisture level also is small (5 ppm to 10 ppm), to achieve better accuracy, the sample should be reanalyzed using a longer sample addition delay (10 minutes for example).

9.2.16 Remove and reweigh the sample cylinder/assembly to the nearest 0.1 g (W_2).

Note: If a small sample size is used, a more accurate balance is recommended and weights should be recorded to the nearest 0.01 g.

9.2.17 Enter the weight from 9.2.16 into the moisture meter if applicable, or record the final weight of the cylinder to the nearest 0.1 g on a worksheet.

9.2.18 Calculate and print-out the ppm or microgram water result. See Figure C2-2 for a sample print-out.

9.2.19 Calculation.

$$\text{Moisture Concentration, ppm} = \frac{\text{micrograms of } H_2O}{\text{grams of sample } (W_1 - W_2)} \qquad \text{C2.2}$$

Report all results to the nearest 1 ppm. If results are < 2 ppm, report < 2 ppm.

Note: Experience has demonstrated that erratic and out-of-specification moisture results are almost always the result of poor and/or improper sampling. Also, be advised that moisture contamination occurs more readily when the relative humidity is high and particular care is required during these times.

Table C2-1. Single Operator Method Precision

	Mean ($\overline{X}$)	Standard Deviation (σ)	95% Confidence Limit
Water (R-12), ppm by weight	10.6	0.11	0.26
Water (R-22), ppm by weight	28.1	0.29	0.77

Table C2-2. Testing for Percent Water Recovery					
	Original Value	Amount Contaminated	Calculated Total	Recovered Total	Percent Recovery
Water (R-12), ppm by weight	6.8	6.9	13.7	13.6	99.3
Water (R-22), ppm by weight	19.2	19.0	38.2	38.1	99.7

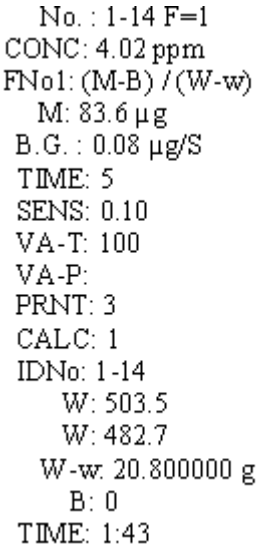


Figure C2-2. Example of Moisture Analyzer Report Print-Out

PART 3

DETERMINATION OF HIGH BOILING RESIDUE IN NEW AND RECLAIMED REFRIGERANTS BY VOLUMETRIC AND/OR GRAVIMETRIC MEASUREMENT AND DETERMINATION OF PARTICULATE RESIDUE BY VISUAL INDICATION

Section C3-1. Purpose

The purpose of this test method is to determine high boiling residue and visible particulates in new and reclaimed refrigerants.

Section C3-2. Scope

This test method is for use with low, medium and high pressure refrigerants.

Section C3-3. Definitions

Definitions for this part are identical to those of ARI Standards 700 and 740.

Section C3-4. Principle

High boiling residue (HBR), also called non-volatile residue, is determined by evaporating a known amount of refrigerant in a Goetz bulb at an ambient or elevated temperature. The remaining residue is then visually measured or weighed. If greater than specification volume is observed, the bulb is placed in a 60.0°C [140°F] oven for 30 minutes and, after cooling, the volume of residue is again measured. For gravimetric determination, the residue is redissolved in a suitable high purity solvent (e.g. R-141b) and quantitatively transferred into a small, tared aluminum pan. The solvent is removed by evaporation and the pan reweighed to obtain the weight of residue.

Prior to evaporation, the measured volume of liquid refrigerant is visually examined for the presence of insoluble materials such as packing fibers, rust, dirt, etc. The residue from high pressure samples is redissolved in a clean solvent, swirled, and then visually examined for any insoluble particulates.

Section C3-5. Applicability

This method is applicable to the routine quantitative determination of HBR and visible evidence of particulates in all low, medium and high pressure new and reclaimed refrigerants. The method was developed to measure HBR and particulates in compliance with AHRI Standard 700 specifications for HBR and particulates.

Section C3-6. Limitations and Interferences

In order to achieve the statistical parameters stated for this method, at least 100 mL of refrigerant sample is required. There are no known interferences to this method.

Section C3-7. Sensitivity, Precision and Accuracy

7.1 *Sensitivity.* Based upon a 100 mL volume of sample, the method will detect 0.01 mL of HBR, which is the first mark on the Goetz bulb buret. This 0.01% value is the AHRI Standard 700 specification for most refrigerants. The detection limit by weight is generally < 0.01% due to the sensitivity of the analytical balance and because 0.01 mL of residue (usually oil) weighs < 0.01 g. Also, except for very high pressure refrigerants, the weight of 100 mL of liquid refrigerant weighs > 100 g.

7.2 *Precision.* The precision for the HBR determination at 0.03 volume percent was found to be $\pm$ 0.005 at the 95% confidence limit. This was based upon an analysis of R-11 by two analysts each of whom used silicone oil as the residue.

7.3 *Accuracy.* The Relative Mean Error at the 0.03% volume level was found to be 3.3%.

Note: These statistical parameters are not applicable to visual observations of particulates.

Section C3-8. Special Apparatus and Reagents

1. Goetz graduated centrifuge tube: 100 mL

2. Boileezers, carborundum crystal

3. Disposable aluminum dish

Section C3-9. Procedure

9.1 *Calibration.* For the HBR procedure, a calibration solution of 0.03% by weight of silicone oil in R-11 may be prepared by weighing 0.220 g of silicone oil and dissolving in 500 mL (738 g) of high purity R-11, mixing thoroughly, labeling and storing in a screw-capped glass bottle in a refrigerator. Alternatively, weigh 0.187 g of oil and dissolve in 500 mL of R-141b or other appropriate solvent.

9.2 *Sample Analysis, HBR Volume Percent Measurement and Particulates.*

9.2.1 Measure 100 mL of refrigerant sample into the Goetz bulb as follows:

9.2.1.1 For low pressure refrigerants (R-11, R-113, R-123): add 100 mL of liquid refrigerant from a glass graduate into the Goetz bulb. Alternatively, add liquid refrigerant from the sample container to the 100 mL mark of the Goetz bulb.

9.2.1.2 While firmly holding the bulb, gently swirl the sample solution and then position the bulb in front of a source light, window, etc. and visually examine for the presence of particulate matter. Record as "pass" if particulates are not observed. Proceed to 9.2.2.

9.2.1.3 For medium and high pressure refrigerants: tare the sample cylinder (to the nearest 0.1 g), invert the cylinder and, by positioning the valve opening just inside the neck of the Goetz bulb, carefully open the valve to allow the liquid phase to discharge inside the bulb. Except for very high pressure refrigerants (R-503, for example), liquid refrigerant will begin to accumulate. Continue to add sample until 60 mL to 75 mL of

liquid has been collected. Turn off the sample valve. Reweigh the sample cylinder and record the difference as the weight of sample added.

9.2.1.4 Repeat 9.2.1.2 above. Use isopropyl alcohol, "thumb," or paper towel to remove frost from the outside of the bulb (create a window) to facilitate the visual observation.

9.2.1.5 For very high pressure refrigerants (R-503, R-13, R-23), the sample cylinder is precooled to approximately 4.4°C [40°F] in ice water (especially on hot days) before carefully flashing the liquid phase into the Goetz bulb. Continue to add liquid phase until the sample cylinder weigh-back shows that between 100 g and 130 g of refrigerant has been flashed into the bulb. At this point, little or no liquid phase refrigerant will have accumulated in the bulb. Record this weight as the "g" of sample added. Add 100 mL of a high purity solvent (e.g. R-141b) to the bulb, put stopper in bulb, swirl to dissolve any residue on the inner walls of the bulb, remove the stopper.

Note: Do not allow any stopcock grease to be present on the glass stopper or on the neck of the bulb.

9.2.1.6 Repeat 9.2.1.2 above.

9.2.2 Add one small boileezer and place the Goetz bulb in a 45.0°C [113°F] constant temperature water bath (60.0°C [140°F] for R-113). Position the bulb such that it is immersed in the bath to about the 20 mL to 25 mL mark. Do not remove the bulb from the bath until all the refrigerant has completely evaporated (determined by observing the disappearance of refrigerant condensation around the neck of the bulb).

9.2.3 Remove the Goetz bulb from the bath, wipe the outside dry and visually measure the mL residue (if any) at the bottom of the buret (ignore the boileezer). Measure to the nearest 0.005 mL.

9.2.4 If the observed residue is ≤ 0.01 mL, proceed to the calculation section below. If the observed residue is > 0.01 mL, proceed to 9.2.5.

9.2.5 Place the Goetz bulb upright in a 60.0°C [140°F] oven for 30 minutes, remove, cool, then measure and record the volume of residue (to the nearest 0.005 mL) in the buret as above. To measure weight percent, save the Goetz bulb-residue for 9.3.

9.2.6 Calculation.

$$\text{HBR Volume \%} = \frac{A \cdot 100}{B} \qquad \text{C3.1}$$

where:

A = volume of residue (mL) in buret.
B = mL of sample added to bulb (9.2.1 above).

Note: To calculate the mL of high and very high pressure refrigerant samples, divide the weight of the sample by the liquid density of the refrigerant at the ambient sample temperature (see Table C3-1).

Report all results to the nearest 0.01% volume. If results are < 0.01%, report as "< 0.01% volume."

9.3 *Sample Analysis, Weight Percent Measurement.*

9.3.1 Prepare an aluminum pan by rinsing it in acetone and placing it in a 60.0°C [140°F] oven for at least 30 minutes. Remove (use tweezers) and place in a desiccator until cool (usually 15 minutes to 20 minutes).

9.3.2 Using tweezers, remove the pan from the desiccator and determine the tare weight (to the nearest 0.0001 g).

9.3.3 Add 20 mL of a high purity solvent (e.g. R-141b) to the Goetz bulb saved from 9.2.5. Stopper the bulb and shake to redissolve the residue and/or to resuspend the particulates (if present) in the solvent.

9.3.4 Carefully pour the solution from the Goetz bulb into the pan. Use two approximately 8 mL portions of the solvent to complete the quantitative transfer of residue. Do not permit the boileezer to fall into the aluminum pan; but, if that should occur, carefully remove using metal tweezers.

9.3.5 Carefully place the aluminum pan inside a hood and allow the high purity solvent to evaporate (alternatively, the pan may be placed on the hot water bath).

9.3.6 Place the pan in the 60.0°C [140°F] oven for 30 minutes, remove and place in the desiccator until cool (20 minutes to 30 minutes).

9.3.7 Using tweezers, remove the pan, reweigh and record the difference in weight (from 9.3.2 above) as the weight of residue.

9.3.8 Calculation.

$$\text{HBR weight \%} = \frac{A \cdot 100}{B} \qquad \text{C3.2}$$

where:

A = grams of residue from 9.3.7 above.
B = grams of sample taken from 9.2.1.

Note: To determine the g of a low pressure sample refrigerant (R-11, R-113, R-123, etc.), multiply the volume taken times the density (see Table C3-1).

Report results to the nearest 0.01% weight. If results are <0.01% weight, report as "<0.01% weight."

Table C3-1. Densities of Some Common Liquid Refrigerants at 25°C [77°F]	
Refrigerant	Density (g/mL)
R-11	1.476
R-12	1.311
R-13	0.907
R-13B1	1.538
R-22	1.194
R-32	0.961
R-113	1.565
R-114	1.456
R-115	1.291
R-123	1.468
R-124	1.364
R-125	1.190
R-134a	1.210
R-141b	1.244
R-142b	1.114
R-143a	0.946
R-152a	0.899
R-290	0.492
R-401A	1.188
R-401B	1.188
R-402A	1.151
R-402B	1.156
R-403B	1.150
R-404A	1.167
R-405A	1.173
R-407A	1.142
R-407B	1.166
R-407C	1.134
R-408A	1.062
R-409A	1.223
R-410A	1.031
R-500	1.168
R-502	1.217
R-503	0.795
R-507	1.170

PART 4

DETERMINATION OF CHLORIDE IN NEW AND RECLAIMED REFRIGERANTS BY SILVER CHLORIDE PRECIPITATION

Section C4-1. Purpose

The purpose of this test method is to qualitatively determine the presence of chloride in new and reclaimed refrigerants.

Section C4-2. Scope

This test method is for use with low, medium and high pressure refrigerants.

Section C4-3. Definitions

Definitions for this part are identical to those of ARI Standards 700 and 740.

Section C4-4. Principle

The qualitative determination of chloride in refrigerants is based on precipitation of the chloride anion as silver chloride:

$$Ag^{+} + Cl^{-} \rightarrow AgCl \qquad \text{C4.1}$$

The refrigerant is added to a solution of silver nitrate in methanol. Visual turbidity indicates the presence of chloride and is reported as "fail." If no turbidity is observed, chloride is within acceptable limits and reported as "pass."

Section C4-5. Applicability

This method is applicable to the routine qualitative determination of chloride in low, medium and high pressure refrigerants.

Section C4-6. Limitations and Interferences

None of the refrigerants tested interfere with the chloride determination. Anions of weak acids can be an interference in the determination, but these interferences are not normally present in new or reclaimed refrigerants. Samples containing insoluble lubricants and oils may show a visual haze or slight turbidity, however, such levels of lubricant or oil necessary to show such visual turbidity are not normally present in new or reclaimed refrigerants.

Section C4-7. Sensitivity, Precision and Accuracy

7.1 *Sensitivity.* The sensitivity of the chloride turbidity test using 5 mL of sample in 5 mL of methanol containing three drops of saturated $AgNO_3$ is approximately 3 ppm. Care must be taken in sample handling to avoid cross contamination when performing this test.

7.2 *Precision.* Data is not available

7.3 *Accuracy.* Data is not available

Section C4-8. Special Apparatus and Reagents

1. Stainless steel capillary tubing
2. Top loading balance, 1000 g with 0.1 g resolution
3. Methanol anhydrous reagent
4. Silver nitrate
5. 75 mL stainless steel double ended 1/4 inch FNPT cylinder
6. Two 1/4 inch stainless steel valves with MNPT fittings
7. Two 1/4 inch FNPT x 1/4 inch flare fittings
8. 1/16 inch x 1/4 inch stainless steel tube compression fitting reducing union
9. 1/4 inch compression fitting x 1/4 inch flare AN female adaptor
10. 1/4 inch x 1/4 inch copper flare connector
11. 1/4 inch inlet MNPT x 1/4 inch outlet FNPT pressure relief valve

Section C4-9. Procedure

9.1 *Stainless Steel Capillary Tubing Connector.* Take 1/16 inch x 0.007 inch stainless steel tubing and attach a 1/16" nut and ferrule. Connect this to a 1/16 inch x 1/4 inch compression fitting reducing union and then connect it to the 1/4 inch compression fitting x 1/4 inch flare adaptor. The 1/4 inch flare adaptor can then be connected to the 1/4 inch flare fitting on the cylinder assembly just before each chloride determination.

9.2 *Cylinder Assembly.* The cylinder assembly is used as the sampling apparatus for chloride determination of medium and high pressure refrigerants. In order to complete this assembly, all pipe fittings must be tetrafluoroethylene taped to ensure a proper seal at each joint.

Attach the pressure relief valve to the 75 mL stainless steel cylinder. Attach one of the 1/4 inch MNPT x 1/4 inch MNPT stainless steel valves to the pressure relief valve. Connect a 1/4 inch FNPT x 1/4 inch flare fitting to the 1/4 inch MNPT valve. To the other side of the 75 mL cylinder, attach another 1/4 inch MNPT x 1/4 inch MNPT valve. Sampling shall always occur from the side of the 75 mL cylinder which does not employ the pressure relief valve.

9.3 *Sample Analysis.*

9.3.1 Thoroughly clean the 75 mL stainless steel cylinder, the valve, the capillary tube, the copper connector and the 100 mL beaker before initiating testing. Heat all of the components to 110°C [230°F] and pull a vacuum.

9.3.2 Weigh the cylinder assembly to the nearest 0.1 g and designate this weight as "X."

9.3.3 Attach the 1/4 inch copper fitting to the gas valve of the sample cylinder and to the cylinder assembly. Loosen the connector and quickly tighten the fitting.

9.3.4 Invert the sample cylinder with the attached cylinder assembly. Open the sample cylinder valve and then the cylinder assembly valve. Allow the refrigerant to be introduced into the cylinder assembly until 30 g to 40 g of refrigerant has been sampled.

Note: For very high pressure refrigerants (R-13, R-23, R-503), it is necessary to precool the sample cylinder and the cylinder assembly to 4.0°C [39°F] in order to provide sufficient liquid phase sample for this test.

9.3.5 Close the cylinder assembly valve and set the sample cylinder upright. Close the sample cylinder valve, loosen the 1/4 inch connector and remove the cylinder assembly.

9.3.6 Reweigh the cylinder assembly with the refrigerant and designate this value as "Y." The weight of the refrigerant is given by Y-X = grams of refrigerant sampled. (Value for “X” is in 9.3.2 above).

9.3.7 Calculate the volume of refrigerant sampled by:

$$\text{volume} = \frac{\text{grams sampled}}{\text{density}} \qquad \text{C4.2}$$

Note: The values of the densities for each refrigerant can be found in Table C3-1.

9.3.8 Add the same volume of methanol as the volume of refrigerant found in 9.3.7 to a 100 mL beaker. For each 5 mL of methanol used, add three drops of saturated silver nitrate solution to the methanol. Also, add one drop of concentrated nitric acid to the solution before adding the refrigerant sample.

Note: This chloride test is valid only if the sample solution being tested is slightly acidic. This prevents: $Ag^{+} + OH^{-} \rightarrow Ag(OH) \rightarrow Ag_2O$ if the sample pH > 7.

9.3.9 Attach the cleaned capillary connector to the cylinder assembly containing the refrigerant sample and slowly introduce the entire sample into the methanolic silver nitrate.

9.3.10 If turbidity is present, the test is reported as "fail." If no turbidity exists, the test is reported as "pass."

Note: For low pressure refrigerants, pour approximately 25 mL of the refrigerant into a 100 mL beaker and proceed as in 9.3.8. After adding the methanol and saturated silver nitrate solution, stir the mixture for 30 seconds. If any turbidity is present in the methanol layer, the result is reported as "fail."

PART 5

DETERMINATION OF NON-CONDENSABLE GAS IN NEW AND RECLAIMED REFRIGERANTS BY GAS CHROMATOGRAPHY

Section C5-1. Purpose

The purpose of this test method is to determine non-condensable gas levels in new and reclaimed refrigerants using gas chromatography.

Section C5-2. Scope

This test method is for use with medium, high and very high pressure refrigerants.

Section C5-3. Definitions

Definitions for this part are identical to those of ARI Standards 700 and 740.

Section C5-4. Principle

Non-condensable gas (NCG) is measured in the vapor space above the refrigerant liquid phase by isothermal gas chromatography using a thermal conductivity detector (TCD) and an external standard calibration. By definition, NCG includes gases such as oxygen and nitrogen (air), carbon dioxide, argon and carbon monoxide. However, in the typical refrigerant sample, air is the only NCG present in significant amounts and the other gases are not routinely analyzed. Very high pressure refrigerants (R-13, R-23, R-503) often contain no liquid phase and these are analyzed directly. NCG equilibrium between refrigerant liquid and vapor phases is temperature dependent and appropriate sample temperature corrections are applied to report results at the 24.0°C [75.2°F] specification temperature.

Section C5-5. Applicability

This method is applicable to the routine quantitative analysis of NCG in medium, high and very high pressure refrigerants.

Section C5-6. Limitations and Interferences

None of the refrigerants interfere with the determination as all chromatographically elute after the air peak. Methane elutes about 0.10 minutes after the air peak and, if present in amounts > 0.10% by volume begins to slightly interfere. However, the amounts of methane (formed during compressor burn-out) in reclaimed refrigerants normally ranges from 0 ppm to 50 ppm by weight and does not interfere at these levels.

Section C5-7. Sensitivity, Precision and Accuracy

7.1 *Sensitivity*. The method will detect about 0.02% by volume NCG in any of the AHRI Standard 700 listed refrigerants.

7.2 *Precision.* The precision was determined at 5.2% by volume concentration and was found to be ± 0.07% by volume at the 95% confidence limit (CL). This was based upon 12 repetitive analyses of an R-12 sample by two technicians over a two-day period.

7.3 *Accuracy.* A 5.1% by volume certified calibration standard (air in helium) was analyzed 9 times following the initial calibration during a one-day period by one technician. The Relative Mean Error was 1.63%.

Section C5-8. Special Apparatus and Reagents

1. Gas chromatograph: Equipped with a manual sample injection valve, 1 mL sample loop and TCD

2. Gas Chromatographic column: 1.8 m x 3.17 mm [6.0 ft x 0.125 in] OD stainless steel, divinylbenzene/ethylvinylbenzene crosslinked polymers, 80-100 mesh

3. Chromatography data system: Capable of electronic integration and processing the chromatographic data

4. Calibration standard: 1.5% by volume, air in Helium, 30 lb. cylinder

5. Digital thermometer

6. Temperature probe

Section C5-9. Procedure

9.1 *Chromatographic Operating Conditions.* Set the GC and data integration system as follows:

Detector sensitivity	low sensitivity
Carrier gas flow	30 cc Helium per minute
Attenuator	x1 (unattenuated)
Detector temperature, ºC [ºF]	100 [212]
Injector port temperature, ºC [ºF]	100 [212]
Head pressure	as required (20 psi suggested)
Column temperature, ºC [ºF]	100 [212]
Sampling valve	load position
Integrator	External Standard method % volume

9.2 *Calibration.*

9.2.1 Refer to the operating manual to gain familiarity with the gas chromatograph (GC).

9.2.2 Attach a 51 cm [20 inch] section of 1/4 inch inside diameter flex line to the GC sample inlet line and terminate the other end with a 1/4 inch female flare connector.

9.2.3 Attach a short piece of flex line to the GC sample exit line and terminate the tubing by placing it inside a small beaker of water.

9.2.4 Connect the sample inlet line to the valve of the 1.5% NCG calibration standard cylinder.

9.2.5 Slowly open the standard cylinder valve, and slowly purge the sample vapor through the sample loop as indicated by bubbles in the exit line beaker of water. Purge for about 10 seconds so as to expel air from the system. One 10 second purge should be equivalent to about 10 mL of vapor.

9.2.6 Close the cylinder valve and, when the bubbling stops, immediately rotate the sampling valve to the "Inject" position and immediately start the GC/integration system.

9.2.7 After the air peak has eluted (about 0.4 minutes), return the sampling valve to the "Load" position and terminate the integration.

9.2.8 Repeat 9.2.5 through 9.2.7 until three consecutive analyses yield essentially reproducible peak areas for the air peak.

9.2.9 Calculate the air peak Absolute Response Factor (ARF) for each of the three analyses as follows:

$$ARF = \frac{A_i}{\%\ \text{by volume air in calibration standard}} \quad \text{C5.1}$$

where:

A_i = area of air peak.

9.2.10 Average the three ARF values and assign the average value as the ARF for the method. The three ARF values should agree within about 1.6% Relative Mean Error.

Note: The calibration standard should be analyzed at least on a daily basis and the ARF updated as necessary.

9.3 *Sample Analysis.* Analyze the sample using the chromatographic conditions described in 9.1.

Note:

See example gas chromatograms in Appendix D.

9.3.1 Record the temperature to the nearest 0.5°C [1ºF] of the sample source liquid phase when the vapor phase is taken for analysis. If this information is unknown (customer samples, for example), record as 24.0ºC [75.2ºF].

Notes:

1. To reestablish equilibrium in a liquid/vapor phase sample cylinder brought into the laboratory and which has changed temperature to a significant degree from the original temperature (standing several hours, for example), the cylinder must be rolled (to mix) for several minutes before sampling the vapor phase for gas chromatography (GC) analysis. The outer wall temperature of the cylinder below the liquid level should be nearly equivalent to that of the refrigerant contents and can be measured using a suitable thermocouple probe.

2. If the vapor phase of a storage tank, road tanker, ton cylinder, etc., is sampled into a small evacuated cylinder, regardless of what temperature the small sample cylinder vapor may be when analyzed by gas chromatography, the contents will represent the vapor temperature at the original sample location point.

9.3.2 Connect the sample inlet line to the sample cylinder valve which directly accesses the sample vapor phase.

9.3.3 Slowly open the sample cylinder valve and slowly purge vapor (about 10 seconds) to expel air from the sample loop and lines.

Notes:

1. When analyzing cylinders containing both liquid and vapor phases, it is especially important that, when purging air from the chromatographic system, a too rapid purge is not used. A too rapid purge may cause some liquid refrigerant to "bump," and such droplets may evaporate resulting in a too rich in refrigerant vapor purge. The presence of refrigerant liquid could result in incorrect NCG values that are lower than the true value in the sample.

2. For samples containing very small total headspace vapor (< 500 mL), the sampling lines, loop, etc., are evacuated to less than 100 microns of Hg pressure [0.013 kPa] to the sample cylinder valve. The vacuum line is then closed and the system brought to the desired pressure (usually 1 atm) by slowly opening the sample cylinder and metering valves and then injecting into the GC as described. In this way, less total volume of headspace vapor is consumed compared to the purging method. See Figure C5-1.

9.3.4 Close the valve and, when the bubbling stops in the exit line beaker of water, immediately rotate the sampling valve to the "Inject" position and immediately start the GC/integration system.

9.3.5 Continue the chromatographic separation until the large refrigerant peak returns to the original baseline (Refer to ASHRAE Handbook of Fundamentals). Stop the integration.

9.3.6 Repeat 9.3.3 through 9.3.5 until the air peak area is reproducible (i.e. until all system air has been expelled). This may require two or three additional consecutive determinations.

9.4 *Calculation.*

9.4.1 The data system will calculate the result for air (NCG) in % by volume, which represents the temperature at which the sample was taken for analysis:

$$\%\ \text{by volume NCG} = \frac{A_i}{ARF} \qquad \text{C5.2}$$

9.4.2 Correct the result to % NCG at 24.0ºC [75.2ºF] as below. Use the Vapor Pressure-Temperature graphs in the ASHRAE Handbook of Fundamentals. For R-403B, use the curve for R-125.

Note:

In all liquid/vapor phase refrigerants, the NCG concentration in the vapor phase increases with decreasing temperature of the liquid phase. This is because the vapor concentration of the refrigerant decreases more so than that of air as the temperature drops.

$$C_1 = \frac{C_2 \cdot P_2 \cdot K_i}{T_2} \qquad \text{C5.3}$$

For K values see Table C5-1.

where:

C_1 = NCG, % by volume, at 24.0ºC [75.2ºF]
C_2 = NCG, % by volume, at the sampling temperature
K_i = Temperature/pressure ratio for refrigerant i at 24.0ºC [75.2ºF], (see Table C5-1).
P_2 = Vapor pressure (psia) of the refrigerant at the sampling temperature, T_2, in ºC [ºF]. This value is determined from the ASHRAE Handbook of Fundamentals.
T_2 = Sampling temperature in K (ºR).
i.e., T_2 = ºC + 273.15 [ºF + 459.67].

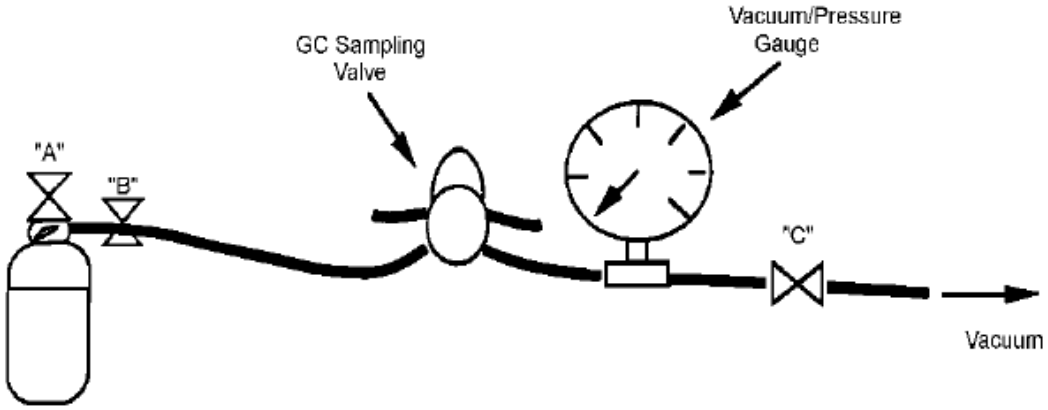
9.4.3 Report results to the nearest 0.01% by volume. If results are < 0.02% by volume, report as "<0.02% by volume."

Table C5-1. K_i Values for Refrigerants at 24.0ºC [75.2ºF]

Refrigerant	K_i (K/MPa)	K_i (ºR/psia)
R-12	478.705	5.941
R-13	87.02	1.08
R-114	1445.54	17.94
R-124	797.71	9.90
R-125	224.406	2.785
R-22	297.086	3.687
R-134a	439.625	5.456
R-115	340.597	4.227
R-142b	906.969	11.256
R-403	224.00	2.78
R-500	402.88	5.00
R-502	269.13	3.34
R-13B1	193.142	2.397
R-152a	552.352	6.855

Note:

1. Source data for this table is the ASHRAE Handbook Fundamentals.



A = Sample Cylinder Valve
B = Metering Valve
C = Vacuum Pump Valve

Figure C5-1. Evacuated System Method of Introducing Vapor Sample into Gas Chromatograph

PART 6

DETERMINATION OF PURITY OF NEW AND RECLAIMED R-11 BY GAS CHROMATOGRAPHY

Section C6-1. Purpose

The purpose of this test method is to determine the purity of new and reclaimed fluorotrichloromethane (R-11) by gas chromatography.

Section C6-2. Scope

This test method is for use with R-11.

Section C6-3. Definitions

Definitions for this part are identical to those of ARI Standards 700 and 740.

Section C6-4. Principle

The organic purity of new and reclaimed R-11 is determined by programmed temperature gas chromatography using a packed column and flame ionization detector (FID). Component peak areas are integrated electronically and quantified by the area normalization response factor method.

Section C6-5. Applicability

This method is applicable to the determination of the impurities typically present in commercially manufactured R-11 and in R-11 recovered and reclaimed from operating refrigeration systems.

Section C6-6. Limitations and Interferences

This method is calibrated for only those impurities commonly present in R-11. Other impurities which have been detected on occasion are listed (with retention times) in Table C6-1. This method will not detect any impurities which may elute within the comparatively large R-11 peak matrix.

Section C6-7. Sensitivity, Precision and Accuracy

Statistical parameters for each impurity are listed in Table C6-2. The data was obtained by analyzing an R-11 calibration mixture 7 times during one day by one operator.

Section C6-8. Special Apparatus and Reagents

1. Gas chromatograph: Equipped with a flame ionization detector (FID), and capable of oven temperature programming.

2. Chromatography data system: Capable of electronic integration and processing the chromatographic data.

3. Gas chromatographic column (Packed): 1 percent high molecular weight compound of polyethylene glycol and a diepoxide reacted with nitroterephthalic acid on (60-80) mesh graphitized carbon with a nominal surface area of 100 square meters per gram in a 7.3 m [24 ft], 3.2 mm [1/8 in] OD stainless steel column. Prepacked columns are commercially available from multiple vendors.

4. Serum bottle: 125 mL, (Note: Bottle holds 160 mL when liquid full).

5. Crimp seal with 20 mm Septa.

6. Glass collecting tube: 125 mL (Enlarge side outlet opening to accommodate a crimp-on 2 cm septum. Apply fiberglass tape outside for protection).

7. Syringe, 10 µL, liquid.

8. R-11 and impurities for calibration standard preparation: CCl_4, $CHCl_3$, CH_2Cl_2 and trichloroethylene (TCE) and all other fluorochemicals are commercially available.

Note: The purity of each calibration component must be predetermined by gas chromatography flame ionization detector (FID) and/or thermal conductivity detector (TCD) and, if necessary, by gas chromatography/mass spectroscopy (GC-MS).

Section C6-9. Procedure

9.1 *Chromatographic Operating Conditions.*

Detector	FID
Carrier gas	30 cc Helium per minute
Initial column temperature , ºC [ºF]	125 [257]
Initial hold	4 minutes
Program , ºC [ºF] per minute	10 [50]
Final column temperature, ºC [ºF]	180 [356]
Post hold	14 minutes
Detector temperature, ºC [ºF]	250 [482] [1]
Injector port temperature, ºC [ºF]	200 [392] [1]
Sample	1 µL (liquid syringe)[2]
Maximum safe column temperature, ºC [ºF]	225 [437] (for conditioning purposes)

Notes:

1. Condition may need to be optimized for specific gas chromatograph used.

2. Externally cool the syringe and sample to 10ºC [50ºF] before sampling.

9.2 *Calibration Standard, Preparation and Analysis.*

9.2.1 Obtain a stock of the highest purity R-11 available as evidenced by the chromatograms using the above procedure.

9.2.2 Determine the tare weight (to the nearest 0.01 g) of a 125 mL serum bottle with septum and cap loosely attached, then fill with stock R-11 to within about 5/8 inch of the top. Crimp-on the septum.

9.2.3 Reweigh and subtract the tare weight in 9.2.2 to obtain the grams of R-11 added.

Note: The purest R-11 will contain some of the impurities listed in Table C6-1. The ppm amounts of impurities already in the stock R-11 are determined via the Method of Standards addition. Individual impurity peak areas in the stock are increased in the calibration standard by the ppm amount of the corresponding impurity added. The ppm already present is combined with the ppm added to give the total ppm component present in the calibration standard.

9.2.4 Individually and in turn add the volumes of each calibration component indicated in Table C6-3 through the septum and below the R-11 liquid surface in the bottle. Use an appropriate sized mL gas tight syringe with a deflected point needle for gases and a liquid µL syringe for liquids. Shake the bottle to mix after addition of each component.

Note: To preserve the stock of calibration gases, it is suggested to load a small evacuated 125 mL gas collecting tube to 1 atm from the liquid phase as illustrated in Figure C6-1. The appropriate volume is then withdrawn and injected into the serum bottle containing the R-11. For impurities which are liquids at ambient temperature, inject the indicated µL volumes of each respective component into the serum bottle.

9.2.5 Total the mass added column and combine this weight with that of 9.2.3 to obtain the total weight (to the nearest 0.01 g) of calibration sample in the bottle.

9.2.6 Calculate the ppm added (to the nearest 1 ppm) for each component by dividing the mass added by the total weight of sample in the serum bottle (9.2.5).

9.2.7 Calculate the ppm present for each component by combining the ppm present in the stock R-11 (if any) and the ppm component added (refer to the Note in 9.2.3). The ppm component present values are those used for determining the method response factors.

9.2.8 Place the serum bottle standard in an ice bath and, after it is ice cold, remove it and immediately replace it with a new septum.

9.2.9 Write the ppm present values for each component on the label, date of preparation, gross weight and total grams of calibration sample. Store in a refrigerator. Discard and prepare a new standard when the sample weight falls below 60% of the original weight (refer to the Note in 9.2.4).

9.3 *Determination of Component Response Factors.*

Note: Depending upon the data system used, it is often more desirable to convert the ppm values to weight % for response factor calculations and for reporting purposes.

9.3.1 Set up the chromatography data system for an area normalization-response factor calibration.

9.3.2 Analyze the calibration standard bulb in triplicate using the chromatographic conditions described in 9.1.

9.3.3 Using R-11 as the reference peak, perform the necessary functions to have the integrator or the chromatography data system determine each component Relative Response Factor (RRF_i) which is then stored. Response Factors are calculated as follows:

$$ARF_i = \frac{\text{weight \% in calibration standard}}{\mathrm{A_i}}; \quad \text{C6.1}$$

$$ARF_{R-11} = \frac{100.0000 - S}{A_{R-11}} \quad \text{C6.2}$$

where:

ARF = Absolute Response Factor of component i
A_i = peak area of component i (average of 3 determinations)
S = weight % sum of all impurities present to four decimal places

Then, using R-11 as the reference peak the Relative Response Factor can now be determined:

$$\mathrm{RRF_i} = \frac{\mathrm{ARF_i}}{\mathrm{ARF_{R-11}}} \quad \text{C6.3}$$

RRF_i values are computed to the nearest 0.0001 unit.

9.4 *Sampling.* Submitted samples should be in either metal cylinders or in glass or plastic bottles such that the containers are at least 80% liquid full.

9.5 *Sample Analysis.* Analyze the sample using the chromatographic conditions described in 9.1. The sample and syringe are precooled (refrigerator, ice bath) to 10ºC [50ºF] before sampling. This is to simplify loading into the µL syringe. To identify an unknown peak, use component spiking and/or GC-MS (if available).

Note:

See example gas chromatograms in Appendix D.

9.6 *Calculations.*

9.6.1 The weight percentage of each component is calculated as follows:

$$\mathrm{W_i} = \frac{\mathrm{RRF_i \cdot A_i \cdot 100}}{\sum(\mathrm{A_i \cdot RRF_i})} \quad \text{C6.4}$$

where:

A_i = peak area of component i
RRF_i = Relative Response Factor for component i
W_i = weight percent of component i
$\sum(A_i \cdot RRF_i)$ = sum of all component peak areas times their respective Relative Response Factors

9.6.2 Report sample component concentrations to the nearest 0.0001% (or to the nearest 1 ppm).

Table C6-1. Retention Time Data for Identified Impurities Not Normally Observed	
Impurity	Retention Time (min)
R-32 [1] R-114 R-290	2.37 4.10 8.00

Note:

1. Coelutes with R-23. To separate, attach 0.30 m [1.0 ft] section of Porapak® T column to detector end of column and rechromatograph (R-23 elutes first).

Table C6-2. Component Statistical Parameters				
Component	Detection Limit, ppm	Range Investigated, ppm	Precision at 95% Confidence Limit, ppm	Relative Mean Error, %
R-23	2.0	15.0	0.37	-2.8
R-13	3.0	20.0	0.53	-3.1
R-152a	1.0	30.0	0.47	1.7
R-22	2.0	50.0	0.98	-0.8
R-115	2.0	30.0	0.80	0.7
R-12	2.0	60.0	1.10	1.1
R-133a	1.0	25.0	0.33	-2.5
R-21	2.0	30.0	0.67	1.2
R-30	2.0	25.0	0.33	-2.5
R-114	2.0	40.0	1.91	-2.7
R-123a	3.0	25.0	2.70	-4.8
R-123	2.0	50.0	1.33	3.3
R-20	2.0	25.0	0.73	0.7
R-113	2.0	60.0	2.31	2.2
R-10	2.0	25.0	1.70	-3.3
R-1120	2.0	25.0	1.77	1.8

Table C6-3. Primary Calibration Standard Components

Component	Molecular Weight	Volume Added	Mass Added[1], µg	Added[2] Concentration, ppm	Total Concentration Present[3], ppm
R-23[4]	70.0	1.2 mL	3436.0	15.0	
R-13[4]	105.0	1.0 mL	4274.0	19.0	
R-152a[4]	66.0	2.5 mL	6748.0	30.0	
R-22[4]	86.0	3.2 mL	11321.0	50.0	
R-115[4]	136.0	1.2 mL	6650.0	29.0	
R-12[4]	121.0	2.8 mL	13845.0	61.0	
R-133a[4]	118.0	1.1 mL	5332.0	24.0	
R-21[4]	103.0	1.6 mL	6740.0	30.0	
R-30	85.0	5.0 µL	6680.0	29.0	
R-114[4]	170.0	1.3 mL	9061.0	40.0	
R-123a	153.0	5.0 µL	7490.0	33.0	
R-123	153.0	10.0 µL	14750.0	64.0	
R-20	120.0	5.0 µL	7445.0	33.0	
R-113	188.0	10.0 µL	15650.0	68.0	
R-10	154.0	10.0 µL	15950.0	70.0	
R-1120	132.0	5.0 µL	7278.0	32.0	

Notes:

1. If necessary, correct the mass added for the purity of the calibration component previously established.
2. Values shown are for illustration; exact values are determined at 9.2.6.
3. Column to be filled in (9.2.7) after determining ppm present in stock R-11 (see the Note in 9.2.3).
4. These impurities are gases at ambient room temperature; the others are liquids with low boiling points.

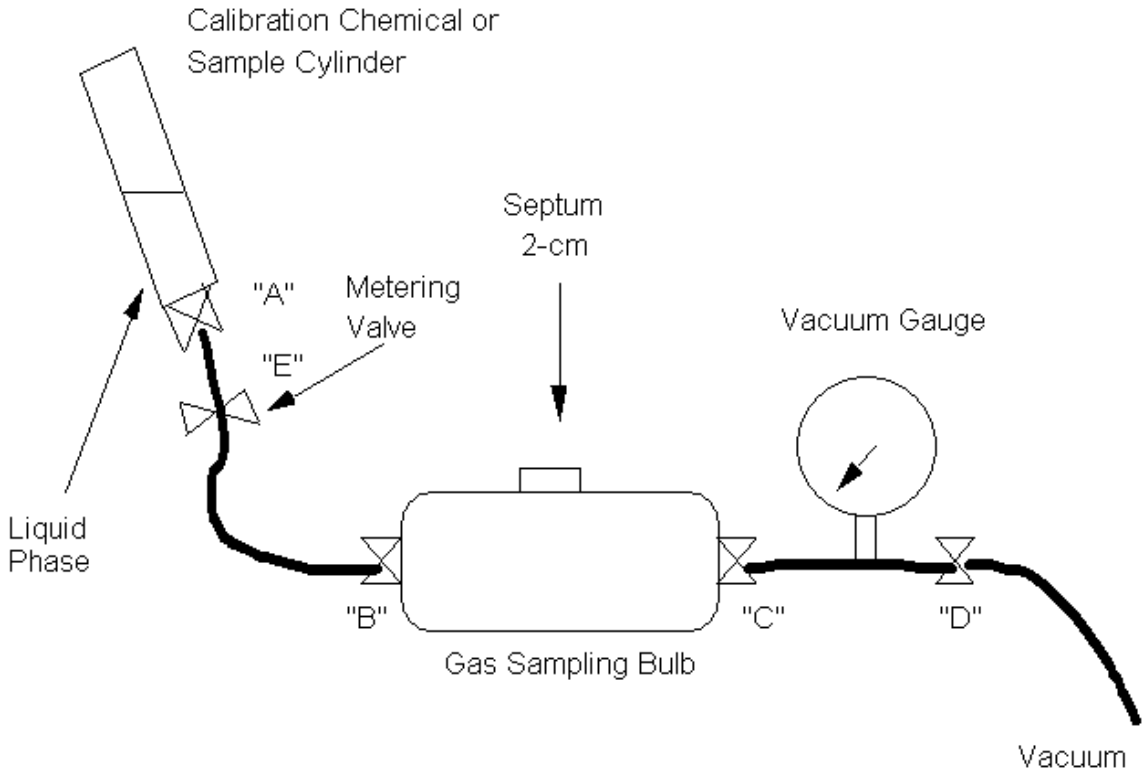


Figure C6-1. Apparatus Used for Calibration Standard Preparation

PART 7

DETERMINATION OF PURITY OF NEW AND RECLAIMED R-12, R-13, R-22, R-23, R-114, R-115, R-116, R-124, R-125, R-143a, R-152a, R-218, R-290, R-600 and R-600a BY PACKED COLUMN GAS CHROMATOGRAPHY

Section C7-1. Purpose

The purpose of this test method is to determine the purity of new and reclaimed R-12, R-13, R-22, R-23, R-114, R-115, R-116, R-124, R-125, R-143a, R-152a, R-218, R-290, R-600 and R-600a by gas chromatography.

Section C7-2. Scope

This test method is for use with new and reclaimed R-12, R-13, R-22, R-23, R-114, R-115, R-116, R-124, R-125, R-143a, R-152a, R-218, R-290, R-600 and R-600a.

Note: R-290, R-600 and R-600a are included because they are components of some fluorocarbon blends.

Section C7-3. Definitions

Definitions for this part are identical to those of ARI Standards 700 and 740.

Section C7-4. Principle

The purity of refrigerants is determined by gas chromatography using a packed column with a liquid phase coated onto a solid support. Separated components are detected using a flame ionization detector (FID) or thermal conductivity detector (TCD). The peak areas from the detector are measured with a data system capable of electronic integration, and component concentrations are quantified by the area normalization response factor method.

Section C7-5. Applicability

This method is applicable to the routine gas chromatographic determination of new and reclaimed R-12, R-13, R-22, R-23, R-114, R-115, R-116, R-124, R-125, R-143a, R-152a, R-218, R-290, R-600 and R-600a.

Section C7-6. Limitations and Interferences

This method is calibrated only for impurities typically found in new and reclaimed refrigerant. Any impurity which elutes within the matrix of the major component will interfere if present in significant concentration.

Section C7-7. Sensitivity, Precision, and Accuracy

The detection limit (DL), 95% confidence limits (95% CL), and accuracy (Relative Mean Error, RME) were established for single operator. Statistical parameters for each impurity are listed in Table C7-2. The data was calculated from seven replicate analyses from one sample of an R-12 calibration standard performed by one technician over a period of one day.

Section C7-8. Special Apparatus and Reagents

1. Gas chromatograph: Equipped with a packed column injector, flame ionization detector (FID) and/or thermal conductivity detector (TCD), and capable of oven temperature programming

2. Chromatography data system: Capable of electronic integration and processing the chromatographic data. The data system must be configured to capture peak areas enabling measurement of peaks greater than or equal to 0.001% by weight. Peaks that are not identified by the data system should be given a default response factor that is the greater of the average response factors for the calibrated components or R-22. If the peak is identified, then it shall be quantified using its measured response factor

3. Gas chromatographic column (Packed): 1 percent high molecular weight compounds of polyethylene glycol and a diepoxide reacted with nitroterephthalic acid on (60-80) mesh graphitized carbon with a nominal surface area of 100 square meters per gram in a 7.3 m [24 ft], 3.20 mm [0.125 in.] OD stainless steel column. Prepacked columns are commercially available from multiple vendors

4. Glass collecting tubes: 125 mL and 500 mL. (Enlarge side outlet opening to accommodate a crimp-on 2 cm septum. Apply fiberglass tape to the outside for protection)

5. Syringe, 1 mL, gas tight

6. Deflected point needle: Standard hub 22 gage x 1-1/2 inch stainless steel

7. Impurities for calibration standard preparation: These impurities are commercially available

Section C7-9. Procedure

9.1 *Chromatographic Operating Conditions.*

Table C7-1. GC Operating Conditions

Condition	R-12, R-22, R-114, R-115, R-116, R-124, R-125, R-143a, R-152a, R-218, R-290, R-600 & R-600a	R-13	R-23
Detector	FID	TCD	TCD
Detector temperature, °C [ºF] [1]	200 [392]	200 [392]	200 [392]
Injection port temperature, °C [ºF] [1]	200 [392]	200 [392]	200 [392]
Carrier gas, cc Helium per minute	20 [68]	20 [68]	20 [68]
Sample size, mL (gas syringe) [1]	0.5	0.5	0.5
Initial column temperature, °C [ºF]	50 [122]	40 [104]	35 [95]
Initial hold, min	6	6	4
Program, °C/min [°F/min]	10 [50]	10 [50]	10 [50]
Final column temperature, °C [ºF]	175 [347]	160 [320]	125 [257]
Post hold, min	15	6	4
Maximum column temperature, °C [ºF]	225 [437] (conditioning purposes only)		

Note:

1. Condition may need to be optimized for specific GC used.

9.2 *Example - Primary Calibration Standard, Preparation and Analysis for R-12.*

Note:

Modify procedure for other refrigerants as necessary.

9.2.1 Determine the internal volume of a 500 mL gas bulb by weighing the bulb empty, then filled to maximum capacity with water. Record the grams of water as mL volume capacity on the outside of the bulb (to the nearest 1.0 mL). Thoroughly dry the inside of the gas bulb then crimp-on the septum.

9.2.2 Assemble the apparatus as illustrated in Figure C7-1.

9.2.3 Attach a cylinder of high purity stock refrigerant to the gas sampling bulb.

Note: The purest stock refrigerant will contain some of the impurities found in the method. The ppm amounts of impurities already in the stock refrigerant are determined via the Method of Standards addition. Individual impurity peak areas in the stock refrigerant are increased in the calibration standard by the ppm amount of the corresponding impurity added. The ppm already present is combined with the ppm added to give the total ppm component present in the calibration standard.

9.2.4 With valve "A" closed, open all other valves and evacuate to less than 100 microns of Hg pressure [0.013 kPa].

9.2.5 Close valve "D" and monitor the gauge for several minutes to insure the system is not leaking.

9.2.6 Close metering valve "E", open valve "A", and then slowly open valve "E" and flash liquid phase stock refrigerant to bring the system to 1 atmosphere pressure. Close valve "A".

9.2.7 Repeat 9.2.4 through 9.2.6.

9.2.8 Close valves "B" and "C" and remove the bulb from the vacuum/sampling apparatus.

9.2.9 Calculate the grams of the stock refrigerant added to the bulb as follows:

$$\text{grams added} = \frac{MW_{ref} \cdot \text{internal volume of bulb (mL)}}{24{,}450} \qquad \text{C7.1}$$

where:

MW_{ref} = molecular weight of the stock refrigerant in g/mole
24,450 = volume (mL) occupied by 1 mole of refrigerant at 25°C [77°F] and at 1 atm

9.2.10 Individually, and in turn, add the volumes of each calibration impurity component of interest indicated in Table C7-3 to the calibration bulb. Use an appropriate sized µL or mL gas tight syringe with a deflected point needle.

Note: To preserve the stock of calibration component, it is suggested to load a small, evacuated 125 mL gas collecting tube to 1 atm from the liquid phase as illustrated in Figure C7-1. The appropriate volume is then withdrawn and injected into the 500 mL calibration bulb.

9.2.11 Preparing a vapor phase standard by weighing the components into the gas bulb is an acceptable alternate for 9.2.10.

9.2.12 Into a 30 mL (37 mL filled) serum bottle, capped and crimped with a septum, add the exact volumes of the liquid impurities from Table C7-3 in the order given. Add by syringe injection through the septum using a 22 gage needle (or smaller) as a vent. After addition, shake bottle vigorously to mix. Label, date and store in a refrigerator.

Note: For calibration components that have boiling points near or slightly above ambient temperature, cool the material and syringe to 10°C [50°F] before transferring.

9.2.13 Refer to Figure C7-1. Evacuate a 125 mL bulb (internal volume premeasured) and fill to 1 atm with refrigerant stock.

9.2.14 Accurately withdraw and inject exactly 5.0 µL of solution from the 30 mL serum bottle into the 125 mL bulb. Allow to equilibrate for 30 minutes.

9.2.15 Using a 5 mL gas tight syringe, withdraw vapor from the 125 mL bulb and inject exactly 5.0 mL into the 500 mL calibration bulb. The mass of each component thus added is calculated as follows and is added to column four of Table C7-3:

$$m = \frac{V_w \cdot 25{,}000}{V \cdot A} \qquad \text{C7.2}$$

where:

25,000	= dilution ratio
A	= internal mL of 125 mL bulb
m	= mass added, µg
V	= total mL of solution from 9.2.12
V_w	= Volume added, mL, from Table C7-3

9.3 *Determination of Component Response Factors.*

Note: Depending upon the data integration system used, it is often more desirable to convert the ppm values to weight % for response factor calculations and for reporting purposes.

9.3.1 Set up the chromatography data system for an area normalization response factor calibration.

9.3.2 Analyze the calibration standard gas bulb in triplicate using the chromatographic conditions described in 9.1.

9.3.3 Perform the necessary functions to have the data system determine each component response factor which is then stored.

9.3.4 Response Factors for each component are calculated as follows:

$$ARF_i = \frac{\text{weight \%}_i \text{ in calibration standard}}{A_i}; \quad \text{C7.3}$$

$$ARF_r = \frac{100.0000 - S}{A_r} \quad \text{C7.4}$$

where:

A_i	= peak area of component i
A_r	= peak area of major refrigerant
ARF_i	= Absolute Response Factor of component i
ARF_r	= Absolute Response Factor of the major refrigerant
S	= weight % sum of all impurities present

Then using the major refrigerant (r) as the reference peak, the Relative Response Factor can now be determined:

$$RRF_i = \frac{ARF_i}{ARF_r} \quad \text{C7.5}$$

The weight percentage of each component is calculated as follows:

$$W_i = \frac{RRF_i \cdot A_i \cdot 100}{\Sigma(A_i \cdot RRF_i)} \quad \text{C7.6}$$

where:

A_i = peak area of component i
RRF_i = Relative Response Factor for component i
W_i = weight percent of component i
$\sum(A_i \cdot RRF_i)$ = sum of all component peak areas times their respective Relative Response Factors

9.4 *Sampling*.

Submitted sample cylinders must contain sufficient liquid phase (80% liquid full is recommended) for analysis.

Note: Special Handling for Low Critical Temperature Refrigerants R-13, R-23, and R-116 - A vapor phase sample is required to determine non-condensables and volatile impurities, including other refrigerants. The vapor phase sample is obtained by regulating the sample container temperature to 5°C or more above the refrigerant critical temperature. Critical temperatures - R-13 = 28.8°C [83.9°F], R-23 = 25.9°C [78.6°F], and R-116 = 19.7°C [67.5°F].

9.5 *Sample Analysis.*

*A*nalyze the sample using the chromatographic conditions described in 9.1. Load the sample injection device by slowly and completely vaporizing the liquid phase. For example, by bubbling the vapor into water through Tygon® tubing and then puncturing the tubing with the syringe needle. An alternative apparatus for vaporizing liquid sample into a glass gas sample bulb allowing repeat injections of the same sample is shown in Figure C7-1.

Note:

See example gas chromatograms in Appendix D.

9.6 *Calculations.*

9.6.1 The weight percentage of each component is calculated as follows:

$$W_i = \frac{RRF_i \cdot A_i \cdot 100}{\sum (A_i \cdot RRF_i)} \qquad \text{C7.7}$$

where:

A_i = peak area of component i
RRF_i = Relative Response Factor for component i
W_i = weight percent of component i
$\sum(A_i \cdot RRF_i)$ = sum of all component peak areas times their respective Relative Response Factors

9.6.2 Report sample component concentrations to the nearest 0.01%.

Table C7-2. Component Statistical Parameters				
Component	Detection Limit, ppm	Concentration Range Investigated, ppm	Concentration Precision at 95% Confidence Limit, ppm	Relative Mean Error, %
Methane	1.0	5	0.07	4.0
R-23	2.0	25	0.54	-2.3
R-1150 (C_2H_4)	1.0	5	0.13	-5.6
R-170 (C_2H_6)	1.0	5	0.10	-4.1
R-13	3.0	30	0.47	-3.8
R-143a	1.0	25	0.30	3.3
R-152a	1.0	30	0.63	1.7
R-40	1.0	20	0.37	2.3
R-134a	1.0	45	0.27	-3.3
R-22	2.0	65	1.75	2.7
R-1170 (C_3H_6)	1.0	5	0.10	3.4
R-115	2.0	115	1.67	1.8
R-142b	1.0	20	0.23	-1.3
R-124	1.0	25	0.37	1.8
R-133a	1.0	35	0.23	1.8
R-21	2.0	50	0.83	1.8
R-600a	1.0	20	0.23	-2.8
R-114	2.0	50	0.83	2.0
R-600	1.0	20	0.18	-3.3
2-butene-T	1.0	5	0.06	-3.8
R-11	4.0	40	0.87	1.1
R-123	2.0	35	1.05	-4.7
2-butanol	2.0	20	0.33	1.6
MEK	2.0	25	0.47	-2.3
R-113	2.0	30	0.87	-4.0
n-pentane	1.0	5	0.25	-3.7

Table C7-3. Primary Calibration Standard Components

Component	Molecular Weight	Volume Added, µL	Mass Added[1], µg	Added[2] Concentration, ppm	Total Concentration Present[3], ppm
Methane	16	20	13.1	5	
R-23	70	22	63.0	23	
C_2H_4	28	12	13.7	5	
C_2H_6	30	11	13.5	5	
R-13	104	20	85.4	31	
R-143a	84	20	68.8	25	
R-152a	66	30	81.0	30	
R-40	50	28	57.8	21	
R-134a	102	30	125.1	46	
R-22	86	50	176.9	64	
C_3H_6	42	8	13.7	5	
R-115	154	50	315.9	115	
R-142b	100	15	61.7	22	
R-124	136	12	67.0	24	
R-133a	118	20	97.0	35	
R-21	103	32	134.7	49	
isobutane	58	25	59.3	22	
R-114	170	20	139.8	51	
n-butane	58	25	59.3	22	
2-butene_T	56	6	13.7	5	
R-11[4]	137	-	-[5]	57	
R-123[4]	153	-	-[5]	38	
MEK[4]	72	-	-[5]	17	
R-113[4]	188	-	-[5]	27	
2-butanol[4]	74	-	-[5]	21	
n-pentane[4]	72	-	-[5]	5	

Notes:

1. If necessary, correct the mass added for the purity of the calibration component previously established.
2. Values shown are for illustration; exact values are determined in 9.2.10.
3. Column to be filled in after determining ppm present in stock R-12 (refer to the Note in 9.2.3).
4. These components are liquids at ambient laboratory temperature and are added to the 500 mL bulb as described in 9.2.12 through 9.2.15.
5. From 9.2.15.

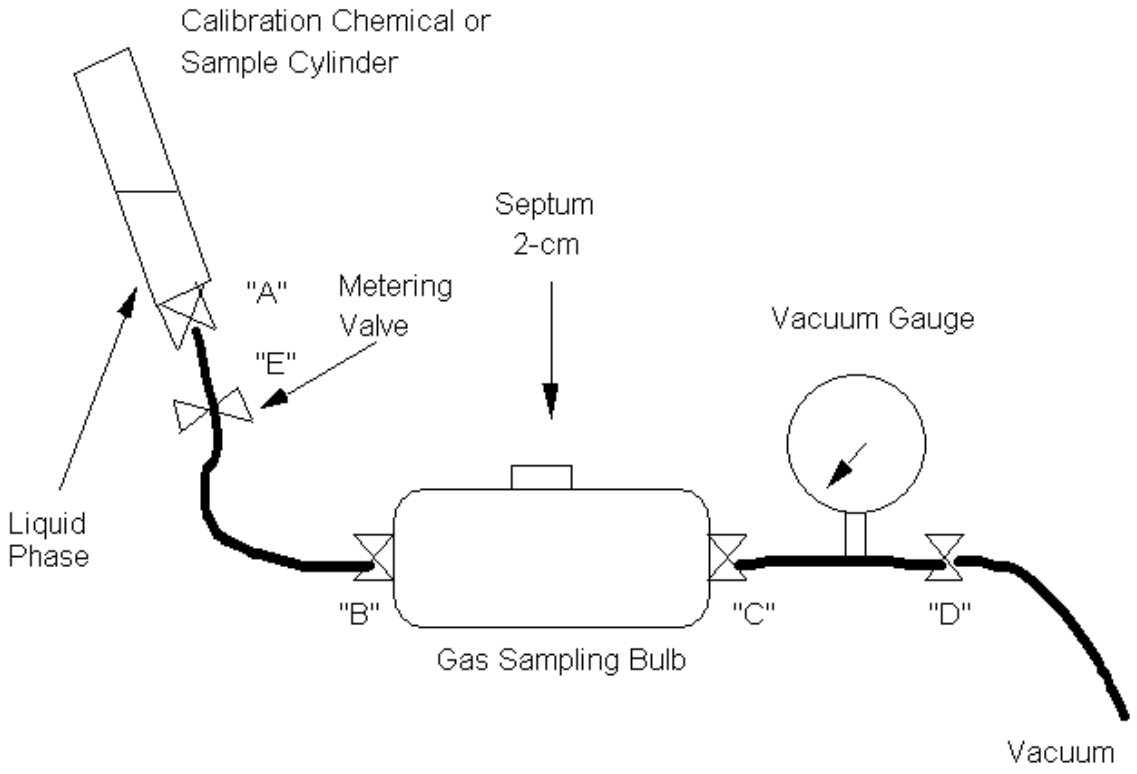


Figure C7-1. Apparatus Used for Calibration Standard Preparation and for Cylinder Sampling

PART 8

DETERMINATION OF PURITY OF NEW AND RECLAIMED R-123 BY CAPILLARY AND PACKED COLUMN GAS CHROMATOGRAPHY

Section C8-1. Purpose

The purpose of this test method is to determine the purity of new and reclaimed 1,1-dichloro-2,2,2-trifluoroethane (R-123) by gas chromatography.

Section C8-2. Scope

This test method is for use with R-123.

Section C8-3. Definitions

Definitions for this part are identical to those of ARI Standards 700 and 740.

Section C8-4. Principle

The organic purity of new and reclaimed R-123 is determined by programmed temperature subambient capillary column gas chromatography, and the R-123 and R-113 isomers determined isothermally using a packed column. Component peak areas are integrated electronically and quantified by the area normalization response factor method.

Section C8-5. Applicability

This method is applicable to the determination of the impurities typically present in commercially manufactured R-123. Although not yet studied at this time, the impurities profile in reclaimed R-123 is expected (more or less) to be similar to that of the new product.

Section C8-6. Limitations and Interferences

This method is calibrated for only those impurities commonly present in R-123 from commercial sources. Other impurities which have been detected on occasion are listed (with retention times) in Table C8-2. The method will not detect any impurity which may elute within the comparatively large R-123 peak matrix on either column.

Section C8-7. Sensitivity, Precision and Accuracy

Statistical parameters for each impurity are listed in Table C8-1. The data was obtained by analyzing an R-123 calibration mixture seven times during one day by one operator.

Section C8-8. Special Apparatus and Reagents

1. Gas chromatograph: Equipped with a flame ionization detector (FID), capillary column split injector, subambient (liquid nitrogen) cooling valve, and packed column capability.

2. Chromatography data system: Capable of electronic integration and processing the chromatographic data.

3. Gas chromatographic column (Packed): One percent high molecular weight compounds of polyethylene glycol and a diepoxide reacted with nitroterephthalic acid on (60-80) mesh graphitized carbon with a nominal surface area of 100 square meters per gram in a 7.3 m [24 ft], 3.20 mm [0.125 in] OD stainless steel column. Prepacked columns are commercially available from multiple vendors.

4. Gas chromatographic column (Capillary): 210 m (connect the two columns below together with the 1st column end attached to the injection port):

   a. 105 m 14 % cyanopropylphenyl-86% methylpolysiloxane, 0.25 mm, 1µm.

   b. 105 m 5 % diphenyl-95% dimethyl polysiloxane, 0.32 mm, 1µm.

5. Glass collecting tube: 125 mL. (Enlarge side outlet opening to accommodate a crimp-on 2 cm septum. Apply fiberglass tape outside for protection).

6. Syringe, 10 µL, liquid.

7. Serum bottle: 125 mL (Note: bottle holds 160 mL when liquid full).

8. R-123 and impurities for calibration standard preparation are commercially available.

Note: The purity of each calibration component must be predetermined by gas chromatography flame ionization detector (FID) and/or thermal conductivity detector (TCD) and, if necessary, by gas chromatography/mass spectroscopy (GC-MS).

Section C8-9. Procedure

9.1 *Chromatographic Operating Conditions, Packed Column.*

Detector	FID
Carrier gas	40 cc Helium per minute
Column temperature, °C [°F]	125 [257] Isothermal
Detector temperature, °C [°F]	250 [482] [1]
Injector port temperature, °C [°F]	150 [302] [1]
Sample	2 µL[2]
Maximum safe column temperature, °C [°F]	225 [437] (for conditioning purposes)

Notes:

1. Condition may need to be optimized for specific GC used.

2. Externally cool the syringe and sample to 10°C [50°F] before sampling.

9.2 *Chromatographic Operating Conditions, Capillary Column.*

Detector	FID
Carrier gas	approximately 1.4 cc Helium per minute
Split flow	40:1
Injector port temperature, °C [°F]	200 [392] [1]
Detector temperature	200 [392] [1]
Sample	2 µL[2]
Initial column temperature, °C [°F]	0 [32] (subambient, liquid N_2)
Initial hold	21 minutes
Program, °C [°F] per minute	15 [59]
Final temperature, °C [°F]	165 [329]
Post hold	18 minutes

Notes:

1. Condition may need to be optimized for specific GC used.

2. Externally cool the syringe and sample to 10°C [50°F] before sampling.

9.3 *Calibration Standard, Preparation and Analysis.*

9.3.1 Obtain a stock of the highest purity R-123 available as evidenced by the chromatograms using the above procedures.

Note: In order to accurately calibrate for R-1112a, select a stock R-123 which does not contain any detectable R-114aB1. The purest R-123, however, will contain some of the impurities listed in Table C8-1 in low concentrations. Individual impurity peak areas in the stock R-123 are increased in the calibration standard by the ppm amount of the corresponding impurity added. The amounts in the stock are thereby determined by the Method of Standards Addition. The ppm amount present (if any) is combined with the ppm added to give the total ppm component present in the calibration standard.

9.3.2 Determine the tare weight (to the nearest 0.0001 g) with a 125 mL serum bottle with septum and cap loosely attached; then fill with stock R-123 to within 5/8 inch of the top. Crimp-on the septum.

9.3.3 Reweigh and subtract the tare weight in 9.3.2 to obtain the grams of R-123 added.

9.3.4 Individually and in turn add the volumes of each calibration component indicated in Table C8-3 through the septum and below the R-123 liquid surface in the bottle. Use an appropriate sized µL or mL gas tight syringe with a deflected point needle. Shake the bottle to mix after addition of each component.

Note: To preserve the stock of calibration component which are gases, it is suggested to load a small evacuated 125 mL gas collecting tube to 1 atm. from the liquid phase of the gas as illustrated in Figure C8-1. The appropriate volume is then withdrawn and injected into the serum bottle containing the R-123.

9.3.5 Total the mass added to the bottle and combine this weight with that of 9.3.3 to obtain the total weight (to the nearest 0.0001 g) of calibration sample in the bottle.

9.3.6 Calculate the ppm added (to the nearest 1 ppm) for each component by dividing the mass added by the total weight of sample in the serum bottle (9.3.5).

9.3.7 Calculate the ppm present for each component by combining the ppm present in the stock R-123 (if any) to the ppm component added (refer to Note in 9.3.1 above and note below). The ppm component present values are those used for determining the method response factors.

Note: The concentration of R-123a in the stock is determined separately by the Method of Standards Addition (adding percent amounts of R-123a to the stock R-123 and chromatographing as in 9.1). The calculated RRF_{R-123a} value is also assigned to the R-123b isomer, as R-123b is not commercially available for separate calibration. The amounts present are added to Table C8-3; the R-123a isomer shown as percent present.

9.3.8 Write the ppm present values for each component on the label, date of preparation, gross weight and total grams of calibration sample. Store in a refrigerator. Discard and prepare a new standard when the sample weight falls below 60% of the original weight.

9.4 *Determination of Component Response Factors.*

9.4.1 Set up the chromatography data system for an external standard area normalization calibration.

9.4.2 Analyze the calibration standard solution in triplicate using the chromatographic conditions described in 9.1 and in 9.2.

9.4.3 Using R-123 as the reference peak, perform the necessary functions to have the integrator determine each component Relative Response Factor (RRF_i) which is then stored. Response Factors are calculated as follows:

$$ARF_i = \frac{\text{weight\%}_i \text{ in calibration standard}}{A_i} \quad \text{C8.1}$$

$$ARF_{R-123} = \frac{100.0000 - S}{A_{R-123}} \quad \text{C8.2}$$

where:

A_i = peak area of component i (average of 3 determinations)
ARF_i = Absolute Response Factor of component i
S = weight % sum of all impurities present to ppm levels

Then, using R-123 as the reference peak the Relative Response Factor can be calculated:

$$RRF_i = \frac{ARF_i}{ARF_{R-123}} \quad \text{C8.3}$$

RRF_i values are computed to the nearest 0.0001 unit.

9.5 *Sampling.* Submitted samples should be in either metal cylinders or in glass bottles such that the containers are at least 80% liquid full.

9.6 *Sample Analysis.* Analyze the sample using the chromatographic conditions described in 9.1 and in 9.2. The sample and syringe are precooled in a refrigerator to 10°C [50°F] before sampling. This is to simplify loading liquid sample into the µL syringe. By spiking components and/or doing GC-MS (if available) unidentified peaks can be identified. Use the Effective Carbon Number (ECN) wherever

applicable to estimate the concentration of any identified components not in the calibration table (see Table C8-2).

Note:

See example gas chromatograms in Appendix D.

9.6.1 *Check for Presence of R-114aB1.* The capillary column procedure will not resolve R-1112a and (if present) R-114aB1. Normally, if the R-114B1 peak is small or absent, then R-114aB1 will not be present. To resolve R-1112a and R-114aB1, the sample is rechromatographed exactly as in 9.2 except the column initial temperature is 40°C [104°F]. The higher starting temperature resolves the R-114B1, R-114aB1 and R-1112a into a triplet in the order given with 0.12 minutes separation between the three peaks. In the absence of R-114aB1, the peak separation between R-114B1 and R-1112a remains at 0.25 minutes. Use the ECN Method (Table C8-2) to estimate the amount of R-114aB1 present.

9.6.2 *Check for R-122 Isomers.* If R-122 isomers are suspected to be present, extend the capillary column procedure post hold an additional 15 minutes (see Table C8-2).

9.7 *Calculations.*

9.7.1 The weight percentage of each component is calculated as follows

$$W_i = \frac{RRF_i \cdot A_i \cdot 100}{\sum (A_i \cdot RRF_i)} \qquad \text{C8.4}$$

where:

A_i = peak area of component i
RRF_i = Relative Response Factor for component i
W_i = weight percent of component i
$\sum(A_i \cdot RRF_i)$ = sum of all component peak areas times their respective Relative Response Factors

9.7.2 Report sample component concentrations to the nearest 0.0001% (or to the nearest 1 ppm).

Table C8-1. Component Statistical Parameters

Component	Effective Carbon Number (ECN)[1]	Detection Limit, ppm	Range Investigated, ppm	Precision at 95% Confidence Limit, ppm[3]	Relative Mean Error, %
R-1113	1.69	1	25	0.37	0.95
R-12	0.35	3	25	0.37	-1.1
R-22	0.40	2	25	0.24	1.4
R-114	1.04	2	50	1.20	-2.1
R-1317mx	3.63	1	30	0.88	4.3 [2]
R-31	0.92	1	10	0.52	2.2
R-216ba	2.16	1	20	0.67	-1.8
R-1326mxz	3.65	1	15	0.33	0.70
R-133a	1.93	1	40	0.67	1.9
R-114B1	0.95	2	50	0.80	2.4
R-1112a	1.64	1	25	0.30	-0.70
R-1112	1.64	1	15	0.27	-0.50
R-123a	1.84	2	50,000	1300	0.30
R-123b	1.80	2	400	12.7	--
R-11	0.43	3	60	2.20	1.8
R-30	0.63	2	50	1.10	0.30
R-113	1.60	3	300	7.30	-0.20
R-113a	1.68	3	250	7.00	-0.15
R-1111	1.90	2	15	0.67	0.80

Notes:

1. Effective Carbon Numbers (ECN) determined experimentally or estimated. Refer to scientific literature on ECN.
2. Combining both isomers
3. Intra-lab, multiple operator

Table C8-2. Additional Impurities Observed in R-123, Quantitation by Effective Carbon Number Method

Impurity	Capillary Column Retention Times (min)	Effective Carbon Number (ECN)[1]
R-1132	9.18	2.00
R-125	9.46	0.79
R-134a	9.80	1.67
R-114a	11.22	1.17
R-124a	11.56	1.27
R-1122	11.57	1.76
R-124	11.77	1.33
R-E328lcc ether[2]	14.59	3.90
R-114aB1	15.00	0.80
R-141b	19.90	2.00
R-1121	23.00	1.75
R-132b	25.35	1.90
R-1130-T	25.64	2.25
R-123B1	28.72	1.70
R-122b	36.28	1.75
R-122a	37.24	1.75
R-122	38.00	1.76
R-112a	43.55	1.48

Notes:

1. Effective Carbon Numbers (ECN) determined experimentally or estimated. Refer to scientific literature on ECN.

   Quantitation by ECN Method

   Select a nearby peak in the chromatogram whose identification and response factor (RF) have been established (the Internal Standard).

   Then:

$$\frac{RF_i}{RF_r} = \frac{ECN_r}{ECN_i} = \frac{MW_i}{MW_r} \qquad \text{C8.5}$$

   where:

   RF = either absolute or Relative Response Factor
   MW_i = molecular weight of the component to be determined
   MW_r = molecular weight of the Internal Standard reference peak

2. Structure tentatively identified as: $CHClF\text{-}CF_2\text{-}O\text{-}CF_2\text{-}CF_3$

Table C8-3. Primary Calibration Standard Components

Component	Molecular Weight	Volume Added, µL	Mass Added[1], µg	Added[2] Concentration, ppm	Total Concentration Present[3], ppm
R-1113	116	1.00	4765	22	
R-12	121	1.00	4946	23	
R-22	86	1.50	5307	24	
R-114	170	1.50	10454	48	
R-1317mx[6]	216	6.0	9289	41[6]	
R-31	68	0.75	2101	10	
R-216ba[5]	221	0.50	4517	21	
R-1326mxz	198	0.40	3270	15	
R-133a	118	1.80	8720	40	
R-114B1[4]	215	6.0	11109	49	
R-1112a	133	1.00	5450	25	
R-1112	133	0.50	2725	13	
R-123a	153	-[7]	-[7]	1000-70,000	
R-123b	153	-[7]	-[7]	200-700	
R-11[4]	137	10.0	14869	65	
R-30[4]	85	10.0	13360	59	
R-113[4]	188	50	78795	361	
R-113a[4]	188	50	78986	362	
R-1111[4]	149	6.0	9279	41	

Notes:

1. If necessary, correct the mass added for the purity of the calibration component previously established.
2. Values shown are for illustration; exact values are determined at 9.3.6.
3. Column to be completed (9.3.7) after determining ppm present in stock R-123 (see Notes in 9.3.1 and 9.3.7).
4. Add by syringe injection of the liquid
5. Although other R-216 isomers comprise the usual R-216 peak multiplet, the R-216ba isomer (available) is used for calibration purposes.
6. The R-1317mx will resolve into the cis and trans isomer peaks with a ratio of 1:2 respectively.
7. Refer to note in 9.3.7

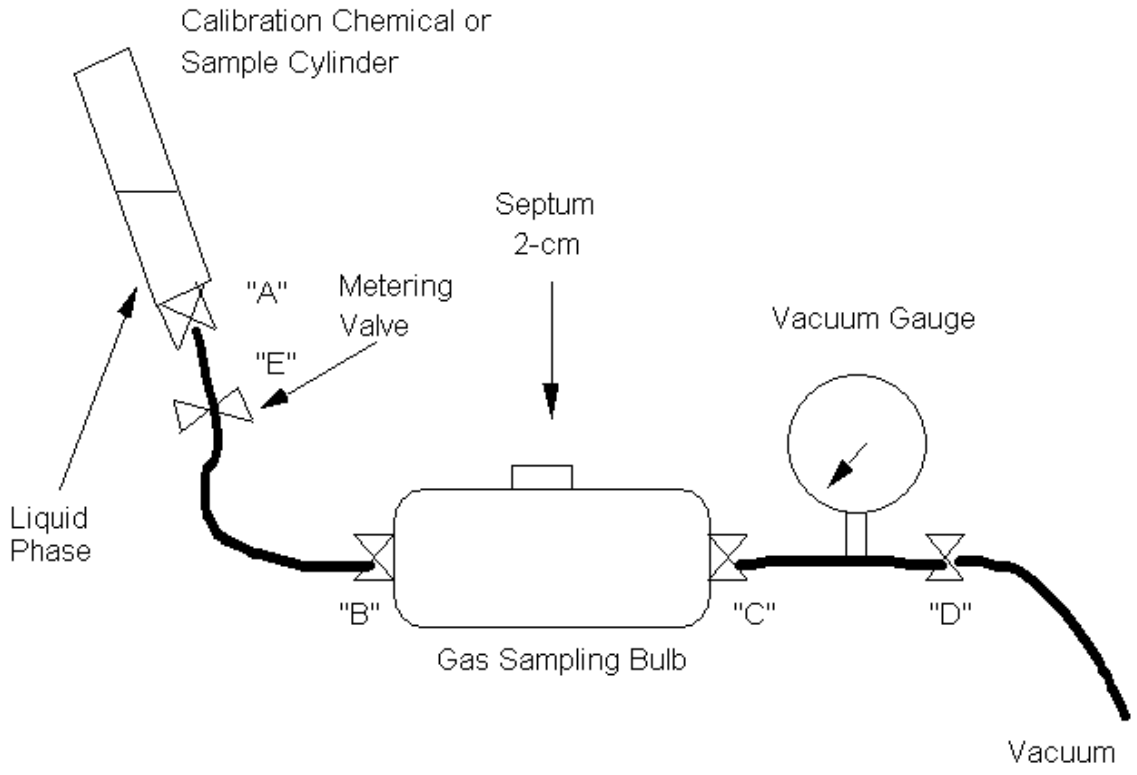


Figure C8-1. Apparatus Used for Calibration Standard Preparation

PART 9

DETERMINATION OF PURITY OF NEW AND RECLAIMED R-22, R-32, R-113, R-134a, R-141b, R-142b, and R-245fa BY CAPILLARY COLUMN GAS CHROMATOGRAPHY

Section C9-1. Purpose

The purpose of this test method is to determine the purity of new and reclaimed R-22, R-32, R-113, R-134a, R-141b, R-142b, and R-245fa, by gas chromatography.

Section C9-2. Scope

This test method is for use with R-22, R-32, R-113, R-134a, R-141b, R-142b, and R-245fa.

Section C9-3. Definitions

Definitions for this part are identical to those of ARI Standards 700 and 740.

Section C9-4. Principle

The organic purity of new and reclaimed R-22, R-32, R-113, R-134a, R-141b, R-142b, and R-245fa is determined by programmed temperature gas chromatography using capillary columns with a flame ionization detector (FID). A capillary column procedure is used because some of the impurities are not resolved by the packed column method. For R-22, because it obscures R-31 on the packed column method (Part 7), R-31 is determined separately by this capillary method. Component peak areas are integrated electronically and quantified by the area normalization response factor method.

Section C9-5. Applicability

This method is generally applicable to the determination of the impurities typically present in commercially manufactured and reclaimed R-22, R-32, R-113, R-134a, R-141b, R-142b, and R-245fa.

Section C9-6. Limitations and Interferences

This method is calibrated for only those impurities commonly present in R-22, R-32, R-113, R-134a, R-141b, R-142b, and R-245fa. Any impurity which elutes within the matrix of the major component will interfere if present in significant concentration. Other impurities that have been detected on occasion are listed (with retention times) in Table C9-1.

Section C9-7. Sensitivity, Precision and Accuracy

Statistical parameters for each impurity are listed in Table C9-2. The data was obtained by analyzing an R-134a calibration standard mixture seven times during one day by one operator.

Section C9-8. Special Apparatus and Reagents

1. Gas chromatograph: Equipped with a FID, capillary column split injector, subambient cooling valve (liquid N_2), and packed column capability

2. Chromatography data system: Capable of electronic integration and processing chromatographic data

3. Gas chromatographic column (Capillary): 135 m x 0.25 mm, 1 µm df, 6% cyanopropylphenyl- 94 % dimethyl polysiloxane

4. Glass collecting tubes: 125 mL and 500 mL. (Enlarge side outlet opening to accommodate a crimp-on 2 cm septum. Apply fiberglass tape outside for protection)

5. Steel cylinder: 1 L, with a single 9 gauge valve

6. Syringe, 1 mL, gas tight

7. Deflected point needle: Standard hub 22 gage x 1-1/2 inch stainless steel

8. Swivel union: 1/4 inch female flare x 1/4 inch female flare

9. R-134a and impurities for calibration standard preparation. The identified impurities R-1336mzz and R-1234yf are not commercially available

   Note: The purity of each calibration component must be predetermined by gas chromatography {flame ionization detector (FID) and/or thermal conductivity detector (TCD)} and, if necessary, by GC-MS

Section C9-9. Procedure

9.1 *Chromatographic Operating Conditions, Capillary Column Gas Chromatography.*

Table C9-1. GC Operating Conditions

Condition	R-22	R-113	R-134a /R-32	R-141b	R-142b	R-245fa
Detector	FID	FID	FID	FID	FID	FID
Carrier gas, cc Helium per minute	1.3	1.0	1.0	1.0	1.0	1.0
Injection port temperature[1], °C [°F]	200 [392]	200 [392]	200 [392]	200 [392]	200 [392]	200 [392]
Detector temperature[1], °C [°F]	200 [392]	200 [392]	200 [392]	200 [392]	200 [392]	200 [392]
Sample, mL	1	1	1	1	1	1
Initial column temperature, °C [°F]	-20 [-4]	35 [95]	-20 [-4]	10 [50]	10 [50]	-20 [-4]
Initial hold, min	14	10	20	12	12	20
Program 1 Ramp - °C/min [°F/min] Column temperature, °C [°F] Hold, min	 20 [68] 175 [347] 6.25	 10 [50] 160 [320] 11.50	 20 [68] 190 [374] 4.50	 10 [50] 100 [212] 5.00	 10 [50] 100 [212] 6.00	 20 [68] 125 [257] 10.00
Program 2 Ramp - °C/min [°F/min] Column temperature, °C [°F] Hold, min	 - -	 - -	 - -	 15 [59] 150 [302] 6.67	 - -	 20 [68] 190 [374] 19.50
Total run time, min	30	34	35	36	27	60
Split ratio	40:1					
Subambient cooling	liquid N_2					
Maximum safe column temperature, °C [°F]	280 [536]					

Note:

1. Condition may need to be optimized for specific GC used.

9.2 *Example - Primary Calibration Standard, Preparation and Analysis for R-134a.*

Note: Modify procedure for other refrigerants as necessary.

9.2.1 Crimp-on the septum, then determine the internal volume of the 500 mL gas bulb by weighing the bulb empty, then fill to maximum capacity with water. Record the grams of water as mL volume capacity on the outside of the bulb to the nearest 1.0 mL. Thoroughly dry the inside of the glass bulb.

9.2.2 Assemble the apparatus as illustrated in Figure C9-1.

9.2.3 Attach a cylinder of high purity refrigerant stock to the gas sampling bulb.

Note:
The purest stock refrigerant will contain some of the impurities found in the method. The ppm amounts of impurities already in the stock refrigerant are determined via the Method of Standards Addition. Individual impurity peak areas in the stock refrigerant are increased in the calibration standard by the ppm amount of the corresponding impurity added. The ppm already present is combined with the ppm added to give the total ppm component present in the calibration standard.

9.2.4 With valve "A" closed, open all other valves and evacuate cylinder. Good practice should be to evacuate to less than 100 microns of Hg pressure [0.013 kPa] to avoid cross-contamination.

9.2.5 Close valve "D" and monitor the gauge for several minutes to ensure that the system is not leaking.

9.2.6 Close metering valve “E”, open valve “A”, and then slowly open valve “E” and flash liquid phase stock refrigerant to bring the system to 1 Atmosphere pressure. Close valve “A”.

9.2.7 Repeat 9.2.4 through 9.2.6.

9.2.8 Close valves "B" and "C" and remove the bulb from the vacuum/sampling apparatus.

9.2.9 Calculate the grams of stock refrigerant added to the bulb as follows:

$$\text{grams added} = \frac{MW_{ref} \cdot \text{internal volume of bulb (mL)}}{24{,}450} \qquad \text{C9.1}$$

where:

MW_{ref} = molecular weight of the stock refrigerant, g/mole
24,450 = volume (mL) occupied by 1 mole of R-134a at 25°C [77°F] and at 1 atm

9.2.10 Individually and in turn add the volumes of each gaseous calibration component indicated in Table C9-3 to the calibration bulb. Use an appropriate sized µL or mL gas tight syringe with a deflected point needle.

Note:
To preserve the stock of calibration component, it is suggested to load a small, evacuated 125 mL gas collecting tube to 1 atm from the liquid phase as illustrated in Figure C9-1. The appropriate volume is then withdrawn and injected into the 500 mL calibration bulb.

9.2.11 Into a 30 mL (37 mL filled) serum bottle, capped and crimped with a septum, add the exact volumes of the liquid impurities from Table C9-5 in the order given. Add by syringe injection through the septum using a 22 gage needle (or smaller) as a vent. After addition, shake bottle vigorously to mix. Label, date and store in a refrigerator.

Note: Cool the syringe and R-1112a to 10°C [50°F] before transferring.

9.2.12 Refer to Figure C9-1. Evacuate a 125 mL bulb (internal volume premeasured) and fill to 1 atm with refrigerant stock.

9.2.13 Accurately withdraw and inject exactly 5.0 µL of solution from the 30 mL serum bottle into the 125 mL bulb. Allow to equilibrate for 30 minutes.

9.2.14 Using a 5 mL gas tight syringe, withdraw vapor from the 125 mL bulb and inject exactly 5.0 mL into the 500 mL calibration bulb. The mass added (µg) of each component thus added is calculated as follows and is added to column four of Table C9-4:

$$\mu g_i = \frac{g_i \cdot 25{,}000}{V \cdot A} \qquad \text{C9.2}$$

where:

A = internal mL of 125 mL bulb
g_i = grams from Table C9-4
V = total mL of solution, 9.2.11
25,000 = dilution ratio

9.2.15 Total the mass added column and combine this weight with that of 9.2.9 to obtain the total weight of sample (to the nearest 0.0001 g) in the bulb.

9.2.16 Calculate the ppm added (to the nearest 1 ppm) for each component by dividing the mass added by the total weight of sample in the gas bulb (9.2.15).

9.2.17 Calculate the ppm present for each component by combining the ppm present in the stock refrigerant (if any) and the ppm component added (refer to the Note in 9.2.3). The ppm component present values are those used for determining the method response factors.

9.2.18 Allow the gas calibration bulb to stand for 20 minutes to 30 minutes to equilibrate. The standard will be stable for three days to four days.

9.3 *Determination of Component Response Factors.*

Note: Depending upon the data integration system used, it is often more desirable to convert the ppm values to weight % for response factor calculations and for reporting purposes.

9.3.1 Set up the chromatography data system for an area normalization-response factor calibration.

9.3.2 Analyze the calibration standard bulb in triplicate using the chromatographic conditions described in 9.1.

9.3.3 Perform the necessary functions to have the data system determine each component Relative Response Factor (RRF_i), which is then stored. Response Factors are calculated as follows:

$$ARF_i = \frac{\text{weight\%}_i \text{ in calibration standard}}{A_i} \quad ; \qquad \text{C9.3}$$

$$ARF_r = \frac{100.0000 - S}{A_r} \qquad \text{C9.4}$$

where:

A_i = peak area of component i (average of 3 determinations).
A_r = peak area of major refrigerant
ARF_i = Absolute Response Factor of component i
ARF_r = Absolute Response Factor of component r
S = weight % sum of all impurities present

Then, using the major refrigerant r as the reference peak, the Relative Response Factor can now be determined:

$$RRF_i = \frac{ARF_i}{ARF_r} \qquad \text{C9.5}$$

RRF_i values are computed to the nearest 0.0001 unit.

9.4 *Example - Secondary Calibration Standard Preparation for R-134a.*

Notes:

1. A secondary calibration standard is prepared in much larger quantity due to the comparatively short lifetime of the primary bulb standard. The primary bulb standard is necessary initially because of inherent phase distribution of added components if simply preparing and calibrating a standard such as described here. The secondary standard is analyzed as a sample against the primary standard and then used subsequently as the daily calibration standard.

2. Modify procedure for other refrigerants as necessary.

9.4.1 Evacuate a 1 L steel cylinder and determine the tare weight to the nearest 0.1 g.

9.4.2 Attach a septum nut and septum to the valve and then cool the cylinder in ice water. Open the cylinder valve.

9.4.3 While keeping cold in ice water, individually and in turn add 500 times the volume of each gaseous component given in calibration Table C9-3 to the cylinder by syringe injection through the septum. Similarly, add 0.10 mL of the liquid refrigerant mixture from 9.2.11. Close the cylinder valve and remove the septum nut and septum.

9.4.4 Evacuate a second clean, dry 1 L steel cylinder and determine the tare weight to the nearest 0.1 g.

9.4.5 Cool the cylinder in ice water and attach a short (up to 61 cm [24 in]) section of flex line from the stock cylinder supply. Purge a small amount of stock refrigerant through the flex line before immediately attaching to the 1 L cylinder.

9.4.6 Open the 1 L cylinder valve, then open the stock cylinder valve and, while keeping cold in the ice water, fill the 1 L cylinder with 1100 g of liquid refrigerant. It may be necessary to reconnect the flex line and add more R-134a until the desired 1100 g has been added. If significantly greater than 1100 g is added, vent the cylinder to give approximately 1100 g.

Note:
During the refrigerant addition to the 1 L cylinder (secondary standard preparation), it is unnecessary to bring the cylinder to ambient temperature between weighings as only an approximate 1100 g weight is required.

9.4.7 Remove the 1 L cylinder from the ice bath and allow warming up to ambient temperature.

9.4.8 Place the 1 L secondary standard cylinder (the cylinder mentioned in 9.4.1, 9.4.2 and 9.4.3) in the ice bath and cool for 30 minutes.

9.4.9 Using a short double female swivel coupler, invert the 1 L cylinder containing the 1200 g of refrigerant and connect to the secondary standard cylinder. Open the valve slightly and purge some of the refrigerant vapor to sweep the coupler before immediately connecting to the secondary standard cylinder. Warm, but do not overheat, the cylinder containing the refrigerant with a heat gun.

9.4.10 Open the valves on both cylinders and allow all of the refrigerant to transfer into the calibration standard cylinder. Close the cylinder valves.

9.4.11 Remove the calibration cylinder from the ice bath and allow the cylinder to reach ambient laboratory temperature before the final weighing. Dry off and then reweigh to the nearest 0.1 g.

9.4.12 Subtract the tare weight (9.4.1) from the total weight (9.4.11) to obtain the total grams of standard in the cylinder. Record this weight together with the cylinder tare weight and date of preparation on the cylinder label.

9.4.13 Roll the cylinder for one hour to thoroughly mix.

9.4.14 Chromatograph the cylinder contents in triplicate as described in 9.1 loading first into an evacuated gas bulb as shown in Figure C9-1.

9.4.15 Average the results calculated electronically (see 9.7, Calculations) and tabulate to the nearest 1 ppm. List each component on the cylinder label with the ppm amount for each. This cylinder is used henceforth as the calibration standard until the loss of standard weight indicates that the internal volume of liquid phase is less than 60% of the total internal volume of the cylinder (for liquid densities, see Table C3-1).

9.5 *Sampling.* Submitted sample cylinders must contain sufficient liquid phase (80% liquid full is recommended) for analysis.

9.6 *Sample Analysis.* Analyze the sample using the chromatographic conditions described in 9.1. Load the sample as illustrated in Figure C9-1 by flashing the liquid phase into an evacuated gas bulb and bringing to 1 atm pressure. Use component spiking and/or GC-MS (if available) to identify questionable peaks. Use the Effective Carbon Number (ECN) Method to estimate the concentration of identified components not in calibration Table C9-1. To separate R-31 and R-1140, see Note 3 below.

Notes:

1. Alternatively, the sample liquid phase may be flashed into a Tedlar bag (1 L recommended) and the sample for gas chromatography analysis withdrawn from the bag.

2. The method will not detect any impurity which may elute within the comparatively large R-134a peak matrix on either column. For example, R-134, R-31 and R-152a elute within the large R-134a peak matrix. The capillary column resolves R-134, R-1234yf, R-31 and the R-152a/R-1243zf pair (which elute together). Note that R-12, if present, elutes on the far shoulder of the R-134 peak.

3. To separate R-31 and R-1140 (which coelute on the capillary column), repeat the capillary column analysis exactly as given in 9.1 except that the column temperature is held at 50.0°C [122°F] (isothermal) throughout. The two components will be resolved at about 15 minutes retention time with the R-31 peak eluting 0.8 minutes before the R-1140 peak.

4. See example gas chromatograms in Appendix D.

9.7 *Calculations.*

9.7.1 The weight percentage of each component is calculated as follows:

$$W_i = \frac{RRF_i \cdot A_i \cdot 100}{\sum (A_i \cdot RRF_i)} \qquad \text{C9.6}$$

where:

A_i = peak area of component i
RRF_i = Relative Response Factor for component i
W_i = weight percent of component i
$\sum(A_i \cdot RRF_i)$ = sum of all component peak areas times their respective Relative Response Factors

9.7.2 Report sample component concentrations to the nearest 0.0001% (or to the nearest 1 ppm). If results are less than the individual detection limits (see Table C9-2), then report less than the detection limit (DL) value given.

Table C9-2. Additional Impurities Observed in R-134a, Quantitation by Effective Carbon Number Method

Impurity	Column Retention Time Capillary(min)	Effective Carbon Number (ECN)[1]
R-1243zf	14.98	2.84
R-1336mzz	-	2.90
R-1234yf	13.75	2.65
R-22	16.40	0.40
R-123a	-	1.84
R-124a	-	1.27
R-245cb	-	2.60
R-1225ye	-	2.42
R-1113	-	1.69
R-263fb	-	2.95
R-1140	21.50	2.08
R-132b	-	1.90
R-13	-	0.23
R-1318my-T	-	2.95
R-1318my-C	-	2.95

Note:

1. Effective Carbon Numbers (ECN) determined experimentally or estimated. Refer to scientific literature on ECN.

Quantitation by ECN Method

Select a nearby peak in the chromatogram whose identification and response factor (RF) have been established (the Internal Standard).

Then:

$$\frac{RF_i}{RF_r} = \frac{ECN_r}{ECN_i} \cdot \frac{MW_i}{MW_r} \qquad \text{C9.7}$$

where:

RF = either Absolute or Relative Response Factor
MW_i = molecular weight of the component to be determined
MW_r = molecular weight of the Internal Standard Reference

Table C9-3. Component Statistical Parameters

Component	Effective Carbon Number (ECN)[1]	detection limit, ppm	range investigated, ppm	precision at 95% Confidence Level, ppm	Relative Mean Error, %
R-23	0.16	4	15	0.70	1.8
R-32	0.62	2	15	0.30	1.2
R-1123	1.93	1	20	0.20	-0.8
R-143a	2.12	1	20	0.20	1.5
R-125	0.79	2	30	0.25	3.2
R-115	0.76	5	60	0.65	-1.3
R-1243zf	2.84	1	10	0.20	-3.6
R-12	0.35	2	40	0.30	1.8
R-1122	1.76	1	15	0.20	2.2
R-124	1.33	1	40	0.45	2.0
R-31	0.92	1	15	0.80	1.7
R-133a	1.93	1	25	0.50	1.7
R-1336mzz	2.90	1	-	0.5[2]	-
R-114	1.04	2	30	1.10	-3.3
R-114a	1.10	2	50	1.20	4.3
R-11	0.43	4	50	2.60	2.6
R-1112a	1.64	1	15	0.30	-0.2
R-1121-C	1.75	1	10	0.30	-6.7
R-123	1.76	2	20	0.90	-3.3
R-1121-T	1.75	1	30	1.00	4.3
R-113	1.60	2	20	1.3	1.7
R-134	1.61	2	30	0.20	1.4
R-152a	1.08	1	30	0.20	0.8
R-1234yf	2.65	1	-	0.5[2]	-

Notes:

1. Effective Carbon Numbers (ECN) were determined experimentally. Refer to scientific literature on ECN.
2. Precision estimated at 10 ppm based upon sample reproducibility.

Table C9-4. Primary Calibration Standard Components

Component	Molecular Weight	Volume Added, µL	Mass Added[1], µg	Added[2] Concentration, ppm	Total Concentration Present[3], ppm
R-23	70.0	12.0	34.73	15.0	
R-32	52.0	16.0	34.03	15.0	
R-1123	82.0	14.0	46.98	20.0	
R-143a	84.0	14.0	48.10	20.0	
R-125	120.0	14.0	68.72	30.0	
R-115	154.0	22.0	139.05	60.0	
R-134	102.0	28.0	116.81	50.0	
R-152a	66.0	25.0	67.49	30.0	
R-12	121.0	20.0	98.89	43.0	
R-1122	98.0	8.0	32.23	15.0	
R-124	136.0	16.0	89.32	39.0	
R-31	68.0	12.0	33.61	14.5	
R-133a	118.0	12.0	58.17	25.0	
R-114	170.0	10.0	69.46	30.0	
R-114a	170.0	20.0	138.92	60.0	
R-11[4]	137.0	-	-[6]	30.0	
R-1112a[4]	133.0	-	-[6]	18.0	
R-1121-C[4]	115.0	-	-[5, 6]	5.0	
R-123[4]	153.0	-	-[6]	19.0	
R-1121-T[4]	115.0	-	-[5, 6]	23.5	
R-113[4]	188.0	-	-[6]	24.0	

Notes:

1. If necessary, correct the mass added for the purity of the calibration component previously established.
2. Values shown are for illustration; exact values are determined at 9.2.16.
3. Column to be filled in (per 9.2.17) after determining ppm present in stock R-134a.
4. These components are liquids at ambient temperature and are added to the 500 mL bulb as described in 9.2.11 through 9.2.14.
5. R-1121 typically contains about 17.5% cis isomer. The mass of R-1121 added times 0.175 is assigned to the cis isomer, the balance to the trans isomer.
6. From 9.2.14

Table C9-5. Primary Calibration Standard Liquid Impurities

Component	Volume Added, mL	Density at 20 °C [68°F]	Mass, g
R-113	6.0	1.565	9.390
R-1121C&T	8.0	1.403	11.224
R-123	5.0	1.470	7.350
R-11	8.0	1.487	11.896
R-1112a	5.0	1.439 (@ 10 ºC [50°F])	7.195

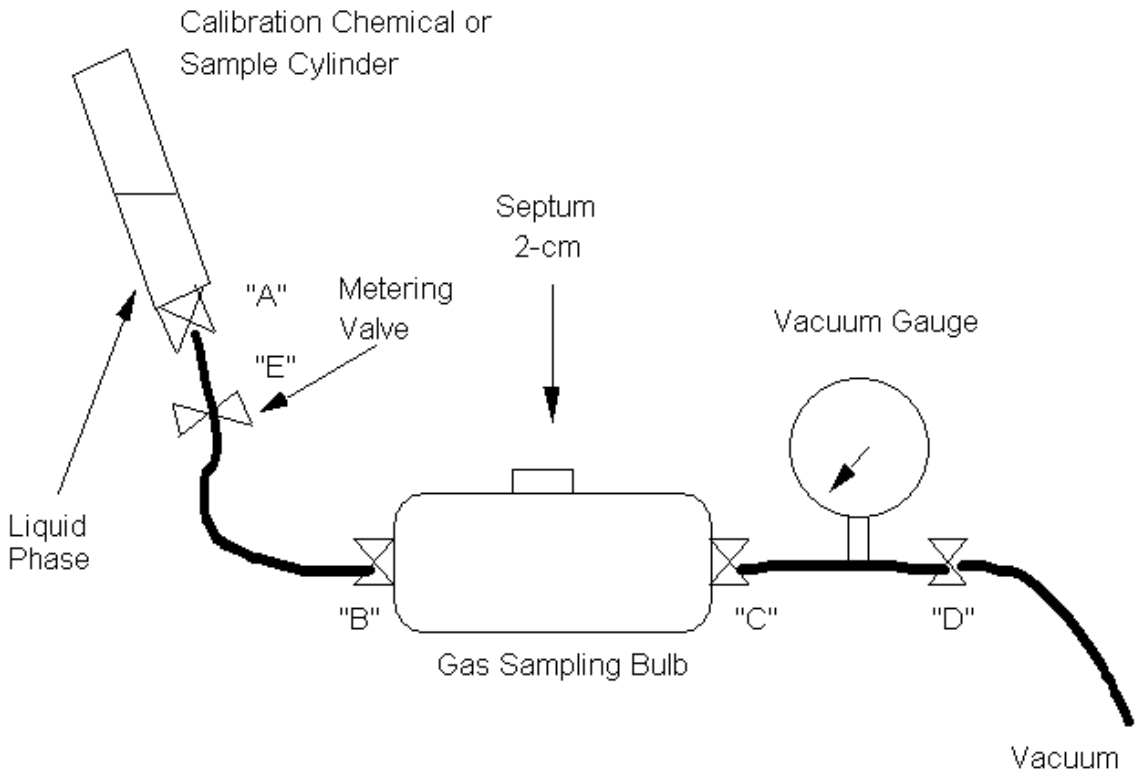


Figure C9-1. Apparatus Used for Calibration Standard Preparation and for Cylinder Sampling

PART 10

DETERMINATION OF COMPOSITION OF NEW AND RECLAIMED 400 SERIES AND 500 SERIES REFRIGERANT BLENDS BY GAS CHROMATOGRAPHY

Section C10-1. Purpose

The purpose of this test method is to determine the composition of all new and reclaimed 400 series and 500 series refrigerant blends by gas chromatography.

Section C10-2. Scope

This test method is for use with all 400 series and 500 series refrigerant blends as listed in ASHRAE Standard 34.

Section C10-3. Definitions

Definitions for this part are identical to those of ARI Standards 700 and 740.

Section C10-4. Principle

400 series and 500 series refrigerant blend compositions are separated by gas chromatography using a packed column with a liquid phase coated onto a solid support. Separated components are detected using a thermal conductivity detector (TCD). The peak areas from the detector are measured with a data system capable of electronic integration, and component concentrations are quantified by the area normalization response factor method.

Section C10-5. Applicability

This method is applicable to the routine gas chromatographic determination of all new and reclaimed blends of 400 series and 500 series refrigerant blends mixture compositions. At laboratory ambient temperature, R-13/R-23 mixtures of R-503 and R-116/R-23 mixtures of R-508 will all be in gas phase, as their critical temperatures are low.

Section C10-6. Limitations and Interferences

This method does not address components other than those found as the major components in the 400 series and 500 series refrigerant blends. R-115 and R-290 elute at nearly the same retention time and will interfere with each other if both compounds are present. Any impurity which elutes within the matrix of any of the major components will interfere if present in significant concentration.

Section C10-7. Sensitivity, Precision, and Accuracy

7.1 *Sensitivity*. This method is sensitive to component concentrations of 0.01 % by weight.

7.2 *Precision.*

7.2.1 Single Operator

The mean of the analysis ($\overline{X}$), standard deviation (σ) and 95 % confidence limits (95 % CL) established for the single operator precision of the test method were as follows:

Component	$\overline{X}$, Weight %	σ	95% CL
R-143a	51.35	0.020	± 0.047
R-125	44.52	0.012	± 0.028
R-134a	4.13	0.017	± 0.040

The above data were calculated from eight replicate analyses of one standard sample performed by one analyst over a period of one day.

7.2.2 Multiple Operators.

The mean of the analysis ($\overline{X}$), standard deviation (σ) and 95 % confidence limits (95 % CL) established for the multiple operator precision of the test method were as follows:

Component	$\overline{X}$, Weight %	σ	95% CL
R-143a	51.59	0.040	± 0.084
R-125	44.01	0.016	± 0.034
R-134a	4.40	0.032	± 0.068

The above data was calculated from 16 replicate analyses of a standard sample performed by four analysts over a two day period.

7.3 *Accuracy*. The accuracy of this method was tested by analyzing a known R-401 blend:

Component	Standard Concentration, Weight %	Relative Mean Error, Weight %
R-22	34.86	0.17
R-152a	25.65	0.16
R-124	39.49	0.05

The above data was calculated from replicate analyses of a standard sample performed by multiple analysts during a single day period.

Section C10-8. Special Apparatus and Reagents

1. Gas chromatograph: Equipped with a packed column injector and thermal conductivity detector capable of oven temperature programming.

2 Chromatography data system: Capable of electronic integration and processing the chromatographic data. The data system must be configured to capture peak areas enabling measurement of peaks greater than or equal to 0.001% by weight. Peaks that are not identified by the data system should be

given a default response factor that is the greater of the average response factors for the calibrated components or R-22. If the peak is identified, then it shall be quantified using its measured response factor.

3. Gas chromatographic column (Packed): 1 percent high molecular weight compound of polyethylene glycol and a diepoxide reacted with nitroterephthalic acid on (60-80) mesh graphitized carbon with a nominal surface area of 100 square meters per gram in a 7.3 m [24 ft], 3.20 mm [0.125 in] OD stainless steel column. Prepacked columns are commercially available from multiple vendors.

4. Glass collecting tube: 500 mL. (Enlarge side outlet opening to accommodate a crimp-on 2 cm septum. Apply fiberglass tape to the outside for protection).

5. 2 L steel cylinder

6. Syringe, 1 mL, gas tight

7. Deflected point needle: Standard hub 22 gage X 1-1/2 inch stainless steel

Section C10-9. Procedure

9.1 *Chromatographic Operating Conditions.*

Detector	TCD
Detector current	Low[1]
Detector temperature, °C [°F]	200 [392][1]
Injection port temperature, °C [°F]	200 [392][1]
Carrier gas	20 mL Helium per minute
Reference flow	as required by your GC[1]
Sample size	0.5 mL (gas syringe)[1]
Initial column temperature, °C [°F]	40 [104]
Initial hold	12 minutes
Program , °C [°F] per minute	15 [59] per minute
Final column temperature , °C [°F]	175 [347]
Post hold	11 minutes
Maximum column temperature, °C [°F]	225 [437] (conditioning purposes only)

Notes:

1. Condition may need to be optimized for specific GC used.

9.2 *Example - Primary Calibration Standard, Preparation and Analysis for R-401.*

Note: Modify procedure for other refrigerants as necessary.

9.2.1 Determine the tare weight of a dry, evacuated empty steel cylinder with a nominal volume of 2 L to the nearest 0.1 g (cylinder size may vary, but size is compensated for in the following procedure).

9.2.2 Calculate the weight of each component to be added to the standard. Fill the empty 2 L steel cylinder to 90% of its loading capacity.

$$\text{g component}_i = \frac{\text{desired weight \% component}_i}{100} \cdot \text{safe load} \qquad \text{C10.1}$$

where:

safe load = liquid density · 0.9 · 2088 mL (allowing for 10% loading factor)

For liquid densities, refer to Part 3, Table C3-1.

Note: The calculations used in this procedure should be corrected for any significant impurities found in the component refrigerants.

9.2.3 Purge the connecting line using the component with the highest boiling point first (i.e., R-124, the higher boiling component) in order to sweep out air; connect the line to the cylinder.

9.2.4 Add the component with the highest boiling point to the cylinder and reweigh the cylinder to the nearest 0.1 g.

Note: If the amount added is less than that desired, more may be added. If the amount added is more than that desired, the cylinder may be purged until the desired weight is obtained. Purging the cylinder is permitted only during the addition of the first component.

9.2.5 Record the weight of the cylinder plus the component with the highest boiling point. This weight minus the tare weight of the cylinder equals the weight of the component with the highest boiling point.

9.2.6 Cool the cylinder in ice water and then add the component with the next highest boiling point in a similar manner. This weight minus the weight recorded in 9.2.5 equals the weight of the component with the next highest boiling point.

Note: It is advisable to add the component with the next highest boiling point so that the weight is less than that desired. If necessary, by adding small additions, it can be brought up to the desired weight. Allow the cylinder and contents to reach ambient laboratory temperature before making the final weighing.

9.2.7 Repeat 9.2.5 except that the refrigerant added here is the component with the next highest boiling point and the tare weight for calculating the component with the next highest boiling point added is the weight in 9.2.5. Repeat this step until all the desired components are added to the steel cylinder.

9.2.8 After the last component is added, agitate the cylinder by rolling for a minimum of one hour to mix the contents thoroughly. The weight percent of each component can be calculated from the measured weights of the components added. Record the weight percent of each component and date of preparation on the cylinder label. Also record the total weight of refrigerant in the calibration standard cylinder.

Note: The blend calibration standard is now ready for use and may continue in service until the liquid phase in the cylinder decreases to 60% of the loading capacity (0.6 · liquid density · cylinder volume in mL) at which time the remaining liquid phase is discarded and a new standard prepared. This is done to avoid the possibility of the vapor/liquid equilibrium changing slightly, thereby changing the composition of the liquid phase. Record the minimum cylinder weight on the cylinder tag.

9.2.9 Preparing a vapor phase standard by weighing the components is an acceptable alternate for 9.2.1 to 9.2.7.

9.3 *Determination of Component Response Factors.*

9.3.1 Set up the chromatography data system for an area normalization response factor calibration.

9.3.2 Analyze the calibration standard in triplicate using the chromatographic conditions described in 9.1. Load the sample injection device by slowly and completely vaporizing the liquid phase. For example, by bubbling the vapor into water through Tygon® tubing and then puncturing the tubing with the syringe needle or using the apparatus as in Figure C10-1.

9.3.3 Perform the necessary functions to have the data system determine each component response factor which is then stored.

9.3.4 Response Factors for each component are calculated as follows:

$$ARF_{component\ A} = \frac{\text{weight \% of component}_A \text{ in calibration standard}}{A_{component\ A}} \quad \text{C10.2}$$

$$ARF_{component\ B} = \frac{\text{weight \% of component}_B \text{ in calibration standard}}{A_{component\ B}} \quad \text{C10.3}$$

$$ARF_{component\ i} = \frac{\text{weight \% of component}_i \text{ in calibration standard}}{A_{component\ i}} \quad \text{C10.4}$$

where:

A	= peak area of component (average of three determinations)
ARF	= Absolute Response Factor
component $_i$	= component 3 or greater

Then, using component i as the reference peak the Relative Response Factor can now be determined:

$$RRF_{component\ B} = \frac{ARF_{component\ B}}{ARF_{component\ i}} \quad \text{C10.5}$$

$$RRF_{component\ A} = \frac{ARF_{component\ A}}{ARF_{component\ i}} \quad \text{C10.6}$$

RRF values are computed to the nearest 0.0001 unit.

Note: The largest peak in the calibration standard chromatogram is selected as the reference peak (RRF = 1.0)

9.4 *Sampling.* Submitted sample cylinders must contain sufficient liquid phase (80% liquid full is recommended) for analysis.

Note: Special Handling for Low Critical Temperature Refrigerants R-503 and R-508 - a vapor phase sample is required to determine non-condensables and volatile impurities, including other refrigerants. The vapor phase sample is obtained by regulating the sample container temperature

to 5 K or more above the refrigerant critical temperature. Critical temperatures- R-503 = 19.5°C [67.1°F], R-508A = 13.5°C [56.3°F], and R-508B = 14.0°C [57.2°F].

9.5 *Sample Analysis.*

Analyze the sample using the chromatographic conditions described in C10-9.1.

Notes:

1. The sample taken into the syringe for injection into the gas chromatograph is vaporized liquid phase from the sample cylinder. One method for obtaining the vapor is to completely vaporize the liquid through soft plastic tubing into water and take the syringe sample by piercing the tubing wall with the syringe needle. An alternative apparatus for vaporizing liquid sample into a glass gas sample bulb allowing repeat injections of the same sample is shown in Figure C10-1.

2. See example gas chromatograms in Appendix D.

9.6 *Calculations.*

9.6.1 The weight percentage of each component is calculated as follows:

$$W_i = \frac{RRF_i \cdot A_i \cdot 100}{\sum (A_i \cdot RRF_i)} \qquad \text{C10.7}$$

where:

A_i = peak area of component i
RRF_i = Relative Response Factor for component i
W_i = weight percent of component i
$\sum(A_i \cdot RRF_i)$ = sum of all component peak areas times their respective Relative Response Factors

Note: The largest peak in the calibration standard chromatogram is selected as the reference peak (RRF= 1.0).

9.6.2 Report sample component concentrations to the nearest 0.01%.

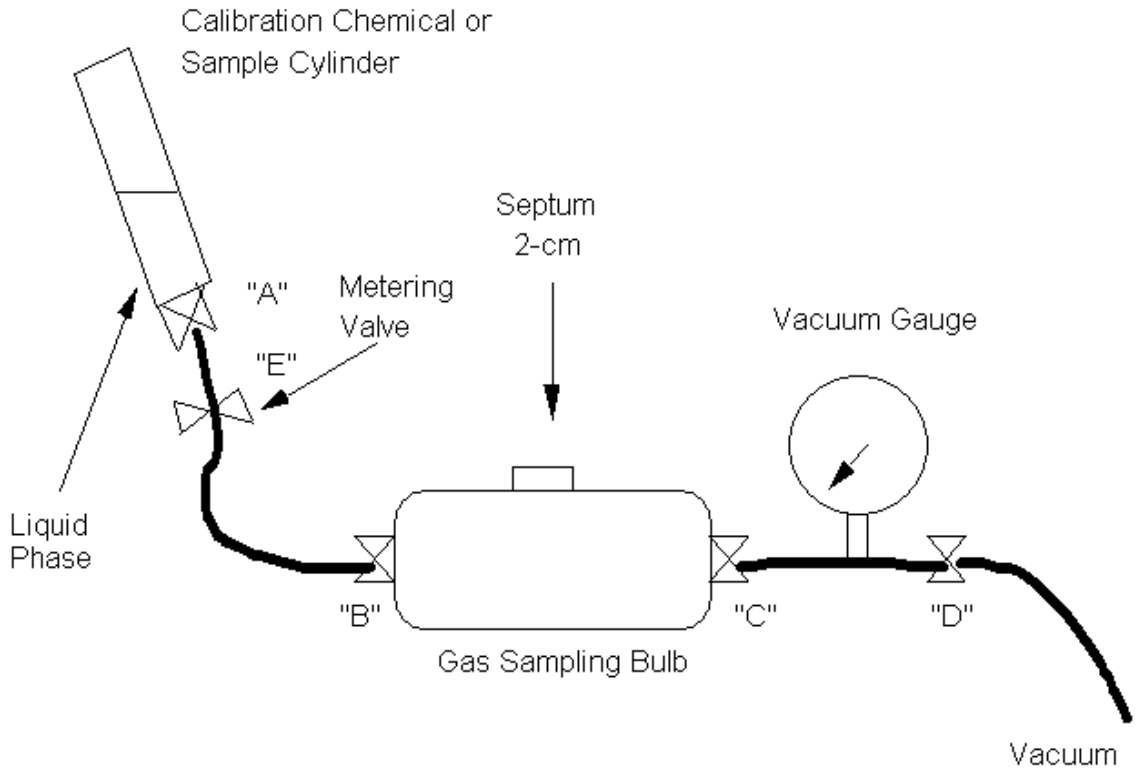


Figure C10-1. Apparatus Used for Calibration Standard Preparation and for Cylinder Sampling.