Status Update on Refrigerant Classification, Specification, and Recovery Standards

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For Discussion Today

- Overview of standards and guidelines involved in the classification, recovery, recycling, and reclaim of refrigerants
- Status of revision activities as they apply to the implementation of low Global Warming Potential (GWP) refrigerants
- Discussion of enabling standard updates to align with the rapid pace of new refrigerant development

International, federal, and state regulations are driving the phasedown of high global warming potential (GWP) refrigerants

Introduction

New refrigerants have been (and continue to be) developed to meet GWP targets for specific applications

Reclaimed refrigerants may play a significant role in meeting the phasedown targets

Anticipated future changes

- Wider variety of refrigerants in the market
- Increased use of recovered and reclaimed refrigerant to meet stepdown targets
- Maintained scrutiny on refrigerant management and tracking (minimizing emissions)



Refrigerant Safety Classification

 Refrigerant <u>designations</u>, and safety classifications for <u>toxicity</u> and <u>flammability</u>, are facilitated by ANSI/ASHRAE 34 and ISO 817

ASHRAE STANDARD

ANSI/ASHRAE Standard 34-2022

(Supersedes ANSI/ASHRAE Standard 34-2019) Includes ANSI/ASHRAE addenda listed in Appendix J

Designation and Safety Classification of Refrigerants

INTERNATIONAL STANDARD

ISO 817

Third edition 2014-05-15

Refrigerants — Designation and safety classification

Fluides frigorigènes — Désignation et classification de sécurité

ANSI/ASHRAE 34 Designation & Safety Classification of Refrigerants

PURPOSE

- establishes a simple means of referring to common refrigerants
- provides a uniform system for assigning reference numbers, safety classifications, and refrigerant concentration limits (RCLs)
- identifies requirements to apply for designations and safety classifications and to determine refrigerant concentration limits

SCOPE

- provides an unambiguous system for numbering refrigerants and assigning composition designating prefixes
- Includes safety classifications based on toxicity and flammability data along with refrigerant concentration limits
- Does not imply endorsement or concurrence that individual refrigerant blends are suitable for any particular application

Safety Classification

ANSI/ASHRAE 34-2022

SAFETY GROUP Higher **A3 B3** N Flammability Α C M R M **B2** A2 Flammable Ε Α Α В S Lower A₂L B₂L Flammability Ν G No Flame Т **A1 B1** Propagation Higher Lower Toxicity Toxicity Adapted from Figure 6-1,

INCREASING TOXICITY

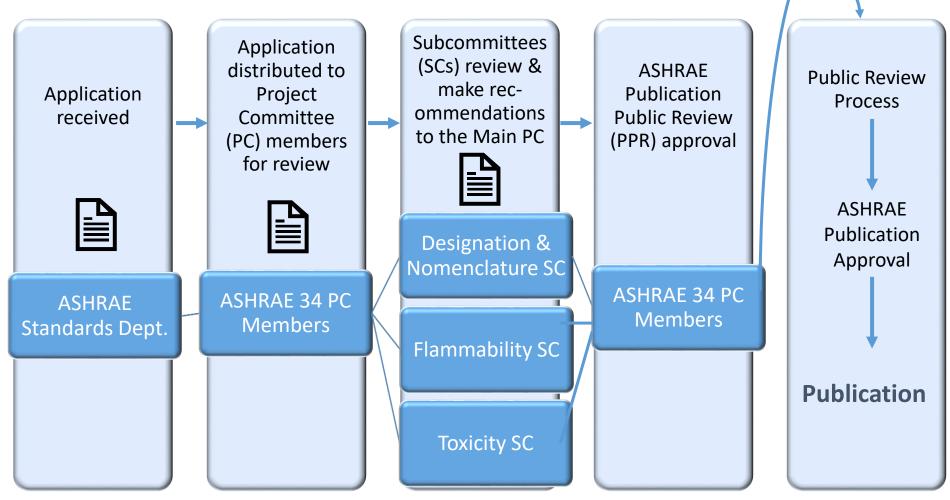
A and B are toxicity classifications

1, 2L, 2, and 3 are flammability classifications

Many of the low GWP refrigerants are Class A2L



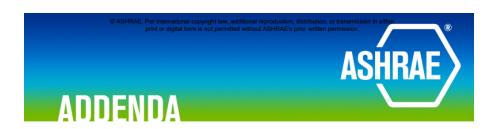
New Refrigerant Application Process – ASHRAE 34



New refrigerants are published as addenda

Example addendum from

https://www.ashrae.org/technical-resources/standards-and-guidelines/standards-addenda



ANSI/ASHRAE Addendum b to ANSI/ASHRAE Standard 34-2022

Designation and Safety Classification of Refrigerants

FOREWORD

Addendum b adds the zeotropic refrigerant blend R-477A to Tables 4-2 and D-2.

Note: In this addendum, changes to the current standard are indicated in the text by underlining (for additions) and strikethrough (for deletions) unless the instructions specifically mention some other means of indicating the changes.

Addendum b to Standard 34-2022

Modify Tables 4-2 and D-2 as shown.

Table 4-2 Data and Safety Classifications for Refrigerant Blends

Refrigerant Number = 477A

Composition (Mass %) = R-1270/600a (84.0/16.0)

Composition tolerances = $\pm 2.0/\pm 2.0$

OEL = 530 ppm v/v

Safety Group = $\underline{A3}$

 $RCL = 1100 \text{ ppm v/v}; 0.13 \text{ lb/1000 ft}^3; 2.0 \text{ g/m}^3$

LFL = 21.000 ppm v/v; 2.4 lb/1000 ft³; 38 g/m³

Highly Toxic or Toxic Under Code Classification = Neither

Table D-2 Data Classifications for Refrigerant Blends

Refrigerant Number = 477A

Composition (Mass %) = R-1270/600a (84.0/16.0)

Average Relative Molar Mass = 44.0 g/mol

Bubble Point (°F) = -48.3

Dew Point (°F) = -35.0

Bubble Point ($^{\circ}$ C) = -44.6

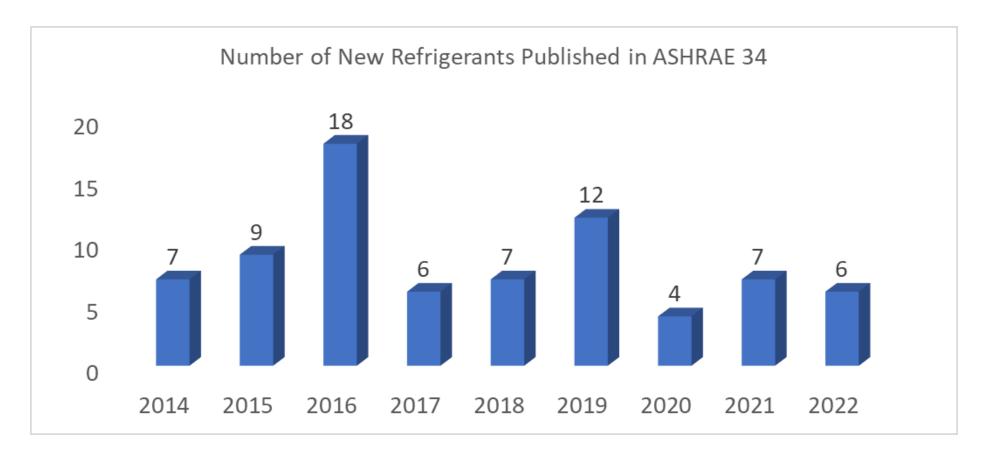
Dew Point (°C) = -37.2

Approved by ASHRAE and the American National Standards Institute on November 30, 2022.

Approved refrigerants are either published in the standard or as addenda on ASHRAE's website



Pace of New Refrigerant Publications



Data provided by ASHRAE staff



Status Update on ASHRAE 34

- New revision published in 2022, superseding the 2019 version
 - 22 new refrigerants were added
 - Lower Flammability (LFL) data were added for flammable refrigerants
 - Some revisions were made to better align with ISO Standard 817
 - Language was added to clarify use of blend toxicity data versus calculated values for the components
- There are already 8 published addenda
 - Five addenda are for new refrigerants:
 - addenda b and c add R-477A and R-477B, respectively (Class A3)
 - Addenda <u>d</u>, <u>e</u>, and <u>f</u> add R-457D, R-478A, and R-479A, respectively (Class A2L)
 - Two addenda are related to flammability
 - Addendum <u>a</u> adds burning velocity data for flammable refrigerants
 - Addendum <u>ac</u> provides clarification on the pressure range for flammability testing
 - Addendum <u>ah</u> revises the composition tolerances for components of refrigerant blends

ISO 817 - Refrigerants - Designation & Safety Classification

SCOPE

- provides an unambiguous system for assigning designations to refrigerants
- Establishes a system for assigning a safety classification to refrigerants based on toxicity and flammability data, along with a means of determining refrigerant concentration limits.
- Tables listing the refrigerant designations, safety classifications, and the refrigerant concentration limits are included based on data made available.

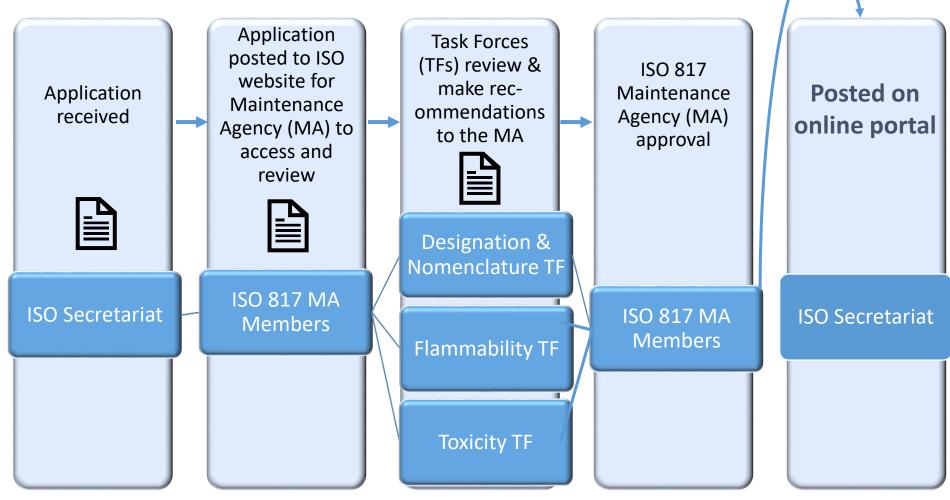
The scope is very similar to that for ASHRAE 34.



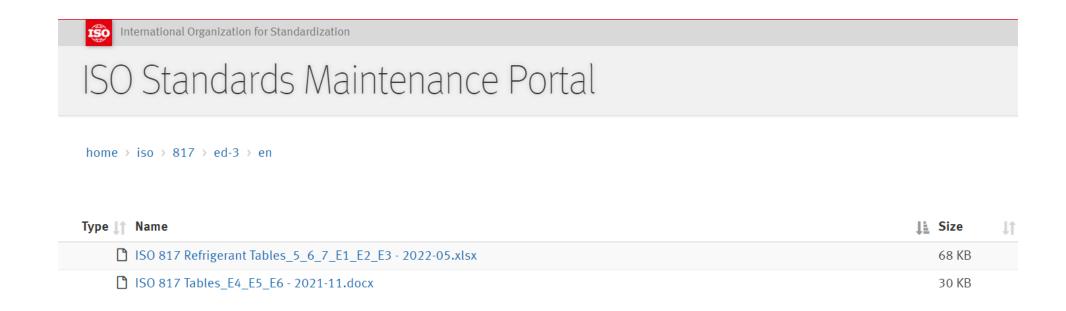
Background on ISO 817

- Most of the refrigerants in ISO 817 were brought over from ASHRAE 34
- Beginning in 2021, new refrigerants were required to be submitted via application to the ISO 817 Maintenance Agency (MA)
 - An applicant can apply to ASHRAE 34, ISO 817, or both
- There are some differences between the two standards
 - Individual applications must be prepared for ISO 817 and ASHRAE 34
- Most, but not all, of the refrigerants in ASHRAE 34 are also in ISO 817 (and vice versa)

New Refrigerant Application Process – ISO 817



New Refrigerants are Posted in Tables in the Maintenance Portal



https://standards.iso.org/iso/817/ed-3/en/

Approved refrigerants are either published in the standard or listed in the tables on the website.



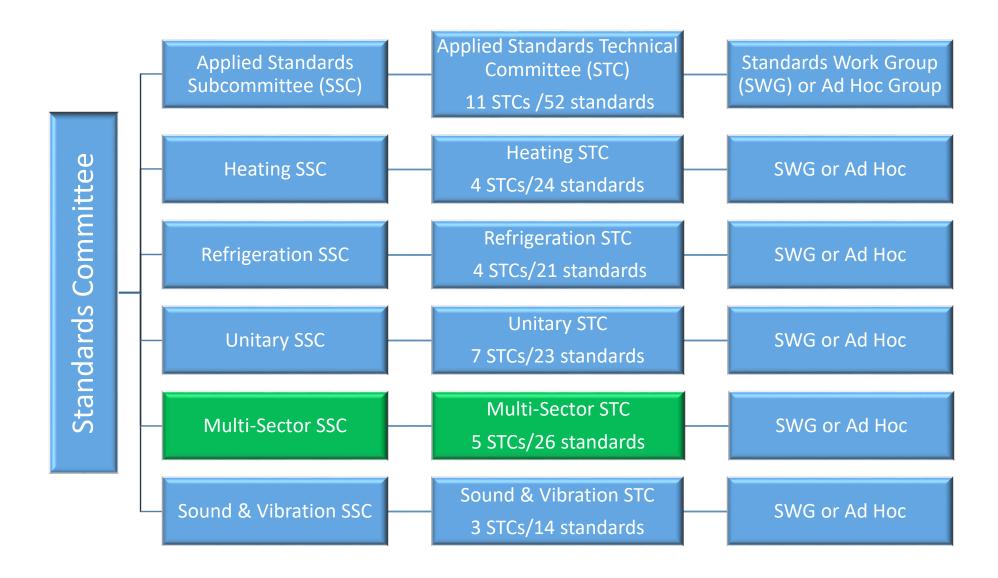
Status Update on ISO 817

- 8 applications have been processed since 2021, and an additional 5 are under review
- Guidelines are being updated to clarify procedures for new refrigerant applications and submission of new data on existing refrigerants
- Work is ongoing to align ASHRAE 34 and ISO 817
 - To minimize the burden on applicants

Review

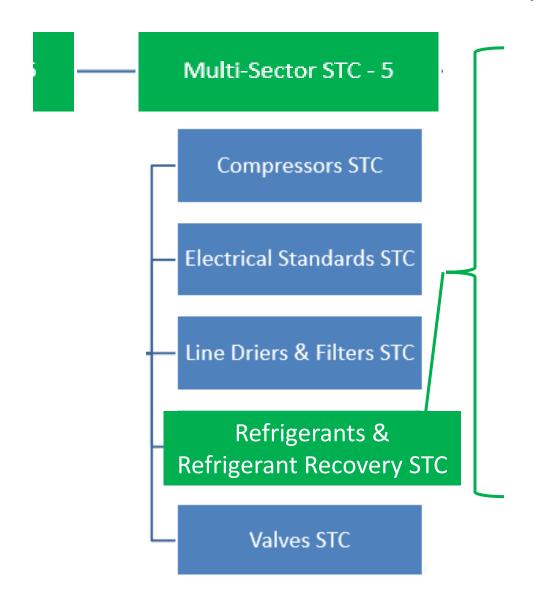
- New refrigerants can be designated and classified for safety through ASHRAE 34 or ISO 817
- Once published, other standards may need to be updated or reviewed to enable the application of these refrigerants
- AHRI standards and guidelines reference ASHRAE 34 and ISO 817
 - Revisions are in process to align these AHRI standards and guidelines

AHRI Standards Structure





AHRI Standards Structure (continued)



Standard 700	Specifications for Refrigerants		
Standard 740	Performance Rating of Refrigerant Recovery Equipment and Recovery/Recycling Equipment		
Guideline K	Containers for Recovered Non- flammable Fluorocarbon Refrigerants		
Guideline N	Assignment of Refrigerant Container Colors		
Guideline M	Unique Fittings and Service Ports for Flammable Refrigerant Use		
Guideline Q	Content Recovery & Proper Recycling of Refrigerant Cylinders		



AHRI Standard 700 – Specifications for Refrigerants

Purpose and Scope – AHRI 700

Purpose

- establish purity specifications,
- verify composition, and
- specify the associated test methods
- for acceptability of refrigerants regardless of source (new, reclaimed and/or repackaged) for use in new and existing refrigeration and air-conditioning products....

Scope

 Specifies acceptable levels of contaminants for refrigerants regardless of source and lists acceptable test methods. These refrigerants are as referenced in ANSI/ASHRAE Standard 34 with addenda and in ISO Standard 817... • Note: AHRI 700 is used in the AHRI Refrigeration Testing Laboratory (RTL) Certification Program.

AHRI 700 - Specifications for Refrigerants

	Specification Catagony	Type of Refrigerant		
	Specification Category	Fluorocarbons	Hydrocarbons	Carbon Dioxide
	Isomer Content	X		
	Air & Other Non-Condensables	X	X	X
	Water	X	X	Χ
	All Other Volatile Impurities	X	X	
	High Boiling Residue	X	X	X
	Particulates/Solids	X	X	X
	Acidity	X	X	
	Chloride	X	X	
	Nominal Composition		X	
	Other Allowable Impurities		X	
	Sulfur Odor		X	
	Total C3, C4, and C5 Polyolefins		X	
	Purity			Χ

Potential contaminants vary by refrigerant type
Different tests are required for different contaminants



Example specifications

R-134a		
Characteristic	Units	Specification
Air & Other Non-Condensables	% by volume at 25.0°C	1.5
Water, maximum	ppm by weight	10
Acidity, maximum	ppm by weight	1
High Boiling Residue	% by volume or % by weight	0.01
Particulates/solids	Pass/Fail	Visually Clean

So what?



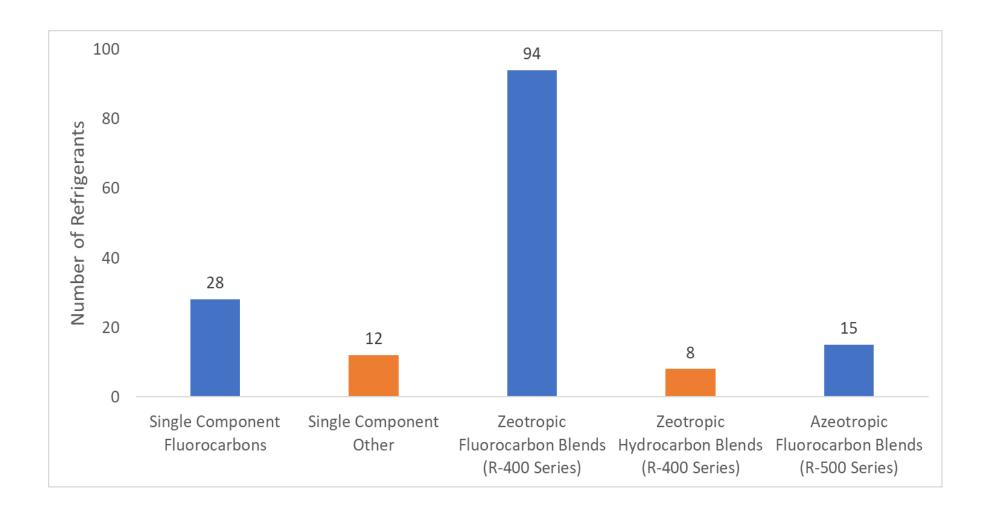


- Equipment performance and reliability
 - Too much air or high boiling residue (oil) may negatively impact system performance
 - Too much water can overwhelm filter drier capacity, leading to corrosion or reactivity issues
 - Particulates may plug orifices, capillary tubes, or otherwise interfere with expansion device function

AHRI 700 specifications are intended to prevent performance and reliability issues in HVACR equipment

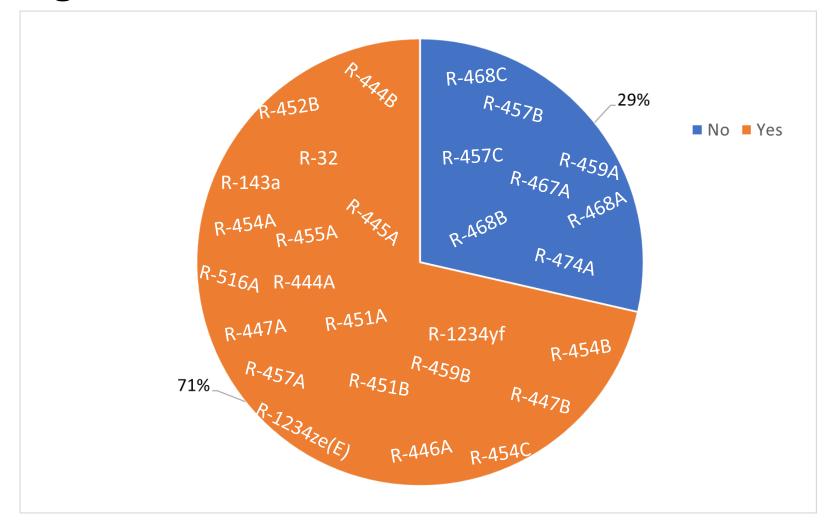


Refrigerant Types in AHRI 700





A2L Refrigerants & AHRI 700 Status





Next Steps/Timeline for AHRI 700

Short term

• Update the current standard to include new refrigerants and specs

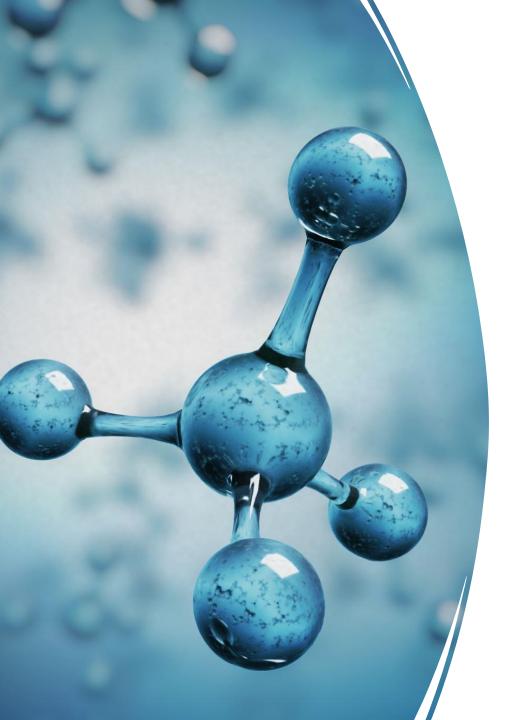
Mid term

- Revise the standard so that portions of it can be more easily and frequently updated
 - To better align with the rapid pace of new refrigerant developments and publications

Long term

- Consider whether every new refrigerant should be specified or only those that meet specific criteria
 - Currently >150 refrigerants listed (and more to add)





AHRI 700 Appendices

- AHRI 700 has two appendices that are published and updated separately from AHRI 700
- Appendix C Analytical Procedures for AHRI Standard 700
 - This appendix contains the procedures for determining different properties of refrigerants such as Acidity, Water, High Boiling Residue, Chloride, Non-Condensable Gas, Purity, and Composition
- Appendix D Gas Chromatograms for AHRI Standard 700
 - This appendix provides examples of gas chromatograms of most of the refrigerants covered in AHRI 700

Appendix C – Analytical Procedures

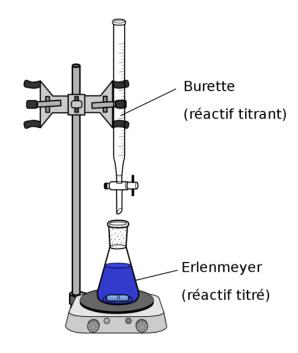
Acidity

 Acidity is determined through titration of the refrigerant added to a solvent of toluene, isopropanol and water using a bromothymol blue indicator

Water

 The amount of water in a sample of refrigerant is determined by Karl Fischer Coulometric Titration. This titration is based upon the redox of water, iodine and sulfur dioxide

$$H_2O + I_2 + SO_2 \rightarrow 2HI + SO_3$$



Appendix C – Analytical Procedures



High Boiling Residue

This is determined through Volumetric or Gravimetric Measurement



Chloride Presence

$$Ag^+ + Cl^- \rightarrow AgCl$$

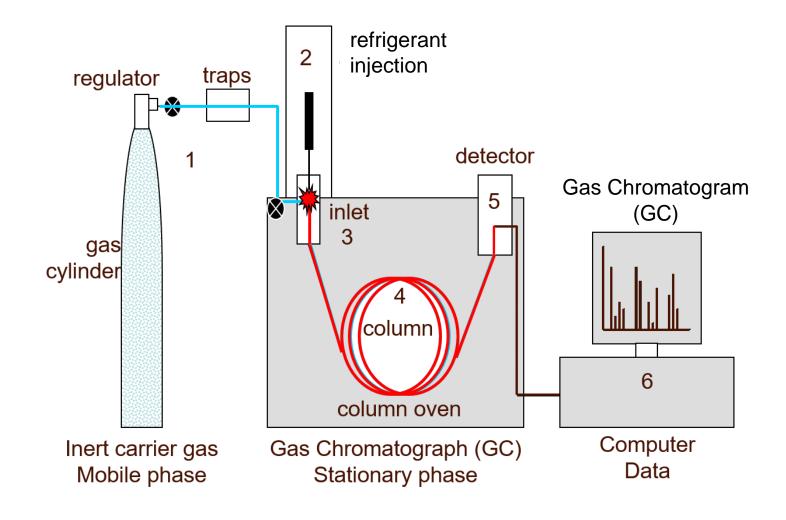
Chloride presence is determined through Silver Chloride precipitation based on the reaction below. The refrigerant is added to a solution of silver nitrate and if chloride is present, it will cause visual turbidity in the solution



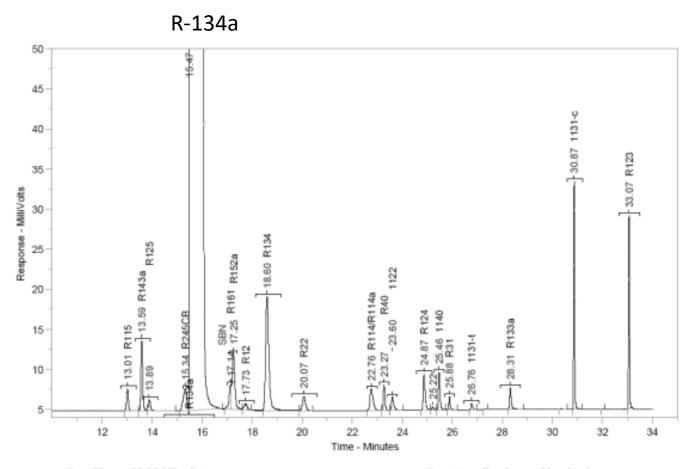
Non-Condensable Gas, Purity and Composition

All these properties are determined using Gas Chromatography (GC)

How Gas Chromatography Works

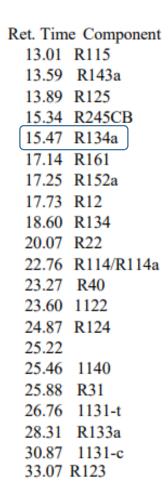


Example Gas Chromatogram from Appendix D (R-134a)



Run Time = 33.99667 minutes

Data Sampling Rate = 20 points/sec





Future changes to AHRI 700 Appendix C and D

- The group is evaluating if any additional properties should be tested, such as for fluorocarbon blends that contain CO₂
- Add any modified procedures for new refrigerants for which current procedures don't apply
- Updating some of the Gas Chromatograms (GCs)
- Adding GCs for newly added refrigerants to AHRI 700



AHRI 740 – Performance Rating of Refrigerant Recovery

Equipment and Recovery/Recycling Equipment

Purpose and Scope – AHRI 740

Purpose

- to establish requirements and conformance conditions for refrigerant recovery and recovery/recycling equipment.
- To establish methods of testing for rating and evaluating the performance of refrigerant recovery and recovery/recycling equipment...

Scope

- applies to equipment for recovering and/or recycling refrigerants, and their normal contaminants from refrigerant systems.
- defines the test apparatus, test gas mixtures, sampling procedures and analytical techniques that will be used to determine the performance of refrigerant recovery equipment and recovery/recycling equipment.

Note: AHRI 740 is used in the AHRI Refrigerant Recovery and Recycling Equipment (RRRE) Certification Program.



Important Definitions



Recover - To remove refrigerant in any condition from a system and store it in an external container



<u>Recycle</u> - To reduce contaminants in used refrigerants by separating oil, removing non-condensables, and reducing moisture, acidity and particulate matter



<u>Reclaim</u> – to process used refrigerant to AHRI Standard 700 product specifications

The standard is for assessing the performance of <u>recovery</u> and <u>recycling</u> equipment. However, either new or reclaimed refrigerant may be used to do so



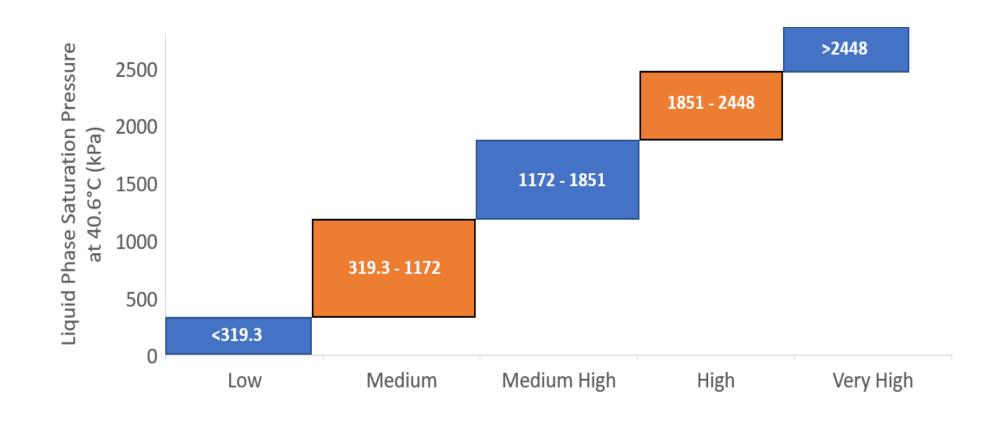
Recovery Performance Testing

Table 1. Performance Ratings for Refrigerant Recovery Equipment and Recovery/Recycling Equipment ^{4,5}									
	Type of Equipment								
Parameter	Recovery	Recovery/ Recycling	Recycling	System Dependent Equipment					
Push/Pull Liquid Recovery Rate, kg/min	X^1	X ¹	N/A	N/A					
Liquid Refrigerant Recovery Rate, kg/min	X^1	X^1	N/A	N/A					
Vapor Refrigerant Recovery Rate, kg/min	X^1	X ¹	N/A	N/A					
High Temperature Vapor Recovery Rate, kg/min	X^1	X ¹	N/A	N/A					
Final Recovery Vacuum Level, kPa	X	X	N/A	X					
Recycle Flow Rate, kg/min	N/A	X	X	N/A					
Refrigerant Loss, kg	X^2	X	X	X^3					
Residual Trapped Refrigerant, kg	X^3	X^2	X^2	X^2					
Quantity of Refrigerant Processed at Rated Conditions, kg	N/A	Х	х	N/A					

Notes:

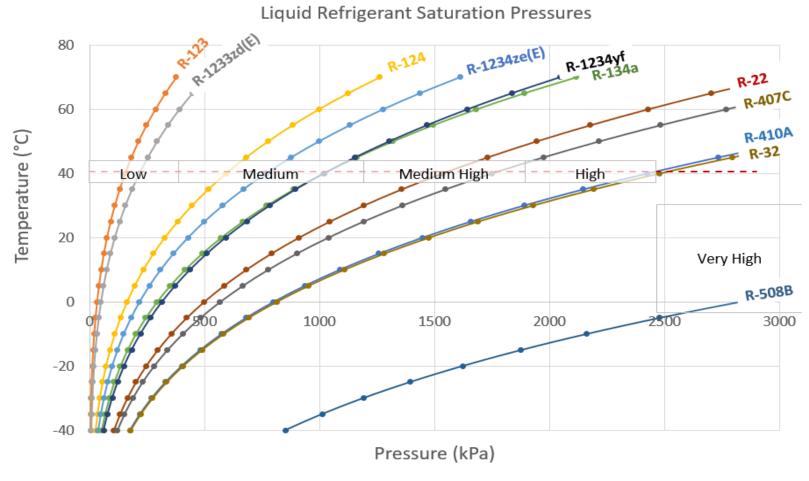
- For a recovery or recovery/recycling unit, establish a rating for either liquid refrigerant recovery rate or vapor refrigerant recovery rate or both. If rating only one, the other rate shall be indicated by N/A, "not applicable."
- 2. Mandatory rating if multiple refrigerants, oil separation or non-condensable purge are rated.
- 3. Mandatory rating for equipment within the scope of this standard tested for multiple refrigerants.
- 4. "X" denotes mandatory rating or equipment requirements.
- 5. "N/A" indicates "Not Applicable" for a parameter that does not have a rating.

Refrigerant Pressure Categories





Representative Refrigerants for each Category







Current Refrigerant Categories in AHRI 740 and Representative Refrigerants

Category	Non-Flammable Representative	Flammable (A2L) Representative		
I – Low Pressure	R-123 or R-1233zd(E)	N/A		
II – Medium Pressure - Low Moisture	R-124	R-1234ze(E)		
III – Medium Pressure	R-134a	R-1234yf		
IV – Medium High Pressure	R-22 or R-407C	N/A		
V – High Pressure	R-410A	R-32		
VI – Very High Pressure – High Moisture	R-508B	N/A		

The standard has representative A2L refrigerants included



Contaminant Removal

Table 2. Contaminant Removal Ratings for Refrigerant Recovery Equipment and Recovery/Recycling Equipment ^{1,2}									
	Type of Equipment								
Contaminant	Recovery	Recovery/Recycling	Recycling	System Dependent Equipment					
Moisture Content, ppm by weight	N/A	X	X	N/A					
Chloride Ions, pass/fail	N/A	X	X	N/A					
Acid Content, ppm by weight	N/A	X	X	N/A					
High Boiling Residue, % by volume	N/A	X	X	N/A					
Particulates/solids, pass/fail	N/A	X	X	N/A					
Non-condensables, % by volume	N/A	X	X	N/A					

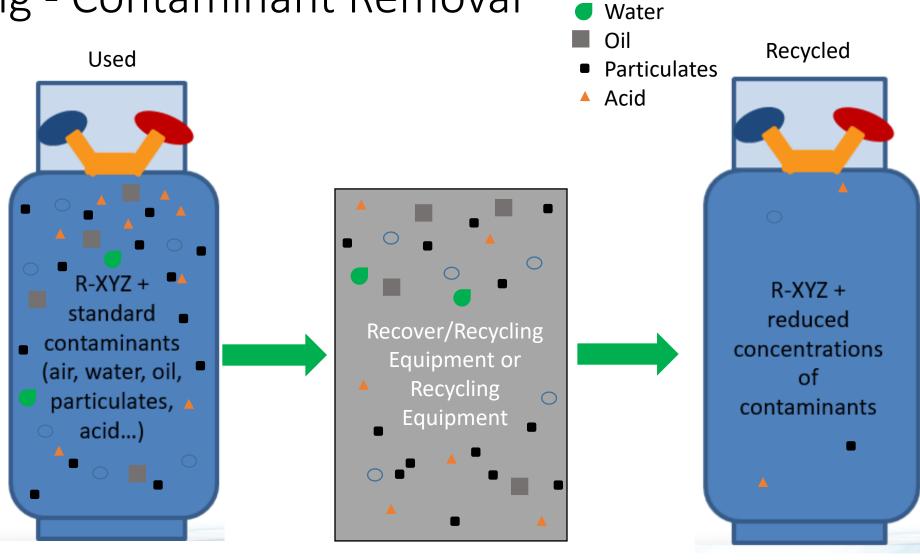
Notes:

- 1. X denotes Mandatory rating.
- 2. "N/A" indicates "Not Applicable" for a parameter that does not have a rating.

Only the recovery/recycling and recycling equipment is assessed for contaminant removal ratings



Recycling - Contaminant Removal



Air

Example of Recycled vs. Reclaimed Refrigerant Requirements

R-134a									
Characteristic	Units	Recycled (AHRI 740)	Reclaimed (AHRI 700)						
Air & Other Non-Condensables	% by volume	2.0	1.5						
Water, maximum	ppm by weight	20	10						
Acidity, maximum	ppm by weight	1	1						
High Boiling Residue	% by volume	0.02	0.01						
Particulates/solids	Pass/Fail	Visually Clean	Visually Clean						

Recycled refrigerant doesn't have the same purity requirements as reclaimed or virgin refrigerant



A2L Flammable Refrigerants & AHRI 740 Status

- A2L flammable refrigerants (R-32, R-1234yf, and R-1234ze(E)) are included as options for the recovery performance testing
- No A2L refrigerants are specified with standard contaminants for the recycling testing

AHRI STANDARD 740-2016_

Table 3. Standard Contaminated Refrigerant Samples (Continued) ⁴														
	Refrigerant Type													
Contaminants	R- 402B	R- 404A	R- 406A	R- 407A	R- 407B	R- 407C	R- 407D	R- 408A	R- 409A	R- 410A	R- 410B	R- 411A	R- 411B	R-417C
Moisture Content: ppm by Weight of Pure Refrigerant	200	200	200	200	200	200	200	200	200	200	200	200	200	200
Particulate Content: ppm by Weight of Pure Refrigerant ¹	80	80	80	80	80	80	80	80	80	80	80	80	80	80
Acid Content: ppm by Weight of Pure Refrigerant ²	100	100	200	100	100	100	100	100	100	100	100	100	100	100
Oil (HBR) Content: % by Weight of Pure Refrigerant	5	5	5	5	5	5	5	5	5	5	5	5	5	5
Viscosity/Type ³	150/ AB	150/ POE	150/ AB	150/ POE	150/ POE	150/ POE	150/ POE	150/ MO	150/ MO	150/ POE	150/ POE	150/ MO	150/ MO	150/ POE
Non-Condensable Gases (Air Content): % by Volume	3	3	3	3	3	3	3	3	3	3	3	3	3	3

Notes

- 1. Particulate content shall consist of inert materials and shall comply with particulate requirements in Appendix D.
- Acid consists of 60% oleic acid and 40% hydrochloric acid on a total number basis.
- 3. POE = Polyolester, AB = Alkylbenzene, MO = Mineral Oil.
- 4. N/A means not applicable.

Next Steps/Timeline for AHRI 740

- Consider replacements for the HCFC and high GWP refrigerants currently specified
- Update the standard contaminated refrigerants to include flammable and nonflammable low GWP options; considering fewer representative contaminated refrigerants to cover categories (like the recovery portion of the standard)
- A revision project charter has been approved by the STC and revisions will commence in 2023

Guideline K-2015: Containers for Recovered Non-flammable Fluorocarbon Refrigerants

Purpose and Scope: Guideline K

Purpose

 To establish a guide of good practice for container design and specifications for the recovery, recycling and reclamation of fluorocarbon refrigerants

Scope

 The guideline applies to cylinders with a service pressure maximum of 400 psig and ton tanks with a maximum service pressure of 500 psig for the receipt, storage, and transportation of recovered non-flammable fluorocarbon refrigerants



Important Definitions: Guideline K

- Reclamation To reprocess refrigerant to new product specifications, by means which may include distillation. Chemical analysis of the refrigerant will be required to determine that appropriate product specifications are met
- Service Pressure The rated pressure marked on the cylinder or ton tank
- Special Permit Cylinder A cylinder that has been authorized by the Department of Transportation (DOT) to be manufactured outside the scope of existing DOT regulations but in accordance with the requirements specified by DOT in a special permit

Topics Covered in Guideline K

- Guideline K covers:
 - Design requirements
 - Label and marketing requirements
 - Filling procedures
 - Best practices for transportation
- For cylinders, ton tanks, and containers

Upcoming Changes: Guideline K

- With the current market shifting to include many A2Ls and other flammable refrigerants, revisions are underway to expand the guideline to include flammable fluorocarbon refrigerants
- Service pressures will be updated to ensure accuracy as well as adding service pressures for flammable refrigerants

Guideline N-2017: Assignment of Refrigerant Container Colors

Purpose and Scope – Guideline N

Purpose

 The purpose of this guideline is to establish assignment of refrigerant container colors; definitions; basic considerations for developing the color guideline; and assignment criteria

Scope

- This guideline provides a means by which PMS
 (Pantone® Matching System) colors can be assigned to
 printed materials, such as printed labels on refrigerant
 containers, for refrigerants currently in use or newly
 developed refrigerants, provided the refrigerant is used
 in significant quantities as defined in this guideline
- Colors should not be relied upon exclusively to determine the type of Refrigerant in the container

Important Definitions/Classifications – Guideline N

- Class I: Liquid Refrigerants Those refrigerants with a normal boiling point greater than 20°C. These products normally are packaged in drums
- Class II: Low Pressure Refrigerants Those refrigerants that meet the definition of a compressed gas and have a minimum cylinder service pressure not exceeding 3447 kPa gage
- Class III: High Pressure Refrigerants Those Refrigerants that meet the definition of a compressed gas and have a minimum cylinder service pressure exceeding 3447 kPa gage
- Class IV: Flammable Refrigerants Those refrigerants that receive a flammability rating of 2, 2L, or 3 in ANSI/ASHRAE Standard 34, Designation and Safety Classification of Refrigerants with Addenda

Color Guidelines – Guideline N

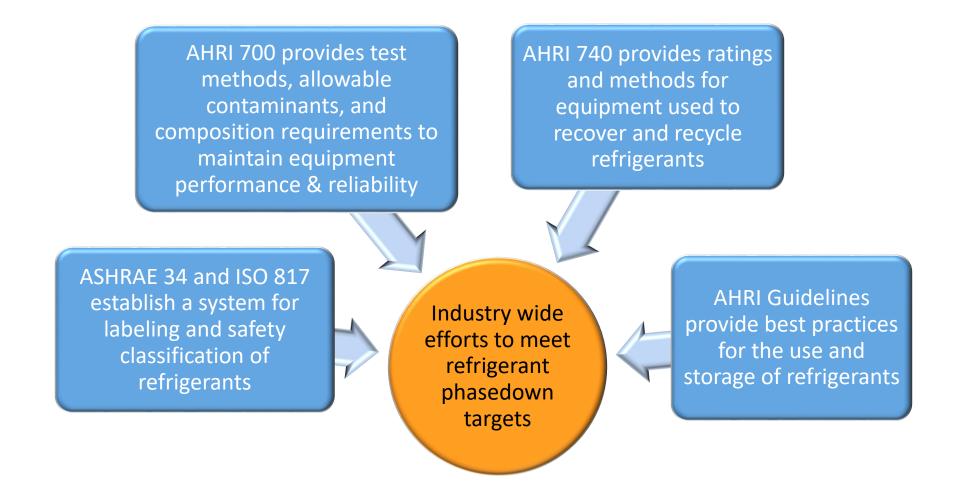
- While Guideline N originally specified unique colors for each refrigerant, the last 2017 revision specified that all refrigerant containers should transition to the same light green-gray paint color (RAL 7044) by 2020
- Any flammable compounds or mixtures should have a red band on the shoulder or top of container
- Existing inventories of previously painted cylinders were not required to be repainted



Next Steps – Guideline N

- The guideline needs to be updated to clarify the current practices.
- The STC responsible for the Guideline plans to start reviewing the guideline in early to mid 2023.

Industry Impact







Summary

- Standards are being updated to enable the use (and reuse) of low GWP flammable and nonflammable refrigerants in HVACR equipment
- Standard revisions are being considered so that update frequency better aligns with the pace of new refrigerant development
- Updates are being made in anticipation of increased recovery, recycling, and reclaim of refrigerants.

If interested in participating on the AHRI Standards/Guidelines updates

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