

Chemical, Physical, and Environmental Properties of ASHRAE 34 and ISO 817

CHAPTER TWO

Chemical and Physical Properties of Class A2L Refrigerants

The HVACR industry's safe transition to low-global warming potential (GWP) refrigerants requires proper training of all stakeholders to safely and responsibly transport, handle, install, and service equipment with ASHRAE Standard 34 Class A2L refrigerants. While the majority of the physical and chemical properties of A2L gases are very similar to the traditional ASHRAE Standard 34 Class A1 refrigerants (CFCs, HCFCs, and HFCs such as R-134a and R-410A), stakeholders must be aware of the properties of these lower flammability refrigerants and trained to mitigate associated risks.

Key Points

- Most of the basic chemical and physical properties of new generation refrigerants are the same as previous generation (CFC/HCFC/HFC) refrigerants.
- The move to sustainable (lower GWP) refrigerants necessitates growth in applications with different flammability and toxicity characteristics.
- Refrigerants are classified according to flammability by ASHRAE Standard 34 & ISO 817 following test protocols under ASTM E681:
 - (1- no flame propagation, 2L lower flammability, 2- flammable, 3- higher flammability)
- Flammable refrigerants may only be used in new systems/applications that are designed and listed by an approved nationally-recognized laboratory to mitigate risks, and where allowed by appropriate codes and standards, or by an Authority Having Jurisdiction (AHJ).
- Compared to traditional (Class A1) refrigerants such as R-410A, A2L refrigerants present the same Hydrogen Fluoride (HF) gas combustion product as all other fluorocarbons.¹ There is no significant change in fuel load (heat of combustion).

What's the Same?

- A2Ls have similar basic pressure/temperature properties to the Class A1 refrigerants they are replacing.
- Appropriate safety procedures, including system evacuation and sufficient work area ventilation, are required.
- System installation and service should be conducted only by properly trained and qualified service technicians.
- First responders still need to use recommended Personal Protective Equipment (PPE) and follow procedures appropriate for the installed systems.

¹ Chlorinated and iodated fluorocarbons such as HCFO-1233zd and R-466A have additional combustion products (e.g. hydrogen chloride and hydrogen iodide)

What's New?

- Systems designed to mitigate flammability risks following UL 60335-2-40, 3rd ed and ASHRAE Standard 15 2019 requirements.
- Service technicians will be required to use tools such as pumps and leak detectors rated for use with Class A2L refrigerants.
- In direct systems (i.e., those where refrigerant can enter an occupied space), newly
 updated safety standards require additional features to enhance safety. These features
 include refrigerant sensors in the product, evaluation of the refrigerant charge and
 conditioned space area following UL 60335-2-40, 3rd ed. A2 and A3 refrigerant charges
 will be limited to 114 g in the U.S. and Canada.
- For indirect systems in machine rooms, there are new requirements for machine room ventilation outlined in ASHRAE 15 (2019).
- First responder training and procedures will need to be updated to incorporate the properties, hazards, and fire-fighting measures associated with Class A2L refrigerants.

What Do I Need to Do?

Read installation instructions before installing equipment. Stay informed and trained on regulations, building codes, and industry adoption and applications, including safe handling and servicing of equipment and systems using A2L refrigerants.

Overview – A2L Refrigerant Properties

Physical and Chemical Properties

- Pressure Temperature Data
- Transport Property Data
- Temperature glide (for refrigerant blends, i.e., those assigned a 400 or 500 series number by ASHRAE Standard 34).
- Material Compatibility Data
- Lubricant Compatibility Data

Safety and Health Properties

- Safety Data Sheets
- Toxicological Data
- Flammability Properties (see below)
- Refrigerant Concentration Limit (RCL)

- PPE Recommendations

Environmental Properties

- Ozone Depletion Potential (ODP)
- Global Warming Potential (GWP)
- Atmospheric Degradation

Flammability Properties

- Flammable Classification per ASHRAE 34 and ISO 817 (Class 1, 2L, 2 or 3)

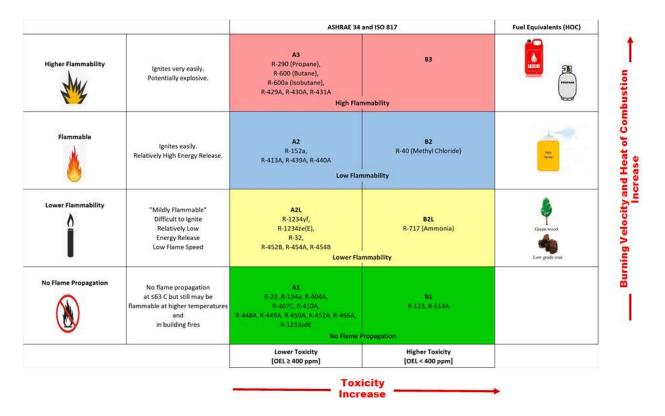


Figure adapted from Richard Lord presentation to IAFF-UL Safety Considerations of the Future Built Environment, Milwaukee, WI, November 8, 2019. ©Carrier.

- Combustion Products
- Heat of Combustion (Fuel Load)
- Burning Velocity (S_u)

- Minimum Ignition Energy (MIE)

Chemical and Physical Properties

<u>Thermodynamic and Transport Properties</u> – Thermodynamic (pressure, temperature, etc.) and transport (viscosity, etc.) properties are unique to each refrigerant and are measured and reported by the American Society of Heating, Refrigeration and Air Conditioning Engineers and other organizations. These basic properties are not dependent on flammability class (A1 vs. A2L) but are critical to equipment design and performance.

<u>Temperature Glide (for blends)</u> – As with A1 products, A2L refrigerants may be either single component (R-1234yf, R-32, etc.) or multi-component blends (R-452B, R-454B, etc.). Refrigerant blends exhibit a property referred to as "temperature glide," which simply indicates that the refrigerant changes state (boils/condenses) over a temperature range ("the glide") rather than at a specific temperature like pure fluids. For blends, the impact of glide needs to be considered when charging, servicing, and/or evaluating system performance.

<u>Material Compatibility Data</u> – The chemical interaction of refrigerants and lubricants with typical materials of construction (metals, plastics, elastomers, etc.) is evaluated and reported by various industry stakeholders including refrigerant producers and system OEMs to guide selection of suitable materials.

Material compatibility interactions are unique to the specific substances being studied and must be evaluated as such. In general, there are no differences in compatibility based solely on flammability classification (A1 vs. A2L).

<u>Lubricant Compatibility Data</u> – Proper interaction between the refrigerant and lubricant is critical to returning lubricant to the compressor and maintaining long term equipment performance. Systems manufacturers run extensive testing to identify the best lubricants for their equipment. As with A1 refrigerants, it is critical to follow the OEM recommendations for lubricants that will perform best with their equipment designed for specific A2L refrigerants.

Safety and Health Properties

- The primary source for safety and health information on refrigerants are the Safety Data Sheets (SDS), formerly known as Material Safety Data Sheets (MSDS).
- SDS are available from refrigerant manufacturers and suppliers, often online.
- Those who handle refrigerants and first responders should read, understand, and follow the guidance in the SDS - especially as it relates to personal protective equipment (PPE) and should follow procedures listed in the applicable service manuals for the equipment.

 Refrigerants are classified by ASHRAE Standard 34 & ISO 817 according to toxicity (based on Occupational Exposure Limit (OEL)) and flammability properties (based on flame propagation at 60°C and 101.3 kPa, burning velocity, and heat of combustion), as shown in the figure below.

	ASHRAE 34 and ISO 817			
Higher Flammability [exhibits flame propagation when tested at $60^{\circ}C$ (140°F) and 101.3 kPa (14.7 psia) and has an LFL < 0.10 kg/m3 (0.0062 lb/ft3) or it has a heat of combustion > 19000 kJ/kg (8169 BTU/lb)]	Higher Fla A3 R-290 (Propane), R-600 (Butane), R-600a (Isobutane), R-429A, R-430A, R-431A	ammability B3	Î	
Flammable [exhibits flame propagation when tested at 60°C (140°F) and 101.3 kPa (14.7 psia), has an LFL > 0.10 kg/m3 (0.0062 lb/ft3) and has a heat of combustion < 19000 kJ/kg (8169 BTU/lb)]	Flam ı A2 R-152a, R-413A, R-439A, R-440A	mable B2 R-40 (Methyl Chloride)	and Heat of Combustion	
Lower Flammability [exhibits flame propagation when tested at $60^{\circ}C (140^{\circ}F)$ and 101.3 kPa (14.7 psia), has an LFL > 0.10 kg/m3 (0.0062 lb/ft3) and has a heat of combustion < 19000 kJ/kg (8169 BTU/lb) and has a maximum burning velocity ≤ 10 cm/s (3.9 in/s) when tested at 23°C (73.4°F) and 101.3 kPa (14.7 psia)	Lower Flam A2L R-1234yf, R-1234ze(E), R-32, R-452B, R-454A, R-454B maximum burning v	B2L R-717 (Ammonia)	Burning Velocity and Heat of Combustion	
No Flame Propagation [does not exhibit flame propagation when tested at 60°C (140°F) and 101.3 kPa (14.7 psia)]	No Flame Pro A1 R-22, R-134a, R-404A, R-407C, R-410A, R-448A, R-449A, R-450A, R-452A, R-466A, R-1233zd(E)	opagation B1 R-123, R-514A		
	Lower Toxicity [OEL ≥ 400 ppm] Toxic incre			

Figure adapted from Richard Lord presentation to IAFF-UL Safety Considerations of the Future Built Environment, Milwaukee, WI, November 8, 2019. ©Carrier.

 As the industry transitions from A1 products (e.g. R-410A), a major change will include measures to mitigate flammability risks associated with new A2L products; such measures are defined in product safety standards like UL60335-2-40, 3rd ed. and ASHRAE 15 – 2019.

- Mitigation is achieved through a combination of OEM system design changes (ignition source protection, refrigerant detectors installed in the product, charge size, and conditioned area), enhanced system tightness and leak detection, piping design and testing requirements, appropriate standards and codes for various applications, as well as service and installation technician training on safe use of A2L refrigerants.
- Burning velocity (S_u) is used to assess potential ignition sources under UL 60335-2-40.
- New labeling requirements for A2L systems will be used, with new symbols indicating that A2L refrigerants are in use.
- Additional labeling may be required for other stakeholders (such as the fire service).



Environmental Properties

<u>Ozone Depletion Potential (ODP)</u> – ODP is the potential for a substance to react with stratospheric ozone, due mainly to chlorine in the molecule. International regulations have shifted the industry away from ODP substances (R-12, R-22, etc.) over recent decades to mostly zero-ODP refrigerants (R-134a, R-410A, etc.). A2L refrigerants are typically HFCs, Hydrofluorolefins (HFOs), or blends thereof and would have zero ODP.

<u>Global Warming Potential (GWP)</u> – GWP is the measure of substance ability to trap heat in the atmosphere ("greenhouse effect").

 The primary source of ODP and GWP values used by the industry and regulators is published by the United Nations Intergovernmental Panel on Climate Change (IPCC).
 GWP values are published by IPCC with both 20-year and 100-year values. The IPCC Annual Report 4 (AR4) is used by all regulating agencies.

<u>TEWI/LLCP</u> – Total Equivalent Warming Impact (TEWI) or Life Cycle Climate Performance (LCCP) and other similar methodologies take a broader view of climate impact beyond GWP. Most significant is incorporation of energy usage when assessing the environmental impact over the lifetime of the system.

Environmental Fate²

According to the Montreal Protocol Environmental Effects Assessment Panel (EEAP) Quadrennial Assessment, trifluoracetic acid (TFA), a chemical that is persistent in the environment, is formed by many unregulated sources with no data on global production and release to the environment of the majority of these sources. TFA is also formed in the atmosphere by several HCFCs, HFCs, and HFOs.

HFCs degrade slowly in the atmosphere (1–100 years) and any TFA produced is globally distributed. By contrast, shorter-lived fluorocarbons, such as HFO-1234yf, degrades to TFA rapidly and breakdown occurs closer to regions where HFO-1234yf is released resulting in possible localized high concentrations of TFA in surface waters than TFA from HFCs. The Assessment Report goes on to state that there is no evidence to date that suggests these local depositions of TFA will result in risks to the environment, especially when eventual dilution occurs in the oceans. Exposure to current and projected concentrations of TFA salts in surface waters present minimal risk to human and environmental health.

Flammability Properties

- Definitions and Terms
- Refrigerant Flammability Classifications
 ASHRAE Std 34 and ISO 817
- Thermal Decomposition
 - Complete Combustion
 - Partial Combustion
 - Pyrolysis
 - Breakdown Products
 - Thermal Load During Combustion Events

² United Nations Environment Programme. 2018. Environmental Effects and Interactions of Stratospheric Ozone Depletion, UV Radiation, and Climate Change 2018 Assessment Report. Accessed from <u>https://ozone.unep.org/sites/default/files/2019-04/EEAP_assessment-report-2018%20%282%29.pdf</u>

Flammability – Definitions and Terminology

Lower Flammable Limit (LFL) or Lower Explosion Limit (LEL)

Minimum concentration of substance in air that will exhibit flame propagation (e.g. volume % in air or kg/m3); below the LFL, not enough fuel is present.

Upper Flammable Limit (UFL) or Upper Explosion Limit (UEL)

Maximum concentration of substance in air that will exhibit flame propagation (e.g. volume % in air or kg/m3); insufficient air is present above UFL. Therefore, ignition/propagation only occurs between the LFL and UFL concentrations.

Flammable Range

The concentration range for a flammable substance in air between and including the LFL and the UFL. Ignition/propagation will only occur in this range.

Minimum Ignition Energy (MIE)

Minimum electrical spark energy (mJ) required to ignite a flammable gas/air mixture. Ignition sources with energies below this value will not ignite the flammable gas/air mixture. This value is assessed for refrigerants following the ASTM E681 test method.

Auto-Ignition Temperature (AIT)

Temperature where material/air mixture does not require an external ignition source to combust.

Burning Velocity (Su)

Velocity of laminar flame under stated conditions of substance concentration in air, temperature, and pressure.

Maximum Pressure Rise

Overpressure: The maximum pressure that can be obtained in a sealed vessel from the combustion reaction (often used to calculate venting requirements in case of an explosion).

Maximum Rate of Pressure Rise

 $(dP/dt)_{max}$: The maximum change in pressure with time during the flame propagation of explosion in a sealed vessel (often used to calculate venting requirements in case of an explosion).

Heat of Combustion (HOC)

Heat per unit mass (or mole) released by the combustion of a substance that produces specified products (this is a calculated value).

Stoichiometric Composition

Composition of flammable gas in air that has the stoichiometric (or optimum) ratio of gas to oxygen for the specified combustion products (this is a measure of the most flammable composition).

Combustion

A chemical process, especially oxidation, accompanied by the production of heat and light.

Thermal decomposition

Decomposition of a compound into one or more substances by heat alone, i.e., without oxidation. This phenomenon is also known as pyrolysis.

Combustion Reaction

An exothermic oxidation (addition of O2) reaction which may occur with any organic compound.

Simple example: combustion of methane

$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$

Reaction products for this equation are CO2 and H2O.

Classifications and Combustion

ASHRAE Standard 34 and ISO 817 Flammability Classifications

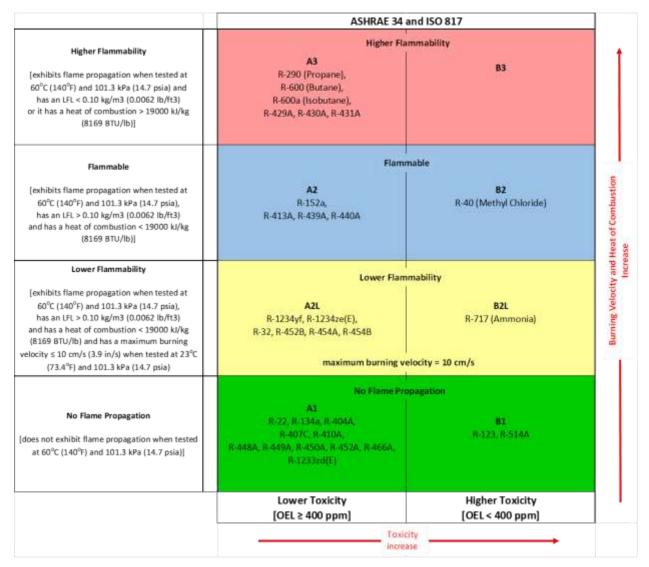
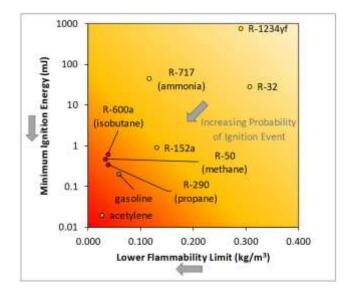


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Flammability – Minimum Ignition Energy (MIE)

- All flammable refrigerants can be ignited once a flammable concentration in the air is reached and a viable ignition source is present.
- A3s require relatively low energy levels to ignite.
- MIEs of A2Ls are orders of magnitude higher than A3s.
- Many potential ignition sources for A3s (e.g., static spark) will not ignite A2Ls.

• A1 refrigerants (which show no flame propagation at 60°C and 101.3 kPa) can also ignite at the higher temperatures seen during an externally-fueled fire.



Refrigerant Decomposition Products

- <u>HF (Hydrogen fluoride gas)</u> can be formed when <u>any fluorine-containing refrigerant</u> (even Class A1 refrigerants) undergo combustion, partial combustion, or thermal decomposition, e.g., exposed to open flames. HF has a very low density and rises in air. Note: Therefore, proper ventilation and removal of refrigerant before use of any flames is recommended for all fluorocarbon refrigerants.
- <u>COF₂ (carbonyl fluoride)</u> is a short-lived, transient, intermediate product, which if produced during combustion, reacts immediately with any moisture to form HF. As a result, there is minimal opportunity for direct exposure to COF₂; the same protective equipment addresses both concerns.
- <u>Others</u> Some refrigerants have been listed by ASHRAE 34 with other compounds (e.g., CF₃I) that can produce new decomposition products (e.g., hydrogen iodide). Please consult the SDS when using any refrigerant for guidance on potential hazards.

Flammability - Degree of Combustion

 <u>Complete combustion</u> (e.g. the production of soot, an incomplete combustion product from burning gasoline) rarely takes place in reality. <u>Complete</u> combustion is almost impossible to achieve.

- The highest probability of <u>complete</u> combustion occurs under conditions where refrigerant and air are <u>well mixed</u>, <u>non-flowing</u>, and in the presence of a strong ignition source. Almost all refrigerants (including Class A1) will combust under these conditions.
- <u>Complete</u> combustion analysis represents a "worst case" scenario when considering HF formation.

Equations for Complete Combustion – Comparison of HFC-134a (A1) to HFO-1234yf (A2L)

HFC-134a: $2CF_3CFH_2 + 3O_2 \rightarrow 2CF_2O + 2CO_2 + 4HF$ $2CF_2O + 2H_2O \rightarrow 2CO_2 + 4HF$

1 mole of HFC-134a combusted produces 4 moles of HF.

1 kg of HFC-134a combusted produces 784g HF

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HFO-1234yf:
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 $\begin{array}{rcl} CF_3CF=CH_2 &+& 2O_2 \rightarrow & 2CF_2O &+H_2O &+& CO\\ 2 CF_2O &+& 2H_2O \rightarrow & 2CO_2 &+& 4HF \end{array}$

1 mole of HFO-1234yf combusted produces 4 moles of HF.

1 kg of HFO-1234yf combusted produces 702g HF

HFC-134a has the potential to generate more HF on a kg basis than HFO-1234yf, given complete combustion <u>rxn</u>.

Complete Combustion of Various Refrigerants

All fluorocarbon refrigerants, including A1 refrigerants, will generate HF if completely combusted				
Refrigerant	ASHRAE Classification	Mol Wt	Moles HF per mole refrigerant	g HF per 1000 g refrigerant
R-410A	Al	72.59	2.9	800
R-32	A2L	52.02	2.0	768
R-452B	A2L	63.53	2.4	756
R-454B	A2L	62.62	2.3	747

R-410A has the potential to generate more HF per kg than A2L candidates, given complete combustion reaction.

Flammability - Partial Combustion

- $CF_3CF=CH_2 \rightarrow CF_3C=CH_2 + F$
- Partial combustion results in only one fluorine atom being removed from refrigerant (HFO-1234yf shown above). This generates one only one mole of HF versus 4 moles of HF found under complete combustion conditions.
- Partial combustion is more representative of many of the scenarios found in real life due to non-ideal conditions:
 - poor refrigerant/air mixing;
 - dynamic flow from the leak source (not stagnant); and
 - slow burning velocity \rightarrow limited flame spread.

Therefore, more realistic scenarios produce significantly less HF than laboratory, well-mixed conditions.

HF Human Response

- HF formation is visibly detected at 1 ppm in air (white fumes).
- HF has a very low density and rises.
- The human nose can detect HF presence at 0.3 ppm in air and noticeable irritation at 3 ppm, which is well below any adverse health effect level.
- SAE CRP OEM group used the AEGL-2 as a Risk Assessment benchmark value.
 - SAE CRP used exposure limits for emergency exposures [AEGLs] for Risk Assessments developed under the National Research Council and supported by the USEPA (agreed upon for use in SAE vehicle CRP setting by an international group of OEM toxicologists).
- HF AEGL-2*:
 - -*95ppm / 10 minutes
 - 95ppm / 1-minute conservative value used by SAE CRP OEMs
 - -*34ppm / 30 minutes

Fuel Value of A2L versus A1 Refrigerants

There is negligible added fuel value in A2L refrigerant usage compared to A1. In the worst-case scenario, which would be an externally fueled fire, complete charge loss (typical residential ducted split unit charge ~ 15 lbs.) would be very similar to today's air conditioning refrigerants.

- Nominal A2L refrigerant He	at of Combustion = 4400 BTU/lb.
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- <u>R-410A refrigerant</u> Heat of Combustion = 2800 BTU/lb.

Assuming all refrigerant leaked and burned, fuel value difference between the A2L and R-410A would be:

This difference (A2L vs A1) is equivalent to additional fuel value of:

- 3.4 lbs. dry wood (~30% of an 8 ft length of kiln-dried 2x4)
- 1.7 lbs. Duraflame[™] wax firelog (~38% of a single firelog)



Summary of A2L Refrigerant Flammability

Compared to higher flammability, A3 class refrigerants (propane) and A2L refrigerants have much lower flammability risk due to:

- higher minimum ignition energy, making them harder to ignite;
- lower burning velocity, making it more difficult for flames to spread; and
- lower heat of combustion, so there is less energy released if burned.

Compared to A1 refrigerants, A2Ls have:

- slightly higher flammability properties, and if burned, produce similar types and amounts of by-products (e.g. HF); and
- somewhat higher heat of combustion/fuel value.

Flammability risks from A2L refrigerants will be mitigated by a variety of equipment design changes, applicable codes and standards, and technician training. The lower flammability limit of A2L refrigerants is very high, which means that a high concentration of refrigerant is needed to create a flammable mixture (ASHRAE 34).³

A2L Refrigerant Properties – Conclusions

- The move to sustainable (lower GWP) fluids to reduce the impact on the environmental temperature will result in the use of some refrigerants with different flammability or toxicity characteristics.
- Many of the basic chemical and physical properties of new generation A2L refrigerants are very similar to previous generation A1 (CFC/HFC) refrigerants and are readily available.
- Refrigerants are classified according to flammability and toxicity by ASHRAE Standard 34 & ISO 817:
 - 1- no flame propagation, 2L lower flammability, 2- flammable, 3- highly flammable
 - A lower toxicity, B higher toxicity
- It is important to also understand the RCL limits that apply to ALL refrigerants and follow requirements defined in standards like ASHRAE 15 2019.
- Flammable refrigerants will only be used in new systems/applications designed and listed by a third-party laboratory to mitigate risks, and where allowed by appropriate codes and standards unless approved by an AHJ.
- Compared to traditional A1 refrigerants (i.e. R-410A), A2L refrigerants present:
 - same combustion products, i.e., both produce HF;
 - similar fuel load (heat of combustion);
 - no additional risk of leaks in a properly installed system; and
 - an opportunity to reduce GWP levels and the possible impact of refrigerant emissions on our global environment.

³ Data from the LIFE FRONT <u>refrigerant leak database</u> suggests that the vast majority (99.2 percent) of leaks are due to small holes forming in equipment (less than 0.004 in²).