

# Hydrogen Gas Safety *Self-Study*

3 Li 6.941	4 Be 9.0122	<b>1</b> <b>1.0079</b> 20.268 14.025 0.0899* <b>H</b> 1s* Hydrogen							
11 Na 22.98977	12 Mg 24.304								
19 K 39.0983	20 Ca 40.078	37 Rb 85.4678	38 Sr 87.62	55 Cs 132.90545	56 Ba 137.327	57 La 138.90487	72 Hf 178.49	73 Ta 180.94788	74 W 183.84
87 Fr [223]	88 Ra [226]	89 Ac [227]	104 Unq [261]	105 Unp [262]	106 Unh [263]				

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# Introduction

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## About This Course

### Course Purpose

This self-study course is intended to provide hydrogen gas users with the fundamental awareness necessary to minimize the risk of accident or injury due to human error.

### Course Objectives

When you have completed this course you will be able to

- identify the physical properties associated with hydrogen gas,
- recognize the physical hazards associated with hydrogen gas,
- recognize the health hazards associated with hydrogen gas,
- list the components of a hydrogen gas supply system,
- identify appropriate precautions for preventing electrical ignition of hydrogen gas,
- identify safe-handling guidelines appropriate for hydrogen gas systems,
- identify the safety considerations for moving gas cylinders,
- identify the safety considerations for storing hydrogen gas cylinders,
- identify the airborne concentrations at which alarm systems will be activated,
- list the four steps required in case a hydrogen alarm is activated,
- list the four steps appropriate for responding in case of a hydrogen fire, and
- list the points of contact for assistance in safely installing a hydrogen gas supply system.

### About This Self-Study Guide

#### What Is Self-Study?

Self-study is a method of instructional delivery that allows you to work independently rather than under the direction of a classroom instructor.

#### In This Guide

This self-study contains two learning units, followed by lessons learned and references.

At the end of this study guide is a cumulative quiz to review the information in all the units. Instructions for accessing and taking the quiz follow this guide. A score of 80% on the quiz is required for course credit.

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# Hazards and Precautions

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## Properties of Hydrogen

### What Is Hydrogen?

Hydrogen is a colorless, odorless, tasteless, flammable nontoxic gas. It is the lightest of all gases, with a specific gravity of 0.0695. The hydrogen content of atmospheric air at sea level is 0.5 ppm.

Hydrogen has two isomers (forms): ortho-hydrogen, in which the two atomic nuclei spin in the same direction; and para-hydrogen, in which they spin in opposite directions. There is no difference in the chemical properties of the two forms of hydrogen, but there are slight differences in physical properties. Gaseous hydrogen is a mixture of 75% ortho-hydrogen and 25% para-hydrogen at room temperature; this mixture is called normal hydrogen (CGA G5 1991).

### Hydrogen Has Unique Properties

Several unique properties contribute to the hazards associated with gaseous and liquid hydrogen systems:

- Hydrogen is flammable over a wide range of concentrations.
- The ignition energy for hydrogen is very low.
- A single volume of liquid hydrogen expands to about 850 volumes of gas at standard temperature and pressure when vaporized. At 7,000 ft elevation, this expansion rate is increased to approximately 1,000 volumes of gas at standard temperature.
- Hydrogen is able to reduce the performance of some containment and piping materials, such as carbon steel.

### Properties of Hydrogen—continued

#### Flammability

Hydrogen burns with a nearly invisible bluish flame, unless it is contaminated with impurities, in which case a pale-yellow flame is easily visible in the dark. The temperature of burning hydrogen in air is high (3,713° F, as compared with 2,276° F for gasoline), and warm hydrogen gas rises rapidly because of its buoyancy. Hydrogen forms a flammable mixture over a wide range of concentrations in air and requires a minimum ignition source, only one-tenth of the energy required for gasoline vapors. It is the combination of these factors that contributes to the flammability hazard associated with hydrogen gas. (See the table below for a summary of the physical properties of hydrogen.)

#### Embrittlement

Because of its small molecular size, hydrogen can easily pass through porous materials and is capable of being absorbed by some containment materials, which can result in loss of ductility or embrittlement. At elevated temperatures, this process is accelerated. Because of the possibility of hydrogen embrittlement of some materials, piping and component materials that are not subject to this form of degradation should be selected. Recommended materials include 300-series stainless steels, copper, and brass.

### Properties of Hydrogen—continued

#### Physical Properties and Characteristics of Hydrogen

The following table lists the physical properties and characteristics of hydrogen and their values.

<b>Physical Properties and Characteristics of Hydrogen</b>	
<b>Property/Characteristic</b>	<b>Values (approximate)</b>
Color	None
Odor	None
Toxicity	Nontoxic
Density, liquid (boiling point)	4.4 lb/ft <sup>3</sup> (0.07 g/cm <sup>3</sup> )
Boiling point (1 atm)	-423.2 F (-252.9° C)
Critical temperature (188.2 psia)	-400.4 F (-240.2° C)
Stoichiometric mixture in air	29 vol %
Flammability limits in air	4–75 vol %
Detonation limits in air	18–60 vol %
Minimum ignition energy in air	20 μJ
Autoignition temperature	1,085° F (585° C)
Volume expansion:	
liquid (-252.9° C) to gas (-252.9° C)	1:53
gas (from -252.9° C to 20° C)	1:16
liquid (-252.9° C) to gas (20° C)	1:848

### Hazards of Hydrogen

#### **Flammability and Explosivity Are Primary Hazards**

The primary physical hazards associated with hydrogen gas are its flammability and explosivity. This is because hydrogen can form a flammable mixture with air over a wide range of concentrations (4%–75%), and very low energy is needed to ignite hydrogen-air mixtures. Once hydrogen is ignited, the reaction can proceed either by deflagration (subsonic propagation) or detonation (supersonic propagation). Deflagration in a closed volume can cause a pressure increase of almost eight times the initial pressure. Detonation from a low-energy ignition source is possible in hydrogen-air mixtures of 18–60% vol that are well mixed and confined. Although hydrogen-air mixtures have the same calorific value per pound as TNT, the rate of energy release is much slower for hydrogen-air mixtures. Hydrogen detonations, although rare, are characterized by pressure increases so rapid that pressure-relief devices are usually ineffective. When using hydrogen in enclosed areas, consult National Fire Protection Association documents 68 and 69.

#### **Effects on Health**

Hydrogen is nontoxic and has even been used as a filler for oxygen sources for underwater diving. The primary health effect associated with hydrogen is the possibility that it could displace air in a poorly ventilated or confined space, resulting in asphyxiation. However, because it is flammable at only 4% in air, the most significant concern should be the physical hazard of flammability and the possibility of burns resulting from fires and explosions. When working with liquid hydrogen, there is an additional health hazard of cryogenic burns.

### Components of the Supply Systems

#### Pressure-Relief Devices

In any pressurized system, each component of the system must have a pressure rating that equals or exceeds the maximum allowable working pressure (MAWP). The MAWP is the maximum pressure at which a system is safe to operate. This is the maximum setting for the primary pressure relief device.

Hydrogen cylinders must be equipped with *pressure-relief devices* to release the gas at or below the MAWP. The relieving capacity of the pressure relief device must be sufficient to prevent the system pressure from increasing more than 10% above the MAWP. The type of pressure relief device used consists of a frangible disk combined with a backing of low melting point fusible metal designed to burst under a combination of high temperature and excessive pressure.

Pressure-relief devices are also necessary on all volumes where liquid hydrogen or cold hydrogen gas can be trapped, and on vacuum insulation spaces surrounding liquid hydrogen. It is important that the discharge of pressure-relief devices is vented outdoors in a way that avoids impingement of escaping gas on adjacent equipment, structures, or personnel. Vents shall not discharge where hydrogen can accumulate, such as below eaves of buildings.

#### Valves

To allow for maintenance activities and emergency response, *isolation valves* are required. An isolation valve shall be installed at an accessible location in a hydrogen pipeline so that hydrogen flow can be shut off when necessary.

A special type of isolation valve is the *emergency isolation valve* (EIV), which provides an automatic or manual means for stopping the hydrogen flow in an emergency. EIVs are used on systems where branch or multiple distribution lines feed different facilities, and are located outside each building to permit emergency isolation of the system.

In some systems, *excess flow valves* may be necessary to ensure that the flow rate of the hydrogen gas does not exceed specifications. *Check valves* prevent reverse flow, which could result in contamination of the hydrogen gas system. All of the valves described in this section must be gas tight and made of materials suitable for use with hydrogen.

### Components of the Supply Systems—continued

#### Regulators

Shutoff valves that come with gas cylinders cannot be used to control the discharge rate of the gas in use. Additional equipment that is required for hydrogen gas delivery systems includes *regulators with pressure gauges*. As with valves and piping materials, these instruments must be intended for use with hydrogen gas.

The following precautions should be observed when using any regulator:

- Provide mechanical shielding for regulators to protect them from mechanical damage.
- Make sure that the regulator that is to be used is intended to be used with hydrogen gas.
- Select a regulator with a delivery gauge range approximately 2 times the operating pressure and at least 1.2 times the MAWP. Gauges are more accurate in midrange, and regulators are designed to operate at about half of the delivery gauge range.
- Never attempt to repair a regulator.
- Never change the delivery gauge on a regulator. Regulators have internal safety devices to protect the delivery gauges, and changing the gauge defeats that protection.
- Never use an adapter.

All component volumes containing hydrogen, including transfer lines, should be evacuated or purged with nitrogen or an inert gas before and after use. The effectiveness of the purge should be verified.

#### Electrical Equipment

Because of the extremely low energy required to ignite flammable mixtures of hydrogen gas, you must exercise caution when using hydrogen around electrical equipment. All flexible hoses and piping systems must be electrically grounded. The National Fire Protection Association has established standards for the specifications of electrical equipment intended to be used around hydrogen gas. The Occupational Safety and Health Administration has also established specifications for electrical equipment used around indoor hydrogen gas systems with a gas volume capacity greater than 400 cubic feet. Contact your area safety engineer for assistance in ensuring that these standards are followed.

### Hydrogen Gas Cylinders

#### Using Hydrogen Gas Cylinders

The following are some safe-handling guidelines that have been established by the Compressed Gas Association for using hydrogen gas cylinders. By following these guidelines you can help assure the safety of your hydrogen gas operations.

- It is very important to secure all compressed gas cylinders in an upright position so that they cannot be knocked over.
- Hydrogen gas cylinders should never be used if pressure has not been reduced by a suitable regulator at the cylinder, or at the outlet of the header valve of a cylinder manifold. Use only regulators intended to be used with hydrogen and never force connections that do not readily fit together.
- Never crack a hydrogen cylinder valve to remove dust or dirt from fittings prior to attaching a regulator. While this practice may be acceptable for other gases, with hydrogen there is a risk of self-ignition.
- Once the regulator is attached, be sure that the regulator adjusting screw is in the closed position before opening the cylinder valve. When opening the valve, turn the hand wheel slowly so that the hydrogen does not enter the regulator suddenly. Never use a wrench, hammer, or other tool to open or close the hand wheel.
- When opening the cylinder valve to extract content, turn the hand wheel all the way open and then back toward the closed position one quarter turn. When the work is finished, turn the cylinder valve off and be sure to bleed off all remaining hydrogen from the regulator before removing it from the cylinder.

### Hydrogen Gas Cylinders—continued

#### Moving Hydrogen Gas Cylinders

When moving cylinders, the following general precautions should be observed:

- Replace cylinder valve cap before moving a cylinder from its secured, in-use position.
- Move cylinders on cylinder carts or with other approved cylinder-transporting devices.
- Never roll or drop cylinders. Severe foot injury or damage to the cylinder could result.
- Before moving cylinders, remove regulator and secure protective valve cap, unless cylinder is part of a mobile system (such as a cart-mounted set). If cylinder is part of a mobile system, close the cylinder valves and bleed the pressure from regulators and hoses.
- Never lift cylinders by their protective caps.
- Wear safety shoes or toe protection.

#### Storing Hydrogen Gas Cylinders

The following points are important to follow for storing hydrogen gas cylinders that are awaiting removal or are anticipated for use.

- Hydrogen gas cylinders should be stored outside and away from doors, windows, and building air intakes. Indoor storage of hydrogen requires specially designed facilities. Consult the Industrial Hygiene and Safety Group (ESH-5) and the Facility Risk Management Group (ESH-3) before setting up indoor storage locations for hydrogen cylinders not in use.
- Cylinders must be protected against heat, corrosive atmospheres, rain, snow accumulation, and direct sunlight. The storage area should be paved and easily accessible to delivery trucks and users with cylinder carts. Cylinder storage areas should drain readily, which may require that cylinders be placed on pallets or otherwise raised above surrounding surfaces.
- Prevent cylinders from toppling by securing them with chains, cylinder racks, or other devices approved by Operational Safety at ESH-5.
- Hydrogen must be separated from oxidizing gases when stored. Acceptable separation is a 5-ft-high fire barrier with a half-hour fire rating or a distance of at least 20 ft.

### Ventilation and Alarms

Because of its small molecular size, hydrogen can leak from apertures through which other gases cannot pass. Ventilation with large quantities of air is vital to dilute small leaks of hydrogen to below the lower flammable limit of 4% in air. Whenever possible, hydrogen should be stored and used outside, with natural ventilation, or under a shed with a nonpeaked roof and no walls. Indoor locations must have ventilation adequate to handle the largest anticipated hydrogen leak or spill. Exhaust fans must be explosion-proof.

Wherever hydrogen is used indoors, flammable gas detection systems must be set to go off when the hydrogen concentration reaches 30% of the lower flammable limit. Sensors should be placed on or at the height of the ceiling immediately above the point of anticipated leakage. The alarm should be calibrated annually (or more often, depending on risk) with a known hydrogen gas mixture.

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# Emergency Procedures

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## In an Emergency

### Cold Burns

Exposure to cryogenic materials may result in serious injury to body tissues similar to heat burns. If a worker comes in contact with liquid or cold gaseous hydrogen, he/she should be transported to the Occupational Medicine Group (ESH-2) or the Los Alamos Medical Center for treatment. If transportation for medical treatment is not available, the affected area can be thawed with tepid water; however, the area should not be rubbed.

### If a Leak Is Detected

When a hydrogen leak is discovered or when an alarm sounds, take the following steps:

1. Evacuate the immediate area of all nonessential personnel.
2. Shut off the hydrogen source immediately and vent all hydrogen to a safe outside location.
3. Increase indoor ventilation with emergency explosion-proof exhaust fans, if possible.
4. Initiate the emergency plan and make the required emergency contacts. Call 911 and 667-6211 [Emergency Management and Response (EM&R)].

### In an Emergency—continued

#### In Case of Fire

To detect a small, local hydrogen fire (the flame is nearly invisible), use a piece of tissue paper on a stick; the paper will readily ignite when it contacts a flame. If fire is present, perform the following:

1. Shut off the hydrogen source.
2. Let the fire burn itself out. (If the flame is snuffed out, it may reignite and cause greater damage.)
3. If you have received hands-on training in the proper operation of a water fire extinguisher then you may use water spray to thermally protect people and equipment if the fire is hot enough to warrant it. However, a venting hydrogen flame cannot normally be extinguished with water.
4. Initiate the emergency plan (which should include calling the fire department) and make the required emergency contacts. Call 911 and 667-6211 (EM&R).

Ultraviolet/infrared detectors and alarms should be installed on systems with the potential for large leaks.

### For Nonemergency Assistance



The following are Laboratory points of contact that may be of assistance in your hydrogen gas system design, set-up, and maintenance needs.

Organization	Service	Contact
Area Industrial Hygienists	identifies the industrial hygienist assigned to your operating group	5-4427
Gas Plant	provides services to meet compressed gas procurement and cylinder disposal requirements	7-4406
EM&R	coordinates response to emergency situations at the Laboratory	7-6211
Operational Safety, ESH-5	provides consultation and assistance to Laboratory pressure system users.	7-4644
Cryogenic and Liquefied Gas Safety Committee	<b>Jim Hoffer, Chairman</b>	7-4049

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# Lessons Learned

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## Lessons Learned

The Rover project (1961), which was never completed, used large amounts of hydrogen as the rocket propellant in a nuclear rocket engine. Back in those days a serious accident occurred when hydrogen gas leaked into a large enclosed space and resulted in an explosion. Ten people inside the space sustained injuries including bruises, ruptured eardrums, and fractured bones.

The space was covered by a removable sheet metal shed, which was completely destroyed by the explosion. Hydrogen had leaked through a valve into 500 ft of piping, and when the valve was opened, the low-pressure hydrogen in the pipe was forced to flow rapidly through a nozzle. It was conjectured that the rapidly moving particles generated sufficient friction upon exiting the nozzle to ignite the hydrogen-air mixture. The ignition energy of a hydrogen-air mixture can be as low as 20 microjoules, an amount approximately equal to the energy in a small ( $1 \text{ mm}^3$ ) particle of sand traveling at 4 m/s (9 mph). The valve was found to be defective and definitely leaking.

The lesson learned from this accident was that more stringent controls needed to be instituted. Administrative controls were implemented by appointing managers for day-in-day-out control, and by setting up a status board to schedule operations on days preceding major experiments. Physical controls were implemented by adding double-block and bleed-valve configurations between the hydrogen source, a tank farm, and the experimental apparatus. In this way, the piping outside the tank farm was guaranteed to be free of gas when none was meant to be flowing.

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## References

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Los Alamos National Laboratory. Laboratory Implementation Requirement (LIR) 402-1200-01.0, *Pressure, Vacuum, and Cryogenic Systems*, October 1, 1999. Los Alamos National Laboratory.

Los Alamos National Laboratory. Technical Bulletin 1403, *Gaseous and Liquid Hydrogen*. Environment, Safety, and Health Manual, Chapter 1 May 24, 1991. Los Alamos National Laboratory.

Los Alamos National Laboratory. Technical Bulletin 1402, *Compressed Gases* Environment, Safety, and Health Manual, Chapter 1 May 24, 1991. Los Alamos National Laboratory.

Compressed Gas Association. CGA G-5, *Hydrogen*. 1991. Compressed Gas Association, Inc., 1235 Jefferson Davis Highway, Arlington, VA 22202.

Compressed Gas Association. CGA G-5.4, *Standard for Hydrogen Piping Systems at Consumer Locations*. 1992. Compressed Gas Association, Inc., 1235 Jefferson Davis Highway, Arlington, VA 22202

## Final Quiz

To receive credit for this self-study, you must complete the final quiz. The final quiz is located in the Training Validation System (TVS).

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### Caution

- You need a SecureID or Crypto Card **that is assigned to you** and Administrative Access to the Lab's Integrated Computing Network (ICN) to complete the final quiz.

If you do not have a SecureID or Crypto Card **that is assigned to you** and ICN Administrative Access, you must complete the final quiz at the ES&H Training Center in White Rock.

To schedule a time to complete the final quiz, contact the ESH-13 Registrar either by phone at 7-0059 between 8:00 am and 12:00 pm or by e-mail at [eshregistration@lanl.gov](mailto:eshregistration@lanl.gov).

- **Do not** complete the final quiz using another person's SecureID or Crypto Card. You can only receive credit for the final quiz using a SecureID or Crypto Card that is assigned to you.
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### Starting the Quiz

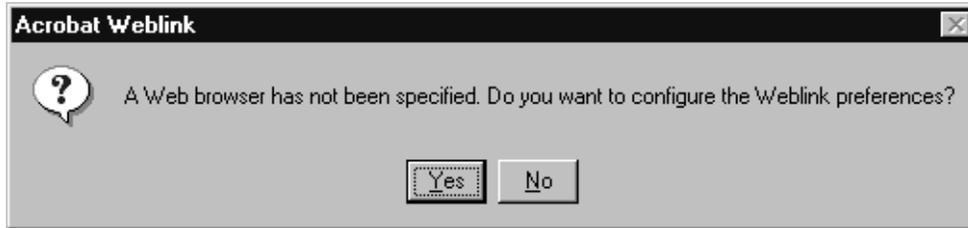
To start the final quiz, click the Start Quiz button below:

### Troubleshooting

- Acrobat Reader for Windows displays error "A Web browser has not been specified. Do you want to configure the Weblink preferences?"
- Acrobat Reader for Macintosh displays "Select Web Browser" dialog box.
- Clicking **Start Quiz** button doesn't bring up Netscape Navigator and/or get error message "The Web browser has not responded to your request for one minute: Terminating request."
- You get an error message after submitting the TVS quiz.
- Other problems: Contact CIC-6 Customer Server at 5-4444.

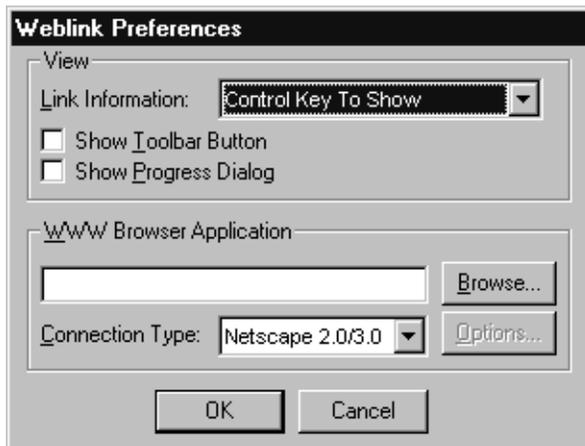
## Acrobat Reader for Windows displays error “A Web browser has not been specified. Do you want to configure the Weblink preferences?”

If you are using a Windows PC, you may see the error message below when you click the Start Quiz button:

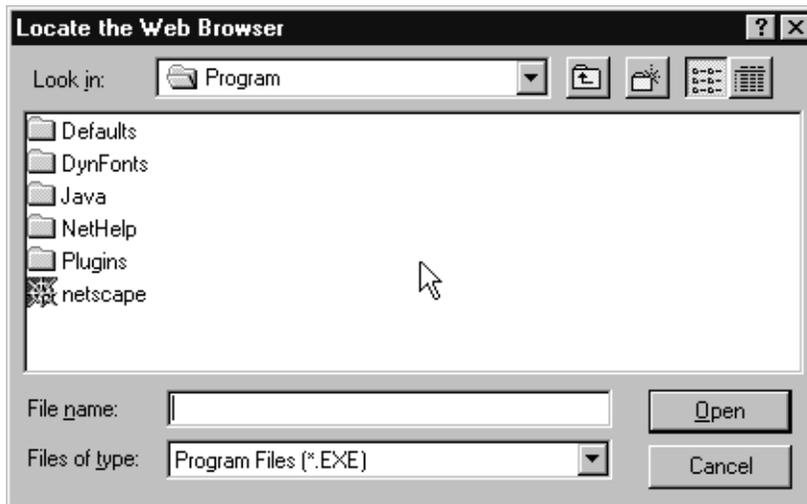


This message appears when a Web browser has not been selected in the Acrobat Reader Weblink Preferences. To select a Web browser, follow the instructions below:

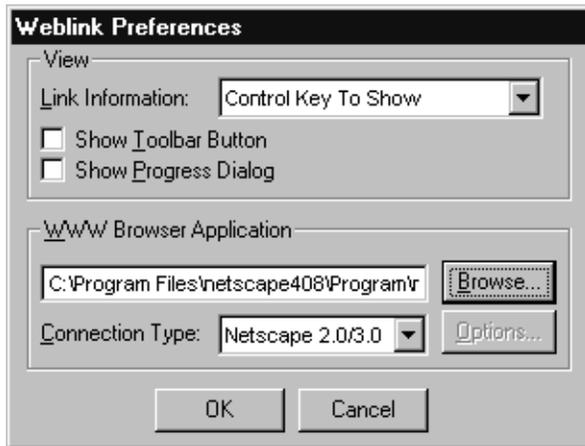
1. Click the **Yes** button on the Acrobat Weblink error dialog box.  
*Acrobat Reader displays the Weblink Preferences window.*



2. Click the **Browse...** button.  
*Acrobat Reader displays the Locate the Web Browser dialog box.*



- Use the dialog box to find your Web browser program, highlight the program name, and click the **Open** button.  
*Acrobat Reader puts the path to the Web browser program you selected into the WWW Browser Application text box on the Weblink Preferences window.*



- Click the **OK** button on the Weblink Preferences window.  
*Acrobat Reader closes the Weblink Preferences window, starts the Web browser you selected, and links to TVS.*

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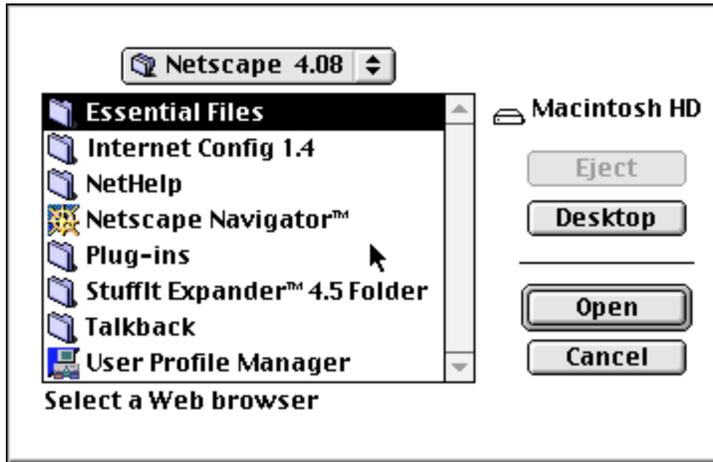
**Note:** If you need assistance configuring Adobe Acrobat Reader, contact CIC-6 Customer Service at 5-4444.

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[Return to Starting the Quiz](#)

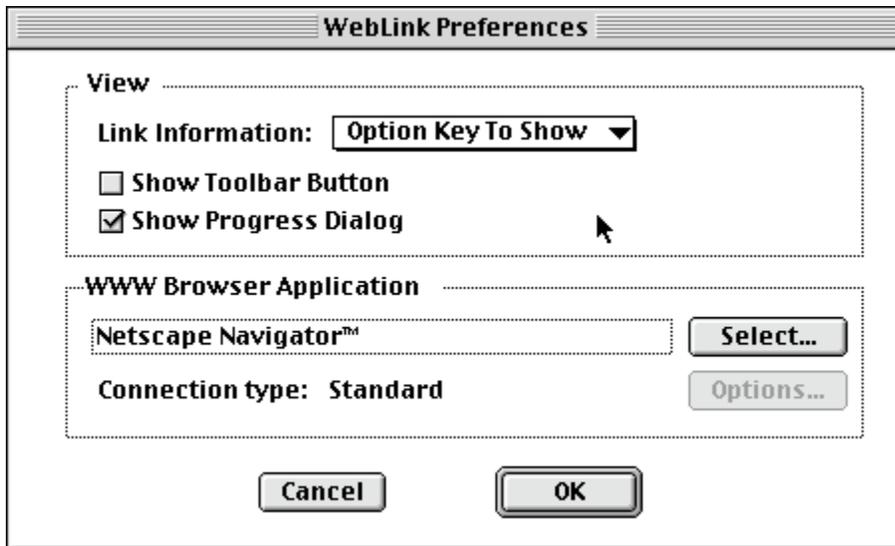
## Acrobat Reader for Macintosh displays “Select Web Browser” dialog box

If you are using a Macintosh, you may see the dialog box below when you click the Start Quiz button:



This message appears when a Web browser has not been selected in the Acrobat Reader Weblink Preferences. To select a Web browser, follow the instructions below:

1. Use the dialog box to find your Web browser program, highlight the program name, and click the **Open** button.  
*Acrobat Reader puts the name of the Web browser program you selected into the WWW Browser Application text box on the Weblink Preferences window.*



2. Click the **OK** button on the Weblink Preferences window.  
*Acrobat Reader closes the Weblink Preferences window, starts the Web browser you selected, and links to TVS.*

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**Note:** If you need assistance configuring Adobe Acrobat Reader, contact CIC-6 Customer Service at 5-4444.

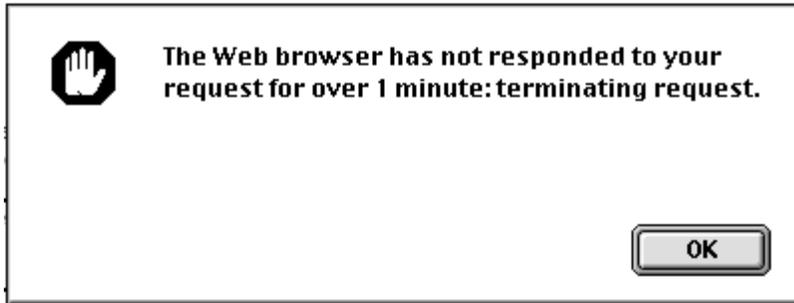
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[Return to Starting the Quiz](#)

## The Web browser has not responded to your request for one minute: Terminating request.

If you are using a Macintosh, Adobe Acrobat Reader 3.x, and Netscape Navigator 4.x, you may see the following problems when you click on the **Start Quiz** button:

- Netscape Navigator will fail to appear and
- You see the following error message dialog box:



There is a bug in Adobe Acrobat Reader 3.x that creates these problems. In fact, a Netscape Navigator window is open behind the Acrobat Reader window. You can work around the problem by following the instructions below:

1. Click the **OK** button on the error message dialog box.  
*Adobe Acrobat closes the error message dialog box and returns to the document window.*
2. Click the **Application Menu** icon on the Mac OS menu bar.  
*The Mac OS displays the Application Menu.*



3. Click **Netscape Navigator** in the Application Menu.  
*The Mac OS displays the Netscape Navigator window.*

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**Note:** If you need further assistance, contact CIC-6 Customer Service at 5-4444.

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## **TVS Error Message After Submitting Quiz**

If you receive an error message from TVS after you submit your quiz, please contact John Conlon at 5-8248 or [jconlon@lanl.gov](mailto:jconlon@lanl.gov) with the following information:

- Your z-number
- Your name
- Your e-mail address
- The approximate time you submitted your quiz
- Your IP address (if available)

John will check TVS to see if your quiz was graded and contact you with the results.

**[Return to Starting the Quiz](#)**