
**Cryogenic vessels — Gas/materials
compatibility**

Réipients cryogéniques — Compatibilité gaz/matériaux

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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

For an explanation on the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the WTO principles in the Technical Barriers to Trade (TBT) see the following URL: Foreword - Supplementary information

The committee responsible for this document is ISO/TC 220, *Cryogenic vessels*.

This second edition cancels and replaces the first edition (ISO 21010:2004), which has been technically revised.

Cryogenic vessels — Gas/materials compatibility

1 Scope

This International Standard specifies gas/materials compatibility requirements (such as chemical resistance) for cryogenic vessels, but it does not cover mechanical properties (e.g. for low temperature applications).

It gives general guidance for compatibility with gases and detailed compatibility requirements for oxygen and oxygen-enriched atmospheres. This International Standard also defines the testing methods for establishing oxygen compatibility of materials (metallic and non-metallic) to be used for cryogenic vessels and associated equipment.

This International Standard focuses on materials that are normally with or could be in contact with cryogenic fluids.

2 Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 10297:2006, *Transportable gas cylinders — Cylinder valves — Specification and type testing*

ISO 23208, *Cryogenic vessels — Cleanliness for cryogenic service*

3 Compatibility of materials with gases other than oxygen

Cryogenic vessels are used in a range of temperatures from very low temperature to ambient temperature. On excluding oxygen, compatibility problems such as corrosion and hydrogen embrittlement normally occur at ambient temperature and become negligible at cryogenic temperatures.

In the case of gases other than oxygen, ISO 11114-1 and ISO 11114-2 can be used as a guide for cryogenic vessels.

4 General requirements for oxygen service

4.1 Evaluation of materials for oxygen service

4.1.1 General

The selection of a material for use with oxygen and/or in an oxygen-enriched atmosphere is primarily a matter of understanding the circumstances that cause oxygen to react with the material. Most materials in contact with oxygen will not ignite without a source of ignition energy. When an energy input rate, as converted to heat, is greater than the rate of heat dissipation, and the resulting heat increase is continued for sufficient time, ignition and combustion will occur. Thus, two things shall be considered:

- the material's minimum ignition temperature;
- the energy sources that will produce a sufficient increase in the temperature of the material.

These should be viewed in the context of the entire system design so that the specific factors listed below will assume proper relative significance.

The specific factors are:

- the properties of the materials, including the factors affecting ease of ignition and the conditions affecting potential resultant damage (heat of reaction);
- the operating conditions: pressure, temperature, gas velocity, oxygen concentrations, and oxygen state (gaseous or liquid) and surface contamination in accordance with ISO 23208;
- the potential sources of ignition: friction, heat of compression, heat from mass impact, heat from particle impact, static electricity, electric arc, resonance, and internal flexing etc.;
- the reaction effect (consequences on the surroundings, etc.);
- additional factors: performance requirements, prior experience, availability, and cost.

CAUTION — This International Standard specifies the minimum acceptance requirements for materials in oxygen and enriched air service. In the cases of severe conditions and when the operating pressure is above 40 bar, additional tests to those specified should be considered.

4.1.2 Evaluation of the insulation system

Insulation systems for cryogenic vessels that can come into contact with oxygen or condensed enriched air, shall be tested in accordance with [4.4.4](#). Any representative sample that passed the tests in [4.4.3](#) need not be tested in accordance with [4.4.4](#).

4.2 Evaluation of metallic materials

Metallic materials commonly used for the construction of cryogenic vessels do not normally present any incompatibility when in contact with oxygen. [Annex A](#) lists the metallic materials commonly used for liquid oxygen.

The cases in which ignition or violent reactions can occur are when very thin materials are used with high surface to volume ratio, and when high ignition energy is available (e.g. pump failure). Materials thinner than 0,1 mm shall be tested in accordance with [4.4.3](#) in conditions as close as possible to the actual operational conditions. Materials to be used in applications where the ignition energy is potentially high should be subjected to special consideration.

For cryogenic vessels intended for oxygen service, the test described in [4.4.3](#) shall be performed with oxygen. When materials are located in an area where contact with condensed enriched air and the presence of potential sources of ignition is a risk, the test described in [4.4.3](#) shall be performed with cryogenic O₂/N₂ mixtures containing at least 50 % oxygen.

NOTE Condensed enriched air can be produced on surfaces with temperatures colder than – 191,3 °C at 1 atm ¹⁾(101,325 Pa).

4.3 Evaluation of non-metallic materials

Example of non-metallic materials include, e.g. plastics, elastomers, lubricants, ceramics, glasses, and glues. Some of these materials present a high risk of ignition when in contact with oxygen and should be avoided or carefully selected and used in limited quantities.

Some fully oxidized materials, such as ceramics and glass, present no risk of ignition provided they are not contaminated.

Any combustible non-metallic materials, used in steady or incidental contact with liquid oxygen, where the presence of a potential source of ignition is a risk, shall be tested in accordance with [4.4.2](#) and [4.4.3](#). Consideration shall be given to testing materials used in those parts of the system where liquid oxygen accumulation might incidentally occur.

1) According to Annex C of ISO 80000-4:2006, the use of this unit is deprecated.

For cryogenic vessels intended for oxygen service, the test described in [4.4.3](#) shall be performed with oxygen. When materials are located in an area where contact with condensed enriched air and the presence of potential sources of ignition is a risk, the test described in [4.4.3](#) shall be performed with cryogenic O₂/N₂ mixtures containing at least 50 % oxygen.

NOTE Condensed enriched air can be produced on surfaces with temperature colder than – 191,3 °C at 1 atm (101,325 Pa).

Any combustible non-metallic materials, used in steady or incidental contact with gaseous oxygen where the presence of potential sources of ignition is a risk, shall be tested in accordance with [4.4.2](#). Consideration shall be given to testing materials used in those parts of the system where gaseous oxygen accumulation might incidentally occur.

4.4 Test methods and acceptance criteria

4.4.1 General

Each material to be tested shall be clearly identified, usually by the commercial name and the manufacturer's name.

4.4.2 Ignition tests

4.4.2.1 Pass criteria

Two alternative test methods are described in [4.4.2.2](#) and [4.4.2.3](#). Materials not satisfying the requirements of [4.4.2.2](#) or [4.4.2.3](#) can still be used providing they successfully pass, in their actual operating configuration, the "oxygen pressure surge test" described in 5.3.8 of ISO 10297:2006 (e.g. for a valve sealing material, the entire valve or a representative assembly shall be tested).

4.4.2.2 Spontaneous ignition test (bomb test)

4.4.2.2.1 Test procedure

The test procedure is given in [Annex B](#).

4.4.2.2.2 Acceptance criteria

The spontaneous ignition temperature determined in accordance with [4.4.2.2.1](#) shall be no less than the values given in [Table 1](#).

Table 1 — Minimum spontaneous ignition temperature

Maximum permissible pressure bar	Minimum spontaneous ignition temperature (SIT) °C	Remarks
3	200	
10	230	
20	250	
40	300	
100	350	
150	375	Complementary test might be advisable (see 4.1)
207	400	
207 < pressure ≤ 345	400	
NOTE Intermediate values can be determined by linear interpolation.		

4.4.2.3 Pressure surge test**4.4.2.3.1 Test procedure**

The test procedure is given in [Annex B](#).

4.4.2.3.2 Acceptance criteria

No reaction shall be observed during five consecutive pressure surge impacts at the intended maximum working pressure.

4.4.3 Mechanical impact test in liquid oxygen (LOX)**4.4.3.1 Test procedure**

The mechanical impact test shall be performed at atmospheric pressure in liquid oxygen generally as described in Reference [4] to [8]. This is an example of preferred test equipment, but the details are not mandatory. The test shall be conducted

- on material with the surface condition that is intended for use,
- on material in a physical form delivered for use (i.e. solid, powder etc.), and
- at an impact energy per unit contact area of at least 79 J/cm².

4.4.3.2 Acceptance criteria

No reaction shall be detected within a series of 10 tests.

4.4.4 Insulation test

Representative samples of the insulation system, when touched with a glowing platinum wire in a 100 % oxygen atmosphere at 1 bar pressure, shall not sustain combustion.

NOTE Representative samples of the insulation system are intended to be installed in the vessel; the full thickness of the insulation can be tested.

4.5 Alternative method of acceptance

The use of materials in cryogenic vessels based on documented evidence of previous long-term satisfactory service or favourable risk assessment is acceptable.

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Annex A (informative)

Metallic materials commonly used for liquid oxygen service

Table A.1

Cryogenic vessels and associated equipment		Metallic materials commonly used				
		Low alloy steels	Nickel steels	Austenitic stainless steels	Copper and copper alloys	Aluminium and aluminium alloys
Large transportable vessels	Inner vessel		×	×		
	Outer jacket	×		×		
Small transportable vessels	Inner vessel		×	×		
	Outer jacket	×		×		
Static vessels	Inner vessel		×	×		
	Outer jacket	×				
Valves and protective devices				×	×	
Flexible hoses				×		
Vaporizers				×		×
Insulation systems						×

Compatibility of all materials should be evaluated before use.

Annex B (normative)

Spontaneous ignition test (bomb test)

B.1 General

[Annex B](#) defines a test method to determine the spontaneous ignition temperature of non-metallic materials in pressurized gaseous oxygen.

Spontaneous ignition temperature is a criterion for the comparison and the classification of materials, and can be used as an aid in the choice of materials used in the presence of pressurized gaseous oxygen.

B.2 Principle

A small quantity of the test material is slowly heated in oxygen under pressure. The continuous recording of pressure and temperature is used to determine spontaneous ignition, which is seen as a sudden increase in temperature and pressure.

B.3 Preparation of test pieces

Test pieces shall be prepared by procedures that prevent contamination.

Test pieces can be in liquid or solid form. In the case of solids, the materials shall be cut into a minimum of six pieces. The total mass of the pieces used in each test shall be at least 60 mg.

B.4 Test equipment

[Figure B.1](#) shows the basic principle of the test equipment. When other methods of heating are used, the heating rate of the specimen is up to 20 °C/min. If an inductively heated furnace is used, the temperature rate can be up to 110 °C/min.

A thermocouple inside a finger of a glove (positioned as close as possible to the test piece) is used to monitor, on a recorder, temperature variation to accuracy of ± 2 °C.

The internal pressure shall be monitored and recorded to an accuracy of ± 2 bar.

The equipment, in particular the autoclave, shall be designed to resist violent internal reactions (e.g. explosions).

B.5 Oxygen purity

The gas used shall contain not less than 99,5 % oxygen. The hydrocarbon content shall be less than 10 ml/m³.

B.6 Test procedure

The test piece contained in the sample holder is put into the bomb. The bomb is then sealed and purged to remove any air and any possible residual combustion products from a previous test. Oxygen is then introduced at a minimum pressure that will produce at least 120 bar at ignition.

While continuously recording the temperature and pressure, raise the temperature at a rate of 20 °C/min by adjustment of the heating power, until the spontaneous ignition temperature or 400 °C or higher is reached.

The spontaneous ignition temperature is indicated on the temperature and pressure recorder by the sudden increase in both temperature and pressure caused by the internal reaction.

B.7 Results

The record of the test is used as shown in [Figure B.2](#), to determine the three parameters, T_i , ΔT , and ΔP where

T_i is the spontaneous ignition temperature;

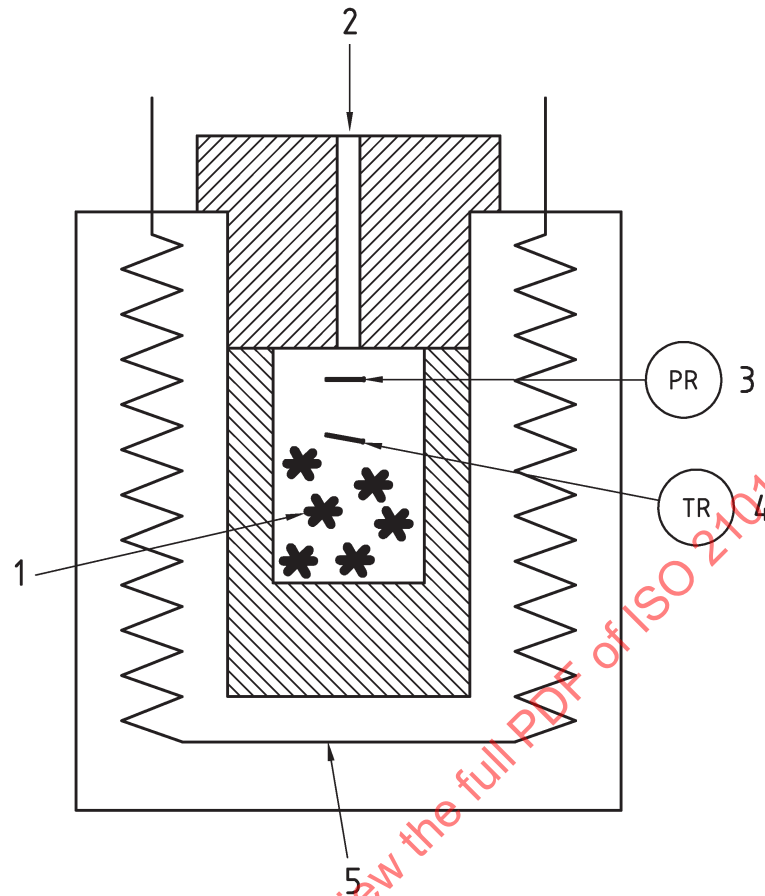
ΔT is the increase in temperature at moment of ignition;

ΔP is the increase in pressure at moment of ignition.

Materials are classified in accordance with their spontaneous ignition temperature.

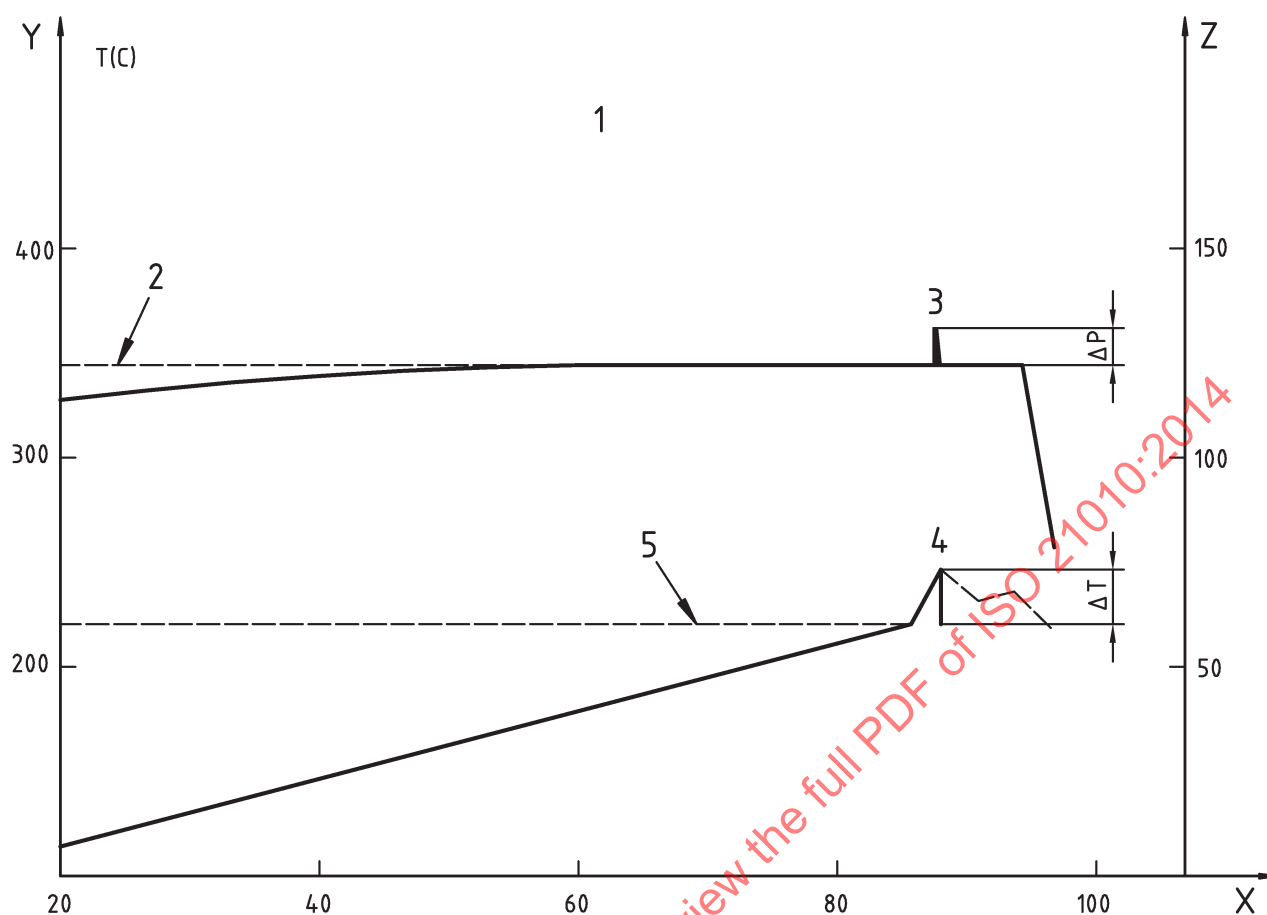
Temperature and pressure increases, ΔT and ΔP , characterize the violence of the reaction.

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**Key**

- 1 test sample
- 2 oxygen inlet: 120 bar at minimum ignition conditions
- 3 pressure transducer
- 4 temperature monitor
- 5 heating element: 20 °C/min to a maximum of 500 °C

Figure B.1 — Bomb for spontaneous ignition test



Key

- X time (minutes)
- Y temperature T (°C)
- Z pressure P (bar)
- 1 temperature and pressure variations against time
- 2 pressure at SIT
- 3 peak pressure
- 4 peak temperature
- 5 spontaneous ignition temperature

Figure B.2 — Spontaneous ignition test — Temperature and pressure versus time

B.8 Test report

Test results are recorded on a report sheet, an example of which is given below.

SPONTANEOUS IGNITION	 Test no.
	 Date
1 - <u>TEST PERFORMED FOR</u> _____	
2 - <u>TESTED MATERIAL</u> _____	
Function _____	
Conditions of use	Temperature in °C _____ Pressure in bar _____
Assumed composition _____	
Condition, shape, appearance _____	
Manufacturer _____	
Supplier _____	
Trade name _____	
3 - <u>RESULTS</u>	
Mass of test piece in grams: _____	

Pressure in bar			Temperature in °C		
At SIT	Peak	ΔP	At SIT	Peak	ΔT

Remarks:
4 - <u>SPONTANEOUS IGNITION TEMPERATURE (°C)</u>
5 - <u>COMMENTS</u>
Authorized signature

Annex C (normative)

Pressure surge test

C.1 General

[Annex C](#) defines a test method for establishing the maximum working pressure by examining the reactivity of non-metallic materials (solids, pastes or liquids) when exposed to a pressure surge of oxygen, air, or of a gas mixture containing oxygen.

This test simulates processes that might occur in service on non-metallic materials (e.g. in shut-off installations when operated too quickly, or on rupture of equipment or pipes, etc.).

This method can be applied to intended working pressures equal to or greater than 10 bar.

C.2 Principle

A small quantity of the test material is exposed to a gaseous oxygen pressure surge generated by operating a quick opening valve between a tube containing the test material and a vessel containing oxygen under high pressure.

The pressure in the tube is raised from initial pressure, P_i , to final pressure, P_f , as near adiabatically as possible, given by the adjustable pressure of an oxygen accumulator.

A possible reaction of the test material with oxygen is indicated by a steep temperature rise, superimposed on the temperature rise obtained by adiabatic compression.

In this method, the maximum working pressure is defined as the maximum final pressure, P_f , at which no reaction of a sample with oxygen can be observed.

C.3 Preparation of test samples

Solid materials are finely divided into a minimum of six pieces, liquids are coated on fibrous ceramic materials.

A total mass of 0,2 g to 0,5 g shall be used for each test.

C.4 Test equipment

[Figure C.1](#) shows the basic components of the test equipment.

The test sample is placed into a steel tube (see [Figure C.1](#), 10) 15 cm³ in volume. This reaction vessel is connected to an oxygen accumulator (see [Figure C.1](#), 7) through a 750 mm long pipe (see [Figure C.1](#), 11, internal diameter of 14 mm) and a pneumatically operated quick-opening valve (see [Figure C.1](#), 6) guaranteeing a pressure-rise time of 20-⁰/₅ ms.

Two heaters (see [Figure C.1](#), 4) are used for heating the oxygen accumulator and the reaction vessel up to (60 ± 3) °C.

After a pressure surge, the reaction vessel shall be allowed to return to atmospheric pressure by aid of a vent valve (see [Figure C.1](#), 8).