

**Committee of Experts on the Transport of Dangerous Goods
and on the Globally Harmonized System of Classification
and Labelling of Chemicals**

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Sub-Committee of Experts on the Globally
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Classification and Labelling of Chemicals (GHS)**

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Item 2 (a) of the provisional agenda

Physical hazards

Determination of chemical instability of gases

**Transmitted by the expert from Germany on behalf of the informal
working group***

Introduction

The Annex to this document describes the method for determining whether a gas is chemically unstable according to the criteria laid down in the UN-GHS, chapter 2.2. Reference to this document and the method in its Annex is made until the method is included into an appropriate document (which probably will be the UN Manual of Tests and Criteria).

* In accordance with ST/SG/AC.10/C.3/70, para. 85 and ST/SG/AC.10/C.4/34, para. 17 to 19.

Annex

“Determination of chemical instability of gases and gas mixtures

1. Scope

This test method is applied for determining chemical instability of gases or gas mixtures by ignition tests in a closed vessel at ambient and elevated temperature and pressure because the ability of dangerous decomposition depends strongly on pressure, temperature and in case of gas mixtures on the concentration of the chemically unstable component. The possibility of decomposition reactions shall be evaluated at conditions which are relevant for handling and use and transport. Therefore two types of tests shall be performed:

- a) at ambient temperature and pressure,
- b) at 65 °C and the corresponding test pressure.

Expert judgement should be applied to decide whether a flammable gas is a candidate for classification as chemically unstable in order to avoid unnecessary testing of gases where there is no doubt that they are stable.

The test method does not cover gas decomposition under process conditions in chemical plants and possible dangerous reactions between different gases in gas mixtures.

Mixtures of gases, where the components can react dangerously with each other, e.g. flammable and oxidizing gases, are not regarded as chemically unstable in the sense of this test method.

2. Concentration limits

2.1. Generic concentration limit

Gas mixtures containing only one chemically unstable gas are considered as chemically stable and therefore do not have to be tested for classification purposes if the concentration of the chemically unstable gas is below the higher of the following concentrations:

- The lower explosion limit (LEL) of the chemically unstable gas or
- 3 mole%.

2.2 Specific concentration limits

In the following table information about some gases with regard to their classification as chemically unstable is given. Furthermore, specific concentration limits for their mixtures are given. Gas mixtures containing only one chemically unstable gas in concentrations below the specific concentration limit are considered as chemically stable and therefore do not have to be tested for classification purposes.

Table 1: Information about gases with regard to their chemical instability and concentration limits for their mixtures below which the mixtures are not classified as chemically unstable

Information about the pure gas					Information about its mixtures
Chemical Name	Molecular formula	CAS No	UN No	Classification	Specific concentration limit (see Note 1 and 2)
Acetylene	C ₂ H ₂	74-86-2	1001 3374	Chem. Unst. Cat.1	See Table 2 For other mixtures: Partial pressure of 1 bar abs
Bromotrifluoroethylene	C ₂ BrF ₃	598-73-2	2419	Chem. Unst. Cat.2?	8,4 mole% (LEL)
Butadiene-1,2	C ₄ H ₆	590-19-2	1010	Not classified as chemically unstable	
Butadiene-1,3	C ₄ H ₆	106-99-0	1010	Not classified as chemically unstable	
Butyne-1, Ethylacetylene	C ₄ H ₆	107-00-6	2452	Chem. Unst. Cat.2?	The specific concentration limits for acetylene may be applied, see Table 2. For other mixtures: Partial pressure of 1 bar abs
Chlorotrifluoroethylene	C ₂ ClF ₃	79-38-9	1082	Chem. Unst. Cat.2?	4,6 mole% (LEL)
Ethylene oxide	C ₂ H ₄ O	75-21-8	1040	Chem. Unst. Cat.1	Specific concentration limits will be added (until December 2010).
Vinyl methyl ether	C ₃ H ₆ O	107-25-5	1087	Chem. Unst. Cat.2?	3 mole%
Propadiene	C ₃ H ₄	463-49-0	2200	Chem. Unst. Cat.2?	The specific concentration limits for acetylene may be applied, see Table 2. For other mixtures: Partial pressure of 1 bar abs
Propyne	C ₃ H ₄	74-99-7	3161	Chem. Unst. Cat.2?	The specific concentration limits for acetylene may be applied, see Table 2. For other mixtures: Partial pressure of 1 bar abs
Tetrafluoroethylene	C ₂ F ₄	116-14-3	1081	Chem. Unst. Cat.2?	10,5 mole% (LEL)
Trifluoroethylene	C ₂ HF ₃	359-11-5	1954	Chem. Unst. Cat.1	10,5 mole % (LEL)
Vinyl bromide	C ₂ H ₃ Br	593-60-2	1085	Chem. Unst. Cat.2?	5,6 mole% (LEL)
Vinyl chloride	C ₂ H ₃ Cl	75-01-4	1086	Chem. Unst. Cat.2?	3,8 mole% (LEL)
Vinyl fluoride	C ₂ H ₃ F	75-02-5	1860	Chem. Unst. Cat.2?	3 mole%

Note 1: The maximum pressure should be limited in order to avoid condensation.

Note 2: The test method is not applicable to liquefied gas mixtures. In case the gaseous phase above a liquefied gas mixture may become chemically unstable after withdrawal, this shall be communicated via the safety data sheet.

Table 2: Specific concentration limits for binary mixtures with acetylene. These concentration limits may also be applied to Butyne-1 (Ethylacetylene), Propadiene and Propyne.

Concentration limit for acetylene in mol-%	Maximum (filling) pressure in bar for a mixture with						
	N ₂	CO ₂	NH ₃	H ₂	CH ₄	C ₃ H ₈	C ₂ H ₄
To be added until December 2010	200.0						
4.0	100.0						
5.0				40.0			40.0
6.0	80.0						
8.0	60.0						
10.0	50.0	38.0	5.6	20.0	100.0	6.0	20.0
15.0	30.0	30.0		10.0			10.0
20.0	25.0	20.0	6.2	5.0	50.0	6.6	7.5
25.0	20.0	15.0					5.0
30.0	10.0	10.0	6.9		25.0	7.3	
35.0			7.3				
40.0					15.0	8.2	
45.0							
50.0					5.0	9.3	
60.0						10.8	

3. Definitions

For the purposes of this test method the following definitions apply:

Chemical instability

Ability of a gas or gas mixture to react dangerously even in the absence of any reaction partner (e.g. air or oxygen) by decomposing and thereby causing a temperature and/or pressure increase.

Test gas

Gas or gas mixture to be evaluated by this test method.

Corresponding test pressure

Pressure at which the test at 65 °C is carried out. For test gases that are completely gaseous the corresponding test pressure is the pressure that a gas develops at 65 °C based on the maximum (filling) pressure at ambient temperature. For liquefied test gases the corresponding test pressure is the vapour pressure at 65 °C.

4. Classification procedures for chemically unstable gases

Chemically unstable gases or gas mixtures shall be classified as “chemically unstable at ambient temperature and pressure” or “chemically unstable at elevated temperature and/or pressure” according to the test results as follows:

- (a) The test gas is classified as “chemically unstable at ambient temperature and pressure” if the test at 25 °C and 101 kPa shows a pressure rise of more than 20 % of the initial absolute pressure.
- (b) The test gas is classified as “chemically unstable at elevated temperature and/or pressure” if the test at 65 °C and the corresponding test pressure shows a pressure rise of more than 20 % of the initial absolute pressure but no such pressure rise at 25 °C and 101 kPa.

The test gas is not classified according to this test method (meaning it is chemically stable) if it does not show a pressure rise of more than 20 % of the initial absolute pressure in either of the tests.

Note: Chemically unstable gases not submitted to the classification procedure in this chapter should be classified as chemically unstable gas, category 1.

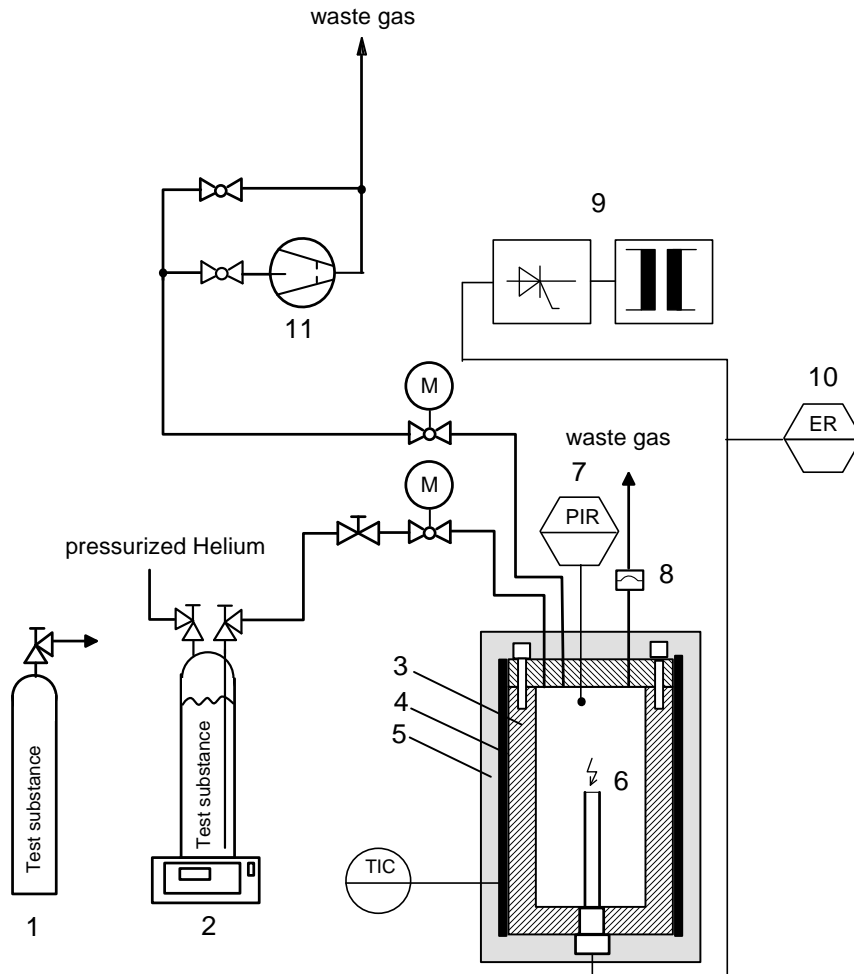
5. Test method

5.1. Abstract

The test gas is charged into a pressure resistant stainless steel vessel at controlled temperature and pressure. The vessel is equipped with a bursting disk. Ignition of the test gas is achieved with an exploding wire igniter. Whether a decomposition reaction has occurred is deduced from the pressure rise produced.

5.2. Apparatus and material

The test apparatus is shown in Fig. 1.



Legend

- | | |
|---|-----------------------------------|
| (1) Test gas supply (gaseous) | (2) Test gas supply (liquefied) |
| (3) Pressure resistant test vessel | (4) Regulated electric heater |
| (5) Thermal insulation | (6) Exploding wire igniter |
| (7) Pressure sensor, pressure indication and registration | (8) Bursting disk |
| (9) Electronic ignition device | (10) Ignition energy registration |
| (11) Vacuum pump | (12) |

Fig. 1.: Schematic diagram of test apparatus

The main parts of test apparatus are:

- Heatable ignition vessel made of stainless steel,
- Ignition source,
- Measuring and recording system to record the pressure inside the ignition vessel,
- Gas supply,

- Venting system with bursting disk,
- Additional piping, fitted with remote-controlled valves and cocks.

Heatable ignition vessel

The ignition vessel is a cylindrical stainless steel vessel with an inner volume of about 1 dm³ and an inner diameter of 80 mm. An exploding wire ignition source is screwed into the bottom of the vessel. The heating jacket is connected to a temperature control unit that heats the outer vessel wall with an accuracy of ± 2 K. The ignition vessel is insulated with temperature resistant insulation material to avoid heat loss and temperature gradients. The vessel shall be pressure resistant up to 50 MPa (500 bar).

Ignition source

The ignition source is an exploding (fusing) wire igniter similar to that described in ASTM E 918 and EN 1839. The igniter consists of two insulated electrodes at 3 mm to 6 mm distance, holding a nickeline wire of 0.12 mm diameter at its ends. The ignition energy is provided by a 1.5 kVA/230 (115) V insulating transformer, which is switched for a short time period to this igniter. The wire melts and then an electrical arc burns between the electrodes for a period extending in maximum to half a period of the supply voltage (10 (8.3) ms). An electronic control unit allows switching different time periods of the mains voltage half wave to the igniter. The corresponding energy delivered shall be in the range of 15 J \pm 3 J. The energy can be measured by recording the current and voltage during ignition.

Pressure and temperature recording equipment

The pressure inside the ignition vessel shall be measured with a calibrated piezoresistive pressure transducer. The measuring range shall be 20 times higher than the initial pressure. The sensitivity shall be at least 0.1 % of the full scale and the accuracy shall be better than 0.5 % of the full scale.

The temperature of the ignition vessel shall be measured and controlled with a 3 mm thermocouple type "K" (NiCr/NiAl) mounted 50 mm below the top inside the autoclave.

After ignition the digitized pressure signal shall be recorded with a computer. The initial pressure (p_0) and the highest pressure (p_{ex}) are derived from the raw data.

Gas supply

Two different types of gas supply are necessary, one for test gases that are completely in the gaseous phase and one for liquefied test gases. Test gases in the gaseous phase are metered volumetric or by flow measurement and liquefied test gases are metered gravimetric.

Bursting disk

The bursting disk is supposed to protect the test vessel. It is connected by a waste gas pipe. The free diameter of the bursting disk is recommended to be at least 10 mm, the inner diameter of the pipe at least 15 mm. The opening pressure of the bursting disk shall amount to 25 MPa (250 bar).

Additional piping and valves

The piping and valves which are fitted directly to the test vessel, shall be pressure resistant up to 50 MPa (500 bar). The test apparatus shall be operated by remotely operated valves.

5.3. Test procedure

The tests shall be executed in the following sequence:

5.3.1 *Test at ambient temperature and pressure*

For the tests at 25 °C and 101 kPa (1.01 bar) the exploding wire igniter shall be arranged in the middle of the test vessel. The test vessel and the piping are evacuated. The test gas is filled into the test vessel by using the remotely operated valves until ambient pressure (initial pressure) is reached. After closing the valves the igniter is fired. The ignition energy should be limited to about 15 J to avoid an over-initiation in the test vessel at this relatively low pressure. Criterion for a reaction is a pressure rise of more than 20 % after ignition ($f = p_{ex}/p_0 > 1.20$). If no pressure rise of more than 20 % has occurred two further re-tests shall be carried out.

If the test gas shows a pressure rise of more than 20 % in either of the tests it is to be classified as “chemically unstable at ambient temperature and pressure”. No further tests are required.

5.3.2 *Test at elevated temperature and pressure*

If in the tests according to 5.3.1 no pressure rise of more than 20 % has occurred, further tests at 65 °C and the corresponding test pressure shall be performed. The procedure is the same as in section 5.3.1 but care should be taken with potentially unstable gases under pressure. The ignition energy shall be about 15 J. If no pressure rise of more than 20 % has occurred two further re-tests shall be carried out.

If the test gas shows a pressure rise of more than 20 % in either of the tests it is to be classified as “chemically unstable at elevated temperature and/or pressure”.

6. Safety precautions

Adequate shielding of the test apparatus must be provided to prevent injury in the event of equipment rupture. The apparatus is set up so that the operator is either separated by a blast proof barrier or - even better - in a separate room as long as the vessel contains test gas. Activation of the ignition source should be possible only from a position shielded from the test vessel.

The test vessel shall be fitted with a bursting disk vented outside any enclosed area to prevent formation of an explosive mixture.

The gas cylinder containing the test gas shall be equipped with a non-return valve and shall be separated from the test apparatus before the igniter is fired to avoid backfiring into the cylinder. The cylinder valve has to be closed immediately after finishing the filling.

Some chemically unstable gases can explode very violently especially at higher pressures. Therefore it is strongly recommended to start with the experiments at atmospheric pressure.
