



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

Sub-Committee of Experts on the Transport of Dangerous Goods

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Item 5 (b) of the provisional agenda

Transport of gases: miscellaneous

Update of LC₅₀ values in P200

Transmitted by the European Industrial Gases Association (EIGA)*

Introduction

1. Following its last plenary meeting on 3 October 2019, ISO/TC58/SC2 asked its working group 7 (WG7) to prepare a paper by 1 February 2020 at the latest with the rationale to agree, as an industry, the correct values for LC₅₀ for some gases to be proposed for the Model Regulations.

2. Indeed, the LC₅₀ values given in the twenty first revision of the Model Regulations and in ISO 10298:2018 *Gas cylinders – Gases and gas mixtures – Determination of toxicity for the selection of valve outlets* (which was developed by ISO/TC58/SC2/WG7) are not aligned for the following gases:

- Ammonia, anhydrous;
- Boron Trifluoride;
- Tungsten Hexafluoride;
- Phosphorous Pentafluoride;
- Hydrogen Fluoride, anhydrous.

Sources and rationale

3. The sources where the LC₅₀ values have been determined from are given in ISO 10298:2018. ISO/TC58/SC2/WG7 recognise that it is important to understand where the values of LC₅₀ have been derived from. For the gases where the proposed changes to the Model Regulations have been made, the source of the value and rationale is given below.

* 2020 (A/74/6 (Sect.20) and Supplementary, Subprogramme 2.

UN No.	Proper Shipping Name	LC ₅₀ in ml/m ³ in P200 (Rev.21)	LC ₅₀ in ml/m ³ in ISO 10298:2018	Source reference from ISO 10298:2018 and rationale
1005	AMMONIA, ANHYDROUS	4000	7338	a)
1008	BORON TRIFLUORIDE	387	864	b)
2196	TUNGSTEN HEXAFLUORIDE	160	218	c)
2198	PHOSPHORUS PENTAFLUORIDE	190	261	d)
1052	HYDROGEN FLUORIDE, ANHYDROUS	966	1307	e)

a) Ammonia, anhydrous

4. The LC₅₀ value is 7338 ppm in ISO 10298 (*Reference: Vernot E.H. et al. Toxicol. Appl. Pharmacol. 1977, 42 pp. 417–423, for all versions (1995, 2010, 2018)*).

5. The value of 7338 ppm is the most conservative (lowest) that can be found in the scientific literature (“1 hour rat” exposure).

6. ISO/TC58/SC2/WG7 agrees this value is based on a valid scientific study.

Note: Currently it is classified in GHS as Category 3 because a value of 4000 ppm has been used based on a value given in the Model Regulations. In terms of GHS, the value of 7338 ppm classifies the gas in Category 4.

7. U.S Department of Transportation (DOT) regulation in the United States of America defines ammonia as non-toxic for domestic transport and the value of 7338 ppm is used.

8. When the Table in P200 was prepared by the working group in the years 2000 to 2001 the LC₅₀ value of 7338 ppm was known and discussed, but it was decided to choose an arbitrary value of 4000 in order to tally with the classification of ammonia as toxic. However, it can be seen by examination of the criteria for classification of toxic gases in the Model Regulations 2.2.2.1 (c) that the working group made an error. It is not necessary for a gas to have an LC₅₀ below 5000 ppm in order to be classified as toxic. It is clear that the first criterion in 2.2.2.1 (c), namely, Gases which: (i) are known to be so toxic or corrosive to humans as to pose a hazard to health; or ...” aptly describes Ammonia, anhydrous. This gas is corrosive to human tissue at low concentrations and being corrosive falls into Division 2.3, even with an LC₅₀ value above the 5000 ppm threshold.

b) Boron trifluoride

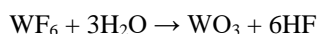
9. The LC₅₀ value given in ISO 10298:1995 (and in the Model Regulations) was originally derived by calculation based on an incorrect assumption regarding a presumed decomposition into Hydrogen Fluoride. Based on *Jones, W. Ransom, “Incorrect Assumption of Boron Trifluoride Hydrolyzation to Hydrogen Fluoride and The Effect on Existing Monitoring Techniques”, SSA Journal, Vol. 12, pp 19-23*, it has been demonstrated that if Hydrogen Fluoride is formed, it will be quickly reacted.

10. As new data became available following a scientific study on Boron Trifluoride (*Rusch G.M. Hoffman, G.M., McConnell, R.F. and Rinehart, W.E. Inhalation toxicity studies with boron trifluoride. Toxicol. Appl. Pharmacol. 1986, 83 pp. 69–78*), ISO/TC58/SC2/WG7 changed the LC₅₀ to a value of 864 ppm in ISO 10298:2010.

11. ISO/TC58/SC2/WG7 agrees that the values given in ISO 10298:2010 and ISO 10298:2018 are correct.

c) Tungsten hexafluoride

12. The LC₅₀ value has always been derived from decomposition into Hydrogen Fluoride (see ISO 10298:1995, ISO 10298:2010 and ISO 10298:2018) based on the following decomposition reaction:

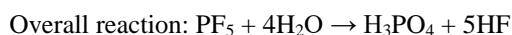
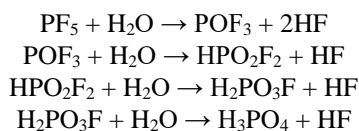


13. Therefore, the LC₅₀ value of Tungsten Hexafluoride is given as 1/6 of the LC₅₀ value of Hydrogen Fluoride.

14. While the method of determining the LC₅₀ value has not been changed since the first edition of ISO 10298, the change of value between ISO 10298:1995 and ISO 10298:2010 is due to the change of reference LC₅₀ value for Hydrogen Fluoride (see e) below).

d) Phosphorous pentafluoride

15. The LC₅₀ value has always been derived from decomposition into Hydrogen Fluoride (see ISO 10298:1995, ISO 10298:2010 and ISO 10298:2018) based on the following decomposition reactions:



16. Therefore, the LC₅₀ value of Phosphorous Pentafluoride is given as 1/5 of the LC₅₀ value of Hydrogen Fluoride.

17. While the method of determining the LC₅₀ value has not been changed since the first edition of ISO 10298, the change of value between ISO 10298:1995 and ISO 10298:2010 is due to the change of reference LC₅₀ value for Hydrogen Fluoride (see e) below).

e) Hydrogen fluoride, anhydrous

18. The LC₅₀ value given in ISO 10298:1995 was 966 ppm.

19. New data being available, ISO/TC58/SC2/WG7 concluded, when preparing ISO 10298:2010, that the LC₅₀ value should be the median of five LC₅₀ values taken from Table 3-4 of the 2004 US National Advisory Committee Acute Exposure Guideline Levels for Airborne Chemicals (AEGL) review for Hydrogen Fluoride.

Note: The change of LC₅₀ from its current value of 966 ppm to the proposed 1307 ppm would result in a change of Category within the GHS.

Proposal

20. In Table 2 of P200 in 4.1.1.4, for the UN numbers below, replace the values under the heading "LC₅₀ in ml/m³", with those in 10298:2018, as follows:

UN No.	Proper Shipping Name	Current LC ₅₀ in ml/m ³ in P200 (Rev. 21)	Replace with
1005	AMMONIA, ANHYDROUS	4000	7338
1008	BORON TRIFLUORIDE	387	864
2196	TUNGSTEN HEXAFLUORIDE	160	218
2198	PHOSPHORUS PENTAFLUORIDE	190	261
1052	HYDROGEN FLUORIDE, ANHYDROUS	966	1307

Justification

21. ISO 10298:2018 and its previous 2010 edition were based on wide-ranging research into the latest toxicological data on these gases and the standard lists the references on which these LC₅₀ values were based. The 1995 edition has proved to be a sound basis for P200 and there are relatively few changes given the fact that scientific knowledge continues to advance.
