



# U.S. ARMY COMBAT CAPABILITIES DEVELOPMENT COMMAND – GROUND VEHICLE SYSTEMS CENTER

## **Purity of Gaseous Fire Suppression Agents (and toxicity of impurities)**

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# AGENT IMPURITIES



- **Both NFPA and ASTM allow impurities in gaseous fire suppression agents:**
  - Halon 1301: up to 0.4% (ASTM D5632 and NFPA 12A)
  - HFC-227ea: up to 1% (ASTM D6064 and NFPA 2001)
- **NFPA: Measurements of impurities in gaseous agents are not directly addressed**
- **ASTM: Both D5632 and D6064 specify how impurities shall be measured**
  - D5632 specs gas chromatography (GC) and, conditionally, mass spectrometry (GC/MS)
    - “6.1.1 Note 1: The GC method described in 6.1.1-6.1.1.6 may not detect certain impurities, for example, impurities that may elute within or near the relatively large Halon 1301 peak. If other tests indicate the presence of unidentified impurities, then the gas chromatography/mass spectrometry (GC/MS) method described in 6.1.2 is recommended.”
  - D6064 only specs GC for purity measurement



## TOXICITY OF IMPURITIES



- Neither ASTM nor NFPA address the toxicity of the allowed impurities
- Since the toxicity of the impurities is not specified, it is possible that an agent that meets the requirements could be toxic in occupied spaces when used in accordance with the relevant NFPA standard
- **Example. HFC-227ea may have up to 1% impurities**
  - The safe air concentration limit for Perfluoroisobutene (PFIB) is much less than 1 ppm (0.0001%)\*
  - This means that at the HFC-227ea design concentration for an occupied space, ~10%, the maximum ambient impurity is 0.1%, and to be safe to breathe, PFIB must be far less than a thousandth of the total impurities

\* <https://pubchem.ncbi.nlm.nih.gov/compound/Perfluoroisobutylene#section=NIOSH-Toxicity-Data>



# HALON 1301



## Excerpted from NFPA 12A-2018

4.1.2\* Quality. Halon 1301 shall comply with the requirements of either Table 4.1.2 or ASTM D5632/D5632M.

**Table 4.1.2 Requirements for Halon 1301 (Bromotrifluoromethane)**

| Property                                       | Requirement  |
|------------------------------------------------|--------------|
| Bromotrifluoromethane, mole percent, minimum   | 99.6         |
| Other halocarbons, mole percent, maximum       | 0.4          |
| Acidity, ppm (by weight), maximum              | 3.0          |
| Water content, percent by weight, maximum      | 0.001        |
| Boiling point, °C at 760 mm Hg                 | -57.75       |
| Boiling range, °C, 5 to 85 percent distilled   | 0.3          |
| High boiling impurities, grams/100 ml, maximum | 0.05         |
| Suspended matter or sediment                   | None visible |

## Excerpted from ASTM D5632/D5632M-12

4.2 *Type II*—Halon 1301 shall conform to the requirements of Type I, as listed in 4.1, and shall contain no more than 1.5 % by volume non-condensable gases in vapor phase, expressed as nitrogen when tested by the appropriate test method(s) listed in Section 6.

4.3 By agreement between the purchaser and the supplier, analysis may be required and limits established for elements or compounds not specified in Table 1.

4.4 Unless otherwise specified, Type I is assumed.

4.5 **Warning**—Exposure to concentrations of Halon 1301 in excess of 7.5 % by volume in air during periods of elevated adrenaline could produce cardiac arrhythmia in some personnel.

**TABLE 1 Requirements**

| Property                              | Requirement                                    |
|---------------------------------------|------------------------------------------------|
| Halon 1301 purity, %, mol/mol, min    | 99.6 (exclusive of any N <sub>2</sub> present) |
| Acidity, ppm by mass, as Hbr, max     | 3.0                                            |
| Water content, ppm by mass, max       | 10                                             |
| Nonvolatile residue, % by weight, max | 0.01                                           |
| Halogen ion                           | Passes test                                    |
| Suspended matter or sediment          | None visible                                   |



# HFC-227EA



## Excerpted from NFPA 2001-2018

4.1.2\* Quality. Agent, including recycled agent, shall meet the standards of quality given in Table 4.1.2(a) through Table 4.1.2(d). Each batch of agent, both recycled and newly manufactured, shall be tested and certified to the specifications given in the tables. Agent blends shall remain homogeneous in storage and use within the listed temperature range and conditions of service that they will encounter.

Δ Table 4.1.2(a) Halogenated Agent Quality Requirements

| Property                                         | Specification |
|--------------------------------------------------|---------------|
| Agent purity, mole %, minimum                    | 99.0          |
| Acidity, ppm (by weight HCl equivalent), maximum | 3.0           |
| Water content, weight %, maximum                 | 0.001         |
| Nonvolatile residues, g/100 ml maximum           | 0.05          |

## Excerpted from ASTM D6064-11 (2015)

4.2 *Type II—HFC-227ea*—HFC-227ea shall conform to the requirements of Type I, as listed in 3.1, and shall contain no more than 1.5 % by volume fixed gases in vapor phase, expressed as air when tested by the appropriate test method(s) listed in Section 6.

4.3 By agreement between the purchaser and the supplier, analysis may be required and limits established for elements or compounds not specified in Table 1.

4.4 Unless otherwise specified, Type II is assumed.

NOTE 1—Prolonged exposure to concentrations of HFC-227ea in excess of 10.5 % by volume in air during periods of elevated adrenaline could produce cardiac arrhythmia in some personnel.

TABLE 1 Requirements

| Property                       | Requirement                                                      |
|--------------------------------|------------------------------------------------------------------|
| HFC-227ea purity               | 99.0 %, mol/mol, min                                             |
| Acidity                        | (exclusive of any $N_2$ present)<br>2.0 ppm by mass, as HCL, max |
| Water content ppm by mass, max | 10 ppm by mass, max                                              |
| Nonvolatile residue            | 0.05 g/100 mL, max                                               |
| Halogen ion                    | passes test                                                      |
| Suspended matter or sediment   | none visible                                                     |

Note: NFPA 2001 does not call out ASTM D6064 requirements



## SUMMARY



- **Current ASTM and NFPA standards for gaseous agents do not prevent a 'properly applied' agent (per the applicable NFPA Standard) from creating a toxic atmosphere in an occupied space**
- **ASTM and NFPA Standards should consider adding language to limit the toxicity of allowed impurities**
- **Also: currently NFPA 12A and 2001 do not harmonize with ASTM the same way; should they?**



## REFERENCES



- ***ASTM D5632, Standard Specification for Halon 1301, Bromotrifluoromethane (CF<sub>3</sub>Br), 2013.***
- ***ASTM D6064, Standard Specification for HFC-227ea, 1,1,1,2,3,3,3-Heptafluoropropane (CF<sub>3</sub>CHF<sub>2</sub>CF<sub>3</sub>), 2015.***
- ***NFPA 12A, Standard on Halon 1301 Fire Extinguishing Systems, 2018.***
- ***NFPA 2001, Standard on Clean Agent Fire Extinguishing Systems, 2018.***