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To cite this article: S N Kopylov *et al* 2021 *IOP Conf. Ser.: Earth Environ. Sci.* **666** 022010

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Dibromomethane as Promising Gaseous Fire Extinguishing Substance with Short Atmospheric Lifetime

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Abstract. Calculation of dibromomethane atmospheric lifetime is carried out, as well as an experimental assessment of its fire extinguishing efficiency. Calculations show that methylene bromide atmospheric lifetime is 15.8 days so it rapidly decomposes in the troposphere. The main mechanisms of the removal of CH₂Br₂ from the atmosphere are its reaction with hydroxyl radicals and the processes of physical removal from the atmosphere. Special experimental equipment allowing to measure fire extinguishing concentration of gaseous fire suppressant having high boiling point is described. Experimentally measured minimum extinguishing concentration of methylene bromide for n-heptane is 2.5 % vol. According to this, CH₂Br₂ is close to the most effective gaseous fire extinguishing agents, such as C₃F₇I and C₂F₄Br₂. LOAEL value for CH₂Br₂ is predicted at the level of 0.3-0.4 % vol. Due to the high boiling point of methylene bromide and its relatively high toxicity, the most appropriate way to use it in fire suppression is to create fire extinguishing mixtures, in particular, with fluorinated hydrocarbons. This approach allows to diminish application of greenhouse gases in fire protection and also to solve the problem of toxicity of extinguishing substance.

1. Introduction

It was shown in [1] that partially halogenated hydrocarbon molecules containing two or more bromine atoms should have a short atmospheric lifetime due to photolysis. Dibromides are considered the most promising for use as extinguishing agents [1], and the simplest representative of this class of substances is dibromomethane (methylene bromide). It was previously widely used in 1960s as a component of fire extinguishing mixtures: in particular, compositions "7" (20 % mass. C₂H₅Br - 80% mass. CH₂Br₂) and BM (70% mass. C₂H₅Br - 30% mass. CH₂Br₂) are known [2]. In this paper the calculation of dibromomethane atmospheric lifetime is carried out, as well as an experimental assessment of its fire extinguishing efficiency.



2. Atmospheric lifetime calculations

According to the generally accepted definition, atmospheric lifetime of a chemical compound is defined as the time during which the initial concentration of this compound in the atmosphere decreases by a factor of e . Below is a summary of the methodology for calculating this parameter (see [3] for more details).

According to existing approach, when estimating the time of removal of a substance from the troposphere, the latter is considered as a quasi-homogeneous medium, mixing in which occurs in a few days. The inhomogeneity of the particle distribution determined by the distance from the source of their formation horizontally and vertically is not taken into account [3].

The main processes responsible for the removal of a chemical compound from the troposphere are the reaction with hydroxyl radicals, photolysis, leaching and the reaction with tropospheric ozone. The atmospheric lifetime t can be represented by the formula

$$\frac{1}{t} = k_{OH}[OH] + \frac{1}{t_{photo}} + k_l + k_{O_3}[O_3], \quad (1)$$

where k_{OH} is the reaction rate constant of the interaction of the substance under consideration with hydroxyl radicals, t_{photo} is the time of a decrease in the concentration of the substance in the consideration by a factor of e due to photolysis; k_l is the constant of the removal of a substance from the atmosphere due to physical interactions (corresponds to the time of a decrease in the concentration of a substance by a factor of e due to the processes of physical removal of a substance from the atmosphere); k_{O_3} is the constant of the reaction rate of the interaction of the compound in question with ozone; $[OH]$ and $[O_3]$ are the average concentrations of hydroxyl radicals and ozone in the troposphere.

The photodissociation time is determined by the expression

$$\frac{1}{t_{photo}} = \int_{290nm}^{700nm} S(\lambda)I(\lambda)\varphi(\lambda)d\lambda, \quad (2)$$

where $S(\lambda)$ is the absorption cross section of the substance depending on the wavelength; $I(\lambda)$ is the intensity of sunlight in the troposphere depending on the wavelength; $\varphi(\lambda)$ is the quantum yield of photodestruction of the compound in question.

According to [4], the average concentration of hydroxyl radicals in the troposphere is $9.7 \cdot 10^5$ molecule \cdot cm $^{-3}$. At a temperature of 298 K, the rate constant of the interaction of CH₂Br₂ with OH radicals is $1.2 \cdot 10^{-13}$ cm 3 \cdot molecule $^{-1} \cdot$ s $^{-1}$. Then $k_{OH}[OH] = 1.16 \cdot 10^{-7}$ s $^{-1}$.

For methylene bromide the quantum yield of photodestruction is close to 1 [6]. Therefore, the time of its photodestruction is determined by the integral of the overlap of the absorption spectrum and the spectrum of solar radiation in the troposphere. Since data on the average intensity of sunlight in the troposphere could not be found, we carried out an estimated calculation using the spectrum of direct solar radiation at different effective thicknesses of the ozone layer. The calculation results are shown in figures 1 and 2.

Figure 1 shows the absorption spectrum of methylene bromide [6] and the spectrum of solar radiation at an effective ozone layer thickness of 3 mm [6] which corresponds to the position of the sun at the zenith.

Figure 2 represents the overlapping of solar radiation spectrum and absorption spectrum of CH₂Br₂ at an effective ozone layer thickness of 3 mm. The area under the overlap spectrum

characterizes the value of the integral $\int_{290nm}^{700nm} S(\lambda)I(\lambda)\varphi(\lambda)d\lambda$.

The calculated value of the integral $\int_{290nm}^{700nm} S(\lambda)I(\lambda)\varphi(\lambda)d\lambda$ is $1.576 \cdot 10^{-8}$ s $^{-1}$ for an ozone layer thickness of 3 mm. Then $t_{photo} = 0.634 \cdot 10^8$ s, or 2.01 years.

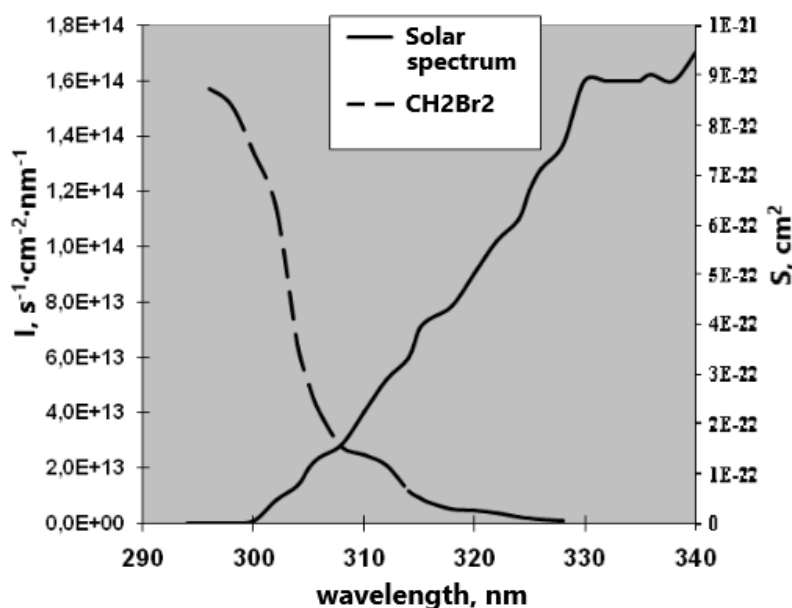


Figure 1. The absorption spectrum of CH₂Br₂ and the solar spectrum in the troposphere when the sun is at the zenith (ozone layer 3 mm thick).

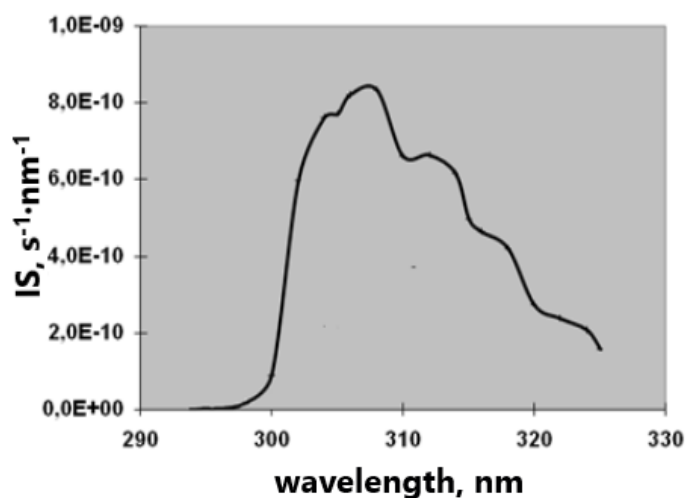


Figure 2. Overlapping of the solar radiation spectrum and absorption spectrum of CH₂Br₂ at an effective ozone layer thickness of 3 mm.

The calculated value of the integral $\int_{290nm}^{700nm} S(\lambda)I(\lambda)\varphi(\lambda)d\lambda$ is $1.576 \cdot 10^{-8} \text{ s}^{-1}$ for an ozone layer thickness of 3 mm. Then $t_{\text{photo}} = 0.634 \cdot 10^8 \text{ s}$, or 2.01 years.

According to the data of [7], for compounds similar to the considered one the value of the parameter k_l at a temperature of 200 K is $< 6 \cdot 10^{-5} \text{ s}^{-1}$ (interaction with an ice film was studied). We could not find any indications of the significance of the reaction of methylene bromide with ozone. Therefore an influence of this process on CH₂Br₂ atmospheric lifetime is not considered in this work.

On the basis of this consideration it is easy to obtain with the usage of formula (1) that even if k_l value is 2 orders of magnitude less than its limiting value, methylene bromide atmospheric lifetime is

1365821 sec, or 15.8 days. The main mechanisms of the removal of CH_2Br_2 from the atmosphere are its reaction with hydroxyl radicals and the processes of physical removal from the atmosphere.

Thus, CH_2Br_2 is a substance that rapidly decomposes in the troposphere and satisfies all modern environmental requirements for such products (atmospheric lifetime is less than 181 days [2]).

3. Experimental

An effect of non-uniformity of distribution of fire extinguishing gaseous agents having high boiling point on their fire extinguishing effectiveness is well known [2,8,9]. In particular, it is impossible to use standard cup burner test method to determine minimum extinguishing concentration [10] for such fire suppressants. Because boiling point of methylene bromide is also high (about 97 C [11]), special experimental equipment was used in this work to measure its minimum extinguishing concentration for n-heptane.

The experiments were carried out at a set-up CYLINDER presented in figure 3. The main element of the set-up is a cylindrical vessel (3) having a volume of 53 dm³. The model fire source (1) also has a cylindrical shape with a diameter of 30 mm and a volume of 20 cm³. In each experiment the model fire source was filled with 19 cm³ of n-heptane.

The experiments were conducted at room temperature and atmospheric pressure in the following order. After evacuation of the vessel (5) using a vacuum pump (6) it was filled with a mixture of extinguishing agent (methylene bromide) and air of the required composition. The mixture was created directly in the vessel by partial pressures. Its composition was determined by a vacuum gauge (3), the mixture was set with an accuracy of 0.1% vol.

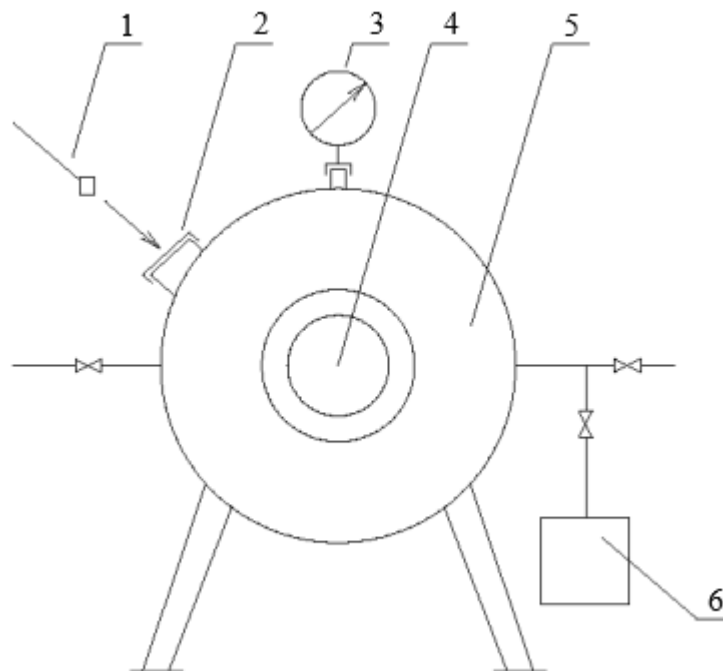


Figure 3. Experimental set-up CYLINDER.

1 – model fire source; 2 – hermetically sealed opening; 3 – vacuum gauge;
4 – window; 5 – vessel; 6 – vacuum pump

The required time to achieve uniformity of the gaseous medium in the vessel (5) was 10 minutes. After its expiration, a pre-filled 19 cm³ of n-heptane was ignited in the model fire source (1). After boiling the fuel in the model fire source it was introduced into the vessel (5) through the opening (2). The moment of extinguishment of the flame was determined through the window (4). The time of 12-

14 seconds was used as the criterion for the absence of extinguishing, since during this time the model fire center is extinguished due to the consumption of oxygen in the vessel (5).

4. Obtained results

The experimental results are shown in figure 4. It was obtained that the minimum extinguishing concentration of methylene bromide for n-heptane is 2.5 ± 0.1 % vol. This result corresponds to the known data [12] that the extinguishing concentration of the composition "7" consisting of 80 % mass. of dibromomethane and 20 % mass. of ethyl bromide is 3 % vol. when extinguishing the flame of n-heptane. According to this, CH_2Br_2 is close in extinguishing properties to the most effective gaseous fire extinguishing agents, such as $\text{C}_3\text{F}_7\text{I}$ and $\text{C}_2\text{F}_4\text{Br}_2$.

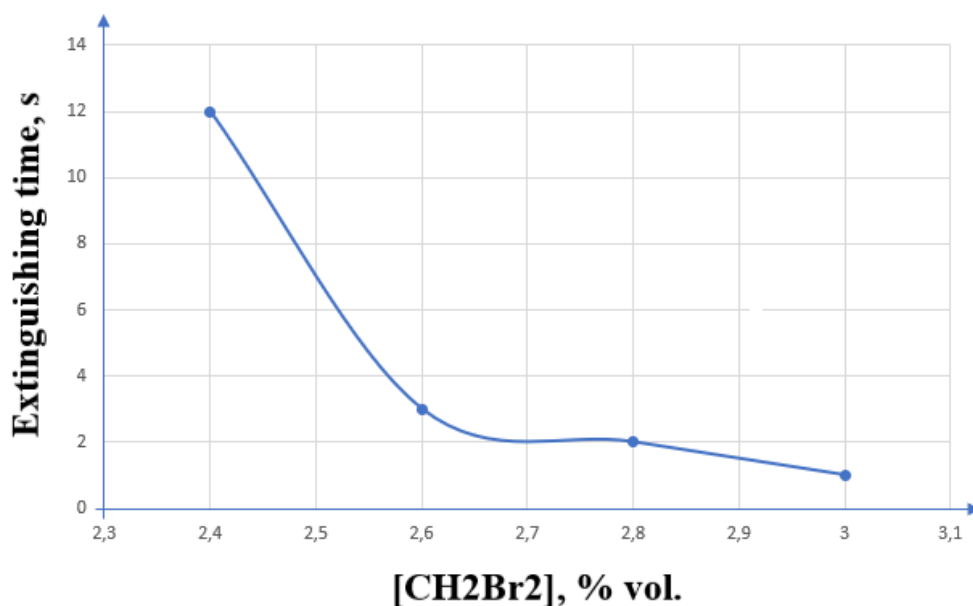


Figure 4. Inhomogeneity of the environment in the room of 40 m³ in 10 sec after the beginning of the agent release.

The value of LOAEL (the most commonly used indicator for assessing the toxicity of gaseous fire extinguishing agents which is determined as the lowest observable adverse effect level for cardiac sensitization in the dog that resulted in death of the animal) is unknown for dibromomethane. The another indicator of toxicity of a substance, TWA (TWA is the employee's average airborne exposure in any 8-hour work shift of a 40-hour work week which shall not be exceeded) is equal to $155 \text{ mg} \cdot \text{m}^{-3}$ for CH_2Br_2 (for comparison, TWA for $\text{C}_2\text{F}_4\text{Br}_2$ is $1000 \text{ mg} \cdot \text{m}^{-3}$, for $\text{C}_3\text{F}_7\text{I}$ - $100 \text{ mg} \cdot \text{m}^{-3}$). It follows from the given data that methylene bromide is less toxic than heptafluoroiodopropane, and on the basis of comparison with $\text{C}_3\text{F}_7\text{I}$ it is possible to predict the LOAEL value for CH_2Br_2 at the level of 0.3-0.4% vol.

Taking into account the high boiling point of methylene bromide and its relatively high toxicity, the most appropriate way to use it in fire suppression is still to create fire extinguishing mixtures. In particular, methylene bromide can be used in mixtures with fluorinated hydrocarbons (HFCs), which allows us to solve two problems: first, the addition of methylene bromide will lead to a decrease in the fire extinguishing concentration of HFC, which will reduce the volume of its use (which is especially important from environmental point of view, since HFCs have very long atmospheric lifetime and large value of the global warming potential). Second, the ratio of the components of the extinguishing mixture can be adjusted so that the LOAEL is not exceeded for either methylene bromide or

fluorinated hydrocarbon when the mixture reaches its fire extinguishing concentration. This is the way to solve the problem of the toxicity of the extinguishing substance.

5. Conclusions

It was obtained that methylene bromide atmospheric lifetime is 15.8 days. The main mechanisms of the removal of CH₂Br₂ from the atmosphere are its reaction with hydroxyl radicals and the processes of physical removal from the atmosphere. Thus, CH₂Br₂ is a substance that rapidly decomposes in the troposphere and satisfies all modern environmental requirements for such products (atmospheric lifetime is less than 181 days).

Experimentally measured minimum extinguishing concentration of methylene bromide for n-heptane is 2.5±0.1 % vol. According to this, CH₂Br₂ is close in extinguishing properties to the most effective gaseous fire extinguishing agents, such as C₃F₇I and C₂F₄Br₂.

It was showed that methylene bromide is less toxic than heptafluoroiodopropane, and on the basis of comparison with C₃F₇I it is possible to predict the LOAEL value for CH₂Br₂ at the level of 0.3-0.4% vol.

Taking into account the high boiling point of methylene bromide and its relatively high toxicity, the most appropriate way to use it in fire suppression is to create fire extinguishing mixtures, in particular, with fluorinated hydrocarbons. This approach allows to diminish application of greenhouse gases in fire protection and also to solve the problem of the toxicity of the extinguishing substance.

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