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Research Summary – Calculating the Inhalation Toxicity of Petroleum Crude Oil

Transportation of Dangerous Goods | Scientific Research Division

SUMMARY

This technical note explains the use of the calculation method for determining the toxicity by inhalation of petroleum crude oil based on the composition of the vapour phase in equilibrium with the liquid phase of the crude oil, in accordance with Section 2.34 of the *Transportation of Dangerous Goods Regulations (TDGR)* [1].

BACKGROUND

Crude oil is a complex mixture of liquid and gaseous components, and its composition varies based on the type of crude oil and the location and time of extraction. Under the *TDGR*, petroleum crude oil is usually classified as a Class 3 Flammable Liquid (UN1267 PETROLEUM CRUDE OIL). However, the presence of components that are toxic by inhalation must be considered when determining the appropriate classification. For example, some petroleum crude oil could contain enough toxic by inhalation components to be assigned to UN3494, PETROLEUM SOUR CRUDE OIL, FLAMMABLE, TOXIC, which is a Class 3, Subsidiary Class 6.1 dangerous good. Because its composition is variable, there is no standard LC_{50} value for petroleum crude oil.

What is LC_{50}?

The LC_{50} value for a substance is the lowest concentration of gas, vapour, mist or dust that, when administered by continuous inhalation to both male and female young adult albino rats for one hour, results in the death of one half of the animals within 14 days after exposure.

Toxicity by inhalation for a mixture of liquids with an unknown LC_{50} can be determined by animal test methods, as per Section 2.35 of the *TDGR*, or by estimation as per Section 2.34 of the *TDGR*. Animal testing may not be practical, feasible or preferable for many transporters. As such, the calculation method found in Section 2.34 is a suitable alternative in determining the toxicity of petroleum crude oil.

OBJECTIVES

The purpose of this work is to explain the calculation methodology found in Section 2.34 of the *TDGR*, for the estimation of the toxicity by inhalation of petroleum crude oil.

METHODS

Toxic Components

Petroleum crude oil is a complex liquid product, with several gasses commonly dissolved within. Some of these liquid and gaseous components are known to be toxic by inhalation, meaning they have an LC_{50} (rat, 1 h) lower than 5 000 mL/m^3, as defined by *Section* 2.28 (c) (ii) of the

TDGR. The LC_{50} value of two toxic gases known to be dissolved in petroleum crude oil are provided in **Error! Reference source not found.** below.

Table 1. LC50 for common toxic components of petroleum crude oil

Component	LC_{50}, 1 h (mL/m^3)
Carbon Monoxide (CO)	4 888 [2]
Hydrogen Sulfide (H_2S)	673 [3]

Since crude oil is a mixture of liquids and dissolved gases that may be toxic by inhalation, it is the toxicity of the vapour in equilibrium with the liquid that must be assessed. The first step in Section 2.34 (1)(a) is to determine the LC_{50} (vapour) of the mixture in accordance with Section 2.33 of the *TDGR*. The components identified in Table 1 as toxic (H_2S, CO) are found in petroleum crude oil as dissolved gases and will evolve into the vapour phase at standard temperature and pressure. The following calculations use the mole fraction of the toxic components in the vapour phase to account for the inhalation toxicity generated by these gaseous components, based on their respective concentration.

Section 2.33 refers to Section 2.17 of the *TDGR* for the determination of the LC_{50} of a mixture of substances that are in the form of a dust, mist, or vapour. In Section 2.17(b), Determination of LC_{50} of a Mixture of Gases, the first step is to calculate the LC_{50} of the mixture using the concentration and LC_{50} of each of the toxic components.

For demonstration, we will use the results obtained from a petroleum crude oil sample analysis campaign conducted by TC [4]. Special attention should be paid to the specificities of every petroleum crude oil shipment when adapting the methodology as the results obtained in this document are only applicable to the samples collected during the campaign.

Based on the results of the campaign, CO and H_2S were identified as the two toxic by inhalation components in the crude oil samples. Therefore, we need to calculate the contributing number (CN) of each gas using the formula in Section 2.17(b)(i):

$$CN\ Gas\ A = \frac{LC_{50}\ Gas\ A}{fraction\ (v/v)\ of\ Gas\ A\ in\ the\ mixture}$$

To use this equation, the fraction by volume of each toxic gas in the vapour phase above the liquid must be known. It has been shown that vapour phase concentration of H_2S over a complex liquid such as crude oil is not derivable from the liquid H_2S concentration, which led to the CCQTA's H2S PVT project to obtain a field measurement of vapour phase H_2S concentration above petroleum crude oil [5, 6]. Work performed by Transport Canada also found that vapour phase H_2S concentration was only weakly predictable based on the properties of a liquid crude oil sample [4]. It was therefore necessary to develop a method to measure the fraction by volume of each toxic component in the vapour space above the petroleum crude oil.

Measurement of Vapour Concentration

Because the evolution of dissolved gases into the vapour phase is influenced by ambient conditions, the objective of this work was to obtain data for classification at conditions similar to petroleum crude oil transported by rail. During the sample analysis campaign, TC therefore measured the vapour phase concentration of the gases at standard temperature and pressure, and at a vapour/liquid ratio of 0.1:1, which represents a tank car which is 90.9% full. A novel method was developed and used, based on ASTM D8236 [7]. This method uses a manual piston cylinder to obtain a vapour sample above the liquid crude oil, so there is no loss of volatile components. Agitation occurs over 5 minutes in a sonicating bath, and then the sample is allowed to settle overnight to reach equilibrium. A sample of the vapour is then passed through a gas chromatograph to measure the fraction by volume of hydrocarbons and fixed gases.

Calculation

Once the vapour fractions of the toxic components were known, the CN of CO and H_2S could be calculated in accordance with Section 2.17(b)(i), using the known LC_{50} (see Table 1) and the fraction by volume of each gas. Then, the CN of both gases were combined using the formula in Section 2.17(b)(ii) to calculate the number T:

$$T = \frac{1}{CN_{H2S}} + \frac{1}{CN_{CO}}$$

The LC_{50} of the vapour mixture above the petroleum crude oil could then be calculated using the formula in Section 2.17(b)(iii):

$$LC_{50,mix} = \frac{1}{T}$$

If the calculated $LC_{50,mix}$ of a specific crude oil is greater than 5,000 mL/m^3, then that crude oil does not meet the criteria to be classified as toxic by inhalation. If it is less than or equal to 5 000 mL/m^3, it meets the toxicity threshold, and the classification must take this into account and assign an appropriate UN number such as UN3494, PETROLEUM SOUR CRUDE OIL, FLAMMABLE, TOXIC.

RESULTS

The above methodology was used on 24 petroleum crude oil samples, to provide a broad overview of crude oils produced across Western Canada. Of these 24 tested samples, none met the criteria for toxicity by inhalation.

CONCLUSIONS

Transport Canada, along with its research partner at InnoTech Alberta, has developed a novel method for measuring the concentration of toxic vapour components above petroleum crude oil and demonstrated the use of the calculation method for determining toxicity by inhalation for the classification of petroleum crude oil as per the *TDGR*.

REFERENCES

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[4] Transport Canada, Crude Oil Sampling and Analysis: Impact of Crude Oil Properties on Flammability Properties, published 2021.

[5] Canadian Crude Quality Technical Association, H2S Measurement Project Report, published 2012.

[6] Canadian Crude Quality Technical Association, Project - H2S PVT Project, updated 2021.

[7] ASTM, D8326 Standard Practice for Preparing an Equilibrium Liquid/Vapor Sample of Live Crude Oil, Condensates, or Liquid Petroleum Products Using a Manual Piston Cylinder for Subsequent Liquid Analysis or Gas Analysis, updated 2019.

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KEYWORDS

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