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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Issues relating to the Globally Harmonized System of Classification and Labelling of Chemicals

Criteria for water-reactivity

Sub-Committee of Experts on the Globally Harmonized System of Classification and Labelling of Chemicals

Twenty-second session

Geneva, 7 – 9 December 2011

Item 2 of the provisional agenda

Updating of the Globally Harmonized System of Classification and Labelling of Chemicals (GHS)

Work on test method N.5 to be used for the assessment of water activated toxicity

Transmitted by the expert from Germany

Introduction

1. In December 2008 the experts from France and Germany submitted a proposal for the program of work in order to include work on test method N.5 to improve its accuracy and precision and to decrease the lower measuring limit in order to enable it to measure the evolution rate of toxic gases emitted by substances upon their contact with water.

2. The proposal was accepted by the Sub-Committees and ST/SG/AC.10/C.4/2008/19 and ST/SG/AC.10/C.3/2008/68, paragraph 6 and UN/SCEGHS/16/INF.18 and UN/SCETDG/34/INF.44, paragraph 8 were supposed to serve as the terms of reference. The focal point is the Sub-Committee TDG and the lead country Germany.

3. Some background information on problems associated with test N.5 was given in the above-mentioned documents and is partly repeated in the Annex to this document in order to recall the reasons for taking up this work.

Developments up to now

4. A first meeting of the informal working group was held in April 2009 in Paris. The participants were from France, Germany, The Netherlands, Qatar and Romania.

5. As it is known that different testing organisations use different testing equipment and apply different methods to determine the gas evolution rate (see also the Annex to this document), the working group agreed that the testing organisations would carry out tests to check the accuracy of their testing equipment. It was foreseen to have a further meeting in December 2009 if the according results were available. However, at that time that was not the case and no meeting was held.

6. Since then BAM has carried out a series of N.5 tests using magnesium and aluminium in order to achieve some kind of a calibration and to determine the order of magnitude of the lower limit of the measurement range. The results were presented to both sub-committees in December 2010 (see UN/SCETDG/38/INF.27 and UN/SCEGHS/20/INF.19).

7. In the meantime one other testing organisation (INERIS, France) has informed BAM about results of tests according to UN test method N.5 with their equipment and gas evolution rate measurement method. So far, no further testing organisations have informed BAM about their tests within the framework of this work item and only one organisation has indicated that it has the intention to do so.

Issues to be solved

8. Further work should focus on the following main issues:

9. One issue is the general improvement of the measurement of the gas evolution rate of water-reactive substances and mixtures. An improvement with regard to the measurement of the gas evolution rate is not only required in order to finally enable the method to be applied to substances and mixtures that in contact with water emit toxic gases but it can also be used to improve the already existing test N.5 for substances and mixtures which in contact with water emit flammable gases. This would be very beneficial as past interlaboratory testing has shown that results based on test N.5 have a very broad range and hence lead to different classification outcomes for one and the same test substance.

10. Furthermore, it is clear that an improvement of test N.5 that aims at achieving consistent and comparative results in different laboratories alone is not enough. The release of toxic gases will be hazardous already in lower concentrations than for flammable gases. Therefore the method must also be adapted (or changed considerably) in order to decrease the lower measuring limit.

11. A third issue is related to those considerations that are necessary in order to derive possible criteria such as the underlying scenario (amount of substance/mixture, toxicity of the gas released, volume of air space, duration of gas release etc.). These finally would have to be reflected in the classification criteria and transformed into the test method by adapting the procedure with regard to the amount of substance to be tested, over-all duration of the gas measurement, intervals in which the gas release is supposed to be measured etc.

Further proceeding and proposal

12. The general improvement of the test method N.5 and its possible adaptation to lower measuring limits can only be achieved based on the results and contributions of different testing organisations and laboratories because otherwise consistent and comparative results all over the world cannot be ensured. The different test equipment used by different testing organisations and the different methods for determining the amount of gas evolved should be compared in order to find the most appropriate equipment and gas evolution rate detection method.

13. Possible criteria for the classification of substances and mixtures that in contact with water emit toxic gases (or at least the order of magnitude) are necessary as directing guidance for adaptations with regard to the lower measuring limit of the test method.

14. The sub-committees are therefore requested to state whether they want to have this work pursued or not. If they want the work to continue, the experts should bear in mind that the work can only continue with the participation of other experts and that especially participation and contributions of other testing organisations and laboratories are required for the improvement of test method N.5. Furthermore, the participation and contributions of health hazard experts (BAM has no expertise to that effect) are required with regard to possible criteria for classification (based on scenarios the health hazard experts deem appropriate). Together the experts then would have to aim at transformation of the criteria to the test method (e.g. amount of substance to be tested, duration of the measurement, should the limiting gas evolution rate be linked to the total amount of gas evolved during the test or should the amount be linked to a certain time frame etc.). Otherwise the working group could only aim at finding the best available test method and possibly indicate the lowest gas evolution rate that can be detected with that method.

Annex

Some problems associated with test N.5

15. Earlier exploratory investigations of BAM showed that the test result and thus the classification depends on the mass of the sample and the volume of water used in the test.

16. In the following the results of one example are shown:
Substance: Mixture based on aluminium granulate;
Test period: 5 days (120 h);
The amount of evolved gas was measured gravimetrically.

Mass of the tested substance	Volume of water	Maximum gas evolution rate	Start of gas evolution after	Resulting classification
10 g	20 ml	0,14 litre/kg.h*	-	Not classified as substance/mixture which in contact with water emits flammable gases (division 4.3)
25 g	40 ml	26,17 litre/kg.h	> 70 h	Classified as substance/mixture which in contact with water emits flammable gases, category 2 (division 4.3, PG II)

* After 6 days (144 h) the maximum rate of gas emission was 35,80 litre/kg.h

17. Within the description of test N.5 the following is stated and is open to different interpretations:

The rate of evolution of gas is calculated over 7 hours at 1 hour intervals. If the rate of evolution is erratic or is increasing after 7 hours, the measuring time should be extended to a maximum time of 5 days.

Depending on the accuracy and precision of the measuring method for the gas evolution rate, the test may be stopped after 7 hours, if the rate of evolution is not erratic and not increasing and consequently the substances will not be classified accordingly. However, sometimes the gas evolution starts later only and the maximum rate gas evolution rate might be much higher than 1 litre per kilogram of substance per hour then.

18. During an inter-laboratory comparison on the evaluation of UN Test N.5 organized by BAM, the same homogenized substance was tested by different testing institutes world-wide. It was observed that there is a very broad range of the test results with regard to the gas evolution rate (range of all single values: 0,4 to 5,7 l/kg per hour, range of the laboratory maximum values: 1,63 to 5,7 l/kg per hour, range of the laboratory mean: 1.0 to 5.2 l/kg per hour, robust mean value over all laboratories (reference value): 3,18 l/kg per hour).

19. During the interlaboratory test it was also found out that the laboratories determine the gas evolution rate with different methods/measuring devices:

- Gravimetry
- Volumetry
- Volumetry with magnetic stirrer
- Volumetry with a pressure gauge
- Volumetry with gas flow meter
- Volumetry with automated gas burette