Contents lists available at ScienceDirect

Process Safety and Environmental Protection

journal homepage: www.elsevier.com/locate/psep

Testing of gas flow measurement methods to characterize substances which emit flammable or toxic gases in contact with water

*Agnès Janès**, *Guy Marlair*, *Douglas Carson*

INERIS, Accidental Risks Division, Parc ALATA, BP 2, F-60550 Verneuil en Halatte, France

ARTICLE INFO

Article history:
Received 10 June 2015
Received in revised form 21 January 2016
Accepted 22 January 2016
Available online 1 February 2016

Keywords:
Dangerous when wet
Water-reactivity
Reaction with water
Hazardous hydro-reactive properties
Classification-testing protocols
Flammability and toxicity of released gases

ABSTRACT

Selecting the most appropriate flow measurement techniques with related devices to characterize potentially hazardous chemicals which emit flammable or toxic gases due to their hydro-reactivity poses a difficult but required task for official classification of such materials. This paper offers a careful examination of three such potential methods that differ from each other by the flow rate measurement device which includes one manual and two automatic systems. Experiments for comparative testing and validation limits have been defined and carried out for two known hydro-reactive chemicals: aluminum chloride and sodium borohydride. The main conclusions are reported here. From the results obtained, the possible selection of the best investigated methods is suggested according to performance based criteria.

1. Introduction and context

In a hazard assessment for the handling, storage, or transport of materials that may produce dangerous gases when wet, the experimental determination of the produced gas flow rate must be performed. When the dangerous gas is flammable, the published UN N.5 test is used. This test is described in the Manual of Tests and Criteria of United Nations (UN, 2009) and mandatory used by international transport regulations as well as the classification of dangerous substances and mixtures according to Globally Harmonized System (GHS) (UN, 2013). In Europe, this test is required for the Classification, Labeling, and Packaging regulations (CLP) (European Parliament and of the Council, 2008). The scientific background and the classification schemes of substances which in contact with water emit flammable gases were extensively described by the authors in a previous publication (Janès et al., 2012).

The UN N.5 test is based on a two step process: (1) three different preliminary tests are performed on small amounts of sample to determine if a violent reaction occurs in contact with water (2) if such a reaction does not occur, the gas flow rate produced must be measured experimentally. The classification threshold is fixed at 1 L of flammable gas per kilogram of substance per hour. If the chemical identity of the gas is unknown, the gas should be tested for flammability. One major difficulty of the current N.5 method is that it does not sufficiently describe the test conditions and therefore too much freedom is left to the potential users leading to a large degree of diversity in actual laboratory practices. Indeed, in previous work (Janès et al., 2012), it was shown that the

* *Corresponding author.* Tel.: +33 344556142.
E-mail address: agnes.janes@ineris.fr (A. Janès).
http://dx.doi.org/10.1016/j.psep.2016.01.016

variation of some parameters influence the results obtained. These influences could be so great that the uncertainty of the measurement can be on the order of the classification threshold. Improvement of test conditions, setting more precisely some of these influential test parameters and optimization of the experimental apparatus have been suggested (Janès et al., 2012).

In the case of substances or mixtures which emit toxic gases in contact with water, no standardized method is yet available however greatly needed insofar that CLP regulations (European Parliament and of the Council, 2008) have introduced this new hazard class. Considering the uncertainties related to the results obtained using the current N.5 method, its direct transposition for the generation of toxic gases cannot be envisaged. Indeed, the classification threshold will be much lower than for flammable gases because of the acute toxicity of certain gases in even a modest overall gas release. It is anticipated though that an improved method derived from the UN N.5 test protocol could be used, if the accuracy and fidelity of gas flow measurement can be achieved.

Several alternative methods to the N.5 test were proposed recently. Rosenberg et al. (2012, 2013) have described an alternative procedure that relies on the variation of the mass of displaced water due to the evolution of gas during the reaction of the sample with water. Their stated motivation is indeed the lack of precision of the N.5 test protocol. This was also the measurement principle that was selected for Round–Robin tests organized by the German Bundesanstalt für Materialforschung und -prüfung (BAM) in 2011 (Kunath et al., 2011). The measuring apparatus was calibrated by means of the reaction of a hydrochloric acid solution with magnesium powder, wherein the flow of released hydrogen can be calculated. The results obtained indicate a discrepancy between the measured and the theoretical volume of 4%. The related uncertainty on the result from the reaction of magnesium with demineralized water was estimated at 17% and the detection limit was reported to be in the order of 3–4 mL.

Later, Smith et al. (2013, 2014) carried out an investigation with a proposed test method based on the reaction taking place in a closed constant volume vessel and deducing by calculation the gas release rate from the pressure elevation in the test vessel. A very detailed description of the system was given with a thorough analysis of results obtained on ten different materials producing flammable or toxic gases in contact with water. Eventually, some classification criteria based on the gas release rate combined with the toxicity of the gas were suggested (Smith et al., 2014). However, it is necessary to exclude a modification of the reaction mechanism with water that is a consequence of the high pressure in the test vessel, which could therefore influence the result and subsequently the classification of the material tested. Such influence was highlighted in 2012 on aluminum (Janès et al., 2012).

The present work is dedicated to the investigation of an innovative test protocol with three different devices, aiming to achieve accurate and reliable measurement of potentially low gas release rate resulting from the reaction of a sample with water. The metrological performances of this protocol and apparatuses are also characterized. These new elements constitute potential breakthroughs that could significantly improve the UN N.5 test method, and possibly provide an alternative method intended for the classification of substances or mixtures which, in contact with water, emit toxic gases.

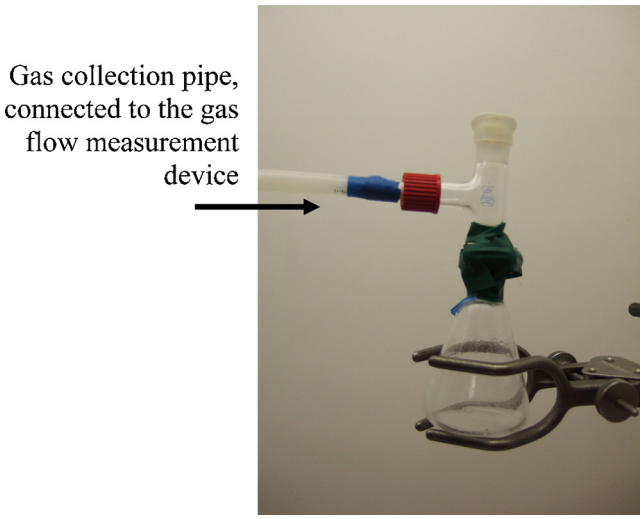

Fig. 1 – Experimental apparatus consisting of a conical flask and a piece of glassware with a gas collection pipe and a membrane cap.

2. Experimental

2.1. *Test apparatus*

The experimental apparatus consists mainly of an assembly of glassware composing a 25 mL conical flask, another glass-made piece with a membrane cap at the end, and a gas collection pipe, as shown in Fig. 1. First, the test sample if put in the flask and then the water is injected using a 1 mL syringe.

A major difference with current UN N.5 procedure is that the dropping funnel is not used in this new set-up. This system reduces the overall free volume of the experimental system, which then reduces the uncertainties on the measured gas flow rate due to the thermal expansion gas when the ambient temperature or atmospheric pressure vary during test runs. The system is assembled before the injection of water and therefore a reaction can take place between the two reactants. As in the case when a dropping funnel is used, it is necessary to subtract the contribution of the water injection to the raw data.

The stopwatch is started at the time of the injection of water into the flask.

2.2. *Tested gas flow measurement systems*

Three innovative experimental devices were identified and assumed particularly interesting for their potential to reduce the uncertainties of the gas volume released. These devices are described below.

2.2.1. *MGC-1 volume meter (PMMA cell) filled with Silox fluid*

The MGC-1 is represented in Fig. 2. It consists in a volumetric device and an automatic flow meter, which contains a cell immersed in synthetic oil, which collects the gas discharged from the reaction between the sample and water. An accumulated gas volume reaching 3.26 mL induces fulfilling of the elemental measurement cell. Each time such event arrives, the cumulative recording of one more volume increment is obtained. The released gas escapes to the open air by another pipe. This cell is not compatible with corrosive gases, since it is made of polymethyl methacrylate (PMMA).