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Committee of Experts on the Transport of Dangerous Goods and on the Globally Harmonized System of Classification and Labelling of Chemicals

Sub-Committee of Experts on the Transport of Dangerous Goods

Fifty-third session
Geneva, 25 June-4 July 2018
Item 2 (e) of the provisional agenda
Explosives and related matters:
stability tests for industrial nitrocellulose

Stability tests for nitrocellulose mixtures

Transmitted by the European Chemical Industry Council (CEFIC) on behalf of the World Nitrocellulose Producers Association WONIPA*

Introduction

1. The stabilization of nitrated cellulose mixture is a decisive and critical step in the production process of nitrocellulose and must be done and controlled properly for each production lot in order to achieve stable nitrocellulose products that can be transported and used safely without the danger of self-ignition over their entire shelf life. The wetting of nitrocellulose mixtures with alcohol, water or plasticizer only reduces the burning speed of the NC; it has no effect on the stability of the nitrocellulose mixtures. Additional measures are necessary to ensure the stability even if the nitrocellulose mixture will get completely dry.

2. At the fifty-first session in July 2017, the Working Group on Explosives of the Sub-Committee endorsed the statements of the German expert in document ST/SG/AC.10/C.3/2017/3, that additional tests are necessary to ensure that different nitrocellulose mixtures are stable, even if these mixtures would get completely dry. The Working Group on Explosives agreed that stabilization was required to ensure safe handling of nitrocellulose but also determined that the 3(c) thermal stability test at 75 °C was not suited for evaluating nitrocellulose stabilization. The Working Group on Explosives unanimously concluded that the Bergmann Junk test and the Methyl Violet

* In accordance with the programme of work of the Sub-Committee for 2017–2018 approved by the Committee at its eighth session (see ST/SG/AC.10/C.3/100, paragraph 98 and ST/SG/AC.10/44, para. 14).

Paper tests were suitable tests for such assessment and recommended their performance in place of the 3(c) test when classifying nitrocellulose.

3. The Working Group on Explosives concluded that CEFIC should lead an intersessional informal group to work out details of implementation, test procedures, placement of the Bergmann Junk test and the Methyl Violet Paper test in the Model Regulations and the Manual of Tests and Criteria, consider some allowance for grandfathering of currently existing nitrocellulose approvals and prepare a new proposal for the next session.

4. The Sub-Committee endorsed the conclusions of the Working Group on Explosives, (refer to the report of the Sub-Committee on its fifty-first session, ST/SG/AC.10/C.3/102, paragraphs 25 and 26).

5. Document ST/SG/AC.10/C.3/2017/35 from Germany was considered by the Sub-Committee at its fifty-second session. As the deadline of 1 September 2017 for submission of official documents was too short for a detailed discussion of the detailed test descriptions in the intersessional informal group, these test description could not be included in the document by Germany.

6. This document provides the detailed descriptions of the tests, a proposal for the details of implementation and the placement of the Bergmann Junk test and the Methyl Violet Paper test in the Model Regulations and the Manual and Tests and Criteria as the result of the discussions within the Working Group on Explosives at the fifty-second session and the work of the intersessional informal group following that session. WONIPA drafted the Bergmann Junk test and SAAMI the Methyl Violet Paper test for inclusion in the Manual of Test and Criteria. - A check of the existing stability test standards for nitrocellulose showed that the 3(c) thermal stability test at 75 °C is not used in any of these standards. Therefore an allowance for grandfathering currently existing nitrocellulose approvals is not needed.

Proposal

7. The expert from CEFIC/WONIPA is of the opinion that the stability of nitrocellulose mixtures is crucial for it being transported, stored and handled safely. A special provisions for Class 1 and division 4.1 entries should be incorporated in chapter 3.3 of the Model Regulations to ensure a sufficient level of stabilisation for worldwide and multimodal transport. The Bergmann Junk Test and the Methyl Violet Paper Test should be included in the Manual of Tests and Criteria as applicable test methods. They could be included in a new appendix 10.

Proposed amendments to the Model Regulations

8. Insert the following special provisions for Class 1 and division 4.1 entries in chapter 3.3 of the Model Regulations:

> Special provision [XXX] for Class 1 entries (UN Nos. 0340, 0341, 0342 and 0343):
>
> "[XXX] The Nitrocellulose is exempted from the UN Test Series 3 (c) thermal stability test requirements, but the consignor must ensure that the material meets the criteria of the Bergmann-Junk test or methyl violet paper test in the Manual of Tests and Criteria Appendix 10".
>
> Special provision [YYY] for Division 4.1 entries (UN Nos.2555, 2556, 2557 and nitrocellulose under UN No.3380):

"[YYY] The consignor must ensure that the material meets the criteria of the Bergmann-Junk test or methyl violet paper test in the Manual of Tests and Criteria Appendix 10".

9. Insert the appropriate special provision in the column 6 of the following entries for the nitrocellulose mixtures of class 1 (UN Nos. 0340, 0341, 0342 and 0343) and division 4.1 (UN Nos.2555, 2556, 2557 and 3380).

Amendments to the Manual of Tests and Criteria

10. Insert a new appendix 10 to read as follows:

"APPENDIX 10

STABILITY TESTS FOR NITROCELLULOSE MIXTURES

1. Introduction

1.1 The Bergmann Junk test and the methyl violet paper test are used to determine whether nitrocellulose mixtures are considered to be stable for transport.

1.2 The methyl violet paper test is a qualitative test and determines the stability of a nitrocellulose mixture by examining the colour change of reagent paper over a period of time.

1.3 The Bergmann-Junk test is a quantitative stability test applicable to all types of nitrocellulose mixtures (NC). The test measures the quantity of NO gas per g NC given off by nitrocellulose heated for two hours at 132 °C determined by titration with alkali. The expression "NO gas" comprises all types of NO-gas formed during the heating for 2 hours at 132 °C. The Bergmann Junk test method allows a reliable and reproducible quantitative assessment of chemical stability. Thus this test is the preferred method.

2. Bergmann-Junk test

2.1 Introduction

The Bergmann-Junk test is a quantitative stability test applicable to all types of nitrocellulose (NC). The test measures the quantity of NO gas per g of NC given off by 1 (one) or 2 (two) gram(s) of nitrocellulose heated for two hours at 132 °C ± 1 °C *(Plasticised NC: 3 (three) grams are heated for 1 hour)* as determined by titration with alkali.

2.2 Apparatus and materials

2.2.1 Analytical balance, precision 10 mg or better.

2.2.2 Bergman-Junk tube made of clear glass, approximately 17.5 mm inner diameter, 19.5 mm, outer diameter, and 270 mm to 350 mm long fitted with a condensing chamber. Several different types of suitable condensing chambers are commercially available. (for examples see figures A10.1 and A10.2).

2.2.3 Stability bath: Oil or suitable fluid bath or metal block capable of maintaining the temperature of the stability tubes at 132 °C ± 1 °C or better. The temperature of the bath

should be monitored with a calibrated thermometer or thermocouple (precision 0.1 ºC) which is located in one of the test wells.

2.2.4 The following apparatus is required:

- 10 cm^3 semi-automatic pipette or equivalent.
- 250 cm^3 conical flash with wide neck.
- 50 cm^3 test tube.
- Titration burette 10 ml to 25 ml; or automated potentiometric titration apparatus with pH-electrode and calibrated class A burette

2.2.5 Sodium hydroxide (NaOH) solution 0.01 mol/l, specification 0.009998 to 0.01002 mol/l for manual titration with a standard burette, or 0.1 mol/l for the titration with an automated potentiometric titration apparatus with pH-electrode and calibrated class A burette, with factor determined to obtain the exact molarity of the sodium hydroxide solution.

2.2.6 Suitable pH indicator e.g. methyl orange, methyl red, methyl red/methylene blue or R8 B3 coloured indicating fluid (Tacchiro). Solution composed of 1 % alcohol mixed with 8 g of methyl red and 3 g of purple methyl (if manual titration is used).

2.2.7 Fully deionized or distilled water with a conductivity < 1 µS/cm (micro Siemens /cm).

2.3 Procedure

2.3.1 Weigh 1 (one) or 2 (two) gram(s) of dry NC to an accuracy of 0.01 g. *(Weigh 3 (three) grams of plasticised NC to an accuracy of 0.01 g)*. The moisture content of the sample must be below 1 % after the drying process and at the time, when it is introduced in the tube. (Drying conditions must be chosen, which avoid a decomposition of the NC, e.g. 50 °C in a vacuum oven) With the help of a funnel introduce this into the tube which must be dry and clean. Wipe the ground section thoroughly and adjust the condensing chamber making sure that the above is well greased with silicone grease; it may also not be greased.

2.3.2 Measure out 15 ml to 50 ml of distilled water, depending on the condenser type, in a test tube and pour into the bulbs of the condenser. Ensure that no water enters the stability tube.

2.3.3 Make sure that the stability bath has reached a temperature of 132 °C ± 1 °C and then insert each tube into one of the apertures in the bath. The depth of immersion of the tube will vary depending on the type of stability bath used but must be between 110 mm and 220 mm. Make a note of the time at which the experiment begins.

2.3.4 Maintain the tubes at a temperature of 132 °C ± 1 °C for two hours unless pronounced fuming is observed. If fuming occurs, the test shall be stopped immediately and the duration of the heating period noted.

2.3.5 After two hours at 132 °C *(1 hour for plasticised NC)* remove the tube from the bath, place it in its stand and allow to cool behind a safety screen. During this time some water may be drawn into the lower tube. After 30 min cooling transfer the contents of the condensing chamber into the lower tube and rinse the condensing chamber with distilled water.

2.3.6 Transfer the contents of the lower tube into the conical flask and rinse with distilled water. The total amount of liquid should not be more than 175 ml.

2.3.7 Titrate with c_{NaOH} = 0.01 mol/l sodium hydroxide solution until the color of the indicator changes.

2.3.8 *Calculations*

$$\mathbf{2\ NaOH + 2\ NO + ½\ O_2 \rightarrow 2\ NaNO_2 + H_20}$$

$$V_{NO} = \frac{c_{NaOH} \times C_{NaOH} \times V_{NO,m}}{m_{NC}} = \frac{C_{NaOH} \times 0.224}{m_{NC}} = C_{NaOH} \times 0.224$$

where:

V_{NO} = volume of the evolved nitrogen oxide in cm^3/g nitrocellulose

c_{NaOH} = concentration of sodium hydroxide solution = 0.01 mol/l

C_{NaOH} = consumption of sodium hydroxide solution in ml.

$V_{NO,m}$ = molar volume of NO gas = 22.4 l/mol

m_{NC} = mass of nitrocellulose in g

If a sodium hydroxide solution with c_{NaOH} = concentration of sodium hydroxide solution = 0.1 mol/l is used, the formula is:

$$V_{NO} = C_{NaOH} \times 2.24$$

The formula is based on the assumption that nitrogen oxide evolves as NO and that NO is an ideal gas; according on the ideal gas law, 1 mol of gas occupies a volume of 22.4 *l*.

The total absence of acidity in the water is verified by a mock test; otherwise the value determined by the mock test is subtracted.

Also aliquot portions of the water containing the NO gas may be used, resulting in different factors in the formula.

2.4 Test criteria and method of assessing results

2.4.1 The tested substance is classified as stable, if the quantity of NO gas given off is not more than 2.5 ml NO gas per g of NC.

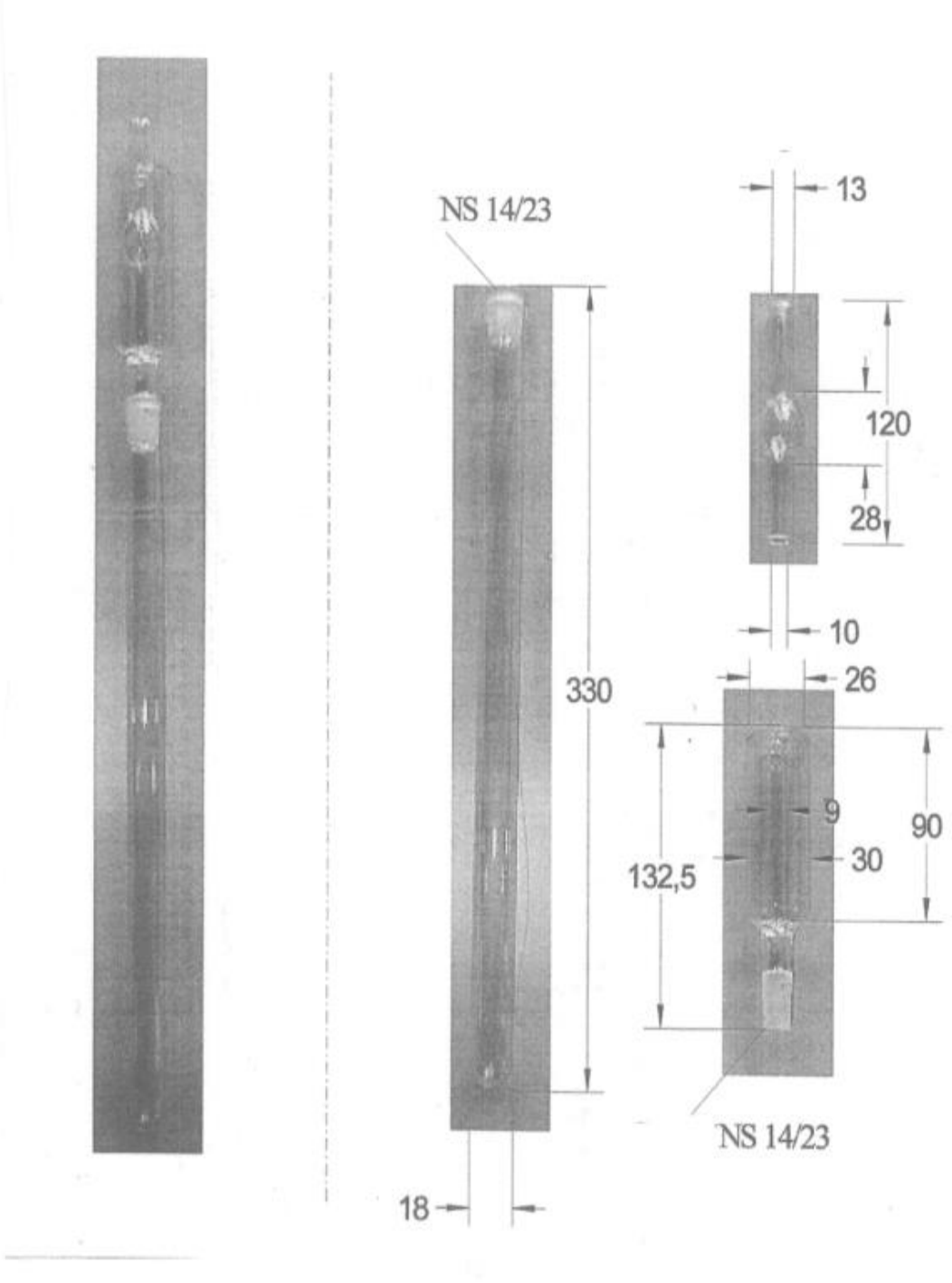

Figure A10.1: Condensing chamber for Bergmann Junk test example 1

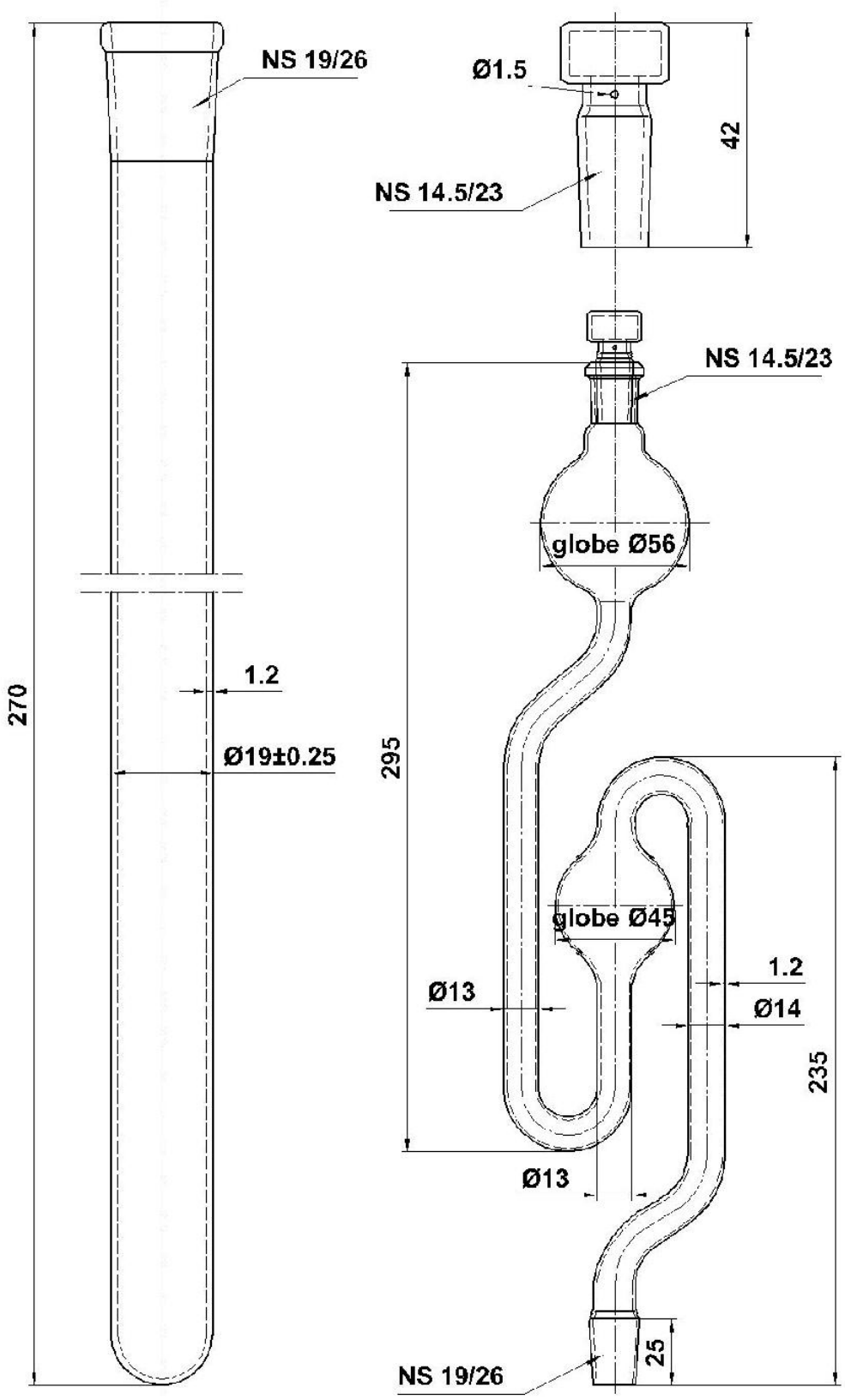

Figure A10.2: Condensing chamber for Bergmann Junk test example 2

3. Methyl violet paper test (134.5° C heat test)

3.1 Introduction

The stability of nitrocellulose is tested by examining the colour change of reagent paper over a period of time.

3.2 Apparatus and materials

3.2.1 *Apparatus*

The following equipment shall be used in the apparatus for 134.5 °C heat test (methyl violet paper test):

(a) Analytical balance, precision 0.01 g or better.

(b) Stability bath: Water-ethylene glycol bath, oil bath, or metal block oven capable of maintaining the temperature of the stability tubes at 134.5 ± 0.5 °C. Temperature of bath has to be monitored with a calibrated thermometer or thermocouple (precision 0.1 °C) which is located in a test tube filled with inert material (e.g., sand); the test tube is placed in one of the thermowells. The inner diameter of each thermowell in the apparatus shall be 19 ± 0.5 mm. Depth of immersion of the stability test tubes shall be such that no more than 6 to 7 mm of the tubes project above the bath.

(c) Stability test tubes made of clear glass, approximately 15 mm inner diameter; 18 mm outer diameter; and 290 mm length.

(d) Powder funnel; metal or conductive plastic funnel with a long tube (to prevent electrostatic charging).

(e) Corks, each containing one breather hole 4 mm in diameter (or notch of equivalent area).

3.2.2 *Materials*

3.2.2.1 A sample of dry nitrocellulose weighing 2.5 ± 0.01 g

3.2.2.2 Standardized reagent methyl violet test papers approximately 70 ± 1.0 mm long and 20 ± 0.6 mm wide (see 6.16) or methyl violet test papers prepared and tested using the following method:

3.2.2.2.1 Preparation of the indicator solution

To prepare 100 ml of indicator solution (note: if different amount of solution is required, it can be prepared while maintaining these proportions): 0.250 g of basic rosaniline (equivalent to CAS number 632-99-5) is weighed into a porcelain dish, and about 10 ml of reagent grade acetic acid is added. The dish is heated on a water bath until all excess of acid is removed. In a 100 ml graduate cylinder, 0.168 g of crystal violet (equivalent to CAS number 548-62-9) is dissolved in 30 ml of high purity water and 5.0 g (4 ml) of reagent grade glycerine is added. The content of the porcelain dish is added to the cylinder using ethanol (minimum 95% v/v) and adjusted to produce 100 ml of solution. The solution is mixed thoroughly.

3.2.2.2.2 Preparation of the methyl violet paper

Sheets of paper are prepared by cutting filter papers (equivalent to Whatman 597, typically 580 mm × 580 mm with approximately 8.5 mg/cm^2) into square parts that will fit into a low edge dish large enough to fit the cut sheet (typically cut in 4 square parts

about 290 mm × 290 mm). In a fume-hood, the methyl violet solution is poured into the low edge dish. Separately, each cut sheet of paper is dipped completely into the solution for about 30 seconds. The strip is removed from the solution and the wet sheet of paper rotated vertically until the solution stops dripping (excess alcohol will evaporate in about 1 minute). The strip is hung up overnight to dry in a room free from deleterious fumes. When dry, the strips are cut in the size of 70 ± 1.0 mm long and 20 ± 0.6 mm wide. Once certified, they are kept in tightly closed amber glass bottles or opaque plastic bottles with a maximum of 200 papers per bottle. The bottle shall be kept closed, stored at room temperature, and out of direct light at all times except to briefly extract indicator papers.

3.2.2.2.3 Certification of the methyl violet paper

A minimum of one paper from each 200 max bottle is tested for the content in water and shall be 7.5 to 15% water content by oven drying. If required, the paper may be rehydrated by keeping the paper in a controlled humidity chamber controlled at 60 to 80% relative humidity until the correct water content is obtained.

To confirm that the reactivity of the methyl violet paper is acceptable, a minimum of 1 paper from each 200 max bottle shall be tested using nitrogen dioxide gas of known concentration in air between 1500 and 2500 ppm (v/v). The gas may be obtained already diluted and certified or obtained by dilution using pure nitrogen dioxide. The gas concentration shall be known with an accuracy of ± 2.5%.

Based on the concentration of the nitrogen dioxide gas, the required flowrate for an end-point centered at 55 min is given by:

Flowrate (ml/min) = 83636 / Gas concentration in ppm (v/v) of nitrogen dioxide gas.

The flowrate shall be maintained within ± 1.5 ml/min of the calculated value during the certification of the paper. The paper is tested using the standard gas and a cylindrical flow cell of about 30 ml containing one paper (the flow cell diameter is similar to the methyl violet paper width). The end-point is obtained when the paper is completely salmon pink after 55 ± 7 min.

Only the batches that meet those 2 criteria (water content and reaction time) will be considered certified methyl violet paper. The paper shall be stored at room temperature and in the shade. The maximum shelf-life of the indicator papers in a sealed bottle is 5 years. Once the bottle is open, the shelf-life of the bottle's contents is reduced to 1 year. After 1 year, the water content of the paper shall be verified and adjusted, if necessary. The bottle containing the verified indicator papers shall be given another 1 year of shelf-life. Under no circumstances shall the indicator paper shelf-life be extended beyond 5 years after manufacture.

3.3 Procedure

3.3.1 Sample and interior of test tubes shall not be touched by bare hands. The test is to be performed in duplicate; with further repetition of test if the two results of the duplicate measurement differ by more than 5 min.

3.3.2 Two portions of 2.5 ± 0.01 g each of dry nitrocellulose sample are transferred into the stability test tubes, preferably by a powder funnel. Each tube is tapped gently in order to settle the material, and any material adhering to the sides of the tubes is brushed down. If the nitrocellulose occupies a greater length than 5 cm, it has to be compressed to that length by means of a flat headed rod. Into each tube a piece of the test paper is placed vertically so that the lower end of the paper is 25 mm above the specimen. Then a cork is placed in each tube. The two tubes are placed in the bath and maintained at a temperature of 134.5 ± 0.5 °C.

3.4 Test criteria and method of assessing results

3.4.1 In order to determine the test time, the test papers are examined after the first 20 min in the bath, and thereafter at 5 min intervals. For each examination of test papers, the tubes are lifted half way out of the bath to monitor test paper colour change, and quickly replaced.

3.4.2 When the test paper in any tube has changed colour completely to salmon pink, the test is considered complete.

3.4.3 The test time is then recorded (for example, if the violet paper is not completely changed in 25 min, but is completely changed in 30 min, the time of the test is recorded as 30 min). The test is discontinued when the salmon pink end point is attained in any of the papers.

3.4.4 The test result is considered "+" and the substance is classified as unstable if the test paper completely changes colour in less than 30 min. If the colour change exceeds 30 min the result is "-" and the substance is classified as stable.

3.5 Examples of results

Time	Result
25 min	+
35 min	–