

Methyl Violet Paper Preparation and Certification

Mario Paquet and Ian Levac

The main method of evaluation of stability of NC in North America is the Methyl Violet Paper test (MVP)

The Bergmann-Junk test (BJ) is now accepted method but is not widespread in North America.



Both tests detect the amount of NO_2 produced during heating under isothermal condition. Exceeding a certain quantity of NO_2 , the test will fail and the material will be deemed not sufficiently stable to be used.

The main negative comments regarding the test are:

- Lack of procedure for the preparation of the papers (not provided in the MIL-DTL)
- No traceability to national standards

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 respecting these proportions):

- 0.250 g of **basic rosaniline (equivalent to CAS number 632-99-5)** is weighed into a porcelain dish, and about 10ml of reagent grade acetic acid is added.
- The dish is heated on a water bath until all excess 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.



Preparation of the MVP papers

- Sheets of paper are prepared by cutting filter papers (equivalent to **Whatman 597**, typically 580mm x 580mm with a grammage of about 8.5 mg/cm²) 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 290mm by 290mm).

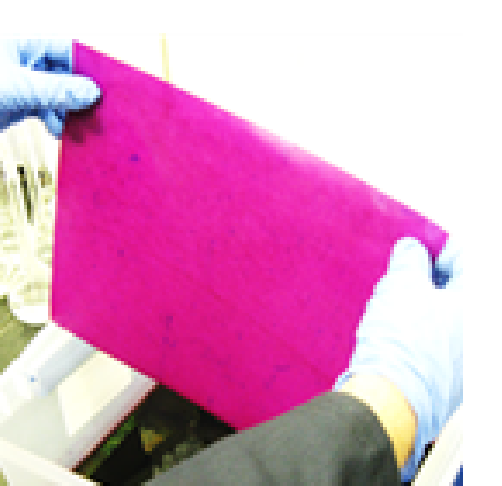
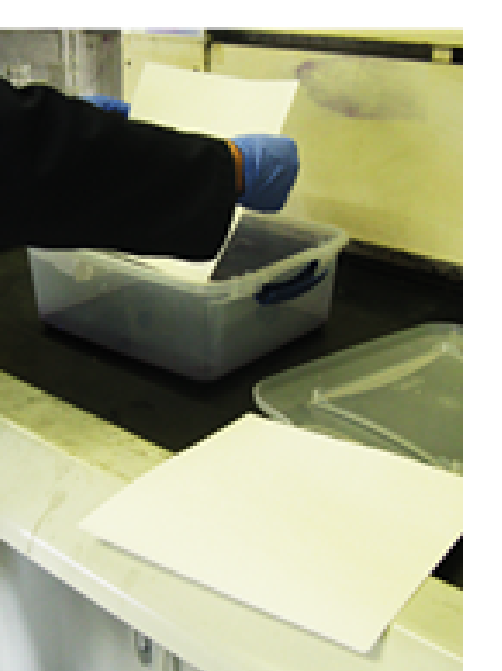
- In a fume-hood, the methyl violet solution is poured into the low edge dish.

- 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 minutes).

- 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 ± 0.6mm 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.



Calibration part 1 (moisture)

The MV indicator requires water for the reaction to proceed.

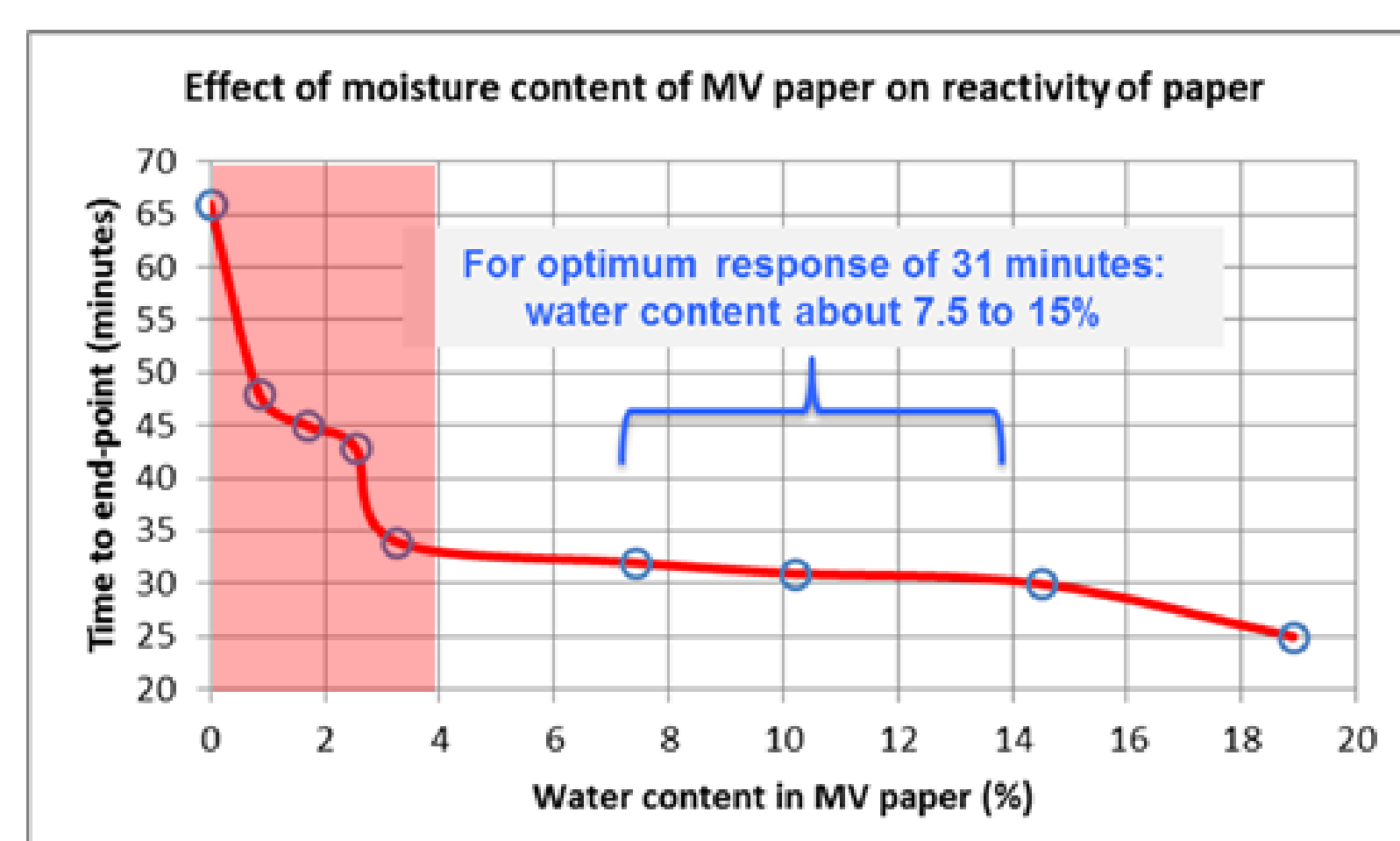
Confirmation of moisture content of MV paper:

- About one paper from each 200 is tested for the content in water by oven drying and shall be between 7.5% and 15%. If required, the paper may be rehydrated by keeping the paper in a controlled humidity chamber set between 60 to 80%RH until the right water content is obtained.

Since the papers are prepared under various %RH in labs, the time to end-point may be affected.

It is therefore recommended to test the moisture content of the MV paper in addition to the certification by standard gas.

If moisture is not provided by the MV paper, it must be acquired from the decomposing NC which takes time and delays the response of the MV paper.



Calibration part 2 (reactivity)

To confirm if the reactivity of the methyl violet paper is acceptable:

Standard gas

- tested using nitrogen dioxide gas of known concentration in air between 1500 and 2500 ppm (v/v) with an accuracy of $\pm 2.5\%$
- gas may be obtained already diluted and certified or obtained by dilution using pure nitrogen dioxide

Flow rate

- the required flowrate for an end-point centered at 55 minutes is given by:

$$\text{Flowrate (ml/min)} = 83636 / [\text{Gaz in ppm (v/v) of NO}_2]$$

- maintained within ± 1.5 ml/min of the calculated value during the certification of the paper.

Flow cell

- 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 MV paper width).

End-point

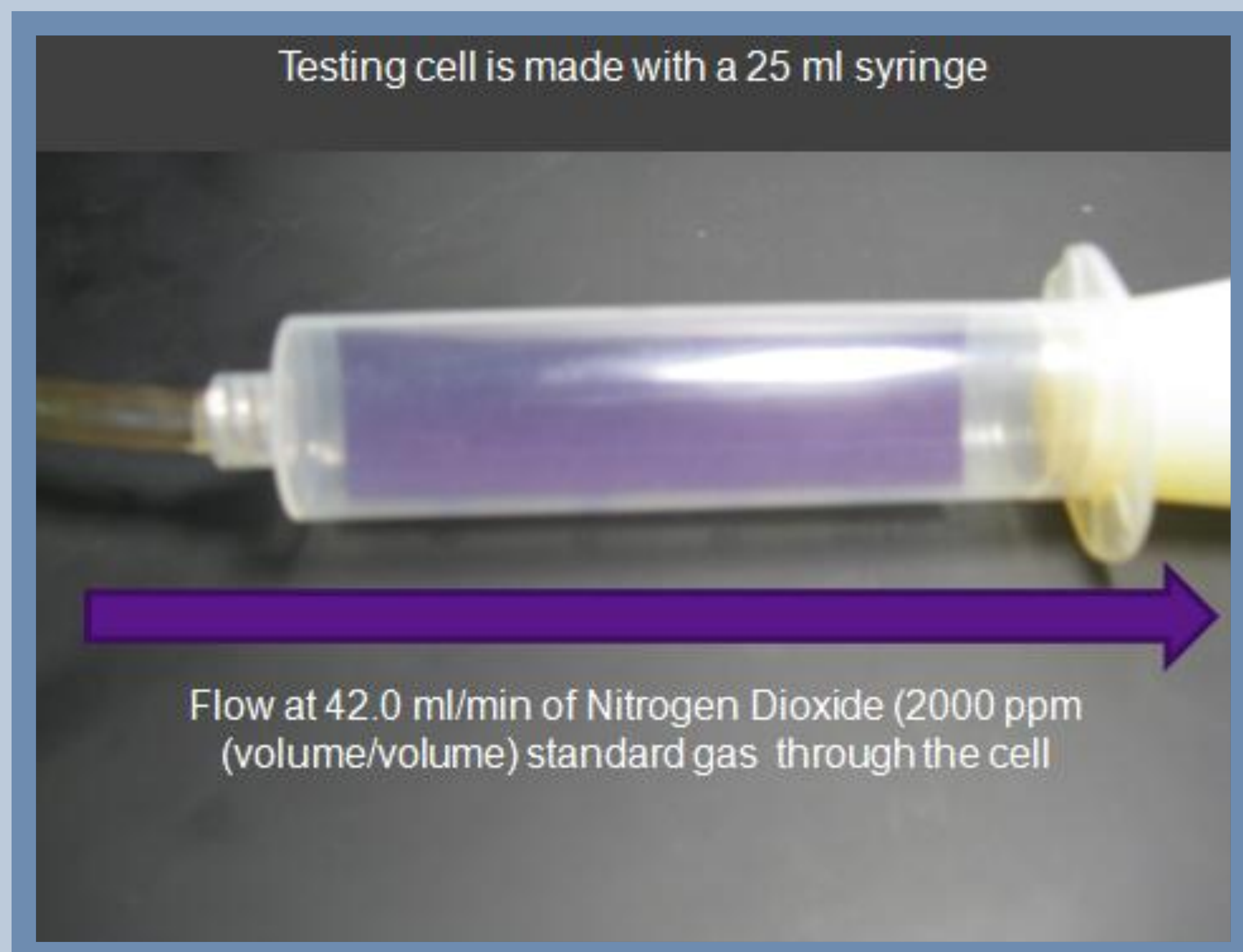
- The end-point is obtained when the paper is completely salmon pink after 55 ± 7 minutes.



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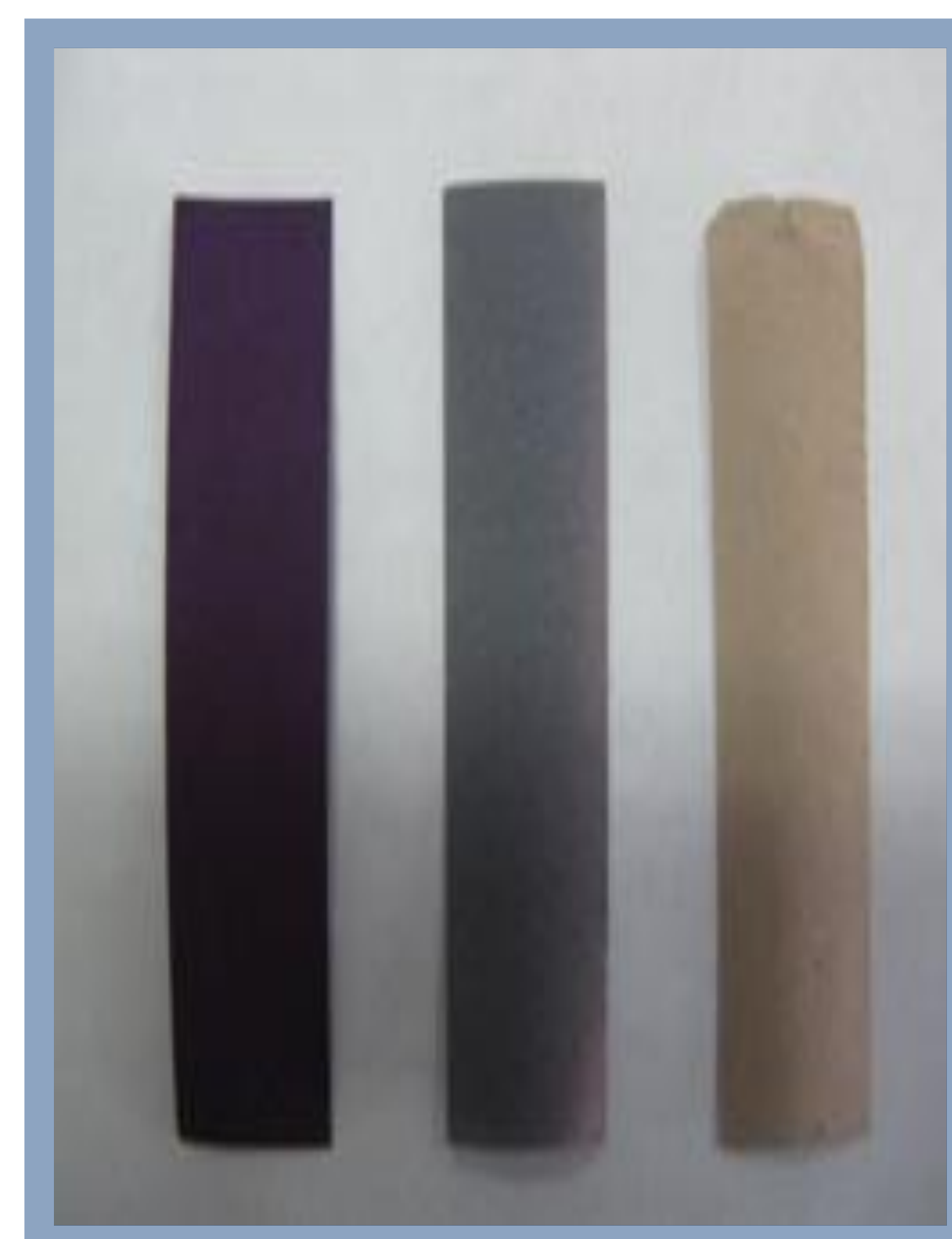
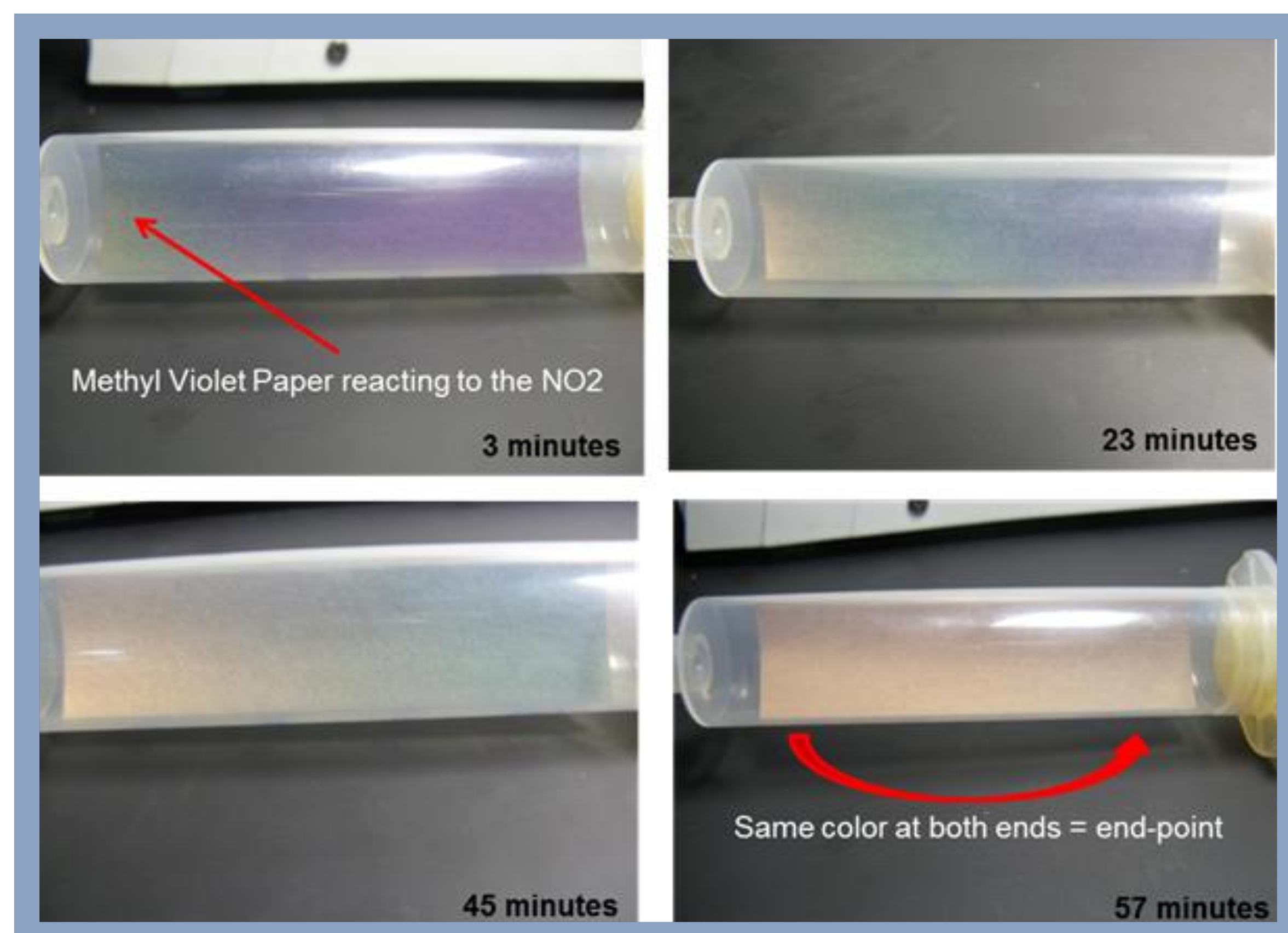
Test cell for certification of MV paper using standard NO₂ gas



A paper will react with about 4.6 ml of NO₂ near room temperature and standard pressure

Note: The use of diluted NO₂ in nitrogen will affect the colour of the end-point of the MV paper (greyish-blue instead of salmon-pink) but not the time. The end-point is more difficult to perceive. *Use of NO₂ in nitrogen is not recommended.*

Changes in color of MV paper during certification using standard NO₂ gas



The greyish-blue fades to salmon-pink when paper is left standing in air for a few hours

Zone 1:

Small variations in flowrate and/or concentration of gas
 → large variations in response times

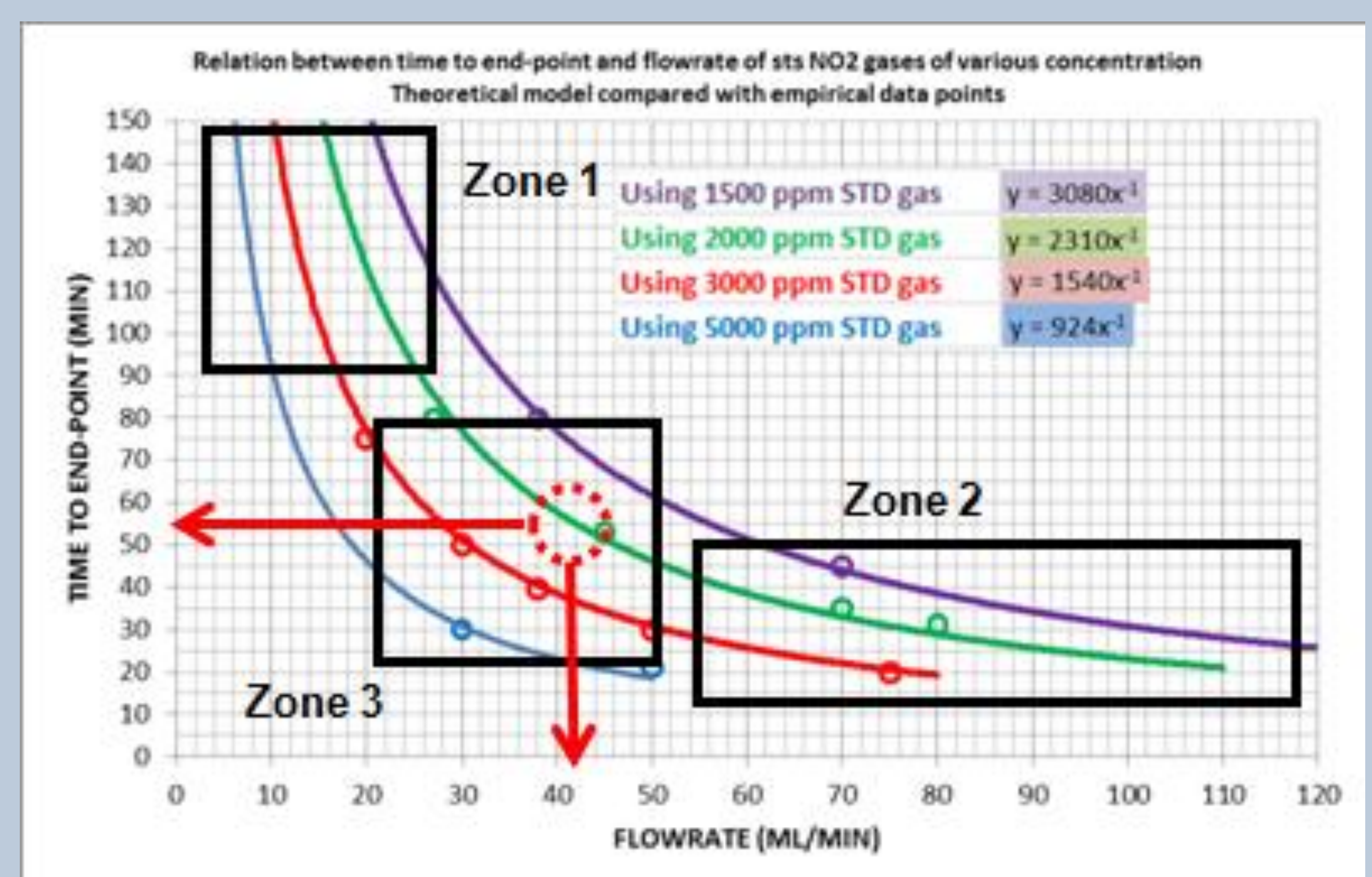
Zone 2:

Small variation in concentration of gas
 → large variations in response times

Paper response time becomes an important variable, short exposure to the gas, NO₂ will not have time to react with the indicator

Zone 3:

Finding the best compromise...



Therefore, standard conditions in zone 3 are preferred

1500-2500 ppm	56-33 ml/min	55 minutes
At 2000 ppm	42 ml/min	55 minutes