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A Program of ASTM International

ROBO Information Letter 21-01
Sequence No. 3
November 3, 2021

ASTM consensus has not been obtained on this information letter. An appropriate ASTM ballot will be issued in order to achieve such consensus.

TO: ROBO Mailing List

SUBJECT: Revisions to ROBO Test Method D7528

The ROBO Surveillance Panel has approved revisions to the D7528 ROBO Test Method. The revisions are attached. The changes add an option to use dilute nitrogen dioxide in air. These changes are effective December 1, 2021.

Justin Mills
Chair
ROBO Surveillance Panel

Frank M. Farber
Director
ASTM Test Monitoring Center

Attachments

c: https://www.astmtmc.org/ftp/docs/bench/robo/procedure_and_ils/IL21-01_ROBO.pdf

Distribution: Electronic Mail

6.7 *Air Supply System*—A gas source cCapable of delivering an uninterrupted flow of dry air into the test oil via a subsurface feed throughout the reaction time period. An in-line, desiccant-charged, drying system has been found suitable.

6.7.2 A second gas source consisting of a gas cylinder containing dilute nitrogen dioxide in air may be added along with a valve to switch between the two gas sources. The concentration of nitrogen dioxide in air needed is 1.13 % by volume. See Appendix X6 for how this is derived. The concentration as certified by the supplier must fall in the range of (1.07 to1.19) % by volume.

6.8 *Nitrogen dioxide delivery system.* There are two options for adding nitrogen dioxide. One uses liquid nitrogen dioxide and the other uses dilute nitrogen dioxide in air.

6.8.1 *Graduated Tube for Liquid Nitrogen Dioxide* (Ace Glass, Inc., part number D120677),[6,7] 12 mL capacity, with 0.1 mL graduations and having appropriate provisions for connection to the reaction vessel's subsurface gas delivery system—see Annex A10 for more details. By receiving liquid phase nitrogen dioxide from a gas bottle, this tube allows measurement of nitrogen dioxide depletion from the tube over the course of the reaction. This graduated tube only used for the liquid nitrogen dioxide option.

6.8.2 *Gas Cylinder Containing Dilute Nitrogen Dioxide in Air.* Second gas source using dilute nitrogen dioxide in dry air as defined in 6.7.2. This is only used for the dilute nitrogen dioxide option.

6.10.2 *Airflow Meter,* with a scale calibrated in mL/min for measuring subsurface airflow of 185 mL/min in 10.3.1 and 10.3.2. Two air flow meters may be used in the dilute nitrogen dioxide configuration depending on the location of the switching valve.

6.10.2.1 A digital mass flow controller may also be used to measure and control the flow rate. This type of flow controller is recommended, but not required, for the dilute nitrogen dioxide in air option.

6.15 *Precision Needle Valve,* having a low Cv for precise control of the flow of nitrogen dioxide. Examples of valves that have been found satisfactory are given in Appendix X3. This valve is used with the liquid nitrogen dioxide option in 6.8.1. It is not required for the dilute nitrogen dioxide option described in 6.8.2.

7.1 ~~*Liquid*~~ Nitrogen Dioxide ~~Produces a reddish-brown gas with a pungent odor. (**Warning**—VERY TOXIC if inhaled or ingested. Explosive if mixed with combustible material. Irritating to eyes and respiratory system. Danger of very serious irreversible health effects.).~~

7.1.1 *Liquid Nitrogen Dioxide —Used with the option in 6.8.1.* Produces a reddish-brown gas with a pungent odor. (**Warning—**VERY TOXIC if inhaled or ingested. Explosive if mixed with combustible material. Irritating to eyes and respiratory system. Danger of very serious irreversible health effects.).

7.1.2 *Dilute Nitrogen Dioxide in Air —Used with the option in 6.7.2.* (**Warning** - Compared to liquid nitrogen dioxide, the exposure risk is greatly reduced, but not negligible.)

Insert new section 9.3.1.3 (below) and renumber current 9.3.1.3 as 9.3.1.4

9.3.1.3 The same nitrogen dioxide delivery configuration must be used to re-verify the calibration status and then continued to be used for subsequent certified runs.

10.5.3 *Charging Nitrogen Dioxide*~~—Transfer 2.0 mL+/- 0.1 mL of liquid nitrogen dioxide (see Section 8 and warning in 7.1) into the graduated tube. See Appendix X2 for examples of how the transfer may be made.~~

10.5.3.1 *Liquid nitrogen dioxide option only.* Transfer 2.0 mL ± 0.1 mL of liquid nitrogen dioxide (see Section 8 and warning in 7.1) into the graduated tube. See Appendix X2 for examples of how the transfer may be made.

10.5.3.2 *Dilute nitrogen dioxide option only.* The amount of nitrogen dioxide introduced can be calculated. An equivalent to

2.0 mL ± 0.1 mL of liquid nitrogen dioxide is required. See Appendix X.6 for example calculation.

10.6.6 Start the nitrogen dioxide flow. ~~Immediately after the previous steps, adjust the nitrogen dioxide precision needle valve to allow introduction of nitrogen dioxide in a controlled and gradual manner into the inlet flow stream. Ensure that the nitrogen dioxide is completely depleted from the tube and introduced into the reactor within 12 h 6 1 h.~~

Revise and renumber current 10.6.6 (below) as 10.6.6.1

10.6.6.1 For the liquid nitrogen dioxide option, ~~I~~immediately after the previous steps, adjust the nitrogen dioxide precision needle valve to allow introduction of nitrogen dioxide in a controlled and gradual manner into the inlet flow stream. Ensure that the nitrogen dioxide is completely depleted from the tube and introduced into the reactor within 12 h ± 1 h.

Revise and renumber current 10.6.6.1 (below) as 10.6.6.2

10.6.6.2 Because changes to the nitrogen dioxide flow rate can affect precision, it is imperative that nitrogen dioxide be introduced to the reactor in a controlled and gradual manner. Using a flow rate target of 0.167 mL/h, monitor nitrogen dioxide depletion closely in the first 2 h to 4 h, the aim being to introduce 0.5 mL during that time period. Introduce the remaining 1.5 mL at a similar flow rate, ensuring that the total of 2.0 mL is delivered between 11 h and 13 h. A run is invalid if the flow of nitrogen dioxide exceeds 0.5 mL during any 1 h period.

10.6.6.3 For the dilute nitrogen dioxide option, switch to dilute nitrogen dioxide for 12.0 hours. A run is invalid if the flow of dilute nitrogen dioxide in air deviates from the required 185 ml/min by more than 6 % during at any of the observations. At least 6 observations during the first 6 hours of the air flow must be made and recorded with the last observation being made at about 6 hours. The air flow may be adjusted at these times. If all of the readings before adjustments are within 5 % of 185 ml/min, then no more observations are required. If the air flow deviates by more than 4% during the first 6 hours, then six more observations are required from hours 6-12. After 12.0 hours, switch back to the dry-air supply for the remaining of the test.

10.6.6.4 If any deviations from 185 ml/min of more than 2 ml/min were observed (or calculated at the 12 hr switching time), then calculate and report the time-averaged flow rate. See Appendix X7 for examples.

13.3.6. The option used to add nitrogen dioxide. Liquid nitrogen dioxide or dilute nitrogen dioxide.

13.3.6.1 If the dilute nitrogen dioxide option was used, calculate and report the total amount of nitrogen dioxide delivered to the reactor to the nearest one-tenth of a ml.

14.3 *Dilute nitrogen dioxide option effect on precision and bias* — The precision and bias in sections 14.1 – 14.2 were determined with the original liquid nitrogen dioxide option. The ASTM ROBO Surveillance Panel approved the use of the dilute nitrogen dioxide option based on the limited data obtained from which no effect on precision or bias was detected.[2]

X6 DILUTE NITROGEN DIOXIDE IN AIR OPTION INFORMATION

X6.1 Calculation of the necessary concentration of nitrogen dioxide in air flowing at 185 ml/min for 12.0 hours to give the same amount of nitrogen dioxide and at that same rate as in the option that uses 2.0 ml of liquid nitrogen dioxide. Typical properties used:

Density of liquid nitrogen dioxide: 1.448 g/ml at 68F (20C)
Density of air = 1.2041×10^{-3} g/ml at 68F (20C)
Vapor density of nitrogen dioxide: 1.58 relative to air = $1.58 * 1.2041 * 10^{-3}$ g/ml = 1.903×10^{-3} g/ml

X6.1.1 Volume of nitrogen dioxide in vapor phase = mass of nitrogen dioxide / vapor density of nitrogen dioxide
= (2.0 ml NO_2 x 1.448 g/ml)/(0.001903 g/ml) = 1521 ml NO_2 in vapor phase

X6.1.2 Concentration by volume = volume of NO_2 / (volume of air + volume of NO_2)
= 100% x (1521 ml NO_2) / ((185 ml/min x 12.0 hr x 60 min/hr) + 1521 ml) = 1.129 % by volume (or rounding to 1.13 % NO_2 in air).

X6.2 Or, the amount of nitrogen dioxide added can be calculated by:

= 2.0 ml x (concentration by volume NO_2 % / 1.13 %) x (time hr / 12 hr) x (time-averaged flow rate ml/min / 185 ml/min)

X7 TIME-AVERAGED SUBSURFACE AIR FLOW RATE

X7.1 If the flow rate never varies outside the range of 185 ± 2 ml/min or if a mass flow meter is used, then the deviations are deemed not significant and the time-averaged value can be estimated as either 185 or whatever value within this range the operator estimates based on the observations.

X7.2 To calculate the time-averaged flow rate, assume any changes observed in flow rate are linear between observations. If the switch from dilute nitrogen dioxide in air to dry-air is done automatically with no opportunity to observe the flow rate at that time, then calculate a flow rate by assuming that the average change in flow rate (change/hour) continues for the period between the last observation and the switching time.

X7.3 An example spreadsheet for calculating dilute nitrogen dioxide flow rate and total nitrogen dioxide delivered is available on the TMC's[2] website.