Designation: D 7558 – 09

Standard Test Method for Colorimetric/Spectrophotometric Procedure to Quantify Extractable Chemical Dialkyldithiocarbamate, Thiuram, and Mercaptobenzothiazole Accelerators in Natural Rubber Latex and Nitrile Gloves[1]

This standard is issued under the fixed designation D 7558; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This test method is designed to quantify the amount of total extractable accelerators in natural rubber latex (NRL) and nitrile gloves. Three common classes of rubber accelerators, the mercaptobenzothiazole (MBT), thiuram, and thiocarbamate type compounds can be detected and quantified by this method. If the specific rubber accelerator(s) present in the glove material is not known, quantification is based on zinc dibutyldithiocarbamate (ZDBC) equivalents. This method will not detect all potential rubber accelerators, including mercaptobenzothiazole disulfide, dimorpholine, thioureas and diphenyl diamine.

1.2 For the purpose of this test method, the range of chemical accelerator measurement is based on the limit of detection (LOD) established in the performing laboratory.

1.3 This test method should be performed by experienced analysts or under the supervision of those experienced in the use of spectroscopy and working with organic solvents.

1.4 This test method has not been validated for measurement of long chain dithiocarbamates or accelerators from other rubber products, such as lubricated condoms (**1**).[2] Although this assay has been reported in the literature for the evaluation of accelerator levels in condoms, further validation for accelerator measurement from other rubber products is required by the testing laboratory prior to use.

1.5 This test method is not designed to evaluate the potential of rubber materials to induce or elicit Type IV skin sensitization reactions (for Type IV skin sensitization reactions see Test Method D 6355). Total extractable accelerator content does not reflect bioavailablity of individual accelerators that are detected and measured by this method. This test method should be used to test and measure the total residual chemical accelerator level in NRL and nitrile gloves under controlled laboratory conditions, and should not be used to describe, appraise, or assess the hazard or risk of these materials or products under actual in-use conditions.

1.6 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.7 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*[3]

D 3577 Specification for Rubber Surgical Gloves

D 3578 Specification for Rubber Examination Gloves

D 4483 Practice for Evaluating Precision for Test Method Standards in the Rubber and Carbon Black Manufacturing Industries

D 6355 Test Method for Human Repeat Insult Patch Testing of Medical Gloves

3. Terminology

3.1 Total thiol vulcanization accelerator includes MBT, zinc dithiocarbamates (ZDTCs) and thiurams.

3.2 *Definitions:*

3.2.1 *limit of detection (LOD), n*—the lowest accelerator concentration that can be measured and be statistically different from the blank.

3.2.1.1 *Discussion*—The LOD is expressed as 3.3 × standard error of the y-intercept of the standard plot regression line divided by the slope of the calibration line.

3.2.2 *limit of quantitation (LOQ), n*—the lowest accelerator concentration that can be measured to produce quantitatively meaningful results with acceptable precision and accuracy.

[1] This test method is under the jurisdiction of ASTM Committee D11 on Rubber and is the direct responsibility of Subcommittee D11.40 on Consumer Rubber Products.

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[2] The boldface numbers in parentheses refer to a list of references at the end of this standard.

[3] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

3.2.2.1 *Discussion*—The LOQ is expressed as 10 × standard error of the y-intercept of the standard plot regression line divided by the slope of the calibration line.

3.2.3 *linear range*, *n*—area of a graph of absorbance versus concentration that approximates a straight line.

3.2.4 *spectrophotometric measurement*, *n*—the unit of measure of the instrument that is proportional to absorbance.

3.2.5 *standard solution*, *n*—the standard analyte to which the test (unknown) sample being measured is compared.

4. Summary of Test Method

4.1 The rubber material is cut into small pieces and approximately 1 g is placed into the extraction vessel. Acetonitrile is added to give a final volume/weight of 10 mL acetonitrile per gram of rubber. The extraction vessel is securely capped, placed onto a rotator and extracted at approximately 200 rpm for a minimum of 2 h at room temperature (25 ± 5°C). The acetonitrile extract is recovered and centrifuged in a sealed centrifuge tube at 500 × g for 20 min at room temperature to remove any residual particulate matter. The acetonitrile extract supernatant fluid is transferred to a clean container and capped. Zinc dibutyldithiocarbamate (ZDBC) standards at 500 to 31.25 µg/mL in acetonitrile and a blank are prepared. Cobalt chloride (10 µL, 420 mmol/L) aqueous solution is added to 1 mL aliquots of each sample extract and standard. Each individual solution is thoroughly mixed and then incubated for 120 min at 50 ± 5°C. The extracts and standards are cooled to room temperature for approximately 15 min after the 50°C incubation. A 100 µL aliquot of each is diluted with 1.9 mL of acetonitrile. All are mixed thoroughly and absorbance of each sample, blank and standard is measured at 320 nm on a UV spectrophotometer. Concentration of residual accelerator is obtained by extrapolation from the standard plot. Depending upon the number of samples tested, this test method takes about 5 h to complete.

5. Significance and Use

5.1 Dialkyldithiocarbamates (DTCs), benzothiazoles, and thiurams are often used as vulcanization accelerators in NRL products. Zinc DTC accelerators are added either directly or are formed in situ during the vulcanization process via reaction between a thiuram(s) and zinc oxide. DTCs, benzothiazoles, and thiurams have been detected in leachates from medical devices made of rubber such as gloves. Studies have shown these chemicals can cause allergic contact dermatitis. A simple selective method to monitor rubber accelerator levels in rubber extracts would be useful for quality control, product screening and research.

5.2 This colorimetric assay measures dialkyldithiocarbamates, including zinc dialkyldithiocarbamates (ZDTC), mercaptobenzothiazole (MBT) and thiurams as a total thiol vulcanization accelerator level in rubber products. A UV spectrophotometer with detection at 320 nm is used to measure the ZDTC, mercaptobenzothiazole and thiurams. Sample extracts diluted at 1:20 prior to measurement on the spectrophotometer is usually sufficient to quantify the residual accelerator level from most commercially available rubber gloves; however, sample dilution can be adjusted (from neat extract to > 1:20 dilution) based on analytical needs. Thiurams and ZDTCs complex with cobalt turning the extract to a concentration-dependent shade of green. ZDTCs reacts quickly while thiurams react very slowly (requiring a heat catalyst). Mercaptobenzothiazole does not complex to Co(III), however, it absorbs strongly at 320 nm. It can be distinguished from both ZDTCs and thiurams by its strong absorbance at 320 nm without the cobalt dependent visible green color. Cobalt complexed thiurams and ZDTCs, but not MBT, also have and absorbance at 370 nm (**2**).

6. Interferences

6.1 Suspended solids such as powder or cotton flock can interfere with spectrophotometric measurements and care must be taken not to resuspend particulate following centrifugation. Some extracts may require additional steps to remove particulate such as higher speed centrifugation or possibly filtration, dependent on the physical nature of the particulate material. The rubber accelerators, mercaptobenzothiazole disulfide, dimorpholine, thioureas, diphenyl diamine, and diphenylguanidine are not detected by this assay and do not interfere with measurement of MBT or ZDTCs. Potential exists for interference from leached dyes or other additives that absorb at 320 nm; however, this has not been reported.

7. Apparatus

7.1 *Polypropylene or Glass Extraction Tubes*, with screw top lids (50 mL, conical bottom).

7.2 *Polypropylene Cryotubes*, (3.6 mL), with screw tops for cobalt reaction of extracts and standards and for the final 1/20 dilution prior to UV analyses.

7.3 *Parafilm*.

7.4 *Adjustable Positive Displacement Pipettes*, (5 to 10 mL, 1 mL and 250 µL).

7.5 *Laboratory Shaker*, (200 rpm).

7.6 *Laboratory Vortex Mixer*.

7.7 *Water or Dry Bath*, capable of maintaining the temperature at 50°C.

7.8 *Centrifuge*, (capable up to 500 × g).

7.9 *UV Spectrophotometer*.

8. Materials

8.1 *Chemical Accelerator Standard*—Use specific thiuram, zinc dithiocarbamate or mercaptobenzothiazole if specific species in the specimen is known.[4]

NOTE 1—Storage problems for zinc diethyldithiocarbamate have been reported and care needs to be taken if this is to be used as the reference standard.

8.2 $CoCl_2$—Cobalt (II) Chloride hexahydrate.

8.3 *Water*, (distilled/deionized (dH_2O)).

8.4 *Acetonitrile*, (HPLC grade).

[4] If species is not known use zinc dibutyldithiocarbamate (ZDBC), the sole source of supply of which known to the committee at this time is ChemService, Inc., 660 Tower Lane, PO Box 599, West Chester, PA 19381 (cat. No. Ou-76 (M.W. = 474.2)). If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,[1] which you may attend.