Designation: E3025 – 16

Standard Guide for
Tiered Approach to Detection and Characterization of Silver Nanomaterials in Textiles[1]

This standard is issued under the fixed designation E3025; 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 guide covers the use of a tiered approach for detection and characterization of silver nanomaterials in consumer textile products made of any combination of natural or manufactured fibers.

1.2 This guide covers, but is not limited to, fabrics and parts (for example, thread, batting) used during the manufacture of textiles and production of consumer textile products that may contain silver-based nanomaterials. It does not apply to analysis of silver nanomaterials in non-consumer textile product matrices nor does it cover thin film silver coatings with only one dimension in the nanoscale.

1.3 This guide is intended to serve as a resource for manufacturers, producers, analysts, policymakers, regulators, and others with an interest in textiles.

1.4 This guide is presented in the specific context of measurement of silver nanomaterials; however, the structured approach described herein is applicable to other nanomaterials used to treat consumer textile products.

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

1.6 *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:*[2]

D123 Terminology Relating to Textiles

D6413 Test Method for Flame Resistance of Textiles (Vertical Test)

2.2 *AATCC Standards:*[3]

AATCC 135 Dimensional Changes of Fabrics after Home Laundering

2.3 *ISO Standards:*[4]

ISO 10136-1 Glass and Glassware—Analysis of Extract Solutions—Part 1: Determination of Silicon Dioxide by Molecular Absorption Spectrometry

ISO 16140 Microbiology of Food and Animal Feeding Stuffs—Protocol for the Validation of Alternative Methods

ISO/IEC Guide 99 International Vocabulary of Metrology—Basic and General Concepts and Associated Terms (VIM)

ISO/DTR 18196 Nanotechnologies—Measurement Technique Matrix for the Characterization of Nano-Objects

ISO/TS 80004-1 Nanotechnologies—Vocabulary—Part 1: Core Terms

2.4 *U.S. Code of Federal Regulations:*[5]

16 CFR Parts 1615 and 1616 Standards for the Flammability of Children's Sleepwear

3. Terminology

3.1 *Definitions*—For additional definitions related to textiles, see Terminology D123; for additional definitions related to nanotechnology, see ISO/TS 80004-1; and for additional definitions related to measurements, see ISO/IEC Guide 99.

3.1.1 *analyte, n*—element or constituent to be determined. **ISO 10136-1**

3.1.2 *consumer textile product, n*—textile product intended to satisfy human wants and needs. **D123**

3.1.3 *manufactured fiber, n*—class name for various genera of filament, tow, or staple produced from fiber-forming substances that may be: (*1*) polymers synthesized from chemical

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[2] 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] Available from American Association of Textile Chemists and Colorists (AATCC), P.O. Box 12215, Research Triangle Park, NC 27709-2215, http://www.aatcc.org.

[4] Available from American National Standards Institute (ANSI), 25 W. 43rd St., 4th Floor, New York, NY 10036, http://www.ansi.org.

[5] Available from U.S. Government Printing Office, Superintendent of Documents, 732 N. Capitol St., NW, Washington, DC 20401-0001, http://www.access.gpo.gov.

compound, (*2*) modified or transformed natural polymers, or (*3*) glass. **D123**

3.1.4 *measurand, n*—quantity intended to be measured or a quantity that is being determined by measurement. **ISO/IEC Guide 99**

3.1.5 *nanomaterial, n*—material with any external dimension in the nanoscale or having internal structure or surface structure in the nanoscale. **ISO/TS 80004-1**

3.1.6 *nanoscale, n*—range from approximately 1 to 100 nm. **ISO/TS 80004-1**

3.1.7 *natural fiber, n*—class name for various genera of fibers (including filaments) of (*1*) animal, (*2*) mineral, or (*3*) vegetable origin. **D123**

3.1.8 *qualitative method, n*—method of analysis whose response is either the presence or absence of the analyte detected either directly or indirectly in a certain amount of sample. **ISO 16140**

3.1.9 *quantitative method, n*—method of analysis whose response is the amount of the analyte measured either directly (enumeration in a mass or a volume), or indirectly (colour absorbance, impedance, etc.) in a certain amount of sample. **ISO 16140**

3.1.10 *textile, n*—general term for fibers, yarn intermediates, yarns, fabrics, and products that retain all the strength, flexibility, and other typical properties of the original fibers or filaments. **D123**

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *characterization, n*—identification and quantification of one or more relevant physical or chemical property values of the analyte.

3.2.2 *detection, n*—qualitative recognition of the presence of the target analyte in a sample.

3.2.3 *silver, n*—element with atomic number 47 that can be in the form of ions, metallic or zero-valent (Ag^0), alloys, oxide, or salt compounds, or combination thereof.

4. Significance and Use

4.1 Natural and manufactured textiles fibers can be treated with chemicals to provide enhanced antimicrobial (fungi, bacteria, viruses) properties. In some cases, silver nanomaterials may be used to treat textile fibers (**1**).[6] Silver nanomaterials are used to treat a wide array of consumer textile products, including but not limited to various clothing; primary garments (shirts, pants), outer wear (gloves, jackets), inner wear (socks and underwear), children's clothing (sleepwear); children's plush toys; bath towels and bedding (sheets, pillows); and medical devices (wound dressings) (**2**).

4.2 There are many different chemical and physical forms of silver that are used to treat textiles and an overview of this topic is provided in Appendix X1.

4.3 Several applicable techniques for detection and characterization of silver are listed and described in Appendix X2 so that users of this guide may understand the suitability of a particular technique for their specific textile and silver measurement need.

4.4 There are many different reasons to assay for silver nanomaterials in a textile at any point in a product's life cycle. For example, a producer may want to verify that a textile meets their internal quality control specifications or a regulator may want to understand the properties of silver nanomaterials used to make a consumer textile product under their jurisdiction or what quantity of silver nanomaterial is potentially available for release from the treated textile during a washing process. Regardless of the specific reason, a structured approach to detect and characterize silver nanomaterials present in a textile will facilitate measurements and data comparison.

4.5 The approach presented in this guide (see Fig. 1) consists of three sequential tiers: obtain a textile sample (Section 7), detection of a silver nanomaterial (Section 8), and characterization of a silver nanomaterial (Section 9). If no forms of silver are detected in a textile sample using appropriate (fit for purpose) analytical techniques then testing can be terminated. If silver is detected but present in a non-nanoscale form, the textile can be treated as a bulk material; however, there still may be potential for release of silver ions that transform into nanoscale silver-containing particles. If silver is detected in nanoscale form it can be concluded that it is a silver nanomaterial in the textile sample and subsequent measurements can be made to characterize its chemical and physical properties.

4.6 Numerous techniques are available for the detection and characterization of silver nanomaterials in textiles which can cause confusion for those interested in developing an analytical strategy and selecting appropriate techniques. Some techniques are applicable only to certain chemical forms of silver and all have limited ranges of applicability with respect to a measurand. No single technique is suitable to both detect and fully characterize silver nanomaterials in textiles. As such, this guide is an attempt to describe and define a tiered approach that uses commercially available measurement techniques so that manufacturers, producers, analysts, policymakers, regulators, and others may make informed and appropriate choices in assaying silver nanomaterials in textiles within a standardized framework. The user is cautioned that this guide does not purport to address all conceivable textile analysis scenarios and may not be appropriate for all situations. In these instances, professional judgment is necessary.

4.7 This guide is intended to provide a tiered approach to be used to determine an efficacious and efficient procedure for detecting and characterizing silver in textiles to make a determination as to whether any silver nanomaterial is present. This tiered approach may also be used to determine whether a reported measurand for silver nanomaterials in a textile was obtained in an appropriate and meaningful way.

4.8 Measurement of many material properties is method dependent. As such, caution is required when comparing data for the same measurand from instruments that operate on different physical or chemical principles or with different measurement ranges.

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

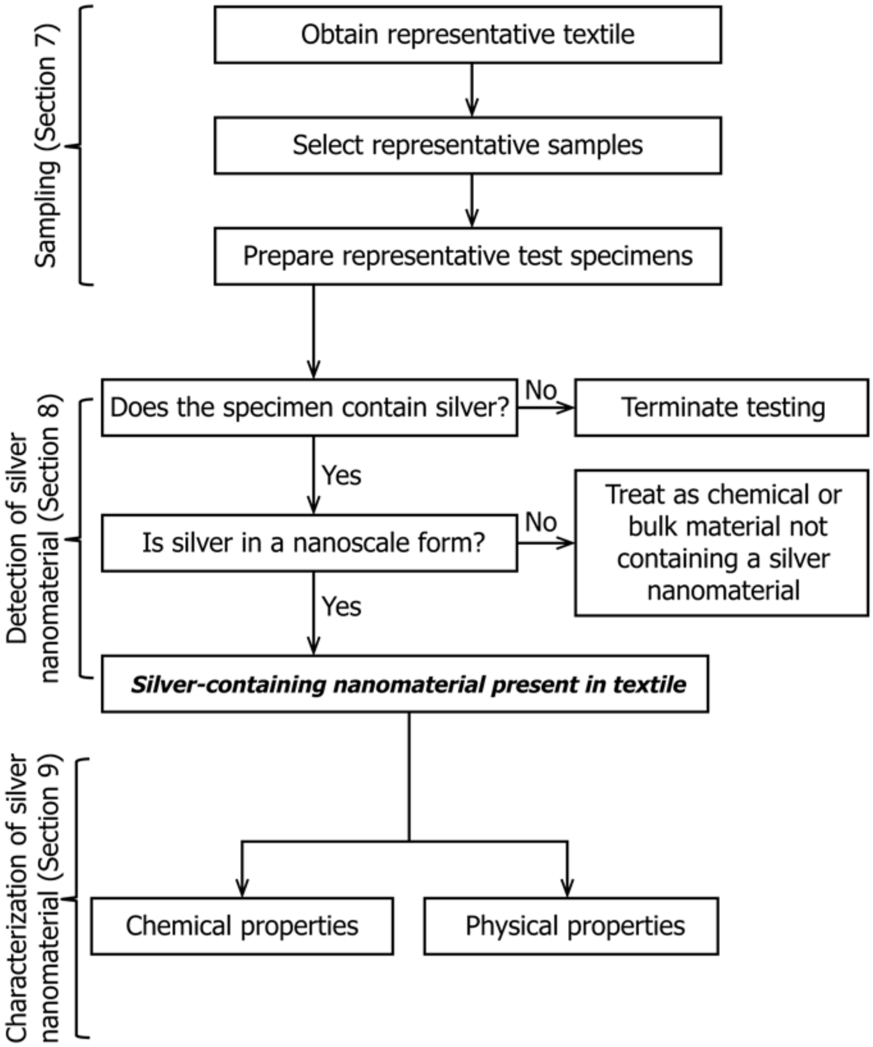

FIG. 1 Tiered Approach for Determining if a Textile Contains a Silver Nanomaterial

4.9 The amount of silver in a textile has a tendency to decrease over time as silver metal and silver compounds can react with oxygen and other oxidation-reduction (redox) active agents present in the environment to form soluble ionic species. These ions are released by contact with moisture (for example, from ambient humidity, washing, body sweat, rain, or other sources). As described in Appendix X1, release of ionic silver species may occur at varying rates that depend on many characteristics, including chemical nature, surface area, crystallinity, and shape of the silver source as well as where the silver is applied to the textile (on the fiber surface, in the volume of the fiber, and so forth) and in what form the silver is applied to the textile (discrete particles, with carriers, and so forth). Hence, if silver is detected in a textile and its properties characterized, the result may only be indicative of that moment in the article's life cycle and great care is necessary in drawing temporal inferences from the results.

4.10 Textile acquisition, storage, handling, and preparation can also affect reported results.

5. Reagents

5.1 *Purity of Reagents*—Reagent-grade chemicals should be used in all tests. Unless otherwise indicated, it is intended that all reagents should conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society where such specifications are available.[7] Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

6. Tiered Approach

6.1 A tiered approach is a cost-effective strategy that uses progressively more specialized instrumentation to elucidate

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[7] *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the United States *Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

whether a silver nanomaterial is present in a textile and to measure its chemical and physical properties (see Fig. 1) (**3**).

6.2 Initially, a robust bulk analytical technique is used for qualitative detection of silver regardless of form (for example, Ag^0, AgCl) or size in a textile specimen.

6.3 If silver is detected in a textile specimen, additional measurements are made to determine if it is a silver nanomaterial.

6.4 Results from these measurements should provide the user with sufficient data to decide whether a silver nanomaterial is present in a textile.

6.5 If a silver nanomaterial is present in a textile, complementary and confirmatory techniques are used to characterize its chemical and physical properties.

7. Sampling

7.1 The first step of the tiered approach is to obtain a textile that is representative of the life-cycle stage for which measurement is needed using an appropriate sampling strategy (Fig. 1). Depending upon the user's specific measurement need, a textile may be obtained from the fabric-processing stage, finishing treatment stage, finished lot or end-product stage, or any other part of its life cycle. Considerations should also be given to obtain threads, decorative trim, and other components used to assemble a textile product. The sampling plan should be fit for its intended purpose and just good enough to deliver the required or specified variation for a heterogeneous material.

7.2 Once obtained, the desired number of representative samples need to be cut from the textile using an appropriate sampling strategy that captures the areas that contain silver nanomaterials. In the absence of knowledge about the distribution of silver in a textile, a conservative approach is to assume that any silver is distributed heterogeneously until proven otherwise. If the distribution of silver in a textile is known or assumed to be heterogeneous, the user should cut samples to capture this variability using some form of random sampling that describes the measurement distribution for their specific needs. A power calculation can be used to estimate the number of samples needed to achieve a desired level of precision.

7.2.1 The locations and dimensions of samples will also depend upon the size of the specific textile article; they may be cut from a portion of a large textile (for example, bed linens, pants) or it may be the entire textile for smaller articles (for example, finger or palm of a glove).

7.3 Finally, a desired number of test specimens are cut from each representative sample. If the distribution of silver in a textile sample is known or could be heterogeneous, test specimens should be cut from the samples to capture variability. The locations and dimensions of the test specimens will depend upon the specific sample.

NOTE 1—If the distribution of silver in a textile is known to be homogeneous, representative samples (and test specimens) can be cut from any location of the article, for example, from different locations across the width of a textile.

7.4 Examples of textile, sample, and test specimen collection practices for processes that span an article's life cycle are described in Test Method D6413, AATCC 135, and 16 CFR Parts 1615 and 1616.

7.5 Textiles, samples, and test specimens should be stored in a manner that will not alter the properties of any silver present and potentially bias the intended data collection objectives. Storage considerations include, but are not limited to, temperature, relative humidity, exposure to direct sunlight, and atmosphere.

8. Detection

8.1 Qualitative determination of silver within prepared test specimens can include indirect or direct measurement methods or both. Test specimens should be initially measured using a robust bulk analytical technique, preferably with capability for high throughput detection of silver (see Appendix X2 for examples). In this step, silver measurements do not need to be made using a quantitative method and do not need to differentiate between forms.

8.1.1 If no silver is detected, a more sensitive bulk analytical technique [lower method detection limit (MDL)] should be used to determine if silver is present in a test specimen. This confirmatory measurement does not need to be quantitative.

8.1.2 If measurement for silver is below the MDL of the more sensitive technique, the result serves as confirmation that silver is not present in a measureable quantity in the textile specimen. Therefore, all testing should be terminated at this step.

8.2 If silver is qualitatively detected above the MDL of either the initial or confirmatory bulk analytical technique, additional measurements are needed to elucidate the form of silver in the textile specimen. This step is necessary because, as noted in Appendix X1, textiles may be treated with silver materials in forms that range from silver salt nanoparticles to micrometre scale silver fibers, and the aforementioned elemental detection step is not designed to discriminate between physical forms. As such, by itself, detection of silver is not sufficient to determine whether a textile contains a silver nanomaterial.

8.3 Available techniques to determine whether a silver nanomaterial is present in a textile include ultraviolet-visible (UV-vis) absorbance spectroscopy, electron microscopy, scanning probe microscopy, and single particle inductively coupled plasma-mass spectroscopy (SP-ICP-MS). A summary of these techniques is provided in Appendix X2.

8.4 UV-vis absorbance spectroscopy measures the absorbance signal due to the surface plasmon resonance (SPR) of metallic silver nanomaterials. The absorbance wavelength will shift as particle size increases or if particles form agglomerates. This technique is applicable if the metallic silver nanomaterial is on or near the surface of the textile fiber and provides only an indirect indication of the presence of metallic silver nanomaterials. Hence, the absence of an UV-Vis absorbance spectroscopy signal cannot be taken as evidence that a silver nanomaterial is not present in a textile because the metallic silver nanomaterial may be encased in the volume of the fibers or the silver may be present in the form of silver ions or in the form of silver alloy, oxide, or salt nanomaterials which do not exhibit SPR.

8.5 SP-ICP-MS is essentially a firmware and software based modification of the traditional ICP-MS analytical technique. In SP-ICP-MS, the observed steady state signal represents the ionic, dissolved contribution form of the element (that is, Ag) and discrete peaks or ion plumes represent individual nanoparticles. Software algorithms are used to identify and separate the two signals and report the ionic, dissolved element concentration as well as the nanoparticle size, size distribution, and concentration of particles. The intensity of each discrete peak is proportional to the number of ions detected at the instrument detector as well as to the mass of the particle and this information is used to convert the observed mass to particle size and particle size distribution. At present, only liquid samples may be analyzed by commercially available SP-ICP-MS instruments and as such textiles must first be prepared for analysis. For determination of silver nanomaterials in the textiles, either the nanomaterials need to be extracted from the textile or the textile fibers needs to be dissolved in an appropriate solvent that will not negatively affect the nanomaterial. It is also necessary to prepare dilute liquid suspensions of the nanomaterials to prevent coincidence or the detection of multiple particles simultaneously which results is positive bias of particle size.

8.6 Among the techniques described in Appendix X2, electron microscopy and scanning probe microscopy provide direct visual confirmation of the form and dimensions of particles, which makes these techniques especially useful for evaluating whether particles are present in nanoscale form. Employing electron and scanning probe microscopy for visualization and measurement of any nanoscale particles present in a textile specimen are of particular use since they can be augmented with chemical detection techniques, such as energy dispersive X-ray analysis or selected area electron diffraction to determine if they actually contain silver. This chemical measurement does not need to be quantitative.

8.7 The type of treatment (ion exchanger, salt, metal) used on a textile is an important consideration when using electron microscopy to determine the form and dimensions of silver present in the detection step of the tiered approach.

8.7.1 With silver ion exchangers, silver is applied to a textile in the form of discrete silver ions (Ag^+) that are distributed within carrier particles such as porous zeolite or glass. Zeolites are alumina silicates that tend to have size in the micrometre scale (**4**). As such, electron microscopy augmented with a chemical detection techniques is useful to verify if visible particles in a textile specimen produced using an ion exchanger treatment are carriers and not a silver nanomaterial.

8.7.2 Textile treatments with silver salts can include both neat silver salt particles (AgCl, Ag_2SO_4, and so forth) and microcomposites comprised of salt particles attached to titanium dioxide as a carrier material. Hence, depending upon the treatment application, the form of particles visible in textiles produced using silver salts could be neat silver-containing salt particles or silver-containing particles attached to the carrier material. The latter would require discrimination using chemical detection techniques to differentiate silver-containing particles from carrier material.

8.7.3 Treatment of textiles with elemental or zero-valent silver (Ag^0) involves a variety of physical forms that potentially makes determination of silver particle dimensions complex. Manufacturers may use silver in the physical form of filaments (threads) or a coating on polymer fibers, apply particles to the surface of textiles or fibers, incorporate particles into the volume of the fibers themselves, or attach microcomposites comprised of silver metal particles adhered to or embedded in an inert carrier material. Hence, inspection of the physical form of particles in textiles produced using silver metal could yield dimensions of silver metal particles in or on fibers or require discrimination of silver metal particles from the carrier material using chemical detection techniques to probe the composition of particles.

8.7.3.1 Determination of the size of elemental silver particles by electron microscopy may be challenging for textiles in which particles were incorporated into the volume of the fibers during manufacturing. In this situation an appropriate solvent may be used to dissolve the fibers without dissolution of silver particles and would minimize sample preparation artifacts. The exact solvent will depend on the specific type of natural or manufactured fiber. For example, spandex fibers can be dissolved using N,N-dimethylformamide, N,N-dimethylacetamide, or by heat-treating and washing with acetone or ethanol (**5**).

8.8 If the silver in the textile is not in a nanoscale form (for example, ions in a carrier or particulate with all dimensions >100 nm), the textile can be treated as a chemical or bulk material that does not contain silver nanomaterial; however, there still may be potential for release of silver ions that transform into nanoscale silver-containing particles.

8.9 If a portion of the silver-containing particles have any external dimension in the nanoscale or have internal structure or surface structure in the nanoscale, then it can be concluded that silver nanomaterial is present in the textile. This conclusion only addresses the dimensional aspect of the silver and does not address any potential or actual nanoscopic-specific chemical or physical properties that might exist (see Section 9).

8.10 It is possible that silver-containing particles can be present as both a nanomaterial and a non-nanoscale form in a textile.

9. Characterization

9.1 If a silver nanomaterial is present in a textile, additional measurements can be made to characterize its chemical or physical properties. A summary of several applicable techniques for characterization of the chemical and physical properties of silver nanomaterials is provided in Appendix X2.

9.2 There are numerous chemical properties of nanomaterials that may be of interest for characterization and the specific properties will depend on the user's measurement goals. Among the most commonly cited chemical properties for characterization of nanomaterials are bulk elemental composition, surface composition, speciation, and crystal structure (**6**).

9.2.1 It is important to recognize that there currently is no chemical analytical technique that can quantitatively differentiate between amounts (in the bulk or on the surface), species, or crystal structures of nanoscale and non-nanoscale silver in a textile (only if all silver in a sample is in the form of a nanomaterial would a measurement correspond only to nanoscale silver). As such, multiple complementary and confirmatory techniques are necessary to characterize the chemical properties of silver in textiles.

9.2.1.1 Quantitative determination of the bulk (total) amount of silver present in a textile specimen can be assayed using solution-based techniques that require acid-assisted digestion of the textile matrix and silver before analysis or certain direct measurement techniques such as X-ray fluorescence spectroscopy. Depending upon the treatment application (see X1.1) and the life-cycle stage, silver ions or particles, or both, may be present in a textile. In these scenarios, separation of ions from particles as part of sample preparation is necessary to avoid bias in the determination of silver nanomaterial mass. Additionally, if the silver is present in a distribution of particle sizes ranging from nanoscale to non-nanoscale then the nanoscale fraction must be measured separately to avoid overstating the silver nanomaterial mass. Acceptable quantitative measurements are characterized by traceability (accuracy based on instrument calibration with known reference material standards or based on first principles), high precision, and knowledge of the uncertainty relating to the result. Appropriate SI units for results are mass of silver (kg)/mass of textile (kg).

9.2.1.2 Surface composition refers to the elemental composition of the surface of a textile sample. Surface analysis is generally method specific. For instance, some surface-sensitive techniques may have deeper penetration than other techniques, so the surface composition shall be given in the context of the method and with an estimate of the surface thickness contributing to the analysis. Appropriate SI units for surface composition are mass of silver (kg)/area of textile (m^2).

9.2.1.3 Speciation refers to the chemical form of silver (for example, zero-valent silver, ionic silver, salt, and so forth). Several techniques are available for determining speciation of silver. These range from commercially available microscopy based techniques of individual or ensembles of particles such as transmission electron microscopy with electron energy loss spectroscopy or with selected area electron diffraction to highly specialized techniques for determining average speciation distributions, such as X-ray absorption near edge structure spectroscopy, which requires access to a synchrotron to make measurements. Speciation is a qualitative property so no unit can be assigned.

9.2.1.4 Crystal structure may include the measurands crystallite size (size of single crystals, typically microscopic or nanoscopic in dimensions and forming polycrystalline materials when held together by then defective or amorphous layers), crystallinity (relative proportion of crystalline and amorphous material in a sample), crystal form, and physico-chemical structure (amorphous, paracrystalline, or crystalline). Crystallite size has SI units of metre, crystallinity has non-dimensional units, and crystal form and physico-chemical structure are qualitative properties, so no units can be assigned.

9.3 There are numerous physical properties of nanomaterials that may be of interest for characterization, and the specific properties will depend on the user's measurement goals. Among the most commonly cited physical properties for characterization of nanomaterials are size, size distribution, shape, and spatial distribution (**6**). In the context of textiles, spatial distribution refers to where the nanomaterial is located in the fibers (on the surface, in the fiber volume, and so forth).

9.3.1 Direct visualization by electron microscopy or scanning probe microscopy is the most suitable technique for determination of particle physical properties though some indirect techniques such as X-ray scattering and spectroscopy may also provide useful information (as described in Section 8).

9.3.1.1 In the detection phase of the tiered approach, electron microscopy (or another analytical technique) is used to identify the presence of silver nanomaterials in textile specimens. In the characterization phase, the same or other techniques or both are used for quantitative determination of the size of silver nanomaterials in a textile specimen. As noted previously, quantitative measurements are characterized by traceability (accuracy based on instrument calibration using known reference material standards such as a grating), high precision, and knowledge of the uncertainty relating to the result. The appropriate SI unit for particle size is the metre. For example, analysis of the size distribution may be limited by the number of particles counted and the ability to differentiate between particles that are touching or overlaid. As a result, size distributions may provide only semi-quantitative or qualitative information about the breadth or general shape of the distribution. The appropriate SI unit for particle size distribution will depend on the type of distribution measured (volume, mass, and so forth).

9.3.1.2 Silver nanomaterials may possess a wide variety of shapes such as spheroidal particles, wires, rods, and agglomerates or aggregates that may be in the form of neat particles or attached to microcomposite carrier material. Measurements that help to define shape such as length and width of a rod have SI units of metre (aspect ratio, length/width, is non-dimensional), though shape descriptors such as "spheroidal" are a qualitative property, so no SI unit can be assigned.

9.3.1.3 It may be desirable to describe the spatial distribution of silver in a textile. As noted previously, silver nanomaterials may be incorporated into the volume of fibers during manufacturing. In this situation, some investigators have used thermal treatment in excess of 500°C to combust the fibers and evaluated the particles remaining in the textile ash using electron microscopy; however, use of heat may cause sintering of neighboring particles to form larger particles. As such, the obtained particle size information may not be representative of the silver particles *in situ* (**7**). Alternatively, dissolution of the fiber using an organic solvent or other means (**5**) may be used to remove the textile matrix prior to inspection by microscopy.

10. Report

10.1 At a minimum, report the following information:

10.1.1 Date and methods by which textile was acquired;

10.1.2 Description of textile (manufacturer, model, fiber type and composition, weight);

10.1.3 Textile storage conditions (light/dark, temperature, humidity);

10.1.4 Textile storage duration from acquisition to measurement;

10.1.5 Methods by which representative samples and test specimens were acquired;

10.1.6 Description of test specimens (dimensions and mass);

10.1.7 Analytical preparation (including manufacturer, expiration date, lot number, and purity of reagents) and handling procedures;

10.1.8 Date(s) of measurements;

10.1.9 Description of instrument(s)—make and model;

10.1.10 Date of last calibration of an instrument (using a reference material standard or other means) and the result (for quantitative measurements) or calibration due date;

10.1.11 Number of replicate measurements, appropriate expression of summary statistics (where applicable), and accompanying measurement units (where applicable) for results; and

10.1.12 Description, results and discussion of analytical findings.

11. Keywords

11.1 analytical methods; characterization; detection; nanomaterials; silver; textiles; tiered approach

APPENDIXES

(Nonmandatory Information)

X1. CONTEXT FOR MEASURING SILVER IN TEXTILES

X1.1 Many Different Chemical and Physical Forms of Silver Are Used in Textile Treatments

X1.1.1 Silver can be applied or incorporated into textiles in a variety of chemical forms. When testing textiles for the presence or concentration of silver in a textile, the test method and interpretation of results shall take into account the particular chemical form of the silver material applied to the textile or fibers where known. Where the chemical form is unknown, testing and interpretation shall take into account that any silver detected may be in any of several different chemical forms, each generally falling into one of three broad classes of treatments widely used in textile manufacturing.

X1.1.1.1 *Silver Ion Exchangers Class*—These are textile treatments comprised of silver zirconium phosphates, silver zeolites, and silver impregnated glass. In these treatments, silver is held in the form of discrete silver ions (Ag^+) distributed within the matrix carrier (that is, zeolite, glass, and so forth). Silver ions (Ag^+) are released from the textile (or the carrier attached to the textile) when the ions come into contact with moisture from body sweat, washing, ambient humidity, and rain or water in the immediate environment.[8]

X1.1.1.2 *Silver Salts Class*—These are textile treatments comprised of both neat silver chloride (AgCl) particles and microcomposites comprised of AgCl particles attached to titanium dioxide as a carrier material. Silver chloride is relatively insoluble in water; however, like silver textile treatments in the ion exchangers class, silver ions (Ag^+) are released from the AgCl particles when they come into contact with water in various forms as described previously. In principle, commercial silver textile treatments also may be made with other insoluble or slightly soluble, particulate silver compounds, including silver carbonate (Ag_2CO_3), silver citrate ($C_6H_5Ag_3O_7$), silver phosphate (Ag_3PO_4), silver iodide (AgI), silver bromide (AgBr), silver oxide (Ag_2O), and silver sulfate (Ag_2SO_4).

X1.1.1.3 *Silver Metal Class*—These are textile treatments comprised of silver metal, that is, not ions or compounds, but in the form of elemental or zero-valent silver (Ag^0). The silver metal may be present in a variety of physical forms, including silver metal filaments (threads), polymer fibers electrolytically coated with a silver layer, or silver metal particles (colloidal silver) applied to the surface of textiles or fibers or incorporated into the volume of the fibers themselves. The textile treatment also may be in the form of microcomposites comprised of silver metal particles attached to or embedded in an inert carrier material. Like the other silver textile treatment classes, silver ions (Ag^+) are released from silver metal particles when they come into contact with water in various forms.

X1.2 All Silver Materials Provide Antimicrobial Function Via The Release Of Silver Ions

X1.2.1 It is generally thought that silver textile treatments (whether of the silver ion-exchange, silver salt, or silver metal class) provide antimicrobial properties to their associated textiles by releasing silver ions (Ag^+) (**1**). It is the ionic form of silver that provides an antimicrobial effect. Several factors influence the release rate of silver ions from silver nanomaterials, including chemical nature and surface area of the silver source, as well as the crystallinity and shape of the material (**8**).

X1.3 Silver Material Particle Size Characterization is Inherently Ambiguous Unless the Measurand is Specified

X1.3.1 Given the variety of chemical and physical forms of commercial silver textile treatments in measuring and reporting the size or size distribution of the silver component of the treatment to avoid ambiguity and improper comparisons, it is

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[8] The presence of ligands is not required for dissolution of any form of silver (**8**) though silver species may be formed when released ions come into contact with ligands (for example, thiols in sweat).

necessary to decide and then report whether the aspect being measured is the size of the silver metal nanomaterial, silver ion, or silver compound particle in the treatment or the size of any entity to which these forms of silver may be attached (for example, a microcomposite particle).

X1.3.1.1 For example, silver chloride microcomposites are composed of an AgCl nanomaterial attached as a separate phase component to a (typically) larger titanium dioxide carrier particle (typically larger than 1 µm). When "activated" by moisture, the AgCl nanomaterial releases silver ions. Any statement about the "size" of the silver in this kind of textile treatment shall identify the particular chemical form of the silver being measured and whether the silver is in the form of (*1*) the micrometre scale composite particle (AgCl and TiO_2), (*2*) the silver chloride nanomaterial, (*3*) the sub-nanometre scale silver ion, or (*4*) nanomaterials formed by reduction of silver ions during drying of a textile.

X1.3.2 Any of these may represent a valid approach depending on the purpose of the study.

X1.4 Commercial Textile Treatment Particles Typically Exist In a Range of Particle Sizes

X1.4.1 "Silver" textile treatment particles of the same chemical and physical form typically will be present in a sample distributed over a large range of particle sizes.

X1.4.1.1 For example, both silver chloride particles (silver salts class) and metallic silver particles (silver metal class) in textile treatments will be present in a range of particle sizes, both less than and greater than 100 nm at their smallest dimension.

X1.4.2 The absence of particle size distribution information as part of any particle size characterization may be misunderstood to imply a monodisperse distribution and lead to erroneous particle-size-related conclusions. Particle size characterizations should include distribution information (and the method used to measure the distribution) to avoid ambiguity and erroneous particle-size-related conclusions.

X1.4.3 Particle size distributions may be calculated and presented either as a function of particle number or particle mass fraction. The choice of which measure to use depends on the purpose of the underlying study.

X1.5 All Sources of Silver Ions Spontaneously Generate Silver Nanoscale Particles

X1.5.1 Silver nanomaterials have been shown to form directly from silver ions (that is, aggregate, nucleate, assemble) (**9**), notably in the presence of ultraviolet light or organic matter (**10**). Because any form of silver metal or silver salt or both will release silver ions when exposed to water in various forms (whether textile "bulk" silver thread; nanoscale silver chloride particle; or silver jewelry, coins, wire, or utensils), each of these types of products has the potential to be a source of any silver nanoparticles found in a sample.

X1.5.2 Under environmental conditions, silver ion and silver metal particles may be in a constant transient cycle through ion-particle transformations.

X1.6 In Textile Samples, It May Not Be Possible to Determine Whether Any Particular Detected Silver Particle Is Man-Made ("Engineered") or Spontaneously Formed

X1.6.1 While analytical methods may detect nanoscale (or larger) particles that contain silver in association with a textile, it may not be possible to know by such measures whether the nanomaterial was originally applied to the textile in that form or whether it formed from the transformation of silver ions released by a macroscale or nanoscale silver source (that is, whether it was engineered or otherwise intentionally added).

X1.6.2 Characterization of "silver"-treated textiles by researchers should include consideration and discussion of this phenomenon as it relates to any conclusions, including consideration of the test parameters (for example, reducing or complex media conditions) that may influence the formation of particles. The proper choice of test method design will depend on the purpose of the underlying study.

X1.7 Amount and Form of "Silver" in a Silver-Treated Textile Is Not Static

X1.7.1 "Silver" textile treatments by design are gradually depleted of silver content by the conversion of silver metal and silver compounds to ionic form and the release of those ions to the treated article or the environment (for example, via laundry wastewater). Bulk "silver" content of the whole article also may be lost by normal physical attrition of the underlying fabric of the article during use or washing (taking any associated "silver" treatment substances with it).

X1.7.2 Characterization of "silver"-treated textiles by researchers should include a description of the age and use state (for example, number of uses or washes) of the sample(s). Study designs should include discussion of the selected age and use state (or preparation) of the textile sample with reference to the aforementioned depletion and conversion phenomena. The proper choice of sample or sample preparation will depend on the purpose of the underlying study.

X1.8 Silver Particles Are Readily and Strongly Passivated by Certain Chemical Species

X1.8.1 Research shows that silver is readily passivated by sulfur-containing species, chlorides, phosphates, and numerous other environmentally ubiquitous substances in sewer pipes and in wastewater treatment plants through oxidation, dissolution, and complexation (**11 and 12**). Many of these same chemical species are present in biological fluids that may contact textiles such as body sweat (that is, sulfur-containing amino acids such as cysteine as well as chloride and so forth) or are present in wash water (for example, phosphates and so forth). As such, it is important to understand that silver nanomaterials in a textile could change their form or size or both if brought into contact with these species (for example, during storage, contact with sweat, wash water, or other forms of water). Hence, it shall be recognized that if a textile is characterized in its neat (unexposed) state and again after exposure to these chemical species and the results compared, there may be transformations and other changes in the physicochemical properties of the silver nanomaterials.

X2. ANALYTICAL TECHNIQUES FOR DETECTION AND CHARACTERIZATION OF SILVER IN TEXTILES

X2.1 Applicable Analytical Techniques for Silver in Textiles

X2.1.1 A wide variety of analytical techniques exist for the detection and characterization of silver in textiles (in all its forms). Each technique provides advantages and limitations, and no single technique encompasses the complete range of measurands, accuracy, and precision required for complete analysis of all samples. Additionally, it is recognized that the cost and availability of instruments varies widely ranging from affordable bench-top models to synchrotron-based systems at large user facilities. This, in part, influenced the development of this guide and is in part responsible for the hierarchical approach chosen.

X2.1.2 Therefore, this section aims to provide a comprehensive, but not all-inclusive, listing of relevant techniques along with their principal measurands and key application details. It does not attempt to prioritize according to cost, ease of use, or general availability. Technical information on specific techniques can be found in the literature as noted in X2.1.3 and is beyond the scope of this guide. Additionally, international standards exist for the general (and nanoscopic) application of many techniques listed in X2.1.3; availability of such standards is growing and the reader is encouraged to consult national and international standards bodies for applicable documents.

X2.1.3 The principles of operation as well as some of the advantages and disadvantages of many of the techniques presented in Table X2.1 are discussed in numerous review articles including those by Powers et al. (**13**), Hassellöv et al. (**14**), Tiede et al. (**15**), Baer et al. (**16**), and U.S. EPA (**17**). Additionally, ISO is developing ISO/DTR 18196 that provides a description of many of the techniques listed in this guide along with information on the measurand, advantages and limitations of the technique, and existing relevant international standards for the technique.

TABLE X2.1 Summary of Analytical Techniques for Detection and Characterization of Silver in Textiles

Technique[A]	Measurand(s)	Comment
AES	Elemental composition	Particle population surface chemistry to depth of approximately 5 nm; depth profiling possible
AFM	Size, shape	Three-dimensional images of individual particles over approximate size range 5 nm to micrometres
EDX[B]	Elemental composition	Individual particle analysis; can do elemental mapping
EELS[C]	Elemental and bonding states	Individual particle analysis but need thin specimens; can do elemental mapping
GF-AAS	Mass concentration	Sensitive analysis of total silver content over wide concentration range
ICP-AES	Mass concentration	Sensitive analysis of total silver content over wide concentration range
ICP-MS	Mass concentration	Highly sensitive analysis of silver content over wide concentration range
SP-ICP-MS	Mass concentration, size	Silver nanoparticles down to approximately 10 nm can be identified and quantified as well as total silver content
PIXE-RBS	Elemental composition	Particle surface chemistry; depth profiling possible
SAED[D]	Crystal structure	Individual particle analysis
SAXS	Size, shape	Highly polydisperse particle sizes in samples may be problematic for accurate analysis
SEM[E]	Size, shape	Two-dimensional images of individual particles; samples shall be conductive or carbon coated
TEM[F]	Size, shape	Two-dimensional images of individual particles on support grid with sub-nanometre resolution
Titration	Mass concentration	Textiles shall be digested in mineral acid before analysis
UV-vis	Size, shape	Absorption at 390-420 nm infers silver nanoparticles; need integrating sphere for textiles
XPS	Elemental and bonding states	Particle population surface chemistry to depth of approximately 10 nm
XRD	Crystal properties	Particle population analysis with high limit of detection (1% to 3 % by mass)
XRF	Mass concentration	Analysis over wide concentration range though less sensitive than atomic spectroscopy

[A] AES = Auger electron spectroscopy, AFM = atomic force microscopy, EDX = energy dispersive X-ray analysis, EELS = electron energy loss spectroscopy, GF-AAS = graphite furnace atomic absorption spectroscopy, ICP-AES = inductively coupled plasma atomic emission spectroscopy, ICP-MS = inductively coupled plasma mass spectrometry, PIXE-RBS = proton-induced X-ray emission-Rutherford backscattering, SAED = selected area electron diffraction, SAXS = small-angle X-ray scattering, SEM = scanning electron microscopy, SP-ICP-MS = single particle inductively coupled plasma mass spectrometry, TEM = transmission electron microscopy, UV-vis = ultraviolet visible absorbance spectroscopy, XPS = X-ray photoelectron spectroscopy, XRD = X-ray diffraction, and XRF = X-ray fluorescence spectroscopy.

[B] In combination with TEM or SEM and their variations.

[C] In combination with TEM or STEM.

[D] In combination with TEM only.

[E] Includes variations such as environmental (ESEM), field emission (FE-SEM), low voltage (LV-SEM), and high resolution (HR-SEM).

[F] Includes variations such as dark field (DF-TEM), high resolution (HR-TEM), energy filtered (EF-TEM), and high angle annular dark field (HAADF) scanning/transmission electron microscopy (HAADF-STEM).

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