Designation: F2102 – 13

Standard Guide for Evaluating the Extent of Oxidation in Polyethylene Fabricated Forms Intended for Surgical Implants[1]

This standard is issued under the fixed designation F2102; 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 a method for the measurement of the relative extent of oxidation present in HDPE homopolymers and ultra-high-molecular-weight polyethylene (UHMWPE) intended for use in medical implants. The material is analyzed by infrared spectroscopy. The intensity (area) of the carbonyl absorptions (>C=O) centered near 1720 cm^{-1} is related to the amount of chemically bound oxygen present in the material. Other forms of chemically bound oxygen (C-O-C, C-O-O-C, C-O-H, and so forth) are not captured by this guide.

1.2 Although this guide may give the investigator a means to compare the relative extent of carbonyl oxidation present in various UHMWPE samples, it is recognized that other forms of chemically bound oxygen may be important contributors to these materials' characteristics.

1.3 The applicability of the infrared method has been demonstrated by many literature reports. This particular method, using the intensity (area) of the C-H absorption centered near 1370 cm^{-1} to normalize for the sample's thickness, has been validated by an Interlaboratory Study (ILS) conducted according to Practice E691.

1.4 The following precautionary caveat pertains only to the test method portion, Section 5, of this specification: *This standard may involve hazardous materials, operations, and equipment. 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 requirements prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method

3. Terminology

3.1 *Definitions:*

3.1.1 *bulk oxidation index (BOI)*—a sample's bulk oxidation index (BOI) is the average of the oxidation indices collected over a 500-µm section at the center of the sample.

3.1.1.1 *Discussion*—Typically, this is a plateau region with the smallest oxidation indices.

3.1.1.2 *Discussion*—For samples less than about 8 to 10 mm thick, this central region may display the sample's highest oxidation indices, depending on its state of oxidation.

3.1.2 *depth locator (DL)*—a measurement of the distance from the articular surface, or surface of interest, that a spectrum was collected and a corresponding OI calculated.

3.1.3 *oxidation index (OI)*—an oxidation index (OI) is defined as the ratio of the area of the carbonyl absorption peak(s) centered near 1720 cm^{-1} to the area of the absorption peak(s) centered near 1370 cm^{-1}, as shown in Fig. 1. Note that the peak areas are computed after subtracting out the appropriate baseline, as further discussed in Section 6.

3.1.4 *oxidation index profile*—an oxidation index profile is the graphical representation of variation of the sample's oxidation index with distance from its articular surface or the surface of interest. This is a plot of an OI versus DL. Typically, the graph will show the profile through the entire thickness of the sample.

3.1.5 *surface oxidation index (SOI)*—a sample's surface oxidation index (SOI) is the average of the oxidation indices from the sample's articular surface, or the surface of interest, to a depth of 3-mm subsurface.

4. Apparatus

4.1 *Infrared Spectrometer:*

4.1.1 A calibrated infrared spectrometer capable of recording a transmission absorption spectrum over the range of about 1200 to about 2000 cm^{-1} using about 200-µsm-thick films at a resolution of 4 cm^{-1} and an aperture of about 200 by 200 µm.

4.1.1.1 Other modes of collection (that is, percent reflection, attenuated total reflection (ATR), and so forth) and aperture and increment sizes may be used to generate the sample's

[1] This guide is under the jurisdiction of ASTM Committee F04 on Medical and Surgical Materials and Devices and is the direct responsibility of Subcommittee F04.15 on Material Test Methods.

Current edition approved Nov. 1, 2013. Published December 2013. Originally approved in 2001. Last previous edition approved in 2006 as F2102 – 06ε1. DOI: 10.1520/F2102-13.

[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.

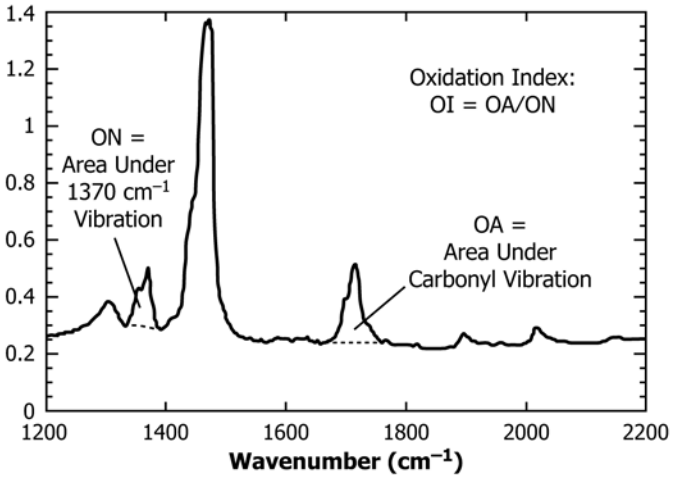

FIG. 1 Typical FTIR Spectra of Oxidized UHMWPE, Showing the Definition of an Area-Based Oxidation Index Based on Normalization Using the 1370-cm^{-1} Peak

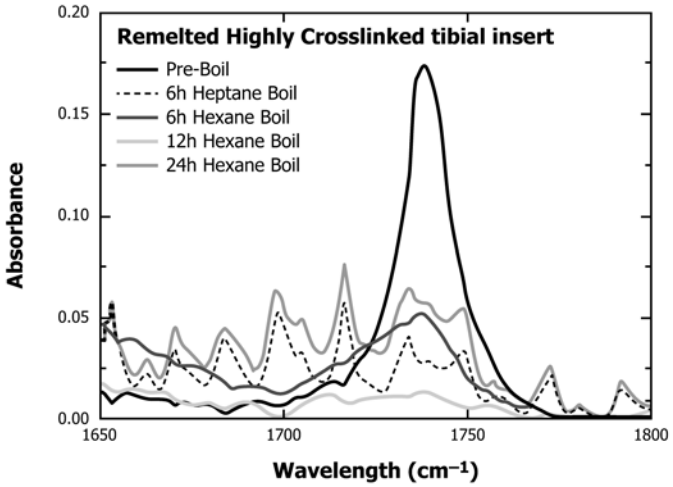

FIG. 2 FTIR Spectra Showing the Carbonyl Absorption Bands

NOTE 1—Note that both reagents effectively extracted the lipids (the lipid absorption peak is centered at approximately 1740 cm^{-1}). The tibial insert was fabricated from highly crosslinked and remelted UHMWPE followed by terminal sterilization in EtO gas (**Ref. 1**).

absorption spectrum provided they can be demonstrated to produce equivalent results. Too large an aperture can result in a loss of profile accuracy.

4.1.1.2 When a Fourier Transform Infrared (FTIR) spectrometer is used, a minimum of 32 scans shall be collected per spectrum.

4.1.1.3 The FTIR instrument and sample compartment may be purged with a moisture-free inert gas (for example, nitrogen, helium, or argon) to minimize spectral interference from these components.

4.2 *Specimen Holder*—Equipment capable of accurately positioning the sample under the orifice in increments at the scale of the aperture dimensions.

4.3 *Microtome*—Equipment capable of producing about 200-µm-thick slices (films) of a sample perpendicular to the articular surface or the surface of interest.

5. Procedure

5.1 *Preparation of the Infrared Spectrometer:*

5.1.1 Prepare the infrared spectrometer for collection of a transmission absorption spectrum from a thin film of the UHMWPE sample according to the manufacturer's recommendations and the conditions described in Section 4 above.

5.1.2 Collect the sequence of spectra per 5.2 and 5.3.

5.2 *Preparation of the Test Specimen:*

5.2.1 Using a microtome, or other appropriate device, prepare a thin slice of the sample about 200 µm thick.

5.2.2 The slice shall be taken near the center of the sample's articular surface or the surface of interest.

5.2.3 The orientation of the slice shall typically be perpendicular to the articular surface or the surface of interest.

5.2.4 For explanted components retrieved after *in vivo* use or *in vitro* samples that have been exposed to lipids (for example, simulator specimens exposed to lubricants containing serum), the film should be submerged in a reagent (heptane or hexane) to extract lipids from the polymer that interfere with the carbonyl peak absorptions. The extraction technique should be verified to confirm that the oxidation level has stabilized.

5.3 *Configuration of the Test Specimen in the Spectrometer:*

5.3.1 The test film (slice) shall be first configured in the spectrometer (after an appropriate background spectrum has been collected) such that the aperture is positioned over the first 200 µm of the film starting at the surface of interest.

5.3.2 Subsequent spectra shall be collected sequentially at increments matching the aperture size (that is, about 200 µm) from the articular surface, or surface of interest, across the width of the film to the opposite surface.

5.3.2.1 Larger increments may be used; however, too large an increment size may result in a loss of profile accuracy.

6. Calculations

6.1 *Oxidation Peak Area (OA):*

6.1.1 For each absorbance spectrum, calculate the total area of the carbonyl peak absorptions centered near 1720 cm^{-1} (Fig. 1).

6.1.1.1 This is the area below the sample's carbonyl absorption curve and above the straight line baseline drawn between the starting and ending points.

6.2 *Normalization Peak Area (ON):*

6.2.1 For each absorbance spectrum, calculate the total area of the peak absorptions centered near 1370 cm^{-1} (Fig. 1).

6.2.1.1 This is the area below the sample's absorption curve and above the straight line baseline drawn between the same starting and ending points.

6.3 *Oxidation Index (OI):*

6.3.1 For each absorbance spectrum, calculate its OI by dividing the area of its oxidation peak (6.1) by the area of its normalization peak (6.2), as shown in Fig. 1.

6.4 *Oxidation Index Depth Locator (DL):*

6.4.1 Calculate the distance from the articular surface, or surface of interest (DL), for each spectrum and its corresponding OI from the following equation.

$$DL = 0.5(A) + n(S)$$

where:

A = the size of the aperture in micrometres in the step direction,

n = the number of steps (increments) the aperture had been moved from its initial location at the articular surface or surface of interest, and

S = the step (increment) size in micrometres.

6.5 *Sample's Oxidation Index Profile*—Construct a plot of a sample's oxidation indices (OI) versus the corresponding depth locators (DLs).

6.6 *Surface Oxidation Index (SOI)*—Calculate a sample's SOI by calculating the average of the sample's oxidation indices (OI) with depth locator (DL) values between 0 and 3000.

6.7 *Bulk Oxidation Index (BOI)*—Calculate a sample's BOI by calculating the average of the sample's oxidation indices (OIs) corresponding to the center 500 mm of material.

6.8 *Maximum Oxidation Index (MOI)*—Calculate the sample's MOI index observed between depth locator (DL) values of 0 and 3000.

7. Report

7.1 The report shall contain at least the following experimental details and results:

7.1.1 *Material Information:*

7.1.1.1 Resin type and resin lot number.

7.1.1.2 Consolidation method and manufacturer and manufacturer lot number.

7.1.1.3 Any special post-consolidation treatments, for example, shot isostatic pressing (HIPing), annealing, sterilization, cross-linking, stabilization, accelerated aging, and storage conditions.

7.1.2 *Sample Information:*

7.1.2.1 Orthopedic implant or laboratory test specimen.

7.1.2.2 Time elapsed between sample preparation and testing in the FTIR.

7.1.2.3 Articular surface or non-articulator surface.

7.1.2.4 Test sample's original dimensions.

7.1.2.5 Any special post-treatments of the original test sample, for example, annealing, sterilization, cross-linking, stabilization, accelerated aging, and storage conditions.

7.1.2.6 Test film thickness and total width.

7.1.2.7 Any special post-treatments of the test films, for example, annealing, sterilization, cross-linking, stabilization, accelerated aging, and storage condition.

7.1.2.8 Describe sample fixturing (for example, pressed between KBr plates).

7.1.3 *Spectrometer Information:*

7.1.3.1 Manufacturer and model number.

7.1.3.2 Analogue or Fourier Transform spectrometer.

7.1.3.3 Aperture dimensions, profile step size, spectral resolution, and number of scans per spectrum.

7.1.4 *Data Analysis Information:*

7.1.4.1 Manual or by spectrometer's software algorithms.

7.1.4.2 Calculated SOI, BOI, and MOI.

7.1.4.3 Calculated SOI, BOI, and MOI values of less than 0 reflect noise or uncertainty in the baseline and shall be assigned a value of 0. The rationale for this interpretation of very low oxidation values is discussed in X1.10.

8. Precision and Bias

8.1 *Precision*—The data in Table 1 is based on a series of international interlaboratory studies using this method which were conducted in 1999 and 2000, in accordance with Practice E691, involving up to twelve institutions across the United States and Europe. Metrics of repeatability and reproducibility between different institutions were calculated as outlined in Practice E691 and normalized with respect to the mean oxidation index to estimate relative uncertainty. The data for the GUR 4150 HP rod stock were collected on as-irradiated microtomed samples. For the long-term shelf-aged tibial implants, the data were collected below the surface at the location of maximum oxidation. All samples were 200-μm-thick microtomed films gamma irradiated in air.

8.2 *Bias*—No statement may be made about the bias of this test method, as there is no standard reference material or reference test method that is applicable.

9. Keywords

9.1 FTIR; implant; oxidation; oxidation index; UHMWPE

APPENDIX

TABLE 1 International Interlaboratory Study Test Results

UHMWPE Resin, Component Type	Shelf Age,	Average Oxidation Index (OI),	Absolute Uncertainty			Standard Relative Uncertainty	
	years	$\bar{x}$	s_x	s_r	s_R	s_r, %	s_R, %
GUR 4150 HP, rod stock	0.0	0.232	0.077	0.017	0.078	7.2	33.8
GUR 1120, tibial insert	5.3	1.28	0.138	0.040	0.142	3.1	11.1
GUR 1120, tibial insert	7.5	4.51	0.823	0.168	0.834	3.7	18.5
GUR 1120, tibial insert	11.5	4.53	0.823	0.483	0.912	10.7	20.2

(Nonmandatory Information)

X1. RATIONALE

X1.1 The extent of overall oxidation and specifically certain oxidation index profiles present in orthopaedic implant components made of UHMWPE have been shown to degrade their mechanical properties and thus potentially adversely affect their *in vivo* performance. It is, therefore, important to have standard methods for assessing the oxidative characteristics of such materials.

X1.2 The method described herein is an adaptation of several similar methods described in the literature. The particular technique used to calculate an oxidation index used here has been validated by interlaboratory studies per Practice E691.

X1.3 For samples that are significantly oxidized, their carbonyl absorption peak(s) is typically very intense and broad. For such samples, a starting and ending wavenumber for the absorption peak(s) and its baseline may be as wide as 1650 cm^{-1} to 1850 cm^{-1}. For samples displaying very small levels of oxidation, their carbonyl absorption peak(s) is typically very weak and narrow in comparison to highly oxidized samples. For such samples, a starting and ending wavenumber for the absorption peak(s) and its baseline may be closer to 1680 cm^{-1} to 1765 cm^{-1}. In any case, one should set the starting and ending points of an absorption peak, and its baseline, to allow the accurate and precise measurement of its area.

X1.4 Although the method described herein has been shown to be useful for comparing the oxidation states of different UHMWPE samples, it is clear that this method does not account for all the different types of oxidative products present or potentially important in a sample.

X1.5 This method is useful for comparing the oxidation state of real-time shelf-aged UHMWPE components and UHMWPE materials assumed to have undergone oxidation via the same mechanisms.

X1.6 This method is also useful for comparing the oxidation state of retrieved components. It is, however, complicated by the effects of biological residues potentially present in retrieved samples. Common methods used to reduce such residuals (for example, extraction with hexane) may improve the comparative power of this technique.

X1.7 Use of this method to make comparisons between real-time shelf-aged components, accelerated aged components, and retrieved components is less useful because of the potential for different, and other, modes of oxidizing the UHMWPE in vivo compared to shelf or accelerating aging.

X1.8 At the present time, there is no clear correlation between the extent of oxidation or the oxidation profile present in a sample of UHMWPE and its functional characteristics.[3] For this reason, no maximum SOI, MOI, or BOI has been specified in this document.

X1.9 Lipid absorption into UHMWPE during *in vivo* use complicates the evaluation of the extent of oxidation since the lipid absorption peak and the carbonyl absorption peak may overlap. Thus, the standard was revised to reflect that lipid extraction should be performed on retrieved implants. By submerging the films in a boiling reagent (heptane or hexane) for at least 6 h, the lipids can be effectively extracted and allow for evaluation of the extent of oxidation **(Ref. 1)**.

X1.10 Analysis of very low levels of oxidation index may result in a negative OI value, which is an artifact of the baseline curvature in the FTIR spectrum. Negative values of OI may be interpreted as noise or undetectable oxidation, and may be assigned a value of 0. The standard has accordingly been revised to include updated advice for reporting of negative OI values.

[3] Gillis, A. M., Furman, B. D., Li, S., "Variations in the Determination of Oxidation in UHMWPE by 10 Different FTIR Protocols and a Proposed Standard Protocol," *Transactions of the 44th Orthopedic Research Society*, 23, 359, 1998.

BIBLIOGRAPHY

(1) Cohen A., Patel H., Medel F.J., Kurtz S.M.,"A Standardized Method For Extraction of Lipids and Oxidation Characterization of Retrieved UHMWPE Components,"*Transactions of the 54th Orthopedic Research Society, Las Vegas, NV.34.2308.2009*.

(2) Collier, J. P., Sperling, D. K., Currier, J. H., Sutula, L. C., Saum, K. A., et al, "Impact of Gamma Sterilization on Clinical Performance of Polyethylene in the Knee," *J Arthroplasty*, 11, 377-89, 1996.

(3) Collier, J. P., Sutula, L. C, Currier, B. H., Currier, J. H., Wooding, R. E., et al, "Overview of Polyethylene as a Bearing Material: Comparison of Sterilization Methods," *Clin Orthop*, 333, 76-86, 1996.

(4) Costa, L. and Brach Del Prever, E. M., *UHMWPE for Arthroplasty*, Edizioni Minerva Medica, S.p.A., Turin, 2000.

(5) Currier, B. H., Currier, J. H., Collier, J. P., Mayor, M. B., Scott, R. D., "Shelf Life and In Vivo Duration. Impacts on Performance of Tibial Bearings," *Clin Orthop*, 342, 111-22, 1997.

(6) Di Maio, W. G., Lilly, W. B., Moore, W. C., Saum, K. A., "Low Wear, Low Oxidation Radiation Crosslinked UHMWPE," *Transactions of the 44th Orthopedic Research Society*, 23, 363, 1998 .

(7) Edidin, A. A., Jewett, C. W., Kwarteng, K., Kalinowski, A., Kurtz, S. M., "Degradation of Mechanical Behavior in UHMWPE After Natural and Accelerated Aging," *Biomaterials*, 21, 1451-1460, 2000.

(8) Greer, K. W., Schmidt, M. B., Hamilton, J. V., "The Hip Simulator Wear of Gamma-Vacuum, Gamma-Air, and Ethylene Oxide Sterilized UHMWPE Following a Severe Oxidative Challenge," *Transactions of the 44th Orthopedic Research Society*, 23, 52, 1998.

(9) James, S. P., Blazka, S., Merrill, E. W., Jasty, M., Lee, K. R., et al, "Challenge to the Concept that UHMWPE Acetabular Components Oxidize In Vivo," *Biomaterials* , 14, 643-7, 1993 .

(10) Kurtz, S. M., Bartel, D. L., Rimnac, C. M., "Post-Irradiation Aging Affects the Stresses and Strains in UHMWPE Components for Total Joint Replacement," *Clin Orthop*, 350, 209-220, 1998.

(11) Kurtz, S. M., Muratoglu, O. K., Buchanan, F., Currier, B., Gsell, R., et al, "Interlaboratory Reproducibility of Standard Accelerated Aging Methods for Oxidation of UHMWPE," *Biomaterials*, 2001.

(12) Kurtz, S. M., Muratoglu, O. K., Evans, M., Edidin, A. A., "Advances in the Processing, Sterilization, and Crosslinking of Ultra-High Molecular Weight Polyethylene for Total Joint Arthroplasty," *Biomaterials*, 20, 1659-88, 1999.

(13) Kurtz, S. M., Muratoglu, O. K., Mounib, L., Buchanan, F., Currier, B., et al, "Confirmed Interlaboratory Validation Studies of a Standard Method for Determining the Oxidation Index of UHMWPE," *Transactions of the 25th Society for Biomaterials*, 22, 46, 1999.

(14) McKellop, H., Shen, F. W., Ota, T., Lu, B., Wiser, H., et al, "Wear of UHMWPE Acetabular Cups after Gamma, Sterilization in Nitrogen, Thermal Stabilization, and Artificial Aging," *Transactions of the 23rd Annual Meeting of the Society for Biomaterials*, 20, 45, 1997.

(15) McKellop, H., Yeom, B., Sun, D. C., Sanford, W. M., "Accelerated Aging of Irradiated UHMW Polyethylene for Wear Evaluations," *42nd Orthopedic Research Society*, 21, 483, 1996.

(16) Sanford, W. M., and Saum, K. A., "Accelerated Oxidative Aging Testing of UHMWPE," *Transactions of the 41st Orthopedic Research Society*, 20, 119, 1995.

(17) Shen, F. W., Yu, Y. J., McKellop, H., "Potential Errors in FTIR Measurement of Oxidation in Ultrahigh Molecular Weight Polyethylene Implants [In Process Citation]," *J Biomed Mater Res*, 48, 203-10, 1999.

(18) Sun, D. C., Scmidig, G., Stark, C., Dumbleton, J. H., "A Simple Accelerated Aging Method for Simulations of Long-Term Oxidative Aging Effects in UHMWPE Implants," *Transactions of the 42nd Orthopedic Research Society*, 21, 493, 1996.

(19) Sun, D. C., Stark, C., Dumbleton, J. H., "Development of an Accelerated Aging Method for Evaluation of Long-Term Irradiation Effects on UHMWPE Implants," *Polymer Reprints*, 35, 969-970, 1994.

(20) Sutula, L. C., Collier, J. P., Saum, K. A., Currier, B. H., Currier, J. H., et al, "Impact of Gamma Sterilization on Clinical Performance of Polyethylene in the Hip," *Clin Orthop*, 319, 28-40, 1995.

(21) Taylor, G., King, R., Devanathan, D., Lin, S., "Stability of N2 Packaged Gamma Irradiated UHMWPE," *Transactions of the 43rd Orthopedic Research Society*, 22, 776, 1997.