INTERLABORATORY VALIDATION OF A STANDARD FOR DETERMINING THE OXIDATION INDEX OF UHMWPE

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Introduction. The level of oxidation in shelf, in vivo, or artificially aged UHMWPE components can be determined using spectroscopic techniques. In the orthopaedics community infra-red (ir) microscopy has been the preferred analytical tool for the quantification of oxidation. The typical quantification of a chemical vibration, in this case the carbonyl, can be carried out by calculating either the height of or area under the vibrational peak. This value should then be normalized to an internal thickness standard (a vibration with an absorbance that linearly varies with sample thickness) to obtain a dimensionless number that is independent of the beam path length, i.e. sample thickness. In the past, several different internal thickness standards have been used in the normalization process, including direct micrometer measurement of the specimen thickness [1-5]. The purpose of this study was to identify an optimal normalization method that minimizes the experimental uncertainties associated with interlaboratory precision (repeatability) and intralaboratory bias (reproducibility) of oxidation index measurements.

Methods. The interlaboratory study was conducted in accordance with ASTM E691-92; a total of seven institutions participated. Identical test samples were prepared from a cylindrical puck of GUR 4150 HP (PolyHi Solidur, Fort Wayne IN). The puck was gamma irradiated in air (25 kGy) and had a shelf age of approximately two years. The puck was divided into pie-shaped wedges and randomly distributed to the participating institutions. Three FTIR spectra were collected at each of the following depths: 0.2 mm, 0.5 mm, 1.0 mm, 1.5 mm, and 2.0 mm below the gamma-incidence surface. The 15 spectra were then analyzed at each institution using 10 different methods, as outlined in Table 1 (one of the institutions was able to perform peak height, but not peak area measurements). For each of the OI methods, statistical metrics of repeatability and reproducibility were calculated as outlined in ASTM E691. Precision and bias estimates were normalized by the average oxidation index for each depth to provide relative measures of experimental uncertainty. Overall estimates of precision and bias uncertainty, u, for each method were calculated as $u = \sqrt{(\sum u_i/5)}$, where u_i is the uncertainty for each of the five depths.

Table 1. Summary of 10 OI Methods and Normalization Procedures

Method	Carbonyl# Region Assessment	Normalization Procedure	Number of Institutions
1	Area	Thickness*	6
2	Max. Height	Thickness*	7
3	Area	2022 cm^{-1}	6
4	Max. Height	2022 cm^{-1}	7
5	Area	1468 cm^{-1}	6
6	Max. Height	1468 cm^{-1}	7
7	Area	1370 cm^{-1}	6
8	Max. Height	1370 cm^{-1}	7
9	Area	4251 cm^{-1}	6
10	Max. Height	4251 cm^{-1}	7

#Carbonyl region was defined as 1650 to 1850 cm^{-1}
*Specimen thickness measured in mils using a micrometer

Results. The uncertainty associated with interinstitutional reproducibility was consistently larger than the repeatability observed within any single institution (Table 2). Consequently, minimization of overall interlaboratory uncertainty was judged to be the primary criterion for selecting a suitable normalization standard. Of the ten methods investigated, Method 7 (Fig. 1) had the lowest overall relative interlaboratory uncertainty (i.e., the greatest reproducibility, Table 2). Reproducibility of the OI varied through the thickness of the sample, but appeared to be greatest near the surface (Fig. 2).

Discussion. The results of this study suggest that with standardization using the appropriate normalization method, interlaboratory comparison of oxidation indexes is currently possible with an overall relative uncertainty of approximately 20%. This result was encouraging, given the variability in FTIR instrumentation and specimen preparation methods employed by the participants in this study. Although an internal reference standard may be limited by sensitivity to crystalline and amorphous content in the polymer, it offers substantial improvement in reproducibility when compared with normalization using direct thickness measurements with a micrometer. The results of this interlaboratory study will be a useful basis for the development of a new national standard under the auspices of the American Society for Testing and Materials (ASTM).

References. [1] Greer et al., 1998 ORS, 52; [2] McKellop et al., 1997 Trans. Soc. Biomaterials, 45; [3] Taylor et al., 1997 ORS, 776; [4] Sun et al., Polymer Reprints, 35: 969-970; [5] Gillis et al., 1998 ORS, 359.

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Table 2. Overall Metrics of Relative Experimental Uncertainty

Method	Reproducibility (Rel. Uncertainty, %)	Repeatability (Rel. Uncertainty, %)
1	44.7	10.3
2	72.2	56.5
3	26.6	6.6
4	29.1	3.1
5	26.4	14.4
6	74.6	16.3
7	**18.6**	**7.3**
8	25.8	3.3
9	37.5	11.1
10	28.7	7.9

Fig. 1. Oxidation Index Definition (Method 7)

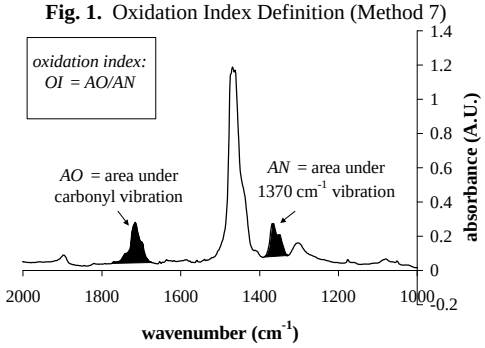
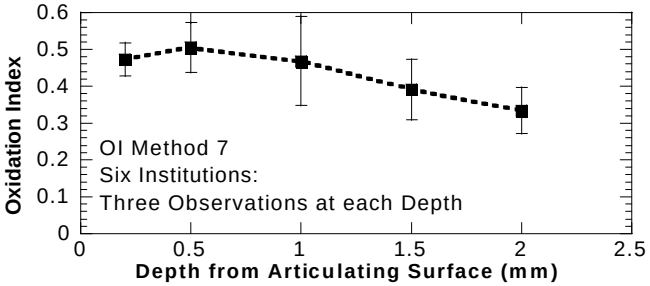


Fig. 2 Reproducibility of Oxidation Index (Method 7) vs. Depth



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