Analysis of Graded Flax Fiber and Yarn by Pyrolysis Mass Spectrometry and Pyrolysis Gas Chromatography Mass Spectrometry

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Pyrolysis mass spectrometry (PyMS) and pyrolysis gas chromatography mass spectrometry (PyGCMS) were used to analyze samples of flax fiber and yarn which had been graded as being of high, medium, and low quality. In-source, low-voltage PyMS spectra were quite similar overall. To identify potential quality markers, we screened mass responses with thresholds for the following criteria: (1) intensity, (2) repeatability, and (3) correlation to quality level. Chemical interpretation of the selected masses suggests the samples may be differentiated based on the levels of pectin, fatty acids, protein, and phenolics. PyGCMS of the graded flax fiber and yarn provided additional information about the identity of some of the selected mass responses. More palmitic acid was detected in the low-quality fiber and yarn samples. Sinapylaldehyde and sinapyl alcohol were present in higher concentrations in the low-quality yarn as compared to the high-quality material. These data suggest that the amounts of cuticular material and waxes are inversely related to quality in both flax fiber and yarn and may be used as markers for certain aspects of flax product quality.

Keywords: *Flax; pyrolysis mass spectrometry; quality measurements*

INTRODUCTION

Flax (*Linum usitatissimum* L.), the source for linen, is a commercially important crop in Europe and gaining interest in the United States (Anderson and Shiavoni, 1994). Flax fibers are freed from the plant by a process called retting. In the predominant retting method, i.e., dew-retting, the flax plant is pulled from the ground and left in the field where, at proper moisture and temperature conditions, indigenous microorganisms degrade pectins and other matrix polysaccharides. Subsequent mechanical processes release bast fibers from the stem. These include scutching (initial removal of woody material) and hackling (combing and straightening fibers and removal of additional foreign material).

The quality of the flax fiber after dew-retting is determined by expert graders and buyers using subjective eye and hand evaluations. Quality factors for the raw fiber considered for quality include weight by hand, strength, fineness, softness, smoothness, pliability, luster, cleanliness, parallelism of strands, freedom from naps and knots, and length and shape of pieces (Archibald, 1992). Prior investigations (Morrison et al., 1997) showed significant differences between high- and low-quality flax fiber and yarn by chemical, microscopic, and instrumental analysis. Compounds attributed to cutin were elevated in low-quality fiber, apparently because they were not completely removed during the retting process. In addition, long-chain fatty acids and alcohols were higher in the low-quality yarn, probably because of the greater wax content. These compounds could be used as a marker of quality. Because chemical analysis is time-consuming, an alternative approach was investigated to provide this information in a much shorter time.

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Pyrolysis gas chromatography mass spectrometry (PyGCMS) and pyrolysis mass spectrometry (PyMS) were evaluated as alternative procedures to wet chemical analysis. The use of these techniques to examine agricultural products has been reviewed by Boon (1989). Ralph and Hatfield (1991) published an inventory of compounds produced on resistive heating PyGCMS of several grasses, and Morrison and Mulder (1994) used PyMS to examine the residue of Coastal bermudagrass cell walls remaining after various chemical treatments. Scheijen (1991) demonstrated that PyMS in conjunction with multivariate analysis provided a method of differentiating flue-cured and burley tobacco. The use of analytical pyrolysis in the textile industry also has been reviewed (Hardin, 1996). These techniques might provide rapid and convenient methods to evaluate flax fiber characteristics and quality levels.

MATERIALS AND METHODS

Raw fiber, which had been dew-retted, scutched, and hackled, and yarn samples were supplied by Linificio & Canapificio Nazionale (Bergamo, Italy). The three fiber samples had been commercially graded as (1) ordinary (low), (2) medium, or (3) high quality according to the following subjective criteria: strength, fineness, luster, color, length, and shape of sticks. Further, the three yarn samples were graded (1) low, (2) medium, or (3) high quality by the following commercial yarn criteria: strength, elongation, and evenness. Samples were stored in plastic bags until analyzed. Fiber samples were taken from the center of the bundle and cut in lengths ranging from 0.5 to 1.0 mm and ground in a SPEX 510 Mixer Mill to form a fine powder.

Pyrolysis Gas Chromatography Mass Spectrometry. PyGCMS was performed using a CDS Pyroprobe 2000 mounted on the GC inlet of a Finnigan GCQ GCMS. Quartz tubes containing the sample were placed in the probe coil. The probe heating rate was 50 °C/ms to 700 °C and held for 10 s. The GC column used was a DB-1 (30 m × 0.25 mm i.d.) with a

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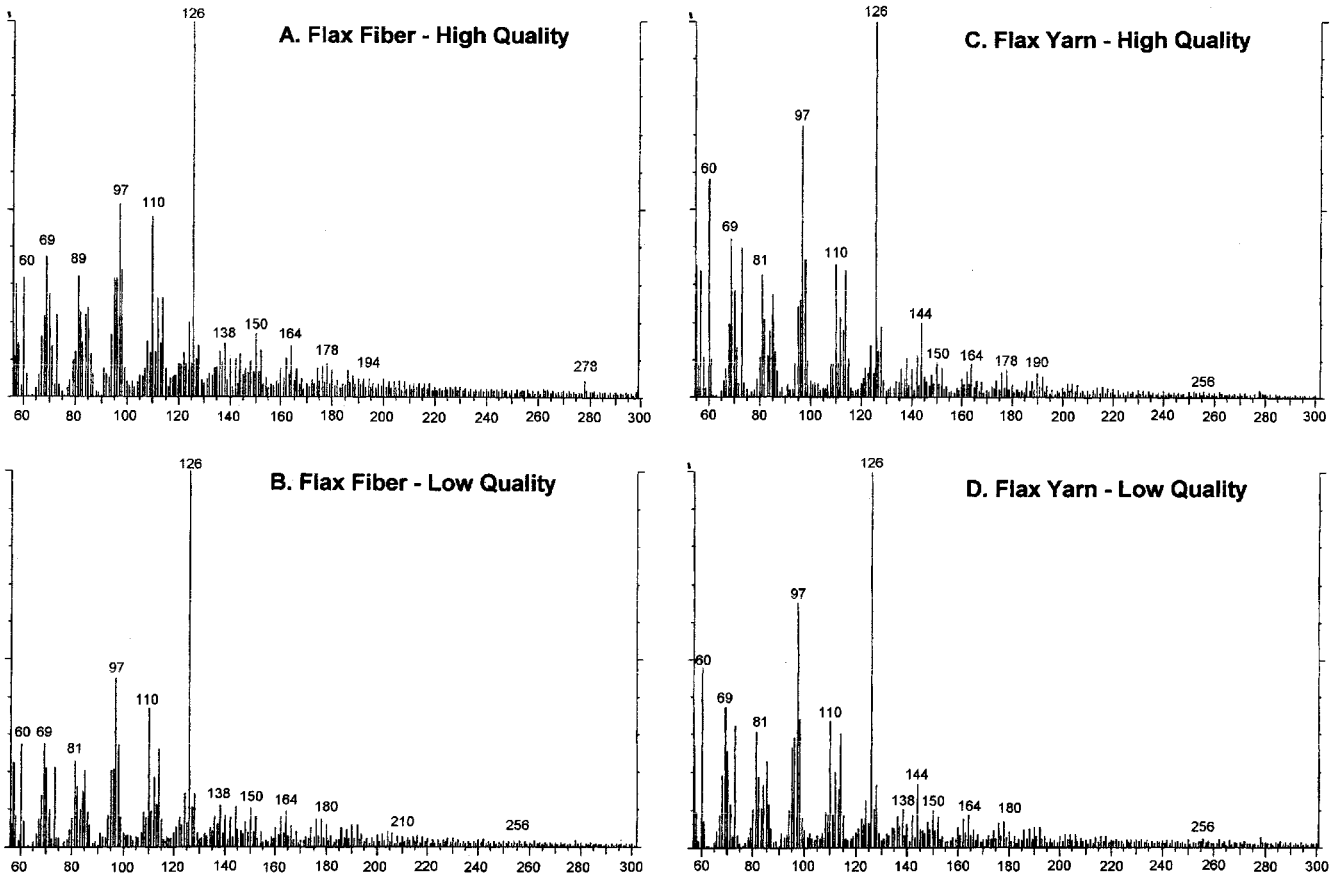

Figure 1. In-source pyrolysis low voltage (22 eV) of (A) flax fiber−high quality, (B) flax fiber−low quality, (C) flax yarn−high quality, and (D) flax yarn−low quality.

hold for 2 min at 50 °C and programmed at a rate of 4 °C/min to 275 °C. Compounds were identified by comparison of their mass spectra with published spectra or that of the authentic compound.

In-Source PyMS. In-source PyMS was performed on a Finnigan GCQ equipped with a direct exposure probe (rhenium loop). Analysis conditions were the following: ionization energy 22 eV; mass range 50−500; scan time 1 s; temperature rise ca. 10 °C/s to 700 °C; ion source temperature 175 °C. Ground samples were analyzed by preparing a suspension of the sample in distilled water using a glass mortar and pestle. A small amount of the suspension was placed on the loop and water was evaporated under vacuum. Each analysis was run in triplicate.

Statistical Analysis. Using the Finnigan software, ASCII mass lists were derived from each pyrolysis mass spectrometry (PyMS) scan by selecting the main pyrolysis peak in the total ion current spectra and subtracting the baseline signal prior to the main peak. Each subtracted mass list was imported into Excel 5.0 for Windows 95 (Microsoft Corp., Redmond, WA). Zeros were added for occasional missing data for individual masses, and mass lists were truncated to the range 51−399 mass units (349 masses total). The flax fiber and flax yarn data were analyzed separately using the same approach. Each set consisted of three samples with three replicates each. Individual mass spectra were first normalized using the total intensity of the 349 masses. Subsequent analyses were performed on the 241 masses of the fiber set and 222 masses of the yarn set which had intensities greater than 1% of the maximum intensity of their respective mean spectra.

Two statistics were calculated in order to identify the most promising masses for distinguishing quality level. For each mass, we applied analysis of variance (ANOVA) (carried out in Excel) on the three replicates of the three quality levels. The confidence level produced for each mass by ANOVA represents the percent probability that the mass can distinguish the three quality levels, though not necessarily in the proper order. Next, arbitrary values of −1, 0, and 1 were assigned to the low-, medium-, and high-quality samples, respectively, and an *r*-squared value was calculated for the prediction of this quality level by each mass. Applying a 90% confidence level threshold for the ANOVA tests yielded 130 of 349 significant masses for the fiber set and 107 of 349 for the yarn set. An *r*-squared threshold of 0.2 yielded 58 of 349 masses for the fiber set and 80 of 349 for the yarn set. When the ANOVA, *r*-squared, and intensity thresholds were applied simultaneously, 20 masses were selected from the fiber set and 44 from the yarn set. These are the masses that would be most likely to distinguish quality levels within the fiber and yarn data sets. Because there were insufficient samples for a statistical proof of the quality/mass relationships, chemical assignment information was incorporated in the mass selection process. A list of 100 assigned masses within our spectral range was derived from our GC−PyMS mass assignment experiments and J. J. C. M. Van Arendonk's mass assignments for electron ionization PyMS of plant material (Van Arendonk et al., 1997). Selecting only masses in this list, the fiber mass list was reduced to 8 and the yarn list reduced to 14. These were subject to multivariate analysis using the software package Unscrambler 6.1 (Camo AS, Trondheim, Norway). The intent of the application of multivariate analysis is primarily to produce graphical representations of the trends among the multiple selected masses. Partial least squares (PLS) with the mass spectra as the X-block and multiple Y-block variables (PLS-2) was used to illustrate the differences among the samples and masses (Martens and Næs, 1994). Glucose content and the total mass of cutin plus wax were used in the Y-block. The Y-block also contained three flag variables representing the classification into the three quality levels. For example, the flag variable for 'LowQual' was assigned 1 for the three measurements of the low-quality sample and −1 for the other six.

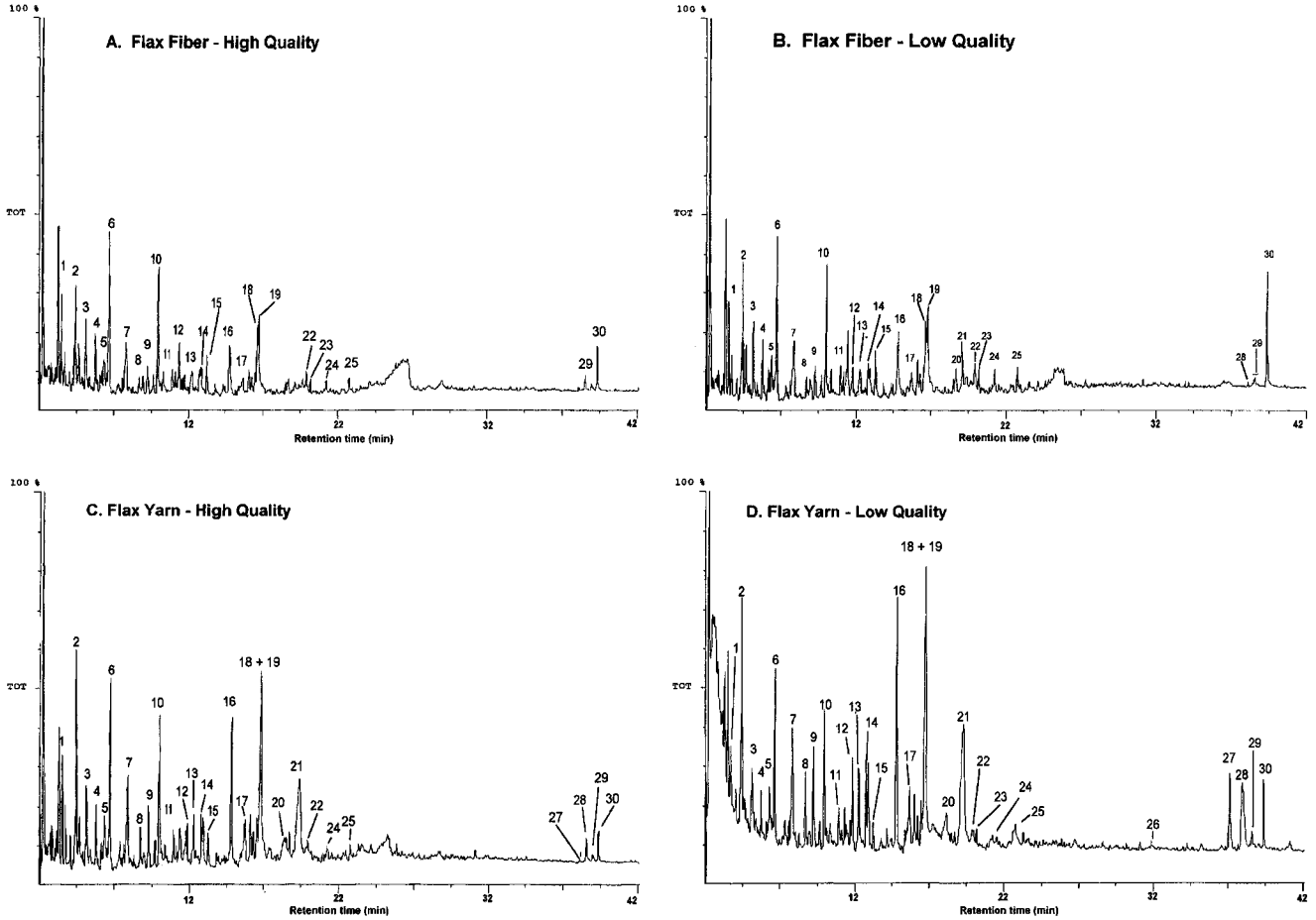

Figure 2. Total ion current chromatogram from PyGCMS of (A) flax fiber−high quality, (B) flax fiber−low quality, (C) flax yarn−high quality, and (D) flax yarn−low quality.

Table 1. Pyrolysis Low-Voltage EI Mass Peaks

compounds	mass peaks[a]
nonspecific polysaccharide fragment ions	31, 32, 43, 55, 60, 72, 74, 82
hexose polymers	57, 60, 73, 85, 86, 96, 98, 100, 102, 110, 112, 126, 144
pentose polymers	58, 85, 86, 114
rhamanose	128
methylgalacturonan	172
phenols	108
phenolic acids	
p-coumaric	120, 147, 164
ferulic	150, 177, 194
guaiacyl lignin	124, 137, 138, 150, 152, 164, 166, 178, 180
syringyl lignin	154, 167, 168, 180, 182, 194, 196, 208, 210
nucleic acids and protein	81, 83, 91, 92, 111, 117, 186
fatty acids	171, 236, 256, 284

[a] Mass assignments from Van Arendonk et al. (1997).

RESULTS AND DISCUSSION

Figure 1A−D shows the pyrolysis mass spectra of high-quality fiber (A), low-quality fiber (B), high-quality yarn (C), and low-quality yarn (D). Mass markers for cellulose, *m*/*z* 57, 60, 73, 85, 86, 96, 97, 98, 100, 102, 110, 112, 126, and 144, and mass markers for hemicellulose, *m*/*z* 58, 85, 86, and 114 (Van Arendonk et al., 1997) (Table 1), showed very little if any differences in relative intensity between high- and low-quality fiber or between high- and low-quality yarn. Chemical analysis showed an increase in glucose with increasing fiber quality and no change with increasing yarn quality (Morrison et al., 1997).

The most striking feature of the in-source, low-voltage electron-impact spectra is the low abundance of mass markers generally associated with lignin in both flax fibers and yarns. This agrees with the results of wet chemical analysis (Morrison et al., 1997). In both high-quality fiber and yarn, lignin markers (*m*/*z* 120, 124, 136, 137, 138, 150, 152, 164, 167, 166, 168, 178, 180, 182, 194, 196, 208, 210, 224) (Van Arendonk et al., 1997) (Table 1) relative to polysaccharide markers appeared slightly increased over the low-quality materials. Histological stains for lignin are positive at discrete sites in the flax fiber, primarily at the cell corners and middle lamella (Akin et al., 1996). At present the exact nature of the areas that stain positively for lignin is not clear. Data suggest that this aromatic material is not affected by retting or processing; thus, its contribution to the PyMS spectra is greater after processing as a result of removal of other constituents. Treatment of plant cell walls with 4 M NaOH at 170 °C cleaves esters and degrades lignin to aromatics which can be isolated and derivatized for GLC analysis. The aromatics can be easily assigned to lignin types (i.e., quaiacyl and syringyl). Chemical analysis has shown that the principal components removed with 4 M NaOH at 170 °C are long-chain fatty acids and alcohols from cutin/waxes and a few aromatics generally derived from lignin (Morrison et al., 1997). When comparing yarn to fiber, the amounts of cellulose fragments (*m*/*z* 97, 110, 112, 126, and 144) have increased slightly compared to hemicel-

Table 2. PyGCMS Data for Flax Fiber and Yarn

peak no.	M_w	compound
1	84	3(*H*)furan-2-one
2	96	furfural
3	98	2-hydroxymethylfuran
4	84	5(*H*)-furan-2-one
5	98	2,5-dihydro-5-methylfuran-2-one
6	98	2,3-dihydro-5-methylfuran-2-one
7	110	5-methyl-2-furfuraldehyde
8	114	4-hydroxy-5,6-dihydro(4*H*)pyran-2-one
9	112	3-hydroxy-2-methyl-2-cyclopenten-1-one
10	112	2-hydroxy-3-methyl-2-cyclopenten-1-one
11	110	5-methyl-2-furfural
12	128	2-(propan-2-one)tetrahydrofuran
13	126	2-furoic acid methyl ester
14	126	3-hydroxy-2-methyl-(2*H*)-pyran-4-one
15	126	a dimethyldehydropyranone
16	144	5-hydroxymethyl-2-tetrahydrofurfuraldehyde-3-one
17	142	3,5-dihydroxymethyl-2,3-dihydropyran-4-one
18	110	catechol
19	126	5-hydroxymethyl-2-furfuraldehyde
20	152	4-ethylguaiacol
21	144	1,4-deoxy-D-glycero-hex-1-enepyranos-3-ulose
22	122	4-hydroxybenzaldehyde
23	150	vinylguaiacol
24	138	1-(4-hydroxyphenyl)ethanal
25	136	4-hydroxyacetophenone
26	196	ferulic acid
27	208	*cis*-sinapylaldehyde
28	210	*trans*-sinapyl alcohol
29	208	*trans*-sinapylaldehyde
30	256	palmitic acid

Table 3. Mass Variables for the Fiber Standards As Selected by the Univariate Statistics[a]

mass	relative intensity	ANOVA probability	R−squared to quality level
82	14.66	90.20	0.259
111	9.38	97.87	0.356
114	34.97	97.72	0.221
117	2.95	99.94	0.426
119	3.00	99.22	0.391
123	6.26	90.41	0.306
128	17.03	96.80	0.515
141	2.56	99.00	0.430
147	4.50	99.96	0.239
155	2.19	99.16	0.228
159	2.77	99.88	0.299
163	4.67	92.90	0.260
177	3.35	99.82	0.217
193	2.35	94.68	0.271
236	2.10	94.61	0.449
248	1.41	93.28	0.226
251	1.16	94.14	0.234
256	2.96	95.96	0.288
284	2.25	92.62	0.241
294	1.32	96.51	0.383

[a] The eight highlighted masses (boldfaced and underlined) have some known chemical assignments for plant material and were used in the multivariate analysis. The ANOVA probability estimates the likelihood that the mass channel could distinguish the three quality standards.

lulose degradation products (*m*/*z* 58, 85, 86, and 114). Loss of hemicellulose is to be expected as a result of the processing of the fiber to yarn, and the PyMS results are consistent with the wet chemical analysis (Morrison et al., 1997).

Another approach for the characterization of flax fiber and yarn is pyrolysis gas chromatography mass spectrometry (PyGCMS). Figure 2A−D shows the pyrograms of high-quality fiber (A), low-quality fiber (B), high-quality yarn (C), and low-quality yarn (D). The peak numbers refer to the compounds listed in Table 2. Compounds generally associated with lignin such as vinylguaiacol (*m*/*z* 150) and vinylsyringol (*m*/*z* 180), which are present in the PyGCMS spectra of the more highly lignified bast tissue from kenaf (*Hibiscus cannabinus*), are present in low amounts in both fiber and yarn, thus indicating a very low lignin content (Morrison et al., 1998). The presence of small amounts of *m*/*z* 150 suggests a small amount of quaiacyl lignin in the fibers. Peak 18, catechol, suggests the presence of ester of caffeic acid. Water extracts of unretted fiber analyzed by HPLC indicate the presence of caffeoyl ester of carbohydrates (unpublished results). The concentration of catechol is somewhat lower in yarn relative to fiber, though it is harder to quantitate because it coeluted with furfuraldehyde. Other phenolic peaks (i.e., 20, 22−26 which probably arise from cutin and/or suberin) appear slightly higher in low-quality fiber. In these samples, palmitic acid, peak 30, is the primary fatty acid associated with cutin/wax from flax. To establish the location of palmitic acid, fiber was extracted for 1 min with chloroform to remove wax. Analysis of the extract by PyGCMS (not shown) revealed a series of hydrocarbons, long-chain alcohols, and fatty acids, with palmitic acid being by far the most abundant compound present, and no aromatic compounds. Scrapings of unretted flax bast (to remove the cuticular layer which would also contain wax) analyzed by PyGCMS (not shown) revealed aromatic markers (guaiacyl and syringyl) characteristic of compounds associated with cutin, long-chain alcohols, fatty acids (palmitic acid being the most abundant), and a small amount of sinapylaldehyde. *cis*- and *trans*-sinapylaldehyde (peaks 27 and 29, respectively) and sinapyl alcohol (peak 28) are in much greater concentration in the low-quality yarn versus high-quality yarn. Together with palmitic acid, these compounds provide good markers of quality. Pyrograms of flax yarn show a very low amount of cutin markers present as indicated by the low amounts of peaks 20 and 22−25, particularly in the high-quality material. Interestingly, the yarns have a relatively higher concentration of sinapyl alcohol and sinapylaldehyde than fiber. This suggests that the aromatic present is predominantly syringyl in nature, and if this is lignin, it has a rather simple structure consisting of β-O-4 ethers (Hage et al., 1993; Ralph, 1996). Higher amounts of sinapylaldehyde and sinapyl alcohol and lower amounts of palmitic acid in the higher quality yarn compared to the low-quality yarn suggest a more efficient removal of wax and also the presence of a more tightly bound lignin and/or cutin. Microscopic examination of high-quality yarn reveals the presence of cuticular material attached to the yarn (Morrison, 1997).

In all evaluations, the medium-quality fiber and yarn fell somewhere between the two extremes but did not exhibit consistent trends. In some cases, the characteristics were more like high quality and in others like low quality. These results mirror those from the chemical studies (Morrison et al., 1997).

The relationship between subtle differences in PyMS spectra can be visualized with the use of multivariate analysis. As described under Materials and Methods, univariate statistics were used to select 8 flax fiber PyMS masses and 14 flax yarn PyMS masses that are good candidates for prediction of the quality levels for each kind of flax product. These mass−variable selections were the result of application of 4 criteria to each mass in the original lists of 349 masses. The criteria

Table 4. Forty-Four Mass Variables for the Flax Yarn Standards As Selected by the Univariate Statistical Analysis[a]

mass	relative intensity	ANOVA probability	*R*-squared to quality level	mass	relative intensity	ANOVA probability	*R*-squared to quality level
59	2.12	94.53	0.405	158	2.61	93.82	0.297
81	32.94	99.29	0.360	**171**	1.79	99.86	0.799
82	21.09	94.67	0.453	**172**	3.14	91.51	0.371
83	11.67	95.19	0.256	175	2.56	99.01	0.342
85	27.25	98.45	0.563	**182**	2.70	97.95	0.438
86	12.19	97.87	0.475	184	2.15	99.61	0.515
87	6.92	91.41	0.370	**186**	4.88	94.81	0.444
88	1.42	98.23	0.250	197	1.14	97.99	0.565
91	3.86	94.34	0.401	200	3.28	91.23	0.202
92	2.48	96.16	0.456	211	1.13	93.45	0.340
93	2.76	96.86	0.520	214	2.85	94.78	0.454
105	2.81	99.52	0.205	215	1.52	98.47	0.545
106	2.35	98.76	0.539	218	3.35	96.12	0.211
108	9.70	93.15	0.261	221	1.20	92.54	0.406
110	35.87	93.92	0.410	223	1.15	90.89	0.240
116	2.45	99.00	0.225	229	1.33	94.03	0.283
130	1.85	98.51	0.418	**236**	1.82	98.03	0.308
132	3.47	91.66	0.357	238	1.65	96.43	0.474
133	3.04	98.17	0.324	244	1.87	98.64	0.398
134	5.11	94.62	0.230	245	1.07	93.78	0.410
147	3.73	99.17	0.200	248	1.32	96.71	0.423
157	1.57	91.89	0.388	259	1.01	97.81	0.534

[a] The 14 highlighted masses (boldfaced and underlined) have some known chemical assignments for plant material and were used in the multivariate analysis. The ANOVA probability estimates the likelihood that the mass channel could distinguish the three quality standards.

were the following: (1) ANOVA indicates that the graded standards can be distinguished with better than a 90% probability; (2) the *r*-squared value for correlation to quality level is better than 0.2; (3) the spectral intensity is greater than 1% of the maximum of the mean spectrum; and (4) the PyMS mass has been previously assigned to at least one plant component. Tables 3 and 4 show the results of applying criteria 1−3 to the fiber and yarn PyMS data, respectively. The results of applying all the criteria are highlighted in the tables. On these subsets of samples, PLS-2 multivariate analysis was used to visualize the relationships among the samples. Because of the small sample set, only the first two PLS-2 latent variables (LVs) were used for the data visualization, and the main conclusions about mass channel trends were drawn from the first LV. The results are presented in Figures 3 and 4. For flax fiber, one latent variable (LV1) is able to distinguish the high-quality sample from the low- and mid-quality standards, while two latent variables are needed to separate all three quality standards (Figure 3A). The *X* and *Y* variable loadings plot indicates that high-quality and *m*/*z* 82, 111, and 117 are correlated positively along the LV1 axis and low quality is positively correlated to the total cutin plus wax and the remaining masses (Figure 3B,C). Masses *m*/*z* 82, 111, and 117 have been assigned to polysaccharide, nucleic acid, and protein, respectively, in PyMS of plant material (Van Arendonk et al., 1997). The polysaccharide signal could be due to increasing purity of higher quality flax fiber, i.e., greater relative concentration of cellulose. The masses *m*/*z* 111 and 117 might be related to the degree of colonization of the samples by the dew-retting microorganisms. Mass 114 has been assigned to hemicellulose (pentosan) and 128 to pectin (rhamnose), and these masses appropriately decrease with increasing quality level. These results are consistent with other studies (Gorschkova et al., 1996) that showed the major pectic sugars are five-linked arabinans, rhamnogalacturonans, and polygalacturonic acid. The remaining masses (*m*/*z* 236, 256, and 284) are probably due to lipid (fatty acids), and these are seen to decrease with improving flax fiber quality.

For the flax yarn standards, the univariate statistical selection procedure yielded 44 masses, 14 of which have been assigned in PyMS of plant material (Table 2). Using these 14 masses for a PLS-2 model, low-, medium-, and high-quality samples are separated by the first latent variable (Figure 4A). Previously reported chemical analyses have indicated that high quality is correlated to glucose content while low quality is correlated to the total quantity of cutin and wax (Morrison et al., 1997). This is supported by the mass variable loadings in Figure 4B,C, which exhibit the correct trends: increasing masses 82 and 110 may be due to the glucose polymer cellulose, while decreasing masses 171 and 236 are fatty acid markers. Mass 171 was shown to arise solely from fragmentation of palmitic acid, *m*/*z* 256. Other mass variables which show decreases with quality seem justifiable: decreasing phenols (*m*/*z* 108), decreasing pectin (methylgalacturonan, *m*/*z* 172), and decreasing syringyl lignin monomer (*m*/*z* 182). Hemicellulose (pentosan, *m*/*z* 85 and 86) is seen to increase with increasing quality, although the intensities seem too great to be purely due to hemicellulose. Complete removal of hemicellulose severely reduces yarn strength (Movan et al., 1989), and thus a certain amount of hemicellulose is needed to maintain fiber strength. The five masses *m*/*z* 81, 83, 91, 92, and 186, which have previously been used as protein markers in plant PyMS analysis (Van Arendonk et al., 1997), are troublesome in that the loadings are both positive and negative to quality level. Since only small quantities of protein would be expected for linen fibers, it is more likely that the strong positive intensities at *m*/*z* 81 and 83 are polysaccharide markers.

CONCLUSIONS

High-quality fiber was characterized by increased glucose- and nitrogen-containing compounds possibly

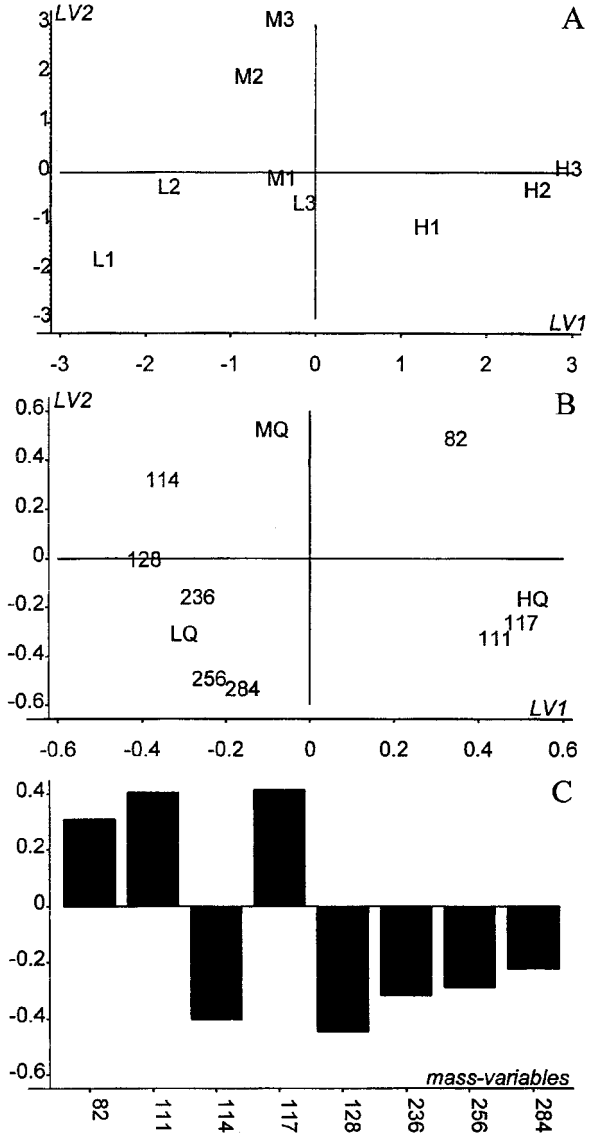

Figure 3. PLS-2 classification analysis of the eight best masses for measuring flax fiber quality level from the nine fiber pyrolysis mass spectra of the three flax fiber quality levels: (A) Sample scores plot of the nine samples versus the first two latent variables. The samples are three repeated measurements each for the low (L), medium (M), and high (H) quality samples. (B) *X* and *Y* variable loadings plot for the first two latent variables (LVs). The *X*-variable is labeled with the mass channel while the *Y*-variable is labeled with the sample attribute. (C) *X*-loadings for the first latent variable. The masses with positive values are positively correlated to high quality, while the negative values indicate channels which are inversely correlated to high quality. The first latent variable explains 36% of the *X*-variance (mass variables) and 50% of the *Y*-variance (quality levels and chemical analysis).

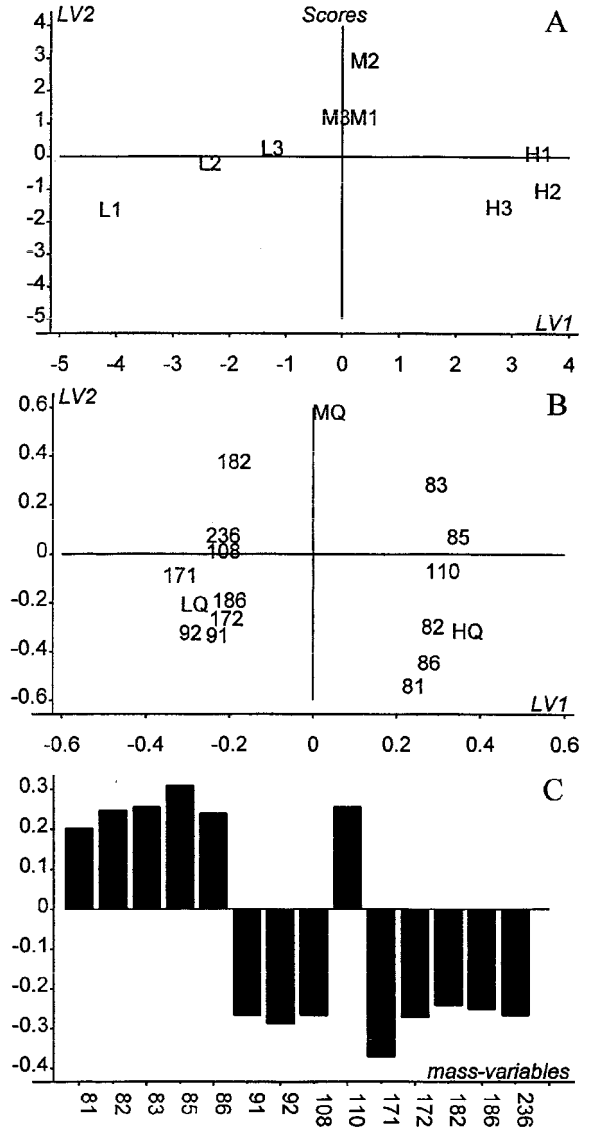

Figure 4. PLS-2 classification analysis of the 14 best masses for measuring flax yarn quality level from the 9 fiber pyrolysis mass spectra of the 3 flax yarn quality levels: (A) Sample scores plot of the nine samples versus the first two latent variables. The samples are three repeated measurements each for the low (L), medium (M), and high (H) quality samples. (B) *X* and *Y* variable loadings plot for the first two latent variables (LVs). The *X*-variable is labeled with the masses while the *Y*-variable is labeled with the sample attribute. (C) *X*-variable loadings for the first latent variable. The masses with positive values are positively correlated to high quality, while the negative values indicate masses which are inversely correlated to high quality. The first latent variable explains 43% of the *X*-variance and 54% of the *Y*-variance.

indicating greater invasion by retting microorganisms, thus resulting in a more efficient ret and accounting for the observed lower amounts of pectin and cutin/wax. High-quality yarn was characterized by high glucose polymers and lower phenolics, pectin, and cutin/wax. The increase in hemicellulose is possibly a result of a greater effective contribution for bound hemicellulose after removal of other materials during yarn processing, particularly scouring.

PyMS was able to distinguish between three quality levels of flax fiber and yarn based on masses corresponding to degradation products of cellulose, wax, cutin, fatty acids, phenolic compounds, and some nitrogen-containing compounds. PyGCMS was able to identify specific pyrolysis products which were correlated to quality levels. The combined techniques can provide a tool to identify carbohydrate, lipid material, and phenolics (specifically syringyl) correlated with quality measurements in flax fiber and yarn. Many of the pyrolysis mass responses which serve as flax quality markers are consistent with wet chemical analyses. Both mass spectral techniques are faster and provide much of the same qualitative information as the wet chemical analyses but initially depend on wet chemistry to validate results with a given sample set. Further, less sample is needed, sample preparation is kept to a minimum, and the use of organic solvents is eliminated.

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