

A quantitative discrimination study of recycled cashmere fibers using MALDI-TOF MS

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Overview

- Chemical damage of the fiber could be responsible for a low *m/z* intensity of the animal specific peptide derived from keratin.
- Cashmere Genuine Index (CGI) was defined from a result of MALDI-TOF MS.
- Multiple regression analysis incorporated with CGI and the ratio of the ruptured fibers enabled a discrimination of recycled cashmere clearly.

1. Introduction

Recently, as the concern of sustainable growth of society is increasing, it has been noted that raising cashmere goats can have a negative impact on our environment. In an effort to reduce the number of grazed animals, there is an increasing demand for recycled cashmere in apparel and textile industries. Meanwhile, the lack of analytical methods to obtain an appraisal parameter for the presence of the recycled fibers in textiles is still a significant issue. Whereas optical microscopy is a useful method to observe changes in shape of the fibers, there is no other testing method to discriminate and quantify the recycled cashmere. We will report a quantitative discrimination method of recycled cashmere using MALDI-TOF MS.

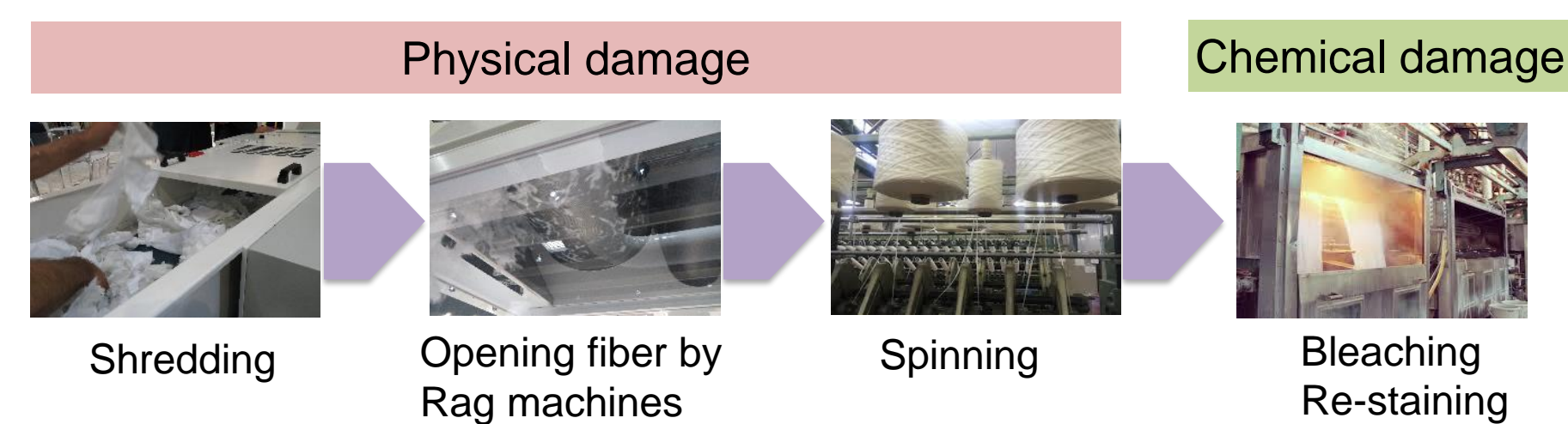


Fig. 1 Recycle process of cashmere textile and conceivable damages

2. Methods

Virgin and recycled cashmere textiles shown in Fig. 3 were kindly provided by The Cashmere and Camel Hair Manufacturers Institute (CCMI).

Protein concentration was measured using 2-D Quant Kit (GE Healthcare).

Optical microscopy observations of the samples were performed by following the Japanese Industrial Standard method (JIS L 1030-2). Shapes of more than 1,000 of the fibers were classified as normal, change of shape, or shortened. Normalized ratio of changed and shortened fibers was estimated as "abnormal" against the normal one.

The animal hair fibers were subjected to typical proteomic analysis by following ISO 20418-2. Briefly, after SDS-PAGE, excised gel-bands containing keratins derived from the animal hair were digested using trypsin.

Mixtures of peptides were analysed in a linear mode MALDI-TOF MS (MALDI-8020, Shimadzu Corp., Japan) in positive mode, using CHCA as matrix. Intensities of animal specific peptides were applied to a quantitative curve in Fig.5 and CGI in Fig.8.

3. Results

3-1. Optical microscopy observation of ruptured fibers.



Fig. 2 Optical view of recycled cashmere fibers (x 300). A) normal, B) change of shape, C) shortened

Virgin						Recycled					
No.	Origin	Normal Cashmere	Change of fiber shape	Short fiber	abnormal	No.	Origin	Normal Cashmere	Change of fiber shape	Short fiber	abnormal
Ne-1	Cashmere 100%	98.1	0.7	1.2	1.9	Re-1	Opened shaded soft waste	97.5	1.3	1.2	2.5
Ne-2	Old knits-1	98.9	0.3	0.8	1.1	Re-2	Sweater "designer brand A"	96.8	1.7	1.5	3.2
Ne-3	Old knits-2	98.9	0.3	0.8	1.1	Re-3	Sweater "designer brand B"	97.8	1.1	1.1	2.2
Ne-4	New yarn & Knitting -1	99.3	0.1	0.6	0.7	Re-4	IT 18.027 CA	96.2	2.2	1.5	3.7
Ne-5	New yarn & Knitting -2	99.1	0.2	0.7	0.9	Re-5	70% Recycled 30% Nergin Cashmere	97.9	1.5	0.6	2.1
Ne-6	New yarn & Knitting -3	99.2	0.1	0.7	0.8	Re-6	Opened yarn from old knits	98.0	0.9	1.1	2.0
Ne-7	Pulled old knits-1	98.7	0.3	1.0	1.3	Re-7	50% Nergin 47% Recycled Cashmere 3% Wool-1	98.4	0.8	0.8	1.6
Ne-8	Pulled old knits-2	98.9	0.6	0.5	1.1	Re-8	50% Nergin 47% Recycled Cashmere 3% Wool-2	98.2	1.0	0.8	1.8
Ne-9	Bleached yarn-3	98.8	0.3	0.9	1.2	Re-9	97% Recycled 3% Wool-1	97.4	0.7	1.9	2.6
Ne-10	Bleached knit fabric-1	99.0	0.3	0.7	1.0	Re-10	97% Recycled 3% Wool-2	97.2	1.5	1.3	2.8
Ne-11	Bleached knit fabric-2	99.0	0.1	0.9	1.0	Re-11	Regenerated From Knit Products	95.8	2.1	2.1	4.2
Ne-12	Bleached knit fabric-3	99.3	0.1	0.6	0.7	Re-12	Regenerated From Woven Products	95.5	1.9	2.6	4.5

Fig. 3 Relative ratio (%) of classified shapes of fibers.

Whereas the abundance ratio of the abnormal fibers in most of recycled cashmere textiles was higher than in the virgin one, some ratios found in the virgin were very similar with those in some recycled samples. The ratios were varied depending on cutting length of the fibers (0.3 to 0.8 mm).

3-2. Cashmere fiber analysis using MALDI-TOF MS.

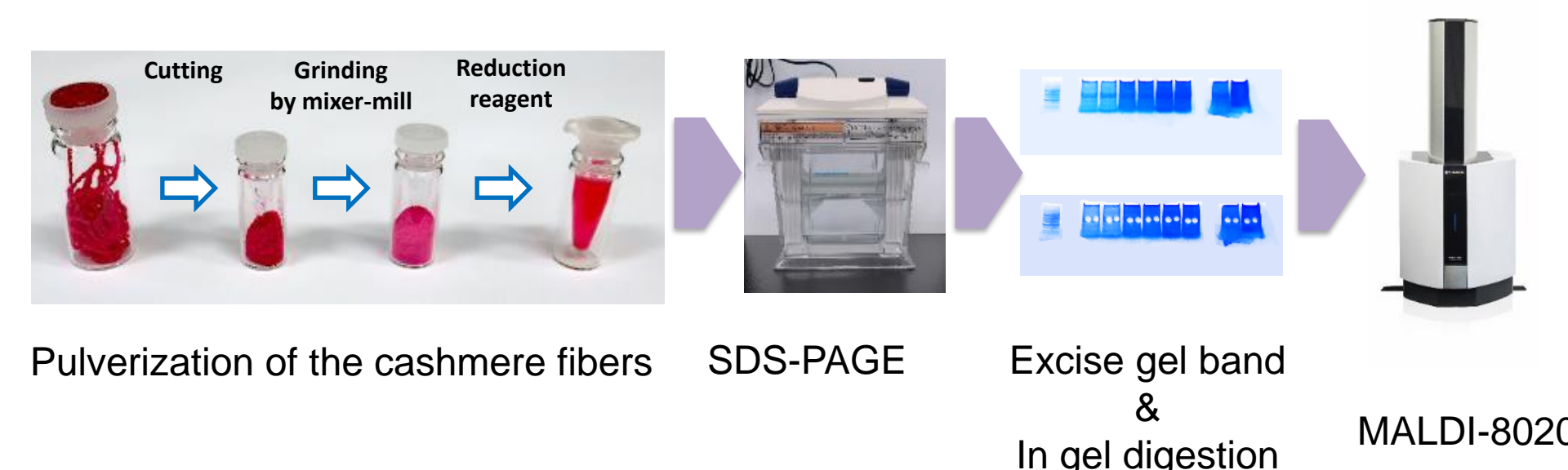


Fig. 4 Workflow of animal hair analysis.

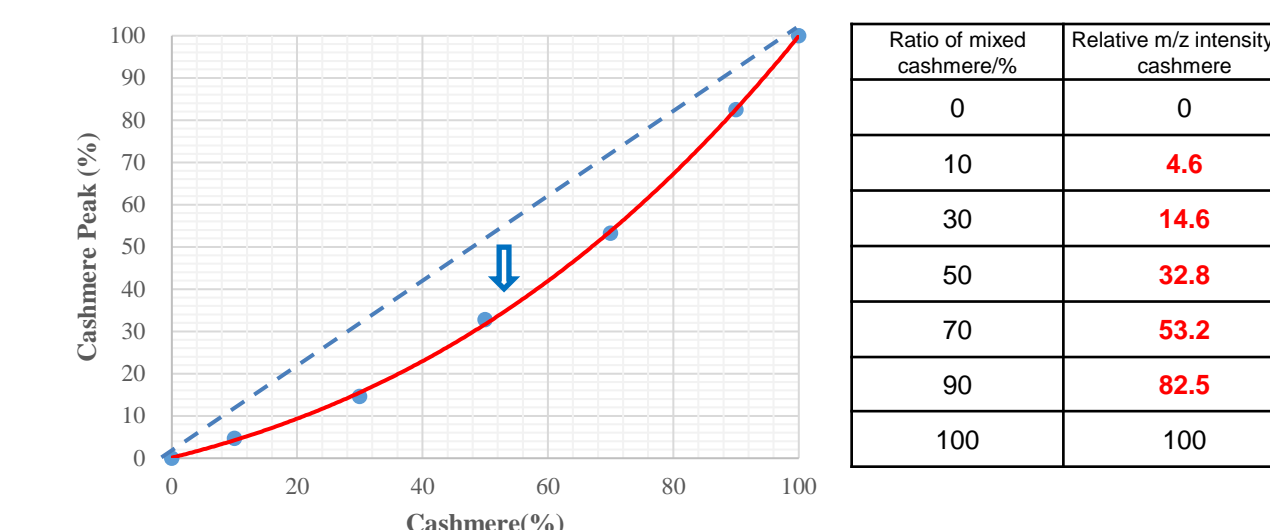


Fig. 5 Quantitative curve of a cashmere specific peptide (m/z 2691)

Bleached cashmere and wool were mixed in a 1: 1 ratio, then digested. The intensity of the cashmere specific peptide was normalized against a wool specific peptide, m/z 2664.

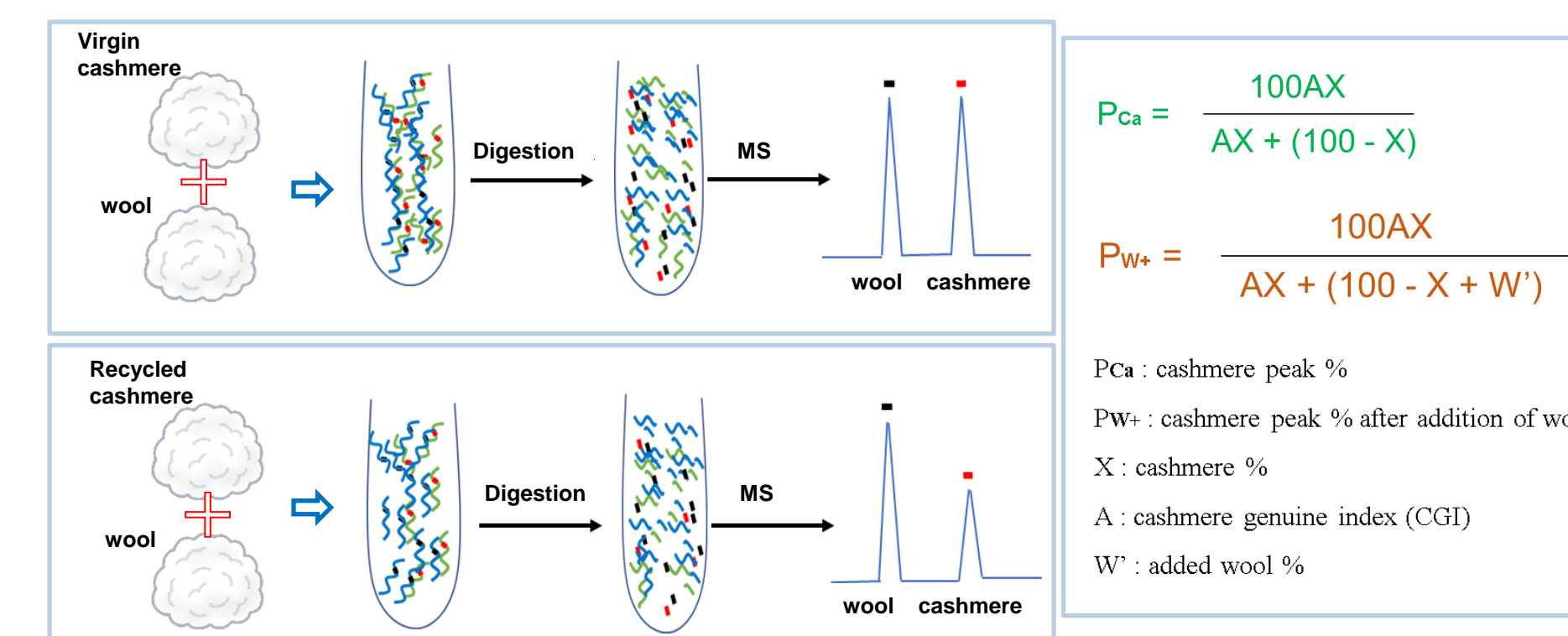


Fig. 6 Concept of Cashmere Genuine Index (CGI)

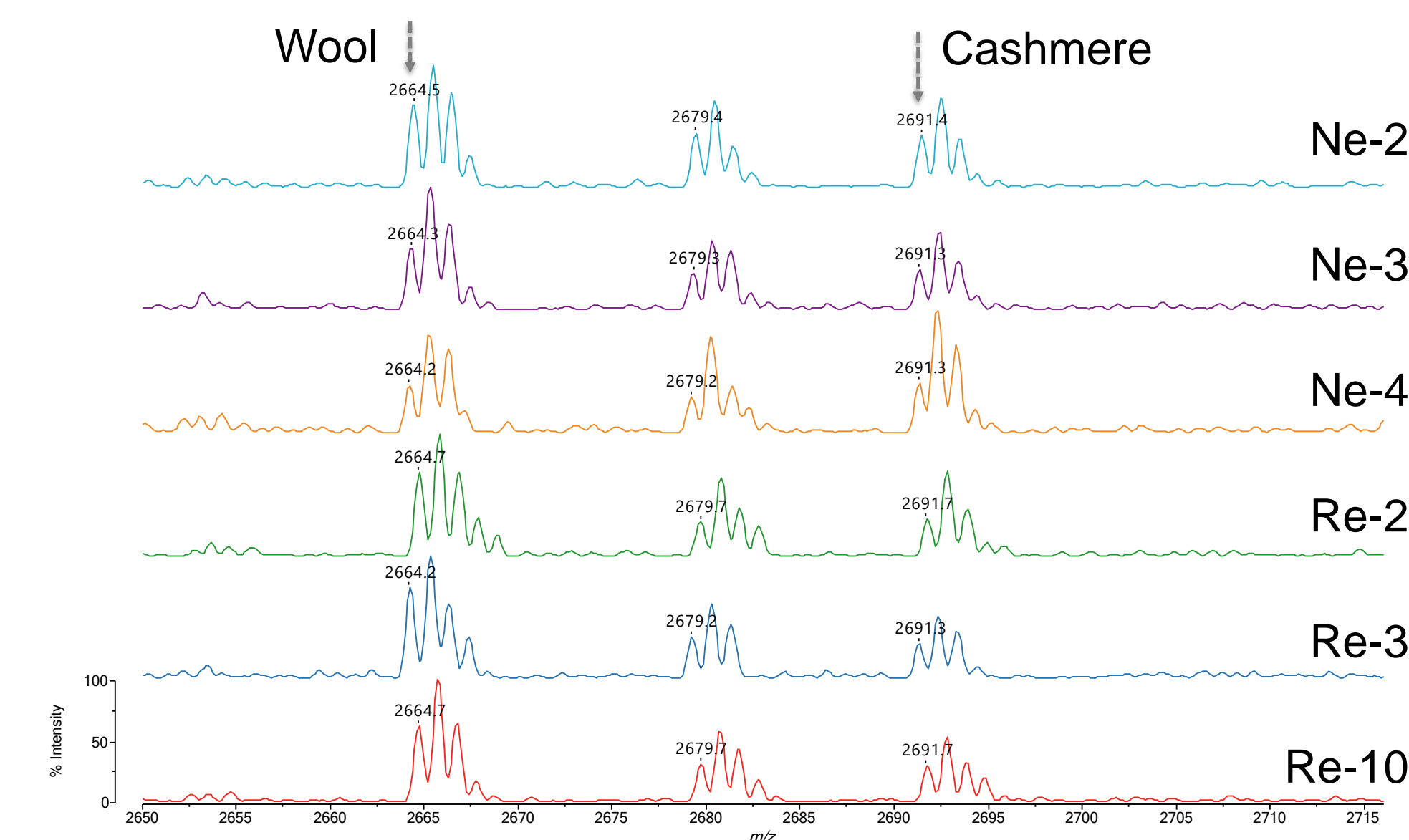
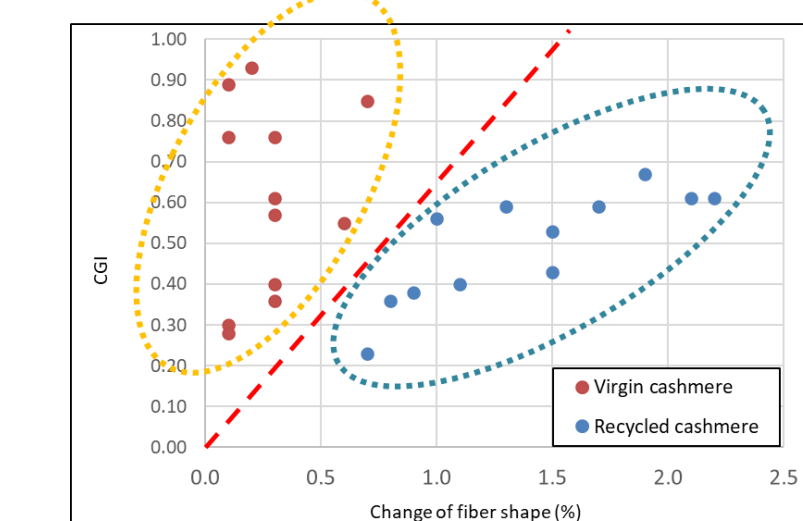


Fig. 7 Expanded MS region of tryptic digests from virgin and recycled cashmere mixed with wool in a 1:1 ratio. The intensity of the cashmere specific peptide was normalized against a wool specific peptide, *m/z* 2664.

3-3. Statistical analysis incorporating CGI and the change of shape.

Fig. 8 Scatter plot with CGI and abnormal fiber shape



This plot indicates that virgin and recycled cashmeres can be classified based on CGI and the change of shape.

	Change of shape / %	CGI	MRE	
Virgin	Ne-2	0.3	0.79	1.018
	Ne-3	0.3	0.68	0.858
	Ne-4	0.1	1.21	1.880
Recycled	Re-2	1.7	0.69	-0.872
	Re-3	1.1	0.54	-0.343
	Re-10	1.5	0.51	-0.885

More than "0", virgin
Less than "0", Recycled

Multiple regression equation (MRE) = -1.246 × Change of fiber shape (%) + 1.457 × CGI + 0.241

Table 1 Multiple regression analysis using CGI and the change of shape.

4. Conclusion

- ✓ Quantitative discrimination between virgin and recycled cashmere was conducted successfully, using MALDI-TOF MS and optical microscope comprehensively.
- ✓ MALDI-TOF MS was able to analyze chemical damage of keratin protein in the fiber, whereas optical microscopy did physical damage of the entire fiber.
- ✓ In this method, MALDI-TOF MS possibly contributes to differentiate the recycled fiber from physically modified virgin one, i.e., treatment for raised fiber or suede.

5. Reference

- 1) Ohashi et al., Journal of Fiber Science and Technology, 68,10,276-281 (2012)
- 2) Ohashi et al., Journal of Fiber Science and Technology, 76,7,267-274 (2020)
- 3) ISO 20418-2; Textiles - Qualitative and quantitative proteomic analysis of some animal hair fibres - Part 2: Peptide detection using MALDI-TOF MS
- 4) JIS L 1030-2; Testing methods for quantitative analysis of fibre mixtures of textiles - Part 2: Testing methods for quantitative analysis of fibre mixtures
- 5) JIS L 1030-3-1; Testing methods for quantitative analysis of fibre mixtures of textiles -Part 3-1: Instrumental analysis of some animal hair fibres -Using MALDI-TOF MS testing methods for quantitative analysis of fibre mixtures
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