Rapid Analysis of Animal Hair Fiber Adulteration in Textiles with MALDI-TOF

MALDI-TOF demonstrates unique advantages in adulteration analysis. In the textile industry, the substitution of inferior fiber components remains a challenging issue in detection, such as in the case of cashmere and sheep wool.

Abstract

In this case, MALDI-TOF was successfully employed to identify different animal hair sources in textiles and quantify adulteration ratios, with the method exhibiting excellent repeatability and reproducibility (RSD<5%). The related procedures could be also applied to adulteration analysis in other application fields such as food adulteration.

Keywords:
MALDI-TOF, Adulteration, Animal hair, Textiles

Introduction

In daily life, textiles such as sheep wool and cashmere, derived from different animal hair, vary significantly in price. Unethical manufacturers adulterate textiles with lower-cost animal hair to reap higher profits, severely harming consumer interests.

Traditional methods for identifying animal hair primarily rely on optical microscopy. However, certain textiles underwent deep processing steps like bleaching and dyeing, making microscopic identification challenging. Methods like fluorescent PCR also face limitations for animal hair samples with damaged DNA during processing. Furthermore, special animal fibers like cashmere, sheep wool, and yak hair overlap in features such as scale height and thickness, posing long-standing challenges in textile testing. These methods heavily depend on inspectors' experience and lack objective evaluation criteria.

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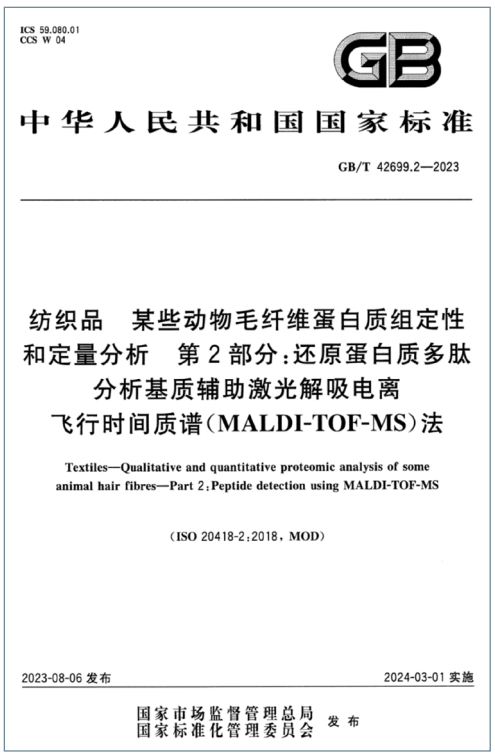
To address the challenge of identifying animal hair in textiles, the Technical Center for Industrial Product and Raw Material Inspection and Testing of Shanghai Customs District established the Chinese national standard GB/T 42699.2-2023 "Textiles—Qualitative and Quantitative Proteomics Analysis of Some Animal Hair Fibers—Part 2: Peptide Detection Using MALDI-TOF-MS" on a Bruker MALDI-TOF platform, which was officially implemented in March 2024. This standard not only accurately identifies the source of animal hair in textiles but also quantifies the proportion of adulterated animal hair, demonstrating excellent reproducibility.

The established workflow demonstrates excellent scalability and has been further successfully applied to the detection of illegal trade in shahtoosh for the first time. Shahtoosh, a Persian word meaning "king of fine wool", is a type of fine wool collected from the underfur of Tibetan antelopes (*Pantholops hodgsonii*). The species is listed in Appendix 1 of the Convention on International Trade in Endangered Species (CITES), and trade for shahtoosh and other Tibetan antelope products has been fully prohibited since 1979 and is illegal. The established method effectively addresses the challenges in distinguishing shahtoosh from other visually similar animal fibers (e.g., cashmere), while quantitative analysis can assist judicial authorities in sentencing determination.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GB/T 42699.2—2023

纺织品　某些动物毛纤维蛋白质组定性和定量分析　第2部分：还原蛋白质多肽分析基质辅助激光解吸电离飞行时间质谱（MALDI-TOF-MS）法

Textiles—Qualitative and quantitative proteomic analysis of some animal hair fibres—Part 2：Peptide detection using MALDI-TOF-MS

（ISO 20418-2：2018，MOD）

2023-08-06 发布　　2024-03-01 实施

国家市场监督管理总局
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Figure 1. Chinese national standard cover page

Methods

- Proteins were extracted from animal hair using a sodium dodecyl sulfate (SDS)/dithiothreitol (DTT)/phosphate buffer.
- The extracted proteins were purified via SDS-PAGE and then digested with trypsin.
- Digested proteins were analyzed on a microfleX LRF (Bruker Daltonics) MALDI-TOF platform. The instrument was operated in reflector mode with positive ion acquisition. For each spectrum, 2000 shots were summed. Characteristic peptides with 2450 *m/z* – 2750 *m/z* were used to identify the animal hair fibers.
- Standard curves based on these characteristic peptides were established and used to quantify the adulterated animal hair contents.

$$G_P = \frac{h_g \times 100}{h_g + h_w + h_y}$$

$$W_P = \frac{h_w \times 100}{h_g + h_w + h_y}$$

$$Y_P = \frac{h_y \times 100}{h_g + h_w + h_y}$$

G_p: cashmere peak height ratio, %.
W_p: sheep wool peak height ratio, %.
Y_p: yak hair peak height ratio, %.
h_g: cashmere peak height.
h_w: sheep wool peak height.
h_y: yak hair peak height.

Results

Animal Hair Species Identification

MALDI-TOF analysis of animal hair in textiles reveals species-specific characteristic peptides in the *m/z* range of 2450–2750, the characteristic peptides could be used to identify sources of fiber species (Table 1). Key characteristic peaks for cashmere, sheep wool, and yak hair are distinct and non-overlapping, overcoming traditional identification challenges (Figure 2).

Table 1. Characteristic Peaks of Different Animal Hair Analyzed by MALDI-TOF-MS.

Characteristic peak (*m/z*)	Latin name	Source of fiber species
2503	*Bos grunniens*	Yak
2556	*Chinchilla*	Chinchilla
2563	*Equus caballus*	Horse
2583	*Camelus bactrianus or Lama pacos*	Camel or Alpaca
2638	*Vulpes*	Fox
2656	*Oryctolagus cuniculus*	Rabbit
2664	*Ovis aries*	Sheep
2684	*Procyon lotor*	Raccoon
2691	*Capra hircus*	Goat (cashmere or mohair)
2698	*Mustelidae*	Mink
2711	*Nyctereutes procyonoides*	Raccoon dog

Quantification of Animal Hair Fiber Contents in Mixed Samples

Mixed samples of cashmere-sheep wool and cashmere-yak hair with varying proportions such as 1:9, 2:8, 3:7, 4:6, 5:5, 6:4, 7:3, 8:2, 9:1 were prepared and processed as described in Methods. Peak height ratios were calculated according to formulas below.

Cashmere contents (X, %) and cashmere peak height ratios (Y, %) were used to establish standard curves (Figure 3-1 and 3-2). Animal hair fiber contents of unknown samples were calculated based on standard curves.

Method Repeatability and Reproducibility Validation

For standards, instrument stability is critical to ensure data accuracy and reliability. Tests over three years on samples with varying contents confirmed excellent repeatability and reproducibility of the established method (RSD<5%).

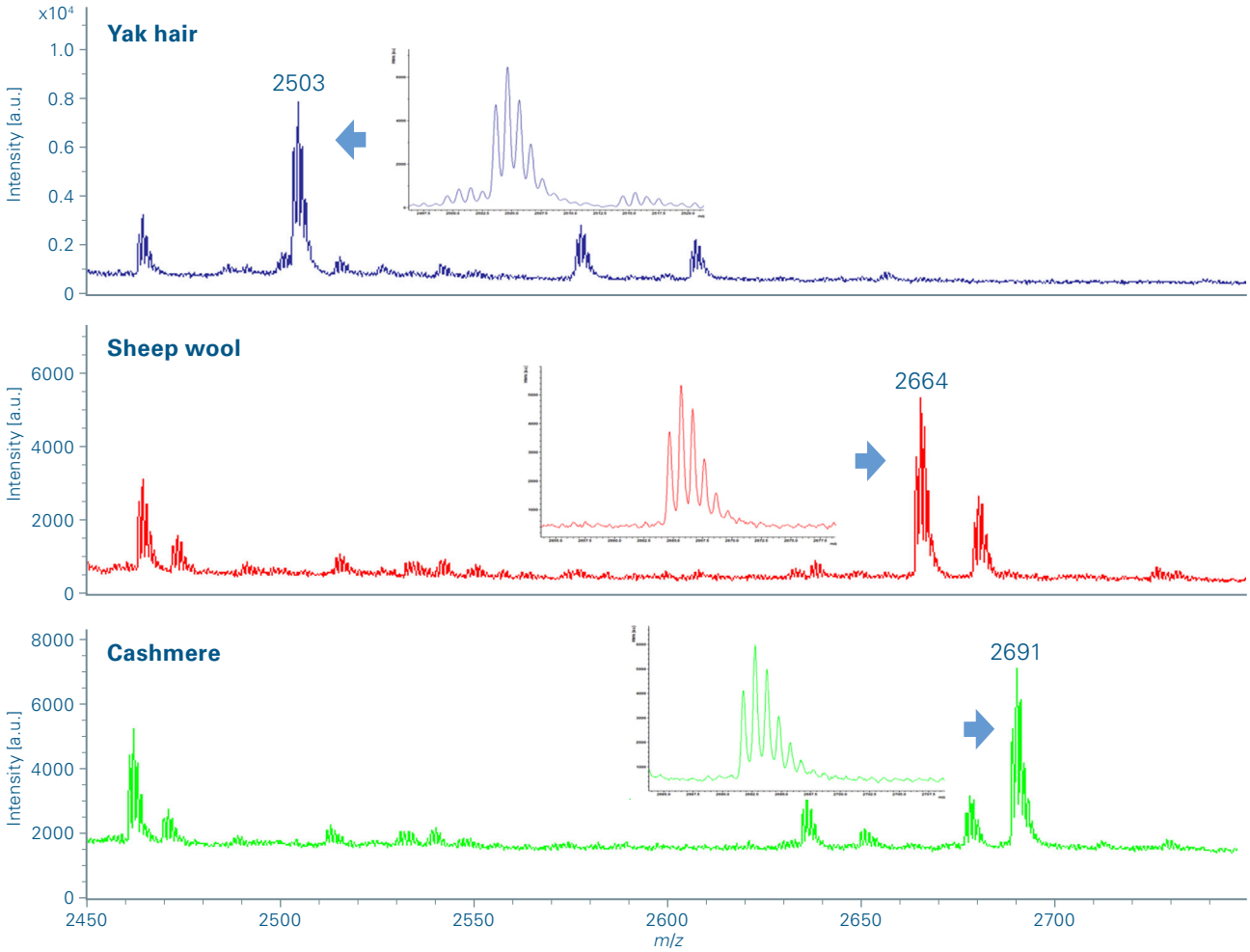

Figure 2. Characteristic peaks of cashmere, sheep wool and yak hair analyzed by MALDI-TOF-MS.

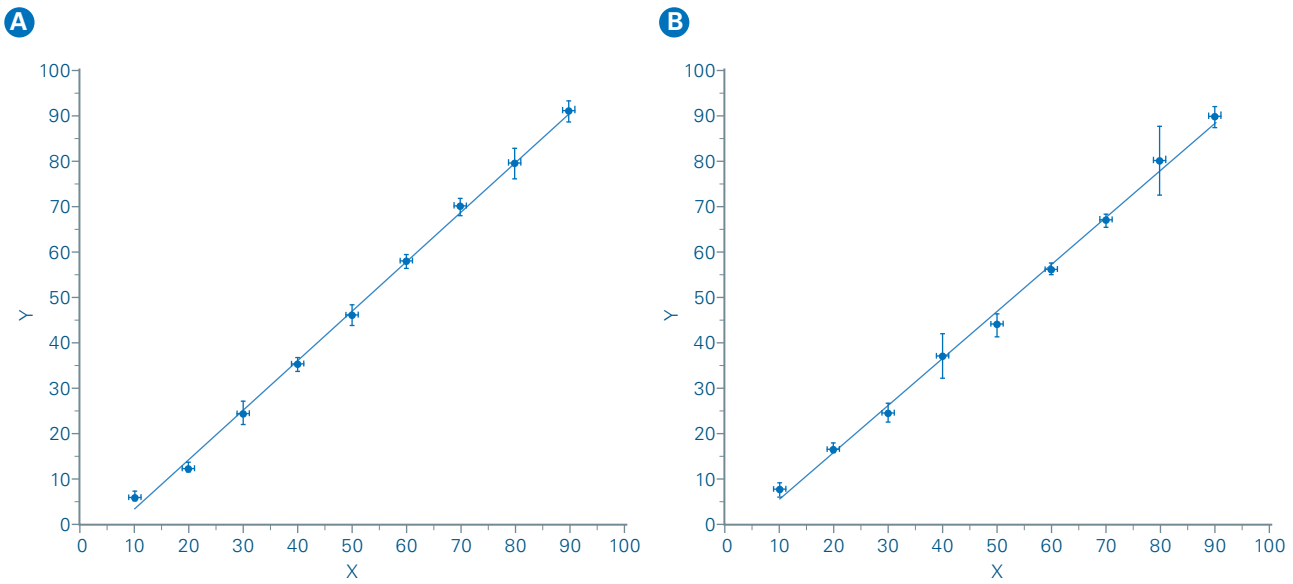

Figure 3. (A) Standard curve of cashmere-sheep wool mixtures. (B) Standard curve of cashmere-yak hair mixtures.

Extended Application: Identification of Shahtoosh in Illegal Trade

Through a similar analytical process, the 2606 *m/z* peak was identified as a characteristic marker for shahtoosh identification (Figure 4).

Experimental verification on blended textiles containing five types of animal hair (yak, alpaca, shatoosh, sheep wool, cashmere) demonstrated clear differentiation between shahtoosh and other animal fibers (Figure 5).

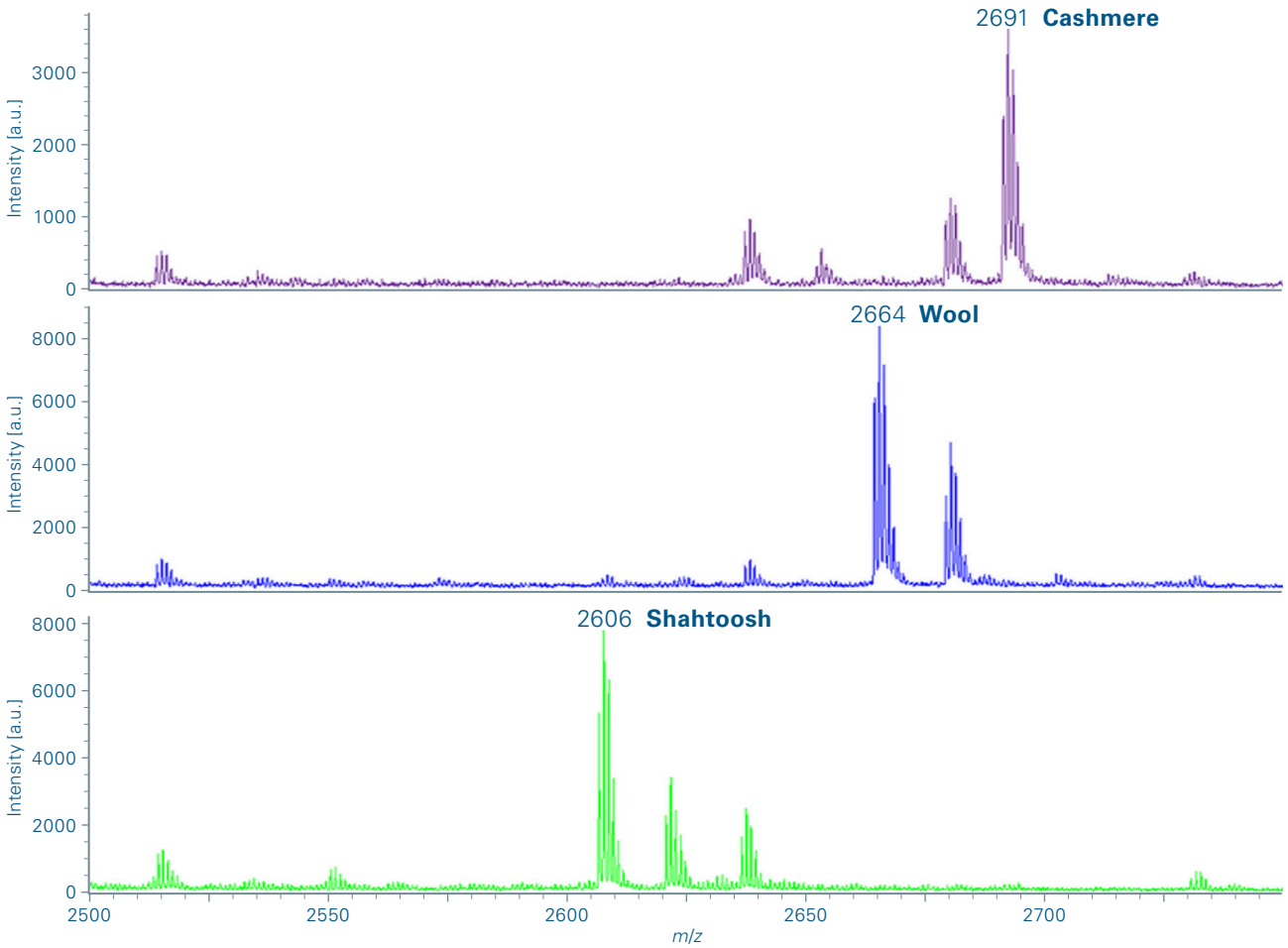

Figure 4. Species-specific peptide peaks of cashmere, sheep wool and shahtoosh.

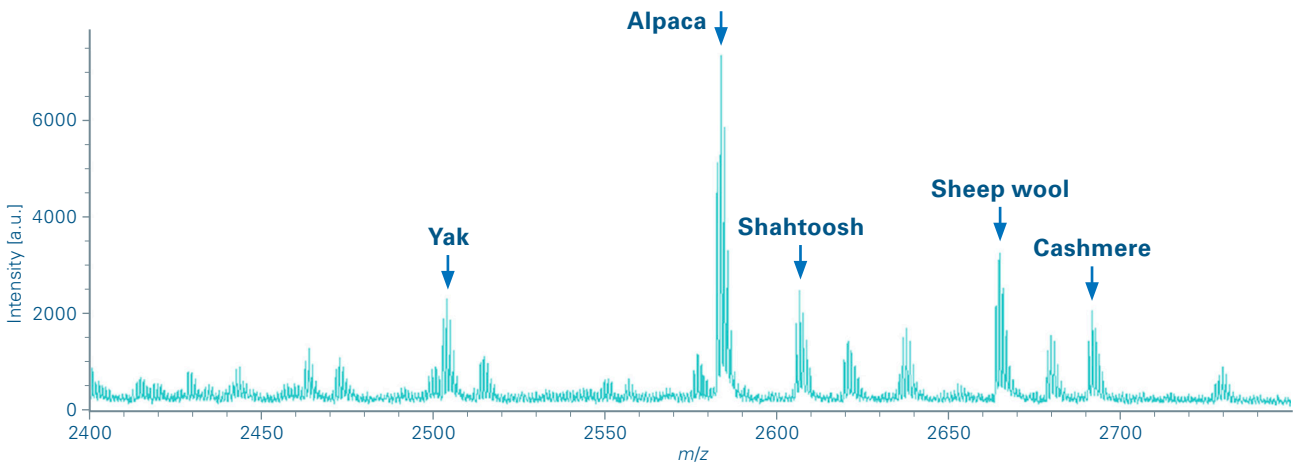

Figure 5. MALDI-TOF mass spectra of the multimixture.
From left to right: 2503 *m/z* (yak), 2583 *m/z* (alpaca), 2606 *m/z* (shahtoosh), 2664 *m/z* (sheep wool), and 2691 *m/z* (cashmere).

Mixed samples of shahtoosh-cashmere with varying proportions were prepared to establish a standard curve (Figure 6). Dyed and processed samples were used for testing, proving the method's effectiveness in accurately quantifying shahtoosh content.

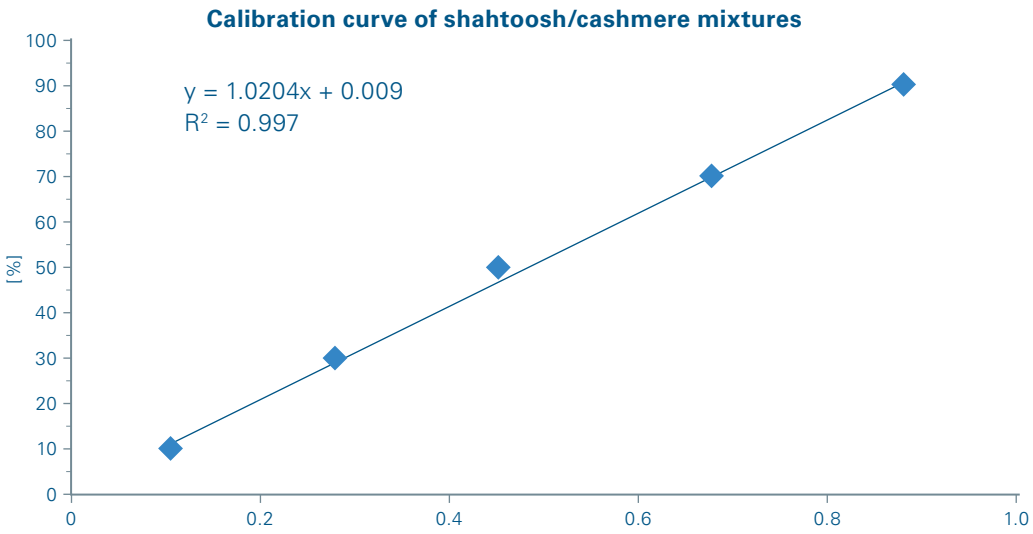

Figure 6. Standard curve of shahtoosh-cashmere mixtures.

Conclusions

Our MALDI-TOF workflow accurately identifies animal hair species in textiles and quantifies their content with high robustness. This technology is also applicable to other fields, such as food adulteration detection.

Advantages of Bruker MALDI-TOF for authentication analysis:

- Accurate Qualitative and Quantitative Data—Identify "what" and measure "how much."
- Easy Data Readout—One sample-One spectrum approach is simpler and more intuitive in getting direct answers compared with conventional LC or LC-MS.

References

[1] GB/T 42699.2-2023. *Textiles—Qualitative and Quantitative Proteomics Analysis of Some Animal Hair Fibers—Part 2: Peptide Detection Using MALDI-TOF-MS.*

[2] Fei J, et al. (2022). *A protein analysis-based method for identifying shahtoosh.* Forensic Science International **336**: 111341.

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