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A Novel Method to Discriminate between Natural and Synthetic Fibers by Stable Carbon, Nitrogen, and Oxygen Isotope Analyses

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We determined stable carbon, nitrogen, and oxygen isotopic compositions (δ^{13}C, δ^{15}N, and δ^{18}O) of fibers to discriminate between plant, animal, and synthetic fibers. The δ^{13}C and δ^{15}N values of synthetic fibers are significantly lower than animal fibers. Cashmere and alpaca have relatively lower δ^{18}O values than other animal fibers. Moreover, there are significant differences between acrylic and cashmere (e.g., in δ^{15}N values). These results suggest that the stable carbon, nitrogen, and oxygen isotope analysis would be useful in discrimination of natural and synthetic fibers.

Cashmere hair is one of the most famous and valuable natural fibers. It is luxuriously soft, lightweight, and warm. Cashmere is an extremely rare fiber and is available in limited supply. One goat yields up to 450 g cashmere fiber. The demand for cashmere continues to grow globally. As a result, cashmere is blended with wool and other fibers and sold as 100% cashmere all over the world.

Mislabeling of luxury fibers in textiles is a growing problem for Japanese retailers. There have been serious mislabeling problems since 2007. In particular, cashmere products blended with acrylic fiber is sold as 100% cashmere in Japan. Acrylic fiber is a synthetic fiber and has a wool-like feel. It has recently been used in clothing as a cheaper alternative to cashmere. Due to the similar feeling of acrylic and cashmere, a great number of cashmere garments are mislabeled. In 2010, Tokyo Metropolitan Bureau of Citizens and Cultural Affairs reported spot testing of garments sampled from internet retailing. They have analyzed the fiber content of 50 textiles such as scarfs and the stoles labeled cashmere using microscope methods.[1] It was reported that 13 items did not reflect their true fiber contents and eight items labeled more than 80% cashmere were not cashmere at all. Furthermore, four items labeled cashmere 100% were made from 100% acrylic.

To protect consumers and manufacturers from deceptively labeled wool fabrics and mislabeled wool garments in Japan, Japanese Industrial Standard (JIS) specifies testing methods to analyze quantitatively the fiber mixtures of textiles.[2] This standard specifies three test methods; release (classifying textiles according to type of fiber with the naked eye), dissolution (removing others except for target fiber in textiles by solvent), and microscopy (use of an optical or electron microscope). In particular microscopy can detect significant differences in the scale structure of the fibers. On the other hand, microscopy requires expert training. Moreover, the analytical time of the microscope method is very long, about 1 h per sample. A simple analytical method, which rapidly finds the fiber content of textiles, is necessary to resolve these problems.

Stable isotope analysis has widely been used to trace the origin of organic materials in various fields, such as ecology, biochemistry, and food authenticity.[3–5] Generally, the isotopic compositions of plant and animal reflect growth environments such as source materials (e.g., CO_2, H_2O, NH_4, and NO_2) and food sources.[6–8] It has also been used for raw material origin and geographical origin of chemical products such as alcohols and plastics.[9,10] Therefore, in this study, we evaluate the applicability of stable carbon, nitrogen, and oxygen isotope analysis to discriminate between natural and synthetic fibers. The recent spread of elemental analyzer/isotope ratio mass spectrometry (EA/IRMS) facilitates a rapid and routine analysis of the isotopic composition of organic materials. This technique will be important for securing reliability of natural products.

We collected fibers: plant fiber from cotton ($n = 4$) and from corn ($n = 1$); animal fiber from wool ($n = 3$), from alpaca, and from cashmere ($n = 3$); and synthetic fibers polyacrylate ($n = 3$), nylon ($n = 3$), and polyester ($n = 3$). A commercial scarf ($n = 1$) was purchased from a retail store. This product was labeled "100% cashmere." Each sample (50–100 mg) was cut to a fine powder. For carbon and nitrogen, 1.0 mg samples were weighed into a tin capsule (5 × 9 mm). Then, each sample was analyzed by EA/IRMS using a Finnigan Delta V (Thermo Electron Corporation) interfaced with a Flash EA 1112 (Thermo Electron Corporation) to determine carbon and nitrogen isotope ratios. For oxygen, each 0.5 mg sample was weighed into a silver capsule (5 × 9 mm). Then, oxygen isotope analysis was carried out by thermocombustion EA/IRMS (TCEA/IRMS) using a Finnigan Delta V interfaced with a Finnigan TCEA (Thermo Electron Corporation). The isotopic composition was reported in the δ notation:

$$\delta(‰) = (R_{sample}/R_{standard} - 1) \times 1000 \quad (1)$$

where R_{sample} is the isotope ratio (i.e., $^{13}C/^{12}C$, $^{15}N/^{14}N$, and $^{18}O/^{16}O$) of the sample, and $R_{standard}$ is the isotope ratio of the international standards: for carbon, Peedee Belemnite (PDB); for nitrogen, Air; and for oxygen, Standard Mean Ocean Water (SMOW). Isotope value is given per mil (‰).

The δ^{13}C values of natural fibers range from −26.8‰ to −25.6‰ for cotton, −10.8‰ for corn, from −25.5‰ to −16.2‰ for wool, from −23.0‰ to −22.8‰ for alpaca, and from −22.2‰ to −19.4‰ for cashmere (Figure 1). The δ^{13}C values of synthetic fibers range from −26.5‰ to −23.3‰ for acrylic, −27.8‰ for nylon, and from −27.3‰ to −27.6‰ for polyester. The synthetic fibers show lower δ^{13}C values than animal tissues. The synthetic fibers are derived from petroleum, of which δ^{13}C values range from −32.5‰ to −23.3‰.[7] These results suggest that the δ^{13}C values of synthetic fibers reflect the raw material. The δ^{13}C value of plant fiber derived from corn is

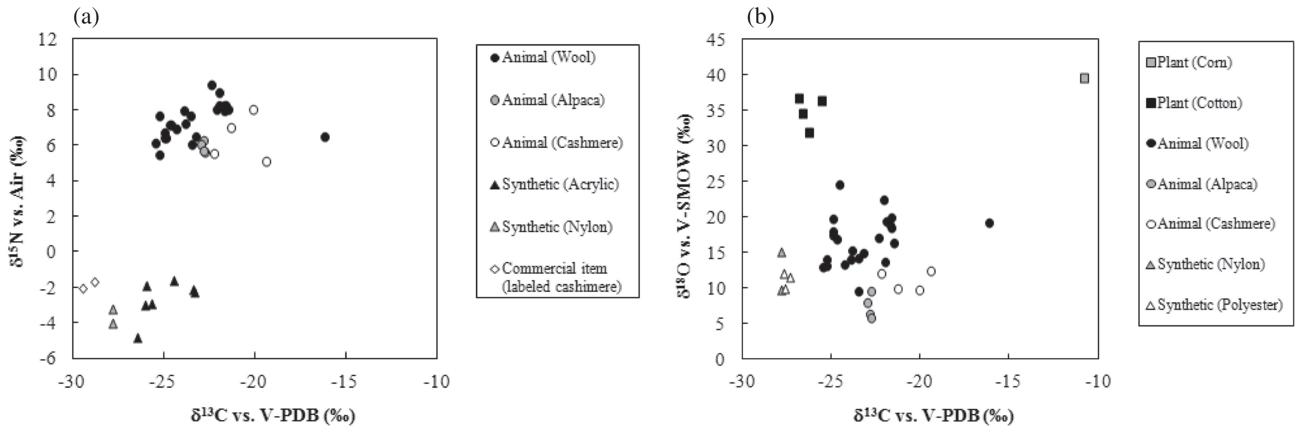

Figure 1. The carbon and nitrogen isotopic compositions (a) and carbon and oxygen isotopic compositions (b) of natural and synthetic fibers.

significantly higher than those from cotton ($P < 0.001$), reflecting the different photosynthesis pathway and resulting in different δ^{13}C signatures between C_3 and C_4 plants[6] (Figure 1b).

The δ^{15}N values of natural fibers range from +5.5‰ to +9.4‰ for wool, from +5.6‰ to +6.3‰ for alpaca, and from +5.1‰ to +8.0‰ for cashmere (Figure 1a). The δ^{15}N values of synthetic fibers range from −4.8‰ to −1.6‰ for acrylic and from −4.0‰ to −3.2‰ for nylon. The nitrogen peak of plant fibers and polyester could not be detected because plant fibers have low nitrogen content and polyester has no nitrogen. The nitrogen in synthetic fibers is derived from atmospheric nitrogen, of which δ^{15}N values are 0‰.[11] Synthetic fibers including nitrogen have significantly lower δ^{15}N values than animal fibers ($P < 0.001$). Thus, δ^{15}N value provides useful information about discriminating between natural and synthetic fibers.

The δ^{18}O values of natural fibers range from +31.6‰ to +36.4‰ for cotton, +39.5‰ for corn, from +9.6‰ to +24.5‰ for wool, from +6.3‰ to +9.5‰ for alpaca, and from +9.7‰ to +12.5‰ for cashmere (Figure 1b). The δ^{18}O values of synthetic fibers range from +9.8‰ to +15.0‰ for nylon and from +9.9‰ to +12.1‰ for polyester. For acrylic, oxygen was not detected because acrylic does not have oxygen. The δ^{18}O values of plant fibers are significantly higher than those of animal ($P < 0.001$). The δ^{18}O values of cellulose generally range from +25 to +35‰,[12] whereas those of international human hair range from +11.9 to +18.1‰.[8] The synthetic fibers have relatively lower δ^{18}O values because the oxygen may originate mainly from meteoric water.

The cashmere and alpaca fibers have lower δ^{18}O values than other wool fibers, probably reflecting the δ^{18}O value of precipitation in their growth environment. The oxygen isotopic composition of animal tissue mainly reflects that of drinking water.[8] The δ^{18}O values of meteoric waters are related to geographical parameters such as air temperature, latitude, altitude, distance from the coast, and intensity of precipitation.[8] Significant supplier countries of cashmere are China, Mongolia, and Tibet, which are located in the high plateaus of Asia. Moreover, alpaca mainly inhabits an altitude of 3500 to 5000 m above sea level in the Andes of southern Peru. Thus, the altitude differences in growth condition are probably reflected in the δ^{18}O values of animal fibers.

The δ^{13}C, δ^{15}N, and δ^{18}O values of commercial cashmere scarf (Figure 1) were compared with the values of reliable samples. The commercial scarf (labeled "100% cashmere") showed a more negative δ^{13}C and δ^{15}N value (−29.5‰ and −2.1‰) than all animal fibers (average −20‰ and +4.5‰). An oxygen peak was not detected. These results suggest that this commercial cashmere scarf mainly consists of synthetic fibers such as acrylic.

Further statistical investigation based on a large number of samples is required. However, this study clearly demonstrates that carbon, nitrogen, and oxygen isotopic composition can discriminate plant, animal, and synthetic fibers (Figure 1). Particularly, it is possible to detect the addition of acrylic to cashmere by measuring the δ^{15}N values. Moreover, the analytical time of the EA/IRMS method (about 20 min per sample) facilitates the investigation of a large number of samples. Therefore, we strongly suggest that stable isotope analysis be employed as a new potential method to identify the synthetic fibers.

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