Analysis of Single Synthetic Fibers Using a Portable Total Reflection X-ray Fluorescence Spectrometer

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In this study, single synthetic fibers obtained from several textile products were analyzed by a portable total reflection X-ray fluorescence spectrometer. Characteristic elements, which would originate from such materials as catalysts, delustering agents, and dyes used for manufacturing synthetic fibers, were detected from single synthetic fiber samples, and the difference in the types of characteristic elements among the single synthetic fiber samples was observed.

Keywords Identification, portable, single fiber, synthetic fiber, X-ray fluorescence

(Received May 13, 2021; Accepted July 9, 2021; Advance Publication Released Online by J-STAGE July 16, 2021)

Introduction

Fragments of textile fibers collected at a crime scene and those collected from a suspect and a crime victim can play a key role in criminal investigations. For example, a case that the criminal and a knife used in a crime were specified by detecting fibers originating from the crime victim’s clothing from the knife was introduced in Ref. 1. Therefore, in order to determine whether a fiber sample originates from a suspect (or a crime victim), a method to distinguish the difference among fibers is needed.

X-ray fluorescence (XRF) analysis and total reflection X-ray fluorescence (TXRF) analysis make it possible to perform non-destructive elemental analysis of textile fibers. Prange et al.2 applied TXRF analysis to single textile fiber analysis. Koons3 conducted energy dispersive XRF analysis of carpet fibers. Nishiwaki et al.4 performed XRF analysis of single white polyester fibers obtained from trunk mats and clothing using synchrotron radiation, and they used the difference in the types of detected elements and the ratio of intensities of fluorescent X-ray peaks of detected elements for distinguishing the difference among polyester fibers. TiO₂ is commonly used as a delustering agent for fibers,5 and Zr6 and Nb7 originating from impurities in TiO₂ were detected from polyester fiber samples by using synchrotron radiation. Takahara et al.7 performed TXRF analysis of single black polyester fibers obtained from trunk mats, and they used principal component analysis for the purpose of classifying these fibers. As described above, the information about elements originating from materials used for manufacturing synthetic fibers can contribute to distinguishing the difference among synthetic fibers with similar colors.

In order to conclude that a textile fiber sample originates from a suspect (or a crime victim), multiple types of information such as chemical component and color obtained from the fiber sample should be compared with those obtained from fiber samples from the suspect’s textile product (or the crime victim’s textile product). Therefore, multiple types of analytical methods should be employed for the identification of fibers. For example, microspectrophotometry is used for comparing colors of fiber samples whose morphologies and color tones are similar to one another, and Fourier transform infrared (FT-IR) microscopy is used for investigating the materials of fibers.8 Raman spectroscopy can be used for identifying main dyes in fibers.8 However, it is not desirable to obtain multiple types of information from all textile fiber samples using multiple analytical methods because the time required for identifying fibers becomes long. Therefore, screening for textile fiber samples needed to be analyzed by multiple methods for performing highly accurate identification should be performed for reducing the time required for identifying fibers. Textile fiber samples, whose origins are obviously different from a suspect’s textile product (or a crime victim’s textile product), would be determined by only comparing the types of detected elements even when the colors and morphologies of these fiber samples observed by using an optical microscope are similar to those of fibers originating from the suspect (or the crime victim). Therefore, qualitative XRF (or TXRF) analysis can be used to screen for fiber samples that are needed to be analyzed by other methods for determining whether these fiber samples originate from a suspect’s textile product (or a crime victim’s textile product). Because multiple elements are detected in one measurement when using energy dispersive XRF (or TXRF) analysis, rapid screening for fiber samples can be performed.

A portable TXRF spectrometer9 was developed in 2006. This portable TXRF spectrometer has been improved since 2006 in...
order to improve the detection limit, and a detection limit of 8 pg\textsuperscript{10} was achieved for Cr in the dry residue of a solution sample. Recently, this portable spectrometer was applied to the elemental analysis of single hog hairs colored with commercially available hair dye products.\textsuperscript{11} This highly sensitive portable spectrometer can be applied to on-site elemental analysis of single textile fiber samples. By performing on-site screening for fiber samples, the time required for identifying fibers using multiple analytical methods will be reduced. In this study, single synthetic fibers obtained from several textile products were analyzed by a portable TXRF spectrometer in order to discuss the possibility that this portable spectrometer can be applied to on-site screening for fiber samples. Single polyester fibers, a single acrylic fiber, and a single nylon fiber were analyzed because these types of synthetic fibers are widely used for clothing.

**Experimental**

In this study, strands of white polyester fibers, which were referred to as polyester fiber A, polyester fiber B, polyester fiber C, and polyester fiber D, were obtained from four different textile products. A strand of polyester fiber A was obtained from a semi dull yarn. Strands of polyester fibers B and D were obtained from two different spun threads, and a strand of polyester fiber C was obtained from a filament thread. Strands of black polyester fibers, which were referred to as polyester fiber E and polyester fiber F in this study, were obtained from two different spun threads. A single white acrylic fiber was obtained from a yarn, and a single black nylon fiber was obtained from clothing. Sewing threads used for obtaining strands of polyester fibers B, C, and F were manufactured by the same Japanese company, and those used for obtaining strands of polyester fibers D and E were manufactured by the same Japanese company. Single fiber samples described above were analyzed by a portable TXRF spectrometer. The setup of the portable spectrometer used in this study is explained in a previous paper.\textsuperscript{12} The tube voltage and the tube current of an X-ray tube 50 kV Magnum (Moxtek Inc., Orem, UT, USA) having a tantalum anode were set to 25 kV and 0.2 mA, respectively. An X-ray waveguide, which was used as the collimator, was placed between the X-ray tube and an analyte, and the sizes of the entrance and exit apertures for passing X-rays of the waveguide were 0.03 mm in height and 1 cm in width. A silicon drift detector VITUS H7 (Ketek GmbH, Munich, Germany) was used as an energy dispersive X-ray detector. Both ends of a single fiber sample, which was placed on a quartz glass substrate with a diameter of 30 mm and a thickness of 5 mm, were attached with adhesive tapes. A quartz glass substrate on which a single fiber sample was placed was tilted at 0.05° to the horizontal in order to set the glancing angle of the incident X-ray beam with respect to the quartz glass substrate to 0.05°. A single fiber sample for the measurement was obtained from a bundle of fibers with a length of about 3 cm that was cut from a textile product. The angle between a single fiber sample on the quartz glass substrate and the irradiation direction of the incident X-ray beam was set to about 90°. The spectra of single fibers were measured in air for 600 s, except for the spectrum of a strand of polyester fiber A, and a strand of polyester fiber A was analyzed in air for 1800 s.

The cross sections of a strand of polyester fiber A, a single acrylic fiber, and a single nylon fiber were observed by an optical microscope ECLIPSE LV100ND (Nikon Solutions Co. Ltd., Shinagawa, Japan) in order to estimate their diameters; the long diameters of these single fibers were ten and several micrometers. An analyte for observing a cross section of a single fiber was prepared as follows: (1) ten single fibers obtained from a textile product were embedded in a glue; (2) they were then sliced using a microtome RM2125 RTS microtome (Leica Biosystems K. K., Germany).

**Results and Discussion**

Figure 1 shows representative XRF spectra of a quartz glass substrate, strands of polyester fibers A, B, C, and D, and a white acrylic fiber. Figures 1d and 1e show the XRF spectra of three different strands of polyester fiber C and those of three different strands of polyester fiber D. Figure 2 shows enlarged views of Figs. 1b, 1c, 1f, and the spectrum denoted by a black solid line in Fig. 1e in the X-ray energy range from 3 to 5 keV. The Si Kα line, Ar K lines, and Ta L lines in Fig. 1 were attributed to the quartz glass substrate, air containing 0.9% of Ar, and the anode material of the X-ray tube, respectively. The spectral backgrounds in Figs. 1c - 1f were as low as or slightly higher than that in Fig. 1a. This result showed that the scattering of the incident X-ray beam from a single synthetic fiber on a quartz glass substrate was weak. Although the backgrounds were low when single fiber samples were measured by using the portable TXRF spectrometer, the measured spectra were referred to as XRF spectra in this study. The Ti K lines were detected from polyester fiber A as shown in Fig. 1b. A peak was observed around 3.65 keV in Fig. 1b. The energy of the Si Lα line (3.61 keV) is near to that of the Ca Kα line (3.69 keV). Therefore, when a peak is observed in the X-ray energy range from 3.6 to 3.7 keV, determining whether this peak originates from Ca or Sb is needed. As shown in Fig. 2a, the energy of the peak observed at around 3.65 keV in Fig. 1b was lower than that of the Ca Kα line in Fig. 1f, but higher than that of the Sb Lα line. A tiny protrusion appeared in the X-ray energy range from 3.8 to 3.9 keV in the spectrum of a strand of polyester fiber A as shown in Fig. 2a, and this tiny protrusion would be attributed to the Sb Lβ line (3.84 keV). Therefore, we concluded that the peak observed around 3.65 keV in Fig. 1b was the sum of the Sb Lα line and the Ca Kα line. The Ba L lines were detected from polyester fiber B as shown in Fig. 1c, and the S and Ca Kα lines also appeared in Fig. 1c. As shown in Fig. 1d, a weak Ca Kα line, whose ratio of the net intensity of the Ca Kα line to the value obtained by multiplying the square root of the background intensity by 10 was lower than 1, was observed from one of three different strands of polyester fiber C, but the Ca Kα line was hardly observed or not detected from the other two. As shown in Fig. 1e, a weak peak at around 4.5 keV, whose ratio of the net intensity of this peak to the value obtained by multiplying the square root of the background intensity by 10 was lower than 1, was detected from one of three different strands of polyester fiber D, but this peak was not detected from the other two. The energy of the Ti Kα line (4.51 keV) is near to that of the Ba Lα line (4.47 keV). When the Ti Kβ line (4.93 keV) and the Ba Lβ line (4.83 keV) were not observed in an XRF spectrum, determining whether a peak observed around 4.5 keV originates from Ti or Ba is needed. As shown in Fig. 2b, the energy of the weak peak observed around 4.5 keV in the spectrum denoted by a black solid line in Fig. 1e was higher than that of the Ba Lα line in Fig. 1c, and was near to that of the Ti Kα line. Therefore, we concluded that this weak peak in Fig. 1e was the Ti Kα line. As mentioned above, weak Ca and Ti peaks were not always detected as shown in Figs. 1d and 1e. This may be attributed to inhomogeneous...
distributions of Ca and Ti. Another possibility is that the Ca peak in Fig. 1d and the Ti peak in Fig. 1e may be due to contamination that occurred during placing a single fiber sample on the sample holder. The S, Cl, and Ca Kα lines were detected from the acrylic fiber as shown in Fig. 1f. Ti detected from polyester fiber A would originate from TiO2 acting as a delustering agent. Antimony compounds are used as catalysts for manufacturing polyethylene terephthalate, which is a type of polyester,13 and Sb detected from polyester A would be due to a catalyst. Biver et al.13 reported that the concentration of Sb in six textile products made from polyester ranged from 125 to 471 μg/g. Therefore, several hundred μg/g of Sb may remain in polyester fibers when an antimony compound is used as a catalyst. Disperse dyes are used for dyeing polyester fibers.15 A disperse dye containing Br (Disperse Blue 291:1) was frequently detected from black polyester fibers obtained from gloves,16 and therefore the Br peaks in Figs. 3a and 3b would originate from a disperse dye containing Br. The Cr K lines in Fig. 3c would originate from either an acid mordant dye or a chromium complex dye. These types of dyes are usually used for coloring nylon fibers.17

In this study, characteristic elements that would be attributed to materials such as catalysts, delustering agents, and dyes were detected by analyzing single synthetic fiber samples using the portable TXRF spectrometer; the difference in the types of characteristic elements among several synthetic fiber samples was observed as shown in Figs. 1 and 3. This result shows that the difference among single fiber samples can be distinguished.

Fig. 1 Representative XRF spectra of (a) a quartz glass substrate, polyester fibers (b) A, (c) B, (d) C, and (e) D, and (f) a white acrylic fiber. Each XRF spectrum in Figs. 1b–1f was obtained from measuring a single fiber sample. In Figs. 1d and 1e, XRF spectra of three different strands of polyester fiber C and those of three different strands of polyester fiber D are shown. The insets in Figs. 1a, 1b, 1d, and 1e show magnified spectra in the X-ray energy range from 3 to 5 keV, and those in Figs. 1c and 1f show magnified spectra in the X-ray energy range from 2 to 4 keV.

d synthetic fibers. As shown in Fig. 3a, Ca and Br were detected from polyester fiber E. S, Ca, Br, and Ba were detected from polyester fiber F as shown in Fig. 3b. S, Ca, Ti, and Cr were detected from the nylon fiber as shown in Fig. 3c. Disperse dyes are used for dyeing polyester fibers. A disperse dye containing Br (Disperse Blue 291:1) was frequently detected from black polyester fibers obtained from gloves, and therefore the Br peaks in Figs. 3a and 3b would originate from a disperse dye containing Br. The Cr K lines in Fig. 3c would originate from either an acid mordant dye or a chromium complex dye. These types of dyes are usually used for coloring nylon fibers.
by only comparing the types of detected elements. However, elements whose fluorescent X-ray peaks were weak in spectra were not always detected as shown in Figs. 1d and 1e. In this study, when the net intensity of a fluorescent X-ray peak was lower than the value obtained by multiplying the square root of the background intensity by 10, this peak was defined as a weak peak. Therefore, the difference in the types of elements whose fluorescent X-ray peaks are clearly observed should be practically employed for determining whether the origin of a single fiber sample is different from that of a sample to be compared. The Ca peaks in Figs. 1c and 3b were also defined as weak peaks in this study. Elemental analysis of single synthetic fiber samples is performed by the portable TXRF spectrometer without the influence of colors of fibers, and this portable spectrometer can be used for distinguishing the difference among single fiber samples that cannot be distinguished by observing the morphologies and colors of these samples using an optical microscope. It is difficult to distinguish the difference among single synthetic fiber samples when the types of elements whose fluorescent X-ray peaks are clearly observed are the same among these samples. In such cases, these single fiber samples are needed to be analyzed by other methods such as microspectrophotometry and Raman spectroscopy for obtaining information other than the elements. Sample preparation for the analysis of a single fiber sample using the portable TXRF spectrometer is to place this fiber sample on a sample holder, and this simple sample preparation is suitable for performing the rapid analysis of multiple fiber samples. A single fiber sample fixed on a sample holder, which has been non-destructively analyzed by the portable spectrometer, can be reused without any change for obtaining information other than the elements using other analytical methods. The portable TXRF spectrometer can be applied to on-site screening for single synthetic fiber samples needed to be analyzed by other methods for performing highly accurate identification of fibers. Especially, by performing this screening method using the portable spectrometer after on-site screening for single synthetic fiber samples using an optical microscope, the number of single fiber samples that are needed to be analyzed by multiple methods will be efficiently reduced, and the time required for conducting identification of fibers will be reduced.

Conclusions

In this study, XRF spectra of single synthetic fibers obtained...
from several textile products were measured by a portable TXRF spectrometer. Characteristic elements, which would originate from materials used for producing synthetic fibers, were detected. The difference among single synthetic fiber samples was able to be distinguished by only comparing the types of characteristic elements detected from each single fiber sample. A synthetic fiber sample, which cannot be determined as to whether the origin of this sample is different from that of a sample to be compared by comparing the types of characteristic elements, is needed to be analyzed by other methods. Qualitative XRF analysis using the portable spectrometer makes it possible to perform on-site screening for synthetic fiber samples that are needed to be analyzed by other methods in order to perform the highly accurate identification of fibers.

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