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Comparison of Individual Carpet Fibers Using Energy Dispersive X-Ray Fluorescence

ABSTRACT: Energy dispersive X-ray fluorescence (XRF) provides the capability for elemental characterization of individual carpet fibers of a few millimeters in length. XRF is rapid, nondestructive, and provides adequate sensitivity to detect the presence of a variety of elements added to carpet fibers during their manufacture. Several metallic elements are commonly observed in automotive carpet fibers and are less frequently present in the residential carpet fibers in this study, making source classification of these fibers at least partially successful. Qualitative comparison of X-ray spectra may also provide some discrimination capability when used in conjunction with optical microscopy and polymer characterization.

A combination of optical, physical, and chemical measurements are used for the identification and comparison of fiber evidence. Historically, fiber examiners have relied most heavily on microscopy for physical and spectroscopic comparison of fiber features. Currently, most forensic laboratories also use chemical and instrumental methods to identify the polymers in synthetic fibers. Manufacturers of synthetic fibers and fiber products often add inorganic and metal-organic compounds to impart desired properties, such as resistance to ultraviolet degradation, colorfastness, and heat resistance. In particular, many automobile carpet fibers contain metallized dyes and other metal containing additives to prevent degradation in the harsh conditions to which these carpets are exposed. Determination of the elemental composition of fibers, might, therefore, provide useful information concerning their manufacture and intended use. Despite this, forensic fiber examinations, for the most part, do not consider inorganic constituents [for example, see (1)]. Reasons cited for the infrequent use of elemental analysis for fiber examination are small sample sizes, limited analytical capabilities, and the destructive nature of some analytical methods. Also, without study of the range of element compositions present in synthetic fibers, their usefulness for source discrimination remains largely conjectural.

Several analytical methods have been used in forensic laboratories to determine elemental concentrations in small solid samples. These include neutron activation analysis (NAA), scanning electron microscopy-energy dispersive X-ray fluorescence (SEM-EDX), X-ray fluorescence (XRF), mass spectrometry, and atomic absorption and emission spectrophotometries. Of these methods, NAA, SEM-EDX, and XRF are the only ones that are, for the most part, nondestructive to the sample. NAA requires access to a nuclear reactor or other source of thermal neutrons and may render the evidence radioactive for a period of time, making it impractical for most forensic laboratories. SEM-EDX is widely available in forensic laboratories, accommodates small sample sizes, and is relatively nondestructive to the fiber. However, a preliminary evaluation of SEM-EDX for direct carpet fiber analysis in the FBI Laboratory showed that the concentrations of most elements needed for fiber source characterization are too low to be readily detectable.[2] XRF is used in forensic laboratories to detect the presence of a wide range of elements present at concentrations of about 10 $\mu g/g$ or greater in trace evidence, such as glass (2,3) and paint chips (4). Despite its sensitivity, XRF has not been widely used for analysis of individual fibers.

A study was undertaken to determine the feasibility of measuring the elemental composition of carpet fibers by XRF for purposes of classification and comparison of sources. This study was designed to address the question of whether elemental compositions can be used to classify carpet fibers into two intended usage classes, automotive and residential. The data from this study was also examined to evaluate the usefulness of elemental composition as a point of comparison for discriminating among similar fibers. This paper presents the results of these studies.

Materials and Methods

Sample Descriptions

Fibers for this study were taken from 100 carpet samples, 50 each automotive and residential. The samples were selected from collections at the FBI Laboratory and from local carpet dealers in 1989. The samples are not meant to be representative of any larger population of fibers, but rather a test set to determine the feasibility of the use of element concentrations for classification and comparison. The samples represent a variety of colors and several polymer compositions. Selected characteristics of the 100 fiber samples are given in Table 1. The fiber type listings in Table 1 were provided by the manufacturers; those fibers listed as olefins or nylons have not been further subclassified. The first letter of each sample designation, A or R, indicates whether the carpet was manufactured

TABLE 1—*Description of carpet fibers used for elemental composition study. (Fiber Types: N = nylon, PP = polypropylene, PE = polyethylene, O = olefin).*

Sample No.	Fiber Type	Color	Carpet Source
A001	PP	Light Saddle 7769	General Motors
A002	PP	Medium Beige 8248	General Motors
A003	PP	Medium Antelope 9102	General Motors
A004	N	Medium Beige 5090	General Motors
A005	N	Light Chamois 8584	General Motors
A006	N	Dark Yellow 8803	General Motors
A007	N	Medium Driftwood 8802	General Motors
A008	N	Medium Saddle 8806	General Motors
A009	N	Medium Saddle 7770	General Motors
A010	N	Dark Rosewood 8843	General Motors
A011	N	Medium Sage 8578	General Motors
A012	N	Medium Pearl Gray 8849	General Motors
A013	N	Medium Dark Gray 8247	General Motors
A014	N	Blue 1208	General Motors
A015	N	Dark Blue 8576	General Motors
A016	N	Dark Sapphire 8841	General Motors
A017	N	Medium Cadet Blue 92969	Ford
A018	N	Medium Cadet Blue 81848	Ford
A019	N	Light Oxford Gray 82257	Ford
A020	PP	Medium Spruce 5083093002	Ford
A021	N	Medium Canyon Red 81819-2	Ford
A022	PE	Dark Teal C2769-3393	Ford
A023	PE	Char Gray C2790-3391	Ford
A024	PE	Char Gray SA-595-B	Ford
A025	PP	Char Gray 84924	Ford
A026	N	Light Sand Beige 82964-10	Ford
A027	N	Aegean 83650-13	Ford
A028	N	Medium Titanium 84849-F3	Ford
A029	N	Light Oxford Gray 500	Ford
A030	N	Taupe 83860-2	Ford
A031	PP	Mahogany	Chrysler
A032	PP	Dark Tundra	Chrysler
A033	N	Dark Tundra	Chrysler
A034	PP	Tundra	Chrysler
A035	N	Medium Buckskin	Chrysler
A036	PP	Medium Almond 5086	Chrysler
A037	PP	Bordeaux 2062	Chrysler
A038	PP	Red 2016	Chrysler
A039	PP	Midnight Blue	Chrysler
A040	N	Dark Blue JB9	Chrysler
A041	PP	Midnight Blue JB8-75	Chrysler
A042	PP	Twilight Blue JB8-46	Chrysler
A043	PP	Blue 238	General Motors
A044	N	Charcoal 1250	General Motors
A045	PP	Black 120	General Motors
A046	PP	Black 904	General Motors
A047	N	Black 848	General Motors

TABLE 1—*Continued.*

Sample No.	Fiber Type	Color	Carpet Source
A048	PE	Black 15BBT	General Motors
A049	PP	White 179	General Motors
A050	N	White 181BT	General Motors
R001	N	Rubellite 70854	Monsanto
R002	N	Persian Sapphire 631	Du Pont
R003	N	Shimmering Taupe 1801	Du Pont
R004	N	Amethyst Shadow 6391	Allied
R005	N	Copenhagen 657	Du Pont
R006	N	Silver Lining 208	Du Pont
R007	N	Sea Sand 394	Du Pont
R008	N	Bateau Blue 14	Du Pont
R009	N	Melon 4389	Monsanto
R010	N	Peach Bud 4327	Monsanto
R011	PP	Opalescence	Du Pont
R012	PP	Faded Denim	Du Pont
R013	N	Volcano	Du Pont
R014	N	Deep Water	Du Pont
R015	N	Plum Sugar	Du Pont
R016	PP	Aqua Tint	Du Pont
R017	PP	Sea Fog	Du Pont
R018	N	Aqua Tint	Du Pont
R019	N	Cerise	Du Pont
R020	N	Soft Dawn	Du Pont
R021	N	Dusty Rouge	Du Pont
R022	N	Star Sapphire	Du Pont
R023	N	Desert Blush	Du Pont
R024	N	Aqua Haze	Du Pont
R025	N	Neutral Tweed 6463	BASF
R026	N	Rose Dawn 3356	BASF
R027	N	Glistening Red 3734	BASF
R028	N	Teal Shadow 87351	BASF
R029	O	Bahama Green 19375	Amoco
R030	O	Mistletoe 19360	Amoco
R031	O	Mint Julep 19373	Amoco
R032	O	Tapestry Rose 19325	Amoco
R033	O	Azure Green 19371	Amoco
R034	O	Vermeil 19441	Amoco
R035	O	Baroque Blue 19496	Amoco
R036	N	Maxton Rose	Allied
R037	N	Essex Blue	Allied
R038	N	Manahasset Gray	Allied
R039	N	Bridgeport Beige	Allied
R040	N	Quoquetoe Blue	Allied
R041	N	Heather 578	Du Pont
R042	N	Golden Straw 851	Du Pont
R043	N	Desert Sand 901	Du Pont
R044	N	Ivory 42	Du Pont
R045	N	Cinnamon 549	Du Pont
R046	N	French Sapphire	Monsanto
R047	N	Jamaican Sea	Monsanto
R048	N	Vinrose	Monsanto
R049	N	Barn Siding	Monsanto
R050	N	Helm Oak	Monsanto

for automobile or residential use. Five of the samples, A023, A024, A025, R012, and R036 contain two fiber colors in the carpet yarn. These samples were each subdivided into light and dark portions, making a total of 53 automotive and 52 residential fibers.

Instrumental Methods

Energy dispersive X-ray fluorescence spectra were obtained using direct X-ray excitation of individual fiber samples. The instrument used for this study (Kevex Model 0700) used a 125-watt rhodium (Rh) X-ray tube operated at 35 KV. The Rh X-rays were collimated through a 3-mm orifice and filtered through a 0.15-mm thick aluminum foil before impinging on the sample. With this configuration, the maximum X-ray intensity falls in an oblong area of approximately 3 by 8 mm in the sample plane.

Emitted X-rays were detected with a Si(Li) detector with a resolution of 160 eV at 6.4 KeV. Spectra were collected on a multichannel analyzer with 1024 channels at a gain of 20 ev/channel to cover the range of 0 to 20.48 KeV. The filter to sample and sample to detector distances were each approximately 10 mm. These conditions produce XRF spectra which have low background intensities and good detection of elements in the 5 to 8 KeV region, the portion of the X-ray spectrum corresponding to the K-lines of the first row transition metals. Removal of the aluminum filter produces more intense X-ray fluorescence because of more effective excitation by the Rh L- lines, but the peak/background ratio is

degraded by higher background count rates. Other excitation and detection conditions yield improved detection of selected elements in specific regions of the spectrum, so in practice the X-ray excitation conditions can be tailored specifically for each fiber sample. However, for this feasibility study, one set of excitation conditions was used for all 105 samples.

The samples were single fibers of 5 mm or greater in length. The samples were suspended in the X-ray path by attaching each end of the fiber to the end of a piece of cellophane tape approximately 0.3 mm wide to form a continuous strip of tape-fiber-tape. The fiber was oriented in the sample holder so as to lie parallel to and centered on the principal energy axis of the incident X-ray beam. The cellophane tape used (Scotch Magic Tape, 3M) was selected because of its low concentrations of elements of interest. The sample chamber was evacuated to approximately 300 mbar during data acquisition. This method of sample attachment proved secure enough so that no loss of samples into the vacuum occurred.

An XRF spectrum was acquired for each sample until the total X-ray counts in the region from 13.5 to 14.5 KeV totalled 3000 counts. This region of the spectrum represents inelastically scattered background from interaction between X-rays and the sample and does not contain significant X-ray fluorescence lines for the samples studied. Data acquisition to a constant background level helps normalize differences in diameter and length among the various samples and provides comparable spectra. For most fibers studied, the acquisition live time was less than 1000 seconds. After acquisition of the spectrum for the fiber and holder, the fiber was removed and a spectrum of the tape holder was obtained. The acquisition time was set to the same length of time as for the fiber plus holder. If significant levels of elements of interest were detected in the tape holder, the mounting tape was replaced and the fiber plus holder spectrum reacquired. The final XRF spectrum used for comparison was then obtained by subtracting the holder spectrum from the total spectrum. This method removes element lines and continuum background associated with the sample holder from the spectra prior to evaluation and provides a consistent basis on which to compare the 105 samples.

Results and Discussion

Examples of XRF spectra of a sample holder, an automotive fiber, A014, and a residential fiber, R037 are shown in Fig. 1. The three spectra are shown with the same vertical scale to facilitate visual comparison. The blank shown in Fig. 1a displays the characteristic scattering background for a small mass of organic material in the X-ray beam and the characteristic K X-ray lines of titanium (Ti). Titanium was always observed as a low intensity peak in the spectra of the tape used in this study. X-ray lines from bromine present in the tape and silver from a collimator ring on the X-ray detector were also occasionally observed in the spectra of the blanks, but they caused no difficulties in spectral interpretation. There are also coherent and incoherent scattering peaks from the Rh K lines appearing at the high energy end of the spectrum. The spectra shown in Figs. 1b and 1c are from single fibers of an automotive and a residential fiber, each with its appropriate sample holder blank subtracted. These two fibers are typical of the nylon fibers in this study. The spectra for the fibers have greater background continuum levels and stronger scattered Rh lines than the tape holder alone because of their greater mass. The middle portion of the XRF spectrum of the automotive fiber in Figure 1b is expanded to show more clearly the X-ray lines for the elements Ti, chromium (Cr), iron (Fe), copper (Cu), and zinc (Zn). As a
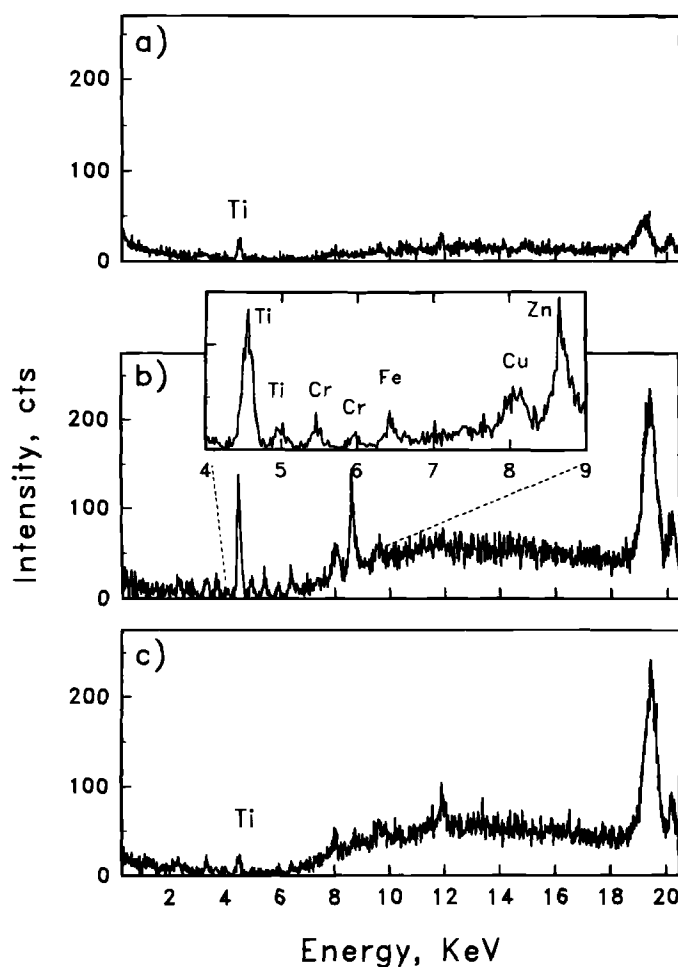

FIG. 1—*X-ray fluorescence spectra.* a) *Sample holder, acquisition time 600 s.* b) *Blue nylon automotive carpet fiber, A014 with sample holder blank subtracted, acquisition time 666 seconds.* c) *Blue nylon residential carpet fiber, R037 with sample holder blank subtracted, acquisition time 693 seconds.*

point of reference, these elements are present at the 20 to 100 μg/g level in this fiber. Titanium is the only element observable in the residential fiber spectrum shown in Fig. 1c. The Ti X-ray count rate in the sample difference spectrum is slightly greater than in its corresponding blank (not shown), indicating that Ti is actually present at low, barely detectable amounts in the R037 fiber.

An XRF spectrum for a polypropylene automotive fiber, A031 is shown in Fig. 2. The vertical scale for Fig. 2 is greater than in Fig. 1, to display the greater fluorescence intensities associated with several elements. Elements present in the fiber sample shown in Fig. 2 include Ti, Cr, nickel (Ni), Cu, lead (Pb), and molybdenum (Mo). The strong intensities and multiple peaks, particularly for Pb, Mo, and Cr in this spectrum contrast sharply with those shown in Fig. 1. The polypropylene fibers in this study generally have a greater variety and stronger intensity of X-ray peaks than do the nylon fibers. It is also interesting to note that, despite the several large X-ray peak intensities, a longer acquisition time was required for the smaller polypropylene fiber than for the nylon fibers shown in Fig. 1.

Prior to comparing XRF spectra of the fibers in this study, observed X-ray peaks were assigned to their corresponding elements and the appropriate peak intensities were determined. In all
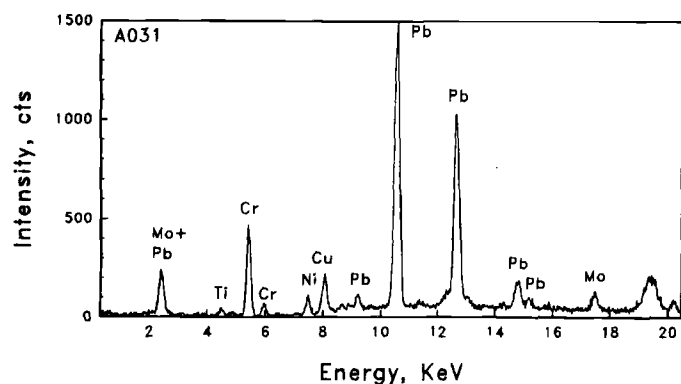
FIG. 2—*X-ray fluorescence spectrum of polypropylene automotive carpet fiber, A031 with sample holder blank subtracted, acquisition time 789 seconds.*

cases, unambiguous assignment of X-ray peaks to their corresponding element was straightforward because of the small number of elements present and consequent simplicity of the spectra. Following escape peak correction, each element present was assigned a value from 1 to 4 according to the intensity of its most intense X-ray emission. The numeric values were assigned based upon the net peak intensity, that is, the maximum intensity of the XRF peak (peak height) minus the mean adjacent baseline intensity. Net peak intensities of less than 32 counts were assigned a value of 1, intensities from 33 to 128 were assigned a value of 2, intensities from 129 to 256 were assigned a value of 3, and intensities greater than 257 were assigned a value of 4. This, rather crude, semiquantitative method of evaluating X-ray spectra provides an approximate measure of the concentrations of elements present in each fiber. It has the advantages of being easy to calculate, requiring only casual observation of a spectrum after some practice and is less dependent upon changes in baseline shape than a method utilizing peak to background ratios. The numeric intensity values are not strongly dependent upon sample size or position in the X-ray beam. Although the numeric intensity values are roughly related to the concentrations of the elements present, there is not a simple, direct relationship because of interelement effects and the different excitation efficiencies for each element. The numeric intensity values also show a strong dependence upon excitation conditions. These conditions were held constant throughout this study, but changing them to enhance X-ray fluorescence for particular elements will greatly affect the observed intensity values. The limited analytical reproducibility of XRF of small samples and the variability within a carpet combine to produce an overall uncertainty that does not warrant more quantitative evaluation of the X-ray data than the categorical analysis used here. Replicate analysis of several fibers and analysis of fibers of varying lengths produce nearly equivalent numeric intensity values for a given carpet sample using this method of data evaluation.

The 105 individual XRF spectra cannot be shown because of space limitations. Instead, the results of numerical evaluation of the spectra are shown in Table 2. An appreciation for the visual appearance of the XRF spectra can be obtained by comparison of the data shown in Table 2 for the A014, A031, and R037 fibers with the XRF spectra shown in Figs. 1 and 2. For example, in Fig. 2, the Pb and Cr peaks correspond to a numeric intensity of 4, Mo and Cu correspond to 3, Ni corresponds to 2, and the other peaks shown in Figs. 1 and 2 correspond to 1. As shown in Table 2, 20 elements are present in one or more of the 105 fiber samples.

TABLE 2—*Results of analysis of carpet fibers.*

Sample No.	X-ray Peak Intensities			
	4	3	2	1
A001			Hg, Zn	Cd
A002		Pb	Ni> Ti, Zn	Cr
A003			Ti, Ni, Zn	
A004				Cu, Zn> Fe K, Ca
A005	Ti			
A006		Ti		Cr, K, Ca, S
A007				Cr, Fe
A008				Ti, Cr, Br
A009				Ti> Cr, Fe, Zn, Ca
A010			Ti	Cu> Cr, Fe, K, Ca
A011				Cr, Co
A012			Cu	
A013		Ti		Cr, Fe, Cu, Zn, K, Ca
A014			Ti, Zn	Cr, Fe, Cu, Ca
A015	Ca	Ti	Co	Cr, Fe
A016		Ti		Cr, Fe, Co, Cu, Zn, Ca
A017			Ti	Mn, Zn
A018				Cr
A019				Cu
A020		Pb	Ti, Cr, Cu	Sr> Zn
A021		Ti	Cr, Co	Cu
A022			Br	Zn, K> Ti, Fe, Ni
A023d			Zn	Fe, Mn, Cu, K, Ca
A023l				Fe, Cu, K
A024d		Ti		Fe
A024l				Ti, Fe, Cu
A025d			Ni> Zn	
A025l				Zn> Ti
A026				Co> Ti, Fe, Cu
A027				Cr> Fe, Ni, Cu, K, S
A028		Cu		Cr, Fe, I
A029				Cr, Cu, Zn, Ca
A030			Ti	Cr> Fe
A031	Cr, Pb	Mo?, Cu	Ni	Ti, Fe, Zn
A032			Ni, Zn, Cd, Hg	Cl> Ti, S
A033			Cr, Cu	Fe
A034		Fe, Pb	Cr, Ni, Zn	
A035			Cu	Cr
A036			Zn	Cl
A037	Ti, Co		Cr, Cu	Fe, S
A038		Ti		
A039		Cu	Ti, Ni, Zn> Fe	
A040			Cr, Co	Ti, Cu
A041		Cu	Ti, Ni	Zn
A042	Fe		Ni, Cu, Zn	
A043			Ti, Cu	Sr
A044			Cr, Ti	Co
A045			Ti	Fe, Sr
A046			Zn	Ti, Cu
A047	Br		Cr	Fe, Cl, K, Ca, S> Cu
A048				Fe, Cu, K, Ca
A049		Ti		Fe, Sr
A050		Zn		Ti> Cu, K, I
R001			Ti	
R002				Fe, Ca
R003		Ti		
R004				
R005			Ti	
R006		Ca> Ti		S
R007			Ti	Ca, S> Fe
R008				
R009			Ti	Ca
R010	Ca		Ti, Cl	Fe> Cu
R011	Ca, Ti		Pb> Zn	Cr, Fe
R012d	Ti	Ca	Cu	
R012l	Ti		Pb	Cr
R013				S
R014				S, Ca

TABLE 2—*Continued.*

Sample No.	\	X-ray Peak Intensities	\	\
	4	3	2	1
R015				S, K, Cu, Fe
R016	Ti	Zn, Pb	Cr	Cu
R017	Ti		Pb> Ca	Cr
R018				S
R019				
R020	Ca			Fe
R021				Fe, S
R022				S
R023		Ti		Ca
R024				S, Fe, Zn, Ca> Mn
R025				Ti, Cu
R026				Fe
R027				
R028				
R029			Ca, Ti	Ni, Cu, Zn
R030	Ti			Ni, Zn
R031	Pb	Ti	Cr> S	Ni, Cu, Zn
R032			Ca, Ti	Ni, Zn> Fe
R033		Ti		Ni
R034		Ti	Pb	Cr> Fe, Ni, Zn
R035d			Ni, Cu, Zn	
R035l				Ni, Cu, Zn
R036				
R037				Ti
R038				Si, Ti, Fe> K
R039				S
R040				S
R041				Ti, Ca, Cl> Fe
R042				
R043			Ca	K
R044			Ca	
R045				Ca
R046				Ca, Mn
R047				
R048				Mn
R049				
R050				

TABLE 3—*Frequency of occurrence of elements in carpet fibers. Values listed are number of occurrences of element at the listed intensity in 53 automotive or 52 residential fibers.*

Intensity	Automotive				Residential			
	4	3	2	1	4	3	2	1
Br	1	0	1	1	0	0	0	0
Ca	1	0	0	11	3	2	5	9
Cd	0	0	1	1	0	0	0	0
Cl	0	0	0	3	0	0	1	1
Cr	1	0	8	17	0	0	2	4
Co	1	0	3	4	0	0	0	0
Cu	0	4	7	18	0	0	2	7
Fe	1	1	1	24	0	0	0	13
Hg	0	0	2	0	0	0	0	0
I	0	0	0	2	0	0	0	0
K	0	0	0	11	0	0	0	3
Mn	0	0	0	2	0	0	0	3
Mo	0	1	0	0	0	0	0	0
Ni	0	0	9	2	0	0	1	7
Pb	1	3	0	0	1	1	4	0
S	0	0	0	5	0	0	1	11
Si	0	0	0	0	0	0	0	1
Sr	0	0	0	4	0	0	0	0
Ti	2	8	12	11	6	6	7	4
Zn	0	1	12	11	0	1	2	7
Total	8	18	56	127	10	10	25	70

TABLE 4—*Results of classification of carpet fibers using several selection rules.*

Selection rule	Number of samples			
	Automobile		Residential	
	Yes	No	Yes	No
For all fibers: Does the fiber contain: Cd, Co, Cr, Cu, Hg, Mn, Mo, Ni, Pb or Zn at any level or Fe at level >1?	48 (91%)	5	19	33 (63%)
Cr, Cu, or Zn at any level?	48 (91%)	5	16	36 (69%)
Cr, Cu, or Zn at level >1?	26 (49%)	27	5	47 (90%)
Any elements at any level?	53 (100%)	0	42	10 (19%)
Any elements at any level except Ca, Cl, Fe, K, S, Si, or Ti at level 1?	53 (100%)	0	29	23 (44%)
For nylon fibers only: Does the fiber contain: Cr, Cu, or Zn at any level?	27 (96%)	1	4	35 (90%)
Cr, Cu, or Zn at level >1?	10 (36%)	18	0	39 (100%)

A wide range of compositions, both in variety of elements present and their relative intensities are displayed by the fibers in this study.

This study was designed to determine whether fibers can be classed into automotive and residential groups based on the combinations of elements present in the XRF spectra of the fibers within each group. A summary of the frequencies of occurrence for each element at each intensity level in the 53 automotive and 52 residential samples is given in Table 3. Casual observation of the data given in Table 3 indicates that the automotive carpet fibers contain a wider variety of elements having greater X-ray intensities than do the residential fibers. The elements most characteristic of automobile carpet fibers are the metals, particularly Cr, cobalt (Co), Cu, Fe, Ni, and Zn. This fact suggests the possibility of a method to source fibers. Several possible selection criteria for fiber classification were evaluated. The results are shown in Table 4. For example, using a criterion that a fiber contain cadmium (Cd), Cr, Co, Cu, mercury (Hg), manganese (Mn), Mo, Ni, Pb, or Zn at any level, or Fe at a level of 2 or greater, puts 48 of the 53 automotive fibers into the "yes" category and 33 of the 52 residential fibers into the "no" category. Clearly, this simple selection procedure offers some degree of product classification. Considering only Cr, Cu, or Zn correctly classifies the same 48 of the 53 automotive carpet fibers and increases the residential group to 36 of 52. The more uncommon metals such as Hg, Cd, and Co are present only

in automobile fibers in this study. The presence of these less common metals in a fiber in addition to Cr, Cu, or Zn increases confidence in the assignment of a fiber to the automotive class.

Low intensity peaks are somewhat difficult to observe in small samples and may not be detectable in all fibers of a given product. A more conservative approach to classification would be to omit the elements with peak intensities of 1. The elements Cr, Cu, or Zn are present at levels of 2 or greater in 26 of the 53 automobile sources and are absent in 47 of the 52 residential fibers. Most of the residential carpet fibers that have elemental profiles similar to fibers in the automotive group are the polypropylene fibers. None of the residential nylon fibers in this study contain Cr, Co, or Zn at levels >1. Thus, for nylon fibers, a lack of detectable levels of

these elements is a good indication of a fiber of residential origin. More definitive classification of the fibers in this study cannot be made using the XRF data. More complete surveys of a wider range of fiber compositions and improvements in analytical sensitivity may improve upon the classification results shown in Table 4.

This study was designed to answer the question of classification. However, the data can also be used to consider the utility of XRF for comparison of individual carpet fibers. The fiber samples in this study are readily distinguishable by morphological, polymeric, and visible spectral features, so this sample set does not represent a critical test of using elemental composition for discrimination. A hint at the possible discrimination capability can be obtained by comparing the element lists in Table 2 for those pairs of auto carpet fiber samples that have the same manufacturers color designation and polymer composition. These five pairs of fibers, A008 and A009, A017 and A018, A023 and A024, A041 and A042, and A045 and A046, are readily distinguishable by their XRF spectra. These few examples provide some support to the belief that elemental composition may add to the discrimination capability obtained by conventional methods. The discrimination capability of elemental profiles can only be evaluated by measuring the variability within and between production runs of carpet fibers and comparison of fibers which are indistinguishable by conventional methods.

The range of elemental patterns displayed by the fiber samples in this study reflects the variety of manufacturing processes and elemental additives used in the production of carpet fibers. Many of the metallic elements observed probably result from the use of metallized dyes, particularly in the automobile carpets. However, metals such as Cr, Ni, and Zn are also used as mordants or are incorporated into polypropylenes so that they can then be dyed with metallized dyes. Because of the multiple uses for individual elements, no simple correlation exists between the observed elemental patterns and specific colors. Titanium is the most frequently observed element in these fibers, primarily because of the widespread use of titanium dioxide as a delusterant. Optical microscopic observation shows that 24 of the 53 automobile carpet samples contain delusterant. The exact nature of the delusterant was not noted in this study. The relationships between the Ti content and whether or not fibers are delustered are shown in Table 5. Fiber delustering is not correlated with the levels of Ti in the XRF spectra of these fibers since Ti is present in some fibers that are not delustered and absent in some of the delustered fibers. Again, this indicates the complex nature of the many elemental additives and the multiple roles of a given element used in the manufacture of carpet fibers. Overall, the elemental composition compliments the microscopic comparison of fibers by providing additional, largely independent, information.

The fibers used in this study were all clean fibers taken from unused carpet samples. A consideration that is paramount in the examination of evidentiary fibers is the effect of contamination on elemental compositions. A brief test was done with a residential carpet fiber to determine how effectively elements associated with contamination can be removed prior to analysis. A fiber from a highly travelled area of a carpet was selected and then contaminated with used motor oil and soil. Portions of the XRF spectrum of the dirty fiber are shown in Fig. 3a. Major X-ray peaks indicating the presence of Fe, Cu, Zn, and strontium (Sr) are evident. The fiber was then removed from the sample holder and cleaned with a dilute solution of an ionic detergent in a bath ultrasonicator for 15 minutes. The cleaned fiber was then rinsed successively with acetone and deionized water and dried. The XRF spectrum of the cleaned fiber is shown in Fig. 3b. The Cu and Zn were completely removed by the cleaning, and the Fe was greatly diminished. The Sr was not affected by cleaning, indicating that it is a manufacturer added element inherent in the fiber. A comparison fiber, taken from an area of the carpet which had not received any traffic is shown in Fig. 3c. The uncontaminated fiber shows the presence of Sr and a minor Fe peak, the intensities of which are in excellent agreement with the washed fiber shown in Fig. 3b. The good agreement between the spectra in 3b and 3c indicates, in this instance, that a simple washing procedure is effective in removing contamination from carpet fibers. In other studies in this laboratory using quantitative methods of elemental analysis, most elemental contamination is readily removed from carpet fibers by simple washing procedures.

Conclusions

X-ray induced XRF has been demonstrated to be a useful method for the elemental characterization of individual carpet fibers of a few millimeters in length. The method described is rapid, nondestructive, and provides adequate sensitivity to detect the presence
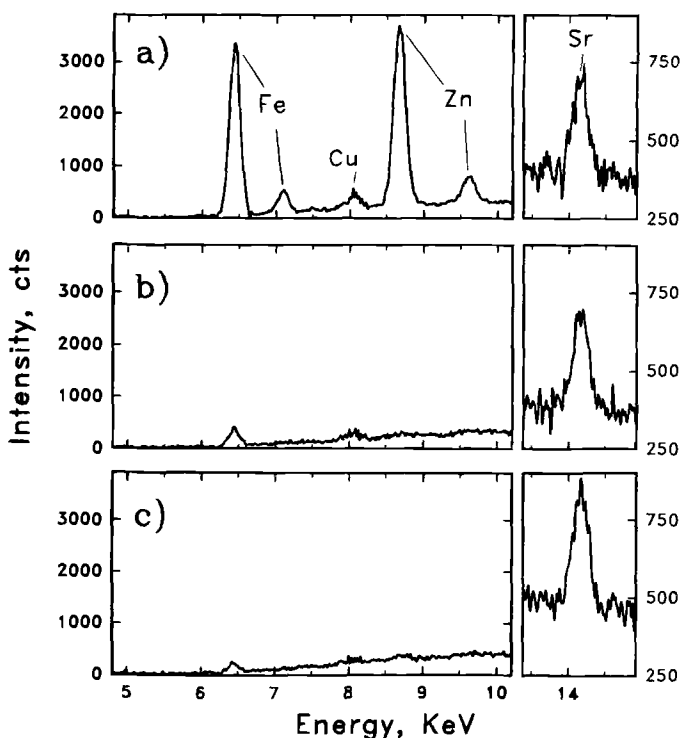

FIG. 3—*Portions of the X-ray fluorescence spectra of residential carpet fibers showing effects of soil removal by ultrasonic cleaning in detergent.* a) *Soiled fiber.* b) *Same fiber after cleaning.* c) *Fiber from unsoiled portion of same carpet. The intensity scales for the low energy portion of spectra are on the left and for the high energy portion are on the right.*

TABLE 5—*Frequency of occurrence and levels of titanium in delustered and nondelustered automobile carpet fibers.*

| | Titanium intensity level | | | | |
	Ti = 4	Ti = 3	Ti = 2	Ti = 1	Ti = 0
Delustered	1	3	8	6	5
Not delustered	1	5	3	4	17

of some 20 elements added to fibers during the various steps of fiber and carpet manufacture.

Attempts to classify the 105 fibers used in this study into automotive and residential use were only partly successful. Several transition metals, notably Co, Cr, and Zn are generally present in the automotive fibers and absent in the residential carpet fibers. Classification results are most promising for nylon fibers, which typically do not contain metallic elements when intended for residential use.

Elemental analysis as a point of comparison following microscopic and colorimetric examination may afford some, as yet unknown, degree of additional discrimination. Further studies, including elemental distributions in finished carpets and comparisons of similar fibers are needed to provide a quantitative estimation of the discrimination capability. The most useful application of XRF measurements may be in identifying the manufacturer of a particular carpet or fiber by detection of manufacturer-specific elemental components.

Although results from this study are promising, they indicate that several additional studies are needed, particularly to establish the viability of using elemental comparisons of fibers. The instrumental operating conditions used in this study were optimized for elements having X-ray emissions in the 5 to 8 KeV range. Changing XRF instrumental operating conditions to enhance low mass elements, particularly sodium, magnesium, and phosphorous, may also provide additional discrimination. Also, setting up instrumental operating conditions to detect one element which is specific to a particular manufacturer may assist in establishing the source of a questioned fiber. This study made no attempt to provide precise quantitative measures of element concentrations or interelement ratios. Combining these measures with studies of inter- and intrasample variability may provide better discrimination than the rather qualitative assessment of spectra used here. Additional studies have shown that such data is better obtained by other analytical methods, such as atomic absorption spectrophotometry.[3] The likely value of the XRF method is as a quick, nondestructive screening method to distinguish among carpet fibers made for different

intended uses or by different manufacturing processes. The work in this study was done using a conventional energy dispersive XRF spectrometer with the exciting X-ray beam collimated through a flat circular aperture. Several recent studies have reported the analytical features of micro-X-ray fluorescence. An excellent discussion of the advantages and pitfalls of several micro-XRF techniques was recently presented (5). These new methods, which produce EDXRF spectra with good intensity and excellent spatial resolution promise to improve significantly upon the results presented in this paper.

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[3]R. D. Koons, unpublished results.