X-ray Fluorescence Spectroscopy Method Development for Quantitative Evaluation of Carpet Cleaning Technology

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Abstract

An X-ray fluorescence method for measuring the quantity of test matter removed from carpet by vacuuming and wet extraction in typical carpet cleaning processes is described. In this cleaning effectiveness analytical method, five different test compounds were incorporated into an artificial soil, which was then applied to a test carpet. X-ray fluorescence was used to quantify these elements after initial addition to the carpet and subsequent to each step of a predetermined cleaning process. Evaluations were conducted with various cleaning process variants including vacuumed and un-vacuumed. X-ray fluorescence identified relative differences in the removal efficacies of the five target compounds from carpet which were associated with the test cleaning processes. This approach appears feasible as a means of assessing the performance of carpet cleaning technologies.

Key Terms

Carpet Cleaning, X-ray Fluorescence

Introduction

Indoor environment cleaning serves several purposes—to maintain a visually pleasing appearance, to protect and preserve material surfaces, and for the health and well being of those who live and work in those environments. Proper cleaning of the built environment involves the collection and removal of contaminants that enter and accumulate in this spaces.[1]

Although the use of textiles as floor coverings dates back to prehistoric human development, the widespread use of "wall-to-wall" carpet in homes and buildings has occurred in only the last 40-50 years. Because of its three-dimensional structure, carpet has a tendency to trap and accumulate debris that tracks or settles onto it. The nature of those soils is diverse, but generically falls into the categories of inorganic particles, fibrous (e.g., plant matter and animal dander), macromolecular dusts (e.g., resins and gums), microbial related (e.g., bacteria and mold spores), and trace contaminants (e.g., pesticides, polycyclic aromatic hydrocarbons, and heavy metals).[2] This diversity of composition also translates to a range of physical properties that cleaning techniques must accommodate. Not surprisingly, the challenge for scientists has been to measure the effectiveness of carpet cleaning technology—both chemistry and equipment.

Some of the earliest approaches to carpet cleaning metrics were appearance assessments. The simplest were subjective human visual ratings. To achieve more objective evaluations, research focused on instrumental light reflectance measures,[3-5] and eventually to ΔE values, which captured contributions of color to changes in appearance after carpet cleaning.[6] ΔE values are still widely used by cleaning scientists.[7] Unfortunately, appearance change is a metric that does not typically provide much insight into contaminant removal effectiveness as it measures only the visible surface.

To develop insights into carpet contaminant removal, gravimetric methods have been evaluated.[8] Although reasonably effective, these techniques tend to be labor intensive and time consuming, thus limiting utility. In the early 1980s, X-ray fluorescence (XRF) techniques were used to measure iron in naturally soiled carpets. XRF analysis was found to correlate reasonably well with gravimetric and reflectance results.[9-11] However, at the time, XRF equipment was expensive and not widely used. In the 1990s, the focus shifted to the accumulation of biological debris in carpet. Analytical techniques involved the microorganism culturing or use of immunoassays to identify markers of biological activity.[12,13] These methods also tended to be analytically specialized and cumbersome in application.

Recently, there has been renewed interest in XRF. Advances in X-ray source technology have dramatically improved portability and significantly reduced costs. This resulted in increased availability and fostered an expansion into a wide range of applications used outside the typical laboratory (e.g., field data on soil contamination, airborne metals, lead in house dusts, and metal composition of alloys).

One application of interest to the carpet and carpet cleaning industries was the use of elemental markers (taggants) to track materials. The original concept was to either use the specific elemental composition of a material or to incorporate a range of XRF-sensitive elements in an object, which could be uniquely coupled to a specific manufacturer, product, and/or manufacturing variables. A joint project between NASA and KeyMaster Technologies Inc. was initiated in 2002 to evaluate critical materials used in launch vehicle construction, and further demonstrate utility of portable XRF techniques.[14-16]

The objective of this study was to develop and assess an XRF analytical method of evaluating carpet cleaning technology based on the ability to remove an array of taggant compounds serving as soil surrogates.

Method Development

The elemental composition of the artificial soils, a carpet substrate, a means of imparting the artificial soils reliably and reproducibly to the carpet, a method for substrate cleaning, and the XRF analytical hardware and techniques were needed for this method development.

Elements with good XRF analytical specificity and sensitivity, and a range of physical characteristics to mimic those of natural soils, were selected for use in surrogate soil compounds. Five compounds were chosen as candidates (Table I). Criteria used were particle size range, hardness, solubility, and surface characteristics.

The carpet substrate used in these tests was a residential cut-pile carpet with the specifications provided in Table II. This is the same style carpet specified in The Carpet & Rug Institute Test Method 111.17.

The method used for conveying the taggants to the carpet substrate was a slight variant of the Carpet & Rug Institute Test Method 111.17 that uses ASTM D6540-2000 to artificially soil carpet samples.[18] The taggant was used in lieu of the AATCC Standard Soil. Nylon pellets, which functioned as the transfer media to the carpet, were pretreated with the taggant(s). The desired quantity of the taggant(s) was added to 2 kg of Zytel pellets in a two-gallon cylindrical container. The container was placed on a jar mill at 60 rpm and allowed to mix for 30 min. This provided a supply of pellets for the treatment of several carpet samples.

This approach worked well for four of the selected compounds—yttrium oxide, zirconium boride, zinc oxide, and iron oxide. Solid potassium bromide did not adhere well to the pellets when applied directly. A solution (in 30 mL of deionized water) was applied to the pellets. An additional 40 mL of deionized water was used to rinse out the container and the mixture tumbled at 40 rpm for 30 min. The wet pellets were then heated to ~140°F for 1 h, and then placed in a 20% relative humidity, 70°F, climate-controlled room to finish drying. While in the climate-controlled room, the pellets were periodically shaken to help ensure even coverage. After the pellets were dry, they were again tumbled on the jar mill for 30 min.

Taggant treated pellets (50 g of each type for a total of 250 g) and 1,193 g of 3/8-in. diameter stainless ball bearings were placed in a cylinder lined with the carpet substrate (~10 × 40 in.). The enclosed cylinder was tumbled on a jar mill at 40 rpm for 30 min. This resulted in a uniform addition of the taggant to about 400 in.^{2} of carpet that was used in subsequent cleaning tests.

Table I.
Elements Chosen for Soil Media

Yttrium Oxide	(< 10 μ) sand-like physical characteristics
Zirconium Boride	(< 44 μ) black in color, dust-like characteristics
Zinc Oxide	(< 74 μ) clay-like consistency.
Iron Oxide	(< 1 μ) common in soil[3]
Potassium Bromide	(water soluble)

Table II.
Carpet Substrate

Style	Residential Cut Pile
Pile Yarn Wt.	848 g/m^2 (25 oz/ yd^2)
Color	Almond White
Pile Height	12 mm (0.470 in.)
Yarn	100% Spun Nylon 6,6
Treatment	No fluorochemical treatment

The soiling process uniformly transferred a small amount of the test soil onto the test carpet. The type of test carpet affected the total amount of soil embedded in the carpet pile. The commercial loop pile carpet retained

Fig. 1. Soiling drum.

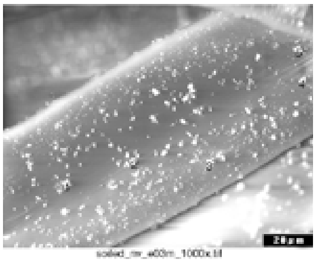

Fig. 2. SEM photo (1,000×) of soiled cut pile material.

Fig. 3. Soil amount required for test carpet substrate.

~2.5 g/m^2 compared to the residential cut pile carpet retention of ~3.1 g/m^2. Fig. 1 shows the soiled nylon pellets and ball bearings inside the soiling drum used to embed the soil in the carpet. Fig. 2 is a scanning electron microscope (SEM) photo of the cut pile material showing the uniformity and depth of distribution. Fig. 3 shows the relatively small amount of soil required to soil the 400 in.^{2} carpet specimen.

The process for cleaning the treated carpets was also taken from Carpet & Rug Institute Test Method 111.17. The carpet sample was secured to a conveyor platform capable of well-controlled speeds in forward and reverse directions. The head of the cleaning equipment (e.g., vacuum cleaner or hot water extraction wand) was fastened in place and the system was activated to run at either 1.8 ft/s for the vacuum cleaner or 1.0 ft/s for the wet extractor. This mitigated variability associated with an operator handling the equipment during the trial.

The XRF spectrometer used was a portable "TRACeR II" (KeyMaster Technologies Inc.). The unit used a small, low power X-ray tube operating at 40-45 kV and 2-10 mA. An integrated multi-channel analyzer (MCA) analyzed the XRF photon energies. The batches of pellets inoculated with the individual soil component compounds were scanned five times for 60 s. Before each scan, the pellets were rearranged in an effort to randomize the sample geometry. The carpets were analyzed by mounting the XRF unit on the conveyer such that the detector face was 3 mm above the fiber tips, and scanning at a rate of 40 in.^{2}/min for 3 min.

Results and Discussion

XRF Methodology

Baseline XRF detection and quantification performance expectations were first evaluated for each taggant system. This was done one compound at a time to avoid cross-contamination, simplify calibrations, and reduce potentially confounding factors.

The first evaluation was on taggant-treated nylon pellets. This was important because of the need to understand the mechanics of taggant transfer to the carpet substrate. Intermediate levels up to 6 g (taggant)/1,000 g (nylon pellet) were measured for each taggant. Fig. 4 illustrates the relationship between signal intensity and XRF energy for each element used. Iron had the lowest sensitivity of the five (as would be expected).[19] The detection sensitivity is a function of the X-ray source, sample distance, and inherent properties of the element. However, all five elements (Fe, Y, Zr, Zn, and Br) responses were in a potentially useful dynamic range.

The relationship between relative signal intensities and concentration was linear through the origin and up to the 6 g/1000 g pellet level for each element (Fig. 5). The lower detection sensitivity for iron gave the relationship with the largest slope. This implies that results for samples with iron may be more variable than those with yttrium and zirconium in this concentration range.

The next phase of the study was to evaluate transfer of the taggants from the nylon pellets to the carpet substrate. This was done by measuring the initial quantity of taggant compound on pellets and comparing it to the quantity on the pellets after "tumbled" with the carpet (using the jar mill method). Although care was taken to minimize loss of material to other surfaces, it is possible that a small amount of test compound was transferred to the

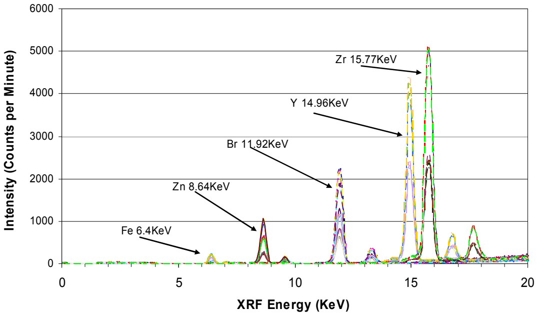

Fig. 4. Pellet scans.

Table III.
Transfer Levels from Pellets to Carpet

	1.5 g/1,000 g Carpet		3 g/1,000 g Carpet		6 g/1,000 g Carpet	
	(g)	(%)	(g)	(%)	(g)	(%)
Iron Oxide	0.07143	85.84	0.11657	71.83	0.21812	65.19
Zinc Oxide	0.05220	71.59	0.09781	61.39	0.21331	69.59
Potassium Bromide	0.02097	28.48	0.08977	49.00	0.18671	57.98
Yttrium Oxide	—	—	0.08393	54.62	0.21094	68.81
Zirconium Boride	—	—	0.12883	87.70	0.22981	83.37

containers and lost in handling. On a relative basis, it is anticipated that this would be small, however, it is possible this would lead to a slight overestimation in the results shown in Table III.

Transfer rates to the carpet substrate were for the most part relatively high. Iron oxide and zirconium boride were in the 70%-80% range. Yttrium oxide and zinc oxide were in the 50%-60% range. Potassium bromide was similar, with the exception of the 1.5 g/1000 g pellet level, which transferred only 28%. It is not clear why this was the case, although it could be an artifact of the wet loading method used for potassium bromide.

It was also observed that the transfer levels appeared to be relatively linear over the 1.5 g to 6 g per 1000 g pellet loading range (Fig. 6). Although not unreasonable, it was interesting that the taggants had various behaviors in their propensity to transfer to the carpet. For example, the percent of zinc oxide and zirconium boride transferred were roughly the same across the concentration range. Potassium bromide and yttrium oxide both increased transfer with higher loading. Conversely, iron oxide decreased in percent transferred with increased pellet loading. The data is insufficient to draw conclusions, but holds out the possibility that it could be related to the relative affinities of these compounds for the nylon polymer. Pellets and carpet fiber were Nylon 6,6 and Nylon 6, respectively, however, the carpet fiber possesses substantially greater surface area than the pellets. Therefore, one might predict that higher transfer rates reflect lower nylon affinity and hence, in the end, easy removal from the carpet as well.

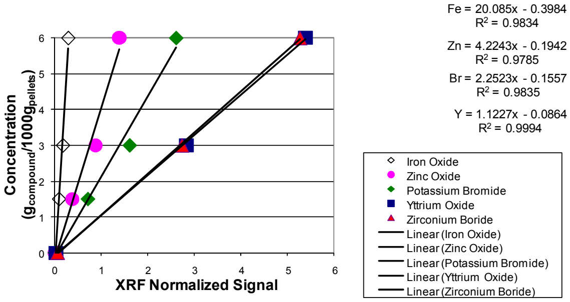

Fig. 5. Regression equations for pellets.

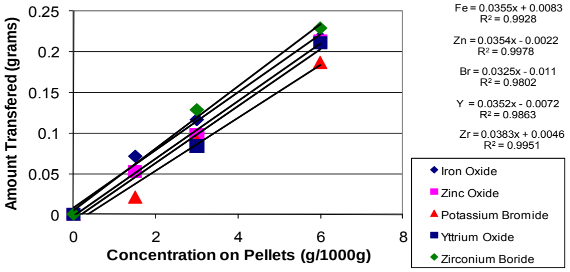

Fig. 6. Concentration on pellets vs. grams transferred.

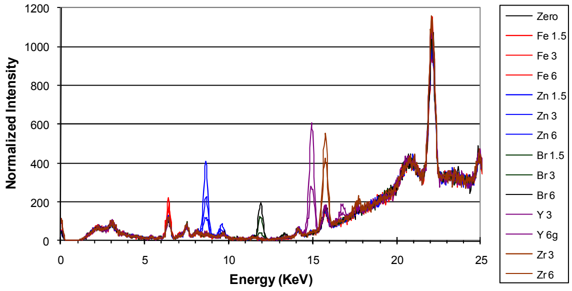

Fig. 7. Carpet XRF scans.

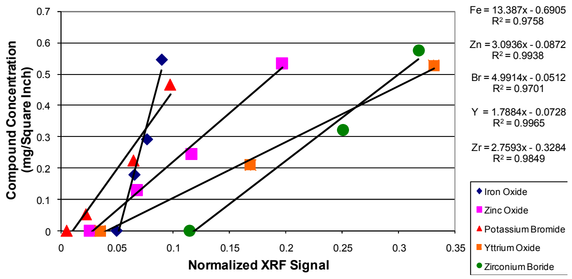

Fig. 8. Regression equations for compounds on carpet.

The test carpet samples were also scanned by XRF to evaluate the signal to loading relationship of the carpet sample matrix, which would be necessary if this method was to have any use in cleaning technology assessment. As seen in Fig. 7, reasonable responses were observed from the carpet samples as a function of loading. Further, these relationships were linear over the range evaluated (Fig. 8). These regressions could then be used to estimate concentrations when the carpet is loaded with all five taggants simultaneously.

Table IV.
Percent of Test Material Removed from Carpet

	Average[a] Percent Removed			
	Pre Vacuum	Wet Extraction	Post Vacuum	Total
(1) Water extraction clean first & post vacuum with an approved CRI vacuum cleaner.	—	57	10	67
(2) Vacuum first with a non-CRI certified vacuum cleaner & post water extraction clean	38	24	—	62
(3) Vacuum first with an approved CRI vacuum cleaner & post water extraction clean	52	15	—	67
(4) Vacuum first with an approved CRI vacuum cleaner & apply a pre-spray before extraction	53	30	—	83

[a] Average removal across five test compounds. (1) & (2) are average of three sets of tests, (3) is average of four sets of tests, and (4) is average of two sets of tests.

These results establish the basis of taggant soil surrogate application to carpet for evaluating carpet cleaning technology.

XRF Taggant Method Application

Two commonly used cleaning techniques were explored. The first was vacuum cleaning, which the vast majority of carpets receive frequently. The other was hot water extraction (HWE), which for a well maintained carpet, should be carried out on a periodic basis determined by end use and foot traffic. It was further understood, based on work prior to the implementation of The Carpet & Rug Institute "Green Label" program for vacuum cleaners, that there were significant differences in equipment performance.[20] The same has been observed for other cleaning systems.[13,21]

A cleaning effectiveness test based on this XRF method was used to assess removal efficacy at various steps in four variations of an HWE process. The variants around the HWE process were 1) no pre-vacuuming of the carpet, 2) vacuuming with a machine that did not meet CRI's Green Label vacuum program criteria, 3) vacuuming with a CRI Green Label certified vacuum, and 4) vacuuming with a CRI Green Label certified vacuum and use of a chemical pre-spray prior to HWE. This phase of the study used vacuum cleaners, HWEs, and chemistry widely used in the trade and viewed as performing at the upper end of the performance spectrum.

The carpet samples for this part of the study were prepared at the 6 g/1000 g pellet loading level. Procedurally, 50 g of each of the five taggant-coated pellets were used to soil a 400-in.^{2} carpet following the ASTM D6540-2000 test method. On removal from the jar mill, each carpet was scanned to obtain the initial concentration of each compound. All XRF scans were conducted with the carpet on the moving conveyor such that in a 3-min scan, approximately 120 in.^{2} of the 400 in.^{2} carpet were analyzed.

The vacuum cleaning step employed the CRI Green Label vacuum cleaner test protocol. This involved securing the carpet to a conveyor, fastening the vacuum cleaner in place, energizing the vacuum, and then allowing the conveyor to move the carpet sample past the vacuum head at 1.8 ft/s in a prescribed number of passes. After vacuuming, the test carpet was scanned using XRF to measure remaining taggants.

On the same conveyor system used for vacuuming, two wet and two dry passes at the rate of 1.0 ft/s were made with the HWE equipment. The test carpet was again scanned using XRF to measure remaining test material. The test procedure was conducted three times for each variation and the results averaged.

Table IV shows the average percent of test material removed from carpet after vacuuming and HWE steps for four different cleaning processes.

The first test was a deviation from normal professional carpet cleaning practice which is to vacuum before HWE, however, it was post-vacuumed. This process resulted in an average of 57% test matter removed from the carpet after HWE only. The carpet was then vacuumed with a CRI approved unit and an additional 10% of test matter was removed. HWE and post vacuuming combined achieved an average of 67% soil removal.

In the second test, a vacuum cleaner that failed to meet CRI Green Label criteria was used to pre-vacuum the carpet. This vacuum cleaner removed 38% of the test matter. The HWE process that followed, using water alone, removed an additional 24% of the test matter. Together, vacuuming with a less than fully efficient vacuum and HWE removed 62% of the test matter.

In the third test, a CRI Green Label vacuum, designed and tested for effective soil removal, was used in the pre-vacuum phase of the process and found to remove 52% of the test matter. The wet extraction phase that followed, using water alone, removed an additional 15% of the test matter for a cumulative removal efficiency of 67%.

In the fourth test, a CRI Green Label vacuum was again used in the pre-vacuuming phase. Similar to Test 3, the Green Label Vacuum removed an average of 53% of the test matter. In the HWE step of the test, a cleaning chemical (pre-spray) was applied to the carpet to promote suspension and removal of the taggants. Overall, pre-vacuuming with a Green Label machine, the application of a cleaning chemical, and wet extraction produced a total removal efficiency of 83%.

Results (Table IV) indicated that vacuuming was a significant factor in test material removal from carpet. This methodology captured the differences expected for the two vacuum cleaners. The CRI Green Label approved vacuum removed 14% more than the machine that did not meet CRI Green Label criteria. These results highlight the potential value of cleaning chemicals (used as pre-sprays here). Without them, wet extraction removed an additional 15% over the 52% removed by the CRI approved vacuum. Additional data is available from the author. Overall, the addition of a chemical pre-spray to the HWE process significantly increased matter removal during the HWE portion of the cleaning process and added 30% removal efficiency to the carpet cleaning process in this example.

Pre-vacuuming and HWE, even with a less than fully efficient vacuum (62%), was better than HWE alone (57%) (Table IV). The order—vacuuming then HWE (67%) or HWE then vacuuming (67%)—did not seem to matter. The best cleaning process was the CRI approved vacuum first, followed by HWE using a chemical pre-spray (83%).

Data in Table V suggest that potassium bromide and zirconium boride were better removed dry by the vacuum cleaner. Alternatively, zinc oxide and yttrium oxide were better removed by HWE. Iron oxide was removed in about the same amounts by either vacuuming or HWE. Differences could be attributed to taggant compound physical properties such as density and substrate affinity. Compounds not easily removed by vacuuming could also become embedded deeper into the carpet pile via the mechanical action of the vacuum. Removal in the HWE process may have increased because the combination of water and air dislodged particles from the carpet.

Table V.
Specific Taggant Removal Per Extraction Process (%)

	Compound	Method 1	Method 2	Method 3	Method 4
Pre Vacuum	Fe_3O_4	—	48	64	66
	ZnO	—	16	22	22
	KBr	—	36	54	61
	Y_2O_3	—	23	36	33
	ZrB_2	—	68	85	84
Wet Extraction	Fe_3O_4	68	74	79	95
	ZnO	47	46	46	83
	KBr	51	57	62	59
	Y_2O_3	54	55	57	85
	ZrB_2	66	80	89	94
Post Vacuum	Fe_3O_4	81	—	—	—
	ZnO	53	—	—	—
	KBr	51	—	—	—
	Y_2O_3	61	—	—	—
	ZrB_2	86	—	—	—

Potassium bromide was unusual in that removal after HWE was about two percent less than after vacuuming. This was likely due to the water solubility of potassium bromide—residual amounts remained in the water left behind after HWE. This also raises the possibility that wicking could have had an impact. Wicking would bring the compound closer to the detector and hence the associated XRF intensity could be greater. Although significant amounts of potassium bromide were removed, the complexity associated with use of it or other water-soluble compounds as a metric precluded its use in future tests.

It was important in this method to expose the carpet fibers in the same position for each scan. Any change in the apparent distribution of the compounds associated with distance could affect the XRF intensity. Therefore, the carpet must be brushed to remove matting and to keep the carpet fibers erect.

Conclusions

The XRF measurement method to assess carpet cleaning efficiency was technically feasible. It was shown to be a reliable means of quantifying the amount of test material removed from carpet during cleaning. Further applications of this methodology will be conducted and published at a later date.

Four XRF method demonstration tests were described and compared in this paper. They suggest that vacuuming in addition to HWE improved the efficiency of the carpet cleaning process over HWE alone. These tests support the view that vacuuming with machines designed to meet CRI Green Label criteria can be expected to be more efficient at matter removal than machines that did not meet CRI criteria. The test data suggest that, on average, slightly higher removal efficiency was achieved when effective vacuuming is done prior to HWE. However, in the absence of chemical pre-sprays, sticky, more clay-like or dense soil components are better removed by HWE followed by vacuuming.

These tests showed that the taggant removal effectiveness of HWE was greatly enhanced by the use of surfactant pre-sprays designed to aid in the suspension and removal of typical soils from carpet. Generally, the carpet cleaning process that employs a CRI Green Label vacuum cleaner and HWE technology combined with chemical pre-spray can be expected to be more efficient in soil removal than other processes tested.

The equipment and protocols described were successfully used in a study of a test cleaning system compared to a standard cleaning system and vacuuming only, replicating the life span of a commercial carpet.[21]

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