Identification of counterfeit sprayed fire-resistive materials and paints by NIR spectroscopy

Nam-Wook Cho[1], Hyun-Jun Shin[1], Byung-Yeol Min[1], Dong-Ho Rie[2], Sung-Yuk Yi[3], Won-Bo Cho[4] and Hyo-Jin Kim[4]*

[1]Department of Fire Disaster Prevention research center, Korea Institute of Construction Technology, IlSan, 411-712 Korea
[2]Fire Disaster Prevention Research Center, University of Incheon, Incheon, 406-772 Korea
[3]Bruker Optics Korea, Sungnam, 463-782 Korea
[4]Department of Pharmacy, Dongduk Women's University, Seoul 136-714 Korea
*Corresponding author: hyojkim@dongduk.ac.kr

Introduction

Sprayed fire-resistive materials and coatings are essential for preventing multi-storied steel buildings from being weakened by fire.[1] Current, standard methods for measuring the efficacy of fire-resistive materials involve real fire tests in dedicated laboratories, which are expensive and protracted (over several months). Therefore, the introduction of a simple test method that can verify the performance of fire-resistive material on-site, without conducting a real scale, fire-resistant test is needed. In this study, near infrared (NIR) spectroscopy was shown to be an effective method of screening for counterfeit fire-resistive materials.

Materials and Methods

Nine sprayed fire-resistive materials and three normal sprayed material sets were used for the analysis. Each material was represented by between 10 and 20 samples. Ten different paint materials, including two counterfeit fire-resistive coatings, were also analysed. Each sample was ground into a fine powder prior to analysis with a FT-NIR spectrometer (MPA, Bruker Optics Ettlingen, Germany). Diffuse reflectance NIR spectra were collected using an integrating sphere with a gold-coated reflection standard. Samples were scanned with a resolution of 8 cm^{-1} and 32 scans were co-added for each spectrum. Analysis of the spectral data was performed using OPUS 6.5 (Bruker Optics, Ettlingen, Germany). The calibration equation was developed with the QUANT software package using partial least squares (PLS) regression. Spectral data were pre-treated by calculating first derivative and standard normal variate (SNV) transformations.

Result and discussion

The major compositions of both the sprayed fire-resistive and non fire-resistive materials were measured by inductively-coupled plasma mass spectrometry (ICP-MS; Table 1). Most of the sprayed fire-resistive materials contained relatively high concentrations of Al_2O_3, MgO and SO_3, while non fire-resistive materials contained high concentrations of CaO. Al_2O_3 and MgO are beneficial in fire-resistive materials, SO_3 is a major component of gypsum ($CaSO_4.2H_2O$), and CaO is abundant in construction cement.[2,3] However, no single compound was indicative of sprayed fire-resistive materials. Figure 1 shows thermogravimetric analysis (TGA) results of nine normal fire-resistive materials and two kinds of normal sprayed materials. Temperature was steadily increased from room temperature to 1400°C at 10°C per minute. The first degradation around 400°C might be due to the water in all normal and fire-resistive materials. However, a second significant weight loss occurred after 500°C in non fire-resistive materials, while fire-resistive materials maintained their weight until around 1200°C.

Table 1. Concentration of major components in nine sprayed fire-resistive materials and three counterfeit materials (A, B, C).

	Escort Nf	Mono-z-106	HI-EF	MK-B	Semi	New HI-SP1	New HI-TP1	New HI-TP2	Escort CF-V	A	B	C
CaO	39.8	54.1	34.2	40.7	22.1	27.8	39.0	33.3	36.9	45.6	44.8	40.9
SO_3	34.5	14.9	35.3	48.2	21.4	23.7	12.7	33.7	23.5	16.4	17.1	31.0
SiO_2	9.51	13.3	5.47	1.03	38.1	5.76	23.2	6.06	20.5	9.18	9.18	8.17
Al_2O_3	4.96	3.65	1.41	0.51	2.66	16.7	5.0	1.64	7.44	1.62	2.00	1.39
MgO	0.39	2.89	11.0	0.45	4.20	8.63	4.0	12.3	0.63	5.34	5.95	0.84

Reference paper as:
Cho, N., Shin, H., Min, B., Rie, D., Yi, S., Cho, W. and Kim, H. (2012).Identification of counterfeit sprayed fire-resistive materials and paints by NIR spectroscopy, in: Proceedings of the 15th International Conference on Near Infrared Spectroscopy, Edited by M. Manley, C.M. McGoverin, D.B. Thomas and G. Downey, Cape Town, South Africa, pp. 17-20.

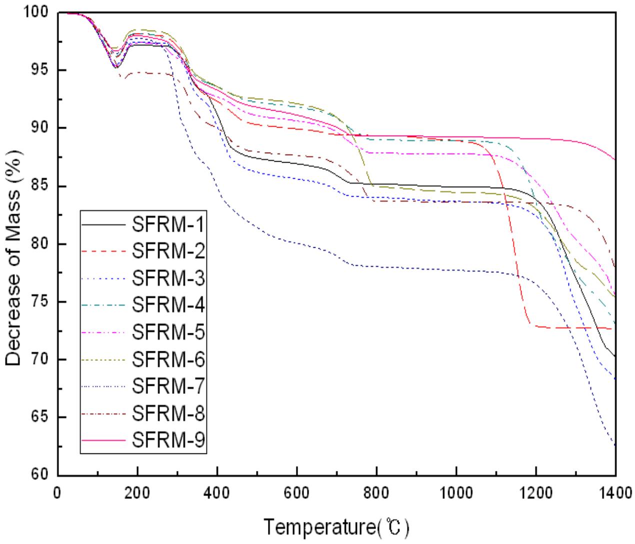

Figure 1. TGA thermograms of nine sprayed fire-resistive materials.

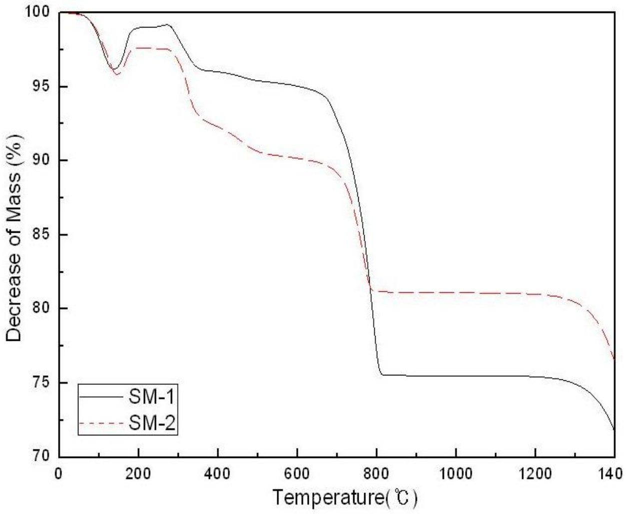

Figure 2. TGA thermograms of two counterfeit sprayed fire-resistive materials.

The average NIR spectra of officially approved fire-resistive materials were obtained (Figure 3). Various pretreatments were investigated to produce the best calibration model, which was then validated with several unknown samples. The average NIR spectra of counterfeit fire-resistive materials were also obtained (Figure 4). The samples was also analysed using various analytical methods such as x-ray fluorescence (XRF) spectroscopy, ICP-MS and thermogravimetric infrared (TG-IR) spectroscopy.

Principal component analysis (PCA) was used to discriminate normal and counterfeit sprayed fire-resistive materials (Figure 5). From an evaluation of the loadings, we found that three spectral regions (7305–6840 cm^{-1}, 5307–4900 cm^{-1} and 4404–4208 cm^{-1}) were heavily weighted, and could be attributed to stretches associated with OH, CaO and SO_3 (respectively).

Reference paper as:
Cho, N., Shin, H., Min, B., Rie, D., Yi, S., Cho, W. and Kim, H. (2012).Identification of counterfeit sprayed fire-resistive materials and paints by NIR spectroscopy, in: Proceedings of the 15th International Conference on Near Infrared Spectroscopy, Edited by M. Manley, C.M. McGoverin, D.B. Thomas and G. Downey, Cape Town, South Africa, pp. 17-20.

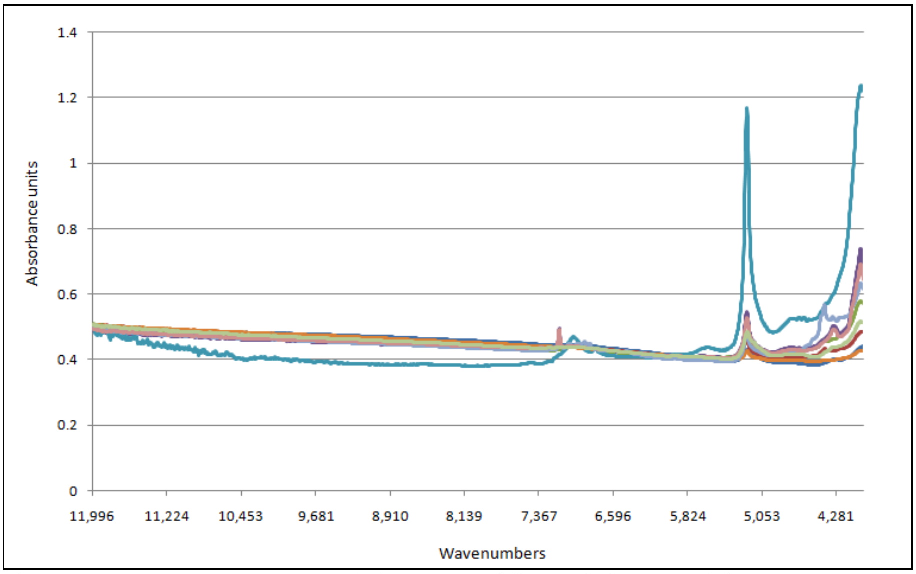

Figure 3. Average NIR spectra of nine sprayed fire-resistive materials.

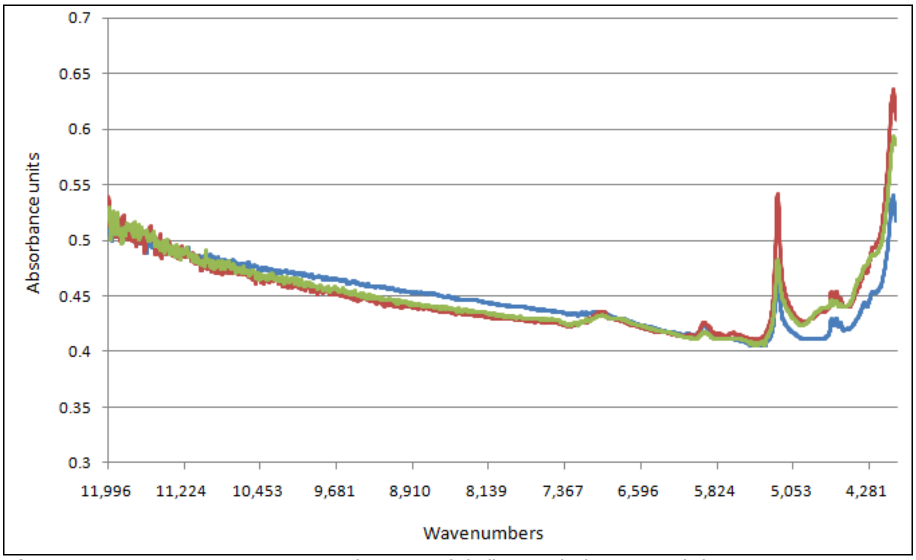

Figure 4. Average NIR spectra of counterfeit fire-resistive materials.

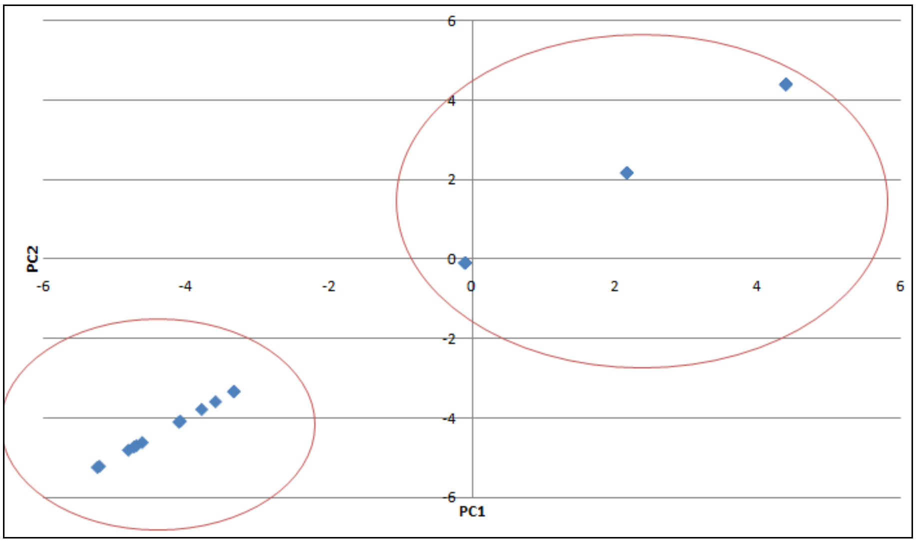

Figure 5. PCA results of normal and counterfeit sprayed fire-resistive materials.

Reference paper as:
Cho, N., Shin, H., Min, B., Rie, D., Yi, S., Cho, W. and Kim, H. (2012).Identification of counterfeit sprayed fire-resistive materials and paints by NIR spectroscopy, in: Proceedings of the 15th International Conference on Near Infrared Spectroscopy, Edited by M. Manley, C.M. McGoverin, D.B. Thomas and G. Downey, Cape Town, South Africa, pp. 17-20.

Conclusions

A fast, accurate and non-destructive NIR method for identifying counterfeit fire-resistive materials was developed. As a result, a NIR-based standard operating procedure (SOP) has been developed and implemented under Korean law.

Acknowledgements

This study was executed as a part of the Research and Development Project by the Korea Institute of Construction Technology for which we would like to extend our sincere gratitude

References

1. E. Arthur and P.E. Cote, *Fundamentals of fire protection*, Jone & Bartlett Pub, MA, p. 151 (2004).
2. L. Webb and J. E. Kruger, *Differential thermal analysis*, Academic Press, London, p. 181 (1972).
3. Y. Liu, A. Wang and J. Freeman, "Raman, MIR, NIR spectroscopic study of calcium sulfates, gypsum, bassanite and anhydrite", in *Proceedings of the 40th Lunar and Planetary Science Conference*, p. 2128 (2009).

Reference paper as:
Cho, N., Shin, H., Min, B., Rie, D., Yi, S., Cho, W. and Kim, H. (2012).Identification of counterfeit sprayed fire-resistive materials and paints by NIR spectroscopy, in: Proceedings of the 15th International Conference on Near Infrared Spectroscopy, Edited by M. Manley, C.M. McGoverin, D.B. Thomas and G. Downey, Cape Town, South Africa, pp. 17-20.