IDENTIFICATION OF ORGANIC COMPONENTS AND COMMERCIAL GRADE DEDICATION USING FOURIER TRANSFORM NEAR INFRARED SPECTROSCOPY

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Abstract

The over all quality assurance programs for the design, fabrication, and construction of nuclear power plants, both in Canada and USA have long been established. A need for an acceptance process to allow the use of commercial grade items to be utilized in safety related applications has been recognized. A guideline in the EPRI NP-5652 report and in the Appendix D of the CAN3-N286.2-86 standard is outlined for testing of commercial grade components. A new non-destructive and cost effective NIR identification technology is now available to meet the above requirements.

The Fourier Transform near infrared spectroscopy (FT-NIR), in the past, has shown to have the capabilities to identify cable insulation non-destructively and in-situ. This paper presents data to show the diversity of the NIR technology in the identification of three different non-metallic materials (wire insulation, o-rings, and greases, all part of the operation of the safety related equipment) for the purposes of quality assurance, quality control, and the commercial grade dedication of components. The enhanced quality control and quality assurance will result in significant savings not only in testing but also in the continuous and reliable operations of power plants.

1. Background

Quality assurance programs for the design, fabrication, and construction of nuclear power plants both in Canada (CAN3-N286.2-86, Appendix D)[1] and USA (10 CFR 50, Appendix B)[2] have been in place for a long time. A reduction in new nuclear power plant construction has resulted in the reduced availability of spare and replacement components designed specifically for nuclear safety related systems. Utilities are consistently facing the necessity to purchase commercial grade parts. The Nuclear Construction Issues Group (NCIG), with the support of the Electric Power Research Institute (EPRI), has prepared a guideline (EPRI NP-5652)[3] for the commercial grade dedication of components intended for use in safety related applications.

A need for an acceptance process that provides reasonable assurance that a commercial grade item received is the item specified is identified in the EPRI NP-5652 report. As part of the acceptance methods, method 1 describes the process for accepting a commercial grade item by conducting special tests and inspections. A similar qualification test is also identified in the Appendix D of the CAN3-N286.2-86 standard. A new non-destructive NIR identification technology offers such capabilities to meet the testing and inspection requirements.

In this paper we intend to demonstrate the diversity of the NIR technology in the identification of three different non-metallic materials (wire insulation, o-rings, and greases, all part of the operation of the safety related equipment) for the purposes of quality assurance and the commercial grade dedication of components. Furthermore, we will show that the FT-NIR technology is a fast, accurate, non-destructive and non-intrusive method for receipt-inspection, quality control and quality assurance and it will result in significant savings not only in testing and commercial grade dedication but also in life cycle management, reliable operations, and environmental qualifications.

2. What is NIR?

1. In spectroscopic terms, NIR means the measurement of the wavelength and intensities of the absorption of near infrared light by a sample. The absorption or reflectance spectrum is directly proportional to the chemical composition of the material.
2. In simple terms, a near infrared light is pointed at a sample using a fibre optic probe and the reflected signal is processed for absorption or reflectance characteristics. In other words, we take a chemical fingerprint of a material using infrared light at a specific point in time.
3. In economical terms, near infrared means fast, accurate, reliable, cost-effective and non-destructive measurements for identification of materials, quality assurance and commercial grade dedication of components.

The Fourier Transform near infrared spectroscopy (FT-NIR) has shown to have the capabilities to identify cable insulation non-destructively and in-situ [4]. The FT-NIR technology is currently used at Ontario Power Generation Inc. (OPGI) in Canada to identify unknown cable insulation and to determine the environmental qualification groups. Significant savings (millions) have now been attributed to the use of this technology. The NIR Technology is also used in other industries such as food, pharmaceutical, chemical, plastic, and medical due to its fast, accurate, and non-destructive characteristics.

3. Near Infrared Spectral Scanning and Analysis (Methodology)

A Vector 22/N model near infrared spectrometer manufactured by Bruker and its associated OPUS software was used in this investigation. The following steps were taken to scan and analyze all wire, grease and o-ring samples:

1. An experimental scanning file with all the appropriate parameters was established.
2. Internal instrument calibration tests were performed.
3. The wire (cable jacket was stripped to reach the wire insulation) and o-ring samples were scanned as received.
4. In the case of grease samples, a small specimen was placed between two microscopic slides and then scanned.
5. Using the standard fibre optic probe each sample was scanned at least 5 times to obtain an average absorption spectrum for that particular sample. In the case of grease samples, three specimens were prepared and scanned for each grease sample.
6. Two separate factorized analysis models were developed consisting of six o-ring samples, thirteen different wire insulation samples from three different manufacturers, and 11 different grease samples from three different manufacturers (see tables 1 and 2 for details).

4. Spectral Analysis and Identification of wire insulation, o-rings, and greases

A typical absorption spectrum for a grease sample, silicone o-ring, PVC (polyvinyl chloride) and XLPE (cross-linked polyethylene) wire insulation is shown in Figure 1. The near infrared light absorption range is between 800nm to 2500nm (12,500 cm^{-1} to 4,000 cm^{-1} wavenumber). The absorption is due to overtones and combination bands of functional group vibrations in the mid-infrared region. The strong vibrational bands include C-H, O-H, C=O, N-H, -COOH, and aromatic C-H groups. It is generally difficult to assign an absorption band in the near infrared region to a specific functional group due to overlapping of several combinations and overtones. Now, with the advancements in computing power and instrumentation in the last decade combined with chemometrics (multivariate calibration methods) we are able to analyze complex systems. For example, using the software analysis tools one can convert the absorption spectrum to its 2nd derivative equivalent as shown in Figure 2 for the above samples. As can be seen, there are significant differences between 4000 to 4750 cm^{-1} (combination region) of these materials. In addition, further differences can be seen in the regions 5300 to 6300 cm^{-1}, 6900 to 7300 cm^{-1}, and 8100 to 8700cm^{-1} (all due to overtones of functional groups).

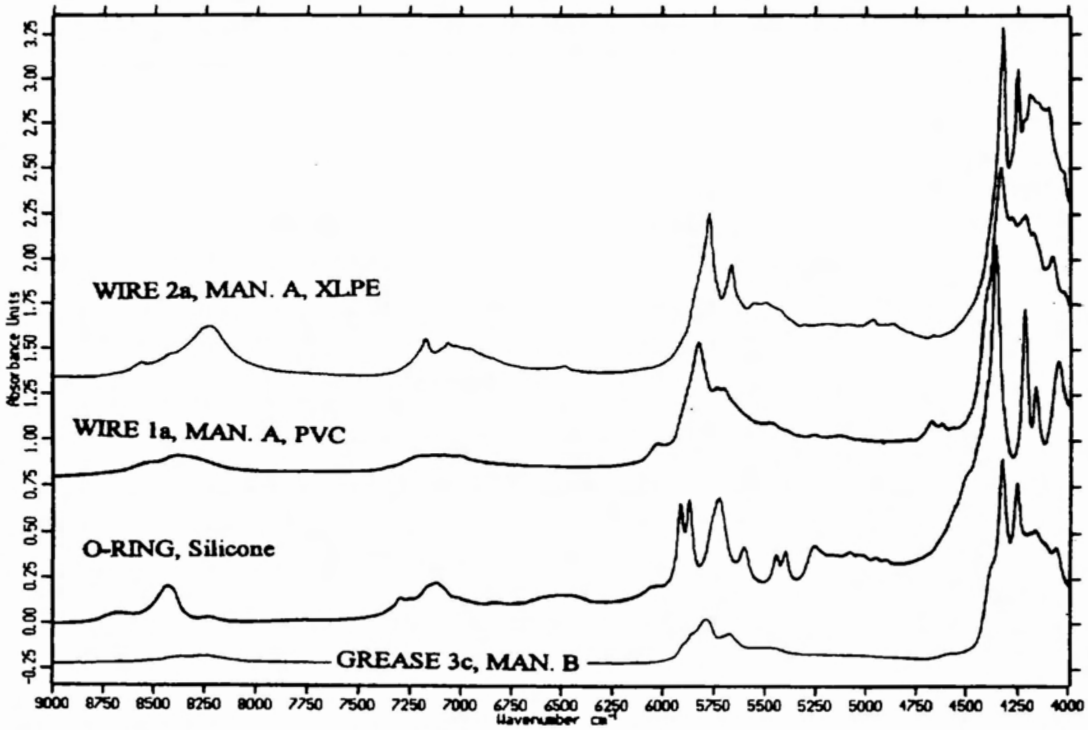

Figure 1 Absorption Spectra of a) Grease, b) Silicone O-ring, c) PVC and d) XLPE wire Insulation

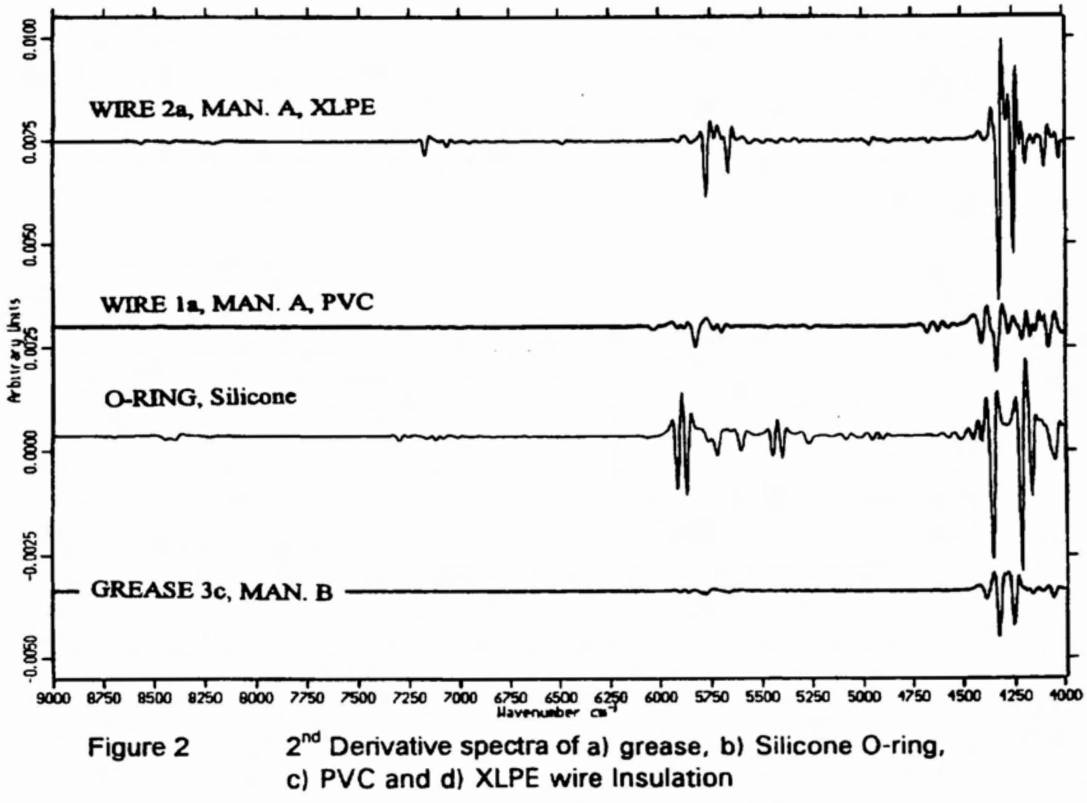

Figure 2 2^{nd} Derivative spectra of a) grease, b) Silicone O-ring, c) PVC and d) XLPE wire Insulation

The existence of combination and overtone absorption is one of the advantages of near infrared over mid-infrared spectroscopy. The other major advantage is the economical use of fibre optic materials in conjunction with the near infrared spectroscopy. The fibre optic probe capability makes the NIR Technology a portable technique allowing in-situ scanning in field applications. The existence of combination and overtone bands in the near infrared region also makes the application of multivariate calibration methods easy. For example, factorization analysis of wire insulation together with o-ring materials and grease samples was conducted and the results are shown in Figures 3 and 5 respectively. As can be seen, similar materials cluster together indicating material similarity. A more detailed analysis is presented in part 4.1, discussion of NIR scanning results.

Multivariate calibration is also applied in the identification of materials. Once a reference spectral model is developed, an analysis of a test sample can be achieved in a few minutes. Analysis of a test sample is comprised of comparison of the test spectrum or the average spectrum of the test sample with all reference spectra in the model. The outcome of this comparison is a spectral distance 'D' also known as 'Hit Quality'. The smaller the 'D' value the more similar the two spectra. A Hit Quality of Zero means that the sample spectrum was compared to itself in the spectral reference model. Tables 4, 5, 6, and 7 show the identification report for a silicone o-ring, a PVC (polyvinyl chloride) and a XLPE (cross-linked polyethylene) wire insulation and a grease sample respectively. The key elements in these reports are the Hit Quality and the Threshold value (obtained from the average of five different measurements) of the reference sample. There are three possible outcomes when a test spectrum is compared to a reference material in the spectral identification model:

1. **Identical** - in this case, the Hit Quality of the test sample is lower than the threshold value of the reference sample therefore the test material is identical to the reference sample.
2. **Can be confused with <N> other hits** - under this result, the test sample spectrum has been found to be identical to more than one reference spectrum (this result occurs because we deliberately placed two similar wires in the reference model to show quality control in manufacturing of materials).
3. **Not identical** - this result happens when the test sample spectrum is compared to a wrong reference material or no similar material can be found in the spectral reference model.

4.1 Discussion of NIR Scanning Results

To protect the identity of the manufacturers, who have generously supplied the various samples for this study and their product specifications, we have labeled all samples as wire 1,2, or 3, or grease 1, 2, 3, 4, 5 or 6, and manufacturers as Man. 'A', 'B', or 'C'. The o-ring samples were generously provided by D&D Packing and Seals Inc. without any reference to their manufacturers. Table 1 shows o-ring and wire insulation samples used for this study. Once all samples were scanned, two separate factorized NIR models were developed for the identification of these materials.

Table 1 List of O-ring and wire insulation

Scan #	Sample description	Manufacturer or supplier
1	Viton O-ring	D&D
2	EDPM O-ring	D&D
3	Neorprene O-ring	D&D
4	Silicone O-ring (red)	D&D
5	Silicone O-ring (white)	D&D
6	Urethane O-ring	D&D
7	Wire 1a, PVC	A
8	Wire 1b, PVC	A
9	Wire 1a, PVC	B
10	Wire 1b, PVC	B
11	Wire 2a, XLPE	B
12	Wire 2b, XLPE	B
13	Wire 2a, XLPE	A
14	Wire 2b, XLPE	A
15	Wire 1a, PVC	C
16	Wire 1b, PVC	C
17	Wire 2a, XLPE	C
18	Wire 2b, XLPE	C
19	Wire 3, unknown	A

Figures 1 and 2, absorption and 2^{nd} derivative spectra respectively show qualitative spectral differences between two wire insulations, a grease, and an o-ring material. Further detailed analysis is obtained when a factorized model is developed for the identification of these materials. Figure 3 shows two components, Vect. 1 and Vect.3 factorized analysis (an alternative mathematical treatment of data) for o-ring and wire insulation samples. As can be seen, samples 1 to 6 (o-ring samples) are scattered from each other with the exception of samples 4 and 5 which are both made of silicone rubber.

The scatter is as expected since they are made of different rubber materials. Figure 3 also shows two additional clusters each representing a PVC and XLPE set of wire insulation. We have also included a wire insulation (scan # 19) from manufacturer 'A' that has a completely different formulation to PVC and XLPE.

4.2 Factorized analysis of wire insulation

A close up of the wire insulation analysis is shown in Figure 4. As can be seen samples 7, 8, 9, 10, 15 and 16 represent three different PVC wire insulation made by three different manufacturers. All three PVC samples could be identified from each other (see part 4.4 below for identification report).

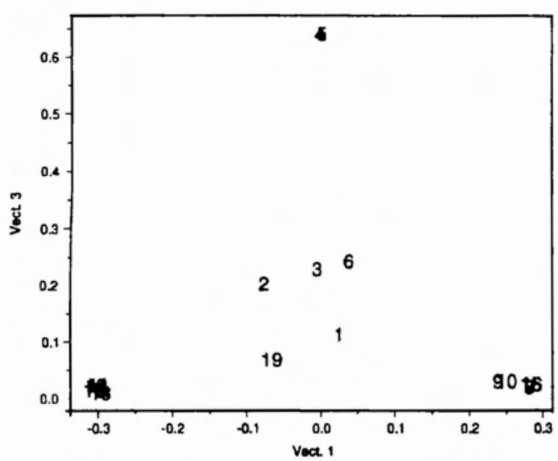

Figure 3 Factorized analysis of wire insulation and o-ring material

A similar pattern is also observed for three different XLPE samples from manufacturers 'A', 'B', and 'C'. Each pair ((11and 12), (13and 14), (17 and 18)) consists of the same insulation within a cable and as expected it is identical to each other. When different XLPE samples were analyzed individually, there were some differences between them.

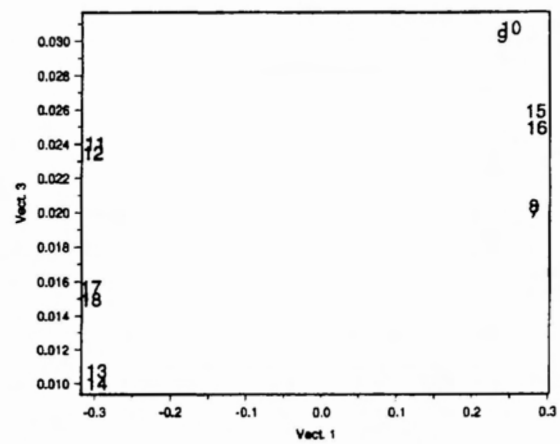

Figure 4 Factorized analysis of wire insulation (PVC and XLPE)

These differences could be due to a number of reasons. For example, batch to batch variation, slightly different formulation, processing conditions, etc. These sample differences may or may not affect the performance of the cable insulation but what is important that the NIR technology has the sensitivity to differentiate between these changes. The quality control and quality assurance is established between the vendor and purchaser. However, once the QA/QC requirements are established between the vendor and supplier, we have the capability to incorporate those requirements within the spectral reference model for future analysis. It is also important to note that the NIR Technology does not determine the performance of these materials. The performance of any material is established by destructive, chemical, physical, mechanical and electrical tests. Once a suitable material formulation is established the NIR Technology will non-destructively identify the chemical composition of the sample and match it to the reference spectrum and eliminate the requirements for the costly and time consuming destructive tests for the purposes of quality assurance and commercial grade dedication of components.

4.3 Factorized analysis of Grease samples

Table 2 shows all the grease samples studied in this investigation. A slightly, different picture emerges with grease samples. For example, Figure 5 shows a factorized analysis of 11 grease samples. As it was indicated above, three specimens were prepared and scanned for each grease sample.

Table 2 List of grease samples

Scan #	Sample Description	Manufacturer or supplier
1	Grease 1a	A
2	Grease 1b	A
3	Grease 1c	A
4	Grease 2a	A
5	Grease 2b	A
6	Grease 2c	A
7	Grease 1a	B
8	Grease 2a	B
9	Grease 2b	B
10	Grease 2c	B
11	Grease 1a	C
12	Grease 1b	C
13	Grease 1c	C
14	Grease 3a	A
15	Grease 3b	A
16	Grease 3c	A
17	Grease 5a	A
18	Grease 5b	A
19	Grease 5c	A
20	Grease 5d	A
21	Grease 3a	B
22	Grease 3b	B
23	Grease 3c	B
24	Grease 1b	B
25	Grease 1c	B
26	Grease 4a	A
27	Grease 4b	A
28	Grease 4c	A
29	Grease 6a	A
30	Grease 6b	A
31	Grease 6c	A
32	Grease 7a	A
33	Grease 7b	A
34	Grease 7c	A

Scan numbers 11, 12, and 13 representing grease '1' from manufacturer 'C' and as can be seen it can be distinguished from the rest easily. Scan numbers 1, 2, 3 (grease '1' from manufacturer 'A') and scan numbers 4, 5, 6 (grease '2' from manufacturer 'A') are for the same grease but different batches. A similar case could be made for scan numbers 14, 15, 16 (grease '3' manufacturer 'A') and 26, 27, 28 (grease '4' manufacturer 'A'). In both cases a batch to batch variation is observed that shows sensitivity of the NIR technology. Once again, this variation from batch to batch may not be a significant factor in the performance of a grease (the performance acceptance criteria are developed by destructive tests and are agreed between the vendor and supplier) but the NIR technology shows capability of distinguishing this variation.

Another separate cluster can be seen for scan numbers 7, 24, 25 (grease 1, manufacturer 'B') and 8, 9, 10 (grease '2' manufacturer 'B') representing two closely related grease samples '1' and '2' from manufacturer 'B'. It is important to note that the intention of this paper was to demonstrate the capabilities of the NIR technology for identification of materials and quality assurance purposes and not a complete investigation of grease formulations. However, it is clear from this study that such an investigation is not beyond the capabilities of the NIR technology.

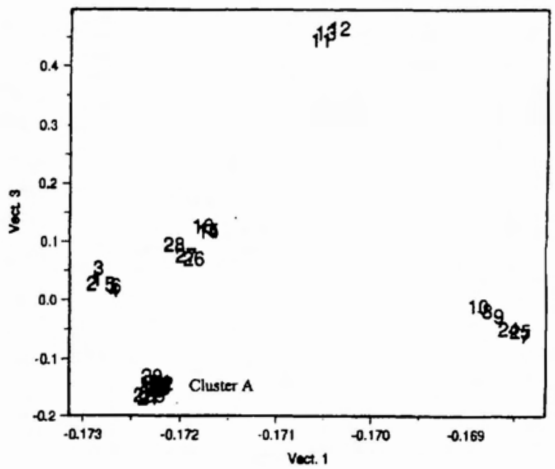

Figure 5 Factorized analysis of different greases

Figure 5, also shows a cluster of several grease formulations from two different manufacturers ('A' and 'B'). An expanded cluster A is shown in Figure 6. Scan numbers 17, 18, 19, 20 (grease '5' manufacturer 'A'), 21, 22, 23 (grease '3' manufacturer 'B'), 29, 30, 31 (grease 6 manufacturer 'A') and scan numbers 32, 33, 34 (grease '7' manufacturer 'A') show very similar responses to NIR analysis. The last two sets are again two different batches of the same grease from manufacturer 'A'. This study shows that several of these grease types could be easily distinguished from each other in less than a few minutes using non-destructive near infrared technology.

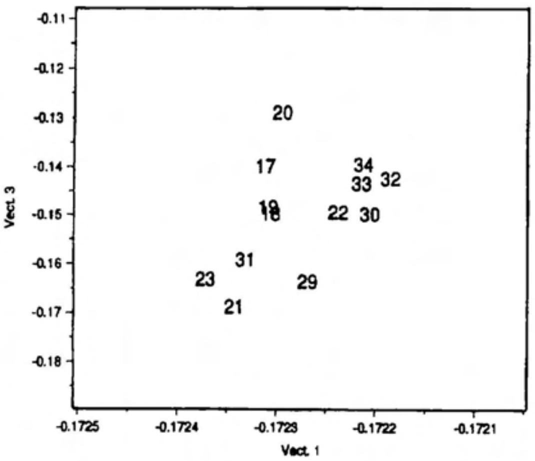

Figure 6 Factorized analysis of grease samples inside the cluster A

As indicated above a batch to batch variation is only significant if the performance of the material deteriorates. Based on the limited number of grease samples a more detailed verification of the batch to batch differences is needed to validate the current NIR spectral model.

4.4 Non-destructive Identification of Materials

Once an acceptable reference spectral model is generated and validated, the identification of incoming material can be done within minutes. The complete receipt-inspection (identification) process for incoming material (scanning, averaging of spectra, and identity test) can be accomplished in less than a few minutes. The following tables show the identity report for O-ring materials, wire insulation and a grease sample. As we explained earlier (see part 4 above), the OPUS software provides three possible outcomes when an incoming sample spectrum is compared to the reference spectra in the reference spectral model. For example, Tables 3 and 4 show the identity test report for EPDM and silicone o-rings and in both cases, materials were identified as "Identical" to the reference spectrum. Table 5 shows the identity report for the wire insulation 1a, Man. A, PVC. You will notice that the description in the report states "CAN BE CONFUSED WITH I OTHER HITS: -1" This was as expected since we had included two different colours of the same wire insulation in the spectral reference model i.e., Wire 1a, Man A, PVC and Wire 1b, Man. A, PVC are identical materials and the result clearly shows that the two wires have the same chemical formulation. A similar outcome for the XLPE insulation is shown in Table 6. Again the result indicates that Wire 2b, Man A, XLPE and Wire 2a, Man A, XLPE have the same chemical formulation. The same outcome was also observed for grease samples 2a, 2b, and 2c from Man. A in Table 7 and again the result indicate that the test spectrum can be confused with 2 other references (we had included three grease specimens per grease sample in the spectral reference model).

5. Component identification and commercial grade dedication using NIR technology

The guidelines for Quality Assurance, Quality Control and Commercial Grade Dedication of components for nuclear power plants are clearly stated in the CAN3-N286.2-86, Appendix D and USA (10 CFR 50, Appendix B) standards. Furthermore, EPRI report, EPRI NP-5652 and Appendix D of the CAN3-N286.2-86 standard suggest that an acceptance test must be conducted to ensure Quality Assurance. The safe and reliable operation of nuclear power plants depends on the use of properly tested and specified components. The cost elements for testing and inspection for the purposes of commercial grade dedication must be assessed against any possible shut down or delays due to the use of inappropriate material.

The FT-NIR technology is a fast, accurate, non-destructive, and non-invasive comparative method that can be used in receipt-inspection, quality control/quality assurance and commercial grade dedication to finger print non-metallic components. As shown before in the cable insulation identification, the use of NIR technology will result in significant savings not only in testing and commercial grade dedication but also in life cycle management, environmental qualification, and safe and reliable operation of nuclear power plants.

References

1. Design Quality Assurance for Nuclear Power Plants, CAN3-N286.2-86.
2. Quality Assurance Criteria for Nuclear Power Plants and Fuel Reprocessing Plants. 10CFR50, Appendix B, November 1987.
3. Guideline for the Utilization of Commercial Grade Items in Nuclear Safety Related Applications (NCIG-07), EPRI NP-5652 (June 1988).
4. Azizian Hormoz "Identification of Nuclear Cables Using a Non-destructive, Non-intrusive Near Infrared (NIR) Spectroscopy Technology", OPT Report: 6692-000-1998-RA-0001-R01 (May 31, 1999).

Acknowledgements

Author would like to express his appreciation to the Canadian Nuclear Society (CNS) for the opportunity to present this paper and to the following individuals and companies for their generous donation of samples for this study: 1) John Janis, Kinectrics; David A. Slack, Imerial oil; Abid Rehman, Shawflex (Shaw Industries Ltd.); Tom Mascardo, Alcatel Canada Wire-Equipment Cables; Bonnie Jones, Belden (Canada) Inc.; Greg Blenkarn, D&D Packing & Seals Inc. Thanks are also due to Michael Younikian, coop student from Sheridan College for his help in the last stages of this work and Pel Castaldo, OPGI for reviewing the paper.

Table 3 Identity Report for EPDM o-ring

File Name:		E:\CNS\S\OPUEPD.500		
Sample Name:		NIR D&D Purple EPDM		
Report of Correlation Search				
Method file:		E:\CNS\S\CNSWO2.FAA		
Description:		IDENTICAL TO: NIR D&D Purple EPDM: 1		
Hit quality with expected reference:		4.10118e-008		
Threshold for expected reference:		0.024106		
Threshold calculation:		Constant confidence level [%] 99.00		
Algorithm:		Factorization		
Hit No.	**Hit Quality**	**Sample Name**	**File name**	**Threshold**
1	4.10118e-008	NIR D&D Purple EPDM	OPUEPD.500	0.024106
2	0.10355	NIR D&D Red Neoprene	ORENEO.500	0.012185
3	0.77344	NIR Wire 2b, Man. A, XLPE	S14G6CG.500	0.003173
4	0.77378	NIR Wire 2a, Man. A, XLPE	S14G6CB.500	0.005409
5	0.79042	NIR Wire 2b, Man. B, PVC	S10TWUW.500	0.008008

Table 4 Identity Report for white silicone 0-ring

File Name:		E:\CNS\S\OWHSIL.500		
Sample Name:		NIR D&D White Silicone		
Report of Correlation Search				
Method file:		E:\CNS\S\CNSWO2.FAA		
Description:		IDENTICAL TO: NIR D&D White Silicone: 1		
Hit quality with expected reference:		3.60844e-008		
Threshold for expected reference:		0.00422139		
Threshold calculation:		Constant confidence level [%] 99.000000		
Algorithm:		Factorization		
Hit No.	**Hit Quality**	**Sample Name**	**File Name**	**Threshold**
1	3.60844e-008	NIR D&D White Silicone	OWHSIL.500	0.0042213
2	0.014122	NIR D&D Red Silicone	ORESIL.500	0.0029123
3	0.809489	NIR Wire 1b, Man. B, XLPE	S12RWW.500	0.0076221
4	0.810695	NIR Wire 1a, Man. B, XLPE	S12RWR.500	0.0036313
5	0.815681	NIR Wire 2a, Man. C, XLPE	S16G4CR.500	0.0123604

Table 5 Identity Report for PVC Insulation

File Name:		E:\CNS\S\S10G5CO.500		
Sample Name:		NIR Wire 1a, Man. A, PVC		
Report of Correlation Search				
Method file:		E:\CNS\S\CNSWO2.FAA		
Description:		CAN BE CONFUSED WITH 1 OTHER HITS: -1		
Hit quality with expected reference:		1.03458e-008		
Threshold for expected reference:		0.00963369		
Threshold calculation:		Constant confidence level [%] 99.000000		
Algorithm:		Factorization		
Hit No.	**Hit Quality**	**Sample Name**	**File Name**	**Threshold**
1	1.03458e-008	NIR Wire 1a, Man. A, PVC	S10G5CO.500	0.0096336
2	0.004288	NIR Wire 1b, Man. A, PVC	S10G5CR.500	0.0097485
3	0.014026	NIR Wire 1a, Man. C, PVC	S16G2PW.200	0.0089985
4	0.014547	NIR Wire 1b, Man. C, PVC	S16G2PW.500	0.0121203
5	0.223164	NIR Wire 2b, Man. B, PVC	S10TWUW.500	0.0080087

Table 6 Identity Report for XLPE Insulation

File Name:	E:\CNS\S\S14G6CG.500
Sample Name:	NIR Wire 2b, Man. A, XLPE
Report of Correlation Search	
Method file:	E:\CNS\S\CNSWO2.FAA
Description:	CAN BE CONFUSED WITH 1 OTHER HITS: -1
Hit quality with expected reference:	1.72863e-008
Threshold for expected reference:	0.00317342
Threshold calculation:	Constant confidence level [%] 99.000000
Algorithm:	Factorization

Hit No.	**Hit Quality**	**Sample Name**	**File Name**	**Threshold**
1	1.72863e-008	NIR Wire 2b, Man. A, XLPE	S14G6CG.500	0.0031734
2	0.0013622	NIR Wire 2a, Man. A, XLPE	S14G6CB.500	0.0054095
3	0.0522667	NIR Wire 1a, Man. B, XLPE	S12RWR.500	0.0036313
4	0.0594458	NIR Wire 1b, Man. B, XLPE	S12RWW.500	0.0076221
5	0.0854735	NIR Wire 2a, Man. C, XLPE	S16G4CR.500	0.0123604

Table 7 Identity Report for Grease

File Name:	E:\MY\G\GUN591.200
Sample Name:	NIR Grease 2a, Man. A
Report of Correlation Search	
Method file:	E:\MY\G\GTHICK3.FAA
Description:	CAN BE CONFUSED WITH 2 OTHER HITS: -1
Hit quality with expected reference:	4.76982e-007
Threshold for expected reference:	0.0137633
Threshold calculation:	Constant confidence level [%] 99.000000
Algorithm:	Factorization

Hit No.	**Hit Quality**	**Sample Name**	**File Name**	**Threshold**
1	4.76982e-007	NIR Grease 2a, Man. A	GUN591.200	0.0137633
2	0.00695914	NIR Grease 2c, Man. A	GUN593.200	0.0078242
3	0.00699799	NIR Grease 2b, Man. A	GUN592.200	0.0055301
4	0.0301099	NIR Grease 1c, Man. A	GUNN23.200	0.0105131
5	0.0351293	NIR Grease 1b, Man. A	GUNN22.200	0.0090751
6	0.0378255	NIR Grease 1a, Man. A	GUNN21.200	0.0088211
7	0.155568	NIR Grease 5d, Man. A	GLONX4.200	0.0313128
8	0.165741	NIR Grease 5a, Man. A	GLONX1.200	0.0150819