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**NRC-CMRC**

## New Technology to Measure Concentration of Cross-linking By-products in Plastics

*A novel optical technique has been developed to determine the concentration of by-products in chemically cross-linked plastic materials. Unlike presently employed analytical techniques, the optical method involves in-situ detection of thermoluminescence (TL) emitted by the cross-linking by-products during the initial thermal treatment. The intensity of the emitted light provides a direct measurement of the concentration of the cross-linking by-products in the material.*

### Advantages of the Optical Technique:

- Provides increased sensitivity and thus enhanced detection of the by-products
- Continuous monitoring of the concentration of the by-products
- Eliminates need to extract by-products from the sample for analysis
- Eliminates interruption of thermal treatment except when desired concentration of the by-products is reached
- Saves time, money and labour

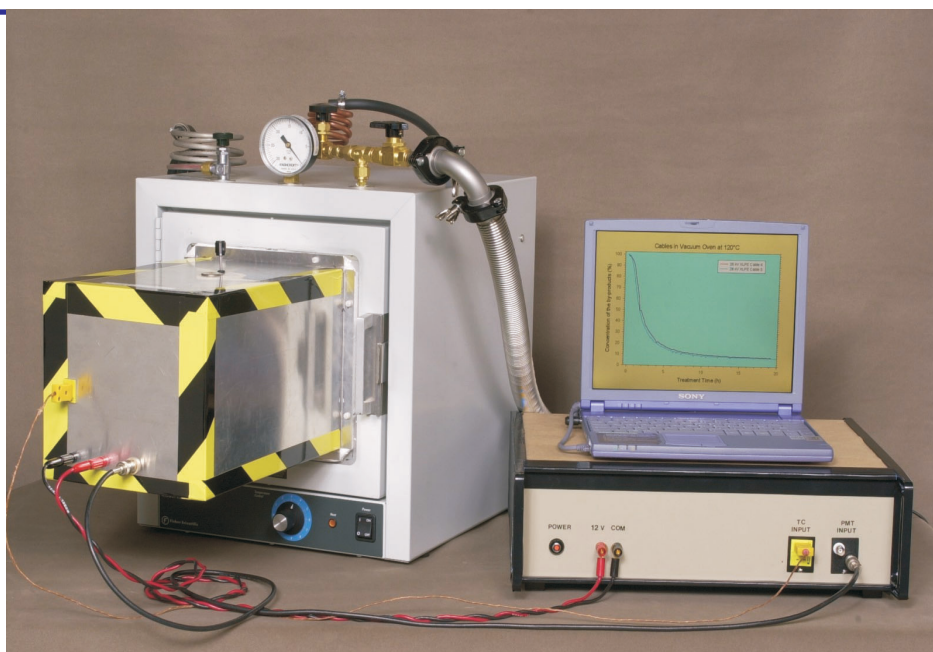


Figure 1. Prototype of the instrumentation for optical measurement of the concentration of cross-linking by-products in polymeric materials.

A setup for the optical technique, which can perform in-situ measurements of the concentration of the by-products, consists of a housing containing the light detection system that is attached to an oven in which the materials are treated at elevated temperatures (Fig. 1). The light emitted by the by-products is monitored by a detector such as a photomultiplier tube (PMT). The detector is connected to a PC for continuous monitoring. The intensity of the emitted light determines the concentration of the by-products present in the material and the thermal treatment can be stopped when the desired level has been reached.

Polymeric materials are extensively used to manufacture a wide variety of goods, such as air-tight plastic boxes to store food. To improve the thermal and dimensional stability the polymers are usually cross-linked. Chemical cross-linking by dicumyl peroxide is widely used but this method creates cross-linking by-products such as acetophenone, cumyl alcohol, and  $\alpha$ -methyl styrene, which remain inside the plastic material for a long time.

A crosslinking by-product such as acetophenone is fugitive and over time it exudes out of the polymer. At temperatures above 40°C, such as during the heating of food containers in a microwave oven, the by-products would exude out of the material and contaminate the food or the articles stored in the plastic container.

At NRC of Canada a novel optical method was developed that performs in-situ measurement and provides continuous monitoring of the residual by-products in plastics. There is no need to stop the treatment and this saves time. This method is non-destructive as there is no need to cut any samples or do any extractions with the solvents.

The optical technique is simple for it detects the Thermoluminescence (TL) emitted by the by-products in the material. The intensity of TL is directly proportional to the concentration of the cross-linking by-products present in the material.

Figure 2 shows a block diagram of the TL set-up, which consists of an oven that can be evacuated or purged with an inert gas such as Nitrogen.

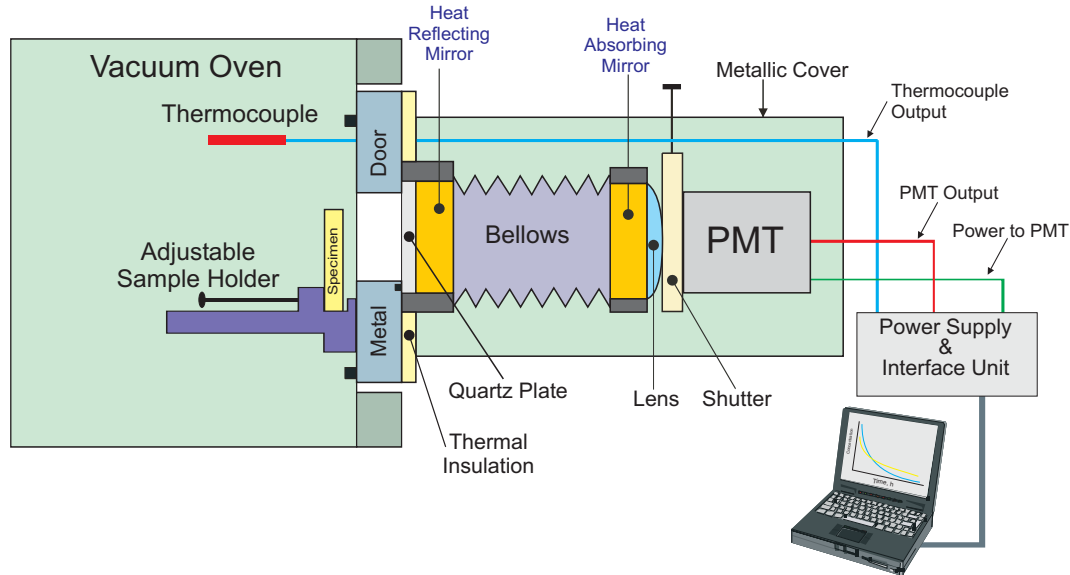


Figure 2. Set-up for Thermoluminescence measurements.

The sample is placed in the oven and during the thermal treatment the TL emitted from the sample is detected by a PMT. Unlike conventional PMT tubes that need to be cooled and require 1500 V to operate this tube operates at RT and only requires  $\pm 12$  V. The light is continuously monitored by a PC, which also records the time of treatment and the temperature of the oven during the treatment.

Figure 3 shows the concentration of the by-products as a function of the treatment time. The residual concentration of the by-products in the material is plotted as the percentage of the initial concentration. The advantage of the TL technique is that it provides continuous monitoring of the concentration of the cross-linking by-products while the treatment is being performed. The three curves are for samples of the same material, which were treated at three different temperatures. The graph shows that, as expected, the concentration of the by-products reduces much faster when the treatment is performed at a higher temperature.

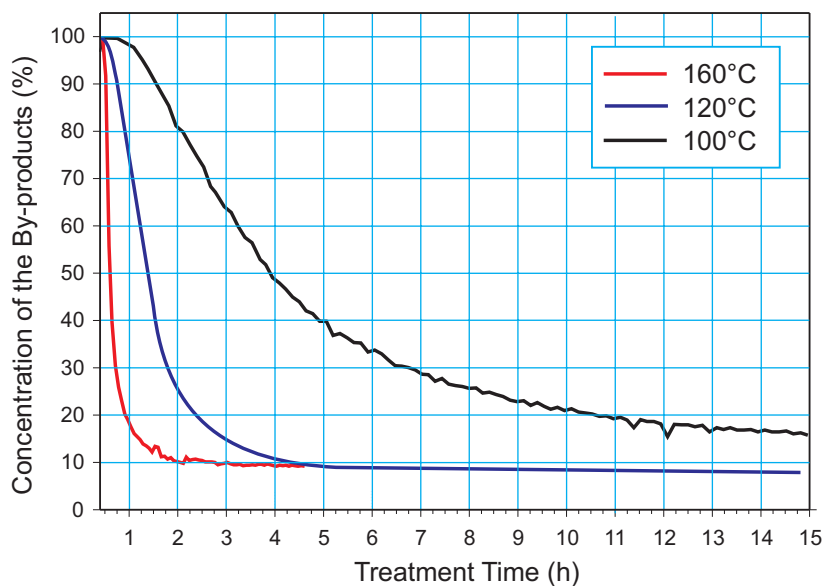


Figure 3. Concentration of cross-linking by-products in Material-A versus time of treatment at various temperatures in vacuum at 0.1 Pa.

Figure 4 compares the TL from two materials (both cross-linked polyethylene), treated at the same temperature of 100°C in a vacuum oven. The graph shows that Material-A has more by-products than Material-B and that they are removed from the polymer at a much faster rate. This illustrates another advantage of this technique i.e., the ability to compare the rates at which the by-products are removed from different materials by thermal treatment.

Another application for this technique is in the electric power industry. Polyethylene has been extensively used in underground transmission and distribution high voltage cables. There are approximately 450,000 miles of cables with extruded polymeric insulation installed in the USA alone. High voltage cables operate at temperatures above ambient, hence the insulation surrounding the conductor is subjected to elevated temperatures and a temperature gradients. To improve the thermal and dimensional stability, the polymer is usually cross-linked. Chemical cross-linking by dicumyl peroxide is widely used but this method creates cross-linking by-products,

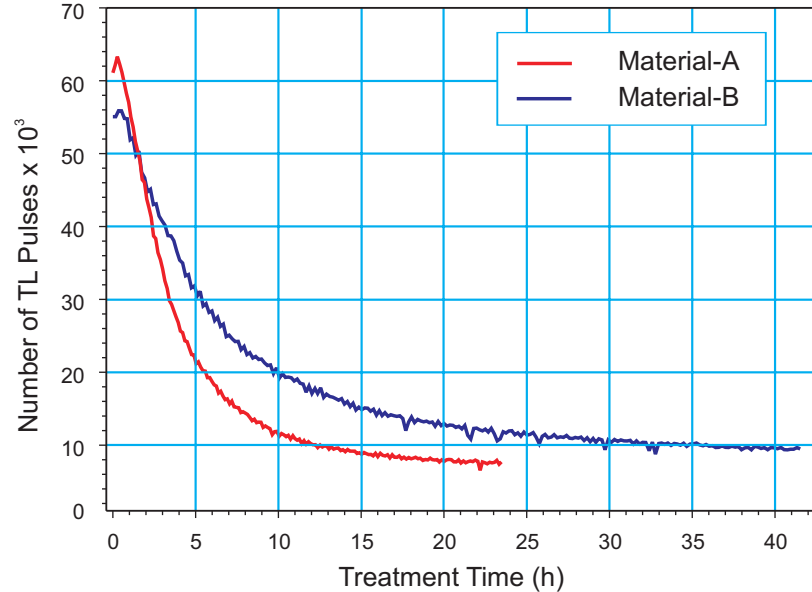


Figure 4. Effect of time of treatment in vacuum oven at 100°C for the concentration of cross-linking by-products in two materials.

which affect insulation properties. Some of these by-products, e.g. acetophenone, decrease the breakdown strength of polymeric cables (Figure 5).

Acetophenone also traps space charge, especially under the application of dc voltage, to form chemically complex degradation products. At high temperatures, such as during the preparation of in-situ molding of cable joints, water is generated from cumyl alcohol. This could lead to water treeing, one of the major forms of degradation of underground cable insulation (Fig. 6).

Water trees consist of numerous cavities filled with water and ionic and other contaminants (Fig. 7). The treed insulation is significantly weaker than the un-treed insulation and water trees are usually the cause of premature cable failures.

Prior to commissioning into service, freshly manufactured cables are

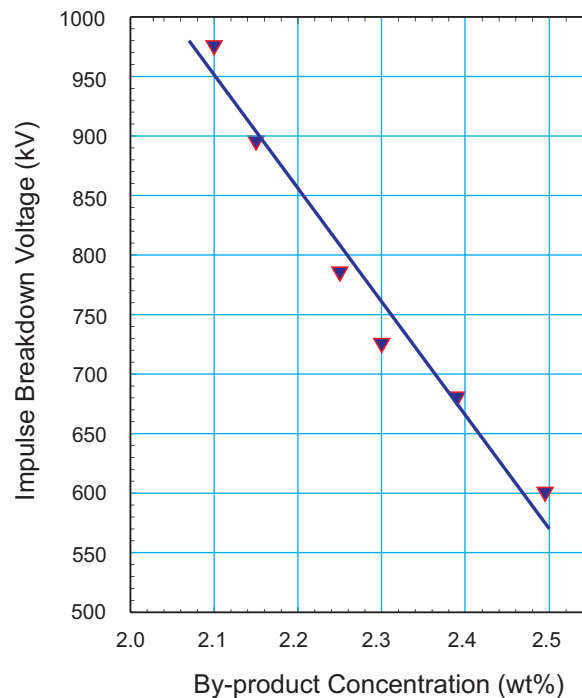


Figure 5. Impulse breakdown strength of a freshly manufactured, 22 kV rated XLPE cable versus concentration of the cross-linking by-products.

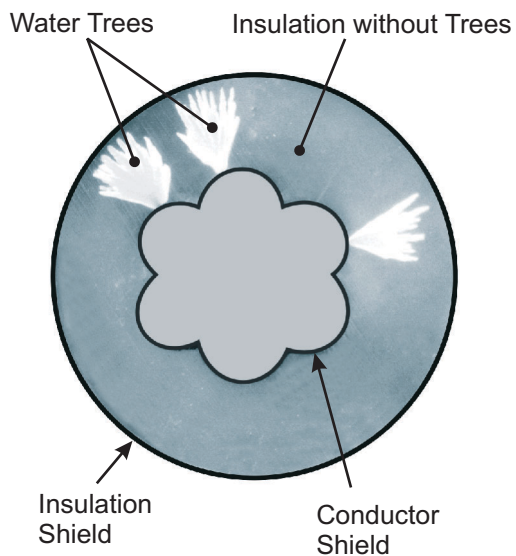
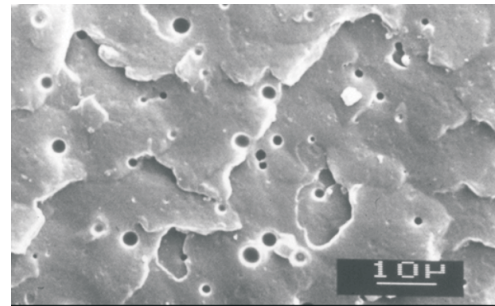
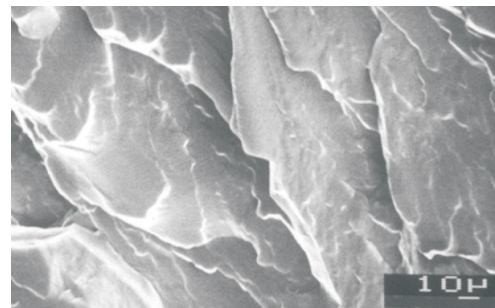


Figure 6. Cross-section of the underground cross-linked polyethylene insulated cable showing water trees.



Water-treed Region



Un-treed Region

Figure 7. SEM micrographs of freeze fractured cross-linked polyethylene insulation with and without water trees.

subjected to high voltage tests to check the integrity of the polymeric insulation. During these tests the cross-linking by-products, which are polar materials, would grade the electric field around defects inside the insulation and could jeopardize their detection. Therefore, prior to installation, underground high voltage cables must be subjected to thermal treatment in order to reduce the concentration of the cross-linking by-products.

At present, to determine the exact concentration of the cross-linking by-products in the cable insulation, the thermal treatment has to be stopped and samples of the insulation have to be removed and analyzed by analytical techniques, which are costly and time consuming. For example, with mass spectroscopy, it may take several hours to extract the by-products with various environmentally hazardous solvents before their concentration can be determined.

Table 1 shows the concentration of the cross-linking by-products in Material-B specimens as measured by mass spectrometer. The concentration in the untreated samples was measured just after cross-linking the polymer.

To reduce the concentration of the by-products in the polymer some samples were treated in a vacuum (0.1 Pa) oven at 120°C for 24 h. This decreased the concentration of the by-products by almost two orders of magnitude and these samples are referred to as Type-I. Further treatment in a vacuum oven at 90°C for 170 h reduced the concentration to very low levels which could barely be resolved by the mass spectrometer. Such samples are referred to as Type-II samples.

Figure 8 shows the temporal behaviour of the light emitted from Material-B samples held at 50°C in vacuum (0.1 Pa). The background level, shown by the black curve, is the dark current of the detector.

Table 1. Concentration of the cross-linking by-products in Material-B measured with a mass spectrometer.

Sample	Treatment	Cross-linking by-products (wt%)		
		Acetophenone	Cumyl Alcohol	$\alpha$ -Methyl Styrene
Untreated	None (Freshly cross-linked)	0.455	1.121	0.014
Type-I	After cross-linking treated in vacuum (0.1 Pa) at 120°C for 24 h	0.007	0.006	0.003
	% Reduction	98.5	99.4	78.6
Type-II	As in Type I and further treated in vacuum at 90°C for 170 h	<0.001	0.002	<0.001
	% Reduction	>99.8	99.8	>92.8

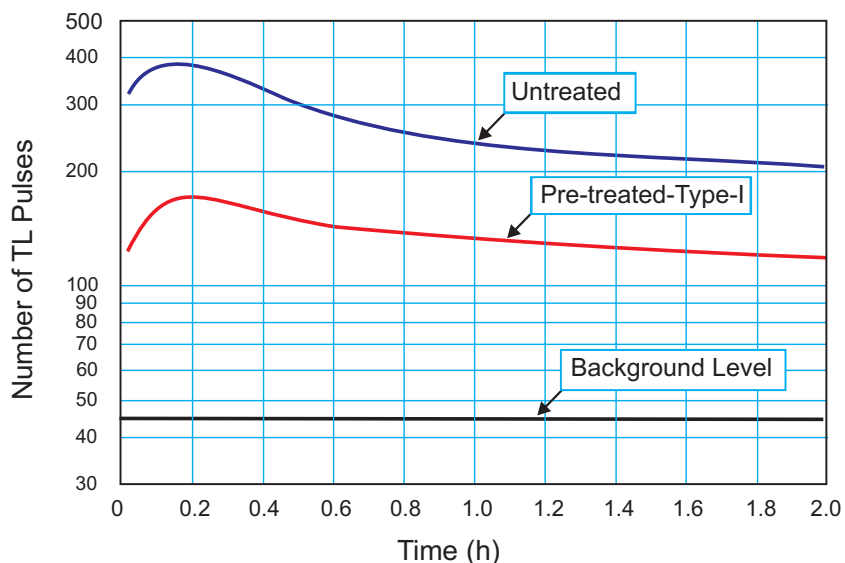


Figure 8. Number of TL pulses for untreated and thermally pre-treated specimens of Material-B versus time of treatment in vacuum at 50°C.

The blue curve shows that the number of light pulses emitted by untreated material decreases with time. This occurs because the light intensity decreases as the volatile cross-linking by-products exude out of the polymer. The red curve shows the light emitted from thermally pre-treated, Type-I, samples, which had a lower concentration of the by-products (see Table 1). As expected, the number of the light pulses is lower than for the untreated polymer.

The product of the number of light pulses and their amplitude gives the intensity of light emitted. Figure 9 shows the temporal behaviour of the intensity of the emitted light. The red curve shows the light emitted from Type-II specimens, which had a concentration lower than Type-I specimens.

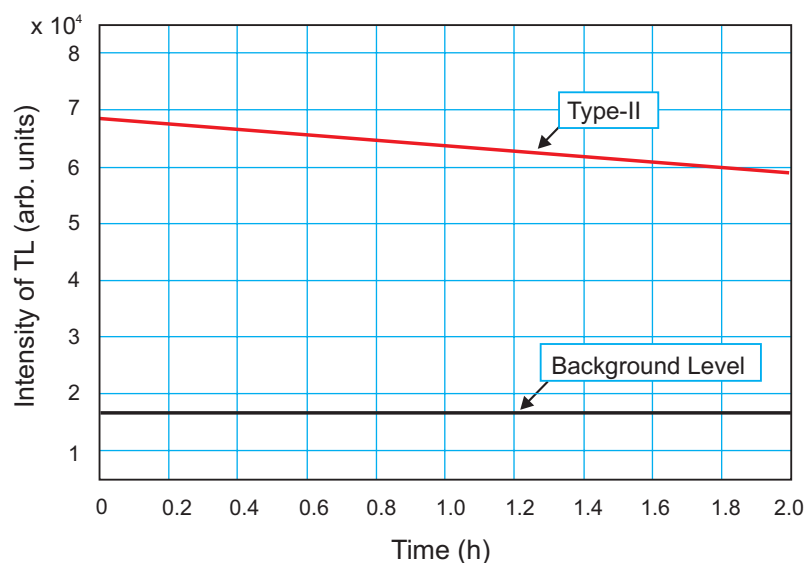


Figure 9. TL intensity measured in Material-B during thermal treatment in vacuum (0.1 Pa) at 50°C.

Although the mass spectrometer could barely resolve the low concentration of cross-linking by-products in Type-II specimens (see Table 1), the optical technique's high signal to noise ratio enabled detection of their presence.

Light emission in XLPE held above room temperature is due to thermoluminescence, which could be attributed to oxidized species and cross-linking by-products. If light emission was due to the oxidized species then at high temperature the intensity of light should increase with time. However, the curves of Figures 8 and 9 show that the light intensity always decreases with time indicating that the cross-linking by-products are the source of thermoluminescence and that the oxidation of the polymer has a negligible effect.

This is substantiated by the FTIR spectra, shown in Figure 10, of XLPE before and after heat treatment. For the treated samples, the intensity of the peaks of the by-products, such as acetophenone, are lower than in the untreated polymer.

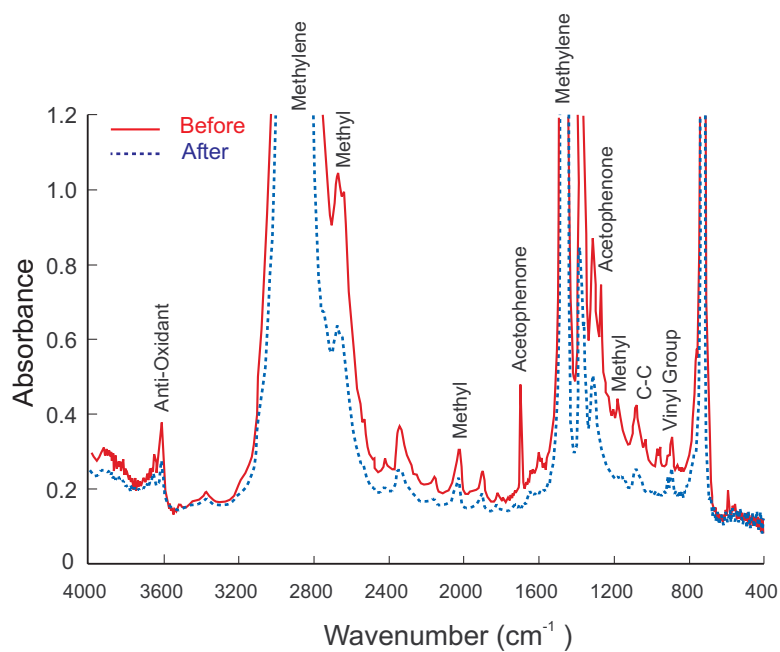


Figure 10. FTIR spectra of XLPE before and after heat treatment.

The fiber-optic version of the TL set-up is shown in Fig. 11. This is very useful for performing in-situ measurements on cables on a drum e.g. during the thermal treatment of large distribution and transmission class cables.

From one end of the cable, the outer jacket, concentric neutral tape (or wire) and the semiconducting insulation shield are removed and the TL emitted from the insulation is monitored continuously. The heat treatment can be stopped as soon as the desired residual concentration of the by-products has been reached.

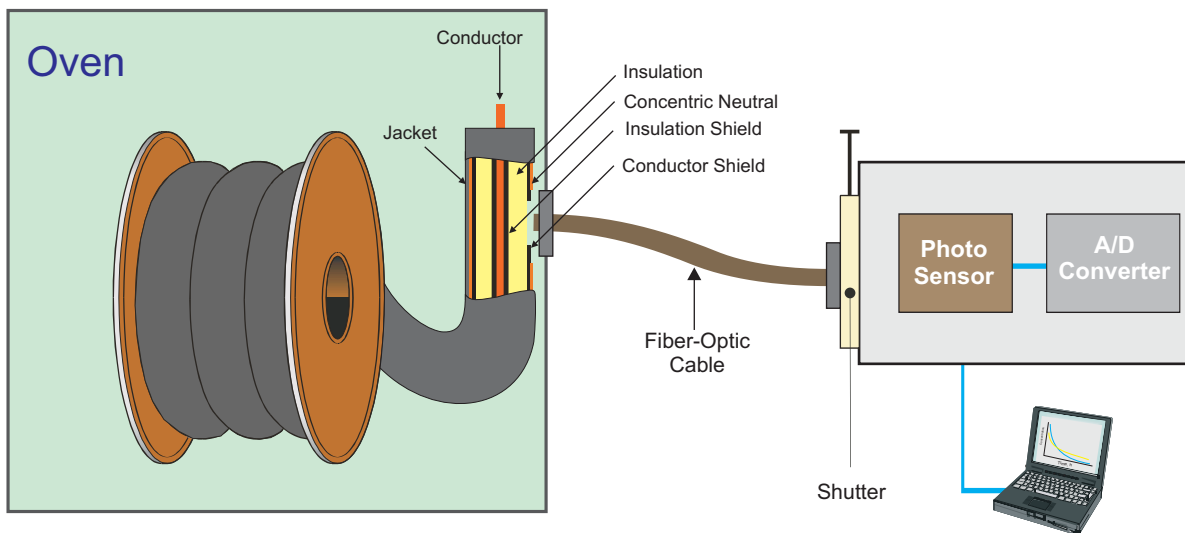


Figure 11. Thermoluminescence set-up with fiber-optic link for in-situ measurements on large cable reels.

**There are several advantages of the optical method for monitoring the cross-linking by-products.** The optical technique is a non-destructive method because pieces of the insulation do not have to be cut from the cable in order to determine the concentration of the by-products during thermal treatment. In-situ measurement gives continuous monitoring of the concentration so the thermal treatment can be stopped when the desired concentration is reached. The optical technique is not time consuming because there is no need to spend several hours to extract the by-products before analysis and the technique is also more sensitive than mass spectrometry.

The new optical technique has been patented in USA [1] and Canada [2] and is available for licensing. By providing in-situ measurement of the concentration of the cross-linking by-products, **the optical technique results in substantial saving of time, money and labour.**



References:

- [1] Bamji, S.S. and Bulinski A., "Measurement of Cross-linking By-Products in Cross-linked Polyethylene". U.S. Patent No. 08/323,108, Issued in March 29, 1996.
- [2] Bamji, S.S. and Bulinski A., "Measurement of Cross-Linking By-Products in Cross-linked Polyethylene". Canadian Patent No. 2,118,197, Issued in January 2002.

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