

COMPARISON OF DIFFERENT ANALYTICAL TEST METHODS TO MONITOR CROSSLINKING BY-PRODUCTS IN XLPE INSULATED CABLES



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ABSTRACT

This study discusses in detail various analytical methods that can be used for the determination of different by-products present in crosslinked polyethylene after production and after degassing. The actual results, obtained by the different methods, are examined as well as the spread. The analytical techniques used are weight loss, TGA, GC, FT-IR line scan and extraction followed by HPLC analysis. To have a detailed understanding of the different by-products a combination of several analytical tools are needed. To use a simple analytical tool as, e.g. TGA, would be recommended as a monitoring tool when detailed knowledge already has been acquired.

KEYWORDS

Crosslinking, degassing, methane, cumylalcohol, acetophenone, by-products, TGA, HPLC, FT-IR, GC

INTRODUCTION

Today the preferred insulation material for cables rated from 1kV up to 500kV is crosslinked polyethylene (XLPE). The crosslinking of the polyethylene chains is accomplished by use of peroxides and dicumylperoxide (DCP) is the most frequently used type. For DCP, every decomposed peroxide molecule, whether it provides a crosslink or not, gives at least three decomposition products, also known as by-products. The main by-products are methane, cumylalcohol (CA) and acetophenone (AP) and these are contained within the crosslinked polyethylene. The ratio between CA and AP is determined by the actual temperature in the polymer matrix used during the crosslinking reaction. An increase of the crosslinking temperature normally results in a higher content of acetophenone and thereby in a higher content of methane as well [1]. Thus the composition of by-products will depend upon the cable type, production technology and the processing conditions used.

For all power cables, especially for high voltage (HV) and extra high voltage (EHV), there is a need to remove by-products or to reduce their concentrations [2]. The most important component to be removed, due to health and safety issues, is the methane. This is a flammable gas that can catch fire or create explosions during jointing and installation procedures. However, presence of methane can also lead to issues in service [3,4] as the gas pressure can create defects in the shielding and in the joints. For cables equipped with a metal barrier the gaseous products can exert a pressure, especially on the joints and terminations, and eventually cause a system failure. The polar by-products such as cumylalcohol and acetophenone mainly have to be reduced as they

contribute to dielectric losses. During degassing, the by-products are redistributed and some are completely removed.

Degassing is a diffusion controlled process and is dependent on many parameters including temperature, thermal processing history, morphology, orientation, crystallinity and degree of crystallinity, annealing, solubility and vapour pressure of the diffusion molecule(s) [5]. The peroxide by-products are most likely confined to the amorphous part of the low density polyethylene (LDPE) as small molecules are excluded from the crystalline areas.

In practice the temperatures used for the degassing operation range between 50 °C and 80 °C. However, care needs to be taken not to damage the core if high degassing temperatures are used, especially for heavy cables [2].

This paper will discuss in detail how the redistribution and removal of by-products from the cable core can be monitored by use of different analytical techniques using different degassing temperatures, 50 °C to 70°C, and after different degassing times. The focus of the discussion will be on the results obtained with the different analytical techniques used as well as on the spread in the data.

EXPERIMENTAL

Sample

The investigated cable is HV cable insulated with conventional material. The insulation thickness is 15 mm and the conductor area is 500 mm². The longer cable sample was taken at the cable core manufacturing line. Samples were cut in 1 meter lengths and each sample was immediately put into an aluminium bag that was sealed.

Sample preparation

The sample preparation started approximately 24 h after the cable core production. For the study cable core samples of around 9-10 cm in length were sealed at both ends with a tightened aluminium foil in order to only allow a removal of the by-products through the outer screen and not via the ends. The cable core pieces were degassed in an oven at the selected temperatures using maximum ventilation. It is understood that these procedures are significantly different from the actual degassing conditions used in practice where the whole cable core reel, with multiple layers of cable cores is put into the degassing chamber.

The repeatability of the analytical techniques used will also be discussed in this paper. The repeatability was investigated on samples before degassing ('zero samples') and on samples taken out after 11 days at 50 °C, 9 days at 60 °C and after 4 days at 70 °C. For the repeatability test three different cable core pieces were analysed at each test condition.

ANYTICAL METHODS

The following methods were selected for this study:

- Weight loss measurements of the cable core
- Weight loss of the insulation by use of a thermogravimetric analyser (TGA).
- Analysis of methane and ethane content by gas chromatography (GC) measurements
- Analysis of the polar by-products by extraction followed by high pressure liquid chromatography (HPLC) analysis
- Analysis of the content of acetophenone by Fourier Transformed Infra Red (FT-IR) analyses

As the degassing exposes the cable core to a thermal treatment, changes in melting characteristics and lamellae thickness is studied by Differential Scanning Calorimetry (DSC).

For the analytical tests, specimens were taken out from the cable cores at three different positions, as close as possible to the inner semicon (1 mm), in the middle of the insulation (7-8 mm) and as close as possible to the outer semicon (15 mm).

Weight loss measurements of cable core

The change in weight as a function of degassing time was monitored by weight measurements. For this a scale with three digit accuracy was used.

GC analysis

A sample of approximately 1 g was taken out for this analysis. Initially a sample was placed in a 20 ml head space bottle with an aluminium crimp cup with seal. However, most of the analysed samples were placed in a larger head space bottle of 120 ml instead. The samples, in the head space bottles, were heat treated at 60 °C for 1.5 h and then 0.3-0.5 ml of the gas was injected into a gas chromatograph. Both the content of methane and ethane were determined. All samples except the 'zero samples' were run on a Perkin Elmer 8500. The 'zero samples' were run on another GC apparatus, a Varian 3400. Both the GC apparatus used were equipped with a column of the same length but of two slightly different diameters. The repeatability of the two apparatus was compared and was found to have a very good agreement. A double sample was tested for each position at each sampling at each degassing temperature. However, some data reported are based on single measurements, due to the large number of samples.

TGA

The TGA analysis was done according to HD632 S1 1998 Part 2 2.4.15., which describes the determination of crosslinking by-product concentration by TGA analysis. The samples should be taken from the inner, middle and outer part of the insulation. In this work an arithmetic mean of 3 samples from each position in the cable has been used instead, due to the large number of samples, using a sample weight of 10±2 mg. For the TGA analysis the temperature is raised to 175 °C with a minimum heating rate of 50 °C/min. The test should be conducted for 30 min at a temperature of 175 ±3 °C. The HD632 requirements are:

- total weight change 0-30 min <1.6%
- rate of change of weight 0-5 min <0.18%/min
- rate of change of weight 15-30 min <0.015%/min

Extraction and HPLC

A sample of 1 g was taken out for this analysis as described above. The sample was placed in a bottle with cover containing 50 ml of a 50/50 solvent mixture of isopropanol and cyclohexane. The samples were then extracted at 72 °C for 2 h. 10 µl from this solution was injected into the HPLC (Waters 2695) using water and acetonitrile as the mobile phase. The amount of cumylalcohol and acetophenone were determined.

DSC

A sample was taken out at each position and 4-6 mg was placed in an aluminium cup with a non-ventilated cover in a nitrogen atmosphere. The measurement was performed as follows:

- first melting from 30 °C to 120 °C using a heating rate of 10 °C/min
- crystallisation from 120 °C to -20 °C with a cooling rate of 10 °C/min
- second melting from -20 °C to 270 °C with a heating rate of 10 °C/min.

FT-IR

This analysis was done as a line scan covering the whole insulation thickness, e.g. the measurement started at the insulation layer closest to the inner semicon and ended at the insulation layer closest to the outer semicon. Only acetophenone was analysed in this way as cumylalcohol unfortunately has too weak absorptions to be monitored with this technique. For the acetophenone the absorption at 1693 cm⁻¹ was recorded and normalised using the peak at 2019 cm⁻¹.

RESULTS AND DISCUSSION

Part 1. Analysis of 'zero sample'

For the analysis of the 'zero sample' three different cable core pieces were analysed. These samples will also give information about the repeatability of the different test methods. The results from the gas measurements are presented in Table 1.

Table 1. Methane spread analysis data on 'zero samples' taken from the inner, middle and outer part of the insulation.

Sample	Methane inner (ppm)	Methane middle (ppm)	Methane outer (ppm)
Sample 1 (20 ml)	591	670	232
Sample 2 (20 ml)	486	552	212
Sample 3 (20 ml)	539*	641*	447*
Sample 3 (120 ml)	703*	943*	462*
Sample 3 (120 ml)***	696**	782**	349**

*single measurements

**single measurements analysed 3 weeks after sampling

***retest of Sample 3 in 120 ml bottles using the Perkin Elmer equipment.

The highest methane contents were detected in the inner and middle part of the cable core. As expected the outer part of the cable core contains less methane as this part probably

Return to Session

looses more methane already in the vulcanising tube. The methane data generated on the small sample bottles show a relatively low spread. However, it seems as if the methane contents are higher than around 500 ppm it is needed to use the large head space bottle for a correct determination of methane. Probably the restricted volume is saturated with methane and thereby the actual value can not be determined. Based on this it was decided to use the data for Sample 3, 120 ml headspace bottle as the initial values even though they are only based on a single measurement. All analysed samples only contained traces, 1-2 ppm, of ethane.

The observed spread in the values could depend on the actual sampling position on the 1 m cable core length. Also the sample preparation may influence as the sample is a thin slices and gaseous components may disappear during this handling step. Possible also the time between sample take out, time before the sample was put into the head space bottle and the time until the actual analysis may influence as well. Methane was also detected in the aluminium bags used for the packaging of the 1 m cable cores. This amount was not quantified but evidently another source for loss of methane.

Another technique to monitor the volatile components is to use the TGA technique. The data for the spread analysis on the 'zero samples' is summarised in Table 2.

Table 2. TGA data spread analysis on 'zero samples' taken from the inner, middle and outer part of the insulation.

Sample	Total weight change 0-30 min (%)	Rate of change of weight 0-5 min (%/min)	Rate of change of weight 15-30 min (%/min)
Inner	-1.4352 -1.1153 -1.1339	-0.2673 -0.2087 -0.1916	Both + and -* Both + and -* -0.0027
Average	-1.2281	-0.2225	N.d.**
Rel.St. dev.(%)	14.6	17.8	N.d.**
Middle	-1.4739 -1.2451 -1.1903	-0.2704 -0.2394 -0.2107	+0.04533 Both + and -* Both + and -*
Average	-1.3031	-0.2402	N.d.
Rel. St. dev. (%)	11.5	12.4	N.d.
Outer	-1.2579 -1.1683 -0.8131	-0.2133 -0.2323 -0.1471	Both + and -* +0.0592 Noth + and -*
Average	-1.0798	-0.1976	N.d.
Rel. St. dev. (%)	21.8	22.6	N.d.

*the weight change was both positive and negative.

**N.d. = not determined

There seem to be a large spread in the data generated by TGA which is also reflected in the relative standard deviations. However, for the TGA analysis it is common to use a carousel with an automatic sampling. This technique was used for the generation of the TGA data presented in Table 2. The spread in these data seems to be closely related to the sample position in the carousel, e.g. the time between sample preparation and the actual analysis. Sample 1 was analysed

first in the order inner, middle and outer. Then Sample 2 was analysed in the order inner, middle and outer, etc. These observations can then explain the large scatter and the constantly lower values obtained on Sample 3. There is a higher content of the volatile components in the interior part of the cable core, the same behaviour as was observed in the methane determination. The rate of change of weight between 15-30 min is very difficult to determine as both positive and negative values are obtained. The analysed data shows that this cable core results in values on the total weight change that indeed are lower than 1.6 wt%. Still, the rate of change of weight between 0-5 min is higher than the specification level.

The amount of the two polar by-products, acetophenone and cumylalcohol, were determined by extraction followed by HPLC analysis. The results from the spread test on the 'zero samples' are presented in Table 3.

Table 3. HPLC data spread analysis on 'zero samples' taken from the inner, middle and outer part of the insulation.

Sample	Inner AP (ppm)	Inner CA (ppm)	Middle AP (ppm)	Middle CA (ppm)	Outer AP (ppm)	Outer CA (ppm)
Sample 1	4862	9461	6384	9860	5173	6490
Sample 2	5102	9601	6701	9653	4830	5940
Sample 3	4566	8921	6442	10409	5930	7692
Average	4843	9328	6509	9974	5311	6707
Rel.St. dev. (%)	5.5	3.8	2.6	3.9	10.6	13.3

As can be seen from Table 3 there is a quite good repeatability. The relative standard deviation is low on the samples taken from the inner and middle part of the insulation. On the other hand, samples taken from the outer layer has a larger relative standard deviation.

Based on the amount of peroxide added to the material, the amount of by-products that should be possible to detect theoretically can not be measured. As the extraction yield is high, around 90%, this difference must originate from that by-products are lost in the vulcanizing tube and possibly also during the sample preparation as this test also uses thin slices.

If it is assumed that the ratios between cumylalcohol and acetophenone are representative, and that the same relative amount of these two by-products are lost in the vulcanizing tube, the methane content could be estimated to be in the range of 1000 ppm. This correlates well with the analysed value of 943 ppm (middle part).

The distribution of the acetophenone within the whole insulation layer can easily be monitored by use of a line scan analysis by FT-IR. The results for the 'zero samples' are summarised in Figure 1.

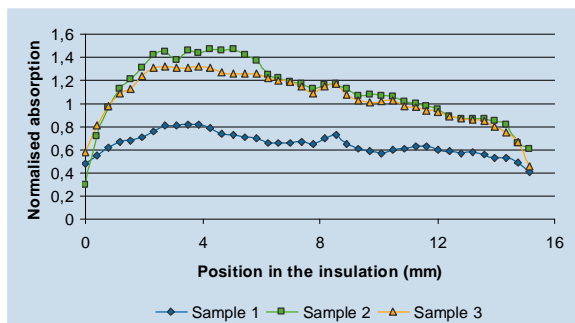


Figure 1. FT-IR data spread analysis on 'zero samples'.

This line scan analysis is a relatively simple method to obtain information about the real distribution of acetophenone within the whole insulation layer as no extraction steps followed by HPLC analysis is needed. The data shows there seems to be an enrichment of the acetophenone in the inner part of the cable. However, there seems also to be a large spread in the analysis. This is possibly related to how and where the slice is taken. This is an interesting measuring technique that can provide very detailed data but needs further refinement due to the large spread.

The thermal properties were determined by a DSC analysis. Table 4 summarises the data analysed on the 'zero samples', only duplicate run.

Table 4. DSC data on 'zero samples' at different position in the insulation, first and second melting.

Sample	Inner T _m (°C)	Inner Cryst. (%)	Mid. T _m (°C)	Mid. Cryst. (%)	Out. T _m (°C)	Out. Cryst. (%)
1-first	107.4	35.3	109.3	33.7	109.2	33.1
2-first	109.2	33.9	108.8	34.6	108.3	35.1
Average	108.3	34.6	109.1	34.2	108.8	34.1
1-second	107.1	41.5	107.0	41.4	107.7	42.4
2-second	106.5	42.8	107.3	43.3	107.9	43.4
Average	106.8	42.2	107.2	42.4	107.8	42.9

Part 2. Analysis of changes in by-product contents as a function of degassing time.

The weight loss measurements are calculated based on the estimated weight of the polymeric part on the cables core parts that are under degassing. The results for the three degassing temperatures are presented in Figure 2.

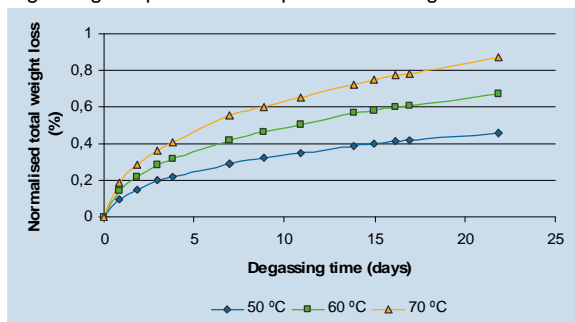


Figure 2. Weight loss vs degassing time.

As mentioned in the introduction the most important

component to remove is the methane. It has been reported [4] that a gas pressure of 1 bar, corresponding to a methane content of 30 to 50 ppm, results in acceptable service and test performance. The degassing of methane as a function of time at different positions is exemplified in Figure 3 with results measured at 60 °C. Based on these data it takes up to 7 days to reach less than 50 ppm of residual methane within the insulation layer for the tested cable. The higher the temperature the faster is the reduction of methane. However, there are not large differences between the different temperatures used to reach the target level of 50 ppm.

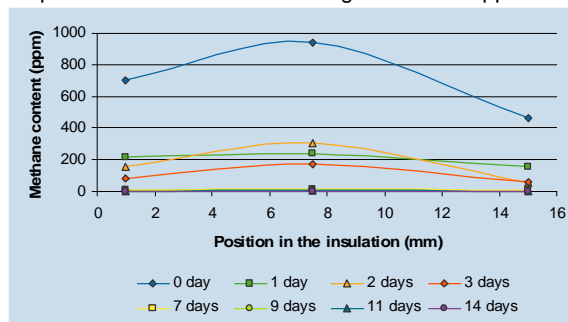


Figure 3. Methane vs degassing time in different parts of the cable at 60 °C.

The results from the TGA measurements are summarised in Figure 4a (middle) and 4b (outer). TGA determines the amount of volatile products that is present in the material at a specific time.

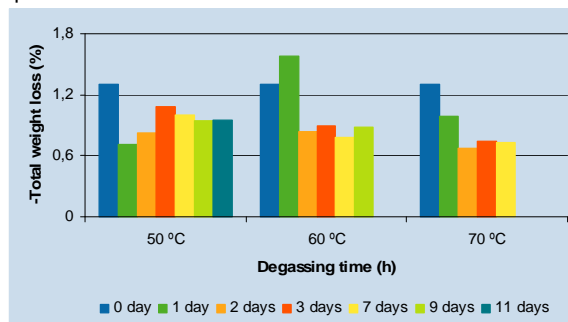


Figure 4a. TGA data at the middle layer vs degassing temperature after different degassing times.

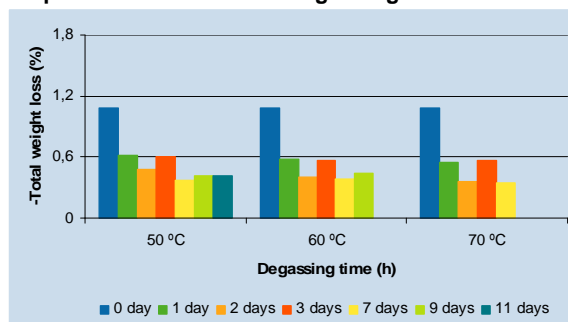


Figure 4b. TGA data at the outer layer vs degassing temperature after different degassing times.

The amount of volatiles in the inner and the outer layers reach a relatively low level after short degassing times. At first sight the data obtained on the middle layer looks a little odd as they first decrease and then seems to increase. This increase probably originates from the redistribution of the by-products

within the insulation layer. Also here there is a spread in the reported TGA data. Sometimes there is a correlation to the position of the sample in the carousel but this does not explain all the variations in the results. What can be noted is that Sample 3 sometimes results in slightly lower values compared to Sample 1 and 2. This could be a result of that the carousel was filled up with samples and Sample 3 was analysed one day after the sample take out. However, all samples were stored in sealed bags from the time at the sample take out until they were analysed.

The following two Figures presents the behaviour of the polar by-product components at the different temperatures at selected degassing times, see Figure 5 for acetophenone after 2 days degassing and Figure 6 for cumylalcohol after 14 days degassing.

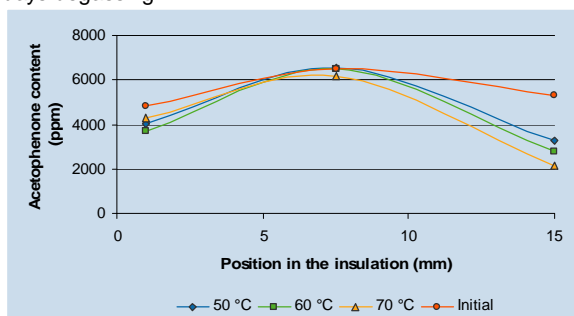


Figure 5. Content of acetophenone at different positions in the cable after 2 days degassing compared to the initial level.

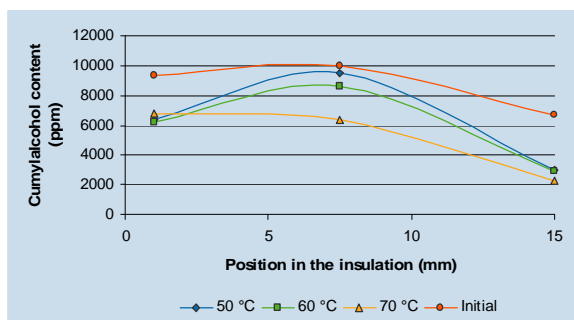


Figure 6. Content of cumylalcohol at different positions in the cable after 14 days degassing compared to the initial level.

As can be seen in Figure 5, there is a reduction of acetophenone at the inner and outer layer, more is removed the higher the temperature. The middle layer is on a similar level as for the initial sample. After 14 days of degassing much more has happened, especially in the outer part of the cable core. There are several explanations for this. First of all the surface area towards the surrounding air is the highest and this facilitates the removal of the by-products. There is also a clear influence of temperature but it is not linear. The results obtained at 50 and 60 °C are more or less the same but significantly lower levels are observed at 70 °C. This difference can not be explained by the change in degree of crystallinity as the reduction is the same between 50 and 60 °C as it is between 60 and 70 °C. Also lower levels of acetophenone are reached compared to the cumylalcohol even if the initial levels of cumylalcohol are higher than for acetophenone. This indicates that the diffusion constant is higher for

acetophenone than for cumylalcohol under the used conditions. Thus it is clear that the use of a higher temperature increases the diffusion rate and thereby the degassing time is reduced. However, the temperature has to be increased to the range of 70 °C to reach significant effects.

At the inner part of the cable, the reached levels of the by-products are almost the same after 14 days as after 2 days of degassing. Due to this observation the by-product level in the inner and outer semicon was investigated as well. In Figure 7 the results for the inner semicon are presented after 9 days of degassing compared with the initial values.

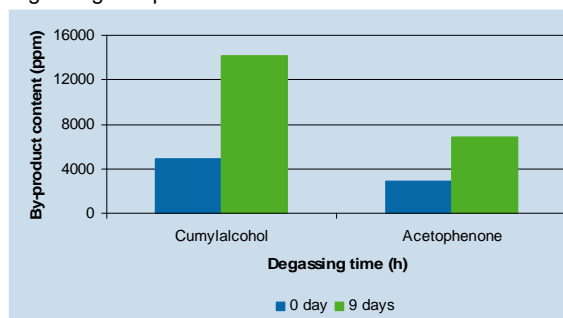


Figure 7. By-product comparison in the inner semiconductive layer before and after degassing.

Clearly there is an enrichment of by-products in the inner semiconductive layer. This is probably partly a result of the sealing of the ends of the cable cores used for this degassing study. If this occurs in reality is not known. This explains the small changes in by-product content observed in the inner layer of the cable with degassing time. On the contrary, tests on the outer semiconductive material clearly show that there is no accumulation of by-products. The analysed levels in this layer are between 1300-2000 ppm of CA and AP respectively, both initially and after 9 days degassing.

The FT-IR line scan results obtained after degassing at 70 °C for 14 days can be found in Figure 9 below.

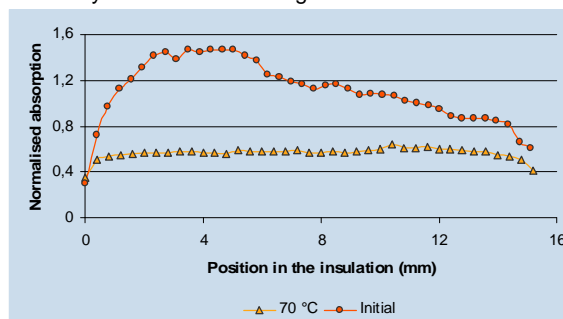


Figure 9. FT-IR analysis at after degassing at 70 °C compared to the initial concentration.

After degassing the content of acetophenone is on a clearly much lower level. The distribution also seems to be flat within the whole insulation layer. The initial enrichment of the acetophenone in the inner parts of the cable is clearly reduced with degassing time.

For the degassing times used in this study no changes in the shape of the first melting curve can be observed. However, a slight increase in the degree of crystallinity can be seen in the

Return to Session

first melting.

As mentioned earlier, spread analyses were also performed on selected samples after degassing. In general the repeatability is good and is exemplified with the 60 °C data after 9 days for TGA, Table 5, and for HPLC, Table 6. Rate of change of weight 15-30 min is not reported as both positive and negative values were obtained this time too.

Table 5. TGA spread analysis on samples degassed 9 days at 60 °C taken from the inner, middle and outer part.

Degassing time	Inner	Middle	Outer
Average Total weight loss (%)	-0.6511	-0.8816	-0.4436
Rel. standard deviation (%)	6.8	1.9	6.0
Average Rate of change of weight (0-5 min) (%/min)	-0.1177	-0.1658	-0.0798
Rel. standard deviation (%)	4.2	5.2	8.7

Table 6. HPLC data spread analysis on samples degassed 9 days at 60 °C taken from the inner middle outer part.

Sample	Inner AP (ppm)	Inner CA (ppm)	Middle AP (ppm)	Middle CA (ppm)	Outer AP (ppm)	Outer CA (ppm)
Average	4012	6298	5039	9615	1871	3656
Rel. St. dev. (%)	9.2	10.5	7.2	5.8	10.4	8.5

Comparison of different analytical techniques

The weight loss data, TGA (total weight loss), methane and HPLC results are compared in Table 7 for a degassing time of 7 days. For this comparison, the part of the by-products that have been removed during the actual degassing was used. This means that the difference between the initial value subtracted with the analysed value after 7 days is used for the comparison and reported in Table 7. The column 'Others' include the contribution from the methane, cumylalcohol and acetophenone (calculated in the same way).

Table 7. Comparison of different analytical techniques.

Temp. (°C)	Weight loss (%)	TGA inner	Other inner	TGA mid	Other mid	TGA outer	Other Outer
50	0.29	0.52	0.35	0.31	0.11	0.70	0.72
60	0.42	0.61	0.42	0.53	0.30	0.69	0.75
70	0.56	0.60	0.40	0.57	0.45	0.73	0.86

TGA analyses performed on the outer part correlates well with the group 'Other'. The TGA measurements correlate less with the weight loss and methane measurements as the TGA results always shows higher values. If the HD632 requirements would be followed, based on total weight loss and rate of change of weight 0-5 min, the degassing time needed would be 3 days at a degassing temperature of 60 °C. At these conditions then around 200 ppm of methane is still present in the middle layer of the cable used for this study.

CONCLUSIONS

One aspect to ensure a reliable long term performance of the cable when put into operation is to secure a proper degassing. Therefore it is important to have a detailed knowledge of the by-product composition within the cable after production and especially after degassing. For this

detailed understanding several techniques have to be used such as GC, HPLC and FT-IR line scan. This study suggests that when this basic knowledge has been acquired for a specific cable, TGA analysis can be used as a tool to monitor the level of degassing as a quality control method.

Regarding the different analytical tools, this study shows that for the determination of methane the choice of sample size/bottle size is very important for a correct analysis. The extraction tests followed by HPLC analysis indicate that the repeatability is quite good but this technique is very time consuming and provides only information on the actual area where the sample was taken. More easy to use, from a sample preparation point of view, is the FT-IR line scan analysis. One drawback with this technique is that many analyses are needed on one sample to obtain reliable data. Also the by-product to be monitored needs to contain absorptions that enable an FT-IR analysis. However, this technique gives very detailed information around the true distribution of the acetophenone within the insulation layer.

The TGA analysis is aimed to be a simple test where many samples can be analysed by automated sampling equipment. This seems not to be an ideal solution, at least not for samples having a high content of volatiles, as a large spread in the results was observed. Probably more reliable data would be obtained if every sample was loaded separately but then this technique becomes quite time consuming. TGA measures a mixture of methane and the polar by-products as the initial results are always quite high and this amount of volatiles can not be explained by methane alone.

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