

NEW method for 2-furfuraldehyde

ABSTRACT

Apart from abnormal faults detected by DGA, one of the most important factors in shortening the lifetime of a power transformer is ageing of paper insulation used in transformer construction. The analysis of furans in transformer oil is one of the best techniques to be used in the assessment of the remaining lifespan of a used transformer.

This technical article aims to describe the development and validation of an analytical method based on ultraviolet-visible (UV-VIS) absorption spectrophotometry, designed to evaluate the content of 2-furfuraldehyde (2-FAL) dissolved in dielectric oil. This is a technique which, despite not reaching the levels of resolution of the more commonly used high-resolution liquid chromatography (HPLC), provides greater efficiency in terms of utilisation of resources, both financial and manpower.

KEYWORDS

insulation ageing, dielectric oil test, life extension, asset management, 2-furfuraldehyde, degree of polymerisation

An easy, rapid and inexpensive spectrophotometric method to analyse furans as paper degradation indicator in transformer oil

1. Introduction

The transformer insulating system is a combination of mineral oil and cellulose paper - a combination which achieves an excellent dielectric and cooling capacity, at a low cost. To perform predictive maintenance of these transformers, it is necessary to periodically assess the occurrence of abnormal faults and degradation of their insulation systems.



analysis

The most commonly used solid insulation (Kraft paper) is composed of 90 % cellulose. This natural polymer degrades throughout the lifecycle of a transformer, resulting in oil soluble subproducts. The degree of polymerisation (DP) is a parameter that evaluates a condition of the paper which deteriorates with ageing of the insulation. New insulation with a high degree of mechanical strength will typically have a degree of polymerisation (DP) from 1000 to 1300. „Middle-aged“ paper will approximately be at 500, while paper with a DP of less than 250 is considered „old-aged“. These estimations are based on a study on GSU mineral oil filled transformers, conducted by Chendong. Severely degraded insulation with a DP of 150 or less will have very little mechanical strength and may result in transformer failure. This is critical, because paper cannot be altered or subjected to regeneration processes, and therefore degradation of solid insulation can lead to the end of transformer's life. The purpose of this article is to describe the

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development and validation of an analytical model based on ultraviolet-visible (UV-VIS) absorption spectrophotometry to be used in evaluating the content of 2-furfuraldehyde (2-FAL) dissolved in dielectric oil. In comparison to the more frequently used high-resolution liquid chromatography (HPLC), this method does not reach the same resolution levels, but it provides greater efficiency with regard to utilisation of financial and manpower resources.

The methodology used during the process was based on several thermal degradations of the oil with the aim of achieving the widest possible range of visual aspects, and the synthesis of a colourimetric reagent so that it reacts with the sought compound. Calibration curves were made with standard solutions, in order for each visual aspect to permit real sample analysis. Finally, UV-VIS method data for real samples was compared with HPLC method data, with good results. The main result of this study was to validate the method for quantification of 2-furfuraldehyde concentrations not exceeding 5 parts per million, dissolved in the oil of transformers used in power generation. In conclusion, the aim was to develop a new methodology for determination of 2-furfuraldehyde, thus leading to significant cost savings, both economic and material. This will enable indirect determination of the status of the solid insulation of transformers for power generation, through a more accessible technique than those currently used.

2. Insulation degradation process

Selection of the most efficient predictive maintenance strategy requires a review of the insulation deterioration process and best methods for early detection. The active part of a transformer

” The new cost-saving method will enable indirect determination of the status of the solid insulation of transformers for power generation using a more accessible technique than those currently used

consists of several subsystems which are designed and tested to sustain the electric and thermal stresses which occur during normal operation. This is why most transformers will provide years of faithful service without developing any problem. However, some units subjected to unusual service conditions, or which suffer from a manufacturing defect, excessive ageing or moisture ingress, may develop problems. These problems should be detected at an early stage to allow for orderly removal from service, and subsequent repair.

Transformer insulation is mostly made of the time-proven combination of cellulose paper or pressboard, fully impregnated with insulating oil. When the insulation is overstressed with high temperature or electric discharges, the chemical bonds within oil and cellulose molecules can break down and new molecules can be created. Such a reaction generates a variety of gases that dissolve in the surrounding oil.

Any problems developing in the winding insulation, the connections, the core or the shields will generate a localised high temperature or electric discharges, resulting in the decomposition of oil and/or paper. The minimum amount of gas dissolved in the oil can alert the operator about a developing problem, and the relative proportion of furans can also indicate the location of the fault.

3. Experimental methodology

New oil was degraded by being heated to 120-140 °C in the presence of copper, in order to achieve different colouration indexes for eight different oils. Degradation time depends on the degree of degradation to be obtained. The greater the time elapsed, the higher the degradation and colouration index. Several 2-furfuraldehyde standards were prepared in order to compare our field samples. After the standards had been prepared, the strategy for development of a new analysis method was created.

4. Results

There are several studies in the literature for determination of 2-furfuraldehyde in dielectric oils using a colourimetric method. However, these methods can be interfered by aged oils and some of them by variation in temperature. These interferences were studied during the development of this method. Figure 1 shows the spectrum between 400 and 700 nm for the new oil with 2-furfuraldehyde added, and the spectrum of three oils without 2-furfuraldehyde, but with high colouration index. Furans were first extracted with 100 % acetonitrile and then analysed using a colourimetric method.

Therefore, it was necessary to modify the treatment of samples from using 100 % acetonitrile mixtures to using acetonitrile/water. Figure 2 shows a single oil which was aged in a laboratory where interferences were eliminated, decreasing the proportion of acetonitrile in the extraction. The same study was performed using both solid-phase extraction and liquid-liquid extraction.

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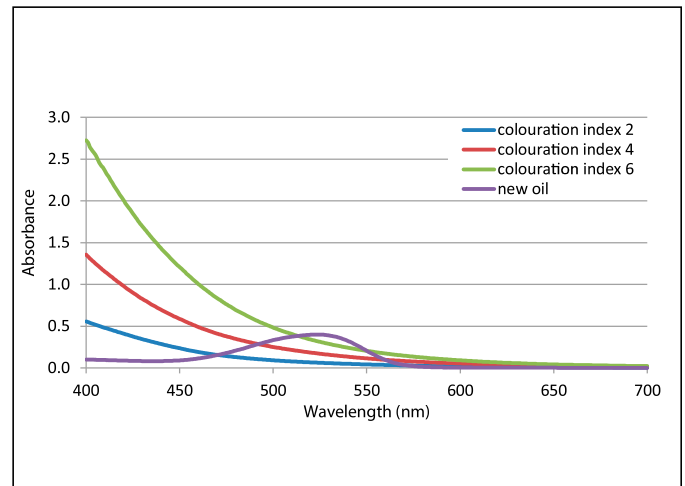
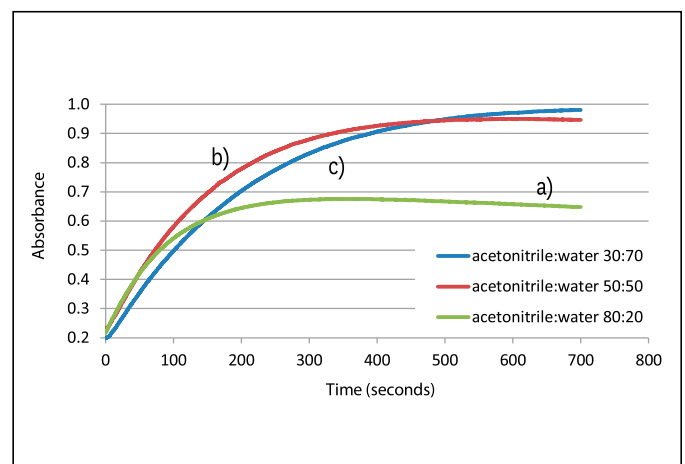


Figure 1: New oil with 2-furfural added and three oils degraded in the laboratory without 2-furfural and with colouration index 2, 4 and 6, respectively. Interferences increase with high oil colouration index; false positives may be reached

In both cases interferences were eliminated by using different proportions of acetonitrile and water.

Studying the kinetics of the reaction, while taking into account the first studies in which the colourimetric reagent was aniline:acetic acid 1:10, a problem was observed when trying to

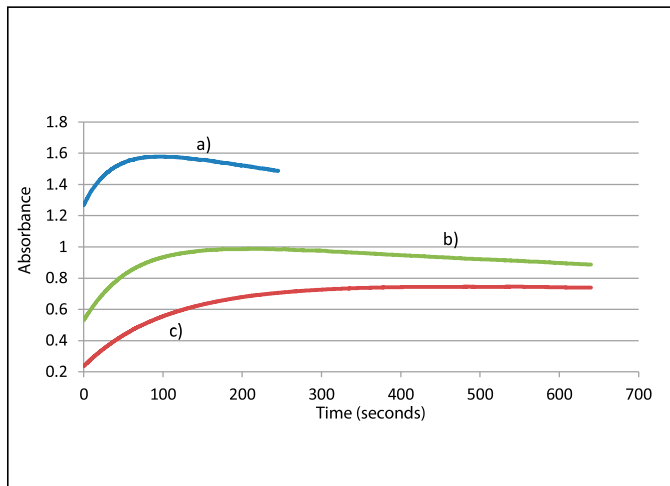


- a) acetone:water = 80:20
- b) acetone:water = 50:50
- c) acetone:water = 30:70

Figure 2: Kinetics of extraction for different acetonitrile and water ratios

modify proportions between acetonitrile/water in the extraction phase. As a result, the reaction became very slow and the sensitivity of the acetonitrile declined.

As illustrated in Figure 2, the kinetics of the reaction starts to drop after reaching the highest absorbance value. In order to eliminate interferences, the proportion of acetonitrile needs to be reduced, but this makes the reaction last too long. This leads to the conclusion that the best solution is to add dimethyl sulfide as a catalyst to accelerate the reaction.



a) Kinetics of the reaction with aniline:acetic acid 1:10
 b) Kinetics of the reaction with aniline:dimethyl sulfide:acetic acid 1:2:7
 c) Kinetics of the reaction with aniline:dimethyl sulfide:acetic acid 1:3:6
 Figure 3: Kinetics of extraction for acetonitrile/water 30/70 %

As illustrated in Figure 3, the greater the proportion of dimethyl sulfide, the higher the speed of the reaction. This means that the proportions for each application need to be optimised, which in this case study was done by selecting colourimetric reagent:dimethyl sulfoxide:acetic acid 1:2:7.

” The new method has been optimised in order to achieve the best performance by using dimethyl sulfide as a catalyst and adjusting the reaction time

To sum up, the parameters chosen for determination of 2-furfuraldehyde were:

- Solid-phase extraction, because it is the easiest extraction method for automation in the laboratory
- Aniline:dimethyl sulfoxide:acetic acid 1:2:7 as the colourimetric reagent, because this yielded the best performance in terms of speed of reaction and sensibility

5. Validation of the method

This is a very selective method. Figure 3 illustrates that for measurements taken at the wavelength of 520 nm only 2-furfural is detected and there are no interferences with other furanic compounds or oils of a high colouration index as they do not react in the same way with aniline as 2-furfural does.

The calibration and linearity are shown in Figure 4.

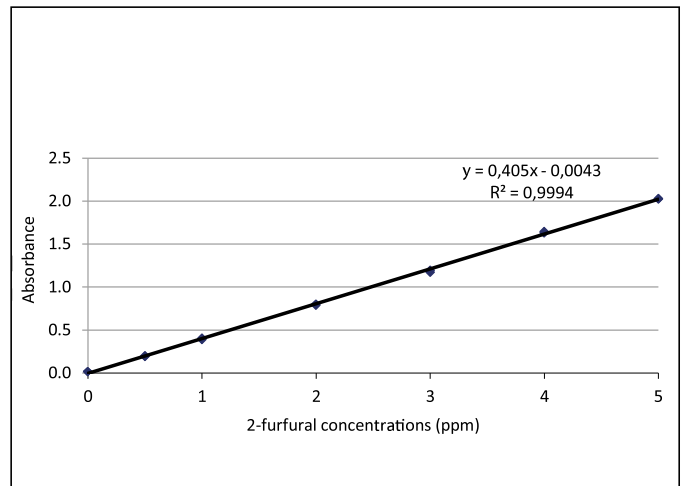


Figure 4: Calibration with standards of new transformer oil doped with 2-furfural with concentrations from 0 to 5 mg/l

The limits of detection (LOD) and quantification (LOQ) were calculated as follows:

$$Y_L = \bar{Y}_{\text{blank}} + k \cdot s_{\text{blank}} \quad (1)$$

$$C_L = k \cdot s_{\text{blank}} / m \quad (2)$$

Where Y_L is the signal for different limits, C_L is the concentration for the limits, \bar{Y} is the mean signal value for the blanks, s is the standard deviation, m is the slope and k is a probability factor. The obtained values were 0.06 ppm for LOD and 0.10 ppm for LOQ.

Repeatability

Table 1: Results of concentration measurements with six replicates each

Concentration (mg/l)	Mean value	Standard deviation	Variation coefficient
0.20	0.20	0.01	5
3.00	2.95	0.04	2

Accuracy

Several transformer oils have been analysed with the new method as well as with the established method recommended in IEC 61198. The comparison is presented in Table 2.

Table 2: Comparison between the concentration of 2-furfuraldehyde obtained through HPLC and the newly developed method

Colouration index	Concentration HPLC (ppm)	New method (ppm)
0.5	<LOQ	<LOQ
3.5	1.06 ± 0.01	1.02 ± 0.05
3.5	0.05 ± 0.01	<LOQ
3.5	<LOQ	<LOQ
3.5	0.23 ± 0.01	0.21 ± 0.05
4.5	0.46 ± 0.01	0.36 ± 0.05
4.5	0.29 ± 0.01	0.25 ± 0.05
4.5	1.77 ± 0.01	1.81 ± 0.05
4.5	1.77 ± 0.01	1.8 ± 0.05

The uncertainties associated with the concentration values obtained colourimetrically have been calculated using the standard deviation of the value predicted by the corresponding calibrated T-student in order to have a confidence level of 95 % and the corresponding degree of freedom.

Conclusion

A new rapid, inexpensive and easy colourimetric method has been developed to determine the content of 2-furfuraldehyde in transformer oils, yielding accurate and reproducible results. Using a small sample volume, the limits of detection and quantification are consistent with the needs of the laboratory. A study of the kinetics of the derivatisation reaction with aniline has also been conducted, showing that dimethyl sulfide can be used to vary the speed of the reaction and sensibility according to our needs. To carry out this analysis, solid-phase extraction was chosen because it is the easiest extraction method for automation in the laboratory.

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