WEAR CHECK
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LIQUID CHROMATOGRAPHY AND ITS APPLICATION IN TRANSFORMER OIL ANALYSIS

WearCheck managing director Neil Robinson

Introduction

The laboratories of condition monitoring specialists WearCheck are equipped to monitor oil and fluids from a wide array of industrial machinery, including transformer oil, utilising a number of sophisticated analytical techniques, one of which is the focus of this Technical Bulletin.

Before I get into the liquid chromatography technique, I would like to briefly cover what it is we would use this technique for, and why.

Paper insulation used in electrical equipment and transformers especially, is a manufactured cellulose-based product. Cellulose, however, is a naturally occurring polymer that nature builds by linking together D-glucopyranose monomers. The average number of monomers in the cellulose chains is called the degree of polymerisation (DP) and it determines its natural strength. As an analogy, consider ethene (gas) and polythene (plastic) - the number of monomers in a chain and the cross linking between chains determine its strength from shopping bags to plastic wheelbarrows.

New insulation paper, or Kraft paper, named after the German word for strong, has a DP in the range of 1000-1300. The physical strength of paper insulation is related to both the average DP and the interaction between adjacent polymer chains. As the paper ages, linkages between adjacent monomers are broken, the DP decreases and the insulation paper and pressboard degrade. This degradation is exacerbated by a number of factors, namely the moisture content of the oil, the temperature, the acidity, oxidation by-products and any metal particles in the oil which may act as catalysts.

The mechanical properties of insulating paper can be established by direct measurement of its tensile strength or by its degree of polymerisation, and these properties can be used to determine the condition and thus potential life of the paper insulation. DP values of 250 and below generally indicate the end of its useful life.[1]

Analysis of the paper insulation, however, requires the removal and analysis of a sample of the paper from the transformer; this is a potentially dangerous, expensive and invasive procedure which requires the transformer to be taken out of service.

However, as discussed above, Kraft paper and pressboard are essentially cellulose polymers, and when cellulose degrades it produces

water, which causes further degradation, carbon dioxide and a number of different molecules as shown below in table 1. However, 2-furaldehyde is the most common. Collectively these compounds are called furanics.

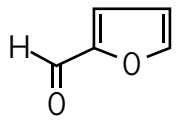	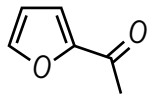	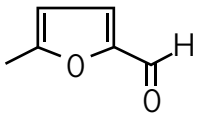	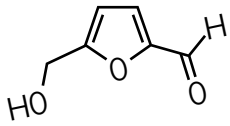	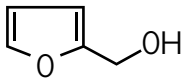
2-furaldehyde	2-furyl methyl ketone	5-methyl-2-furaldehyde	5-hydroxymethyl-2-furaldehyde	furfuryl alcohol

Table 1

Furanics dissolve in the transformer's oil and it is generally accepted that their concentration can be directly related to the amount of degradation of the solid insulation in the transformer.

Log [Fur] = 1.51 - 0.0035 DP

where [Fur] = concentration of the furanics in ppm

This equation, though not exact, does allow one to estimate the DP of cellulose insulation.

Content (ppm)	DP Value	Significance
0-0.1	1200-700	Healthy transformer
0.1-1.0	700-450	Moderate deterioration
1-10	450-250	Extensive deterioration
>10	<250	End of life criteria

Table 2

The technique we use to measure the concentration of these furanics is High Performance Liquid Chromatography or HPLC.

Wiktionary defines chromatography as: *Any of various techniques for the qualitative or quantitative separation of the components of mixtures of compounds all characterised by the use of a mobile phase (gas or liquid) moving relative to a stationary phase (liquid or solid) – the difference between the rates of migration of the compounds between the two phases effects the separation.*[2] Or as I would say: A method for the separation of components in a mixture.

Chromatography was first described by a Russian botanist (Mikhail Tswett) in the early 1900s. He used a glass column packed with chalk to separate the pigments in a plant extract. As this extract moved through the column in a solvent, coloured bands appeared.[3]

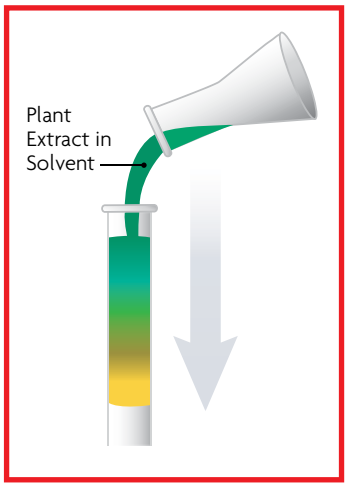

Figure 1

Tswett coined the name *chromatography* [from the Greek words *chroma*, meaning colour, and *graph*, meaning writing—literally, *colour writing*].

There are many Chromatographic techniques available - such as gas chromatography (GC), thin layer chromatography (TLC), ion chromatography (IC), including others. Here, we will concentrate on liquid chromatography (LC), and specifically reverse phase liquid chromatography.

As a sample passes through a column packed with an appropriate material [stationary phase], carried through by a solvent [mobile phase], as in Tswett's experiment, the different components or compounds in the sample are then separated by travelling at different individual speeds through the column.

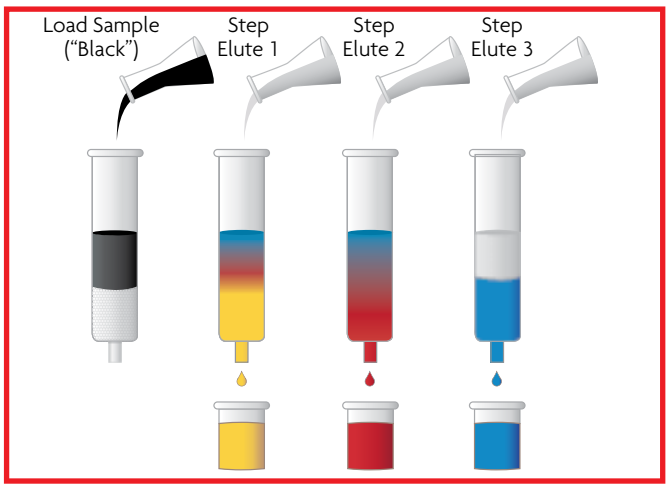

Figure 2

This is due to the various compounds of the sample having differing affinities to either the stationary phase or the mobile phase.[4] Over time, stationary phases have evolved and now are specifically designed to have affinities for different types of compounds to effect superior separations.

Early in the development of the theory of LC it was noticed that the efficiency of separation could be vastly improved by reducing the particle size of the stationary phase. However, it was not until the late 1960s that the technology for producing the stationary phases in sizes as small as 5-10μM was developed.

Modern stationary phases are generally complex organic compounds bonded to fused silica (e.g. octyldecylsiloxanes).

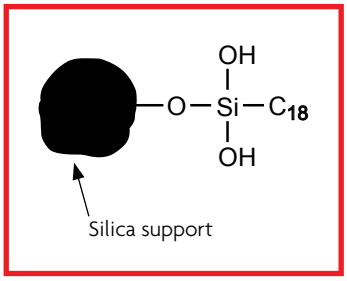

Figure 3

However, these smaller particles tended to cause a greater resistance to flow of the sample through the column, so pressure was introduced to push the sample at a reasonable rate through specially designed stainless steel columns.

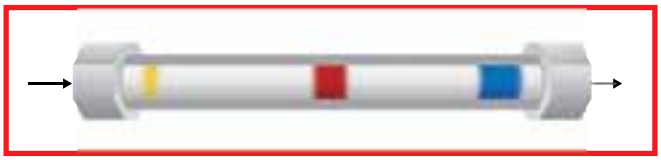

Figure 4

And the phrase *high pressure* liquid chromatography [HPLC] was introduced. The early 1970s saw a tremendous leap in technology. These new HPLC instruments could develop up to 400 bar of pressure, and incorporated improved injectors, detectors, and columns. HPLC really began to take hold in the mid- to late-1970s. With continued advances in performance during this time [smaller particles, even higher pressure], the acronym remained the same, but the name was changed to *high-performance* liquid chromatography.

High-performance liquid chromatography is now one of the most powerful tools in analytical chemistry, and state-of-the-art machines can operate at pressures approaching 7000 Bar with <l μM particle sizes. They have the ability to separate, and quantify, the compounds that are present in any sample that can be dissolved in a liquid with detection levels approaching 0.01 trillionths of a gram (10^{-14} of a gram).

So how does a HPLC work? Reservoirs hold the mobile phase, often either a single or mixture of solvents

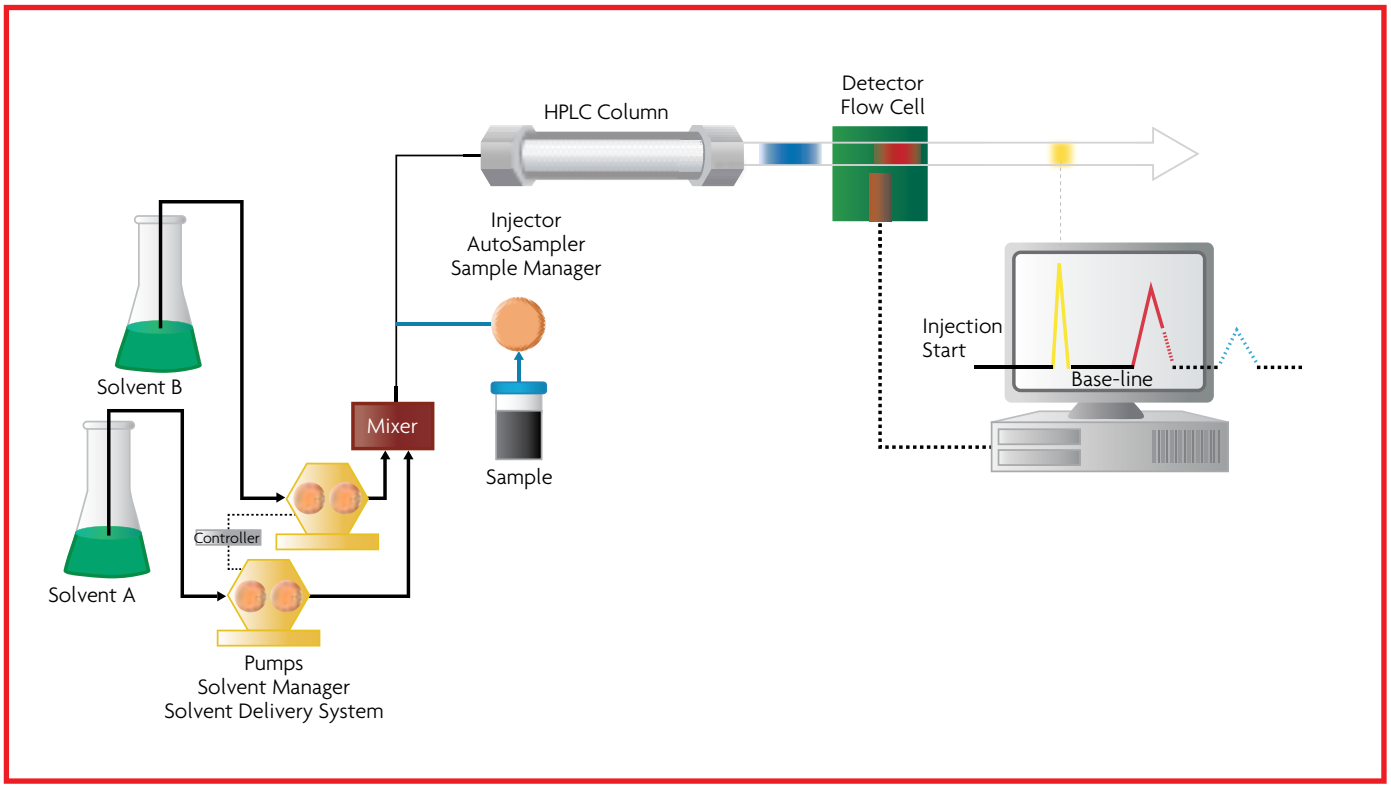

Figure 5

(Isocratic elution) or as a number of single solvents with a mixer that allows us to change the mobile phase mix during the course of a run to effect better separation (gradient elution). We need an injector that allows us to put the dissolved sample onto the column; the stationary phase as discussed briefly above is held in place in a column and finally, since most compounds - including those of interest to us - have no colour, a detector is needed to see them as they elute from the column. The detector sends this information to a computer where the result or chromatogram (a series of peaks representing each compound) is displayed. This peak is effectively a Gaussian curve of the amount of each compound in the mobile phase as it passes through the detector, so in order to calculate its concentration, the area value under the peak is integrated and calculated automatically by the computer.

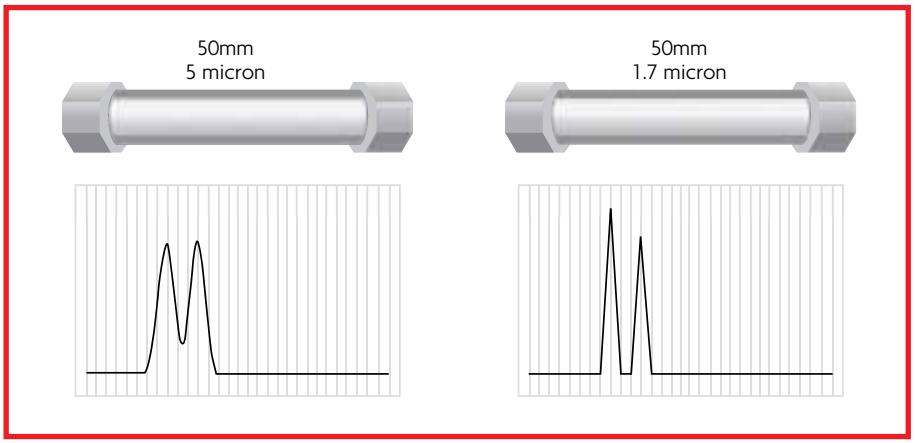

Figure 7

The efficiency of a column to separate a mixture is affected by two main parameters, its mechanical separating power and its chemical separating power or, the size of the column and the packing material inside it and the chemistry of the column and solvents used.

If a column is stable and uniformly packed, its mechanical separation power will be determined by the length of the column and the size of the particles inside. For any given particle size, more mechanical separation is gained by increasing column length. However, this results in longer chromatographic run times, greater solvent consumption and an increase in the backpressure.

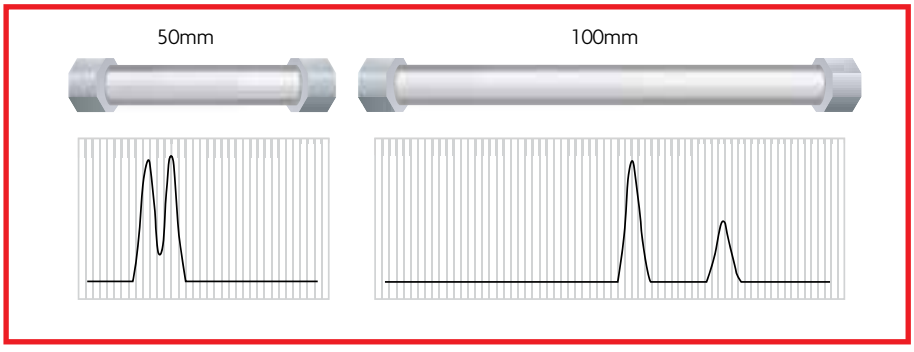

Figure 6

Alternatively, a column of the same length and diameter, but with a smaller particle size, will deliver more mechanical separation in a shorter time and use less solvent, however its backpressure will be much higher. Therefore trade-offs between these two parameters are needed.

Secondly, the chemistry of the packing material and chemistry of the solvents used are defined as its chemical separation power, and optimising the selectivity of these is the most powerful means of creating a separation. This will allow us to reduce the brute force required to gain the highest possible mechanical efficiency. To create a separation of any two specified compounds, an analytical chemist may choose among any number of combinations of stationary phases and mobile phases. This decision is determined by the characteristics of the compounds that our chemist wishes to separate.

A molecule's structure and how it reacts to its environment is determined by the arrangement of its constituent atoms and the bonds that hold them together. Within any molecule, there is a specific arrangement or group of certain atoms that are responsible for its properties and predictable chemical reactions, this is called the functional group; this functional group will often determine whether the molecule is *polar* or *non-polar*. Organic molecules are generally sorted into classes according to the principal functional group it contains, e.g. alcohols, esters, ketones, aldehydes etc.

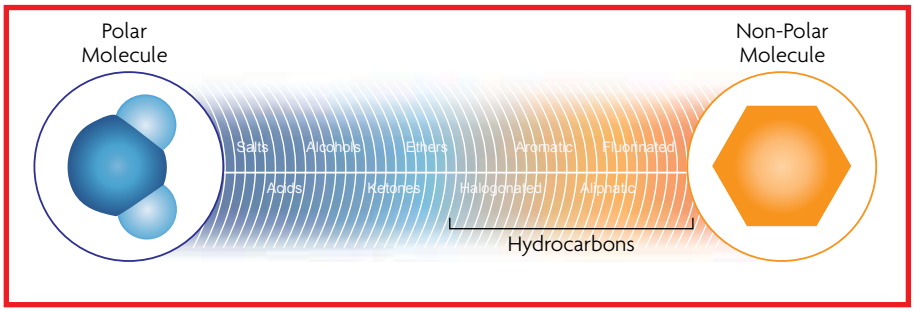

Figure 8

Water, for example, is a polar compound, whilst benzene is non-polar. In chemistry, unlike physics, substances with a similar polarity tend to be attracted to each other; those with dissimilar polarity exhibit weaker attraction, or even repel one another, for example, oil and water. Analytical chemists are able to use this property as the basis for chromatographic separation. Remember, that in chromatography and chemistry in general "*like attracts like*" or "*like dissolves like*".

To make use of this property to effect a separation, the chemist must choose a mobile phase and a stationary phase with different polarities. After considering the polarity of both phases, the chemist must choose a stationary phase in which the compounds of interest are retained, but not so strongly that they cannot be eluted from the column. Among solvents, the chemist must choose those of similar polarity to that of the compounds, but not so much so that they are washed straight through the column without separating. In other words, the chemist must choose which phase combination may best exploit the more subtle differences in any given compound's polarity and solubility to maximise the selectivity of the chromatographic system. Remember - like attracts like. But, as you can imagine, creating a separation based upon polarity involves knowledge of the sample and experience with various kinds of compounds and retention modes.

So, how do we know what we are looking at and how much of it is there by simply seeing the peaks on a computer screen? In the case of transformer testing, this is "relatively" straightforward, since we know what the compounds are that we are looking for - these are purchased from a chemical supply company in an extremely pure form and used to calibrate our instrument. A number of solutions of each of these compounds of exactly-known concentration are prepared in a suitable solvent and run on the instrument. These elute at a specific location (retention time) to produce a chromatogram and by comparing each peak's chromatogram and its area we are able to accurately identify which peak is which compound and produce a calibration curve. (Fig.9). So, when a sample of unknown concentration is tested, provided that temperature, pressure, mobile and stationary phases remain the same, the chemist will be able to identify and quantify each compound, by comparing the reference standard chromatogram with the unknown.

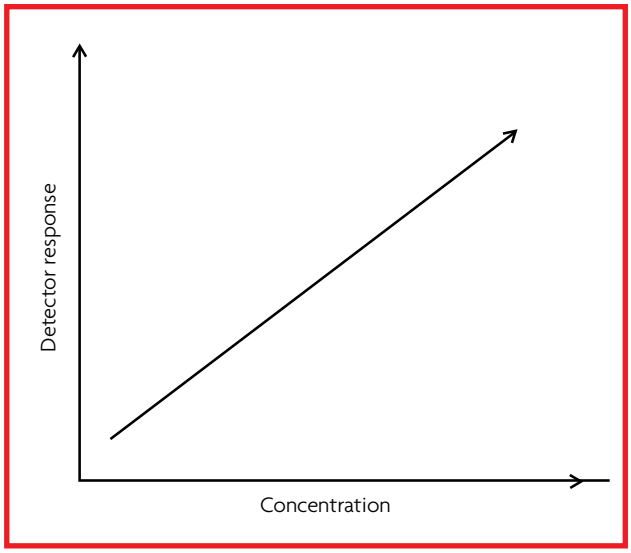

Figure 9

Unfortunately in this case there is a problem: furanics dissolve in the transformer oil and transformer oil is not a pure compound, it is made up of hundreds of different compounds including additives such as antioxidants to improve its lifespan, so we cannot simply inject the oil into the HPLC and compare the chromatogram with our standards, as we would end up with hundreds of peaks. We need a way to extract the furanics and then inject our extracted solution. Again, we turn to the chemistry to solve this.

As before, a number of solutions of known concentration of each compound are made, but this time by diluting them in virgin oil. These are now our reference standards. Then using a solvent of a polarity close to that of our compounds but not close enough to the oil that it will dissolve it, we vigorously mix the two and allow the oil / solvent mix to separate.

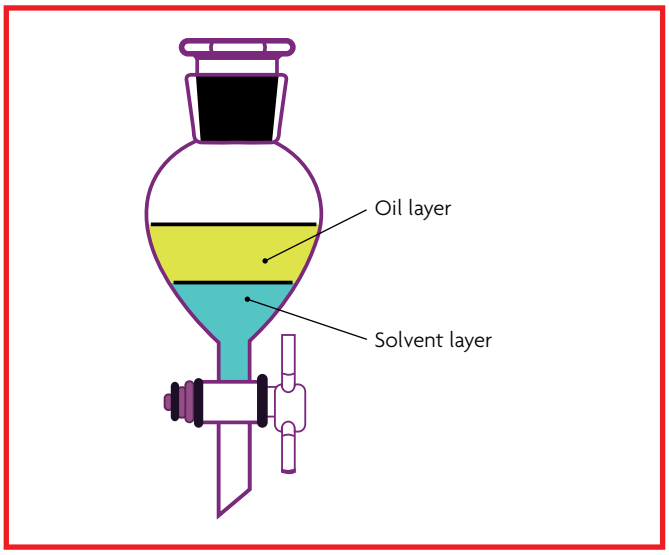

Figure 10

Our compounds of interest will now be partitioned between the solvent and the oil in differing proportions depending on how like they are to the solvent, but there will be very little, if any, oil in our solvent. Remember - like dissolves like. We now take a sample of each of our solvent layers and inject these into the HPLC, and compare the chromatograms to our calibration curve (figure 9) in order to determine the concentration and thus the partition coefficient of each of our compounds (ratio of how much compound is in the oil versus the solvent).[5]

Knowing the partition coefficient, we are finally in a position to test our unknown sample, and providing it is treated in exactly the same way as the calibration samples as described above, before injecting in the HPLC, we will know its partition coefficient, its retention time (from our chromatogram) and thus can calculate its concentration in the original oil sample, and last but certainly not least, can calculate the degree of polymerisation and thus the condition of the paper insulation....Phew!

To conclude, HPLC is one of a number of chromatographic techniques in the analytical chemist's tool box, and along with gas chromatography, one of the more sophisticated techniques used in the analysis of transformer oil. However, considering the value of transformers both in their cost and the cost of their downtime, the complexity and expense of the testing techniques to ensure continued service is easily justified.

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Head Office KwaZulu-Natal
9 Le Mans Place,
Westmead, KZN, 3610
PO Box 15108,
Westmead, KZN, 3608
t +27 (0) 31 700 5460
f +27 (0) 31 700 5471
e support@wearcheck.co.za
w www.wearcheck.co.za

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