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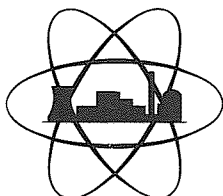
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For many years, analysis of the gaseous decomposition products of the insulating oil has had an important place in the monitoring of transformer operation. It offers practically the only possibility of at least an indirect look into the normally hidden interior of a transformer.

The primary task of the insulating fluid is to remove the heat which unavoidably forms in the iron core and windings of a transformer under load. In addition it must be a good insulator, which prohibits the use of liquids such as water. Because of its relevant good properties, a fluid having a mineral oil basis has generally proved most satisfactory. At an early date, *Buchholz* developed the Buchholz relay named after him (Figure 1). This is a device for the protection of oil-filled transformers; its action is based on the fact that gaseous decomposition products caused by electrical faults, short circuits or overloads collect at the highest point of the oil system. This is where the Buchholz relay is placed; when gas collects, a float switch activates an alarm. The analysis of the "Buchholz gas" is generally most helpful in tracing the fault. Few of the faults which occur are actually spontaneous, however, and it was soon recognized that slowly developing faults leave their traces in the oil long before the Buchholz relay is activated [1, 2]. With a routine analysis of the gaseous decomposition products of the insulating oil, electrical weak points in the system, such as:

— hot spots,
— poor contacts,
— arcing and general discharges,

Fig. 1. The Buchholz relay.

Fig. 2. Structure and decomposition products of the insulating oil.

— poor impregnation (air inclusions in solid insulations),

can be detected in good time and corrected at a suitable moment. When slow faults occur and decomposition gas is formed, some of the decomposition products remain dissolved in the oil. Analysis of the decomposition gas is useful not only in timely detection of a fault, but also in the identification of the cause of the fault, on the basis of the proportions of various gaseous components which are present. The oils used are pure hydrocarbons, hence the decomposition products are either also hydrocarbons or hydrogen proper (Figure 2). For example, acetylene is the typical compound formed during discharges of high energy density; this refers to discharges ranging from those found in poor contacts to full dielectric breakdown. The presence of the saturated hydrocarbons methane and ethane is an indicator of thermal oil decomposition; the higher the temperature, the more ethylene is in the mixture. Poor impregnation of the solid insulation (e.g. air inclusions) will lead mainly to hydrogen formation.

The presence of carbondioxide or carbon monoxide will indicate the decompositionf cellulosic material, i.e. of the solid insulation, as they cannot be formed by the mere decomposition of the oil. The oxides of carbon are, however, not a definitive indication of the decomposition of paper. On the one hand, oxides of carbon are produced from cellulose already under normal thermal loading, and on the other hand,

there is a general oxidation of the insulating oil, when it is in direct contact with air. If therefore the condition of the paper insulation is to be evaluated, other indicators have to be examined.

For this purpose, especially furan and its derivatives have proved suitable. All furan derivatives are built up on the heterocyclic ring C_4H_4O (Figure 3). Furans are produced industrially from agricultural residues such as straw and corncobs; in the same way, it is produced in the decomposition of cellulosic materials such as paper (Figure 4). Cellulose is a long-chain polymer, with up to several ten-thousands of glucose units in each chain. The length of the cellulose chain indicates the degree of polymerization, hence is referred to as the D.P., indicating the average number of glu-

Fig. 3. Chemical structure of Furan C_4H_4O.

structure:

decomposition products:
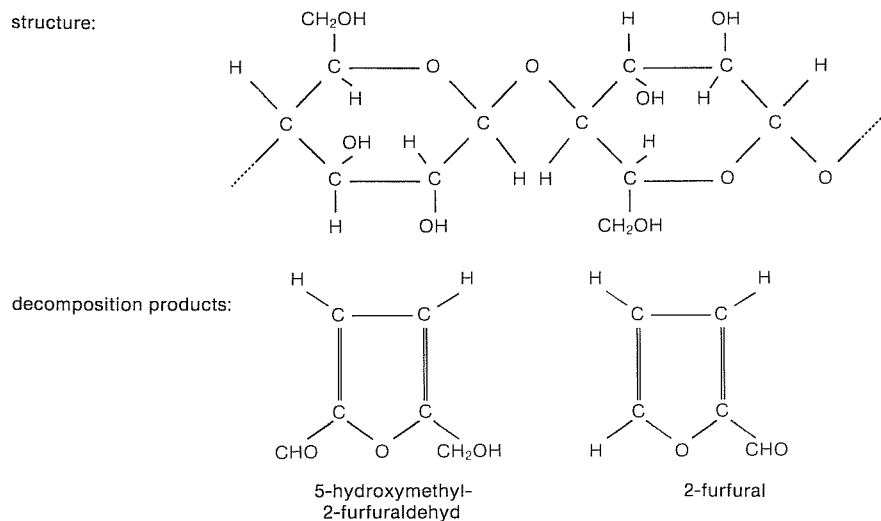
5-hydroxymethyl-
2-furfuraldehyd

2-furfural

Fig. 4. Structure and decomposition products of cellulose.

cose units per cellulose molecule. New paper, before aging, has D.P. values of over 1000, whereas aged paper may have D.P. values below 200. In the latter case, the paper will already have almost completely lost its original strength; it will be brittle and broken. During decomposition, a series of furans are formed, the main one being hydroxymethyl-2-furfuraldehyde. This compound is relatively unstable and can break down to form further derivatives. The specific products depend on many parameters. The present investigations have been limited to the following six furan compounds, which is not to say that others which are not mentioned could not also be formed:

— 2-furoic acid,
— 5-hydroxymethyl-2-furfuraldehyde,
— 2-furfural,
— 2-acetylfurane,
— methyl-5-furfural,
— 2-hydroxymethylfurane.

The basic structure of all these compounds is similar to 5-hydroxymethyl-2-furfuraldehyde, and all of them are soluble in oil; this means that with a suitable analytical method they should provide a practical indication of the condition of the paper or other solid insulation. The by far best method is the high-performance liquid chromatography (HPLC).

As early as 10 years ago, *H.-J. Krabbe* presented a paper at the VGB Conference "Chemie im Kraftwerk 1980 (Chemistry in Power Plants 1980)" entitled "Application of Gas Chromatography in the Power Plant Laboratory" [3]. The main subject was the use of gas chromatography for monitoring transformers, as we have already mentioned. It will be useful here to review briefly the principles of chromatography in general, with particular reference to HPLC.

Chromatography is a method of separating and identifying the components of a mixture. All types of chromatography follow the same basic procedure, which involves the following parts (Figure 5):

— a mobile phase: in gas chromatography, this is the carrier gas; in HPLC, it is a liquid.

— a stationary phase: in our case, the separation column.

— a detector for qualitative and quantitative determination of the separated components.

First the mobile phase is passed through the separation column at a constant rate. The mixture to be investigated is then added to the mobile phase, whether gas or liquid, so that it also passes through the column. Interactions then ensue between the individual components of the mixture and the fil-

ling in the column, and a dynamic equilibrium is established between the stationary and mobile phases. Usually the individual components have different coefficients of distribution between the two phases, thus giving rise to different migration velocities. The task of the detector placed at the column outlet is to recognize and quantify the various substances which have thus been separated on the basis of their different velocities. For the problem we are concerned with, an ultraviolet detector has proven to be a most useful solution. Its effectiveness depends on the ability of each of the various substances to absorb ultraviolet light of a specific wave-length. In order to utilize this characteristic, ultraviolet light of suitable wavelength is passed through the substance to be checked; comparison of the output signal with the input signal gives the amount of light which has been absorbed. This amount is proportional to the concentration of the substance to be detected, so that with a simple calibration the amount of the substance which is present becomes known.

The result of such a measurement using HPLC is shown in Figure 6. At time $t = 0$, 20 μℓ of a 5-component standard solution was injected into the HPLC apparatus through a sample tube. In accordance with the interaction mechanism described above, the various components reached the end of the column at different times. These times, referred to as the retention times, are plotted as abscissa. Under the same conditions, the times are always the same, therefore the times can be used to identify the components. The quantity of a substance is found either from the height of a peak in the curve, i.e. the ordinate, or from the integral over the peak width, when that can be determined. For the problem we are discussing, there is an even more suitable detector, referred to as a diode-array detector. This a further development of the ultraviolet detector, and permits material identification on the basis of two characteristics. The first ultraviolet detector we mentioned can determine the absorption of only one freely selectable wave-length at a time, whereas the diode-array detector can cover the whole ultraviolet spectrum at the same time. An example of the resulting chroma-
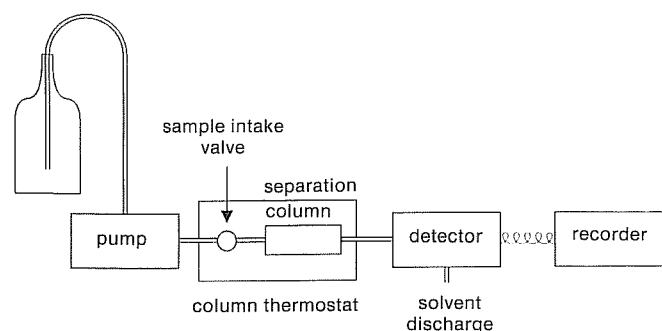
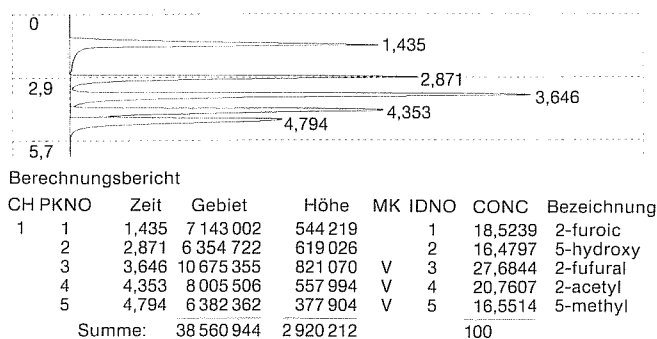

Fig. 5. Scheme of an HPLC apparatus.

Berechnungsbericht

CH	PKNO	Zeit	Gebiet	Höhe	MK	IDNO	CONC	Bezeichnung
1	1	1,435	7 143 002	544 219		1	18,5239	2-furoic
	2	2,871	6 354 722	619 026		2	16,4797	5-hydroxy
	3	3,646	10 675 355	821 070	V	3	27,6844	2-fufural
	4	4,353	8 005 506	557 994	V	4	20,7607	2-acetyl
	5	4,794	6 382 362	377 904	V	5	16,5514	5-methyl
	Summe:		38 560 944	2 920 212			100	

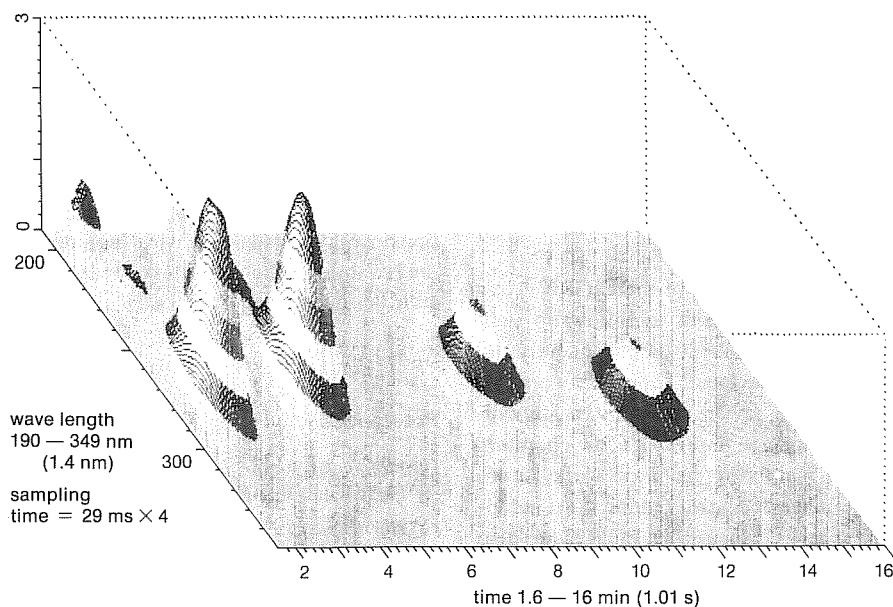*Fig. 6. HPLC chromatogram of furans.*

Fig. 7. "DIODE-ARRAY"-chromatogram.

togram is shown in Figure 7. Each substance is now characterized not just by one parameter, the retention time (also shown here as the abscissa) but by two, the retention time and the wave-length at which maximum absorption occurs (shown as the ordinate).

The various individual furanic compounds have their maximum ultraviolet absorptions at different wave-lengths, therefore each substance can be clearly identified on the basis of two different properties. This can be of particular importance when the sample contains other substances having similar retention times. The third dimension in the illustration shows the amount of ultraviolet radiation which is absorbed; this is a measure of the amount of the substance in question. It is in the nature of things, of course, that an analytical method of this sort produces a great amount of data; this can be handled quite well with a standard data processing system and suitable software.

Analytical Method

For determining the furanic compounds, only a small amount of the insulating oil is required. The oil, however, cannot be introduced directly into the apparatus for analysis. The compounds of interest first have to be separated from the oil by means of a "solid-phase extraction". For this purpose, 20 ml of the oil sample are mixed with an equal quantity of n-pentane and are then passed through a silica-gel cartridge in which the furances are retained. The cartridges are standard, commercially available analytical items; they can be used only once. The cartridge containing the furans is next washed through with the eluent, yielding a solution suitable for the HPLC analysis. For the analysis, 20 µl of this solution are then introduced into the HPLC appar-

atus through the sampling tube. Good separation efficiency for the individual furan compounds is obtained with a methanol-water solution, under isocratic flow conditions; a mixture of 30 % methanol and 70 % water has been found best. In special cases, however, other eluents have also been found useful.

Very good separations are obtained with a "C-8 Octyl" column 25 cm in length. A C-18 column of the same length is also useful for the present problem.

The individual furanic compounds are best determined with the diode-array detector already referred to; maximum ultraviolet absorption is attained at the following wave-lengths:

5-hydroxymethyl-2-2furfur-aldehyde	280 nm
2-furfural	274 nm
2-acetylfuran	272 nm
methyl-5-furfural	288 nm
2-furoic-acid	242 nm
2-hydroxymethylfuran	194 nm

When using apparatuses which do not include the above detector, it is possible to determine the first four compounds at a fixed wave-length of 276 nm, while 2-furoic acid, which has the lowest retention time and which can be well separated from the other compounds, can be determined in the same analysis, at 242 nm (Figure 6). 2-hydroxymethylfuran has then to be determined in a separate analysis at 194 nm.

Comments on the Results

The method described permits determination of 1 mg of compound per litre of oil with a high degree of certainty. The question as to whether even smaller amounts can be determined and with what accuracy, is presently under investigation by working groups in CEGRE and the IEC; more will

be said about this in a later paragraph. In the light of recent experience, we judge that 0.1 mg furan per litre of oil can be determined with suffcient accuracy, and this is an amount that already indicates a very small amount of abnormal paper decomposition.

How much experience already exists, either in our company or in others, in the field of transformer monitoring with HPLC? This has been an important topic in the meetings of the CEGRE Working Group 15-01 over the past four years. At first the question was handled by the group called Task Force 01, whose subject is the analysis of the decomposition gas from insulating oil. Starting this year, it comes under the new Task Force 03, which deals exclusively with the problem of HPLC analysis of insulating oil. From the work of these groups, it is apparent that a number of power companies already use the HPLC method for checking their oil-insulated transformers. ENEL in Italy, for example, reported four years ago that a series of investigations covering over 200 transformers had been made using HPLC. Also, for a number of years, oil-insulated transformers in England have been checked for paper decomposition products, using the HPLC method, and similar systematic investigations have been reported from Australia. The main compound found to occur is furfural, but in some cases methyl-5-furfural and 2-acetylfuran have also been observed. ENEL [4] reports a case of an interturn fault in the low-voltage winding of a 19-year old 15/250 kV, 190 MVA transformer. An HPLC analysis made shortly before the event indicated 3.2 ppm furfural in the insulating oil, with traces of other furans. Investigation of the insulating paper after the event yielded D.P. values of 130 to 450. A comparison with the D.P. value of about 1000 for new paper shows that the insulating paper in the transformer was already in a badly aged condition.

Closer investigation revealed that large amounts of furans were absorbed on the paper, these being exactly those compounds which had been presumed as paper decomposition products. It is interesting to note that for 15 years regular analyses of the decomposition gas had been made; these had indicated generally low and, in particular, stable quantities of saturated hydrocarbons, which as a rule is to be interpreted as natural aging. Carbon dioxide and carbon monoxide, which normally are the indicators of paper decomposition, were found only in small quantities which would not point to any abnormal decomposition of the paper.

This case thus serves to illustrate the advantages of investigations using the HPLC method; it offers a valuable supplement to the analysis of the decomposition gases given off by the insulating oil, as a means for monitoring the operation of oil-insu-

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lated transformers, bushings, and instrument transformers. The gas analysis will, without doubt, remain the most important tool in the early detection of faults, but the additional information which an HPLC analysis can give must not be disregarded.

Especially with the instrument transformers referred to above, there are still a number of unsolved problems. It is, unfortunately, a well known fact that periodically one of these transformers will suffer a dielectric breakdown, or will even explode, spontaneously and without warning. Not only is adjacent equipment damaged, but also the staff is considerably jeopardized. It is known, for example, that high-frequency transient disturbances in instrument transformers, as can occur in connection with breaking operations, can lead to discharges. These discharges are of low intensity, but are sufficient to cause gradual perforation of the paper. Then at some later time the insulation becomes so weak that there is

a danger of a high-power flashover, with all of its consequences. In such situations, there is a justifiable hope that HPLC analyses would offer a timely warning, particularly when the analyses of the decomposition gas have indicated by the presence of, for example, acetylene, that electrical discharges may be occurring.

It is the declared aim of the CIGRE group which was mentioned, to follow up such information and events. Consequently, an appeal is made to all those who operate instrument or power transformers, to support this work. In the end, it is the operators who will gain most from the work, i.e. to avoid outages occurring at the most inconvenient times. Since 1989, the IEC has also had a similar working group in the form of the Technical Committee No. 10, "Fluids for electrotechnical applications". Their aim is to develop a standard method for the analysis of furanic compunds in insulating oil,

which is analogous to the proven Standard 567 for the analysis of the decomposition gas.

In concluding, we should like to repeat that with the HPLC, an analytical method is now available which permits timely detection of abnormal decomposition of the solid insulation in oil-insulated electrical equipment, thus enabling action to be taken before possible serious damage occurs.

References

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