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Note

Reversed-phase high-performance liquid chromatographic analysis of polar oxidation products in transformer oils

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Oxidation is the main cause of the deterioration of transformer oils in service, apart from the more severe but abnormal faults such as arcing, hot spots and partial discharges¹. Oil resistance to oxidation has therefore been studied extensively over the years, and the results have been reviewed^{2,3}. The dielectric and physical properties of oils, such as their breakdown strength, conductivity, power factor and interfacial tension, are affected by the polar compounds formed during oxidation, and measurement of these properties is used routinely in the industry to evaluate the extent of oil degradation. However, the interpretation of the results may be misleading^{4,5}, owing to the variety of parameters involved, and a more direct method of determination of the polar compounds formed would be preferable.

Infrared measurements⁵⁻⁷ could be a solution but they are limited to cases where relatively extensive oxidation has already taken place. Among other possible methods, high-performance liquid chromatography (HPLC) has been applied successfully to transformer oils in this laboratory: in the gel-permeation chromatographic mode for oil fingerprinting, x-wax formation⁸ and flow-improver content⁹, in the normal absorption mode for aromatic group-type composition⁸ and in the reversed-phase mode for antioxidant content¹⁰. A certain degree of separation of the polar compounds extracted from coal liquefaction products¹¹ and insulating oils¹² using reversed-phase HPLC, has also been reported. A more complete and systematic study of the separation of polar compounds in transformer oils is presented here.

EXPERIMENTAL

The HPLC instrument was equipped with a Model M6000 high-pressure pump from Waters Assoc., a Model 7120 injection valve from Rheodyne and a differential UV detector from Waters Assoc., operating at 254 nm. The reversed-phase column was LiChrosorb RP-18 (10 μm) (250 \times 3.2 mm I.D.) from Altex Scientific.

The solvents (HPLC grade), methanol (Omni-Solv) and water were obtained from BDH (Canada), filtered on 0.5- μm Millipore filters prior to use. The flow-rate was 1.0 ml/min.

New samples of Voltesso 35, Sunelect HT and Diala A were obtained from Imperial Oil, Sun Oil and Shell, respectively. Samples of these new oils were subjected to accelerated oxidation tests according to ASTM method D2440 (25 g of oil at

110°C, under oxygen at 1 l/h and atmospheric pressure, with 30 cm of copper wire, for up to 164 h) or D2112 (50 g of oil at 140°C, with 300 cm of copper wire, in a rotating bomb under 630 kPa of oxygen, until the pressure dropped to 420 kPa. Samples of aged Voltesso 35 were also obtained from Hydro-Québec transformers that had been in service for up to 25 years. The antioxidant in Voltesso 35 is 2,6-di(*tert.*-butyl)-4-methylphenol (DBPC).

The model compounds listed in Table I were obtained from Pfaltz and Bauer and ICN Pharmaceuticals and were used without further purification.

RESULTS AND DISCUSSION

Transformer oils are complex mixtures of aromatic, alkane and cycloalkane hydrocarbons, totalling hundreds and possibly thousands of individual compounds, although the precise number has never been reported accurately¹³. Dielectric losses in new purified oils are very low and are attributed to the small permanent dipole moment or polarity of the aromatic molecules¹⁴. During the operation of transformers, dielectric losses increase markedly owing to oil oxidation and the formation of oxygen-containing compounds, which are more polar than the parent hydrocarbons, with functional groups such as aldehydes, ketones, alcohols, phenols, peroxides and carboxylic acids².

In reversed-phase HPLC, despite the fact that the precise mechanism of retention is still under debate, it is generally accepted that the most polar solutes are the

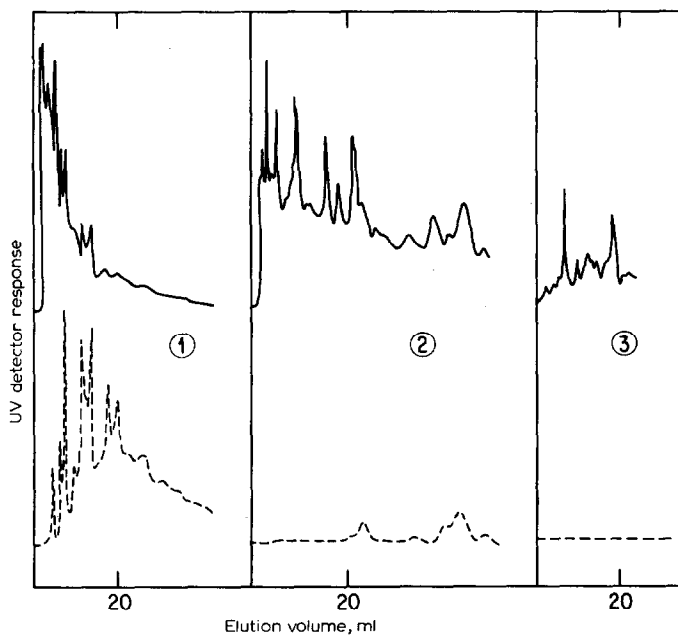


Fig. 1. Influence of methanol to water ratio on the separation of oxidation products and aromatic compounds in Voltesso 35 transformer oil: ---, new unoxidized oil; —, highly oxidized oil (15 days at 120°C over copper). Methanol-water ratio: (1) 80:20; (2) 60:40; (3) 20:80. Injection volumes: (1) and (2), 1 μ l; (3), 10 μ l. UV detector sensitivity: 0.08 a.u.f.s.

least retained and are eluted first¹⁵. It should therefore be possible, using reversed-phase HPLC, to separate the more polar oxidation products from the oil. To optimize the separation conditions, samples of new and oxidized Voltesso 35 transformer oil were examined with solvent mixtures of increasing polarity (Fig. 1). This was achieved by decreasing the methanol to water ratio in the solvent mixture¹⁶, which resulted in an increase of the overall elution time.

At a methanol to water ratio of 80:20, all components in the new and oxidized oils are eluted completely and rapidly. The separation obtained for the UV-detected aromatic compounds in the new oil is related to the number of aromatic rings and alkyl substituents⁸. After oxidation, additional peaks appear at shorter elution times, indicating that more polar oxidation compounds have been formed, as could be expected. Aromatic compounds and oxidation products still interfere considerably, however.

At a methanol-to-water ratio of 20:80, all the aromatics and a large part of the oxidation products are irreversibly retained on the column (10 μ l were injected at a methanol-to-water ratio of 20:80 compared with 1 μ l in the other instances in Fig. 1).

A methanol-to-water ratio of 60:40 therefore appeared to be the best compromise for the separation of the oxidation products, which may be divided into two categories: (i) relatively non-polar compounds, eluting with the aromatic compounds after an elution volume of 20 ml; these compounds are not more polar than the aromatic compounds naturally present in new oil and therefore will have only minor effects on the electrical properties of oil, especially as they are formed in smaller amounts, even after extensive oxidation (Figs. 1 and 3); (ii) oxidation compounds eluting before the first aromatic peaks, at an elution volume of less than 20 ml. Eluting more rapidly, these oxidation products are more polar; they are also formed in larger amounts and will therefore contribute most to the dielectric losses of the oxidized oil. Further, as they are not affected by interferences from the aromatics, peaks eluting before an elution volume of 20 ml can be unequivocally attributed to oxidation compounds only and are easily quantitated by surface measurements. Only these oxidation products (ii) will be considered in the remaining part of this paper, where they are referred to as the "polar oxidation products" of oxidized oil.

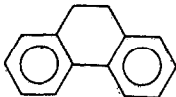
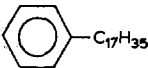
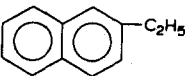
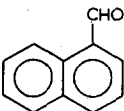
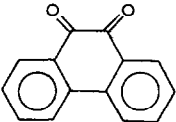
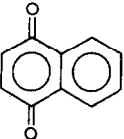
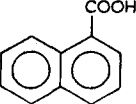
The identification of the hundreds of individual polar oxidation products would be virtually impossible, even with such powerful methods as gas chromatography-mass spectrometry. Further, it is outside the scope of this paper, which is rather to analyse them as a chemical class of compounds.

It is possible, however, to obtain an idea of the types of compounds present in this fraction by using oxygen-containing hydrocarbon model compounds with chemical structures close to those suspected in oxidized oils^{2,3}. The results shown in Table I confirm that the polar models, like the polar oxidation products, elute more rapidly than the non-polar aromatic model compounds and the aromatic compounds in new oils. The elution times increase in the order carboxylic acid > quinones > aldehyde.

Accelerated oxidation

Various types of transformer oil were oxidized under the same accelerated oxidation conditions (according to ASTM method D 2112) and examined by HPLC

TABLE I
ELUTION BEHAVIOUR OF MODEL COMPOUNDS

Name	Structure formula	Elution volume (ml)
9,10-Dihydrophenanthrene		33
Heptadecylbenzene		31
2-Ethynaphthalene		29
1-Naphthaldehyde		6
9,10-Phenanthraquinone		5
1,4-Naphthoquinone		3
1-Naphthoic acid		2.8

using methanol-water (60:40) (Fig. 2). The smaller amounts of polar oxidation products in Shell Diala A oil can be related to its lower overall aromatic content of 3.3% compared with 15.9 and 12.8% in Sunelect HT and Voltesso 35 oils, respectively⁸. The absence of polar peaks in the 7–20-ml elution volume range of Shell Diala A oil may also be related to the absence of di- and triaromatics in this oil⁸.

The build-up of polar oxidation products during the accelerated oxidation of Voltesso 35 (according to ASTM method D 2440) as a function of oxidation time is illustrated in Fig. 3. It is progressive up to 84 h, then increases dramatically after 90 h, which corresponds to the end of the induction period when all the DBPC antioxidant additive has been consumed¹⁰.

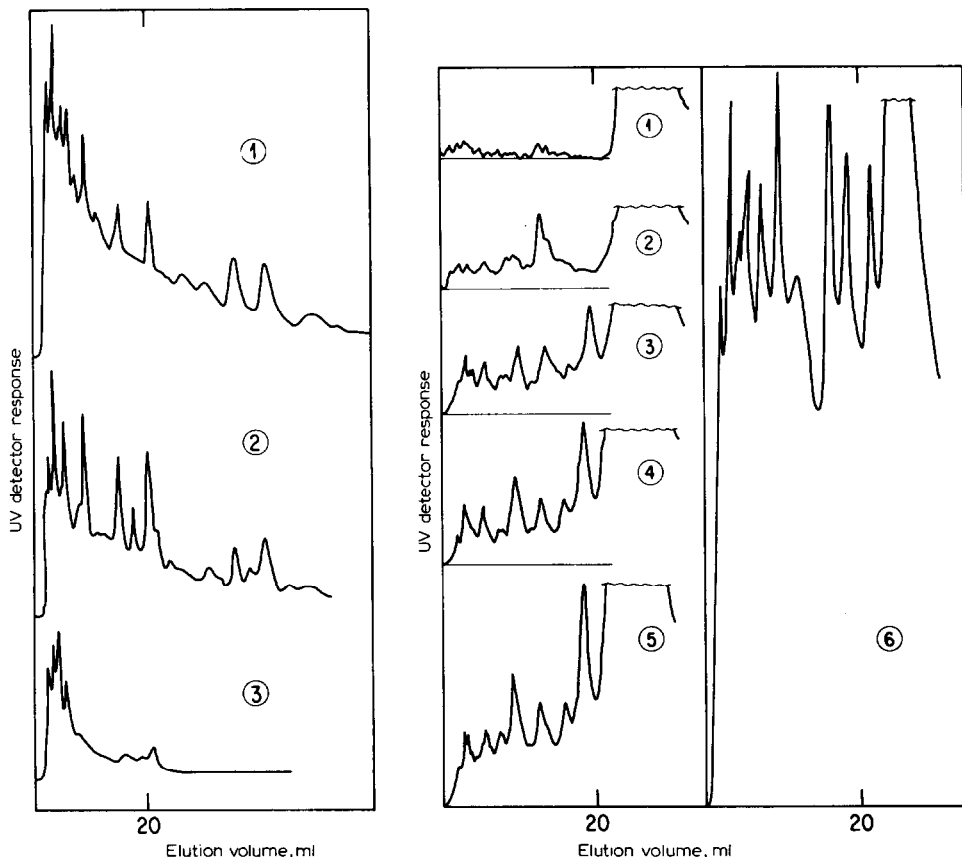


Fig. 2. HPLC of oxidized samples of commercial transformer oils. Oxidation according to ASTM D 2112. Methanol-water ratio: 60:40. Injection volume: 1 μ l. UV detector sensitivity: 0.08 a.u.f.s. Sample: (1) Sunelect HT; (2) Voltesso 35; (3) Shell Diala A.

Fig. 3. HPLC of oxidized samples of Voltesso 35 transformer oil as a function of oxidation time. Oil samples: (1) treated on Fuller's earth; (2) left for several weeks under artificial light; (3) after 48 h of accelerated oxidation according to ASTM D2440; (4) after 72 h; (5) after 84 h; (6) after 90 h. Methanol to water ratio: 60:40. Injection volume: 25 μ l. UV detector sensitivity: 0.04 a.u.f.s.

Subjecting a sample of new oil to artificial light at ambient temperature for a few weeks surprisingly leads to the formation of significant amounts of polar oxidation products compared with those found in a sample of oil freshly treated on Fuller's earth (Fig. 3). This may be related to the unexpected increase in interfacial tension also observed under these conditions⁴; and is due to photochemical oxidation.

Transformer oils aged in service

Typical HPLC traces of oil samples taken from transformers in service in the Hydro-Québec power system are shown in Fig. 4. It appears that the deterioration of the oil is not directly related to its number of years in service: one transformer oil was still in good condition after 21 years whereas another was considerably degraded

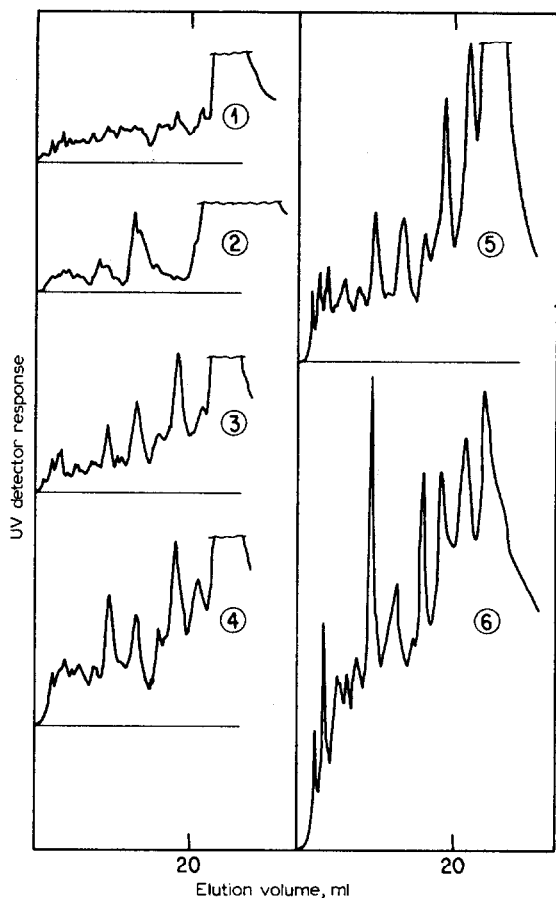


Fig. 4. HPLC of aged samples of Voltesso 35 from transformers in service. Age of transformers: (1) 21; (2) 1; (3) 25; (4) 20; (5) 7; (6) 13 years. Methanol-water ratio: 60:40. Injection volume: 25 μ l. UV detector sensitivity: 0.04 a.u.f.s.

after only 7 years. The operating load and the transformer type are obviously more important than the age of the transformers in this instance.

Before an elution volume of 20 ml aromatics do not interfere with the oxidation products, as mentioned previously and as can be seen in Fig. 3 for oil purified on Fuller's earth. The area under the HPLC curve up to this volume can therefore be used to compare the relative amounts of polar oxidation products in different oil samples run under the same HPLC conditions. The results are summarized in Fig. 5, where it can be seen that the relative amounts of polar oxidation products in oxidized and aged oils increase very rapidly towards the end of the induction period (when most of the DBPC antioxidant has been consumed), whereas the changes in the interfacial tension are much less important. HPLC therefore appears to be a more sensitive method for assessing the state of deterioration of transformer oils than the conventional interfacial tension and antioxidant content methods⁴.

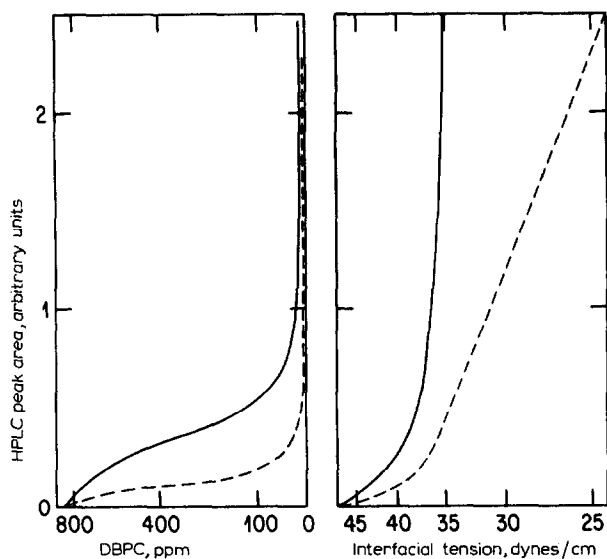


Fig. 5. Amount of polar compounds in aged and oxidized samples of Voltesso 35 (evaluated from the area under the HPLC curve, up to an elution volume of 20 ml) as a function of DBPC content¹⁰ and interfacial tension: —, aged oil from transformers in service; - - -, oxidized oil from accelerated oxidation tests according to ASTM D2440.

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REFERENCES

- 1 M. Duval, *IEEE PES SM Conference, Anaheim, July 14-19, 1974*, IEEE, New York, 1974, Paper C 74476-8.
- 2 A. C. M. Wilson, *Insulating Liquids: Their Uses, Manufacture and Properties*, Peregrinus, Stevenage, U.K., 1980.
- 3 R. W. Sillars, *Electrical Insulating Materials and their Applications*, Peregrinus, Stevenage, U.K., 1973.
- 4 J. P. Crine, M. Duval and C. Lamarre, *Proceedings of IEEE International Symposium on Electrical Insulation, Philadelphia, PA, June 7-9th, 1982*, IEEE, New York, 1982, p. 35.
- 5 T. Ishii and M. Ueda, *Proceedings of Conference on Electrical Insulation and Dielectric Phenomena, Washington, October 1973*, National Academy of Sciences, Washington, DC, 1975, p. 175.
- 6 J. J. Melchiorre and I. W. Mills, *IEEE Trans. Electr. Insul.*, 12 (1967) 150.
- 7 T. J. Gedemer and G. Maller, *IEEE PES SM Conference, Los Angeles, July 16-21, 1978*, IEEE, New York, 1978, Paper A 78561-3.
- 8 M. Duval and C. Lamarre, *IEEE Trans. Electr. Insul.*, 12 (1977) 340.
- 9 M. Duval, S. Lamothe, D. Cauchon, C. Lamarre and Y. Giguere, *J. Chromatogr.*, 244 (1982) 169.
- 10 C. Lamarre, M. Duval and J. Gauthier, *J. Chromatogr.*, 213 (1981) 481.
- 11 W. Dark and W. H. McFadden, *J. Chromatogr. Sci.*, 16 (1978) 283.

- 12 I. Webber and A. D. Mitchell, *Canadian Electrical Association Project RP 77-70 Final Report*, CEA, Montréal, 1980.
- 13 L. Ehrart, E. Rey and H. Sutter, *CIGRE Conference, June 8-18, 1966*, No. 119.
- 14 R. Bartnikas, *IEEE Trans. Electr. Insul.*, 5 (1970) 36.
- 15 S. R. Bakalyar, R. McIlwrick and E. Roggendorf, *J. Chromatogr.*, 142 (1977) 353.
- 16 L. R. Snyder, *Principles of Adsorption Chromatography*, Marcel Dekker, New York, 1968.