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DETERMINATION OF ORGANIC COMPOUNDS IN THE HYDROGEN USED FOR COOLING LARGE ELECTRICITY GENERATORS

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SUMMARY

An analytical method based on the pre-column technique has been developed for the analysis of the hydrogen used for cooling generators. A wide range of degradation products of the generator insulating materials can be determined at levels down to 1 pg/l and may provide an early warning of a developing fault. The procedures for pre-column preparation and sampling, retention volume determination, analysis and calibration are given together with typical results.

INTRODUCTION

Large electricity generators contain a number of organic insulating materials which may degrade to give gaseous products, either by ageing or because of electrical faults which produce hot spots or arcing. The value of gas analysis in the detection of faults in oil-filled transformers is well established¹. Similar techniques can be applied to generators. By regular analysis of the hydrogen used for cooling the generator, impurities known to result from the degradation of a particular insulating material or from a specific degradation process can be identified. This may provide an early warning of a developing fault and so permit steps to be taken to prevent a major failure.

A method for analyzing a wide range of possible degradation products as impurities in the hydrogen has been developed and is described. A typical example of the compounds which are found is given in Fig. 1. In order to determine which of the impurities are characteristic of the degradation of a particular insulating material, samples have been degraded in the laboratory and the products analysed. This work is reported elsewhere².

PRINCIPLE OF THE METHOD

The results of direct analysis of generator hydrogen for organic compounds using a gas chromatograph and flame ionization detector (FID)^{3,4} have shown that only methane, ethane and ethylene were normally present at levels which were above the detection limits. Early work to analyse generator hydrogen for insulation degradation products² confirmed that most of the organic compounds present could not be

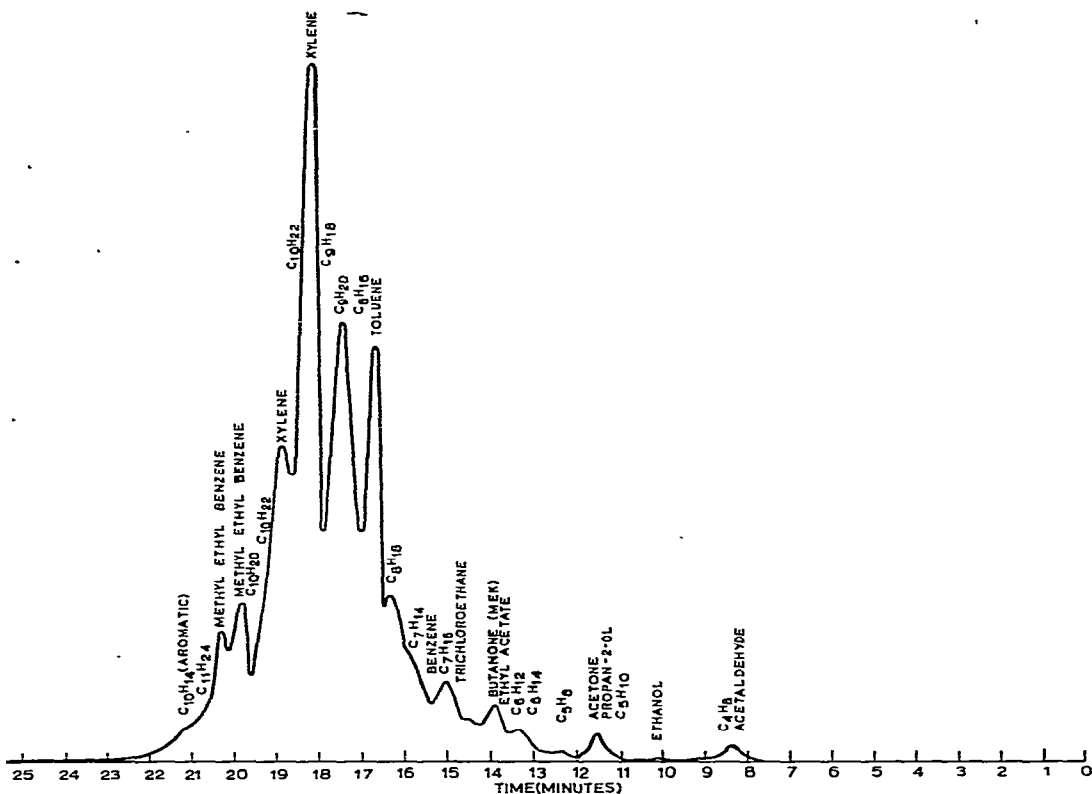


Fig. 1. Gas chromatogram of generator hydrogen impurities desorbed from a Tenax GC pre-column (reconstructed to the same attenuation).

determined without a concentration technique. A number of concentration techniques have been reported⁵⁻⁸. Of these the pre-column technique, in which the impurity is adsorbed on a gas chromatographic stationary phase contained in a short tube, was used for this work. Desorption is achieved by placing the pre-column in the carrier gas stream of a gas chromatograph and then heating rapidly. The released impurities are flushed into the gas chromatograph or combined gas chromatograph-mass spectrometer for analysis.

Calibration for each compound of interest is carried out by injection of known amounts of the compound on to a pre-column followed by desorption into the gas chromatograph. The retention volume V_T of each compound for a pre-column is defined as the volume of hydrogen which can be passed through the pre-column, at the working temperature T , without eluting the compound in question. For many compounds, the retention volume will be greater than the sample volume V_S and therefore concentrations can be calculated directly using the sample volume.

If the weight of an impurity trapped on a pre-column is W_i , then the concentration C_i of that impurity in the generator hydrogen will be given by

$$C_i = \frac{W_i}{V_S} \quad (1)$$

When $V_T < V_S$ the retention volume is determined for each compound of interest and is used instead of the sample volume to calculate the concentration of the compound, so that

$$C_i = \frac{W_i}{V_T} \quad (2)$$

EXPERIMENTAL

Pre-column preparation

Two different pre-column packing materials were used for this work. Low-boiling-point compounds ($< 100^\circ\text{C}$) were concentrated on Porapak T pre-columns since they show high retention volumes on this packing. Porapak T is the commercial name for a porous polymer of ethylene glycol dimethacrylate. Tenax GC (2,6-diphenyl-*p*-phenylene oxide porous polymer) was used for the concentration of higher-boiling-point compounds ($> 50^\circ\text{C}$) since its stability at relatively high temperatures eliminated the possibility of significant sample contamination due to column bleed during desorption.

The Porapak T pre-column was prepared by packing a U-shaped, 160-mm length of clean 6.35 mm ($\frac{1}{4}$ in.) O.D. stainless-steel tubing with approximately 2.5 ml (0.75 g) of 250–180 μm (60–80 U.S. standard mesh) Porapak T. Stop valves were then attached to each end. The Tenax GC pre-column was prepared in a similar manner using a straight 100-mm length of tubing and 1.5 ml (0.5 g) of the same mesh Tenax GC. The Porapak T pre-column was conditioned by coupling it into a gas chromatograph in place of the normal analytical column. The helium carrier gas flow-rate was set at 50 ml/min and the oven and detector temperatures were maintained at 150°C . The FID output signal was then monitored until a flat baseline was achieved. The Tenax GC pre-column was conditioned in the same way, except that a flow rate of 25 ml/min and oven and detector temperatures of 350°C were used.

Retention volumes for different compounds on the Porapak T pre-column were determined by cooling the pre-column, still coupled into the gas chromatograph but using hydrogen as the carrier gas, to -78°C in a cooling mixture of crushed, solid carbon dioxide and methylated spirits. This procedure required that the chromatograph injection, oven and detector heaters were switched off. The chosen compound was then injected onto the pre-column and the retention time t_R , recorded. After repeating this procedure several times to obtain a mean value, the retention volume V_T could be calculated from the relationship $V_T = ft_R$ where f is carrier gas flow-rate. Typical retention volumes determined in this way were 0.125 l (methane) and 10.5 l (ethylene). Retention volumes for the Tenax GC pre-columns were determined in a similar manner by injecting 1% solutions of the chosen compound at pre-column temperatures of 80, 100, 120 and 140°C . V_{ambient} was determined using a linear regression analysis of $1/T$ on $^{10}\log V_T$ (where T is the temperature in $^\circ\text{K}$). Following this procedure using a 1% solution of toluene in methanol, a value of 132.5 l for V_{293} was obtained from the regression line. Other typical retention volumes at 293°K , determined on a Tenax GC pre-column, were 72 ml (methanol) and 151 ml (ethanol).

Sampling

The sampling systems are shown in Figs. 2 and 3. The short lengths of nylon tubing are necessary to provide electrical insulation from induced currents in the generator pipe-work. The flow-rate was adjusted to 100 ml/min using the flow control valve and hydrogen was allowed to flow through the pre-column for a sampling period of 30 min. At the end of this period the flow control valve was closed and the pre-column sealed, either with stop valves (Porapak T) or stop ends (Tenax GC). The pre-column was then removed for laboratory analysis. The precise volume of hydrogen passed was recorded, together with the ambient temperature.

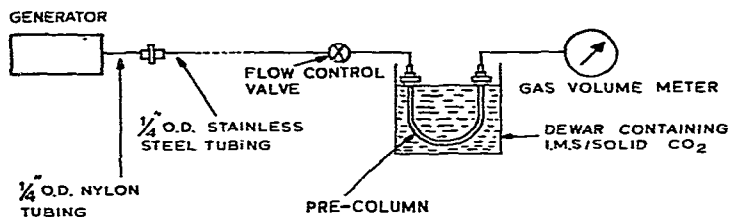


Fig. 2. Sampling of generator hydrogen. Pre-column, Porapak.

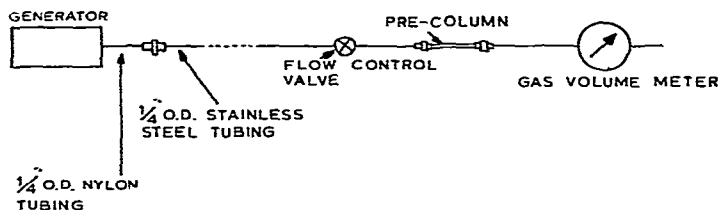


Fig. 3. Sampling of generator hydrogen. Pre-column, Tenax GC.

Analysis

The low boiling point impurities from the Porapak T pre-column were analysed on two 1.5 m × 6.35 mm O.D. stainless-steel analytical columns in series, the first packed with Porapak Q (a porous co-polymer of ethyl vinyl benzene and divinyl benzene) and the other with Porapak T. This arrangement allowed the three C₂ hydrocarbons to be easily separated. The column oven was kept at 110°C for the first 10 min of the analysis after which it was increased, at the maximum rate, to 150°C. A helium carrier gas flow-rate of 50 ml/min was used.

The pre-column was connected to the gas chromatograph sampling valve as shown in Fig. 4. The desorption and subsequent injection of the hydrogen impurities was achieved by immersing the pre-column in an oil bath at 150°C and rapidly switching the sampling valve to position A and opening the pre-column stop valves.

The high boiling point impurities from the Tenax GC pre-column were analysed on a 1.5 m × 3.17 mm O.D. stainless-steel analytical column packed with Tenax GC. After an isothermal period of 5 min at 50°C the column oven temperature was increased by 10°C/min to 340°C. A helium carrier gas flow-rate of 25 ml/min was used. The pre-column was connected to the gas chromatograph using the arrangements shown in Fig. 5, designed to prevent condensation of the impurities in

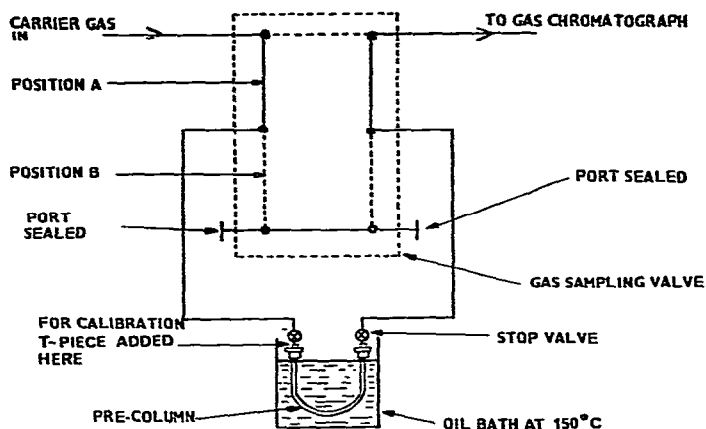


Fig. 4. Sample analysis. Pre-column, Porapak.

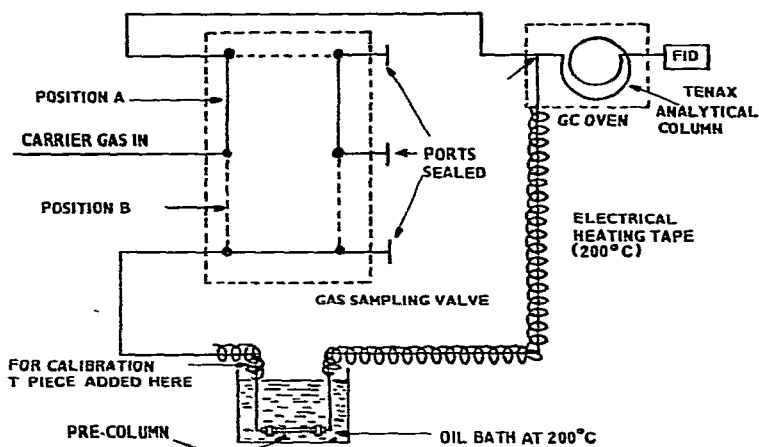


Fig. 5. Sample analysis. Pre-column, Tenax GC.

the inlet line. Analysis was started by immersing the pre-column in the oil bath and switching the valve to position B.

Calibration

Calibration was carried out by injecting a known amount of a chosen compound onto the pre-column, either as a gas or as a 1% solution in a suitable solvent. The solvent was chosen to have a retention time sufficiently different from that of the compound of interest for the two peaks to be well resolved. The material was then desorbed as described above and its retention time and peak area noted. This procedure was repeated for different quantities of the material and a calibration curve plotted of peak area against the volume of sample injected. When the sample was injected as a solution, the liquid volume was converted to the equivalent volume of vapour at the ambient temperature.

RESULTS

Typical gas chromatograms of generator hydrogen impurities desorbed from a Tenax GC pre-column and from a Porapak T pre-column are shown in Figs. 1 and 6, respectively.

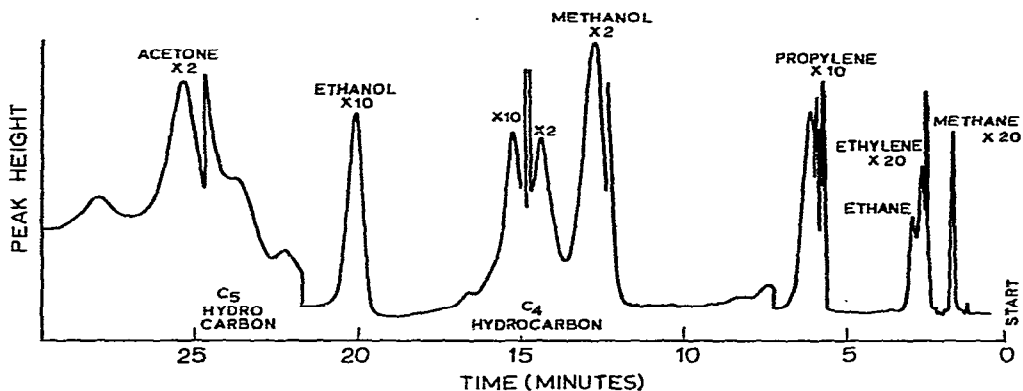


Fig. 6. Gas chromatogram of generator hydrogen impurities desorbed from a Porapak T pre-column.

To obtain a full quantitative analysis it is necessary to prepare a calibration plot for all of the known impurities in the sample. Fig. 7 shows a typical calibration plot for toluene obtained by injecting samples of a 1% solution of toluene in *n*-hexane.

Using the calibration plot shown in Fig. 7, the area of the toluene peak shown

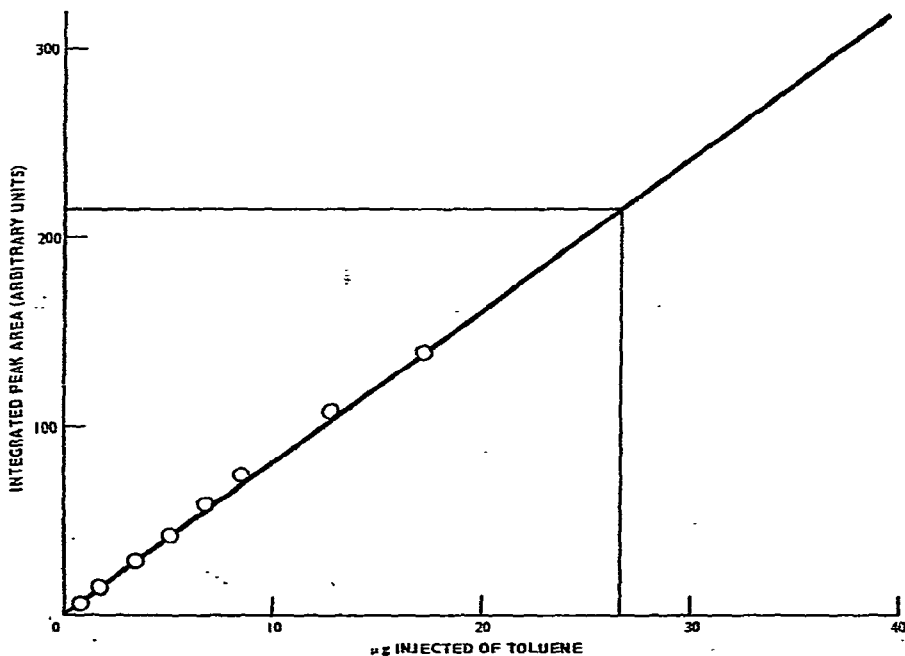


Fig. 7. Calibration plot for toluene.

in Fig. 1 is equivalent to 26.7 μg . This weight of toluene was collected from 3 l of hydrogen, equivalent to 2.8 l (V_S) at normal temperature and pressure; from the retention volume calculation for toluene above $V_T = 132.5$ l and so $V_T \gg V_S$. Therefore substitution of the above data in eqn. 1 gives a concentration of 9.5 $\mu\text{g/l}$ for toluene in the hydrogen sample.

The gain in detectability of organic species in a gas sample, achieved by the pre-column concentration technique, is determined by the volume of sample gas passed through the pre-column. The largest volume of sample gas that is normally injected into a chromatograph via a conventional sample loop without causing an unacceptable loss of resolution is approximately 0.005 l. Based on this volume, the concentration factor, G , achieved by concentrating V_S litres of gas in a pre-column is given by

$$G = 200 V_S \quad (3)$$

A practical limit on this factor is reached for a particular impurity when $V_S \geq V_T$, so that

$$G_{\text{max.}} = 200 V_T \quad (4)$$

Given that an FID system can detect a minimum of 10^{-10} g of any organic species, it follows that the minimum detectable concentration, $C_{\text{min.}}$, of an organic impurity in a gas is given by

$$C_{\text{min.}} \approx \frac{10^{-10}}{V_T} \text{ g/l} \quad (5)$$

when using the pre-column technique. Values of $C_{\text{min.}}$, based on the stated approximate values for V_T for ethanol, toluene and *n*-decane are shown in Table I. These were determined using a Tenax GC pre-column. However, it should be borne in mind that it would be impractical to sample volumes of gas in excess of say 100 l at a time, so that a detection limit of 10^{-12} g/l for all compounds exists. Also, this practical limit may be raised by several orders of magnitude when an impurity has a low retention volume on the pre-column, or when the impurity peak in the chromatogram is only partially resolved.

TABLE I
MINIMUM DETECTABLE CONCENTRATIONS

Compound	$C_{\text{min.}}$ (g/l)	V_T (l)
Ethanol	10^{-9}	10^{-1}
Toluene	10^{-12}	10^2
<i>n</i> -Decane	10^{-14}	10^4

CONCLUSION

A sensitive method has been developed specifically for the analysis of very low levels of organic gases and vapours in generator hydrogen. The method can be applied with equal facility to the analysis of any inorganic inert gas containing organic gases and vapours.

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