CHROM. 25 528

Determination of dissolved gases and furan-related compounds in transformer insulating oils in a single chromatographic run by headspace/capillary gas chromatography

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(First received January 5th, 1993; revised manuscript received August 26th, 1993)

ABSTRACT

A static headspace/capillary gas chromatographic technique has been developed allowing dissolved gases and furan-related compounds in power transformer oils to be determined in a single chromatographic run. The simultaneous determination of these two classes of compounds from a single sample injection represents a definite advantage over current procedures for the detection of impending performance failure of the unit. The method uses gas chromatography with porous-layer open tubular (PLOT) columns and a valve operated in sequence for flowpath selection. Also, comparison with the current method using packed columns showed that dissolved-gas analysis with PLOT columns provides better peak shapes and lower detection limits ($S/N_b = 3$): 5, 3 and 1 ppm (v/v) for hydrogen, carbon oxides and light hydrocarbons respectively. Detection of 2-furaldehyde is possible down to 0.5 ppm (w/w).

INTRODUCTION

Analysis of dissolved gases in insulating oils is an efficient diagnostic tool for routine performance monitoring of power transformers. As a result of a malfunction, gases such as H_2, CH_4, C_2H_2, C_2H_4, C_2H_6, C_3H_8 and C_4H_{10} may evolve from thermal or electrical degradation of insulating oil [1]. When paper insulation is involved, CO and CO_2 are also produced. The

concentrations and proportions of the dissolved gases can be related to the type of fault occurring in a transformer without taking the equipment out of service [2,3]. However, the production of carbon oxides cannot be specifically associated with cellulose degradation since they can also be formed as a result of long-term oxidation of the oil or introduced by equilibration of a limited surface of oil with air in the transformer expansion chamber. Also, it has been shown recently that the degradation of paper insulation results in the formation of furans, such as 2-furaldehyde, which dissolve in oil [4–7]. Thus, moni-

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toring these compounds can give complementary information specifically related to the state of the solid insulation.

The analytical methods used for dissolved-gas analysis generally comprise vacuum extraction [8] or stripping [9] of the gases followed by gas chromatographic separation. Analysis of less volatile furan-related compounds requires a second technique involving liquid- or solid-phase extraction followed by high-performance liquid chromatography [4,5]. A headspace method allowing automated analysis has recently been reported [10] as an alternative to vacuum gas extraction. This procedure, coupled with gas chromatographic separation, offers a precision better than 5% with detection limits ($S/N_b = 3$, where S and N_b are the net signal and the background noise, respectively) for hydrogen, carbon monoxide and methane, carbon dioxide and hydrocarbons of 7, 10, 5 and 1 ppm (v/v) respectively. The analytical performance of this technique was shown to be similar to that of the ASTM D3612 vacuum method [8] currently used for routine dissolved-gas analysis, while allowing a larger number of oil samples to be analysed by the same operator as a result of automation.

Gas chromatographic separation for dissolved-gas analysis is generally achieved using dual-packed columns to separate permanent gases and light hydrocarbons: a molecular sieve column is connected at the outlet of a porous polymer column through a valve used for column isolation [10]. Recently commercialized porous-layer open tubular (PLOT) capillary columns have not yet found an application in this field [11–15].

Firor [16] has used PLOT columns for the analysis of natural gas, refinery gas and process stream and has found that these columns provide shorter retention times, better resolution and lower detection limits than packed columns. The shorter retention times obtained could allow heavier insulation breakdown products such as the furan-related compounds to be determined.

This paper reports on the application of PLOT columns for the analysis of dissolved gases and furan-related compounds in transfer oils by the headspace/gas chromatographic technique. The possibility of measuring dissolved gases and cellulose insulation breakdown products in a single chromatographic run could simplify routine monitoring procedure for public utilities. In addition, compared with the previous packed column system, greater sensitivities for the dissolved gases are expected.

EXPERIMENTAL

Instrumentation

The instrumentation used for this study is depicted schematically in Fig. 1. It is the same as that used in a previous work for packed columns [10]. An HP-19395A static headspace unit (Hewlett-Packard, Palo Alto, CA, USA) equipped with a six-port injection valve (V1) and a 1-ml sample loop is used to extract the dissolved gases from transformer oil. An HP-5890 gas chromatograph (also from Hewlett-Packard) equipped with a thermal conductivity detector, a nickel catalyst unit to convert CO and CO_2 into CH_4, and a flame ionization detector was used for all
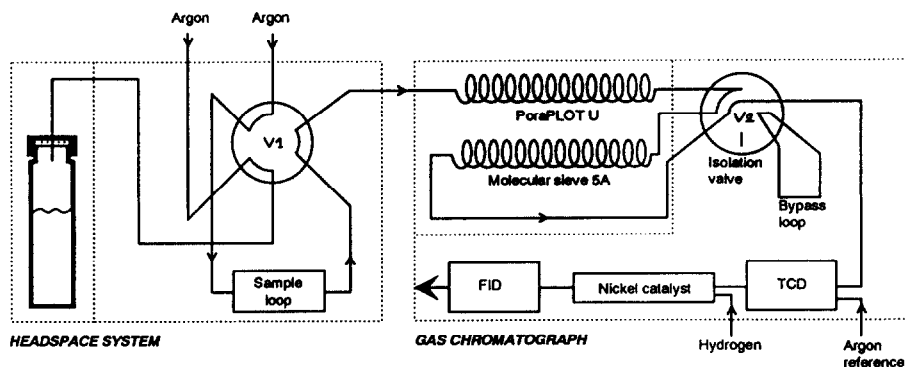

Fig. 1. Schematic diagram of the headspace/gas chromatographic instrumentation. FID = Flame ionization detector; TCD = thermal conductivity detector.

analyses. The methanizer was maintained at 350°C and fed with pure hydrogen serving both as reactant for the catalyst and fuel for the flame ionization detector. A ten-port pneumatic valve (V2) for column isolation (Valco, Houston, TX, USA) with 1/16-in. (1 in. = 2.54 cm) fittings was installed on the gas chromatograph and maintained at 150°C. A 10 m × 0.53 mm molecular sieve 5A capillary column with 50 μm adsorbant thickness (Chrompack, Raritan, NJ, USA) was connected at the outlet of a 35 m × 0.53 mm PoraPLOT U column with 20 μm adsorbant thickness (also from Chrompack) through the isolation valve to separate the lighter gases (H_2, O_2, N_2, CH_4 and CO) poorly resolved on the porous-polymer column. The event controller used for valve action (V2), thermal conductivity detection and flame ionization detection signal acquisition and the instrumental conditions for the headspace unit were identical to those previously described [10]. For packed columns, the system configuration was the same as in capillary mode with an HP molecular sieve column (0.8 m × 1/8 in., 45–60 mesh) connected at the outlet of an HP Porapak N column (4 m × 1/8 in., 80–100 mesh). The chromatographic conditions used for both systems are given in Table I. Positive identification of the furans was accomplished using an HP-5971 mass spectrometer that was connected to the outlet of the columns

through a splitter. A tenth of the total flow was directed to the mass spectrometer used in chemical ionization mode. The peaks were identified using the mass spectral library NTIS/EPA/NIH obtained from Hewlett-Packard (G1033A).

Chemicals and standards

The capillary and packed chromatographic systems were evaluated for gas separation by headspace/gas chromatographic analysis of sealed vials purged with different standard gas mixtures of 100, 1000 and 5000 ppm of each gas (H_2, O_2, N_2, CH_4, CO, CO_2, C_2H_2, C_2H_4, C_2H_6, C_3H_8) in argon (Scott Specialty Gases, Plumsteadville, PA, USA). A special gas mixture was also used with concentrations specified in Fig. 2.

Dissolved-gas oil standards were used for the calibration and analytical performance evaluation of the method. The preparation of these standards was done according to Duval and Giguère [17]. Sub-standards were obtained by diluting the dissolved-gas oil standard with degassed oil in the headspace vials. The dilution factor was determined by weighing. Preparation of headspace vials for analysis was done as follows: after being sealed with PTFE-lined septa, the vials were purged with argon; 15 ml of oil sample were then introduced into the vial, releasing pressure build-up through a 0.5 mm

TABLE I

CHROMATOGRAPHIC CONDITIONS

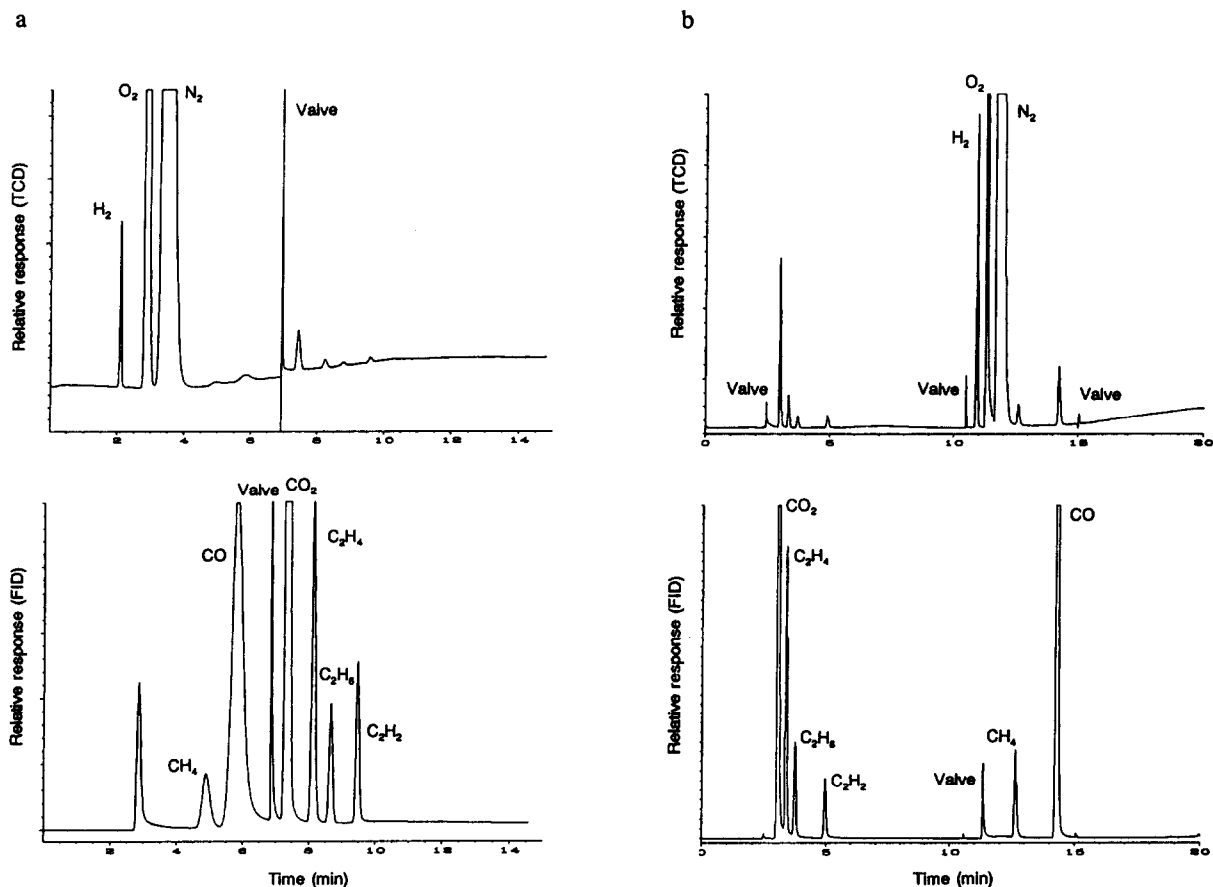|	Packed columns	Capillary columns
Carrier gas	Argon, 40 ml/min	Argon, 15 ml/min
Catalytic gas	Hydrogen, 70 ml/min	Hydrogen, 40 ml/min
Valve operation	0–7 min, columns in series	0–2.5 min, columns in series
	7–18 min, molecular sieve bypassed	2.5–10.5 min, molecular sieve bypassed
		10.5–15.0 min, columns in series
		15.0–20 min, molecular sieve bypassed
Oven programme	40°C for 4 min	40°C for 4 min
	40 to 180°C at 20°C/min	40 to 65°C at 8°C/min
	180°C for 7 min	65°C for 4.9 min
		65 to 115°C at 10°C/min
		115 to 190°C at 20°C/min
		190°C for 3.75 min
Detection	Thermal conductivity at 250°C	Thermal conductivity at 250°C
	Flame ionization at 350°C	Flame ionization at 350°C

a

b

Fig. 2. Chromatograms of 1 ml gas standard injection. (a) Packed columns and (b) capillary columns. Certified gas mixture concentrations (ppm, v/v): 1485 H_2, 423 CH_4, 4365 CO, 7221 CO_2, 569 C_2H_4, 205 C_2H_6, 292 C_2H_2, in air (Matheson Gas Products, Secaucus, NJ, USA).

O.D. needle. The vials were weighed before and after filling to control the volume introduced. A 30-ml syringe (Perfectum, Thomas Scientific, Swedesboro, NJ, USA) with an 1.2 mm O.D. stainless-steel needle was used for this transfer. The 20-ml glass vials were purchased from Wheaton (Millville, NJ, USA).

The following procedure was used to prepare a solution of furans in oil: after purging 1 l of Voltesso 35 (Esso Imperial Oil Company, Sarnia, Ontario, Canada) transformer insulating oil with helium, a few microlitres each of 2-furaldehyde, 5-methylfurfural, 2-acetylfuran and furfuryl alcohol at 99% purity (Aldrich, Milwaukee, WI, USA) were added and homogenized by manually shaking the solution for a few seconds. This

solution was introduced into vials as for dissolved-gas oil samples.

RESULTS AND DISCUSSION

Capillary columns for dissolved-gas analysis

Chromatograms from packed and capillary columns for a standard gas mixture injected from the headspace unit are compared in Fig. 2. The retention times for non-permanent gases obtained with capillary columns are shorter than those obtained with packed columns. The permanent gases appear at later retention times as a result of the valve operating sequence used for column isolation. When packed columns are used (Fig. 2a), the two columns are initially in

series and the permanent gases elute from the molecular sieve just before column isolation is achieved to ensure bypass of the hydrocarbons. When the capillary columns are used (Fig. 2b), the permanent gases do not elute from the molecular sieve as fast as the hydrocarbons from the PoraPLOT U with the result that column isolation is achieved while the permanent gases are still in the molecular sieve column. In order for these gases to elute, the time window in the hydrocarbon peak elution sequence must be long enough to allow the second column to be switched back in series. By adjusting the chromatographic conditions, this can be achieved between propane ($t_R \approx 9$ min) and butane ($t_R \approx$ 16 min). Later, the molecular sieve is again isolated for the remainder of the chromatographic run to allow higher hydrocarbon elution. Dual-capillary column separation of dissolved gases requires three valve actions (V2) compared with only one with packed columns.

The peak widths and detection limits obtained with both column technologies are compared in Tables II and III. As expected, the peaks are sharper with capillary columns, especially for CH_4 and CO, resulting in slightly better sensitivity in the determination of dissolved gases in

TABLE II

COMPARISON OF PEAK WIDTHS AND RETENTION TIMES t_R FROM PACKED AND CAPILLARY COLUMNS[a]

Gas	Packed columns[b]		Capillary columns	
	Peak width (min)	t_R (min)	Peak width (min)	t_R (min)
H_2	0.06	2.13	0.06	10.91
O_2	0.10	2.92	0.05	11.32
N_2	0.25	3.45	0.18	11.79
CH_4	0.25	5.03	0.10	12.63
CO	0.38	5.98	0.10	14.30
CO_2	0.12	7.56	0.07	3.01
C_2H_4	0.12	8.37	0.08	3.40
C_2H_6	0.12	8.91	0.08	3.71
C_2H_2	0.11	9.74	0.10	4.92

[a] Peak widths measured at half-height.
[b] Results obtained under the conditions given in ref. 10.

TABLE III

COMPARISON OF DETECTION LIMITS ($S/N_b = 3$) FOR PACKED AND CAPILLARY COLUMNS

Gas	Concentration in ppm in oil (v/v)	
	Packed columns[a]	Capillary columns
H_2	7	5
CO, CH_4	10	3
CO_2	5	3
C_2H_2, C_2H_4, C_2H_6	1	1

[a] From ref. 10.

power transformer oils. In addition, the resolution of two adjacent peaks is higher with the capillary column system and is at least 2.3. This allows a more than adequate resolution for quantitative analysis of dissolved gases. The noise on the background signal was approximately the same for both systems. However, the background signal was more stable in capillary mode, allowing easier peak detection and better reproducibility. It is not possible to compensate for the sensitivity loss of the packed columns by increasing the injection volume: first, the methane and carbon monoxide peaks would start to overlap while, second, the higher vial pressurization required to fill the loop would result in dilution of the headspace, thus offsetting the volume increase.

The time required for complete chromatographic analysis is approximately the same for both systems; C_4H_{10} elutes at 17 min in packed mode compared with 16 min with capillary columns (species not present in the sample of Fig. 2).

Extension of the analytical capabilities

Since capillary columns have a lower retention volume than packed columns, it could be possible to determine compounds otherwise retained on the porous-polymer packed column. Fig. 3 shows a headspace/gas chromatogram of an in-service transformer oil sample. On the flame ionization detector, peaks appearing after 19 min could not be observed with packed columns, even over an extended chromatographic run. It
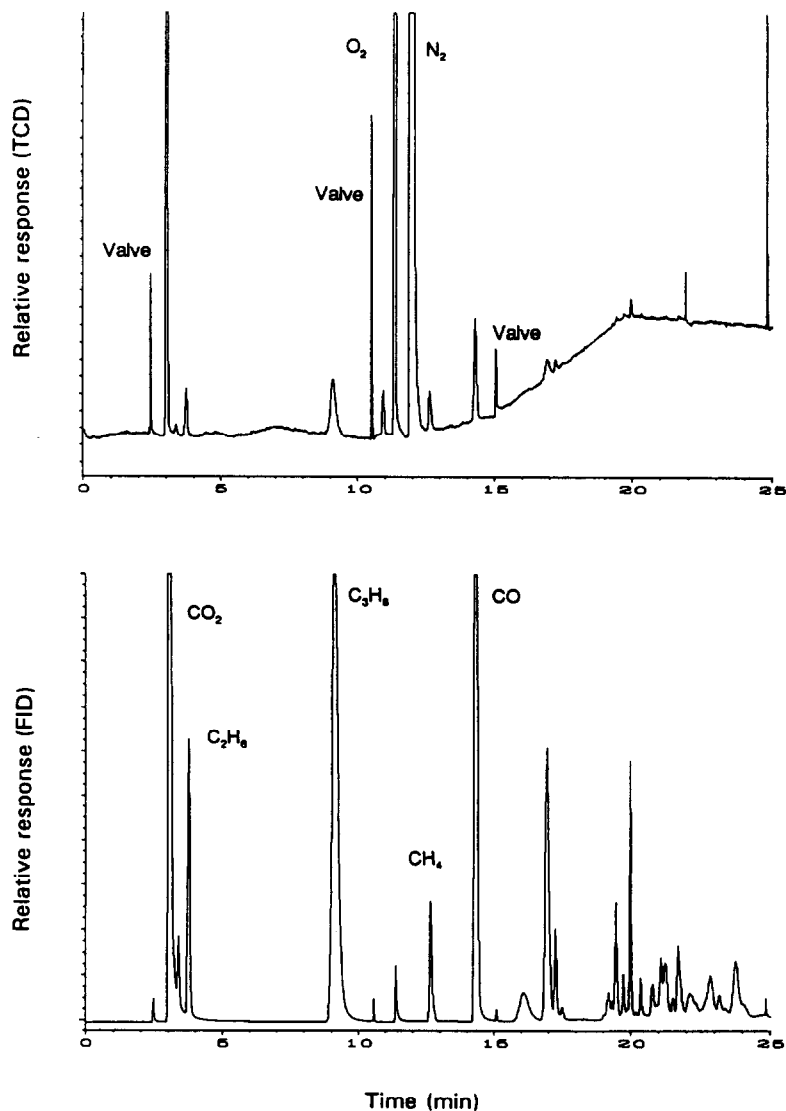
Fig. 3. Chromatograms of an in-service transformer oil sample by headspace/gas chromatography. Conditions as in Table I.

has been noted that this region of the chromatogram varies from one transformer oil sample to another and could possibly be representative of the internal condition of equipment. However, some of these peaks also noted in new Voltesso 35 might be attributed to volatile compounds normally present in this type of insulating oil.

An additional important benefit of replacing the packed columns by the capillary columns for dissolved-gas analysis is that furan-related compounds resulting from cellulose insulation breakdown can be analysed by the same chromato-

graphic technique as dissolved gases by extending the run, as seen in Fig. 3. To demonstrate the potential of this approach, Fig. 4 shows a headspace/gas chromatogram from an oil standard containing 25 ppm (w/w) of each furan compound. Single furan oil standards provided the retention times observed. The identity of the chromatographic peaks labelled 1–4 in Fig. 4 was further confirmed by GC–MS: molecular ions and fragments were observed for each compound studied. For example, Fig. 4 shows the mass spectrum of the chromatographic peak labelled
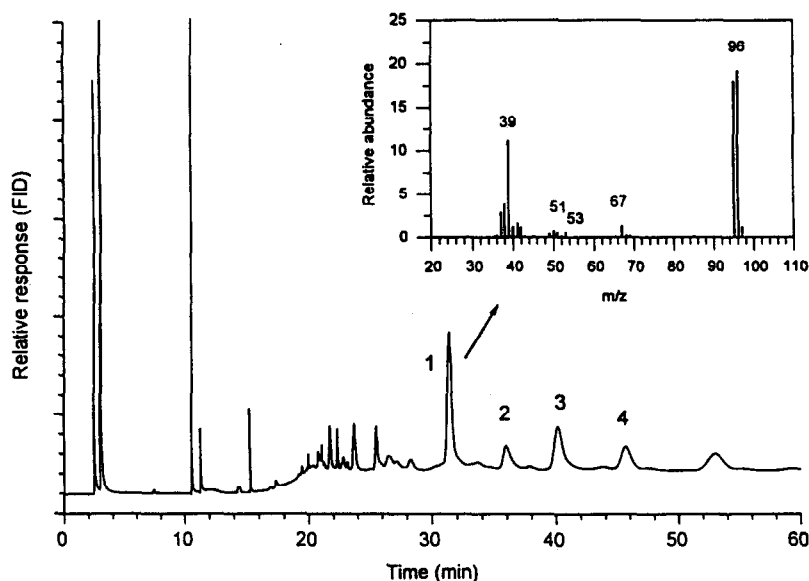
Fig. 4. Chromatogram of a Voltesso insulating oil standard containing 25 ppm (w/w) furans —FID channel only. Peaks: 1 = 2-furaldehyde; 2 = furfuryl alcohol; 3 = 2-acetylfuran; 4 = 5-methylfurfural.

"1". It was identified as 2-furaldehyde with a 97% match to the spectral database. Peaks 2, 3 and 4 were also identified by the same method with a minimum of 91% spectral match. Under the instrumental conditions given in Table I, the detection limits are 0.5 ppm (w/w) for 2-furaldehyde and 5 ppm (w/w) for 5-methylfurfural, 2-acetylfuran and furfuryl alcohol.

In order to validate this method on real samples, a series of analyses on in-service transformer oil samples were performed. 2-Furaldehyde was observed in a sample taken from a unit known to be defective. Fig. 5a shows the resulting chromatogram of selected ions specific for the furans investigated (m/z = 29, 37, 38, 39, 95, 96, 97, 98, 110 and 112). From the total ion chromatogram, we were able to focus on 2-furaldehyde by tracing the ion chromatogram for mass 96, which is the molecular ion (Fig. 5b).

On the basis of the results so far, it is obvious that the technique represents a useful means of pinpointing defaults in transformers, an aspect which requires further investigation. In this respect, the headspace/capillary gas chromatographic method presents a breakthrough over the techniques already available for routine dissolved-gas analysis.
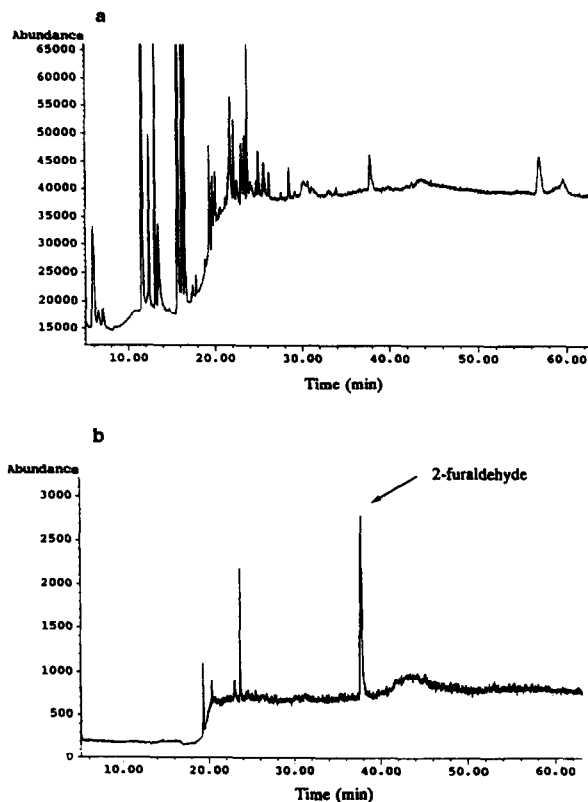

Fig. 5. Selected ions chromatograms of an in-service oil sample with 2-furaldehyde. (a) Total from selected-ion chromatograms (m/z = 29, 37, 38, 39, 95, 96, 97, 98, 110 and 112) and (b) ion chromatogram of m/z = 96.

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