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Short communication

Gas chromatographic analysis of freons and chlorinated solvents in aviation breathing oxygen

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Abstract

This paper describes a gas chromatographic technique that simplifies the analysis of freons and chlorinated solvents which could pollute liquid oxygen used by flight crews for breathing. This is possible by using, as a gas chromatographic stationary phase, a solid phase normally used in liquid chromatography, Porasil B, size 100–150 mesh, with electron-capture detection.

Keywords: Freons; Organochlorine compounds

1. Introduction

Liquid oxygen, due to its low boiling point (−183°C), suffers, during storage and distribution phases, a continuous evaporation, that causes a constant increase of the incidentally present contaminants.

For this reason, liquid oxygen appointed for breathing of flight crews, must be submitted to a continuous analytical control, from production to the customer, to maintain acceptable contamination levels.

The need to rapidly carry out contaminant analysis, by mobile units, imposes a continuous attempt to simplify instrumental procedures, without loss in sensibility and precision.

In this study some instrumental parameters were found to allow freon and chlorinated solvent analysis by a single chromatographic column, instead of the two or three employed before [1–3].

This analytical method can be employed also for high purity liquid oxygen for other purposes, such as the product for therapeutic use, of which requirements, in Italy, were recently established by the Health Superior Institute [3].

2. Experimental

In previous works [1–3], it was suggested to employ the following instrumentation for freon and chlorinated solvent analysis:

(1) A Porasil B column with flame ionization detection (FID) for freon 12, freon 22, freon 113, CH_2Cl_2, $CHCl=CCl_2$;

(2) A Chromosorb 102 (or Porapak Q) column with electron-capture detection (ECD) for freon 13 B1, freon 12, freon 114, freon 11, freon 113;

(3) A Apiezon L column with ECD for CH_2Cl_2, $CHCl_3$, CCl_4, $CHCl=CCl_2$.

Now it is possible to do a similar job, clearly saving time, employing only one Porasil B column

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Table 1
Comparison between the previous and new methods[a]

	Previous methods			New method: ECD, Porasil B
	ECD, Apiezon L	ECD, Chromosorb 102	FID, Porasil B	
CH_2Cl_2	Yes	No/S	Yes	No/S
$CHCl_3$	Yes	No/S	No/D	Yes
CCl_4	Yes	No/S	No/D	Yes
$CHCl=CCl_2$	Yes	No/S	Yes	Yes
Freon 11	No/S	Yes	No/D	Yes
Freon 12	No/S	Yes	Yes	Yes
Freon 13	No/S	No/S	No/D	Yes
Freon 113	No/S	Yes	Yes	Yes
Freon 114	No/S	Yes	No/D	Yes
Freon 13B1	No/S	Yes	No/D	Yes
Freon 22	No/D	No/D	Yes	No/D

[a] ''Yes''=''separated and detected'', ''NO/S''=''not separated'' and ''NO/D''=''not detected''.

with ECD, under different conditions with respect to previous work [1].

Table 1 shows that there is a comparison between the previous and new analysis methods.

2.1. Instrumentation

A Perkin-Elmer Model 8500 gas chromatograph is employed equipped with a 3-ml gas sampling valve, an ECD system and a 2 m×2 mm I.D. stainless steel column, packed with Porasil B, size 100–150 mesh.

2.2. Conditions

The best results are obtained under the following operative conditions: helium carrier gas at 40 ml/min flow; argon–methane (90:10) make-up gas; initial oven temperature: 40°C for 8 min; subsequent temperature rate: 7°C/min; final oven temperature: 100°C for 10 min.

2.3. Sampling

Fig. 1 shows the scheme for sampling [2,4,5].

It consists of an ~0.5 l sampling cup (a) whose external wall is continuously cooled by liquid oxygen before and during entrapment.

In particular, after connecting the sampler to the container, the sampling valve b is closed and the liquid only passes through the intermediate space to cool the sampling cup.

Valve b is then opened and the liquid sample pours into the cup.

Finally, after reclosing valve b and disconnecting the sampler from the container, the transformation of oxygen from the liquid to the gaseous phase occurs.

After all the gas has been diffused, the sampler is connected to a gas chromatograph for analysis.

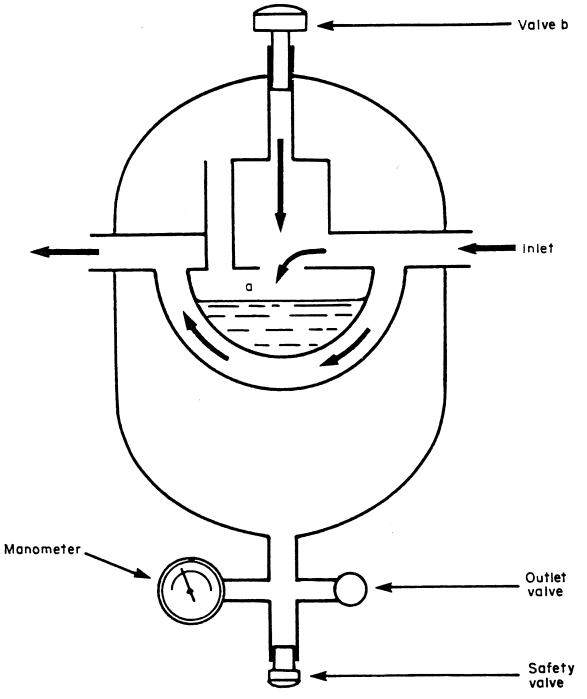

Fig. 1. Sampler.

Table 2
Standard mixture composition

Substance	Contents	SD (ppm)	LD (ppb)[a]
Oxygen	ca. 100%		
Freon 13	1 ppm	±0.03	17
Freon 13B1	0.1 ppm	±0.003	0.8
Freon 12	1 ppm	±0.03	1.8
Freon 114	1 ppm	±0.03	9
Freon 11	0.1 ppm	±0.003	0.05
Freon 113	1 ppm	±0.03	0.5
CCl_4	0.1 ppm	±0.003	0.05
$CHCl_3$	0.1 ppm	±0.003	4
$CHCl=CCl_2$	0.1 ppm	±0.003	3

[a] LD=Limit of detection.

When the available quantity of sampling liquid is small (less than 4 l), the sampler can be pre-cooled by means of a different oxygen.

2.4. Standard

A gas mixture of freons and chlorinated solvents in oxygen is employed with the composition as shown in Table 2.

The table also shows the standard deviation (± 3%) and the limits of detection of the method.

2.5. Procedure

A 3-ml sample of standard mixture and of an oxygen sample are directly injected into the gas chromatograph and the two chromatograms obtained are compared.

Fig. 2 shows a gas chromatogram obtained with the mixture in Table 2 and the peak sequence in the chromatogram corresponds to the pollutants sequence in the table.

3. Results and discussion

The most probable contaminants of breathable liquid oxygen are: (i) light hydrocarbons, carbon monoxide, carbon dioxide, nitrous oxide that can come from the air used in the distillation plant; (ii) refrigerant fluids (freons) that can come from the air coolers of the same plant; and (iii) chlorinated solvents not removed well after the periodical cleaning of the liquid oxygen stockage containers.

The analysis of the oxygen samples are carried out by various gas chromatographic methods [1–3], for example: (a) light hydrocarbons (C1–C3) on Carbosieve G or Porasil B column with FID; (b) CO_2 and N_2O on a Porapak Q Column with HID (helium ionization detection); (c) CO on a 5A molecular sieve column with HID; and (d) freon and chlorinated solvents as in Table 1.

Apiezon L is a high boiling point hydrocarburic liquid stationary phase supported on a polymeric powder solid phase (Chromosorb W) and allows the separation of some chlorinated solvents because of their different solubility in the liquid, but does not allow the same for freons.

Chromosorb 102 is a solid stationary phase (styrene–divinylbenzene powder) that allows the separation of some freons because of their different physical absorption on the solid microsurfaces, but does not allow the same for chlorinated solvents.

Porasil B is a solid stationary phase (silica gel-powder) that allows simultaneous separation of some freons and chlorinated solvents because of their different physical absorption on the solid microsurfaces.

The freons and the chlorinated solvents are more or less detectable by ECD or FID depending on their molecular content of halogen or hydrogen atoms and on the type of halogens: Br>Cl>F prefer ECD, H prefers FID.

As can be seen in Table 1 the present new method allows the simultaneous analysis of all the compounds separately measured by the previous methods, except CH_2Cl_2 and freon 22.

This is not a problem because it is very unlikely that CH_2Cl_2 is used as a cleaner for the containers and freon 22 is detectable and measurable together with light hydrocarbons on the Carbosieve G column with FID.

4. Conclusions

The present new method allows the analysis of the freons and chlorinated solvents more rapidly, and with a simplified instrumental procedure, without loss in sensibility and precision.

This is very useful when it is necessary to

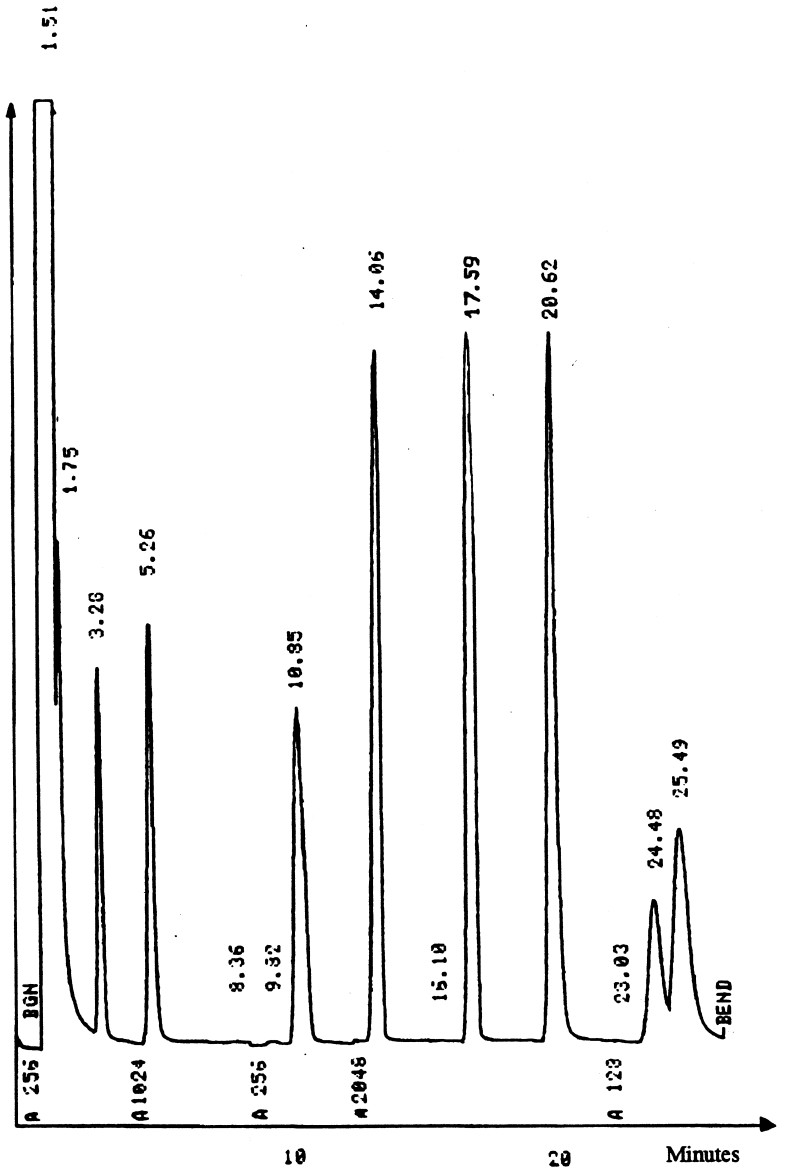

Fig. 2. Gas chromatogram obtained with the mixture in Table 2. The peak sequence corresponds to the pollutant sequence in the table.

intervene directly with a mobile unit where oxygen is employed, as in an airport or hospital.

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