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ANALYSIS OF TRACES OF CONTAMINANTS IN BREATHING OXYGEN WITH A HELIUM DETECTOR AND AN ELECTRON CAPTURE DETECTOR

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SUMMARY

A method is described which allows the determination of a few parts per billion of impurities in breathing oxygen for pilots and for therapeutic purposes. Fixed gases and chlorinated solvents are analysed by gas chromatography and detected with a helium detector and an electron capture detector, respectively. The analysis time is about 15 min.

The method can be applied to the analysis of air pollutants and to the determination of the purity of gases.

Very high purity is required for therapeutic oxygen for breathing and for liquid oxygen used for pilots of aircrafts and for the atmosphere in space capsules. Very pure oxygen must be used in these cases, as it has to be breathed by people that are in both critical health and environmental conditions.

The values for the threshold limits of contaminants in air[1-3] reported in Table I have to be drastically reduced, because of the possible synergistic effect of various contaminants, especially in unusual conditions. In this case, low concentrations of several impurities may have an effect greater than a higher concentration of a single contaminant.

For this reason, the limits allowed by the regulations are very small in comparison with the data reported in Table I. The maximum allowed concentrations of contaminants in aviator breathing liquid oxygen[4,5] are given in Table II.

Analysis of these contaminants has been carried out previously by several methods, and standard procedures have been developed. The combustible gases (methane and other hydrocarbons) were analysed by a flame ionisation detector, by means of direct injection of several ml of gas. The inert gases were analysed with a thermal conductivity detector, after concentration from several litres of oxygen by means of a cold trap[6]. The chlorinated compounds were analysed by IR analysis, using cells with an optical path[7,8] of 10 m.

All these systems have the disadvantage that several instruments are necessary for a complete analysis, and that the concentration of the impurities from a large volume of oxygen is very time consuming.

Gas chromatography provides a rapid separation and a sensitive means of

TABLE I

THRESHOLD LIMIT VALUES FOR CONTAMINANTS IN AIR

Contaminant	*Italy (p.p.m.)*	*U.S.S.R. (mg/m^3)*	*U.S.A.*	
			(p.p.m.)	*(mg/m^3)*
CO	50	20	50	55
CO_2	5000	—	5000	—
CH_4	—	—	1000	—
Hydrocarbons	500	100	500	—
Nitrogen oxides	5	5	5	9
CCl_4	10	20	10	65
$CHCl_3$	50 max.	—	50	240
$CHCl=CCl_2$	100	10	150	520
CH_2Cl-CH_2Cl	50	10	50	—
CH_2Cl_2	250	50	500	—

detection without need of concentration, if a helium detector (HeD)[9,10] and an electron capture detector (ECD) are used to measure the compounds separated.

Fig. 1 shows the practical arrangement of the analytical system. For complete separation three parallel columns were used:

(1) A Porapak Q column, 100–120 mesh, $\frac{1}{8}$ in. diameter and 3 m length, operated at room temperature with a helium flow of 60 ml/min, allowed the separation of CH_4, CO_2, N_2O, C_2H_2, C_2H_4, C_2H_6, C_3H_6 and C_3H_8, which were detected by a HeD.

(2) A molecular sieve column, Linde 5A, $\frac{1}{8}$ in. diameter and 6 m length, heated at 60°, with a helium flow of 60 ml/min, and connected to another HeD, separated H_2, N_2, CH_4 and CO.

TABLE II

MAXIMUM ALLOWED CONCENTRATION VALUES (IN P.P.M.) OF CONTAMINANTS IN BREATHING OXYGEN FOR PILOTS[4,5]

Contaminant	*Concentration*
CO	5
CO_2	5
CH_4	25
C_2H_2	0.05
C_2H_4	0.2
C_2H_6	2
Other hydrocarbons	1
N_2O	1
Cl solvents	0.1

(3) A column filled with 20% Apiezon L on Chromosorb W 80/100, $\frac{1}{8}$ in. diameter and 1.5 m length, heated at 60° and connected to an ECD, allowed the analysis of chlorinated hydrocarbons. The nitrogen flow was 20 ml/min.

The detectors and electrometers that were used were manufactured by Varian Aerograph, and the arrangement shown in Fig. 1 was obtained by partial modification

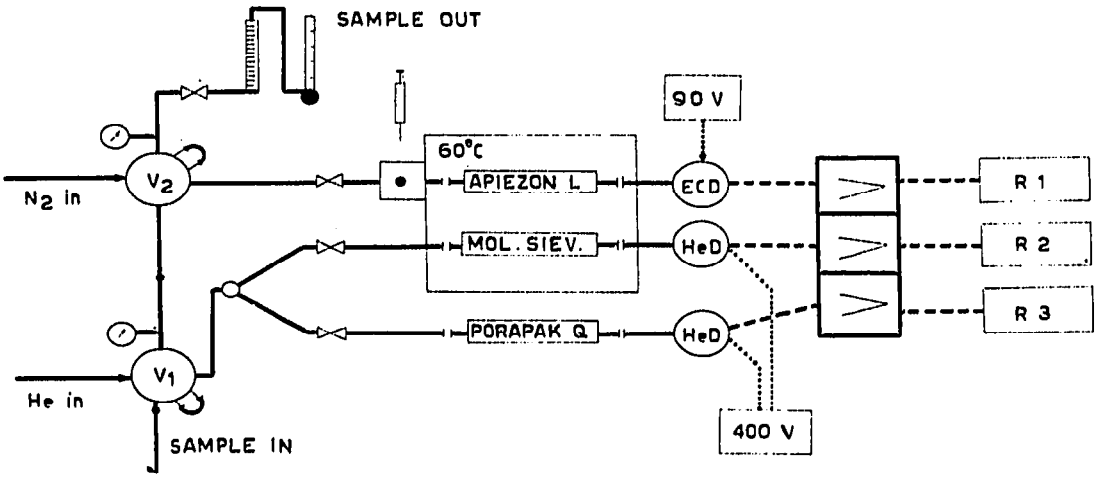

Fig. 1. Schematic drawing of the apparatus. V = sampling valves, R = recorders.

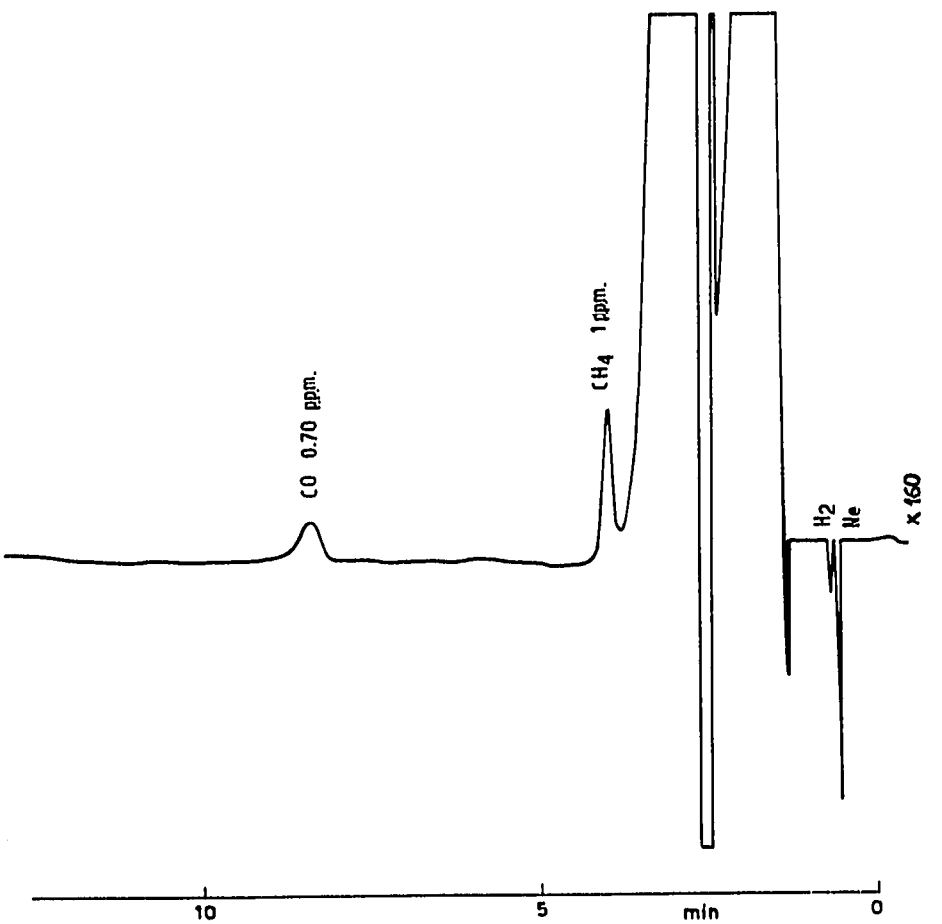

Fig. 2. Analysis on molecular sieves column; sensitivity 16×10^{-9} A/mV.

of a Trace Analyser Mod. 1532 by adding a third column with an injector and an ECD to the standard dual column system.

As helium detectors need very pure helium as carrier gas[10], a molecular sieve trap held at the temperature of liquid nitrogen was used for purification and was installed before the gas sample valve No. 1. The nitrogen for ECD was purified with a molecular sieve trap at room temperature to remove moisture and CO_2.

The two gas sampling valves, of the rotary type, were connected in series to the oxygen flow, and two precision gauges were used to monitor the actual pressure in the two sample loops. For proper quantitative analysis, a knowledge of the sample pressure is required. It is essential that the oxygen first flows through the valve connected to the helium detectors, because traces of helium that contaminate the oxygen flow when the valve is operated do not disturb the ECD. The reverse arrangement would introduce a certain amount of nitrogen into the oxygen flow that would be detected by the HeD.

The sample was introduced into the apparatus from a flow of oxygen with a pressure of 1 atm, and a volume of 1 ml was injected. Figs. 2–4 show different analyses on molecular sieve and Porapak columns. The sensitivity to impurities is very satisfactory.

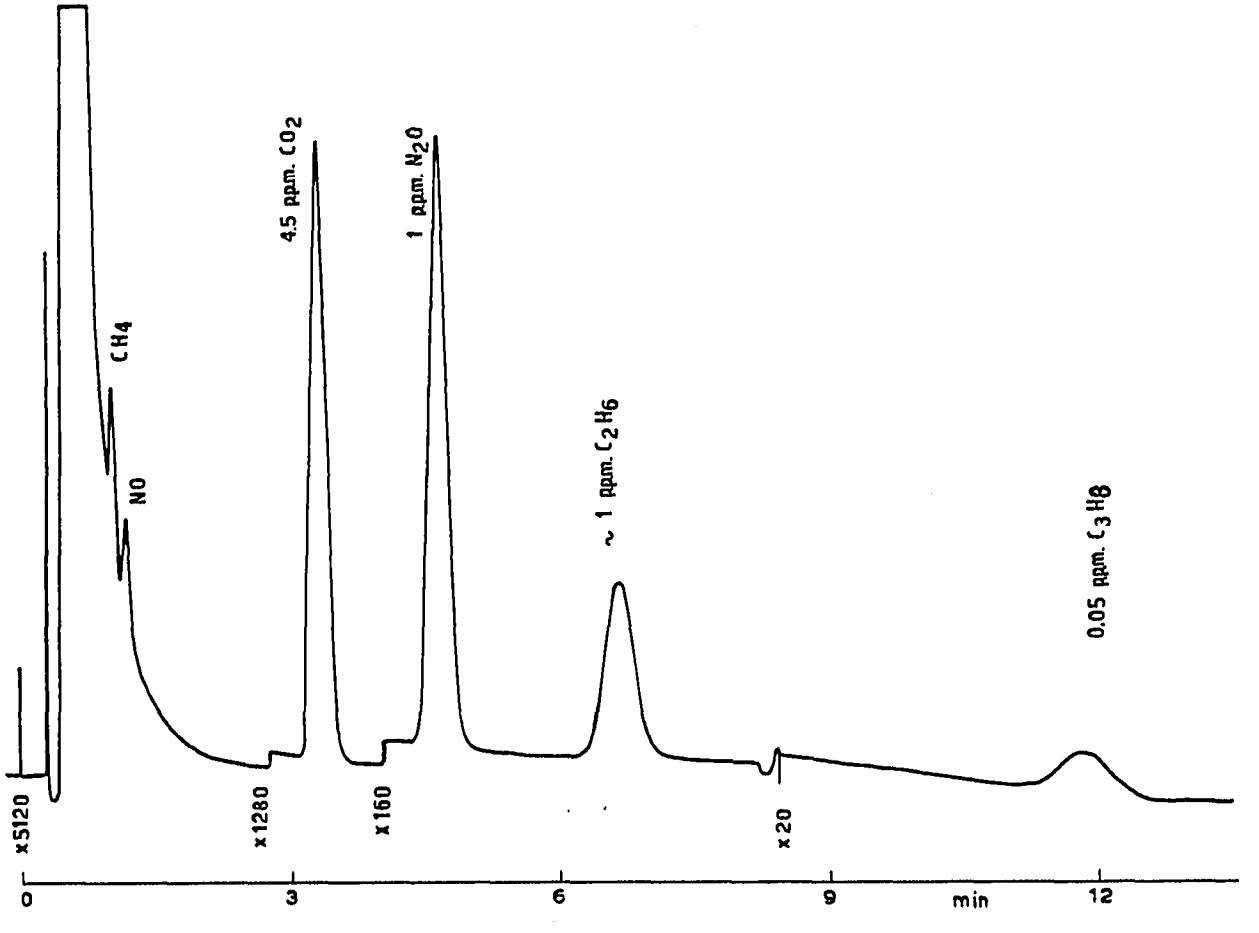

Fig. 3. Analysis on Porapak Q column. Standard mixture containing CO_2, N_2O, ethane and propane.

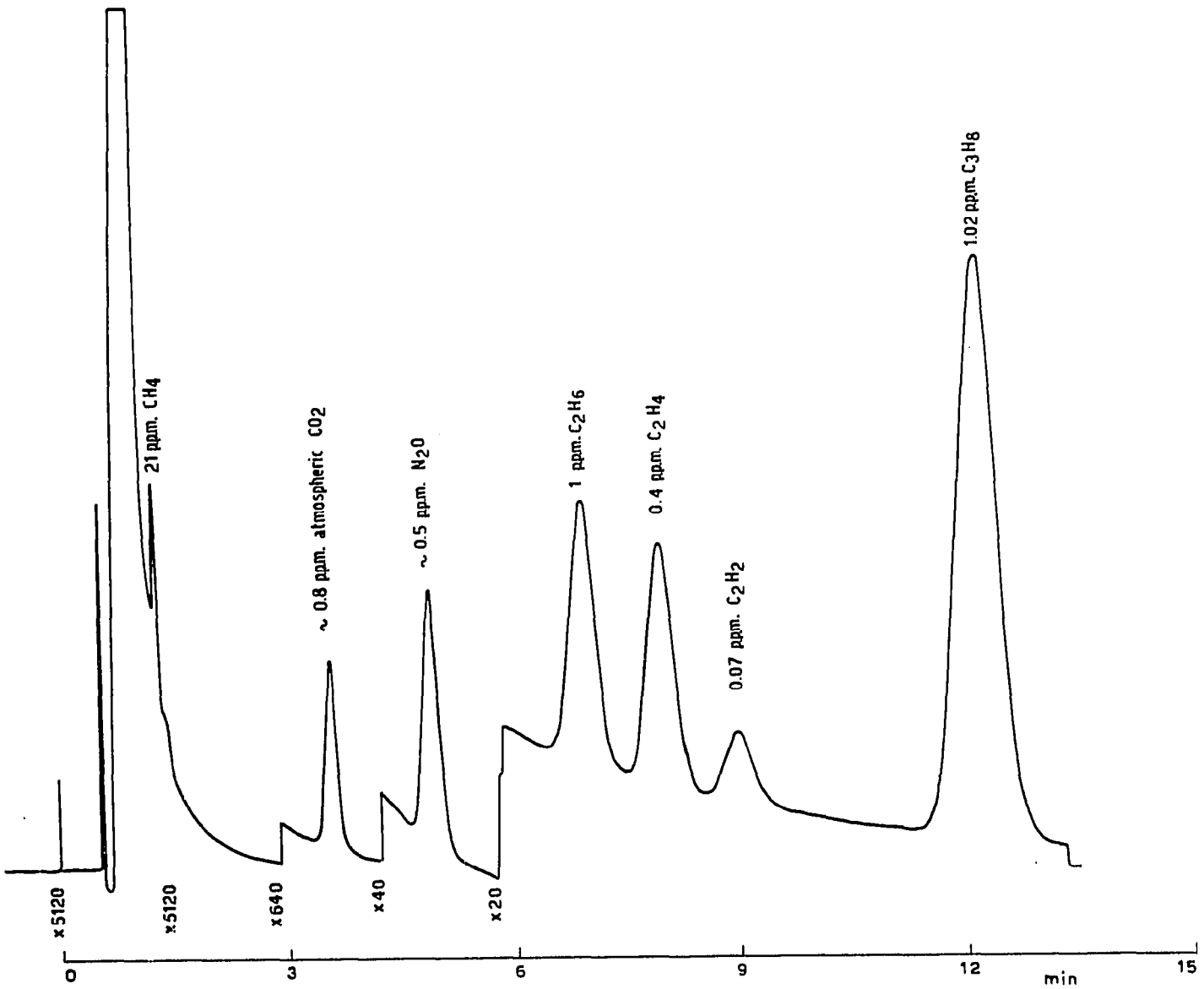

Fig. 4. Analysis on Porapak Q column. Standard mixture containing CH_4, N_2O, ethane, ethylene, acetylene and propane.

For calibration, standard mixtures, containing known amounts of contaminants diluted in oxygen, were used. This allowed an every day check on the performance of the instrument. The preparation of these mixtures was difficult, and the concentration changed over several weeks from the initial preparation, due to adsorption of contaminants on the inner surface of the vessel[11–13]. For this reason the composition of standard mixtures was tested by comparison with an absolute calibration, made with an exponential dilution flask[14,15]. Several calibration curves are reported in Fig. 5. The dilution flask was used both with pure helium and with the oxygen flow, to take into account during the calibration the effects on sensitivity due to the tailing of the oxygen peak. In fact, if the tail of the main peak is very long, it is impossible to reduce the attenuation of the amplifier sufficiently to detect the

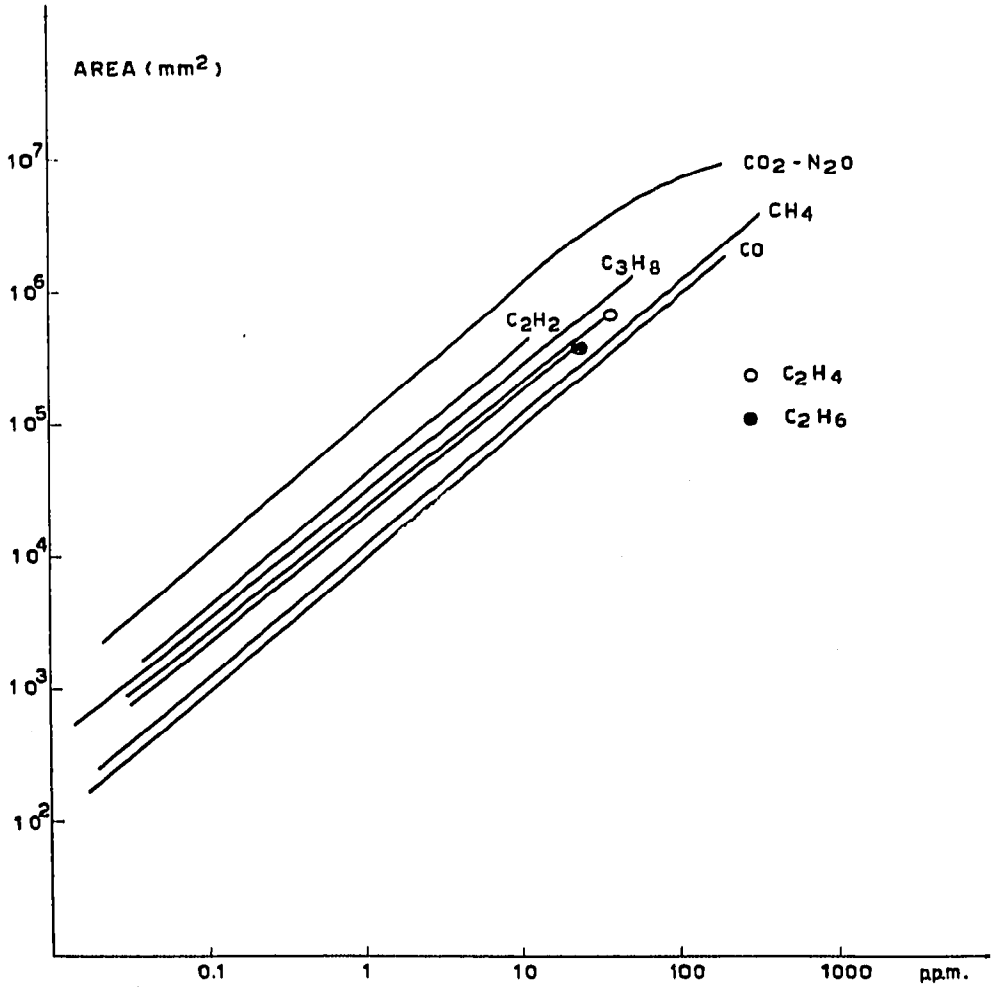

Fig. 5. Calibration curves obtained with the exponential dilution flask. Volume of the sample, 1 ml at atmospheric pressure; peak areas determined at maximum sensitivity (10^{-10} A/mV).

impurities, and a high sensitivity obtained during the calibration with the helium flow, does not mean that a similar sensitivity would be reached when the sample is mainly composed of oxygen. The true sensitivity of the instrument to a certain gas therefore depends on various factors: ionisation efficiency, sharpness of the peak, background and signal noise.

The sensitivity of helium detector to contaminants is given in Table III. Absolute values in coulombs per mole are reported. The observed current corresponds to an ionisation efficiency of 1.57–13.50% if one supposes that the ionisation of all the molecules of the eluted compounds gives 96 500 C per mole. Of course, the values reported in Table III do not represent the real efficiency of ionisation, as the collecting efficiency of the electrodes must be taken into account. Notwithstanding this, the sensitivity is very high, if one considers that the ionisation efficiency of a flame ionisation detector is about 0.0005% for hydrocarbons[16]. For practical purposes, the sensitivity can be expressed as mm² of peak area for a concentration of 1 p.p.m. of contaminant per ml of sample.

TABLE III

SENSITIVITY OF HELIUM DETECTOR TO CONTAMINANTS

	Response factor (C/mole)	*Ionization efficiency (%)*	*Peak area (mm^2/p.p.m.·ml)*
CH_4	1 510	1.57	12 × 10^3
C_2H_6	2 600	2.70	20.8 × 10^3
C_2H_4	2 780	2.88	23 × 10^3
C_2H_2	5 200	5.40	41.5 × 10^3
C_3H_8	3 800	3.95	30.6 × 10^3
CO	1 200	1.57	12 × 10^3
CO_2	13 200	13.70	105.5 × 10^3
N_2O	13 000	13.50	103.8 × 10^3

The separation of the chlorinated hydrocarbons was carried out on an Apiezon L column, as their separation on a Porapak column, though possible, was too long and not satisfactory. As the ECD tolerates a certain bleeding from the column, especially if the column is packed with a hydrocarbon stationary phase, gas–liquid chromatography was more convenient than gas–solid or gas–gel chromatography.

Fig. 6 shows the separation of chlorinated compounds in oxygen and in air. The sensitivity to the chlorinated compounds is given in Table IV, and it is interesting

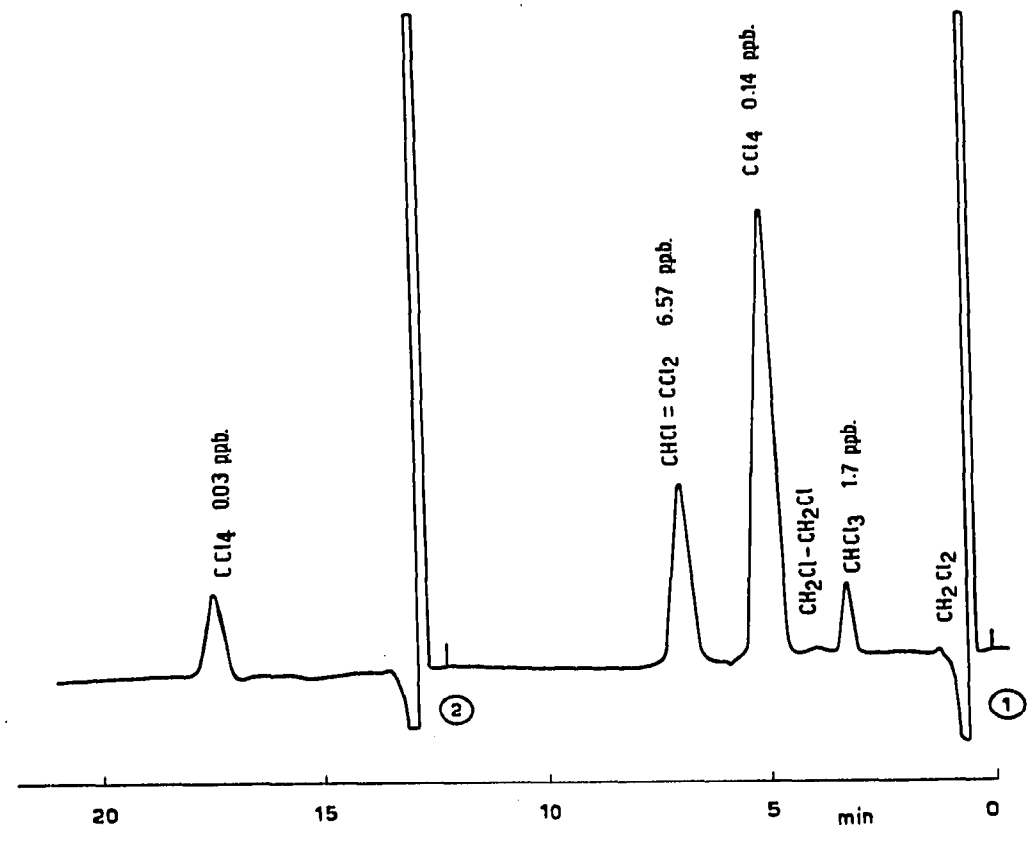

Fig. 6. Analysis of chlorinated compounds on an Apiezon L column with ECD. (1) in oxygen; (2) in air.

TABLE IV

SENSITIVITY OF THE ECD TO CHLORINATED SOLVENTS

On the recorder 1 mV full scale deflection, speed 20 in./h, a peak area of 1 mm^2 is equivalent to 0.56×10^{-10} C at an attenuation of × 20.

Contaminant	$C \cdot mole^{-1}$
CCl_4	3.00×10^6
$CHCl=CCl_2$	4.39×10^3
$CHCl_3$	3.28×10^3
CH_2Cl-CH_2Cl	3.53
CH_2Cl_2	2.84

to observe that the sensitivity is proportional to the number of chlorine atoms in the molecule. The calibration for the chlorinated compounds, due to the difficulties in preparation of a gaseous standard[13], was accomplished by injecting liquid standards with known concentrations of chlorinated compounds in pure *n*-hexane. As ECD is not so sensitive to contamination from air as the HeD, a conventional injector was installed between the gas sampling valve No. 2 and the column.

The sensitivity of the system to all the gases analysed is shown in Table V. The amount of contaminant that produces a peak area of about 50 mm^2 at the highest sensitivity is given. The values refer to a sample volume of 1 ml at atmospheric pressure. An increase of sensitivity may be achieved by using a greater sample volume and/or a higher pressure. Attention must be paid to the increase of the oxygen tail when increasing the quantity of sample. If the methane peak is overlapped by this tail, a still better separation can be obtained by using a longer molecular sieve column, but the time of analysis increases.

With the arrangement described, the whole analysis of a sample of oxygen for breathing or therapeutic use can be completed within 15 min. No interval is needed between the elution of the last peak (for example propane) and the introduction of

TABLE V

PRACTICAL LIMIT OF DETECTION (PEAK AREA ABOUT 50 mm^2) AT MAXIMUM SENSITIVITY FOR 1 ML OF SAMPLE AT ATMOSPHERIC PRESSURE

Contaminant	*Detection limit (p.p.b.)*
CH_4	4
C_2H_6	2
C_2H_4	2
C_2H_2	1
C_3H_8	1
CO	5
CO_2	0.4
N_2O	0.4
CCl_4	0.01
$CHCl=CCl_2$	1
$CHCl_3$	1
CH_2Cl-CH_2Cl	1000
CH_2Cl_2	1000

a new sample, but if the oxygen contains a lot of moisture, water eluting with a retention time of about 1 h from the Porapak column will saturate the corresponding HeD. It is convenient to make three analyses during the shortest possible interval and, when water begins to elute, to wait for a complete restoration of the initial baseline level.

The sensitivity data reported in Table V are very satisfactory if compared with the purity required by the regulations. The proposed method is therefore sufficiently sensitive and rapid for routine analysis of contaminants in breathing oxygen. It can obviously be applied to the analysis of contaminants in air or other gases, by proper selection of the column lengths and temperatures.

REFERENCES

1 K. NABERT AND G. SCHÖN, *Sicherheitstechnische Henzahlen Brennbarer Gase und Dämpfe*, 2nd Ed., Deutscher Eichverlag G.m.b.H., Berlin, 1963.
2 *Threshold Limit Values, 27th Ann. Meeting Amer. Conf. Governmental Ind. Hygienists, Houston, 1965.*
3 *Prontuario delle Sostanze Chimiche Pericolose*, E.N.P.I., Roma, 1968.
4 *U.S.A.-Mil-o-27210 A.*
5 *Norma Aeronautica Militare-M-532* (1964).
6 E. CIANETTI, G. PECCI AND G. SCUDERI, *Riv. Med. Aeron. Sp.*, 28 (1965) 26.
7 C. MARANGONI AND A. GIUSTI, *Riv. Med. Aeron. Sp.*, 29 (1966) 106.
8 C. MARANGONI, A. GIUSTI AND E. DI CARLO, *Riv. Med. Aeron. Sp.*, 30 (1967) 693.
9 C. H. HARTMANN AND R. P. DIMICK, *Pittsburgh Conf. Anal. Chem. Appl. Spectroscopy, Pittsburgh, March, 1965.*
10 G. CASTELLO AND S. MUNARI, *Chim. Ind.*, 51 (1969) 469.
11 S. BRUNAUER, *The Absorption of Gases and Vapours*, Oxford University Press, London, 1945.
12 S. ROSS AND J. P. OLIVIER, *On Physical Adsorption*, Interscience, New York, 1964.
13 C. MARANGONI AND A. TRONCA, *Riv. Med. Aeron. Sp.*, 32 (1969) 281.
14 J. E. LOVELOCK, in D. H. DESTY (Editor), *Gas Chromatography* 1960, Butterworths, London, 1958, p. 26.
15 C. H. HARTMANN AND K. P. DIMICK, *J. Gas Chromatogr.*, 5 (1966) 163.
16 C. H. HARTMANN AND K. TOMPSON, *Aerograph Research Notes*, (1967) 3.