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Investigation of the use of oxygen doping of the electron-capture detection for determination of atmospheric halocarbons

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Abstract

The development of a GC–electron-capture detection instrument to determine accurately certain important trace C_1 halocarbons in a single analytical procedure from ambient air is reported. The procedure utilizes preconcentration at room temperature on an efficient microtrap filled with a commercially available adsorbent, Carboxen, followed by direct thermal desorption in a single stage on to a high-resolution capillary column. Detection is achieved with dual electron-capture detectors in series; the second being oxygen doped to dramatically enhance the sensitivity of the detector towards those halocarbons (hydrofluorochlorocarbon 22, CH_3Cl) which normally react feebly with thermal electrons.

1. Introduction

Recent studies [1–3] have provided clear evidence of the significant reduction in fluorochlorocarbon (CFC) 11 and 12 concentrations in Europe over the period 1987–1990 following the phase-out in CFC use. In addition to the principal CFCs, HCFCs (hydrofluorochlorocarbons) and the replacement HFCs (hydrofluorocarbons), there are a number of other trace halogenated gases which are of environmental concern for which no continuous monitoring programmes exist. The present study concentrated on the group of halogenated methane compounds of both natural and anthropogenic origin; HCFC 22 ($CHClF_2$), the primary interim

replacement compound, already in widespread use, was included in this group. Due to the single chlorine and partial removal in the troposphere by hydroxyl radicals, HCFC 22 was excluded from the controls under the Montreal Protocol while the search was initiated for safer, chlorine-free chemicals. Its rapidly increasing use [4] suggests a need for careful atmospheric monitoring, due to an uncertain atmospheric lifetime of between 12 and 40 years [5] and because HCFC 22 is a significant absorber of infrared radiation. The first measurements of HCFC 22 in the atmosphere were made in 1979 by GC–MS and GC–electron-capture detection (ECD) techniques [6]. Long-term, high-frequency atmospheric measurements are relatively sparse and improved techniques are therefore required.

The first measurements of CH_3Cl , a major

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contributor to the total chlorine budget of the atmosphere, were reported by Grimsrud and Rasmussen [7] and by Lovelock [8]. Both indicated that the primary source was from natural emissions from the oceans, however, a significant contribution also arises from biomass burning [9]. CHCl_3 has approximately equal natural and anthropogenic sources with a substantial seasonal ocean flux [10]. Although CHCl_3 can be determined by existing GC-ECD techniques, the precision is poor due to the proximity of the limit of detection to its atmospheric concentration. Similarly, CH_2Cl_2 has limited data, and will contribute chlorine to the atmosphere. There are almost no reliable estimates for the relative emissions from their different natural sources. To understand fully the role of CH_3Cl , CH_2Cl_2 and CHCl_3 in the global environment, there is a need for contiguous measurements to establish accurate trends and atmospheric lifetimes.

The atmospheric chemistry of bromine containing compounds plays an important role in the stratosphere — with synergistic interactions of chlorine and bromine in the lower stratosphere [11,12]. Brominated compounds have up to 60 times the ozone depletion potential of the CFCs, although bromine is in the atmosphere at a hundredth of the concentration of chlorine species. The large uncertainties in CH_3Br atmospheric abundance, which range from 10 to 20 ppt [12], is due to difficulties of absolute calibration and poor understanding of relative sources (natural versus anthropogenic), although studies are increasing, as this compound is implicated as an important player in stratospheric ozone depletion [13,14]. The two Halons, 13B1 (CF_3Br) and 12B1 (CF_2ClBr), are entirely manmade and used almost exclusively as fire extinguishers. Before implementation of the Montreal Protocol, the use of the Halons was increasing (ca. 15–20%/year) [15]; now, recent results indicate this rate of increase has substantially decreased [16] although they may induce significant ozone depletion in the short term [11]. There are at present no long-term observational records of sufficient frequency and duration to determine accurate trends in these brominated species.

The special challenge comes for the group of

compounds, 13B1, 12B1, HCFC 22, CH_3Cl , CH_3Br , CH_2Cl_2 and CHCl_3 , from the low concentrations and/or low ECD response which prevent their direct measurement. Although determination of halocarbons down to the ppt level has been achieved by concentration from ambient air cryogenically [17], the associated problem of collection of large quantities of water during sampling is an inherent drawback — presenting a problem in the subsequent chromatographic analysis. The method used here is based on a single microtrap developed in earlier work in these laboratories [18]. A small ambient air sample is trapped at room temperature, thereby avoiding the use of cryogenics which is expensive, time consuming and technically demanding in field analysis or automated operation. A single desorption stage directly onto the column suffices, due to the small design of the microtrap with near capillary dimensions, thereby avoiding the need for a second cryofocusing stage, while maintaining suitable chromatography. This eliminates additive errors obtained in each stage of desorbing when using several trapping and desorbing stages.

Grimsrud and co-workers [19–21] demonstrated that the response of the ECD to certain compounds which normally produce very low signals can be considerably enhanced by addition of oxygen as a dopant of the carrier gas. It has, therefore, become apparent that the presence of certain electron-attaching molecules as part of the carrier gas produced both interesting and analytically useful effects [20], increasing the ECD response to many compounds by reactions of the additional O_2^- negative ions which are then present. Specific applications of the oxygen doped ECD to atmospheric analysis have been shown [9,21,22]. As yet, the number of research groups working in this area is limited and the ultimate importance of the method to the broad scope of chemical analysis has yet to be determined. The fact that oxygen can alter the response characteristics of the ECD leads to the improved sensitivity desired for detection of the ultra low concentrations of the target species.

The basis of this work was the development of a single GC-ECD instrument using two elec-

tron-capture detectors in series, the second ECD apparatus sensitized with oxygen, and the use of a microadsorption trap to concentrate trace atmospheric contaminants. The Halons, despite their low atmospheric concentrations, are strong electron absorbers, and do not need oxygen doping provided there is a reasonable preconcentration ratio and, in fact, show no response enhancement with oxygen doping. A similar situation pertains to CHCl_3 , which only shows a minor response enhancement with an oxygen doped ECD. The method will allow construction of a near real-time/field portable GC instrument to determine these trace halocarbons accurately in a single analysis of air samples, ultimately for use in a remote field station.

2. Experimental

2.1. Preconcentration

The microtrap was constructed from thin-walled type 304 [0.023 in. I.D. \times 0.035 in. O.D. (1 in. = 2.54 cm)] stainless-steel tubing (Coopers Needle Works, Birmingham, UK) and filled with Carboxen 1003 and Carboxen 1000 (Supelco, Bellefonte, PA, USA), which were held in by end plugs of stainless-steel wire (0.017 in. O.D.) with flattened ends. The adsorbents were select-

ed from studies of the breakthrough volume of the halocarbons, on a variety of materials, by a procedure which is reported in an earlier paper [23]. Desorption was facilitated with direct ohmic heating to 200°C by application of 90 V a.c. from a Variac transformer for 3 s to the microtrap. The dimensions of the microtrap and gas flows were equivalent to those of the capillary column (1–2 ml/min) allowing flow path uniformity and preventing possible pressure differentials in the system and turbulence in the flowing gas stream, which may alter sample residence time. The method of measuring the volume of a sample passing through the microtrap involved a three-way valve (Hamilton, HVP 3-3) connected to an appropriate sized syringe (100 ml). Fig. 1 shows the entire system configuration for the preconcentration and detection of atmospheric halocarbons.

Two Valco valves (Valco Instruments, Houston, TX, USA) were incorporated in the system: the first (a four-port valve) enabled the system to be purged to this point with either sample or nitrogen; the second (a six-port switching valve) allowed sample or nitrogen to be passed through the trap in one mode, while column nitrogen carrier gas flowed through the trap in the other mode. Pressurized air samples, contained in 3.5-l passivated stainless-steel canisters (SUMMA polished), were connected via a three-way valve

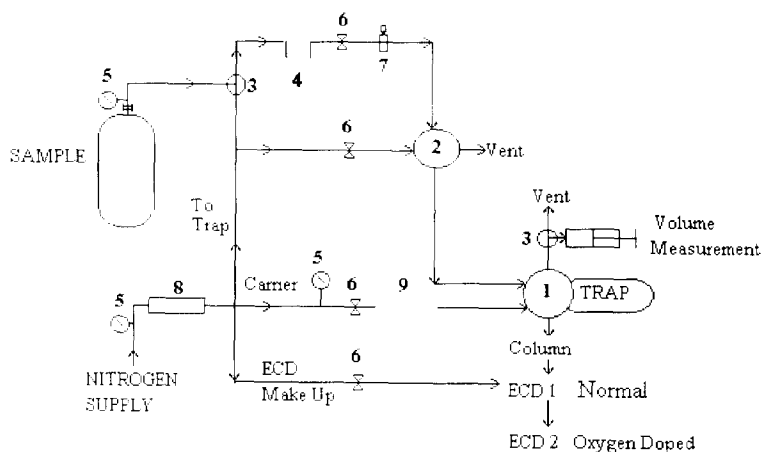


Fig. 1. Apparatus for halocarbon preconcentration and detection. 1 = 6-Port Valco valve, 2 = 4-port Valco valve, 3 = 3-way valve, 4 = Nafion drier, 5 = pressure regulator, 6 = needle valve, 7 = toggle valve, 8 = molecular sieve/charcoal trap, 9 = particle filter.

(Whitey ss-41 xs2) to permit either sample or nitrogen purge gas to be passed through a Nafion Permeation Drier to reduce sample moisture content reaching the trap. Consequently, the microtrap was always under an atmosphere of pure nitrogen when not sampling and during any pre-conditioning thermal desorption cycles. Flow-rates were controlled by Nupro fine metering valves (Bristol Valve and Fitting, Bristol, UK). The optimum flow-rate for air sampling was 10 ml/min to avoid the possibility of component breakthrough and incomplete trapping.

2.2. Chromatography

Studies, detailed in an earlier paper [24], concentrated on optimizing the chromatographic separation on a variety of high-resolution capillary columns including PoraPLOT, Alumina PLOT and WCOT columns, of the target halocarbons, as well as other components of atmospheric air, e.g. CFCs, HFCs, other HCFCs and the ubiquitous hydrocarbons, which could complicate the interpretation of results. However, in such a complex matrix (air), it is unlikely that a single chromatographic column will resolve all the individual compounds. The similar physical properties of HCFC 22 to CFC 12 which it replaces makes their complete chromatographic separation difficult. Table 1 gives details of the halocarbons identified in this study. GC-MS studies [25] confirmed the identities of the other compounds eluting in this important region, with propene and propane eluting after HCFC 22 and propyne eluting on the shoulder of the CFC 12 peak. These hydrocarbons are fortunately less susceptible to response enhancement and therefore unlikely to cause any interference with HCFC 22 determination in the second detector, which is oxygen doped.

Separation was carried out on the WCOT CP Sil 5 CB column (Chrompack, Middelburg, Netherlands) (50 m × 0.32 mm I.D.) with a temperature programme of 30°C (8 min) to 80°C at a rate of 10°C/min. This column and temperature programme gave the best resolution of the problematic HCFC 22/CFC 12 peak pair. Connection of the capillary column to the six-port

Table 1
Major atmospheric halocarbons

Chemical formula	Trade name or abbreviation	Boiling point/°C
CF ₃ H	HFC 23	-82.2
CF ₃ Cl	CFC 13	-81.4
CF ₃ Br	13B1	-57.8
CHClF ₂	HCFC 22	-40.8
CF ₂ ClCF ₃	CFC 115	-38.7
CF ₂ Cl ₂	CFC 12	-29.8
CH ₂ Cl	-	-24.2
CF ₂ ClBr	12B1	-4.0
CH ₃ Br	-	3.6
CF ₃ ClCF ₂ Cl	CFC 114	3.7
CFCl ₃	CFC 11	23.8
CH ₂ Cl ₂	-	40.0
CH ₃ I	-	42.4
CF ₂ ClCFCl ₂	CFC 113	47.4
CHCl ₃	-	61.2
CH ₂ CCl ₂	-	74.0
CCl ₄	-	76.3
CCl ₂ CHCl	TCE	87.0
CCl ₂ CCl ₂	PCE	121.0

injection/microtrap valve was achieved via a short length (25 cm) of deactivated fused-silica (0.32 mm I.D.) capillary tubing. Nitrogen was used as the column carrier gas (BOC Gases) and was purified by passage through a molecular sieve 5Å and activated charcoal filter.

2.3. Instrumentation

The GC used was a Varian 3700 Aerograph with a constant current, pulse-modulated 8 mCi ⁶³Ni detector. The detector cell had displaced coaxial cylinder geometry, 0.3 ml internal volume and was polarised with a negative voltage pulse of 50 V amplitude and 0.64 μs width, and a pulse frequency output range of 1.57 kHz to 1.4 MHz. The output signals were recorded with both a standard potentiometric recorder and a 3390A Hewlett Packard integrator. The final instrument involved the simultaneous use of normal and oxygen doped detection. The procedure is achievable via two electron-capture

detectors coupled in series with the first, the Varian ECD apparatus, in normal mode, using 20 ml/min of nitrogen gas as make up. The second ECD apparatus, a Shimadzu constant-current Ni⁶³ ECD instrument, combined the effluent from the first ECD apparatus with a make up of 2% oxygen in nitrogen (20 000 ppm) (BOC Special Gases) at ca. 2 ml/min to give a concentration of nominally 2000 ppm oxygen in nitrogen in the detector.

2.4. Procedure

Preliminary studies on a standard mixture of HCFC 22, CH₃Cl, CH₂Cl₂ and CHCl₃, via sample loop injection, were performed to observe response enhancement and allow selection of the oxygen doped ECD conditions. A standard mixture was prepared by static dilution with nitrogen from pure samples to give concentrations at the 100 ppb level. The ECD response was observed over the temperature range 250 to 350°C, since electron capturing compounds are known to have widely varying responses as a function of detector temperature [21] and will have a similar influence on oxygen doped detection. Various oxygen concentrations in the ECD apparatus were investigated to confirm Grimsrud and Miller's finding [19] that 2000 ppm oxygen in nitrogen in the ECD apparatus was the most suitable concentration for the response enhancement of these halocarbons. Detector cell current was varied to determine the effect on signal response for specifically HCFC 22 and CH₃Cl.

The linearity of the entire system was tested by trapping increasing volumes of an air sample over the range of 20 to 120 ml on the microtrap at room temperature and desorbing each time under the same conditions. Extensive checks of system blanks were run to estimate interferences from other sources due to the ubiquitous nature of halocarbons. A blank analysis involved passing the same amount of nitrogen as used in the air sampling procedure, from either the carrier line or the purge and trap line, through the trap using the normal thermal desorption procedures on to the capillary column.

3. Results and discussion

The variation in ECD baseline frequency as a function of detector temperature and oxygen doping is represented in Fig. 2. The baseline frequency increases dramatically at lowest temperatures as the concentration of oxygen in the ECD apparatus is increased, while the lowest frequencies, i.e. "cleanest", are observed at high temperature, because the instantaneous O₂⁻ concentration (the reagent thought to be responsible for response enhancement [19,21]) is reduced at elevated temperatures. Further results in Table 2, for the standard mixture, show that for the susceptible target halocarbons, response enhancement by oxygen doping of the ECD is least at the highest ECD temperatures.

The increase in response enhancement is most impressive on reducing the ECD temperature from 350 to 300°C, particularly for HCFC 22, but was less marked for CHCl₃ due to its higher normal ECD response. For example, from the peak area data for HCFC 22, the ECD response was increased by a factor of 2.4 on reducing the ECD temperature from 350 to 300°C, while reducing the ECD temperature to 250°C only increased the response by a further factor of 0.4. Overall, higher ECD temperatures are preferable with respect to providing minimum baseline noise with oxygen doping, but provide lower response enhancement. Therefore, a fine balance between the two (i.e. least noise gave the least response enhancement) has to be achieved. Signal-to-noise ratios allowed selection of the optimum ECD operating temperature of 300°C. This temperature provides maximum response for the weakest electron capturing compounds, HCFC 22 and CH₃Cl, with adequate, although not the greatest, signal-to-noise ratio for CH₂Cl₂. CHCl₃ is most sensitively determined by operating the ECD apparatus in the normal mode with modest sample preconcentration.

A detrimental side effect is that the oxygen enhancement process will also increase the instrument's sensitivity to column bleed molecules as well as to the analytes of interest. It is therefore important to select the optimum detector standing current since with oxygen doping,

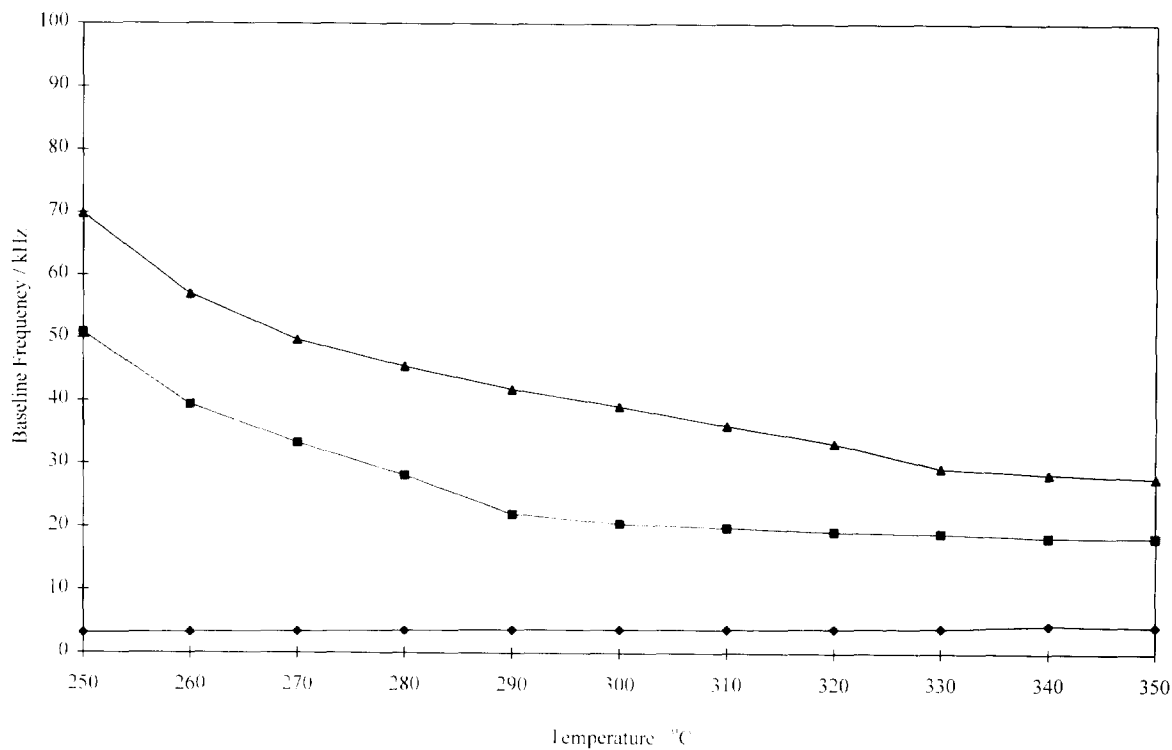


Fig. 2. Effect of oxygen on the baseline frequency at various ECD temperatures. \blacktriangle = 2000 ppm O₂, \blacksquare = 1000 ppm O₂, \blacklozenge = normal.

unavoidably column bleed results in a high baseline frequency. The present work showed that a detector current of 0.5 nA current should be used for both the Varian and the Shimadzu ECD systems in the oxygen doped mode. With the Varian ECD apparatus in the normal mode, a detector current of 0.5 nA causes the baseline

Table 2
Effect of ECD temperature on compound response with 2000 ppm O₂ in the ECD apparatus

ECD temp (°C)	HCFC 22	CH ₃ Cl	CH ₂ Cl ₂	CHCl ₃
<i>Peak area/counts</i>				
250	245703	129240	351440	55591
300	207997	109517	152183	49607
350	87512	47291	62768	44324
<i>Signal-to-noise ratio</i>				
250	196	103	280	44
300	295	155	216	70
350	175	95	126	89

frequency to fall below the minimum operating frequency of the system of 1.57 kHz, and is unusable without a minimum current of 1 nA. Similarly, for the Shimadzu ECD apparatus in the oxygen doped mode, satisfactory responses were achieved at 0.5 nA and 1 nA, with only the 2-nA current being unsuitable, while the normal mode required a detector current of 1 nA. Signal-to-noise ratios are shown for HCFC 22 and CH₃Cl, from a trapped air sample (80 ml), using the Shimadzu system in Table 3, which illustrates the favoured conditions for an oxygen doped detector at 2000 ppm and 300°C for these specific target compounds.

The following conditions were found to be the optimal for the target halocarbons on this particular GC system: (i) 2000 ppm oxygen in nitrogen to give sufficient compound response enhancement in the second ECD; (ii) 300°C for optimum detector operating temperature for the oxygen doped mode and 330°C for the normal

Table 3
Signal-to-noise ratios for HCFC 22 and CH₃Cl at different ECD currents

ECD current (nA)	Signal-to-noise ratio	
	HCFC 22	CH ₃ Cl
0.5	104	440
1.0	39	165
2.0	25	16

mode; (iii) ECD cell current of 0.5 nA in oxygen-doped mode, and 1 nA for normal ECD operation.

The efficacy of the analytical procedure was explored by analysis of samples of rural air in SUMMA-polished stainless-steel canisters, collected from the west coast of Ireland and from the Mendip Hills. A wide range of air volumes trapped have been quantitatively retained, and have shown to provide linearity in the range required for determination of the target compounds (Fig. 3). The precision from replicate Irish air samples adsorbed and desorbed from the microtrap are given in Table 4. Precisions are presented as peak areas relative to CFC 12 from the ECD mode which gives the highest signal-to-noise ratio for each target halocarbon. The precision levels are very acceptable for this type of analytical procedure.

From the examination of the Mendip Hills air sample, the necessity of the concentration procedure is illustrated in Fig. 4, from a sample loop of air (5 ml) compared with a trapped air sample (80 ml). The CFCs, known to be in the air at trace levels, could easily be detected in rural air samples of <20 ml sample volume. Overall results demonstrated clearly that sufficient sensitivity had been achieved via the trapping system for trace gas analysis: even CH₃I, at an atmospheric concentration of 2–3 ppt, could be detected routinely from 80 ml air samples by the normal ECD mode. Chromatograms of blank analyses are shown in Fig. 5 indicating adequate clean up procedures have been used within the system, preventing interference from contaminants.

The advantage of this technique over earlier methods [6,9] is that the major contaminant peaks (e.g. CFC 12, CFC 11) will be reduced in their passage through the first ECD apparatus, thereby, reducing their response in the second, highly sensitized detector, selectively revealing the remainder of the target compounds by response enhancement. The percentage reductions of the major chlorinated compounds and target halocarbons, from an air sample from Ireland, via passage through the first ECD apparatus are shown in Fig. 6. All the target compounds can be accomplished in a single analytical procedure, significantly reducing analysis time and allowing higher frequency routine analysis.

The additional sensitization of the second ECD with oxygen extends the range of the ECD to the weak electron adsorbers, HCFC 22, CH₃Cl and CH₂Cl₂. Further compounds shown to be responsive in the present work were: SO₂, COS, CS₂, CFC 1113 (CCIFCCl₂), HFC 134a (CF₃CH₂F) and the HFCs 141b (CH₃CFCl₂), 124 (CF₃CFHCl) and 142b (CH₃CF₂Cl). Other workers have also recently demonstrated the potential application of oxygen doping for certain HCFCs and HFCs [26]. It is important to be aware of their possible interference with and response to oxygen doping of the ECD. Some are of particular concern due to the predicted increase in usage and therefore atmospheric release as they replace the CFCs. Therefore, the potential exists for the analysis of a much wider range of halocarbons [25], subject to judicious capillary column choice. Additionally, atmospheric hydrocarbons would be suitably determined by this preconcentration procedure with separation using an Alumina/KCl PLOT column, which is specifically made for the analysis of such compounds, followed by flame ionization detection.

4. Conclusions

This work has demonstrated the development of a practical GC-ECD instrument to determine accurately seven important trace atmospheric halocarbons with a combination of adsorption on

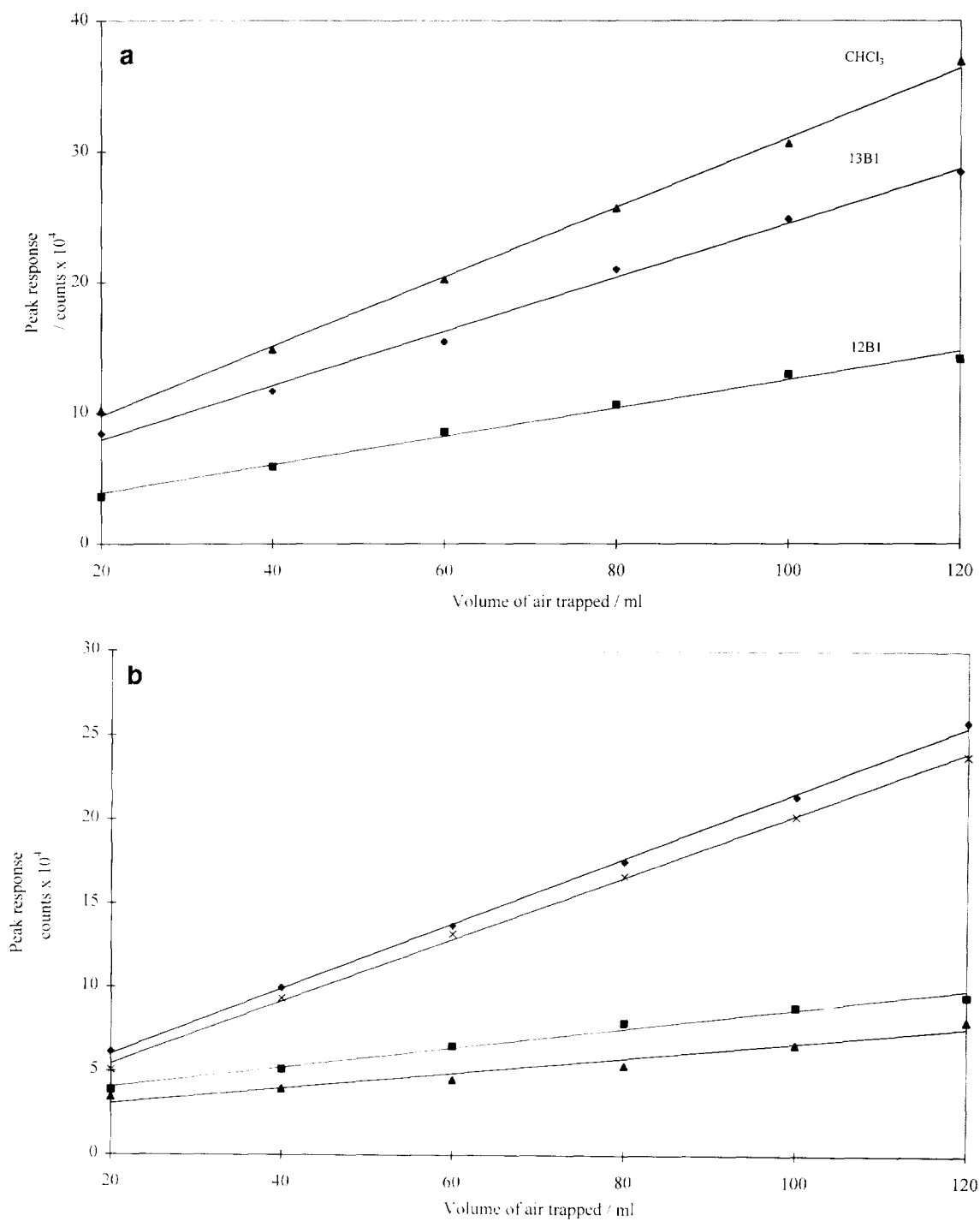


Fig. 3. Linearity of the ECD for trapping increasing volumes of air. (a) \blacktriangle = CHCl_3 ($r = 0.999$), \blacklozenge = 13B1 ($r = 0.995$), \blacksquare = 12B1 ($r = 0.989$). (b) \blacklozenge = HCFC 22 ($r = 0.999$), \times = CH_2Cl_2 ($r = 0.998$), \blacksquare = CH_3Cl ($r = 0.985$), \blacktriangle = CH_3Br ($r = 0.956$).

Table 4
Precision levels for the analytical procedure for $n = 10$

Compound	Peak area ratio %R.S.D.	
	Normal ECD	Oxygen doped ECD
13B1	0.8	—
HCFC 22	—	1.3
CH ₃ Cl	—	3.6
12B1	1.7	—
CH ₃ Br	—	3.9
CH ₂ Cl ₂	—	1.8
CHCl ₃	1.6	—

a microtrap and detection with an oxygen doped ECD, due to their low concentration and low ECD response. It was directed towards the continuous long-term monitoring of specifically HCFC 22, 13B1, 12B1, CH₃Cl, CH₃Br, CH₂Cl₂ and CHCl₃ from ambient air at near real time in a single analysis with high-frequency, high-precision measurements.

Complete trapping efficiency at ambient temperatures and efficient band-focusing (without the need for cryogenics) was achieved with a microtrap of near capillary dimensions packed with a small amount of the adsorbent, Carboxen.

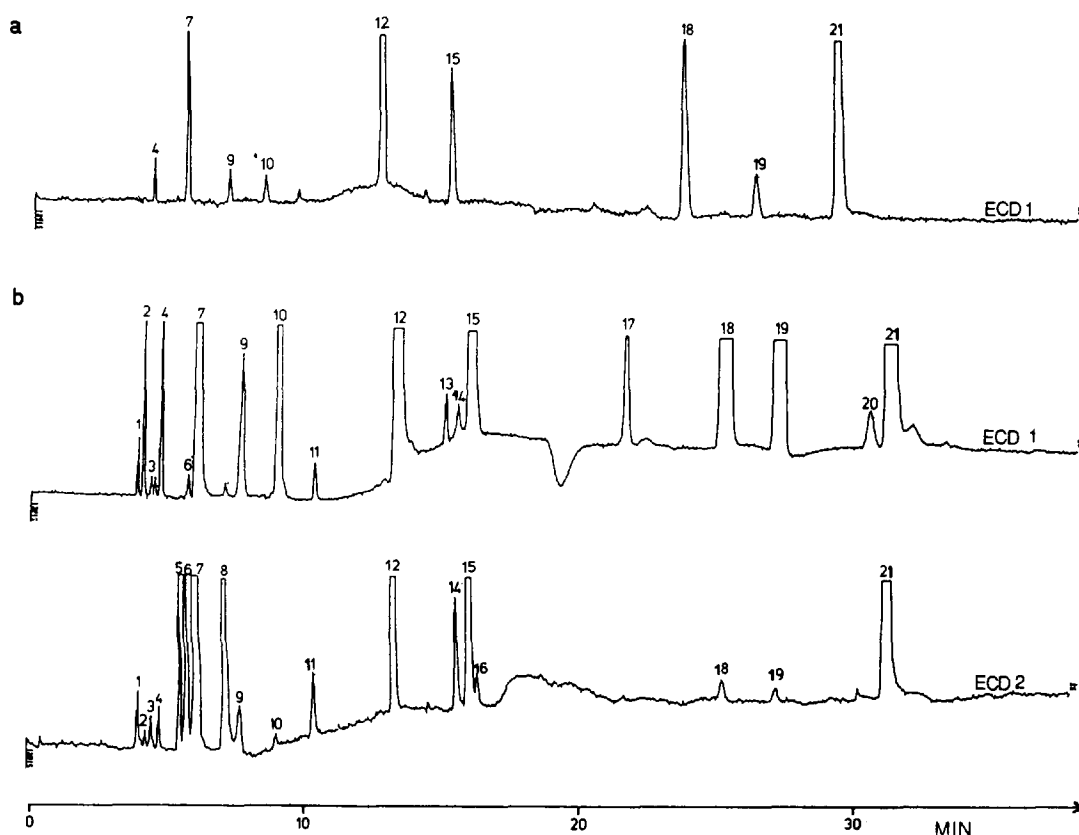


Fig. 4. Chromatograms of (a) a 5-ml and (b) an 80-ml Mendip Hills air sample on the WCOT CP Sil 5 CB column with nitrogen carrier gas flow-rate of (a) 1.8 ml/min and (b) 1.6 ml/min, with ECD 1 in normal and ECD 2 in oxygen doped mode. Peak identification: 1 = CFC 13, 2 = CFC 23, 3 = CFC 115, 4 = 13B1, 5 = HCFC 22, 6 = COS, 7 = CFC 12, 8 = CH₃Cl, 9 = CFC 114, 10 = 12B1, 11 = CH₃Br, 12 = CFC 11, 13 = CH₃I, 14 = CH₂Cl₂, 15 = CFC 113, 16 = CS₂, 17 = CHCl₃, 18 = CH₃CCl₃, 19 = CCl₄, 20 = TCE, 21 = PCE.

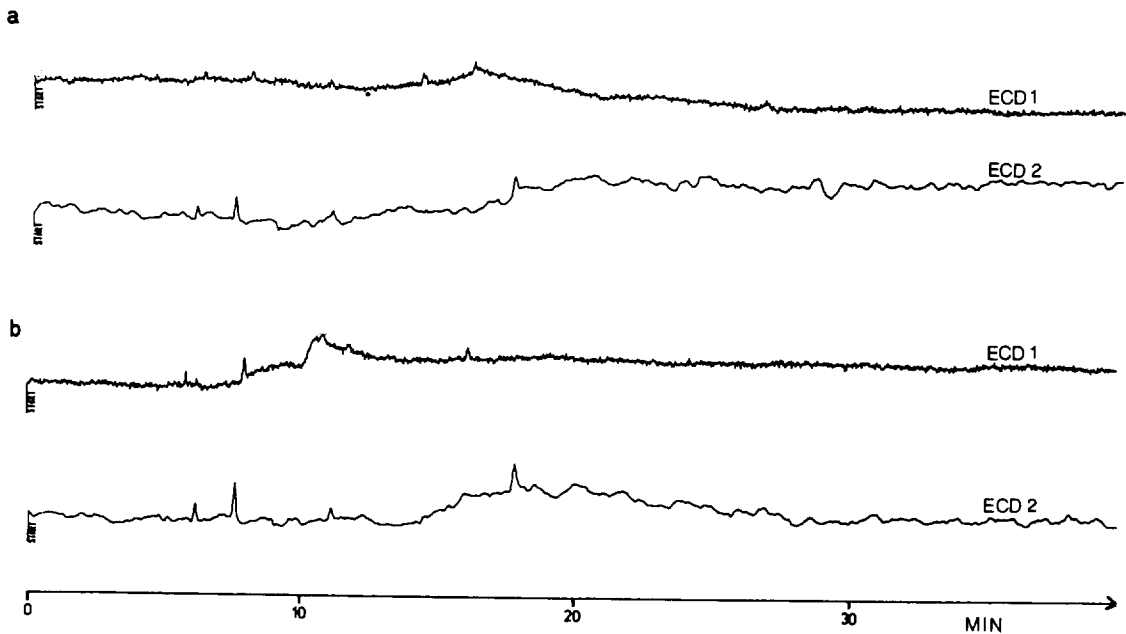
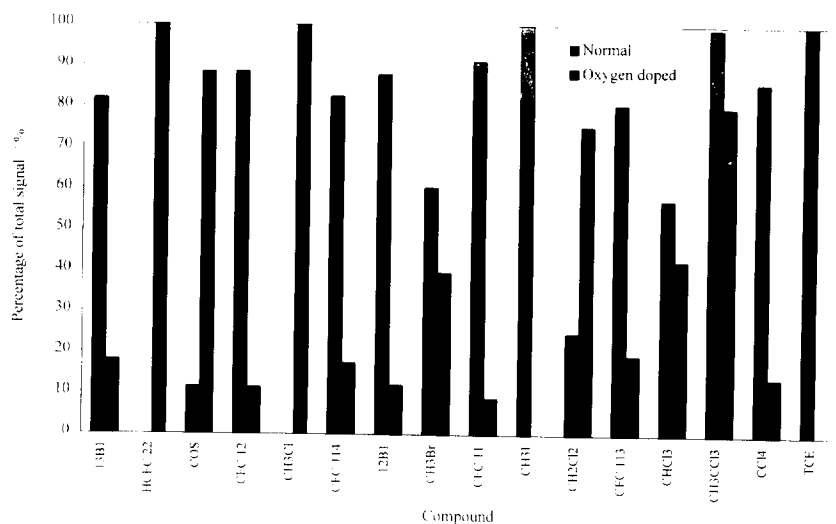


Fig. 5. System blanks: (a) 100 ml nitrogen carrier gas and (b) 100 ml nitrogen purge gas, with the same conditions as for Fig. 4.

Maintenance of the trap at ambient temperature during the concentration procedure was a key requirement for this work, thereby avoiding the need for expensive liquid nitrogen supply. Desorption on to the capillary column from the one-stage multibed trap was facilitated, under

carrier gas flow reversion, using direct ohmic heating. Subambient temperature programming for the GC was also unnecessary. Investigations using oxygen doped ECD to enhance the response of certain halocarbons, which react feebly with thermal electrons, were successfully made



with selection of operating parameters such as the required oxygen concentration for sufficient compound response enhancement, detector temperature and cell current. The use of two ECD instruments in series allowed simultaneous determination of the CFCs and oxygen-enhanced compounds from an air sample in a single analysis. The method has wider application, in addition to the group of compounds in this study, to atmospheric analysis.

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