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Use of adsorbents to collect selected halocarbons and hydrohalocarbons of environmental interest from large air volumes

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ABSTRACT

Hydrohalocarbons are the proposed replacement compounds for the chlorofluorocarbons. They will initially have very low concentrations, on the order of a ppt (v/v), in the global atmosphere. Neither gas chromatography–electron-capture detection, nor gas chromatography–mass spectrometry, have adequate sensitivity to measure such concentrations directly from air samples; concentration techniques are required to achieve this. We have examined a range of commercially-available adsorbents, including activated charcoals, carbon molecular sieves, porous polymers, and graphitized carbons, for their suitability as ambient temperature concentrating traps for a range of man-made halocarbons and hydrohalocarbons (CFC-12, CFC-11, CFC-13, HCFC-22, HCFC-123 and HFC-134a). From our measurements of specific retention and desorption volumes it was found that no one adsorbent could both collect all of the target compounds with high efficiency, and also allow efficient recovery by thermal desorption. A sequence of adsorbents is required. We designed a 30 cm long × 0.64 cm O.D. trap containing HayeSep D₈ (a porous polymer), Carboxen 1000 and Carbosieve S-II (both carbon molecular sieves) to collect all of the target compounds from a 5 l air sample at 25°C and allow efficient recovery with 500 ml of nitrogen carrier gas at 200°C. Good comparability was demonstrated between the adsorbent trapping system and direct loop injection analysis for CFC-12 in ambient air. Precision for all of the compounds analyzed with the adsorbent trap was better than 4%, and improved to better than 1% when ratioed to CFC-12.

INTRODUCTION

The chlorofluorocarbons (CFCs) are man-made compounds used in refrigeration and cooling systems, foam blowing, aerosol propellants and industrial solvents. In the atmosphere they can migrate to the stratosphere where photolysis releases the chlorine atoms, which can in turn participate in reactions which remove ozone [1]. As a result of this threat to the ozone layer the CFCs, and other selected man-made halocarbons, have been targeted for elimination by the end of the year 2000 by countries ratifying the Montreal Protocol [2]. In many

Western countries, including the USA and Canada, national regulations now require the elimination of CFC usage by the end of 1995 [3]. Industry is turning to alternative compounds to replace the CFCs, in particular the hydrohalocarbons (HHCs) [2]. These include the hydrochlorofluorocarbons (HCFCs), which are non-fully-halogenated analogues of the CFCs, and the hydrofluorocarbons (HFCs) which are both non-fully-halogenated and contain no chlorine. The presence of the hydrogen atom in these molecules makes them accessible to OH radical reaction in the troposphere, so reducing their atmospheric lifetime relative to the CFCs, and

thus the amount reaching the stratosphere [4]. The HFCs, since they contain no chlorine, should have no impact on stratospheric ozone but are strong infrared adsorbers and may contribute to “greenhouse warming” [5].

We anticipate a rapid rise in HHC concentrations over the next decade or more as the CFCs are phased out and replaced. HCFC-22 is already in use and is present in the atmosphere at about 100 ppt (v/v) [6]. HFC-134a is the first HFC to be used commercially with its recent introduction in some automotive air conditioners [7]. This compound has not yet been detected in the ambient atmosphere. With the exception of HCFC-22, the HHCs will initially have minute atmospheric concentrations, on the order of a few ppt, compared with tens or hundreds of ppt for the CFCs. Direct gas chromatographic (GC) analysis of small loop injections of air will not be sufficiently sensitive for such concentrations. In addition, GC–electron-capture detection (ECD) sensitivity for HHCs is moderate to very poor compared with the CFCs.

Whether GC–ECD or GC–mass spectrometry (MS) is used, sample concentration is required. In

our experience, large volume sample concentration of the condensable gases by cryogenic techniques (cryotrapping) results in frequent blockage of the traps by carbon dioxide and water vapor, and is often not suitable for field use. Adsorbents offer the possibility of ambient temperature collection and selective trapping to remove interferences such as water vapor. Adsorbent tubes are small, light, and cheap compared to metal flask samples, and might be used for portable multiple sampling units. In addition, some of the artifacts of flask sampling might be avoided.

We examined a variety of adsorbents for their suitability for trapping some representative CFCs and HHCs at ambient temperature, and subsequent recovery by thermal desorption. This information was used to design a trap for field use to concentrate the target compounds from several liters of air.

METHODS

The adsorbents tested are listed in Table I. Each adsorbent was used to make one or more short chromatographic columns in 0.64 cm or 0.32 cm

TABLE I

ADSORBENTS EXAMINED IN THIS STUDY

Adsorbent types: A = activated charcoal; CS = carbon molecular sieve; G = graphitized carbon; P = porous polymer; MS = molecular sieve. Suppliers: Alltech, Deerfield, IL, USA; Supelco, Bellefonte, PA, USA; Hayes Separations, Bandera, TX, USA.

Adsorbent	Supplier	Type	Mesh	Specific surface area (m ² /g)	Bulk packed density ^a (mg/ml)	Column dimensions, length × O.D. (cm)
SK4 Carbon	Alltech	A	80–100	n/a ^b	460	2.86 × 0.32
CT Carbon	Alltech	A	80–100	n/a ^b	470	2.54 × 0.32
Carbosieve S-II	Supelco	CS	80–100	1000	680	2.54 × 0.32
Carbosieve S-III	Supelco	CS	60–80	550	700	3.18 × 0.32
Carboxen 1000	Supelco	CS	60–80	1200	490	5.08 × 0.32
Carboxen 1001	Supelco	CS	60–80	500	580	3.18 × 0.32
Porapak Q	Supelco	P	100–120	510	340	22.9 × 0.32
HayeSep D _B	Hayes Separations	P	80–100	781	360	22.9 × 0.64
						6.99 × 0.32
						3.51 × 0.64
Carbopak B	Supelco	G	60–80	100	460	15.9 × 0.32
Graphpac GB	Alltech	G	Granular	100	450	15.2 × 0.64
Tenax TA	Alltech	P	20–35	35	220	15.2 × 0.64
Tenax GR	Alltech	G/P	80–100	24	320	15.2 × 0.64
Molecular sieve 5A	Supelco	MS	80–100	700–800	660	22.9 × 0.64

^a Determined by weighing 7.62 × 0.64 cm O.D. tubes packed with adsorbent using a column vibrator.

^b Information not available.

TABLE II
CFC, HCFC AND HFC COMPOUNDS STUDIED IN THIS WORK

Halocarbon	Formula	M_r (g/mol)	Boiling point (°C)	Standard concentrations (v/v, by mole fraction)
HFC-134a	$C_2H_2F_4$	102.02	-26.0	1021, 734, 156 ppm
HCFC-22	$CHClF_2$	86.47	-40.7	1058, 150, 56 ppm, 494 ppb
CFC-12	CCl_2F_2	120.91	-29.8	2.48 ppm, 438 ppb
CFC-11	CCl_3F	137.37	23.8	264, 253 ppb
HCFC-123	$C_2HCl_2F_3$	152.9	27.9	16 ppm, 581 ppb
CFC-113	$C_2Cl_3F_3$	187.38	47.5	357, 193 ppb

O.D. stainless-steel tubing (dimensions in Table I). The columns were connected to a gas chromatograph (Hewlett-Packard, Sunnyville, CA, USA; Model 5890A) equipped with an electron-capture detector operated at 350°C and a standing current of 1 nA. The compounds of interest (Table II) were introduced to the front of the column by making loop injections of gaseous gravimetric standards (in air) into the nitrogen carrier gas stream (Fig. 1) with a 6-port gas sampling valve (Valco Instruments, Houston, TX, USA). High-concentration standards (Table II) were used to account for the non-optimal chromatographic conditions and the poor ECD sensitivity of the hydrohalocarbons (particularly HFC-134a). Various loop volumes, from 0.05 to 5 ml, were used to obtain a satisfactory peak for individual compounds, concentrations, and experimental conditions. In later stages of the study, HCFC and HFC sensitivities were improved by adding a mixture of 2% oxygen in nitrogen to the carrier gas at the ECD inlet to give O₂ concentra-

tions in the ECD of around 0.2%. This allowed smaller loops and/or lower concentration standards to be used (Table II).

Peak retention, start, and end times were obtained by examining the ECD signal output to a recording integrator (Hewlett-Packard, Model 3396A). Times were corrected by reference to a non-retained species (oxygen from the standard air balance). Experiments were conducted at a range of column temperatures and carrier flow-rates. Since the primary interest in this study was collection of samples at ambient temperature, and subsequent thermal desorption of collected species at 200°C, attempts were made to include measurements at, or approaching, these temperatures. We also examined flow-rates in the range likely to be used under actual sampling conditions (order of 10–100 ml/min).

It is customary to evaluate adsorbent efficiency by calculating the specific retention volume (V_R) for each compound of interest [8]:

$$V_R = (t_r - t_0) \frac{T_c}{T} \frac{3(P_i/P_0)^2 - 1}{2(P_i/P_0)^3 - 1} \frac{F}{V_s} \left(1 - \frac{P_w}{P_a}\right) \quad (1)$$

where t_r and t_0 are the retention times of the compound and non-retained species respectively (min), P_i and P_0 are the column inlet and outlet pressures respectively, T_c and T are the trap operating and ambient temperatures (K) respectively, F is the carrier gas flow-rate at ambient temperature (ml/min), V_s is the volume of adsorbent in the column (ml), P_w is the vapor pressure of water at ambient tem-

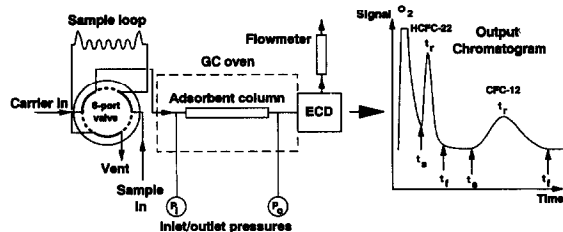


Fig. 1. Schematic of system used to test adsorbents for specific retention volumes and specific desorption volumes, together with an idealized chromatogram. t_s = Peak start time; t_r = compound retention time; t_f = peak finish time.

perature, and P_a is ambient pressure. This equation corrects for gas compressibility in the adsorbent column and yields retention volumes that are appropriate for conditions of ambient pressure and temperature in the adsorbent column. The last term corrects the volumetric flow-rate measured by soap bubble flow meter, and is omitted where solid state flow sensors are used.

Note that V_R in this expression is normalized to adsorbent volume, rather than the more conventional use to adsorbent mass. This is more useful in the present study where the quantity of adsorbent to be used in sampling tubes of given or maximum dimensions is considered. Conversion to units of volume per adsorbent mass can readily be achieved using the adsorbent densities in Table I.

Eqn. 1 measures the approximate 50% breakthrough volume (BTV) of the compound. A measure of the maximum sample volume (V) can be derived from [9]:

$$V = V_R(1 - 2/\sqrt{N}) \quad (2)$$

where N is the number of theoretical plates at the experimental conditions at which V_R is measured. Rather than attempt to estimate N , but to still obtain a measure of maximum sample volume, the visually determined peak start time, t_s (see Fig. 1), was used in place of t_r in eqn. 1. The detection threshold varied with peak height and width, but we estimate that in no case did it exceed 1% of the peak area. We therefore refer to the specific retention volume so calculated as the 99% specific retention volume: $V_{R,0.99}$.

We can similarly measure the desorption time, t_d , for peaks returning to the baseline. Again we esti-

mate that the detection threshold was $>99\%$ for all peaks, and calculate the 99% specific desorption volume, $V_{D,0.99}$, from eqn. 1 using t_d in place of t_r .

Further tests were conducted using a multiple stage adsorbent trap (Fig. 2). This was a 30 cm \times 0.64 cm O.D. stainless-steel tube containing 3.5 ml HayeSep D_B, 1 ml Carboxen 1000 and 1 ml Carbo-sieve S-II, separated by deactivated pesticide-grade glass wool (Alltech, Waukegan, IL, USA). The tube exterior was coated with Omegabond 200 high-temperature epoxy (Omega, Stamford, CT, USA), which has a high electrical resistivity and thermal conductivity, close-wound with glass fiber double-insulated 30 gauge E-type thermocouple wire (Omega) as the heating element (largely achieved through the nickel-chromium conductor), and sheathed with Nextel sleeving (Omega).

Gas samples could be loaded on to the adsorbent trap by making loop injections into the nitrogen carrier gas used to flush the tube, and then analyzed by backflushing the trap with carrier gas at around 50 ml/min for 5–10 min while heating the tube. The compounds desorbed from the trap were refocused on a 0.53 mm I.D. fused-silica capillary with a 10- μ m thickness Al₂O₃/KCl wall coating (Chrompack column 7518, Raritan, NJ, USA) cooled to -165°C by liquid nitrogen with the cryogenic trapping section of a Chrompack Model 16400 purge-and-trap injector. This was in turn interfaced to a 30 m \times 0.32 mm I.D. DB-1 (dimethylpolysiloxane) capillary column (J&W, Folsom, CA, USA), with a 5- μ m film thickness, in a Shimadzu (Columbia, MD, USA) GC-9A chromatograph equipped with dual in-series ECD cells. ECD temperatures in the range 275–350°C, and standing currents of 0.2–1 nA, were used in different experiments (see Results section). UHP nitrogen, purified with a Supelco (Bellefonte, PA, USA) Model 3800 heated getter gas purifier, was used as the carrier and make-up gas, with the addition of 10% (v/v) of 2% oxygen-doped nitrogen (UHP grade, further purified with molecular sieve 13X) into the second ECD in series to improve the response of HCFC-22 and HFC-134a. A dramatic improvement in the HFC-134a response was observed, as will be reported in a later paper.

The cryogenic trap was desorbed at 200°C for 5 min at the column flow-rate (approximately 2 ml/min) on to the analytical column, which was held at

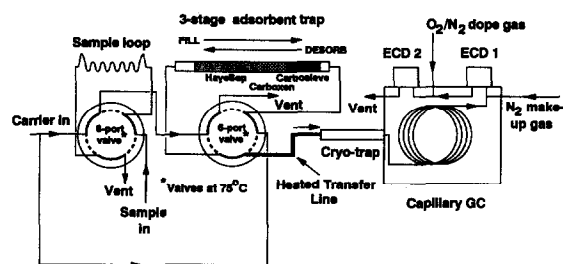


Fig. 2. Schematic of system used to test the design triple-stage adsorbent trap. The adsorbent trap was filled and flushed in one direction, and desorbed at elevated temperature in the reverse direction.

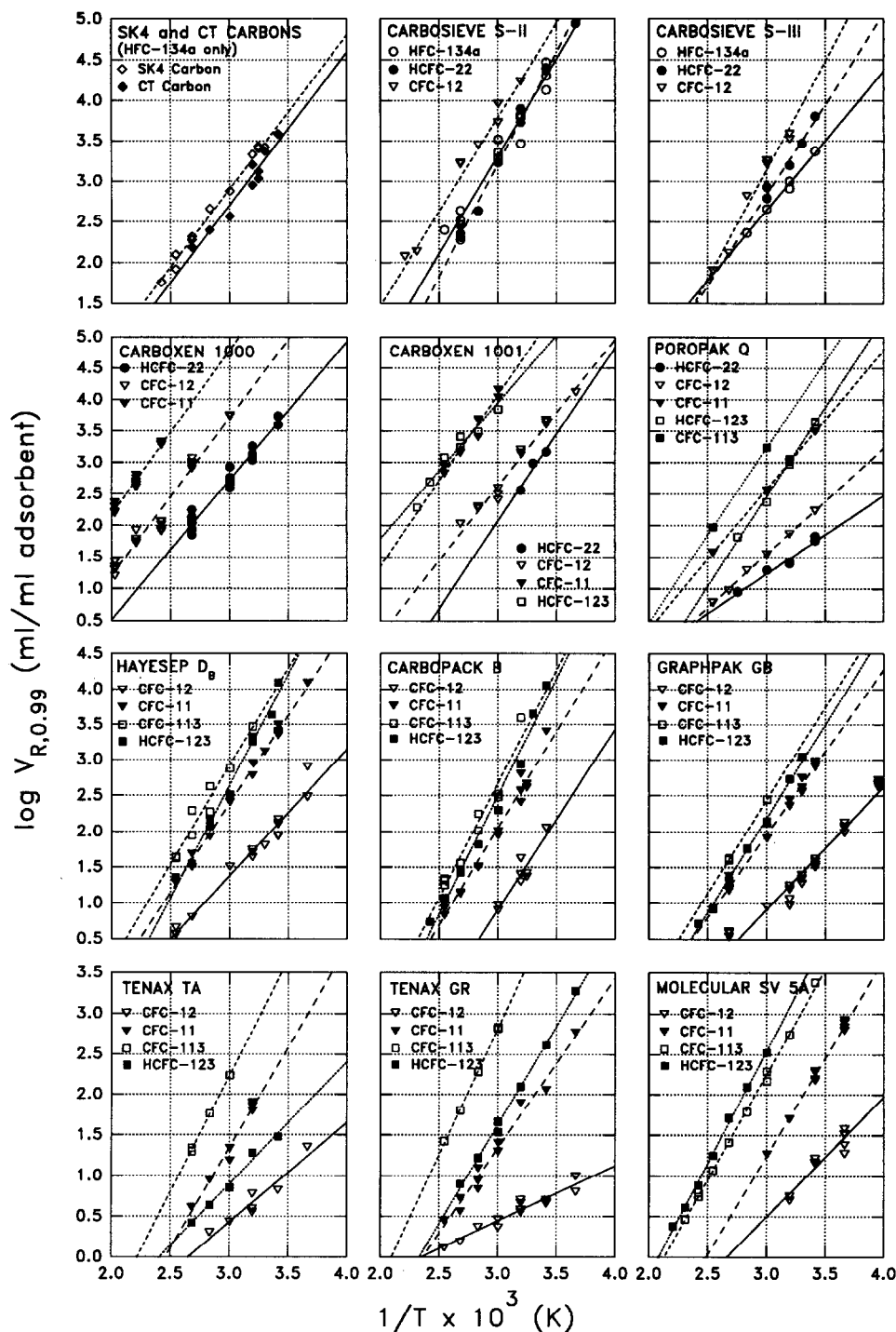


Fig. 3. Summary plots of $\log V_{R,0.99}$ versus $1/T$ for all compounds tested with each adsorbent. Lines are linear regression fits to the data.

0°C. After a further 3 min, the column temperature was raised to 100°C at 8°C/min.

RESULTS

A technique that has commonly been used to estimate specific retention volumes for adsorbents at near or sub-ambient temperatures is to extrapolate linear fits of $\log V_R$ versus $1/T$, from data obtained at elevated temperatures, to the lower temperatures of interest [8]. Others have shown that this can lead to errors in the calculated retention volume due to non-linearity effects [9, 10]. Pankow [10] demonstrated a method of *estimating* and correcting for such errors in the extrapolation technique, but this requires a knowledge of the enthalpy of desorption from the adsorbent, and enthalpy of vaporization of the pure compound, and still may not account for all errors. We have therefore aimed to make measurements at temperatures close to ambient using short adsorbent-packed columns.

Fig. 3 shows plots of $\log V_{R,0.99}$, normalized to a 1-ml volume of adsorbent, versus $1/T$ for all of the compound retentions that could be determined on the selected adsorbents, together with linear fits to

the data. Compounds that were either too strongly retained on an adsorbent and did not appear to elute within about 30 min, or were negligibly retained and consequently not separated from the oxygen peak, are not reported. A table of regression data for all of the plots in Figs. 3 and 5 can be obtained from the authors on request.

In most cases the plots showed a high degree of linearity. In some cases, however, there was a significant amount of scatter. Generally this scatter was related to differences in carrier flow-rates between experiments. Examples of variations in $V_{R,0.99}$ with flow-rate are shown in Fig. 4. Retention volumes generally increased with decreasing flow rate, but this varied between compounds, adsorbents, and column temperatures. The plots in Fig. 3 include only experiments with flow-rates ≤ 200 ml/min since this is the range of flow-rates that we anticipate using in actual ambient air sampling. It is recommended that flow-rates below 100 ml/min be used to achieve retention volumes estimated from the linear fits.

It should also be noted that the values of $V_{R,0.99}$ in Fig. 3 are for ambient pressure in the adsorbent tube. This will normally be valid where samples are collected by drawing ambient air through an adsorbent tube. Where air is pumped through the tube, or where an adsorbent tube is used as a focusing trap on a GC system, then corrections should be made for internal tube pressure.

Of equal importance to the retention volume of a compound on a particular adsorbent is its desorption volume. An adsorbent may be a highly efficient sampling material, but will not be useable if the retained species cannot be thermally desorbed within a reasonable time and at a practical temperature. Fig. 5 shows plots of $\log V_{D,0.99}$ versus $1/T$ for most of the adsorbents. Tenax TA, Tenax GR and molecular sieve gave desorption volumes that were too low to be determined at the higher temperatures. During desorption the tube will be at elevated pressure and temperature, and therefore corrections must be made (eqn. 1). For example, with a tube inlet pressure three times that of the outlet pressure, and a temperature of 200°C, a value of $V_{D,0.99}$ obtained from Fig. 5 must be increased by a factor of 1.25.

Table III summarizes retention and desorption values for ambient temperature sampling (25°C)

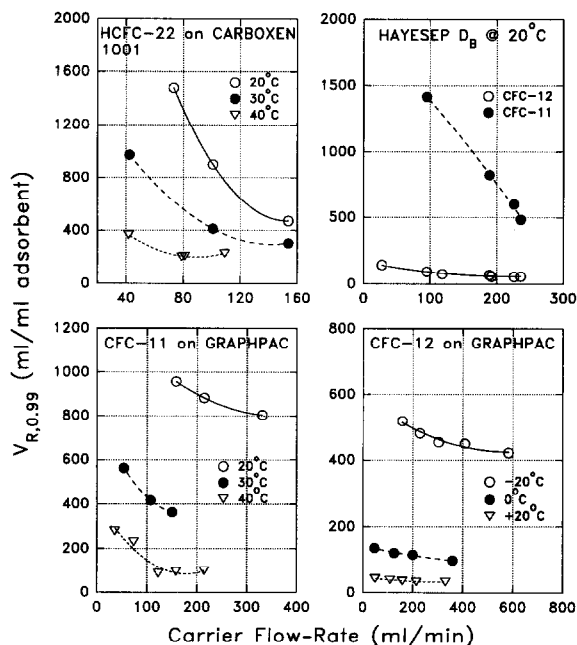


Fig. 4. Examples of variations in specific retention volumes with flow-rates through the tubes.

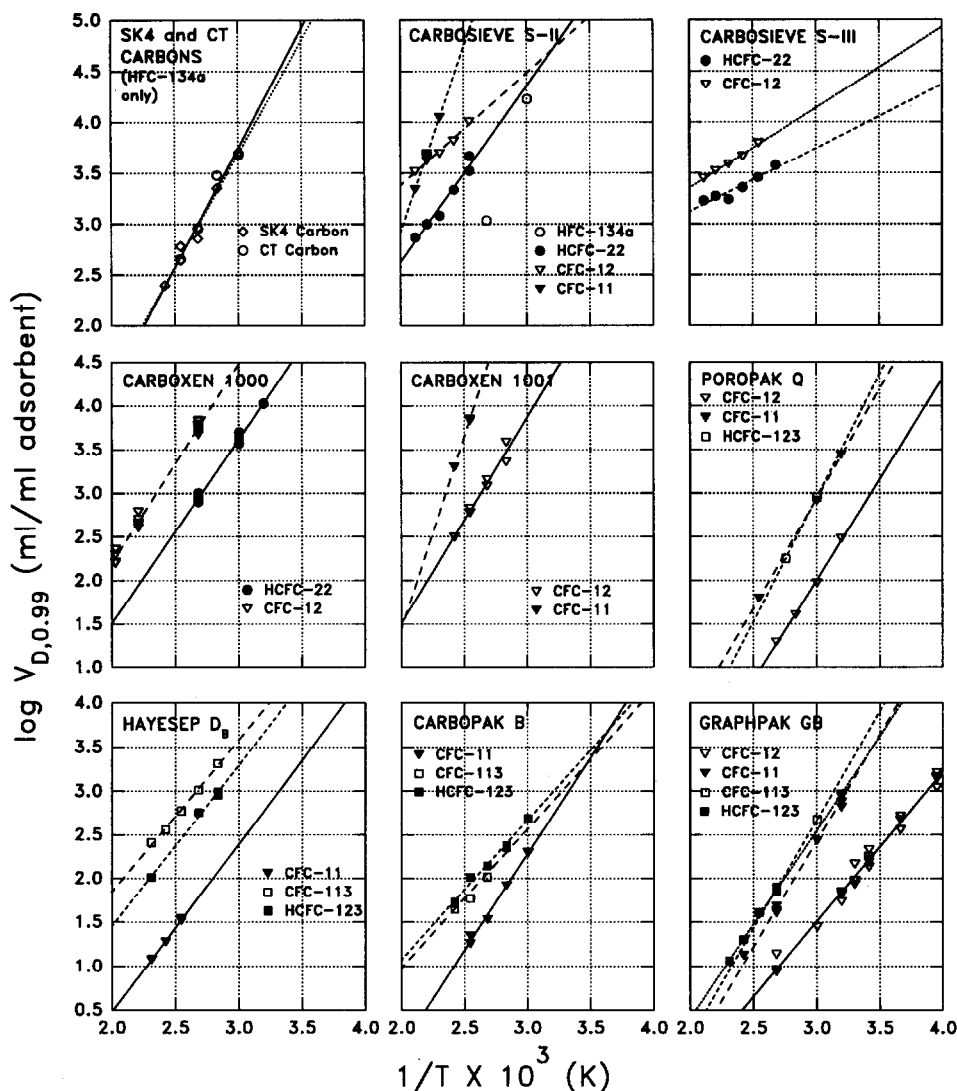


Fig. 5. Summary plots of $\log V_{D,0.99}$ versus $1/T$ for all compounds tested with each adsorbent, except the two Tenax formulations and molecular sieve 5A (see text). Lines are linear regression fits to the data.

and desorption at 200°C. Note the different units for retention volumes (l/ml) and desorption (ml/ml). From the table it can be seen that retention volumes generally increase in the order (by halocarbon number): 134a < 22 < 12 < 11 < 113. This is in boiling point order for the CFC compounds, but the same is not true for the HHCs. HFC-134a, with a boiling point similar to that of CFC-12 (Table II), is less effectively trapped than CFC-12. The same effect will likely be seen for all HFC compounds due

to the absence of chlorine atoms. HCFC-123 is not included in the above ranking as it shows some remarkable variations between adsorbents. Its boiling point is between that of CFC-11 and CFC-113 (Table II). All the porous polymers, except Tenax TA, and both graphitized carbons, gave HCFC-123 retention volumes that fell between those of CFC-11 and CFC-113. Carboxen 1001, however, gave values lower than that of CFC-11 at lower temperatures, whilst Tenax TA gave values between

efficient for HCFC-123 and CFC-113. HayeSep D_B has other desirable features over Porapak Q, including higher thermal stability (maximum temperature of 300°C versus 250°C for Porapak Q), and smaller desorption volumes for HCFC-123.

Carbopak B and Graphpac GB are both graphitized carbons of similar composition. Graphpac GB is in a coarse granular form designed to produce sampling traps of lower pressure drop. Carbopak B was somewhat more efficient than Graphpac GB for all of the compounds.

Tenax GR is manufactured by coprecipitating the same polymer used in Tenax TA with 30% graphitic carbon. Both Tenax forms had low collection efficiencies for all of the compounds except CFC-113. Efficiencies for CFC-12 and CFC-11 were similar, or slightly lower in the GR form. Given the higher density of GR (Table I), this equates to a significantly lower efficiency for GR on a per gram basis. For the heavier halocarbons, however, the situation was reversed with much higher retention volumes for HCFC-123 and CFC-113 on the GR form.

An important conclusion from Table III is that no one adsorbent is suitable to make ambient measurements of all of the listed compounds, due to the limitation of desorption volume. Two or more adsorbents need to be used in series to successively remove less easily trapped species from the sample air stream. This ensures that compounds do not penetrate to a large extent into an adsorbent from which they cannot be readily desorbed. The adsorbent tube must be desorbed by flowing carrier gas in the reverse direction to the sample flow.

DESIGN OF A MULTIPLE BED ADSORBENT TRAP

The information in Table III was used to design a trap that could be used to collect all of the compounds listed from a large enough air sample to permit low ambient concentrations (few ppt, v/v for the HHCs) to be determined. A portable automated multiple-tube sampling device is being developed in which the tube size is limited to about 30 cm × 0.64 cm O.D. The interior volume of a trap with these dimensions is about 6.7 ml.

In designing the trap, due attention must be paid to both the desorption and retention volumes. Some breakthrough of a species from its target ad-

sorbent stage to the next can be tolerated since the molecules will be concentrated at the front of the next adsorbent stage and, during backflushing to desorb the trap, the whole volume of the adsorbent will not need to be desorbed to remove them again. However, to ensure rapid desorption, it is recommended that such breakthrough be kept to a minimum.

In the example given here the design sample volume was 5 l at ambient pressure and 25°C. For desorption we considered 200°C to be a safe temperature to avoid any thermal decomposition effects for these or any other halocarbons. A flow-rate of 50 ml/min can be achieved with the cryogenic refocussing system used, and 10 min was taken as a reasonable desorption time. Therefore desorption volumes should be less than 500 ml in total for the amount of adsorbent used.

CFC-11, HCFC-123 and CFC-113 are not readily desorbed from either the carbon molecular sieves or the activated carbons (Table III). The graphitic carbons and both Tenax formulations have relatively low retention volumes for CFC-11. Porapak Q has higher retention volumes than HayeSep for CFC-11 and CFC-113, but lower values for HCFC-123. HayeSep was selected to collect these three species due to its lower desorption volume for HCFC-123 relative to Porapak, and its higher thermal stability. A volume of 3.5 ml was selected to retain CFC-11 from volumes of up to 6.7 l, HCFC-123 from volumes up to 20 l, and CFC-113 from volumes up to 28 l. At 200°C all of the CFC-113 should be desorbed with 385 ml of carrier gas, and lesser volumes for the other two species. A 1-ml volume of Carboxen 1000 was selected to retain CFC-12 from up to 39 l of air and desorb with 290 ml of carrier at 200°C. A 1-ml volume of Carbosieve S-II was selected to retain HFC-134a from 9 l of air. The desorption volume could not be assessed, but is presumed to be less than that of HCFC-22 (670 ml), and within the 500 ml criterion. HCFC-22 will be collected partly on the Carboxen 1000 (up to 3.2 l), and partly on the Carbosieve S-II (up to a further 16 l). It is readily desorbed from the Carboxen (58 ml at 200°C). The given desorption volume for HCFC-22 on Carbosieve S-II is, at 670 ml, a little higher than the criterion, but it is considered that with a 5 l air sample, HCFC-22 will only penetrate part of the way into the Carbosieve S-II stage, and therefore be more readily desorbed.

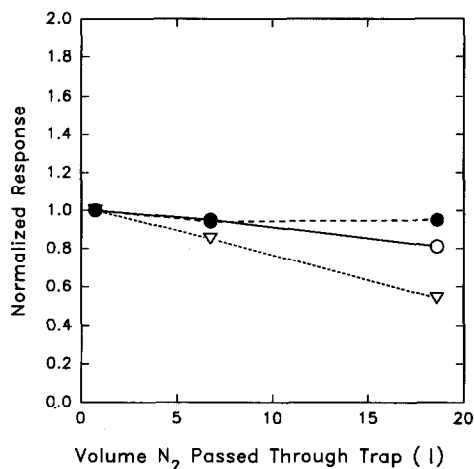


Fig. 6. Long period flushing tests of the triple-stage adsorbent trap: 10 ml standards in air were injected at 33°C, followed by nitrogen carrier gas at 114 ml/min to the volumes shown. Peak area responses were normalized to the experiment in which the trap was flushed with 300 ml nitrogen. ∇ = HFC-134a; \bullet = HCFC-22; \circ = CFC-12.

The design triple-stage trap was tested with large flushing volumes using the apparatus in Fig. 2 (see Methods section). A 10-ml loop injection of a standard was made into the nitrogen carrier flowing through the trap at 114 ml/min and 33°C. The carrier was allowed to continue flowing for a set time to give a total volume of nitrogen flushed through the trap. The trap was then desorbed at 200°C and analyzed. The results are shown in Fig. 6, normalized to the experiment in which only 300 ml of carrier were used to flush the trap. This experiment gives the “worst case” breakthrough since the sample is loaded at the start of the flushing period, whereas in the sampling of real air the analyte molecules enter the trap continuously through the sampling period. In addition the tube temperature was higher than the standard used in Table III (25°C), and the flow-rate was above the recommended maximum (100 ml/min). Nevertheless, the experiment demonstrated that the values used to design the tube are, for the most part, conservative. About 20% breakthrough (or non-recovery) of HFC-134a had occurred with 9 l of flushing. High collection efficiency of HCFC-22 was obtained up to almost 19 l of flushing, indicating that it was still being efficiently recovered after breaking through to the Carbosieve

stage. A small reduction in CFC-12 efficiency was evident at the highest volume.

The triple stage trap was also used to determine accuracy and precision for the adsorbent trapping technique (Fig. 7). Loop injections (10 ml) of a series of CFC-12 gravimetric standards (accuracy better than 1% [11]) were made on to the trap, followed by 550 ml of nitrogen carrier. The trap was desorbed at 200°C. The same procedure was then used to determine the CFC-12 concentration in a cylinder of dried air filled at Niwot Ridge in the Colorado Rocky Mountains (40°02'N, 105°35'W, 3018 m above sea level). Two measurements gave results of 484 and 475 ppt, in good agreement with an earlier analysis (461 ppt CFC-12) of the same cylinder using direct loop injections into the GC system used by the National Oceanic and Atmospheric Administration (NOAA) Nitrous Oxide and Halocarbons group for their flask-sampling network [12].

Precision was determined by replicate measurements of 10-ml loop injections of a multiple standard mixture flushed on to the adsorbent tube with 400 ml of air at 30°C, and desorbed at 200°C. The results are shown in Table IV. The atmospheric concentrations that would yield the same CFC concentrations on the trap from a 5-l air sample can be obtained by dividing the concentrations in Table IV by 500. These resultant concentrations are well be-

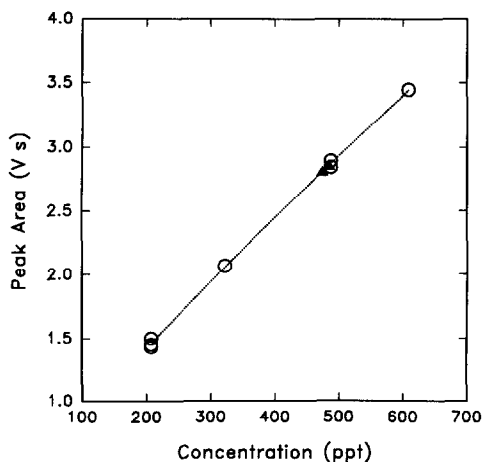


Fig. 7. CFC-12 calibration curve (second order polynomial) and analysis of dried air from Niwot Ridge using the triple-stage adsorbent tube. \circ = CFC-12 standards in air; \blacktriangle = ambient air (Niwot Ridge, CO, USA).

TABLE IV

ANALYTICAL PRECISIONS FROM THREE ANALYSES OF 10-ml LOOP SAMPLES OF A MIXED HALOCARBON STANDARD DEPOSITED ONTO A TRIPLE-STAGE ADSORBENT TRAP WITH 400 ml N₂ CARRIER GAS AT 30°C AND DESORBED AT 200°C

Compound	Concentration (ppb)	Precision (sample standard error, $n = 3$) (%)	
		Peak area	Ratio to CFC-12
CFC-12	15.6	2.8	—
CFC-11	3.00	3.3	0.47
CFC-113	1.27	3.7	1.26
CH ₃ CCl ₃	6.37	2.2	0.57
CCl ₄	10.2	2.5	0.28
HCFC-22 (O ₂ -doped ECD)	4.99	4.3	0.86

low present-day background air values. Standard errors of the peak areas were 4% or less, and improved to 1% or less when ratioed to CFC-12. The ratio technique might be used to account for errors arising from sample volume measurement, and collection/recovery efficiency variations, at stations where independent CFC-12 measurements are available (*e.g.*, NOAA Baseline Monitoring Stations [12]).

It has been shown that ambient levels of CFC-12, CFC-11, CFC-113 and HCFC-22 can all be detected in 500-ml air samples using the Chrompack cryotrap/Shimadzu GC-9A system used in this work [12]. The question remains as to whether adequate sensitivity can be obtained for ultra-trace levels of HFC-134a and HCFC-123. Direct injections of HFC-134a and HCFC-123 standards were made into the cryotrap to assess detection limits. HFC-134a was measured with an ECD temperature of 275°C, a standing current of 0.5 nA, and oxygen doping to a final concentration of 0.2% within the ECD cell. A 10-ml loop injection of a 47.4 ppb HFC-134a standard gave a peak area 15.8 times the peak threshold; *i.e.* a detection limit of 3.0 ppb for a 10-ml sample. This implies a detection limit of 6 ppt in a 5-l air sample concentrated on an adsorbent trap. Fig. 8, however, indicates that at the cryotrapping temperature of -165°C, HFC-134a was inefficiently trapped, thus improved detection limits should be possible with a more efficient refocussing trap. We are presently addressing this issue.

The detection limit for HCFC-123 was determined with a 3- μ l gas syringe injection of a 16.0

ppm HCFC-123 standard into the carrier gas entering the cryotrap. It was found that although oxygen doping enhanced the HCFC-123 signal it also enhanced the baseline noise. A lower *S/N* was obtained without oxygen doping. In this instance the ECD temperature was 325°C and the standing current was 0.5 nA. The peak area was 80.8 times the area threshold, giving a detection limit of 0.198 ppm for the 3- μ l injection, equivalent to a detection limit of 0.12 ppt for a 5-l air sample.

These detection limits are, however, ideal in that no account has been made for interference from other compounds in real air samples. The presence of large amounts of water vapor or CO₂ can severely affect chromatographic separation. We noted that when ambient air samples of several liters volume were collected directly on to the traps, without

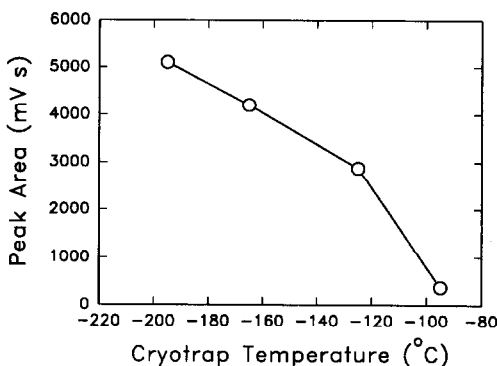


Fig. 8. Effect of cryotrapping temperature on HFC-134a peak size.

any attempt to remove water vapor or CO₂, the cryotrap became plugged during trap desorption. Both Carbosieve and Carboxen are carbon molecular sieves, and as such are strong adsorbers of CO₂. The carbon molecular sieves are hydrophobic, but the manufacturer's information for HayeSep D_B shows that it can be used to separate water vapor in near-ambient temperature chromatography, thus we suspect that some water vapor may be retained by this trap.

Flushing the trap with dry nitrogen prior to desorption should remove the water vapor, but it is unlikely that CO₂ can be similarly removed without also losing some of the desired analytes. We have been able to prevent trap plugging by sampling air through a trap filled with Aquasorb (P₂O₅ on a vermiculite base: Mallinckrodt, Paris, KY, USA) and Ascarite (NaOH on a silicate base: Thomas Scientific, Swedesborough, NJ, USA) to remove water vapor and CO₂ respectively. CO₂ collection might also be avoided by selection of different adsorbents, although there appears to be no suitable alternative for Carboxen in the present application, or by reflushing with an adsorbent trap operated at a temperature above the freezing point of CO₂. We are currently investigating this latter option.

CONCLUSIONS

Adsorbents can be selected to perform sample concentration of volatile halocarbons and hydrohalocarbons at ambient temperature. Due to the large variations in boiling point and adsorbent affinity between the compounds of interest, it is necessary to use a multiple-stage adsorbent to be able to both trap and recover all of the species. Further work is needed to validate these findings in the field: in particular the effects of humidity and CO₂ adsorption on collection efficiency.

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