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Evaluation of Carboxen carbon molecular sieves for trapping replacement chlorofluorocarbons

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ABSTRACT

A method has been developed for trapping and preconcentrating the very volatile replacement chlorofluorocarbons (hydrofluorocarbons and hydrochlorofluorocarbons) using microtraps filled with Carboxen, a carbon molecular sieve type material, without the need for extensive cryotrapping using liquid nitrogen. We present here the adsorption characteristics of four Carboxen materials, Carboxen 569, 1000, 1001, and 1002, used to trap a range of replacement chlorofluorocarbons varying in boiling point from −48.4 to −9.8°C. The application of these traps for the automated analysis of trace gases in atmospheric and environmental chemistry could prove extremely useful.

INTRODUCTION

Since the signing of the Montreal Protocol (1987) agreeing to phase out the production and use of ozone depleting chlorofluorocarbons (CFCs), much emphasis has been directed towards the replacement of these compounds with environmentally more acceptable alternatives. A group of compounds currently being tested as alternatives are the hydrochlorofluorocarbons (HCFCs) and the hydrofluorocarbons (HFCs, the name which is adopted to describe all alternatives for this study). It is envisaged that these very volatile compounds will react more readily with tropospheric hydroxyl radicals thus reducing their atmospheric lifetimes and therefore their ozone depleting potential [1]. As a consequence it is anticipated that the atmospheric mixing ratios for the HFCs will initially be in the ppt to sub-ppt (v/v) range. The accurate measurement and long-term monitoring of these compounds, as well as other trace organic contaminants in air, therefore requires a preconcentration step before analysis using gas chromatography (GC) or GC-mass spectrometry (MS).

The use of sampling tubes packed with adsorbent materials has proved a popular method for trapping organic pollutants present at trace levels in the atmosphere [2–6]. However, the commonly used adsorbents such as Tenax TA, Porapak Q, Porapak T, and Carbopak do not have the adsorptive capacity necessary to trap the very low boiling HFCs unless a cryogenic preconcentration step is used. The usual approach would be to use a fairly large primary trap and then thermally desorb into a small secondary trap or short length of capillary tubing (or column), which is cooled in liquid nitrogen [7–10]. This ensures that the sample is cryofocussed into a narrow band in order to optimise chromatographic res-

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TABLE I

PHYSICAL CHARACTERISTICS OF CARBOXEN ADSORBENTS

Carboxen adsorbent	Mesh size	BET surface area (m^2/g)	Porosity volume[a]		
			Micropore (3–20 A)	Mesopore (20–500 A)	Macropore (> 500 Å)
569	40–60	485	0.20	0.14	0.10
1000	60–80	1200	0.44	0.16	0.25
1001	60–80	500	0.22	0.13	0.11
1002	60–80	1100	0.36	0.28	0.3

[a] Approximate values.

olution during a rapid final desorption step. In remote atmospheric monitoring stations there are considerable technical and logistical difficulties in routinely providing liquid nitrogen. Furthermore, the maintenance of automated cryogenic traps is equally difficult in remote field locations. It would therefore be desirable to use adsorbents which can be maintained at practical operating temperatures for both trapping and desorption steps.

Preliminary experiments with a number of the more commonly used adsorbents indicated that they had insufficient capacity to trap the trace HFCs from several litres of ambient air. It was found that the most suitable adsorbents for trapping the HFCs were carbon molecular sieve type materials called Carboxens [11] (Supelco). The adsorbent characteristics of these materials were evaluated for the HFCs using two different methods: (a) indirect sample introduction [12–14] and (b) direct sample introduction [14–16], a full description of the two types of method is described later in the paper.

TABLE II

PHYSICAL CHARACTERISTICS OF HFCs

Compound	Structure	Boiling point (°C)	M_r
HFC 125	CF_3CF_2H	-48.4	120
HFC 143a	CF_3CH_3	-41.6	84
HCFC 22	$CHClF_2$	-40.8	86
HFC 134a	CF_3CH_2F	-25.9	102
HCFC 124	CF_3CFHCl	-11.8	136
HCFC 142b	CH_3CF_2Cl	-9.8	101

EXPERIMENTAL

Adsorbents and adsorbates

The physical characteristics of the Carboxen materials evaluated in this study are listed in Table I, and cover the range of HFCs being currently evaluated by industry as replacement compounds for existing CFCs. The physical characteristics of these compounds are described in Table II.

Indirect method of sample introduction

Sample preparation and chromatographic conditions. Gas samples were prepared by static dilution of individual pure gases (supplied by ICI, Cheshire, UK). A known volume of each HFC (200 μl) was transferred using a gas syringe to a glass flask (100 ml) equipped with a rubber septum cap. The flask had previously been purged with nitrogen to reduce possible sample contamination. A 20-μl portion of the sample gas was then injected into the gas chromatograph.

The instrument used was a Varian Model 3700 gas chromatograph (Varian, Palo Alto, CA, USA) equipped with a flame ionization detector. A variety of adsorbent traps were used and their dimensions are listed in Table III. Each trap was conditioned at 200°C for at least 12 h in a stream of nitrogen (20-30 ml/min). Nitrogen was used as the carrier gas at a flow-rate of 2-4 ml/min depending upon which trap was being evaluated.

Specific retention volume data for each adsor-

TABLE III

DIMENSIONS OF CARBOXEN TRAPS

Carboxen material	Trap dimensions (cm)	Adsorbent bed weight (mg)	Mesh size
569”	27 × 0.08 O.D. × 0.05 I.D.	15	40-50
1000^b	57 × 0.63 O.D. × 0.51 I.D.	560	60–80
1000’	30 × 0.16 O.D. × 0.05 I.D.	40	60-80
1001^b	60 × 0.63 O.D. × 0.51 I.D.	786	60-80
1001’	30 × 0.16 O.D. × 0.05 I.D.	48	60–80
1002”	30 × 0.08 O.D. × 0.05 I.D.	80	80–100

[a] Trap used for indirect injection method.
[b] Trap used for direct injection method.
[c] Trap used for both injection methods.

bent-adsorbate interaction were obtained by injecting duplicate samples of each HFC standard at 3-5 different column/trap temperatures. These adsorbate retention volumes were used to construct a straight line plot of the specific retention volume (log V_g^1) *versus* temperature $(1 \cdot 10^3/K)$. This straight line was subsequently extrapolated via linear regression analysis to obtain V_g^1 values at ambient and sub-ambient temperatures.

Direct method of sample introduction

Sample preparation and chromatographic conditions. A 30-l electropolished stainless-steel canister containing a pressurised sample of HFC 125 (1.46 ppm) was prepared by injecting 1 ml of pure HFC 125 into the evacuated cylinder and pressurising to 325 p.s.i. (1 p.s.i. = 6894.76 Pa) with halocarbon-free nitrogen to give an approximate concentration of 1.5 ppm. A laboratory-made system was constructed to enable direct injection of the HFCs into the microtraps. A diagram of the system is shown in Fig. 1. The HFC sample canister was connected to the microtrap via a pressure regulator (Porter Instruments Model 8286) and a flow controller (Brooks Instruments Model 8744A, Hatfield Co., Hatfield, PA, USA). Nitrogen and the HFC 125 standard was passed into a six port gas sampling valve (Rheodyne Model 7010, Cotati, CA, USA) and flowed either to vent or the microtrap depending upon the position of the valve. The flow rate of the gases were balanced using a flowmeter and a needle valve on the vent side and a mass flow transducer (Scott Speciality Gases, Plumsteadville, PA, USA) situated in line after the microtrap. A flame ionization detector, part of a Carlo Erba Model 490 gas chromatograph was connected in line with the microtrap via a short length of deactivated fused-silica tubing.

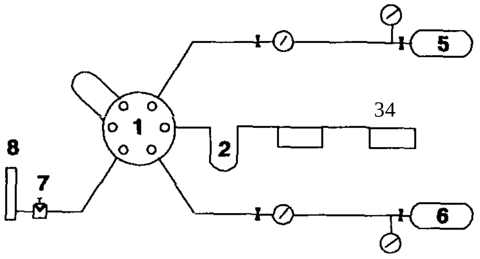

Fig. 1. Schematic diagram of the direct injection apparatus. 1 = Six-port valve; 2 = microtrap; 3 = flow transducer; 4 = flame ionization detector; 5 = carrier gas; 6 = HFC sample; 7 = needle valve; 8 = flow meter.

RESULTS AND DISCUSSION

Indirect method of sample introduction

A trap packed with Carboxen material can be regarded as a short chromatographic column, therefore, injection of a vaporized sample of each HFC will produce a chromatographic peak with a retention time dependent upon sample-adsorbent interactions and oven temperature.

Sample retention time data at a range of oven temperatures can be used to calculate the specific retention volume, V_g^1

$$V_g^1 = \frac{3}{2}\left(\frac{(Ip/Op)^2-1}{(Ip/Op)^3-1}\right)Fa\left(\frac{Tc}{Ta}\right)\left(\frac{(t_r-t_a)}{Wa}\right)$$

where ***Ip*** and ***Op*** are the trap inlet and outlet pressures respectively, ***Fa* is** the carrier flow-rate through the trap at ambient temperature (ml/min), ***Tc*** is the trap operating temperature (K), ***Ta*** is the ambient temperature, t_r and t_a are retention times (min) of the sample and methane, respectively, and ***Wa*** is the weight of adsorbent (g).

The breakthrough volume (BTV) at any trapping temperature of interest can be obtained by linear extrapolation of the graph log V_g^1 vs. 1/T determined at temperatures higher than the trapping temperature. This method is useful as a relatively quick means of estimating a particular trap capacity, and is typically more precise when using temperatures which approach the boiling points of the analytes.

Specific retention volumes *versus* $1/T$ values were plotted for each HFC on Carboxens 569, 1000, 1001 and 1002. The resulting straight line plots were extrapolated to give BTV data at temperatures as low as − 50°C. It was assumed that the extrapolated lines would be linear at sub-ambient temperatures. and correlation coefficient data was used to determine the variances associated with the plots. The results of the BTV calculations for the compounds of interest at temperatures between 20 and − 50°C are presented in Tables IV–VII, and these results are illustrated graphically in Figs. 228. CFC 13B1 has been included in some of these experiments as it acts as a useful surrogate for the HFCs when using an electron capture detector, which is insensitive to most HFCs.

The results indicate that no single characteristic trend exists for the HFC group of compounds. The elution order for the HFCs on carboxen 569 and 1000 follow. however, an expected pattern taking into account the compounds boiling points, molecular sizes and possible surface interactions.

The order in terms of BTVs is: 143a < 125 < 134a < 22 < 142b < 124. It is interesting to note that this is also the elution order for these HFCs when chromatographed on a Poraplot Q column [17]. One unexpected observation is the exceptionally high BTV for HFC 125 on Carboxen 1001 (see Table VI). At this stage, we believe that HFC 125 has a very non-linear adsorption isotherm. Since the pore size of Carboxen 1001 has been expanded this could result in HFC 125 fitting perfectly into the pores of the adsorbent material and thus being

TABLE IV

BTVs FOR HFCs AT VARIOUS TEMPERATURES ON CARBOXEN 569

Temperature (°C)	BTV (ml/mg)						
	143a	125	134a	22	13B1	142B	124
20	1.3	4.8	1.3	28.0	3.1	44.x	204.9
15	1.7	6.5	10.0	37.1	4.0	61.9	303.5
10	2.1	9.0	13.8	49.8	5.2	86.6	456.0
5	2.7	12.6	19.2	67.4	6.8	122.4	694.9
0	3.5	17.9	27.0	92.4	9.1	175.3	1075
-5	4.6	25.7	38.6	128.1	12.2	254.4	1692
-10	6.1	37.3	56.0	179.8	16.5	374.8	2710
−15	8.2	55.0	82.3	255.8	22.6	560.2	4419
-20	11.1	82.4	122.8	368.9	31.5	850.7	7344
-25	15.2	125.4	186.1	539.8	44.3	1313	12452
-30	21.2	194.3	287.1	802.8	63.2	2065	21594
-35	29.7	306.5	451.1	1213	91.6	3309	38327
-40	42.4	493.0	722.32	1867	134.9	5410	69670
-45	61.5	810.1	1181.5	2930	202.1	9042	130137
-50	90.6	1360	1974.5	4687	308.1	15457	249783

TABLE V

BTVs FOR **HFCs** AT VARIOUS TEMPERATURES ON CARBOXEN 1000

Temperature (°C)	BTV (ml/mg)						
	143a	125	**134a**	22	**13B1**	142b	124
20	7.65	10.90	13.18	14.34	–	198.57	351.52
15	9.68	13.98	16.90	18.40	–	266.87	481.83
10	12.37	18.10	21.88	23.84	–	362.62	668.23
5	15.93	23.63	28.57	31.15	–	497.92	937.17
0	20.72	31.17	37.69	41.11	–	691.95	1331.2
-5	27.19	41.53	50.22	54.81	–	973.18	1915.4
-10	36.09	55.96	67.69	73.92	–	1387.3	2795.7
-15	48.40	76.26	92.26	100.82	–	2004.4	4139.9
-20	65.68	105.21	127.31	139.20	–	2938.4	6225.1
-25	90.18	146.98	177.89	194.64	–	4372.5	9513.1
-30	125.53	208.28	252.15	276.08	–	6618.0	14802
-35	177.17	299.53	362.71	397.42	–	10193	23465
-40	253.68	437.31	529.69	580.82	–	15984	37918
-45	369.20	649.55	786.99	863.63	–	25585	62626
-50	546.17	981.58	1189.6	1306.5	–	41799	105719

retained longer. Betz *et al.* [12] reported that the diameters of the micropores and the percentage of micropores present for a particular sieve are directly responsible for variances in specific retention volumes for different sized adsorbents. Supelco also reports [11] that the adsorbent strength of the carboxens increases towards volatile materials as follows: 1001 > 1000 > 569. However, our research

TABLE VI

BTVs FOR **HFCs** AT VARIOUS TEMPERATURES ON CARBOXEN 1001

Temperature (°C)	BTV (ml/mg)						
	143a	125	134a	22	**13B1**	142b	124
20	1.59	65.34	3.61	6.34	3.07	31.76	50.40
15	2.10	106.46	4.91	7.93	3.98	43.28	69.96
10	2.82	176.64	6.75	10.01	5.20	59.68	98.30
5	3.81	298.22	9.37	12.74	6.86	83.19	139.74
0	5.22	513.52	13.19	16.36	9.15	117.43	201.31
-5	7.22	901.93	18.78	21.20	12.32	167.87	293.89
-10	10.12	1619.7	27.12	27.76	16.79	243.36	435.50
-15	14.38	2974.5	39.72	36.12	23.15	357.84	655.07
-20	20.70	5594.4	59.05	49.10	32.32	534.20	1001.3
-25	30.23	10785	89.16	66.41	45.73	810.09	1556.1
-30	44.86	21384	137.02	90.99	65.65	1250.5	2464.5
-35	67.69	43642	214.40	126.34	95.71	1966.0	3979.4
-40	103.91	91748	341.79	177.82	141.72	3149.7	6555.1
-45	162.65	199514	556.56	254.21	213.64	5155.5	11045
-50	259.6	448782	925.73	369.10	327.87	8621.4	19040

TABLE VII

BTVs FOR HFCs AT VARIOUS TEMPERATURES ON CARBOXEN 1002

Temperature (°C)	BTV (ml/mg)						
	143a	125	134a	22	13B1	142b	124
20	1.71	1.50	2.05	1.90	–	40.51	60.22
15	2.16	1.88	2.57	2.37	–	53.75	80.82
10	2.74	2.36	3.25	2.97	–	72.07	109.65
5	3.50	2.99	4.15	3.77	–	97.60	150.33
0	4.51	3.82	5.35	4.81	–	133.70	208.57
-5	5.88	4.92	6.95	6.20	–	185.26	292.84
-10	7.74	6.41	9.12	8.07	–	260.04	416.71
-15	10.29	8.43	12.10	10.61	–	369.74	600.99
-20	13.84	11.21	16.23	14.10	–	533.04	879.33
-25	18.83	15.07	22.02	18.94	–	779.56	1305.9
-30	25.95	20.52	30.28	25.78	–	1158.7	1972.4
-35	36.25	28.31	42.18	35.53	–	1751.4	3031.5
-40	51.36	39.58	59.58	49.64	–	2693.0	4743.2
-45	73.91	56.17	85.50	70.40	–	4222.9	7574.3
-50	108.08	80.95	124.62	101.39	–	6752.8	12343

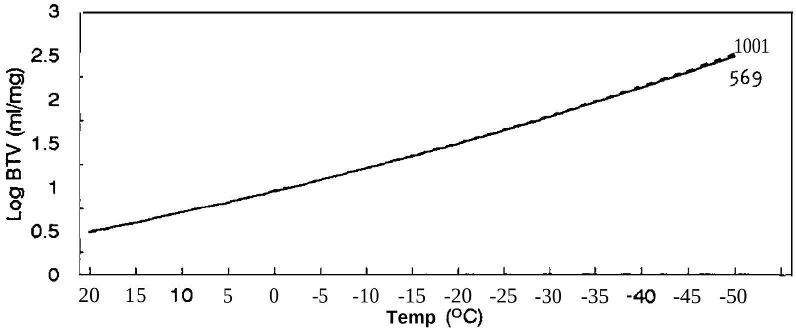

Fig. 2. Log BTV of CFC 13B1 *versus* temperature using Carboxen 569 and 1001.

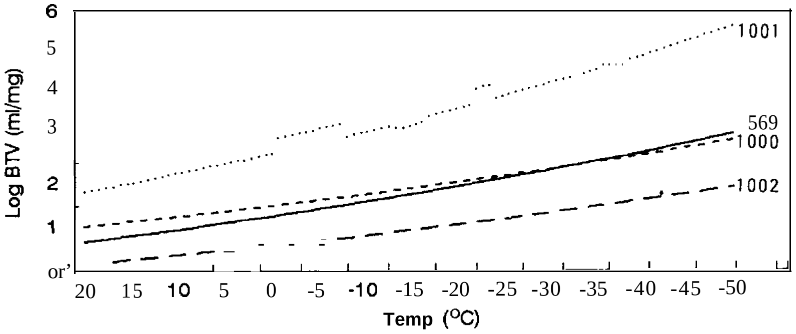

Fig. 3. Log BTV of HFC 125 *versus* temperature using Carboxen 569, 1000, 1001 and 1002.

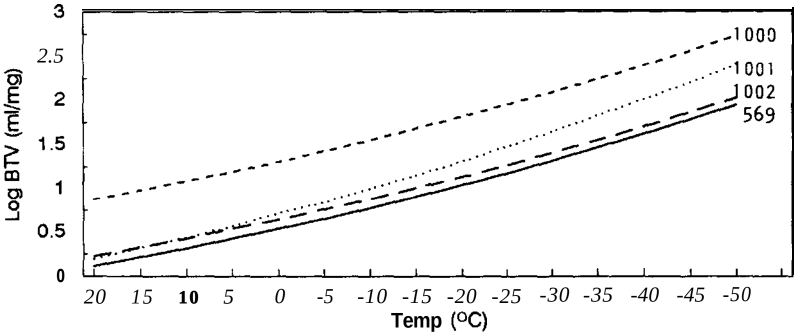

Fig. 4. Log BTV of HFC 143a *versus* temperature using Carboxen 569, 1000, 1001 and 1002.

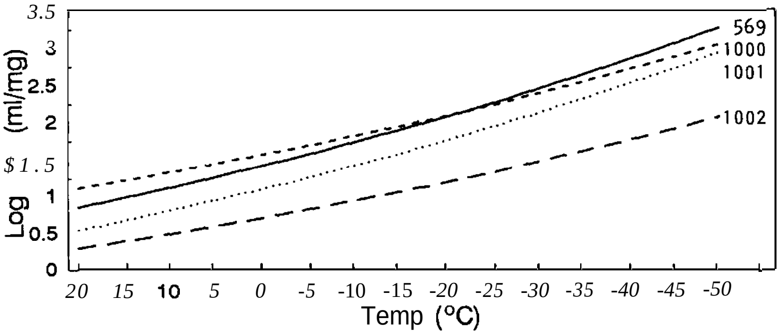

Fig. 5. Log BTV of HFC 134a *versus* temperature using Carboxen 569, 1000, 1001 and 1002.

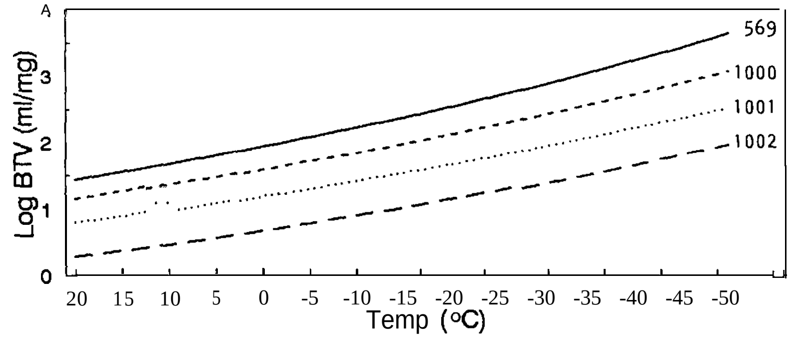

Fig. 6. Log BTV of HFC 22 *versus* temperature using Carboxen 569, 1000, 1001 and 1002.

indicates that for the HFCs at a sub-ambient temperature of -50°C the adsorbent strength of the different Carboxens is very compound dependent, as summarised in Table VIII. Clearly from these results either Carboxen 1000 or 569 would be the best general adsorbent for most HFCs. One other important observation is that although HFC 125 (b.p. −48.4°C) has a slightly lower boiling point than HFC 143a (b.p. −47.6°C) it is more strongly retained on both Carboxen 569 and 1000. Similarly, HFC 22 (b.p. −40.8°C) is again more strongly retained than the higher boiling HFC 134a (b.p.

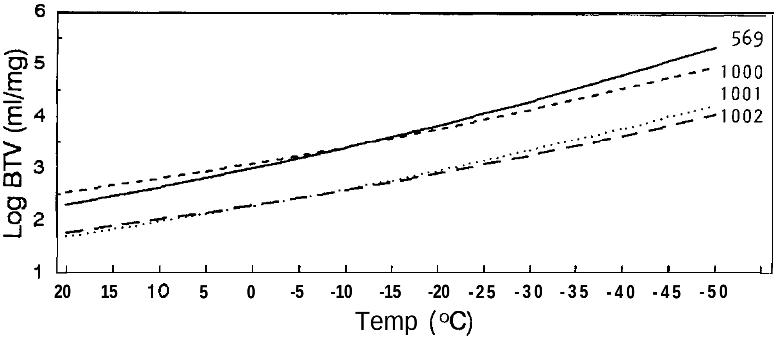

Fig. 7. Log BTV of HFC 124 *versus* temperature using Carboxen 569, 1000, 1001 and 1002.

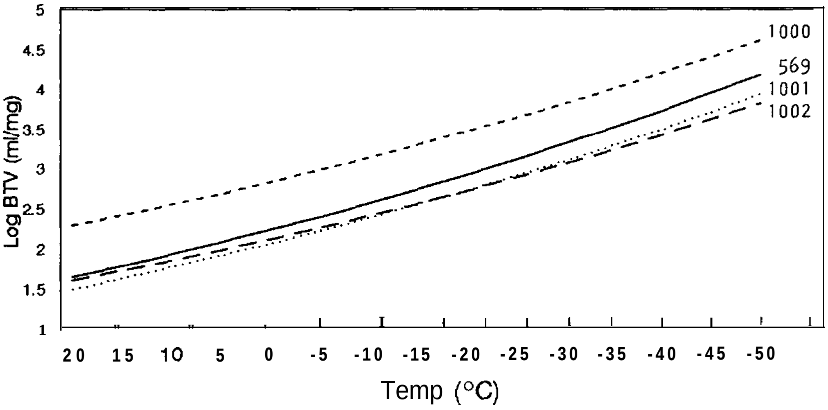

Fig. 8. Log BTV of HFC 142b versus temperature using Carboxen 569, 1000, 1001 and 1002.

−25.9°C). We attribute this to the presence of a single hydrogen atom in HFC 125, and HFC 22 which undergoes stronger interaction through hydrogen bonding with the adsorbent. The molecular size and shape (*i.e.* surface area, volume) is also thought to be responsible for differences in adsorption in the micropores. Previous work [18] utilizing dichloromethane indicates the presence of larger (i.e. macro, meso) pores in the sieve structure which permits greater usage of the microporous region due to the more effective transfer within the porous regions. Micropore diameters also play an important role in the adsorption process.

TABLE VIII

ACTIVITY ORDER OF DIFFERENT CARBOXENS

Boiling point (°C)	HFC	Carboxen activity order
-48.4	125	1001 > 569 > 1000 >1002 (indirect)
		1000 > 569 > 1002 > 1001 (direct)
-47.6	143a	1000 > 1001 > 1002 > 569
-40.8	22	569 > 1000 > 1001 > 1002
-25.9	134a	569 > 1000 > 1001 > 1002
− 11.8	124	569 > 1000 > 1001 > 1002
-9.8	142b	1000 > 569 > 1001 > 1002

Since the BTVs are reported in terms of ml per mg of adsorbent in all of our tables, we can quickly estimate the amount of adsorbent required to quantitatively trap each HFC for any size air sample. For all practical purposes, it is only necessary to determine the amount of adsorbent required for the least strongly retained HFC, since all other more strongly retained HFCs will also be trapped quantitatively. As an example, HFC 143a is one of the

TABLE IX

COMPARISON OF **BTVs** FOR HFC 125 ON VARIOUS CARBOXEN MATERIALS USING A DIRECT AND INDIRECT METHOD OF SAMPLE INTRODUCTION

Carboxen	Temperature (“C)	Direct injection		Indirect injection	
		BTV (1)	BTV **(ml/mg)**	BTV (1)	BTV **(ml/mg)**
569 (15 mg)	17.9	0.10	6.55	0.09	6.03
569 (15 mg)	18.2	0.10	6.17	0.09	5.98
1002 (80 mg)	17.5	0.36	4.50	0.14	1.79
1000 (560.5 mg)	18.4	> 12.22	>21.80	1.25	12.94
1000 (40 mg)	21.3	1.03	25.84	0.41	10.24
1000 (40 mg)	-1.4	1.35	33.74	1.35	33.75
1001 (48 mg)	21.0	0.08	1 .77	2.85	59.85

most difficult compounds to trap, and if we assume a trapping temperature of − 40°C and a 2-l air sample, then the following amounts of each Carboxen would be needed: Carboxen **569, 47** mg; Carboxen **1001, 19** mg; Carboxen **1000, 8** mg; Carboxen 1002, 39 mg. The small amounts of adsorbent required, especially for Carboxen 1000, are consistent with the design of our microtraps where we expect to maintain good chromatographic resolution without the need for post desorption cryogenic focusing. Preliminary desorption studies carried out in our laboratory support this view. These results will be published as soon as trials have been completed.

Because of the large extrapolation needed to obtain retention volumes at ambient temperatures with the indirect method described above, the same carboxen traps were also evaluated by the direct (continuous flow) method of sample introduction.

TABLE X

COMPARISON OF **BTVs** FOR THE CFC **13B1** FOR INDIRECT METHOD OF INJECTION AND THE DIRECT INJECTION RESULTS USING 50 mg OF CARBOXENS IN ADSORPTION TUBES

Carboxen material	Temperature (‘C)	Direct injection BTV **(ml/mg)**	Indirect injection BTV **(ml/mg)**
569	-21.6	14.35	31.47
1001	-22.1	38.90	32.33
1001	− 22.0	39.66	32.33

Direct method of sample introduction

Carboxen microtraps were used under frontal analysis conditions, whereby a constant concentration of individual **HFCs** flowed continuously at a nominal flow-rate of 20 ml/min through a microtrap maintained at a constant temperature. Initially the sample was completely retained by the adsorbent material, however, over time the gas volume flowing through the trap exceeds the retention volume of the sample, resulting in sample breaking through the adsorbent. Sample breakthrough was monitored by the flame ionization detector and the signal response displayed on a chart recorder. **BTVs** are normally quoted as the point at which 5% breakthrough occurs, however in order to directly compare the indirect and direct analysis results BTV was taken when the detector signal reached 50% of its maximum value.

It was not possible to determine **BTVs** for Carboxen 1000 and 1001 on the original columns used in the indirect method since they contained large amounts of adsorbent material (1000: 560.5 mg, and 1001: 786.1 mg), and their expected **BTVs** would be very large. Therefore, two new micro-columns were prepared containing substantially less of each adsorbent (1000: 40 mg, and 1001: 48 mg). A comparison of **BTVs** achieved using the two methods of analysis can be seen in Table IX. As a further check BTV results achieved at an earlier date using glass adsorption tubes and CFC **13B1** were also compared as is shown in Table X.

With the exception of HFC 125 on Carboxen

1001, the results indicate that the two methods of determining BTV correlate well, if anything the faster indirect method has underestimated the BTVs for the HFCs. The BTV for HFC 125 on Carboxen 1001 by the direct method is substantially lower than predicted using the indirect method of injection, where the steep slope of the regression line did appear anomalous. Therefore, as indicated in Table VIII, Carboxen 1000 would be the preferred adsorbent for all of the HFCs if we discount the unexpected and anomalous behaviour of HFC 125 by the indirect method.

CONCLUSIONS

The HFCs are only weakly adsorbed on most of the conventional adsorbents used in air pollution studies. To quantitatively trap these volatile compounds requires the much stronger adsorbents of the carbon molecular sieve type (Carboxens). Extrapolation of BTVs to ambient and sub-ambient temperatures from plots of the log of their retention volumes *versus* temperature provides a reasonable estimate of adsorbent capacity. However it is recommended that comparison of sample breakthrough also be checked by the more direct method of frontal chromatography, particularly where adsorbates have unusual adsorption isotherms.

Our detailed studies of the Carboxens indicate that several hundred milligrams of these adsorbents would be needed at ambient temperatures to ensure complete trapping of trace concentrations of the HFCs from a 1-2-1 atmospheric sample. However, maintaining the strongest carbon molecular sieve, Carboxen 1000, at sub ambient temperatures (− 40°C) during the trapping process, reduces the amount of adsorbent required to about 10-20 mg. This small amount of adsorbent permits the design of a small microtrap with near capillary dimensions, thus reducing the dependancy on liquid nitrogen for cryofocussing. Research is continuing in our laboratories to assess quantitative recoveries of various HFCs and CFCs from the Carboxen materials.

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