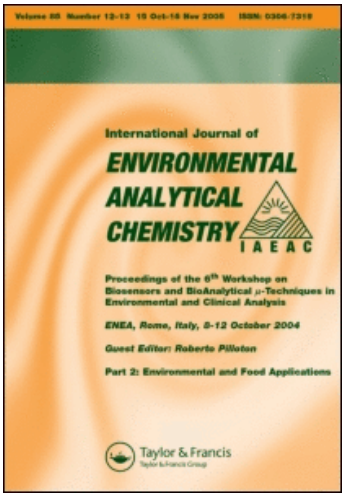

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Measurement of Methyliodide and Halocarbons in the Atmosphere

Y. G. Gritsun[a]; S. F. Watts[a]; J. Wibrow[ab]
[a] School of Biological and Molecular Sciences, Oxford Brookes University Headington, Oxford, UK [b] Division of Atmospheric Research, CSIRO, Mordialloc, Victoria, Australia

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MEASUREMENT OF METHYLIODIDE AND HALOCARBONS IN THE ATMOSPHERE

Y. G. GRITSUN, S. F. WATTS and J. WIBROW*

School of Biological and Molecular Sciences, Oxford Brookes University Headington, Oxford, OX3 0BP, UK

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Current methods of chlorofluorocarbons (CFCs), and some halocarbons (including methyliodide (MeI)) calibration and measurement are reviewed and compared. A new hybrid calibration system is described and assessed. Trapping systems with different media (Tenax GC, Porasil C, and Porapak Q) have been compared experimentally. Of these Porasil B was found to be the most appropriate. A novel dual capillary gas chromatography (GC) method, and one involving dual packed columns, have been set up with these trapping and calibration systems. Our results indicate that the dual capillary method performs better in terms of detection limits, resolution and analysis time for MeI than other previously published methods. Detection limits for MeI are 0.1 pptv, with a total error over the whole calibration/trapping/separation process of 25% (±12%) in the pptv range. This compares very favourably with literature data. Results of measurements of MeI at Oxford using the capillary system are reported.

KEY WORDS: Halocarbons, methyliodide, CFCs, gas chromatography, atmospheric chemistry.

INTRODUCTION

The concentrations of MeI and other halocarbons in the atmosphere and oceans have been the subject of intense interest for a sustained period of time[5,15,16,18,20,25,34]. Numerous analytical systems have been employed to different ends in different environments. Examples range from atmospheric emission of methylbromide from strawberry fields using long-pathlength Fourier Transform InfraRed spectroscopy (FTIR)[14], to the distribution of MeI-131, produced by accidental leaks (or explosions) from nuclear power stations, using wet chemical methods[24].

The most widely used technique for these quite demanding analyses is GC with electron capture detection (ECD)[8,21,25]. The main problems which make these analyses demanding are: (i) the very low ambient concentrations of the species of interest; this is demanding in itself, but places extra strain on the calibration systems in use; (ii) the very divergent concentrations of species of interest; (iii) the presence of water in the atmosphere which must be excluded from most of the column systems used.

There are a number of methods in use for the analysis and sampling of halocarbons in air[10,11,17,29,35]. They vary in the method of trapping and preconcentration, injection systems employed, type of chromatographic columns used, method of calibration (if any), *etc.* Most methods employ a cold trap to preconcentrate the halocarbons from the air[12,26].

*Current address: Division of Atmospheric Research, CSIRO, Private Bag Number 1, Mordialloc, Victoria, 3195, Australia.

Sample air is pumped through the trap and the halocarbons are stripped. The volume of air passing through the trap is measured. The trapping preconcentration system consists of glass beads at 90 K (liquid oxygen temperature)[26] or Porasil C[12], at 200 K (dry ice temperature). Some of the automated systems use different strategies (to exclude water), *e.g.* the use of micro-traps packed with organic polymer and molecular sieve sorbents[7,10]. Other methods preconcentrate at room temperature[23], whilst yet others use direct injection without preconcentration[29]. Both capillary and packed columns are used.

The methods employing a packed column usually require a pre-column, which allows back-flushing of high-molecular-mass compounds and water to exclude them from the main separation column[12,17,26]. Other methods which employ wide-bore capillary columns of different polarity connected in series[7], give better resolution but slightly less good detection limits, and still need the preconcentration stage[4,22].

Recent work on MeI in the atmosphere describes a method which uses direct injection of the sample without any preconcentration procedure[29]. Although as published there are no details of detector modification, as written the method requires a detector sensitivity of *ca.* 0.1 fg MeI s^{-1}. Clearly this is considerably better than the standard ECD detector (see Table 4) below.

A variety of calibration methods are in use for the halocarbons and CFCs, but probably the most reliable is the permeation tube method[2,6]. The lowest concentrations of MeI reported in air are 0–10 pptv[25–27,29]. These authors used different calibration procedures based on permeation tubes and standard mixtures.

Given the very active interest in this area, the aims of this work were to improve selectivity and sensitivity of the GC method for halocarbons (especially MeI) and CFCs in air, as well as to evaluate the precision and accuracy of the method.

EXPERIMENTAL

The instruments used in this work were Hewlett-Packard 3390A ECD GCs. The MeI used in the calibration was BDH laboratory-grade. Chloroform and carbon tetrachloride where BDH Analar grade. Samples of various CFCs were kindly donated by ICI. The GC calibration strategy employed a hybrid diffusion-dynamic method (using a permeation tube to provide the MeI and CFC sources, and a volumetric mixing chamber (Figure 1)).

Standard additions of halocarbons (including MeI) and various CFCs were used to calibrate the system, using standard gas sampling loops (10, 50, 250, 1000 µl) and Valco automated gas sampling valves. Two separation methods were compared in this work, one a modified dual packed column system[12], and the other using a novel dual capillary column set. The use of open-tubular wide-bore capillary columns allowed the use of low splitting ratios, hence better detection limits. Trapping techniques were also examined (see later), and this resulted in adoption of Porasil C in the trapping stage for all subsequent comparison work.

RESULTS AND DISCUSSION

The permeation tube was weighed over a several day period to generate the mass loss/time curve necessary to standardise the system. The permeation tubes used were standard polypropylene centrifuge tubes into which the MeI or halocarbons were sealed. The time required for the system to come to equilibrium and the rate of permeation through the ampoules depended mainly on the ambient temperature (Figure 2).

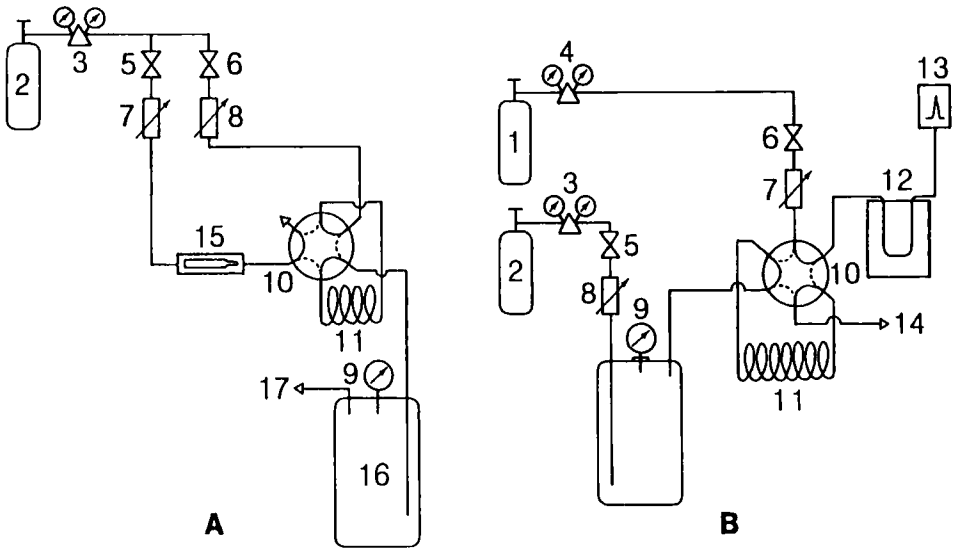

Figure 1 Schematic diagrams for the preparation of gas mixtures (A) and trap testing (B). Key: (1) nitrogen cylinder; (2) argon (with 5% methane) cylinder; (3,4) pressure regulators; (5,6) needle valves; (7,8) butterfly valves; (9) vacuum gauge; (10) six-port valve; (11) standard gas sampling loops; (12) testing trap; (13) ECD; (14) exhaust; (15) tube with ampoule containing MeI; (16) Monel steel dilution chamber; (17) to GC.

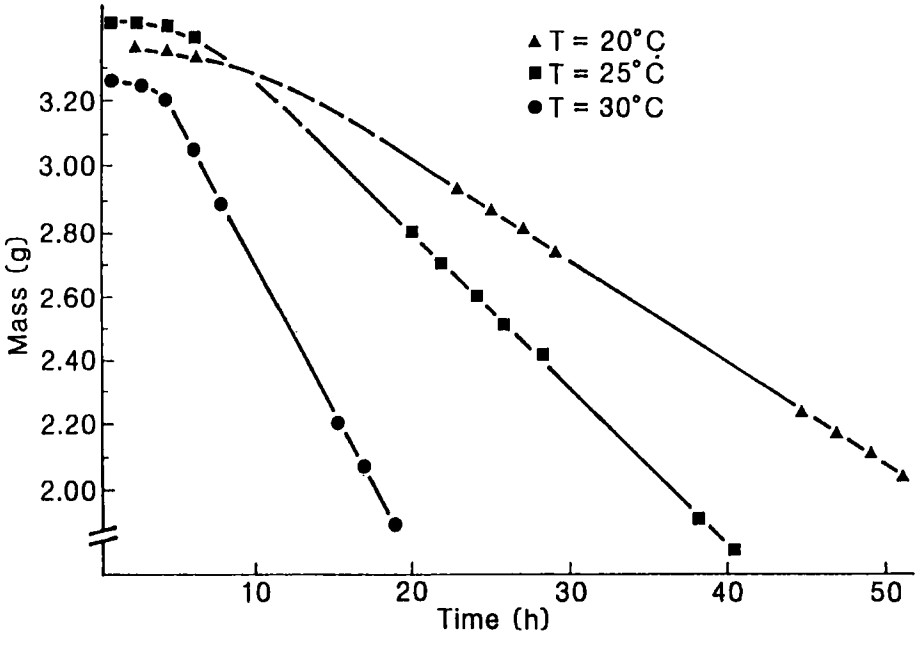

Figure 2 Results of experimental evaluation of MeI diffusion from polypropylene ampoules at temperatures near ambient.

Although the lifetime of the tubes was quite short, this was very convenient and reduced the 'lead in' time of the calibration. Variability of permeation rates between different tubes was less than 5%. The diffusion rate for MeI through the polypropylene tubes was (6.6–10.0) $\times$ 10^{-6} g s^{-1}. Experiments with the flow rate of carrier gas (dry oxygen-free nitrogen (OFN)) showed that the rate of permeation did not vary significantly with flow rate, hence by varying the flow rate of the carrier gas different concentrations of MeI, other halocarbon or CFC in the nitrogen stream were obtained. Calibration mixtures were prepared by injecting a standard volume of MeI, other halocarbon or CFC in nitrogen (from permeation tube) into the volumetric mixing chamber using a standard sample loop (cf. Figure 1). The initial concentration of MeI, other halocarbon of CFC in the volumetric mixing chamber was calculated using the ideal gas law. The absolute accuracy of the overall process depends on that of several parameters; the diffusion rate of the permeation tubes, flow rate of the carrier gas and volumes of the volumetric mixing chamber and standard gas loops. The estimated absolute error of the standard preparation procedure was generally 10%. Our calculations indicate that this is about normal for any permeation tube method operating in the concentration range of this work, including those systems with in-line permeation tubes.

The reactivity and general chemistry of MeI dictate certain requirements of the preconcentration/calibration/GC system. As with reduced sulphur compounds[30,33], glass was excluded from the sample path, and glass syringes were not used in the calibration procedure. As the preparation of gas mixtures of MeI in cylinders under pressure is not possible (for calibration purposes), we used exponential dilution in open system[1]. The pressure in this system was only marginally greater than atmospheric to achieve a slow stream (10–15 cm^3min^{-1}) of the mixture from the volumetric mixing chamber. Clearly, the concentration of MeI decreased exponentially:

$$[MeI]_t = [MeI]_o exp^{(-bt)} \quad (1)$$

where $[MeI]_o$ is the starting concentration in chamber (t = 0), $[MeI]_t$ is the concentration at time t, and b is a constant equal to the flow rate from chamber/volume of chamber.

Using a slow flow rate (5–8 cm^3min^{-1}) this dilution allowed the GC to be calibrated with a random error of less than 5%. The absolute precision of the calibration is about 3%. The systems were calibrated over a range of 2–400 fmol (not maximum) using this method. The slopes of the calibration lines for the packed and capillary column systems were different; the raw data appear in Table 1. The calibration curve for the capillary system was linear (R^2 = 99.4%, σ = 3%), and nearly so for the packed system (R^2 = 98.7%, σ = 4.2%). Instrument stability was excellent over the period of measurements.

Trapping

Preconcentration of a species from a gas stream by stripping onto a solid adsorbent is central to many atmospheric analyses[30,33]. Provided temperature conditions *etc.* are optimised, quantitative trapping will continue until the volume of gas through the trap is equal to the retention volume minus half the base width of the peak. The maximum sample volume (MSV) can be calculated from the retention volume (V_R) and the plate number (N) of the trap:

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

Table 1 Data from two separate calibration events, repetition of calibration was possible over a six-month period with differences in calibration line slopes of ± 2%.

Capillary column		*Packed column*	
MeI /fmol	*ECD detector voltage (mV)*	*MeI /fmol*	*ECD detector voltage (mV)*
2	15	5	28
4	35	10	42
10	65	19	68
20	111	27	120
48	280	52	180
96	410	90	240
190	990	100	420
		205	610
		340	900

Three types of trapping material were tested (Porasil C, Tenax GC and Porapak Q). 250 mg of each were each packed into identical stainless-steel columns (ID 2 mm; length 140 mm), and connected direct to the ECD detector, in the thermostatted oven (Figure 1). Preliminary tests on a cooled glass bead packed column[26] showed it to be considerably less effective than the other packing materials, and so it was not used.

A standard MeI mixture in OFN was injected directly onto each of the columns using a large (3 cm^3) sample loop and gas injection valve. The MSV was taken as the amount of nitrogen that passed through the trap before the ECD signal reached 5% of the maximum value and was determined at different temperatures (Table 2).

Although the adsorption capacities of the Tenax GC and Porapak Q are appropriate, they both require too high temperatures to effect dynamic desorption. (A better use for these adsorbents in this context might be in a cryofocussing system[22], although the use of this type of preconcentration system would almost certainly decrease the precision of the method). Consequently, Porasil C was used in all further work.

Figure 3 shows the capacity of the Porasil C trap with real (air) samples used in the packed column method for MeI and CFC113. These were chosen as they represent extremes of the suite of species of interest. 0°C was chosen as the trapping temperature both to reduce condensation of water in the trap, and also to avoid the trapping of bromine containing halocarbons (found in marine air). These compounds require much colder traps (–20°C < T < –80°C). Clearly the optimum time for trapping is 4 min at 30 cm^3min^{-1} at 0°C. Desorption took place at 150°C by plunging the cooled trap into glycerol at that temperature[32].

GC separation

Two separation methods were compared: one employed packed columns with a backflushing arrangement, and was a variation of a previously published procedure[12]. The other involved a novel system with two wide bore capillary columns in series, largely adapted from references[4,28]. Table 3 and Figure 4 show the conditions of analysis, and schematic diagrams of the apparatus for both methods.

Table 2 MSV (cm^3) for MeI (6 ppb in OFN; flow rate 30 cm^3min^{-1}) on different adsorbents at different temperatures.

Temperature (°C)	*Porasil C*			*Tenax GC*			*Porapak Q*		
	MSV	*n*	*σ*	*MSV*	*n*	*σ*	*MSV*	*n*	*σ*
100	–	–	–	43	3	2	–	–	–
75	–	–	–	55	2	3	1218	2	–
50	52	3	2	120	4	3	1832	6	16
25	99	5	2	348	3	9	> 2000	2	–
0	196	4	3	> 2000	2	–	–	–	–
-25	> 2000	2	–	–	–	–	–	–	–

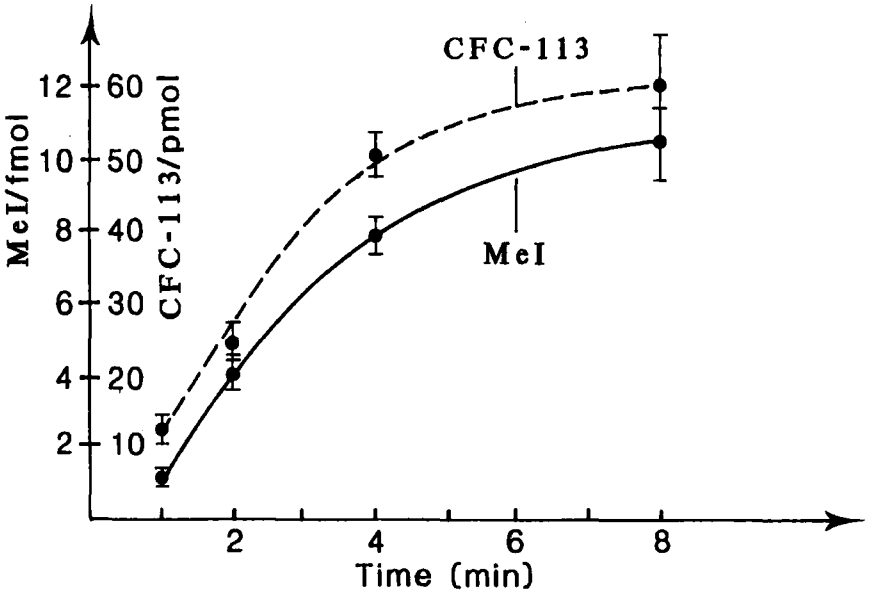

Figure 3 Porasil C trapping efficiency at 0°C: MeI and F113 (error bars 2.5σ).

Table 3 Comparison of several parameters of the two methods used in this work.

	CFC22	*CFC12*	*CFC114*	*CFC11*	*CFC113*	*MeI*	*CCl_4*	*$CHCl_3$*
PACKED COLUMN METHOD								
Relative retention time	1.39	1.39	1.17	1.00	0.77	0.63	0.62	0.48
Relative coefficient of sensitivity	0.004	0.404	0.298	1.00	0.168	1.57	–	–
Number of theoretical plates	$N = 16/a^2 \sim 2000$ (for CFC11)							
Maximum sample size	$V_s = b(Vr/\sqrt{N}) \sim 1.35\ cm^3$ (gas sample)							
CAPILLARY COLUMN METHOD								
Relative retention time	–	–	4.71	1.00	0.78	0.35	0.17	0.09
Number of theoretical plates	$N = 16/a^2 \sim 9200$ (for CFC11)							
Maximum sample size	$V_s = b(Vr/\sqrt{N}) \sim 1.25\ cm^3$ (gas sample)							

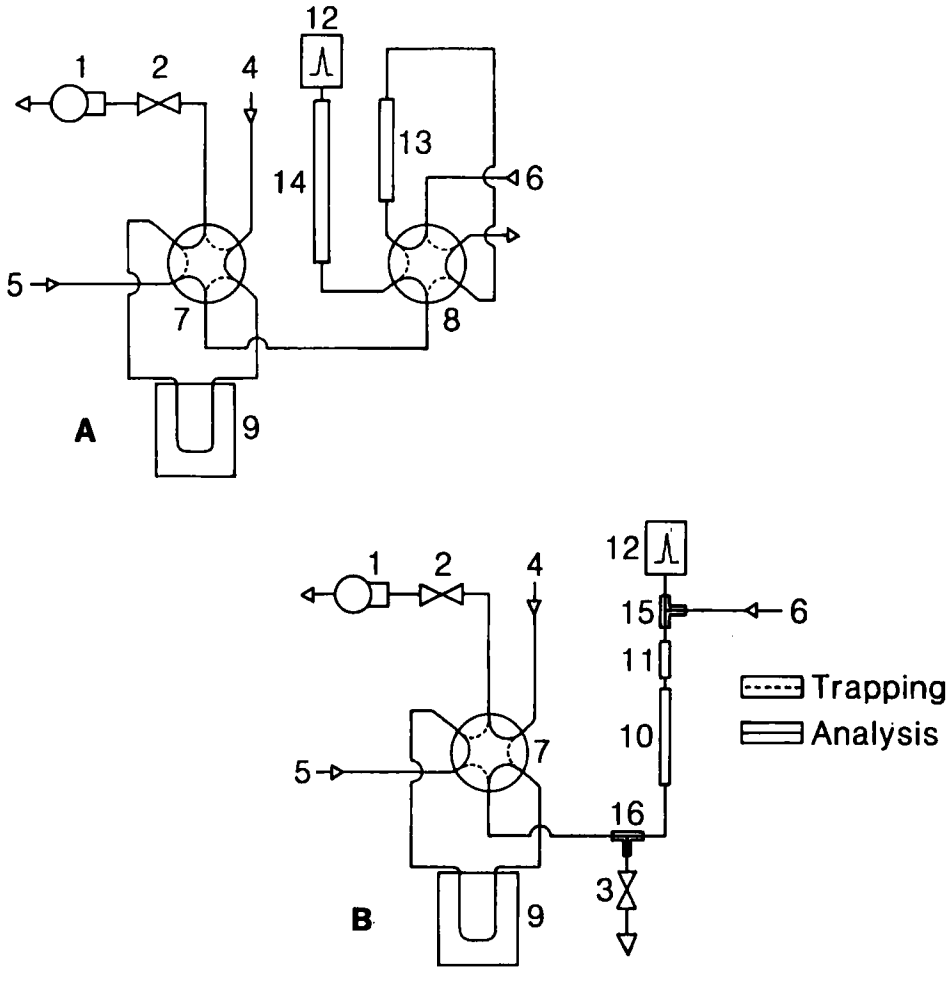

Figure 4 Schematic diagrams for GC analysis using (A) packed and (B) capillary systems. (1) pump; (2,3) needle valves; (4) air inlet; (5,6) argon (with 5% methane) (7,8) six-port valves; (9) trap; (10) capillary [Supelcowax 10; id 0.53 mm, 1–30 m]; (11) capillary [SE 30; id-0.53 mm; 1–15 m]; (12) ECD; (13,14) pre-column [Porasil C 80/100#] and main column [Porasil B, 80/100#]; (15,16) T-splitter.

Typical chromatograms of a standard gas mixture of various halocarbons and CFCs appear in Figure 5. Using these methods, overall repealability for a given standard with repeated injections (automatic six-port sampling valve), was typically 0.5–1.5% for CFCs, and 1–2% for MeI.

The dynamics of the GC separation process and the limits of detection are sensitive to a number of variables including oven and detector temperature, carrier gas flow rate, splitting ratio, and gas scavenger flow rate. Sensitivity analysis on these parameters to determine optimum conditions and the limitations of the methods employed a half-fraction (2^5) orthogonal experiment[3,13]. Peak selectivity, α, was assessed on the basis of neighbouring-peak resolution and number of theoretical plates, N:

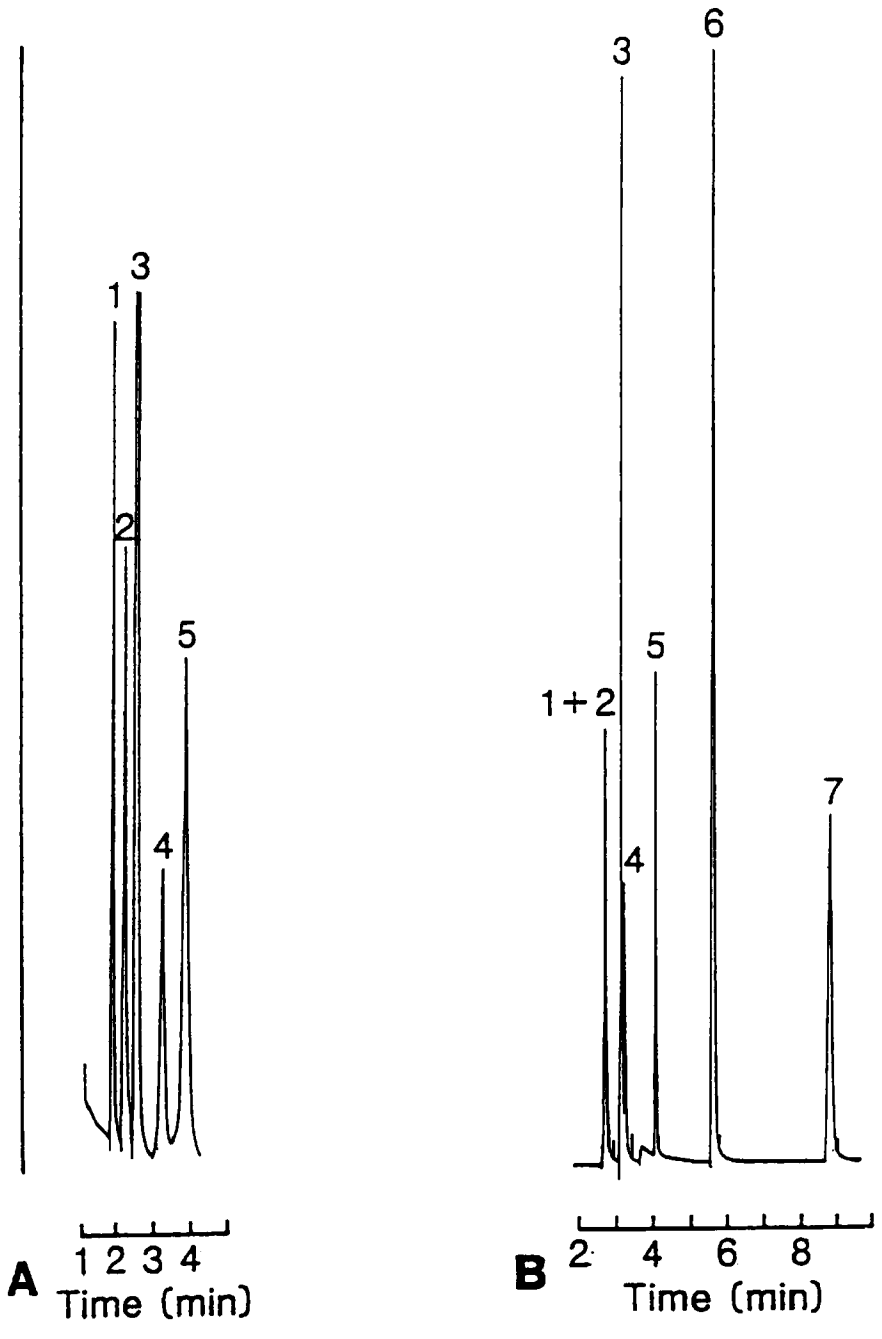

Figure 5 Chromatograms of a standrad halocarbon mixture on the packed (A) and capillary (B) systems. Peaks: 1, CFC12; CFC114; 3, CFC11; 4, CFC113; 5, MeI; 6, CCl_4; 7, $CHCl_3$. Concentrations; MeI 7.6 ppb, CFCs 6 ppb in nitrogen.

$$\alpha = 2(t_2 - t_1)/(w_1 + w_2) \quad (3)$$

and

$$N = 16(t/w_i)^2 \quad (4)$$

where t_1, t_2 are the times of peaks 1 and 2, respectively, and w_1, w_2 are the distances between tangents of the peaks at baseline.

Optimisation of the separation on the capillary system (Figure 6) revealed that increasing the flow rate decreased the theoretical plate height and resolution, but at the same time increasing split ratios increased the detection thresholds making the method more sensitive. The optimum parameters for the capillary system appear to be a flow rate of 4–5 cm^3min^{-1} with a total flow rate of 20 cm^3min^{-1}. This gives a detection limit of 1 fmol of MeI in the detector, a resolution of 0.95 between CFC11 and CFC113, and a selectivity of about 10,000. The detector temperature was found to be critical with best detector sensitivity above 250°C.

The differences between packed and capillary columns are well known: the much lower theoretical plate height in the latter usually result in much better resolution of neighbouring peaks, whereas packed columns with their higher sample loading can often attain slightly better sensitivity than their capillary counterparts. In the case of atmospheric halocarbons, both the resolution and detection limits are important, because of the vast differences in concentration of neighbouring components. It has been pointed

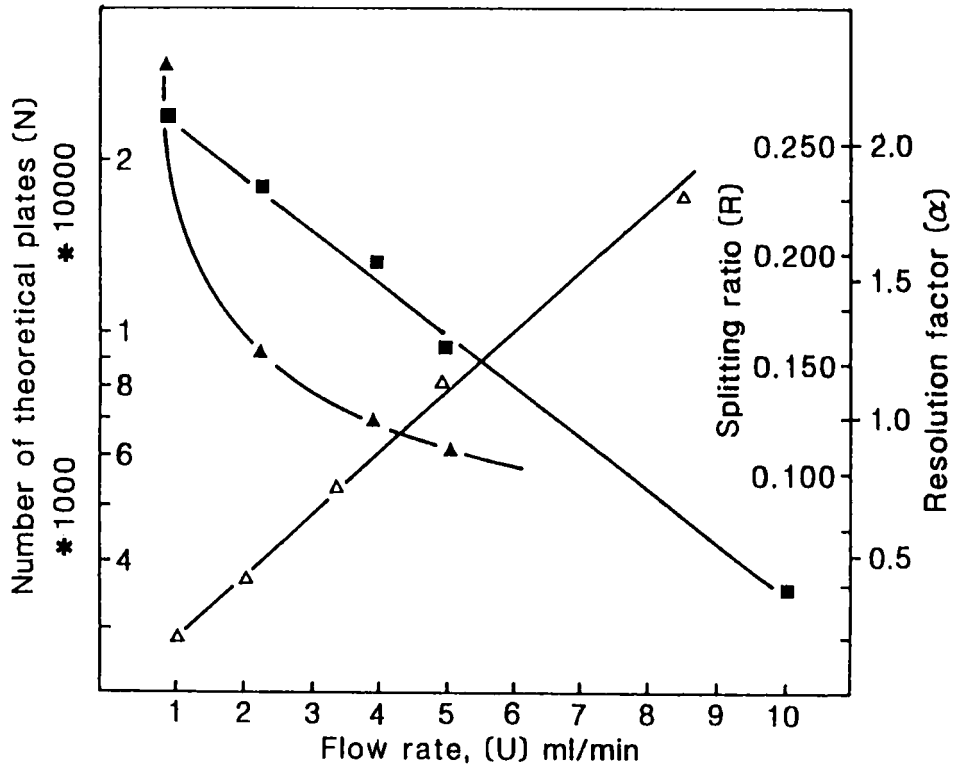

Figure 6 Relationship between carrier gas flow rate (U), number of theoretical plates (n), splitting ratio (D), and resolution factor between CFC11 and CFC113 on the capillary system (s).

out[9] that in most analyses in this field, there are interferences between CCl_4 and MeI. This is inconvenient as CCl_4 is often a hundred times more concentrated than MeI in the atmosphere. Additionally, there are often peaks present that are not readily identifiable. The packed column method[12], which was originally designed for CFCs, avoids some of these problems by 'cutting' the large CCl_4 peak and thus excluding CCl_4 and water from the main column. However, when the halocarbons are also of interest (present at much lower concentrations), the resolution of a packed column system (even with temperature ramping) is not able to distinguish CFC113 or CFC11 from MeI (the atmospheric concentrations of these CFCs are typically 50–150 times greater than those of MeI). The situation becomes worse in marine areas when other natural halocarbons (typically the organic bromides) are present[32]. The packed column method used in this work was based on that previous method[12], and although representing an improvement over that work, it still suffers from the limitations of the original—CFC113 and MeI are not resolvable from each other.

Comparison of the capillary method for MeI adopted in this work with previously published methods for MeI shows it to have improved detection limits, but with a faster analysis cycle, and crucially no interferences from CCl_4 or CFC11 or CFC113 (see Table 4).

Conventional packed columns (see Table 4) employ temperature ramping to effect separation, giving total cycle times of *ca.* 30 min per sample[26], whereas the adopted capillary method is isothermal with a cycle time of *ca.* 10 min per sample. The capillary method adopted also has better detection limits than most of the other methods reported (packed or capillary), and lacks the problems of major interferences by other species. The sensitivities of the ECD detectors used in this work are comparable to those used in other works, with one remarkable exception[29]. The sensitivity reported by these authors seems about twenty times better than that in this or other works.

The total errors of the various parts of the process have been experimentally determined and appear in Table 5. This gives a total error of *ca.* 25% (±12%) on the assembly of processes involved in making a calibrated measurement of a halocarbon (e.g. MeI) in air. This experimental error compares well with other published error estimates[12,26,27], although these authors do not report whether they have assessed the errors in their calibration standards.

Measurements

Figure 7 shows typical chromatograms of air from each of the two systems. The immediate observation is that the chromatogram obtained from the capillary system shows much better resolution of more components than the packed system, as might be expected.

Atmospheric MeI has been measured intermittently at Oxford (UK) for six months between October 1991 and May 1992 with over 300 individual measurements using the capillary method. The sampling site was in a sheltered but essentially urban area of Headington (East Oxford) about 20 m above ground level on the University Campus (Lat 51°41"N, Lon 1°15"W). The data appear in Figure 8 as a temporal plot. Although the data set is not continuous (NB timescale), measured levels of MeI do appear to be lower in the winter than the autumn. This is broadly consistent with the results of other work[25], although the variability of MeI concentrations encountered does not seem as great as in that work. This may be because this work was conducted over the winter months when both general levels and variability seem reduced[25,34].

Table 4 Intercomparision of the GC methods for MeI analysis in atmospheric air.

Preconcentration method	*Separation method*	*Detection limit (*)*
Rasmussen *et al.*, 1982[26]		
100 cm^3 air from flasks; −183°C and 70°C trap/desorb.	Column 10' × 1/4" OD SS, Supelcoport 100/120# + 10% SP2100,	0.25 pptv
6 × 0.25 mm SS trap, glass beads 60/80#	carrier gas: Ar + 5% CH_4, 63 cm^3min^{-1}; detector: 350°C; oven: programmed,	
	start 10°C, 16°C min^{-1}, end 80°C, approx. cycle: 30 min	1.2 fg s^{-1}
Singh *et al.*, 1983[27]		
400 cm^3 air; −183°C and 90°C trap/desorb.	Column 10 m' × 1/8" Nicel, Supelcoport 80/100# + 20% DC200	0.5 pptv
0.16 mm SS trap, glass wool	carrier gas: nitrogen, 40 cm^3min^{-1}, detector: 275°C; oven: 40°C, approx. cycle: 10 min	1.2 fg s^{-1}
Tsetsi *et al.*, 1990[29]		
1.88 cm^3 air;	Column 4 m (?) × 1/8" stainless steel, Chromosorb 80/100# + 10% OV101;	0.1 pptv
direct injection gas sampling valve	carrier gas: nitrogen, 10 cm^3min^{-1}, detector: 150°C; oven: 40°C, approx. cycle: 10 min	0.08 fg s^{-1}
Gammon *et al.*, 1982[12]		
Water samples stripped by sparging	Column 15 cm Porasil B(T = 80°C) + 3 m Porasil B (T = 100°C) both 1/8" SS (?)	–
15 cm 0.32 cm OD SS Poracil C −75°C	detector: 350°C	1 fg s^{-1}
This work		
100 cm^3 air; 0°C and 150°C trap/desorb.	3 m and 3 m (2 mm ID) SS, col and precol; Porasil B 80/100#,	0.1 pptv
14 × 0.2 cm ID stainless steel trap, Poracil C 80/100#	carrier gas: Ar + 5% CH_4, 30 cm^3min^{-1};	
	detector: 300°C; oven: 110°C, backflush gas: Ar + 5% CH_4, 25 cm^3min^{-1},	1.5 fgs^{-1}
	approx. cycle: 10 min	
This work		
200 cm^3 air; 0°C and 150°C trap/desorb.	Fused quartz, wide bore 0.53 m, film 1 m, (1)15 m SE 30, (2) 30 m Supelcowax-10;	0.1 pptv
28 × 0.2 cm ID stainless steel trap, Poracil C 80/100#	detector: 300°C; oven: 55°C, split ratio 1/40, gas scavenger 20 cm^3min^{-1}	1.5 fgs^{-1}
	carrier gas: Ar + 5% CH_4, 30 cm^3min^{-1}, approx. cycle: 12 min	

*Detection limit estimated very roughly as best value for published methods: (1) minimal detectable concentration (pptv) for exactly known volume of air (2) detectability (g s^{-1}) which describes the sensitivity of the ECD detector.

Table 5 Total errors for different parts of the calibration/trapping/analysis process.

Accuracy of gas mixtures from calibration method	< 10% at 1 pptv
Non-linearity of detector and amplifier	3%
GC analysis from factor analysis	5%
Trapping/injector system (experimental)	< 10%

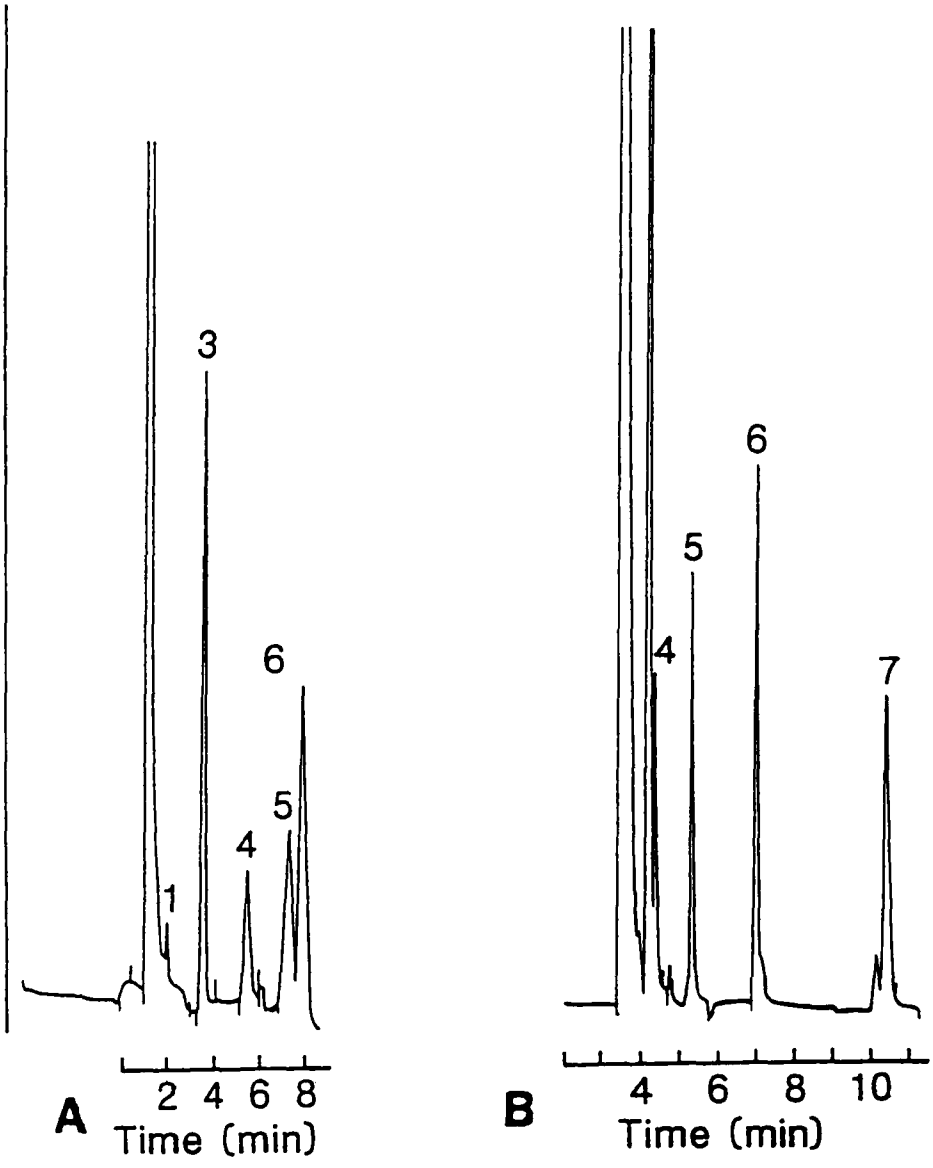

Figure 7 Chromatograms of atmospheric samples on both the packed column with back-flushing (A) and capillary (B) systems. Peaks; 1, CFC12; 2, CFC114; 3, CFC11; 4, CFC113; 5, MeI; 6, CCl_4; 7, $CHCl_3$. Table 4 contains conditions.

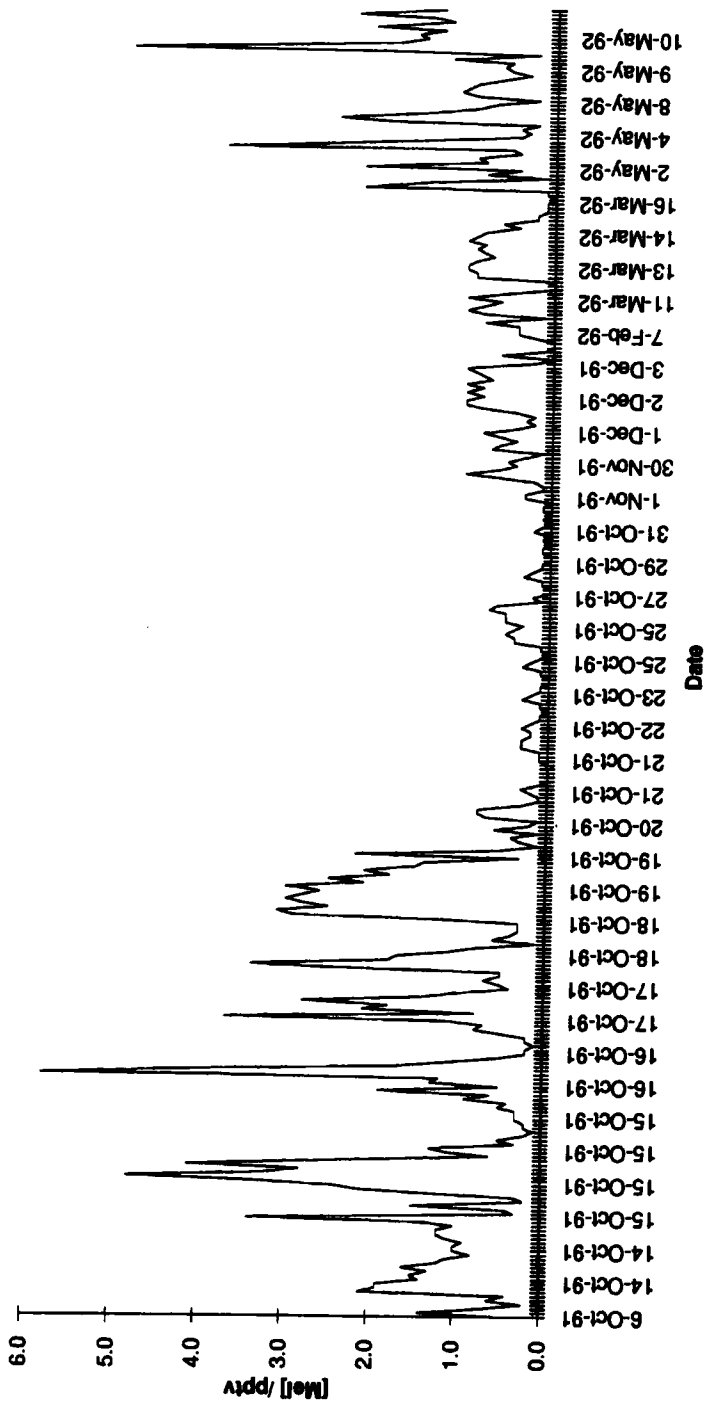

Figure 8 Plot of the atmospheric concentration of MeI as measured at Oxford over the period from October 1991 to May 1992. (Note timescale is not continuous).

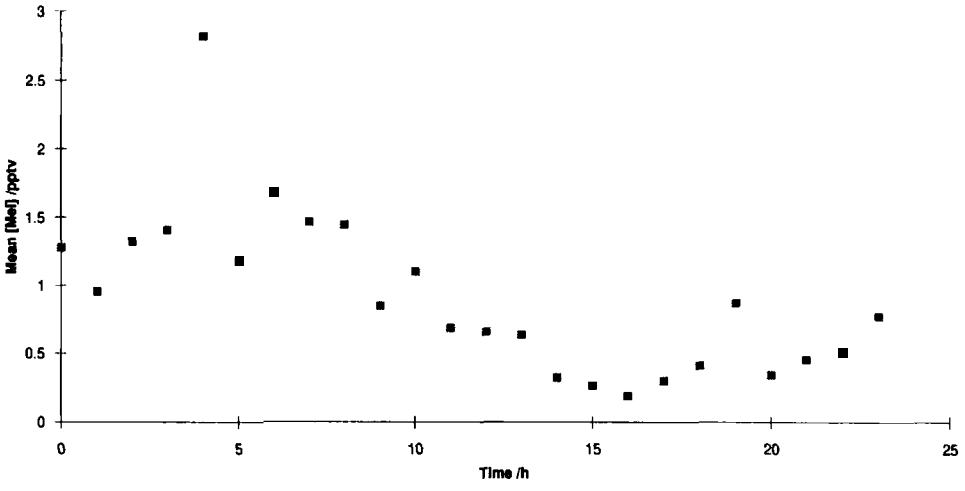

Figure 9 Plot of atmospheric concentration of MeI as measured at Oxford averaged hourly (all data). The error to the determination is ± 12%.

Figure 9 shows the same data plotted on an hourly timescale. There seems to be a marked diurnal variation of MeI with a nightime maximum of *ca.* 2 pptv and average amplitude of more than an order of magnitude. Whilst the explanation for a diurnal cycle in MeI *per se* is not straightforward, careful examination of data from measurements at other terrestrial sites in Norfolk[25] imply a daytime maximum. The phase of the diurnal variation found at Oxford has a nightime maximum. It is possible that Oxford is much more of a terrestrial site than those in Norfolk, or that there are other sources of MeI in the vicinity, either anthropogenic or vegetative[34]. The quoted authors[25] explain most of the variation in their MeI data by the history of the airmass; they hypothesize that marine (Atlantic) trajectories contain more MeI than terrestrial ones and that this is the reason for the [MeI] maxima they observe. However, they also point out that this scenario is a little difficult because MeI has not been detected at measurement sites on the west coast of Ireland where, if their hypothesis is correct, it should be present at high concentrations. Also if their calculated dry deposition rate is correct then most of the MeI should have deposited out before the air mass reached Norfolk. The results of this work would seem to indicate either a terrestrial or anthropogenic source for MeI at Oxford. A meteorological analysis of the full data set (including CFCs and other halocarbons) will appear elsewhere.

CONCLUSIONS

The calibration system described allows the generation of calibration mixtures for MeI and other halocarbons to less than 0.1 pptv with a total error of less than 10%. For the complete system (standard preparation and analysis of air samples), the total error is 25% (± 12%) for low pptv levels. This compares very favourably with other procedures which typically appear to be in the range 15–30%, although many do not report the errors in their calibration standards. Precision on consecutive analysis is better than 2%. A one-

stage preconcentration procedure (trapping at 0°C) reduced the effect of water vapour on the ECD. Halocarbons were easily and completely desorbed at 150°C from the Porasil C. There was no breakthrough with sample sizes of less than 150 cm^3.

Using wide-bore open tubular capillary columns of different polarities connected in series and a high splitting ratio (1:5), a number of halocarbons have been separated and quantified (pptv levels). Limits of detection with this system were found to be about 1 fmol MeI (inj).

Measurements of atmospheric MeI at Oxford using this system indicate that there appears to be variation of MeI on both the seasonal and diurnal timescale.

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