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THE SAMPLING AND DETERMINATION OF HALOCARBONS IN AMBIENT AIR USING CONCENTRATION ON POROUS POLYMER

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SUMMARY

The levels of halocarbons have been determined in rural air in central Michigan using a sampling procedure employing pre-concentration on a porous polymer. The samples were analyzed by gas chromatography (GC) with an electron capture detector. Both qualitative and quantitative confirmation of the results were achieved by GC–mass spectrometry.

Trichlorofluoromethane, chloroform, 1,1,1-trichloroethane, carbon tetrachloride, trichloroethylene and perchloroethylene were determined in the range of 30–130 parts per trillion. These concentrations agree well with data obtained by others in Washington state and Ireland indicating even distribution of the halocarbons in these latitudes.

INTRODUCTION

Recently published reports have stated that air remote from obvious sources of contamination has measurable (parts per trillion, ppt[*]) chlorocarbon and chlorofluorocarbon content[1–6]. Murray and Riley[2] have suggested that the observed levels of chlorocarbons in the troposphere originate from evaporation of commercially produced solvents. Others have proposed that chlorofluorocarbons used as aerosol propellants and refrigerants are contaminating the stratosphere, which may result in partial destruction of the earth's ozone layer[7–9]. Current controversy includes the question of whether chlorofluorocarbons or chlorocarbons would be more significant in ozone depletion. And whereas chlorofluorocarbon presence is accepted as being entirely man-made, the anthropogenic *versus* naturally occurring proportions of chlorocarbon concentrations in the atmosphere are not well understood. The successful resolution of these questions requires the gathering of extensive data.

Existing analytical techniques for the determination of ppt halocarbons include concentration from air cryogenically[10] or on activated charcoal[1,2] followed by gas

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[*] Throughout this article, the American trillion (10^{12}) is meant.

chromatography–electron capture detection (GC–ECD), or the analysis of unconcentrated samples by GC–ECD[5,11], or gas chromatography–mass spectrometry (GC–MS)[5].

The use of specially treated stainless-steel vessels to collect samples may present difficulties for certain substances due to strong adsorption on the vessel walls or even decomposition catalyzed by the metal (or metal oxide) surface. The use of a small (1/4 in. O.D.) sampling tube containing a porous polymer (a non-catalytic surface) to entrain the sample organics, allowing the "fixed" gases to pass through, greatly diminishes the possibility of decomposition. Using thermal desorption, the collected sample is swept off the porous polymer greatly diminishing the irreversible adsorption possibilities.

Attempts to determine ppt halocarbons in air samples without sample concentration have encountered difficulties in purifying GC carrier gases sufficiently to permit these determinations. This is especially true of argon–methane. The use of a pre-concentration technique transforms a ppt analysis into the ppm range, increasing the quantitative ratio of sample halocarbons to carrier gas halocarbons. Thus the purity of the carrier gas need not be as extreme. Moreover, preparation of standards in the ppm range is much more certain than at ppt levels.

Both water and oxygen interfere with electron capture detectors and may cause quite erroneous responses. Oxygen is mostly eliminated from air samples by pre-concentration on sampling tubes and water is removed by use of drying tubes.

Sampling tube pre-concentration is particularly advantageous because of sampling simplicity and to a lesser extent for increasing sensitivity. Ninety percent of the GC column effluent (and thus of the sample) may be discarded via a flow splitter before the electron capture detector to minimize contamination by variable column bleed during temperature programming. Sensitivity is more than ample, avoiding errors in measuring response due to relatively high detector noise at low attenuation.

Air samples were obtained in Midland County (Mich., U.S.A.), an area differing from previously reported work in that it is mid-continent and, at the times of sampling, was roughly 200 miles downwind of the Chicago megalopolis, an urban source of halocarbons.

The halocarbons concentrated from air on a sampling tube were thermally desorbed through a drying tube into an electron capture gas chromatograph with the column at $-40°$. When desorption was complete, the column was temperature programmed to elute the halocarbons and allow their quantitation. The identities and concentrations of the halocarbons detected by electron capture were confirmed by GC–MS.

EXPERIMENTAL

Sampling

Stainless-steel tubes (4 in. × 0.25 in. O.D. × 0.19 in. I.D.) fitted with Swagelok stainless-steel nuts and ferrules were packed with Porapak N porous polymer (80–100 mesh; Waters Assoc., Milford, Mass., U.S.A.) held in place with glass wool plugs. A series of 15 packed tubes was conditioned overnight at 200° with 20-ml/min filtered pre-purified nitrogen flow. The nitrogen filter was a 12 in. × 0.5 in. O.D. aluminum tube containing activated charcoal (60–80 mesh). After conditioning, the

tubes were tightly sealed (except during sampling, analysis or conditioning) with Swagelok stainless-steel caps.

A portable 12 V d.c. air pump (oil-less pump, Model 0333-127-149, Gast Manufacturing Corp., Benton Harbor, Mich., U.S.A.) was used to pull 0.3–3 l of air at flow-rates of 30–150 ml/min through individual Porapak N sampling tubes suspended 1 ft. above ground. Samples were taken at two sites 14 miles apart to check data agreement between locations. The first site, 3 miles south of the city of Midland, was in a farming region, while the second was in a clearing in a deciduous forest, 16 miles southwest of Midland. Both sites were selected to be remote and up-wind (in a southwest wind) of industrial, residential, automotive or other likely sources of halocarbon contamination.

GC apparatus

Sampling tubes were analyzed by GC using the apparatus shown in Fig. 1. The chromatograph was a Hewlett-Packard Model 5700 with linear ECD and carbon dioxide cooling for sub-ambient temperature programming. The front end of the GC column was inserted through the injection port to the outside to allow attachment of sampling tubes with a Swagelok union. The carrier gas, charcoal-filtered argon–methane (95:5) was routed to the injection T which was attached to sampling tubes. A 10:1 splitter was employed at the column exit to discard 90% of the column effluent and thus reduce both detector contamination from column bleed and base-line rise from temperature programming while still providing sufficient sensitivity.

Porapak N sampling tubes collected water from air in addition to halocarbons. This water interfered seriously with operation of the electron capture detector during halocarbon elution. Investigation of inorganic salts as drying agents showed that a 3 in. × 0.25 in. O.D. stainless-steel tube packed with partially dehydrated
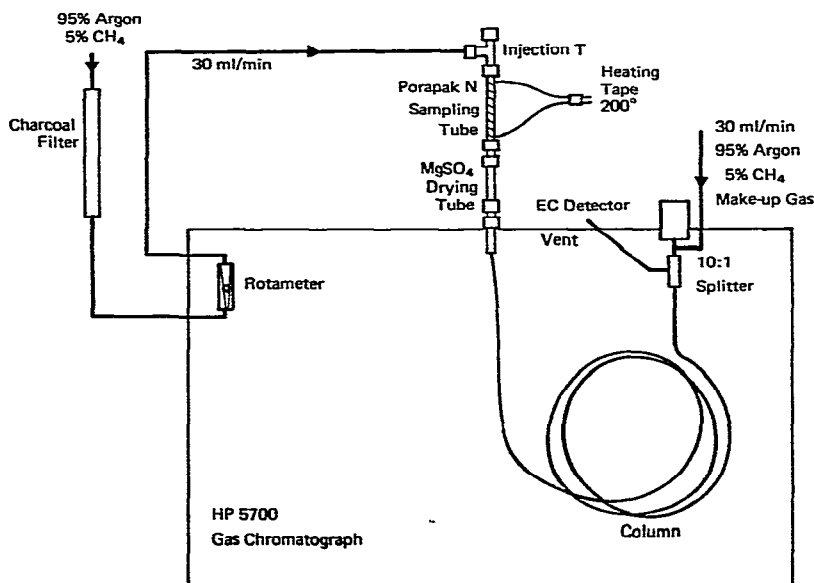

Fig. 1. Electron-capture GC apparatus for trace halocarbon analysis.

$MgSO_4 \cdot 7H_2O$ (ACS grade; Fisher Scientific, Pittsburgh, Pa., U.S.A.) would quantitatively adsorb water desorbed from Porapak N tubes yet permit at least 95% recovery of the halocarbons analyzed. Several other salts were tried as drying agents with the results shown in Table I.

TABLE I

ABILITIES OF DEHYDRATED SALTS TO ADSORB WATER AND PASS HALOCARBONS UNDER CONDITIONS OF ANALYSIS

+ = Yes; − = no; ± = somewhat.

Hydrate of salt	Temp. of dehydration (°C)[13]	Adsorption of water	Passing of halocarbons
$CaSO_4 \cdot 2H_2O$	163	+	−
$Na_2SO_4 \cdot 10H_2O$	100	−	+
$CuSO_4 \cdot 5H_2O$	110 ($-4H_2O$)	+	−
$Na_2WO_4 \cdot 2H_2O$	100	±	+
$CoCl_2 \cdot 6H_2O$	110	+	±
$MgSO_4 \cdot 7H_2O$	150 ($-6H_2O$), 200	+	+

The magnesium sulfate tubes were partially dehydrated by heating a series of eight tubes at 120° for 1 h with 20 ml/min charcoal-filtered pre-purified nitrogen flow. Excess drying was found to result in adsorption of halocarbons, particularly 1,1,1-trichloroethane, in the salt. The series of partially dehydrated tubes was checked for drying ability and absence of halocarbon contamination by attaching the last tube in the series to a conditioned Porapak N tube spiked with 20 mg of water in the apparatus shown in Fig. 1. The water was desorbed and the procedure continued as in a sample analysis. Freedom from water reaching the detector was shown by lack of the characteristic baseline rise and freedom from halocarbon contamination by lack of peaks. Non-adsorption of halocarbons was checked on the first tube of the series by desorbing a standard from a sampling tube through the drying tube in a similar manner. Each drying tube was used for one analysis and then was again partially dehydrated.

Halocarbons were desorbed from Porapak N tubes by heating the tube rapidly to a temperature of 200°, which was then maintained for 15 min. The GC column was maintained at −40° for 8 min and then temperature programmed to produce a chromatogram as in Fig. 2.

GC conditions were as follows. Column: 6 ft. × 0.125 in. O.D. × 0.081 in. I.D. stainless-steel packed with 20% DC-200 silicone oil on 100–120 mesh Chromosorb W AW DMCS HP. Temperatures: oven, (a) −40° for 8 min, (b) program 16°/min to 140°, (c) 140° for 4 min; ^{63}Ni ECD, 250°. Carrier gas flow–rate: 30 ml/min argon–methane (95:5); make-up gas flow [30 ml/min argon–methane (95:5)] was added between effluent splitter and ECD.

Standardization

A stock standard solution of halocarbons was prepared in 2,2,4-trimethyl-pentane. An aliquot of this solution was transferred using a microliter syringe to a
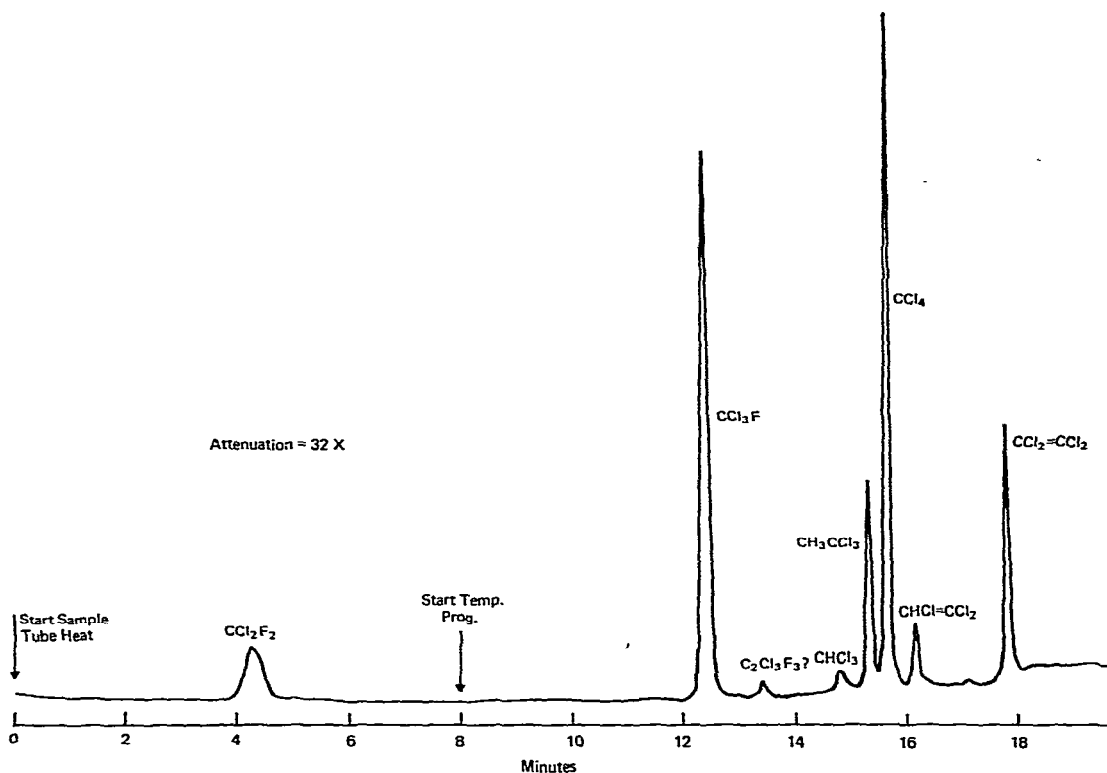
Fig. 2. Electron-capture chromatogram of 1-1 air sample collected 3 miles south of Midland.

300-ml gas sampling bottle containing charcoal-filtered pre-purified nitrogen giving a gas standard with an actual concentration of the order of 1 ppm of each halocarbon. An aliquot of this gas standard (equivalent to 200 ppt of each halocarbon in concentrated air samples) was injected into the GC carrier gas stream flowing into a halocarbon-free Porapak N tube. The tube was reversed and the halocarbons thermally desorbed (back-flushed) into the GC with the oven temperature at $-40°$. The procedure then continued in the same manner as a sample analysis.

Blanks

        Because of the ubiquitous nature of the halocarbons, blanks were repeatedly checked to insure freedom from halocarbon contamination. The GC carrier gas was checked regularly by performing the analysis with an unpacked tube substituted for a Porapak N tube. Sampling and drying tubes after conditioning were also checked. Occasionally, an air sample was taken using two Porapak N tubes in series. When the second tube was analyzed, blank values were obtained which would combine any contamination from the GC carrier gas, sampling tube and drying tube conditioning, sample manipulation, and break-through of halocarbons from the first tube during sampling. Halocarbon levels in blanks were generally less than 10% of the quantities detected in air samples.

Breakthrough volumes

The volume that may be directed through a sampling tube before a particular compound begins to elute (the break-through volume) had been determined for some halocarbons using the technique described previously[12]. Break-through volumes at 23° and 100% humidity were 2 l for methyl chloride, 7 l for carbon tetrachloride and >10 l for 1,1,1-trichloroethane using Porapak N tubes of the dimensions noted. Since sampling of ambient air was performed near 0°, break-through volumes were appreciably greater than these values. Proof that break-through did not occur was obtained by sampling with two tubes in series and confirming that the second tube was halocarbon-free, as described above. Analysis of the second tube indicated that dichlorodifluoromethane broke through under the conditions employed whereas trichlorofluoromethane and the other halocarbons determined did not.

GC–MS confirmation

Sample preparation. Air samples concentrated on Porapak N tubes were analyzed by GC–MS to qualitatively and quantitatively confirm all of the halocarbons detected by electron capture. In order to prevent overpressuring the mass spectrometer, water was removed from the samples by thermally desorbing the halocarbons and water from a sampling tube through a magnesium sulfate tube to a halocarbon-free Porapak N tube. The carrier gas was charcoal-filtered argon–methane (95:5) flowing through the tubes at a rate of 30 ml/min. Blanks were prepared by similarly desorbing halocarbon-free Porapak N tubes through drying tubes into halocarbon-free Porapak N tubes.

GC–MS procedure. The prepared sampling tubes were analyzed on an LKB Model 9000 spectrometer equipped with the batch inlet system and accelerating voltage alternator (AVA) attachment. The trapped organics were desorbed thermally using the
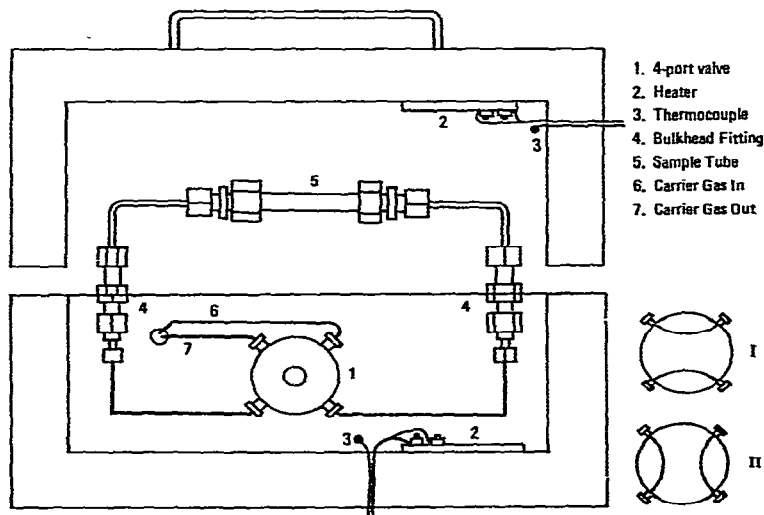

1. 4-port valve
2. Heater
3. Thermocouple
4. Bulkhead Fitting
5. Sample Tube
6. Carrier Gas In
7. Carrier Gas Out

Fig. 3. GC–MS sampling tube desorption apparatus.

apparatus shown in Fig. 3. The tube is attached to the loop and the heated lid replaced. The valve is in position I so that the carrier gas (50 ml/min) flows through the valve and onto the analytical column, and the sampling tube is sealed. The tube is maintained at 180° for *ca.* 5 min when the valve is moved to position II sweeping the volatilized organics onto the analytical column. After 5 more min the valve is moved back to position I and the lid removed to cool the sampling tube.

The analytical column (9 ft. × 0.25 O.D. glass, 20% DC-200 silicone oil on Gas-Chrom Z, 80–100 mesh) is maintained at ambient temperature while the volatilized organics are swept onto the column and is consequently temperature programmed at 12°/min to elute the organics. The mass spectrometer is set to monitor specific *m/e* values during elution of the sample. To tune the spectrometer to the exact *m/e* values, the components are injected into the batch inlet system, and the magnet and AVA controls adjusted. One ion was monitored at a time and the AVA switched manually between component elution times.

The ion current was displayed on a strip-chart recorder after being filtered with an active filter to increase the signal to noise ratio. Fig. 4 shows a typical output from a standard and sample at *m/e* 121 and 129 for the determination of carbon tetrachloride and tetrachloroethylene.
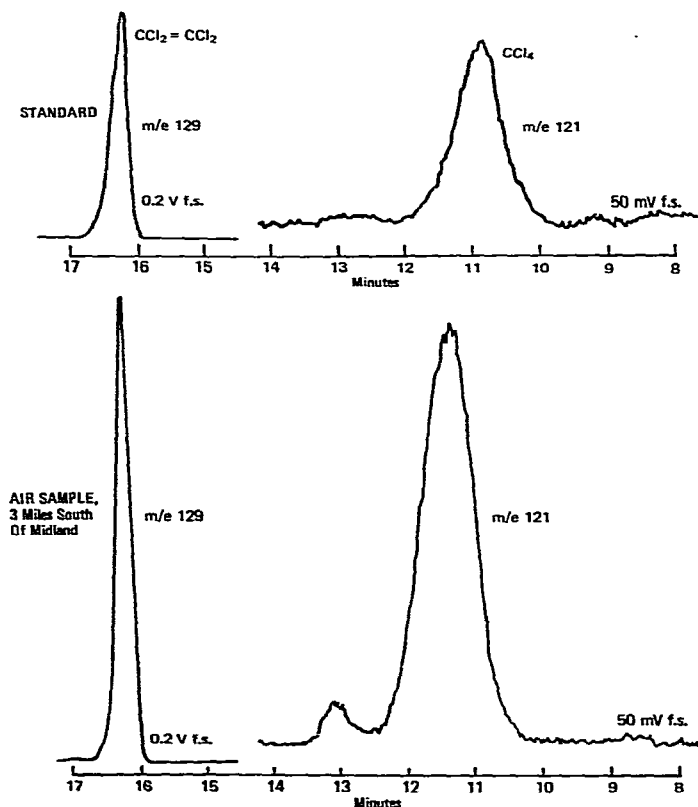

Fig. 4. GC–MS chromatograms of carbon tetrachloride and perchloroethylene.

TABLE II

HALOCARBONS DETERMINED IN AIR SAMPLES COLLECTED SIMULTANEOUSLY AT SITES 14 MILES APART

All samples were 1 l except C and D, (3 l). Sample D was analyzed 2 weeks later than C.

Site	Sample	CCl_3F		$CHCl_3$		CH_3CCl_3		CCl_4		$CHCl=CCl_2$		$CCl_2=CCl_2$	
		ppt	ng/m^3	ppt	ng/m^3	ppt	ng/m^3	ppt	ng/m^3	ppt	ng/m^3	ppt	ng/m^3
16 Miles	A	110	700	30	180	80	500	80	600	30	150	30	200
SW of	B	120	700	—	—	90	500	90	600	30	150	30	200
Midland	C	130	800	20	100	110	600	100	700	30	150	40	300
	D	110	700	—	—	120	700	100	700	40	200	40	300
3 Miles	E	140	800	—	—	110	700	100	700	90	500	50	300
S of	F	100	600	30	140	80	500	80	500	60	300	40	300
Midland	G	110	700	30	140	90	500	80	500	70	400	30	200

Methyl chloride analysis

Because of poor ECD sensitivity, methyl chloride was determined by GC–MS only. Samples of 300 ml air at −4° were taken 3 miles south of Midland. These were analyzed by a procedure similar to the above GC–MS analyses except that the column was a 9 ft. × 0.25 in. O.D. glass Chromosorb 101 (80–100 mesh) porous polymer, m/e 50 was monitored and water removal prior to analysis was not necessary. The precision of the analysis was not as good as that for the other halocarbons because of high blank values, from unknown sources, equal to almost half of the quantity of methyl chloride detected in air samples.

RESULTS AND DISCUSSION

Table II lists data from samples collected the same afternoon (March 6th, 1975) at two sites 14 miles apart. Halocarbon concentrations are expressed as ppt (v/v) and ng/m³. Sample reproducibility is better than ±20% as is agreement between locations. Exceptions are trichloroethylene, which was present at different concentrations at the two sites, and chloroform, which appeared to be subject to random contamination.

GC–MS data are shown in Table III and compared to concentrations of halocarbons determined by GC–ECD to be present in Midland County in March, 1975. In addition to qualitatively confirming the compounds detected by electron capture, MS analyses provided excellent quantitative confirmation.

Data published by three other researchers are compiled in Table IV. The good agreement with Lovelock[4], and Grimsrud and Rasmussen[5], corroborates the methods used. In addition, the levels of halocarbons in these latitudes from Washington state to Ireland appear to be evenly distributed. The detected halocarbons are apparently wide-spread and well mixed in the air at sea level. The higher levels of carbon tetrachloride found over the Atlantic compared to over land may be indicative of a natural marine source of carbon tetrachloride.

The high levels of trichloroethylene and perchloroethylene observed can be attributed to higher local levels or perhaps output from the Chicago megalopolis.

TABLE III

GC–MS CONFIRMATION OF GC–ECD

All samples (except CH_3Cl) were taken March, 1975.

Compound	Samples from 16 miles SW of Midland		Samples from 3 miles S of Midland		m/e monitored	Intensity (%) **
	ECD (ppt)	MS (ppt)	ECD (ppt)	MS (ppt)		
CCl_3F	130	130	110	140	101	100
CH_3CCl_3	110	100	90	80	99	63
$CHCl=CCl_2$	26	24	70	60	130	100
CCl_4	90	90	90	80	121	32
$CHCl_3$	30	50*	30	30	83	100
$CCl_2=CCl_2$	40	50*	40	50	83	4
	40	50	50	50	129	83
CH_3Cl	—	—	—	520	50	100

* Interferences present.
** Intensity of m/e chosen expressed as percentage of most intense ion in spectrum of that compound.

The data shows that halocarbons evolved from that area had been diluted sufficiently by mixing with cleaner air to preclude gross contamination 200 miles downwind.

Two general approaches to sampling atmospheric halocarbons have been attempted by various scientists involving either air sampling with or without concentration of the samples. Each has its own advantages and disadvantages. Whole-air sampling collects all the components into the sample container without the possibility of losses due to incomplete trapping. However, the storage of the sample prior to analysis may lead to difficulties for some substances due to adsorption or reactions on the container surface. The analysis of the sample requires the detection and quantitation of picogram quantities with concomitant difficulties in the preparation of standards for calibration. In other words, the difficulties encountered are mainly in the calibration and detection portion of the analysis.

The sample concentration procedures reported using cryogenic trapping present nanogram quantities of materials to be analyzed making the preparation of

TABLE IV

COMPARISON OF DATA (ppt)

Compound	Murray (NE Atlantic, 8–72)[1]	Lovelock		Grimsrud (Pullman, Wash., 1–75)[5]	Midland county, 3–75
		W. Ireland, 6–74[4]	N. Atlantic, 10–73[4]		
CCl_3F	—	80	89	125	120
$CHCl_3$	0.3	27	19	20	30
CH_3CCl_3	—	65	75	100	90
CCl_4	0.04	111	138	120	100
$CHCl=CCl_2$	1.0	15	<5	<5	30
$CCl_2=CCl_2$	0.7	28	21	20	40
CH_3Cl	—	—	—	530	520

standards less difficult but still utilizing relatively large (several liters) sample volumes and, therefore, surface area. The sampling apparatus is larger than with the whole-air method due to the use of liquified gases requiring well insulated containers. Also, due to the condensed nature of the sample, reactions may occur among the various constituents. Here the burden of possible difficulties lies in the sampling, with the calibration and detection being more conventional.

We report here a sampling method which employs a small container (and battery-operated pump) which may minimize surface effects during storage of the sample prior to analysis. Thermal desorption of the sample minimizes irreversible adsorption. However, very low boiling substances (*e.g.*, dichlordifluoromethane) may elute through the sampling tube under certain conditions which limits the extent to which these substances may be concentrated. As with other pre-concentration procedures, the preparation of standards is less difficult than with whole-air sampling. This, then, is a complementary method to the others reported. An additional advantage may lie in the ability to greatly concentrate compounds less volatile than the halocarbons studied and still deliver them for analysis, thus extending the analysis of ambient air to these types of substances.

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