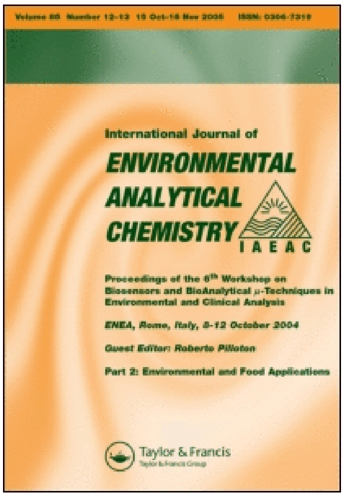

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Development and Application of a Method for Monitoring Methyl Chloride in Ambient Air

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A method is presented for the routine measurement of methyl chloride in air at sub-ppb levels. Methyl chloride in 1–2 liter of air is trapped onto active charcoal, then desorbed and concentrated onto a capillary trap, and subsequently analyzed by gas chromatography using an Al_2O_3/KCl PLOT capillary column and flame ionization detector. Levels of CH_3Cl range from 200 ppb at points near a factory known to use this compound in its manufacturing processes to 0.2 ppb, corresponding to background levels, at points 1.5 km from the factory. Proper placement of the sampling locations is essential when measuring CH_3Cl emissions from a point source.

KEY WORDS: Methyl chloride, CH_3Cl, air pollution.

INTRODUCTION

Methyl chloride (CH_3Cl) is one of the more difficult compounds to quantify at low ppb* levels in environmental samples due to its high volatility and low response to conventional GC detectors. However, the advent of commercially available "cold trap" injectors allows more and more chemists to tackle such analytical problems. Earlier studies have demonstrated the feasibility of such analyses and discuss the problems involved.[1–4]

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*ppb = parts per billion. All concentrations in this study are expressed as volume CH_3Cl/volume air.

In this report we present the application of a method, developed at our laboratory for the analysis of CH_3Cl concentrations in ambient air at different distances from a factory using this compound in its manufacturing process.

The analytical method is based on pre-concentration of CH_3Cl in a 1–2 liter air sample onto active charcoal, thermal desorption from the charcoal onto a capillary trap maintained at $< -90°C$, subsequent thermal desorption and separation on an Al_2O_3/KCl PLOT fused silica capillary column, and detection using a flame ionization detector. The method is reasonably rapid (total GC analysis time ca. 25 min), reproducible, and sensitive. The detection limit is ca 0.05 ppb, corresponding to ca 0.2 ng CH_3Cl in 2 liters of air. This is sufficient for monitoring background levels of methyl chloride.

EXPERIMENTAL

Sampling

Charcoal tubes for sampling were prepared by packing glass tubes (160 mm long, 3 mm i.d.) with 250 mg coconut-based active charcoal (Catalog No. 226-09, SKC Inc., Eighty Four, PA, USA). Glass wool was used to plug both ends of the tubes. Glass drying tubes (ca 100 mm long, 5 mm i.d.) containing 50 mm powdered $MgClO_4$ were prepared in the same way. The $MgClO_4$ had been passed through sieves to remove particles larger than 2 mm and smaller than 0.5 mm, which otherwise could produce irregularities in air flow during sampling. The charcoal tubes were purged with ca. 10 ml/min N_2 gas at 300 °C overnight to remove contaminants, then sealed with Swagelock plugs using Teflon ferrules.

Between one and two liters of air were collected using battery-powered pumps (SKC Universal Sampler model 124). Two charcoal tubes were connected in parallel to each pump, each preceded by a drying tube to remove moisture, which could otherwise greatly reduce the adsorptive capacity of the charcoal. All connections were made using short lengths of silicone tubing. A capillary restrictor was used to insure reliable operation of the pump at the low flow rates.

Prior to and after the sampling period, all pumps were calibrated using a soap-bubble flow meter connected in series to a charcoal tube and a drying tube. The pressure drop across these tubes was negligible. Flow rates were typically 100–125 ml/min, and were controlled using a calibrated rotameter during sampling. The pumps were started by automatic timers, permitting sampling of different locations during the same time period.

In order to obtain a representative picture of the emissions, samples were taken at three different periods under different meteorological conditions (see Table 1). During each sampling period one sample was taken near to and upwind from the factory, and the remaining 7 to 8 were taken downwind, grouped around two different distances from the factory (see Figure 1). Selection of the sampling locations was based on the wind's direction and velocity as well as local topography.

Two charcoal tubes were used at each point to allow for duplicate analyses. In addition, the charcoal tube's efficiency in adsorbing CH_3Cl was tested during sampling period no. 2 using two parallel pairs of charcoal tubes connected in series (point T in Figure 1A). Immediately after sampling, the tubes were securely capped, wrapped in aluminium foil, placed in Dewar flasks over dry ice, and analyzed within one week. Unopened charcoal tubes followed the sample tubes and were stored with them to serve as blanks.

Analysis

The analytical apparatus consisted of a Chrompack thermal desorption cold trap injector (Chrompack, Middleburg, The Netherlands) mounted on a Packard Model 428 GC with flame ionization detector and a 50 m Al_2O_3/KCl PLOT fused silica column (0.32 mm i.d.). A piece of this column was used as the capillary trap in the cold

Table 1 Sampling periods and meteorological conditions

Period no.	*Date*	*Time*	*Wind*		*Temp. (°C)*
			Direction	*Velocity (m/s)*	
1	Nov. 6, 1985	10.45–11.01	160	10	7
2	Nov. 13, 1985	11.50–12.06	340	3	0.3
3	Nov. 13, 1985	15.05–15.21	300	3	0.4

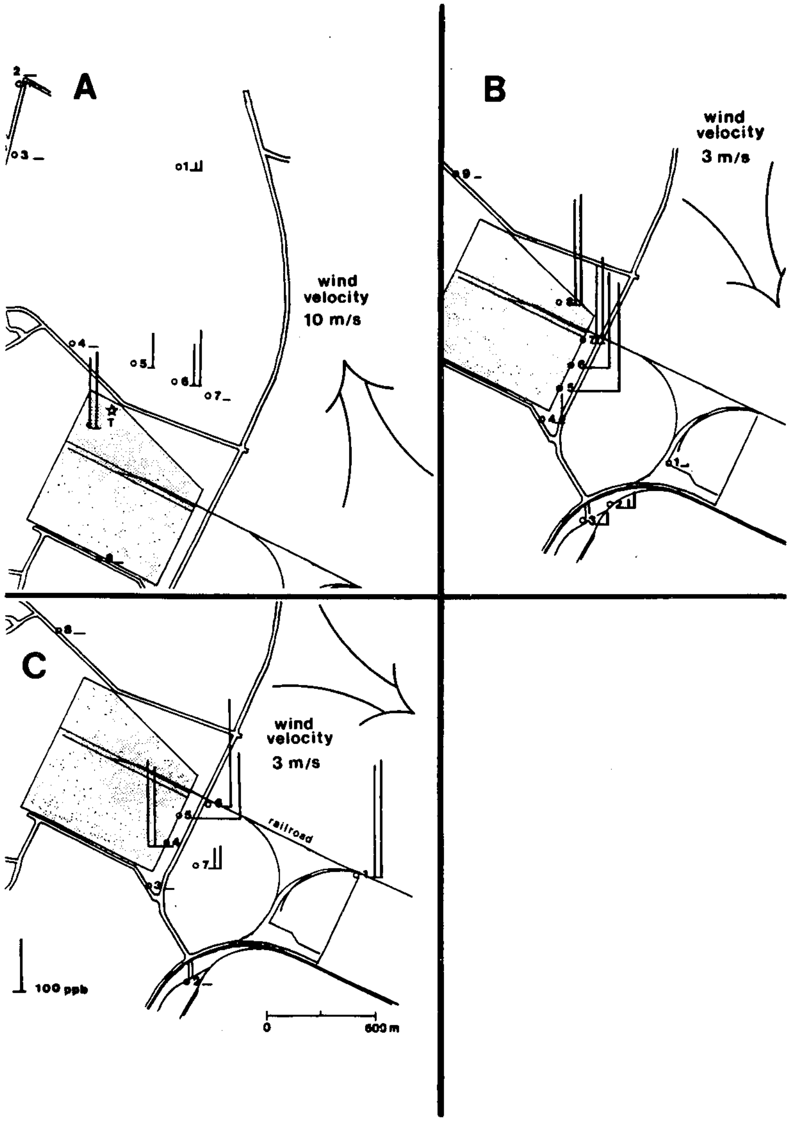

Figure 1 Locations of sampling sites for the three sampling periods: (A) Nov. 6, 1985, 10.45–11.01; (B) Nov. 13, 1985, 11.50–12.06; (C) Nov. 13, 1985, 15.05–15.21. Location of the factory using CH_3Cl in its manufacturing processes shaded in gray. CH_3Cl concentrations are represented by vertical bars.

trap injector. Peak areas were calculated using a Hewlett–Packard 3385A integrator. The GC operating parameters were as follows: injector temperature 200 °C, detector temperature 250 °C, helium carrier gas at 1.1 kp/cm^2 constant pressure, oven temperature programmed at 10 °C/min from 50 °C to 200 °C. Preliminary trials indicated that compounds in the carrier gas were adsorbed onto the charcoal tube in the injector and desorbed along with the sample, interfering with its analysis. An on-line charcoal filter solved this problem.

The charcoal tube containing the sample was analyzed by placing it in the cold trap injector immediately after removing it from storage in dry ice. The tube was then warmed to 250 °C for 5 min (10 ml/min helium purge flow) while the capillary trap was held at < -90 °C using liquid N_2-cooled air. The capillary trap was then heated to 200 °C for 3 min, and at the same time the GC oven temperature program was started. The cold trap injector was cooled down to less than 30 °C using a fan prior to the next analysis.

Standards were prepared by static dilution of 99% pure CH_3Cl gas in pure nitrogen, using a Hamilton 1 ml gas-tight syringe and 100 ml septum-capped bottles, to achieve a working concentration of 17.4 ppb. 500 μl of this standard was slowly injected onto the cold trap injector containing an empty glass tube during the 5 min desorption phase, after which the capillary trap was heated to 200 °C in the same way as for the sample tubes. The standard was injected within 30 min of preparation, and a fresh standard was injected prior to each batch of samples analyzed.

RESULTS AND DISCUSSION

Chromatograms of samples containing high and low levels of CH_3Cl are presented in Figure 2, showing that the CH_3Cl peak is well separated from the surrounding ones. The chromatograms of the blank tubes were free from CH_3Cl.

Table 2 lists the concentrations measured at each site for the three sampling periods. At several points only one concentration is given, due to the fact that the end(s) of the second sample tube was broken from overtightening the Swagelock plugs. Analysis of these broken tubes revealed that most or all of the CH_3Cl had disappeared. The

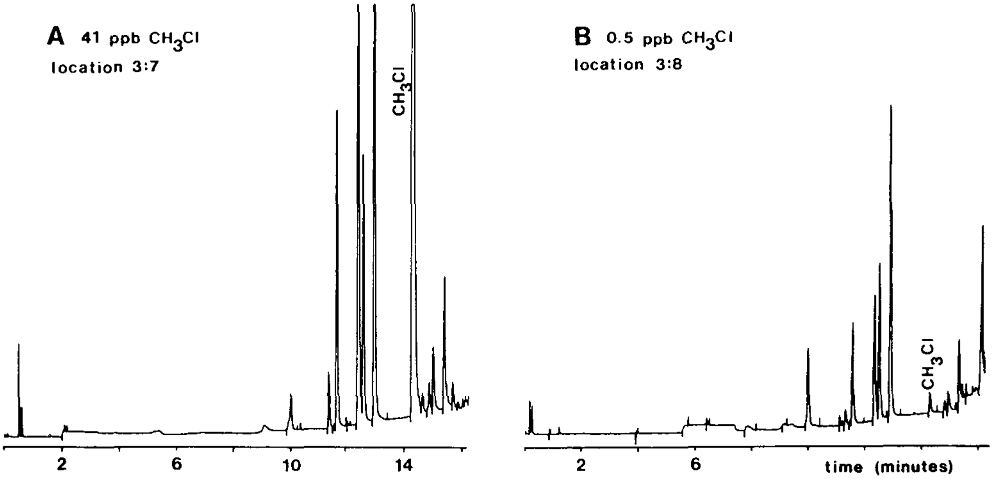

Figure 2 Gas chromatograms of high (A) and low (B) concentrations of CH_3Cl. Column: 50 m Al_2O_3/KCl PLOT fused silica (0.32 mm i.d.), temperature program 50 °C, then 10 °C/min up to 200 °C, helium carrier gas at 1.1 kp/cm^3 constant pressure.

Table 2 Concentrations of CH_3Cl around the factory

Sampling period 1		*Sampling period 2*		*Sampling period 3*	
Location (see Figure 1A)	*Concentration (ppb)*	*Location (see Figure 1B)*	*Concentration (ppb)*	*Location (see Figure 1C)*	*Concentration (ppb)*
1:1	13	2:1	4.2	3:1	210
1:1	14	2:1	4.8	3:1	220
1:2	0.7	2:2	16	3:2	1.2
1:2	—	2:2	27	3:2	0.5
1:3	0.6	2:3	20	3:3	0.6
1:3	0.5	2:3	—	3:3	—
1:4	2.1	2:4	53	3:4	140
1:4	3.5	2:4	—	3:4	150
1:5	66	2:5	200	3:5	120
1:5	—	2:5	—	3:5	—
1:6	76	2:6	180	3:6	200
1:6	100	2:6	—	3:6	—
1:7	0.1	2:7	150	3:7	38
1:7	—	2:7	160	3:7	41
1:8	0.2	2:8	200	3:8	0.5
1:8	0.2	2:8	200	3:8	—
		2:9	0.2		
		2:9	—		

mean CH_3Cl concentration for the downwind locations nearest the factory was 100 ppb (range, 0.1 to 200). At the downwind sites a greater distance from the factory (700 to 1500 m), the mean level was 7.2 ppb (range, 0.1 to 27), with the exception of point 3:1, which had an unexpectedly high value. This may be due to some temporary source, possibly from transport on the nearby railroad. Levels at the points upwind from the factory, which correspond to background, ranged from 0.2 to 0.5 ppb, which compares well with 0.6 ppb measured in rural air.[2]

Variations between the duplicate analyses were generally small, i.e., from ±0% to ±14% of the mean for concentrations above 75 ppb. Larger variations were observed at some of the lower concentrations. These variations can be due to leakage of the samples during storage and/or analysis, and to imprecision in quantifying the CH_3Cl peak at low levels. One weakness of the cold trap injector was in the connection between the charcoal tube and the capillary trap, which is made using a 1/4 inch graphite or Teflon ferrule. It was found that it was easier to obtain reproducible injections when using a Teflon ferrule, but that one had to change the ferrule after every five to ten injections, as it was deformed by the repeated heating cycles.

The very low levels observed at points 1:4, 1:7 and 3:3, which are downwind and near the factory, demonstrate that the choice of sampling locations is critical. It appears that these points lie just outside of the plume of the CH_3Cl emission, which is quickly diluted in the surrounding air (see Figure 1). It is therefore necessary to spread the sampling sites to insure that some of them will fall inside the plume.

The charcoal tubes were 99.9% efficient in trapping the atmospheric CH_3Cl, as demonstrated by the test at point T, sampling period 1. The first tube in each pair contained 130 and 140 ppb, while the second tube had 0.1 and 0.2 ppb, respectively.

The efficiency of the cold trap injector was tested by injecting 230 ng CH_3Cl onto an empty glass tube in the injector, which was warmed to 200 °C for 3 min, while the capillary trap was maintained at < -90 °C. The trap was maintained at this low temperature for an additional 15 min, while the oven temperature program was started as in a normal analysis. No peak appeared with a retention time corresponding to CH_3Cl. The GC oven was then cooled to the initial temperature, the capillary trap heated to 180 °C for 3 min, and the temperature program restarted, producing a peak with the expected retention time and peak area. Thus no 'breakthrough' of this compound was observed using the stated operating parameters.

CONCLUSIONS

This study demonstrates that by using "off the shelf" instrumentation, routine quantitation of sub-ppb levels of volatile organics such as CH_3Cl is practical for any well-equipped analytical laboratory. The method is simple and rapid, allowing the analysis of up to 12 samples per working day. It should be emphasized that the choice of active charcoal as adsorbent and the Al_2O_3/KCl PLOT capillary column for GC separation, and of the capillary trap in the cold trap injector, was critical to the success of this study. By proper selection of the sampling sites it is possible to map the dilution of CH_3Cl from a point source into ambient air.

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