

Automated analysis of C₁- and C₂-halocarbons in ambient air.

W. Frank¹, H. Frank¹ and R. Englert²

¹ Institut für Toxikologie; ² Institut für Pharmakologie
Universität Tübingen
7400 Tübingen, Federal Republic of Germany

ABSTRACT Airborne C₁- and C₂-halocarbons are determined with an automated system by sorbent-sampling at ambient temperature followed by thermodesorption and capillary gas chromatography. The system has been operated at various rural sites over several weeks, taking one sample every 30 minutes.

INTRODUCTION

Atmospheric concentrations of volatile halocarbons in Central Europe may fluctuate over two orders of magnitude. For monitoring their dynamic behaviour, actual air levels must be determined at short intervals; statistically significant comparison of different sites requires large numbers of data. Application of conventional packed-column gas chromatography is time-consuming. Therefore, an air-autosampling system for capillary gas chromatography has been developed for unattended operation.

EXPERIMENTAL

Autosampler: A scheme of the automated system is depicted in Fig. 1. Air (50 mL) is drawn with a membrane pump from a transfer line through a microtrap packed with segments of two different sorbents [1]. Flow is in such a direction that high-boiling compounds are retained by the the sorbent with lower affinity but do not enter the sorbent with high affinity; otherwise thermodesorption would be too slow to ensure an eluting profile compatible with capillary GC. After sampling, the six-port valve is actuated; now the microtrap is inserted between carrier gas line and the gas chromatographic capillary. Air is purged out of the system for 1 min, the trap is heated for thermodesorption at a rate of 20 K/sec to 200°C and held until 5 min before the next sampling cycle. At the same time temperature program and data acquisition are started.

All timed events are switched by a programmable electronic timer in a 30-min cycle.

Gas Chromatography: The compounds released from the micro-trap are separated with a glass capillary (28 m x 0.3 mm), coated with 2 μ m SE 54 and immobilized with DCUP. Carrier gas is hydrogen (60 cm/sec at 20 °C) purified with a Pd-diffusion cell (Aadco, model 560, Rockville, USA). A typical chromatogram is depicted in Fig. 2. The gas chromatograph (Carlo Erba, model Vega, Milan, Italy) is equipped with an ECD which is operated in the constant-current mode.

Data acquisition and management: Data acquisition is done with an analogue/digital interface and chromatographic software (type 2600, PE Nelson, Sinsheim, FRG) installed on a personal computer (IBM-AT standard). Calculated concentrations are saved in files which are transferred on-line to a Lotus 123 data management program (Lotus Inc., Berkshire, GB) for further mathematical operations and graphics generation.

Calibration: Standards are generated by diluting the vaporized compounds in septum vials with gas-tight syringes. Aliquots of 50 μ L are withdrawn and injected into a glass tube injector connected to the fused-silica capillary inlet of the autosampler.

RESULTS AND DISCUSSION

Airborne halocarbons have been determined at various times and sites; typically, 350 air-samples are analyzed automatically per week. The levels of C₂-chlorocarbons determined between 30 May and 19 June 1990 in the National Park Berchtesgaden (Southern Bavaria) are shown in Fig. 3. Tetrachloroethene with a tropospheric half-life of a few months and relatively high emissions exhibit strongest fluctuations. The effect of inversions at night are seen during a period of fine weather in the first week of the series. Trichloroethene concentrations are low, due to its fast tropospheric degradation and relatively small emissions. The smaller emissions of trichloroethane and trichlorotrifluoroethane generate moderate fluctuations and their relatively high tropospheric stabilities result in high base levels of 1 and 0.6 μ g/m³, respectively. The base level for tetrachloroethene is 0.15 μ g/m³.

REFERENCES CITED

- 1) Frank, W.; Frank, H. Chromatographia 1990, 22, 571-574.

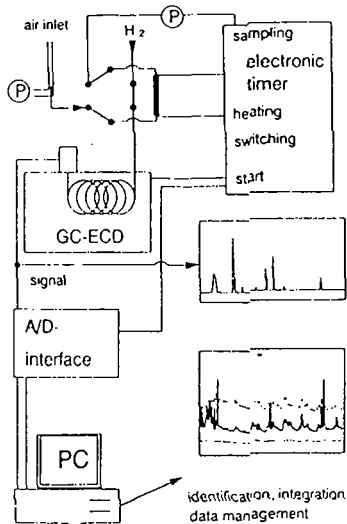


Figure 1
System for unattended automated analysis of airborne halocarbons

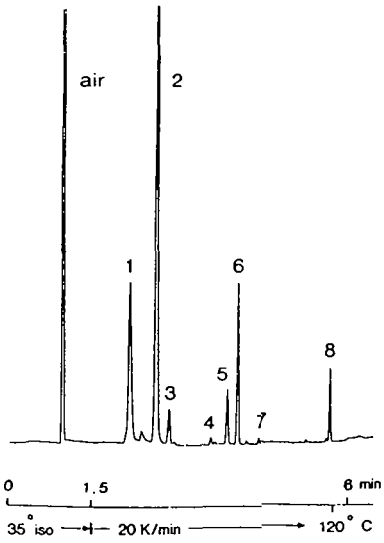


Figure 2
Chromatogram of halocarbons from a 50 mL air sample.
1: CF_2Cl_2 2: CCl_3F 3: $\text{C}_2\text{Cl}_3\text{F}_3$ 4: CHCl_3
5: CH_2Cl_2 6: CCl_4 7: C_2HCl_3 8: C_2Cl_4 .

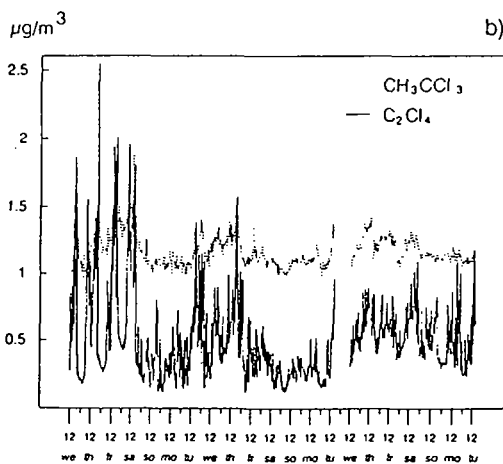
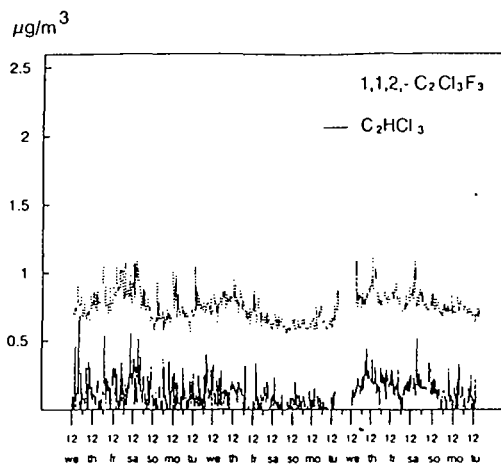


Figure 3 - Atmospheric concentrations of C_2 -halocarbons in the National Park Berchtesgaden (Southern Bavaria) during a three-week period in May/June 1990.