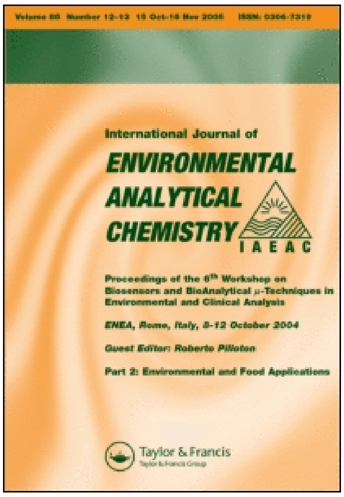

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AN IMPROVED SAMPLING STRATEGY FOR THE MEASUREMENT OF VOCS IN AIR, BASED ON COOLED SAMPLING AND ANALYSIS BY THERMODESORPTION-GC-MS/FID

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Reliable and comprehensive sampling methods are required to obtain accurate data for VOC concentrations in air samples. The major drawback of the adsorption tube sampling method, widely employed in environmental studies, is the fact that C_2 compounds are usually not trapped quantitatively.

The focus of this work was thus to improve sampling based on adsorption tubes packed with Molsieve and Carbosieve. To improve the sampling efficiency for the C_2 compounds, a cooling device, based on Peltier cooling was constructed, which could be operated at a temperature down to -30°C.

Experiments under laboratory and field conditions were carried out to study the influence of the sampling temperature on the recovery of ethane and ethene as the most volatile VOCs. The results clearly demonstrate the need for a cooled sampling device for the analysis of C_2 compounds in air. Under the investigated conditions, the recoveries with ambient temperature sampling were only in the range of 38–46% for ethane and 33–59% for ethene respectively, in comparison to the cooled sampling device. These findings are only valid for the described conditions and can change significantly with temperature and concentration. A generalisation of the recovery is thus very difficult to give.

The use of the sampling device for a field study is reported, where samples were collected simultaneously at three different altitudes in a diurnal profile on the slope of the Schulterberg mountain in Tyrol (Austria).

Keywords: Atmospheric pollution; organic trace gases; sample preconcentration; adsorption tubes; cooled sampling; C_2 hydrocarbons

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INTRODUCTION

Analysis of VOCs is of increasing importance for the evaluation of air quality. Since it was found that these compounds are of both biogenic and anthropogenic origin there is a growing interest in determining the concentrations and sources of these compounds. In fact, they have an effect on the environment on a local and global scale: ozone depletion in the stratosphere above the Antarctic[1,2] due to halocarbons, increased ozone formation due to hydrocarbons in the troposphere[3], suspected direct phytotoxic effects[4] of some of these compounds (especially ethene), and a contribution to global warming[5–7] have been reported.

Requirements for a monitoring technique are the sensitivity to detect compounds in the low $\mu g/m^3$ range, the maintenance of sample integrity and the absence of sampling and analysis artefacts. Besides it should be possible to follow diurnal cycles (time resolved measurements) and the dynamic range should be sufficient to monitor concentration changes of one order of magnitude or more during a measuring cycle. Reliable and comprehensive sampling methods are required to obtain accurate data. The most commonly used methods are canister sampling and sampling on adsorption tubes packed with solid adsorbents.

SAMPLING CONSIDERATIONS

Canister Sampling

For this sampling technique passivated stainless steel canisters are used[8–10]. Unfortunately automation is precluded and problems associated with sample integrity during transport and storage for some less stable compounds arise.[11]

The canisters are well suited for sampling C_2-C_6 hydrocarbons. However, the risk of irreversible losses due to wall adsorption increases with increasing boiling point and polarity of the sampled compound. Very low blank values can be obtained and the samples can be stored for several weeks without observable changes in sample composition. Furthermore the cleaning of the canisters after use is relatively easy. Nevertheless there are some major drawbacks: The use of sampling canisters in the field is less practical due to their size, weight and the fact that a suitable infrastructure is needed (for transport, storage, etc.). They have high prime costs (due to the special pre-treatment of the inner canister surface and the contamination-free shut-off valves), the samples contain a relatively large amount of water (air humidity) which has to be removed before analysis by a drying agent (which may cause losses of the less volatile ($>C_6$) compounds), and the risk of contamination and adsorption losses by the sampling pump cannot completely be excluded.[11]

Adsorption Tubes

The sampling on adsorption tubes is a good alternative to the canister sampling, as adsorption tubes can readily be prepared at low cost and they are easy to handle during sampling, storage and analysis[12–15]. Selectivity can be tuned by choosing appropriate adsorbents or combinations of different adsorbents in the same or in different tubes. With Tenax TA only insignificant amounts of water are retained on the solid adsorbent surface. Sampling over a longer period (up to 24 h) and of a larger volume (10–60 L) is possible as long as the sampled volumes are lower than the breakthrough volumes.

A major drawback is the partly incomplete collection of compounds of low molecular weight. Also the cleaning methods are rather time-consuming and at least for the polymeric adsorption materials the blank values increase during storage due to slow degradation of the polymer and migration of contaminants out of the porous structure. Also a slow decomposition of the adsorbent structure by reactive gases during sampling is possible. It can be problematic to obtain sufficiently low blank values for aromatic compounds.[11] Automation is possible but at high cost for the thermodesorption.

The approach of the work presented here was thus to improve the sampling strategy with adsorption tubes with the goal to sample also compounds of low molecular weight (especially the C_2 compounds) quantitatively. As a demonstration of the practicability of this strategy data were collected during a field study simultaneously at three different heights in a diurnal profile on the slope of the Schulterberg mountain in Tyrol.

EXPERIMENTAL

Sampling

The basic configuration was as follows: sampling on two separate adsorption tubes in series[16], the first filled with Tenax, then a Nafion dryer between the two tubes and the second tube filled with Molsieve and Carbosieve. In this set-up, the compounds $>C_6$ are trapped on the first adsorption tube, then the water vapour is removed and finally the C_2-C_5 compounds are trapped.

Adsorption tubes: 18 cm × 6 mm o.d. × 4 mm i.d. Duran glass; filled with either ca. 375 mg of Tenax TA 60/80 mesh (internal surface ca. 35 m^2); or with ca. 425 mg Molsieve 5 Å 60/80 mesh and ca. 500 mg Carbosieve S-III 60/80 mesh (internal surface ca. 820 m^2); the adsorbent beds were fixed by a plug of silanized glass-wool (all adsorbents were ordered from Supelco).

The advantage of such a configuration is that it separates the VOCs in 2 fractions, one with $C < 6$ and one with $C \geq 6$. This allows both the sampling conditions and the analysis to be optimised separately by the choice of suitable adsorbents or adsorbent combinations for the former and the optimisation of chromatographic conditions (column, temperature and inlet pressure programming) for the latter.

The sample humidity can be significantly reduced which is essential for improving the sampling of the light fraction. As the second adsorption tube is cooled to temperatures below the freezing point, the water has to be removed first. In the literature it is reported that drying the sample air is a quite complicated step, which can lead to substantial loss in sample and to the formation of artefacts. The major methods reported are the use of conventional bed desiccants such as $Mg(ClO_4)_2$ and K_2CO_3, or drying with a semipermeable Nafion-tube (a perfluorosulfonate polymer).

In this work a Nafion dryer was used as described by Foulger and Simmonds[17](water is removed by adsorption on molecular sieve (Molsieve 5 Å, pellets, Supelco) after it has permeated through the membrane tubing ("static drying"). The dryer type was a DP–3S from International Science Consultants, Ringwood, Hants, UK, equipped with a 1 m length Nafion 815 tubing, 1.14 mm internal diameter, 0.13 mm wall thickness, desiccant: molecular sieve 5 Å). It has a low dead volume, a constant pressure drop (almost no flow restriction) compared to conventional bed desiccants, and a high inertness towards most inorganic gases, hydrocarbons, chlorinated or fluorinated hydrocarbons, esters, aldehydes and some ethers. For some polar compounds, such as amines, ketones, the lower alcohols and some ethers losses are reported, as they can permeate through the polymer-like membrane. In some studies, this dryer was unsuitable for drying hydrocarbons, oxygenated compounds and unsaturated cyclic hydrocarbons emitted from vegetative sources because it caused rearrangement of the monoterpenes and removed several important oxygenated compounds from the sample.[18,19]

However, in this sampling configuration all critical compounds whose recovery might be affected by the Nafion dryer (such as the polar and oxygenated compounds) are already trapped on the Tenax tube. Therefore, no negative effects of the Nafion dryer have to be anticipated.

The only but important disadvantage of the described configuration is that the analysis is more time consuming, since both adsorption tubes have to be analysed separately.

Development of the Sampling Device

The difficulty of quantitatively trapping light hydrocarbons on adsorbent tubes at ambient temperatures has been demonstrated.[11] Particularly as this temperature is variable over a wide range (10–35°C in summer, several degrees below zero in winter), the influence of the temperature is probably the most important parameter for the breakthrough-volume (BTV) of a single compound: a change in temperature by 10°C can lead to a change of the BTV by a factor of 2 (as reported for the BTV on Tenax[20]). Therefore, an uncontrolled sampling temperature implies an uncontrolled BTV, which leads to completely unreproducible sampling efficiencies.

No reports on adsorption sampling of VOCs at subambient temperatures are available up to now. Therefore conclusions have to be obtained from the experiences of other authors in the analysis of VOCs by using traps packed with various adsorbents at different temperatures. Different kinds of capillary cold traps were tested by Cao and Hewitt[21] for their trapping efficiency. For the C_2-C_5 hydrocarbons the trapping efficiency was in ascending order: deactivated capillary trap ~ coated capillary trap < Tenax-TA capillary trap < Chromosorb 101 capillary trap. They concluded that stronger adsorbents such as Carbotrap (internal surface 100 m^2/g) or Chromosorb 106 (internal surface 800 m^2/g) are needed for packing capillary traps in order to trap the most volatile hydrocarbons such as ethene completely. There exists a linear relationship between the boiling point of each substance and the maximum trapping temperature for each trap, which is the highest temperature at which a quantitative recovery of the analytes is still possible. Trapping efficiencies of various compounds on a Chromosorb 101 capillary trap are given in Figure 1. It is evident that this adsorption tube does not provide a sufficient sampling efficiency for light hydrocarbons at reasonably low temperatures.

To improve the unsatisfactory sampling efficiency for the C_2 compounds, stronger adsorbents, like Carbosieve and effective cooling have to be employed. Therefore, a suitable cooling device was developed. Requirements were as follows: no exhausts should be released, a temperature down to –30°C should be reached, the unit should be easily transportable and it should be also independent from a fixed power supply to enable the use in field sampling campaigns.

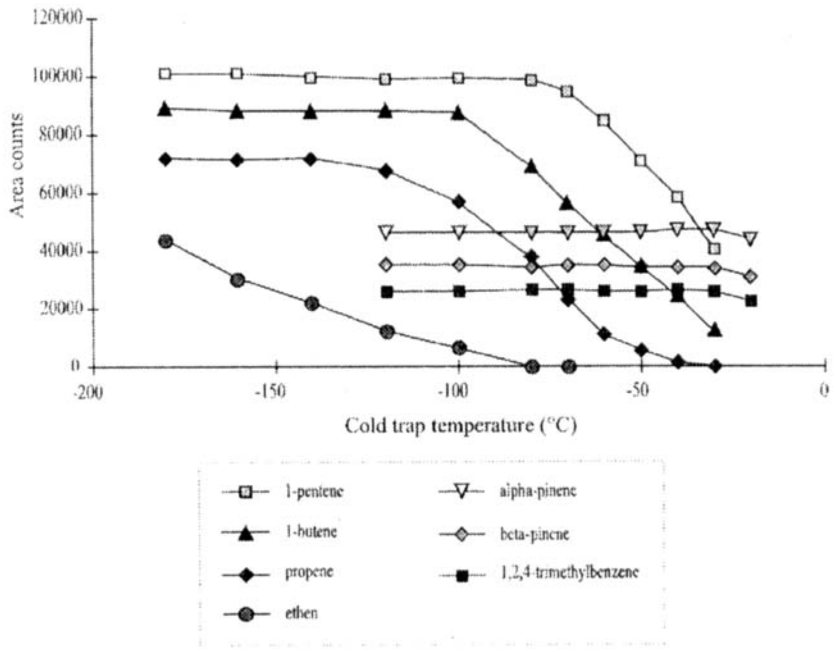

FIGURE 1 Trapping efficiency of different hydrocarbons as a function of the temperature of the Chromosorb 101 capillary cold trap of the thermodesorption unit (redrawn after reference 21)

Only electric cooling with Peltier elements and power supply by accumulators met all these requirements as cooling with dry ice or liquid nitrogen were not practical because of the lack of supply in the sampling area.

The cooling device (see Figure 2) was constructed of an isolated aluminium block which supported the sample tube and transported the heat from the sample tube to the Peltier elements. The efficiency of the Peltier elements is strongly dependent on the temperature difference between their warm and cold side. To maintain high efficiency (electric power was limited) and to reach a working temperature down to -30°C, a water circuit cooled the warm side of the Peltier elements. The cooling water was pumped back into a heat exchanger built in a cold box with cooling accumulators. Thus a water temperature of approximately 10°C could be maintained even at 30°C ambient temperature.

The control electronics kept a constant temperature within ±0.1°C around the setpoint and stabilised also the power supply for the air pumps as this was essential to provide a constant flow. The flow was adjusted by a needle valve and measured by a calibrated flowmeter (ADM 1000, J&W), placed at the membrane-pump exhaust. As the membrane pump is strongly pulsating, a pulse

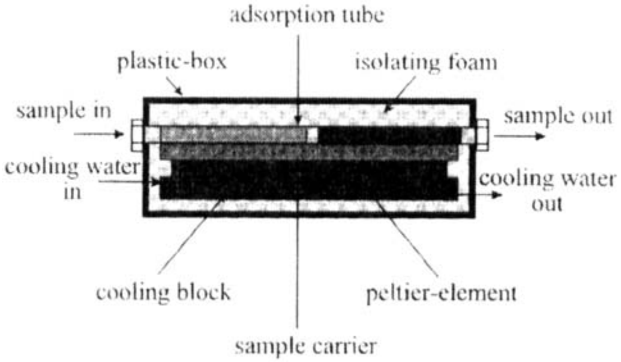

FIGURE 2 Schematic drawing of the cooling stage of the sampling unit

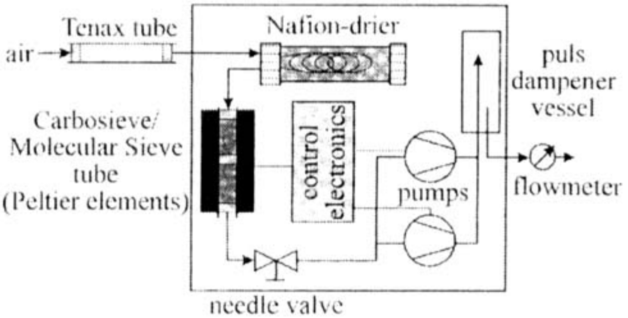

FIGURE 3 Schematic drawing of the sampling device

dampener vessel was inserted between the flowmeter and the pumps. All components were housed in a solid aluminium box (see Figure 3) which could stand the rough conditions present in a field campaign. For sampling it was placed together with the cold box on top of a tripod.

Analysis

The analysis of the adsorbed hydrocarbons was done by thermodesorption with a two stage cryofocusing at liquid nitrogen temperature (Tekmar AEROTrap 6000 with external cryofocusing module). This allowed a quantitative transfer of the analytes onto the capillary column of the GC (HP 5890 Series II). A precolumn split was used to distribute the sample between a MS detector (HP MS Engine) for the qualitative analysis and a FID for the quantitative analysis. Different columns are used for the two sample fractions: the C_2-C_5 hydrocarbons are analysed on a 50 m × 0.32 mm Chrompack Al_2O_3-PLOT-column with a 5 μm Al_2O_3/KCl coating, and the hydrocarbons $\geq C_6$ on a 50 m × 0.2 mm × 0.33 μm HP-Ultra 1, a

100% polydimethylsiloxan-phase coated capillary column. This optimised technique enables qualitative and quantitative analysis of around 80 different substances.

Parameters of analysis for the C_2-C_5 hydrocarbons: GC: 40°C for 4 min; then at a rate of 5°C/min to 195°C which is held for 10 min (run time: 45 min); Flow: stand-by 0.1 psi (until start of desorption of the second cryo trap), then with a rate of 84 psi/min to 13.0 psi–constant flow (=3.6 mL/min); FID: 250°C, MS transfer line: 205°C; Thermodesorber: 20 min sample desorb time at 300°C and a He flow of 7 mL/min; first cryo trap: –180°C during cooling and 250°C during trap desorb; second cryo trap: –196°C during cooling and 100°C during trap desorb. transfer line: 200°C. For quantitation the FID detector signal was used (see Figure 4 for a chromatogram). It was calibrated by an external propane gas standard and results were calculated by the use of response factors[22,23] from the literature.

For the analysis of the C_2-C_5 hydrocarbons the thermodesorption unit had to be modified, as the second stage cryo trap could not trap the C_2 hydrocarbons efficiently. Since the length of 9.5 cm of liquid N_2 cooled capillary column was too short, the automatic trap had to be replaced by a manually operated trap of the following dimensions: 1 m × 0.51 mm i.d. Ni-capillary which in previous experiments was shown to provide complete recovery of ethane and ethene (see Table I). During the cooling step, the capillary was immersed in liquid nitrogen. To desorb the analytes, it was heated up by immersing in boiling water.

TABLE I Recovery of ethane/ethene in dependence of the dimensions of the second stage cryo trap: values related to the sample amount of 8.7 ng ethane and 8.2 ng ethene

trap diameter	*material*	*cooled length*	*recovery*
0.32 mm	fused silica	9.5 cm	38%
0.25 mm	fused silica	9.5 cm	48%
0.51 mm	Nickel	100 cm	100%

RESULTS

Blanks

Initial investigations were directed towards the quality of zero gas. A zero gas with a blank as low as possible is needed for the determination of the temperature dependent recovery of ethane/ethene under laboratory conditions, and to clean the adsorption tubes prior to sampling. The importance of low blank values becomes obvious in comparing the blank values of different laboratory gases (see Figure 5).

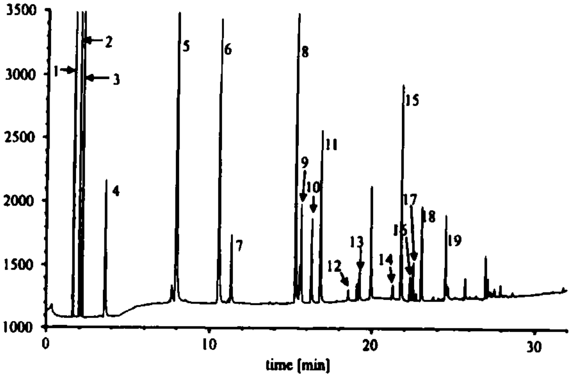

FIGURE 4 **Chromatogram: Sample collected on the 26.9.95 at 17:30–18:00, at an altitude of 1686 m on top of the Schulterberg mountain in Tyrol.** Substances: 1) methane; 2) ethane; 3) ethene; 4) propane; 5) 1-propene; 6) i-butane; 7) n-butane; 8) trans-2-butene; 9) 1-butene; 10) i-butene; 11) cis-2-butene; 12) i-pentane; 13) n-pentane; 14) 3-methyl-1-butene; 15) trans-2-pentene; 16) 2-methyl-2-butene; 17) 1-pentene; 18) cis-2-pentene; 19) methyl-cyclopentane; **Sampling:** Temperature: –20.1°C; **Analysis:** Column: 50 m x 0.32 mm Al_2O_3-PLOT-column with a 5 μm Al_2O_3/ KCl coating; Concentrations between 0.04 and 3.21 μg/m^3 have been found

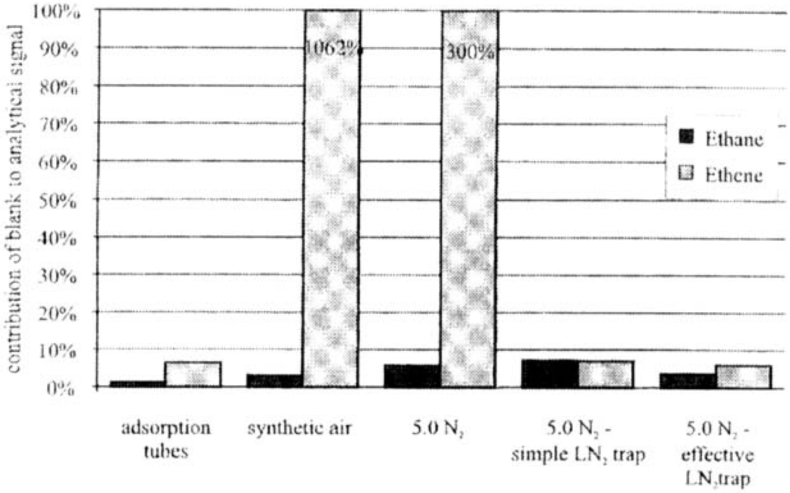

FIGURE 5 **Blanks of different laboratory gases:** Blank values related to the sample amount of 8.7 ng ethane and 8.2 ng ethene (sampling conditions: 3 L were aspirated at 100 mL/min; Sampling temperature: –20.1°C)

Only with an effective cryotrap immersed in liquid nitrogen a sufficiently clean zero air could be obtained. This special trap consists of a 25 cm length 1/4" i.d. copper tube filled with glass-beads, followed by a 1.5 m, 1/8" copper tube. The cold gas leaving the trap was warmed up again to room temperature by means of a heat exchanger, immersed in a water bath.

Determination of the Recovery of Ethane/Ethene with Simulated Air Samples for Different Sampling Temperatures

For this experimental series the configuration was the same as presented above. The cryotrap was used to clean the nitrogen 5.0 used as zero gas. After the start of the air pumps, a sample of 8.7 ng ethane and 8.2 ng ethene was injected with a gastight syringe into the gas flow of 100 mL/min. After 30 min and a volume of 3 L the sampling was stopped. The cooled sampling device was operated at different temperatures to investigate the recovery as function of the temperature of the sampling tube (see Figure 6). At each temperature three samples were taken (standard deviation s ≤ 2%). The tube blanks of 0.11 ng ethane and 0.53 ng ethene (1% and 6% of the injected sample) were subtracted.

Determination of the Recovery of Ethane/Ethene with Laboratory Air Samples

To verify the results of the laboratory study, a further sampling series was performed under ambient conditions. Air samples were taken simultaneously in the laboratory with two sampling devices in parallel: one operating at ambient tem-

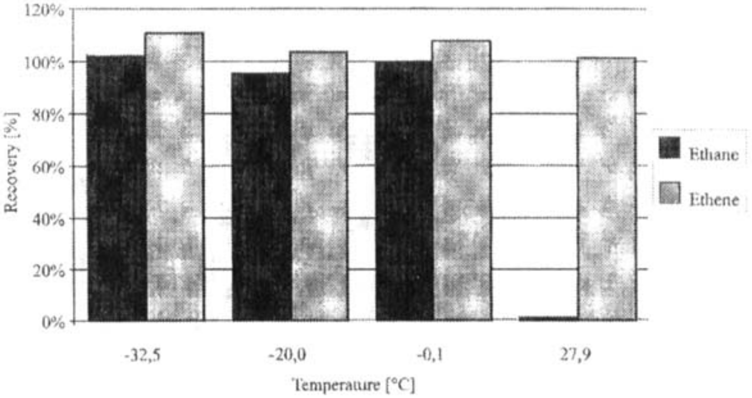

FIGURE 6 **Recovery of ethane/ethene dependent of the sampling temperature under laboratory conditions** (sample amount of 8.7 ng ethane and 8.2 ng ethene; sampling conditions: 3 L were aspirated at 100 mL/min during 30 min)

perature and the other at –20.1 °C. A constant atmosphere, and notably a constant temperature was provided by the air-conditioning in the lab. For each sample the recovery was calculated as ratio of the signal intensities obtained from the cooled and uncooled sampling device (see Table II).

TABLE II Recovery of ethane/ethene dependent of the sampling temperature of the air samples (sample amount of 3–10 ng ethane and 127–150 ng ethene; sampling conditions: 3 L were aspirated at 100 mL/min during 30 min)

	Ethane	*Ethene*
Recovery with cooled sampling T = –20.1°C	100%	100%
Recovery with sampling at ambient temperature T = 23°C	42%	46%
RSD of the recovery with sampling at ambient temperature	3.9%	12.9%

Analysis of Background Air Samples

After successful tests in the laboratory, the sampling unit was employed in a field campaign. The aim of this study was to estimate the contribution of anthropogenic and biogenic sources to the total concentration of VOCs in this Alpine background area. To investigate the variations in the analyte concentrations during a diurnal cycle as well as along an altitude profile, samples were collected simultaneously at three different heights at 1030 m, 1220 m and 1686 m in a diurnal profile on the slope of the Schulterberg mountain in Tyrol. The presented data are from a sampling campaign carried out on 26.6.95. Only the samples taken at the highest point (1686 m) were cooled during the sampling procedure, as only one cooled sampling unit was available. But still the data between the different stations are comparable, as a quantitative coverage of all compounds with $\geq C_3$ can be expected. Only for the C_2 compounds the recoveries of the uncooled sampling are too low. Thus only the absolute amounts are not comparable, whereas the observed trends are comparable.

The concentration of ethane varies only slightly during the day and shows only little difference between the sampling points. The highest concentrations are found in the valley. With increasing altitude, atmospheric dilution becomes effective, so that at the middle sampling point the ethane concentration is generally lower. The apparent increase in concentration at the highest located sampling point is more likely due to a more efficient sampling as a result of the use of the cooled sampling unit than due to an actually higher ethane concentration (the two lower sampling stations were equipped only with uncooled sampling devices).

For the phytotoxic ethene, a different trend can be observed: Ethene has been found to correlate with the hydrocarbons from automobile exhausts. At the sampling station in the valley a clear maximum of ethene is visible at midday and after decrease in concentration a second one in the early afternoon. This indicates increases in local emissions as a result of increased traffic. In part, this trend can still be followed at the middle station, although the significantly lower concentrations are already an indication of dilution due to atmospheric transport. At the sampling station on top of the Schulterberg mountain, the lowest ethene concentrations were found throughout, although the cooled sampling unit provides a complete recovery of the ethene. The total VOC load of the air is comparable with other studies in forest areas[24,25].

DISCUSSION

The work presented here clearly points out the importance of a cooled sampling device for quantitative trapping of C_2 compounds on adsorption tubes. As the trapping efficiency is strongly temperature dependent, and as a quantitative trapping cannot be achieved at ambient temperature, cooling to subambient temperature during the sampling presents the only alternative to canister sampling. The varying sampling conditions of the different experimental series are listed in Table III.

There are three factors of great influence on the recovery of ethane/ethene: the form of sample application, the sampling temperature and the sample concentration.

TABLE III Conditions for the different sampling experiments

	simulated air samples	*laboratory air samples*	*background air samples*
Absolute amounts of ethane	8.7 ng	7–11 ng	3.2–4.9 ng
Absolute amounts of ethene	8.2 ng	128–146 ng	0.2–32.9 ng
Sample amounts determined by	injected amount	amount found with the cooled sampling device	amount found with both the cooled and the uncooled sampling device
Sampling temperature	27.9°C	-20.1°C (cooled sampling) 23°C (ambient temperature)	-20°C (cooled sampling) 4–11°C (ambient temperature)
Form of sample application	injected over a short period	continous	continous
ethane: recovery RSD	1.0% 58% for (n = 4)	42% 3.9% for (n = 3)	
ethene: recovery RSD	101.5% 13% for (n = 4)	46% 12.9% for (n = 3)	

Form of Sample Application

For the simulated air samples the sample was injected over a short interval at the beginning of the sampling procedure. For the rest of the sampling duration, only zero gas was aspirated and the substances were chromatographed through the adsorbent packing. This caused probably almost complete ethane breakthrough at a temperature of 27.9°C (only 1% recovery). Only ethene was trapped quantitatively as it stronger interacts with the adsorbent material.

In contrast to this, the laboratory air samples came closer to the real sampling situation, as the concentration was rather constant in the aspirated air. This leads to a continuous adsorption process rather than a mixed chromatographic process as is the case for the sample being applied in a rather narrow zone. In addition to this point, the substances were accumulated on the adsorbent packing at a temperature 5°C lower than for the simulated air samples. Probably the different way of aspirating the sample (almost the same ethane amount as in the simulated air samples) and the lower sampling temperature led to an ethane recovery of 42% compared with the cooled device, which is much higher than in the simulated air samples.

Sampling Temperature

The effect of sampling temperature becomes clearly visible in the simulated air samples (see Figure 6). Ethene still is trapped quantitatively at -0.1°C, while at a temperature of 27.9°C it is almost not detectable. Brown and Purnell[20] found for Tenax that a change in temperature by 10°C can lead to a change of the breakthrough-volume (BTV) of a single compound by a factor of 2.

For the laboratory air samples, sampling on the adsorbent packing at a 5°C lower temperature than for the simulated air samples had also a significant effect, beside the different form of sample application. This resulted in a higher recovery of ethane.

Effect of Sample Concentration

The third important factor on the recovery of a substance is the concentration, as can be seen by ethene (see Table III). In the simulated air samples a concentration of 8.2 ng is trapped quantitatively even at a temperature of 27.9°C. A 15 times higher amount of 128 ng as present in the laboratory air samples could only be trapped with an efficiency of 46% at a temperature of 23°C. It is obvious that the breakthrough-volume had been exceeded significantly and a substantial breakthrough occurred.

Results of the Background Air Samples

Comparing the data of the field campaign presented in Figure 7, one has to keep in mind that for ethane and ethene the data from the highest located sampling point must not be compared to the results of the two other stations in terms of absolute concentrations, but only with regard to the observable trend, as it was not possible to collect air samples with and without cooling in parallel. Only at the highest sampling station on top of the Schulterberg mountain cooled sampling was available, while sampling at the middle station and in the valley was carried out uncooled.

This limitation is acceptable, however, since it is only valid for the C_2 compounds, as substances $\geq C_3$ are trapped quantitatively also without cooling. As explained before, the trends, the diurnal variations in concentration found at the

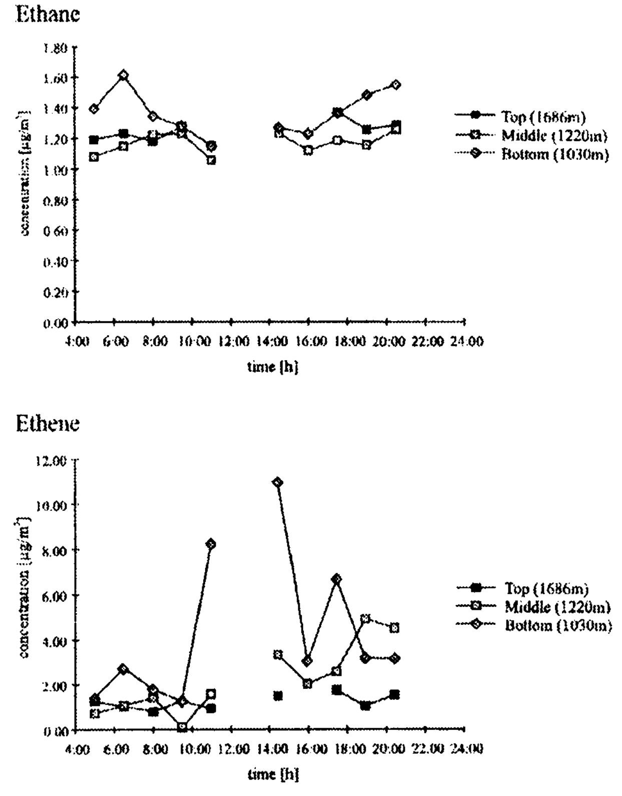

FIGURE 7 **Ethane (top) and Ethene (bottom) values of a diurnal profile at the Schulterberg mountain in Tyrol on 26.9.95** (sampling conditions: 3 L were aspirated at 100 mL/min; only the samples from the sampling point at 1686 m were cooled to T = -20.1 °C during sampling)

three stations are still very well comparable also for the C_2 compounds ethane and ethene. Only the absolute concentrations found with uncooled sampling are too low compared with cooled sampling.

Since it was not possible to keep the sampling temperature constant at the sampling sites equipped only with an uncooled sampling device during the back-ground sampling campaign, no correction for the recovery is made to the values found. The ranges of recovery have been studied in the laboratory and were 38–46% for ethane and 33–59% for ethene, respectively. But it has to be pointed out that these findings are only valid for the described conditions, and that they may change significantly with temperature and concentration.

Where possible, only cooled sampling should thus be carried out to achieve accurate results for C_2-compounds. For measurements in background areas at ambient temperature recoveries for C_2-compounds of less than 100% are obtained, but they are rather constant and therefore measurements at different locations are comparable due to the anticipated small variations in concentration and the low concentration levels (different from the urban atmosphere).

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