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Review

Headspace sampling with capillary columns

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Abstract

A headspace sample is in principle a gas sample which has been previously in contact with a liquid or solid sample from which volatile compounds were released into the gas with subsequent analysis by gas chromatography. Headspace gas chromatography (HS-GC) is thus a technique of gas extraction and can be carried out comparable to a solvent extraction as a one-step extraction (static or equilibrium headspace) or as a continuous extraction (dynamic headspace). If the concentration of the volatile analytes is sufficiently high, a small volume of the gas sample can be injected directly with all common devices, known for gas sampling. The resulting sensitivity depends, except from detector sensitivity, from the capacity of the column for a gas sample. Packed columns are traditionally preferred for gas analysis. Trace analysis on the other hand requires in most cases high resolution also and thus the application of capillary columns. The critical problem relating to sample introduction for headspace (viz. gas) analysis is a function of column capacity and the initial sample bandwidth. The admissible volume of a gas sample is limited by beginning of band broadening. Although the capacity of a capillary column for a gas sample depends on its cross section, the increase of the inner diameter gives a marginal improvement only and is paid off with reduced separation efficiency. Cryogenic trapping of the volatile analytes is a more efficient way and the variety of such techniques can be classified in methods for cryogenic condensation where the volatiles are trapped just by condensation at very low temperatures followed by instantaneous evaporation. Alternatively, with a technique, called cryogenic focusing here, the volatile compounds are trapped directly into a coated capillary column but at moderate low temperatures where the liquid phase is still effective as a chromatographic phase. Band concentration here is achieved by decelerated chromatographic migration at the lower column temperature and even more efficiently if an additional temperature gradient is included in the system. Cryogenic trapping in both cases, however, has to deal with water, which is often present at a high concentration in the headspace and may block a cooled capillary column by an ice plug. The need to remove the water before cryogenic trapping is more urgent with the dynamic headspace procedures due to the higher amount of accumulated water compared to static HS-GC and the techniques to remove the water from the headspace sample therefore differ also. Diffusion through semipermeable membranes and condensation in a reflux condenser are mainly applied for the dynamic headspace procedures, while the much smaller water amount in static HS-GC is easier removed by chemisorption on an inert hygroscopic salt. When comparing and evaluating the various techniques of headspace sampling, the deciding criterions are not only method sensitivity but equally important is the degree of automation. It improves precision and provides for more effective use of laboratory personnel, particularly for industrial routine analysis. It also helps to process the high number of samples, necessary to get the many data for method validation to certify an analytical method.

Keywords: Reviews; Headspace analysis; Sample handling; Cryogenic trapping

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Contents

1. Introduction

The term *headspace gas chromatography* (HS-GC) is applied for various gas extraction techniques, where volatile sample constituents are first transferred into a gas with subsequent analysis by gas chromatography. The sample, placed in a closed container may be in contact and in equilibrium with the extracting gas (*static* or *equilibrium headspace*) or the volatile compounds my be stripped off in a continuous flow of an inert gas (*dynamic headspace*). HS-GC is straightforward, when volatile compounds have to be separated from a solid or liquid matrix prior to GC analysis. As a gas extraction procedure it replaces a solvent extraction, thus avoiding the many problems with solvents.

HS-GC can be performed with both packed and capillary columns. In the early times of gas chromatography, packed columns were used exclusively, but already as early as 1965 a capillary column made of copper, 100 m long with an inner diameter (I.D.) of 1.0 mm was used for the headspace analysis of flavor compounds in beer and hop [1]. The general acceptance of capillary columns was established since the year 1979 with the introduction of fused-silica capillary columns by Dandenau and Zerenner [2], which displaced the fragile glass capillary columns due to their ruggedness and flexibility and the heavy metal capillary columns due to inertness.

The various techniques of headspace sampling may be classified as a one-step procedure, such as static HS-GC where an aliquot of the vapor phase in a closed container (vial, jar) is transferred directly to the gas chromatograph or as a two-step procedure, where the volatile analytes are first separated from the matrix of the headspace gas in a ‘trap’. *Dynamic HS-GC* or the procedure of *solid-phase microextraction (SPME)* may fall in this category and in both cases the trapped compounds are released by thermal desorption in a stream of carrier gas and transferred

to the column. Independent of the particular headspace technique the actual headspace sample is in any case a more or less diluted gas sample.

Samples in which the volatile components have to be analyzed at low concentrations levels generally need the high separation efficiency of capillary columns. Such samples, on the other hand, need also high sensitivity. In the case of a gas sample, sensitivity depends among other parameters on the capacity of the capillary column to accept a gas sample. A small starting solute profile is required to maintain the separation efficacy of a high resolution capillary column and only small volumes of the headspace gas are therefore admissible. Hence, there is again the classical conflict of chromatography between resolution and sensitivity. If the concentrations of the target analytes in the headspace gas are too low, a preseperation step is required to separate first the volatile compounds from the bulk of the headspace gas and to get a more concentrated sample for the following analysis by gas chromatography. The possibilities for such enrichment techniques depend much on the type of the various headspace techniques.

Although the techniques of headspace sampling are quite different, they all end up with a diluted gas sample and encounter finally the same problem: how to introduce such a gas sample as large as possible for the required sensitivity and as fast as possible to avoid delayed sample injection with accompanying band broadening. This common problem can therefore be discussed on a general basis and independent from the particular technique of headspace sampling.

The main emphasis of this review paper is on the instrumental aspects of capillary headspace gas chromatography. Neither the many practical applications nor the quantitative methods are treated here. The interested reader may be referred to a recent book in which a comprehensive review on static HS-GC is presented [3].

2. Classification of headspace sampling techniques

The various techniques of headspace sampling comprises static HS-GC, dynamic HS-GC and SPME. The instrumentations are completely different and will be described briefly to understand the common situation with all of them, which finally introduce a diluted gas sample into a capillary column.

2.1. Principles and instrumentation of static HS-GC

(a) A peculiar problem in static HS-GC is the internal pressure in the headspace vial generated during thermostatting by the sum of partial vapor pressures from all volatile sample constituents, from which in general the humidity of the sample is predominant. Thus, the vapor pressure of water contributes mostly to the internal pressure. Moreover, some sampling techniques pressurize the vial prior to sample transfer with the inert carrier gas. For these reasons it is necessary to close the vial pressure tight by a septum (preferably PTFE-lined) and to crimp-cap it by an aluminum cap.

(b) The most popular device for headspace sampling is a gas syringe. Besides the risk of sample carry-over and significant memory effects there is the inherent problem that the internal pressure in the vial extends into the barrel of the syringe and after withdrawal from the vial, the pressurized headspace gas then expands through the open needle to the atmosphere. Part of the headspace gas will thus be lost. This drawback may be avoided by a using a gas-tight syringe equipped with a valve. Such syringes may be adequate for manual sampling, but are hard to automate.

(c) The headspace sample is a gas mixture and every sampling device to inject a gas sample into a gas chromatograph can in principle be used. Gas sampling valves with sample loops are very common for this application. Filling the loop with headspace gas is achieved by pressurizing the vials first up to a certain pressure level above the original pressure in the vial. The pressurized headspace then is temporarily connected to the sample loop and the pressurized headspace gas expands through the loop to the atmosphere, thus filling the loop with headspace gas. By rotating the valve, the content of the loop is swept onto the column as shown in Fig. 1.

(d) However, instead of filling first a loop, a pressurized headspace gas can expand directly into the column. Such a sampling system, called *balanced*

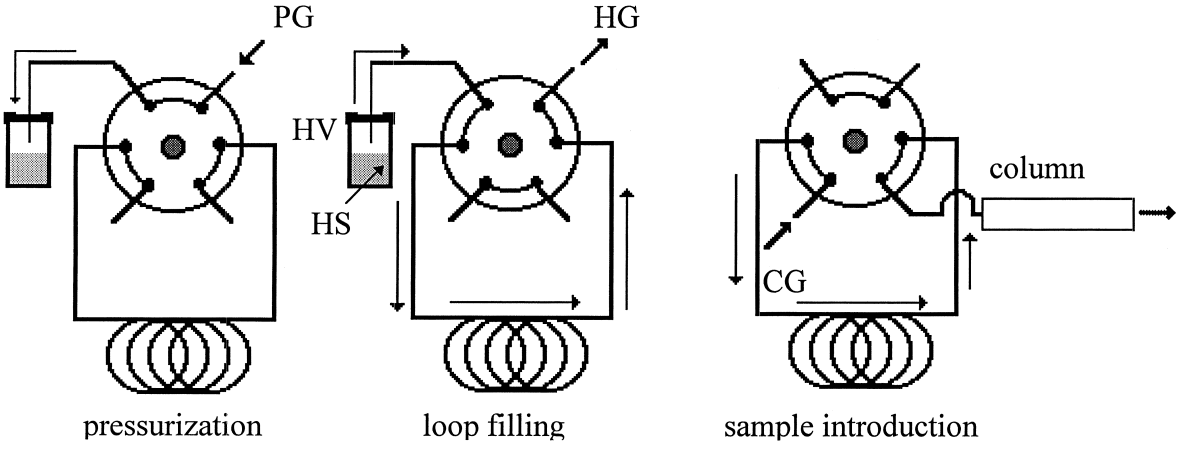

Fig. 1. Schematic of the 'pressure/loop' headspace sampling system. PG = Pressurization gas, HV = headspace vial, HS = headspace sample, CG = carrier gas.

pressure sampling system was already introduced in 1968 in the first automated headspace sampler by Perkin-Elmer [4] and its principle is shown in Fig. 2, while a detailed description is shown later in Fig. 11 when techniques for cryogenic trapping are discussed.

Inert carrier gas enters the gas chromatograph through a solenoid valve V and branches before the column. Part of the gas is directed to the sampling needle SN. The needle penetrates the septum of the headspace vial and carrier gas pressurizes it usually up to the column head pressure, but any other pressure value may be applied as well during this cycle period (cf. Fig. 4). Sample transfer is subsequently performed by closing solenoid valve V for a short time (usually few seconds), thus disconnecting the carrier gas flow. The pressurized headspace gas in the vial expands now directly onto the column and no headspace gas is wasted by unnecessary expansion to atmosphere. The headspace gas replaces the carrier gas flow during the sampling time and the volume of headspace gas transferred into the column is therefore time-controlled and the injected volume can precisely be adjusted by varying the

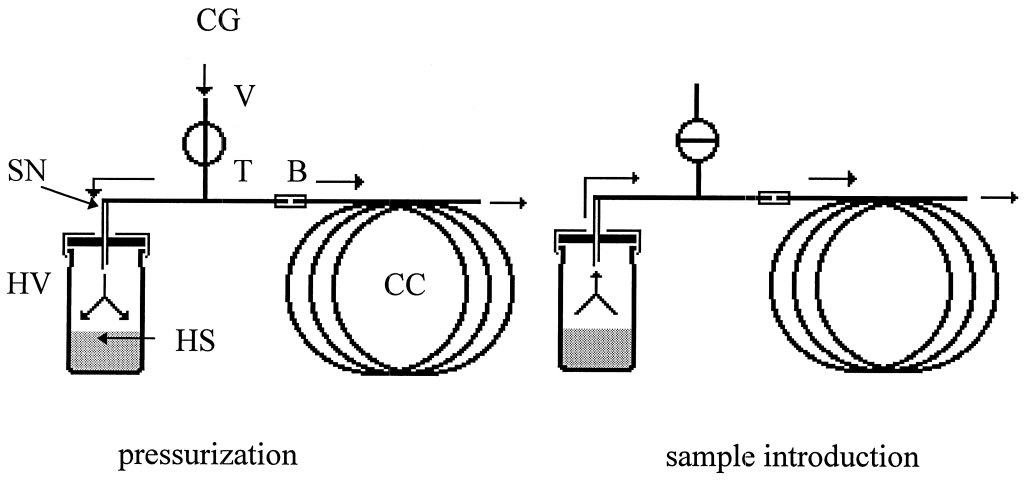

Fig. 2. Schematic of the 'balanced pressure' headspace sampling system in splitless configuration. CG = Carrier gas, V = solenoid valve, SN = sampling needle, HV = headspace vial, HS = headspace sample, T = fused-silica transfer line, B = butt connector, CC = capillary column.

sampling time in a wide range. Any time event is part of a GC method and can thus be automatically varied under computer control in an unattended run contrary to the pressure/loop system where the loop must be changed mechanically.

(e) The technique of SPME is a two-step procedure applied also to static HS-GC [5–7]. A fused-silica fiber coated on the surface with a stationary phase and mounted on a modified GC syringe is either immersed into a liquid sample or exposed to the headspace above the sample (Fig. 3). After achieving equilibrium the fiber is removed and the analytes are thermally desorbed in the injector of a gas chromatograph and transferred to the column. The absorption in the fiber coating adds one more equilibrium process to the existing one between the sample in the vial and the surrounding gas phase. This additional equilibrium constant should also be included in the whole calibration procedure, but in practice equilibrium is often not achieved. Rather the analyte is pumped from the liquid sample through the headspace to the fiber if the distribution constant favors the non-vapor phase. However, the different solubilities of volatile compounds in the fiber coating introduces an additional selectivity into the whole procedure. For example: if a non-polar dimethylsilicone fiber coating is used for a typical headspace application to determine residual solvents in a sample, the non-polar toluene will dissolve reasonably well in the coating while methanol will not. The resulting sensitivities therefore will vary correspondingly, depending much on the polarity of the compounds in the solvent mixture. The technique of SPME is mainly applied for aqueous samples, but not for samples dissolved in organic solvents. Fiber exposure time must be carefully matched across runs to avoid accumulation of air contaminants in the fiber coating. The influence of sample temperature is different compared with the other headspace techniques: an increase in the sample temperature increases in any case the volatility of the analytes and finally the headspace sensitivity, but with SPME this effect is paid off by lowering simultaneously the concentration in the fiber coating. Heating the samples therefore makes not much sense with SPME.

The desorption from the fiber takes some time –

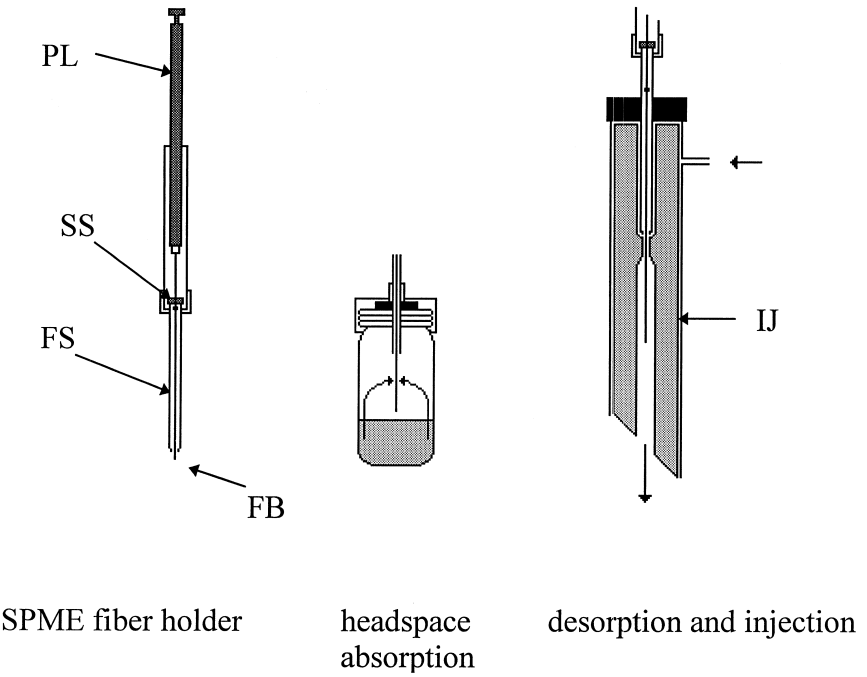

Fig. 3. Schematic of the 'SPME' headspace sampling system. PL = Plunger, SS = sealing septum, FS = fiber sheath (pierces septum of sample vial and GC-injector), FB = SPME fiber, IJ = GC-injector.

often desorption times up to several minutes are applied – depending on analyte volatility, desorption temperature and thickness of the coating, which vary between 7 and 100 μm. High injector temperatures are recommended for a fast desorption. This, however, is in contrast to the general trend in gas chromatography where cold injection techniques are preferred. The resulting gas volume containing the desorbed analytes depends on the flow of carrier gas during the desorption step and similar problems with band broadening may exist, making sometimes a refocusing necessary.

2.2. Principles and instrumentation of dynamic HS-GC

The dynamic headspace technique separates the volatile sample constituents from the sample by a continuous flow of an inert gas either through or above a solid or liquid sample. The variant where the extracting gas flow is bubbling through a liquid – preferably an aqueous – sample, is known as *purge-and-trap.* Quantitative analysis requires an exhaustive gas extraction and this needs more or less time, depending on sample properties (size, viscosity, diffusion, possibility of shaking, etc.) but is in any case too long for an instantaneous sample introduction into a column. It is therefore necessary to focus the volatile analytes in a trap, in general a cartridge packed with an adsorbent (e.g. Tenax), from which they are released by thermal desorption and transferred by the carrier gas into the column. Since the desorption takes also some time, during which the adsorption trap is continuously swept by the carrier gas, again a diluted gas extract is produced. The problem with long desorption time and resulting broadening of the starting band profile is the same if such an adsorption trap is used to collect air samples for pollution analysis rather than accepting the purge gas from a sparging vessel [8,9]. Air sampling, however, using the technique of thermal desorption will be covered by another article in this volume. The use of capillary columns in combination with packed adsorbent tubes therefore has to deal with two problems, a flow problem and a time problem.

The original simple configuration consisting of the sparging vessel, a packed adsorbent tube, connected to a packed column had meanwhile undergone many modifications, to fullfil the rigid demands of capillary columns. The various solutions to this problem are briefly described next.

A high flow-rate is necessary to achieve an exhaustive extraction from the sample in a reasonable time and this requires an adsorption trap with a sufficiently big capacity to avoid breakthrough during the purge time. Such a trap therefore has in general the dimensions of a short packed column and accepts comparable flow-rates, e.g. 20–30 ml/min for both adsorption and desorption. The desorption is the critical step in connection with capillary columns due to the high flow-rate of the desorption gas and also because it takes a longer time than is acceptable for an instantaneous sample introduction into a capillary column. Although the desorption is often carried out at a reduced flow-rate (e.g., 10 ml/min), this may still be too high for the flow requirements of a capillary column and a capillary inlet splitter [10,11] is used to solve the flow problem. Such a splitter, on the other hand, reduces the sensitivity since most of the headspace gas is wasted and a few percent of the sample only is actually used for the analysis. A splitter solves the flow problem but not the time problem because the desorption from the trap may also take a longer time than a high resolution capillary column would allow. These time and flow problems are often handled by a compromise such that a wide-bore capillary column (0.53 mm I.D.) is operated with a high flow-rate, practically under packed column conditions. Although such a compromise may be useful for some practical applications it masks the problem proper.

If the full separation efficiency of capillary columns has to be maintained, an additional refocusing zone becomes necessary, usually by a cryogenic trap. The techniques of cryogenic trapping, however, are discussed in Sections 5 and 6.

3. Properties of capillary columns for HS-GC

3.1. Capacity of capillary columns for gas samples

Headspace analysis is solely a method of sampling and there are, in principle, no limitations for capillary columns and any type may be used. The many

varieties, concerning diameter, length and film thickness as well as carrier gas flow-rate are selected as usual in GC according to the demands of a particular analytical problem. Sensitivity, resolution and analysis time are the most important criteria. Sensitivity depends on the capacity for a gas sample and thus on the diameter of a capillary column; the analysis time, with the carrier gas flow-rate adjusted according to the optimum value, depends on column length while the resolution depends on both column length and diameter. However, it is common practice to run a capillary column at somewhat higher carrier gas flow-rate than the optimum to get a faster analysis while the loss in resolution is, in general, marginal only. Often a compromise has to be found for all these requirements and a capillary column of 0.32 mm I.D. with moderate length, for example 30 m is a good work horse for headspace analysis. However, if high resolution is required, a longer column with a smaller I.D., for example a 50 m×0.25 mm capillary column provides a better separation. According to the fundamental chromatographic theory, resolution increases with the square root of the column length only, while the analysis time increases proportional to column length and the better resolution of such a long column is paid off with a longer analysis time. However, in the case of an automated headspace sampler a long analysis time is less unfavourable, because the samples are analyzed anyway unattended overnight. If, however, a fast analysis is of prime interest, even very short capillary columns with inner diameters of 100 or 50 μm can be used. For example, Russo [12] has separated 11 volatile hydrocarbons ranging from *n*-pentane to cumene in less than 3 min with a 3 m×50 μm fused-silica capillary column at a concentration of 1–2 mg/l in an aqueous sample by static HS-GC with syringe injection and using flame ionization detection (FID), while the electron-capture detection (ECD) allowed the detection of halogenated hydrocarbons in water at a concentration level of few μg/l only under the same chromatographic conditions.

Film thickness is also an important parameter in column technology, but there is a difference between normal GC with liquid injection and the introduction of a gas sample. In normal GC, a thicker film is often preferred to provide a higher sample capacity for compounds of high concentrations to avoid peak broadening of the big peaks by overload and hence loss in resolution. Sample capacity is in general defined in GC as the highest admissible solute amount in a column which does not yet affect the sharpness or the symmetry of the corresponding peak by overload. This, however, is not the problem here. A headspace sample is a diluted gas sample and the absolute amounts of the analytes are in general small enough to avoid peak broadening. Capillary columns with thick films (>1 μm) are mainly used in HS-GC for highly volatile compounds to provide the necessary retention at convenient column temperatures above ambient. Disadvantages of thicker films are longer analysis times, loss in resolution, higher temperatures for less volatile sample constituents, often combined with excessive baseline drift during temperature programming, particularly at the necessary high detector sensitivity for trace analysis. On the other hand, a thick-film fused-silica capillary column has attractive properties for cryogenic trapping.

Column capacity in HS-GC has a different meaning and concerns the gas volume which can be introduced without significant band broadening. To avoid any confusion with the conventional definition of capacity, the term *headspace capacity* is more adequate and will be used instead. The volume of a gas sample, if introduced with the same pressure of the carrier gas at the column head (*isobaric headspace sampling*), replaces an equivalent volume of carrier gas. Its introduction therefore needs some time, depending on the cross section of the capillary column, carrier gas flow-rate and sample volume. A long sampling time therefore causes band broadening just at the beginning of chromatography. The relationship of sample volume and sampling time is immediately obvious with the time controlled balanced pressure sampling system. If we accept a maximum time of 3 s to introduce a gas sample at a linear carrier gas flow-rate of 30 cm/s at the column head, the corresponding volumes of gas samples with capillary columns of varying inner diameters are listed in Table 1.

From the data in Table 1 we see that the volume of headspace gas during an acceptable sampling time is surprisingly small and less than 1% of the available total headspace gas in a headspace vial of typically ca. 20 ml volume. It is obvious that the

Table 1
Headspace sample volume (H.V.) as a function of the inner diameter (I.D.) and cross section (C.S.) of capillary columns during a sampling time of 3 s at a linear flow-rate of 30 cm/s

I.D. (mm)	C.S. (mm^2)	H.V. (μl)
0.10	0.008	7.1
0.18	0.025	22.9
0.25	0.049	44.2
0.32	0.080	72.4
0.53	0.785	198.5

admissible sample volume increases with the cross section of the capillary column. For this reason, fused-silica capillary columns with an I.D. of 0.53 mm (wide-bore capillary columns) are often used for HS-GC, particularly when packed columns should be replaced and if high resolution is not required. Such columns are often recommended in official procedures, for example to determine volatile organic impurities (OVIs) in pharmaceutics by USP [13]. There is, however, a serious limitation if such wide-bore capillary columns are used for GC–MS, since most quadrupole mass spectrometers cannot accept carrier gas flow-rates >5 ml/min which are usually applied for those columns and flow reduction by using an outlet splitter again reduces the sensitivity.

3.2. Example for headspace sensitivity depending on column type and detector sensitivity

The following practical application should be used to give an example for the determination of concentrations in the low range of $\mu g/l$ even with the simple balanced pressure headspace sampling technique by a reasonable combination of column diameter and appropriate detector sensitivity without the need for any further refocusing procedures. The total available volume of the headspace gas in the usual vials with about 20 ml volume as used for static HS-GC is large enough to allow simultaneous sample introduction into parallel capillary columns. With such a dual channel arrangement it is possible to find optimized conditions for both resolution and headspace capacity to meet the specific requirements of a

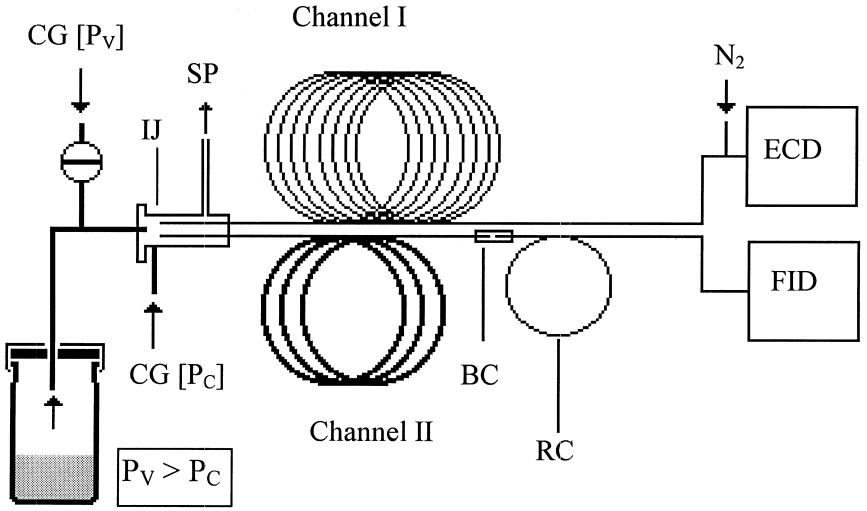

Fig. 4. Schematic dual channel ECD–FID configuration for simultaneous static headspace analysis of volatile halogenated and aromatic hydrocarbons in water. Balanced pressure system in sampling position and in split mode. *Instrumentation*: Perkin-Elmer AutoSystem, HS40 Automatic Headspace Sampler. CG = Carrier gas, IJ = GC-injector, SP = split vent; dual capillary column arrangement with a two-hole ferrule at the injector; channel I: 60 m × 0.32 mm I.D. fused-silica capillary column Rtx-volatiles (Restek), 1.5 μm film thickness, detector: ECD at 350°C, make-up gas: N_2, 50 ml/min; channel II: 15 m × 0.53 mm I.D. fused-silica capillary column, Stabilwax (Restek), 1.0 μm film thickness, connected by a butt connector (BC) to the end-restrictor (RC): 0.6 m × 0.15 mm I.D. deactivated fused-silica capillary, detection: FID; temperature program: 40°C (5 min), 5°C/min, 110°C (15 min), 20°C/min, 150°C (2 min); carrier gas: helium, 205 kPa vial pressure [P_V], 160 kPa column headpressure [P_C], split flow: 50 ml/min. *Headspace conditions*: pressurization time: 3 min, sampling time: 0.08 min, sample: 5 ml, equilibrated at 80°C for 30 min with shaking.

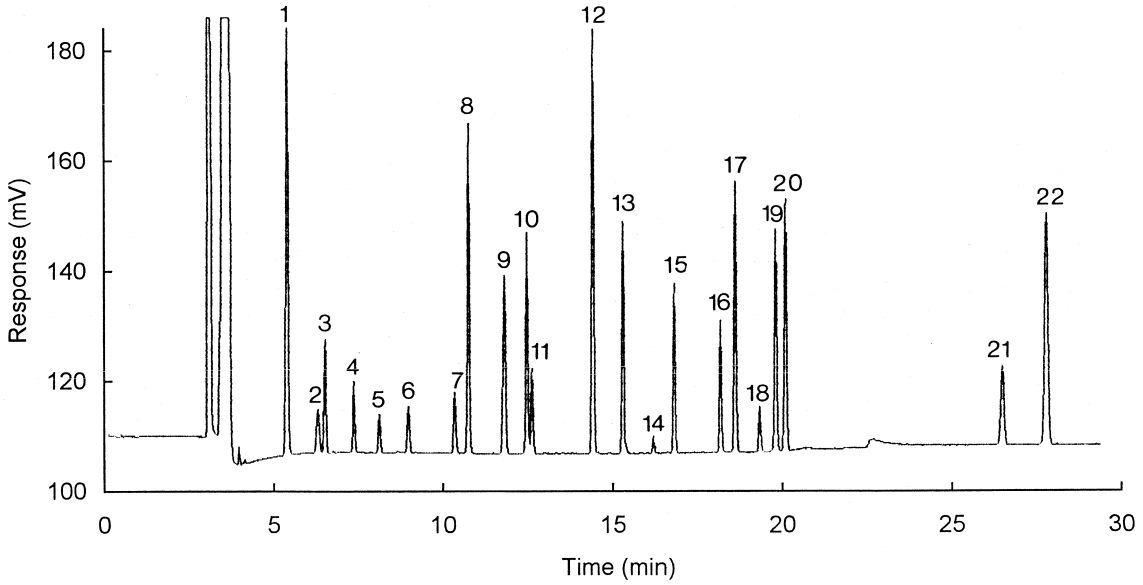

Fig. 5. Determination of volatile halogenated hydrocarbons from water by static HS-GC. Instrumentation and headspace conditions as given in Fig. 4 for the ECD channel (channel I). *Identified peaks*: 1=dichlorofluoromethane+trifluoromethane, 2=1,1,2-trichlorotrifluoroethane, 3=1,1-dichloroethylene (1.95 μg/l), 4=dichloromethane (5.4 μg/l), 5=*trans*-1,2-dichloroethylene (3.0 μg/l), 6=1,1-dichloroethane (4.7 μg/l), 7=2,2-dichloropropane (2.6 μg/l)+*cis*-1,2-dichloroethylene, 8=chloroform (0.6 μg/l), 9=1,1,1-trichloroethane (0.1 μg/l), 10=carbon tetrachloride (0.05 μg/l), 11=1,2-dichloroethane (5.0 μg/l), 12=trichloroethylene (0.44 μg/l)+1,2-dichloropropane, 13=dichlorobromomethane (0.16 μg/l), 14=2-chloroethyl vinyl ether, 15=*cis*-1,3-dichloropropylene, 16=*trans*-1,3-dichloropropylene, 17=1,1,2-trichloroethane (3.5 μg/l), 18=1,3-dichloropropane (2.6 μg/l), 19=tetrachloroethylene (0.66 μg/l), 20=dibromochloromethane (0.4 μg/l), 21=bromoform (0.3 μg/l), 22=1,1,2,2-tetrachloroethane (1.3 μg/l). From Ref. [14], with permission.

particular analytical task. An example is given in Figs. 4–6 [14]. The determination of volatile aromatic and halogenated hydrocarbons in water and soil is of widespread importance and a vast number of samples need to be processed routinely. A high degree of automation therefore is required for cost reduction reasons and static HS-GC in this respect is best suited and is widely used for this application. Both classes of compounds can be analyzed with such a dual channel arrangement under optimized conditions. The class of halogenated hydrocarbons comprises many compounds, and a long capillary column with good resolution is required, for example, a 60 m×0.32 mm I.D. fused-silica capillary column. This column is already standardized according to the US Environmental Protection Agency (EPA) Method 624. ECD is used here for the determination of the halogenated compounds (channel I). The high detector sensitivity for this class of halogenated compounds compensates the lower sample capacity of the 0.32 mm I.D. capillary column. The other channel (channel II) is used to separate the volatile aromatic hydrocarbons (benzene, toluene, ethylbenzene, xylene, BETX) with FID, but here a better sensitivity is more important than high resolution, since the interesting compounds are easily to separate, even with a short 0.53 mm I.D. capillary column. However, both columns need different headpressures for optimized flow conditions and to achieve a common carrier gas pressure, for both types of columns a restrictor capillary (60 cm×0.15 mm I.D. deactivated fused-silica capillary) was connected to the end of the 0.53 mm I.D. capillary column providing a flow-rate of 11 ml/min to the detector. It should be mentioned that simultaneous sample introduction in the two parallel columns does not affect the sensitivity, because from the huge reservoir of headspace gas in the vial the same volume is withdrawn for each channel as in the case of a single column during the time-controlled sample transfer. This dual channel configuration is shown in Fig. 4.

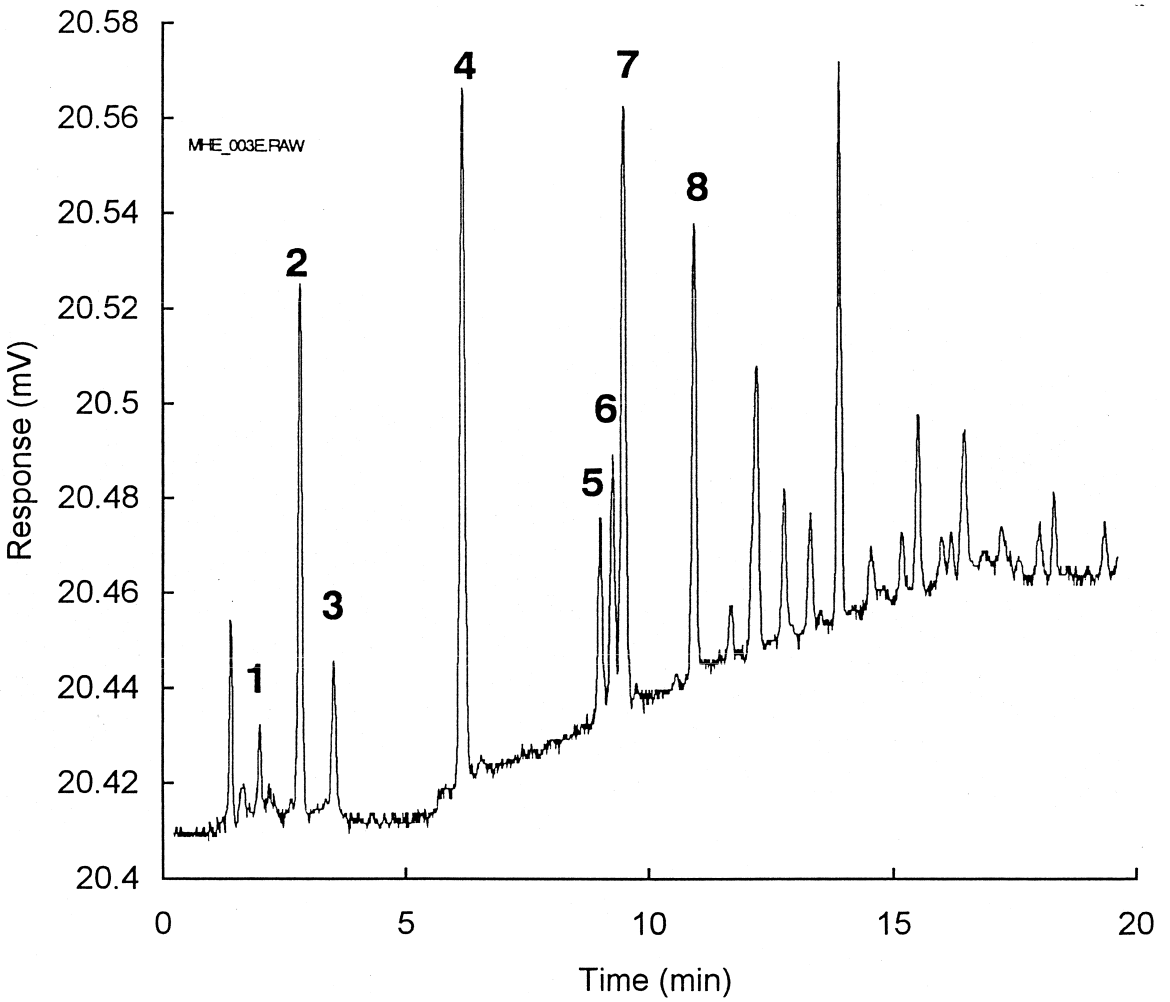

Fig. 6. Determination of residual gasoline constituents in a wheathered water sample. Instrumentation and conditions as given in Fig 4 for the FID channel (channel II). *Identified peaks*: 1=MTBE (3.8 μg/l), 2=methanol (1.9 mg/l), 3=benzene (2.9 μg/l), 4=toluene (22.3 μg/l), 5=ethylbenzene (3.9 μg/l), 6=*p*-xylene (4.9 μg/l), 7=*m*-xylene (13.0 μg/l), 8=*o*-xylene (10.3 μg/l). From Ref. [14], with permission.

The resulting chromatogram from a standard test sample of halogenated hydrocarbons in water is shown in Fig. 5 and that from a water sample collected from a river, polluted with gasolin, in Fig. 6. A polyethylene glycol (Carbowax) phase was used to separate the aromatic compounds, including *m*- and *p*-xylenes The latter sample is of particular interest, because the paraffins have already evaporated from the river water approximately 5–8 h after a gasoline spill, thus making room in the early part of the chromatogram for the peaks of methyl *tert.*-butyl ether (MTBE) and methanol. Due to the low volatility of methanol in water and assuming a concentration of about 1% methanol in gasoline an original pollution in the river water of approximately 200 mg/l can roughly be estimated.

This example is presented here to show that good sensitivities can be obtained by selecting carefully the column type to reach the analytical objective without resorting to focusing techniques. Such a dual channel configuration is very flexible concerning the types of columns and its combination. This example

also demonstrates that sensitivity depends on the type of the detector too. There is a wide range of standard GC detection methods, such as electrolytic conductivity detection (ELCD) for halogenated compounds, photoionization detection (PID) for aromatic compounds or nitrogen–phosphorous detection (NPD). A mass spectrometer is also already a standard GC detector and a quadrupole mass spectrometer in the single-ion monitoring (SIM) mode provides good sensitivity [15] as shown in Fig. 7 and comparing the sensitivities with the ECD chromatogram in Fig. 5 for similar compounds.

If, however, even a good combination of column type and detector lacks the required headspace sensitivity, enrichment techniques can provide a remarkable improvement, mainly by using thermal

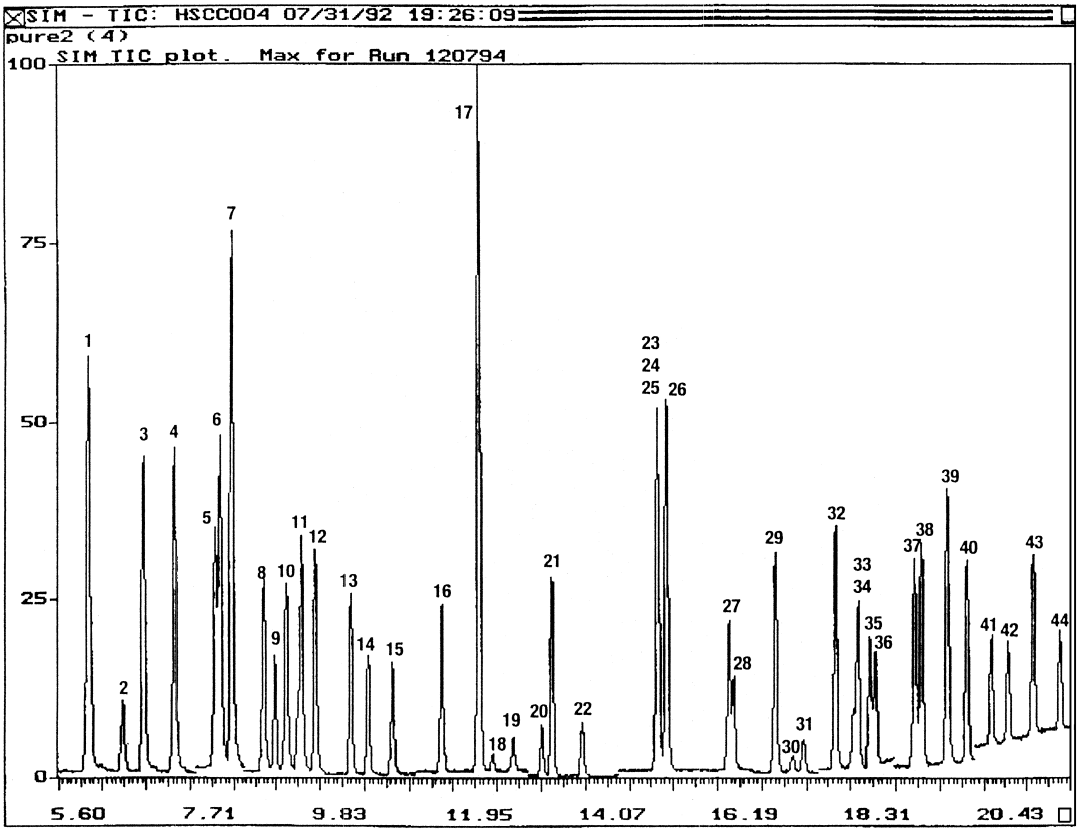

Fig. 7. Single-ion monitored total-ion chromatogram of a water standard containing 44 halogenated and aromatic hydrocarbons at the 10-ppb level, by directly coupled static HS-GC–(quadrupole) MS. *Instrumentation*: Perkin-Elmer AutoSystem, HS40 Automatic Headspace Sampler, Qmass 910 mass spectrometer; 60 m×0.32 mm I.D. fused-silica capillary column, VOCOL (Supelco), 3 μm film thickness, programmed: 40°C (5 min), 25°C/min, 100°C, 5°C/min, 189°C. *Headspace conditions:* sample: 5 ml of the standard, equilibrated at 40°C for 30 min, sampling time: 4.8 s. *Identified peaks*: 1=1,1-dichloroethylene, 2=dichloromethane, 3=*trans*-1,2-dichloroethylene, 4=1,1-dichloroethane, 5=2,2-dichloropropane, 6=*cis*-1,2-dichloroethylene, 7=chloroform, 8=1,1,1-trichloroethane, 9=1,1-dichloropropane, 10=carbon tetrachloride, 11=1,2-dichloroethane, 12=benzene, 13=trichloroethylene, 14=1,2-dichloropropane, 15=bromodichloromethane, 16=*cis*-1,3-dichloropropylene, 17=toluene, 18=*trans*-1,2-dichloropropylene, 19=1,1,2-trichloroethane, 20=1,3-dichloropropane, 21=tetrachloroethylene, 22=dibromochloromethane, 23=chlorobenzene, 24=ethylbenzene, 25=1,1,1,2-tetrachloroethane, 26=*m*-+*p*-xylene, 27=*o*-xylene, 28=styrene, 29=isopropylbenzene, 30=bromoform, 31=1,1,2,2-tetrachloroethane, 32=*n*-propylbenzene, 33=bromobenzene, 34=1,3,5-trimethylbenzene, 35=*o*-chlorotoluene, 36=*p*-chlorotoluene, 37=*tert*-butylbenzene, 38=1,2,4-trichlorobenzene, 39=*sec*-butylbenzene, 40=*p*-isopropyltoluene, 41=*m*-dichlorobenzene, 42=*p*-dichlorobenzene, 43=*n*-butylbenzene, 44=*o*-dichlorobenzene. From Ref. [15], with permission.

refocusing at low temperatures (cryogenic trapping). These enrichment techniques are discussed in the following Sections 5 and 6.

3.3. Headspace sampling with split or splitless?

The problem whether a headspace sample should be introduced into a capillary column either splitless or using an inlet splitter is different compared to the injection of a liquid sample in normal gas chromatography. A diluted liquid sample needs splitless injection to get the necessary sensitivity for the low concentrated analytes but requires subsequent refocusing of the accompanying broad starting sample band by thermal focusing or by the solvent effect. A solvent effect is not feasible for a gas sample and only thermal refocusing remains for band sharpening, usually by cryogenic trapping.

Split injection of a liquid sample in normal GC is prone to mass discrimination, which is caused by several effects during evaporation of the injected liquid sample in a hot injector. Such effects are incomplete evaporation from the syringe needle, rapid pressure increase by solvent evaporation with fractionated evaporation of a wide boiling mixture and accompanying change of the split ratio. There are some more effects involved, but all are related to the evaporation process in a hot injector. Sampling of an already homogenous gas sample, particularly under isobaric conditions does, in principle, not have such problems and mass discrimination therefore is unlikely to occur and was never observed with split injection of a headspace sample. But, independent from these fundamental differences to liquid sample injection, the situation is different either between the various headspace sampling techniques.

The dynamic headspace techniques try to achieve an exhaustive gas extraction of a sample mainly for quantitative analysis and not in any case to get high sensitivity. If the resulting gas extract is sufficiently concentrated, the loss in sensitivity by using an inlet splitter may therefore be acceptable. Refocusing techniques in this case are applied more for band sharpening due to a delayed sample introduction (time problem). If, however, further enrichment techniques become necessary for low analyte concentrations, splitless sample introduction is mandatory. The procedures and instrumentation will be discussed in Sections 5 and 6.

The same considerations apply for the SPME procedure, but here splitless sample introduction is in general preferred (cf. Fig. 3) because the available sample amount is confined by the absorbed amount of the analytes in the fiber coating and any loss by a splitter reduces sensitivity while further enrichment is not feasible. Thermal focusing and even cryogenic trapping is sometimes necessary but again for band sharpening rather than for sample enrichment.

In static HS-GC the total volume of the headspace gas is large enough to allow sample introduction using an inlet splitter. If we assume an admissible sample volume of, say 100 μl, in a capillary column, a split ratio of 1:20 will require a total volume of 2 ml and this is 10% only from the whole available headspace gas in a 22 ml vial containing, for example, a 2 ml sample. In the case of split sampling, the gas volume withdrawn by time-controlled headspace sampling from the vial is larger due to the high split flow but will immediately be split before the column and the volume which actually enters the capillary will be the same as in the case of splitless sampling and not much differences therefore are to be expected [16]. The same situation applies with syringe or loop injection, where a correspondingly higher sample volume can be injected to compensate the loss by the splitter. Whether split- or splitless mode is used here depends more on practical or instrumental aspects. It is often easier to attach an automated headspace sampler to the gas chromatograph by connecting a heated transfer line to an existing standard split/splitless injector (cf. Fig. 4). But, if the incoming headspace gas is mixed in this injector with carrier gas, it will be diluted and the sensitivity be lowered. A small split ratio is therefore recommended.

Split sampling is also recommended in the case where a headspace sampler is attached by a long transfer line to the gas chromatograph, because due to the split flow the sample transfer through the transfer line will be accelerated. Also if in a not well designed instrument some dead volumes are present, a higher flow of the headspace gas may be helpful. Whenever a splitter is used for reasons as discussed above, a low split flow is recommended in any case and particularly for the balanced pressure sampling

system, because otherwise the pressure in the pressurized vial during the sampling period will decrease and the sample transfer will thus be decelerated. While for practical reasons, split-sampling has some benefits, splitless sample introduction is mandatory for any further enrichment techniques to avoid wasting of headspace sample by an unnecessary splitter.

4. Headspace sampling time and band broadening

4.1. Band broadening during sample introduction

If a gas sample has to be introduced into a capillary column the problem is how large can the volume be before band broadening becomes intolerable. Ideally, sample introduction should be instantaneous and the starting band width should approach zero time, but in practice a compromise for resolution and sensitivity – as usual in gas chromatography – has to be found. However, if for trace analysis a large sample volume is injected to get the necessary high sensitivity together with high resolution, the relationship between sample volume, sampling time and band broadening must be discussed, particularly since many recommended techniques or published applications hide this fundamental problem.

The sharpness of peaks is determined by the starting band profile at the beginning of the chromatographic process and later by band broadening during the chromatographic migration in the column by various diffusion processes in the stationary and the mobile phase. The first effect is the result of the sampling technique, while the second can be influenced by column technology and operating conditions. The starting band profile affects particularly the early eluting peaks while with increasing retention times the second effect becomes more dominant. The discussion here on band broadening will be strictly confined to the influence of the sampling procedure and will briefly summarize a more detailed discussion on headspace sampling technique [16].

The volume a gas sample occupies in the capillary column and also the individual length of the zone for each compound dissolved in the stationary phase is in principle proportional to the sampling time. This, however, is correct for isobaric conditions only, when the pressure of the headspace gas sample equals the carrier gas pressure. Depending on the various headspace sampling techniques, however, the pressure may be different and may even change during sample introduction. For example: the gas sample in a gas syringe is at atmospheric pressure, when the needle is open to atmosphere, even if it was originally filled with pressurized headspace gas. Immediately when the needle penetrates the septum of the GC-injector, the syringe is connected to the carrier gas and will be filled up with the carrier gas pressure faster than the plunger can be pressed forward. The headspace gas volume may be injected rapidly or slowly. If the plunger is rapidly pressed forward, the pressure in the gas sample by compression will exceed the carrier gas pressure and the headspace gas sample will enter the column as a pneumatic pulse at a higher flow-rate and thus in a shorter time compared to a slow injection. Although the actual injection time differs, the volume of the headspace gas is the same and will finally occupy the same volume in the column because it will soon acquire the carrier gas pressure by expansion or compression inside the column. Therefore, the plug of the headspace gas extends the same distance into the capillary column and the individual zones for each compound too. This example should demonstrate that the sampling time does not necessarily determine the starting band width. More or less the same relationship is found with other techniques of headspace sampling.

In the case of time-controlled balanced pressure headspace sampling, where the vial is connected to the capillary column, the length of the sample plug in the column corresponds to the linear flow-rate of the carrier gas during the sampling time under isobaric conditions. If, however, the pressure in the vial is adjusted above carrier gas pressure, sample transfer is faster and there is the same situation as described above. An opposite effect is achieved when the headspace gas is transferred from a small vial with a limited gas volume into a column with a high flow-rate, for example a packed column or a capillary column operated with a high split ratio, since the pressure in the vial will decrease during sampling time and the sample transfer into the

column will be decelerated and it will take longer to introduce the same volume of headspace gas. The distance, however, the sample volume extends inside the column will finally be the same as under isobaric sampling conditions.

In the case of loop sampling the situation is comparable, since for these considerations the volume of the loop may be considered analoguous to the volume of the vial or the syringe. Immediately when the filled loop is connected to the carrier gas it will first be pressurized. The situation may be further complicated, if the headspace gas is exponentially diluted by carrier gas during the elution from the loop.

This discussion of the interrelationship of gas volume and sampling time should show that the resulting starting band profile and thus the chromatographic resolution does not necessarily depend on how long the sample introduction takes. This is not a problem for practical headspace application, where sample volume, sensitivity, resolution and injection time are usually adjusted empirically, it only complicates a theoretical treatment. The real starting band profile can be determined by the ABT-concept of Kaiser [16,17]: the peak width in an isothermal chromatogram increases with retention time and by linear regression calculation the peak width at zero retention can be derived. This method was applied to measure the effect of cryogenic trapping on separation efficiency by investigating the peak width at the start of the chromatographic separation [18].

4.2. Temperature influence on band broadening

However, independent of all the different sampling techniques, the situation is the same when sample introduction is finished and the chromatographic process starts: the plug of the headspace sample extends a certain distance into the capillary column depending on the volume of the headspace gas at carrier gas pressure conditions, on the diameter of the capillary column and the flow-rate. The length of the zone for each solute depends on its chromatographic properties under given conditions and is a fraction of the headspace sample plug. This common situation at the begin of chromatography allows now to discuss band broadening effects on a more general basis and independent from the various sampling techniques. Again we ignore the additional chromatographic band broadening due to the various diffusion processes in both phases which overlay the original rectangular starting profile.

The distribution of a solute in a gas–liquid equilibrium system is described by the *distribution constant* (K), also called *partition coefficient* which is the ratio of solute concentration in the liquid phase (C_L) to that in the gas phase (C_G):

$$K = C_L / C_G \tag{1}$$

Since the concentrations are given as mass per volume, the distribution constant (K) can be split in the the *mass distribution ratio*, this is the ratio of the solute amounts in both phases, ($k = m_L / m_G$) and the *phase ratio* (β), this is the ratio of the volumes both phases occupy in the capillary column ($\beta = V_G / V_L$)

$$K = k\beta \tag{2}$$

The mass distribution ratio (k) determines the retention behaviour of the solute in the column and is therefore also called retention factor: it is the ratio of the adjusted retention time (t'_R) of the solute to the hold-up time (t_M), this is the time an inert and not retarded compound needs to travel through the column with the velocity of the mobile phase. The retention factor (k) is therefore the ratio of solute residence time in the two phases.

$$t'_R = t_R - t_M \tag{3}$$

$$k = t'_R / t_M \tag{4}$$

The main compounds in a headspace sample is the air in a headspace vial, often mixed with the carrier gas. The distribution constant of this gas mixture is zero ($K = 0$) at any temperature and it passes a capillary column with the velocity of the carrier gas flow with no retention. The length of the resulting plug of the headspace gas in the capillary column is determined from the volume of the headspace gas and the cross section of the capillary. The solute band, however, is shorter because already during the sampling time the solute dissolves in the liquid phase and migrates slower due to the retention. This delayed migration can be visualized and described by the *relative migration rate* (Rf) which is identical to the retardation factor (R_F) used in thin-layer chroma-

tography and which is the migration rate of the solute relative to that of the mobile phase. The relative migration rate of an analyte therefore is expressed as the ratio of migration rate of the sample (u_S) to that of the carrier gas (u_C):

$$Rf = u_S / u_C \quad (5)$$

Rf also describes the retention behaviour of the solute and is related to the retention factor (k):

$$Rf = \frac{1}{1+k} \quad (6)$$

After all, the relative migration rate (Rf) is related to the distribution constant (K):

$$Rf = \frac{1}{1+K/\beta} \quad (7)$$

The solute dissolves in the liquid stationary phase and the length of the solute zone depends on *Rf* and finally on the distribution constant (K) and the phase ratio (β). At a given column temperature and thus a given distribution constant (K), the length of this zone can be varied by modifiying the film thickness. A thicker film and thus a smaller phase ratio (β) causes a smaller zone for each solute at the column inlet. It is often recommended in practice, to use a thick film to focus the slowly arriving compounds at the column head, but such a thicker film does not by itself help to sharpen a band. With a thicker film and hence a lower migration rate the starting band width becomes smaller, compared to a thinner film at the same sampling time, but the molecules now migrate slower. When this zone arrives at the column end, the molecules at the front of the zone already leave the column, but the molecules at the rear of this zone still have to travel the same distance across the band width with the same migration rate. The elution of this zone therefore requires the same time period as was applied for sampling. The elution time therefore is identical with the sampling time and independent from film thickness. Of course the actual eluted peak is broader due to the various diffusion effects during the chromatographic migration as described by the *Golay–van Deemter Equation*. These effects, however, are outside the scope of these considerations which should be confined strictly to the contribution of the sampling process on peak broadening.

The advantage of a thicker film can be utilized only in combination with a temperature rise. When increasing the column temperature after sampling, the initial band width in units of length is not affected and remains the same. But the volatility (migration rate) increases with temperature and this zone when arriving at the column end is emptied much faster now due to enhanced migration. Since the chromatogram is finally traced in a time scale, the peak width at column end in units of time now becomes smaller as it would be under isothermal conditions at the lower temperature of sampling. This *thermal focusing effect* is shown by comparing both chromatograms in Fig. 8, which were obtained with the balanced pressure headspace sampling technique. The early peaks (acetaldehyde and ethanol) in the headspace chromatogram (A) are sufficiently small due to the short sampling time of 4.8 s, while a sampling time of 24 s (chromatogram B) apparently was too long for these early eluting peaks, which therefore are unduly broad. The peak shapes of the fatty acids, which are eluted later by temperature programming are not affected, but the longer sampling time increased the sensitivity correspondingly due to the larger sample volume.

The same effect on peak broadening is obvious in the chromatogram in Fig. 9, obtained by SPME, where the time of 60 s to desorb the fiber in the injector at 250°C was apparently too long for the early eluted peak of chloronitromethane. The later eluted peaks are all sharpened by the thermal focusing effect. The chromatogram in Fig. 9 contains another type of peak broadening: the last peak is broadened by overload, because it is the dominant compound *trans*-anethol from an anise drop.

4.3. Conclusions

The foregoing discussion showed that the starting band profile of a gas sample depends on sample volume and the diameter of a capillary column, but on the time of sample introduction only under isobaric conditions. Film thickness has no effect on the band width in units of length and causes no focusing effect under isothermal conditions. Only temperature programming helps to elute an originally broad band profile as a sharp peak in units of time. However, the application of this thermal focusing effect for highly volatile compounds needs, in gener-

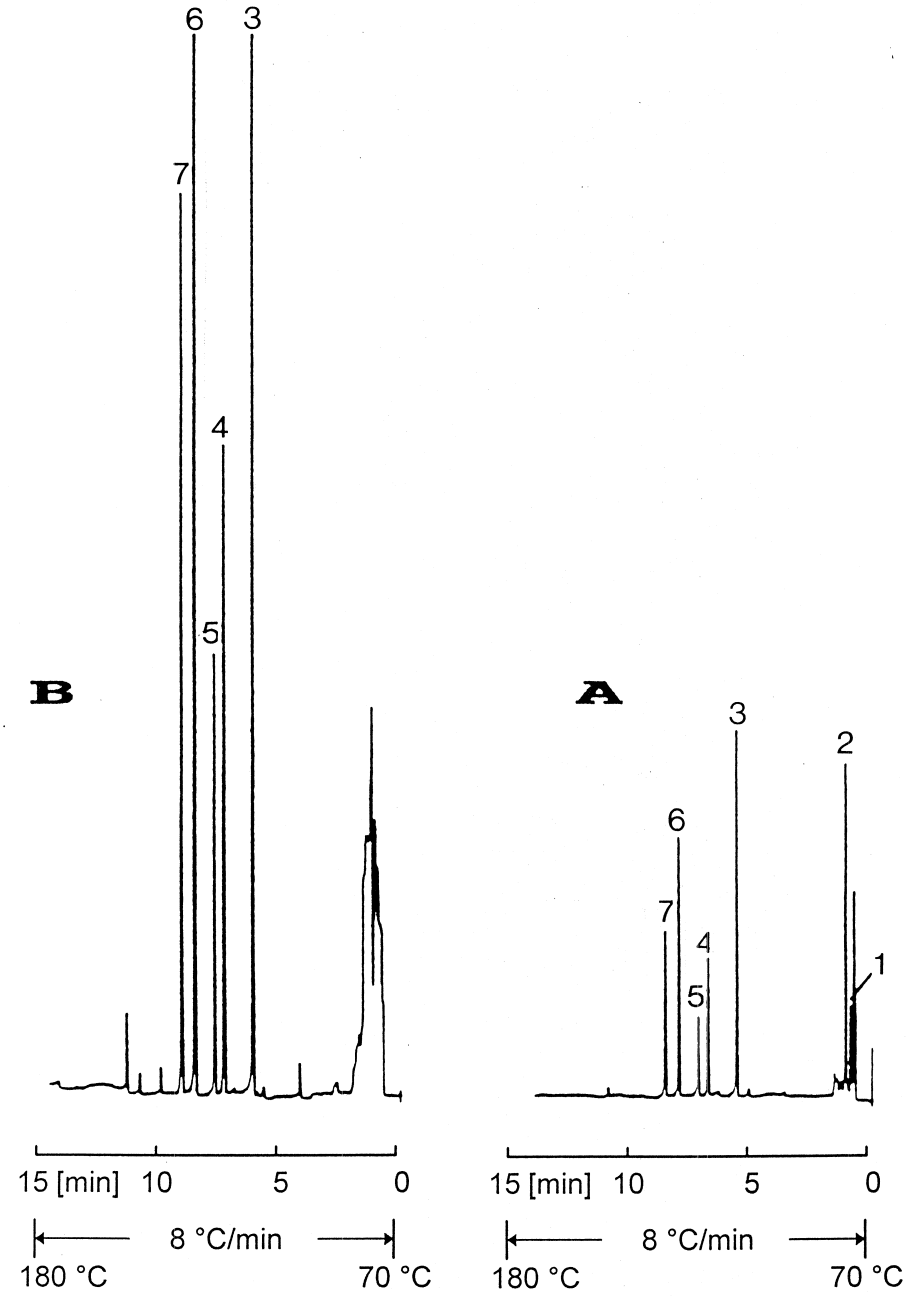

Fig. 8. Free fatty acids in cheese by static HS-GC. *Instrumental conditions*: Perkin-Elmer SIGMA 2000 GC, Automatic Headspace Sampler HS100; 25 m×0.32 mm I.D. fused-silica capillary column, FFAP liquid phase, 1 μm; programmed as given; FID. *Headspace conditions*: sampling time: (A) 4.8 s, (B) 24 s, sample: 2 g ground cheese, equilibrated 60 min at 90°C. *Identified peaks*: 1=acetaldehyde, 2=ethanol, 3=acetic acid, 4=propionic acid (130 ppm), 5=isobutyric acid, 6=butyric acid, 7=isovaleric acid (85 ppm). From Ref. [19], with permission.

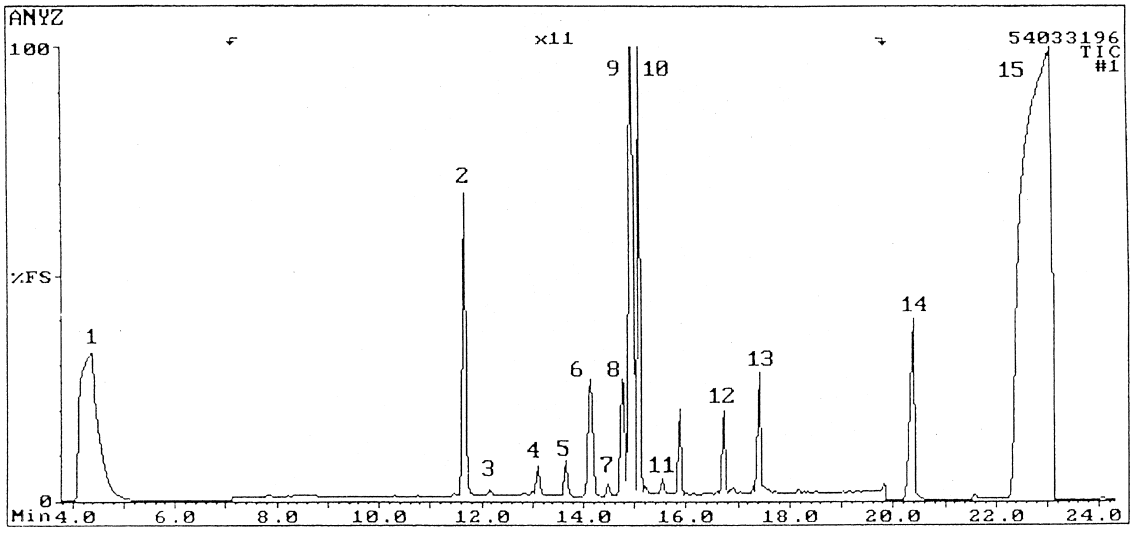

Fig. 9. Analysis of volatile ingredients of anise drops by SPME. *Instrumental conditions*: FISONS GC-8000 and MD-800 quadrupole mass detector, SPME holder (Supelco), 10 mm fiber coated with dimethyl silicone, 100 μm; precolumn: 2 m×0.32 mm I.D., phenyl methyl deactivated (Restek), analytical column: 30 m×0.32 mm I.D. fused-silica capillary, DB-5 ms, 0.5 μm (J&W Scientific), programmed: 30°C (2 min), 2°C/min, 120°C, 5°C/min, 270°C; injection: splitless, desorption 60 s at 250°C. *Identified peaks*: 1=chloronitromethane, 2=4-carene, 3=camphene, 4=β-pinene, 5=β-myrcene, 9=limonene, 14=estragol, 15=*trans*-anethol. From Ref. [20], with permission.

al, low starting temperatures and this leads finally to the techniques of cryogenic trapping, which is discussed in the following Section 5.

5. Enrichment techniques by cryogenic trapping

Enrichment techniques become necessary if the analyte concentration in the headspace gas sample is below detectability. For this purpose the target analytes must be separated from the headspace gas either by absorption into a liquid or by adsorption onto a solid adsorbent and also by condensation in a cold trap. The vast numbers of different methods in comprehensive reviews on general preconcentration techniques for headspace volatiles [21] and particularly by cryogenic trapping [22,23] indicate the need for such enrichment purposes to increase sensitivity and also to improve chromatography by band concentration (focusing). Solvent-free techniques are particularly desirable in case of trace analyses to avoid the cumbersome problems with solvent impurities. Cryogenic trapping therefore is the preferred choice and will be discussed here exclusively.

Cold traps are used for two main reasons: enrichment purposes and solute band concentration. There are so many instrumental possibilities for cold trapping and the selection of the technique which should be applied depend much on other aspects, for example whether a single analysis from a unique sample only should be carried out or if the whole headspace procedure including cryogenic trapping should be carried out routinely and completely automated. Most published constructions of cold traps are home-made and are operated manually, requiring more or less skill and experience of the operator. According to the general trend in analytical instrumentation, however, any technique will be successful only if it can be operated automatically and unattended. For this reason, the main emphasis in the following discussions is clearly on automated instrumentation. Any headspace sample as mentioned earlier, is a diluted gas sample and some of the techniques described in this section were not developed explicitly for headspace analysis but were often applied just for the analysis of gas samples, e.g. for air samples, but are included here also because they are likely to work for headspace samples as well.

5.1. Methods of cryogenic trapping

The various underlying physical principles and the many versions of cold traps requires a clear definition of the nomenclature to classify the different instrumental configurations in a systematic approach. Therefore a distinction is made between *cryogenic condensation* and *cryogenic focusing* while the common term *cryogenic trapping* is applied for both.

The term *cryogenic condensation* is used here for techniques where the volatile compounds are trapped simply by condensation in traps which usually contain no stationary phase. Condensation is also the prevailing mechanism if a coated capillary is cooled down to such a low temperature, that the liquid phase will solidify and lose its property as a chromatographic phase. This limiting temperature is determined by the glass transition temperature (*T*g) of the liquid phase. The *T*g of a dimethyl silicone rubber is −125°C [24] and may therefore be representative also for a crosslinked immobilized silicone in a capillary column. Other and particularly polar liquid phases are less applicable, although even a Carbowax-type phase was reported to act as a liquid phase at a temperature as low as 0°C [25]. In general, however, empty tubes of glass or metal, sometimes filled with some inert packings (glass beads) are preferred, but wall coated fused-silica capillary columns can also be used as cold traps since chemically crosslinked liquid phases allow cooling even by liquid nitrogen (LN_2) without damaging the film, e.g. by droplet formation, although the stationary phase will have lost its chromatographic properties at such a low temperature.

The term *cryogenic focusing* is used if the volatile compounds are trapped in the liquid phase of a column at a low temperature which, however, is still above the glass transition temperature. Cryogenic focusing is identical with thermal focusing, discussed before, and the difference in the nomenclature should only indicate the difference in the applied temperature, with cryogenic focusing carried out below and thermal focusing above ambient temperature. During the sample introduction the compounds dissolve in the liquid phase and migrate already but slowly downstream the cold column. The focusing effect is achieved in the same way as the thermal focusing effect by subsequent temperature rise at the end of the headspace sampling period. The longitudinal bandwidth is thus transformed into a smaller bandwidth in time units, as the peak leaves the cold zone or the column end. In addition to thermal focusing, however, there is another and even more effective focusing effect, if a temperature gradient during trapping and/or desorption can be applied. Advanced versions of cryogenic focusing use this technique of *cryogenic gradient focusing* and examples are given in the Figs. 8, 12–15, 18, 21, 23–25.

5.2. Instrumentation for cryogenic trapping

It was already discussed that dynamic HS-GC meets a flow problem and a time problem whenever the analytes are transferred from the adsorbent tube into a capillary column. Due to the importance and widespread use of dynamic HS-GC it is not surprising that many technical solutions to incorporate a cold trap in this instrumentation have been published. The original configuration for purge-and-trap comprising a sparging vessel, an adsorption tube and a packed column was modified to meet the rigid requirements for capillary GC and a typical arrangement for dynamic capillary HS-GC including such a cryogenic trap (CT) is shown schematically in Fig. 10.

During the first step (A) in the whole procedure the target analytes are stripped off by a flow of an inert purge gas (IG) from the sample vessel (SV) and transferred into the adsorbent tube (TB). During the second step (B) the tube is heated rapidly usually in backflush position and the adsorbed compounds are desorbed more or less fast but hardly fast enough to start in the capillary column with the necessary narrow band width. To refocuse the band of the analytes again, an additional cold trap (CT) is included in the instrumental configuration and indicated schematically in Fig. 10 by a Dewar vessel, filled with a liquid cryogen.

(a) Such a cold trap is not necessary in the case where a packed column is used, but even for wide-bore capillary columns (0.53 mm I.D.) such a refocusing was found necessary [9,26]. The time problem can thus be handled by cryogenic trapping while for the problem with a high desorption flow a splitter may help [10,11]. Whether or not such a splitter sacrifices the sensitivity depends where it is

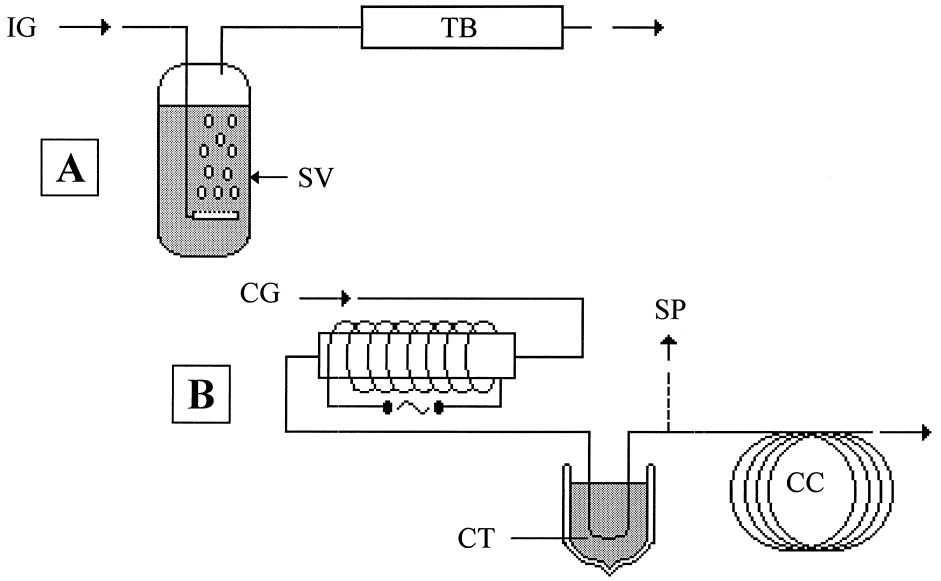

Fig. 10. Schematic of dynamic capillary HS-GC ('purge-and-trap') with cryogenic trapping. (A) Sample purge and collection of the stripped volatiles in a trap and (B) desorption from the trap and introduction into the gas chromatograph. IG = Inert purge gas, CG = carrier gas, TB = adsorbent tube, SV = sample vessel, CC = capillary column, CT = cryogenic trap, SP = split (optional).

located. No sample will be lost if the splitter (SP) is arranged behind the cold trap (dotted line in Fig. 10). The high flow-rate during desorption is vented through the open split whereupon the splitter is closed for transferring the trapped compounds from the cold trap into the capillary column. However, efficient cooling of the high flow of hot desorption gas requires a large cold trap which acts as a heat exchanger.

(b) If, however, such a cold trap becomes too large, the subsequent vaporization of the trapped compounds and the sample introduction into the capillary column may be too slow and even two cold traps in series were used to trap first the compounds desorbed from a Tenax tube in a cold metal tube from which they were transferred into a cooled fused-silica trap to refocus again the sample into a narrow band for injection into the capillary column [28]. However, if a cold trap is included in the system, it is not necessary to desorb the adsorption tube (e.g., Tenax tube) with a high flow-rate to enhance sample transfer because the cold trap refocuses the desorbed compounds again and a prolonged desorption time with a reduced desorption flow is meaningless then [29].

(c) The usual packed adsorption tube can be replaced by a capillary, coated with a thick film of a liquid phase and this configuration has the advantage that desorption can be carried out under capillary flow conditions thus eliminating the flow problem and the need for using a splitter; but the remaining time problem by slow desorption requires refocusing by cold trapping [30].

(d) Finally, if cryogenic trapping is necessary in any case for the requirements of high resolution capillary separation, the use of an intermediate adsorption trap is in principle obsolete, because the purge gas may be trapped directly in the cryotrap and introduced splitless into a capillary column by the *purge- and cold-trap injection* (PTI) technique [31–34]. Such an arrangement has the advantage to avoid problems with decomposition or isomerization of labile compounds on an adsorbent due to the released adsorption energy followed by the necessary high temperature for desorption. Of course it is in any case an advantage to avoid such a risk, but the elimination of one problem here is paid off by another one and this is the water problem. The excess of water vapor in the purge gas may block a cold trap by ice plugging. With an adsorption tube

the excess of water can be removed by a preliminary 'drying step', before thermal desorption starts. Without an adsorption tube provisions are required to remove the water vapor prior to cryogenic trapping. The details of these techniques are discussed later in Section 6.

5.3. Trapping by cryogenic condensation

The schematic principle of cryogenic trapping for dynamic HS-GC as shown in Fig. 10 is varied in numerous modifications by applying both the method of cryogenic condensation and also that of cryogenic focusing.

(a) U-shaped traps made either from a glass [32,35], or metal tube [8,35–38] sometimes filled with glass beads [32,35,36,38], or from fused-silica capillaries [11,25,39–42] are immersed in a cooling bath, for example a Dewar flask filled with the cryogen. Trapping of a compound in this case is by condensation and depends therefore not only on temperature but also on the concentration in the gas phase. Since the concentrations are usually very low – therefore the need for enrichment – very low temperatures are required. These cold traps therefore are usually immersed in a bath of liquid cryogen, for example liquid nitrogen (LN_2) or Argon [43], which has to be removed manually for desorption before the traps are heated, in most cases electrically. Depending on how the cold traps are heated, a very narrow band width of less than 10 ms can be achieved [41].

(b) Manual operation can be avoided by a design where the Dewar flask is replaced by a U-shaped PTFE tube around a flexible fused-silica trap [44]. This tube is filled with LN_2 during sample introduction while evaporation of the trapped compounds is achieved by displacing the LN_2 by a flow of warm water or oil.

(c) Handling of liquid cryogen, however, is inconvenient and difficult to automate. As an alternative, trapping may be performed by a flow of cold gas and then a U-shaped trap is not necessary and manually removing the cooling bath is avoided. This is already a progress to automation since the cooling gas can be switched on and off automatically by a valve. With a bare metal trap tube cooled by cold nitrogen gas and heated by a capacity discharge power supply, sample plugs of 5–10 ms width were introduced into a short capillary column for high-speed gas chromatography [45–50]. Some sample decomposition was reported by rapidly heating such a metal tube [49], but may be avoided if a deactivated and inert fused-silica capillary [27,51] or an adsorbent-lined fused-silica trap tube [50] is inserted inside of such a metal tube. A fused-silica trap can also be heated directly by ohmically heating, if coated outside by a layer of aluminum [52] or of gold [53].

(d) Similar reasons which favor to cool a low mass fused-silica trap by cold gas rather than by a liquid cryogen, suggest heating it up again by hot gas [38,39]. But taking into account the low heat capacity of a gas, it is important that the fused-silica trap should not come in contact with bulky metal parts (e.g. screws, fittings, tubes) which all have a high thermal mass and will not follow sufficiently fast a rapid temperature rise. The remaining cold spot may then cause peak splitting or peak tailing.

(e) But even heating by an additional flow of hot gas is unnecessary if the fused-silica trap is placed inside the GC oven since immediately when the flow of cooling gas is stopped, the low-mass fused-silica capillary acquires the temperature of the surrounding oven sufficiently fast [38]. Kuck [54] who has first applied the technique of cold trapping for static HS-GC, has cooled the first part of a glass capillary column inside the GC oven with cold nitrogen gas and immediately after the flow of cooling gas was stopped, the cold zone rapidly accepted the temperature of the GC oven. The cold nitrogen gas was prepared outside the gas chromatograph by directing it through a metal coil immersed in a Dewar flask with LN_2. This instrumentation was already simple enough to be incorporated into a fully automated headspace sampler. The same effect is achieved if LN_2 or CO_2 are directly blown onto at the entrance of a straight fused-silica capillary column inside the GC oven, where the coolant vaporizes, thus creating a short cold zone [18,55,56].

So far cryogenic trapping was discussed in the variant of cryogenic condensation which may be assumed in all cases, where LN_2 or cold gas at the same deep temperature is used as the cryogen. However, if a coated fused-silica trap is cooled with LN_2 and the solutes thus trapped by condensation, it may occur that during the subsequent warm up

period when the column temperature exceeds the glass transition temperature the trapped compounds dissolve in the stationary phase. In this case the trapping process may already approach the principle of cryogenic focusing.

5.4. Trapping by cryogenic focusing

Cryogenic focusing requires a wall coated (or adsorbent coated) fused-silica capillary column operated under temperature conditions where the stationary phase is still chromatographically effective. The underlying principle is only a rigid deceleration of the migration rate rather than freezing and immobilisation of the trapped compounds. For this purpose the cooling temperature can be much higher than is required for trapping by cryogenic condensation because it should remain above the glass transition temperature of the stationary phase.

(a) This allows to cool the whole oven of the gas chromatograph including the column because most commercial gas chromatographs limit the lower temperature to −100°C. The capillary column in the oven is cooled over its whole length and this technique therefore was called *whole column cryotrapping* (WCC) by Pankow [57–60]. Most gas chromatographs are equipped with a so-called subambient accessory, where the cryogen, either LN_2 or CO_2 is introduced into the oven through a valve under controlled temperature conditions and cryotrapping therefore can be performed automatically [61,62] with commercially available equipment. After the cooling period is finished, the supply of the cooling medium is stopped and the cold oven rapidly heated up to the pre-set higher temperature, required for the chromatographic separation. Band concentration is thus achieved by the same thermal focusing effect of the temperature program as discussed earlier, but now shifted to lower temperatures. The WCC-technique was applied by Wiley [63] for static headspace sampling to trap the volatile compounds from several rapid injections from a sample which, however, was distributed in several vials. This multiple headspace injection technique (MHI) was found useful to introduce a large gas volume for the required enrichment, despite the limited volume of a loop in the pressure/loop system. These multiple samples are all cryotrapped as a plug at the column head and eluted jointly by temperature programming the column. However, cooling a column over its whole length is in fact necessary only if the chromatographic separation requires low temperature, while for the intended purpose of generating a narrow starting band profile it is sufficient to cool only the begin of a coated capillary column, which should be called *on-column cryogenic focusing* (OCF) here.

(b) A very effective band concentration is achieved if cryogenic focusing is combined with an additional focusing effect by a negative temperature gradient. In this case the front of the moving zone is colder than its rear and during the sampling time the molecules at the rear end of the moving zone are accelerated and migrate with a higher relative migration rate (*Rf*), while the migration rate at the front may already approach zero. Such a temperature gradient was already used by Kaiser [64] to trap and desorb volatiles in the so-called gradient tube, a short packed column. The formation of a temperature gradient needs a certain length (e.g. 20 to 60 cm) of a fused-silica capillary column. Rijks et al. [65] have found a 20 cm coated capillary column sufficiently long if cooled by cold gas (−60°C), prepared externally by a dry-ice–ethanol mixture. The cooling gas was moving counter to the carrier gas flow, whereupon the trapped compounds were flash-vaporized by hot gas flowing in the same direction as the carrier gas, thus creating a negative gradient for both trapping and vaporization. With a similar configuration such a double-focusing effect was obtained [39] also by alternate cooling and heating with cold and hot nitrogen gas.

(c) Additional hot gas to accelerate the migration of the trapped compounds is unnecessary, as was already discussed above, if the trap is located in the GC oven [38,54]. Kolb et al. [66] modified the arrangement of Kuck [54] for cryogenic condensation into an advanced version for cryogenic focusing. Since most of the chromatograms shown here were obtained with this instrumentation a detailed presentation is given in Fig. 11.

The cryogenic trap is a PTFE tube similar to the design of Jennings [44] which jackets the first coil of a fused-silica capillary. The coolant here is cold nitrogen gas rather than LN_2, and is usually prepared outside the gas chromatograph by passing it through

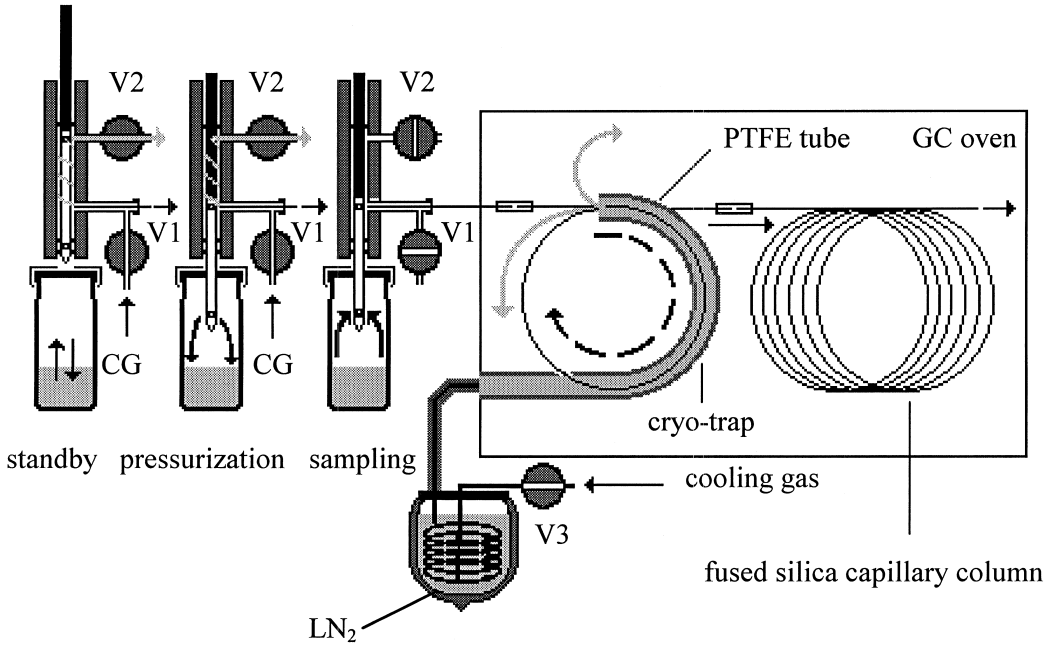

Fig. 11. Schematic principle of the balanced pressure sampling system for splitless static HS-GC with cryogenic gradient focusing in the Perkin-Elmer Automated Headspace Samplers in sampling position. V1 = Solenoid valve for the carrier gas (CG), V2 = solenoid valve for the purge gas, V3 = solenoid valve for the cooling gas.

a copper coil, immersed in LN_2. Without using LN_2, the cooling gas can also be generated by a refrigerator as will be described below. The flow of the cooling gas is opened and closed by the automatically operated valve V3. During the sample introduction period the cold nitrogen gas flows through the PTFE tube outside the fused-silica capillary column but counter to the warm headspace gas inside. Thus, a strong temperature gradient is created already during sample introduction. If the cooling gas was prepared by a bath of LN_2 it comes with the temperature of -196°C while at the end of the trap the temperature can be adjusted by the flow-rate of the cooling gas, and is usually set at -30°C with flow-rate of the cooling gas of about 5 l/min. A strong negative temperature gradient is thus generated. The headspace gas enters the trap at the higher end temperature (e.g. -30°C) where the volatile analytes dissolve in the liquid phase and move slowly into the colder zone, where they come nearly to a stop. At the end of sample introduction (e.g. after a few minutes) the flow of cooling gas is stopped. Now the incoming warm headspace gas heats the fused-silica capillary from inside and a second negative temperature gradient is created, where the rear of the solute band is warmer, while the front is still cold. Due to this double focusing effect the trapped compound leaves the trap in a very narrow band at the temperature of the oven. Fig. 11 shows also the whole sampling cycle of the balanced pressure sampling system as it is used in the automatic headspace samplers (HS100, HS40) from Perkin-Elmer.The hollow sampling needle contains two vents and moves in a heated compartment. In the 'standby' position the carrier gas enters the chromatographic system through valve V1 and branches in the T where one part flows down the capillary column while a small flow of purge gas flows back through the heated compartment and leaves the system through valve V2. This purge gas flow is adjusted by a needle valve (not shown in Fig. 11). The sampling procedure is started when the needle moves down into the headspace vial. Carrier gas flows through the upper and the lower vent into the vial and pressurizes it ('pressurization' in Fig. 11). Sample transfer ('sampling' in Fig. 11.) is started by closing both valves V1 and V2. The

pressurized headspace gas expands through the sampling needle onto the capillary column in the cryogenic trap. Sample injection is stopped when both valve V1and V2 are opened again after the pre-set injection time. The purge gas flow cleans the system from any residual headspace vapors through valve V2. The flow of the cooling gas is opened by the valve V3 already during the pressurization period to cool the cryogenic trap for the subsequent sampling period and is stopped after sample transfer is finished.

The effect of the enrichment is shown by comparing both chromatograms in Fig. 12, where residual solvents from an adhesive tape were determined. Chromatogram A shows the normal headspace analysis with a 3 s sampling time, while in chromatogram B 10 times higher peaks were obtained due to the 10 times longer sampling time of 30 s. In practice it is often only the factor 10 for a better sensitivity, which is desired.

The cryogenic trap may contain the first coil of the coated fused-silica capillary column used for subsequent chromatography or a different one, coated with another liquid phase and connected to the separation capillary column by a butt connector. For example, a thick film silicone coated capillary column in the cryogenic trap may be connected to a Carbowax-type capillary column for specific chromatographic separations. Such a combination was used for the determination of hydrocarbons in the air of a car park (cf. Fig. 13). The xylene isomers were separated with a Carbowax capillary column, which on the other hand could not be used in the cryogenic trap due to the low temperature of -80°C.

Particularly useful for highly volatile compounds is an adsorption capillary with a coating of porous polymer or aluminum oxide as the stationary phase. The chromatogram in Fig. 14 gives an example for the determination of 85 ng/g vinyl chloride monomer in a PVC resin with a fused-silica capillary column coated with Al_2O_3/KCl (Chrompack Intern. BV).

5.5. Experimental example: influence of temperature and film thickness on the retention of vinyl chloride

The objective of this example is to verify the chromatographic migration even at low column temperatures and to demonstrate thus the difference between cryogenic focusing and cryogenic condensation. For this purpose the temperature dependence of the chromatographic migration at low temperatures was investigated. Vinyl chloride with a boiling point of -14°C was used as a representative example for a highly volatile compound; it is also of analytical interest, because it has to be determined in a variety of samples, such as polymer resins (cf. Fig. 14), plastic materials and consumer products at low ppb concentrations.

Fig. 15 shows the separation of vinyl chloride from other compounds of similar volatility such as 1,3-butadiene (b.p. -3°C), ethylene oxide (b.p. $+11$°C) and trichlorofluoromethane (b.p. $+25$°C) with a 50 m$\times$0.32 mm I.D. fused-silica capillary column, coated with crosslinked dimethyl silicone at a film thickness of 3 μm under isothermal conditions at $+50$°C. This chromatogram was achieved by the technique of on-column cryogenic focusing (OCF) with the instrumentation as shown in Fig. 11. The chromatographic conditions are apparently adequate to separate vinyl chloride from all other compounds in this mixture and these conditions were maintained to investigate the influence of temperature and film thickness on the retention behaviour of vinyl chloride. For this purpose, however, isothermal conditions over the whole column length are required and the WCC-technique had to be applied. The measurements were carried out isothermally at various temperatures with two 50 m$\times$0.32 mm I.D. capillary columns with crosslinked dimethyl silicone liquid phase, one column coated with a 3 μm film, as used for the separation in Fig. 15 and the other one with a 1 μm film.

The retention of a compound is described by the retention factor (k), which is determined from the retention time (t_R) according to Eqs. 3 and 4 with the hold-up time (t_M). The method of Petersen and Hirsch [67] was applied to calculate t_M at each temperature by extrapolation from the retention times of the *n*-alkanes ethane, propane, *n*-butane and *n*-pentane, because FID does not detect the inert peak (air peak) and, on the other hand, the usual method to replace the inert peak by methane was not applicable here either with thick-film columns at low temperatures. With t_M and the retention time for vinyl

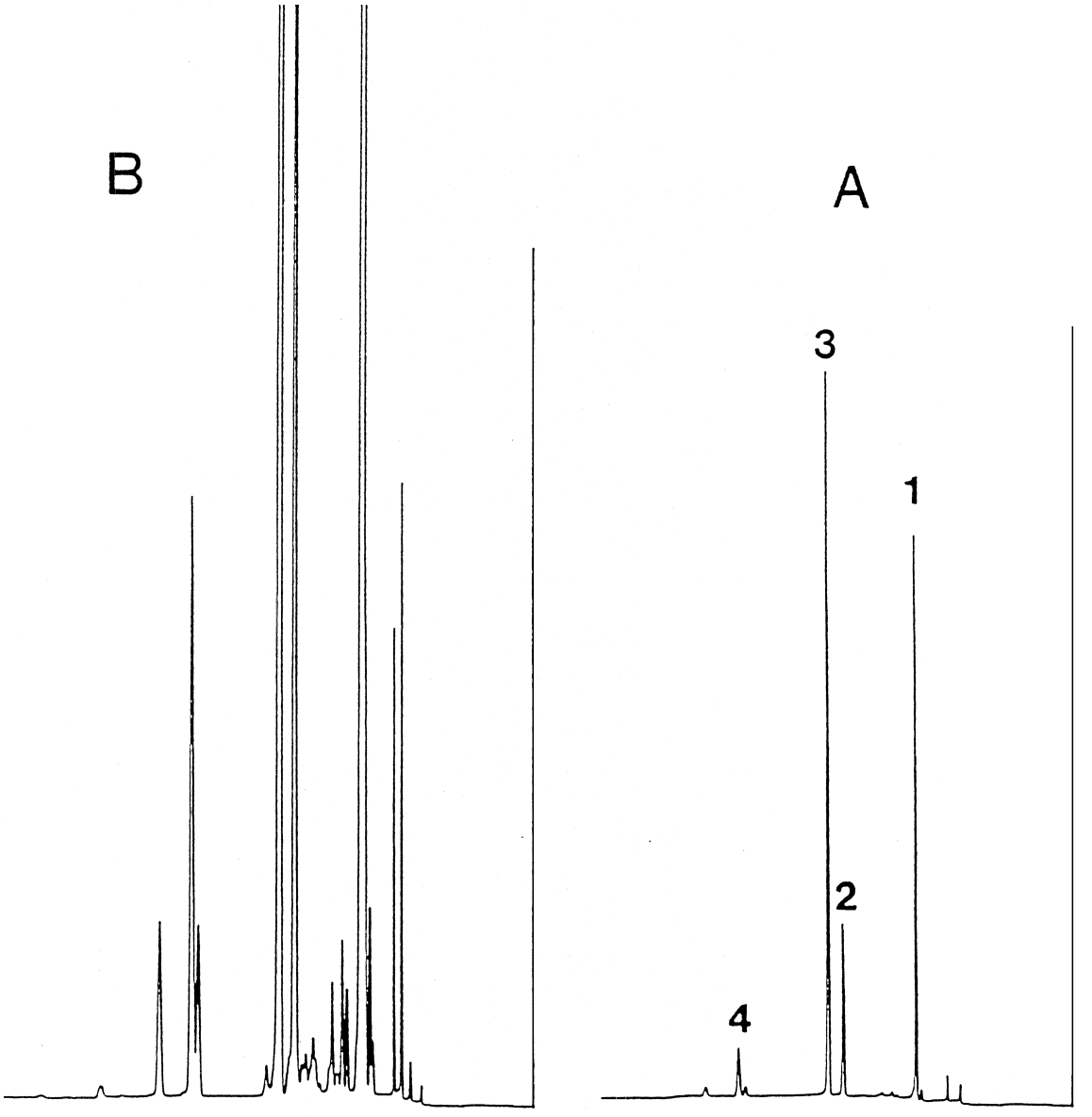

Fig. 12. Enrichment effect of cryogenic focusing for the headspace analysis of solvents in an adhesive tape. *Instrumentation*: as shown in Fig. 11, 50 m×0.32 mm I.D. fused-silica capillary column, crosslinked phenyl (5%) methyl silicone, 5 μm film thickness, programmed: 80°C, 15°C/min, 160°C; FID. *Headspace conditions*: chromatogram (A) 3 s sampling time, chromatogram (B) 30 s sampling time with cryogenic focusing. *Identified peaks*: 1=acetone, 2=*sec*.-butanol, 3=toluene, 4=*m*-, *p*- xylene.

chloride, the retention factor (k) for vinyl chloride was calculated for each temperature. The temperature influences primarily the distribution constant (K) which changes exponentially with absolute temperature (T) like any other equilibrium constant (e.g. vapor pressure). The retention factor (k) is affected in the same way, because it is related to K by Eq. 2 and the temperature function is described by the ex-

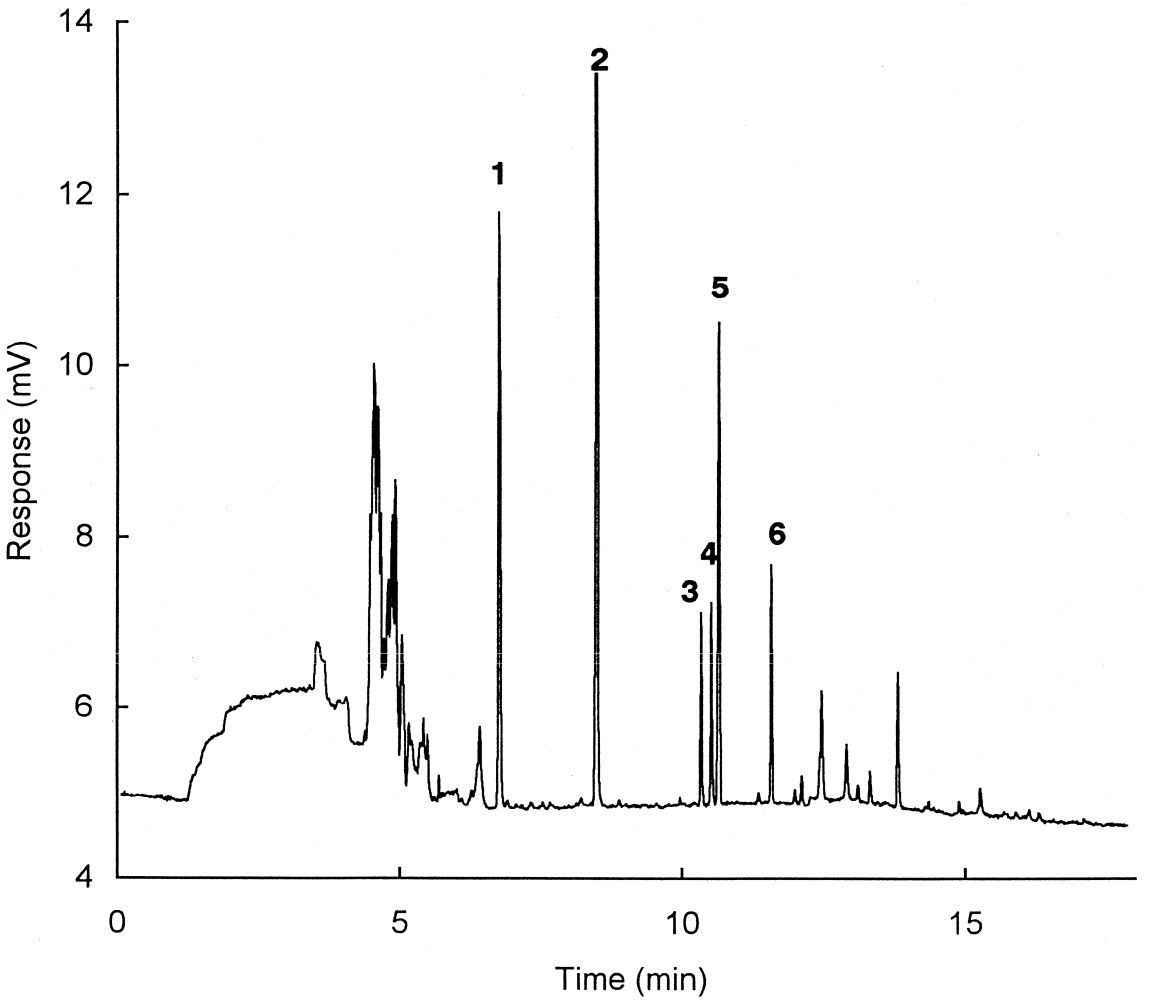

Fig. 13. Determination of BETX in the atmosphere of an underground car park by cryogenic-HS-GC. *Instrumentation*: Perkin-Elmer AutoSystem, HS40 Automatic Headspace Sampler, cryogenic accessory with water trap and gas cooler; 60 m×0.25 mm I.D. fused-silica capillary column, Stabilwax (Restek), film thickness 0.25 μm, programmed: 40°C (1 min), 20°C/min, 65°C (4 min), 10°C/min, 120°C; FID. *Headspace conditions*: cryogenic trap 60 cm×0.32 mm I.D. fused-silica capillary column, crosslinked dimethyl silicone, film thickness 1 μm., 3 min splitless sampling, sample collection by vial sampling technique [14]. Calibration by external vapor standard. *Identified peaks*: 1=benzene (807 μg/m^3), 2=toluene (1596 μg/m^3), 3=ethylbenzene (228 μg/m^3), 4=*p*-xylene (228 μg/m^3), 5=*m*-xylene (531 μg/m^3), 6=*o*-xylene (245 μg/m^3). From Ref. [14], with permission.

ponential function (Eq. 8), where ΔG° is the difference of the free enthalpies in the stationary and mobile phase.

$$k = \frac{1}{\beta} \cdot e^{\Delta G^\circ / RT} \tag{8}$$

Few experimental retention data at different temperatures are sufficient to calculate any other k value by using linear regression of the form $Y = AX + B$, since Eq. 8 can also be expressed by Eq. 9, with $X = 1/T$ and $Y = \log k$, and with A and B as the two regression coefficients:

$$\log k = A \cdot \frac{1}{T} + B \tag{9}$$

The retention factors of vinyl chloride were de-

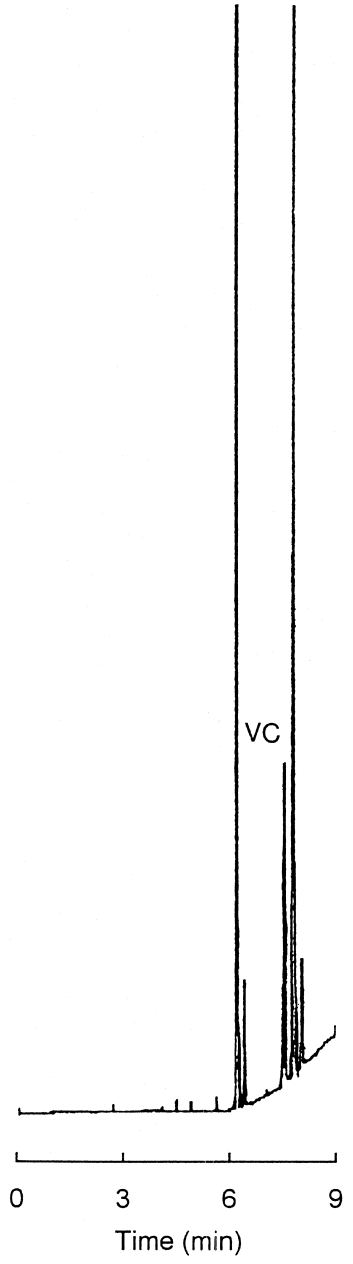

Fig. 14. Determination of 85 ppb (μg/kg) vinyl chloride monomer (VC) in a PVC resin by static cryogenic-HS-GC. *Instrumentation*: Perkin-Elmer SIGMA 2000, HS100 Automatic Headspace Sampler,cryogenic accessory, 50 m×0.32 mm I.D. fused-silica capillary column, coated with a porous Al_2O_3/KCl layer (Chrompack Intern. BV), programmed: 50°C, 10°C/min, 150°C (5 min), 30°C/min 180°C; carrier gas: N_2, 180 kPa; FID×2. *Headspace conditions*: 2 min splitless sampling, sample: 2 g PVC resin, equilibrated 30 min at 110°C with stirring; quantitation by MHE and calibration by external vapor standard.

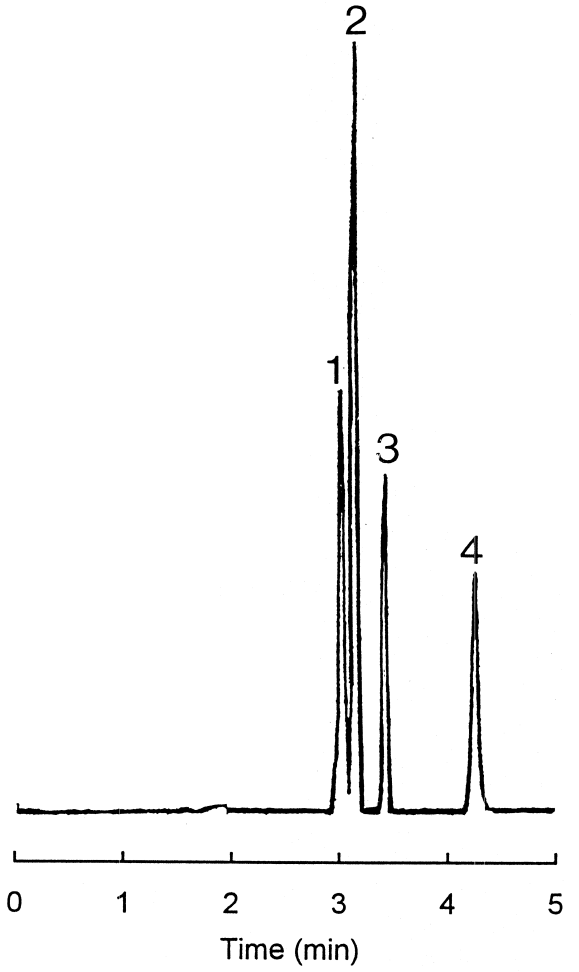

Fig. 15. Determination of highly volatile compounds by static cryogenic-HS-GC. *Instrumentation*: Perkin-Elmer SIGMA 2000, HS100 Automatic Headspace Sampler, cryogenic accessory, 50 m×0.32 mm I.D. fused-silica capillary column, crosslinked phenyl (5%) methyl silicone, 3 μm film thickness, programmed: 50°C (4.5 min), 10°C/min, 120°C; detection: FID. *Headspace conditions*: 27 s splitless sampling, sample: vapor mixture. *Identified peaks (boiling points)*: 1=vinyl chloride (−14°C), 2=1,3-butadiene (−3°C), 3=ethylene oxide (+11°C), 4=trichlorofluoromethane (+25°C).

termined with both capillary columns in a temperature range from +75 to −75°C under isothermal conditions by the WCC technique and the result is shown in Fig. 16 by the plot of log k versus the reciprocal of the absolute temperature ($1/T$). The results from the regression calculation are listed in Table 2.

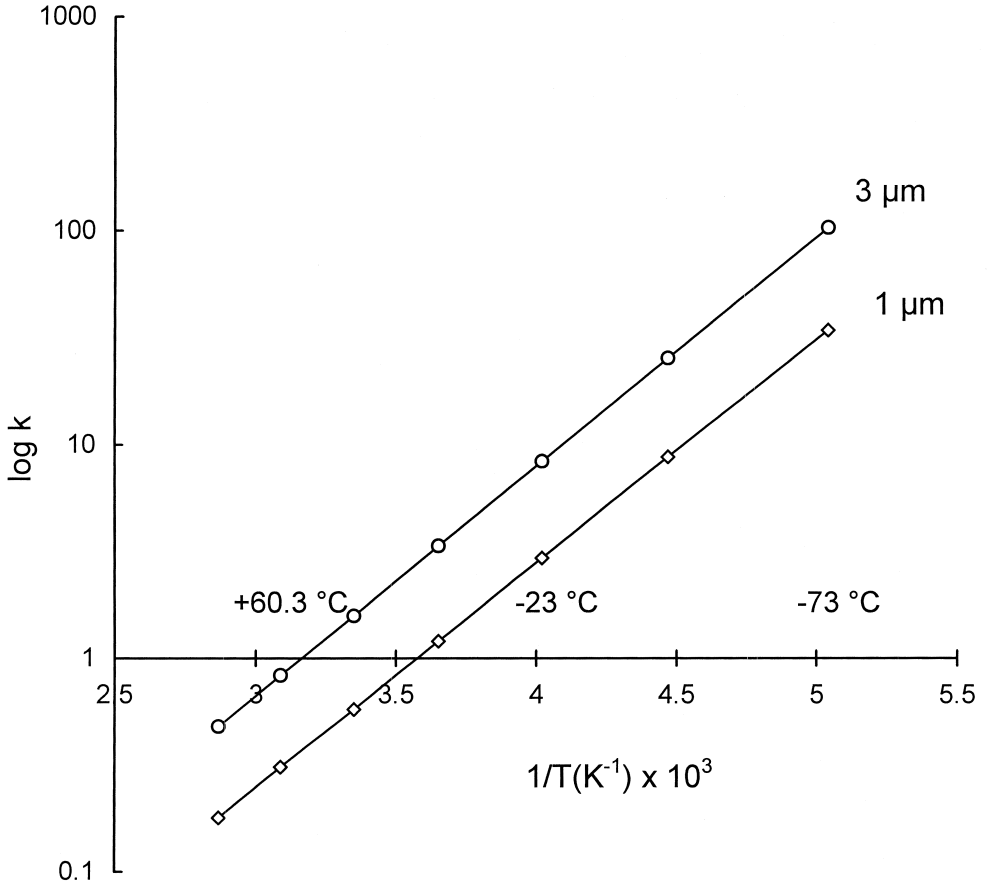

Fig. 16. Temperature function of the retention factor (k) of vinyl chloride in a temperature range from +75 to −75°C on two 50 m×0.32 mm I.D. fused-silica capillary columns coated with crosslinked dimethyl silicone and a film thickness of 1 and 3 μm, respectively.

The decreasing migration of vinyl chloride in the column with falling temperature is best visualized by the decreasing values of the relative migration rate (Rf), which are derived from the k values with Eq. 6. Table 3 contains data for k and Rf in steps of 25°C in the range from +50 to −75°C. These data allow to calculate the band width of vinyl chloride in the column from the linear flow-rate at the column entrance which was 20 cm/s in this example. During the sampling time under isobaric conditions, the headspace gas replaces the carrier gas flow and after one-second sampling time the whole headspace sample plug extends 20 cm into the capillary column. From the Rf -values at various temperatures the length of the solute zone for vinyl chloride is then derived. Although in this example the solute zone of vinyl chloride corresponds always to the one-second sampling time, it becomes smaller (in units of length) with decreasing temperature as shown in Fig. 17.

Table 2
Temperature function of the retention factor (k) of vinyl chloride in the range of +75 to −75°C by linear regression (cf. Eq. 9) with two 50 m×0.32 mm fused-silica capillary columns with different film thickness

	Film thickness	
	1 μm	3 μm
Regression coefficient A	1052.31	1075.81
Regression coefficient B	−3.767	−3.404
Correlation coefficient r	0.99988	0.99999

The total length of the headspace plug remains

Table 3
Retention factor (*k*), relative migration rate (*Rf*) and enrichment factor (EF) for vinyl chloride in steps of 25°C as a function of the temperature (°C) measured with 50 m×0.32 mm I.D. fused-silica capillary columns, coated with crosslinked dimethyl silicone at a film thickness of 1 μm and 3 μm; sampling time 1 s at a sample transfer rate of 20 cm/s

Temperature (°C)	*k*		*Rf*		EF	
	1 μm	3 μm	1 μm	3 μm	1 μm	3 μm
+50	0.305	0.832	0.77	0.55	1.0	1.0
+25	0.573	1.585	0.64	0.39	1.2	1.4
0	1.186	3.332	0.46	0.23	1.7	2.4
−25	2.906	8.332	0.26	0.11	3.0	5.0
−50	8.65	25.40	0.10	0.04	7.4	13.6
−75	34.41	104.25	0.03	0.01	27.4	54.6

unchanged, because air has no retention in the liquid phase. The decreasing band width of vinyl chloride allows to calculate an enrichment factor (EF): at a temperature of +50°C the peak of vinyl chloride with the 3 μm column has a retention factor (*k*) of 0.832 and thus a relative migration rate (*Rf*) of 0.55 (cf. Table 3). The flow-rate of the headspace sample during sample transfer equals the linear carrier gas flow-rate at the column entrance of 20 cm/s and with a one-second sampling time the plug of the whole headspace sample extends 20 cm into the column and the zone of vinyl chloride 11 cm. With decreasing column temperature this zone becomes smaller and this allows to increase the sampling time to maintain the same distance of 11 cm in the column. According to the longer sampling time the volume of the headspace sample becomes larger and the sensitivity will be enhanced. The ratio of the relative migration rate at the lower temperature to that of the reference temperature at +50°C gives the enrichment factor (EF) which is listed in Table 3 also. For example: at a column temperature of −75°C during headspace sampling the sensitivity can be increased by a factor of 55.

The influence of the film thickness is obvious by comparing the two capillary columns with 1 and 3 μm film thickness. If we want to maintain the same chromatographic resolution (cf. Fig. 15) of the 3 μm column at +50°C with the 1 μm column, a *k* value of 0.832 (*Rf*=0.55) is required but this value now needs a lower column temperature of +12.2°C as can be calculated using Eq. 9 with the regression coefficients from Table 2. In other words: the column with a three-times thicker film can be operated at a +37.8°C higher temperature for the same retention and peak resolution (cf. Fig. 15). Doubling the film thickness thus corresponds to a temperature difference of 25.2°C and this result is in reasonable agreement with the general rules in gas chromatography that doubling the film thickness doubles the retention time while on the other hand a temperature increase of 25–30°C compensates this

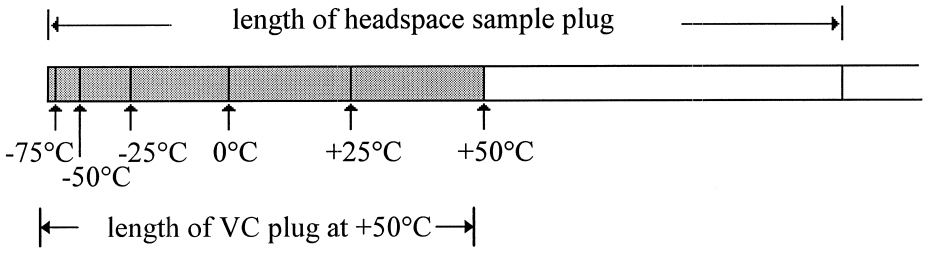

Fig. 17. Length of the sample plug of vinyl chloride (VC) at the head of a fused-silica capillary column with 3 μm film thickness (cf. Table 3) at the given temperatures, resulting from a one-second sampling time and a carrier gas flow-rate (=sample transfer rate) of 20 cm/s. The length of the total headspace plug is independent of the temperature.

effect by reducing the retention time by a factor of two. This practical rule is apparently applicable for lower temperatures also. For a given temperature, the enrichment effect is smaller with the 1 μm column as shown by the data in Table 3.

The increase of the retention factor (k) of vinyl chloride with falling temperature shows clearly that even at the lower temperatures of −75°C there is still chromatographic migration, contrary to popular belief, which often considers the compounds as frozen or dormant. The migration rate is simply slowed down by increasing the retention factor. It can be assumed that the chromatographic properties extend down to the glass transition temperature of the silicone phase of about −125°C, but this could not be proved experimentally due to instrumental constraints.

5.6. Discussion of the various techniques of cryogenic trapping

Cryogenic focusing has some benefits compared to trapping by cryogenic condensation for several reasons: the latter technique needs temperatures lower than the dewpoint of the volatile analyte and considering the low concentrations in headspace samples, very low temperatures are required and for this reason LN_2 is the preferred cryogen. On the other hand a rapid temperature rise of the trap is required to achieve sample introduction as a narrow plug into the capillary column, since a trap for cryogenic condensation may be considered comparable to a PTV injector (*programmed temperature vaporizer*), where the starting band width is determined by the time for sample transfer. Rapid heating of an external cold trap, particularly a metal bar tube may cause decomposition of labile compounds [46,49]. Moreover, cryogenic trapping by condensation has some other inherent problems such as breakthrough by aerosol formation. Graydon and Grob [40] have observed significant breakthrough of volatile organics from a simple open cold trap immersed in LN_2. Trapping may be incomplete by droplet formation, causing peak splitting or distorted peaks. Particularly polar compounds, by rapid cooling from the hot gaseous state may form aerosols which are often electrically charged and can pass the cooling zone unretained. A theoretical treatment of sample breakthrough and dependences of trapping from dewpoint and trap geometry is given by Hagman and Jacobsson [35]. Aerosol formation can successfully be suppressed by offering large surfaces and glass beads are sometimes used as packing material for glass tubes [35] or capillaries [36].

Some more reasons clearly favor on-column cryogenic focusing: the stationary phase maintains its property as a chromatographic phase and the trapped solutes dissolve in the liquid phase or are adsorbed in case of an adsorbent coated fused-silica capillary. Therefore, any aerosol formation is avoided. Sample decomposition is also unlikely to occur since a trapped compound does not come in contact with any other material than it would do during the rest of the chromatographic separation. The main advantage, however, is the fact that the compounds are already trapped inside the capillary column. Any effect on band broadening during sample transfer as in the case of cryogenic condensation does not therefore exist. For the same reason it is less important to heat the trap as fast as possible, since the trapped compounds migrate already in the stationary phase more or less slowly depending on the temperature and this chromatographic process is identical with thermal focusing in a temperature programmed column. The rate of heating the trap determines how fast this band migrates and thus influences the final retention time, but not the band width. This is the reason why, in the arrangement shown in Fig. 11, already the warm carrier gas inside the fused-silica trap evaporates the trapped compounds, or more precisely: accelerates their migration rate, despite the slow carrier gas flow-rate and the low heat capacity of the carrier gas.

From the various instrumental configurations of cryogenic focusing, the WCC-technique is simple, but less attractive for routine analysis, where a high sample throughput is required, since the WCC-technique suffers from the high consumption of cryogens and the time expenditure since a high amount of cryogen and a long time therefore is required to cool a hot oven down to low temperatures.

An important aspect of cryogenic trapping is the selection of a suitable cryogen. Due to the strong influence of the techniques of cryogenic condensation with its rigid demands for low temperature, LN_2 is very popular; it is inexpensive and easily available

in most laboratories. Dry-ice or liquid CO_2 may also be used and allows a temperature as low as −78.5°C, which, however, is sometimes not enough. Mixtures of dry-ice with acetone, methanol or other solvents have no advantage and are not useful for routine application either. Handling of all these liquid or solid cryogens is not ideal for unattended routine analysis. Particularly the techniques of cryogenic focusing do not need extremely low temperatures and alternative cooling devices might become feasible. Cold gas for cryogenic focusing can be produced by a Ranque–Hilsch vortex tube [68]. The vortex tube is a pneumatically operated device, containing a concentric aperture, that splits compressed air (at a minimum pressure of 0.6 MPa) into a cold and a hot airstream. A minimum of −50°C can be obtained for the cold air stream while the hot airstream can reach +225°C. The lower temperature of −50°C may be sufficient to trapp less volatile compounds, but may not be cold enough for more volatile solutes. Bertman et al. [69] developed a two-step cooling device to cool a section of a coated fused-silica trap as low as −100°C. It features a single-stage, closed-cycle, Freon refrigerator to cool a heat sink for a three-stage cascaded thermoelectric (Peltier) heat pump which achieves a 40°C temperature differential with the hot junction starting at −60°C. A closed-cycle Freon refrigerator aggregate was applied also to cool first an aluminum block through which in a coiled tube the cooling gas was directed. This cold gas generator (National Lab, Mölln, Birkenweg 20, Germany) allows to set any temperature in steps of 1°C in the temperature range down to −80°C. It was already used to replace the bath of LN_2 for generating a flow of cold air in the arrangement shown in Fig. 11. and an example for using this device is the analysis of the air from a car park by cryogenic-HS-GC in Fig. 13. It is a very convenient device to produce cold gas requiring only electric power supply and (clean) nitrogen or compressed air. The temperature of −80°C was found sufficient to trap compounds with boiling points $>+50$°C, while higher volatile solutes were trapped partially only. However, if a thicker film is used in the fused-silica cryogenic trap and connected to a capillary column with smaller film thickness (cf. Fig. 13), the limit of trapping may be lowered by about 30°C and more volatile compounds with boiling points around +20°C will be trapped completely. The air sample was collected using the vial-sampling technique by pumping the air through an open headspace vial, which in this case is used as a minicanister [14] with subsequent crimp-capping it as usual. The baseline hump at the beginning of the chromatogram is caused by a slightly reduced carrier gas flow due to the additional flow resistance of the water trap during the sampling time of 3 min. However, the application of a water trap to remove excess of water from a headspace gas to avoid ice plugging of the cryogenic trap will be discussed next.

6. The water problem in cryogenic-HS-GC

In the foregoing chapters a variety of technical solutions for headspace enrichment by cryogenic trapping was presented. With the exception of SPME both static and dynamic HS-GC have to deal more or less with the ‘water problem’. Most samples in GC contain water and the accompanying water problem is immediately obvious if a capillary is blocked by ice formation. Another, though less apparent, detrimental influence of the trapped water is peak distortion, particularly when it occurs in the early part of the chromatogram, where highly volatile compounds are eluted together with water. Although the water is present in the headspace sample of both static and dynamic HS-GC, there is a big difference in the resulting water amount and the technical solutions to handle the water problem are different either.

Most techniques to handle the water problem were developed for dynamic HS-GC, mainly for the purge-and-trap procedure where the water problem is much more prominent than with static HS-GC for the simple reason that during the long time of purging an aqueous sample, the stripped gas remains permanently saturated with water vapor, while the concentration of the analytes decreases exponentially. A high amount of water is thus accumulated in the final gas extract. For example: if an aqueous sample is purged 11 min with a flow-rate of 40 ml/min at +60°C temperature, as set by the EPA methods, the total volume of the water saturated purge gas is 440 ml, containing 57 mg of water (density of saturated water vapor at +60°C: 0.130 g/l).

In the case of the static headspace technique, the headspace gas above the sample has the initial and therefore the highest ratio of the analyte concentration to the water vapor and this favorable ratio remains constant during the whole sampling time because the headspace is not further diluted by a water saturated purge gas. There is not so much a need therefore to remove the water in static HS-GC. For example, a volume of 10 ml headspace above an aqueous sample in a 20 ml vial at +60°C contains only 1.30 mg of water. If 5 ml are introduced into a capillary column by cryogenic trapping such a small droplet of 0.65 μl water is not enough to block e.g. a 0.32 mm I.D. fused-silica trap by an ice plug, particularly not in the case of cryogenic focusing, where the water is spread over a certain length in the area of the temperature gradient. The form of the deposited ice plug depends also on the polarity of the liquid phase in the coated capillary column and its wettability [70]. In other words: in the case of balanced pressure headspace sampling the injection time can be increased from normally a few seconds (e.g., 3 s cf. Table 1) up to about 1.5 min before a 0.32 mm I.D. fused-silica trap will be blocked. This provides a sensitivity enhancement, for example of 30, which is more than enough for most practical applications. An example is given in Fig. 18, where the aroma compounds of a juice from sage were analyzed by cryogenic-HS-GC. This aqueous sample was equilibrated at a temperature of +80°C and despite the high concentration of 0.293 mg/ml water vapor in the headspace at that temperature, the 0.32 mm I.D. fused-silica capillary column was not ice blocked during the sampling time of 1 min, corresponding to a headspace volume of about 1.5 ml.

It is only if the sensitivity should be increased even further or if water causes other problems, depending often on the type of detector, that it may become necessary even for static HS-GC to remove the water vapor in the headspace sample prior to cryogenic trapping. Ice formation is particularly critical depending on the inner diameter of the capillary column. The smaller this diameter, the shorter the allowable injected volumes. Narrow-bore capillary columns therefore suffer particularly from ice plugging, while a 0.53 mm I.D. fused-silica capillary in the cryogenic trap accepts several milliliter headspace, saturated with water vapor.

This is one of the principle differences in the water problem between both headspace techniques and may explain why most techniques to eliminate the water before cryogenic trapping have mainly been developed for purge-and-trap procedures or for air sampling by thermal desorption of adsorption tubes. These techniques will be discussed briefly for their potential to be applied for static HS-GC.

6.1. Water removal in dynamic HS-GC

(a) Pankow and Rosen [58] described a technique where all volatile analytes, including water, were trapped in an adsorption tube from which the water was first removed by a 'trap drying step', while the analytes were subsequently thermally desorbed and transferred onto a capillary column, cooled down to −80°C by WCC. This technique has to cope with the risk of also losing the highly volatile compounds during the 'trap drying' step.

(b) Werkhoff et al. [51] avoided this problem by using a reflux condenser, cooled at +5 to +10°C, between sparging vessel and the adsorption tube packed with Tenax TA. After thermal desorption the analytes were trapped in an uncoated deactivated fused-silica capillary (retention gap) at −130°C cooled with LN_2 and finally transferred into the capillary column by flush heating this cold trap up to +150°C within 40 s. An example for this headspace technique is given by the fingerprint chromatogram in Fig. 19 from the headspace volatiles of 200 g freshly picked rose flowers.

(c) Badings et al. [31] have shown that an intermediate adsorption trap (Tenax tube) is unnecessary and can be eliminated from the system if the water is removed by such a condenser since the purge gas can be transferred directly into a cooled capillary column. Such an arrangement is commercially available (Chrompack, Middelburg, Netherlands) and shown in Fig. 20.

The purge flow (carrier gas) passes the condenser, which is cooled by a cryostat at −15°C where most of the water is frozen out. The purge gas containing the volatiles streams through a heated compartment into the cold trap made of fused-silica tubing (30 cm×0.32 mm I.D.) and coated with CP sil 5 CB (crosslinked dimethyl silicone) at a film thickness of

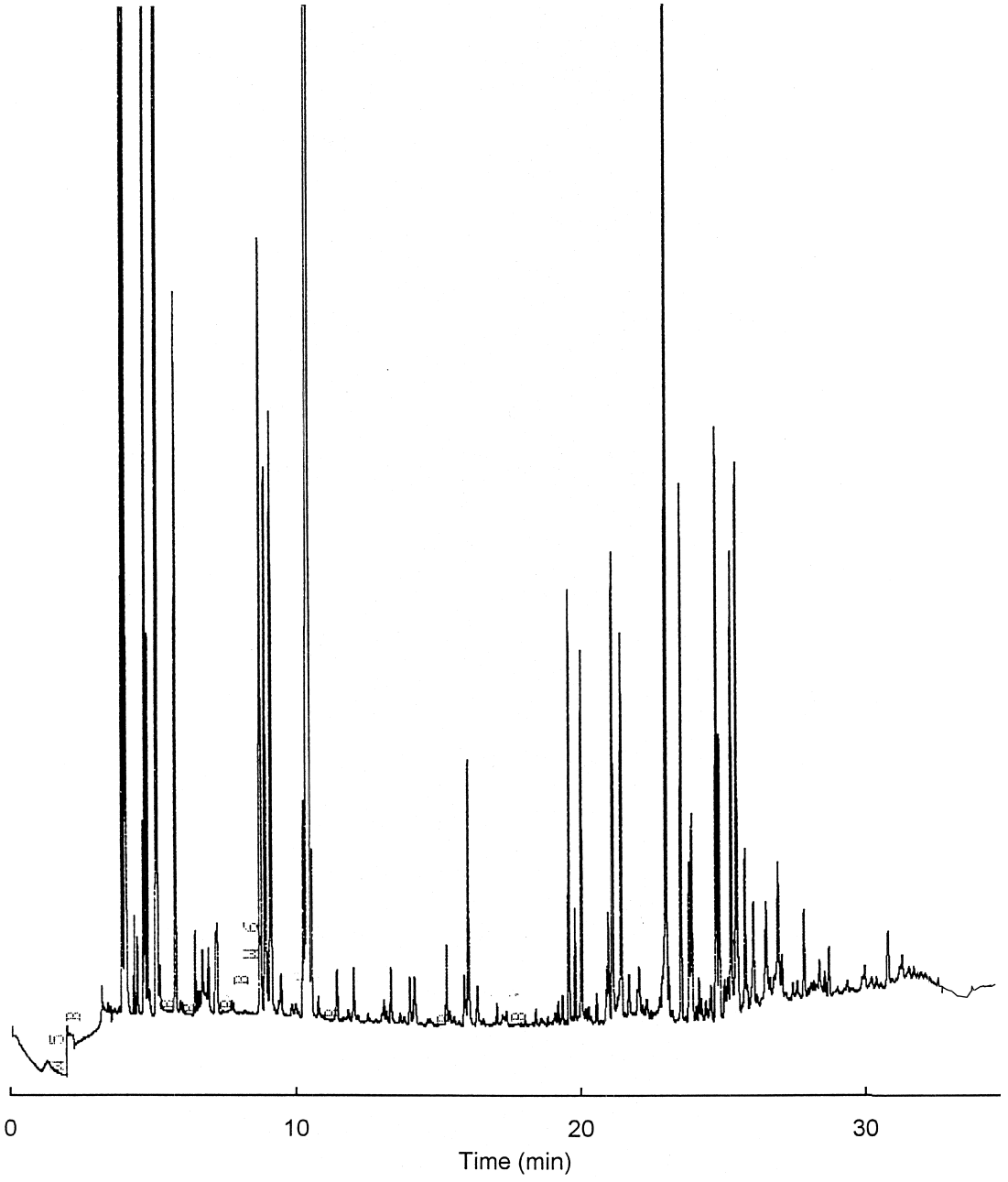

Fig. 18. Aroma analysis from sage juice by cryogenic-HS-GC. *Instrumentation*: Perkin-Elmer SIGMA 2000, HS100 Automatic Headspace Sampler, cryogenic accessory, 50 m×0.32 mm I.D. fused-silica capillary column, coated with crosslinked phenyl (5%) methyl silicone, 1 μm film thickness, programmed: 45°C (8 min), 8°C/min, 120°C, 6°C/min, 250°C; carrier gas: H_2; FID×4. *Headspace conditions*: 1 min splitless sampling, cryogenic trap: 0.8 m×0.32 mm I.D. fused-silica capillary, coated with crosslinked phenyl (5%) methyl silicone, 5 μm film thickness, sample: 1 ml sage juice, equilibrated 30 min at +80°C.

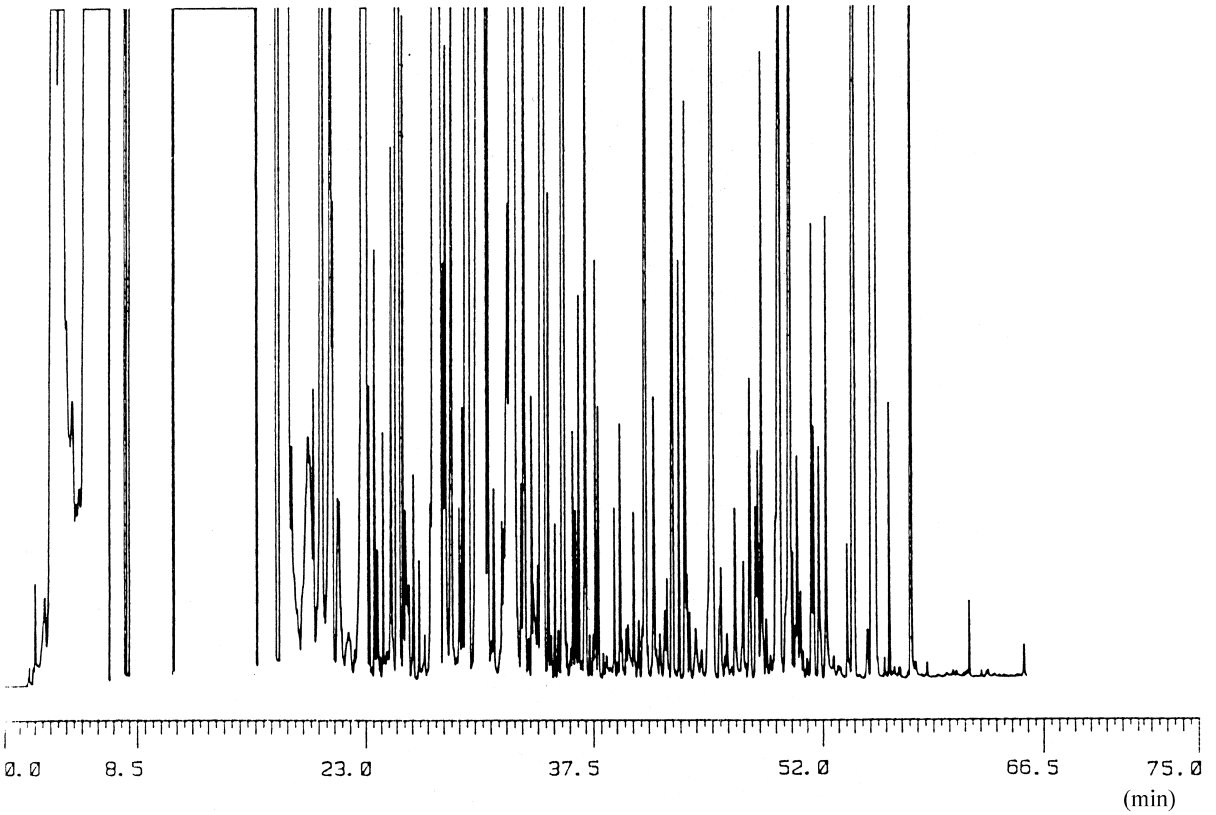

Fig. 19. Chromatogram of headspace volatiles from 200 g rose flowers after enrichment on Tenax TA. *Instrumentation*: Carlo Erba HRGC 5300, 60 m×0.32 I.D. fused-silica capillary column, column temperature: −30°C to 0°C at 50°C/min, then with 3°C/min to 250°C; carrier gas: He, 2.5 ml/min; FID. *Purge conditions*: total purge volume 9 l helium, purge gas flow-rate 50 ml/min, sample at +20°C. *Desorption*: temperature 250°C, desorption flow-rate ca. 30 ml/min, desorption time 30 min, total desorption volume 0.9 l (helium). *Cryogenic trap conditions*: retention gap 2.5 m×0.53 mm I.D. fused-silica capillary deactivated with octamethylcyclotetrasiloxan (D4) (J&W Scientific) at −130°C, oven temperature −30°C. From Ref. [51], with permission.

1.2 μm, maintained at −120°C by an air stream, cooled with LN_2 from a Dewar vessel. A high purge flow is achieved without disturbing the column flow by a splitter in the oven, where the purge flow is vented through solenoid valve V (cf. Fig. 20). This solenoid valve V is closed, when sample purge is finished and the system switched to the injection mode.

(d) Such a condenser was modified by Pankow [71], using a tube, filled with glass beads and cooled to −10°C, through which highly volatile compounds pass unretained, while the less volatile and polar compounds which may be condensed in the trapped water are finally transferred to the column by drying the water trap at room temperature.

6.2. Water removal in static cryogenic-HS-GC

It was already mentioned above that there is not so much a need for static HS-GC to care about the water problem and this difference may be apparent by comparing the two fingerprint chromatograms from flower heads in Fig. 19 obtained by dynamic HS-GC and in Fig. 21 by static HS-GC. The chromatogram in Fig. 21 was obtained with a much smaller sample amount of 250 mg flower heads of *lily of the valley* and was obtained with the instrumentation for static cryogenic-HS-GC shown in Fig. 12 without any provisions to remove water from the headspace. Both chromatograms are a comparable whealth in peaks.

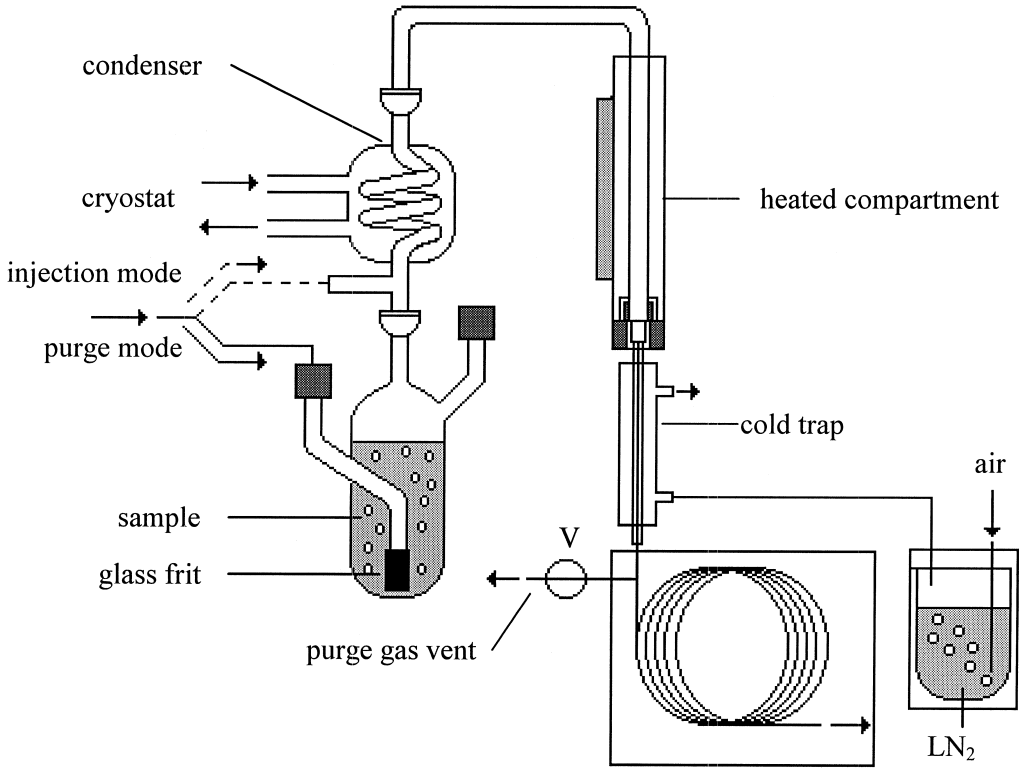

Fig. 20. Schematic principle of water removal with the Chrompack purge- and cold-trap-injection system (PTI) in the purge mode. Details of flow switching, arrangement of needle valves, solenoid valves and trap backflush are not included. After Badings et al. [31].

If, however, for some reasons, the water content in the headspace gas becomes in fact a problem, even with static HS-GC, and should therefore be removed before cryogenic trapping, the following techniques may be used for that. But considering the much smaller water amounts, it does not seem reasonable to design a miniaturized condenser to eliminate, for example, 0.5 μl of water only. Alternatives are either diffusion of the water through a semipermeable membrane or elimination by chemisorption.

The diffusion approach by using, e.g. a Nafion drier, has mainly been developed for the purge-and-trap techniques [33,36,70–74] or for air samples [75] but has not yet been applied for static HS-GC. It seems to be less attractive due to some selectivity of the Nafion membrane for various classes of compounds. It has been found that light, polar and oxygenated compounds such as alcohols, ketones, and aldehydes are partially or completely removed [33,71]. Moreover, memory effects of Nafion driers have also been documented [33,72–74].

More promising for static HS-GC appears the principle of selective chemisorption of water onto a hygroscopic salt. $Mg(ClO_4)_2$ was used by several workers but with differing experience. While Matuska et al. [76] found quantitative recoveries for all C_2–C_{10} hydrocarbons, Doskey [77] has reported losses of long chain olefins and C_1- to C_3-substituted benzenes and therefore did not recommend this salt any longer. Another dessicant applied for this purpose was K_2CO_3 [78,79] and good recoveries were found for both aliphatic and aromatic hydrocarbons with significant losses for heavier aromatic compounds [78]. It has been experienced, however, that pure salts will alter by caking after prolonged use. To avoid this problem Kolb et al. [80] have coated a porous support material with the sorbent and LiCl was found particularly useful from all these hygro-

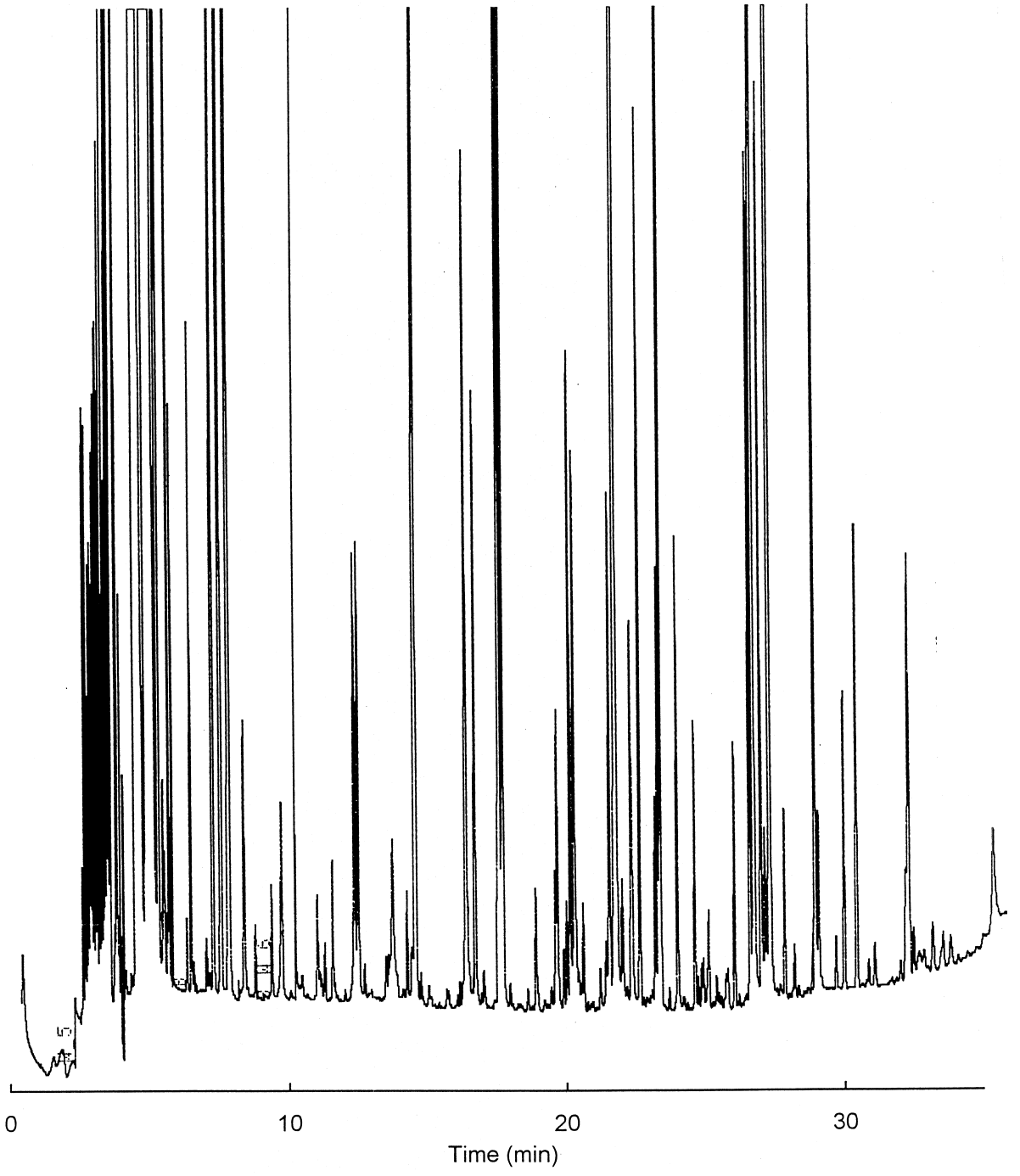

Fig. 21. Chromatogram of headspace volatiles from 250 mg flowerheads of 'lily of the valley' (*Convallaria majalis*), after static cryogenic-HS-GC. *Instrumentation*: Perkin-Elmer SIGMA 2000, HS100 Automatic Headspace Sampler, cryogenic accessory, 50 m×0.25 mm I.D. fused-silica capillary column, crosslinked methyl phenyl (5%) silicone, 1 μm film thickness, programmed: 45°C (8 min), 8°C/min, 120°C, 6°C/min, 250°C; carrier gas: hydrogen; FID×4. *Headspace conditions:* cryogenic trap and transfer line 1 m×0.32 mm I.D. fused-silica capillary column, crosslinked methyl silicone, film thickness 5 μm; sample: eight flower heads, equilibrated at +80°C for 30 min; 1 min splitless sampling.

scopic salts. It is an inert salt, contrary to K_2CO_3 and has a high capacity for water [81]. Similarly important, on the other hand, is the ease of reconditioning, because the water must be removed from the water trap after each run and this is done by increasing the temperature since LiCl already releases the water at +120°C sufficiently fast. The water trap consists of a small glass lined tube (6 cm×0.8 mm I.D.) packed with 10 mg of a material composed of Chromosorb W, AW, 60/80 mesh and coated with 65% (w/w) LiCl. This water trap can be included as part of the standard cryogenic accessory of the HS40 Automatic Headspace Sampler from Perkin-Elmer (Norwalk, CT, USA) already described in Fig. 12, and this extended modification is shown in Fig. 22.

The head of the fused-silica capillary column which extends out of the cryogenic trap is connected to a 1/16 in. Swagelok-T, onto which both the water trap and a stainless steel capillary (for carrier gas to backflush the water trap) are connected (1 in. = 2.54 cm). The other end of the water trap is connected to a 0.32 mm I.D. deactivated fused-silica capillary which is threaded through the heated transfer tube up to the sampling needle. The two solenoid valves V1 and V4 operate the carrier gas flow while V2 operates a purge flow and V3 the flow of the cooling gas nitrogen. Fig. 22 shows the 'standby' position (identical with the position during chromatography). The carrier gas enters the chromatographic system through valve V4 while valve V1 is closed and branches in the T between the water trap and the cryogenic trap where one part flows down the capillary column, while a small flow of purge gas streams back through the water trap, the transfer capillary, further through the heated needle compartment and leaves the system through valve V2. This purge gas flow can be adjusted by a needle valve (not shown) at the outlet of V2. In the 'standby' position the instrument is either idle or the chromatographic separation is proceeding in the capillary column. This position, where the water trap is permanently

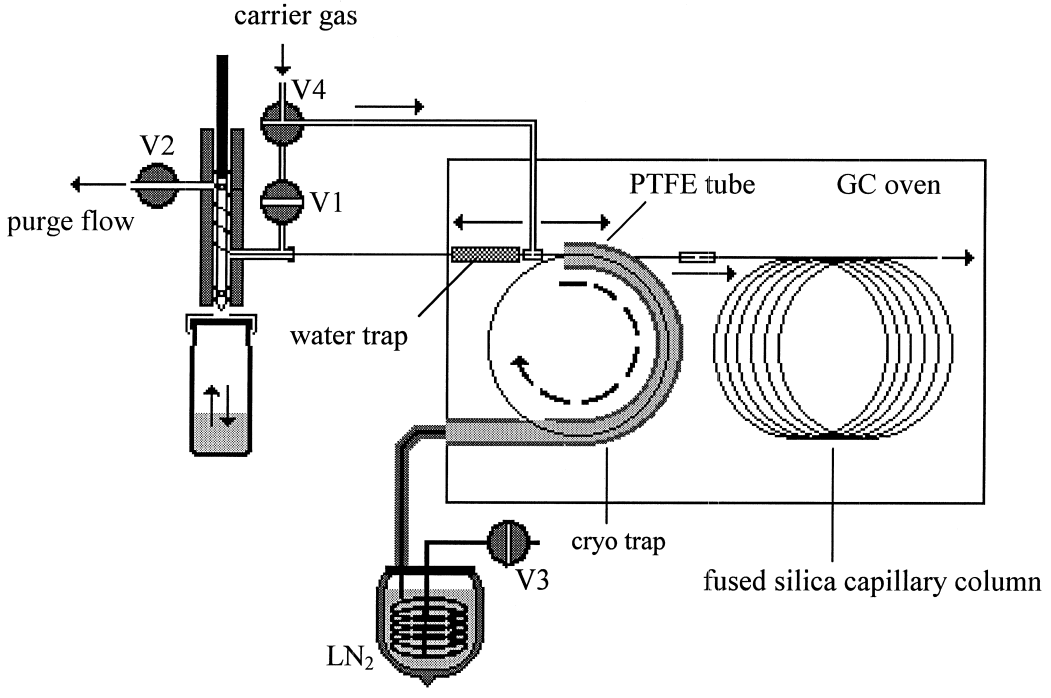

Fig. 22. Schematic principle of water removal for static cryogenic-HS-GC with the Perkin-Elmer balanced pressure headspace sampling system using a water trap. The system is shown in the 'analysis mode' (also 'standby mode') with backflushing of the water trap for regeneration. V1–V4 solenoid valves. The whole sampling cycle (cf. Fig.11) comprises the additional steps: pressurization (needle down, V1, V2, V3 open, V4 open to V1), sampling (needle down, V1, V2 closed, V3 open, V4 closed to cryogenic trap).

backflushed, is also maintained till the end of each analysis where the water trap is regenerated when increasing the oven temperature above +120°C. The sampling procedure is started by pressurizing the vial (cf. Fig. 11). The needle moves down into the headspace vial. Valve V4 is in the position where the carrier gas is directed to the open valve V1 and closed to the T. Carrier gas streams through V1 and the upper and lower vent of the sampling needle into the vial and pressurizes it. Independent of this 'pressurization' period is the possibility of starting the cooling gas by operating valve V3 either shortly before or after the beginning of 'pressurization'. This is to precool the cryogenic trap and to stabilize its temperature before sampling. Sample injection is started when both valves V1 and V2 are closed and valve 4 closed to the T. The pressurized headspace gas then expands through the needle, through the transfer capillary, passes the water trap and enters the cryogenic trap. Water is retained in the water trap, while the other compounds are trapped in the cryogenic trap. Sample injection is stopped, when valve V1 opens, while V4 is still in the position to direct the carrier gas to V1. In this 'withdrawal' position the carrier gas continues to flush the water trap in the forward direction and any volatile compounds which may still be in the water trap either by some sorption or by dissolution in the trapped water, are thus flushed by the carrier gas into the cryogenic trap. It is thus a type of miniaturized purge-and-trap, which may explain why even polar compounds such as alcohols pass the sorbent. At the end of the withdrawal time the system again goes into the 'standby' position. The chromatographic process starts when the flow of cooling gas is stopped by closing valve V3. The fused-silica capillary column in the cryogenic trap is rapidly heated up to the oven temperature in a few seconds by the warm carrier gas, which comes through the heated transfer capillary.

6.3. Properties of the LiCl-water trap

Lithium chloride in the water tap removes the water content in the headspace gas not completely. Depending on the oven temperature a small fraction pass through according to the vapor pressure above LiCl. For example, at +40°C oven temperature, 0.6% of the incoming water was found to break through [80]. This small amount of water helps to avoid the system to become absolutely dry and thus too strongly adsorptive. On the other hand, when LiCl becomes saturated with water, it liquifies and recoats the porous support smoothly again. Thus, caking by the crystallized salt after regeneration above +120°C is prevented.

6.4. Applications of static cryogenic-HS-GC with water removal

It was already discussed above that the need to remove water from the headspace gas is less urgent for static HS-GC due to the much smaller water content compared to the dynamic headspace procedures. Therefore, most applications for cryogenic-HS-GC can be carried out without removing the water from the headspace gas. However, although ice plugging of the capillary column is not the main problem, water can disturb the baseline in the chromatogram or the detector response, particularly with the ECD and PID which are often used for the headspace analysis of volatile halogenated and aromatic hydrocarbons in water at sub-ppb concentrations and also with GC–Fourier transform (FT) IR combination. The improvement in baseline stability is shown in Fig. 23.

A comparison of both chromatograms shows the effect of the water trap on an ECD chromatogram. Without the water trap a serious baseline distortion can be noticed by the excess of water and also peak broadening during the elution of water, which affects the resolution, as shown by peaks 2/3. Peak broadening comprises the whole range from trichlorofluoromethane up to chloroform. Ultra high sensitivity can be achieved for this type of analysis by static cryogenic-HS-GC with the water trap as shown by the peak 6 which corresponds to 3 ppt of carbon tetrachloride and by comparing with peak 10 in the chromatogram in Fig. 5 corresponding to 50 ppt without cryogenic enrichment. Detection limits in the ppq (parts per quadrillion) range are feasible, because the system was not yet at the highest possible sensitivity as indicated by the stable baseline with no noise on it. However, in practice the sensitivity is limited by the ubiquitous blanks rather than by the instrumentation including enrichment

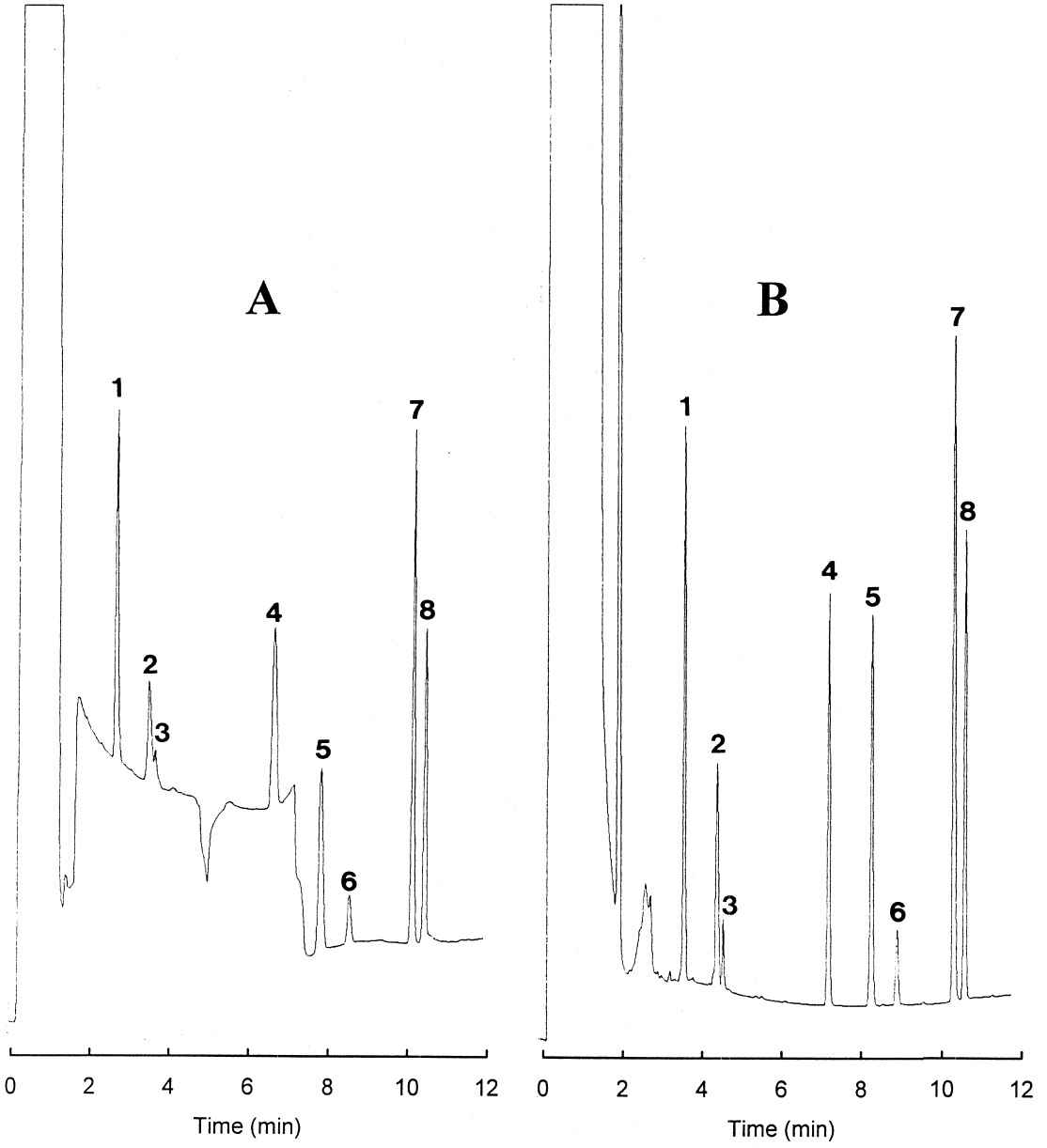

Fig. 23. Volatile halogenated hydrocarbons in water by static cryogenic-HS-GC–ECD without (A) and with (B) the water trap. *Instrumentation*: Perkin-Elmer AutoSystem, HS40 Automatic Headspace Sampler, cryogenic accessory with water trap, 50 m×0.32 mm I.D. fused-silica capillary column, crosslinked phenyl (5%) methyl silicone, film thickness 2 μm, programmed: 40°C (5 min), 6°C/min, 150°C (6 min), 200°C (5 min); carrier gas: He, 160 kPa; ECD. *Headspace conditions*: 2 min splitless sampling, sample: 2 ml, equilibrated 30 min at +80°C. *Identified peaks*: 1=trichlorofluoromethane, 2=1,1,2-trichlorotrifluoroethane, 3=dichloromethane (1.1 μg/l), 4=chloroform (0.1 μg/l), 5=1,1,1-trichloroethane (0.05 μg/l), 6=carbon tetrachloride (0.003 μg/l), 7=trichloroethylene (0.15 μg/l), 8=dichlorobromomethane (0.03 μg/l).

techniques. A similar baseline distortion by excess of water vapor as shown here for ECD was found with PID [80] and was improved also by the water trap.

The water trap was originally developed for the determination of low concentrations of nonpolar aromatic and halogenated hydrocarbons in water by static cryogenic-HS-GC, but even polar compounds pass the water trap unchanged. This is shown by an

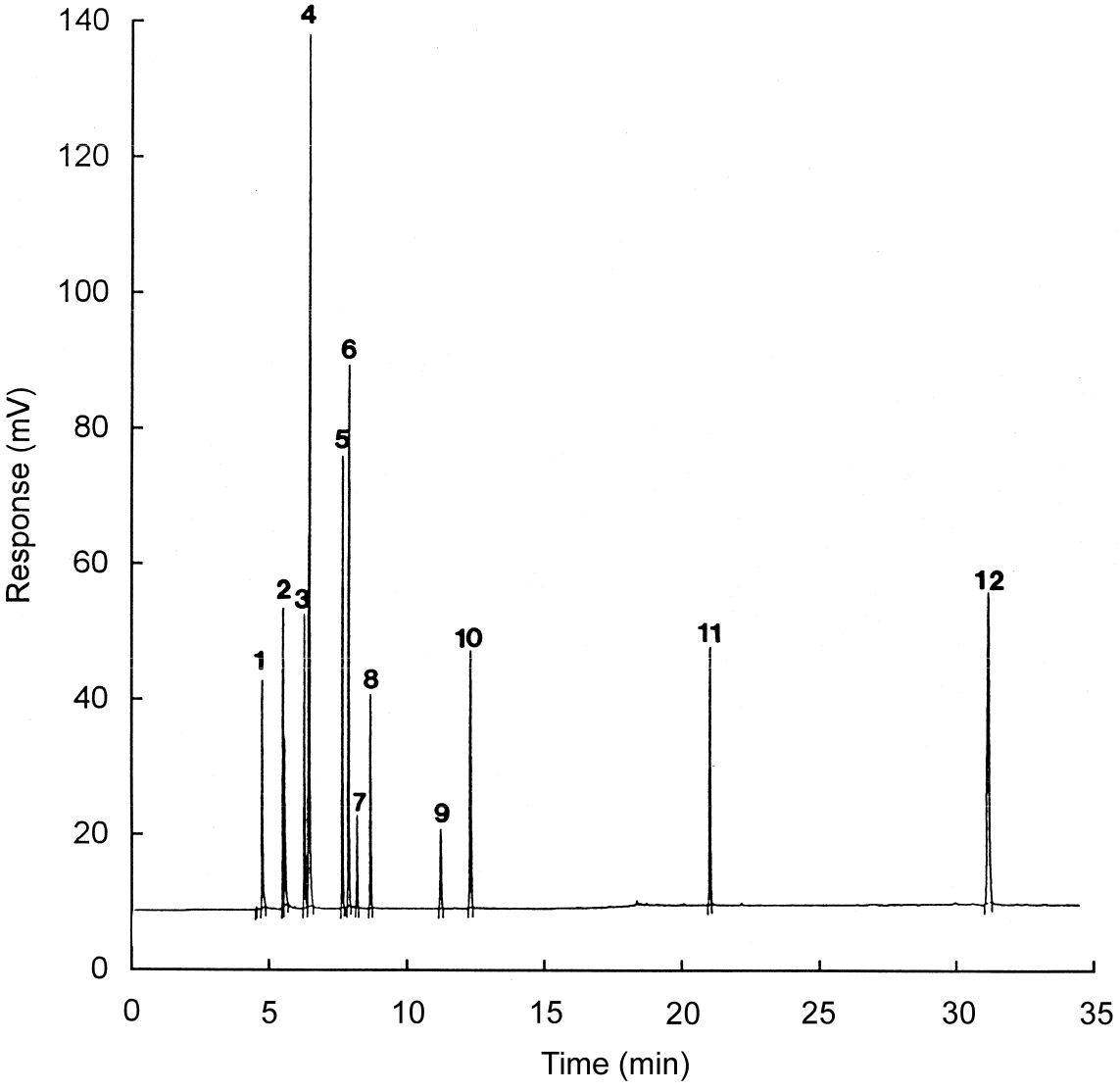

Fig. 24. Polarity test mixture in water by static cryogenic-HS-GC with water trap. *Instrumentation*: Perkin-Elmer AutoSystem, HS40 Automatic Headspace Sampler, cryogenic accessory with water trap, 50 m×0.32 mm I.D. fused-silica capillary column, crosslinked cyanopropylphenyl (14%) methyl silicone, film thickness 1 μm, programmed: 40°C (1 min), 8°C/min, 80°C (8 min), 20°C/min, 160°C (10 min); carrier gas: He: 205 kPa; FID. *Headspace conditions*: cryogenic trap 50 cm×0.32 mm I.D. fused-silica capillary column, phenyl (5%) methyl silicone, film thickness 1 μm, 1 min splitless sampling, sample: 2 ml, equilibrated 1 h at +80°C. *Identified peaks*: 1=methanol (6.5 mg/l), 2=ethanol (6.2 mg/l), 3=dichloromethane (0.28 mg/l), 4=*tert*.-butanol, (2.5 mg/l), 5=ethyl acetate (0.52 mg/l), 6=2-butanone (1.0 mg/l), 7=*n*-heptane (87.7 μg/l), 8=benzene (20.1 μg/l), 9=*n*-octane (9.4 μg/l), 10=toluene, (25.7 μg/l), 11=1,2,4-trimethyl benzene (26.3 μg/l), 12=naphthalene, (68.6 μg/l). From [81], with permission.

aqueous polarity mixture in Fig. 24 which comprises a wide range of various polar compounds from methanol up to naphthalene.

No adsorption and memory effects were observed and a linear relationship of peak areas with concentrations were found in the investigated working range of 1:80 [80]. Regression coefficients (r) were found close to unity with $r = 0.9998$ as the worst for naphthalene. This is particularily remarkable, considering the low volatility (b.p. 217.9°C) of this compound and the fact that it had to pass the water trap in the GC oven, which is only at +45°C at this early part of the procedure. The detection limit for naphthalene under these conditions is below the 1 ppb level. However, reactive compounds such as free acids did not pass the water trap, probably by reaction with LiCl.

The chromatogram in Fig. 25 shows the potential application of static cryogenic-HS-GC for flavor and aroma analysis. Such determinations are mostly

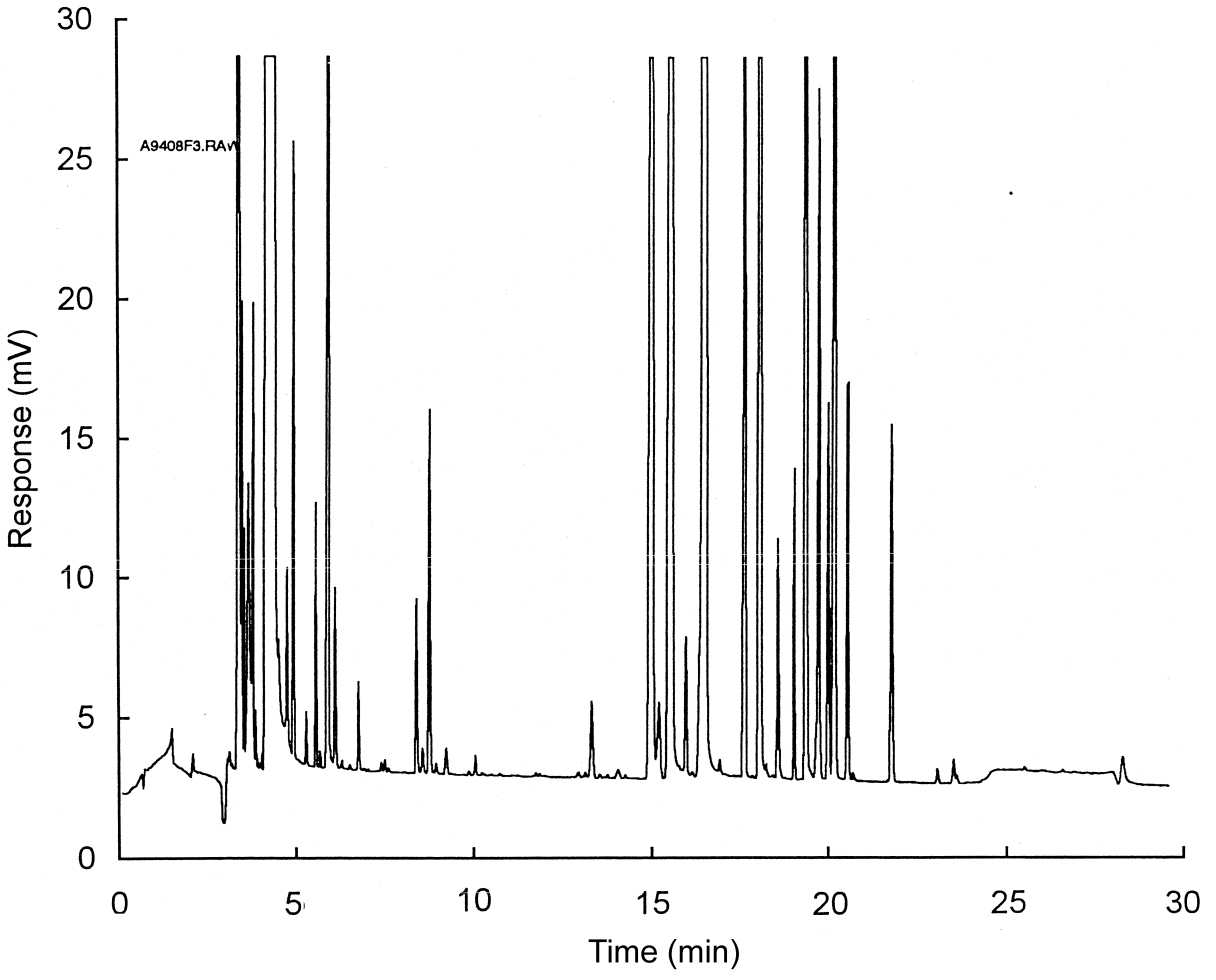

Fig. 25. Flavor analysis of pine needles at ambient temperature by static cryogenic-HS-GC. *Instrumentation*: Perkin-Elmer AutoSystem, HS40 Automatic Headspace Sampler with cryogenic accessory and water trap, 50 m×0.25 mm I.D. fused-silica capillary column, crosslinked cyanopropylphenyl (14%) methyl silicone, film thickness 1 μm, programmed: 40°C (1 min), 3.5°C/min, 90°C, 8°C/min, 120°C (20 min), 20°C/min, 200°C (10 min); FID; carrier gas: He, 200 kPa. *Headspace conditions*: cryogenic trap 0.55 m×0.32 mm I.D. fused-silica capillary, crosslinked phenyl (5%) methyl silicone, film thickness 1 μm, splitless sampling: 9.9 min, sample: 500 mg pine needle at room temperature.

carried out by dynamic headspace techniques, but both the adsorption and subsequent thermal desorption often causes artefact formation. Static cryogenic-HS-GC can avoid heating of such samples, since the headspace analysis can be carried out with the sample even at room temperature, allowing much longer injection times (volumes) to compensate for the corresponding lower sensitivity. The chromatogram in Fig. 25 shows the volatile compounds released from pine needles at room temperature (25°C) with a long injection time of 9.9 min, corresponding to a volume of 11.5 ml headspace gas. This sample volume was 53% of the available headspace volume in the 22.3 ml headspace vial and was transferred splitless into the 0.25 mm I.D. fused-silica capillary column.

Static cryogenic-HS-GC if compared to other headspace techniques has the main advantage that it runs completely automatic. For example 40 vials, each containing 2.0 ml of an aqueous solution of aromatic hydrocarbons with 25 μg/l for each component were analyzed under cryogenic conditions (2 min injection time) including the water trap with the Perkin-Elmer HS40 Automatic Headspace Sampler using the balanced pressure sampling technique. A good long term reproducibility with a relative standard deviations from ±2.4 to ±2.8% for benzene, toluene and *o*-xylene were found [80]. A total amount of only 6 kg of liquid nitrogen was consumed for this overnight run.

7. Conclusions

Headspace sampling is nothing else but the introduction of a gas sample into a column. Not much problems were encountered as long as packed columns were used which are better adapted for gas samples than capillary columns. The need for high separation efficiency and high sensitivity, however, called for capillary columns. Their drawbacks of low sample capacity and hence low sensitivity stimulated the development of various headspace techniques including numerous enrichment procedures and the variety of those techniques indicate the complexity of this problem. But regardless of whether dynamic or static HS-GC including SPME is used, they all encounter, in principle, the same problem of band concentration and sample enrichment. After all, however, the sensitivities of all these headspace techniques are in general more or less comparable, particularly if for trace analysis the potential instrumental sensitivity cannot be utilized due to the ubiquitous blank problems. Therefore, when comparing the various headspace techniques, the sensitivity should not be considered as the main criterion, since other aspects are important as well, such as the degree of automation or the ease of calibration for quantitative analysis. Automation is necessary not only for industrial routine analysis but in general for any analytical technique, which will be accepted as a certified method only after extensive evaluation for method validation. For this purpose a tremendous amount of data is required which can be determined by automated instrumentation only with reasonable expenditure. Equally important is the applicability for quantitative analysis. The inherent problem of any headspace analysis is the inclusion of the matrix effect in a calibration factor, but this makes in general no difficulty and proven methods are available, just to mention the method of standard addition. However, it is obvious that any calibration technique becomes more complicated the more parameters are involved in the overall procedure. In practice, therefore, the most simple technique of headspace sampling should be preferred.

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