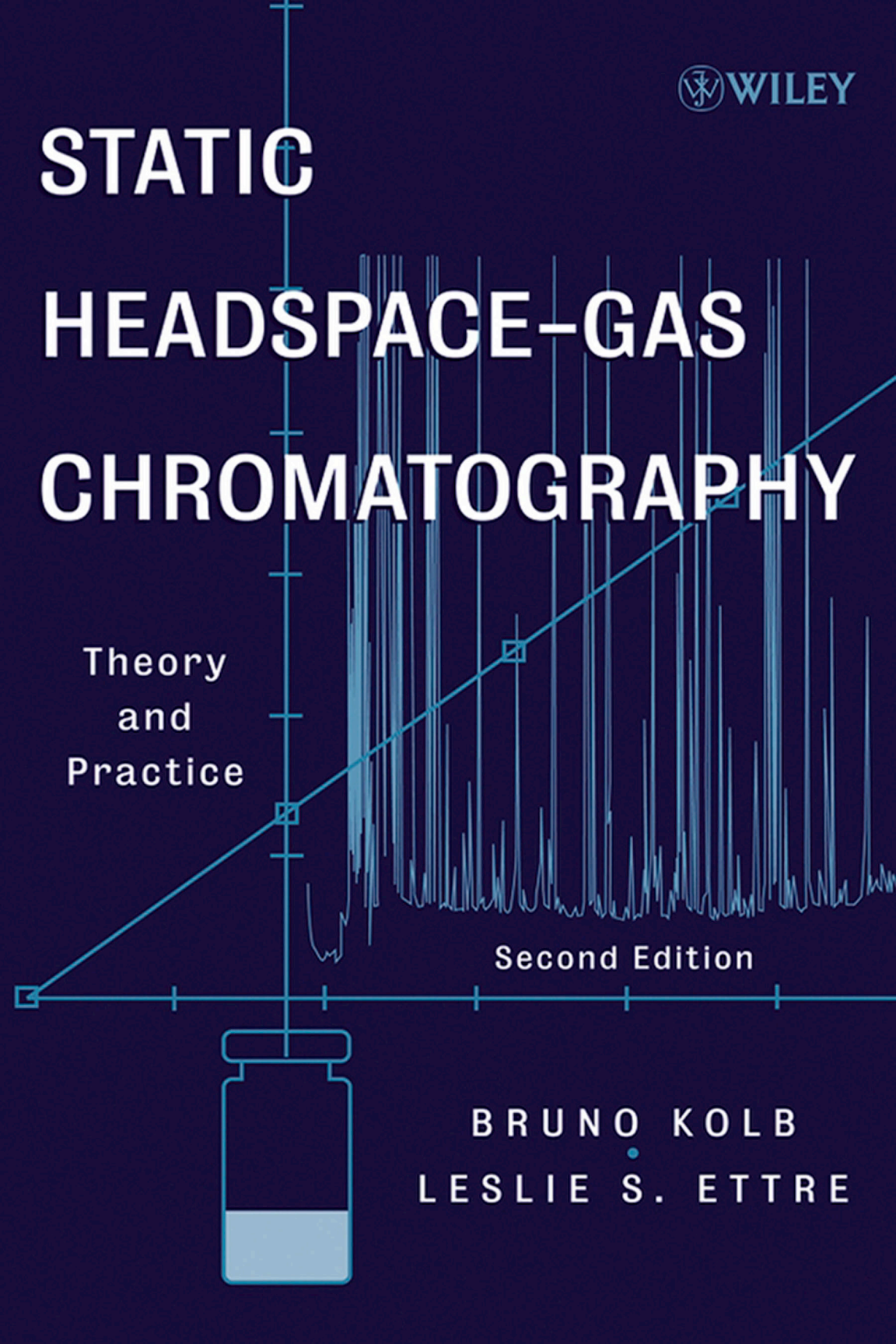
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STATIC
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CHROMATOGRAPHY
Theory
and
Practice
Second Edition
BRUNO KOLB
LESLIE S. ETTRE

Static Headspace–Gas Chromatography

Static Headspace–Gas Chromatography:

Theory and Practice

Second Edition

Bruno Kolb
and
Leslie S. Ettre

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Preface

The first edition of our book was published in 1997. In it, we tried to cover not only the theory and instrumentation of headspace–gas chromatography, but also give many examples for its use in quite diverse fields, indicating always the best conditions for optimization. We also tried to present a step-by-step guide for the potential user on how to select the best approach to solve a particular problem. It has been very gratifying for us to see that our approach was successful; even today, eight years later, practicing chromatographers find our book a useful help in their daily work.

However, in instrumental analysis eight years represents a long period of time, during which improved models of established instruments are introduced, and systems based on different principles developed. This has also been the case with headspace – gas chromatography; well-established techniques have been further improved and new techniques and systems introduced. Thus, we felt the need to prepare a new, enlarged edition of our book.

Solid-phase microextraction (SPME) is the most important among these new techniques. It can be used in two ways: by immersing the coated fiber in a liquid sample, and by sampling the headspace above a liquid or solid sample. In this way, it became complementary to the well-established static headspace sampling. The other traditional headspace sampling technique, *dynamic headspace sampling* ("purge and trap") has also undergone an expansion in its use in the last decade and is now the method recommended by various official standard procedures. In addition, systems combining its principles with static headspace sampling have recently developed. This broadening of the ways of headspace sampling induced us to include a comprehensive overview of these two gas extraction techniques and present their comparison with static headspace sampling.

Both classical static headspace sampling and SPME analyze an aliquot of the headspace of a closed vial; on the other hand, the purge-and-trap method represents exhaustive gas extraction, collecting all volatile vapors from the sample and analyzing them after further concentration. A fourth headspace sampling technique, multiple headspace extraction (MHE), is essentially exhaustive gas extraction, but carried out stepwise as a sequence of static measurements and not as a continuous process as purge-and-trap. MHE has important advantages. It permits easy calibration by a simple vapor standard, simplifying this important step in quantitation. It also helps to classify a new sample and to establish the most important analytical parameters (such as time and temperature) necessary to achieve the state of equilibrium. Additionally, it can provide the data needed to evaluate the

linearity and precision of a determination, and permit the evaluation of detector properties such as linear working range and limit of detection. A particular advantage of MHE is that it can be performed automatically (e.g., overnight), without the need of the user's attention. In the first edition of our book we have already dealt in detail with the principles and applications of MHE. Essentially we kept this discussion in the new edition, but have further emphasized its advantages in routine analysis.

In the last decade the demand to determine trace concentrations of a wide variety of samples has greatly increased. Such measurements require the use of large inert gas volumes for sampling and extraction and the large inert gas volumes must be separated from the compound(s) of interest prior to introduction to the gas chromatograph. This can be done in two ways, by adsorption-desorption or condensation. The use of *adsorption* requires a careful selection of the adsorbent and the analytical conditions. The enriched compounds suffer from the thermal stress, first by the adsorption energy and then the high temperature needed for quick desorption, and labile compounds can easily decompose, resulting in artifacts occurring in the analyzed final sample. On the other hand, *condensation (cryotrapping)* only needs lower temperatures; thus, thermal decomposition is avoided. The first edition of our book dealt with the various cryotrapping techniques, but we have greatly expanded this discussion, particularly by explaining the difference between simple *cryocondensation* and the advanced technique of *cryofocusing*. The latter technique utilizes the dissolution properties of the stationary phase in the GC column at lower temperatures, and accomplishes additional band focusing by temperature gradients during both trapping and warming-up. Cryofocusing does not necessarily need very low temperatures, so the need for a liquid cryogen can be avoided, (replaced just by cold air). In our opinion this possibility has great potentials, and therefore, we are illustrating it here with some examples. At this moment, such systems are not yet commercially available. We hope that this more extensive discussion will induce a further development of this technique as an integral part of automated instruments.

Today, all analytical laboratories are facing increasing sample leads; as a result, *automation* has become increasingly important, particularly in routine analysis. HS-GC is ideally suited for such operation. Therefore, when preparing this new edition, important consideration was given to the selection of various application examples and their suitability for automation.

Naturally we considered the newest developments in HS-GC, and whenever necessary we added some new application examples. However, we did not feel it necessary to replace the numerous examples already included in the first edition, only to have more recent dates in the respective references. All the practical examples given here are the results of extensive and laborious development work; they are fully valid and up-to-date even today and it would be practically impossible to find equivalent newer examples with sufficient detailed data. Unless otherwise noted all application examples are the result of the activities of the former lab of one of us (BK).

The subject of our book is static headspace—gas chromatography. Recently, the use of headspace sampling for other instrumental analytical techniques has increased, and we should note that the techniques discussed in our book are

generally also applicable in other applications. However, at this time we did not feel it possible to treat such usage in our book. Hopefully in a decade or so, someone will pick up the thread and present an even more comprehensive discussion of headspace sampling in general.

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November 2005

Preface to the First Edition

Headspace–gas chromatography is not new; the technique has been practiced since the early days of gas chromatography. However, there is still an increasing interest, apparently driven by the need for cost reduction in every analytical laboratory. This calls for automation of each part of an analytical procedure. Computer-controlled automated analytical instruments including autosamplers and data systems were the first step in this process of automation and were carried out very effectively by the instrument manufacturers. While the actual time needed to perform the analysis could thus be dramatically reduced, sample preparation remains a time-consuming task. Despite variation from laboratory to laboratory, our experience, which has been confirmed by statistical surveys, is that in most laboratories about two-thirds of the time is spent on sample preparation, while only 10% goes for actual analysis, and the rest for documentation and organization. Whenever the efficiency of an analytical laboratory has to be improved, it is worthwhile to look at and begin with sample handling.

Most samples need to be modified for the specific requirement of a particular analytical technique. Most of these cleanup procedures use some type of initial extraction procedure such as solvent extraction, solid-phase extraction, or supercritical-fluid extraction. However, if we are interested in highly volatile compounds, we can use an inert gas for this purpose; gas is an ideal "solvent" for volatile compounds, since it is easy to handle and is available in a much higher purity than most organic solvents—an aspect that is particularly important for trace analysis. A gas extract is ideally suited for analysis by gas chromatography, and this combination is called "headspace–gas chromatography"—HS-GC. Gas extraction techniques can be carried out in several variants: as a single step (static headspace) or by stepwise repeating of the extraction (multiple headspace extraction) and also by stripping the volatiles (dynamic headspace) by a continuous flow of an inert purge gas. All these gas extraction techniques are called headspace techniques for historical reasons (the name "headspace" was originally given to the gas content of the bulge that forms at the top of a can of food, whose composition had to be analysed).

If gas extraction is considered to be suitable cleanup procedure for a particular sample, we may ask which of these variants should finally be applied. The following criteria may help to make this decision:

- simplicity of operation
- degree of automation

- flexibility for changing requirements
- sensitivity
- quantitation

The simplicity of static HS-GC is unsurpassed by any other cleanup techniques: the sample (either a gas, a liquid, or a solid) is filled into the headspace vial, which is closed immediately and remains closed until an aliquot has been withdrawn form the closed vial and transferred directly to the gas chromatographic system, thus guaranteeing sample integrity. This simplicity enabled the early automation of the whole procedure. It is interesting to note that Bodenseewerk Perkin-Elmer introduced the first automated headspace sampler for gas chromatography as early as 1967 and prior to any liquid autosamplers. Automation also helps to overcome the only drawback of static HS-GC, the sometimes long equilibration times.

The flexibility of a system in adapting to varying sample properties is also an important factor in saving time if a laboratory receives samples of different types for analysis. This argument favors static against dynamic HS-GC: it has fewer parameters to be tailored and optimized for specific sample properties, such as selecting the various adsorbents for filling a trap in the case of dynamic HS-GC. In principle, static HS-GC needs to determine only the purely physical parameters (i.e., time and temperature) to achieve the necessary state of equilibrium in the vial.

As far as sensitivity and the possibilities for quantitative analysis are concerned, one would at first favour dynamic HS-GC. Its inherent purpose is to perform an exhaustive extraction, contrary to static HS-GC, and therefore the composition of the resulting gas extract is often considered to be the same as that of the original sample. As this book shows, however, the modern techniques of cryogenic focusing also allow the sensitivity range to be extended to determine concentrations down to the level of parts per trillion, or even parts per quadrillion (ppt, $1:10^{-12}$; ppq, $1:10^{-15}$).

With static HS-GC, the quantitative aspects are often rendered difficult, or at least complicated, by the somewhat mysterious matrix influence. A few words of clarification are necessary here. The first application of automated static HS-GC was the quantitative determination of ethanol in blood samples. No other analytical technique has been investigated and tested worldwide for precision, accuracy, reliability, and robustness by so many independent experts. If static HS-GC works so well with such a complex matrix as blood, there is no reason for it to fail in other cases and other matrices. Therefore, it is the main concern of the authors of this book to focus on the quantitative aspects of static HS-GC.

The need to give a comprehensive discussion of all the possible calibration techniques for gas, liquid, or solid samples in HS-GC was recognized by the authors during many headspace training courses—for example, the course entitled Headspace Gas Chromatograpy: Equilibrium and Purge-and-Trap Analysis, which we have held for several years at the Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy. The many questions and discussions with the participants stimulated the writing of this book, which we hope will prove to be a real practical textbook. For this reason, we have included many practical examples

with all the original data (peak area values), to enable the interested reader to go through all the calculations and also to use these data for alternative methods. We have compared the quantitative results of various calibration techniques as appropriate, to demonstrate that there feasible alternative techniques often exist.

Although this book emphasizes techniques, methods, and procedures rather than applications, we have selected the many practical examples to cover at least the most important applications of static HS-GC in environmental, polymer, and food analysis, and in some other interesting fields of application. Most of these applications, if not otherwise referred to literature, were developed in the GC laboratory at Bodenseewerk Perkin-Elmer, which pioneered in the automated HS-GC, most of these are unpublished results. It is natural therefore that these practical examples were carried out by the "balanced pressure headspace sampling technique," specific to the Perkin-Elmer headspace samplers. However, this is not mentioned explicitly in the figures, because a headspace sample is in fact a gas sample, and any other technique for the introduction of gas sample into a gas chromatograph should in principle also be suitable. The use of a particular sampling technique, therefore should not be considered a biased preference.

This book would not have been possible without the great commitment of many co-workers in this GC laboratory. Of these we thank particularly Maria Auer and Petr Pospisil, who made many valuable contributions to both instrumental engineering and applications. If this book contains many useful practical hints, it is due to the highly skilled experimental work and experience of Mrs. Auer, who carried out most of the quantitative examples in this book. We also thank Meredith Harral-Schulz for preparing the manuscript and Albert Grundler for the design of many of the figures.

BRUNO KOLB
LESLIE S. ETTRE

List of Acronyms and Symbols

In general, we follow the recommendations of the Nomenclature for Chromatography* of the International Union of Pure and Applied Chemistry (IUPAC); for new symbols not included in that nomenclature, we try to use its principles whenever possible.

In the symbols, further differentiation is provided by the use of certain *subscripts:* Generally, 1, 2, and so on are used for subsequent measurements, *i* to express in general an analyte, *st* to indicate a standard, and *ex* for the external standard. Subscripts *o*, *S*, and *G* refer to the original situation, the sample, and the gas phase, respectively; subscript *o* may also indicate conditions at column outlet or a base situation.

The use of *superscripts* is avoided except when specifically distinguishing between sample and calibration measurement, when the latter is indicated by superscript *c*, and in the symbols for saturated vapor pressure (p^o) and for the energy of mixing (ΔG^M).

In expressing concentration, we always use *parts per million (ppm), parts per billion (ppb)*, and *parts per trillion (ppt)* according to the American usage: *ppm* means $1:10^6$ (e.g., mg/L), *ppb* $1:10^9$ (e.g., µg/L) and *ppt* $1:10^{12}$ (e.g., ng/L).

* *Pure Appl. Chem.* **65**, 819–972 (1993).

Acronyms*

AA	acetaldehyde
ASTM	*American Society for Testing and Materials*
AT	adsorption tube
BF	backflush technique
BFB	1-brumo-4-flurobenzene
BP	boiling point
BTEX	benzene, toluene, ethylbenzene and the xylenes
CEN	*Comité Européen de Normalization* (European Committee for Standardization)
DIN	*Deutsche Industrienormen* (German Industrial Standards)
DMA	dimethyl acetamide
DMF	dimethyl formamide
DVD	divinylbenzene
EC	equilibrium constant
ECD	electron-capture detector
EF	enrichment factor
EG	ethylene glycol
EHA	2-ethylhexyl acrylate
ELCD	electrolytic conductivity detector
EN	*European Norm*
EO	ethylene oxide
EPA	*Environmental Protection Agency (U.S.A)*
FDA	*Food and Drug Administration (U.S.A)*
FET	full evaporation technique
FID	flame-ionization detector
FPD	flame-photometric detector
FTIR	Fourier-transform infrared spectroscopy, spectrophotometer
GC	gas chromatography
GPA	gas-phase addition
HPLC	high-performance liquid chromatography
HS	headspace
HSA	headspace analysis
HS-GC	headspace–gas chromatography

* Names of associations and official groups are given in italics.

HS-SPME	headspace solid phase microextraction
IC	ionization constant
I.D.	internal diameter
IF	improvement factor
INCA	inside needle capillary adsorption trap
ISO	*International Standards Organization*
IUPAC	*International Union of Pure and Applied Chemistry*
KF	Karl Fischer titration
LN_2	liquid nitrogen
MDQ	minimum detectable quantity
MEK	methyl ethyl ketone
MHE	multiple headspace extraction
MHI	multiple headspace injection technique
MS	mass spectrometer, spectrometry
MTBE	methyl-*tert*-butyl ether
NPD	nitrogen-phosphorus detector (thermionic detector)
OVI, OVIs	organic volatile impurity (impurities)
PA	polyacrylate
PAH, PAHs	polynuclear aromatic hydrocarbon(s)
PCB, PCBs	polychlorinated biphenyl(s)
PDMS	poly(dimethyl siloxane) (silicone)
PET	poly(ethylene terephthalate)
PFB-Br	pentafluorobenzyl bromide
PFBHA	pentafluorobenzyl hydroxylamine
PFPDE	1-(pentafluorophenyl) diazoethane
PFPH	pentafluorophenyl hydrazine
PGC	propylene glycol carbonate
PID	photo-ionization detector
PRV	phase-ratio variation method
PS	polystyrene
P&T	purge and trap
PTV	programmed-temperature vaporizer
PVA	poly(vinyl alcohol)
PVC	poly(vinyl chloride)
RF	response factor
RR	rate of release
RSD	relative standard deviation
SC	stability constant
SIM	single-ion monitoring
SM	styrene monomer
SPA	sample-phase addition
SPME	solid-phase microextraction
TCD	thermal-conductivity detector
TCE	tetrachloroethylene
TCTA	2,4,6-trichloro-1,3,5-triazine

TMSPMA	(3-trimethoxysilyl)-propyl methacrylate
TVT	total vaporization technique
TWA	time-weighted average
UNIFAC	universal functional group activity coefficient
USP	*United States Pharmacopeia*
VC	vinyl chloride
VCM	vinyl chloride monomer
VDI	*Verein Deutscher Ingenieure* (Association of German Engineers)
VOC, VOCs	volatile organic compound(s)
VPC	vapor-phase calibration method
WCC	whole-column cryotrapping technique

Symbols

a, a'	constant (in general)
a, a'	constant (slope) of a linear regression equation
a_c, a_G	constant (slope) in the linear regression evaluation of the peak area in the VPC method
A	peak area
A^*	peak area corrected for sample volume in the vial
A_c	peak area corresponding to C_c
A'_c	peak area corresponding to W_c in the determination of K by the VPC method
A_{ex}	peak area of an external standard
A_1	in MHE, the measured area of the first extraction
$A_1{}^*$	in MHE, the theoretical area corresponding to the first extraction (the intercept value)
ΔA	peak area corresponding to an added amount of the analyte (standard addition method)
b, b'	constant (in general)
b, b'	constant (intercept) of a linear regression equation
b_c, b_G	constant (intercept) in the linear regression evaluation of the peak area in the VPC method
b_o	peak width at half height
B, B'	constant (e.g., in Antoine-type equations)
c	calibration factor
c_n	number of carbon atoms in a molecule (carbon number)
C	concentration (in general)
C, C'	constant (e.g., in Antoine-type equations)
C_c	concentration of the analyte in the calibration vial in the VPC method

* In the general chromatography nomenclature, H and N are the symbols of plate height (HETP) and plate number, respectively. In this book, however, column efficiency is never specified, so H and N are given the meanings listed here.

C_F	analyte concentration in the fiber coating of SPME
C_o	original concentration of the analyte in the sample
C_e	actual concentration of a compound during exponential gas dilution
C_G	analyte concentration in the gas phase (headspace)
C_S	analyte concentration in the sample phase
d	density
d	diffusion path length
d_c	inside column diameter
d_f	coated stationary phase film thickness
D	diffusion coefficient
DL	minimum detectable limit
f	proportionality factor, calibration factor, correction factor, or response factor (in general)
f	friction factor
f_c	calibration factor
f_v	volume correction factor
F	flow rate (in general)
F_a	carrier gas flow rate at column outlet (without corrections)
$F_{c,o}$	carrier gas flow rate at column outlet, corrected to vial temperature and dry gas conditions
F_i	carrier gas flow rate at column inlet
ΔG^M	total free energy of mixing
ΔG_i^M	partial free molar energy of mixing
H	peak height*
H	Henry's law constant*
i	reference to a certain compound or to a stage in a measurement (e.g., in MHE)
k	retention factor
K	partition (distribution) coefficient
$K_{G/S}$	distribution constant of the analyte between the gas phase and the sample
$K_{F/G}$	distribution constant of the analyte between fiber coating and the gas phase
L	column length
M	molecular weight
M_{ref}	molecular weight of a reference compound
n	number of moles of a compound
n	number of measurements
n_{total}	total number of moles present
N	noise level*
p	pressure (in general)
p_a	ambient pressure
p_h	in MHE, pressure in the headspace vial
p_i	partial pressure of a compound

p_i	inlet pressure to a column (absolute)
p_L	pressure in the sample loop
p^o	saturation vapor pressure of a compound
p_o	in MHE, pressure in the headspace vial after venting
p_p	pressurization pressure
p_{ref}	partial pressure of a reference compound
p_{total}	total pressure of a gas mixture
p_v	sample vapor pressure in the headspace vial
p_w	partial pressure of water at ambient temperature
Δp	pressure drop along the column
$p\%$	precision of a detector's linear range
q	constant in the exponent describing MHE
Q	area ration of two consecutive peaks in MHE
Q_c	cross section of a column
r	correlation coefficient (in linear regression)
r	ratio of amounts in the determination of K by the VPC method
R	gas constant
R	peak area ratios (in the standard addition method)
Rf	relative migration rate
RF	response factor
RR	rate of release
S	selectivity
S_{sample}	surface area of sample
t	time
t_M	holdup time
t_R	retention time
t'_R	adjusted retention time ($= t_R - t_M$)
T	temperature, absolute (in general)
T_a	ambient temperature
T_c	column temperature
T_g	glass transition temperature
T_v	vial temperature
u	average linear carrier gas velocity
V	volume (in general)
V_e	the expanded volume of the headspace gas at p_o
V_F	volume of fiber coating in SPME
V_G	volume of the gas phase (headspace) in the vial
V_H	volume of transferred headspace gas
V_L	gas volume filling a sample loop
V_{mole}	g-mole volume of a pure compound in gaseous (vapor) form
V_o	volume of the original sample
$\mathrm{V_S}$	volume of sample phase in a vial
V_v	total volume of a vial
V_{vent}	volume of gas vented in the MHE procedure

W	amount (in general)
W_a	added amount of the analyte
W_A	amount of the analyte in the aliquot withdrawn form the headspace
W_c	amount added to the vial in the determination of K by the VPC method
W_{ex}	amount of analyte in the external standard
W_F	amount of analyte absorbed by the fiber coating in SPME
W_G	amount of analyte in the gas phase (headspace)
W_o	original amount of analyte present in the sample
W_S	amount of analyte in the sample phase
x	mole fraction (in general)
$x_{G(i)}$	mole fraction of a component in a gas mixture
$x_{S(i)}$	mole fraction of a component in solution
$Y\%$	extraction yield in the full-evaporation technique
α	proportionality constant
β	phase ratio
Φ_S	phase fraction (sample volume as a function of the vial's volume)
γ	activity coefficient
η	carrier gas viscosity
σ	relative pressure ($=p_o/p_h$) in MHE
φ	fraction of the vented solute vapor

CHAPTER

1

General Introduction

1.1 Principles of Headspace Analysis

Gas chromatography (GC) is an analytical technique for the investigation of volatile compounds. If the sample is a gas, then an aliquot of it is introduced into an inert moving gas stream—the *mobile phase* or the *carrier gas*—which carries it into the column containing the *stationary phase*. If the sample is a liquid, then an aliquot of it is heated and its vapor is transferred by the carrier gas into the column. There the sample components are separated by means of selective interaction (partitioning) between the stationary and mobile phases. Thus, they emerge at the end of the column at different times and can be detected. The time (*retention time*) that has passed between sample introduction and the emergence of the individual analyte bands—the *peaks*—is, under given conditions, characteristic of the individual analytes, while the size—height or *area*—of the individual peaks is proportional to their amount.

It is not our task to discuss the theory and practice of GC; the reader is referred to the general textbooks (e.g., [1–11]). However, from the brief summary just given, one can immediately draw two conclusions about the sample and its introduction. First, it is obvious that sample introduction must be instantaneous: after all, if the

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sample vapor band introduced into the column already has a significant width, then analyte separation will be hindered by the initial broadness of the analyte mixture's band. Second, it is obvious that all sample components must be volatile; otherwise, a solid residue will remain in the inlet system. Since this zone is heated, the solid residue may eventually decompose, creating volatile breakdown products which get into the column and thus into the chromatogram, creating the impression that these compounds were present as such in the original sample. Also, sample residue may interfere with subsequent injections due to adsorption and/or catalytic decomposition.

Because of this problem, one may have to follow an indirect procedure in handling complex solid samples (or samples containing nonvolatile solid particles) by first extracting the analyte(s) of interest and then introducing an aliquot of the resulting solution into the gas chromatograph. A typical example is the determination of low molecular weight compounds, such as monomers, in a polymer sample. The traditional methods use solvents either to extract the chemicals of interest or to dissolve first the polymer, which is then precipitated. The resulting solution is then injected and analyzed by GC. There are several problems with this approach. First, it is obviously time-consuming. Second, the analyte will generally be more diluted in the solution than it was in the original sample. And finally, it is difficult to avoid getting polymer into the injector of the gas chromatograph, where any nonvolatile sample constituents will accumulate, causing degradation of the chromatographic performance.

Solvent extraction of low molecular weight compounds from a complex solid sample is useful only if the high molecular weight or nonvolatile sample constituents are insoluble in the solvent; otherwise, these compounds will also be injected with the solvent extract, causing severe problems, as discussed above. Moreover, solvents always contain annoying impurities which may interfere with the subsequent chromatography. In GC, however, we analyze volatile compounds, and it is therefore natural to use a gas to extract the volatile analytes rather than a liquid solvent. A gas is an ideal solvent for volatile compounds and is available with much higher purity than any liquid solvent; this is an important factor, particularly for trace analysis at high sensitivity. Every extraction technique combines two immiscible phases, between which the compound to be extracted distributes partially. There are several versions of extraction procedures: a single extraction, a repeated stepwise extraction, or a continuous extraction. Which technique is preferred depends largely on the intended purpose. In liquid extraction, the goal is usually complete separation of the compound of interest to have it available for further processing. Stepwise extraction, for example in a separation funnel, is quite common for this purpose, while continuous extraction is applied mainly for industrial processes.

For analytical purposes, however, one does not need to have the pure compound at hand, because it is the information, for example the concentration of a certain compound in a sample, which is of interest. How much of an extracted compound is necessary to get this information depends on the sensitivity of the final measurement. For this reason, complete extraction yield by an exhaustive extraction is less important.

Gas extraction techniques are quite similar to those of liquid extraction. They can be carried out by a single extraction step, and for this purpose the original sample (liquid or solid) is placed in a closed vial. Volatile compounds vaporize partially from the sample into the gas phase above it and back again into the sample. After some time the system comes to an equilibrium, where the concentration of the volatile analyte in the gas phase remains constant. The equilibrium of both concentrations is controlled by the equilibrium constant (distribution constant, partition coefficient, Henry's law constant). In common practice, we refer to the gas phase in contact and in equilibrium with an essentially nonvolatile (or lesser volatile) sample as the *headspace* (*HS*) and its investigation as *headspace analysis (HSA).* By taking an aliquot of the gas phase, we can analyze the volatile compounds without interference by the nonvolatile matrix. In this procedure, the two phases in the sample vial are under static conditions and sample transfer is carried out after they have reached equilibrium. Therefore, we call this type of headspace analysis *static* or *equilibrium headspace* analysis.* If we want to determine the original concentration of the analyte in the sample from this analysis, we must include the equilibrium constant in the calibration procedure. Various techniques for this purpose are described in this book. If for some reason this is not possible, the single extraction step may be repeated until exhaustion is achieved and aliquots from the resulting gas extracts are analyzed again. The combined information (sum of peak areas) of these analyses corresponds to the total amount of that analyte in the original sample, and the resulting sum of peak areas is thus independent of the unknown equilibrium constant. This is the principle of the stepwise gas extraction procedure multiple headspace extraction (MHE).

There is, however, another way to carry out gas extraction. In this version we do not wait for equilibrium: gas extraction is carried out by continuously removing the gas phase; therefore, we rely on the volatile analytes to try to reestablish the equilibrium state, which, however, is never reached. Thus, at the end, the total amount of the volatile analytes is removed from the sample. The underlying idea is to collect the total amount of the various analytes in the sample and to have it available for analysis. This is *continuous gas extraction.*

1.2 Types of Headspace Analysis

In principle the headspace can be investigated by various analytical techniques, for example spectroscopic methods (mass spectrometry [MS], Fourier-transform infrared spectroscopy [FT-IR], etc.), but GC is particularly well suited for such measurements, since GC is an ideal method for gas (vapor) analysis. In headspace–gas chromatography (HS-GC), the vapor (gas) phase in contact with a condensed (liquid or solid) phase is analyzed by GC.

* Because with certain precautions calibration is also possible under nonequilibrium conditions, we prefer the term *static HS-GC* rather than *equilibrium HS-GC*.

Although the subject of this book is static headspace analysis by GC (static HS-GC), we have found it worthwhile to include a discussion of the various versions of gas extraction procedures in order to better understand the differences and the specific application of each technique and also to clarify some misunderstandings.

1.2.1 Principles of Static HS-GC

HS-GC analysis consists of two steps. First, the sample—a liquid or a solid—is placed in a vessel having a gas volume above it, and the vessel—usually a vial—is closed. This vial is then thermostatted at a constant temperature until equilibrium is reached between the two phases. Then an aliquot of the vial's gas phase (the headspace) is introduced into the carrier gas stream which carries it into the column, where it is analyzed in the usual way. Figure 1-1 visualizes the two steps of HS-GC. Sample transfer can be carried out in a number of ways: either manually, for example, by using a gas-tight syringe, or automatically, by means of pressurization of the sample vial and a time- or volume-controlled transfer of an aliquot of the headspace into the column. Instead of transferring an aliquot of the headspace gas directly into a GC column (direct static HS-GC), newer techniques have emerged, which include additional adsorption traps. The purpose of such a trap is to separate the volatile analytes from the excess of the diluted headspace gas. With the method of *solid-phase microextraction* (*SPME*), a thin fiber of fused silica, whose outer surface is coated with an immobilized stationary phase and mounted on a modified GC syringe, is inserted into a vial containing the sample. The fiber may be immersed in a liquid sample or in the headspace above a liquid or solid sample. In this case,

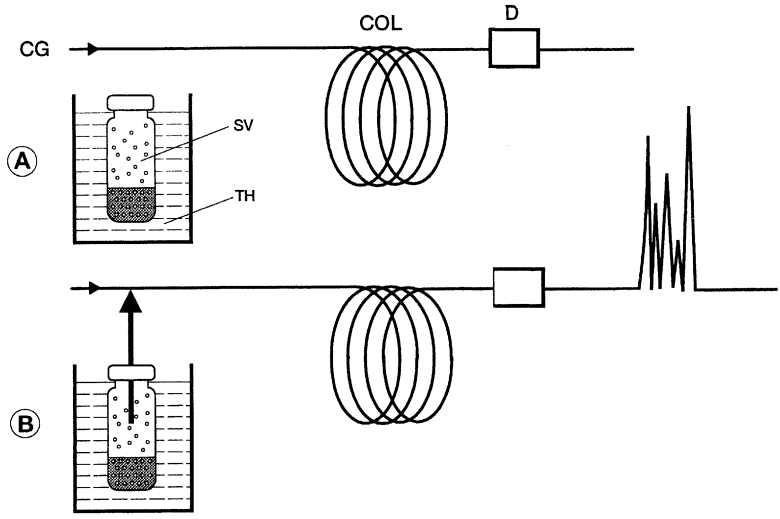

Figure 1-1. Principles of static (equilibrium) headspace-gas chromatography. (*A*) equilibration and (*B*) sample transfer. *CG* = carrier gas, *SV* = sample vial, *TH* = thermostat, *COL* = GC column, *D* = detector.

volatiles are absorbed in the fiber coating and the charged fiber is subsequently desorbed in the hot injector of the gas chromatograph. This technique, if used to collect volatile analytes from the headspace of a sample, is called *headspace solid-phase microextraction* (*HS-SPME*). Such an intermediate trap can also be an adsorption tube packed with traditional packings, from which the adsorbed compounds are released by thermal desorption and transferred to the gas chromatograph. This method, however, is a hybrid system between classical static HS-GC and continuous gas extraction.

1.2.2 Principles of Dynamic HS-GC

The dynamic headspace technique is principally a continuous method of gas extraction and separates volatile sample constituents from the matrix by a continuous flow of an inert gas either above a solid or liquid sample or by bubbling through a sintered glass of high pore density through a liquid sample, preferably an aqueous one; this technique is known as *purge and trap* (*P&T*). A high surface is required for rapid mass transfer from the aqueous matrix to the purge gas, and the sintered glass disc provides the necessary small gas bubbles. In an alternative technique, called the *chromatomembrane* version by Moskvin and Rodinkov [12] for monitoring a continuous flow of an aqueous sample, sintered Teflon particles, packed in a tube of a microporous Teflon membrane, provide a three-dimensional porous structure with gaps of open macropores through which the water moves continuously while the purge gas enters the tube through the micropores of the enveloping membrane and those of the sintered particles. The stripped volatiles are finally transferred to the sample loop of a gas chromatograph.

The underlying idea of P&T is to completely separate the volatiles of interest from the sample in order to have them all available for quantitative analysis in the finally diluted gas extract. Such an exhaustive extraction proceeds exponentially and therefore takes some time. The purged volatiles are thus present in a diluted gas extract and must be subsequently focused in a trap; this can be a cold trap, but in general, a cartridge packed with an adsorbent is used from which the trapped compounds are released by thermal desorption and transferred by the carrier gas into the column. The charged adsorbent, however, may also be desorbed by a small amount of a liquid solvent, as used in the *closed-loop stripping* procedure of Grob [13–15]. Figure 1-2 shows a typical configuration for P&T instrumentation for capillary GC, comprising an adsorption tube (AT) with multisorbent packing, various possible split positions (SP-1, SP-2, and SP-3), and a cryo-trap (CT). This schematic P&T set-up, however, has been modified by many workers, and the various variants are discussed briefly here following mainly the historical evolution.

1.2.2.1 The Trap

A high flow rate is necessary to achieve an exhaustive extraction from the sample in a reasonable time. This requires an adsorption trap with a sufficient capacity to

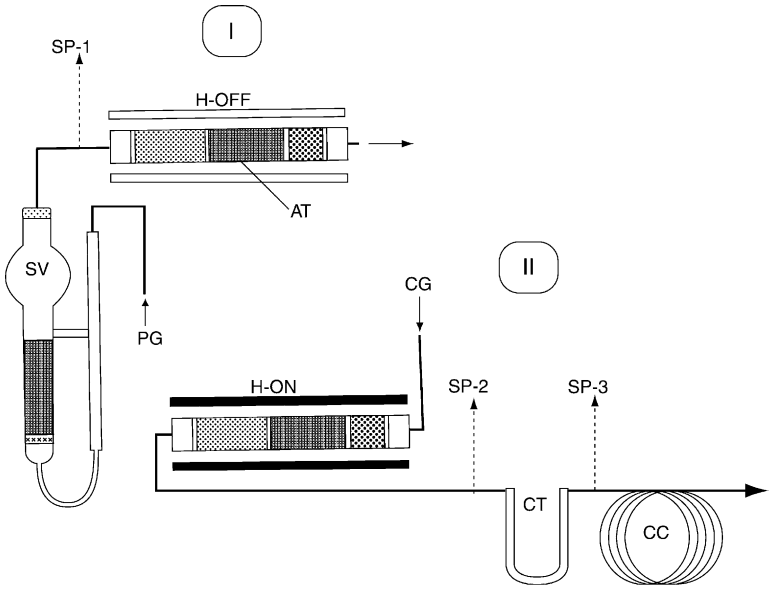

Figure 1-2. Principles of dynamic headspace-gas chromatography ("purge-and-trap"). (I) Sample purging and collection of the removed volatiles from the sparging vessel (*SV*) in an adsorption trap (*AT*) with multisorbent packing. (II) Desorption from the adsorption trap by backflushing of the heated trap (*H-ON*), refocusing in a cryo-trap (*CT*), and transfer into the capillary column (*CC*). *PG* = inert purge gas, *CG* = carrier gas, *SP-1; SP-2* and *SP-3* are optional positions of a splitter; *H-OFF* = trap heating off, *H-ON* = trap heating on.

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, for example 20–40 mL/min for both adsorption and desorption. Tenax, a porous polymer, is a very popular adsorbent. Since it is a weak adsorbent, particular care must be taken to avoid breakthrough of volatile compounds. Breakthrough volumes for Tenax TA have been published by Kroupa et al. [16] in the temperature range from -10 °C to $+170$ °C. Less care is necessary if the trap is filled with several adsorbents in series with increasing adsorptivity, forming an adsorption gradient where the most volatile compounds are finally adsorbed on the strongest adsorbent at the end of the multisorbent packing. The trapped compounds are then thermally desorbed and backflushed onto the capillary column but often are also trapped for refocusing in a cryo-trap. It should be noted, that a strong adsorbent may have the drawback of artifact generation from labile compounds, particularly flavor compounds, and safe solvent extraction is preferred in this case [17]. Artifacts are formed not only by the energy released during adsorption, but also by thermal stress during thermal desorption. However, high temperatures are often needed for rapid desorption from strong sorbents. Moreover, porous polymer sorbents such as Tenax at high desorption temperatures can release artificial decomposition products which produce spurious peaks in the chromatogram [18].

Thermal desorption from such a tube is the critical step in the whole P&T procedure, especially if combined with capillary columns for GC separation. Apparently there are three problems: (a) the *water problem*, caused by the large amount of water vapor also stripped off, particularly from an aqueous sample; (b) the *time problem*, caused by slow desorption of the trapped compounds from the trap; and (c) the *flow problem*, caused by gas flow during desorption, which in general is too high to be used directly as carrier gas for capillary columns.

1.2.2.2 The Water Problem

The resulting diluted gas extract contains not only the analytes of interest but also stripped water vapor, which may deteriorate the chromatographic process. The compounds of interest are usually trapped by adsorption on a hydrophobic adsorbent (Tenax, Carbopack, Carbotrap, Carboxen, etc.) where the excess of water vapors passes through unless the trap is at a lower temperature than the sparging container or if it is cooled during adsorption [19–21], when water becomes trapped by condensation. However, even at room temperature, some water may still be trapped in such a tube by capillary condensation in the micropores of the adsorbent rather than by superficial adsorption processes. This residual amount of water may still cause problems, particularly for further MS analysis, and either desiccants or other water-removal techniques have been adopted [22] to remove the trapped water (see also Section 3.7). This is also achieved by a very common technique called *dry purge*, in which the adsorbent is flushed at a temperature near ambient while the adsorbed volatile compounds remain adsorbed.

1.2.2.3 The Flow Problem

The adsorption tubes generally have the dimensions of a short packed column, since they have to accept a high purge flow from the sparging vessel, for example 20–40 mL/min. For the subsequent step of thermal desorption a similar flow rate is required. Although desorption is often carried out at a reduced flow rate (e.g., 10–20 mL/min), this may still be too high for the flow requirement of a capillary column which is around 1 mL/min, depending on its diameter and other chromatographic parameters. Therefore, a capillary inlet splitter is often applied [23, 24] and provides the appropriate flow rate through the capillary column (see Split SP-3 in Figure 1-2). Such a splitter, on the other hand, reduces the sensitivity since most of the headspace gas is wasted and only a small percentage of the sample is actually introduced into the column. These problems are often handled by a compromise in which a wide-bore capillary column (0.53 mm I.D.) is operated splitless but 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. Since such a splitter reduces the sensitivity of analysis, it could be placed before the trap (Split SP-1 in Figure 1-2). In this case, the trap may be miniaturized, and such a micro-trap with its lower mass could be heated up much faster; therefore it would fit much better capillary GC systems (see the following section).

1.2.2.4 The Time Problem

The high resolution capability of capillary columns requires a small concentration profile of the sample at the beginning of the chromatographic separation process. This is the crucial problem in GC for all injection techniques, but it is particularly serious for a diluted gas sample. A splitter solves the flow problem but not the time problem. Desorption, therefore, is the critical step in connection with capillary columns because generally it takes more time than is acceptable for instantaneous sample introduction into a capillary column. It is, of course, feasible to direct the charged gas flow for a short time, for example a few seconds, to the column, but such an approach would further decrease sensitivity. The delayed sample transfer therefore requires focusing of the analytes even further, for example by a cryo-trap; this can conveniently be achieved by the thermal focusing effect of a temperature-programmed capillary column. A low initial column temperature can compensate for delayed sample transfer when the analytes are trapped in the stationary phase or migrate very slowly. Naturally, the initial column temperature required for such a focusing effect depends on the volatility of the analytes and on some column properties, such as film thickness, in the case of coated capillary columns. Since both dynamic and static HS-GC are used mainly for the analysis of highly volatile compounds, these compounds require low initial column temperatures, often below ambient, and this leads to the various techniques of cryo-trapping (see Section 3.7). Most published papers on P&T applications report the use of such a two-step focusing procedure comprising adsorption/desorption together with cryo-trapping. However, in principle, one trapping step should be enough and either the cryo-trap or the adsorption/desorption trap may be omitted.

Traditionally, adsorption/desorption traps have had the dimensions of a short packed column from the time when packed columns were used for chromatography. However such traps do not follow fast enough the temperature rise during desorption and therefore need an additional refocusing step. On the other hand if the trap is miniaturized, it will allow rapid heating, thus producing a narrow desorption plug sufficiently sharp for direct transfer into a capillary column. Such microtraps are packed with Tenax TA either in a 11 cm $\times$ 2.17 mm I.D. stainless steel tube [25] or in a 5 cm $\times$ 0.53 mm I.D. fused silica capillary [26]; a multi-sorbent packing of Carboxen 1000, Carboxen 1003, and Carbotrap B in series in a 8 cm $\times$ 2 mm I.D. stainless steel [27] tube has also been used. Such miniaturized adsorption traps are in some respect similar to the charged fiber used with HS-SPME (see Section 3.5.2), which, due to its low mass, can also be desorbed sufficiently fast in the hot GC injector, often eliminating the need for an additional cryo-trapping.

The thermal focusing effect of a temperature-programmed capillary column may already be so effective that a previous adsorption/desorption trap may be unnecessary since the purge gas flow from the sparging vessel may be directed immediately onto such a capillary column [28]. In this case, however, the water problem becomes serious, particularly when the procedure comes to a stop due to ice plugging in the capillary column. Unless precautions are taken to remove water, a cryo-trap made of a 0.32 mm I.D. capillary became clogged after 3.22 mL of

water-saturated purge gas volume has passed through (after 2.18 mL in the case of a 0.25 mm I.D. capillary [26]). Such small sample volumes of a few milliliters, however, are typical of static cryo-HS-GC, and under these conditions both techniques are comparable. Because the various ways of managing the water problem are quite similar for both dynamic and static HS-GC, and also for air sampling by adsorption, the various techniques of cryo-trapping are treated separately and more extensively in Section 3.7.

The practical work with P&T deals with several severe problems. These include sample foaming [25, 28], as well as aerosol formation with transfer of inorganic and organic compounds such as salts, silicate, humus, and so on and its deposition in valves and tubes, thus creating the source of memory effects. These problems can be avoided if the gas flow is not bubbled through the liquid sample but instead is directed continuously through the headspace above the sample, which in this case may also be a solid or a viscous material. This variant of continuous gas extraction is often called *dynamic headspace analysis* in contrast to P&T. It is usually performed by using the sample vials for static HS-GC, which are closed by a septum and crimp-capped by an aluminum cap. Hino et al. [25] named this method the *whole headspace injection* (*WHSI*) method. It was carried out by piercing the septum by two parallel needles through which a continuous gas flow was directed, thus sweeping the gas phase. The volatile organic compounds (VOCs) from an aqueous sample were further trapped in a microtrap, as discussed above. The use of two parallel needles may cause problems with leaking septa. Markelov et al. [29] used a needle-in-needle version, in which the septum is punctured only once. The gas extract resulting from this *vapor phase sweeping* may be directed through any type of trap or a sample loop, or even directly onto a GC column. Calibration and quantitation, however, are complicated, because sweeping starts while the sample is in equilibrium with the headspace.

Although dynamic HS-GC is not the subject of this book, a comparison with static HS-GC is appropriate, since such a comparison is often made in the literature. It has been concluded that the dynamic version is supposed to have higher sensitivity [25, 30, 31] and it does not have to deal with matrix effects, because it is taken for granted that all VOCs are stripped off and used for the analysis. This may be true if a packed column is used where neither the flow problem nor the time problem is particularly important, but in capillary GC such a conclusion, if not wrong, is at least not fair for reasons that will now be discussed.

1.2.2.5 Comparison of Static HS-GC with P&T

We consider the following example representing typical instrumental conditions: 10 mL of a liquid sample originally containing 100 µg of a volatile analyte is transferred into a 20 mL vial and equilibrated. Assuming that half of the VOC is present in the gas phase, its concentration there is 5 µg/mL. With static HS-GC 2 mL should be sampled, and if it is transferred with a split ratio of 1 : 20, the corresponding volume entering the capillary column is 100 µL, which contains 0.5 µg of the analyte. P&T may be successful to strip off the total amount (100 µg) of the volatile analyte, and if it is transferred with the same split ratio of 1 : 20 to the capillary

column, 5 µg will go to the column. Thus, P&T appears to be 10 times more sensitive. If, however, cryo-trapping is necessary in the P&T procedure, this comparison favors static HS-GC. Cryo-trapping applied to P&T helps to achieve a band-sharpening effect but no enrichment, while when it is used in static HS-GC, both band sharpening and enrichment are obtained. By cryo-trapping in static HS-GC, it is thus possible to transfer several milliliters of the headspace gas splitless onto the capillary column, while only 1 mL would be required to equal the sensitivity of P&T. However, since several milliliters can easily be transferred, static HS-GC with cryo-trapping exceeds the sensitivity of the P&T procedure.

Nouri et al. [32] used both static HS-GC and P&T procedures for the analysis of methyl-*tert*-butyl ether in water samples. They found a detection limit of 50 µg/L for the static procedure and 2 µg/L for the P&T procedure, which, however, used such a cryo-trap. A further sensitivity enhancement by a factor of 25, however, would easily be possible for static HS-GC with such an additional cryo-trap. It is interesting to note that these authors used both techniques: static HS-GC for routine screening, due to its high degree of automation, and P&T in the case of a negative result for additional confirmation due to its higher sensitivity under the conditions indicated above.

Besides its allegedly superior sensitivity, another argument which is often used in favor of P&T is its elimination of the matrix effect. This, however, is true only if all analytes are completely purged, but such an exhaustive extraction can hardly be achieved in practice, considering the wide range of volatilities and polarities in a multicomponent mixture. The matrix effect influences the volatility of each dissolved compound to a different degree; therefore, the purge time needed to achieve an exhaustive extraction for each compound will also vary. Dunn et al. [33] have found that the dynamic headspace technique suffers from dependence of the calibration data on the sample matrix composition, thus making complicated multivariate calibration techniques necessary to obtain accurate results.

When comparing analytical methods, sensitivity is not the only criterion. Other factors are equally important, primarily the degree of automation. Automation is not only required for high sample throughput in practical routine analysis, but is also a prerequisite for method development. To validate an analytical method, a tremendous amount of analytical data are required, and these need automated instrumentation so that the series of samples can be analyzed unattended overnight. With its simplicity and high degree of automation, static HS-GC is unsurpassed by other headspace techniques because fully automated instruments are commercially available.

1.3 The Evolution of the HS-GC Methods

Headspace analysis—analyzing a gas in contact with a liquid or solid sample and drawing conclusions from the results concerning the nature and/or composition of the original sample—had been carried out long before the development of GC and before the combination of the two techniques. A comprehensive historical review of