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APPLICATION OF AN AUTOMATED HEAD-SPACE PROCEDURE FOR TRACE ANALYSIS BY GAS CHROMATOGRAPHY

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SUMMARY

Head-space gas chromatography (HSGC) is a useful method for the analysis of trace compounds in samples that cannot be handled with a syringe or involve too many difficulties if injected with a syringe. However, as HSGC requires expensive calibration, an automated instrument is essential for routine work and also eliminates problems related to contamination and sample carry-over.

Practical examples are given for the sensitivities that can be achieved with flame-ionization, electron-capture and nitrogen-specific detectors. The quantitative analysis of liquid and solid samples is discussed and emphasis is placed on the quantitative determination of monomers in polymers. A new method, called "discontinuous gas extraction", which is useful for the quantitation of volatile compounds in solid matter, is described briefly as an alternative method that can be used if the static head-space analysis fails.

INTRODUCTION

Head-space analysis by gas chromatography (GC) is a familiar technique and is widely used for samples that otherwise cannot be handled with a syringe, such as solids, and for samples that consist mainly of non-volatile material. Such samples could be extracted with a solvent, but as the compounds that are to be analyzed are volatile, it is obviously better to use a gas for extraction and to combine the extraction step directly on-line with the GC separation. A gas is usually available in a higher purity than any liquid solvent and hence problems with trace impurity interferences are avoided, apart from the fact that a gas does not cause a solvent peak with a solvent tail in the chromatogram.

Head-space analysis is usually carried out in the following way. The sample, either a solid or a liquid, that is to be analyzed for its content of volatiles is placed in a glass bottle that is closed with a rubber septum. The bottle is carefully thermostated until each compound has established an equilibrium between the sample and the gaseous phase. The equilibrium constant (partition coefficient for a liquid sample) is unique for each compound and must be determined by calibration if quantitative analysis is required. A known aliquot of the gas phase is then transferred to the gas chromatograph with either a gas-tight syringe or a similar device and analyzed for its

content of volatiles. The resulting chromatogram represents the composition of the gas phase, but by careful calibration it is also possible to determine the concentration of each compound initially present in the sample. It follows that every quantitative analysis by head-space gas chromatography (HSGC) requires much more calibration work than normal GC analysis, and therefore an automated instrument is desirable for this application. The additional expense of calibration could be justified only if a series of samples were subsequently analyzed under constant conditions, which again points to automation. Automation in this respect, however, does not mean the simple mechanization of a manual operation, but better precision and accuracy. For this reason, an electropneumatic dosing system has been used instead of a gas-tight syringe in all the applications described in this paper, because such syringes show undesirable memory effects, which are always a nuisance, particularly for trace analysis.

This electropneumatic dosing system, which is an accessory of the Perkin-Elmer F-42 gas chromatograph, has been described by Jentzsch *et al.*[1] and Kolb[2]. It is not only a well accepted device for forensic blood alcohol analysis, but it also works equally well for trace analysis in the parts per million and billion ranges because any contamination by condensation or adsorption is avoided. This paper considers the analytical aspects of HSGC with this particular instrument, thermodynamic applications having been discussed in a previous paper[2]. It is, however, not intended to give a comprehensive review of HSGC and the interested reader should consult, for example, papers by Binder[3], Vitenberg *et al.*[4] and Kolb[5].

HEAD-SPACE ANALYSIS OF LIQUID SAMPLES

Basic relationship for quantitative analysis

When an aliquot of the head-space gas is dosed, the resultant peak area (A_i) from a compound i is a measure of the amount of this compound in the gas space above the sample and is thus proportional to its partial vapour pressure, p'_i:

$$A_i = c_i p'_i \tag{1}$$

So far, only a simple gas analysis is concerned here, and as a result the sample bottle used for HSGC can in fact be used as a simple gas sampling tube, particularly for collecting gas samples at various locations, as these bottles can be conveniently evacuated by piercing a septum needle through the rubber septum and applying a vacuum. These evacuated bottles can be filled with an air sample at any location for environmental control simply by piercing the septum with a septum needle. The chromatogram in Fig. 1 shows the analysis of such an air sample with 1 ppm of vinyl chloride monomer together with other unidentified air pollutants.

The result of such a head-space analysis, in the form of the gas composition, may also be sufficient when the composition of an aroma, for example, is to be determined, and HSGC is widely used for this purpose. More frequent, however, is the task of determining the concentration of the components in the sample itself. This is also feasible, as the partial vapour pressure, among other parameters, is dependent on the concentration of that particular component in the sample. From the large number of possible examples, a binary liquid mixture will be considered as the simplest model,

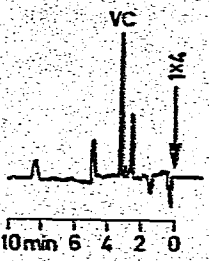

Fig. 1. Analysis of 1 ppm of vinyl chloride (VC) in air. Instrument: Perkin-Elmer F-42 with FID; 2 m × 1/8 in. stainless-steel packed column with 10% DC-200 on Chromosorb R at 80°C (isothermal). Sample volume, 0.5 ml.

in which a solute i is dissolved in the solvent; the solute i should be sufficiently volatile to be suitable for GC analysis.

The partial vapour pressure of the solute above the solution, according to Henry's law (eqn. 2), depends on the mole fraction, x_i, of the solute i, and the vapour pressure, p_i^0, of the pure compound i at a given temperature corrected for any deviation from ideality by the activity coefficient, γ_i:

$$p'_i = x_i \gamma_i p_i^0 \tag{2}$$

Combination of eqns. 1 and 2 results in eqn. 3, which is the basis of any quantitative head-space analysis, as already shown by Kolb[2,3]:

$$x_i = A_i / c_1 \gamma_i p_i^0 \tag{3}$$

Hence, the desired concentration, x_i, can be calculated provided that the product $\gamma_i p_i^0$ is known. However, as the activity coefficient is usually not known, this product must be included in the calibration and thus eqn. 4 describes the practical equation, where c_2 is the overall calibration factor:

$$x_i = A_i / c_2 \tag{4}$$

As a result of eqn. 3, the calibration has to be carried out not only with the pure compound itself, as p_i^0 is a unique property for each compound at a given temperature, but also under the same instrumental conditions, as the calibration factor c_1 represents a specific apparatus factor that also includes the temperature. Consequently, both the analysis and the calibration sample must be analyzed at the same temperature.

The application of eqn. 3 to quantitative HSGC requires a constant activity coefficient, which is realized only in dilute solutions, while at higher concentrations the activity coefficient becomes a function of the concentration itself. This effect, however, is not a problem in HSGC, because it is always possible to dilute a sample, if the concentration of its compounds is too high. According to our experience, dissolution below 1% is always sufficient to remain in the linear range of the activity coefficient. Solid samples and samples of heterogenous composition, however, must be carefully checked for linear behaviour of the activity coefficient. For colloids, a linear relationship similar to that for liquids can be assumed, as shown in Fig. 2.

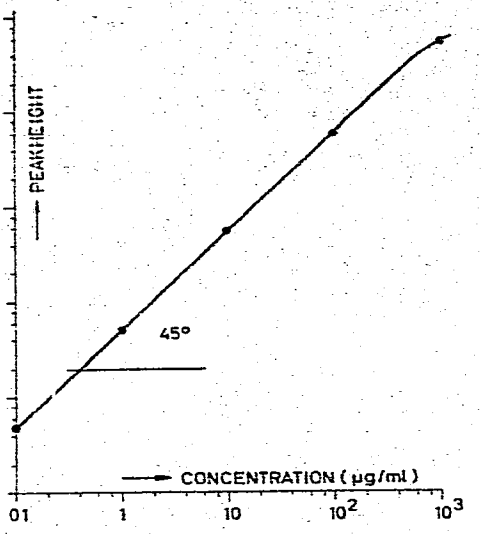

Fig. 2. Linearity of peak area versus concentration of acrylonitrile monomer in a dispersion of an acrylonitrile copolymer by head-space gas chromatography. Conditions as in Fig. 7.

where a dispersion of an acrylonitrile copolymer was tested for the linear relationship between the acrylonitrile monomer concentration and the resulting peak height in the head-space chromatogram (see also the chromatogram in Fig. 7).

Subsequently, calibration has to be carried out in the same matrix, as the activity coefficient represents the influence of the intermolecular interaction between the solute and the solvent. This requirement can sometimes cause serious problems if the matrix of the sample is not available in a pure form or cannot be simulated to a sufficient extent. If, for example, the concentration of a trace compound in waste water has to be determined, it is convenient to perform a calibration with pure water, but the result can be considerably in error if the waste water sample has a high content of salts, which changes the matrix and thus the activity coefficient in an unpredictable manner. The following solutions to such problems exist:

(1) The composition of the matrix is known and can be reproduced or at least simulated for calibration purposes. For example, for the determination of fusel oils in spirits, it is sufficient to execute the calibration in an aqueous alcoholic solution[6].

(2) The composition of the matrix is not known, but is available in pure form. For example, for the determination of trace amounts of trichloroethylene in blood (see Fig. 5), pure blood is available for calibration purposes. One must be careful, however, even in such simple cases, as blood has slightly different properties depending on the individual concerned, owing to differences in the lipid or salt content, which influences the activity coefficient of alcohol, as has been found in forensic blood alcohol analysis. This effect can be compensated for if a second alcohol is added as a standard at a constant amount in every blood sample, and the peak area ratio is used for both calibration and analysis. For this reason, it has been suggested[5] that such a standard should be called a "compensation standard" in order to prevent confusion with the usual internal standard in quantitative analysis. This compensation standard should compensate only for slight matrix effects and for this purpose should be chemically

as similar as possible to the compound that is to be determined, in order to achieve similar intermolecular interactions and thus a similar effect on the partial vapour pressure of both compounds.

(3) The composition of the matrix is unknown, and it is also not available in a pure form. In such a case, the calibration can be carried out by the method of known addition, in which the sample is analyzed twice, with the addition of a known amount of the compound to one of the two samples. The increase in the peak area thus corresponds to the amount added and permits the calculation of the original concentration.

The use of an internal standard in HSGC for the quantitative analysis of a multi-component mixture is possible, provided that not only the temperature of the samples but also the matrix does not change for all the samples, as each compound again must be calibrated under the same conditions with respect to the concentration of such an internal standard. The resulting factor, usually known as the detector response factor, now includes, however, not only the difference in the detector response but also the differences in the partition of each compound and thus all of the relevant experimental conditions, and the method with an internal standard should therefore be applied carefully in HSGC with these limitations in mind.

Practical application of HSGC to liquid samples

The basic relationship in eqns. 3 and 4 makes a quantitative analysis by HSGC very simple, provided that the sample is a liquid, because it is easy to prepare a calibration mixture from the pure compounds as discussed above. The sensitivity with which a certain compound is determined depends on its partial vapour pressure and thus on all of the parameters expressed in eqn. 3. If in trace analysis the highest possible sensitivity is required, the following aspects should be taken into account.

Increasing the absolute amount of sample in a head-space bottle does not improve the sensitivity, as it is the concentration of a compound in the gas phase that is in fact determined, and not the total amount of that compound in the bottle. For a liquid sample, the concentration in the gas phase is related to the concentration in the liquid phase by the partition coefficient, and changing the volume of sample in the bottle does not change the concentration of that compound in the sample. Hence the volume of sample is determined mainly from practical considerations, such as ease of handling the sample with syringes or pipettes.

Improvements in sensitivity can be achieved by increasing the temperature of the sample. Thus, as a rough rule, an increase in temperature of about 30°C doubles the peak height. This is not as much as might be expected, because in general the sample temperature should not exceed 100°C, mainly owing to chemical reactions such as oxidation and hydrolysis, which are likely to be initiated in the environment of air and water with most natural samples. The application of higher temperatures in polymer analyses will be discussed later.

The partial vapour pressure of a compound can be increased and hence its detection limit improved by changing the activity coefficient, *e.g.* by a salting-out effect. This effect is particularly useful for compounds that form strong hydrogen bonds in aqueous solutions, such as phenols or fatty acids. It has been found[7] that the detection limit for volatile fatty acids in water can be improved by a factor of 10–20 by adding sulphuric acid (50%) to give a pH of less than 1 in the solution and by the salting-out

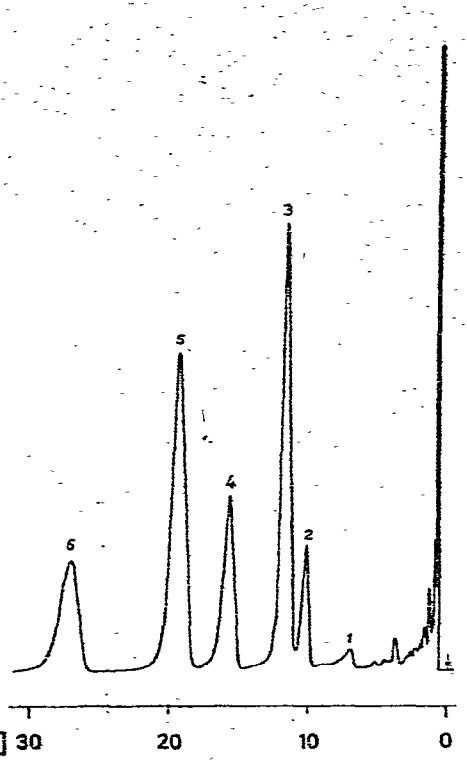

Fig. 3. Head-space analysis of an aqueous solution of free fatty acids. Instrument: Perkin-Elmer F-40 with FID; 2 m × 1/8 in. stainless-steel packed column with 5% FFAP on Chromosorb G, AW-DMCS, at 110°C (isothermal). Sample temperature, 55°C. Attenuation, ×8. Components (0.1%): 1 = acetic acid; 2 = propionic acid; 3 = isobutyric acid; 4 = *n*-butyric acid; 5 = isovaleric acid; 6 = *n*-valeric acid. Reproduced with kind permission of M. J. House[7].

effect achieved by adding magnesium sulphate. Table I gives a comparison of the practical detection limits of some fatty acids in pure water and after the addition of sulphuric acid plus magnesium sulphate. Fig. 3 shows a chromatogram with a concentration of 0.1% of each compound.

TABLE I

DETECTION LIMITS OF FREE FATTY ACIDS IN AQUEOUS SOLUTION AT 55°C SAMPLE TEMPERATURE[7]

Conditions as in Fig. 3.

Compound	*Detection limit (ppm)*	
	Solution in water	*Solution in water + H_2SO_4 + $MgSO_4$*
Acetic acid	10^3	80
Propionic acid	250	15
Isobutyric acid	35	3
n-Butyric acid	200	10
Isovaleric acid	125	5
n-Valeric acid	600	15

Another approach for increasing the sensitivity of the overall procedure is to use a more sensitive or a more selective detector, such as an electron-capture detector (ECD) or an element-specific detector, provided that the compounds to be analyzed have the necessary properties. Very often it is not the enhanced sensitivity that can be achieved with such detectors, but the better selectivity, which enables the determination of trace amounts, particularly in complex mixtures, as shown for example in Fig. 7.

Practical example of HSGC with a flame-ionization detector

The practical example given in Fig. 3 is not representative of the sensitivity that can be achieved with a flame-ionization detector (FID). Depending on the parameters outlined above, less polar compounds with higher vapour pressures can be determined with a sensitivity several orders of magnitude higher. Such an example is shown in Fig. 4, which demonstrates the analysis of some aromatic hydrocarbons in water that had been polluted with gasoline. The concentrations were found to be 170 ppb for benzene and 390 ppb for toluene, and thus the detection limit for both compounds would be about 10 ppb.

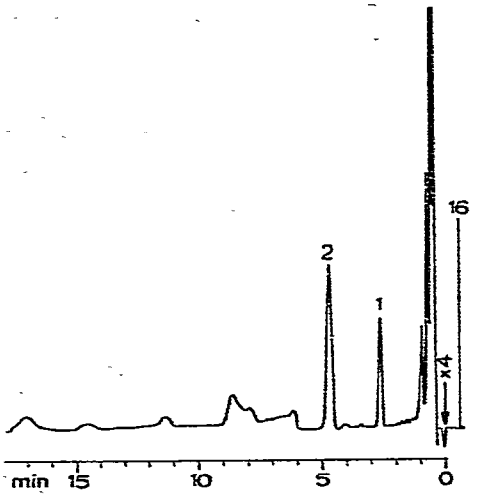

Fig. 4. Head-space analysis of aromatic hydrocarbons in gasoline-polluted water. Instrument: Perkin-Elmer F-40 with FID; 2 m × 1/8 in. stainless-steel packed column with 15% Carbowax 1500 on Celite (60–80 mesh) at 60°C (isothermal); sample at 75°C. Components: 1 = 0.17 ppm of benzene; 2 = 0.39 ppm of toluene.

Practical examples of HSGC with an ECD

Compounds with strong electron-capture properties, such as halogenated hydrocarbons and diketones, have found interesting application in head-space analysis using an ECD. Head-space analysis is carried out preferably with the original sample without any clean-up, and as a result mainly aqueous solutions such as beverages or body fluids are investigated. The proper choice of the ECD is very important in order to avoid deterioration of the radioactive source by water vapour. Tritium-

containing detectors are not suitable for this purpose owing to possible hydrogen exchange and only nickel-63 detectors should be used, because they are not influenced by water vapour.

Head-space analysis of halogenated hydrocarbons. The environmental control of halogenated hydrocarbons has become important in recent years, and HSGC has provided an interesting means of measuring the uptake of such compounds in man. Gostomzyk[8] investigated the pharmacokinetics of halothane and its uptake and elimination in fat tissues, and Gostomzyk *et al.*[9] investigated the stress of the anaesthetic staff in operating theatres by chronic exposure to anaesthetics such as halothane by combined electron-capture and head-space gas chromatography of blood samples and tissues.

The same instrumentation has been used for the surveillance of workers exposed to trichloroethylene vapour, and this compound together with its metabolites trichloroethanol and trichloroacetic acid were determined in blood by Lindner and Weichardt[10,11]. Trichloroethanol has been detected by HSGC after conversion into chloroform by the haloform reaction[11], which was carried out directly in the sample bottles prior to HSGC analysis.

The chromatogram in Fig. 5 shows an example of the sensitivity that can be achieved, using the head-space analysis of 0.5 ppm of trichloroethylene in blood.

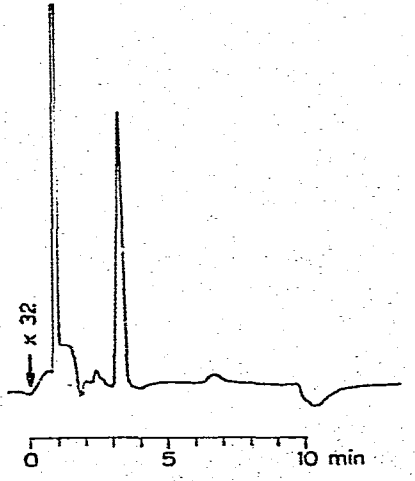

Fig. 5. Head-space analysis of 0.5 μg/ml trichloroethylene in blood. Instrument: Perkin-Elmer F-40 with Ni^{63} ECD (1 mCi); 2 m × 1/8 in. stainless-steel packed column with 15% polyethylene glycol on Kieselguhr at 80°C (isothermal). Sample, 0.1 ml of blood at 85°C. Attenuation, ×32.

Head-space analysis of diketones in beer. Diketones such as diacetyl and pentane-2,3-dione also show strong electron-capture properties, and their analysis in beer is of considerable interest as both compounds have a strong influence on the taste of the beer even at extremely low concentrations. For this reason there is a need for process control, which is best carried out by automated HSGC with an ECD[6]. The chromatogram in Fig. 6 shows such a head-space analysis of beer using a nickel-63 ECD. The concentration of each dicarbonyl compound is about 0.06 mg/l.

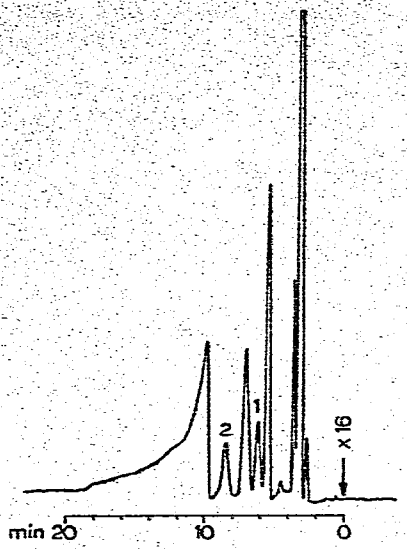

Fig. 6. Headspace analysis of diketones in beer. Instrument: Perkin-Elmer F-40 with Ni^{63} ECD (1 mCi); 2 m × 1/8 in. stainless-steel packed column with 5% Carbowax 20M on Chromosorb G (60–80 mesh) at 60 °C (isothermal). Sample, 1 ml of beer at 50 °C. Attenuation, ×16. 1 = Diacetyl (0.06 mg/l); 2 = pentane-2,3-dione (0.05 mg/l).

Apart from this special application to beer analysis, all other volatile compounds in beer, such as fusel oils and other carbonyl compounds, have also been analyzed by HSGC with an FID[6,12,13].

Practical examples of HSGC with a nitrogen-specific detector

The chromatogram in Fig. 7 shows the result of a head-space analysis of a dispersion from an acrylonitrile copolymer with both the FID and a phosphorus- and nitrogen-specific detector (PND). By using a stream splitter after the column, both chromatograms were recorded simultaneously with a dual-pen recorder. A comparison of the two chromatograms demonstrates clearly that the FID is not suitable for the analysis of the acrylonitrile monomer in such a complex mixture. The linearity of the acrylonitrile concentration with the peak height has already been demonstrated in Fig. 2.

Even very polar compounds, such as the amphetamines, can be analyzed directly from urine sample by HSGC with such a nitrogen-specific detector, and the urine can be used directly without extraction. It is necessary only to make it alkaline by adding sodium hydroxide. The chromatogram in Fig. 8 shows as an example the analysis of 0.7 μg/ml of amphetamine in urine.

HEAD-SPACE ANALYSIS OF SOLID SAMPLES

Only liquid samples have been considered in the examples above. As already mentioned, such samples are easy to handle and the necessary calibrations are in general without problems. The situation, however, is different if solid samples are analyzed by HSGC and whenever possible such solid samples should always be analyzed in solution.

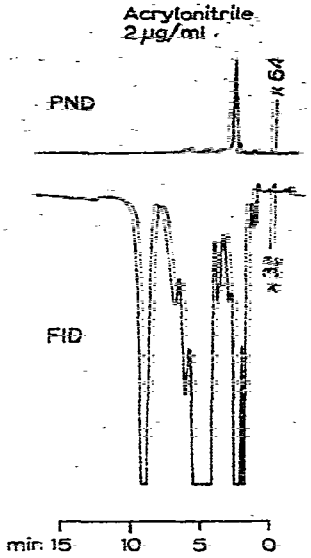

Fig. 7. Head-space analysis of acrylonitrile monomer from a dispersion of an acrylonitrile copolymer. Instrument: Perkin-Elmer F-42 with FID + PND; 2 m × 1/4 in. glass packed column with 10% DEGS on Chromosorb A, AW, at 70°C (isothermal), split 1:1 after the column. Sample, 1 ml at 80°C. Attenuation: FID, ×32; PND, ×64. Component, 2 µg/ml of acrylonitrile monomer.

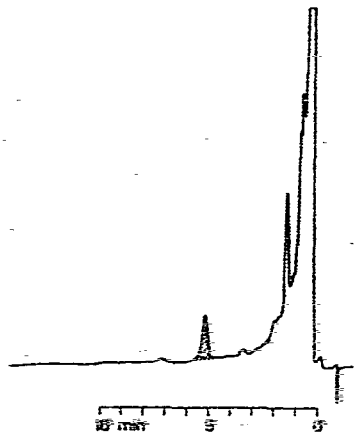

Fig. 8. Head-space analysis of amphetamine in urine. Instrument: Perkin-Elmer F-42 with PND, 2 m × 1/8 in. stainless-steel packed column with 8% Carbowax 20M + 2% KOH on Chromosorb W, NAW, at 130°C (isothermal). Sample, 2 ml of urine + NaOH at 80°C.

Typical examples of the HSGC of solids are monomers in polymers, adsorption material with adsorbed compounds and residual solvents in printed foils. It is not difficult to obtain good chromatograms if such samples are analyzed by HSGC, but problems arise if calibrations have to be carried out for quantitative purposes, as it is difficult, if not impossible, to mix a certain amount of a volatile compound homogeneously into a polymer, for example. The examples described below are used to discuss

these problems in general terms, but it is beyond the scope of this paper to deal with detailed working procedures.

Monomers in polymers

It has been shown by Rohrschneider[14] that the period required for a monomer to become equilibrated between the polymeric sample and the gas phase above it can sometimes by excessive. As a result, it is strongly recommended that whenever possible the polymer should be dissolved in a suitable solvent and the solution obtained analyzed by HSGC for its content of monomers or other volatile compounds. The methods are then the same as those outlined above for liquid samples. It is preferable in this instance to use a solvent with a longer retention time than those of the compounds to be determined in trace concentrations in order that the small peaks of the trace compounds should occur before the large solvent peak, which subsequently can be removed rapidly by back-flushing the column.

The chromatogram in Fig. 9 shows a cut from a series of repetitive analyses of a solution containing 0.6 ppm (w/w) of vinyl chloride monomer in dimethylacetamide. Using an automatic back-flush accessory, the peak of the dimethylacetamide was removed after each analysis. The precision of five repetitive analyses expressed as the relative standard deviation was 1.4% at the 1 ppm level.

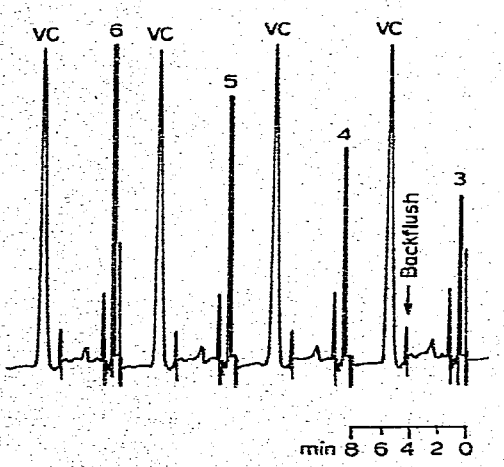

Fig. 9. Head-space analysis of vinyl chloride monomer solution with back-flushing. Instrument: Perkin-Elmer F-42 with back-flush accessory; 2 × 0.5 m stainless-steel packed columns with Chromosorb 102 (140–200 mesh) at 110°C (isothermal). Sample, 1 ml of a solution containing 0.6 ppm (w/w) of vinyl chloride monomer in dimethylacetamide at 90°C. Attenuation, ×1. The tracing at the beginning of each chromatogram indicate sample number.

This procedure can be used for the analysis of all types of PVC, regardless whether it is a powdered resin, pellets, foils or finished products, and the detection limit has been determined to be about 50 ppb (w/w)[15]. The calibration is carried out with a solution of vinyl chloride monomer (VC) in such a solvent and such calibration standards can easily be made up by injecting a certain volume of 100% VC gas into a sealed vial filled completely with the solvent without any remaining gas space. The

VC gas dissolves rapidly in the solvent and the solution obtained is further diluted so as to cover the total concentration range. With slight modifications, this procedure can be adopted for every polymer material for which a suitable solvent can be found.

The use of a solvent, however, introduces the disadvantage that the sample is further diluted, usually by a factor of 5–10, if 10–20% solutions can be made up, depending on the solubility of the polymer. As a result, the detection limit deteriorates by the same factor. If the highest possible sensitivity is required, the use of solvents should therefor be avoided. According to Behrens *et al.*[16], this is possible for finely powdered polymer material if the polymer is heated above its glass transition point, which is about 85°C for PVC. At this temperature, the amorphous polymer or the amorphous portion of a semi-crystalline polymer changes from a rigid glass to a rubberlike state. As a result, not only is the diffusion of small molecules such as the monomer in the polymeric matrix rapidly enhanced but also the motion of polymer segments of about 20–40 carbon atoms is possible owing to the availability of free volume. At temperatures below the glass transition, these free volumes are "frozen in" and most of the monomer is included in these holes. Thus, the amount of the monomer is determined below the glass transition point by normal dissolution that follows Henry's law, in addition to a so-called "hole filling contribution", according to Behrens[17]. Above the glass transition point, the amount of the monomer that is included in these holes is suddenly liberated and the remaining monomer is normally dissolved in the polymer and thus follows Henry's law, which in any event is the basis of every quantitative head-space analysis.

Behrens *et al.*[16], for example, found that the release of VC from a finely powdered PVC sample was completed in about 10 min if the sample was heated at 90°C. A typical example of such an analysis is shown in Fig. 10. The sample was a finely powdered PVC resin (4 g) with a content of 0.4 ppm (w/w) of VC monomer. The detection limit that can be achieved with this procedure[15] is about 1 ppb and the analysis time can be even shorter, as shown in Fig. 9, as no further solvent peak must be back-flushed. Quantitative calibration is carried out either by determining Henry's constant under the prevailing conditions[16] or by using a reference sample that has first been quantitatively analyzed by the method of dissolution.

This procedure can be applied to every kind of polymer material that has a suitable glass transition point, provided that it is sufficiently fine, but it is less satisfactory for pellets or fused samples owing to the very long equilibration times, depending on the thickness of the particles.

Head-space analysis of adsorption material

It is a common technique in environmental control to collect a sample of air pollutants first by adsorption on, for example, activated charcoal, and to analyze it after desorption either by thermal desorption or by replacement with a solvent such as carbon disulphide. HSGC now offers an interesting means of automating at least the last step of this procedure, the analysis of the adsorbed compounds, as desorption and analysis can be carried out on-line in the glass bottle of the head-space instrument. If the charcoal, for example, is transferred from the collection tube into the glass bottle for head-space analysis, an additional calibration becomes necessary in order to compensate for the gas adsorption equilibrium. This additional calibration effort can be considerable and is worthwhile only if a large number of samples can

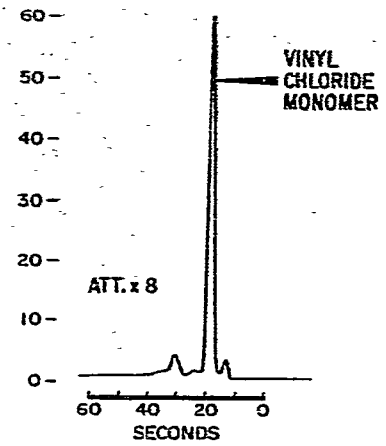

Fig. 10. Head-space analysis of 0.4 ppm (w/w) of vinyl chloride monomer from a PVC-sample Instrument: Perkin-Elmer F-40 with FID; 2 m × 1/8 in. stainless-steel packed column with 0.4% Carbowax 1500 on Carbopack A at 110°C (isothermal). Sample, 4.0 g of PVC resin at 90°C. Reproduced with kind permission of N. A. Sebestyen[15].

then be analyzed automatically, as reported by Lindner and Langes[18], who carried out 10,000 quantitative analyses of trichloroethylene in the environment of workers by the combined method of charcoal tube adsorption followed by automatic HSGC of the charcoal.

The calibration problems, however, are considerably simplified if the desorption is effected by replacement with a solvent. Bencsath[19] reported the determination of air pollutants at concentrations of 10^{-2}–10^{4} ppm. The first step of the procedure was adsorption on 400 mg of charcoal, which, after transferring it into a head-space bottle, was desorbed by adding 2 ml of a suitable solvent. The desorbed compounds were dissolved and analyzed by HSGC in which this procedure is based on the fact that aromatic hydrocarbons are strongly adsorbed preferably on activated charcoal and consequently high-boiling aromatic compounds are used for this purpose, such as tetrahydronaphthalene, benzyl alcohol and benzyl esters. Even benzene and toluene are nearly quantitatively desorbed after 1 h. This procedure has the advantage that the adsorption equilibrium, which is difficult to calibrate, is replaced by a partition equilibrium that can easily be calibrated as outlined above. The charcoal suspended in the solvent then has no further influence on the equilibrium between the liquid and the gas phase.

This procedure seems to be suitable for a high throughput of samples if carried out with an automated head-space instrument, including a back-flush system to remove the large solvent peak rapidly.

Analysis of residual solvents in printed foils

Printed foils that are used as packaging material for food items contain usually trace amounts of solvents, which may influence the taste of the foodstuff. The sample here is neither soluble nor sufficiently finely powdered to allow for "dry measurements" above the glass transition point. Nevertheless, it is possible to obtain a satisfactory chromatogram from such a sample by HSGC, but owing to calibration

problems such a chromatogram is at best only semi-quantitative. In such instances, an empirical calibration according to the quality of the product is often suitable for the intended purpose of the analysis. If, for example, the printing process used on packing foils has to be analytically controlled, purely empirical boundary values can be determined for the individual solvent peaks by which, as shown by experience, the flavour of the packed food items will not be influenced. Such an analysis report is obviously not suitable for inter-laboratory comparisons, because for these purposes the result should give the amount of each solvent compound in mass units per square metre, for example. Such a result now cannot be obtained by the static head-space analysis, as it is not feasible to mix a certain amount of a solvent homogeneously into the foil. The only possible way is to remove all of the volatile compounds by heating the sample in a stream of a purging gas, to collect the volatile compounds, *e.g.*, by cold-trapping and to analyze them as usual. Such an exhaustive extraction can be time consuming and, as a wide-boiling solvent mixture is frequently used for such printed foils, condensation by cold trapping and transfer of the sample to the gas chromatograph is often not satisfactory.

Following a suggestion from Scharfenberger[20], we have developed a method that we call a "discontinuous gas extraction" procedure[21]. This procedure can be carried out with any dual-channel gas chromatograph with a thermostated injection block. Both injection tubes are connected to the column by a Swagelok T-piece and the carrier gas is directed by an external switch through one of the two injection tubes, the other being by-passed, as shown in Fig. 11.

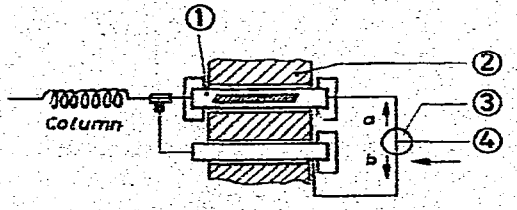

Fig. 11. Injection block arrangement for "discontinuous gas extraction". 1 = Glass tube with the sample (foil); 2 = thermostated injection block; 3 = valve; 4 = carrier gas; a = purging gas flow; b = by-pass gas flow.

The sample is now placed in the glass tube of one of the injection tubes and heated at a suitable injection block temperature for about 10 min, while the carrier gas is by-passed and directed through the other injection tube. After the sample has been thermostated for a sufficient period for equilibration, the volatile compounds that are now in the gas space of this sample tube are flushed on to the column by directing the gas flow through this tube for a few seconds. During the subsequent time period necessary for developing the chromatogram, the residual volatile compounds in the sample can evaporate again. After the first analysis, the tube is again flushed for a few seconds and the whole procedure is repeated, resulting in the same chromatogram but with smaller peaks. This stepwise extraction with subsequent analysis can be repeated until the sample is exhaustively extracted. The quantitative analysis is carried out if, for each compound, the corresponding peaks from each of the chromatograms are summed and the sum corresponds to the total amount of this compound in the sample.

This procedure works fairly well, but for practical purposes it is too time consuming. However, as it is not the extracted material, but only the analytical information, that is of interest, the procedure can be stopped after the second or third extraction step and the remainder can be calculated, because the extraction follows exactly an exponential relationship. If the resulting peak areas for each compound are plotted against the number of extraction steps on a semi-logarithmic scale, a linear relationship is found, as shown in Fig. 12, which can be used for extrapolation to give the total amount of a compound present initially in the sample.

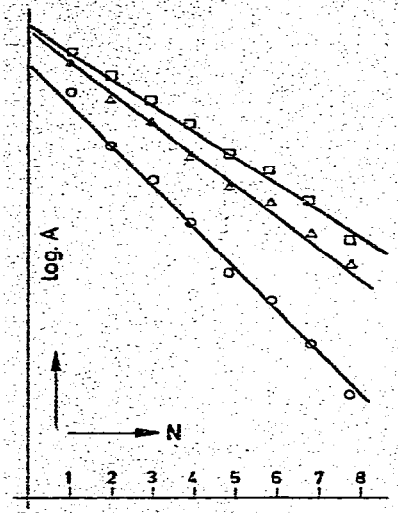

Fig. 12. Semi-logarithmic plot of the resulting peak areas (*A*) from a printed foil *versus* number of extractions (*N*). Peak areas in arbitrary units. □, Ethyl acetate; △, ethanol; ○, toluene.

As this "discontinuous gas extraction" procedure does not work at an equilibrium, however, it is not covered by the term for head-space analysis as used throughout this paper, it will therefore not be discussed here any further, but will be published elsewhere. It was mentioned only to show the limits of the static head-space analysis for such difficult samples and to indicate a means of solving these difficult problems.

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