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QUANTITATIVE ANALYSIS OF RESIDUAL SOLVENTS IN FOOD PACKAGING PRINTED FILMS BY CAPILLARY GAS CHROMATOGRAPHY WITH MULTIPLE HEADSPACE EXTRACTION

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SUMMARY

A procedure for stepwise gas extraction at equal time intervals has been developed, which is called "multiple headspace extraction" (MHE), because it uses the same equipment as for a standard headspace analysis. The method is suitable as a calibration method for the headspace analysis of volatile trace compounds in solid samples which otherwise cannot be analysed quantitatively. A BASIC program has been used to perform the necessary calculations for quantitative determinations.

The application of the MHE procedure is demonstrated on the example of the analysis of residual solvents in printed films which are used as food packaging material, and for the determination of vinyl chloride monomer in a PVC resin. Particularly for the solvent analysis a good glass capillary column is required to separate the complex mixtures which are used for printing the films.

INTRODUCTION

Volatile compounds in solid samples can easily be determined by headspace gas chromatography (GC), but any attempt to quantitate the results meets with the problem of how to prepare calibration standards. It is difficult, if not impossible, to add trace amounts of volatile compounds to a solid material. Such problems are known where residual solvents have to be determined quantitatively in printed plastic or aluminium films which are used as food packaging materials. In any case, headspace analysis needs an equilibrium based on the partition of the volatiles between the sample and the surrounding gas phase in a closed sample vial. The prevailing partition coefficient of each compound is included in the calibration factor, together with the detector response, the sample volume and other instrumental parameters[1]. This calibration factor is always determined experimentally under the conditions of analysis, and it is obvious that the calibration sample must therefore reproduce exactly the prevailing equilibrium system. If, for practical reasons, such a calibration standard cannot be prepared, the method of headspace analysis can be used for quantitative determinations only if the sample is analysed independently by a different method and is used further as a calibration standard for headspace analysis.

A stepwise gas extraction procedure, as has been used by Suzuki *et al.*[2] for the

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determination of occluded solvents in adhesive tape seems to be attractive for this purpose, as a few extractions are sufficient to be able to calculate, from the exponential decrease in the concentration of each solvent in the resulting gas samples, its original concentration in the solid sample. Kolb and Pospisil[3,4] determined volatiles such as monomers, solvents, ethylene oxide and water in solid plastic materials by a similar approach and even aqueous samples have been analysed by McAuliffe[5,6] and by Ioffe and Vitenberg[7] by such a stepwise gas extraction method.

Such a stepwise extraction procedure is usually too time consuming, even if only a few extractions are carried out, to be applied for routine analysis, where a high sample throughput is required, particularly if the printing process of such films must be controlled. Automated headspace analysis is apparently the method of choice, but a stepwise gas extraction procedure, if used for calibration purposes only, can take more time and is not necessarily carried out automatically. Such a combinations eems to be ideal, therefore, provided that both methods can be performed with the same equipment, particularly using the same vials. However, this meets with the following problem. The various applications of a stepwise gas extraction as cited above use a heated tube or chamber as a sample container, from which, after equilibration, the gas phase is completely separated from the sample and transferred on to the column for subsequent GC analysis. Such a complete separation of both phases is not possible with the sampling device for headspace analysis as used here, because only an aliquot is taken from the gas phase and this aliquot is usually not large enough to cause a significant extraction effect. An additional problem arises if capillary columns must be used owing to their small sample capacity, particularly for gas samples. The gas sample which is taken from the sample vial should be as large as possible in order to achieve an effective extraction, but the capillary column requires a small gas sample only for capacity reasons and in order to avoid peak broadening during a long sampling time. We first used a high splitting ratio to combine both requirements, but this was often difficult to achieve with columns of low back-pressure, such as glass capillary columns. High-efficienty glass capillary columns, however, are indispensable for separating solvent mixtures, which are mostly of very complex composition; a typical example is given in Fig. 1. Capillary columns work well with the pneumatic sampling system used here, as has first been shown by Kuck[8] and discussed later more in detail[9,10].

For all of these reasons it has been found necessary to modify the stepwise gas extraction in such a way that the extraction is carried out independently of the analysis. This becomes possible if not the gas extract is used for the analytical determination, but rather the remaining sample, which can be used equally well if the extraction yield is to be determined. It is necessary only to perform the gas extraction between two sample analyses, which in this instance are carried out by the simple headspace technique. The extraction of the sample by a gas also becomes very simple, because with the pneumatic sampling system used here the sample vials are under pressure after each headspace analysis and it is necessary only to vent the pressure to the atmosphere in order to achieve an effective extraction.

Based on these considerations, a procedure of stepwise gas extraction has been developed which we shall call "multiple headspace extraction" (MHE) in order to indicate that it is in fact a repeated headspace analysis with a gas extraction in between, and that it uses the standard headspace sampling system.

This MHE procedure is demonstrated on the determination of residual solvents in printed films which are used as food packaging material. The need for and the possibilities of analysing such samples by headspace GC for their content of solvents and monomers have been discussed by Jeffs[11] and Lüthi[12].

MULTIPLE HEADSPACE EXTRACTION PROCEDURE

The procedure of MHE needs an electropneumatic sampling system as used in a special headspace instrument, the F45 Automatic Headspace Analyzer, as well as in the HS6 Semiautomatic Headspace Injector, an accessory for gas chromatographs of the Sigma series (Perkin-Elmer, Norwalk, CT, U.S.A.). This sampling system has already been described in detail[9,13], but will be discussed briefly again here.

The sample to be analysed is placed in a glass vial which is closed by a septum and secured against pressure by crimping an aluminium cap on it. The vials are thermostated in a heated aluminium block, which is mounted as a turntable in front of the headspace sampling system, which comprises a dosing needle and a solenoid valve in the carrier gas supply line and which is operated from a control unit.

When the dosing needle pierces the septum, the sample vial is first pressurized up to the head pressure of the column. After a short pressurization period, the sample transfer on to the column is performed by stopping the carrier gas supply for a few seconds by means of the solenoid valve, thus causing the pressurized gas in the vial to expand together with all of the volatiles along the needle on to the column. The injection is stopped when the solenoid valve opens the carrier gas supply again and it is important to note that the vials thus remain under pressure after each headspace analysis.

It is possible now to achieve an effective extraction of the sample if the pressure in the vial is released to the atmosphere simply by puncturing the septum manually with a dosing needle from a syringe. If, for example, the internal pressure is 1 bar, half of the gas content in the vial is vented and with higher pressures even more. This extraction is followed by the necessary equilibration time, during which the chromatographic separation is performed, after which the next headspace analysis can be carried out. This procedure can be continued several times and a series of chromatograms are obtained with decreasing peak heights for each solvent peak, as shown in Fig. 1, in which the first two chromatograms from a series of five extraction steps are presented. If this procedure were to be continued experimentally until exhaustive extraction, it would be necessary only to add the peak areas from each component in all of the chromatograms to obtain the total peak area, which corresponds to the total amount or the original concentration of this compound in the sample. This value must, of course, be calibrated, and it is necessary for this purpose to repeat the whole procedure with a calibration sample, which is easily prepared by injecting a few microlitres of the respective compounds into a closed and empty glass vial through the septum. After complete vaporization at the prevailing temperature, the whole procedure is repeated, and again a series of chromatograms are obtained, in which the peak heights usually decrease at a faster rate compared with the decrease in the chromatograms from the analysis. It has been found, as with all other such stepwise extraction techniques, that a straight line is obtained if the logarithm of the peak areas is plotted against the number of extractions[2,3,6,7], and such a plot is shown in

Fig. 2 for three extractions of ethyl acetate from a printed aluminium film by the MHE procedure. This relationship enables the total peak areas from each solvent to be determined from only a few extractions as the sum of a geometric progression. At least two extractions are necessary and have often been found sufficient for practical purposes. Applying a statistical evaluation by linear regression calculation improves the precision of the measurement, but at the expense of an increased number of experimental determinations.

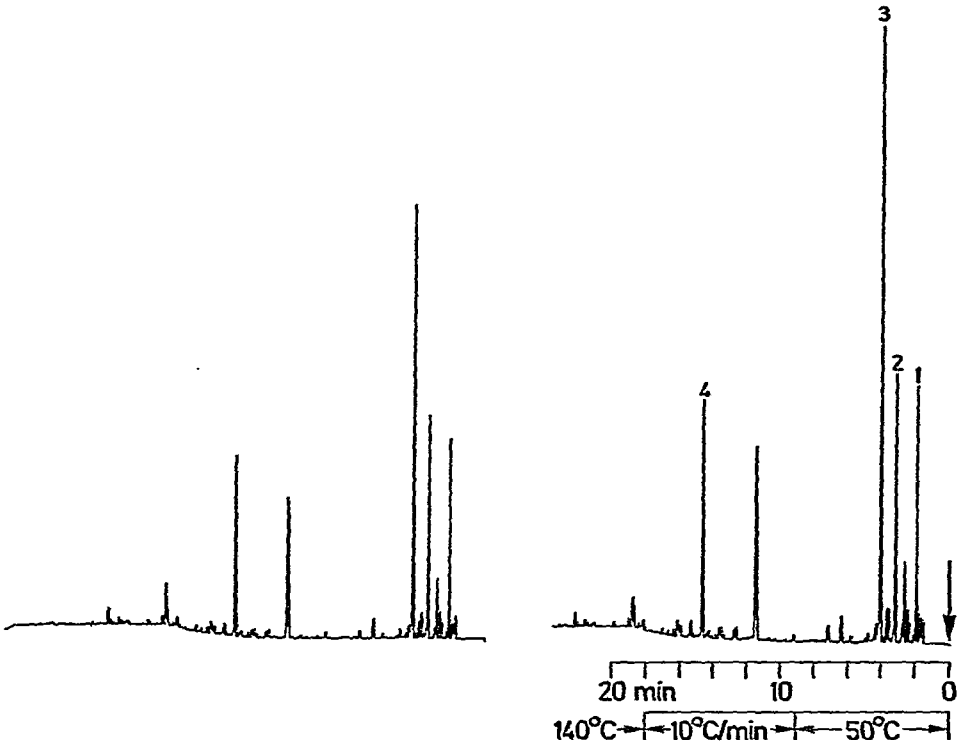

Fig. 1. Analysis of residual solvents in a "sandwich-structured" printed aluminium film by multiple headspace extraction. Instrument, Sigma 2 and HS6 semiautomatic headspace injector (Perkin-Elmer); 35 m × 0.3 mm I.D. glass capillary with Marlophen M87 liquid stationary phase; temperatures, column programmed as indicated, sample 140°C for 45 min; detector, FID, 10 × 16; sample, 50 cm². Compounds: 1 = *n*-hexane, 1.8 mg/m²; 2 = methanol, 9 mg/m²; 3 = ethanol, 12 mg/m²; 4 = ethyl glycol, 6 mg/m².

RESULTS AND DISCUSSION

A printed aluminum film with ethyl acetate as the main volatile constituent was extracted three times by the MHE procedure. Three peak area values were obtained both from the foil sample (shown in the computer printout in Fig. 2) and from the calibration sample, from which the area total was calculated and is given in Fig. 2. The calibration sample was prepared by injecting 1 μl of ethyl acetate into an empty vial with a 10-μl syringe. The analysis was carried out using the F45/FID automatic headspace analyzer with the Sigma 10 Chromatographic Data System (Perkin-Elmer)

and with a 50 m × 0.25 mm I.D. glass capillary with Carbowax 1000 as the stationary phase. A 150-cm² sample was used and thermostated at 110°C for 50 min.

Fig. 2 gives the result of a linear regression calculation using a BASIC program with the Sigma 10 Chromatographic Data System. A concentration of 1.018 μg/cm² of ethyl acetate in the aluminium film sample was determined.

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/BR GASEX.1
PROGRAM   57
OK
57 : 1
                    MULTIPLE HEADSPACE EXTRACTION
                    -----------------------------

      CALIBRATION RUNS  Y/N  ?N
      NO. OF EXTRACTION STEPS?3
      COMPOUND NAME           ?ETHYLACETATE

                       PEAK AREA
      1 .EXTRACTION    ?12.8441
      2 .EXTRACTION    ?6.3510
      3 .EXTRACTION    ?3.2955
      CONCENTRATION OF CALIBRATION SAMPLE MG/ML?900.5
      VOLUME OF CALIBRATION SAMPLE  UL          ?1
      SAMPLE WEIGHT(MG) OR SAMPLE AREA(CM2)     ?150,CM2
      PEAK AREA OF CALIBRATION COMPOUND         ?152.247
      PEAK AREA OF BLANK                        ?0
      PEAK AREA FOR ADDITION                    ?0

                 -------->LOG PEAK AREA  ETHYLACETATE
      1 -I-----------------------------------------------+------
         I                                                12.8441
         I
         I
      2 -I                          +   6.351
         I
         I
         I
      3 -I      +   3.2955

                       EXTRAPOLATED FINAL AREA   S= 25.82
        CONCENTRATION MG/M2 OF ETHYLACETATE      C= 10.1812

57 : 1  1000 H 100
```

Fig. 2. Print-out from the Sigma 10 chromatographic data station for the analysis of ethyl acetate in a printed aluminium film by multiple headspace extraction with three extraction steps. Concentration of ethyl acetate in this 150-cm² sample = 1.018 μg/cm².

From this result, it is now possible to derive a correction factor that can be applied to further headspace analyses of similar samples. This correction factor is obtained from the first peak area with 12.8441 units and the corresponding ethyl acetate concentration of 1.018 μg/cm²; the resulting value of 0.7926 can be handled

as a response factor (RF) for further data processing by using external standard calibration.

This method was then applied to the analysis of three more samples, which were cut out in equal sizes from the same roll of printed film. These three samples were analysed by the standard headspace procedure but using the correction factor, and a mean value for the ethyl acetate concentration of 0.92 $\mu g/cm^2$ was determined with a relative standard deviation of 11%. Despite the fact that this precision is an order of magnitude worse than the precision of the measurement, it is sufficiently good for the practical purpose of this analysis, and is caused mainly by the inhomogeneous distribution of the ethyl acetate across the film areas of these three samples. Sample homogeneity is the main problem with solid samples, particularly if the reproducibility has to be determined, and this situation is different from that with liquid samples.

The accuracy which is obtainable by the MHE procedure cannot be determined with samples such as printed films, because there is no alternative method available for comparing the results. The MHE procedure was therefore applied to the determination of vinyl chloride monomer (VCM) in a PVC resin, because this sample offered the possibility of analysis by a different approach with no calibration problems according to the method of Puschmann[14] by headspace analysis of a solution, and a concentration of 1.28 ppm (w/w) of VCM was found. Four further samples from the same batch of PVC resin were analysed by the MHE procedure and a concentration of 1.35 ppm (w/w) of VCM was determined, with a relative standard deviation of 3.4%, thus showing much better sample homogeneity in this instance and fairly good agreement between the results of the two methods.

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