Journal of Chromatography, 395 (1987) 437–444
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

CHROMSYMP. 1152

AUTOMATIC GAS CHROMATOGRAPHIC EVALUATION OF THE PERFORMANCE OF MEMBRANES USED FOR PERMEATION PROCESSES

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SUMMARY

The separation of liquid mixtures by permeation through membranes from a liquid stream to a gas phase is influenced by the permeability and the selectivity of the polymeric layer. These properties depend on various parameters: time, temperature, swelling of the membrane in water and in organic solvents, composition of the permeating mixture, etc. The evaluation of a given membrane is accomplished by measuring the distribution of the compounds to be separated over the liquid and the gas phase. This procedure is time-consuming because many analyses of both phases must be performed in order to investigate the effect of the various parameters.

Full automation of the analysis and of the evaluation of the results has been achieved by connecting an external events module to a digital integrator in order to connect an automatic gas-sampling valve and a small-volume liquid-sample valve to the carrier gas source and to the permeating streams, respectively. Each valve is automatically filled with samples coming from the liquid or gas circuit and activated to deliver the sample to the gas chromatographic unit, through a low-dead-volume injector, suitable for on-column introduction of both liquid and gaseous samples.

The gas chromatographic columns were packed with various amounts of porous polymer-bead stationary phases (Porapak or Chromosorb "Century Series") in order to separate water efficiently from the organic components of the permeating mixture (alcohols, glycols). A thermal conductivity detector was used.

Computer programs were developed for automatic evaluation of the quantitative results, recording of the data, calculation of the retention-index values, plotting of the time–composition graphs, and calculation of the membrane selectivity as a function of time, temperature and composition of the permeating mixture. Low-cost personal computers are suitable for this application. With minor modifications and by using other columns and detectors, the system can be used for automatic analysis of any combination of liquid or gas streams.

INTRODUCTION

Permeation (or pervaporation) processes permit the composition of a liquid mixture to be changed by selective diffusion of one of the components trough a polymeric membrane in order to perform separations or enrichment that cannot be

0021-9673/87/$03.50

easily obtained with other techniques (*e.g.* distillation). A polymeric membrane permits the permeation of a component from a liquid mixture when it is swollen by a permeant compound, and the permeation rate depends on the interaction between the permeating molecules and the membrane. The interactions between the membrane and the components are influenced by synergistic effects that control the concentration gradients through the membrane and, therefore, the efficiency cannot be easily predicted on the basis of the permeation of pure components.

Many analyses of the permeating mixture and of the permeate are therefore necessary to study the behaviour of a membrane as a function of time and of the concentration of the components. Liquid samples must be extracted from the stream of the mixture at regular intervals and analyzed by proper techniques (gas chromatography, liquid chromatography, refractive index, density, etc.) in order to check the variations in the amount of each component. The permeated compounds, which are in the vapour phase, can be analysed directly (on-line) by injecting a suitable volume into a gas chromatograph, or can be condensed in a cold trap and analysed later with the same techniques as used for the liquid samples. The two methods yield instantaneous and averaged values of the permeate composition respectively.

Manual collection and injection of the samples is very time-consuming, and therefore, the evaluation of the behaviour of a membrane with many different mixtures, at various temperatures, flow-rates and amount of swelling takes a long time. Gas chromatographic techniques combined with autosampling systems permit many liquid samples to be sequentially and automatically analysed off-line (*i.e.* overnight) but do not avoid the troublesome extraction of these samples from the circulating liquid stream and the repeated sampling of the gas stream by means of manually operated gas sampling valves (GSV).

Full automation of the analysis and of the evaluation of the results has been achieved by connecting an external events module to a digital integrator (Varian CDS-111C) (Varian, Palo Alto, CA, U.S.A.) in order to install an automatic GSV and a small-volume liquid-sample valve (LSV) in the carrier-gas stream and in the permeating stream, respectively. Each valve is automatically filled with samples coming from the liquid or gas circuit and is activated to deliver the sample to the GC unit, through a low dead-volume injector, suitable for on-column introduction of both liquid and gas samples.

EXPERIMENTAL

Fig. 1 shows a schematic diagram of the permeation circuit (above) and of the sampling and analysis system (below). An initial volume of the permeating mixture, contained in the reservoir, R, is continuously recirculated with the pump over the membrane, M, supported by a porous polyethylene disc that separates the two compartments of the permeation cell. PTFE or rubber seals avoid any liquid or gas leaks that could bypass the membrane and influence the results of the pervaporation. Structures of the permeation cell and circuit were previously described[1–3]. The stripping-gas flow (nitrogen or helium coming from the bottle, G) is controlled by the pressure regulator, PR, and continuously removes the compounds permeating through the membrane. The liquid and gas samples, respectively, are connected upstream of the restrictor valves, V_1 and V_2, by means of stainless-steel capillary tubing.

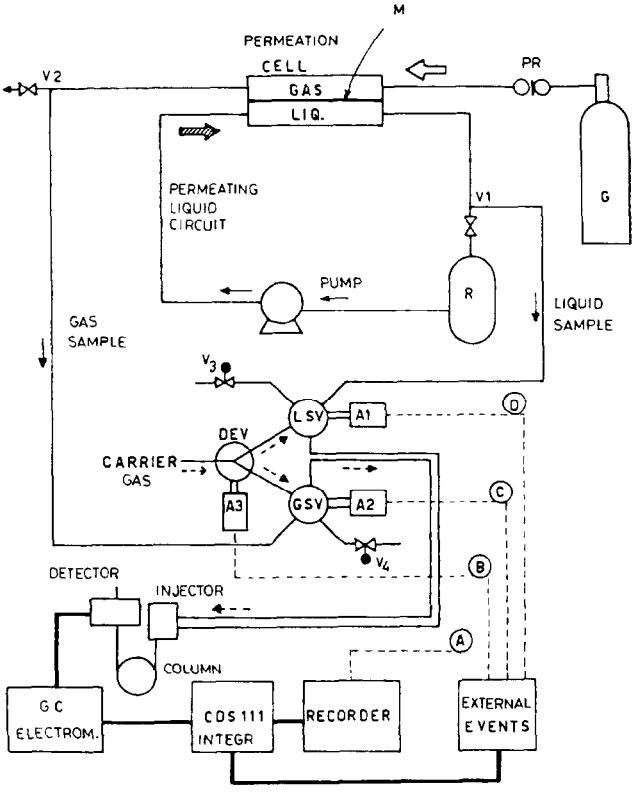

Fig. 1. Schematic diagram of the permeation and analysis system. M = permeation membrane; G = stripping gas bottle; R = permeating mixture reservoir; DEV = valve that switches the carrier gas flow to gas sampling valve (GSV) and liquid sampling valve (LSV); A_1, A_3 = pneumatic actuators for valves; V_1, V_2 = valves (restrictors) for sample pick-up; A,B,C,D = connection of actuators to external event module (refer to text).

The sample stream can be continuous or can be activated by opening the electric valves, V_3 and V_4, just before the sampling points. Usually, the gas sample is continuously fed to the GSV, because the stripping gas is discarded. For very long permeation experiments, the sampling of the liquid stream is controlled by valve V_3, in order to avoid too great a loss of the circulating mixture. For experiments carried out over several hours, the loss of liquid mixture is negligible when a liquid sample stream of 10–20 μl/min is extracted from the permeation circuit and the volume of reservoir R is sufficiently large.

In order to simplify the description of the analysis sequence, continuous sample flows are considered here, and the time sequencing of V_3 and V_4 are therefore not taken into account.

Valco valves with pneumatic actuators are used for sampling. The GSV and the LSV are alternatingly connected to the GC column (COL) by switching the carrier-gas flow using a two-way valve, DEV (Fig. 2). The on-column introduction of the liquid samples is carried out with a needle, soldered in a Swagelock tee which is connected to the column inlet (Fig. 3). The gas samples are injected through the side

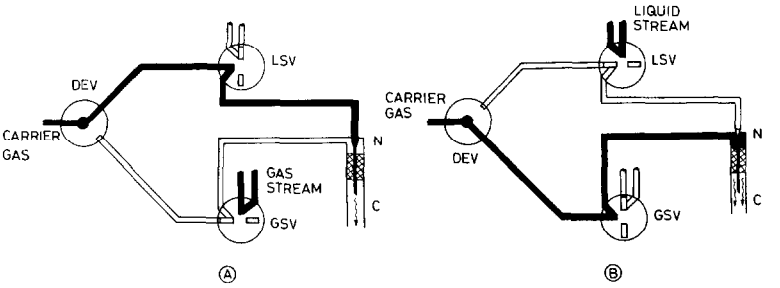

Fig. 2. Circuit for automatic selection and delivery to the GC of (A) liquid and (B) gas samples from the permeation cell See detailed drawing of the injection needle in Fig. 3.

port of the same tee. Backflushing of liquid or gaseous samples in the other line is avoided by closing the line not used for sampling at the DEV. The DEV, GSV, and LSV are pneumatically operated by actuators A_1, A_2 and A_3.

The sampling and analysis sequence was controlled by a Varian Chromatography data system CDS-111C, with the time sequencing shown in Fig. 4. The chromatograms of permeate and feed obtained in the permeation of water–ethanol are also shown. The CDS can be automatically switched between four states: stand-by, monitor, inject, and compute. Other components have two possible positions: the strip chart recorder is activated only when injections take place in order to record the chromatograms; the DEV selects the gas or liquid sample; the GSV and LSV are

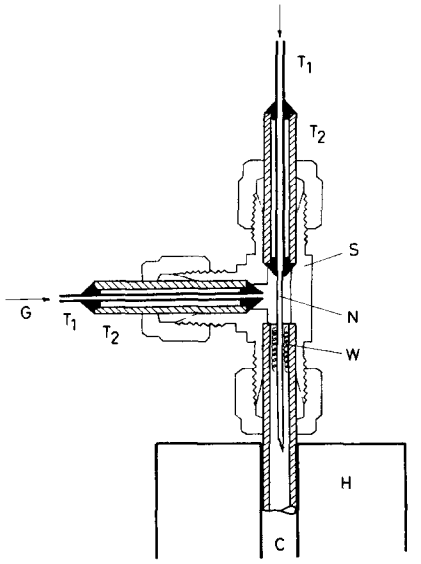

Fig. 3. Detailed drawing of the injection system. G and T = gas and liquid sample streams; S = Swagelok 1/8 in. stainless-steel tee union; T_1 = stainless-steel tubing 1/16 in. (1.6 mm O.D.); T_2 = stainless-steel tubing 1/8 in. (3.4 mm O.D.); N = hypodermic needle; W = glass wool at the inlet of column C; H = injector heating block. All the manifold is thermally insulated with glass wool.

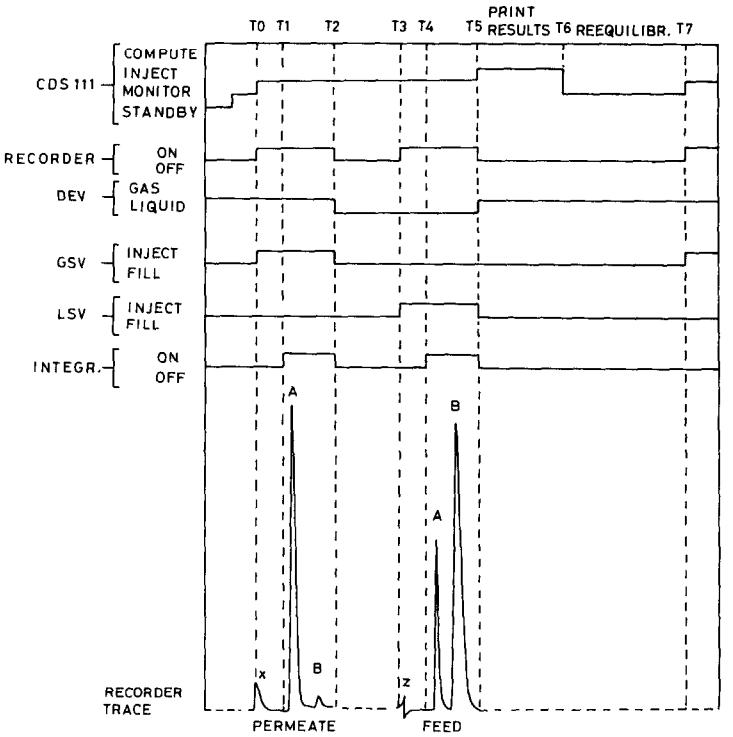

Fig. 4. Time sequence of events for sampling of liquid and gas, analysis, and peak integration (refer to text). Chromatograms of permeate and feed mixture in the water (A) ethanol (B) separation are shown.

in "fill" or "inject" position. The last timing sequence in Fig. 4 (integr. on/off) indicates that the integration is only activated when the peaks of the components are eluted from the column, whereas it remains in "forced-baseline" condition when sample introduction, flow switching, equilibration, etc. produce non significant detector signals.

The complete automation sequence (see Fig. 4) is as follows: at the beginning of the experiment the recorder is off, DEV delivers the carrier gas to GSV, both GSV and LSV are in fill position (*i.e.* the samples are flowing through the calibrated loops), and the integrator is off. The CDS is switched to the "monitor" state, which checks the gas chromatograph parameters and records the drift and noise of the recorder baseline. When all the conditions are within the set limits, the sequence starts:

At T_0: the CDS is in "inject" position, the recorder chart on, the GSV delivers the gas sample to the column. Elution of the stripping gas is very fast but the peak (X) is not integrated because the integrator is in the "forced-baseline" mode.

At T_1: when the X peak has been eluted, integration is activated, and the peaks of the component mixture (A and B) are recorded and integrated.

At T_2: after elution of the component peaks, the recorder chart and integration are switched off, the GSV returns to "fill" position and the DEV delivers the carrier gas flow to the LSV.

At T_3: after a suitable equilibration time, the LSV injects the liquid sample, and the recorder chart is switched on. Baseline oscillations due to the injection (z) are not integrated.

At T_4: integration is switched on, the peaks of components A and B in the feed mixture are detected and integrated.

At T_5: integration and recorder chart are switched off, the DEV is connected again to the GSV, the LSV in "fill" position, the CDS switched to "compute".

At T_6: computation ends and the systems goes into "monitor" state until the instrument is re-equilibrated.

At T_7: the sequence starts again automatically.

Between T_5 and T_6 the calculation of the results is performed by the CDS by automatic linking of three of the nine available "files" or programs of the integrator. File 1 contains all the instructions for setting up the instrument Varian 3700, *i.e.* the initial temperature, detector sensitivity, and the temperature program, and for operation of the external events module that controls the Valco valves and relays. Peak recognition, acquisition, and integration are also programmed in File 1. By using of the "forced baseline" function, only four peaks are integrated. P_1 and P_2 are the peaks of components A and B in the gas sample, and P_3 and P_4 are the corresponding peaks in the liquid sample. In order to calculate the composition of the gas phase in weight percentages, File 1 is automatically linked to File 2, where proper correction factors are given to P_1 and P_2, while P_3 and P_4 are cancelled by setting their factors equal to zero.

File 2 is linked to File 3, where the composition of the liquid is calculated, and the system then returns to File 1. By linking other available files and programs, other results can be obtained, *i.e.* composition in volume or mole percent, A/B ratio, etc. Equivalent results can be obtained with other integrators and data systems that permit the control of external events. The Varian Vista 401 and the Spectra Physics 4270 were found suitable for this application after some modifications of the automation programs.

The choice of the GC column obviously depends on the composition of the permeating mixture. Porous polymer-bead stationary phases (Porapak from Waters Assoc., Framingham, MA, U.S.A. or Chromosorb "Century series" from Johns-Manville, Denver, CO, U.S.A.) and thermal-conductivity detection were used for separation of water–ethanol and water–glycerol mixtures. PTFE membranes were modified by means of radioinduced grafting, by following the previously described method[1–3]. The use of the automatic sampling system described here allowed characterization of the membranes in a few days, in contrast to the several weeks previously needed. With different feed mixtures, other columns and detectors can be used. The timing sequence of the system needs to be modified, taking into account the retention times of the compounds to be analysed and the column and temperature programming conditions.

The calculation of the parameters which characterize the permeating membrane are carried out as follows. The selectivity factor, α, is defined as

$$\alpha = \frac{Y_A/Y_B}{X_A/X_B} \tag{1}$$

where X and Y are the volume fraction of components A and B in the feed mixture and in the permeate, respectively, and A is the component that is preferentially permeated.

The permeation rate, φ, can be measured by evaluating the decrease of the volume of the permeating mixture in the reservoir, R, taking into account the loss due to sampling. The value of α changes as a function of time, of the permeation rate, φ, of the membrane swelling, etc. Therefore, its dependence on time and on concentration of the permeating mixture has to be evaluated.

BASIC programs for automatic calculation and plotting of the selectivity factor were written for use on low-cost personal computers (Commodore CBM 4016, Commodore 64, Apple II C). The main program "SELETT" has two options:

(i) a program "SELCO" which evaluates the selectivity as a function of the concentration of the components in the mixture, calculated by eqn. 1 with the X and Y values measured at various concentrations of the permeating mixture.

(ii) a program "SELTE" which investigates the effect of the cell temperature on the selectivity.

Both programs are linked to the dedicated programs "GRAF 1" and "GRAF 2", which plot the results in tabular or graphic form, depending on the initial choice made in the "SELETT" program menu.

The input of data in the CPU was performed manually using the tabulated output of the CDS-111C printer. This procedure is slow, but permits operator control of the integration performance, thus avoiding the elaboration of defective GC runs. Direct interfacing of the CDS output to an APPLE II computer is also possible by means of a standard serial interface, RS 232C. The above described programs were designed to permit an easy conversion, by giving a vectorial structure to the input variables. This permits the routines devoted to the keypad input to be replaced by PEEK instructions, which sequentially read area and composition data coming from CDS-111 and store the values in the CPU memory. Modification of the programs is required for use on different computing systems.

CONCLUSIONS

With the system described, a greater speed and accuracy of analysis is achieved than with a manual procedure. Automatic sampling enhances the reproducibility of the sampled amounts and avoids the loss of volatile components that can evaporate from the sample when an off-line procedure is used. The reproducible intervals between gas and liquid sampling permit the selectivity, α, to be followed as a function of time. This is necessary for evaluating the time needed for the membrane to reach its standard performance, *i.e.* for α and φ to become stable after initial fluctuations, the trend and length of which depend on the membrane structure and on the composition of the permeating mixture[1–3]. The evaluation of the conditioning time takes a long time and large volumes of the feed mixtures are needed to avoid changes in composition, especially when the pervaporation rate, φ, is high.

ACKNOWLEDGEMENT

This work was supported by the Ministero della Pubblica Istruzione (Italy).

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