4 Chromatomembrane Method

In early 1949, Martin, founder of the liquid- and gas-liquid chromatography, said that chromatography would be a technological method only when it became possible to make the chromatography separation process continuous. This continuous separation process of the substances will be possible when phases move independently at right angles each other. Some numerous attempts were made to realize this idea since 1950, but it did not provide in any practical results, mainly owing to technical difficulties of releasing a separation scheme with mechanical transfer of one of phases. The search for continuous separation methods shifted more and more in the field of membrane process. This can be shown by the use of selective membrane in the liquid extraction process with accomplishing a fundamental work during 1960-1970's. The main result was experimental evidence for the conceptional possibility of realizing membrane extraction process in the dialysis and the electrodialysis regions, until L. N. Moskvin [97] presented his idea in the development of selectively permeable membranes for the continuous selective extraction of substances based on his experiment on the retention mechanism of the stationary gas phase in the liquid gas chromatography. He found that with virtually totally degassed aqueous phases the volume of the stationary gas phase retained in the pores of micropores hydrophobic supports can reach up to 50% of the total free volume of the column. The explanation is that increasing of capillary pressure of non wettable water in the support pores prevents them from filling while the pressure of a liquid does not exceed the sum of the capillary pressure and the pressure of gas in the pore space, the liquid cannot fill the pores.

4.1 Principle and Development of the chromatomembrane cell (CMC)

The chromatomembrane method is based on capillary effects that arise in hydrophobic porous media. Mass transfer between the flows of immiscible liquids or a liquid and a gas flow is accomplished in a hydrophobic porous material with open pores. The flows of the two phases move independently, due to the presence of two types of pores in the porous material significantly differing in their size. The macropores are selected so that the capillary pressure in them is negligibly small and does not hinder the transport of the polar liquid phase. In contrast, the micropores are so narrow that the capillary pressure prevents the polar liquid phase from penetration into them. At the same time, the micropores must assure the substantial permeability of the biporous medium to a gas or a nonpolar liquid flow.

Polytetrafluoroethylene (PTFE), which is characterized by the maximum wetting angle for aqueous solutions, is used as a hydrophobic biporous matrix in the CMC. CMC consists of two types of pores, micropores and macropores. The size of macropores is varied in the range 0.1-1.0 mm, depending on the required permeability of the cell to aqueous solutions. The size of micropores is 0.1-1.0 µm. Each cm^3 of biporous PTFE is capable to take 0.3 cm^3 polar- and 0.3 cm^3 non polar phases on average. The size of the surface boundary, where the two phases are in mutual contact, was determined to be in the range of 60 cm^2/cm^3 biporous PTFE. The most characteristics property of the biporous PTFE should be emphasized, independent fluxes of the polar as well as the non polar phase can be realized within this material. The mass exchange process is carried out in the capillary porous media of hydrophobic material with two preferential pore types differing in pore size, which is bounded on two sides by microporous hydrophobic membrane as shown in Figure 4.1.

The absence of mutual phase mixing is guaranteed by the difference in pressures under which polar (P_1) and non polar (P_3) phases are supplied into the system. The pressure within all the volume occupied by the non polar phase is maintained lower than the polar phase pressure.

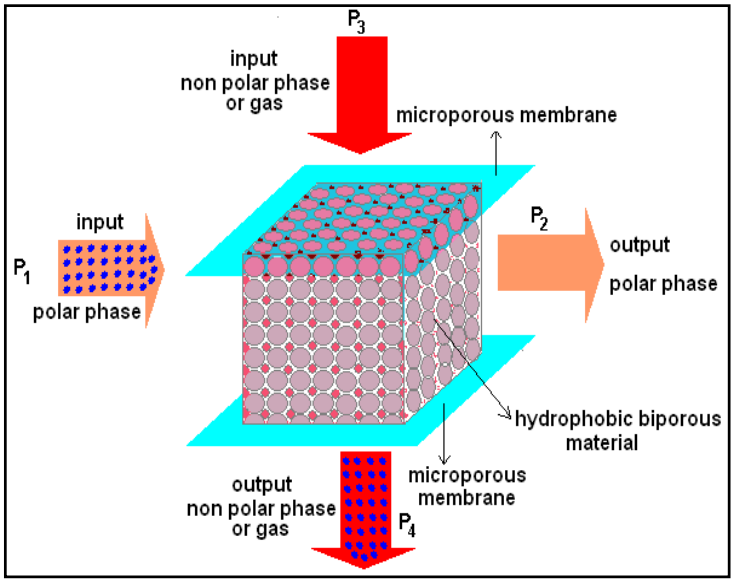

Figure 4.1 Schematic diagram of the CMC

Hence the polar phase pressure at the outlet from the mass exchange chamber (P_2) must exceed the pressure at the inlet of the non polar liquid or gas in it (P_3)

$$P_3 < P_2 \quad \text{..... 4.01}$$

As a result, the non polar liquid phase or gas can not penetrate from the micropores to the macropores. In turn, the capillary pressure (P_c) prevents its displacement out of the micropores by the polar phase. The value of P_c depends on the surface tension (σ), the contact angle of the porous material (θ) and the pore radius (r):

$$P_c = \frac{2\,\sigma\cos\theta}{r} \quad \text{.....4.02}$$

For liquids that do not wet the pore walls the P_c value is negative. As long as the condition

$$P_1 < P_4 + |P_c| \quad \text{.....4.03}$$

is valid, micropores remain inaccessible to the polar phase. When the limiting conditions in equations 4.01 and 4.03 are fitted, the possibility of transferring two phases independently within a mass exchange space formed by the hydrophobic biporous medium arises.

Combining equations 4.01 and 4.03, the following expression can be obtained.

$$P_1 - P_2 + P_3 - P_4 < |P_c| \quad \text{.....4.04}$$

It is known that

$$P_1 - P_2 = \Delta P_{\text{polar phase}} \quad \text{.....4.05}$$

$$P_3 - P_4 = \Delta P_{\text{non polar phase}} \quad \text{.....4.06}$$

Thus $\Delta P_{\text{polar phase}} + \Delta P_{\text{non polar phase}} < |P_c|$ 4.07

Hence it is necessary for the chromatomembrane process that the sum of pressure gradients for the polar phase and non polar phase should be less than absolute capillary pressure value.

Possibilities of the chromatomembrane method for the continuous pre concentration and isolation of individual substance can be described below. The volume rate of shift of that zone front along the direction of

aqueous phase flow (U_i) is expressed by the ratio known from the theory of chromatography:

$$U_i = \frac{U_o}{1 + K_{D1}(V_1/V_2)} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 4.08$$

where K_{D1} is the distribution coefficient at the extraction stage, U_i the rate of the shift of the *i*th component zone with aqueous solution flow, U_o the rate of supply of the solution and V_1/V_2 the ratio of the volumes occupied by the micro- and macropores. A complete extraction will be realized by a continuous flow mode as well under the condition that:

$$l/U_i > h/U_{ex} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 4.09$$

where l is the length of the rectangular biporous PTFE block, U_{ex} is the flow rate of the non polar phase, and h denotes the height of the rectangular biporous PTFE block and also the direction of the non polar phase.

Continuous preconcentration is possible if the ratio between flow rate of the non polar phase and flow rate of the aqueous phase in certain time, which contains analyte, is very small. In the chromatomembrane method, the ratio of non polar and aqueous phase flow rates 1:100 can even be implemented.

In these works, a rectangular block of PTFE was used as a hydrophobic biporous matrix in the CMC which contains micropores and macropores. The average radius of the macropores is 250-500 μm and of the micropores about 1 μm. The PTFE block has a thickness of 8 mm, width of 10 mm, and length of 17 mm, giving the extraction volume around 1.2 mL,

which is surrounded by a shell of a chemically resistant material, being equipped with inlets and outlets for the aqueous phase and non polar phase so that the direction of both phases is 90° each other. Development of the CMC used in the experiment is shown in Figure 4.2, where a is outside part of CMC, b is porous PTFE, c is micropores membrane, d is biporous PTFE block, and e is center part of CMC .

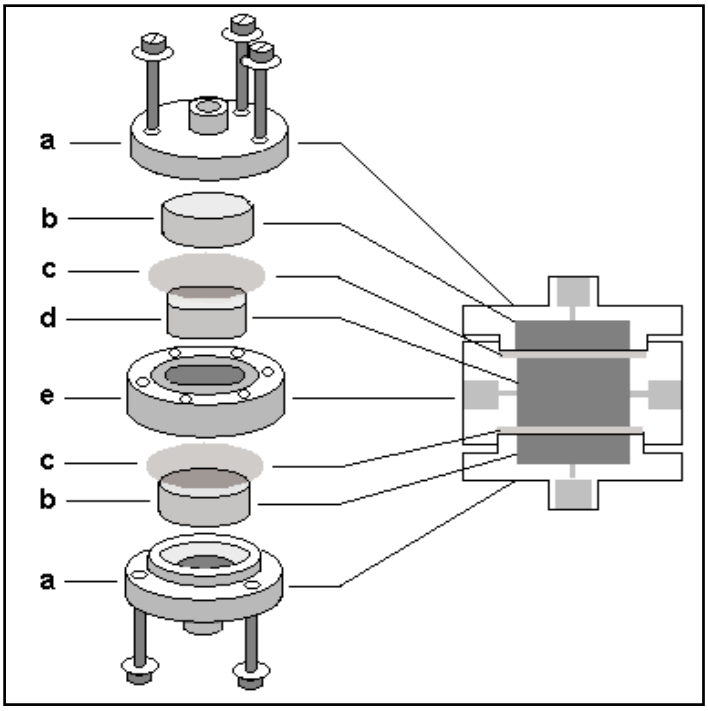

Figure 4.2 Schematic of the CMC used in the experiments

4.2 Application of the CMC

The CMC is mainly used in sample preparation step of substances before their detection or analysis with several detectors or instrumental analysis. The chromatomembrane process can be implemented in two versions: continuous, when the flows of the two phases are simultaneously passed through the biporous material, and discrete (stop flow), when the flows of the two phases are successively passed through a CMC and the inlet and outlet channels of the CMC are shut off each time for the stationary phase. The principles of chromatomembrane mass transfer were used in FIA for determining NO_2 [98], with the potometric detection and ammonia [99] with

potentiometric detection of ions forming in the absorbing layer. In addition, the determination of polar inorganic and organic impurities in the atmosphere was also proposed. They involved chromatomembrane extraction and ion chromatographic (for nitrogen and sulfur oxide, nitrous acid, ammonia, and fluorinated and chlorinates hydrocarbons) and gas chromatographic (for alcohols, formaldehyde, and hydrazines) substance determination after their chromatomembrane transfer to aqueous solutions. Rodinkov et al [100] used chromatomembrane gas extraction method in gas chromatographic determination of hydrocarbons (methane, ethane, acetylene, propane, isobutene, and butane) dissolved in water. The headspace analysis with the chromatomembrane separation of the flows of an aqueous and a gas phase was implemented, and its advantages over the conventional schemes of dynamic headspace analysis were demonstrated in [101]. The efficiency of the chromatomembrane liquid extraction was illustrated by examples of the photometric determination of trace Cu(II), nitrite ions, phenols, and anionic surfactants and luminescence determination of petroleum products and phenols in natural waters.

The chromatomembrane method was also used as an efficient method for the removal of dissolved oxygen from aqueous solution [102] which is one of the problems in electrochemistry. The application of this method has been demonstrated by Reinke and Simon [103] in the determination of cadmium and lead in water. They combined the CMC with a flow-through system allows an online deaeration of solution used in voltammetric measurements. They found that no differences in the background currents was observed when voltammograms of solutions deaerated with the chromatomembrane method were compared to those of solutions purged with nitrogen for several minutes immediately before the measurements.

Kirchhof [104], a member of the Prof. Simon group work at the Department of Chemistry, Free University of Berlin, presented the recent work on the application of the CMC. The chromatomembrane method was coupled with gas chromatography for the determination of semi volatile organic compounds and non-volatile organic compounds. Sample containing these substances was continuously pumped through the CMC and continuously extracted with heptane as an organic solvent. Extractant was collected in adsorbent, Chromosorb in which the organic solvent was reduced in a nitrogen stream. After thermal desorption, the analyte was introduced to gas chromatograph and analyzed. This system allows sensitive determination for the substances that have boiling points around 130-300^{o}C. Compared to head space or purge and trap technique the CM extraction with a small amount of an organic solvent allows accumulation times and small sample volumes because of the mostly complete accumulation in the organic phase. For determination of the substances that have boiling points 200^{o}C or higher, the more compact unit should be created in order to reach the temperature required. This system included the solvent elimination which is integrated with the injector of the GC.

The coupling of CMC and HPLC was also conducted. In this system, pentane was used as organic solvent. The extract was introduced through the sample loop of the HPLC and transported to the column when needed. The influence of several matrix components on the PAH extraction (i.e the addition of humic acid and surfactants and the increasing of the electrolyte concentration) were also investigated.

The indirect determination of extractable organic halogens (EOX) was conducted by coupling the CMC with the closed combustion system and ion chromatograph. After CM extraction of the halogen organic substances out of the water sample the extract is combusted. The exhaust gases are

extracted a second time and the halogen compounds are accumulated as halides in the water phase, which is then analyzed with the ion chromatograph.

Paz [105], another member of the group work, used the gas-liquid chromatomembrane extraction coupled with inductively coupled plasma-atomic emission spectrometry (ICP-AES) for simultaneous determination of mercury, arsenic, and selenium compounds in the air. The air containing those compounds was passed through the CMC that has been filled with absorbing solution/reducing agent so that the reduction-oxidation reaction takes place. The oxidized metal ions were then transported to ICP-AES. Potassium dichromate, potassium permanganate and nitric acid were tested as absorbing solution. 4M nitric acid was chosen as the best absorbing solution. The main analytical characteristics of procedures using chromatomembrane sample preparation are presented in Table 4.1.

Table 4.1 The main analytical characteristics of procedures using chromatomembrane sample preparation

Analyte	Determination method	Detection limit (µg/L)	Refe-rences
SO_2	Photometry	0.025	106
	Ion chromatography	0.003	106
HNO_2, NO_x	Ion chromatography	0.005	107
Ammonia	pH-electrode	1.0	99
	Ion chromatography	6 *	99
HF, HCl	Ion chromatography	0.001	109
Hydrazine	Photometry	10	110
Ozone	Conductometry	7 *	108
Copper (II)	Photometry	1	111
Nitrites	Gas chromatography	0.2	112
Phenol	Photometry	1	113
	Luminescence	1	114
Anionic surfactants	Photometry	8	115
Petroleum products	Luminescence	1	116
Methane	Gas chromatography	1	100
Ethane	Gas chromatography	2	100
Acetylene	Gas chromatography	1	100
Propane	Gas chromatography	1	100
Isobutane	Gas chromatography	3	100
Butane	Gas chromatography	2	100

* $\mu g/m^3$