Review

Gas/Liquid and Liquid/Liquid Solvent Extraction in Flow Analysis with the Chromatomembrane Cell

Leonid N. Moskvin [1] and Juergen Simon [2,*]

[1] Department of Chemistry, St. Petersburg State University, 198904 St. Petersburg, Russia

[2] Institute of Chemistry and Biochemistry, Inorganic and Analytical Chemistry, Free University of Berlin, Fabeckstrasse 34/36, D-14195 Berlin, Germany

[*] Author to whom correspondence should be addressed. Email: jsimon@zedat.fu-berlin.de

Abstract: Since twelve years the Chromatomembrane Cell has been proposed as a new and versatile device for extraxtion procedures in the flow based analysis. In the meantime a remarkable number of papers was submitted dealing with applications of the novel method to all the conceivable varieties of flow injection and sequential injection analysis. The device supports important analytical procedures such as sampling, sample preparation, and preconcentration each being combined with a phase transfer of the analyte. The Chromatomembrane Cell can be coupled to most of the modern detectors which work computer aided in the laboratories of today. Centrepiece of the cell is a block made from biporous hydrophobic PTFE, inside which polar (in the macropores) and nonpolar (in the micropores) solvents come into a close contact with each other and might flow independently with different flow rates. Microporous PTFE membranes prevent polar phases from their flowthrough into directions which are reserved for nonpolar fluids only. Thus, a strict control over the fluxes can be established at the analysts request. Especially, that PTFE block offers outstanding possibilities as a sampling unit for air monitoring.

Keywords: Flow injection analysis, chromatomembrane-cell, automated extraction procedures, preconcentration, sampling, sample-preparation

1. Introduction

During the past decades the Flow-Injection methods became a versatile instrumental tool that contributed substancially to the development of automation in chemical analysis. A wide ranging field of its application is within bounds of possibility, and on top of that the main steps such as sampling, sample preparation and analyte detection can be integrated into only one set-up of instrumentation. But one problem arises in numerous cases, i.e., whenever the analyte has to be separated from a complex matrix, the classical techniques of solvent extraction are difficult to be realized with common devices of Flow Analysis. In principle three various steps have to be performed following each other: First, two immiscible phases must be dispersed together with constant volume ratio each, then the two phases have to remain in close contact attaining effective mass transfer, and finally, a physical separation of both of the phases has to be established [1, 2]. Later on such problems were solved by a segmental flow moving in narrow tubes followed by a separation step [3]. All these devices suffer for their restricted possibilities in analyte preconcentration. The application of membranes proved to be reliable in particular, and yet the supplement of further devices is mostly required. Moreover, for liquid/liquid extraction procedures it has been turned out, that one of the liquids is a non-polar solvent, which is a hazard to the environment and therefore should be avoided. Alternative techniques were introduced to the Flow Analysis such as the solid phase micro extraction (SPME) [4] using suitable filters or surface treated beads [5].

The traditional and well tried extraction will get appropriate prospects for its use in modern analysis only when the quantity of the organic solvent can be held extremely small, and when the process comes together with remarkable preconcentration of the analyte. Our group presented a new concept for the implementation of extraction procedures inside a novel material, namely the biporous PTFE, which contains two types of pores, micropores and macropores. Polar liquids fill the macropores whereas the micropores remain available for non polar liquids or gases only. The penetration of polar liquids into the micropores prevents their capillary pressure therein [6,7]. Due to the fact, that gases are able to substitute the non polar liquid within the micropores, the new method especially provides a lot of applications in the field of automated gas analysis. The biporous PTFE can be used for both, the collecting of air samples and a more than hundredfold preconcentration of the analyte in an adequately prepared aqueous solution. The new technique combines partition chromatography with the use of microporous PTFE membranes as barriers against the flowthrough of aqueous solutions. Accordingly, this technique was named "chromatomembrane method", and its most important device is the "chromatomembrane cell" (CMC) with separated inlets and outlets for the both phases. Within the block of biporous PTFE the analyte transfer is made possible across the extended interface between the contacting phases.

2. The Chromatomembrane Method

Biporous PTFE consists of solid material (PTFE), macropores (250 – 500 µm in diameter), and micropores (0.1 – 0.5 µm), each of them contains roughly a third of the entire volume. The aqueous phase in the macropores and the organic one in the micropores safely coexist as long as $P_{org} < P_{aq} < P_{org} + P_{cap}$ (P_{aq}, P_{org} pressures of aqueous and organic phase, P_{cap} capillary pressure). The size of the surface boundary, where the two phases are in mutual contact, was determined to be in the range of 60

cm²/cm³ biporous PTFE [8]. This mostly guarantees to avoid kinetic hindrance for the analyte transfer between the two phases.

The chromatomembrane cell, which was introduced to the instrumentation of flow analysis by L.N. Moskvin [7], contains a rectangular block of the biporous PTFE as its main part. The special construction of the cell (Fig. 1) allows independent flows of two immiscible phases. Inlet and outlet of the aqueous phase result from direct supply to the macropores and effluence from the opposite side of the PTFE block respectively. Rectangular to this direction flows the organic phase, which is made possible by covering opposite sides of the block with microporous PTFE membranes.
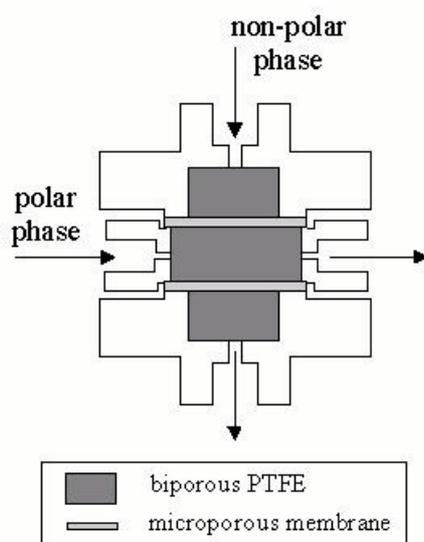

Figure 1. The Chromatomembrane Cell (from [11]).

In order to reduce the flow resistance of the organic phase these membranes are completely embedded now between biporous PTFE. (CMC models of the first hour contained a PTFE block with microporous membranes connected to the surface by sintering. Due to its high flow resistance the cell often suffered from leakages.) The enclosure of the CM body is constructed from non-corroding metals like steel or Titanium. Varying the flow rates of the two phases continuously working extraction processes can be established. Using a "stopped flow" mode the preconcentration of the analyte in the extracting phase is possible. The partition of a dissolved substance between the two solvents, which flow inside the CMC independently and rectangular to each other, may be considered as a two dimensional chromatography and, if required, multiple extraction procedures could be managed by adopted flux rates. The adequate parameter adjustment and the benefits from the application of the chromatomembrane cell for sample preparation and extraction procedures were explained in paper [9]. A physico-chemical model of the CM process and its application in chemical analysis were discussed in details by Moskvin [10].

Let us consider the continuous flux of the two phases to be rectangular to each other as shown in Fig. 1: The partition of the analyte is given by the distribution coefficient

$$k = c_n / c_p \tag{1}$$

which produces the retarding of its shift related to the flow-rates of the two fluxes (c_n and c_p are the equilibrium concentrations in the non-polar and the polar phase).The same retarding goes for an injected component-zone in flowing systems. Such zone-shift u_{ip} of the analyte with the polar flux results in

$$u_{ip} = \frac{u_p}{1 + k(V_n / V_p)} \tag{2}$$

and the zone-shift u_{in} with the non-polar flux according to

$$u_{in} = \frac{u_n}{1 + (1/k)(V_p / V_n)} \tag{3}$$

(u_p and u_n are the flow-rates and V_p and V_n the contacting volumes of the two phases). These volumes correspond with the volumes of the macropores and the micropores inside the biporous PTFE block. A system of a two dimensional chromatography is described in such a way. The times t_{zp} and t_{zn} of the respective breakthroughs result in:

$$t_{zp} = u_p/u_{ip} \text{ and } t_{zn} = u_n/u_{in}. \tag{4}$$

As long as $t_{zp} > t_{zn}$, the analyte has no time to reach the outlet for the polar phase, in other words, the separation from that phase occurred completely. But, whenever $t_{zp} < t_{zn}$, the analyte remains partially in the polar phase, whereas the outflow of the non-polar phase will be saturated from the substance extracted. Under that condition a procedure of "ultimate equilibrium saturation" can be realized. Further calculations reveal that complete analyte separation takes place in case of $u_p/u_n < k$, and the ultimate equilibrium saturation in the extracting phase is realized by setting the ratio of flow rates to be $u_p/u_n > k$ respectively.

There are two independent variables which characterize the state of a partition equilibrium, i.e. the partition constant and the ratio of the volumes of the two immiscible solvents being in contact with each other. That ratio can not differ remarkably from 1 : 1 using the customary extraction techniques. But in flow systems with continuously streaming fluids coming into contact with another inside a cell with a given volume, the ratio of the flow rates substitutes that of the volumes. Because of the fact, that immiscible solvents flow independently within the biporous PTFE (even in different directions) preconcentration can be provided in accordance with the highest possible ratio of flow rates which may increase up to 1 : 150 inside a CMC. Assuming a partition constant of $k = 10^3$ and a ratio of flow rates set to be 1 : 100, a hundretfold preconcentration will occur linked with an analyte transfer of 91 % [11], i.e., the calculated recovery of the analyte being concentrated hundredfold in the extracting phase. This is a further and efficient mode of preconcentration being possible in case the CM-method will be employed.

Moreover, the CM-method provides alternative variants of its application. Fig.2 shows an extraction cell filled with biporous PTFE. The two immiscible fluids can flow inside the tool with optional rates together or against each other. Nothing else but a T-shaped tubing is required for the mixing and a suitable phase-separator for moving the solvents apart from each other.
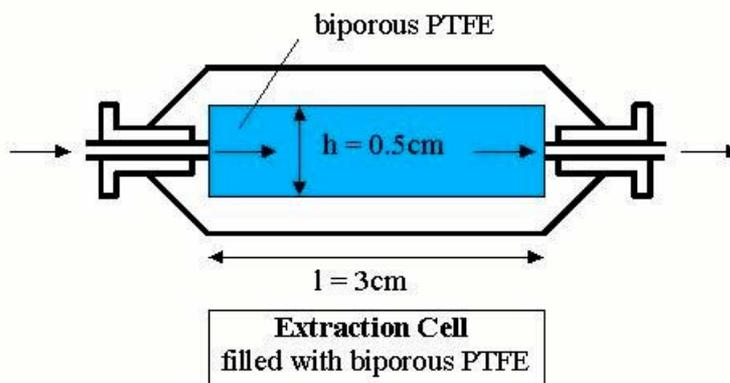

Figure 2. Extraction Cell without phase separation (from [11]).

Gaseous fluids were normally supplied to the CMC via the microporous membrane. But analyzing ambient air into its trace constituents it might happen, that such traces are adsorbed at aerosol particles which cannot pass a microporous membrane of hydrophobic material. This would mean, that the analyte extraction into an aqueous phase is strongly hindered. Because of that the "three-hole" CMC is constructed which uses a port of the polar phase as the gas inlet at first and after it as the outlet for the extracting aqueous phase [12, 13]. This requires to operate in a stopped flow mode preconcentrating the constituents of the air in an absorbing aqueous solution. It's obvious that after the supply of the gas sample the outflow of the extracting solvent must be diverted to the analyzer circuit by means of a suitable valve. In the cases dicussed at first, the block of biporous PTFE inside the cell has been used for the extraction procedure only, for the analysis of gases, however, the entire gas sample gets collected within that block. In other words the CMC also takes part in the sampling process. This fact allows the set-up of fully automated FIA-systems for monitoring the ambient air as Motomizu's group [14] realized for the detection of several pollutive constituents. These papers especially show the robustness of CMCs working integrated in analyzer-modules as units for sampling and separation. The cells do not need any maintenance over extended periods, so that their application is possible in fully equipped and automated systems, which do their job anywhere in the field. It should be emphasized that both, liquid/liquid and gas/liquid extraction procedures can be established without problems.

In conclusion the CMC works as an effective tool in all extraction procedures with preconcentration of the analyte in the extracting phase. The method requires small sample sizes and therefore reduces the consumption of organic solvents. The quality of its results bears comparison with the established methods in every respect. The versatility of the proposed method may be understood from the possibility to realize the analyte transfer between any desirable combination of two immiscible solvents even in the both conceivable directions.

3. Application in Analytical Chemistry

As mentioned above stable working conditions inside the CMC will exist if the pressure of the polar phase exceeds somewhat that of the non-polar one. A simple possibility of its realization is to make sure that the outflow of the polar phase is higher than the level of the CMC, so that a hydrostatic pressure will be produced in addition.The flow rates of polar liquids through a block of biporous PTFE with a volume of about 2 cm^3 can be set up to several ml/min, non-polar liquids should flow with rates of 1 ml/min at the most, whereas flowrates of more than 100 ml/min are possible for gaseous phases. In principle, the flow diagrams for the CMC preconcentration from an aqueous phase or a gas phase were shown in Fig. 3. The scheme can be adjusted to every special analytical requirement for FIA and SIA applications.
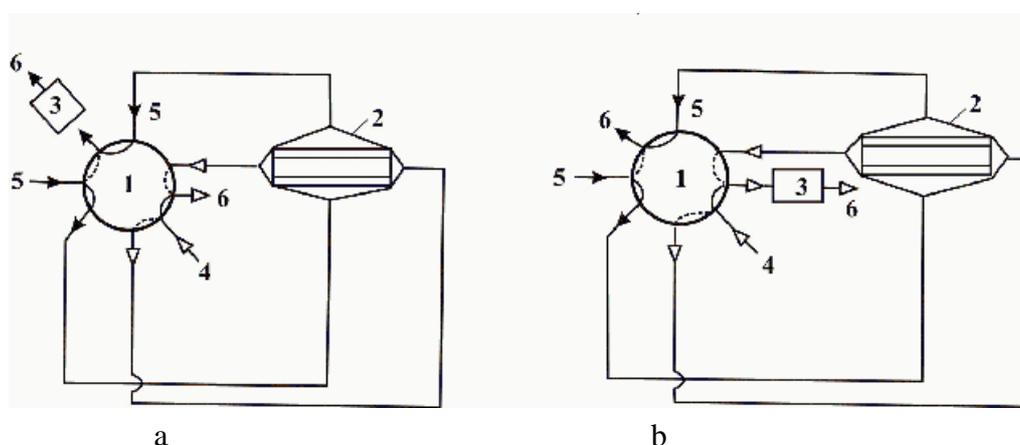

a   b

Figure 3.   Scheme for chromatomembrane preconcentration from (a) an aqueous and (b) a gaseous phase. 1 valve, 2 CMC, 3 detector, 4 aqueous sample (a) or aqueous absorber solution (b), 5 polar extractant (a) or gas sample (b), 6 waste.

3.1 Liquid/liquid solvent extraction

Let us consider the micropores of the biporous PTFE to be filled with an organic extractant and its flux to be stopped completely. If the aqueous phase containing the analyte flows through the macropores, a partition between the two phases will take place like in common chromatography and a retention results in accordance with the partition law. The zone shift inside the PTFE block in the direction of the flux of the polar phase determines the time up till the break-through of the analyte. In case the entire volume of the organic solvent is removed within that period, the extraction of the analyte will completely occur. The optimum efficiency of the process will be given if the flux rate of the organic phase is exactly calculated for the condition discussed before. On this basis a continuous extraction procedure can be established.

Several examples related to continuous solvent extraction:
-   Chromatomembrane method coupled to photometric detection for the
    determination of phenol in water (phenol-index, the limit of detection is in the
    range of 5 μg per liter aqueous phase [8]. ($R^2 = 0,99$ for calibration graph).
-   Luminescence determination of oil products and phenols in natural water [15] and [16].

- Determination of nitrite traces with chromatomembrane extraction [17]
- Monitoring of PAH and EOX in waste water. Flow based procedures with chromatomembrane cells coupled to gaschromatography and ion-chromatography respectively [18]. (LOD's for PAH: 1 - 2 µg l^{-1}, R^2 =0,999, LOD's for EOX: ~ 0,5 mg l^{-1}, R^2 = 0,999, even the simultaneous detection of the three halogens is possible).

Whenever higher analyte preconcentration is required, the "stopped-flow-mode" may be the method of choice. In this case the flux of the extracting solvent has been stopped as long as the capacity for the analyte uptake from the flowing sample (its rate is u_w) is still not exceeded. Then the sample flux becomes stopped (after the preconcentration time t_p) and the extracting solvent starts to flow for the transportation of the taken analyte to the detecting device. The calibrated detector records the mass m of the analyte, and its concentration c_w in the original sample can be calculated from the equation: $m = c_w * u_w * t_p$.

Further details of the application of the "stopped-flow-mode" are disussed in some published papers:

- Photometric determination of anionic surfactants by separation from the aqueous phase with the chromatomembrane cell ((MBAS-Index) [19]) (LOD = 20 µg l^{-1} for dodecylsulfate, R^2 = 0,998).
- The chromatomembrane method used for sample preparations in the spectrophotometric determination of zinc and copper in pharmaceuticals (extraction of the Me(PAN)$_2$ complexes) [20]) (LOD's = 40 µg l^{-1}, R^2 = 0,996).

At least, the natural progression of the well established membrane methods towards the CMC filled the lack of new procedures for the continuous and selective extraction of substances from a complex matrix. Solvent extraction by the CMC is a promising technique in the flow based analysis, by which the three steps necessary for a complete extraction procedure are combined in one small and robust device only. A sophisticated automation is provided to FIA and SIA applications [21].

3.2 Gas/liquid extraction

The use of chromatomembrane methods in the analysis of gases such as ambient air is pretty unsurpassable. The extracting solvent is a suitable aqueous solution which is able to absorb selectively the constituent desired, and therefore hazardous organic solvents can be completely avoided. A measured volume of the gas becomes supplied to the micropores of the biporous PTFE, whereas its macropores are filled with absorbing solution, so that the gas sample will be collected in the CMC. In other words the sampling procedure fully occurs in the biporous PTFE, and the CMC proves itself to be the sampling unit.

At first investigations started with the absorption of ammonia from loaded air into an aqueous phase and the electrochemical detection of the pH-shift [22]. For a better adaption to the requirements of gas analysis the "three-hole"-cell was constructed as discussed above. It allows the preconcentration of nitrogen oxides in a solution of 0.2 % triethanolamine (TEA) in water and the following detection of

the formed nitrite ions with a coupled ion-chromatograph [23]. Using the same technique the ozone content of air was measured after its preconcentration in a 0.1 % potassium iodide solution (pH 4.2). The oxidation of the I^- to I_2 produces a change in the conductivity of the solution, which was determined conductometrically in a flowthrough cell (LOD = 7 µg O_3 per m^3 air) [24]. A flow injection analyzer coupled to a photometric detector was used for the CMC absorption of formaldehyde from air [25]. All these procedures require the calibration with standard gases. Only in case of high quality instrumentation the conductometric method allows the direct mass detection by mathematical evaluation. The versatility of the biporous PTFE gives analysts the idea of developing special cell designs for solving analytical problems. So it happens that arsine can be formed from arsenic species inside a CMC and be removed with a nitrogen flux for its adsorption in a column filled with a solution of special reagents for the photometric detection which follows.

In case of using 5-(1,3-benzodioxol-5-yl)-3-(4-iodophenyl)-2-phenyl-3H-1,2,3,4-tetraazol-2-ium chloride for absorption a limit of detection in the range of 1 µg l^{-1} is possible [26].

Providing a micro-FIA system Motomizu's group succeeded in going a remarkable step forward in the automation of flow based gas analysis. A three-hole CMC was used for collecting NO_2 [14,27,28] or SO_2 [29] from air and for their simultaneous absorption in aqueous solutions. The absorbing solutions were supplied to a detection circuit where a dye will be formed for the photometric determination. It was shown that the absorption of the air pollutant occurs completely in the biporous PTFE by forming nitrite (in 0.2 % TEA) or sulfite respectively. On request the system calibrates itself by analyzing NO_2^- or SO_3^{2-} standard solutions. Thus, this "intelligent" device allows the fully automated air monitoring. (By using 20 ml air the LOD for NO_2 is 0,9 ppb and 0,5 ppb for SO_2).

3.3 Liquid/gas extraction

The objectives and features of the gas extraction from a stationary liquid phase were discussed by Rodinkov et al. [30] in details. In this context alternativ applications of the CMC to the determination of volatile organic compounds (VOC) should be mentioned [12,31,32]. In this way compounds such as methane, ethane, acetylene, propane, isobutene or butane can be extracted from aqueous phases in the CMC for their detection in a gas chromatograph [33]. (LOD's for the different VOC's range from 0,01 to 10 µg/l^{-1}). In electrochemical investigations the problem arises, that dissolved oxigen disturbes measurements with electrodes. It became a habit to remove it by rinsing with nitrogen, but in case of very sensitive measurements the use of purified nitrogen or argon is necessary. In order to reduce the quantities of such expensive gases an alternative technique is required. Thus, a CMC should help in the removal of oxygen [34,35]. The efficiency of the proposed oygen removal is comparable to that of the degassing system of Colombo and van den Berg [36]. Working with high sensitive mercury film electrodes this method allows to deposit online the Hg-films on glassy carbon electrodes inside a closed flowthrough cell, and a high-performance SIA enables inverse voltammetric studies in the lower range of nano A currents [35]. The LOD's for Cd^{2+} and Pb^{2+} in aqueous solutions are about 0.5 µg l^{-1}.

4. Conclusion

Since more than one decade the chromatomembrane method has succeeded in a wide spread field of different analytical applications. One of its many advantages is the flexibilty of trace separation from complex matrices for all types of flow analysis. This is especially based on the

- small volumes of the contacting phases (100 – 200 µl)
- fast adjustment of distribution equilibria because of the short distances to the phase boundary
- uncomplicated phase separation
- continuous extraction and preconcentration by varying the ratio of flux rates between 1 : 1 and 1 : 100.
- preconcentration by using a "stopped flow mode"
- fully automated sample pretreatment on request, i.e.: process analysis can be realized.

S. Motomizu [37] and K. Higuchi [38] contributed very much to the common knowledge of the new method within Japan and described the CMC as an "intelligent device".

Later on S. Kawakubo and T. Yamane [39] reviewed the features of online extraction devices and in this context they discussed the feasibility of the CMC in details. New constructions of especially designed cells keep options open for analysts being creative in solving separation problems. The possibilties have been discussed above, which CMCs offer for integrating separation and detection in only one modul for doing its job outside of the laboratory.

The CMC can be handled quite easily and is a low cost offer to flow based techniques. It is a supplement which improves the quality not only of routine but also of process analysis. It decreases the waste production (hazardous organic solvents) and enhances the repeatabilty in combination with online processing because of the flexibility of the CM-method and its suitability for coupling to the most of common sensor-systems. The on-line sampling of ambient air with automated FIA-systems is a key feature of the Chromatomembrane Cell.

Acknowledgement

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