9   Summery

The CM Method has been proved being a robust method for sample preparation, with a high automating potential. For the direct coupling to GC and HPLC capable flow systems were built. For the analysis of the EOX parameter (extractable organic halogens) a flow system was developed. By combination with IC the differentiated determination of Chlorine, Bromine and Iodine was possible. For the determination of naphthalene from water samples a flow system including CM cell and spectral photometer was created.

The flow system for the determination of naphthalene from water samples was used for the examination of the effectivity of the CM module. Because of its simpleness and high steadiness this system was chosen to characterize flow conditions and properties of the filling material of the extraction cell.

It could be shown that beside PTFE other chemically inert, non-polar materials can be used as filling for the CM cell. The determining criterion for the usability in the cell is the wetting behavior of the material. The less the surface was wetted by the polar water phase, the better conditions for the second, the non-polar fluid were found. A steady film flow along the polymer surface was possible. A rough surface structure assists because of the Lotus Effect this behavior even like a positive interaction between the polymer surface and the non-polar fluid.

The model of the flow through a bulk commodity gives a good description for the flow conditions of the polar phase. The flow of the non-polar phase is additional described as film flow through a widely ramified grit of channels along the polymer surface. The model explains the experimental found huge contact area of the fluids in the cell corpus even like the independent flow conditions of both phases. Smaller pore diameters shortens the distance, the analyt has to pass by diffusion and increase so the effectivity of the cell. Best results were received using the PTFE material of the Bohlender Company with standardized pore diameters of 50 µm.

The coupling of CM method and gas chromatography was managed in two ways. For the determination of semi volatile organic compounds the liquid extract flew into a sorbens filled, tempered sample loop. The organic solvent was reduced in a nitrogen stream. After thermal desorption the analyts were conducted into the GC and analyzed. For substances boiling between ca. 130 to 300°C this system allows sensitive determination. Even the separation of the sampling unit from the GC is given. Compared to headspace or purge and trap technique the CM extraction with a small amount of an organic solvent allows low accumulation times and small sample volumes because of the mostly complete accumulation in the organic phase. No washing or drying steps are needed.

A second assembly was used for the analysis of non-volatile organic matter. The solvent elimination here was integrated inside the injector of the GC system. So a more compact unit was created, which could reach higher temperatures. Substances boiling at ca. 200°C or higher could determined

this way. Using only 20 mL water sample several PAH components were determined in the lower ppb level. For a complete analysis including all washing steps and three determination steps only ca. 100 mL sample were necessary. The complete operation takes nearly an hour. Lowering the detection limit by increasing the sample volume is possible. There was no effect to the capacity of the adsorber inside the injector after passing of 1 mL organic extract that means nearly 500 mL sample.

The coupling of CM method and HPLC worked in a similar way. The extract was conducted through the sample loop of the HPLC and could be injected when needed. Only problems were caused by the desiderative miscibility of solvents for the extraction step and the eluent. Without any washing or preconcentration steps detection limits for the used PAH components were found between 1,3 and 0,07 µg L^{-1}. The limits were found by using an UV-detector so that the essential lowering of the detection limits would be easy to reach by the use of a fluorescence detector.

The influence of several matrix components were tested by the PAH extraction from water samples using the CM cell. No influence was found by the pH of the sample. Even humic acids up to an amount of 20 mg L^{-1} caused no effect. Neither the flow through the cell was affected, nor PAH were masked by the humic acid.

The increasing of the electrolyte concentration causes no effect. Only the affinity of adsorption to the surfaces of the apparatus increase, if the concentration of the PAH near their solubility.

The addition of surfactants caused a decrease in the detected PAH. Also the volume of extract decreases. Anyhow there was an extraction up to the highest used concentration of surfactant possible. The phases left the cell module separated. The detected PAH amount depend to the PAH concentration in the water sample so that analysis of PAH even in surfactant containing water is possible.

A more complex flow system was developed for the halogen differentiating determination of organic halogens. 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 analyzed in the ion chromatograph. Other then normally the amounts of chlorine, bromine and iodine can be detected separately. Iodine is only by using a reducing absorber solution possible.

Because of the necessity of the complete extraction of more polar substances the residence time in the contact range a small column filled was inserted before the CM cell. The accumulation rates for the samples were increased this way ca. 30%. The organic extract also can be collected and analyzed for getting differentiated information about special compounds

For the combustion unit from Haberkorn & Braun was very sensitive for pressure variations the normally used CM module only could work in continuous flow mode. For the more effective stopped flow accumulation some changings were necessary. Either both membrane fitted openings of the cell were used as gas outlets or a special absorber unit, including only two openings, gave good results. An especially for the gas extraction constructed type of CM cell, including 3 openings, was

not useable. Best results were found by using a new built absorber type, which is only fluffily filled with PTFE fiber. This new type of extraction module shows interesting options. The small column is first filled with the absorber solution and after this the gas phase is conducted through. The gas flows consistent along the PTFE fiber so that no solution escapes with the gas phase.

The EOX analysis in a fully automated flow system simplifies the monitoring of process water and environmental samples. The continuous extraction of the water sample allows the retention of extract for the analysis of interesting components by GC or HPLC later on.

A larger cell module was shown to be useless in all applications. The extra long module caused instabilities in flow conditions.

The development of an online filtration step in front of the extraction module would be an interesting ambition for the near future. Especially for the analytic of environmental samples the separation of sediment and suspended load would accelerate and simplify the investment for the analysis. As could be shown, the passage of smaller aggregates of humic acids causes no problems for the cell extraction. However the critical value of particles to pas the pores not was found.

An other target could be the development of a cell geometry that allows the passage of suspended load through the cell corpus. Because of the high adsorption affinity of various organic substances an extraction module without the necessity of a preceding filtration seems interesting. A CM module with wide and preferably straight pores which only has to separate the before the passage merged phases possibly could afford this.

For all surfactant-containing solutions an easy separation of the phases at the outlet of the CM cell was guaranteed, so that the possibility of the analysis of steady emulsions like milk or cosmetic lotions should be checked.

All applications and studies of this work show the flexibility of the CM method and the potential for new variations. The studies of the flow conditions allow the specific modification of the extraction conditions and enlarge the spectrum of possible applications. All presented applications show a high value of automation and a low need of sample volume. They easily reach the detection limits needed, so that they offer a good alternative to more similar techniques.