Photometric Determination of Phenol with a Flow-Injection Analyzer that includes a Chromatomembrane-Cell for Sample Preconcentration by Liquid-Liquid Solvent Extraction

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Abstract

A computer-controlled Flow Injection Spectrophotometric Analyzer (FISA) has been proposed which is now applied to determine the phenol according to the rules and regulations of the ISO for monitoring the Phenol-Index. Our group introduced a new concept for the implementation of extraction procedures in flow systems combining partition chromatography with membrane techniques. We developed the Chromatomembrane-Cell (CMC), that allows preconcentration and extraction procedures for automatical sample pretreatment. By coupling the CMC to an UV/VIS-Spectrophotometer a set-up is obtained that makes possible to detect the coloured phenol-complex which is produced by oxidation of 4-Aminoantipyrine in the presence of phenol. The computer controlled FISA permits a LOD (3σ) of 5 µg phenol per Liter aqueous phase in case that a preconcentration time is kept of at least four minutes.

Keywords Phenol-Index, liquid-liquid solvent extraction, Chromatomembrane Cell

Introduction

Phenols are chemicals of today which are commonly used in the industrial production of polymers, dyes, pharmaceuticals, antioxidants, herbicides, fungicides, pesticides etc. But even the nature causes phenols to exist without any human influence whenever foliage, fir-needles or something similar decay. Nevertheless, all phenolic compounds are toxic to an exceptional degree for the most aquatic organism. The quantitative determination of phenols in natural waters is carried out by HPLC, GC, GC/MS, or, however, using an UV/VIS photometer for the measurement of the absorbance of the coloured phenol-complex, which was extracted from aqueous phase after having condensed the phenol with 4-Aminoantipyrine and then oxidized [1-4]. The procedure proposed in this paper is established for an automized FI-system including preconcentration facilities. It allows to detect phenolic compounds at the level of micro grams. The processing comprises four steps:

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1) chemical interaction of phenol with 4-Aminoantipyrine (4-AAP)
2) oxidation with potassium peroxidisulfate or potassium hexacyano-ferrate
3) extraction of the coloured phenol complex from the aqueous phase and its preconcentration in chloroform inside the Chromatomembrane-Cell
4) measurement of the absorbance of the coloured complex in a flow-through-cell by a photometer.

As customary until now the FIA-extraction procedures operate in three distinct steps, e.g., the application of a phase segmentor, an extraction coil and a phase separator. This process is even not satisfying with regard to easy handling and, however, preconcentration facilities do not exist. The CM-method shows the difference when compared:
The link-up with modern instrumentation can be established, preconcentration is possible by using the "stopped-flow"-mode, and the waste production is minimized remarkably. The CMC was developed and introduced for every traditional extraction procedure within any chain of automated sample pretreatment. The CMC realizes independent flows of polar- and non polar phases through a block of hydrophobic PTFE with two types of pores -

micropores (0.1 - 0.5 μm) and macropores (250 - 500 μm). Polar liquids fill the macropores whereas the micropores remain available for non-polar liquids or gases. The capillary pressure of polar liquids prevents their penetration into micropores. Now, the size of the surface boundary, where the two phases are contacting with each other was determined to be 60 cm^2 per cm^3 biporous PTFE. That resulted from studies on the kinetical behaviour of a two-phase-reaction of which the reaction-rate depends on the size of the contacting area, i.e., the saponification of benzoylchloride with NaOH. Each cm^3 of the biporous PTFE is capable to take 0.3 cm^3 polar and 0.3 cm^3 non polar phase as average. Distinct conditions have to be complied in order to make possible an independent flux of two immiscible phases inside the block of biporous PTFE. Two opposite sides of the block are covered with microporous PTFE membranes stopping the water passage there. Only the non-polar liquid is allowed to flow in this direction. Two sides are open for the flux of the polar liquid whereas any flux in the third direction is excluded by sealing the pores completely on the matching sides (Fig.1) The enclosure of the biporous PTFE block is constructed from non-corroding materials providing inlets and outlets for the two phases. If these are supplied to the CMC a difference in their inlet-pressures must be maintained which is set by the capillary pressure of the polar liquid within the micropores of the PTFE membrane. We reported in detail on the construction of the CMC and its application to extraction procedures in flow systems [5-12].

Experimental

Chromatomembrane Cell

We proceeded to extract and preconcentrate the coloured phenol complex inside the CMC according to the "stopped-flow-mode": the aqueous phase flows with a constant pump rate through the cell while the flux of the non polar phase is stopped. An ordinary partition chromatography takes place with its specific rate of component zone shift (loading up to capacity). The polar liquid must be stopped before the analyte breaks through.

When starting the flux of the chloroform-phase the extracted and enriched analyte becomes rewashed from the CMC (Fig.2). The computer controlled processing is possible using a multifunctional valve. The CMC is on-line coupled with a UV/VIS-Photometer, which measures the absorbance of the phenol complex when passing a flow-through-cell.

Since the detected mass equals the product of (a) the phenol concentration in the aqueous phase, (b) its flow rate and (c) the preconcentration time, the controlling computer is enabled to optimize the procedure by changing the preconcentration time in such a way, that the absorbance can be detected within the range of best confidence.

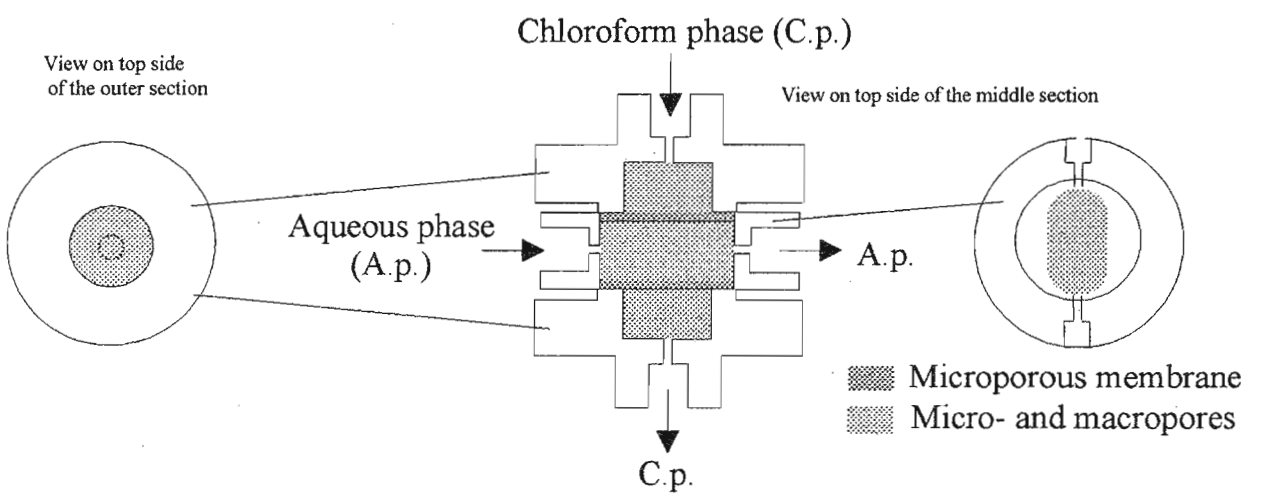


Fig.1. Construction of the CMC with a biporous PTFE block insinde

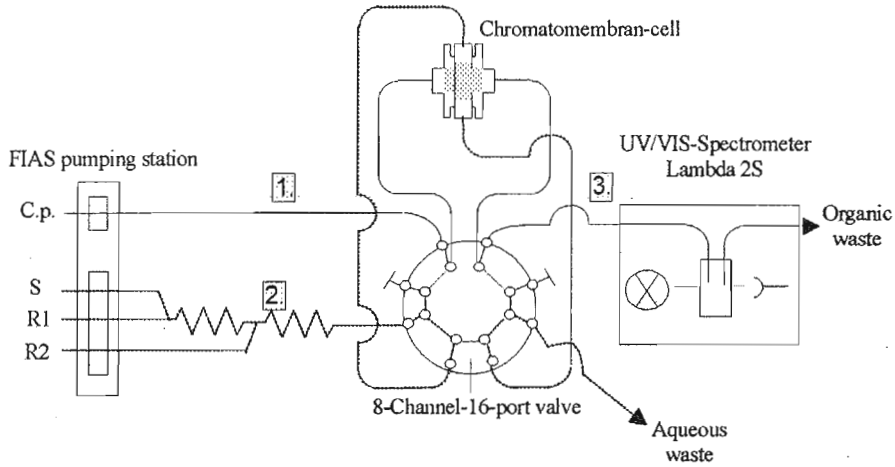


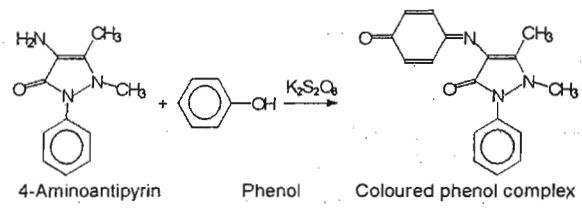
Fig.2. Time sequence of the sample pretreatment steps using the CMC
(S: Sample, R1: 4-AAP/buffer, R2: oxidizing reagent, C.p.:Chloroform phase)
1. CM-cell gets filled with the chloroform phase (C.p.)
2. Preconcentration and extraction of Phenol from the solution
3. Transportation of the extractant to the UV/VIS-Spectrometer

Equipment

The photometric measurements were carried out by an UV/VIS Spectrophotometer (Lambda 2 S) which was equipped with a Flow-Injection-Analysis-System (FIAS 300) from Perkin Elmer. The FIAS-device was fitted with a 8-channel-16-port valve and two peristaltic pumps in order to perform computer-aided preconcentration procedures. The absorbance of the phenol complex was measured at its maximum of absorption (460 nm).

Reagents and Flow-Rates

R1 contains the required quantity of 4-AAP in 100 mL buffer. This buffer consists of 23 g/L $NaHCO_3$, 27 g/L H_3BO_3 and 35 g/L KOH. The 4-AAP concentration should not exceed 2.5 g/L, because it dyes the sample by itself, what would enlarge the extent of later corrections when comparing with a blank-plot. R2 is prepared by dissolving 47 g/L $K_2S_2O_8$ in water and adjusting with potassium hydroxide to pH 11.
Both reagents became freshly prepared every day. All the solutions were carefully degassed by ultrasound. The flow rates of R1 and R2 were 0.25 mL/min, the phenol sample S was flowed with 0.60 mL/min. The optimized flow rates of chloroform and the aqueous sample through the CMC were determined to be 0.60 mL/min [11].



Results and Discussion

The influence of preconcentration time on the scale of mass transfer into the organic phase was studied at constant phenol concentration (200µg/L) in the aqueous solution. The same procedure was carried out with a blank solution as the not converted 4-AAP causes absorption too. The linear dependence of preconcentration time upon extracted phenol quantities reveals a remarkable fact: The lowest limit of detection is inversely proportional to the volume of the aqueous phase where the phenol becomes extracted from (Fig.3). The LOD of phenol amounts to 26 ng in the chloroform phase (3σ). From this it follows that a calibration graph for the aqueous phase is linear between 20 and 200 µg/L phenol, if a preconcentration time of two minutes and a flow rate of 0.65 mL/min are chosen for instance (Fig.4). The Departments of the Environment do recommend limits of phenol content to be 50µg in natural water and 0.5µg in drinking water.

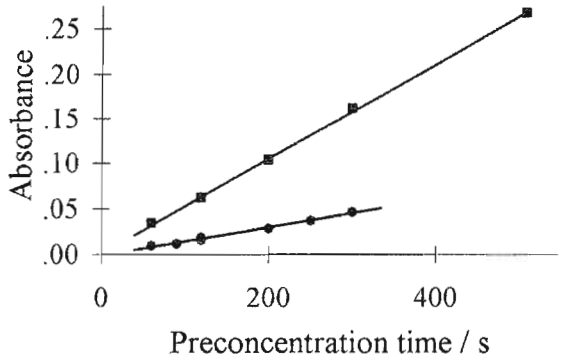


Fig.3. Effect of preconcentration time on the extracted quantity of phenol
■ 200µg/L (R^2=0.9993) ● blank solution (R^2=0.9877)

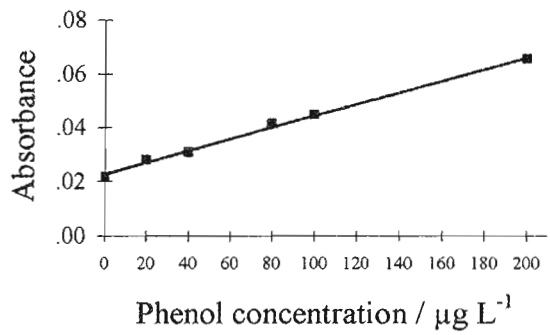


Fig.4. Calibration graph of phenol at constant preconcentration time of 120 s

Conclusions

This paper shows the CMC to be a fast working extraction device in case of quantitative phenol determinations according to the regulations of the Phenol-Index. Applying the "stopped flow mode" the CM-method reveals supplementary facilities for analyte enrichment. Don't neglect the possibility of computer aided operating with CMCs whenever extraction procedures are required in process analysis. Even that completes the versatility and low cost offer which have often been cited as two of the major strengths of FIA and SIA.The CMC is a supplement which improves the quality of routine analysis, which helps to decrease the waste production, to enhance the reproducibility in combination with on-line processing. As a result we observed an increased sample throughput, and manual processing faults do not occur. Finally, the workload of expensive instrumentation improves. The CMC is suitable for establishing sampling and sample pretreatment units for operating anywhere in the field. Analytical laboratories of today are required to validate their procedures in accordance with governmental orders. It is important to become acquainted with the presented techniques as to be compatible with Analytical Assurance Programs.

Acknowledgments

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