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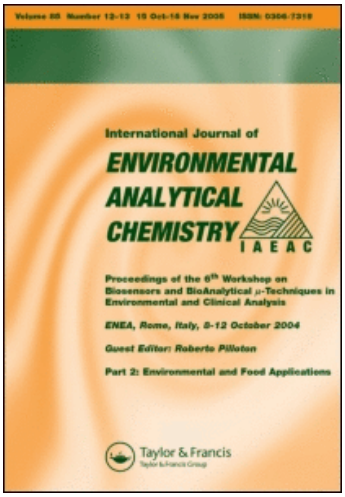

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Liquid Film Pertraction—A Liquid Membrane Method for Recovery and Preconcentration of Aromatic Amines from Their Dilute Aqueous Solutions

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LIQUID FILM PERTRACTION—A LIQUID MEMBRANE METHOD FOR RECOVERY AND PRECONCENTRATION OF AROMATIC AMINES FROM THEIR DILUTE AQUEOUS SOLUTIONS

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A new liquid membrane method is proposed for selective extraction and preconcentration of aromatic amines from their diluted aqueous solutions. The Liquid Pertraction Technique applied for preconcentration of pyridine and *m*-toluidine provides high extraction efficiency and stable continuous operation. It was shown that the main factors affecting the mass transfer efficiency and hence the enrichment factor and preconcentration accuracy are the mean residence time of the donor (sample) solution in the apparatus and the motion intensity of the membrane liquid.

KEY WORDS: Liquid membrane, pertraction, amines, amine analysis, preconcentration, purification.

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INTRODUCTION

In most cases, trace analysis of organic species in aqueous effluents requires the samples to be pretreated prior to their introduction into the gas or liquid chromatograph. The pretreatment step involves a selective separation of the analyte component from the matrix and its preconcentration in an appropriate medium. The separation of aromatic and aliphatic amines from the matrix which often represents a very dilute aqueous solution, is usually performed by solvent extraction[1]. For this purpose the sample is alkalinized as to obtain the free amines[2,3] or ion pairs are formed by the addition of suitable reagents which are extracted into the organic phase[4,5]. The second approach is applied especially to the determination of amines in biological matrices as blood plasma, urine, etc.

The classical extraction procedure is not efficient for the preconcentration of amines and other organic compounds with relatively low distribution coefficients. Its application is limited to the preconcentration of substances of low polarity and low solubility in water.

More favorable in this respect proved to be the separation methods using liquid membranes. Compared to the classical extraction procedure, they provide a more complete transfer of the analyte from strongly diluted donor solutions into a suitable acceptor phase. A large number of organic solvents may be used, also when the distribution coefficients are lower than 1.

Recently the first studies of the analytical application of liquid membrane preconcentration methods appeared: recovery and preconcentration of metal ions—U, Mn, Co, Sr, Cs, Ce, Tc, Cd, Zn and Hg by the widely studied Emulsion Liquid Membranes (ELM)[6–8]; recovery of U[9], Li[10] and Cu[11] by the method of Supported Liquid Membranes (SLM), which uses impregnated porous polymeric supports. An aqueous membrane supported on cellulose paper has been used for the separation of enantiomers and other isomers[12].

The weak organic bases, to which belong amines, have been the subject of a few studies, focused on the demonstration of the adequacy of developed mathematical models for describing the transfer processes in the ELM systems[13–17]. The only study aiming at the purification and preconcentration of amines for analytical purposes using supported liquid membranes has been performed by Audunsson[1,18] on a porous polymeric membrane impregnated with undecane.

The purpose of the present work was to study another liquid membrane technique, the Liquid Film Pertraction (LFP), which has been recently introduced[19,20] as an alternative of the above mentioned ELM and SLM methods for the analytical preconcentration of traces of substances, especially of aromatic amines from aqueous solutions.

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EXPERIMENTAL SECTION

LFP method and apparatus used

Figure 1 shows the principal idea of the liquid film pertraction method. The donor solution F and the acceptor solution R are flowing as thin films down the vertical

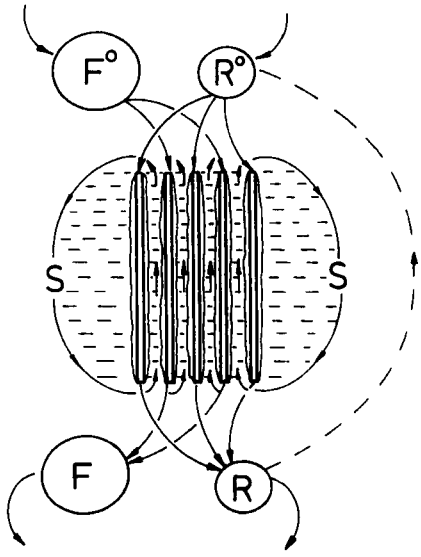

Figure 1 Principal diagram of liquid film pertraction. F = Donor solution; R = Acceptor solution; S = Membrane liquid.

hydrophilic solid supports, alternatively arranged at a small distance. The support package is immersed in the liquid membrane—the organic liquid *S*, which fills up the gaps and the whole apparatus volume. In contrast to the ELM and SLM methods mentioned, in the LFP all three liquids including the liquid membrane are in motion. This increases the rate of the mass transfer process. The three-phase liquid system thus created is very stable and permits a long-term continuous operation. Differently from ELM, this method tolerates any donor-to-acceptor flow ratios with no effect on the phase contact area. Under appropriate conditions, particularly high pre-concentration effects may be achieved.

All experiments were carried out at 20°C. The concentrations are expressed in mg l^{-1} and each experimental point represents an average value of three independent concentration measurements.

Experimental set-up

The laboratory experimental set-up used is shown in Figure 2. The solutions F^0 and R^0 are fed into the corresponding pertractor feeding chambers by means of two peristaltic pumps P-1 and P-2. They are operated by the timer device *T* which provides independent periodical supply of the solutions thus ensuring their homogeneous distribution along the width of the supports, maintaining the desired plug flow.

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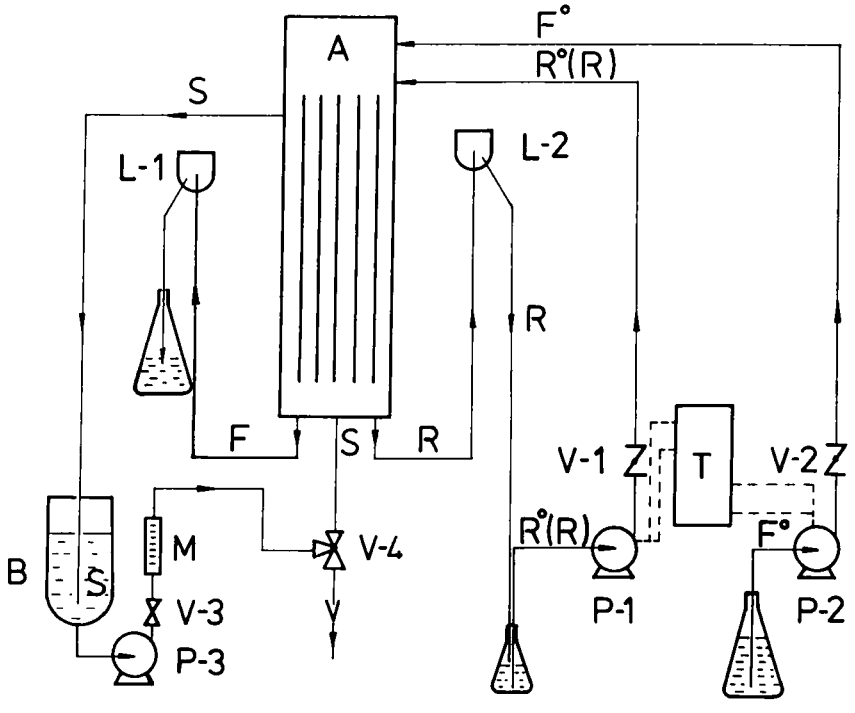

Figure 2 Experimental set up.

The latter cannot be realized at low flowrates under forced continuous supply of the liquids into the chambers. These flowrates may be varied in a broad range by appropriate adjustment of the active and passive cycle periods. The one-way valves V_1 and V_2 stop the back-flow of the liquids F^0 and R^0 during the passive periods. After being passed through the feeding and mass-transfer parts of the apparatus, the treated (F) and enriched (R) solutions are led out via the corresponding level-legs L_1 and L_2. The solution R is circulated in a closed loop. The membrane liquid is set into motion by a chemical magnetically driven centrifugal pump P-3 (March MFG Co). The flow rate of this liquid is controlled and measured by the valve V-3 and the flowmeter M. A buffer vessel B and a three-way valve V-4 are coupled to this line for draining the apparatus.

Two LF-pertractors, representing rectangular prisms, made of organic glass were used in this study. Their main characteristics are given in Table 1.

Figure 3 shows the flow paths of the three liquids—F, S and R in apparatus No. 1, having the minimal number of supports (one for the donor solution F and two one-side exposing supports for the acceptor solution R). The feeding top part of the pertractor involves two compartments (1 and 2), which serve as reservoirs—distributors of the donor and acceptor liquids F^0 and respectively R^0. A disposable entry filter 5 for the donor liquid F^0 is provided for. The mass-transfer part involves the space from the upper level of the membrane liquid S to the lower end of the supports. When porous solid materials are used as the supports, the solutions F and R not only form a liquid film on their surface, but penetrate into the support interior, providing in this way a stable plug flow.

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Reagents and analytical methods used

The organic solvent NORPAR 10/13, employed as the liquid membrane, was a standard fraction of medium-boiling normal paraffins (C_{10}–C_{13}), produced by Neftokhim Co, Bulgaria ($\rho = 750$ kg m^{-3}, $\nu = 1.76.10^{-2}$ m^2 s^{-1} at 20°C). The model donor solutions were prepared by dissolving pyridine (purum from Fluka AG) or *m*-toluidine (Merck-Schuchardt, FRG) in distilled water. For preparing the acceptor solution, sulphuric acid (p.a. from KZ Co, Bulgaria) and distilled water were used. The aqueous solutions were alkalinized with 1M solution of sodium hydroxide (p.a., Lachema, Czechoslovakia).

Table 1 Characteristics of the apparatus used.

Characteristic		*Apparatus No. 1*	*Apparatus No. 2*
Number of supports	[—]	3*(2R + 1F)	5*(3R + 2F)
Support width	[mm]	70	80
Thickness of F-supports	[mm]	4	4
Thickness of R-supports	[mm]	0.5	4
Active support height	[mm]	500	500
Membrane thickness	[mm]	5	8

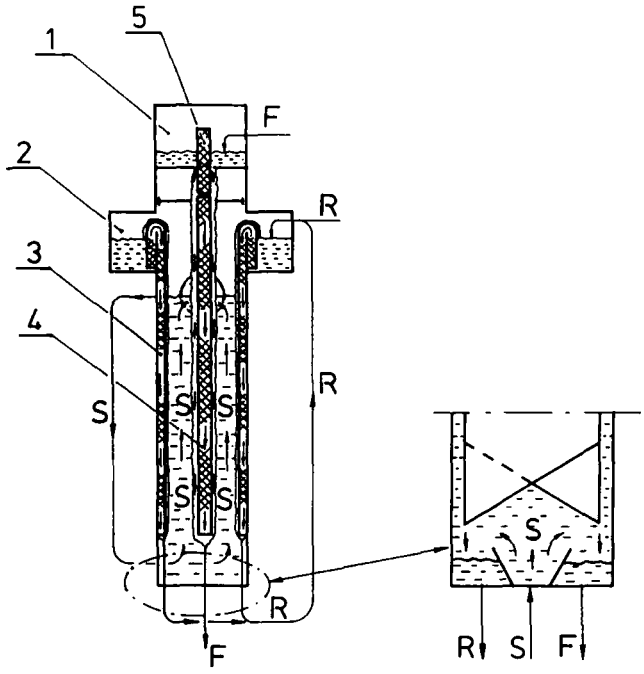

Figure 3 Introduction, flow pattern and collection of donor (*F*) and acceptor (*R*) solutions in the apparatus No. 1.

The concentration of the amines in the aqueous solution was measured by a UV-VIS spectrophotometer SPECORD (Germany) at $\lambda = 257$ nm for pyridine and at $\lambda = 287$ nm for *m*-toluidine, respectively[21].

The pH-values were monitored by a pH-meter (LP-17, Bulgaria).

RESULTS AND DISCUSSION

Distribution coefficients

The pertraction experiments were preceded by the determination of the equilibrium distribution of pyridine and *m*-toluidine between distilled water and the membrane liquid. The analysis of the data obtained showed that in both cases constant distribution coefficients (0.315 for pyridine and 1.5 for *m*-toluidine) were achieved when the donor phase had a pH value between 6 and 10.

Reaching the steady-state regime

The comparative studies performed on the two pertraction apparatus (see Table 2) showed that the time necessary for reaching a steady-state transport, provided a circulating membrane liquid *S*, depends on the mean linear velocity U_S of this liquid.

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Table 2 Pertraction efficiency during the steadying period.

m-toluidine, apparatus No. 1 $X_F^0 = 105$ $(mg\ l^{-1})$, $U_f = 0.04$ $[cm\ s^{-1}]$				*Pyridine, apparatus No. 2* $X_F^0 = 94$ $(mg\ l^{-1})$ $U_f = 0.008$ $[cm\ s^{-1}]$	
$U_s = 0.15$ $[cm^{-1}]$		$U_s = 0.33$ $[cm\ s^{-1}]$		$U_s = 0.15$ $[cm\ s^{-1}]$	
t $[h]$	X_f $(mg\ l^{-1})$	t $[h]$	X_f $(mg\ l^{-1})$	t $[h]$	X_F $(mg\ l^{-1})$
0	43.0	0	43.0	0	47.0
1	35.2	1	26.0	1	37.0
2	31.5	2	23.6	2	28.0
3	29.2	3	23.6	3	24.0
4	27.4	4	23.6	4	20.6
5	26.0			5	20.5
6	26.0			6	20.5

No significant differences in the extraction efficiency of the two pertractors were further established when the linear velocities of both donor solution U_F were equal and the other conditions were kept constant. The obtained results show that the steady-state regime can be reached at membrane superficial velocity $U_S = 0.3$ cm s^{-1} after the second hour since the operation start.

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Effect of the initial amine concentration

Solutions with initial amine concentrations between 1 and 100 mg l^{-1} were treated using apparatus No. 1. Figure 4 shows the dependence of the normalized final amine concentration in the donor phase (X_F^E/X_F^0) on its initial concentration X_F^0. The obtained results revealed that the concentration of amine in the initial aqueous phase has a considerable effect on the extraction efficiency of amine, i.e. on the purification extent of the initial matrix, the donor phase F. This effect was more pronounced with a circulating membrane liquid (curves 2 for pyridine and 3 for *m*-toluidine) compared to a non-circulating one (curve 1), since in the former case the hydrodynamic and concentration changes in the donor phase are the major factors determining the total resistance of the transfer processing the three-phase system.

It is worth mentioning that the effect in question was not manifested at amine concentrations in the donor solution above 80–100 mg l^{-1}. This could be related to the lower dissociation level of the amine at the higher concentrations, as only undissociated amine molecules are transferred through the oil membrane. Vice versa, the high dissociation levels of amines in very diluted solutions may be the cause for the relatively poor extraction.

Effect of the liquid membrane circulation

As it was already mentioned, the intense continuous motion of the liquid membrane contributes to the faster reaching the steady-state regime. The experimental results

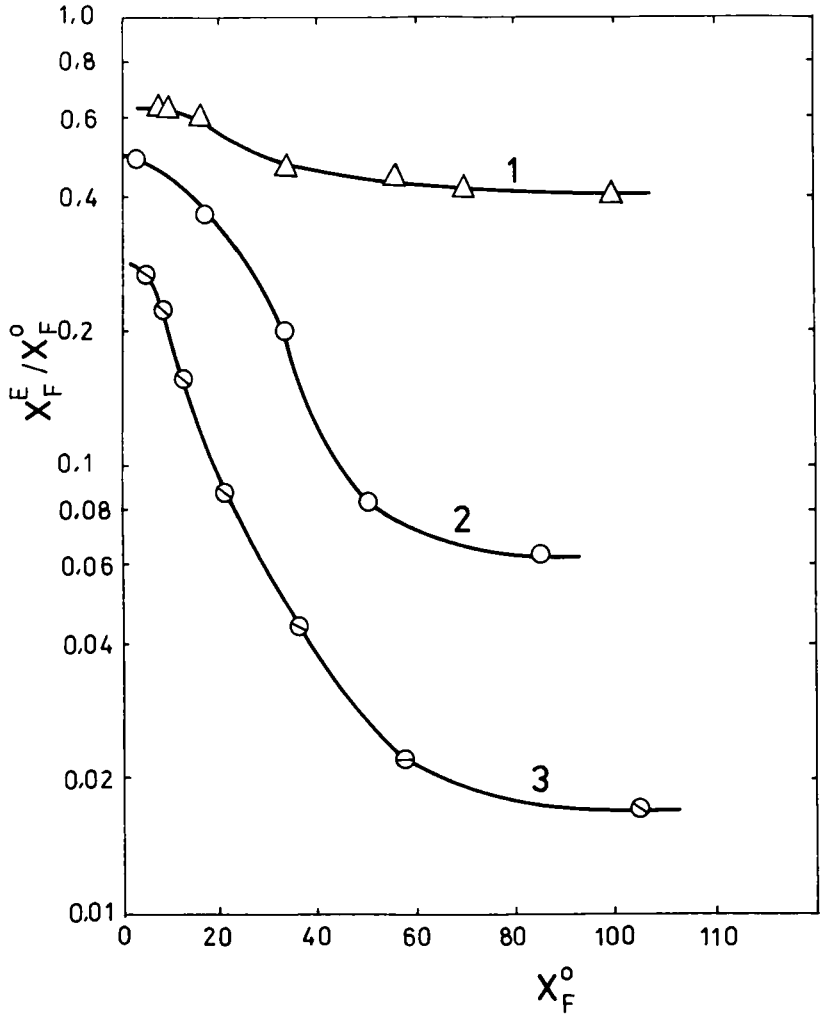

Figure 4 Effect of the initial amine concentration in the donor phase on the pertraction efficiency. (1) (△)-*m*-toluidine, $U_F = 0.04$ cm s^{-1}, $U_S = 0$, $U_R = 0.016$ cm s^{-1}. (2) (○)-pyridine, $U_F = 0.004$ cm s^{-1}, $U_S = 0.187$ cm s^{-1}, $U_R = 0.016$ cm s^{-1}. (3) (∅ ≅ ≠*m*-toluidine, $U_F = 0.004$ cm s^{-1}, $U_S = 0.187$ cm s^{-1}, $U_R = 0.016$ cm s^{-1}.

presented in Figure 5 give grounds to assume that the velocity U_S which affects the extraction extent for both model systems under the above described experimental conditions is about 0.3 cm s^{-1}.

It should be stressed, however, that stopping the pump P-3 (cf. Figure 3) does not mean that this liquid is completely motionless. The experimental results for $U_S = 0$ did not correspond to these, calculated for a completely motionless organic membrane *S*. It follows then that in this case the membrane should be regarded as pseudo-motionless. Obviously the aqueous solutions flowing down the supports and the mass transfer itself, induce some displacements in the membrane liquid.

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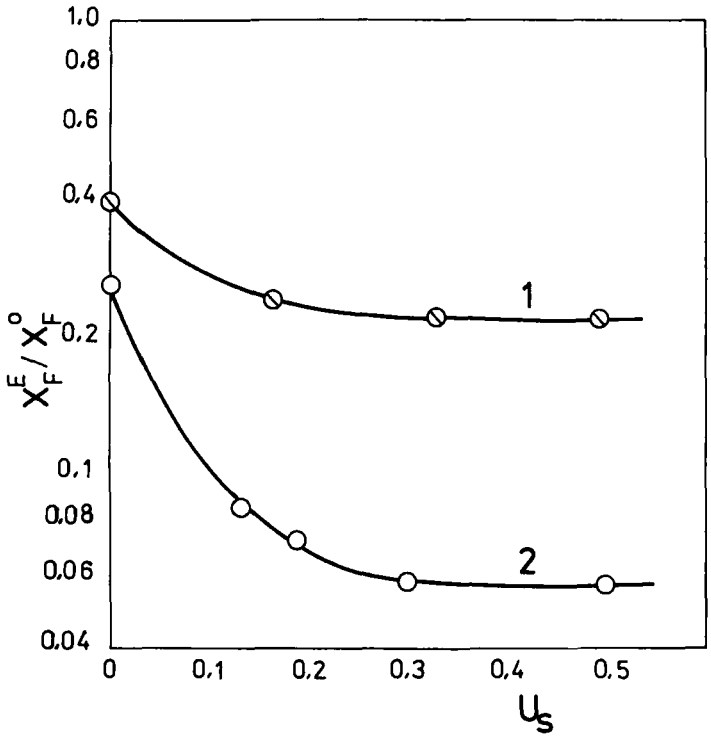

Figure 5 Effect of liquid membrane circulation velocity (U_S) on the pertraction efficiency. (1) (∅)-*m*-toluidine, $X_F^0 = 105$ mg l^{-1}, $U_F = 0.04$ cm s^{-1}, $U_R = 0.025$ cm s^{-1} (2) (○)-pyridine, $X_F^0 = 98$ mg l^{-1}, $U_F = 0.004$ cm s^{-1}, $U_R = 0.0025$ cm s^{-1}.

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Effect of donor solution flowrate

Figure 6 illustrates the effect of the flowrate of the donor solution F expressed as mean linear velocity U_F of this liquid solution through the device. The increase in U_F (or decrease of the mean resistance time of the donor solution in the apparatus) has an unfavorable effect on the extraction efficiency. The important role of this parameter may be estimated from the fact that this effect is strongly expressed both for a pseudo-motionless (curve 2) and circulating (curve 3) membrane in the case of *m*-toluidine preconcentration.

Effect of acceptor solution flowrate

Upon varying the acceptor solution flowrate Q_R in a broad range from 0.003 to 0.14 cm^3 s^{-1}, no noticeable effect on the transfer efficiency was established. This assertion is only valid when excess of acid is available in the acceptor liquid R.

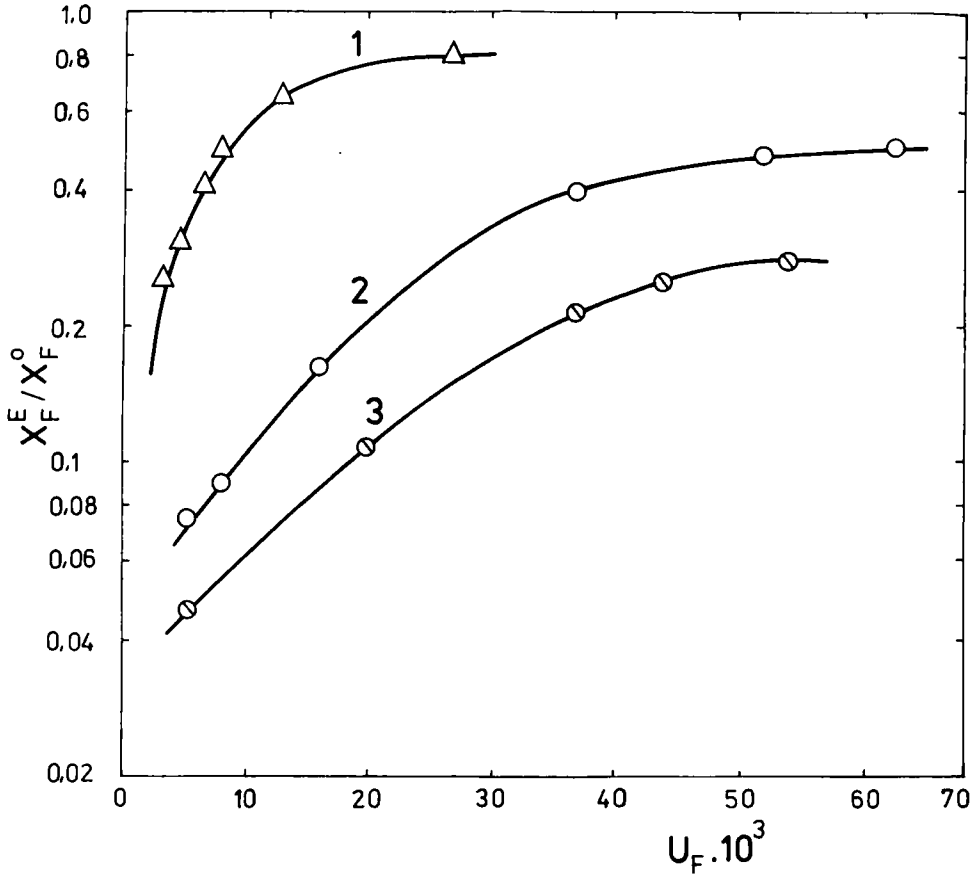

Figure 6 Effect of the mean linear velocity of the donor solution (U_F) on the pertraction efficiency for circulating and non-circulating membrane liquid. (1) (△)-pyridine, $X_F^0 = 105$ mg l^{-1}, $U_S = 0$, $U_R = 0.01$ cm s^{-1}. (2) (○)-*m*-toluidine, $X_F^0 = 109$ mg l^{-1}, $U_S = 0$, $U_R = 0.01$ cm s^{-1}. (3) (∅)-*m*-toluidine, $X_F^0 = 109$ mg l^{-1}, $U_S = 0.3$ cm s^{-1}, $U_R = 0.01$ cm s^{-1}.

Preconcentration of amines

As above mentioned, the pertraction technique provides for the simultaneous separation of the amine from the initial matrix (the donor solution F^0) and its preconcentration into a suitable medium (the acceptor liquid R). The mechanism of the transfer process of amines across the three liquids F, S and R, involves three transport steps: amine transfer from the donor aqueous solution into the organic membrane, owing to the difference in its chemical potentials in two liquids; diffusion of the amine molecules from the F/S-interface to the S/R-interface due to the concentration gradient; and stripping of the amine from the liquid membrane into the acidic acceptor solution. The transfer of amine from the F to the R solution will continue as long as the restriction $pH_R < pK_a$ is valid. The values of the latter are: 5.25 for pyridine and 4.73 for *m*-toluidine, respectively[1]. The much smaller volume of the

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acceptor solution R compared to the donor solution F permitted to achieve high enrichment factors (EF). The latter represents the ratio between the final amine concentration in the acceptor phase (X_R) and its initial concentration in the treated sample (X_F^0). It may serve as an efficiency criterion of the studied preconcentration method.

Prior to the determination of the enrichment factor, the equipment was thoroughly washed for 2 hours with distilled water along the path of the donor solution F and with 1M H_2SO_4—along the path of the acceptor solution R. This procedure was necessary for elimination of the amines or other transported substances, dissolved in the organic membrane during the previous experiments. Subsequently, the donor solution containing, for example, 1 mg l^{-1} of the amine specified was let to flow through the device and a limited volume of the acceptor solution was put in recirculation. Finally, the donor liquid was replaced by distilled water in order to achieve a complete removal of the amine from the membrane. The flow rates of the donor and acceptor solutions were maintained constant in all runs—Q_F = 140 ml h^{-1} and Q_R = 17.6 ml h^{-1}. The total amount of the membrane liquid was 600 ml, that of the recirculated acceptor solution—between 40 and 55 ml. Experiments without membrane circulation (for 24 h) as well as with a circulation rate U_S = 0.3 cm s^{-1} (for 5 or 24 h) were performed. The results are summarized in Table 3.

It follows from the obtained results that the method is characterized by a high accuracy ($\Delta X_R < 9\%$), provided a reliable information about the extraction efficiency, which depends, as mentioned above, on the donor solution flowrate (Q_F), the nature of the transferred solute and on its concentration in the treated solution (X_F^0). The latter imposes on the use of at least two experimental runs to obtain the real value of X_F^0.

The cited complication arose from the relatively low pK_a value of the used amines, as a result of which at concentrations about 1 mg l^{-1} one half of pyridine and one quarter of *m*-toluidine are present in dissociated ionic forms which are a priori not transferable. The preconcentration of substances of lower polarity and hence higher pK-values would not be probably related to such problems.

Table 3 Preconcentration of aromatic amines by the LFP method.

Run no.	*Amine*[a]	X_F° [mg l^{-1}]	V_F [ml]	V_r [ml]	U_S [cm s^{-1}]	E[b] [—]	X_R [mg l^{-1}]		ΔX_R [%]	EF [—]
							calc.	*found*		
1	P	1.0	3360	55	0	0.24	14.66	13.4	+8.5	13.4
2	P	1.0	700	55	0.3	0.50	6.36	6.0	+5.6	6.0
3	T	1.1	3700	50	0.3	0.72	58.6	54.0	+7.8	49.0
4	T	1.1	770	40	0.3	0.72	15.24	14.6	+4.1	13.3
5	T	35.0	770	50	0.3	0.95	512.0	530.0	−3.5	15.4

[a] P = pyridine, T = *m*-toluidine.
[b] Values determined from preliminary experimental data.

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CONCLUSIONS

The liquid film pertraction is a liquid membrane method suitable for selective preconcentration of aromatic amines e.g. pyridine and toluidines from their diluted aqueous solutions. The continuous motion of the thick (5 mm) membrane of *n*-paraffins reduces its mass-transfer resistance to that of a completely stagnant membrane of few μm thickness only. The method proposed provides relatively high enrichment factors ($EF = 49$ for *m*-toluidine). Solute preconcentration is a continuous operation which does not need a supervision; the "membrane" is not subjected to exhaustion or destruction hazards.

Difficulties may be encountered in the precise determination of the analyte concentration in the donor solution when very diluted solutions of species with relatively high dissociation constants are treated. A longer residence time of the donor solution in the pertractor or the usage of iterative calculation and multiple procedures may be employed in these cases.

Acknowledgment

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LIST OF SYMBOLS

E extraction efficiency [—], $E = 1 - X_F^E/X_F^0$
EF enrichment factor [—], $EF = X_R^E/X_F^0$
F donor (treated) solution [—]
K dissociation constant [—]
m distribution coefficient [—]
Q flowrate [ml h^{-1}]
R acceptor solution [—]
S liquid membrane [—]
t time [h]
U linear velocity [cm s^{-1}]
V volume [ml]
X concentration of analyte [mg l^{-1}]
ν kinematic visocosity [m^2 s^{-1}]
ρ density [kg m^{-3}]

INDICES

$F(R)$ refers to the aqueous solution $F(R)$
S refers to the organic membrane S
0 initial value
E final value

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