

Separation and Preconcentration of Ionic Solutes by Transport Extraction Based on Solvent Sublation*

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Dedicated to Professor J. Tölgyessy, in honour of his 65th birthday

The experimental capabilities of transport extraction were investigated by the help of a complex of molecular iodine with ionic surfactants. The extraction efficiency up to 95 % was obtained with a 400-fold preconcentration of iodide into benzene, using *N*-cetylpyridinium chloride. Moreover, a new method of sorbent-supported transport extraction by means of a resilient open-cell polyurethane foam has also been elaborated. The method was demonstrated in the separation of radioiodine from 4 dm³ of deionized, drinking or surface waters with N₂ carrier gas in about 60–90 min. The intercomparison showed that the nonequilibrium transport extraction gives some distinctive advantages over equilibrium solvent extraction. The kinetics of the transport extraction has also been established, from which the mass-transfer rate constant of the process can be evaluated, and the separation efficiency can be predicted in dependence on time.

Separation and preconcentration of solutes from aqueous solutions by solvent extraction is one of the most intensively used techniques in analytical practice. Nevertheless, the extraction procedures in liquid–liquid systems have a common drawback that the separation efficiency decreases with increasing ratio of aqueous phase to organic phase volume, as it follows from Nernst distribution law. This fact seriously detracts from the preconcentration performance of this technique. In normal solvent extraction the passage of the solutes into the organic phase is a result of a spontaneous distribution process during a more or less intensive mixing of phases. Under these physical conditions, it is impossible to overcome the above-mentioned drawback neither practically, nor theoretically [1, 2].

Preconcentration techniques based on the use of *adsorptive bubble (adsubble)* separation processes have received increasing attention in inorganic trace analysis. Different adsubble (flotation) techniques were used, including solvent sublation [3–13]. *Sublation* is a collection process opposite to precipitation [11], where the complex formed between a surface-active agent and an oppositely charged species, called the *sublate*, is lifted up by gas bubbles [13]. The solvent

sublation technique is an option to ion flotation where the solute (colligend) alone, which is surface-active itself or is made surface-active with a surface-active agent (collector), is adsorbed on the bubble surfaces of an ascending gas stream in water as a sublate and then collected in an immiscible liquid layer (usually an organic solvent lighter than water) placed on top of the water column [4, 10–16]. At least, a stoichiometric amount of colligend is required theoretically. In fact, this technique can be recognized as an alternative to solvent extraction and viewed as a process of nonequilibrium transport extraction.

The main difference between transport extraction and normal solvent extraction is in the role of thermodynamic parameters controlling the extent of the separation and the state of equilibrium of the process [3, 10–14]. The separation yield in normal solvent extraction is determined both by equilibrium distribution ratio of the solute between two immiscible liquid phases and their volume ratio. The mass transfer of solutes between phases is realized through immeasurably large contact surface area of phases during mixing. In transport extraction, the passage, or mass transfer of the hydrophobized solutes from stationary bulk aqueous phase into the organic layer is forced by

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the stream of bubbles of a carrier gas and the contact of the phases takes place at their interface only. Thus, thermodynamic equilibrium cannot be established in the bulk aqueous and organic phases. Therefore, the quantity of trace solute collected in the organic solvent is independent of the extraction equilibrium distribution ratio and the volume ratio of the phases as well [11–14].

Each phase separation in extraction processes is subject to loss of material, which decreases the efficiency of separation. In this paper a new technique of solvent sublation is also suggested, the so-called sorbent-supported transport extraction, which may facilitate easy manipulation of the organic phase and minimize losses. This is based on the use of an open-cell type resilient polyurethane (PU) foam sorbent and is motivated by the already successful application of PU foams in separation chemistry as quasi-solid separating media with unique geometrical and membrane properties [17, 18].

The separation of iodine from aqueous solution by solvent sublation, *i.e.* transport extraction, has been reported rather scarcely, *e.g.* by *Liu* and *Yue*, who used cetyltrimethylammonium bromide (CTMAB) [15]. The separation of iodine by ion flotation in the form of I^- [15, 19], or I_2 [16], has also been reported. The cationic surfactants used in ion flotation can apparently also be used in transport extraction. Among these, mainly *N*-cetylpyridinium chloride (CPC) proved to be the most effective, especially for molecular I_2 in the aqueous phase [16, 20, 21]. The high efficiency of the separation of iodine in this case has indicated the suitability of this surfactant for the effective preconcentration of iodine from relatively large-volume samples. Polyurethane foam-supported solvent extraction has been used previously in the separation of radioiodine from various water samples [17, 18]. The different radioiodines still evoke considerable interest in radiochemical analysis; not only ^{131}I , as a well-known important radionuclide (*e.g.* from nuclear reactor accidents [22, 23]), but also ^{129}I , a long-lived environmental radioactive contaminant [22, 24] is important. Recently, an increased attention has been paid to the determination of ^{125}I in aqueous or gaseous effluents, in connection with its medical use [22–26].

The aim of this paper was to investigate the experimental possibilities of this procedure and its intercomparison with conventional batch liquid–liquid extraction, with regard both to the separation and preconcentration efficiency, in order to verify the above-mentioned assumptions. A molecular iodine (colligend)—cationic surfactant (collector) complex pair in aqueous phase was chosen as a model system with benzene as nonmiscible solvent. The transport extraction has been carried out under static conditions with a stationary organic phase. The separation processes and this application were studied by using a radioindicator technique with ^{131}I as tracer.

THEORETICAL

There are many theoretical models available to explain the mechanism of bubble separation techniques and to predict the separation efficiency of the processes with different degree of simplifying assumptions [3, 10, 13, 14, 27]. A useful equation has been derived by *Vallebona et al.* [8] to find a relation between the separation yield and the adsorption constant and the column volume in the bubble extraction process. Essentially, the same equation can also be derived, supposing a linear adsorption distribution of trace colligend concentration (c) between liquid phase (aq) and gas bubble surface (gas). Then a respective equilibrium distribution constant (k_s), independent of the colligend and/or collector concentration, can be defined as

$$k_s = c_{\text{gas}}/c_{\text{aq}} \quad (1)$$

The other simplifying assumptions are the constant size of gas bubbles independent of the constant gas flow-rate, independence of the gas volume in the column from the gas flow-rate, the homogeneous gas distribution in the aqueous phase, and a sufficient excess of the surface-active agent to ensure the independence of collector–colligend pair formation from its concentration.

Considering a material balance

$$m_{\text{aq}}(0) = c_{\text{gas}} V_{\text{gas}}(t) + c_{\text{aq}} V_{\text{aq}} \quad (2)$$

where $V_{\text{gas}}(t)$ denotes the volume of the gas phase passed through the column in gas bubbling time t , $m_{\text{aq}}(0)$ is the initial amount of the solute in the aqueous phase ($t = 0$) and $c_{\text{gas}} V_{\text{gas}}(t) = m_s(t)$ is the amount of the solute adsorbed on the surface of the gas bubbles and transport extracted into the water-immiscible liquid in bubbling time t , a simple equation of the theoretical nonequilibrium transport extraction efficiency under static (batch) condition with stagnant organic phase can be derived in terms of transport extraction (solvent sublation) coefficient (K_s)

$$E_s(t) = m_s(t)/m_{\text{aq}}(0) = K_s/(K_s + V_{\text{aq}}) \quad (3)$$

where

$$K_s = k_s V_{\text{gas}}(t) = k_s \cdot v_{\text{gas}} \cdot t \quad (4)$$

If $m_s(t)$ is expressed as the mass fraction, then $m_{\text{aq}}(0) = 1$. From eqn (4) it is obvious that $E_s(t)$ is independent of the volume of the organic phase (V_{org}).

By comparison of eqn (3) with the well-known equation for the separation efficiency of conventional equilibrium solvent extraction under static (batch) conditions [1, 2] (E_e)

$$E_e = m_e/m_{aq}(o) = K_d/[K_d + (V_{aq}/V_{org})] \quad (5)$$

where m_e is the extracted and $m_{aq}(o)$ is the initial amount of a solute and K_d is the equilibrium distribution ratio of a solute between phases of respective volumes, it is possible to evaluate the theoretical separation and/or preconcentration potentials of these two techniques.

During the process of transport extraction an enrichment of the sublute at the upper end and its depletion at the lower end of the column takes place [12–14, 27]. This results in accumulation of the colligend at the organic phase–aqueous phase interface, where true equilibrium distribution of the solute is only established between phases. The value of K_s , which contrary to the dimensionless K_d , has the dimension of volume (eqn (4)), is increasing during transport extraction and reaches its maximum value at the end of the process. Combining eqn (3) and eqn (4) it follows that for a given time of bubbling t

$$E_s(t) = (K_s/V_{aq})/[(K_s/V_{aq}) + 1] = \text{const} \quad (6)$$

From eqn (6) it is evident that the transport extraction efficiency is independent of the volume of the aqueous phase (V_{aq}). Contrary to the transport extraction efficiency ($E_s(t)$), the solvent extraction efficiency (E_e), as it follows from eqn (5)

$$E_e = (K_d \cdot V_{org})/[(K_d \cdot V_{org}) + V_{aq}] = [1 + (V_{aq}/\text{const})]^{-1} \quad (7)$$

is dependent on the V_{aq} (at constant V_{org}) and it decreases with increasing value of V_{aq} . These findings reveal the theoretical principles of transport extraction separation and explain the basic difference between transport extraction and conventional extraction from the theoretical point of view. It is assumed that these observations are valid for ideal liquid–liquid systems, and where the capacity of the organic phase for the separated compound will not be exhausted. In real analytical separations some decrease in the efficiency may be expected in handling larger volumes of water due to possible deviations from the ideality and losses.

Literature data show that the transport extraction based on precipitate flotation does not follow any of the usual rate laws [28, 29]. In the ion-flotation the kinetics of the removal of a solute can be approximated mostly by a direct or reversible first- or second-order chemical reaction [9, 10, 28–31]. One of the possible solutions could also be made by the application of eqn (3), which can be rewritten using eqn (4) as

$$m_s(t)/m_s(\infty) = 1/[1 + (V_{aq}/k_s \cdot v_{gas} \ t)] \quad (8)$$

where $m_s(t)$ and $m_s(\infty)$ are the amounts of a solute subluted into the organic phase in time t , and $t = \infty$, respectively and $v_{gas} = V_{gas}(t)/t$ is the carrier

gas flow-rate. Since $E_s(t)$ is directly proportional to $m_s(t)$ and $E_s(\infty)$ is directly proportional to $m_s(\infty) = m_{aq}(o)$ (where $m_{aq}(o) = c_{aq}(o) \ V_{aq}$ at $t = 0$),

$$E_s(t) = E_s(\infty) [1 + (k_r \ t)^{-1}]^{-1} \quad (9)$$

where $E_s(t)$ and $E_s(\infty)$ are the theoretical transport extraction efficiencies at time t and $t = \infty$, respectively, and

$$k_r = k_s \cdot v_{gas}/V_{aq} \quad (10)$$

is the transport extraction (mass-transfer) rate constant. (It is obvious that $E_s(\infty)$ theoretically is equal to 1 (or 100 %) and the possible deviations can be caused by the insufficiency of idealized approach to the real transport extraction system, when $m_s(\infty) \neq m_{aq}(o)$.) The final equation used for theoretical calculations was derived from eqn (9) in the following linearized form

$$t/E_s(t) = (t/E_s(\infty)) + (1/k_r \ E_s(\infty)) \quad (11)$$

Obviously, the $t/E_s(t) = f(t)$ function can be used for fitting the obtained experimental values of the transport extraction efficiency ($E_{s,\text{exp}}$) and in either of its forms (eqn (9) or (11)) also for the calculation of both the theoretical transport extraction efficiency ($E_{s,\text{theor}}$) and k_r for each particular case. On the other hand, eqn (10) can also be used for the calculation of the actual values of k_s and K_s as well as using eqn (4).

EXPERIMENTAL

Reagents and solvents were of anal. grade. As cationic surfactants, cetyltrimethylammonium bromide (CTMAB) and *N*-cetylpyridinium chloride (CPC) were used of DAB purity (Merck, Darmstadt, BRD). Sodium laurylsulfate (NaLS) (Reanal, Budapest, Hungary) was used as anionic surfactant. The nitrogen gas was of technical purity and was neither purified nor wetted before use.

Deionized, tap (drinking) and Danube river waters were used. The deionized water was prepared from common distilled water passing through a column of specially treated cellulose according to the method described in [32]. The river water samples were filtered through a laboratory filter paper to remove coarse mechanical impurities.

As a sorbent support, polyether-type open-cell polyurethane (PU) foam, Type A-32, of 32 kg m⁻³ specific mass (Chemical Works, Sajóbáony, Hungary) was used and cut into plugs of 5 cm in diameter and of 4 cm thickness and cleaned by the method described, *e.g.* in [18, 33].

Two different simple laboratory transport extraction equipments were used. The smaller consisted of a glass column (inner diameter 4.4 cm and height 80

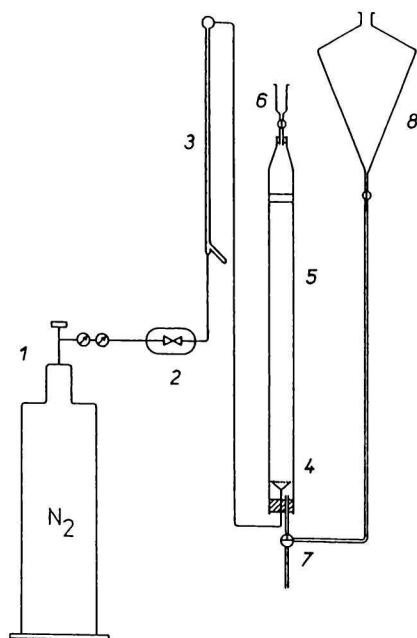


Fig. 1. Schematic representation of the transport extraction equipment: 1. gas cylinder with regulator, 2. fine needle valve, 3. flow meter, 4. sparger, 5. column filled with water sample and benzene layer, 6. separatory funnel, 7. three-way stopcock, 8. separatory funnel.

cm), equipped with a sintered glass sparger frit (G3 porosity and 4 cm in outer diameter) at the bottom and a three-way glass stopcock for aqueous sample inlet, connected to a separatory funnel, and outlet. On the top of the column a 25 cm³ glass funnel was attached, fitted with a ground joint and a stopcock for sampling the organic phase (Fig. 1). The larger flotation set-up consisted of a 4.5 dm³ glass column (6.2 cm in inner diameter and 150 cm height), equipped with a sintered glass sparger frit G3 (6 cm in outer diameter) and a two-way glass stopcock for sample outlet at the bottom. No separatory funnel was attached to the larger column. Both the sparger and the vertical tube of the stopcock were fitted to the columns through a suitable bored rubber stopper. The sparger of each column was connected to a pressurized N₂ gas cylinder, equipped with a pressure regulator, through a fine pressure needle valve for controlling the gas flow. For measuring the gas flow-rate through the column, a soap-bubble flow meter was inserted between the pressure valve and the column.

Static (batch) solvent extraction was made in a conventional 2 dm³ glass separatory funnel.

The activity of ¹³¹I in the aliquots of the aqueous and organic phase was measured with suitable well-type NaI(Tl) scintillation detector coupled to a single channel amplitude analyzer. The counting conditions were chosen in such a way that they can approximately be made with the same counting statistics. The uncertainties of these measurements never exceeded 1 % of

relative standard deviation (RSD) and were included into the overall uncertainties of the analysis.

Transport extraction: Water samples up to 1 dm³ were analyzed in the smaller column and treated in the attached separatory funnel. The procedure is described for 1 dm³, containing a required amount (0.5–10 cm³) of freshly prepared 0.01 mol dm⁻³ NaI solution. A sufficient amount of ¹³¹I tracer (as NaI) was added and the pH was adjusted to about 1 by 2.5 cm³ of concentrated H₂SO₄. After mixing for about 2 min, the iodide in the sample was oxidized to I₂ with 0.5 cm³ of 1 mol dm⁻³ NaNO₂ solution. After shaking for about 1 min, a required amount of an aqueous solution of a given surfactant in 0.01 mol dm⁻³ concentration was added (in the case of CPC, 7.5 cm³ was found to be the optimum). Following the addition of 10 cm³ of ethanol (to control the size and ensure uniform N₂ bubble generation and to prevent micelle formation) and careful mixing, the sample was transferred onto the column. Finally, 10 cm³ of benzene was poured onto the top of the aqueous sample from the upper funnel and the stopcock was left in the open position to allow the gas to leave the column. When sample solutions of different volumes were taken into the experiment, the volumes of the used reagents were proportionally adjusted to keep their volume ratios constant, except that of the organic phase. After filling the column, nitrogen was passed through the column at a constant flow-rate of 15 cm³ min⁻¹. If the transport extraction lasted more than 60 min, some losses of organic phase have occurred by evaporation. Therefore, during the bubbling, several cm³ of benzene were added to maintain the volume at exactly 10 cm³.

Samples of higher volumes than 1 dm³ were analyzed in the larger column, treated as described above, in a 2 dm³ separatory funnel or in a 5 dm³ beaker. The sample solution was carefully mixed by swirling for about 3 min to avoid froth formation. The content of the separatory funnel or beaker was poured into the column by its upper end. After filling the column with the sample 10 cm³ of benzene was placed onto the top of the aqueous phase. Then a stream of N₂ was introduced into the column through the frit at a constant flow-rate between 15–60 cm³ min⁻¹. It has to be noted that higher flow-rates than 30 cm³ min⁻¹ led to increasing formation of bubbles in the column, followed by a very rich froth formation over the organic layer escaping from the column. If necessary, this froth can be destroyed, e.g. with ethanol sprayed on the top of the column.

In the course of each run, 20 cm³ aliquots of the aqueous sample were taken from the lower part of the smaller column through the sample outlet for activity counting. After counting, the aliquots were returned to the column in 3 min. The separation efficiency was determined by difference from the respective countings before and after the transport extraction. Completing the separation, the organic solution was ele-

vated into the upper funnel of the smaller column lifting the aqueous solution in the separation funnel filled with a sufficient amount of added deionized water, and prepared for further analysis. In the larger column, completing the separation and destroying the froth by standing for several minutes, the benzene layer was pipetted off from the column and adjusted to 10 cm³. Finally, 1 cm³ of this transparent orange yellow solution was diluted to 20 cm³ with benzene and counted. The colour of this solution was found to be stable over several weeks.

Sorbent-supported transport extraction: After filling the larger column with the 4 dm³ sample treated as above, 10 cm³ of benzene was pipetted onto the surface of the aqueous phase. Then the PU foam cylinder was placed on the top of the column so that the cylinder was fully soaked with the benzene layer. In this operation, swelling of the foam support takes place, which causes a tight contact between the foam plug and the wall of the column. Finally, the foam plug was fixed by means of an inverted glass beaker placed on the column. Nitrogen carrier gas was then introduced into the lower end of the column, maintaining a flow-rate of about 55–60 cm³ min⁻¹ (In the case of intensive froth formation see the procedure as above.) The separation efficiency for each observed time interval was determined as above. After completing the separation in 1–1.5 h and stopping the gas stream, the foam plug was removed from the column. Following air drying on a sheet of filter paper, the foam disc was prepared for direct ¹³¹I activity counting [18, 25, 33], or for indirect activity measurement of radioio-

dine after its elution with acetone from the PU foam sorbent [18]. In the direct activity counting, the foam plug can be measured either in released, or compressed geometry when the best counting efficiency is attained [33]. If the elution technique is applied (*e.g.* for the determination of stable iodine) the iodine–surfactant associate is back-extracted from the PU foam plug by causing 3 to 4 pulsations with several (*ca.* 5) 25 cm³ aliquots of acetone while the tip of a syringe is kept in the solvent. This extract can be used for further analysis.

Solvent extraction: In these experiments the same reagents were used under identical conditions. The phases were shaken for 2 min, then left to stand for phase separation as required. After standing, 20 cm³ aliquots were taken from the aqueous phase. The separation efficiency was determined from the activities of ¹³¹I of the respective aliquots of the aqueous phase before and after separation, respectively.

RESULTS AND DISCUSSION

Preliminary experiments were made with smaller transport extraction column at constant N₂ flow-rate of 15 cm³ min⁻¹. Favourable results were obtained by modifying a method of *Liu and Yue* [15], using an aliphatic CTMAB cationic surfactant. These indicate a marked dependence of the separation efficiency on the I₂ concentration. The decrease of the extraction efficiency for concentrations of iodide lower or higher than the optimum concentration range is caused by the inherent nature of the ion flotation as it is ex-

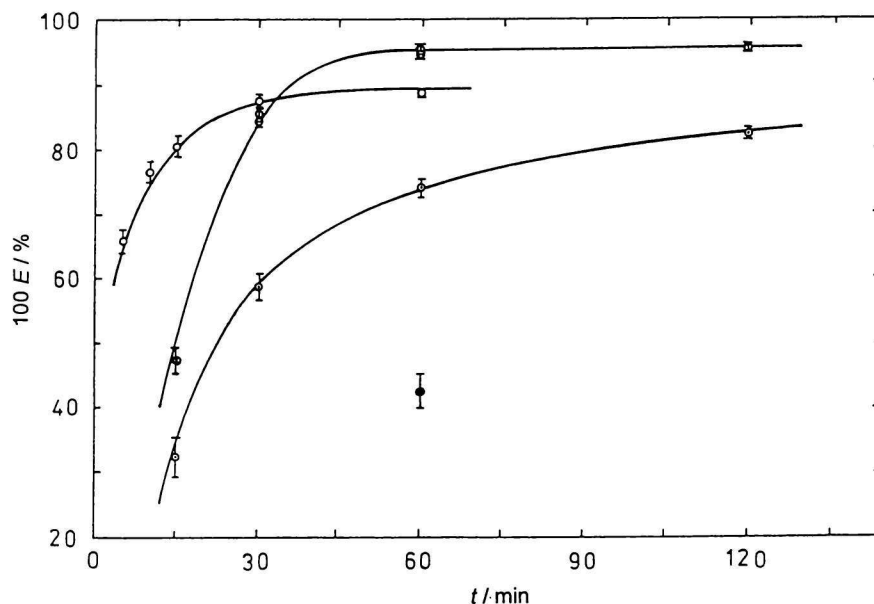


Fig. 2. Transport extraction efficiency 100 *E* of I₂ from 200 cm³ of its 2.5 × 10⁻⁵ mol dm⁻³ solution at pH 1 and surfactant to I₂ mole ratio of 3:1 as a function of bubbling time at 15 cm³ min⁻¹ gas flow-rate: ○ with CTMAB, ◊ with CPC, ◐ with NaLS and ● without surfactants into benzene, and ◑ with CPC into xylene; average of 3 runs.

Table 1. Experimental Transport Extraction and Solvent Extraction Efficiency of $2.5 \times 10^{-5} \text{ mol dm}^{-3} \text{ I}_2$ ($V_{\text{org}} = 10 \text{ cm}^3$, Average of 3 Runs, RSD = 0.5–3 %)

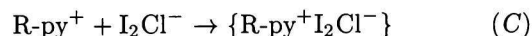
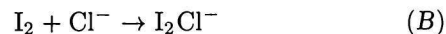
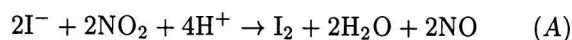
V_{aq} cm ³	t min	100 × Separation efficiency/%		
		Transport extraction with CPC	Solvent extraction	
			with CPC	without CPC
200	15		90	91
	30	86	93	90
	60	96	97	
500	15			80
	30	83	89	80
	60	93	91	–
	120	96	93	
1000	15			66
	30	59	82	66
	60	86	87	
	120	95	87	
	180	96		

Note: Time of solvent extraction includes phase separation.

plained in detail, *e.g.* in [13, 14, 19]. From this explanation it follows that the optimum concentration of the colligend is in the range of 10^{-5} to $10^{-3} \text{ mol dm}^{-3}$. It was also found that the efficiency of transport extraction does not differ considerably when changing the pH from 1 to 6 and that the collector to colligend mole ratio between 1:1 and 5:1 has a moderate effect on the separation efficiency. Nevertheless, it seems that the ratio of the surfactant to I_2 of about 3 gives optimum results.

Further experiments were done with another, aromatic CPC cationic surfactant, as recommended previously by Koizumi [16]. These experiments, under the same conditions led to better results. The effect of the bubbling time on the transport extraction efficiency is presented in Fig. 2. It can be seen that it is possible to obtain an almost quantitative transport extraction of iodine in about 60 min. The organic solvent showed no effect on the separation efficiency, when instead of benzene other immiscible solvent, *e.g.* *o*-xylene was used. From the figure it is also evident that I_2 itself has certain surface-active properties and it can be transport-extracted not only with NaLS, a typical anionic surfactant, but also alone, with a moderate separation efficiency. Similarly, as in the case of CTMAB, iodide cannot be extracted effectively even with CPC and under identical conditions only *ca.* 10 % separation efficiency was obtained.

In the case of I_2 , the interaction with CPC cationic surfactant is quite different from that of I^- . Some authors assume a formation of a molecular complex between CPC and I_2 [16, 34], resulting in a precipitate [35, 36]. This interaction proceeds through three steps, involving the oxidation of iodide to iodine (A), formation of a complex anion (B), and precipitation of the formed ionic associate (C)



where py^+ denotes the pyridinium cation and R the cetyl group. The above described complex formation may also occur in the CTMAB and I_2 interaction, but apparently not with subsequent precipitate formation. A higher separation efficiency of iodine obtained with CPC can be attributed to higher hydrophobicity of the $\text{CP}^+\text{I}_2\text{Cl}^-$ ionic precipitate in comparison with less hydrophobic CTMAB: I_2 molecular associate.

The results in Table 1 show that the separation efficiency of the transport extraction is independent of the volume of the aqueous phase in the studied range from 200 to 1000 cm³. The time of bubbling to reach maximum separation efficiency is dependent on the volume of the aqueous phase and for volumes higher than 200 cm³ it takes more than 60 min.

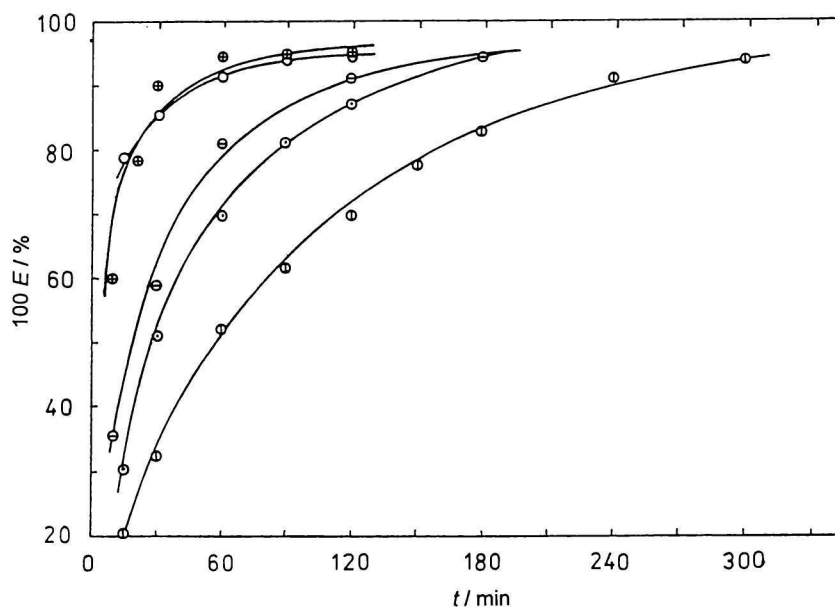
In parallel with the transport extraction, solvent extraction experiments were carried out under the same experimental conditions shaking the respective phases in a separatory funnel. The data given in Table 1 show that the separation efficiency in conventional solvent extraction is dependent on the volume of the aqueous phase, *i.e.* on the volume ratio of the aqueous phase to the organic phase and decreases with its increasing values, especially in the case when no surfactant is used. In shaking the phases, when CPC was also added, a copious froth formed, which makes necessary to wait 60–120 min for the froth settling down before radioactivity counting. In fact, some froth formation over the organic phase was also observed during transport extraction, but its amount was far less than in the solvent extraction and it can easily be destroyed by adding several drops of ethanol on the froth. The use of this froth destroying method in the case of solvent extraction is less effective and it can

Table 2. Calculated Values of K_s and K_d , Using Eqns (3) and (5), under Conditions Given in Table 1

V_{aq} cm ³	100 $E_{s,exp}/\%$		K_s cm ³	K_d	
	with CPC	without CPC		with CPC	without CPC
200	96	97	4800	647	180
500	96	93	12000	664	200
1000	96	87	24000	669	194

Table 3. Effect of I_2 Concentration on the Transport Extraction Efficiency of I_2 at 15 cm³ min⁻¹ N₂ Flow-Rate ($V_{aq} = 1$ dm³, 3 Runs, RSD < 3 %)

Concentration of I_2 mol dm ⁻³	$n(CPC):n(I_2)$ mol mol ⁻¹	100 × Transport extraction efficiency/%		
		Bubbling time/min		
		60	120	180
2.5×10^{-6}	30.0	69	71	73
1.0×10^{-5}	7.5	88	90	93
2.5×10^{-5}	3.0	92	94	95
5.0×10^{-5}	1.5	79	92	94

**Fig. 3.** Transport extraction efficiency 100 E of I_2 as a function of bubbling time for various volumes of aqueous phase: \circ 1 dm³, \odot 2 dm³, and \oplus 4 dm³ at constant gas flow-rate of 15 cm³ min⁻¹ and for various gas flow-rates: \ominus 15 cm³ min⁻¹, Θ 30 cm³ min⁻¹, and \oplus 60 cm³ min⁻¹ at constant aqueous phase volume of 4 dm³; average of 3 runs, RSD < 3 %; respective solid curves: theoretical values.

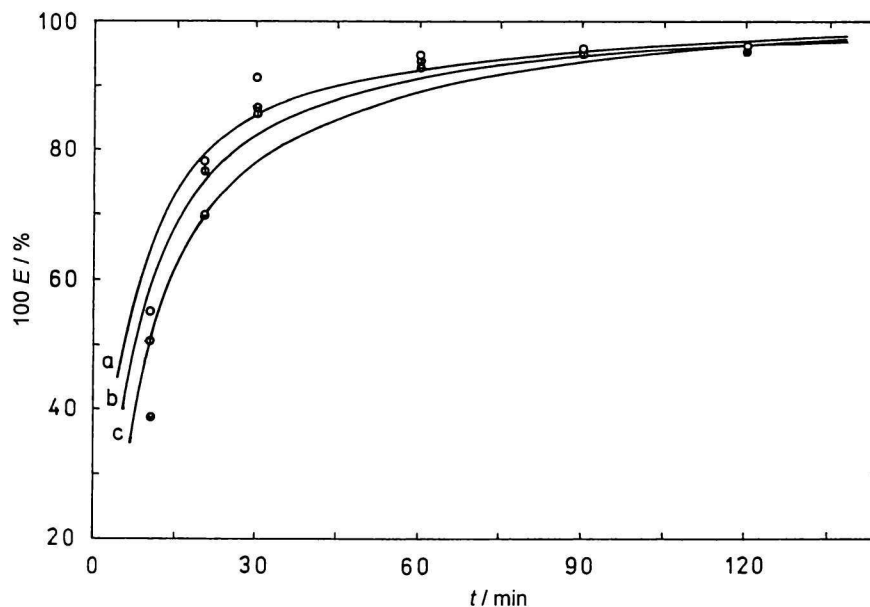
also cause dissolution of a thin benzene layer in the bulk aqueous phase. The results presented in Table 1 fully confirm the assumptions given in the introductory and theoretical parts of this paper in respect to the unlimited independence of the separation efficiency from the aqueous phase volume in transport extraction.

From Table 2 it can be seen that the value of K_d in the solvent extraction of I_2 with CPC, is more than 600. Without CPC it is around 200. K_d is practically

constant and independent of the aqueous phase volume. In agreement with eqn (3), K_s increases proportionally with increasing volume of the aqueous phase; however the ratio of K_s to V_{aq} remains constant, as follows from eqn (6). Under given conditions K_d/V_{aq} is around 24. The value of 100 E_s is close to its maximum value and practically independent of the volume of the aqueous phase. This fact makes possible to obtain relatively high values of preconcentration also at unchanging high value of the separation effi-

Table 4. Dependence of Mass-Transfer Rate Constant (k_r), Maximum Theoretical Transport Extraction Efficiency ($E_s(\infty)$), and Colligend Equilibrium Distribution Constant (k_s) on the Volume of Aqueous Phase and on the Carrier-Gas Flow-Rate (Correlation Coefficient, $r^2 = 0.9982$ – 0.9999)

Sample volume	Carrier-gas flow-rate	k_r	100 $E_s(\infty)$ calculated	k_s
dm ³	cm ³ min ⁻¹	min ⁻¹	%	
1	15	0.2460	97.94	16.4
2	15	0.0263	114.82	3.5
4	15	0.0126	119.34	3.4
4	30	0.0482	106.07	6.4
4	60	0.1993	100.23	13.3

**Fig. 4.** Transport extraction efficiency 100 E of ^{131}I from various water samples as a function of bubbling time at 60 cm³ min⁻¹ gas flow-rate: ○ deionized, ⊙ tap and ⊗ river water; average values of 3 runs, RSD 3 %; solid curves: theoretical values for a deionized, b tap, and c river water.

ciency. Further results and discussion are based on the experimental study carried out with larger transport extraction column. Table 3 shows that for a I^- concentration of about 1–10 mg dm⁻³, the efficiency is practically independent of the iodine concentration if sufficiently long bubbling time is applied. It was confirmed that the optimum surfactant to iodine ratio is around 3 (mol/mol). The activity measurement of the benzene solutions showed that the separation efficiencies calculated from the organic phases and from the aqueous phases are within the experimental error.

The results presented in Fig. 3 again confirm the theoretical assumptions that the volume of the aqueous phase has no influence on the separation efficiency in the studied range of volumes, but for a higher volume longer bubbling time is needed. Since the required bubbling time for the analysis of samples of higher volumes than 1 dm³ has been proved to be rather long, in the next experiments the effect of the N_2 -gas flow-

rate on the transport extraction efficiency was investigated in order to accelerate the separation process. From Fig. 3 it is evident that the increase of the gas flow-rate considerably reduces the duration of the separation, which can be accomplished even from a 4 dm³ sample with 60 min bubbling time at a transport extraction efficiency of about 0.95 and a 400-fold preconcentration. A good agreement has been found between experimentally observed and theoretically calculated values of the transport extraction efficiency using eqn (11).

Table 4 shows, according to eqn (10), that the value of k_r decreases as the volume increases, but it increases with increasing the gas flow-rate. It is seen that with increasing volumes of the aqueous phase the $t/E_s(t) = f(t)$ function, calculated according to eqn (11), begins to deviate from the reality ($E_s(\infty)$ has to be 1), whereas it becomes more realistic with increasing flow-rate. Throughout the experiments, the size of

Table 5. Transport Extraction Efficiency ($E_{s,\text{exp}}$) of ^{131}I after 60 min Gas Bubbling at $60\text{ cm}^3\text{ min}^{-1}$ Flow-Rate with Values of k_r and $E_s(\infty)$ for Various Water Samples (3 Runs, RSD < 1 %, $r^2 = 0.996\text{--}0.999$)

Water sample	100 $E_{s,\text{exp}}$ from aqueous or organic phase		k_r	100 $E_s(\infty)$ calculated	k_s
4 dm ³	%		min ⁻¹	%	
Deionized	95	95	0.1799	100.85	12.0
Tap ^a	94	94	0.1434	101.35	9.6
River ^b	93	92	0.0925	104.73	6.2

a) Composition (mg dm⁻³): chlorides (10.1), phosphates (0.1), nitrates (13.4), nitrites (0), sulfates (66.8), ammonia (0), Fe (0), Mn (0), organic substances (0.9), total hardness 15.7 and permanent hardness 4.2 German degrees, pH 7.6. b) Composition (mg dm⁻³): chlorides (11.5), phosphates (0.01), nitrates (12.6), nitrites (0.2), ammonia (0.1), Fe (0), Mn (0), O₂ (9.8), total hardness 11.4 German degrees, pH 7.8.

the gas bubbles was kept constant and apparently did not change in the range of the gas flow-rate of 15 to $60\text{ cm}^3\text{ min}^{-1}$.

Experiments with sorbent-supported transport extraction have shown that the used PU foam effectively absorbed the solution of $\text{CP}^+\text{I}_2\text{Cl}^-$ ionic associate in benzene and that the sorbed associate could also be back-extracted from the foam into acetone [37]. This enabled the PU foam sorbent to be used as a solid support in transport extraction of iodine. The results and discussion presented here are based on the experimental study made with larger transport extraction column at $55\text{--}60\text{ cm}^3\text{ min}^{-1}$ carrier gas flow-rate. In the experiments described here only the effect of bubbling time and/or carrier gas flow-rate on the PU foam-supported transport extraction efficiency was investigated. As expected from previous results, 60 to 90 min bubbling time was sufficient for maximum separation efficiency amounting to 0.95 for all water samples (Fig. 4). Table 5 shows some slight differences in the values of separation efficiencies of ^{131}I between deionized and environmental water samples. Such but slight variation in the efficiency may be explained by a decrease in the mass-transfer rate constant (k_r) of iodine from environmental waters in comparison with deionized water. A higher salt content and ionic strength in tap water and also other impurities in river water should increase the content of interfering substances decreasing the k_r of $\text{CP}^+\text{I}_2\text{Cl}^-$ from aqueous phase to bubble surface ascending into the organic phase. The values of k_r and $E_s(\infty)$ were calculated according to eqn (11).

In Tables 4 and 5 the values of k_s calculated from eqn (10) are also presented. A statistical investigation of the data shows a good correlation between k_s and k_r for the calculated average values of $100 E_s(\infty)/\% = 100.1 \pm 1.5$, the ratio of k_s to k_r being 67.0 ± 0.5 , independently from the sample volume and carrier gas flow-rate. Under these conditions the average value of k_s is 12.8 ± 2.8 . Table 5 also shows that almost no differences were observed between measurement in organic and aqueous phase provided that the ^{131}I activ-

ity counting was made under identical geometry. The best counting efficiency was obtained, when the PU foam plug was compressed into the smallest possible volume of about $12\text{--}15\text{ cm}^3$, e.g. in a suitable plastic syringe [18, 33]. A preconcentration of about 300-fold can be obtained by this direct method.

The possibility of the indirect counting of ^{131}I after its back-extraction from the PU foam plug was also investigated. This method is particularly useful in the determination of stable iodine separated from water samples, e.g. by spectrophotometry [15]. The $\text{CP}^+\text{I}_2\text{Cl}^-$ ionic associate can easily be back-extracted by successive extractions with several portions of acetone. Using a pulsating syringe technique, the average back-extraction efficiency after 6 extractions with 25 cm^3 aliquots of acetone was 0.94, with a RSD of less than 2 %. This value indicates that the overall separation efficiency of ^{131}I (transport extraction and back-extraction) from the water samples used lies between 86–89 %. The colour of the slightly turbid solution was lemon yellow. After standing for several minutes, the solution became transparent and some white precipitate, most probably K_2SO_4 , settled out. This precipitate did not carry any ^{131}I radioactivity, so it does not interfere in the radioiodine or iodine determination. In the indirect method even higher preconcentration can be obtained than in the direct method after suitable evaporation of the acetone extract.

CONCLUSION

Transport extraction can be advantageously used in the effective preconcentration of trace amounts of solutes in liquid–liquid systems, where the normal equilibrium solvent extraction fails owing to the low distribution ratio of the solutes and the strong dependence of its separation efficiency on the volume ratio of the aqueous to organic phase. In the nonequilibrium transport extraction technique, the aqueous and organic phases are in contact only at the measurably small surface area, which is negligible in comparison with the surface area formed in conventional static or

dynamic solvent extraction techniques. Therefore, the transport extraction is not governed by the Nernst distribution law and its theoretically high constant separation efficiency, even at low distribution ratios, is not dependent on the volume of the aqueous phase or on the ratio of the phases.

Transport extraction proved to be convenient in the separation of iodine and appears to be competitive to conventional solvent extraction or precipitation techniques also from the kinetic point of view. Its further advantages over normal solvent extraction are the easy handling of both large-volume samples and small-volume extracts. The main limitation of transport extraction in this particular case could be the relatively high and narrow concentration range of iodine, which may restrict the use of this method to, *e.g.* mineral or wastewater. However, the preconcentration of radioiodine from water with properly adjusted iodine carrier concentration, is very effective. Since iodine is in an oxidizing medium, it may be possible to use air as the bubbling gas in place of nitrogen. This would simplify the gas system for the extraction equipment, using a commercially available cheap peristaltic air pump.

Polyurethane foam sorbent-supported transport extraction has proved to be effective in the separation and preconcentration of both radioiodine and stable iodide also from environmental water samples. The proposed new technique avoids the escape of the organic solvent and minimizes the losses of the separated solute. The selectivity of the iodine separation has not been investigated, however, possible coextractions of anions and cations (commonly present, *e.g.* in environmental waters), which may decrease the separation efficiency of iodine, are not to be expected. Further, it is unlikely that the other important cationic uranium fission products, in the case of ^{131}I and ^{129}I , or some medically important radionuclides, in the case of ^{125}I , would interfere seriously under the conditions described.

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