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SOLVENT EXTRACTION IN FLOW-INJECTION ANALYSIS A REVIEW

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A review with 63 references presents fundamentals and applications of solvent extraction in flow-injection analysis. The factors affecting the efficiency of solvent extraction in flow conditions and problems associated with design of particular flow-through modules of measuring systems are discussed. Applications of flow-injection analysis involving on-line solvent extraction with various detection methods such as VIS spectrophotometry, fluorimetry and AAS are reviewed.

Przegląd dokonany w oparciu o 63 pozycje literaturowe dotyczy podstaw i zastosowań ekstrakcji rozpuszczalnikowej w przepływowej analizie wstrzykowej. Przedstawiono czynniki wpływające na efektywność ekstrakcji w warunkach przepływowych oraz podstawowe problemy związane z konstrukcją poszczególnych modułów układu przepływowego, które umożliwiają prowadzenie tego procesu. Przedstawiono zastosowania ekstrakcji w układach przepływowo-wstrzykowych z różnymi rodzajami detekcji, takimi jak spektrofotometryczna, fluorymetryczna i metoda atomowej spektrometrii absorpcyjnej.

One hundred years since the law of distribution of given substance between two immiscible liquid phases was formulated by Nernst, the solvent extraction plays a significant role among separation and preconcentration methods of modern chemical analysis. Numerous authors have contributed to the theoretical development of solvent extraction basing on solution chemistry and ionic equilibria in solutions. Analytical literature provides a large number of examples of the use of chelate complexes, ion-association compounds with high-molecular amines, acidocomplexes and salts solvated by coordination of phosphoroorganic compounds in solvent extraction. Although those methods are very often burdensome because of necessity of the use of volatile and harmful solvents, they are

inclued in many standard analytical procedures, where they are performed manually or in continuous or automated extractors.

The distribution of a given substance between two immiscible phases can be also carried out in low pressure column processes in extraction chromatography, where extracting phase is immoblized on porous stationary support or in high performance partition liquid chromatography.

Another concept of performing solvent extraction was developed in sixties, initially for continuous flow analysis, where streams of solutions were segmented with air bubbles. The segmentation of sample zone with extracting solution and transportation of such a multiphase immiscible system along appropriate distance of coiled tubings could be easily incorporated into a given manifold for clinical, environmental or food analysis.

Later the same concept of solvent extraction in flow conditions was adapted for more advanced flow measurements with strictly controlled dispersion and without air segmentation, which is commonly known as flow-injection analysis [1]. Appropriate design of extraction modules with thorough chemical and hydrodynamic optimization of the flow system performance, enables to preserve in flow-injection systems with on-line solvent extraction all basic advantages of flow-injection analysis. They include a large sample throughput and small sample consumption, whereas due to on-line solvent extraction the improvement of detectability and selectivity can be usually expected.

The aim of this review is to present basic problems involved in the optimization of solvent extraction sample pretreatment in flow-injection analysis and its applications reported in analytical literature.

FUNDAMENTALS OF SOLVENT EXTRACTION PROCESS IN FLOW-INJECTION SYSTEMS

A general scheme of the flow-injection manifold with solvent extraction step is shown in Fig. 1. The sample to be analyzed is injected into the stream of aqueous carrier solution and then one of the following processes can occur:

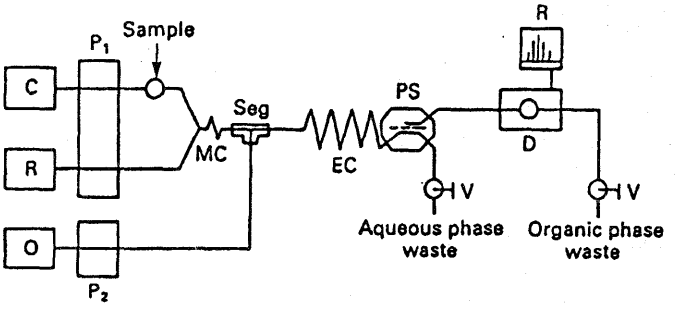

Fig. 1. Typical arrangement of a flow-injection extraction system [19]. P_1, P_2 – peristaltic pumps, C – carrier (aqueous phase), R – reagent stream (aqueous phase), O – organic phase, S – injection valve, MC – reaction coil, Seg – segmentor, EC – extraction coil, PS – phase separator, D – detector, R – recorder, V – waste

a) chemical reaction takes place in the aqueous phase and its product after segmentation of the sample zone with extracting solvent is extracted to the organic phase,

b) aqueous solution serves as a carrier stream only, and after sample zone segmentation species to be determined are extracted by the appropriate reagent supplied in the organic phase.

Extraction process for separation and/or preconcentration of a given analyte, takes place in the extraction coil. From the extraction coil the segmented aqueous–organic stream is usually directed to the phase separator, although several authors reported already the flow-injection systems with on-line solvent extraction, where separation of organic and aqueous phases was not necessary [2–7]. Most frequently the separated pure organic phase is transported to a suitable detector, whereas aqueous phase usually with some excess of organic phase is disposed.

Mechanism of segmentation

The segmentation process concerns the formation of a mixed liquid stream composed of regularly sized segments of aqueous phase divided by segments of organic phase. The purpose of liquid segmentation is to ensure the optimum contact between two phases. It is carried out in different segmentor modules, which are discussed below.

The segmentation process takes place in two stages. First, a drop of organic phase is shaped at the nozzle of a capillary transporting this phase. Then, the drop formed is broken off by the flowing stream of aqueous solution and the segment of organic phase is transported to the segmentor outlet.

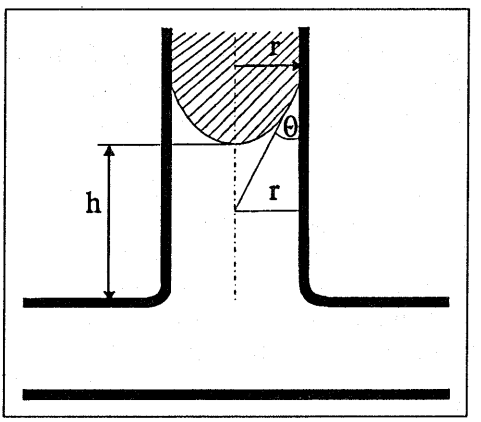

Fig. 2. Schematic of a liquid–liquid interface [9]

A detailed study of the mechanism of segmentation process was reported by Cantwell and Sweileh [8]. As segmentor they used reversed T-connector, where organic phase was introduced by a vertical capillary, whereas aqueous solution, in which organic segments are formed, is transported by horizontal capillary. In

mathematical treatment of observed phenomena the gravity was neglected. The aim of that study was to estimate the magnitude of hydrodynamic forces affecting the segmentation process in order to find a relationship between flow-rate of both phases and size of segments formed for different organic solvent-water systems.

The mathematical treatment was based on theory of interfacial forces [9], according to which the contact surface of two immiscible liquid phases in a capillary of circular cross section has a shape of hemisphere (Fig. 2). In such conditions the solid–liquid–liquid contact angle (θ), between the capillary surface and the contact surface of liquid phases is related to the height of the capillary rise, h, by the expression:

$$\cos\theta = \frac{\Delta\rho g h r}{2\gamma_{o/a}} \tag{1}$$

where $\Delta\rho$ is the density difference between the organic solvent and water. $\gamma_{o/a}$ is the liquid–liquid interfacial tension between organic and aqueous phases, g is the gravitational constant, and r is the radius of the capillary. The magnitude of angle θ significantly affects the length of segments formed for a given total flow-rate of both liquid phases. The exact description of this relationship requires several additional assumptions:

1) because of a continuous flow of both phases, the breaking off a droplet of organic phase occurs instantly after it is formed;

2) the spreading of an organic phase towards the segmentor outlet does not occur until droplet is formed (before dislodgement);

3) the droplet grows in size straight down, along the extrapolated axis of the vertical branch of reversed T-connector (although visual observation shows some bending down-stream);

4) the cross section of the space below the growing drop is assumed to be elliptical, with its major axis D_H equal to the diameter of the horizontal tube and its minor axis, a, equal to the difference between D_H and the vertical length of the drop.

The formation of segment of the organic phase (drop dislodgement) results from the competition of two forces. The hydrodynamic force f_{hyd} is due to the perpendicular flow of aqueous phase, which tends to break off the drop from the column of organic phase above and move it along the surface of the horizontal branch of segmentor. The interfacial force (f_{int}) holds the droplet onto the vertical column of organic phase. The drop is dislodged, when those two forces are equal.

The value of hydrodynamic force is directly proportional to the surface area of the drop formed (B) and the pressure difference (ΔP) across the drop due to the aqueous flow:

$$f_{hyd} = B\Delta P \tag{2}$$

The pressure difference ΔP depends on volumetric flow-rate of aqueous phase F_A, the density ρ_A of aqueous phase and its viscosity:

$$\Delta P \cong \frac{F_A 8\eta_A(D_V + 1.64R)}{\pi R^4} + \frac{1.12\rho_A F_A^2}{\pi^2 R^2} \tag{3}$$

where R is the equivalent radius of the ellipse:

$$R \cong \frac{a^2 D_H + aD_H^2}{2a^2 + 2D_H^2} \tag{4}$$

and a the minor axis of the ellipse given by:

$$a = D_H - \frac{\pi L D_c^2}{4D_V^2} \tag{5}$$

D_H and D_V are the internal diameters of the extraction coil and the vertical branch of the segmentor, respectively. L is the length of segment of organic phase.

Surface area of the drop may be expressed as:

$$B \cong \frac{D_H D_c^2}{4D_V^2} \tag{6}$$

The drop is dislodged, when hydrodynamic force is equal to the interfacial force, which can be given by the following form of the Tate equation:

$$f_{int} = 2\pi\,(D_V/2)\,\gamma_{o/a}\,(1 - \cos\theta) \tag{7}$$

The value of interfacial force is independent of drop size. The above expressions indicate that when a larger flow-rate of an aqueous phase is used the shorter segments of organic phase should be formed.

Sample dispersion

The signal broadening in the flow-injection systems occurs due to the physical dispersion of the sample segment in the flowing stream of liquid, widely discussed in a fundamental monographs [1, 10]. It results in dilution of analyte during its transport to the detector, causing the deterioration of detectability of determination and a decrease of sampling rate.

In the flow-injection systems with on-line solvent-extraction step the additional contribution to the total dispersion can be attributed to the transport backward of organic phase into following organic segments *via* the wetting film along the wall of the extraction coil. Band broadening, verified in experimental model studies [11], is intermediate in magnitude between that predicted by using a mixing chamber model, assuming that all of the liquid in the wetting film adjacent to the aqueous segment mixes completely and instantly with next organic segment and that predicted by assuming only diffusional mixing between the segments and the wetting-film on the tube wall [11]. It was shown, that an increase of flow-rate may cause an additional dispersion due to an increase of

thickness of the inorganic wetting layer. This results in an increase of backwards transport because of shortening of diffusion time from the wetting layer to segments of or- ganic phase. Analogous relationships at constant flow-rate can be caused by an increase of inner diameter of extraction coil. The sample dispersion is practically not affected by the extraction coil diameter.

Nord and Karlberg [12] have also shown, that all factors leading to a decrease of thickness of organic phase layer on the wall of extraction coil diminish the dispersion in extraction flow-injection system. Of great importance is the appropriate selection of the organic solvent used with low ratio of viscosity to interfacial tension and the material for the extraction coil.

In a well designed extraction system the contribution of dispersion in a phase separator to the total dispersion in measuring system is negligible [7]. Therefore, in flow-injection systems, where separation of organic and aqueous phases is almost complete a large volume separators can be used with a large flow-rate of segmented stream. In the systems, where certain loss of organic phase occurs in the separator, the contribution of dispersion in the phase separator depends on the volume of phase separator.

Kinetics of solvent extraction in flow-injection systems

During the solvent extraction process in flow conditions in the extraction tubing or coil, a solute extracts from an aqueous segment through the ends of the segment into the adjacent organic segments and also radially through the sides of the aqueous segment into the wetting film of organic phase along the walls of the tube. If no chemical reaction is involved, the extraction process depends on the mass transfer to and from the aqueous–organic interface and follows an exponential behaviour, which can be treated similarly to a first-order chemical reaction.

Evaluation of parameters, which affect the extraction rate in straight tubes, including two major factors, namely the ratio of interfacial area to volume and mass transfer to and from interfaces was reported by Nord *et al.*[14]. The significant contribution of secondary flow to convection in coiled extraction tubes was pointed out by Lucy and Cantwell [15]. Experimental verification of mathematical considerations requires a careful design of solvent extraction flow-injection system, where random turbulence within segments in the extraction tube should be minimized. Therefore numerous precautions were taken such as preequilibriation of solvents, thermostating the system in order to avoid thermal gradients, avoiding surface-active compounds and minimization of the flow pulsations.

Several essential conclusions on the rate of extraction for the practice of the solvent-extraction flow-injection analysis can be found in mentioned above papers [14, 15]. The extraction rate is increased by increasing the interfacial area to volume ratio, which can be most effectively achieved by decreasing the tubing diameter. The extraction rate increases rapidly with decreasing segment length for short segments and is approximately constant for longer segments. Increasing the linear velocity increases the extraction rate with respect to time, but not in a

linear proportion. In coiled tube the extraction rates are much higher than in comparable straight tube. The tightening of coilling of the tubing increases the extraction rate with respect to time to greater extent for long than for short segments. The tangential secondary flow within long segments is more efficient than within short ones.

Other factors affecting the signal magnitude

Fossey and Cantwell [16] examined the effect of the flow-rates of aqueous phase F_a, organic phase F_o and the part of organic phase, which is transported through the membrane in separator F_m on the area S of the recorded flow-injection peak. For detectors with linear dependence of signal *vs.* concentration the peak area was inversely proportional to the flow-rate through the detector (F_m). The peak area is proportional in more complex way to the molar fraction k' of solute present in the organic phase in comparison with amount present in the aqueous phase:

$$S = K \frac{n}{F_m} \frac{F_m}{F_o} \frac{k'}{1 + k'} \tag{8}$$

where n is amount of solute (in moles) present in the injected sample and K is proportionality factor.

k' can be expressed by means of extraction coefficient D (concentration ratio in both phases) and volume ratio of both phases equal to the flow-rate ratio:

$$k' = D(F_o/F_a) \tag{9}$$

From the above equations one can obtain the following expression:

$$S = \frac{nDK}{F_a + DF_o} \tag{10}$$

showing independence of peak height from the flow-rate of organic phase through the detector. For sufficiently effective extraction, where $DF_o >> F_a$, a simplified relation can be obtained:

$$S = K(n/F_o) \tag{11}$$

which shows that for quantitative extraction process of given analyte to the organic phase, the peak area S depends only on the amount of analyte n in the injected sample and the flow-rate of organic phase F_o. The practical limitation of that dependence is that below certain value of F_o/F_a ratio partial transport of aqueous phase through the membrane can occur.

The same authors [16] discussed also the effect of the length of extraction coil and injected sample volume on the signal magnitude. Both peak area and peak width at half of its height increase with an increase of the length of extraction coil until the equilibrium values are obtained at certain length of extraction coil.

As far as the sample volume is concerned two different regions were observed. For smaller sample volumes, with Gaussian shape of signal a constant peak width was observed, whereas its surface area depends on the sample volume. For a large sample volumes the plateau of signal value in the centre of the signal is observed. In this region the peak width becomes influenced by the sample volume.

DESIGN OF SOLVENT EXTRACTION MODULES FOR FLOW-INJECTION ANALYSIS

Delivery of organic solvent

The handling of organic solvents in flow-injection system limits the variety of materials, which can be used for tubing and for producing detector cells, connectors, segmentors or phase separators to very resistive chemically materials such as glass, PTFE, Kel-F or several other polymers. Some of those modules are commercially available from specialized manufacturers, which already included solvent extraction to their offer for flow-injection equipment.

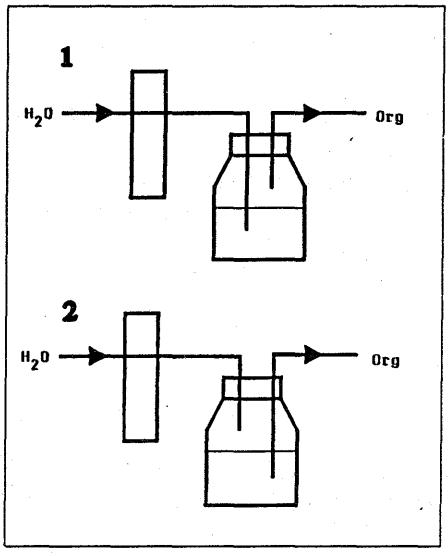

Fig. 3. Typical arrangements of replacement pumping of an organic phase in flow measurements for solvents of smaller (1) and larger (2) density than water

This concerns also appropriate choice of pumping system. Very often in such systems HPLC pumps are used, however, because of their large cost, they can not be widely recommended. For the use of peristaltic pump it is necessary to replace common tygon or silicon rubber pumping tubing for those resistant to organic solvents. PVC based pumping tubing can be used for aqueous–organic mixed solvent with contents of organic component not exceeding 15 to 30%.

The easiest method of delivery of the organic solvent is the use of replacement bottles (Fig. 3). Depending on a relative density in comparison with the water, organic solvent occupies the upper or lower part of tightly sealed bottle, into which water is

pumped using a peristaltic pump with the conventional tygon tubing and the corresponding amount of organic solvent is delivered from the bottle.

Segmentor

The aim of this module in the flow-injection system is to merge in the most reproducible and effective way the aqueous and organic streams to form a segmented stream with a given size of segments, which is directed to the extraction coil.

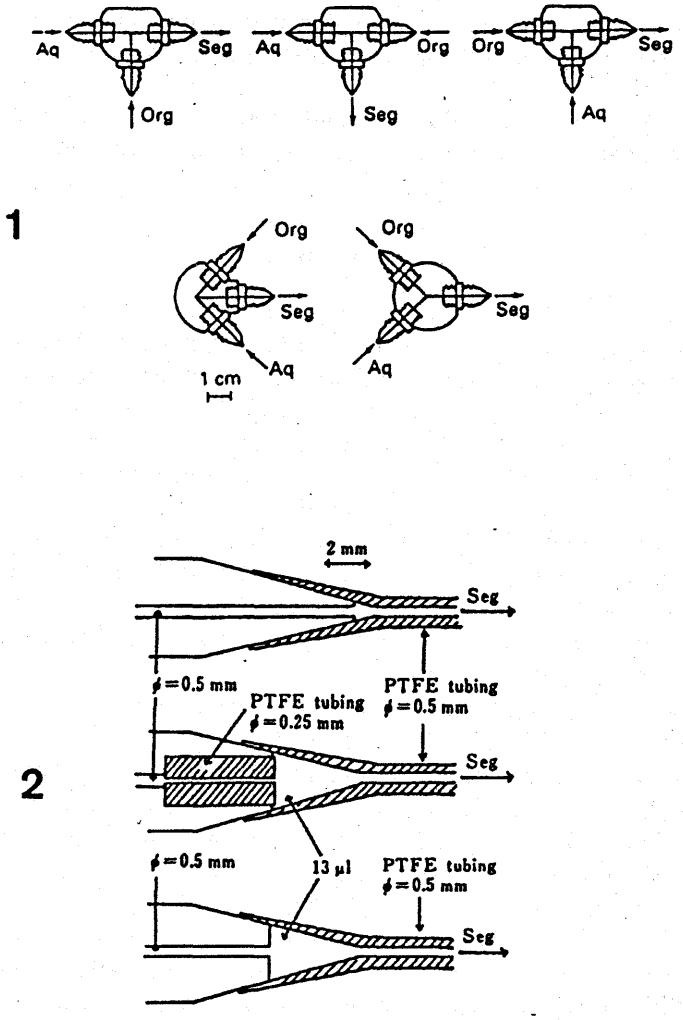

Fig. 4. Design of segmentor modules used in flow-injection extraction systems: 1 – segmentors with various arrangements of confluence points (Aq – aqueous phase, Org – organic phase, Seg – segmented stream) [19], 2 – examples of outlets used in segmentors [17]

The reproducibility of segmentation depends mostly on the quality of machining and smoothness of the inner surfaces, which are in contact with both solutions. The size of segments can be governed by flow-rates and the geometry of segmentor.

Most frequently segmentation is carried out in T-connectors, where aqueous and organic solvents are merged at 90 or 180° angle (Fig. 4). Sometimes they are additionally equipped with special inserts [8, 17] (Fig. 4-2). It was reported by Cantwell and Sweileh [8], that for segmentors without Teflon inserts irregular segmentation was observed, due to penetration of organic phase to the arm, which was used as the aqueous phase inlet. Less often are used segmentors, where both streams are merged at 60° [18, 19] or 45° [19]. As segmentor also a modified Technicon A-8 connector was used, where glass capillary was used as aqueous phase inlet and perpendicularly mounted platinum capillary as organic phase inlet [20].

A very regular and reproducible segmentation was also obtained, when as segmentor a small volume mixing chamber equipped with the magnetic stirrer was applied [21].

Extraction coil

In this element of the flow-injection system a main process of interfacial transport of analyte from aqueous to organic phase takes place. In glass coils, their inner wall is wetted by water and organic phase forms bubbles. In extraction coils made of organic polymer (most often PTFE) the organic phase wetts the inner wall, whereas aqueous phase forms bubbles.

Following Rossi *et al.* [22], certain rules of design of extraction coils can be formulated:

1) the choice of material for extraction coil should be made in such a way, that the phase initially containing analyte should form bubbles in order to diminish the carry-over between the injected samples;

2) the maximum value of the ratio of interfacial surface to the volume of injected sample should be ensured;

3) the optimum conditions for transport of analyte from the sample solution to the interfacial surface should be provided.

In order to fulfil last two requirements a phase initially containing analyte should form bubbles in the segmented stream. Therefore it can be concluded, that for most common extraction carried out from aqueous to organic phase extraction coils should be made of material, which is not wettable by aqueous solutions.

The extraction efficiency observed usually in flow-injection systems is within 70 to 90% and depends substantially on the design of flow system and its modules. Too long extraction coils improve the extraction efficiency, however, usually introduce significant dispersion of sample. There were also several other methods reported to improve the interfacial contact in order to increase the extraction efficiency such as using special insert to the extraction coils, elevating the temperature, ultrasonication or vibrations. Precautions should be made to avoid the formation of emulsions which makes difficult phase separation.

Separator

Phase separator is usually the most complex module of the on-line solvent extraction part of flow-injection manifold. The separation of aqueous and organic phases in developed and reported devices is never complete practically and its efficiency is varying from 80 to 95%. Most often it is required that the phase to which analyte is extracted should not be contaminated by the other phase, which can interfere in the detection.

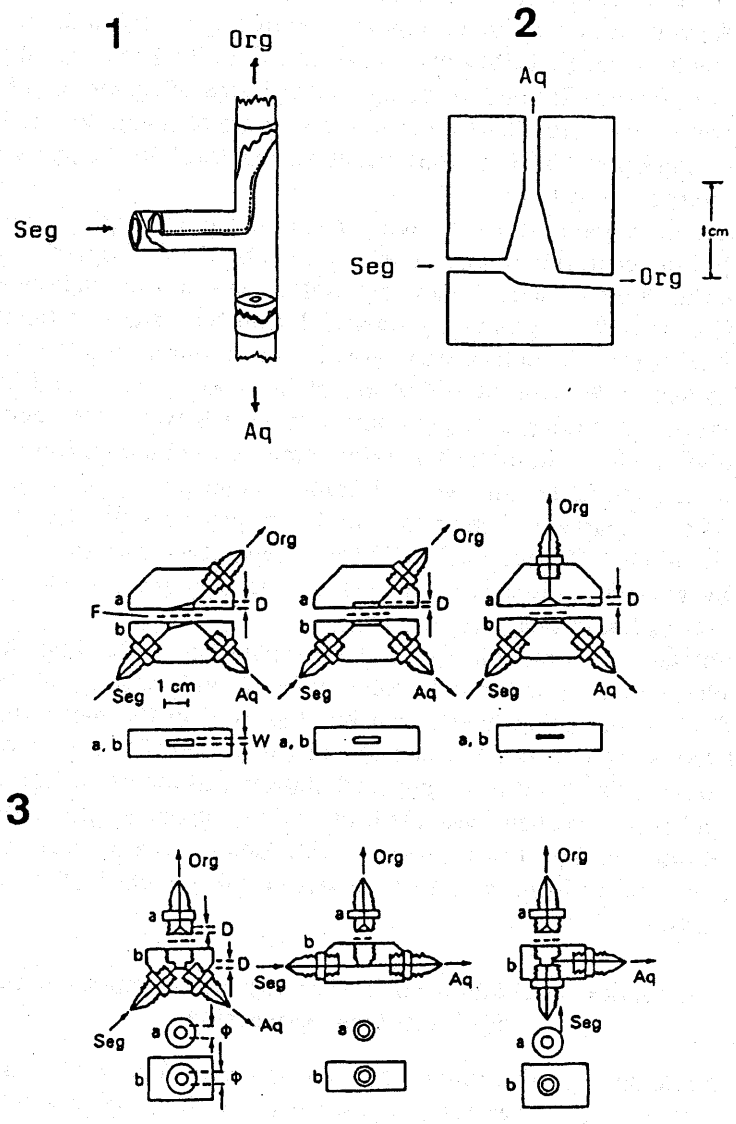

Fig. 5. Phase separator units used in flow-injection extraction systems: 1, 2 – separators relying on differences in density of aqueous and organic phases [20, 23], 3 – membrane separators with various shapes of a separator cavity (Seg – segmented stream, Org – organic phase, Aq – aqueous phase) [19]

Different types of phase separators described in the literature are based on differences in density and different wetting of various materials by solutions to be separated, on selective permeability through different membranes or on selective sorption of one phase by an appropriate sorbent.

The examples of design of phase separators based on differences in density of solvents are shown in Fig. 5. The device reported by Shelly *et al.* [20] was based on a commercial Technicon A4 connector equipped with Teflon inserts facilitating the phase separation due to differences in wetting.

Phase separation in membrane separators is mostly based on the permeability of organic phase through Teflon membrane of 0.7 to 0.9 μm pore size. Because of some overpressure formed in separator and flexibility of membrane it is advantageous to use some inert mechanical support of membrane [24]. Also in this case the appropriate Teflon insert can be very helpful for the phase separation due to differences in wetting.

The membrane separators reported for flow-injection applications have different shapes of separation compartment divided by the hydrophobic membrane. Most often this compartment is manufactured in the shape of shallow straight [4, 13, 26, 27] or coiled [3] groove symmetrically on both sides of the membrane. In order to increase the contact area between the solutions and the membrane it is advantageous to decrease the thickness of the solution layer and increase the width of groove providing a larger contact surface between the membrane and flowing solution [4]. Cylindrical separators are designed with different geometry of solution inlet and outlet, and with different volume and shape of the separation chamber. The comparison of their functioning to groove separators [13] and the comparison of the efficiency of cylindrical separators of various design was reported by several authors [13, 24, 25]. Figure 5 shows the most often used constructions of liquid phase separators.

A completely different concept of phase separation is based on absorption of aqueous phase in a flow-through column filled with appropriate hydrophilic loading. Such a separation device can be employed in the measuring systems, where relatively small volume of aqueous phase is used. The choice of absorbent is very critical with regard to its physical stability. In the extraction of caffeine, when the gel-type absorbent was used, the column pressure gradually increased with the number of injections, however with cotton-type absorbent, pretreated with methanol–chloroform mixture a satisfactory functioning of the system was observed [28].

Detection methods used in flow-injection systems with on-line solvent extraction

Spectrophotometric absorptive detection is most often employed in flow-injection analysis. A great variety of known reagents forming products absorbing visible radiation with numerous inorganic and organic species and usually simple and widely available instrumentation results in a wide application of these procedures in routine chemical analysis. In real samples with complex matrices,

especially for trace level of analytes the use of sample pretreatment by preconcentration or separation procedures is very often indispensable. Introducing on-line extraction modules into the flow-injection manifold offers a convenient method of mechanisation and automation of such procedures.

Table 1. Applications of on-line solvent extraction in flow-injection systems with spectrophotometric detection

Determined species	Analyzed sample	Extracted species	Solvent	Detection limit, $\mu g\ l^{-1}$	Reference
Anionic surfac-factants	river and treatment waters	ion-pair with Methylene Blue	chloroform	4	32
	tap water	"	1,2-dichloro-benzene	3	17
	tap and river waters	"	1,2-dichloro-benene +benzene (1+1)	5	27
	river water	ion-pair with 1-methyl-4--(4-diethylamino-phenylazo)-pyridinium ion	chloroform	0.01*	33
	wastes	ion-pair with Ethyl Violet	toluene	10	54
	water	ion-pair with Methylene Blue	chloroform	0.5*	35
Bitterness	beer	not indicated	isooctane	NE	53
Caffeine	coffee, coca cola	caffeine	chloroform	NE	41
Codeine	pharmaceuticals	ion-pair with picrate	chloroform	20000	40
Phenol	waters	reaction with 4-amino-antipyrine and potassium persulfate	chloroform	50	37
Organo-phospho-rus pesticides	–	pesticides	*n*-heptane	40–90	18
Procycli-dine	drugs	ion-pair with picrate	chloroform	50	16
Cd	urine	complex with dithizone	chloroform	0.2	39
ClO_4^-	potassium chlora-te	ion-associate with Brillant Green	benzene	36	45
Co	steels	ion-associate ethylenebis-(triphenylphosphonium)-tetrathiocyanato-cobaltate(II)	chloroform	230	21

Determined species	Analyzed sample	Extracted species	Solvent	Detection limit, $\mu g\ l^{-1}$	Reference
$Cr_2O_7^{2-}$	steels	ion-associate tetramethylene bis-(triphenylphosphonium) dichromate	chloroform	440	36
K	river water	complex with 4-(4--diethylaminophenyl)azo--2,5-dichlorobenzene sulphonate and benzo-18-crown-6	benzene+ chlorobenzene(1+1)	40	48
	river water	complex with 4-(4-phenylamino)phenylazo-2,5-dichlorobenzene sulphonic acid and dibenzo-18-crown-6	benzene	NE	49
	fruit juices and beverages	complex with dibenzo--18-crown-6 and Bromothymol Blue	chloroform	NE	50
K, Na	river and tap water	complex with benzo-18-crown-6 and tetrabromo phenolphtalein ethyl ester anion	chlorobenzene +benzene (1+3)	NE	51
Li	blood serum	complex with dodecyl-14-crown-4-dinitrophenol	chloroform	16000	43
	blood serum	complex with 2″, 4″-dinitro-6″-trifluoromethylphenyl-4′--aminobenzo-14-crown-4	1,2-dichloroethane	14000	42
Mn	steels	ion-pair with ethylenebis-(triphenylphosphonium) ion	chloroform	580	44
Mo	plant extracts	complex with thiocyanate	isoamyl alcohol	50	23
Pb	soil extracts	complex with dicyclohexyl-18-crown-6 and dithizone	chloroform	50	46
PO_4^{3-}	river water	ion-associate of phosphomolybdate with Malachite Green	benzene +4-methylpentan-2-one (1+2)	0.1	19
	human seminal plasma and urine	phosphomolybdic acid	isobutyl acetate	10	38
U	nuclear waste processing solutions	U(VI) salted-out with aluminium nitrate	isobutyl methyl ketone	50	29

NE – detection limit not estimated. *$\mu mol\ l^{-1}$

Reported applications of flow-injection analysis with on-line solvent extraction and spectrophotometric detection are listed in Table 1. Several authors developed fast and sensitive methods for determination of anionic surfactants in

natural waters and wastes [17, 27, 32, 33, 35, 54], which are based on extraction of appropriate ion-pairs. Among other organic species determined were phenol [37], organophosphorus pesticides for further HPLC analysis [18], codeine [40] and caffeine [28, 41]. Among inorganic species trace determination of heavy metals predominates, however several anions like phosphates [19, 38] or perchlorates [45] were also determined. Extraction of crown complexes was utilized for flow-injection determination of lithium in blood serum [42, 43], potassium in surface waters [48, 49] and fruits and beverages [50] and simultaneous determination of sodium and potassium in waters employing on-line separation on microcolumn packed with silica gel [51].

The use of solvent extraction in flow-injection systems with atomic absorption spectrometric (AAS) detection is mostly utilized for trace determination of heavy metals (Table 2). Organic solvents allow not only preconcentration and separation from the matrix of the determined species but due to more efficient combustion in the flame and easier evaporation additionally improve the detectability of the detection with flame atomization. For continuous sample aspiration from 15 to 20 [55] and up to 60-fold [59] improvement of detectability was observed. The extraction of zinc thiocyanate after preliminary reduction of iron to Fe(II) allowed the elimination of the iron interferences observed usually for the AAS zinc determination [60]. The extraction flow-injection systems with AAS detection can be also utilized for indirect determinations, where the analytical signal of a metallic element is proportional to the concentration of anion coextracted into the organic phase [61–63].

Table 2. Applications of on-line solvent extraction in flow-injection systems with flame atomic absorption spectrometric detection

Determined species	Organic phase	Detection limit, $\mu g\ l^{-1}$	Reference
Cu	APDC in MIBK	0.8	55
Ni		9.0	
Pb		5.0	
Zn		0.4	
Cu	APDC in MIBK	NE	56
Cd, Co, Cu, Ni, Pb	Freon 113	20	57
Pb	KI in MIBK	20	59
Zn	KSCN in acetone and MIBK	200	60
NO_2^-	Cu(I) neocuproine	40	61, 62
NO_3^-	complex in MIBK	400	
ClO_3^-	Cu(I) 6-methylpicolinealdehyde azine complex in MIBK	70	63

APDC – Ammonium pyrolidinedithiocarbamate.
MIBK – Methyl isobutyl ketone.
NE – not estimated.

Table 3. Applications of on-line solvent extraction in flow-injection systems with fluorimetric detection

Determined species	Analyzed sample	Solvent	Detection limit, $\mu g\ l^{-1}$	Reference
Ga	–	isoamyl alcohol	70	26
K	–	1,2-dichloroethane	NE	52
Vitamin B_1	pharmaceutical preparations	chloroform	NE	58

NE – not estimated.

In several applications reported for solvent extraction in flow-injection systems with fluorescence detection (Table 3), the detection is based on measurement of the fluorescence of extracted complex [26] or the anion forming extracted complex [52]. In determination of vitamin B_1 the fluorescence of thiochrome is measured, which is oxidation product of vitamin B_1 [58].

Flow-injection solvent extraction without phase separation

Several other concepts of the on-line separation of analyte based on partition between two liquid phases were reported in the literature without the need of stream segmentation and phase separation. Instead of partition between segments of two immiscible liquids the extraction module contains a PTFE porous membrane, and each phase is fed to only one side of the membrane [2–4]. The extraction cell has a similar construction to a dialysis cell, where the contact area between the aqueous and the organic phase is reduced to a "stagnant" zone in the cell. The organic solvent groove was filled with a porous support of polyethylene. Such a system is suitable for coarse liquid–liquid extraction of concentrated samples.

An interesting concept to avoid the phase separation in extraction flow systems was proposed by Memon and Worsfold [5, 6]. An introduction of large amount of surfactant allows the formation of stable microemulsion, in which detection can be carried out. This concept was demonstrated for the determination of copper with neocuproine [5] and zinc with dithizone [6].

Another methodology of solvent extraction in continuous flow systems without phase separation was proposed by Canete *et al.* [7]. It consist of a single plug of organic phase inserted into the carrier stream of aqueous solution, which contains the analyte. The flow is subjected to an iterative reversal, and the gradual enrichment of the organic phase with the solute is monitored photometrically. It is similar in some aspects to manual shaking of both phases except for the reduced and defined contact area between both phases. Schematic diagram of the functioning of such a system and obtained signal recordings are shown in Fig. 6. Each experiment provides much information because multidetection with a single detector is performed. This allows to use conventional reaction-rate measurements and the use of concentration and dilution methods to manipulate the sensitivity of the determination. The disadvantage of such a set up is the need of use of an electronic programmer to obtain programable and reproducible reversal

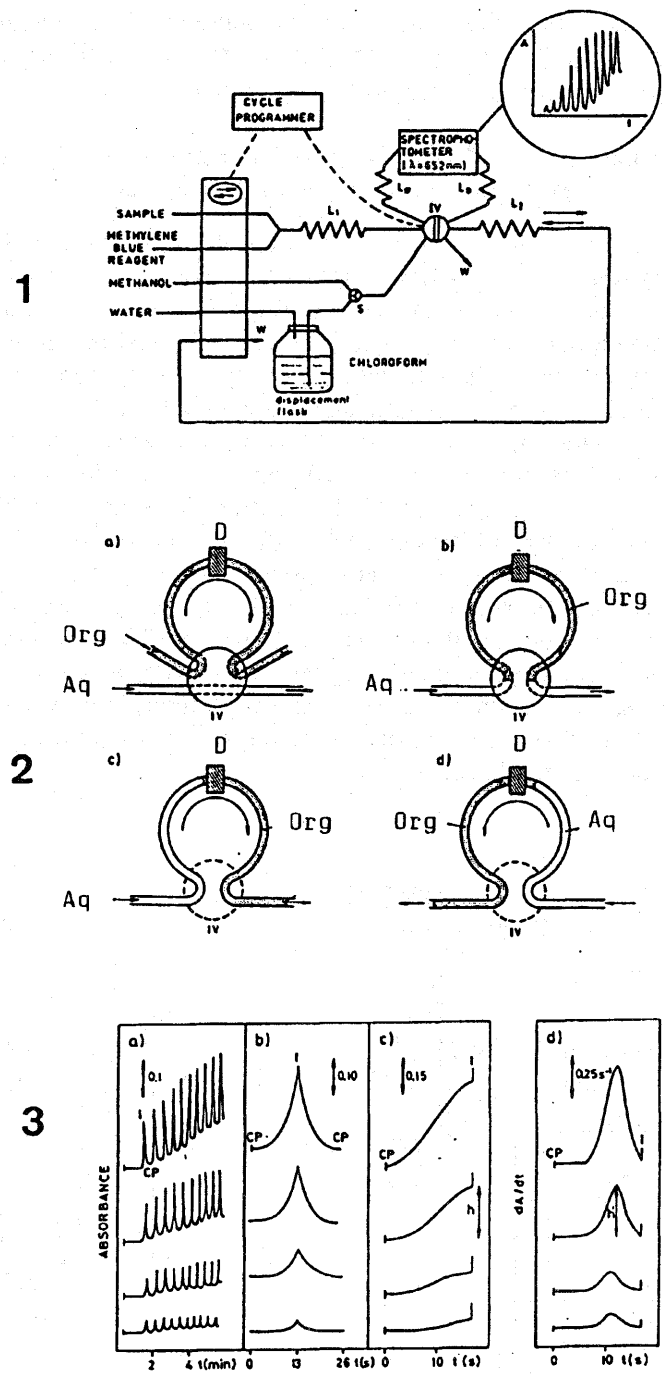

Fig. 6. Flow-injection extraction system based on a single plug technique [7]: 1 – general arrangement of the system, 2 – stages of measurement (D – detector, Org – organic phase, Aq – aqueous phase, IV – injection valve), 3 – signals obtained

cycles of the flow from the pump. The methodology has been tested on the determination of anionic surfactants in water by conventional ion-pair formation with Methylene Blue using chloroform as the organic phase [7].

Enhancement of sensitivity and selectivity of solvent extraction procedures in flow systems

The use of recirculation of solution in a closed loop with multiple measurement of analytical signal is often employed in flow systems to improve the detectability of determination [1, 10]. It was also employed for the on-line preconcentration of analytes from aqueous solution by continuous extraction into organic solvent circulating in a closed loop of system consisted of a segmentor, an extraction coil, a phase separator and a switching valve [29, 30]. With the organic phase circulating in the loop, it can be contacted with fresh aqueous stream, which continuously enters the extraction coil and leaves to waste (Fig. 7). As it was shown by Atallah *et al.* [30] for extraction of copper with chloroform solution of zinc diethyldithiocarbamate high preconcentration factors can be reached, depending on several system parameters such as flow-rates, loading time, loop volume, extraction efficiency and organic loss through the phase separator. A unique feature of the system is the possibility to perform several washing steps on the organic phase trapped in the loop to remove interferences or to strip the analyte. Such a concept of the continuous flow solvent extraction was applied to the determination of trace amounts of uranium in nuclear waste with spectrophotometric detection [29].

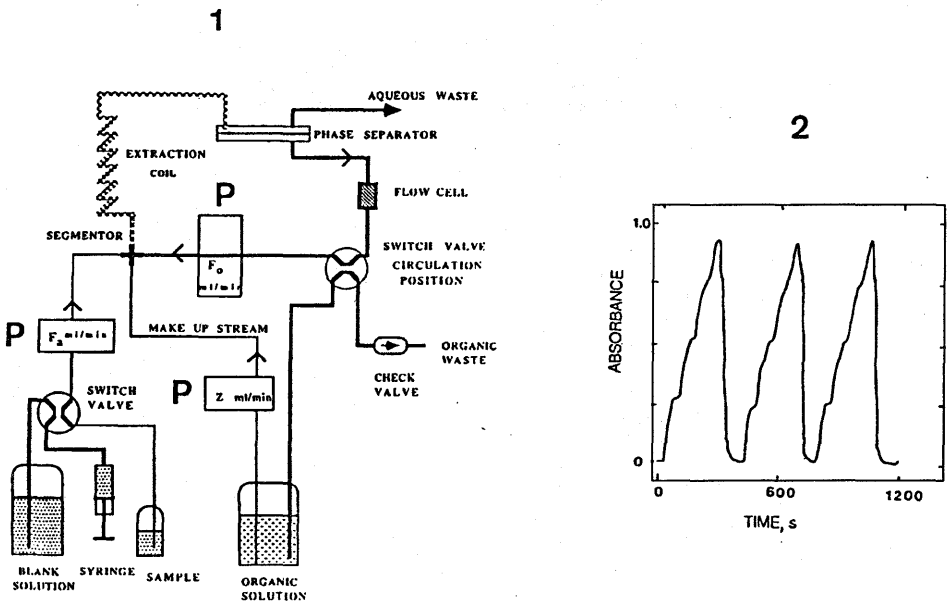

Fig. 7. Flow-injection extraction closed-loop system [30]: 1 – general arrangement of the system (P – peristaltic pump), 2 – signal recorded for triplicate measurement of 1 ppm Cu(II) solution

Certain improvement of detectability and sampling frequency in the continuous flow system with solvent extraction and AAS detection was observed, when sample was injected to the segmented organic–aqueous stream instead of aqueous stream [31].

The multiple repetition of the solvent extraction process is a commonly known method for the improvement of sensitivity and selectivity of conventional analytical procedures. A three-stage extraction procedure in the flow injection system was proposed for the isolation of polycyclic aromatic compounds from the Soxhlet extracts of burned oil residues [20, 22]. Three single-step liquid–liquid extractions are linked together by multichannel pumping and resampling. The performance of the system was evaluated by HPLC and visual fluorimetry. The flow-injection system developed was found rapid, reproducible and quantitative as compared with manual procedure.

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