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# SEPARATION AND PRECONCENTRATION OF TRACE ELEMENTS AND THEIR PHYSICO- CHEMICAL FORMS IN AQUEOUS MEDIA USING INERT SOLID MEMBRANES

(Technical Report)

*Prepared for publication by*

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# Separation and preconcentration of trace elements and their physico-chemical forms in aqueous media using inert solid membranes (Technical Report)

**Abstract:** A survey is given over various methods for separation and enrichment of trace elements and their speciation in aquatic media using membrane filtration. The methods are mainly used for three purposes: (1) studies of size distribution patterns for trace elements in order to estimate the association of the elements with suspended particles and soluble compounds of different nature, (2) pre-separations of interfering constituents of solutions to be analysed in continuous flow instruments, (3) separation and preconcentration of inorganic ions in membrane filtration cells with and without chemical reagents. The capabilities and limitations inherent in the methods are critically discussed. The most interesting results have been obtained for size fractionation techniques and for membrane separations in the presence of separating reagents. These and especially other membrane methods require further research to identify more clearly their respective advantages and limitations.

## 1. INTRODUCTION

Membrane processes are among the most promising technologies for enrichment of various species from solutions and for their separation [1-4]. However to date, membrane separations have relatively seldom been used in analytical chemistry, particularly in inorganic analysis. There are only two monographs devoted to membrane methods which mention analytical applications of inert solid membranes [3, 4]. An interesting review [5] is only partially dedicated to utilization of such membranes, and partially to application of better known ion-exchange, liquid and other so-called active and reactive membranes. The authors of reviews [5-7] and books [1-4] have paid much attention to the principles of membrane methods and to the equipment used. Therefore, in this report we only briefly describe some properties of the membranes, general principles and capabilities of the techniques. Attention will be mainly paid to analytical applications of membrane filtration, critical evaluation of the methods developed and their comparison with other techniques.

Use of inert solid membranes enables separation to be achieved which cannot be successfully carried out by other means. Thus, membrane-based size fractionation is useful for the determination of the distribution pattern of trace elements in natural waters and other fluids. Elements associated with suspended particles, colloids and polymers as well as the ionic forms of these elements can be determined separately after membrane separation and preconcentration. Physico-chemical forms of solutes can also be differentiated in speciation studies. The possibility of preconcentration and separation of different species without separating agents is another advantage of some membrane techniques. This is of particular interest in trace and ultratrace analysis to decrease the probability of contamination.

Membrane separation is most selective, however, if soluble reagents are added. Such techniques may supplement two-phase distribution methods (e.g. solvent extraction, sorption and precipitation) which are frequently applied to extract inorganic species from dissolved matrices, industrial fluids or natural waters. Although many such methods have been developed and successfully used, their application is still sometimes troublesome. Some problems are caused by heterogeneous reactions and transfer between phases. Other problems can arise from the composition of the solution finally obtained which has to be submitted to the final determination method. In such cases, additional procedure may be required, e.g. back-extraction, desorption or dissolution of solid concentrates, which render analytical procedure more complex and can cause additional contamination. Membrane separations can yield homogeneous aqueous phases suitable for subsequent analysis by many instrumental methods.

Microfilters, ultrafilters and dialysis and osmosis membranes can be used for analytical separations. The membranes are usually made of polycarbonate, cellulose (esters), polyamide, polysulfone, etc. The principal factors that should be considered for application of membranes to aqueous media are [8]: pore size and pore size distribution, solution flow, potential drop over the

membrane, degree of hydrophilicity. Brock [3] and Matteson [4] give detailed lists of commercially available membranes appropriate for analytical applications. The methods described below are based on utilization of "inert" membranes, i.e. membranes which hardly adsorb the species to be separated. Of course, any membrane has some adsorption ability, so certain conditioning should be provided to minimize the adsorption.

## 2. MEMBRANE SEPARATIONS WITHOUT CHEMICAL REAGENTS

### 2.1. Studies of size distribution patterns for trace elements

Trace elements in natural waters and other fluids may be present in different physico-chemical forms varying in size, charge and density. They may be associated with ligands ranging from simple ions to large molecules and may, via products of hydrolysis, form colloids, or they may be absorbed onto or incorporated in organic or inorganic particles [8-10]. The binding of trace elements and radionuclides can enable the determination of transport, distribution and biological uptake. Because of their impact on human and animal organisms, the distribution patterns of trace elements are important for environmental and biological studies. Membrane methods are appropriate for the study of such patterns. A classification of membrane size separation methods and some principles of the application of such methods for the investigation of element distribution in aquatic systems have been described [8, 13]. Examples of membrane separations in water analysis are reported [3-5, 8-13]. Some standard methods based on microfiltration, ultrafiltration and dialysis have been recommended in the USA for characterization of water quality [3].

Dialysis, osmosis (reverse)	Ultrafiltration			Microfiltration	
	1 nm	10 nm	0.1 $\mu\text{m}$	0.45 $\mu\text{m}$ 1 $\mu\text{m}$	10 $\mu\text{m}$
Molecular mass	$10^2$	$10^4$	$10^6$	$10^8$	$10^{10}$
Simple compounds	hydrolyzates/colloids			suspended particles	
Hydrated inorganic or organic ions, complexes, molecules	polyhydroxo complexes, polysilicates, fulvic substances, fatty acids		metal hydroxides, clay minerals, humic substances, proteins	inorganic mineral particles, organic particles, microorganisms	
	viruses			bacteria	

Fig.1. Scheme for speciation of trace elements in river water by size fractionation techniques

Fig.1 gives some characteristics of the size separation techniques which can be used to study the distribution of trace elements associated with various constituents of natural waters. It is obvious that the dimensions given in the figure are tentative as various factors influence the association/dissociation and aggregation/dispersion processes [13]. However, preservation of real equilibria and labile species of elements, especially at their concentrations of less than  $10^{-6} \text{g l}^{-1}$ , prior to analysis is a much more serious problem encountered with methods which are not based on a direct physical separation. From this point of view, membrane filtration has advantages although some uncertainties connected with equilibria shifts always exist.

The pore size distribution in the membranes is another factor which may influence the reliability of size distribution patterns. Membranes with a relatively narrow distribution are produced. For example, the pore size distribution in some MF Millipore membranes are: 0.025-0.05, 0.1-0.22, 0.45-0.65, 1.2-3.0, 5.0-8.0  $\mu\text{m}$  [3]. Vary narrow pore distribution (geometric standard deviation being smaller than about 1.1) is obtained when a thin (10  $\mu\text{m}$ ) sheet of polycarbonate or other polymer material is

irradiated with a collimated beam of fission fragments from uranium-235 and the damaged material is removed in an etching bath. Such sheets for use as filters are produced by the Nuclepore Corp. and are called Nuclepore filters [3, 4, 14]. Also commercially available are nuclear track membranes developed in Joint Nuclear Research Institute (Russia) [14]. These membranes are made of a chemically very inert material (polyethylene terephthalate) and have a pore diameter ranged from 0.025 to 25  $\mu\text{m}$ . Nuclear track filters are often applied if fine solid particles are to be separated [3, 4].

Rather informative distribution patterns can be obtained using only two or three filters having different pore size if the membrane filtration is combined with acidification of water fractions. Thus, an analytical scheme for determining the speciation of aluminium in natural waters has been described. The scheme is based on sizing by filtration of acidified and unacidified water sample portions through 0.1 and 0.4  $\mu\text{m}$  polycarbonate membrane filters (Nuclepore) [15]. The following aluminium species have been detected using spectrophotometric and atomic absorption measurements after the separation: particulate, colloidal and soluble, large colloidal, fine colloidal and soluble, fine colloidal complexed forms, labile aluminium forms such as  $\text{Al}^{3+}$ ,  $\text{Al}(\text{OH})^{2+}$ ,  $\text{Al}(\text{OH})_2^+$  as well as total aluminium.

Membrane filtration was used in the speciation of trace 32 elements in river water [16]. A 30-l water sample was immediately pre-filtrated using a 8  $\mu\text{m}$  Millipore filter in order to remove large particles. Another 5 l of the sample was taken in a polyethylene bottle without filtration and acidified with 30 ml of nitric acid. Two 5-l portions of the filtrate were filtered through 0.45 and 0.05  $\mu\text{m}$  Millipore membranes respectively. The other 4 portions were ultrafiltrated through membranes having molecular-mass cut-off  $2 \times 10^5$ ,  $10^4$ ,  $10^3$ ,  $5 \times 10^2$   $\text{g mol}^{-1}$ , and then acidified to prevent any adsorption on the walls of the polyethylene bottles used. The concentrations of the 32 elements were determined for the filtrates and non-filtrated sample by neutron-activation analysis. The studies of the mass balance of the trace elements during the ultrafiltration showed that the loss due to adsorption was 20-50% for Fe, Ag, U and rare-earth elements. The loss or contamination for alkali, alkaline-earth, most of transition elements was less than 10%.

In the described experiments, the filtration was carried out under stirring. Acidification procedures and utilization of stirred filtration cells should be used with care because they may result in equilibria shifts.

Stirring can influence not only the equilibria between solution and suspended colloidal forms but also the flux through ultrafiltration membranes [17]. Besides, the membranes of stirred ultrafiltration cells clog relatively fast in the presence of dissolved organic carbon and the polarized membrane surface changes its retention behaviour. In contrast, in the use of the tangential flow technique, the surface of the membrane is continuously cleared of small particles, and allows high flow rates [18].

Hollow fibre cartridges having a nominal molecular mass cut-off of  $10^6$ ,  $10^5$ ,  $10^4$  and  $10^3$   $\text{g mol}^{-1}$  respectively have been used for successive filtration separations in natural water analysis [9, 19, 20]. Sorption of Zn and Cr on hollow fibers (Amicon Corp.) from synthetic solutions was studied using radionuclides of these elements. Clogging and sorption effects were also investigated for aluminium in natural waters [20]. On the basis of the results obtained and of the studies of distribution patterns for Al, Fe and Zn as well as some radionuclides [11] in natural waters, it has been shown that the main advantages with hollow fibre fractionation are mainly minimal clogging and sorption problems (compared to disc filtering techniques) and a high filtering capacity.

Different methods for the determination of the physico-chemical forms of metals in waters have been compared [13, 21, 22]. If the fractionation is rapid, the risk of equilibria shifts during membrane filtration is less than for other fractionation techniques. The absence of gels or other separating materials, which can more readily adsorb trace elements and their species than polymer membranes, enables minimization of sorption. The adsorption effects may also be reduced if preconditioning of the filtration unit with a sample aliquot is used. This can be easily done because membrane filtration is faster than gel filtration to say nothing of such a fractionation techniques as sedimentation. Both membrane filtration and sedimentation of particulate matter can be performed with large volume samples that is convenient for comparative analysis of the fractions by different determination methods.

Table 1 gives some typical examples of the determination of trace elements present in water in different particulate and dissolved species.

Table 1. Identification of physico-chemical forms for trace elements in waters by using membrane filtration

Water type	Trace elements	Membrane, pore size	Determination method	Reference
Natural	Cu, Cd, Hg		AAS	[23]
Natural	Li, B, Be, C	Nuclear track filters	Nuclear-physical method	[24]
Natural	Hg, Zn, Co	Nuclear track filters, 0.45 $\mu\text{m}$	NAA	[11]
Natural	$^{58}\text{Co}$ , $^{60}\text{Co}$ , $^{54}\text{Mn}$ , $^{64}\text{Zn}$	Amicon hollow fibres	$\gamma$ -Spectrometry	[9, 19, 20]
Natural	Al	Polycarbonate membrane filters, 0.1- 0.4 $\mu\text{m}$	Spectrophotometry, AAS	[15]
Natural and mine River	Be	Sheet filters, 0.45 $\mu\text{m}$	ICP - OES	[12]
River	Fe, Al	Polymer filters, 8, 1 and 0.4 $\mu\text{m}$	ICP - OES	[25-27]
River	32 elements	Millipore filters, 0.05, 0.45 $\mu\text{m}$	NAA	[16]
Lake	Al, Fe, Zn	Amicon hollow fibres	AAS	[20]
Sea and other	Np, Am	Sheet filters, 0.45 $\mu\text{m}$	Radiometric method	[28]
Sea	Tl, Ag, Cu, Cd, Pb, Ni, Zn	Nuclepore membranes	Isotope dilution mass spectrometry	[29]
Sea	16 elements	Nuclepore membranes	NAA	[30]

Size distribution studies can be of interest in the analysis of liquids other than natural waters; so far important results have been obtained in the determination of products of corrosion in cooling systems of nuclear reactors [31]. Methods for identification of trace element species in natural and synthetic biological materials have been described [32], various techniques including ultrafiltration and dialysis were used. Membrane methods have been used in the analysis of various samples, e.g. in the determination of bound and free calcium, magnesium [33], aluminium [15, 34], and non-protein-bound zinc in human serum [35].

Different techniques are in use for the analysis of filtration fractions and concentrates ( Table 1 ). Most often multielement techniques such as neutron-activation analysis (NAA) [16, 19, 30], radiometric measurements [28, 34-36], X-ray fluorescence spectrometry (XRF) [24], inductively coupled plasma optical emission spectrometry (ICP OES) [25-27] are applied. The application of electrochemical methods [38, 39] and different techniques of atomic absorption spectrometry (AAS) [23, 38, 40] is also possible. Such determinations are usually carried out after washing out the particles from the filter [9, 19, 20], after their transfer onto a metallic substrate [24], after acid digestion of the concentrate and the filter [12, 25], or after dissolution of the concentrate and the membrane in chloroform in the presence of 0.1 mol l<sup>-1</sup> HNO<sub>3</sub>. Fractions separated on the membrane can be directly analysed by electrothermal AAS [23].

It is obvious that the use of one membrane filtration method as a single separation technique cannot give comprehensive information on metal speciation in aqueous media. Combinations of ultrafiltration with dialysis [11], coprecipitation and centrifugation, ion exchange [11, 21], and liquid-liquid extraction [11, 12, 22] are useful for the identification of the species of an element. However, the membrane filtration itself is a rather powerful means if a number of membranes, having different pore size, are applied for studying one sample. On the other hand, the use of many different membranes in one procedure requires a number of operations and takes a long time, if off-line separations are used. Therefore, important efforts should be focused on the development of on-line multimembrane devices, preferably based on tangential-flow discs [41] or hollow-fibre cartridges.

## 2.2 Membrane prepreparations in continuous flow instruments

Dialysis cells are amongst the most practical units of systems for flow injection analysis (FIA) which serve to exclude any unwanted sample material so that only the analyte reaches the reaction or sensing zone [37, 42]. Solid particles and larger interfering molecules can be separated by membrane dialysis from the smaller species of analytical interest. Several dialysis units have been described [43-47]. In the processes used, the sample passes through the module where particulate and dissolved macromolecular fractions are retained whilst the analyte molecules diffuse across the membrane into a recipient stream. Inorganic ions can be separated on the basis of different rates caused by different rates of reactions between the migrating ions and a reagent in the recipient stream. The theory of the processes has been described [48, 49].

Mass transfer in on-line parallel-plate dialyzers was studied in the continuous and flow injection modes [50]. The dialysis of both cations ( $\text{Ca}^{2+}$ ) and anions ( $\text{Cl}^-$ ) was investigated with different membranes made of cellophane, cellulose acetate and natural cellulose. It was shown that the fraction of analyte transferred from the donor to the acceptor stream depended on the membrane used, membrane surface and porosity, concentration of analyte in the donor stream, flow-rates of the donor and acceptor streams.

Dialysis was used in FIA of nitrate and nitrite in dairy product [46] to improve the selectivity for various anions detected by ion-selective electrodes [51-54]. Trace quantities of cyanide and thiocyanate were simultaneously determined by the pyridine/barbituric acid method after diffusion through a microporous membrane [47]. Dialysis was combined with coulometric titration with potentiometric end-point detection [54]. Bromine generated at a platinum electrode diffused across the membrane into the test solution and reacted with the analyte. A rapid, indirect diffusion FIA method with amperometric detection has been developed for the determination of bromide [55]. The method is based on permanganate oxidation of bromide to bromine which diffuses through a polytetrafluoroethylene (PTFE) membrane and is quantified amperometrically. The throughput of 30 samples per hour was reached with as low relative standard deviation as 0.7% at  $10 \mu\text{mol l}^{-1}$ . Other applications of membrane modules have been reported [56-58].

It is worthwhile mentioning that membrane filtration can be used in sample preparation for chromatography, e.g. in the ion-chromatographic determination of  $\text{Fe}^{\text{II}}$  and  $\text{Fe}^{\text{III}}$  in water samples [59] or of  $\text{Cl}^-$ ,  $\text{NO}_2^-$ ,  $\text{NO}_3^-$ ,  $\text{SeO}_3^{2-}$  and  $\text{PO}_4^{3-}$  [60]. Membrane filters (pore diameter 0.45-0.22  $\mu\text{m}$ ) were used to remove particulate and organic materials from the mobile phase in liquid chromatography [61, 62]. Tubular membrane interfaces were recently used for sample introduction in capillary zone electrophoresis to separate low-molecular-mass organic constituents in blood plasma [63]. Similar dialysis membranes may be recommended for the separation of inorganic ions.

It is obvious that physical separation of inorganic ions and other low-molecular analytes from particulate and dissolved macromolecular fractions of the sample is useful in continuous flow instruments. Further investigations seem to be necessary to compare the analytical capacities of the methods involving both membrane filtration and chemical reactions with those of other on-line separation techniques.

## 2.3. Separation and preconcentration of inorganic ions in solutions

For aqueous media the methods described above enable the separation of particulate matter and dissolved macromolecules from inorganic ions. However, membrane separations can also be used to obtain charge distribution patterns for low-molecular-mass species in true solutions. For example, charge distribution profiles (concentration ratios for metal complexes having different charges as a function of ligand concentration) were obtained for complexes of platinum metals in sulfate and sulfate-chloride solutions [64].

An effective simultaneous concentration of various trace element ions in very diluted solutions is achieved by use of such membrane processes as osmosis and reverse osmosis. The latter is utilized in water desalination technologies and for production of special purity water [5]. Such processes are only seldomly applied to analytical preconcentration although some interesting examples have been reported. Thus, acetylcellulose membranes have been successfully used for preconcentration of Cd, Cu, Ni, Mn, Zn by reverse osmosis [65].

Methods, in which two parameters (e.g., pressure drop combined with electrical potential drop in electroosmosis or concentration and potential drop in electrodialysis) control the total flux passing through the membrane, are more effective and more frequently used. Electroosmosis is of particular interest for preconcentration of ultratrace elements in the analysis of extremely pure water [5]. Concentration factors of  $10^2$  -  $10^3$  have been achieved for inorganic cations and anions. Membrane filters (pore diameter 0.45 and 0.50  $\mu\text{m}$ ), containing quaternary nitrogen and having a positive charge at the surface at  $\text{pH} < 9$ , were used for electroosmotic preconcentration of various metal cations. Acetylcellulose and PTFE 0.45  $\mu\text{m}$  membranes with a negatively charged surface were applied for simultaneous enrichment of anions ( $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ) [66].

A combination of two control parameters can also result in better separation of different ions. High separation factors have been obtained for metal cations by simultaneous application of electric potential and pressure differences to the filtration systems [67-70]. A preconcentration of the ions is also possible [71].

Amongst the techniques described above, reverse osmosis and electroosmosis are attractive from the point of view of the capability to preconcentrate practically all the solutes present in the solution. On the other hand, the advantage of high absolute enrichment factors and, therefore, the subsequent determination sensitivity may be not very important because of the interferences from the major sample constituents preconcentrated together with the trace elements. The described methods for the membrane separation of inorganic ions without chemical reagents can hardly at present compete with the reagent-based membrane and other techniques known.

### 3. MEMBRANE SEPARATIONS USING CHEMICAL REAGENTS

#### 3.1. Collection of trace elements on a membrane filter

A chemical reagent added to the aqueous sample, to the recipient solution or built in the membrane can improve the separation or increase the concentration efficiency. If the reagent is built in, the membrane is called chemically active. Applications of active membranes have been reviewed elsewhere [5]. If an inert solid membrane is used, an inorganic reagent or organic monomeric or polymeric agent is added to the sample to obtain insoluble compounds of analytes.

A combination of membrane filtration and XRF was used for the determination of molybdenum in sea water after precipitation of molybdenum diethyldithiocarbamate [72], for the determination of orthophosphate in waste water after precipitation of iron(III) hydrogen phosphate [73]. Preconcentration of trace levels of cadmium in water was combined with the determination by electrothermal AAS [74]. Cadmium was collected on an acid-soluble nitrocellulose membrane filter as the 1-(2-pyridylazo)-2-naphthol complex and then dissolved in concentrated sulphuric acid. The resultant solution was diluted with water and subjected to the determination. The detection limit was 1.5  $\text{ng l}^{-1}$  in river and sea water samples.

A precipitation - membrane filtration procedure can be combined with UV-visible spectrophotometry. Direct spectro-photometric determination of a coloured precipitate at the membrane is possible as shown in the determination of aluminium in tap water after collection on a membrane filter with Chromazurol S and Zephiramine [75]. The concentrate can also be dissolved in an organic solvent together with the nitrocellulose or acetylcellulose filter prior to spectrophotometric measurement. A method was described for the determination of germanium [76]. A coloured complex of germanium with phenylfluorone was collected on a membrane filter. The complex, together with the filter, was dissolved in dimethylformamide, and the absorbance of the solution was measured. The time required for one run was about 10 min and germanium at  $1 \mu\text{g l}^{-1}$  levels could be determined. Similar procedures were applied to the determination of arsenate, arsenite, phosphate and silicate as heteropoly species [77-80]. Phosphate was also determined spectrophotometrically after the collection of ion pair of molybdophosphate with bis[2-(5-chloro-2-pyridylazo)-5-diethylaminophenolato]cobalt(III) and dissolution in dimethylformamide [81]. This enrichment procedure was used before capillary isotachophoretic determination of phosphate [82].

Removal of the analyte-containing precipitate with a thin membrane filter is similar to conventional filtration with a filter paper. However, there is a difference: the precipitate does not penetrate the membrane filter material thus facilitating its quantitative removal from the membrane surface for subsequent analysis.

### 3.2. Liquid-phase polymer-based retention

Soluble complexing polymers are being used in selective membrane separations of inorganic ions in homogeneous aqueous phase. Such polymeric reagents form soluble polymer complexes which are separated from low-molecular compounds by membrane filtration processes [83]. Thus, uncomplexed inorganic ions can be removed with the filtrate, whereas the water-soluble polymer complexes are retained. To separate and preconcentrate metal ions, their solution to which a polymer is added can be passed from a reservoir into the filtration unit. In earlier studies this procedure was designed for the recovery of elements from dilute solutions [83,84]. Later another procedure of absolute preconcentration was recommended in which the polymer reagent was added directly to the cell and then a large volume sample passed through a solution of a relatively high and constant polymer concentration [85] (see Fig. 2).

However, interfering components of the test solution partly remain in the cell after the filtration run, even when they do not interact with the reagent. This can cause difficulties, e.g. in trace analysis of highly mineralized waters. Therefore, a combined procedure is of interest: a sample with a large volume is passed from reservoir II through a much smaller volume of polymer solution in the cell and then washed with pure water from reservoir I to remove remaining amounts of constituents not complexed by the polymer. Thus, both absolute and relative preconcentration are achieved.

To separate components of a small volume of sample, the liquid sample is placed in the polymer-containing cell solution and washed with water. The pH is adjusted to a value at which the elements of interest are retained and other species removed.

Fig. 2 shows the principles of the procedure used for preconcentration of elements from a large volume sample (dashed lines) and of the procedure for separation of ions present in a small volume sample (solid lines). The main features of a liquid-phase polymer-based retention system are a membrane filtration cell, reservoirs and a pressure source, e.g. a nitrogen bottle. Conventional stirred filtration cells or a specially designed tangential-flow cell [41] equipped with a pump can be used. Membranes made of polysulfone, polyamide, cellulose, etc. are suitable. Essential parameters are the molecular mass exclusion rate in wide pH ranges (1-10), an appropriate permeate flow rate (1-10 ml min<sup>-1</sup>), retentate volume (2-10 ml) and gas pressure (300 kPa is a suitable pressure in most cases). A nominal exclusion rate of 10 kg mol<sup>-1</sup> proved to be convenient for polymers having a molecular mass between 30 and 50 kg mol<sup>-1</sup>. A polymer concentration of 1-4% in the cell solution is most appropriate for both retention of elements and their subsequent determination in the retentate.

Poly(ethyleneimine) (PEI), poly(acrylic acid) (PAA), poly(1-vinyl-2-pyrrolidone) (PVP) and other widely used polymers were applied to preconcentration and separation of various elements. For example, PEI can be used for the retention of Cu, Ni, Co, Zn, Cd, and Pb at pH 5-7. Reagents were also utilized which had typical acidic chelating groups - 8-quinolinol and iminodiacetic groupings, neutral thiourea groups; trimethyl-ammonium-based anion-exchange groups [86]. Introduction of strong chelating groups into the basis polymer backbone results in more effective retention of metals. Thus, at pH 1-3 PEI-based reagent bearing 8-quinolinol functions retains quantitative Fe, Bi, Zr, Nb and W. At pH 4 this reagent completely concentrates triply charged rare earth and transplutonium cations, U and Pu used in radioanalytical studies [87].

Thiourea-containing derivatives of PEI, PVP and PAA are effective reagents for separation of mercury and noble metals from other elements. The reagents quantitatively retain Hg, Ag, Au, Pd, Pt from chloride solution at pH 1 and separate these elements not only from alkali metals but also from non-ferrous metal ions such as Co, Zn, Cd and others. Of practical interest are also polymers bearing quaternary ammonium function which serve as reagents for retention of anions, e.g. of halide ions and oxo anions such as selenite, chromate, arsenate and phosphate [86]. Poly(vinylamine), polyurethanes, poly(vinylalcohol) and its phosphorus-containing derivatives, poly(acryloylphosphonic acid) [88, 89] as well as reagents containing allylamine, vinylpyridine, 15-crown-5 and 18-crown-6 groups [90] can also be recommended for analytical separation.

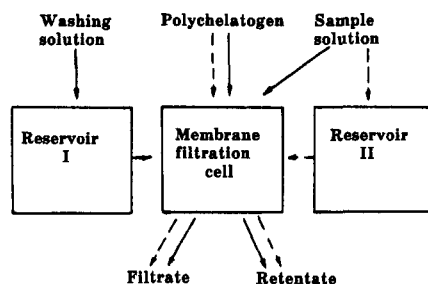


Fig. 2. Principle of the liquid-phase polymer based retention method



Preconcentration of elements by the liquid-phase polymer-based retention (LPR) method combines with different determination methods e.g., with AAS, ICP OES, stripping voltammetry and other techniques applicable to the analysis of aqueous solutions. The final solution (concentrate) obtained after the separation, is an aqueous solution of 1-4% polymer which does not interfere significantly with the determination methods mentioned.

A combination of AAS and LPR has been used for water analysis using both flame and electrothermal procedures [91]. Because PEI retains Cu, Ni, Hg and Cd quantitatively, these elements can be determined in river waters with preconcentration factors between 20 and 250. The combination of 250-fold preconcentration with ICP-OES analysis of a PEI-based retentate enables the detection limits well below  $\text{ng ml}^{-1}$  levels to be reached for Cu, Ni, Cd, Zn, Pb, Fe and Cr. After 50-fold preconcentration of Cd, Pb, Hg and Co from water using PEI for metal retention and acidification of the concentrate to pH 1, stripping voltammetry makes it possible to determine down to a few  $\text{pg ml}^{-1}$  of these elements [86].

The LPR method, like other flow techniques, can be easily automated. Radiometric, spectrophotometric and other flow-through detectors may be recommended to measure the element concentration in the retentate. The viscosity of the retentate, containing more than 2-3% polymer may cause some difficulties if flame AAS or ICP OES are used for the retentate analysis. Another problem is encountered in the studies by stripping voltammetry and other electroanalytical techniques: retentates containing thermodynamically very stable or kinetically inert complexes may be difficult to analyse as too strong acidification is required.

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