A Highly Effective Dynamic Method of Membrane Concentration

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A new method of chemical concentration of elements is presented.

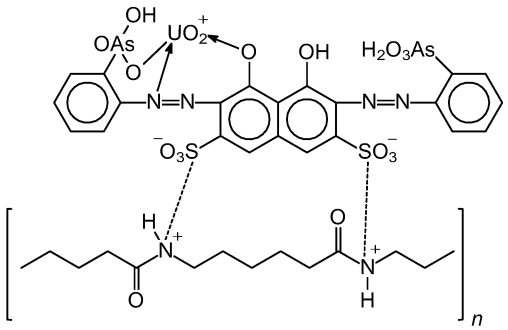
Preconcentration prior to the determination of trace inorganic elements in different environments significantly enhances the potential of spectrophotometric methods using organic reagents. The theory and application of preconcentration methods *e.g.* extraction, co-precipitation with organic co-precipitants, ion exchange, use of chelating resins and other sorbents and membrane filtration being developed are very well elaborated and are described in the current literature.[1]

The sorption method with chelating resins has been used widely as the most effective method and by means of this method the greatest coefficients of concentration (K) can be achieved.[2] However, the theoretical K-values (in the range of 10^4–10^5) are not often realized in analytical detection because it is necessary to convert the concentrate into a form suitable for measurement of the signal. We can illustrate this approach by a procedure that includes concentration of uranium on the polyarsenaso-n sorbent and its spectrophotometric determination in the eluate by arsenazo III reagent.† The concentration coefficient is 10^2n in this case only.

The method suggested above is based on the principle of elements concentration by co-precipitation with organic co-precipitants from dilute solutions[3,4] using the new analytical technique. The principal difference is the concentration of metal ions in the form of complexes with specific organic reagents using membrane filtration and their determination by diffusion reflectance spectroscopy directly on this membrane filter.

Based on this assumption, the ion-pair type of co-precipitate elements exist in the form of complexes with organic reagents which contain SO_3^- groups, *e.g.* analogues of arsenazo III.[3] The principle of this procedure implies that complex formation of the elements determined is carried out with selective organic reagents in solution and subsequent sorption of this complex on the membrane in the course of filtration. This can be shown graphically, Scheme 1.

Selective preconcentration can be performed by creating and optimizing special conditions for the most sensitive,



Scheme 1

selective and reliable reagents in particular applications. The retention mechanism of the metal ion and organic reagent complex on the anion-exchange membrane filters is based not only on electrostatic forces but also on non-hydrophobic interactions between the polymer matrix and molecules of organic reagent.[5]

This method allows for the concentration of ultratrace elements and the elimination of unfavourable effects due to the high concentration of salts. The complex is evenly distributed over the membrane. The concentration coefficient value is high because the elements are transferred from a large volume (1 l) of the solution to a small one (membrane volume 0.02 cm^3). Diffusion reflectance spectroscopy is the detection method (analyser PFKD-1000, firm Eureka, Russia).

The organic reagent and its metal ion complex uniformly cover a membrane. We emphasize that this complex can be distributed over the membrane surface. Consequently, in this case the concentration coefficient must be higher. In this study arsenazo III and UO_2^{2+} was the model system. The concentration coefficient 3×10^5–6×10^6 (Table 1) with a concentration of 0.5 ppb uranium(VI) from 1 l of solution has been found. No concentration coefficient values as high as that have been reported in the literature.[1]

New, porous polymeric films are important for selective concentration of organic reagents and their complexes with elements. This material is of white colour, non-transparent, 100–105 mcm thick. The membrane is a slightly basic ion-exchange polymer with the $(-NH-(CH_2)_5-CO-)_n$ group as the structural unit of the polymer chain (firm Mehis, Estonia). It has been proposed that the SO_3^- groups of arsenazo III interact with amino-nitrogen groups converting the membrane amino groups into the protonated form. In this case the membrane plays the role of macrocomponent used as collector.[3,4] Organic precipitating agents are certainly not needed in this method.

The process of sorption has been illustrated by the example of the model system arsenazo III–UO_2^{2+}. A sample of artificial sea water has been used[3] with pH 1–2. The control of uranium(VI) content in water is of great importance because of its dangerous effects on the metabolism, in particular, on enzymes. Since the most harmful impact of uranium upon the human organism is its influence on the kidneys, uranium is called "kidney poison".[6]

The dependence of sorption effectiveness upon arsenazo III concentration is shown in Fig. 1, where R is the relative

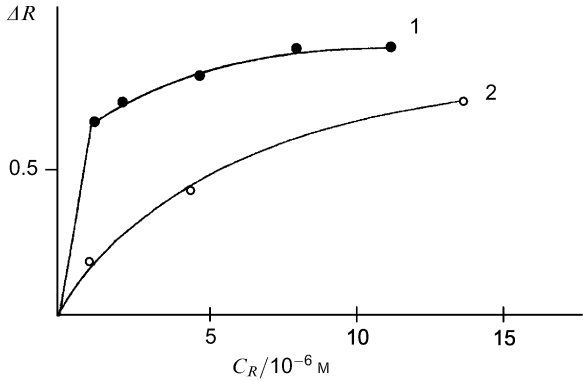


Fig. 1 Diffusion reflection of arsenazo III, membrane diameter 25 mm, dimensions of pore 0.2 mcm, 0.5 M NaCl, pH 2: (1) dynamic sorption of arsenazo III, $V = 40\,cm^3$, flow velocity 80 $cm^3\,min^{-1}$; (2) static conditions, $V = 25\,cm^3$, 5 min.

† [2,2′-(1,8-Dihydroxy-3,6-disulfonaphthylene-2,7-bisazo)bisbenzenearsonic acid].

Table 1 Concentration coefficients of uranium(VI) using arsenazo group reagents.

Method of concentration	Composition	Determination	Concentration coefficient	References
Co-precipitation with organic co-precipitants	Arsenazo I and chloro-*N*,*N*′,*N*″-triphenylguanidine	Spectrophotometric	2.8×10^2	3
Chelating sorbents	Polyarsenazo-n	Spectrophotometric	2.0×10^2	2
Optical sensors	Arsenazo I and pyridylazonaphthol-fibre, weak-base anion exchanger	Diffusion reflectance spectroscopy	1.9×10^4–3.0×10^5	9
Filtration with liquid membrane	Arsenazo III and glycine	Spectrophotometric	4×10^2	10
Filtration with membranes of a specific kind	Arsenazo III and poly-ε-caproamide membranes	Diffusion reflectance spectroscopy	3×10^5–6×10^6	our data

reflection coefficient. As can be seen from Fig. 1, the hydrodynamic situation in the filtration allows for the best isolation of complex from solution. It is known from the kinetic parameters of the UO_2^{2+} reaction with arsenazo III that the interaction is rather fast.[7] Thus, complete complexation occurs within 3.5–22 μs, in spite of the low uranium concentration.

The principal limitation on the analytical concentration has been overcome in the procedure suggested. This was possible firstly, due to the realization of high *K* values that are reliable in sorption methods. Secondly, an equilibrium state for the distribution of the elements to be concentrated between two phases can be reached. The combination of the advantages of preconcentration using co-precipitation with organic co-precipitant reagents with a dynamic method of concentration gives good results. Therefore, membrane filtration[8] in combination with subsequent photometric measurements of the concentrate on the membrane can be considered as a new method of obtaining a high concentration coefficient in microelement determination.

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