

Behaviour of chromatographic separation of rare earth elements on dynamic membranes that formed in the process of ultrafiltration

S. M. Ilina, Yu. V. Alekhin, S. A. Lapitsky, M. N. Sokolova
Lomosov Moscow State University, Moscow
alekhin@geol.msu.ru, fax: 8 (495) 939 48 08, tel.: 8 (495) 939 49 62

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The works on modeling object have been spent to solve the problem of the various elements balance of the individual components of runoff, estimates of migration, research on the transformation and natural differences in the truly dissolved and colloidal forms of individual metals with organic matter migration in natural waters. The object is a classic watershed with soil sampling and soil extracts, samples of bog and river water with an analysis of the composition and distribution of dissolved organic matter (DOM) and trace elements in the components supply and runoff. There was a sampling of large volumes (40–80 liters) with consistent use of methods of stepwise cascade filtration and ultrafiltration to divide these groups on various types of filters and to study molecular weight distribution of OM. Objects of study are the small rivers of Russia (North Karelia and Vladimir region). Composition of isolated fractions of filtrates and sediments were analyzed sequentially and separately by different methods. All filtrates and dialysate were analyzed for a wide range of elements by ICP-MS, the DOM - using three methods: catalytic combustion; spectrophotometrically in the range of 400–590 nm (differential spectra of DOM) and chromatographic HPLC method. Using the method of cascade (series) filter allows us to obtain analytical information about correlations of organic content and other elements in a series of Using the method of cascade (sequential) filter allows us to obtain analytical information about correlations of organic content and other elements in a series of sequential filtrates. In the latter case it is sufficient to effectively apply the method of «elimination curves», when a series of sequential filtrates compared themselves to reduce the concentration of trace elements and their values are normalized to the total, and also changes the number of macro components - the complexing compounds and potential of sorbents. Fresh and ultrafresh river water of boreal zone with the usual predominance of bog nutrition, and small rivers of the taiga boreal forest area was generally dominated among macro-components of OM humic nature complexes and iron hydroxide sols, and a relatively small amount of suspended clay particles. For the separation of such mixtures on size fractions, so that the last filtrate is contained only «truly» dissolved forms, requires a combination of filtration, ultrafiltration and hyperfiltration. The overall cascade consecutive filters, technologically and chemically different nature, usually not more than 5-7 denominations. But the basic principle procedures are the branches coarse, so sedimentation volatile fraction more 0,2-0,4 microns (filtering), the separation of humic and fulvic acids by ultrafiltration and the separation of narrow molecular fractions of dissolved OM in the range of molecular weights of 1 - 100 kDa by methods hyperfiltration. Hyperfiltration in the standard version is already an example of reverse-osmosis filtration and is widely used for desalination of water. But on the basic physico-chemical mechanism of separation of solution components is different enough from the processes of filtration and ultrafiltration. The last two processes on the mechanism of separation is a process analogous to the usual sieve separation, in which principal are steric constraints - the ratio of particle sizes and then. Hyperfiltration of natural waters, especially OM solutions with a wide range of molecular masses, is always a combination of reverse-osmosis process and sieve separation. The nomenclature «kilodaltons» filter based on the molecular density of spherical protein molecules. With some degree of conditionality can be assumed that the passage of molecules of 100 kDa correspond to the pore diameter of 68 Angstroms (0.0068 micron) for the 10 kDa - 0.0037 micron, 1 kDa - 0.0017 microns. The last membranes (1 kDa) are very similar to the declared limit of 10 - 20 Angstroms, after which the filtrate was assumed to contain only the solute free ultracoloidal size matter. Conformity of the border is obvious, because for the humic acids molecules formally colloidal size with a mass of 100

kDa and a more satisfied sedimentation stability. They are «truly dissolved», while changes in pH is not specifically provoked by their aggregation and precipitation. The 1 - 100 kDa range is the most interesting for a detailed study of the natural humic OM properties in all respects. Cascade filtration as a new method for isolating narrow fractions OM and determination of associated trace element composition has a very important advantage over methods of studying the molecular weight distribution adopted in the chemistry of soils. For example, methods of chromatographic separation, is always complicated by adsorption losses of trace elements. However, the use of filters for hyperfiltration as a method of separating the factions methodically have not proved and does not rely on electrokinetic theory of reverse-osmosis separation, formally inherits the sieve-method. The ion concentration polarization (an increase of concentration of the solution to the reverse-osmosis filter for desalting) is not accompanied by excretion of much components in the sediment and sedimentation. This is a fact for OM in the filter, when the ability to aggregate in concentration and the shift of adsorption equilibrium. Therefore, the use of bilayer membrane hyperfiltration to study the molecular weight distribution requires a number of conditions, reducing concentration polarization and mechanism of reverse-osmosis delay. In standard conditions of desalting ratio of delay dissolved electrolytes typically seek to maximize. For this filter in conditions of optimal polarization, so under conditions where the concentration of dissolved electrolytes to the filter (filtrant) and demineralized water (filtrate) is stationary differ when the coefficient of delay reach 0,97-0,99. For optimal regime realizing, when $R = 0$ and no the concentration and reverse-osmosis mechanism delay, filtrant must not stirred, filtered in a current flow (the vast potential of the flow) and have retarding layer on the output of the filter for bilayer asymmetric membranes. In this case, the filter substrate gruboporistoy quickly formed a stationary area of high filtrant concentration for a loose matrix membranes prevents the aggregation of molecules dissolved OM. In this case most effectively realized version of the division only on the sieve separation mechanism. This special area under cascade filtration, we studied in our experiments, in order to assess the proportion of reverse-delay and delay associated with the separation of large molecules and their associates by the usual sieve separation mechanism. It was obvious that the integral coefficient of seeming delay, R_{Σ} , is the sum of these two effects. For information about the true molecular weight distribution (MWD) is necessary to reduce reverse-osmosis desalination. There is significant capillary backpressure in bilayer membranes, where the radius of the substrate pores, $r_1 = 0,11$ micron, and in starving layer $r_2 = 0,0014$ micron. In according with the law of Laplace, $\Delta p = 2\sigma (1/r_2 - 1/r_1)$ for membranes of 10, 1 kDa, it is close to 3 atm. When the reverse-osmosis desalination has to overcome the capillary backpressure, filtering at high differential of applied pressure. If the filter through an inverted bilayer membrane, the direction of the applied pressure coincides with the direction of the capillary pressure and effective filtering possible even at low applied pressures about 0,1-0,5 bar. If we filter mode the minimum concentration polarization (without mixing the initial solution), then go to a regime with $R \rightarrow 0$. The stationary of high concentration area, when $C_1 = C_2$, formes in a loose layer of a bilayer membranes. If $C_1 \neq C_2$ in these conditions filtration, then this effect is associated with the conventional size delay filter.

The natural water samples were filtrated through 0,22 mcm and concentrated in the column, then they were analysed by the high-efficiency liquid chromatography (HELIC) method to determine the aromatic acids presence and their concentrations. So the concentrations (mcg/L) of the acids are - gallic - 0,11; phthalic - 1,05; protocatechuic - 0,62; p-hydroxobenzoic - 0,045; vanillic - 0,18; salicylic - 3,83; ferulic - 0,025; benzoic - 1,79. The total molar concentration of these acids as well as cinnamylic, oxalic, acetic, hydroxy tricarballic and vnic acids is less then the molar concentration of the low-molecular fulvic acids.

MWD of humic OM in aqueous solutions are often studied by the methods of chromatography and cascade filtration separation with the construction of terns, as the distribution functions of the diameters and masses of the molecules. Spectra of molecular weights of humic and fulvic acids in river waters and soils are sufficiently wide, continuous (0,5 - 500 kDa), bad reproducibile. The main part of the complexes is the truly dissolved forms. It is therefore there aren't any noticeable trace elements elimination in the fulvate complexes forms up to 10-1 kDa filters. Our HPLC analysis showed that the molecules with a mass 1 kDa are dominated (Fig. 1, Table. 1). The mole (not weight!) concentrations of OM present in the formulas for the constants of complexation. So in the interval 0,2 mcm-10 kDa (0,0028 mcm) while retaining the DOC mass concentration at the level of 5,2 mg/L 8 molecules with a mass 5200000 corresponds to 4,400,000 molecules with a mass of 10 kDa. Thus, the fulvic acids molar concentrations are responsible for the main transport of trace elements, but not adsorption on the large molecules of OM. So their MWD can be studied only by the cascade filtration

method.

Table 1. Dissolved organic matter (DOC), nitrogen, macro-anions concentrations and the weight-average molecular weight (WAMW) values for the samples of the river Senga (Seng), the lake Ignatkovo (Ignat) – Vladimir Meshchyora; the stream Vostochniy (OR), the river Palojoki (KAR), the bog «ZPBL» –North Karelia.

sample	DOC mg/L	N mg/L	C/N	Cl ⁻ mg/L	SO ₄ ²⁻ mg/L	NO ₃ ⁻ mg/L	WAMW
Seng-1	23,81	1,47	16	3,71	46,10	0,10	970
Seng-2	25,39	1,11	23	4,40	40,90	0,24	960
Ign	12,40	0,58	21	-	-	-	920
OR-9	51,15	0,49	104	1,10	0,76	0,003	1260
OR-6	19,26	0,33	58	0,52	1,10	0,01	1020
OR-1	16,20	0,34	48	0,40	0,85	0,05	1010
OR-8	4,27	0,18	24	0,76	2,44	-	960
KAR-1	10,84	0,42	26	0,83	2,40	0,17	910
ZPBL-1	38,99	0,54	72	0,70	1,54	0,002	1080

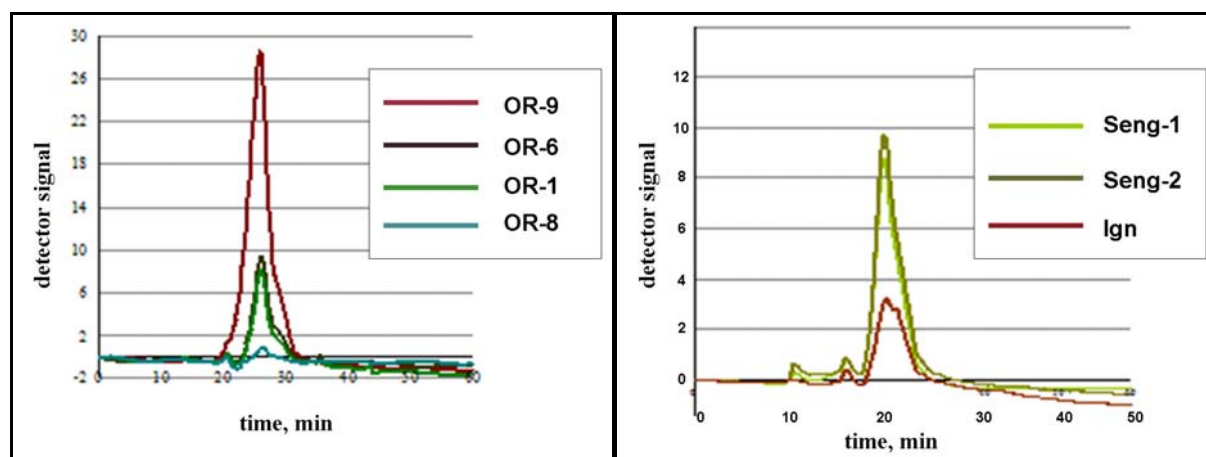


Fig. 1. The humic substances weight-average molecular weight distribution in filtrates 0,2 mcm for the natural water samples of the North Karelia (left) and Vladimir Meshchyora (right), measured by the high-efficiency liquid chromatography (HELIC) method

WAMW of the large molecular aggregates can be understood on the basis of the thermodynamic description of the analysis of their relative stability during the polymerization. On the example of the organic complexes with a large number of associated molecules I. Prigogine have showed that the solubility of these compounds can be simply related to the reactions of sequential complexation of type: $A_n + F = A_{n+1}$, where F - monomer fragment, under the assumption that for $\gg 1$ $K_n \approx K_{n+1} \approx K_{n+2} \approx K_{n+3}$, etc. This realistic assumption is equivalent to saying that for large cluster polymers the free energies of joining of the elementary fragment in a consecutive series of associates are almost indistinguishable. We developed this approach to the properties of more complex real forms of transfer - clusters of humic acids that sedimentation stability, i.e., they have Stokes diameters up to 0,2-0,4 mcm (filtrates of the conventionally dissolved forms are not capable for the fast aggregation). At a density of humic acids 1,6 g/cm³ the associates of this size have large molecular weights ($4,03 \cdot 10^6$ and $32,28 \cdot 10^6$ kDa, respectively), and actually observed (often dominated by mass) in the filtrates of bog waters and streams of the primary hydrographic network. Our calculations of the constants of humic acid sequential polymerization made from the condition that the kinetic stability of the largest associations determined by the proximity of energy addition of the monomer fragment to the energy of thermal vibrations of RT (600 cal/mol at 25°C). Calculation of association constants is made in the coordinates $\lg K_n - 1/n$ for the interval of values of n 1 - 8000000 (maximum diameter of 0,2 mcm at a mass of fulvic monomer 500 Da), when at $1/n \rightarrow 0$ $\lim RT \lg K_n \rightarrow 600$ cal/mol and $\lg K_n \rightarrow 0,44$ (Fig. 2). Using of the results of cascade filtration and HPLC allows to specify diffraction

patterns on the relative amounts of the dominant first associates (monomers, dimers, trimers) and to agree their association constants, which, may not exceed ($\lg K_n$) values of 5,5. Small binding energy predetermine stochasticity exposure mass fraction of large aggregates fluctuations of the hydrodynamic conditions and temperature at the absolute dominance of the mole (not weight!) amounts in solution of fulvic acids with a mass of 500-1500 Da.

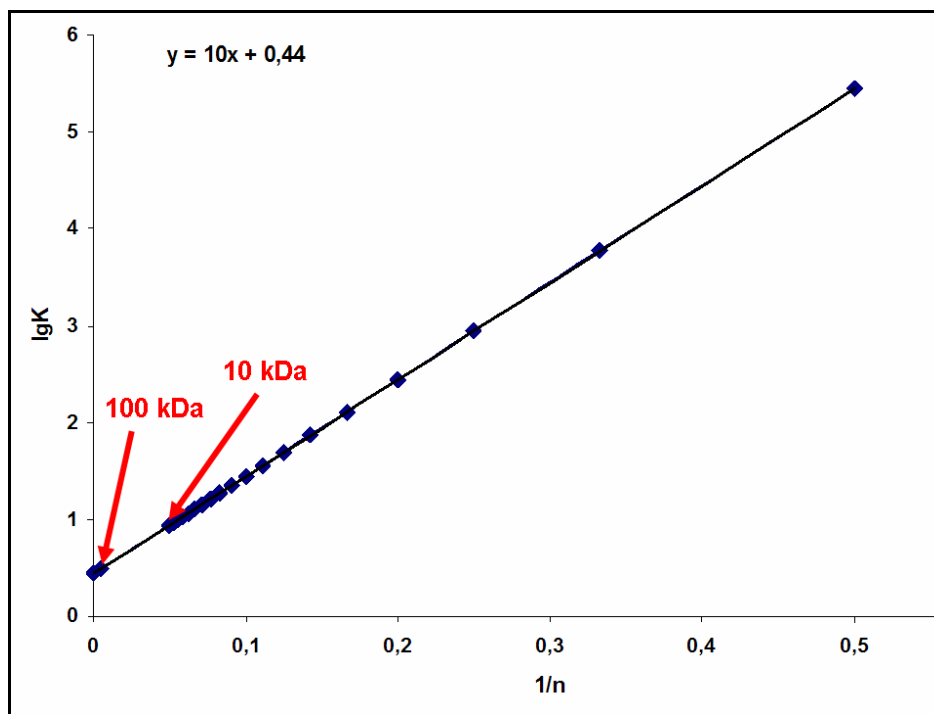


Fig. 2. The dependence of the humic cluster association constant ($\lg K$) for the sequential reactions of addition for the 500 kDa-weight unit (for illustration purposes the means of the constants were dissembled for the molecular weights range 10-100 kDa)

When the filtering volumes are large formed sediment layer can itself act as an adsorption-precipitation barrier with chromatographic separation of components in this layer. The most demonstrative example of this behavior of sediment are experiments with reverse osmosis (Fig. 3, B) and inverted membrane (Fig. 3, C). There is a progressive separation of REE in series of successive portions of the filtrate. All REE patterns of the filtrates and the initial solutions (Fig. 3, A) were normalized to their individual global prevalence for its smoothing in the samples of continental waters. But we see (Fig. 3, B) that in the first samples of filtrates the concentration of light REE is significantly lower than in the initial solutions due to the reverse-delay. In the case of inverted membrane (Fig. 3, B) the content and the patterns of REE are approximate to the initial ones in the first portions of filtrate. However, in both cases by the filtering there is a general increase of REE concentrations in sequential filtrates. By the end of experiments, we see increasing of the concentrations by 2-10 times and REE patterns complete smoothing. On the background of a general increase of the concentrations the solutions are progressively enriched in odd REEs but even REEs are delayed adsorptionally due to the ion exchange of macrocomponents within the membrane. This significant accumulation of the odd REEs in the last filtrate completely turn the usual pattern - in these solutions odd elements with lower global prevalence are dominated. This experimental fact is analogous in the different REE patterns of the initial solutions of two regions. That repetition of these elements adsorption-desorption in the long history of forming flyuvio-glacial sediments and soils of Meshchyora lowland is reflected in the smoothing of the REE patterns with the removal of lighter elements and adsorptional retention of heavy ones. For both regions the rocks of Fennoscandia are the initial substrate, but the processes of transformation of the REE patterns are far from complete in the North Karelia, which is also reflected in higher concentrations of REE in the waters of this region.

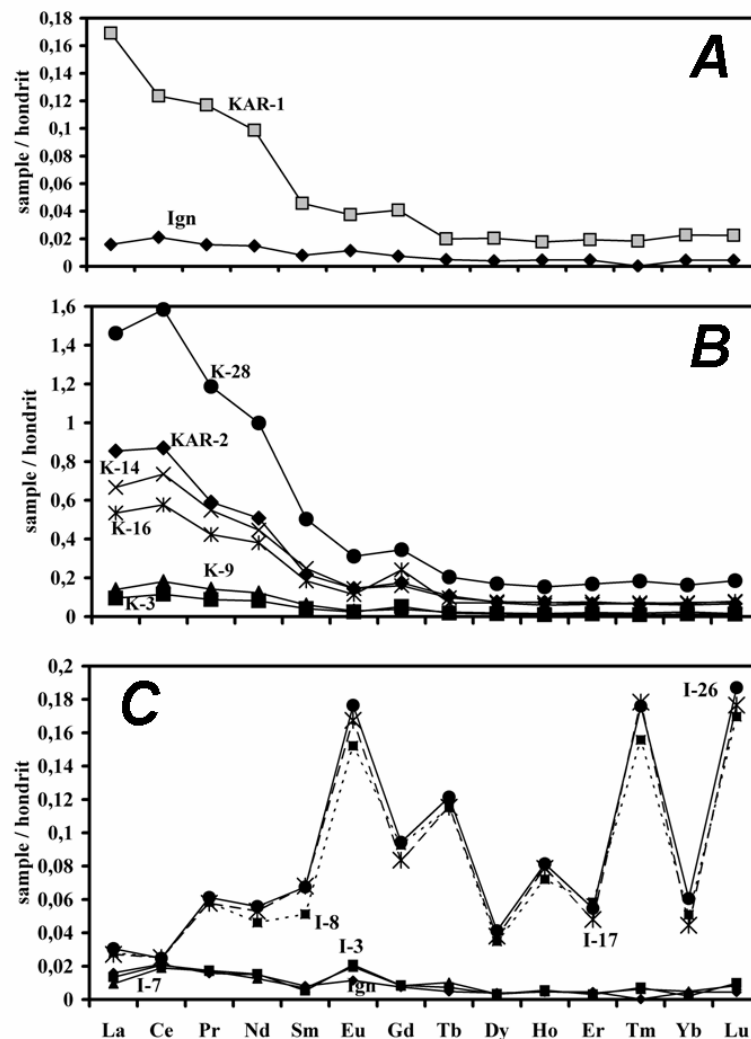


Fig. 3. (A) REE normalized patterns for the natural water samples of the North Karelia (KAR-1) and Vladimir Meshchyora (Ign); (B) REE normalized patterns distortion in the sequential samples of the reverse osmosis filtration mode; (C) REE normalized patterns distortion in the sequential samples of the filtration mode of the chromatographic fractionation on the formed sediment.

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