

Continuous-flow membrane filtration (CFMF) as a new method to study the narrow size fractions of colloidal dimension

Yury Alekhin^{1,*}, Svetlana Ilina¹, and Elena Ivleva¹

¹Moscow State University, Geochemical Department, 119234 Leninskie Gory 1, Russia

Abstract. In addition to the cascade filtering method, a new method of continuous-flow gel filtration (CFMF gel filtration) without replacing the filter septum has been developed and tested. The results of narrow size fractions separation from water samples with a high content of colloids (cascade filtration and continuous filtration) and the study of their migration with microelements are presented. An experimental investigation of the joint migration of a large number of elements (up to 40-60) and organic matter in continental waters demonstrates the high prospects for the methods to establish stable geochemical associations of trace elements adsorbed on colloids.

1 Introduction

Recently, the analysis of cascade filtration with replacement of filter septums led us to create a new and effective method to study the dynamics of separation of size fractions without replacing filters, in which the pore clogging and the permanently formed sediment layer serves as the main separation membrane in “continuous filtration” mode. Filtration through such a sediment layer as a separation membrane has a number of characteristic features and obvious advantages. When clogging the pores of the septum (cake filtration) by the colloidal fractions and increasing the thickness of the sediment, an asymptotic slowing of the volumetric filtration rate is observed, which can be linearized with the normalization functions $\lg D - \lg V_t$ and D^2/d^2 [1] (Fig. 1, A- B). The continuous gel filtration method allows obtaining reliable quantitative data of the molecular mass distribution of colloids in narrow size fractions using the value of varying hydraulic diameters, without replacing the filter septum. There is no need for an experimentally complex cascade filtering method. Using the function $D^2/d^2 = V_t$ (current value) / V_t (reference value), where D is the time-varying effective hydraulic pore diameter of the porous medium at the current volumetric flow rate, V_t (current value), the average initial known geometric pore diameter, d , and determined initial volume flow for distilled water, V_t (reference value), allows to determine the effective hydraulic diameter with the required degree of discreteness.

* Corresponding author: alekhin@geol.msu.ru

All calculations of D and data treatment from the time dependent variables V_t must be performed at a fixed and constant value of applied hydraulic pressure defined by filtration under a slight vacuum of 0.05 atm. The same calculation with knowledge of the initial flow rate for distilled water as well as the nominal value of the mean pore diameter can be applied to any filter with a complex geometry of pore spaces (Fig. 2). Usually, the hydraulic diameter is used as a characteristic of the flow cross - section in calculations of the dimensionless criteria Re, Nu, Pe (Reynolds number (Re), Nusselt number (Nu), Peclet number (Pe)). The hydraulic diameter, $D = 4S/P$ [2], cm, is the ratio of the flow cross-section to the circumference, and its value is used in a number of dimensionless parameters when solving problems associated with fluid flow in pipes, as well as in porous materials. When describing fluid flow in pipes or pores with a variable shape and cross-section, it is preferable to use the hydraulic diameter D . With a decrease in the wetted flow cross-section with a constant total flow area, the Darcy constant in the Darcy law decreases in proportion to the decrease in the flow rate, where the decrease in the effective cross-section is proportional to D^2 . The perimeter, P , becomes unproductive, and does not unambiguously characterize the pore size and porosity. In this case, there is a need for a test calibration of the pore size through diameters of passing or non-passing molecules, usually spherical "globular" proteins. However, it turned out that there is the possibility of a direct solution of the problem without using test molecules of a known size using the proposed method of continuous-flow gel filtration (CFMF gel filtration).

2 Methods of research

Water samples were taken from 2 different reservoirs, eutrophic lake Ershevik and dystrophic lake Ignatkovo. The samples were initially taken in 5-liter plastic cans. Fifty-ml aliquots were withdrawn from the 5L reservoir for further filtering.

A large number of microelements (up to 40-60) were analyzed in the filtered samples by ICP MS (ELEMENT-2).

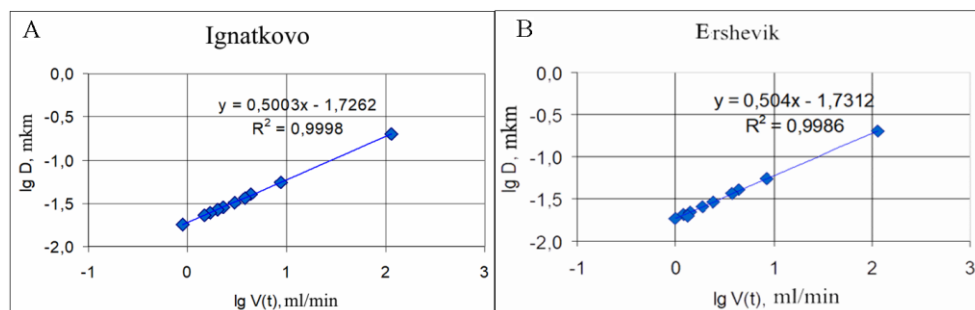


Fig. 1 (A-B). Normalization functions for determining the hydraulic diameters of colloidal particles. With large volumes of filtration, clogging of the pores leads to the appearance of osmotic effects.

The initially developed approach used polyethylene terephthalate membranes with cylindrical pores of known permeability for distilled water, constant hydraulic pressure, known pore diameter and initial porosity. With this baseline, the task was reduced to a simple recalculation of the flow rate in terms of the hydraulic diameter for any time.

We do not expect new patterns to appear when filtration rate drops, that is, when the permeability of the gel phase with respect to water changes. It asymptotically tends to the limit determined simply by the diameter of the monomers of water (solvent), that is, 2.9×10^{-8} cm (2.9 Å). This limit allows us to constrain physically the normalization function (Fig. 1A and 1B) and use it to estimate the required filtering volumes. The phenomenon of

the same retardation for macromolecules, for example, humic acid, will be observed with much larger pore diameters [3]. If the volume flow rate decreased by 100 times, which corresponds to the same decrease in the wetted cross-section, then the hydraulic diameter decreases by 10 times due to the quadratic relationship between the pore wetted cross-section and the hydraulic diameter. Clogging of the pores of gel-like sediment with an initial diameter of 0.2 μm with a hundredfold reduction of the flow rate corresponds to a decrease in the effective cross-section and the average hydraulic diameter to 0.02 μm . In this case, the initial porosity, equal on average to 7.5% for the FiTreM-0.4 μm filter, also decreases by a factor of 100, or to 0.075%. However, if the main task is to extract sufficient quantities of suspensions so that the solids can be studied, a sample of 50-100 liters should be filtered slowly, without stirring; a process that takes 3-5 days.

3 Results

Let us focus once more on the importance of determining the volume flow of distilled water. Although in track lavsan membranes, all pores are ideally "calibrated" (a small dispersion of single pore diameters is 5-10%), but the pore distribution is not spatially uniform, since the share of cluster pore mergers is significant. SEM micrographs of the membranes (Fig. 2, 3) show that the filter nominal values do not correspond to the actual ones, and for each filter used, it is required to control the initial volumetric filtration rate in distilled water. In order to justify applicability of the FiTreM membranes for the separation of narrow size fractions by gel filtration, statistical treatment of the micrographs was performed. To calculate the pore area and distribution of the geometric forms (single and merged) for the track membrane, the STIMAN computer code was used [4].

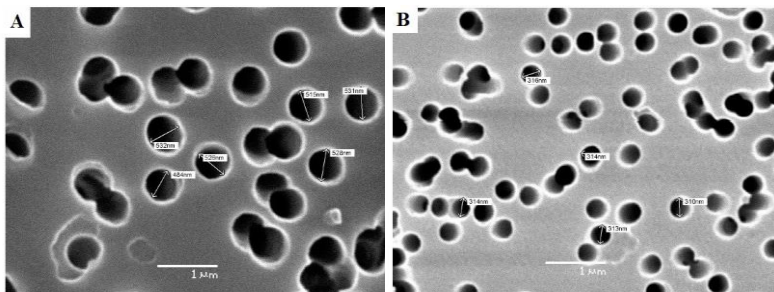


Fig. 2. Filter with a pore diameter of A 0.4 μm , B 0.2 μm

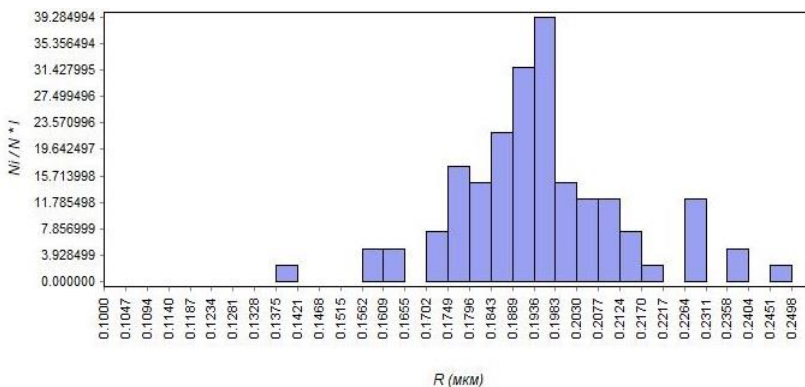


Fig. 3. Histograms of the pore size distribution for a filter with a nominal pore size of 0.2 μm .

A key feature of dynamic approach developed here is the continuous filtration of the original colloidal solution, but by definition it is always in equilibrium with the truly dissolved forms of elements, which are only partially in the adsorbed state. The consequence of this process is the continuous removal of colloidal particles on the filter, but only with a fraction of the microelements adsorbed on them. Therefore, the curves of apparent dissolved concentration change over time (with the total filtrate volume) and have the form of regular asymptotes (Fig. 4, 5), where the lower limit for the element is its steady-state concentration, and represents the truly dissolved form. Figures 4, 5 show dependencies of the element contents on the filtered volume. In these figures, the main y-axis is concentration of the elements, and the right-hand y-axis is the filtration rate (blue and green). As seen in the figures, some of the elements behave conservatively - the concentration does not change as the filtering proceeds (V, Co, etc.). The others correspond to the proposed elimination model - concentration of the elements asymptotically decreases during filtration (As, V, Cr, Co, Zr, Mo, Cd, Sb).

An important task in the experimental data treatment is the correct mapping of the dynamics of elimination of the element proportion with the colloidal fractions. The easiest way to do this is to plot data in the coordinates $\Delta C - D$, where $\Delta C = C - C_0$. However, it is preferable to use the plots of C / C_0 vs. $\lg D$ with a good linearity of the dependence between $\lg D$ and $\lg V$. This is a consequence of the fact that the hydraulic diameter and the volumetric flow similarly depend on the dynamics of the decrease of the effective flow cross-section.

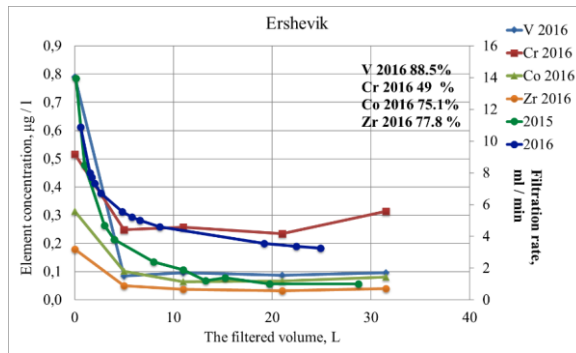


Fig. 4. The curves for deducing V, Cr, Co, Zr from the experimental data (Ershevik, 2016).

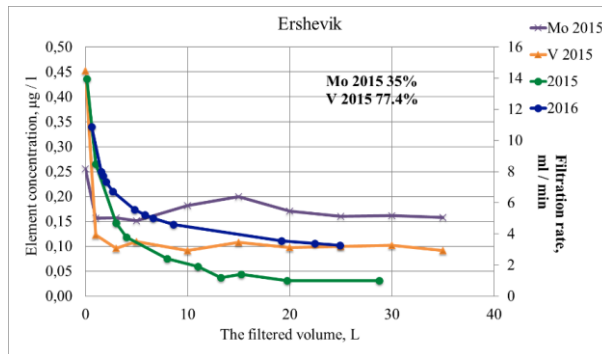


Fig. 5. Curves and percent removal of V and Mo (continuous filtration, Ershevik, 2016).

4 Conclusions

Comparison of experimental results and capabilities of data treatment methods for continuous and cascade filtering suggests that it is preferable to conduct a detailed study of colloidal fractions in the case of continuous filtering, when the main patterns of retardation (i.e., removal from the filtrate into the forming sediment layer on the filter surface) can be more correctly investigated with membranes, where the gel phase itself occurs with colloids of continuously decreasing diameter. Application of this approach guarantees the study of the distribution of the colloid molecular masses with unbiased estimates of particle size fractions, in contrast to the capabilities of the flow-field-flow fractionation method [5]. In combination with the analysis of the composition of microelements of consecutive filtrates, we can determine the ratio of the fractions of truly dissolved and colloidal forms for a wide range of microelements and water reservoirs. Analysis of the results obtained in [6-8], with our methodological support [1, 9-11] using the cascade filtering method [7] when replacing (up to 7-11 partitions) shows that it does not lead to easily interpretable dependencies of the proportions of microelements which are not retarded on a large series of filters. It is difficult, if not impossible, to control the exact pore size, the dynamics of their partial clogging with such filtration. Analysis of membrane phenomena in the sediment, as in the main separation membrane, in the CFMF gel filtration method does not have such significant drawbacks. Using this method of microcomponent separation, the percentage content of colloidal forms can be clearly defined and interpreted.

References

1. Yu.V. Alekhin, S.M. Ilina, S.A. Lapitsky, Sitnikova M.V. / *Bul. MSU. Geology*, **6**, 49 (2010)
2. Yu. I. Dytnerky. Processes and devices of chemical technology. Part 1. Theoretical foundations of chemical technology processes. Chemistry (1995)
3. Y. Wei, A.L. Zydney, *Journal of Membrane Science*, **157** (1999)
4. V.N. Sokolov, D.I. Yurkovets, O.V. Razgulina, V.N. Melnik / *Izvestiya: physics*. **68**, 9 (2004)
5. J.C. Giddings, F.J. Yang, M.N. Myers / *Science*, **193**, 4259 (1976)
6. S.M. Ilina, F. Poitrasson, S.A. Lapitskiy, Y.V. Alekhin, J. Viers, O.S. Pokrovsky / *Geoch. Cosm. Acta*, **101** (2013)
7. S.M. Ilina, J. Viers, S. Mialle, V. Mavromatis, J. Chmeleff, P. Bruner, S.A. Lapitskiy, Y.V. Alekhin, H. Isnard, O.S. Pokrovsky / *Chem. Geol.*, **304** (2013)
8. S.M. Ilina, S.A. Lapitskiy, Y.V. Alekhin, O.Yu. Drozdova, J. Viers, O.S. Pokrovsky / *Riparian zones. Characteristics, management practices, and ecological impacts*. Nova Science Publishers Inc. New York (2016)
9. Yu.V. Alekhin, S.M. Ilina, S.A. Lapitsky, O.S. Pokrovsky, J. Viers, O.Yu. Drozdova / *Bul. MSN. Geology*. **87**, 5 (2012)
10. Yu.V. Alekhin, S.M. Ilina / *Proc. Conf. GEIWR*, 587 (2015)
11. Y.V. Alekhin, M.A. Makarova, E.A. Kozachenko (Markova), E.S. Shipilova, I.U. Nikolaeva, M.I. Makarov / *Experiment in GeoSciences*, **23**. 1 (2017)