

## MEMBRANE GAS SEPARATION MODULE WITH PULSED RETENTATE FOR LOW-PERMEABLE COMPONENT RECOVERY

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The paper presents the experimental study of a novel unsteady-state membrane gas separation approach for recovery of a slow-permeant component in the membrane module with periodical retentate withdrawals. The case study consisted in the separation of binary test mixtures based on the fast-permeant main component ( $N_2O$ ,  $C_2H_2$ ) and the slow-permeant impurity (1% vol. of  $N_2$ ) using a radial counter-current membrane module. The novel semi-batch withdrawal technique was shown to intensify the separation process and provide up to 40% increase in separation efficiency compared to a steady-state operation of the same productivity.

**Keywords:** membrane gas separation, unsteady-state operation, process intensification, separation efficiency, membrane module

### 1. INTRODUCTION

Currently, the main trends of membrane gas separation development include the synthesis of new membrane materials with required properties (Akhmetshina et al., 2017; Friess et al., 2017; Válek et al., 2017; Rezakazemi et al., 2018) and also the development of novel engineering approaches for the improvement of membrane apparatus performance (Atlaskin et al., 2019; Baker et al., 2017; Castel et al., 2018; Chen et al., 2014; De Almeida et al., 2017; Kundu et al., 2016; Trubyanov et al., 2017; Wang et al., 2011). It is known that transient regimes could give a considerable increase in separation efficiency compared to a steady-state operation at the expense of a productivity loss (Wang et al., 2011). Recently it has been shown that novel pulsed retentate separation approach holds great promise for the improvement of a single membrane module separation ability without productivity loss (Trubyanov et al., 2017). The enhancement of the separation efficiency up to 80% (depending on membrane selectivity) was demonstrated in a fast-permeant impurity removal during pulsed retentate operation in comparison with a steady-state process. Current research aims at exploring the capabilities of the novel process intensification logic for slow-permeant component recovery. The principal objective is to achieve higher separation performance of a single module by periodical product withdrawals keeping the desired level of productivity. Such a technique constitutes the essential novelty as compared to the intensification methods considered in the literature so far (Wang et al., 2011).

In this study, the separation of two binary mixtures under unsteady-state operational conditions has been studied against the conventional steady-state separation in order to identify the influence of the operating

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parameters and compare the behavior of the novel separation technique both for fast-permeant impurity removal and for slow-permeant component recovery.

## 2. MATERIAL AND METHODS

The two-step semi-batch separation process with pulsed retentate was conducted for the high-efficient countercurrent radial membrane module (Drozdov et al., 2002) through the cyclic alternation of a so-called “closed mode” operation (no product flow) (Drozdov et al., 2003) and a short-time product withdrawal according to the description given elsewhere (Trubyanov et al., 2017). The experimental setup designed for testing the performance of a steady-state and a pulsed retentate operation is shown in Fig. 1.

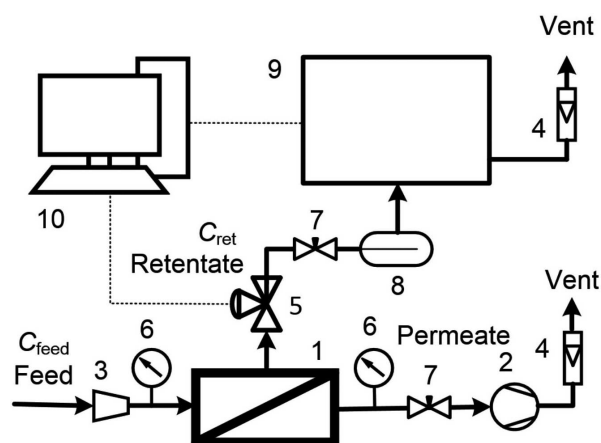


Fig. 1. Principal scheme of the experimental setup for testing the performance of a pulsed retentate operation: 1 – radial counter-current membrane module; 2 – vacuum pump; 3 – feed pressure regulator; 4 – flow meters; 5 – automated pneumatic valve; 6 – high precision pressure gauges; 7 – needle valves; 8 – mixing chamber; 9 – gas chromatograph with thermal conductivity detector (GC/TCD); 10 – workstation

The crucial component of the setup is a radial countercurrent membrane module made of AISI 316 stainless steel with PTFE sealing. The scheme and the flow scheme of the membrane radial module are shown in Fig. 2. An automated pneumatic valve was mounted on the retentate line to carry out periodical withdrawals of impurity concentrate. The high-performance elastomeric poly(-arylate-siloxane) SILAR™ membrane with 5 μm selective layer was used in the current study of separation of binary mixtures based on a fast-permeant 99% of basic component (nitrous oxide or acetylene) and a slow-permeant impurity (1% vol. of

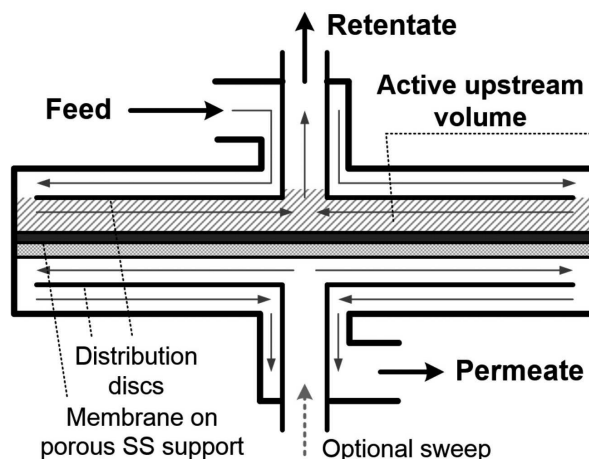


Fig. 2. Principal flow scheme of the radial countercurrent membrane module (adopted from Drozdov et al., 2002)

nitrogen). Gas mixture was supplied from the cylinder to the feed side of the membrane module through a pressure regulator with a constant pressure maintained at  $120 \pm 5$  kPa. The permeate was evacuated with a vacuum pump with a constant flow of  $100 \text{ cm}^3/\text{min}$  controlled by a flowmeter. In a steady-state operational mode, the retentate flow was regulated by a needle valve in the range of  $4\text{--}100 \text{ cm}^3/\text{min}$ . The impurity concentration variation during the separation process was monitored by the gas chromatograph with thermal conductivity detector (GC/TCD) CvetAnalytik (Dzerzhinsk, Nizhny Novgorod Region, Russia). Controlled operating parameters included time of a “closed mode” operation (enrichment time), time of retentate withdrawal, flow and amount of retentate sample withdrawal, transmembrane pressure, feed and permeate flows. The system automatically executed 50 cycles of retentate withdrawals at a given set of operating parameters (opening and closing times, transmembrane pressure, feed and permeate flow rates, and retentate sample amount), and then the average composition of the retentate sample is determined by starting the GC analysis. The experimental procedure was analogous to that described in detail elsewhere (Trubyanov et al., 2017).

### 3. RESULTS AND DISCUSSION

According to the research aim, the behavior of the pulsed retentate mode under different operating parameters (enrichment time, time of retentate withdrawal, flow and amount of retentate sample withdrawal) was experimentally studied for slow-permeant component recovery, and its performance was compared with the conventional steady-state process.

At the first step of the cyclic process, the membrane module operates in a so-called “closed mode” implying continuous supply of the feed mixture under constant pressure, continuous evacuation of the permeate, and zero retentate flow (pneumatic valve is closed for the given period of time referred to as  $\tau_{\text{close}}$ ). During this step, some near-stationary state is gradually achieved in the upstream side of the membrane module, and the concentration profile is established in the active upstream volume (Fig. 2) from the feed inlet towards the retentate outlet along the membrane.

During the first set of experiments, the “closed mode” operation of the membrane module was studied in order to determine the time needed to reach the near-stationary state of the closed operation. The retentate valve closing duration was varied stepwise from 3 to 60 s at other operating parameters set as described in the experimental section. The valve opening duration for a retentate sample withdrawals was 0.5 s.

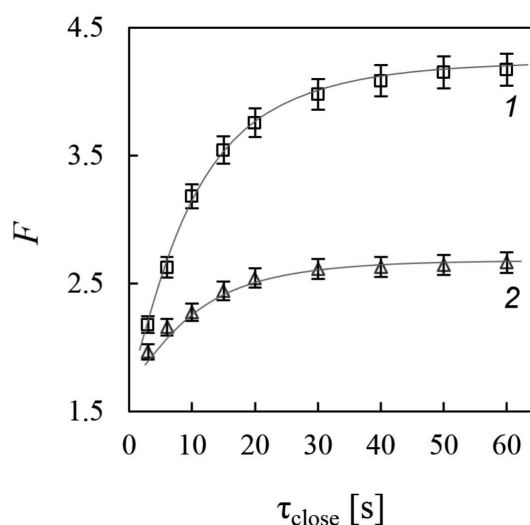


Fig. 3. Approaching a near-stationary state during the “closed mode” operation:  
1 –  $\text{N}_2\text{O}/\text{N}_2$  system; 2 –  $\text{C}_2\text{H}_2/\text{N}_2$  system

Experimental results are presented in Fig. 3, showing the value of the separation degree  $F = C_{\text{feed}}/C_{\text{ret}}$  determined as the ratio of the feed/retentate slow-permeant component concentration depending on the closing time  $\tau_{\text{close}}$  (enrichment time) for 9 different  $\tau_{\text{close}}$ . Six to eight parallel measurements were carried out for each experimental point giving an error of less than 7%. It was calculated as the uncorrected sample standard deviation according to the method described (Upton and Cook, 2014).

As can be seen from the graph, the concentration ratio in the upstream side of the membrane module gradually increases with time and approaches a stable value similarly to the total reflux operation of a batch distillation column. During the “closed mode” operation, the maximum separation degree can be achieved inside the membrane module, and the maximum slow-permeant component concentration is realized in the active upstream volume near the retentate outlet.

The small portion of this slow-permeant-enriched mixture is to be withdrawn as a retentate sample at the second step of the cyclic process when the retentate line is opened for the given period of time referred to as  $\tau_{\text{open}}$  (withdrawal time). The practical active volume of the feed side available for gas separation is situated in the 1 mm gap between the distribution disc and the membrane (shaded area in Fig. 2) and equals to approximately  $50 \text{ cm}^3$  ( $V_0$ ). Fig. 4 reflects the variation of the slow-permeant component concentration depending on the retentate sample volume ( $V_s$ ) withdrawn after the “closed mode” operation for 8 different  $V_s$ . The volume of retentate sample was varied stepwise from  $1.2 \text{ cm}^3$  to about  $40 \text{ cm}^3$  by changing the opening duration of the retentate withdrawal valve and the withdrawal flow. The closing time period was set corresponding to the time required to reach the near-stationary state. Such experimental technique allows to estimate the concentration profile being established in the active upstream volume during the “closed mode” operation from the center ( $V_s/V_0 \rightarrow 0$ ) to the periphery ( $V_s/V_0 \rightarrow 1$ ). The graph shows that the concentration of the slow-permeant component in the withdrawn sample is the highest if the ( $V_s/V_0$ ) value is close to zero, which means that the smallest possible retentate sample is withdrawn from the center part of the active upstream volume. Then the concentration in withdrawn samples decreases exponentially with the increase of the retentate sample amount.

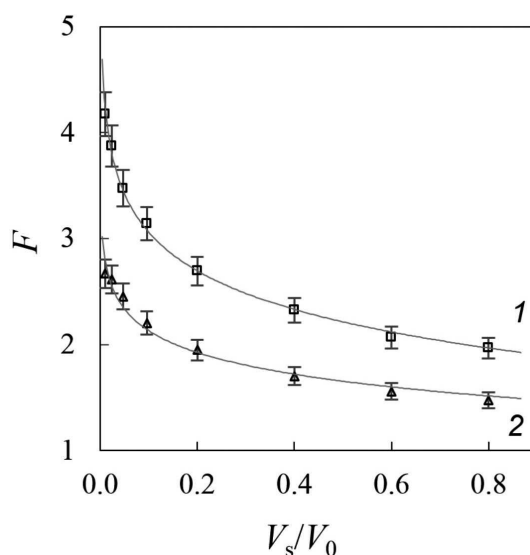


Fig. 4. The concentration of the slow-permeant component depending on the retentate sample amount: 1 –  $\text{N}_2\text{O}/\text{N}_2$ ; 2 –  $\text{C}_2\text{H}_2/\text{N}_2$

Similar trends were obtained earlier for the case of the fast-permeant impurity removal by the same periodical retentate withdrawal technique (Trubyanov et al., 2017). It should be noted that the current dependencies correlate very well with the previously obtained results, but are slightly less pronounced due to the fact that the membrane module used for the experiments generally exhibits lower separation

efficiency for the case of concentrating the slow-permeant component in comparison with the removal of the fast-permeant impurity (Drozdov et al., 2002). Nevertheless, it is of immediate interest to compare the novel semi-batch pulsed separation approach with the conventional steady-state process concerning the performance of the slow-permeant component recovery.

Since in our case the retentate flow is the target product flow enriched with the slow-permeant component, the ratio between the retentate flow ( $L_{ret}$ ) and the feed flow ( $L_{feed}$ ) directly reflects the process productivity. During the steady-state separation tests, the retentate flow constantly goes through the sampling valve of the gas chromatograph for on-line determination of the impurity content. Therefore, it is possible to estimate the variation of the separation degree ( $F = C_{ret}/C_{feed}$ ) against the process productivity. The obtained experimental data for the various pulsed retentate conditions were summarized in terms of separation efficiency – productivity tradeoff. Fig. 5 shows the performance of the two modes for the selected gas mixtures depending on the productivity. For the pulsed retentate operation, the time-averaged retentate flow, which depends on both the opening and closing times, was calculated from the experimental data on the volume of withdrawn retentate samples.

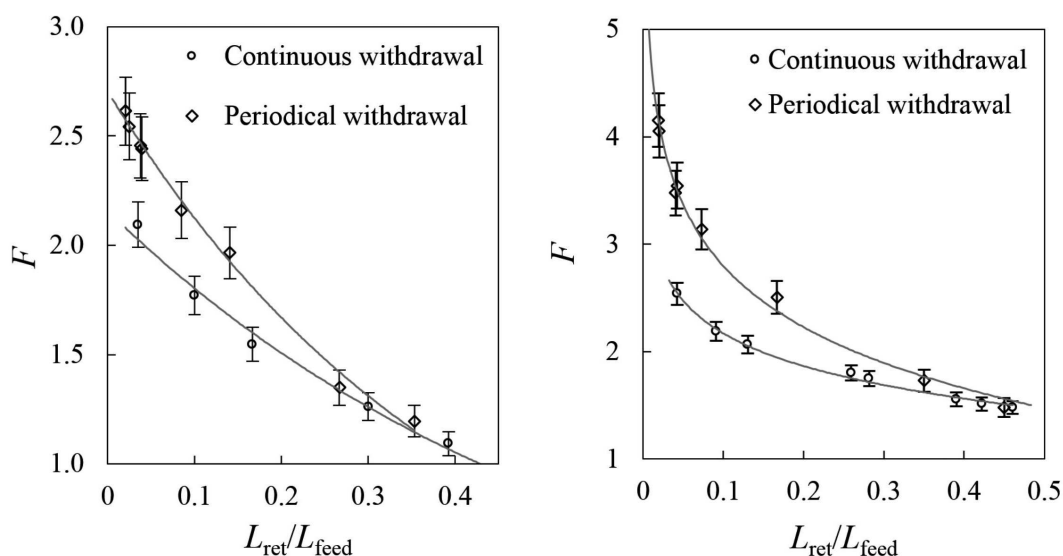


Fig. 5. Comparison of a continuous withdrawal mode and a periodical withdrawal mode in terms of productivity and efficiency during low-permeable component recovery: 1 –  $C_2H_2/N_2$ ; 2 –  $N_2O/N_2$

As can be seen from the graphs, the unsteady-state operation provides enhanced separation performances observed under the decrease of  $L_{ret}/L_{feed}$  ratio, which means that just the use of a pulsed product withdrawal technique allows to improve the separation ability of the membrane module while keeping the productivity level the same as for the steady-state withdrawal. The same behavior was demonstrated for the case of the fast-permeant impurity removal according to both experimental and modeling data (Trubyanov et al., 2017). The modeling essence was as follows.

To obtain the analytical solution for the purpose of a parametric study, a number of assumptions were made:

1. The main component (matrix) concentration is much higher than impurity concentration; gas dynamics in the membrane module is exclusively determined by the matrix, the impurity influence can be neglected.
2. In the membrane module, a cross flow mode (as shown in Fig. 6) with ideal displacement (plug flow) on the feed side is realized; there is no longitudinal mixing in the feed side; there is complete mixing in the permeate side due to low pressure.
3. The membrane permeability is the same for both pulsed and steady-state modes and remains constant over time.

4. The mixture concentration in the direction perpendicular to the membrane surface is constant.
5. The feed and permeate side pressures are assumed to be constant.
6. The process is carried out under isothermal conditions.
7. Ideal gas behavior is assumed.

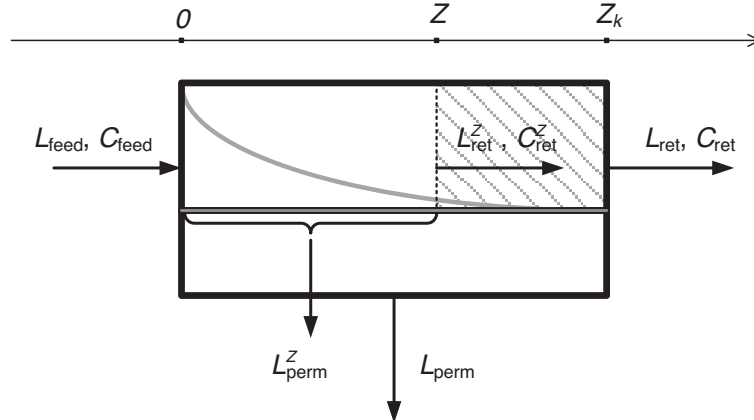


Fig. 6. Flow scheme of a plane-parallel membrane module in a cross flow mode:  $Z_k$  – membrane total length;  $L_{feed}$ ,  $L_{ret}$ ,  $C_{feed}$ , and  $C_{ret}$  – feed and retentate gas flow ( $\text{mol}\cdot\text{s}^{-1}$ ) and impurity concentration (mole fraction), respectively;  $L_{perm}$  – gas flow passing through the whole membrane area ( $\text{mol}\cdot\text{s}^{-1}$ );  $L_{perm} = L_{feed}$  in the closed mode;  $L_{ret}^Z$ ,  $C_{ret}^Z$  – gas flow ( $\text{mol}\cdot\text{s}^{-1}$ ) and impurity concentration (mole fraction) at  $Z$  point;  $L_{perm}^Z$  – gas flow passing through the membrane with  $Z$  length. The grey solid line illustrates an exemplary fast-permeant impurity concentration profile on the feed side for the closed mode. The shaded area represents a retentate sample to be withdrawn

According to modeling, the following main equation (1) describing a relative efficiency parameter to compare the two modes depending on  $\frac{Z}{Z_k}$  value (Fig. 7) was obtained (Trubyanov et al., 2017):

$$E\left(\frac{Z}{Z_k}\right) = \frac{\overline{F}\left(\frac{Z}{Z_k}\right)}{F_{st}\left(\frac{Z}{Z_k}\right)} \quad (1)$$

where:

$F_{st}\left(\frac{Z}{Z_k}\right) = \frac{C_{feed}}{C_{ret}}$  is the separation efficiency of the steady-state mode;

$\overline{F}\left(\frac{Z}{Z_k}\right) = \frac{C_{feed}}{\overline{C^Z}\left(\frac{Z}{Z_k}\right)}$  is the separation efficiency of the pulsed mode;

$\overline{C^Z}\left(\frac{Z}{Z_k}\right) = \frac{C_{feed}}{\alpha_{ef}} \left(1 - \frac{Z}{Z_k}\right)^{\alpha_{ef}-1}$  is the average impurity concentration in the segment from  $Z$  to  $Z_k$ .

Thus, the conclusion that can be drawn from the results obtained in this work and (Trubyanov et al., 2017) is that the novel process intensification logic is based on some universal principle of dynamic driving force increase in the module. The periodical disturbances of the near-stationary state established in the module under the “closed mode” conditions promote a higher average driving force for more intense mass transfer process. During the pulsed retentate withdrawals the concentration gradient cyclically established in the active upstream volume of the membrane module may become higher than that of a steady-state operation depending on the opening and closing time periods, sample volume, and the total cycle time. Besides that, it is possible to optimize the total cycle time for a given productivity, selecting a longer cycle time, which

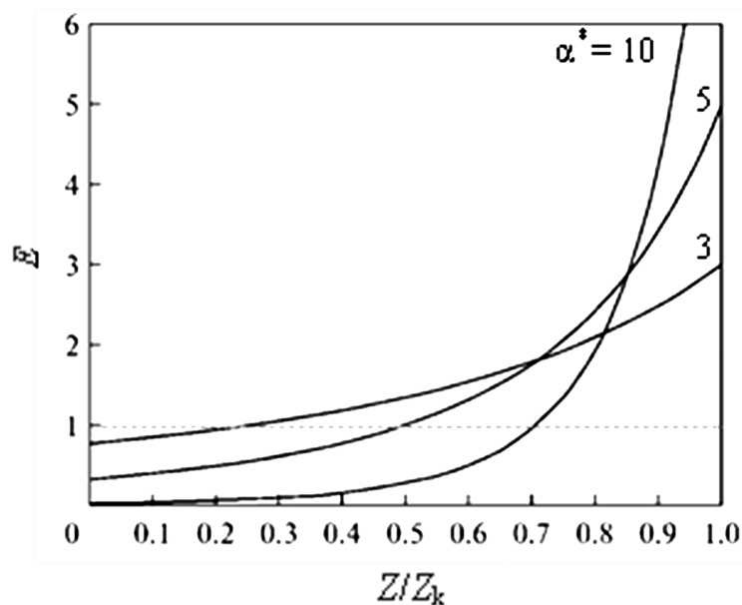


Fig. 7. Relative efficiency of pulsed and steady-state operation depending on  $\frac{Z}{Z_k}$  value for systems with different effective selectivities; grey dashed line shows equal efficiency for both modes (Trubyanov et al., 2017)

is desirable from an operating standpoint, as less frequent valve switching will be favorable for process control and operation.

#### 4. CONCLUSIONS

The experimental study of the unsteady-state membrane gas separation process with pulsed retentate withdrawals has been conducted for the case of a slow-permeant component recovery showing the possibility of increasing the separation performance of the membrane module as compared to the conventional steady-state operation. The kinetics of the “closed mode” operation has been studied experimentally as well as the dependence of the separation efficiency on the retentate withdrawals for different test systems has been obtained. The improvement of the membrane module separation ability in the pulsed retentate operation is associated with the higher driving force of unsteady-state cyclic process in which the module periodically works at a distance from the stationary-state “closed mode” condition attempting to achieve it. The enhancement of the separation efficiency obtained for the slow-permeant impurity recovery under the unsteady-state operation was up to 40% depending on the selectivity of the membrane as compared to the conventional steady-state process of the same productivity. The experimental evidence clearly shows that the periodical withdrawal technique is efficient both for the slow-permeant component recovery as well as for the fast-permeant impurity removal (according to (Trubyanov et al., 2017)) thus providing a universal and simple way to intensify the separation process keeping the desired productivity. Much longer cycle time can be used compared to the transient permeation processes (Wang et al., 2011), which is favorable from the operational point of view. The transmembrane pressure difference is not affected in this process. Consequently, there are no additional costs to increase the pressure difference.

The novel semi-batch membrane separation technique can be particularly beneficial and useful in analytical applications (impurity pre-concentration) and also may offer a series of promising perspectives for use in continuous membrane columns, comprising the stripping and enrichment sections to which the periodical withdrawal technique can be applied. A semi-empirical optimization model needs to be developed for

evaluation of each operating parameter contribution and for identification of the best set of operating conditions for a given system and target performance.

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## SYMBOLS

$C_{\text{feed}}$	feed slow-permeant component concentration, %
$C_{\text{ret}}$	retentate slow-permeant component concentration, %
$F$	separation degree
$L_{\text{feed}}$	feed stream flow rate, cm <sup>3</sup> /min
$L_{\text{ret}}$	retentate stream flow rate, cm <sup>3</sup> /min
$V_0$	active volume of the feed side available for gas separation, cm <sup>3</sup>
$V_s$	retentate sample volume, cm <sup>3</sup>

### Greek symbols

$\alpha_{\text{ef}}$	effective selectivity
$\tau_{\text{close}}$	closing duration of the retentate valve, s
$\tau_{\text{open}}$	opening duration of the retentate valve, s

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