Optimization Criterion for Two-Stage Countercurrent Cascade for Molybdenum Isotopes Separation by the method of laser-assisted retardation of condensation (SILARC)

K.A. Lyakhov
National University of Science and Technology MISIS, Leninskii Av. 4, Moscow, 119049, Russia
E-mail: lyakhov2000@yahoo.com

Abstract.
The application of the method of laser-assisted retardation of condensation has been considered for molybdenum isotope separation. Enrichment factor as a function of pressure and temperature of gas flow cold-core have been evaluated. Since the maximal value of the enrichment factor is not high (≈ 1.8), to achieve desired enrichment level in products an iterative procedure is applied. To reduce the amount of wastes and increase the performance of the SILARC method, two-stage countercurrent cascade is considered. Relations between the molar and isotopic fractions of target isotopologues on the first and second stages of the cascade at each iteration are found. The optimization problem is formulated to evaluate optimal physical parameters of this cascade.

1. Introduction
The search for efficient ways of molybdenum isotopes separation is very important because they can be used for creating safe materials with improved thermophysical properties in nuclear industry [1], and in nuclear medicine [2]. Today molybdenum isotopes are mainly produced by the gas centrifuging [3]. However, consequences of industrial scaling up of molybdenum isotopes production by the laser assisted methods are still unexplored.

Popular laser assisted methods are following: isotope separation in atomic vapors (atomic vapor laser isotope separation-AVLIS method) [4], and in molecular gases (molecular laser isotope separation-MLIS methods). AVLIS has high selectivity, but its equipment and maintenance costs are also high. MLIS methods are based either on selective multi-photon dissociation or excitation of molecules. AVLIS and MLIS, based on multi-photon dissociation (also known as molecular obliteration laser isotope separation-MOLIS), methods have been industrially deployed for uranium and carbon isotope [5] separation respectively. MLIS method, based on selective excitation, is known as SILARC method (separation of isotopes by laser assisted retardation of condensation). This method has an advantage of relatively high selectivity and much less equipment and maintenance costs than traditional methods. Moreover, isotope scrambling effects in this method are believed less pronounced comparing to other MLIS methods. A more detailed comparison of laser-assisted methods can be found in [6, 7].
In this paper application of the method of laser-assisted retardation of condensation, proposed in [8], has been considered for separation of molybdenum isotopes. Since the enrichment factor is rather small (∼1.8), to achieve desired enrichment level an iterative procedure is required. To minimize tails and setup volume, introduction of the second stage into the separation cascade is considered. Relations between molar and isotopic fractions of target isotopologues on the first and second stages of the cascade at each iteration are found. Optimization problem is formulated to evaluate optimal physical parameters of a two-stage iterative isotope separation cascade. All calculations for this paper were carried out by Maple 2017.03 [9].

2. Design of a two-stage molybdenum isotopes recovery cascade

In industry countercurrent cascade is mostly used due to its high performance, [10]. Hence, this cascade will be considered. Schematic of two stages molybdenum isotope separation cascade is shown in Fig.1. Feeding gas flow composed of mixture of target and carrier gas comes from the feed camber FC. Mixing tanks, denoted by MT#1-2, correspond to the first stage, and MT#3 to the second. Irradiation chambers, denoted by IC#1-2, correspond to the first stage, and IC#3 to the second. Automatic valve AI is actuated at the end of enrichment process in order to provide access of the $^{98}Mo$ enriched gas stream to the cryotrap CT#2. Gas flow fraction, enriched by $^{98}Mo$, is indicated by the dashed line, and the depleted one is indicated by the dotted line. Brown lines refer to the first stage, and the green ones to the second. Cryotrap CT#1 purifies carrier gas from depleted gas flow fraction residuals. Since irradiation cells are

![Figure 1: Two-stage cascade scheme.](image)
implemented as absorbers in the cavity of the $CO_2$ laser, laser beam moves back and forth between mirrors M#1-8, laser cuvettes L#1-2, diffraction gratings G#1-2 and beamsplitters BS#1-3. The laser beam is shown by the solid red line, which is hidden if laser beam gets inside the object. Forward gas flow, which has optimal conditions inside the irradiation cells, is provided by diffusion vacuum pumps DVP#1-2, and backward flow is provided by diffusion vacuum pumps DVP#3-4 (vacuum pump exhaust serves as feed for the next stage).

3. Product cut and enrichment factor

Product cut on the $j$th iteration can be introduced as

$$\theta^{(j)}_\alpha = \frac{Q_{\alpha,esc}^{(j)}}{Q_{\alpha,feed}^{(j)}}, \quad \alpha = I, II,$$

where $Q_{\alpha,feed}^{(j)} = q_{\alpha,feed}^{(j)}$, $N_{\alpha,feed}^{(j)} = Q_{\alpha,f}^{(j)}$, $N_{\alpha,esc}^{(j)}$ is the number of $MoF_6$ molecules in the feeding gas flow and $Q_{\alpha,esc}^{(j)}$ is the number of $MoF_6$ molecules in the gas flow fraction escaped from its cold core.

Gas flow rate through iteration by iteration changing nozzle throat area $A_{\alpha}^{(j)}$ is given by:

$$Q_{\alpha}^{(j)} = \int C_{\alpha, nozz}(x,y) J_{\alpha, nozz}(x,y) dxdy;$$

$$J_{\alpha, nozz}^{(j)} = \rho_{\alpha, nozz}^{(j)} U_{\alpha, nozz}^{(j)};$$

$$\rho_{\alpha, nozz}^{(j)} = \frac{\rho_{\alpha,0}^{(j)}}{\gamma; \frac{T_0}{T_{flow}}; \frac{\gamma^{(j)}}{-1}};$$

$$P_{\alpha,0}^{(j)} = p_{flow} \left( \frac{T_0}{T_{flow}} \right);$$

$$U_{\alpha, nozz}^{(j)}(T) = \frac{\alpha^{(j)}_{\alpha, nozz}(T) \lambda^{(j)}_{\alpha, nozz}(T)}{\tilde{\alpha}^{(j)}_{\alpha, nozz}(T) \lambda^{(j)}_{\alpha, nozz}(T)};$$

$$\gamma^{(j)}_{\alpha, nozz}(T) = \left( \frac{\gamma^{(j)}_{\alpha, nozz}(T)}{\lambda^{(j)}_{\alpha, nozz}(T)} \right);$$

$$M^{(j)}_{\alpha, nozz}(T) = \left( \frac{\gamma^{(j)}_{\alpha, nozz}(T)}{\lambda^{(j)}_{\alpha, nozz}(T)} \right);$$

where it is assumed that

$$\int C_{\alpha, nozz}^{(j)}(x,y) dxdy \Rightarrow C^{(j)}_{\alpha} A^{(j)}_{\alpha},$$

where factor $C^{(j)}_{\alpha}$ cuts nozzle throat area according to effective boundary layer thickness. Average transition time of infinitely narrow transverse gas flow layer across irradiation cell of given length $L_{IC}$ is given by

$$t_{\alpha, tr}^{(j)} = \frac{L_{IC}}{U^{(j)}_{\alpha, nozz}(T_{flow})}. \quad (2)$$

According to the transport model, developed in [11], product cut $\theta^{(j)}_{\alpha}$ and factor of enrichment by $i$th isotope $\beta^{(j)}_{\alpha}$ on the $j$th iteration of $\alpha$th stage can be represented as

$$\theta_{\alpha}^{(j)} = a^{(j)}_{\alpha} + b^{(j)}_{\alpha}; \quad (3)$$

1 in order to prevent turbulent mixing of gas flow cold core with ambient gas as far as possible from nozzle throat, adjacent nozzle walls should also change to avoid boundary layer detachment.
\[ \beta_{\alpha}^{(j)} = \frac{\left( iQ_{\alpha,\text{esc}}^{(j)}/Q_{\alpha,\text{esc}}^{(j)} \right)}{\left( iQ_{\alpha,\text{feed}}^{(j)}/Q_{\alpha,\text{feed}}^{(j)} \right)} = \frac{\alpha_i}{\beta_{\alpha}^{(j)}} \]  

(4)

where

\[ a_{\alpha}^{(j)} = \sum_{k=1}^{7} x_{k,\alpha}^{(j)}, \quad a_{\alpha}^{(j)} = (1 - f_{kd}) \Theta_{\alpha}^{(j)} + f_{kd} \Theta_{d,\alpha}^{(j)}; \]

\[ b_{\alpha}^{(j)} = x_{\alpha}^{(j)} \alpha_i, \quad \alpha_i = (1 - f_{id} - f_{id}) \Theta_{\alpha}^{(j)} + f_{id} \Theta_{1,\alpha}^{(j)} + f_{id} \Theta_{d,\alpha}^{(j)}. \]

Relative target \( i \)th isotopes abundance on the \( \alpha \)th stage \( j \)th iteration is denoted as \( x_{\alpha}^{(j)} \equiv x_{i,\alpha}^{(j)} \). The fraction of monomers \( \Theta_{\alpha}^{(j)} \), epithermals \( \Theta_{1,\alpha}^{(j)} \), and dimers \( \Theta_{d,\alpha}^{(j)} \), escaped gas flow cold core, can be calculated as

\[ \Theta_{\alpha}^{(j)} = 1 - e^{-k_{Wt}^{(j)}/\alpha}\; ; \]

\[ \Theta_{1,\alpha}^{(j)} = 1 - e^{-\mu_{1}k_{Wt}^{(j)}/\alpha}\; ; \]

\[ \Theta_{d,\alpha}^{(j)} = 1 - e^{-\psi_{d}k_{Wt}^{(j)}/\alpha}, \]

where

\[ \psi_{d} = \frac{\sigma_{Q/G}M_{1}^{1/2}}{\sigma_{Q/G}M_{1}^{1/2}}. \]

Relative \( i \)th isotope abundances on the \( j \)th iteration in the initial gas flow and in its escaped fraction are given by \( \left( iQ_{\alpha,\text{feed}}^{(j)}/Q_{\alpha,\text{feed}}^{(j)} \right) \) and \( \left( iQ_{\alpha,\text{esc}}^{(j)}/Q_{\alpha,\text{esc}}^{(j)} \right) \) respectively. Our results for enrichment factor evolution as functions of temperature and pressure are shown in Fig. 2.

Figure 2: Enrichment factor on the first iteration for the case of \( ^{100}MoF_{6} \) selective excitation as a function of gas flow temperature at \( p_{\text{tot}} = 2 \) torr in the left panel, and as function of gas flow pressure at \( T_{\text{flow}} = 66 \) K in the right panel. All other parameters are fixed at \( I_{\text{CW}} = 100 \) W, \( y_{Q}^{(0)} = 0.5, \ W_{t} = 10 \) cm, \( H_{t} = 360 \) \( \mu \)m, \( L_{IC} = 85.6 \) cm, \( R_{L} = 3 \) mm, \( T_{\text{flow}} = 66 \) K.
4. Iterative scheme for isotope separation

Since $^{12}$C$^{16}$O$_2$ can be excited by CO$_2$ laser and its volatility at room temperature is good enough, it was chosen as a target gas. As a carrier gas, argon was selected due to its perfect aerodynamic properties. According to [12, 6], combinational mode $\nu_3 + \nu_5$ for different $^1$MoF$_6$ ($i = 92, 94, 95, 96, 97, 98, 100$) isotopologues at low gas flow pressure and temperature can be assumed to have the following emission lines of $^{12}$C$^{16}$O$_2$ laser [13]:

$$\{\lambda_{\text{exc}}\}_{i=1}^{7} \approx \{1057, 1059, 1060, 1061, 1062, 1063, 1065\} \text{ cm}^{-1}.$$  

First four of them in the same order can be selectively excited by the following emission lines of $^{12}$C$^{16}$O$_2$ laser [13]:

$$\{\lambda_{\text{laser}}\}_{i=1}^{4} = \{1057.3, 1058.949, 1060.571, 1062.166\} \text{ cm}^{-1}.$$  

Two CO$_2$ laser beams with photons of given frequency are delivered into three chambers of the cascade, as shown in Fig.1. The laser beam in each chamber moves back and forth, directed by a corresponding system of mirrors, to provide the most complete overlap with overcooled gas flow and save expensive laser photons. In each of the two stages, overcooled gas flow is recirculated until the required enrichment level in the product collecting cryotrap is reached.

We assume that physical conditions in the cold core of gas flows, corresponding to the first and to the second stage, coincide, while laser beam intensities, as seen from Fig.1, are different: $I_1 = I_2 = \frac{3}{4} I_0$ are in the separation cells of the first stage and $I_3 = \frac{1}{2} I_0$ is in the separation cell of the second stage. Therefore, product cuts should be $\theta_1 = \theta_2 = \theta_{i}^{(j)}$; $\theta_3 = \theta_{II}^{(j)}$.

Mole fraction on the first stage $j$th iteration $y_{Q,J}^{(j)}$ can be obtained from the following set of balance equations:

$$\begin{align*}
\sum_{j} y_{Q,J}^{(1)} \sum_{j} & \left(1 - y_{Q,J}^{(0)} \right) N_{I,\text{feed}}^{(0)} + \left(1 - \theta_{II}^{(0)} \right) Q_{II,\text{feed}}^{(0)} \right] = \left(1 - \theta_{II}^{(0)} \right) Q_{II,\text{feed}}^{(0)}; \\
\sum_{j} y_{Q,J}^{(2)} \sum_{j} & \left(1 - y_{Q,J}^{(0)} \right) N_{I,\text{feed}}^{(0)} + \left(1 - \theta_{II}^{(1)} \right) Q_{II,\text{feed}}^{(1)} \right] = \left(1 - \theta_{II}^{(1)} \right) Q_{II,\text{feed}}^{(1)}; \\
& \cdots \\
\sum_{j} y_{Q,J}^{(j)} \sum_{j} & \left(1 - y_{Q,J}^{(0)} \right) N_{I,\text{feed}}^{(0)} + \left(1 - \theta_{II}^{(j-1)} \right) Q_{II,\text{feed}}^{(j-1)} \right] = \left(1 - \theta_{II}^{(j-1)} \right) Q_{II,\text{feed}}^{(j-1)}. \\
\end{align*}$$  

(5)

Mole fraction and nozzle throat area $A_{II,J}^{(j)}$ on the $j$th iteration of the second stage are determined from the following set of balance equations:

$$\begin{align*}
N_{II,\text{feed}}^{(j)} &= 2 N_{I,\text{feed}}^{(j)} \left[ y_{Q,J}^{(j)} \theta_{II}^{(j)} + 1 - y_{Q,J}^{(j)} \right], \quad j = 0, N_{I,\text{II}} \\
Q_{II,\text{feed}}^{(j)} &= 2 Q_{I,\text{feed}}^{(j-1)} \theta_{II}^{(j-1)} + Q_{II,\text{feed}}^{(j-1)} \theta_{II}^{(j-1)} \theta_{II}^{(j-1)} \\
\end{align*}$$  

(6)

Target isotopes relative abundance on the second and first stages are related as follows

$$\begin{align*}
& x_{II}^{(j)} Q_{II,\text{feed}}^{(j)} = \theta_{II}^{(j-1)} \beta_{II}^{(j-1)} x_{II}^{(j-1)} Q_{II,\text{feed}}^{(j-1)} + \\
& + 2 x_{II}^{(j-1)} \beta_{II}^{(j-1)} \beta_{II}^{(j-1)} Q_{II,\text{feed}}^{(j-1)}. \\
\end{align*}$$  

(7)

In general, the first stage can consist of an arbitrary number of cells, which must be configured in this way. In this case, the 1st stage is defined as shown in Figs. 1,2 from [14]. Initial value of the mole fraction on the second stage can be calculated as

$$y_{Q,II}^{(0)} = \frac{2 \theta_{II}^{(0)} Q_{I,\text{feed}}^{(0)}}{N_{I,\text{feed}}^{(0)}}.$$  

(8)

The initial value of the relative abundance of isotopes on the second stage is given by

$$x_{II}^{(0)} = \beta_{II}^{(0)} x_i,$$  

(9)

where $x_i$ is the relative $i$th isotopes abundance in the natural mixture.
5. Optimization criterion

The efficiency of isotope separation can be determined by the rate of energy consumption and isotope separation, so that an objective function can be introduced as

$$\Psi_i = \frac{dE}{dt} \frac{dN_{i,II}}{dt}. \quad (10)$$

The minimum of this function meets requirement to separate the largest amount of target isotopes over the shortest possible time at lowest energy footprint. Therefore, optimization problem can be formulated as

$$\min \Psi_i; \quad \Omega = \{y_{Q,I}^{(0)}, P_{flow}, T_{flow}, L_{IC}, H_t, W_t, I_{CW}\}. \quad (11)$$

Energy consumption rate is given by

$$\frac{dE}{dt} = \frac{E_{tot;i}}{T_{proc}}. \quad (12)$$

Enrichment rate by target isotopes can be introduced as

$$\frac{dN_{i,II}}{dt} = \frac{iQ_{esc}^{(N_{i,II})}}{T_{proc}}, \quad (13)$$

where

$$T_{proc} = \sum_{j=0}^{N_{i,II}} t^{(j)}_{II,\text{tr}} \quad (14)$$

is total processing time. The number of MoF_6 molecules in the enriched product with the enrichment level $x^{(N_{r,II})} = x_{\text{fin}}$ can be estimated as

$$iQ_{esc}^{(N_{i,II})} = \sum_{j=0}^{N_{i,II}} t^{(j)}_{II,\text{tr}}\ b^{(N_{i,II})}. \quad (15)$$

The total electricity consumption for the separation of $i$th isotopes is defined as

$$E_{tot;i} = \int_0^{T_{proc}} dt \frac{dE}{dt} = \sum_{\alpha=l,II}^{N_{i,\alpha}} \sum_{j=0}^{N_{i,\alpha}} (E^{(j)}_{\alpha,\text{vac,core}} + E^{(j)}_{\alpha,\text{vac,rim}}) + W_{\text{las}}T_{proc}. \quad (16)$$

6. Summary

In this paper, an iterative scheme for countercurrent two-stage cascade (enriched gas flow is returned back into the mixing tank, passing through three separation cells in the cascade until the required level of the product enrichment is reached) for the separation of molybdenum isotopes has been proposed. For this, the enrichment factor and the extraction were estimated depending on the temperature and pressure in the cold core of the gas flow. The absorption line corresponding to the $\nu_3 + \nu_5$ combination mode can be resonantly excited by a CO_2 laser. The enrichment factor was calculated from the system of transport equations for the case of continuous irradiation of a stationary gas flow. The rate of formation and decay of dimers was estimated from the temperature dependence of the parameters of the interaction potential (modified Lennard-Jones potential), based on the model proposed in [15]. Relations between molar and isotopic fractions of target isotopologues on the first and second stages of the cascade at each iteration are found. Optimization problem is formulated to evaluate optimal physical parameters of a two-stage cascade.
Acknowledgments
Author acknowledges the Ministry of Science and Higher Education of the Russian Federation in the framework of the State Program(project No. 0718-2020-0025) for financial support. There is no conflict of interests.

References
[1] Shmelev V A, Smirnov A Y, Bonarev A K et al. 2016 Theor. Found. Chem. Eng. 50(6) 1049–1057
[2] Zykov M P and Kodina G E 1999 Radiochemistry 41 198–204
[3] Palkin V A 2020 Atomic Energy 128(3) 155–161
[4] Bokhan P A, Buchanov V V, Fateev N V, Kalugin M M, Kazaryan M A, Prokhorov A M and Zakrevsky D E 2006 Laser Isotope Separation in Atomic Vapor (Weinheim: WILEY-VCH Verlag GmbH & Co. KGaA)
[5] Evseev A V, Laptev V B, Puretskii A A, Ryabov E A and Furzikov N P 1988 Soviet Journal of Quantum Electronics 18 385
[6] Eerkens J W 1998 Laser and Particles Beams 16 295–316
[7] Parvin P et al. 2004 Progress in Nuclear Energy 44 331–345
[8] Lee Y T 1977 Isotope separation by photodissociation of Van der Waal's molecules, US patent 4032306, June’28
[9] Maplesoft 2017.3 http://www.maplesoft.com
[10] Cohen K 1951 The Theory of Isotope Separation as Applied to the Large Scale Production of U-235 (New York: McGraw-Hill)
[11] Eerkens J W 2005 Laser and Particle Beams 23 225–253
[12] Freund S M and Lyman J L 1978 Chemical Physics Letters 55 435–438
[13] Witteman W J 1987 The CO2 Lasers (Berlin: Springer-Verlag) pp 23–52
[14] Lyakhov K A, Lee H J and Pechen A N 2017 Separation and Purification Technology 176 402–411
[15] Eerkens J W 2001 Chemical Physics 269 189–241