Production of high-enriched carbon-13 by two-stage laser method

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Abstract. A variant of a two-stage laser process for production highly enriched carbon-13 (¹³C) with a concentration of more than 99% is being investigated. The first laser stage provides effective enrichment of ¹³C up to 30-50% based on the isotopically selective multiphoton dissociation of freon-22 (CF₂HCl) by pulsed radiation of a CO₂ laser. Then the product of the first stage tetrafluoroethylene, enriched in ¹³C, is converted into the working substance of the second stage, freon-12B₂ (CF₂Br₂). At the second stage of enrichment, a component with an undesirable isotope ¹²C undergoes to selective dissociation, until its concentration in the residual gas decreases to 1% and the concentration of the ¹³C isotope is increased to 99%. In preliminary experiments, high parameters of the elementary act of separation were achieved - the dissociation yield of the ¹²CF₂Br₂ up to 20% and selectivity (for ¹²C) up to 100%. A productivity of the second enrichment stage for a reactor of ideal displacement is estimated, that is 0.6 and 1.2 g¹³C/h for initial concentrations of ¹³CF₂Br₂ 30 and 50%, respectively.

1. Introduction
The production of pharmaceuticals labeled with the carbon-13 isotope is continuously growing [1-3]. This is mainly caused with the introduction and widespread use in medical practice of the "Diagnostic Breath Test" (DBT) [1-3]. The constantly growing demand for the ¹³C isotope [3] requires the development of its production, including on new principles.

In the industrial production of the ¹³C isotope from a natural concentration 1.1% to 99%, traditional separation technologies are mainly used, namely, the methods of low-temperature rectification of CO or CH₄ and the enrichment by gas centrifuges [3]. However, the classical separation methods are characterized by high capital and energy costs connected with a large number of separating elements, as well as a long time for the separation stage to reach a stationary operating regime.

In Russia the method of carbon isotope separation, based on isotopically selective multiphoton dissociation of molecules by IR laser radiation (IR MPD), was brought to industrial implementation and proved its competitiveness in comparison with traditional methods [1, 4]. At the beginning of the 2000s, up to 30 kg / year of carbon-13 were produced at the laser complex "Carbon", which consists of 4 laser modules. The technology was based on the isotopically selective dissociation of Freon-22 (CF₂HCl) molecules by radiation of a repetitively pulsed CO₂ laser. Carbon-13 was accumulated in the dissociation...
product tetrafluoroethylene (C\textsubscript{2}F\textsubscript{4}), which was then separated from the irradiated gas mixture in a conventional rectification column.

At the same time, the production practice has shown that it is economically profitable to carry out the laser enrichment of \textsuperscript{13}C in one stage only up to a concentration of 30-50%. Therefore, to achieve the \textsuperscript{13}C concentration 99% required for the market, it is necessary to use the second enrichment stage. At the second stage, traditional enrichment methods can also be used (low-temperature rectification, gas centrifuges, etc.). However, the use of the laser method of \textsuperscript{13}C enrichment from 30-50% to 99% is more expedient for a number of reasons.

A large number of works [5-18] were devoted to the development of various variants of the implementation of the second stage of laser enrichment by the IR MPD method. Practically all of them were based on the selective dissociation of the \textsuperscript{13}C-containing component in compounds preliminarily enriched in \textsuperscript{13}C. It turned out that in this way it is difficult to realize high productivity of the enrichment process, since the required final concentration of \textsuperscript{13}C = 99% was either not achieved or was achieved at low productivity of the process and a small degree of depletion of the \textsuperscript{13}C-containing component [7]. The main physical reason for this is the insufficient value of the IR MPD selectivity of the studied compounds.

In early works the method of enrichment of carbon-13 based on the selective “burning off” of the \textsuperscript{13}C-containing component was also studied. This way of enrichment of \textsuperscript{13}C was first proposed in [19] and then developed in [20-22]. A theoretical analysis of such method was given in [23], where a possibility of its application at the second enrichment stage was considered. Using the example of the MPD of CF\textsubscript{3}I [19, 20, 22], CF\textsubscript{3}Br [21], and CF\textsubscript{3}HCl [22] molecules with a natural concentration of \textsuperscript{13}C = 1.1%, the fundamental possibility of the using such a scheme was demonstrated. For instance, in [21] the concentration 90% of \textsuperscript{13}CF\textsubscript{3}Br molecules in the residual gas was achieved.

At the same time, the method of selective “burning out” of undesirable \textsuperscript{12}C-containing component has extremely low efficiency for compounds with natural \textsuperscript{13}C abundance, since 99.99% of the substance must be dissociated to reach a \textsuperscript{13}C concentration 99%, that dramatically increases energy consumption. In addition, the huge amount of formed dissociation products must be continuously removed from the reactor since they can affect the dissociation selectivity. This is extremely inconvenient in view of technology.

In this work, the authors propose the following scheme for organizing a two-stage industrial technology of obtaining \textsuperscript{13}C with a concentration ≥99%. At the first stage, the dissociation product a tetrafluoroethylene enriched in \textsuperscript{13}C up to 30-50% is obtained due to the method of isotopically selective dissociation of CF\textsubscript{3}HCl molecules by a radiation of a repetitively pulsed CO\textsubscript{2} laser. Then, in a separate chemical cycle, tetrafluoroethylene must be converted into \textsuperscript{13}C-enriched freon-12B2 (CF\textsubscript{3}Br\textsubscript{2}). The synthesis of this compound from tetrafluoroethylene is quite simple [24]. At the second stage of enrichment, the method of selective “burning off” of the \textsuperscript{12}CF\textsubscript{3}Br\textsubscript{2} molecules is used. The principal advantage of the proposed enrichment method of \textsuperscript{13}C is the ability to achieve any final concentration of \textsuperscript{13}C, including \textsuperscript{13}C less than 1%. In this case, the value of the MPD selectivity determines only the value of the loss of the \textsuperscript{13}CF\textsubscript{3}Br\textsubscript{2} component, but not its final concentration.

To confirm the economic feasibility of the proposed \textsuperscript{13}C enrichment method at the second stage, it was necessary in the experiments to achieve high values of the parameters of the elementary act of separation: the yields and selectivity of MPD of \textsuperscript{12}CF\textsubscript{3}Br\textsubscript{2} molecules. The main results of these experiments are given below.

2. Experiment
The amount of freon-12B2 enriched in \textsuperscript{13}C up to 30% required for the experiments was synthesized by us through laser conversion of enriched CF\textsubscript{3}HCl (\textsuperscript{13}C = 30%) in medium of bromine. The content of CF\textsubscript{3}Br\textsubscript{2} in the synthesized product was about 98% [25].

The selective dissociation of \textsuperscript{12}CF\textsubscript{3}Br\textsubscript{2} was carried out by tuning the CO\textsubscript{2} laser radiation frequency to the long-wavelength wing of the absorption band v\textsubscript{1} = 1090 cm\textsuperscript{-1}. In the experiments, the decreases of the concentration of both isotopic components were measured as a function of the number of laser pulses

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for different irradiation conditions (radiation frequency, CF$_2$Br$_2$ pressure, O$_2$ acceptor gas pressure). The reducing of a concentration of each component was used to determine the dissociation yields and selectivity, as well as their change during the enrichment process. Selective dissociation of CF$_2$Br$_2$ in mixture with oxygen results in the conversion of the component with $^{12}$C mainly into the dissociation product COF$_2$, and the residual CF$_2$Br$_2$ was enriched in $^{13}$C up to a concentration of ≥ 99%.

A computerized two-beam IR spectrophotometer Specord-M82 was used to determine the concentration of each component when a $^{12}$CF$_2$Br$_2$ content was from 70 to ~5%. The concentrations were determined by measuring the intensity of the absorption bands of $^{12}$C- and $^{13}$C-containing components of the mode $\nu_8 = 831$ cm$^{-1}$ ($^{12}$CF$_2$Br$_2$). When the concentration of $^{12}$CF$_2$Br$_2$ was dropped below ~5%, a highly sensitive chromatmass-spectrometer Clarus 500 was applied.

The experimental technique was as follows. For irradiation, a stainless steel cell with KBr windows 11.2 cm long was used. The cell was evacuated by a forepump through a nitrogen trap to a residual pressure of $7.5 \times 10^{-3}$ Torr (1 Pa) and after that it was filled with a mixture of enriched CF$_2$Br$_2$ with a concentration of $^{13}$C = 30% and oxygen. Then the gas was irradiated with series of N pulses. After each series of laser pulses, the yields and selectivity of MPD were determined. The selectivity of dissociation for the $^{12}$C component was determined as the ratio of the yields $\alpha(12/13) = \beta_{12}/\beta_{13}$. The dissociation yields $\beta_i$ (i=12, 13) were calculated from the partial pressure of each component before ($p_{i,0}$) and after ($p_i$) irradiation with N laser pulses. In this case, $p_{i,0}$ was taken to be the current partial pressure of the components before the start of a new series of laser pulses. To calculate $\beta_i$, we used the following formula from [26]

$$\beta_i = \Gamma^{-1}[1 - (p_i / p_{i,0})^{1/N}]$$

where $\Gamma$ – is the ratio of the irradiated volume to the volume of the cell.

When measuring the $^{13}$CF$_2$Br$_2$ concentration below ~5% by the chromatmass-spectrometric method, we used mass peaks with $m/e = 129, 130$ from fragment ions $^{12}$CF$_2$Br$^+$ and $^{13}$CF$_2$Br$^+$.

### 3. Results and discussion

The kinetics of an increase in the concentration of the desirable component $^{13}$CF$_2$Br$_2$ in the residual gas with an increase in the number of laser pulses is shown in Figure 1 for a laser frequency of 1084.6 cm$^{-1}$ (9R30 generation line of CO$_2$ laser). It can be seen that the concentration of $^{13}$CF$_2$Br$_2$ over 99% is confidently achieved.

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**Figure 1.** The dependence of $^{13}$CF$_2$Br$_2$ concentration on a number of the laser pulses in result of consecutive irradiation of CF$_2$Br$_2$ + O$_2$ mixture. Initial pressures of CF$_2$Br$_2$ – 1 Torr, O$_2$ – 30 Torr. Laser radiation frequency is 1084.6 cm$^{-1}$ (9R30 generation line of CO$_2$ laser), radiation fluence is 2.6 J/cm$^2$. 

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The dependences of $\beta_{12}$ and $\beta_{13}$ dissociation yields of molecules $^{12}$CF$_2$Br and $^{13}$CF$_2$Br and selectivity $\alpha(12/13) = \beta_{12}/\beta_{13}$ on a number of the laser pulses in result of consecutive irradiation of CF$_2$Br$_2$ + O$_2$ mixture are presented on Figure 2.

Figure 2. The dependences of $\beta_{12}$ (1) and $\beta_{13}$ (2) dissociation yields and selectivity $\alpha(12/13)$ (3) on a number of the laser pulses in result of consecutive irradiation of CF$_2$Br$_2$ + O$_2$ mixture. Initial pressures of CF$_2$Br$_2$ – 1 Torr, O$_2$ – 30 Torr. Laser radiation frequency is 1084.6 cm$^{-1}$ (9R30 generation line of CO$_2$ laser), radiation fluence is 2.6 J/cm$^2$.

Three main points should be noted that are characteristic of these dependencies. First, at a moderate laser radiation fluence 2.6 J/cm$^2$, high (15–20%) yields of MPD $\beta_{12}$ are achieved with respect to the undesirable component $^{12}$CF$_2$Br$_2$. In the long term, this allows to realize high productivity of the enrichment process. In addition, the value of $\beta_{12}$ is practically independent on the current concentration of $^{12}$CF$_2$Br$_2$. Secondly, a high selectivity of dissociation $\alpha(12/13) = 40$–80 has been achieved, which makes it possible to have acceptable (~15%) losses of the desirable component $^{13}$CF$_2$Br$_2$. Third, at the beginning of irradiation, a selectivity growth is observed. It is in this region that the concentrations of $^{12}$CF$_2$Br$_2$ and $^{13}$CF$_2$Br$_2$ become approximately equal. Thus, a significant reserve for reducing the losses of the component with the desirable isotope $^{13}$CF$_2$Br$_2$ consists in the use of enriched CF$_2$Br$_2$ with a $^{13}$C concentration of 50% and higher.

We proposed to use a laser reactor of ideal displacement at the second stage for realization of an enrichment technology of $^{13}$C base on the method of selective “burning off” of a $^{12}$C-containing component in CF$_2$Br$_2$. The scheme of such reactor is shown in Figure 3.

Figure 3. The scheme of a laser reactor of ideal displacement. 1 – laser beam, 2 – low-pressure circulation fan, 3 – separate sections of reactor.
In this type of reactor, the space is divided into separate sections, in each of which the gas mixture is intensively pumped across the laser beam. At the same time, the mixture is pumped between the feeding tube and a tube for the selection of irradiated mixture at the channel where laser beam passes. For this type of reactor, the estimation was made of the possible productivity of $^{13}$C enrichment to a concentration of 99.2%. for $\text{CF}_2\text{Br}_2 + \text{O}_2$ mixture at an initial pressures of $\text{CF}_2\text{Br}_2$ = 1 Torr and $\text{O}_2$ = 30 Torr. A estimated productivity was found to be 0.6 and 1.2 g$^{13}$C/h for initial concentrations of $^{13}\text{CF}_2\text{Br}_2$ 30 and 50%, respectively.

4. Conclusion
In this work, we propose a new method for organizing a two-stage process of carbon isotopes separation, which makes it possible to obtain carbon-13 with a concentration $\geq 99\%$ with high productivity. At the first stage of the process, tetrafluoroethylene enriched in $^{13}\text{C}$ up to 30-50% is obtained due to isotope selective dissociation of $\text{CF}_2\text{HCl}$ molecules by radiation of a repetitively pulsed $\text{CO}_2$ laser. At the second stage, freon-12B2 ($\text{CF}_2\text{Br}_2$) with $^{13}\text{C}$ enrichment from 30% and higher is used as a working substance. Freon-12B2 synthesized from the enriched product of the first stage $\text{C}_3\text{F}_7$. In this case, for enrichment $^{13}\text{C}$ the method of selective deep “burning off” of the $^{13}$C-containing component is applied.

Experiments on selective dissociation of $^{13}\text{CF}_2\text{Br}_2$ in a isotope mixture with an initial concentration of $^{13}\text{CF}_2\text{Br}_2$ 30% have been carried out. The possibility of reaching a concentration of $^{13}\text{CF}_2\text{Br}_2 \geq 99\%$ was shown. High values of the dissociation yield for the $^{13}\text{CF}_2\text{Br}_2$ component ($\beta_2 = 15-20\%$) and selectivity ($\alpha_{12/13} = 40-80$) were obtained at a moderate laser radiation fluence 2.6 J/cm$^2$. The obtained results allow us to hope for the construction of an efficient, purely laser process for the production of carbon-13 with the required concentration $\geq 99\%$.

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