



CRYOADSORPTION AS UNIVERSAL ROUTE TO DIHYDROGENS OF HIGH AND ULTRAHIGH INDIVIDUAL PURITY

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ABSTRACT

The paper describes a new efficient cryoadsorptive method of dihydrogens p-H₂, o-H₂, HD, o-D₂, p-D₂, HT, DT, T₂ separation with moving temperature gradient on the adsorbent fixed bed. The method was developed at the Department of Chemistry, Moscow State University, as a result of many years' experimental and theoretical investigations. The separation method, and corresponding periodical action apparatus named MTGA (Moving Temperature Gradient Adsorption), and MGU DETRA (Multispecious Gas Separator-Upgrader: DEuterium, TRitium, Adsorption), respectively, are applied to prepare individual dihydrogens in very pure isotopic or nuclear-spin forms. In this paper, the basic design and possibilities of a typical three – stage laboratory adsorption separative cascade are given. The cascade was used to prepare two gases of ultrahigh isotopic purity (99.9998 mol.% deuterium and 99.98 mol.% deuterium hydride HD) for the first time. Moreover, the paper presents the results of successful studies on enriching microquantities of tritium-containing molecules HT, DT, T₂ from macrocomponents H₂ and D₂.

Keywords: Dihydrogens; Ultrahigh individual purity; Cryoadsorptive separation cascade

INTRODUCTION

Three hydrogen isotopes – protium, deuterium and tritium – give nine individual diatomic molecules (dihydrogens) [1-3]. Owing to their unique properties, individual high- and ultrahigh-purity dihydrogens become more

and more widely used recently in different fundamental researches and applied fields. One can see the continuing growth of requirements concerning individual purity of dihydrogens and, at the same time, the amounts needed for each experiment in nuclear physics, metrology, NMR and optical spectroscopy, cryogenics, laser techniques, study of quantum crystals, fusion experiments [4-9]. In fact, a new chapter of hydrogen isotopes history is opened.

The most elaborated older methods of gaseous hydrogen isotopes separation such as cryogenic distillation [10-12] or thermodiffusion [13,14] do not satisfy current level of purity, quantity, and especially time requirements. The main reason for this is the fact that artificially prepared individual dihydrogens are unstable and undergo back-conversion into the temperature dependent equilibrium state. The rate of such undesired decrease in purity depends on many factors and may be only partially diminished by applying special measures. There are even cases in which purity decreases so quickly that one needs to re-enrich an individual dihydrogen in the "on-line" mode. A real answer to this challenge is to develop an efficient, universal, and quickly acting separation technology and compact apparatus, allowing "on-line" applications.

Such a technology was developed at the Department of Chemistry of Moscow State University as a result of many years' experimental and theoretical investigations. Up to now, the information about our new separation method has been dispersed among hardly available dissertations, deposited papers, reports, symposium abstracts and patents [15-28]. The goal of this paper is to give a concise but reasonably detailed description of the new technology.

Phenomenological fundamentals of the method

As it is known, dihydrogens can be subdivided into 3 subfamilies depending on the rotational quantum number J [1]:

J-even homonuclear diatomics	– p-H ₂ , p-T ₂ , o-D ₂ ; $J = 0, 2, 4, \dots$
J-odd homonuclear diatomics	– o-H ₂ , o-T ₂ , p-D ₂ ; $J = 1, 3, 5, \dots$
heteronuclear diatomics	– HT, HD, DT; $J = 0, 1, 2, 3, 4, \dots$

Due to the quantum character of dihydrogens, the members of the three subfamilies have different properties and behave differently as the temperature is lowered, especially below about $T = 150\text{K}$.

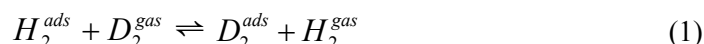
Pure J-even dihydrogens are thermodynamically stable only near absolute zero and undergo ortho-para conversion at nonzero temperatures.

Individual J-odd dihydrogens: a) are unstable at any temperature and go back to the equilibrium o-p-mixture by giving up the conversion heat; b) are magnetically active.

Pure heteronuclears: a) are only kinetically stable in the absence of catalyst; b) unlike homonuclears, exhibit no known complications due to o-p-conversion; c) have the small dipole moment, and thus, are active in the infrared spectral area.

The physical base of cryoadsorption separation method is the preferential adsorption of dihydrogens at sufficiently low temperature. According to our experimental data, there is, in general, the following sequence of dihydrogens adsorptive affinities: $T_2 > DT > o\text{-}D_2 > p\text{-}D_2 > HT > HD > o\text{-}H_2 > p\text{-}H_2$.

By, applying formally the Mass Action Law, one can describe the equilibrium adsorption of dihydrogens mixture as a quasi-chemical interphase exchange reaction [15]. For example, for the binary mixture of $H_2\text{-}D_2$, we can write the reaction (1), where superscripts describe gas and adsorbed phases:



The Van't Hoff equation for the reaction (1) is as follows:

$$RT \ln K = -\Delta H + T\Delta S \quad (2)$$

where T – is the temperature, K – is the equilibrium constant, ΔH , ΔS – is the standard enthalpy, and entropy of reaction (1), R – gas constant. Using molar concentrations in brackets, the equation for the equilibrium constant, which approximately is equal to the separation factor α :

$$K = [D_2^{ads}][H_2^{gas}] / [D_2^{gas}][H_2^{ads}] = \alpha_{D_2\text{-}H_2} \quad (3)$$

The analogical equations can be written for any pair of dihydrogens, index i indicating the more adsorbable component, and index j , the less adsorbable one:

$$RTK_{ij} = -\Delta H_{ij} + T\Delta S_{ij} \quad (4)$$

Equations (1-4) give thermodynamic description of the selective dihydrogens adsorption; its model quantum mechanical microscopic approach was developed earlier [26].

Several representative values of brutto separation factors are shown in Table 1. Before we have to explain the situation with “brutto” factors. These values refer to undetermined ortho-para dihydrogens' composition; as such, they are useful only for making various technological calculations. Unlike that, the data for NaX zeolite (Table 2), referring to individual dihydrogens, have strict thermodynamic meaning and can serve as a source of thermodynamic information. Note that the sets of data concerning NaA and NaX were obtained by a new chromatographic technique elaborated by the authors [18,23], but the two adsorbents behave differently. Zeolite NaA acts as an effective ortho-para conversion catalyst, while the activity of NaX is very low. Bearing the fact in mind we can return to the data presented in Table 1 and 2.

Tab. 1. Brutto separation factors for cryogenic adsorption of hydrogen isotopic molecules on zeolites NaA (upper triangle - II) and NaX (lower triangle -I) at $T = 77.3$ K and high degree of adsorbent filling ($\Theta = 0.6$)
The data are presented in chess table form

I \ II	H ₂	HD	HT	D ₂	DT	T ₂
H ₂		1.43	1.87	2.42	3.30	4.24
HD	1.40		1.31	1.70	2.31	2.97
HT	1.69	1.21		1.30	1.77	2.27
D ₂	2.12	1.52	1.26		1.37	1.76
DT	2.73	1.95	1.62	1.29		1.29
T ₂	3.38	2.42	2.00	1.60	1.24	

Tab. 2. Separation factors for individual dihydrogens at cryogenic adsorption on zeolite NaX (upper triangle $T=77$ K - II; lower triangle $T=62$ K - I)
The data are presented in chess -table form

I \ II	p-H ₂	o-H ₂	HD	o-D ₂	p-D ₂
p-H ₂		1.44	1.54	2.49	6.74
o-H ₂	1.69		1.07	1.62	2.71
HD	1.79	1.06		1.51	1.68
o-D ₂	3.36	1.88	1.77		1.11
p-D ₂	14.3	4.25	2.27	1.28	

Firstly, a general conclusion can be drawn from the data analysis : even at $T=77$ K, NaA and NaX have very high potential to separate any mixture of dihydrogens, and they make it possible to prepare highly enriched individual dihydrogens (except ortho- and paratritium, still unseparated).

Secondly, zeolite NaA is more efficient for separating isotopic dihydrogens, while NaX - for ortho-para-modifications separation.

Thirdly, by lowering the operation temperature one can greatly increase the adsorption selectivity (for example see value 14.3 for p-D₂ - p-H₂ separation factor at $T=62$ K on NaX).

In the conclusion we enumerate the most important parameters determining the selectivity of dihydrogen cryogenic adsorption found in the experiments: an adsorbent type, temperature, equilibrium pressure or a degree of volume filling, ortho-para-concentration, an ortho-para-catalyst. While varying these parameters one can find the optimum conditions for a separation of any pair of dihydrogens.

The principle of cryoadsorptive separation of dihydrogens with moving temperature gradient

Our separation technology is based on the moving temperature gradient on the fixed adsorbent bed column principle, formulated as early as

in 1936 by German scientists Euken and Knick for the automatic microanalytical separation of low-boiling hydrocarbons [29]. The essence of this technique is to provide a countercurrent movement of fluid against a fixed sorbent bed. In our variant of the technique we will use MTGA (abbreviation for Moving Temperature Gradient Adsorption).

The single column MTGA operation

Fig. 1. demonstrates the principal design and action of a single MTGA separation column.

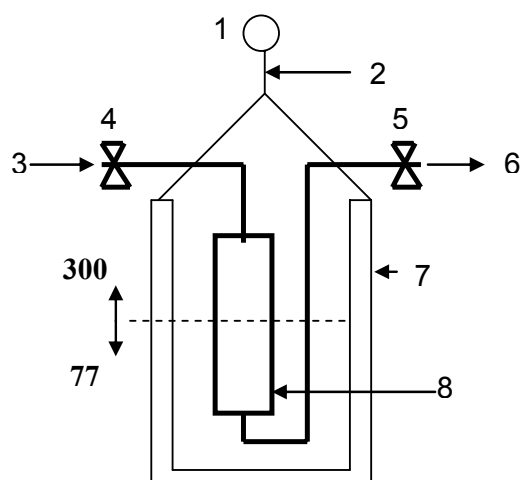


Fig. 1. Basic design of a MTGA single column: 1 – reversible motor; 2 – steel string; 3 – gas mixture to separate; 4 – valve “IN”; 5 – valve “OUT”; 6 – gas fractions collectors; 7 – liquid N₂ Dewar vessel; 8 – separative column.

The process is divided into 4 steps: 1) cooling down the column with the dehydrated adsorbent at 77 K; 2) opening the valve “in” while the valve “out” is closed and adsorbing the predetermined quantity of the gas mixture; 3) closing the valve “in”, opening the valve “out”, turning on the motor in the direction “down”, lowering a Dewar with a fixed rate and collecting the separated fractions in the preevacuated vessels (single column mode) or sending the gas into the next column (cascade mode); 4) returning to the initial state of the cascade and repeating the steps.

The optimum speed of the temperature gradient ΔT movement was experimentally found to be between 6 and 15 cm/min. In our experience one column is insufficient to solve different separation problems, and a 3-stage cascade scheme is more appropriate. The enrichment efficiency of one column is in the range 10⁻¹⁵, while three-stage cascade provides enrichment in the 10³ - 10⁴ range.

Universal three-stage separation cascade MGU DETRA

A schematic diagram of a universal 3-stage laboratory adsorption separative cascade named MGU DETRA (Multispecies Gas separator-Upgrader: DEuterium, TRitium, Adsorption), designed to operate with non-radioactive dihydrogens H_2 , HD, D_2 is shown in Fig.2. The main goal of the cascade is to upgrade 99.7 % commercial deuterium gas up to 99.99 – 99.9998 mol.% D_2 , as well as to separate and enrich hydrogen deuteride up to 99.98 mol.% HD from feed with the molar composition $H_2/HD/D_2=25/50/25$. The last ternary mixture is prepared by isotopic equilibration of an equimolar protium and deuterium binary mixture.

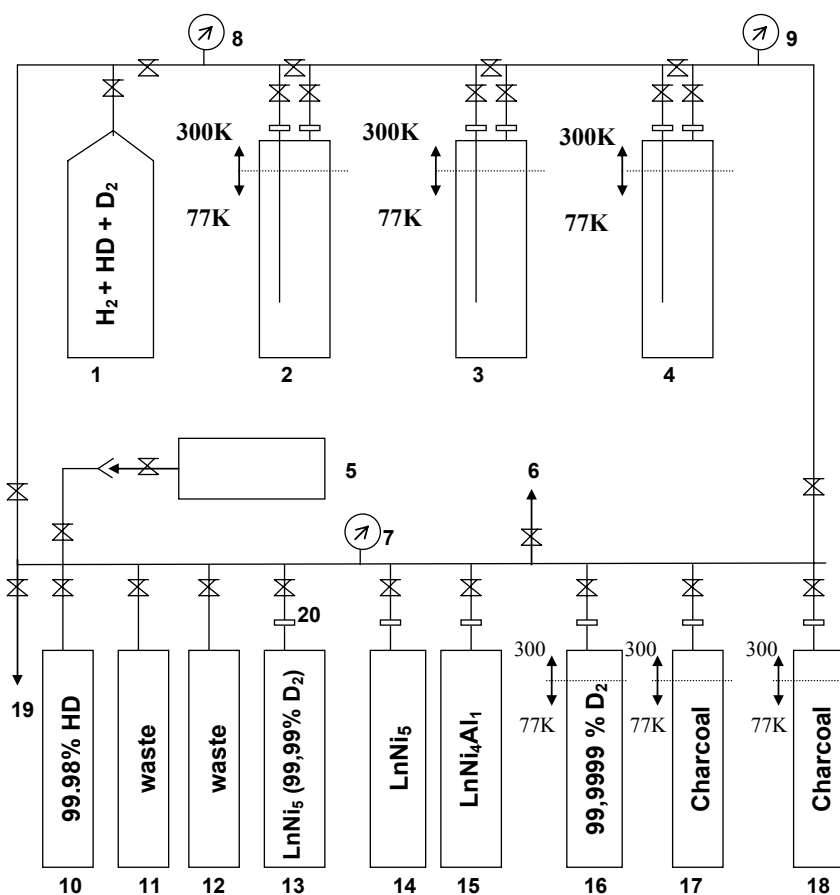


Fig.2. Schematic diagram of the arrangement of a MTGA separative cascade.

1 – vessel with feed dihydrogens mixture; 2,3,4 – separative columns;
 5 – enriched product recipient; 6 – mass spectrometer for isotope analysis
 and gas chromatograph for ortho-para-analysis; 7,8,9 – manometers;
 10,11,12 – fraction collectors; 13, 14, 15 – hydride adsorbers-compressors
 for $T=300-500$ K, $P \leq 15$ MPa; 16, 17, 18 – charcoal adsorbers-compressors
 for $T=77-300$ K, $P \leq 5$ MPa; 19 – vacuum; 20 – metal-ceramic 1 μ filters.

The appointment and operation of different parts are explained in Fig. 2. To separate isotopic mixtures, columns with commercial zeolite NaA, and interchangeable columns with commercial NaX for ortho- and para-isomers enrichment were used. The current cascade could produce enriched para-H₂ (99 %), ortho-D₂ (98 %) and ortho-H₂ and para-D₂ of 97-95 % purity even at 77 K [20,21]. The preparation of higher purity spin-isomers is a far more complex problem which requires specially synthesized ultra pure adsorbents and temperature below 77 K.

Similarly to the preparation of highly enriched tritium dihydrogens HT, DT, T₂, there are no fundamental restrictions to do it by our MTGA technique, but the corresponding cascade design and operation has to fulfill legal radioactive safety requirements.

The current laboratory cascade consists of the following main components: separative columns, vessels for the initial and product gases, containers with intermetallic hydrides LaNi₅ and LaNi₄Al and with charcoal adsorbents, vacuum equipment, measuring devices. Both the columns and the containers are equipped with 1 micron metalloceramic filters. The containers with hydrides and charcoal have three functions: 1) gas gathering and transportation from one part of system to the other; 2) compression of gases up to 50 atm (charcoal) or 150 atm (hydrides); 3) temporary storage of the enriched products up to 300 normoliters. For the analysis of the enriched dihydrogens a MI-1201 mass-spectrometer and a home-made cryogenic chromatographic system were used. The separative columns and adsorbent-compressors are equipped with Dewars for liquid nitrogen (not shown on Fig. 2). Dewars can be moved up and down with special electric reversible motors. The adsorbent and hydride compressors are equipped with heating ovens and water coolers.

The main characteristics of the described cascade are as follows: operation temperature 77 K with an applied moving temperature gradient $\Delta T = 300 - 77 = 223$ K; the separative columns are made of stainless steel tubes, with 4-5 mm internal diameter, loaded with 0.25-0.5 mm zeolite NaA or NaX. The interchangeable columns of 35 to 65 cm high were explored for different separation tasks.

The cascade has been used for more than 20 years for the preparation of pure and ultrapure dihydrogens. The efficiency of the cascade was proved by the successful preparation of ultrapure deuterium and highly enriched hydrogen deuteride (99.9998 mol.% D₂ and 99.98 mol.% HD) for their triple points implementation as the fixed points in the new version of International Temperature Scale ITS-90 [27,28]. To check and certify the quality of such highly enriched isotopic products we had to develop special analytical procedures. Moreover, about 100 normoliters of enriched HD were prepared for our chromatographic experiments in which dihydrogens are used as carrier gases.

The productivity of the described cascade version ranges from 1 to 10 normoliters per hour, depending on the desired individual dihydrogen

purity. Two ways to increase the cascade productivity were experimentally verified: several identical columns acting in parallel or one column of a greater diameter were used. The second way results in diminished efficiency, and we preferably used the first one. The effective packeted columns with 2, 4 and 8 identical parallel “barrels” were designed and developed.

The cascade operation in the case of non-radioactive dihydrogens H_2 , HD, D_2 , is illustrated with the following real examples.

The breakthrough curves for the first isothermal step of the cascade action (or, in other words, the frontal adsorption of the ternary mixture H_2 , HD, D_2) on the double column are shown in Fig. 3. One can see that to reach the equilibrium state, about 1,2 l of the initial feed should be passed through the column. The curve of the middle component HD exhibits a hump near 0,2 l, while highly retained D_2 component appears at the exit only after 0,2 l of gas has been collected. Starting with the first step isotopic distribution one can continue next nonisothermal step(s).

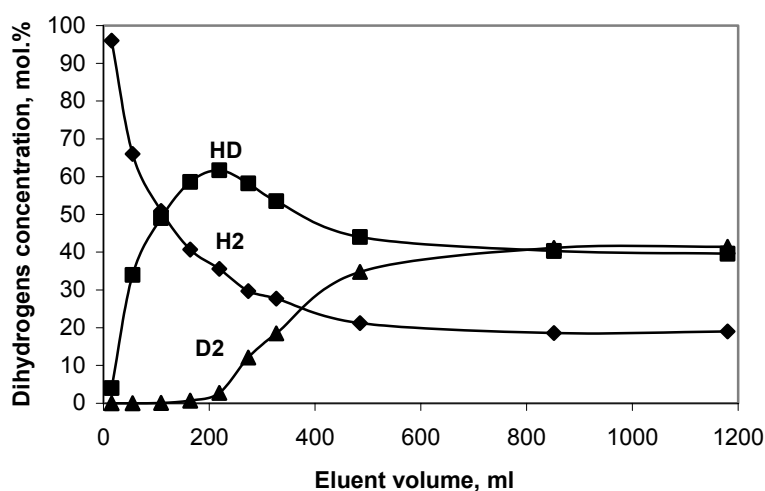


Fig.3. Frontal adsorption of triple H_2 , HD, D_2 mixture on the double 65 cm \times 4 mm column with zeolite NaA.

The results of the double enrichment are shown in Fig.4, where a new dimensionless gas volume unit was used (this unit is equal to the ratio V/V_m , where V is the sum of collected gas fractions, V_m is the maximum column capacity). The concentration of the target component HD is close to 100% in the range of collected dimensionless gas volume V/V_m from 0.4 to 0.6. This middle enriched fraction of HD was collected in parallel experiments and additionally enriched on the third column to yield 99.98 mol.% HD.

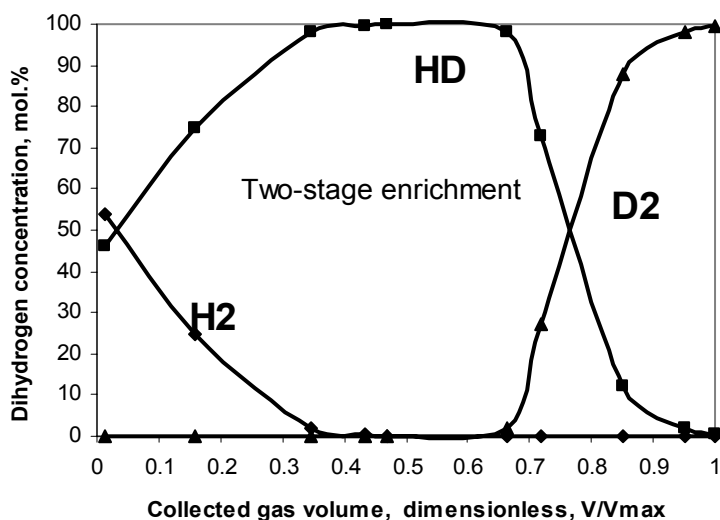


Fig.4. Enrichment of HD from triple mixture on a double-stage MTGA cascade.

The operation of a high productivity single 8-barrels column for HD enrichment is shown in Fig.5. As expected, the column efficiency was diminished: the enriched (72-75% HD) middle fraction was found to be only 10% of the maximum column capacity, but the volume of the enriched gas was increased 4 times.

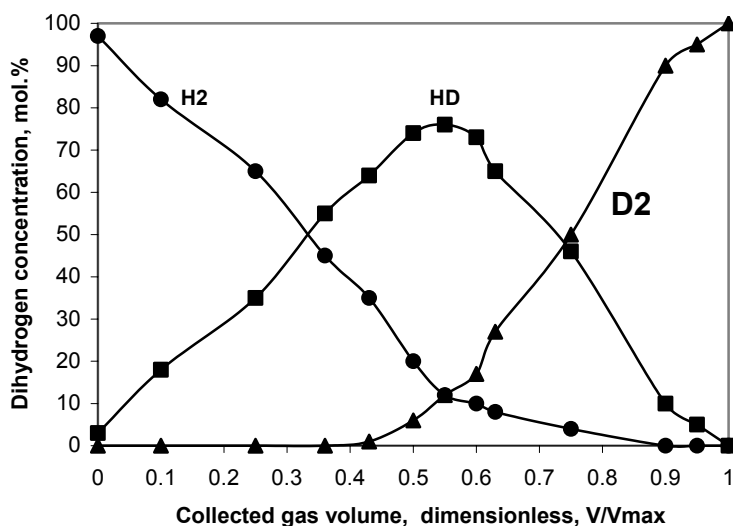


Fig.5. MTGA enrichment of HD from triple mixture on a single 8-barrel column.

Figures 6 - 9 describe the cascade operation with specially prepared protium and deuterium macrocomponents containing microconcentrations of radioactive tritium-containing dihydrogens HT, DT, T₂. The increase in HT, DT and T₂ concentrations at the column exit are shown in Fig. 6. The relative positions of curves reflect different affinities of these molecules to NaA adsorbent: HT, DT, T₂, respectively. Additionally, the data also demonstrate the possibility of using cryoadsorption for efficient T-contaminated hydrogen flow detritiation.

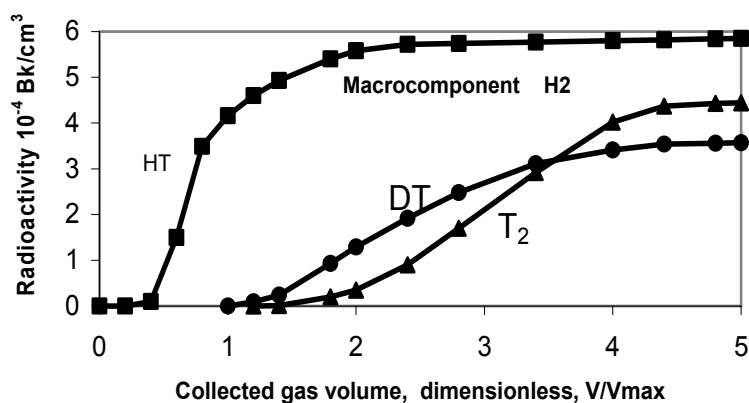


Fig.6. Breakthrough curves for frontal adsorption of HT, DT, T₂ from macrocomponent H₂.

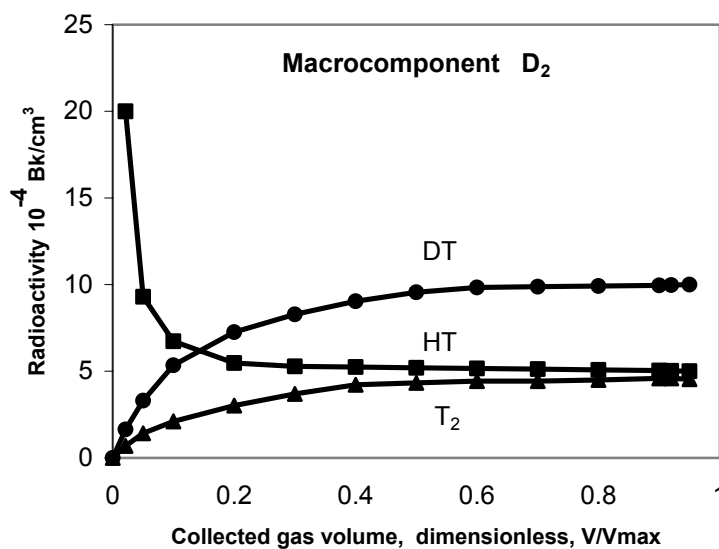


Fig.7. Breakthrough curves for frontal adsorption of HT, DT, T₂ from macrocomponent D₂.

Fig. 7 shows the results of similar frontal operation for HT, DT, T₂ adsorption from D₂ macrocomponent. In this case, the breakthrough curves have no horizontal parts, which is explained by separation factors for the DT-D₂, T₂-D₂ pairs much lower than those for HT-H₂, DT-H₂, T₂-H₂, (for example, $\alpha_{T_2-H_2} = 4.24$ and $\alpha_{DT-D_2} = 1.6$ [see Table 1]).

The cryoadsorbative method is relatively inefficient for detritization of D₂ at 77 K, but it could be successfully applied for the separation and enrichment of DT and T₂ dihydrogens (Fig.8) even at this temperature. By using the single column mode, one can enrich T₂ 7 times and DT 4 times, while HT concentration diminishes to zero.

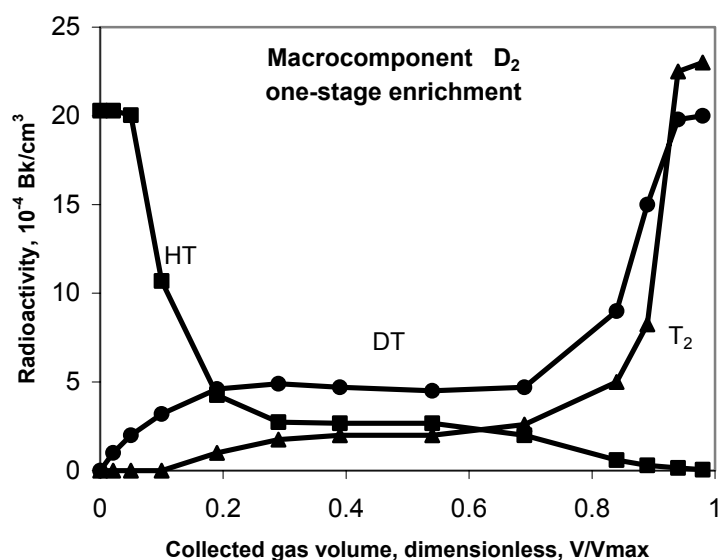


Fig.8. One-stage MTGA enrichment of HT, DT, T₂ from macrocomponent D₂.

The results of the two-stage enrichment are presented in Fig.9. They illustrate the high efficiency of cryoadsorption for the enrichment of tritium-containing dihydrogens: the total separation degree for DT is equal to 35 and for T₂ up to 60. So for the first time, it was experimentally demonstrated that the cryoadsorption method can be successfully applied for solving different “tritium” problems, including the regeneration of the spent thermonuclear fuel.

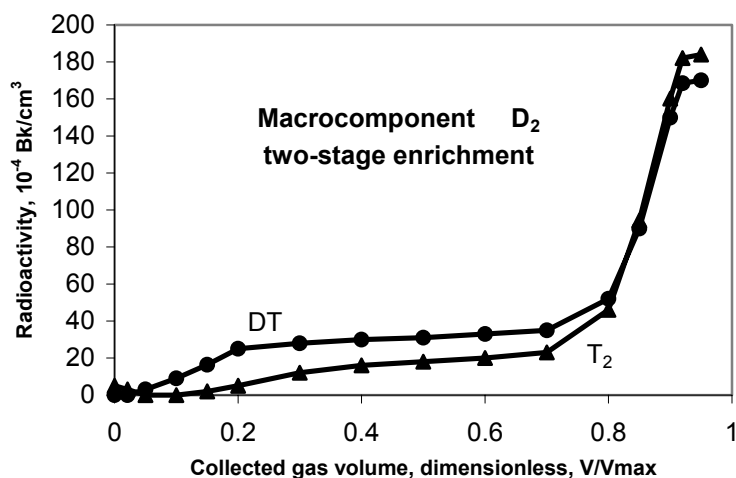


Fig.9. Two-stage MTGA enrichment of HT, DT, T $_2$ from macrocomponent D $_2$.

CONCLUSIONS

The efficient cryoadsorptive dihydrogen separation technique with a moving temperature gradient on the fixed adsorbent bed column and the corresponding cascade were developed and experimentally tested during many years of operation.

The MTGA- method has the following main advantages:

- 1) universality of the method for the preparation of ultrapure dihydrogens (except for ortho-, para-T $_2$);
- 2) able to be used in an "on-line" mode due to the short time needed to prepare the cascade for operating;
- 3) flexibility in terms of the feed concentration of the target component(s);
- 4) simple process manipulating in both manual and automatic modes;
- 5) stability of the system against possible disturbances of the process due to slow isotopes redistribution in the adsorbent phase;
- 6) low risk of radioactive tritium emissions at cryogenic temperature and high safety due to low tritium inventory in the separative columns;
- 7) high radioactive stability of zeolites to tritium β -rays bombardment;
- 8) inflammability of inorganic zeolite and liquid nitrogen;
- 9) economical advantages due to the fact, that the commercial adsorbents are used and liquid nitrogen is more accessible and much cheaper than liquid hydrogen or helium;
- 10) due to applying low temperature adsorption, the enriched product(s) is/are highly purified from usual chemical impurities (the sum of N $_2$, O $_2$, Ar, CO, CO $_2$, H $_2$ O is under few parts per million by mass spectrometry).

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