An Experimental Setup and Results of Investigations of the Xenon Sorption Characteristics for a Number of Adsorbents

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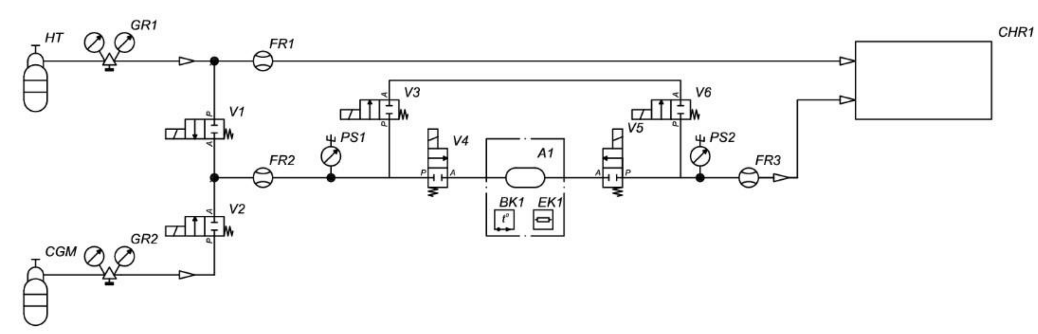
Abstract

The comparative investigations of the methods for extracting xenon from atmospheric air resulted in the selection of the pressure swing adsorption (PSA) technology as a basis for developing the draft system design for noble gas sampling directly on traps.
It was proposed that the selection of the sorbent for use in the system prototype should be experimentally selected by making comparative measurements of the sorbing properties of various sorbents.
The experimental setup and the program of investigations are described. The experimental results are presented, based on which it is possible to estimate the sorbing properties of a number of adsorbents for xenon.
Conclusions are made, which allow us to proceed to the development of appropriate design and technology solutions for the draft system design for noble gas sampling directly on traps.

Current noble gas monitoring systems have similar flow diagrams, which can be conditionally divided into the following component parts: air sampling (ambient or subsoil air), concentration using different gas separation methods, final enrichment of a sample, and measurement of the isotope volumetric activities using a detector. Differences in the implementation of this diagram are caused by the use of different techniques, designs, and technology solutions, e.g., by the use of various sorbents and various adsorption, gas-separation, and air-drying techniques.
A number of industrially produced sorbents are available today. For example, in [1], it was reported that AG-2, AG-3, SKT-M, and SKT3 activated carbons produced in Russia found application in various devices that often have similar destination: a chromatographic column, an adsorber, a krypton sampler, a replaceable xenon sampler and a radon trap in a facility for obtaining krypton and xenon samples, and high-temperature radon and xenon traps in a mobile xenon monitoring system.
In this connection, while developing the draft system design for noble gas sampling directly on traps in which sampling is based on the pressure swing adsorption (PSA) technology, we proposed to experimentally select the sorbent by making comparative measurements of the sorbing properties of various sorbents.

An Experimental Setup for Determining the Sorption Characteristics

The experimental setup is intended to determine the sorption characteristics of sorbents at different temperatures.
The gas-pneumatic diagram of the experimental setup for determining the sorption characteristics of sorbents using a chromatograph is presented in Fig. 1.



CGM – Xe or Ar tank; *HT* – He tank; *GR1,GR2* – gas pressure regulators; *FR1–FR3* – flow regulators; *V1–V6* – valves; *A1* – adsorber; *EK1* – heater; *BK1* – thermocouple; *PS1, PS2* – pressure sensors; and *CHR1* – chromatograph.

Fig 1 – The gas-pneumatic diagram of the experimental setup for determining the sorption characteristics of sorbents using a chromatograph

The sorbent is placed inside the tube of adsorber *A1* with a length of 20 cm and is pressurized using an air blasting pistol to provide the maximum fill density.
Measurement of the Xe or Ar breakthrough curves is performed according to the following procedure.
Pure helium is fed over the *V1–V3–V6* line to adjust the required gas flow rate using flow regulators *FR1* and *FR2* and to set the zero line of the chromatograph. Thereafter, valves *V1* and *V2* are switched, and a calibration gas mixture (1% Xe) or an argon (2,7%) mixture with helium is fed to the system. After the calibration of the maximum chromatograph reading, the valves are reversed in order to remove the calibration mixture from the pipelines. After the calibration is complete, the gas flow is redirected to the *V1–V4–V5* line for measuring the breakthrough curve.
The appearance of the setup for studying the sorption characteristics of sorbents is presented in Fig. 2.

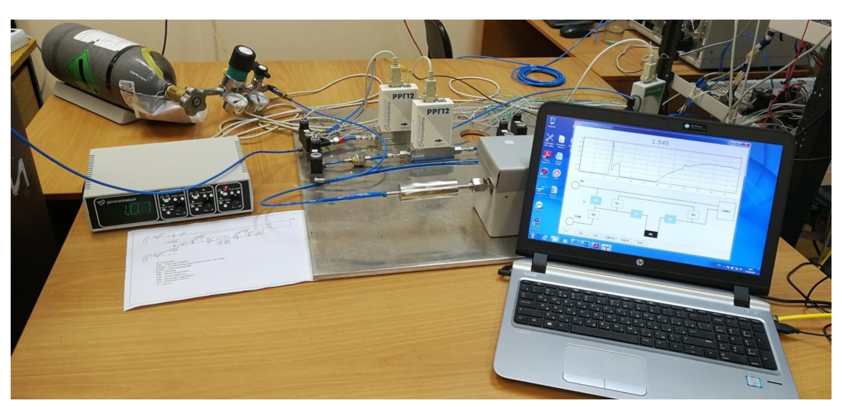


Fig. 2 – The setup for studying the sorption characteristics of sorbents

Experimental Results

Over 100 experiments for determining the characteristics of various sorbents were performed in the course of the study.
Activated carbon and coconut-shell activated carbon [1] are the most widely used sorbents for noble gases, but the sorbents based on silver-loaded zeolites are getting popular today [2–8]. We investigated two sorbents of this type: Ag-ETS-10 provided by the PTS of the CTBTO PC and Ag-ZSM-5. Table 1 lists the sorbents and the scope of the experiments. VNIIA has Ag-ZSM-5 in the form of standard pellets and a powder with natural boehmite (15%, PWD+clay) used as a binder.
Table 2 presents the packing density of sorbents broken into particles with dimensions of 0,25–0,50 mm, into the adsorbers, which should be taken into account in the comparison of the sorption characteristics, i.e., the half-time of gas release ($T_{0.5}$), dynamic adsorption coefficient (*Kd*), and adsorption capacity (*q*).

Table 1 – The list of sorbents and the scope of the experiments

Sorbent	Group	Temperature, °C			Flow, ml/min			Gas	
		30	40	50	126	87	56.5	Xe	Ar
Ag-ETS-10	1	x	x	x	x	x	x	x	x
Ag-ZSM-5	1	x	x	x	x	x	x	x	x
Ag-ZSM-5 (PWD+clay)	1		x		x			x	
Activated Carbon SKT3 No.1 (VNIIA)	2	x	x	x	x			x	
Activated Carbon SKT3 No.2 (SPB)	2	x	x	x	x			x	
Coconut-shell carbon No.1 (Geizer)	2		x		x			x	x
Coconut-shell carbon No.2 (Filter)	2	x	x	x	x			x	
Coconut-shell carbon NWC 8*30 'REGULAR'	2	x	x	x	x	x		x	x
Activated Carbon AG-3	2	x			x	x		x	x
Li-LSX	2	x	x	x					
ZSM-5	2	x	x	x	x			x	x
NaX	2	x			x			x	x

Table 2 – The mean sorbent packing density

Sorbent	ρ, g/cm³
Ag-ETS-10	0.994
Ag-ZSM-5	0.750
Ag-ZSM-5 (PWD+clay)	0.605
Activated Carbon SKT3 No.1	0.473
Activated Carbon SKT3 No.2	0.486
Coconut-shell carbon No.1	0.565
Coconut-shell carbon No.2	0.593
Coconut-shell carbon NWC 8*30 REGULAR'	0.694
Activated Carbon AG-3	0.694
Li-LSX	0.599
ZSM-5	0.759
NaX	0.754

Special emphasis was placed on silver-loaded sorbents, since they have high Xe sorption properties as references [2–7] say. The Ag-ETS-10 zeolite possesses best properties for Xe sorption, but it does not possess Ag sorption. Regardless of the scientific articles [2–7], Ag-ZSM-5 zeolite that we investigated revealed low sorption properties for Xe. At the same time, it demonstrated a certain capability of sorbing Ar, and this result turned out to be the highest in this study.
The small scope of experiments with Ag-ZSM-5 and only two samples available for analysis make it impossible to consider it as unsuitable for our purposes. In order to clarify the picture, the results of the experiments with a conventional ZSM-5 zeolite, which had even higher Xe sorption relative to Ag-ZSM-5, were added.
Figures 3 and 4 depict the Xe breakthrough time as a function of the temperature and the flow rate of the calibration mixture. The hold-up time is seen to increase as the flow rate or temperature goes down and the function itself looks like an exponential curve. Note that, for the Ag-ETS-10 sorbent, the breakthrough time as a function of the flow at a temperature of 30ºC has a substantially larger slope than others do, which can be the indication of a higher rise in the dynamic adsorption coefficient and the adsorption volume with a decrease in the temperature.

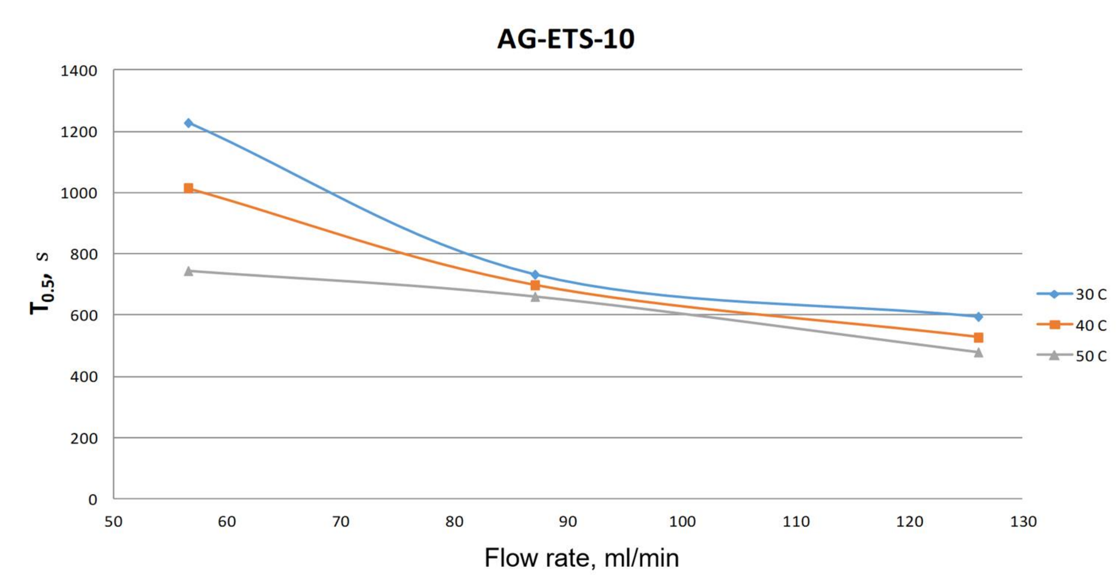


Fig. 3 – The Xe breakthrough time from the absorber with an Ag-ETS-10 as a function of the calibration-mixture flow rate at different temperatures

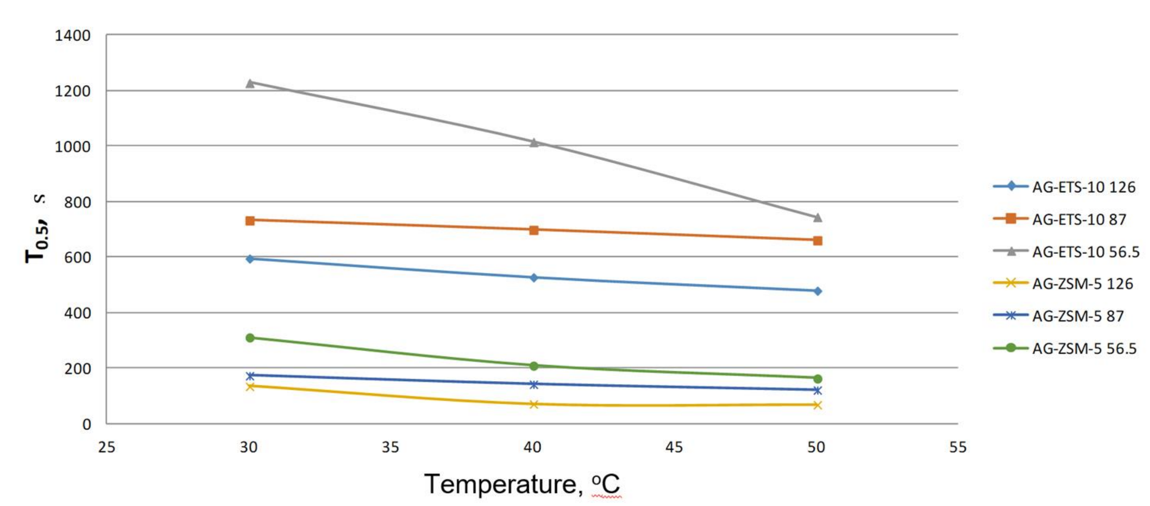


Fig. 4 – The Xe breakthrough time as a function of temperature

Figure 5 shows the Ar (2.7%) breakthrough curve for Ag-ETS-10 and Ag-ZSM-5. Though Ag-ETS-10 offers better Xe sorption, it sorbs Ar six times worse, and Kd_{Xe}(Ag-ETS-10) is 18 times higher than Kd_{Ar}(Ag-ZSM-5).

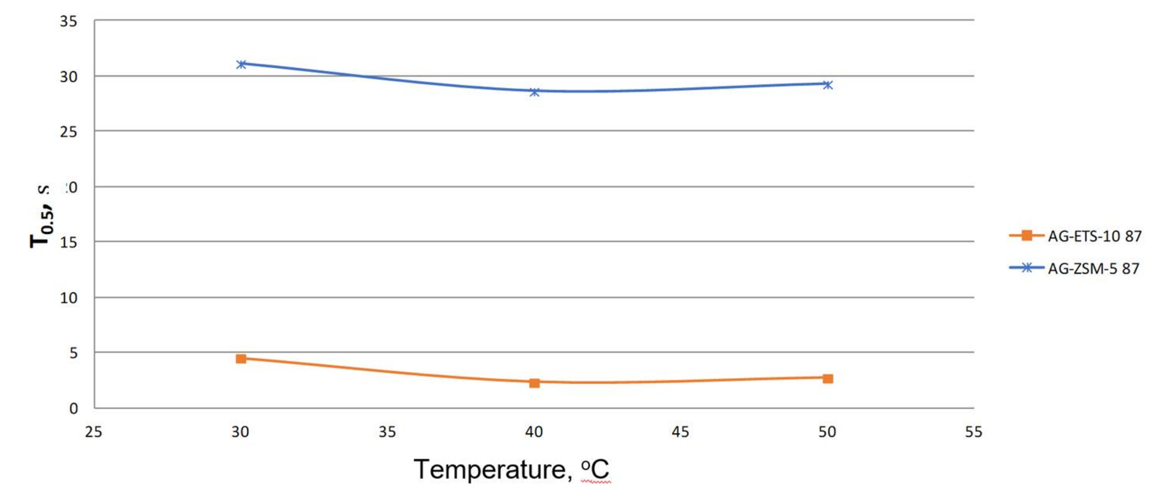
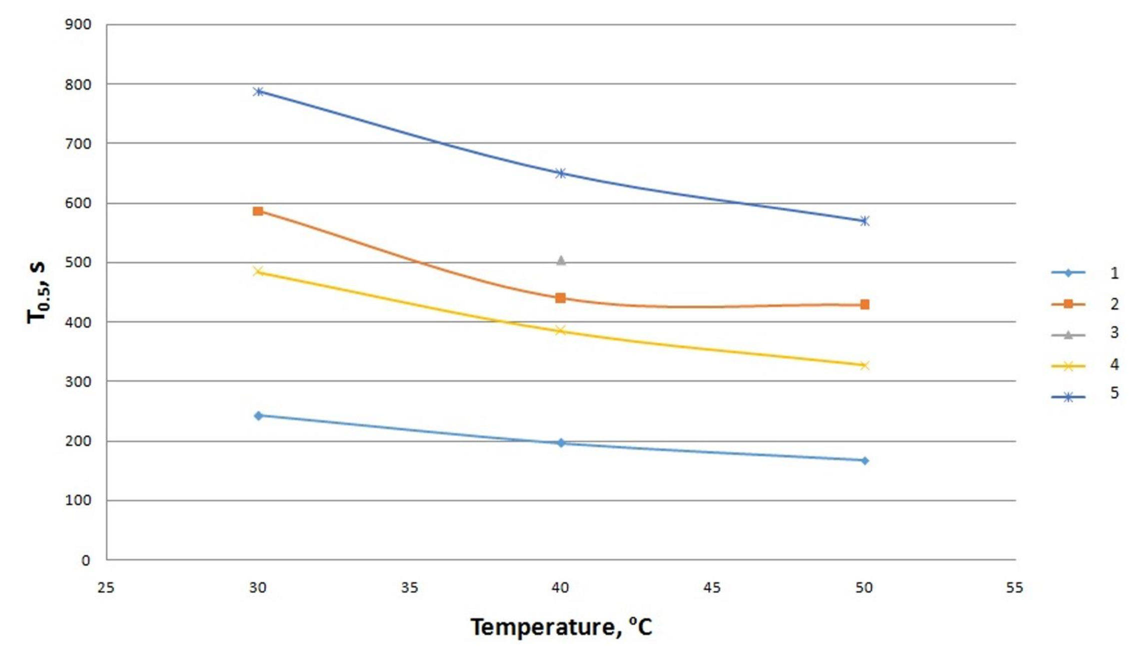


Fig. 5 – The Ar breakthrough time as a function of temperature

Figure 6 shows the temperature dependence of the Xe breakthrough time in experiments with various activated carbons used for sorption. The selected carbon types differ mainly in the raw material (charcoal and coconut-shell carbon), batch, and manufacturer. The curve confirms that the same rank of carbon can have different separation properties depending on the batch or the manufacturer. For example, Activated Carbon SKT3 No.1 purchased in 2015 offers 2.5 times worse properties than Activated Carbon SKT3 No.2 bought in 2001. The coconut-shell activated carbons No.1 and No.2, which are intended for water filtering, have lower Xe sorption than coconut-shell activated carbon NWC 8*30 'REGULAR' of the same destination, which was manufactured in Ceylon.



1 – Activated Carbon SKT3 No.1;
2 – Activated Carbon SKT3 No.2;
3 – Coconut-shell activated carbon No.1;
4 – Coconut-shell activated carbon No.2;
5 – Coconut-shell carbon NWC 8*30.

Fig. 6 – The temperature dependence of the Xe breakthrough time for different activated carbons

Unfortunately, the Li-LSX and NaX sorbents offer no significant sorption both for Xe and for Ar, and it is senseless to analyze or use them for separation of these gases.
Table 3 presents experimental results for Ar. As mentioned above, neither of sorbents demonstrated good Ar separation. However, we note that Ag-ZSM-5, ZSM-5, and NWC 8*30 'REGULAR' shall be more thoroughly analyzed at lower temperatures and lower gas flow rates, which may provide significant increment of the dynamic adsorption coefficient.

Table 3 – Experimental results for argon

Sorbent	Temperature, ºC	Flow, ml/min	Gas	$T_{0.5}$, s	Kd, ml/g	q, ml/g
Ag-ETS-10	30	87	Ar	4.5	5.10	0.14
Ag-ZSM-5	30	87	Ar	31.1	50.11	1.35
ZSM-5	30	87	Ar	10.5	5.29	0.14
Coconut-shell carbon NWC 8*30 'REGULAR'	30	87	Ar	15.1	8.33	0.22
Activated Carbon AG-3	30	126	Ar	1.2	0.96	0.03
Li-LSX	30	87	Ar	0	0	0
NaX	30	87	Ar	0	0	0

Figures 7 and 8 present the experimental dependences of the chromatograph readings as a function of time in a set of experiments. The fit of the breakthrough curves by a two-phase S-shaped curve is presented in the graphs with red color.

The breakthrough curves are S-shaped curves of an asymmetric type.
Various models based on a simple symmetric logistic function were proposed earlier to estimate the sorption efficiency until R.M. Clark combined the logistic function with the Freundlich isotherm of adsorption [9]. The general logistic function obtained thereby adequately describes the asymmetric breakthrough curves.
The general logistic function has the form:

$$C = [\frac{C_i^{n-1}}{1+A\times e^{-rt}}]^{1/(n-1)},$$

- where *C* is the sorbate concentration at the outlet of the column filled with activated carbon;
- C_i is the sorbate concentration at the inlet;
- *R* and *A* are the constant coefficients of the logistic function;
- *t* is time;
- *n* is the reverse inclination of the Freundlich isotherm.

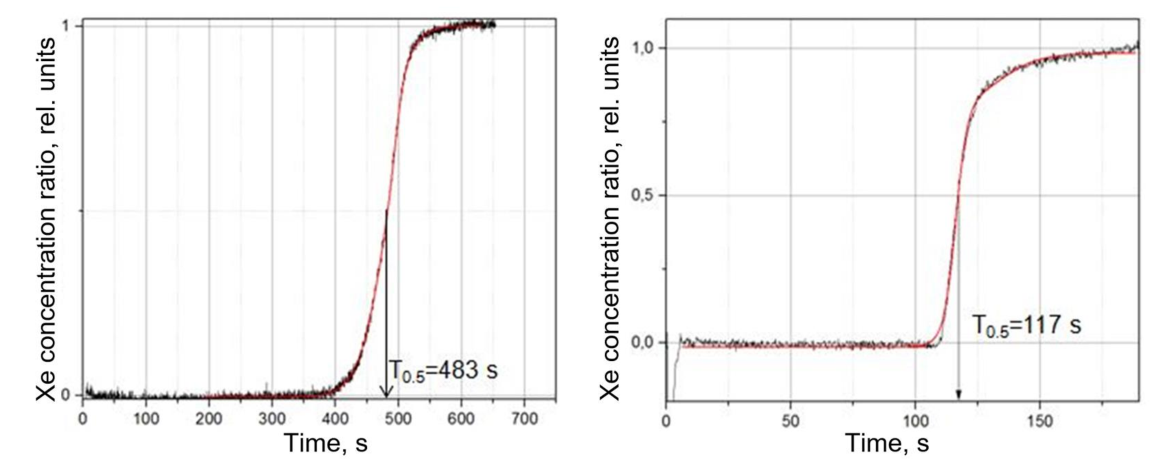


Fig. 7 – Measurements of the Xe passage through the Ag-ETS-10 (left) and Ag-ZSM-5 (right) sorbents

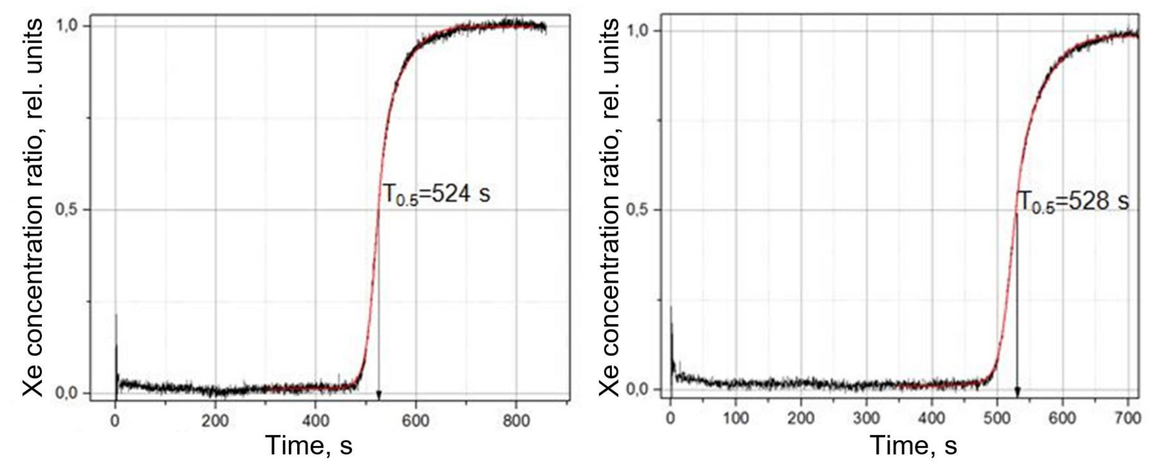


Fig. 8 – Measurements of the Xe passage through the NWC 8*30 'REGULAR' activated coconut-shell carbon. The measurements were made with an interval of 26 h

The adsorption curves in all diagrams are approximated well by this function. The fit of the breakthrough curves of noble gases by the S-shaped curve is presented in Figs. 7 and 8 with red color.

Conclusions

The results of the experimental study aimed at determining the sorption capabilities of various substances ranging from activated carbon to state-of-the-art nonnatural compounds are presented in the report.
The principal task was to measure the breakthrough curves for different sorbents in order to compare their properties and select sorbents most suitable for gas separation technologies with the aim of developing the design and technology solutions for future gas-separating devices.
The experimental results were processed and presented in tables and in diagrams.
The most promising sorbent is Ag-ETS-10 provided by the Preparatory Commission for the Comprehensive Nuclear-Test-Ban Treaty Organization. It demonstrated the highest Xe sorption capacity (the dynamic adsorption coefficient is 800–1000 ml/g) in all measurement modes.
The second place can be shared between SKT3 activated carbon produced in Russia in 2005–2010 and the modern NWC 8*30 'REGULAR' coconut-shell activated carbon (its dynamic adsorption coefficient is 400–600 ml/g).
The unexpected result was obtained for the Ag-ZSM-5 zeolite that showed low sorption properties for xenon inspite of its excellent characteristics known from the literature. However, it is this zeolite that demonstrated an ability to sorb argon.
In general, for practical implementation of the system for noble gas sampling directly on traps, to our mind, the sampler should the be developed based on the pressure-swing adsorption (PSA) method using cocunur-shell activated carbon and filling the final Xe trap with Ag-ETS-10 sorbent.
The results of our study show that development of devices based on the chromatographic separation technology calls for careful preparation: sorbents must be preliminarily selected and their properties must be determined, since even sorbents of the same declared type may differ in the sorbing properties.
VNIIA will carry out further work on the determination of the adsorption capabilities of various substances with broader range of external effects.

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