Technical Note

Selection of a carrying agent for obtaining radioactive methyliodide vapors under dynamic conditions

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A R T I C L E   I N F O

A B S T R A C T

A method for preparing "reagent" for radioactive methyliodide vapors production using an isotopic exchange reaction has been developed. Based on the obtained data of the isotopic exchange efficiency and hydraulic resistance, white fused alumina (700—840 μm) was selected as the carrying agent material for "reagent" production. The radioiodine isotopic exchange dependences on such parameters as temperature, gas flow velocity, and the methyliodide concentration in it were determined. Optimal conditions have been selected to achieve 85% of the isotopic exchange rate in 1 h of the experiment. The obtained data allowed to develop an approach to the test of iodine filters for nuclear power plants and to determine their efficiency.

1. Introduction

During the routine nuclear power plant operation, radioactive aerosols and gases inevitably enter the industrial premises air. Gaseous iodine radioactive isotopes are the main danger for personnel and the population [1,2]. It gets into production premises with uncontrolled leaks of the primary coolant. The ventilation systems efficiency designed for air purification depends directly on the sorbents quality. In Russia, a unified approach to assess the iodine sorbents quality based on the standard procedure of granular activated carbon testing under laboratory conditions has been developed [3,4].

However, the iodine filters installed at nuclear power plants are necessary to conduct "in-situ" tests to confirm their further operation capacity or the need to replace the sorbents that have reduced or lost their sorption qualities. The main reasons are temperature and humidity effect on the iodine sorbent, as well as aging and poisoning during the operation [5—9]. The gaseous methyliodide ($CH_3^{131}I$) labeled with the I-131 isotope pulsed into the adsorber is used as a test agent for such tests [10,11]. $CH_3^{131}I$ is present in the

gaseous radioactive waste of nuclear power plants and is the most difficult to capture chemical radioiodine form [1,2,12].

Radioactive methyliodide is often obtained by the reaction of dimethyl sulfate with metal iodide labeled I-131 [13,14]. Another way of obtaining is by isotopic exchange, when a portion of liquid methyliodide reacts with an aqueous solution of $Na^{131}I$ without a carrier [4,15]. However, there is a risk of spillage and indoor air contamination with liquid radioactive methyliodide vapors during testing or in cases of safety violations when handling this substance.

In our opinion, the optimal approach to obtain gaseous $CH_3^{131}I$ is the isotopic exchange reaction under dynamic conditions. That should be two-phase system between methyliodide vapors, which do not contain radioactive isotopes, and metal iodide, labeled with the isotope iodine-131. This process can be carried out safely in a small portable radioactive methyliodide generator during acceptance tests and regular monitoring of iodine filters efficiency installed at the nuclear power plants ventilation systems. Thus, optimal parameters determination of isotopic exchange process will provide basic guidelines on hardware-technological scheme for obtaining the gaseous methyliodide labeled with the isotope iodine-131.

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The aim of this work is to obtain data on heterogeneous isotopic exchange between radioactive iodine deposited on an inert carrying agent and gaseous methyliodide, as well as to determine the optimal conditions for obtaining gaseous methyliodide labeled with the isotope iodine-131.

2. Material and methods

A number of materials traditionally used in the column chromatography were selected for research and selection of the optimal carrier: calcined silica − Chezasorb AW-DMCS, Chromaton N; silica gel Kieselgel 40; aluminum oxide Al_2O_3. Table 1 shows the characteristics of the selected porous carrying agents. The specific surface area was calculated using the BET method, and the porous structure parameters were calculated using the DFT model based on low temperature nitrogen adsorption isotherms obtained on the Quadrasorb Kr/SI (Quantachrome) device using a high-purity nitrogen as an adsorptive at 77.4 K.

The other group includes non-porous materials: glass spheres (60−160 µm), white fused alumina WFA F20 (crystalline Al_2O_3, 700−840 µm), white fused alumina WFA F120 (100−125 µm), cubic zirconia F100 (crystalline ZrO_2, 100−150 µm).

2.1. The "reagent" preparation method

For application of radioactive iodine to the materials surface, several microliters of $Na^{131}I$ aqueous solution without an isotope carrier were added to a small amount of water-ethanol solution in order to obtain a pasty mixture of the carrier with the liquid phase. The water-ethanol volume ratio of the labeled I-131 solution in all cases was 2:5. Then the obtained "reagent" was dried to a constant mass at temperatures from room one to 200 °C and loaded into a dismountable column (Fig. 1) for the isotopic exchange.

2.2. The testing and calculating method for isotopic exchange efficiency

The "reagent" column was a hollow PTFE cylinder (I) with a height of 70 mm and an internal diameter of 20 mm. The upper and lower covers (II) with pipes intended for the supply (discharge) of a gas mixture were screwed on the cylinder hermetically by thread. There is a nylon mesh (III) on a collar made on the inner surface of the covers. Thus, the mesh was fixed with a tightened cylinder and cover, forming an internal space of ≈ 22 cm^3 for placing the "reagent", which volume was the same in all experiments (17 cm^3). The top cover also has an external collar for mounting the column in a dry-air thermostat. A medical drug for injection "Sodium Iodide-131″ was used as radioactive label source, which is an aqueous solution (2 ml) of $Na^{131}I$ without a carrier with an activity of 200 MBq.

The study of iodine isotopic exchange kinetics between the prepared "reagent" and the methyliodide vapors was carried out on a laboratory stand developed by us [16] (Fig. 2). For the experiment, a portion of methyliodide (1.5−2.0 ml) was poured into a hermetically sealed test tube (2), which was thermostated using a circulation thermostat (7) at 25 °C to ensure a constant rate of liquid

methyliodide evaporation during the experiment. The methyliodide vapors were supplied into the main gas stream by a peristaltic pump (4) at a controlled speed. The construction of the peristaltic pump does not allow backflow of the gas stream. The methyliodide concentration in the stream in the range from 10 to 250 mg/l was varied by adjusting the pump rotor rotation speed (4). The methyliodide consumption was determined by weighing a test tube (2) with an analytical balance with an accuracy of 0.1 mg. The main gas stream (air) was supplied to the system using a diaphragm compressor (3). Air flow was monitored using an adjustable rotameter LZM-4T (8) with a flow measurement range of 0.1−1.0 l/min. Both streams (air and methyl iodide vapors) were mixed at the junction point of 2 tubes without an expansion volume. The gas stream with CH_3I vapors entered the column filled with "reagent" (1). The test column was previously thermostated in a dry-air thermostat (6) for an hour. Radioactive methyliodide vapors were captured in a protective column (5). The protective column consisted of 15 steel sections (Ø50 mm, 10 mm section height) filled with the industrial iodine sorbent VSK-5IK based on granular charcoal impregnated with 5% triethylenediamine (TEDA). The isotopic exchange efficiency (E) was calculated by measuring the "reagent" column activity in the same geometry before (A_0) and after (A) the experiment on a scintillation gamma-ray spectrometer with a crystal-based detector NaI(Tl):

$$E = \left(1 - \frac{A}{A_0}\right) \cdot 100\% \tag{1}$$

2.3. The hydraulic materials resistance determination

The hydraulic resistance measurement of non-porous carrying agents at different air flow rates was performed under the same conditions, using a differential pressure gauge (CEM DT-8890A). To do this, the air flow at a known speed was fed into the column and the pressure drop was measured. The material hydraulic resistance value was found as the difference between the pressure drops on an empty and filled column.

3. Results and discussion

At the initial stage of the study, the isotopic exchange efficiency on porous materials containing I-131 without an isotopic carrier was determined. The experimental conditions were as follows: the air flow with $CH_3^{131}I$ vapor through the column − 0.2 l/min; the column temperature − 120 °C; the methyliodide concentration in the gas stream with approximately 55 mg/l; the test duration − 60 min. The relative humidity of the gas stream taken from the laboratory was not controlled. The isotopic exchange results are presented in Table 2.

As a result of the conducted research, it was found that Kieselgel showed the highest isotopic exchange efficiency among the considered porous carriers − 62 ± 3%. Its advantages include the fact that this material is less prone to dusting and has a larger particle sizes. The next series was carried out with this material.

Table 1
The physical characteristics of the porous carrying agents.

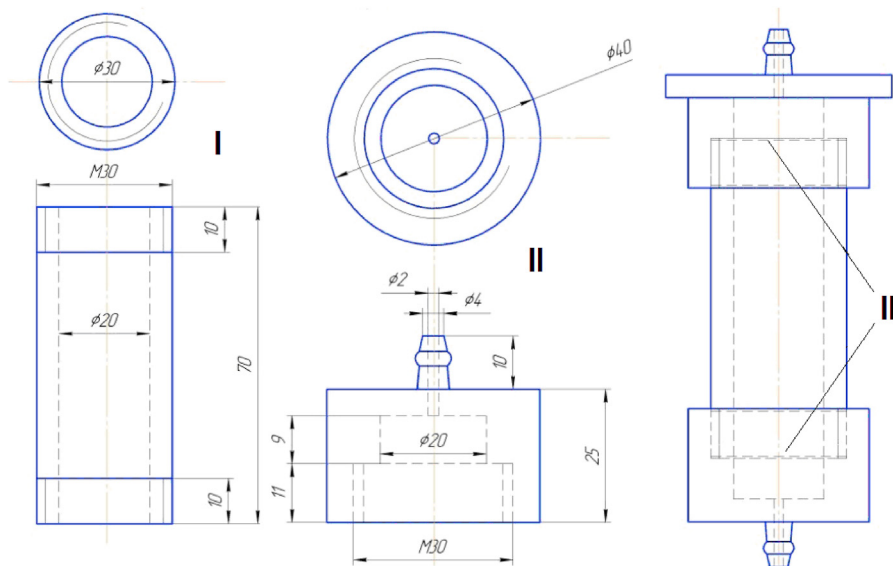| No	Designation	Specific surface area, m^2/g	Total pore volume, cm^3/g	Particle size range, mm
1	Chromaton N	1.132	0.002	0.16−0.2
2	Chezasorb AW-DMCS	3.915	0.006	0.2−0.36
3	Alumina	252.6	0.517	0.315−0.5
4	Kieselgel 40	734.3	0.391	0.2−1

Fig. 1. The "reagent" test column: I — threaded cylindrical shell; II — cover with inlet (outlet) pipe; III — nylon mesh placement.
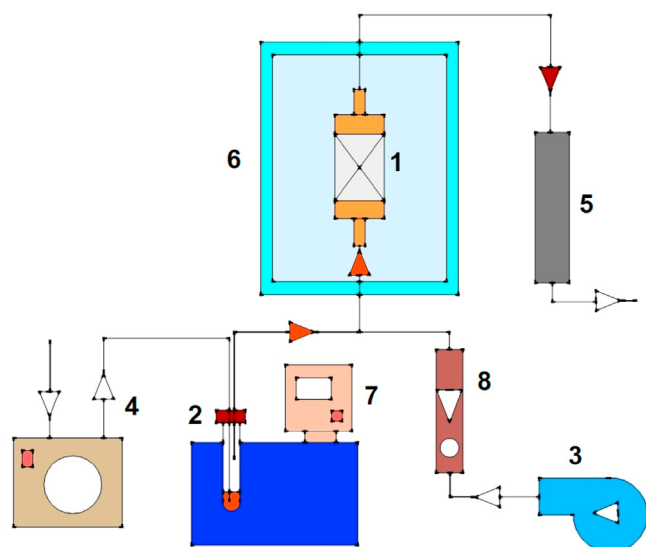

Fig. 2. The test facility simplified scheme [16]: 1 — "reagent" test column; 2 — methyl iodide thermostatic tube; 3 — compressor; 4 — peristaltic pump; 5 — protective charcoal column; 6 — dry-air thermostat; 7 — circulation thermostat; 8 — rotameter.

Table 2
The isotopic exchange process results with porous carrying agents (Q = 0.2 l/min, c = 55 mg/l, solid phase volume is 17 cm^3).

Parameter	Chtomaton N	Chezasorb AW-DMCS	Al$_2$O$_3$	Kieselgel 40
Solid phase mass, g	4.22	9.07	9.42	13.47
CH$_3$I input, mg	710	620	720	640
E, %	55 ± 2	23 ± 2	27 ± 2	62 ± 3

The gas flow rate and CH$_3$I concentration effect on the exchange efficiency between I-131 in the solid phase and stable I-127 in the gas phase was studied. For this purpose, a series of Kieselgel samples labeled with iodine-131 without an isotope carrier was prepared. The samples drying time was 2 h at 120 °C. Test conditions: the "reagent" column temperature — 120 °C; the gas flow rate (Q) through the column was 0.1—0.8 l/min; the relative gas stream

Table 3
The kinetic conditions effect on isotopic exchange efficiency (carrying agent — Kieselgel).

No	Q = 0.2 l/min		m(CH$_3$I) ≈ 1000 mg	
	c, mg/l	E, %	Q, l/min	E, %
1	55	31 ± 2	0.1	55 ± 3
2	110	55 ± 3	0.2	31 ± 2
3	230	61 ± 3	0.8	11 ± 1

humidity was 70—75%; the methyliodide concentration (c) in the gas phase was 10—230 mg/l; the test duration — 60 min. The total iodine amount (m) supplied to the column was calculated as the product of its concentration, gas flow rate, and test duration. The isotopic exchange efficiency increase was observed up to methyliodide concentration of 110 mg/l (Table 3). With a further increase in the concentration to 230 mg/l, the effectiveness increased slightly. An increase in the gas flow rate above 0.1 l/min (Table 3) did not lead to the process intensification and was considered impractical. As a result, in an hour of testing under the most favorable conditions, it was possible to achieve an isotopic exchange efficiency of about 55—60%.

Previously obtained results [16] showed (Fig. 3) that the air humidity practically does not affect the isotopic exchange efficiency of labeled "reagent" dried at room temperature. The kinetic curves corresponding to the "wet" material are convex at the initial stage (it is re-dried and the exchange is slow), regardless of whether dry or wet air is supplied to the column. Then (starting, approximately, from 40th minute) the isotopic exchange process accelerates. It should be noted that the radioactive iodine proportion that passed into the gas phase during 1 h of testing from the air-dried samples surface does not exceed 40%. The kinetic curve is completely different when the dry air is applied to the dried carrier. We guess that the water desorption from the Kieselgel pores affects the isotopic exchange rate. The form of these curves can be explained by diffusion hindrance for the methyliodide molecules which creates a counter flow of water vapor from the pore volume into the intergranular space. The isotopic exchange efficiency per hour of testing with the material dried at 120 °C is already more than 50%.
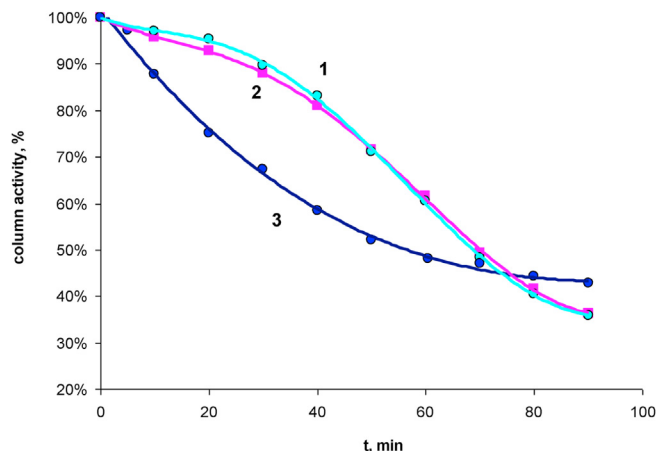
Fig. 3. The isotopic exchange kinetics with the "reagent" preparation [16]: 1 − dry air and uncalcined Kieselgel; 2 − humid air and uncalcined Kieselgel; 3 − dry air and calcined Kieselgel.

Based on the all data obtained, it became clear that the Kieselgel material is not optimal for the "reagent" production for a number of reasons. First, the maximum isotopic exchange efficiency, which was achieved, was a little more than 60% during 1 h at 120 °C. Secondly, due to the sufficiently developed specific surface area of the material, the exchange between radioactive and stable iodine is significantly affected by the preparation conditions of both the "reagent" itself and the gas stream humidity. Therefore, when performing further research, it was decided to abandon porous materials.

At the next stage of the research, data on the isotopic exchange efficiency on non-porous carrying agents were obtained (Fig. 4a). The "reagents" samples based on WFA, glass spheres and cubic zirconia were prepared in accordance with the procedure described above and dried at a temperature of 150 °C for an hour. The experimental conditions were as follows: the air flow with CH$_3$I vapor through the column − 0.2 l/min; the column temperature − 120 °C; the radioiodine concentration in the gas stream was ~55 mg/l; the relative humidity of the gas stream taken from the laboratory − 68−72%.

The isotopic exchange efficiency for all carrying agents, except for the glass spheres, after an hour of testing was 66−70%. When using glass spheres, the efficiency was significantly lower and was comparable to the "reagent" prepared on the basis of Kieselgel −

55%. In addition, to select the optimal carrying agent, comparative tests were performed on the hydraulic resistance of these materials (Fig. 4b). After comparing the data obtained, we selected the WFA F20 material for further research as having the lowest hydraulic resistance.

A series of experiments was carried out with this material to determine the "reagent" drying temperature effect on the isotopic exchange efficiency. In accordance with the procedure above, several samples of the "reagent" based on WFA F20 were prepared. The samples were kept in a drying oven at temperatures of 100, 150 and 200 °C for an hour. The remaining experimental conditions were as follows: the air flow with CH$_3$I vapor through the column − 0.2 l/min; the column temperature − 120 °C; the methyliodide concentration in the gas stream was ~55 mg/l.

It was found that with drying temperature increase from 100 to 200 °C, the isotopic exchange efficiency decreases (Fig. 5). We suppose that drying temperature affects the morphology of the active Na^{131}I layer on the carrying agent surface which in turn affects the isotopic exchange rate.

To find out the nature of the isotope carrier additives effect on the isotopic exchange efficiency, a number of experiments were carried out where a certain amount of KI (not labeled with I-131) was added to the radioactive solution before it was impregnated with the solid phase. Experiments have shown that the provision of
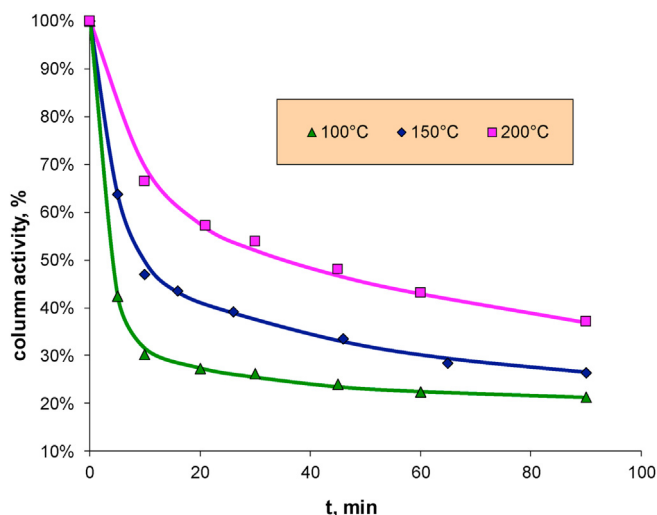

Fig. 5. The isotopic exchange kinetics with the "reagent" drying temperature.
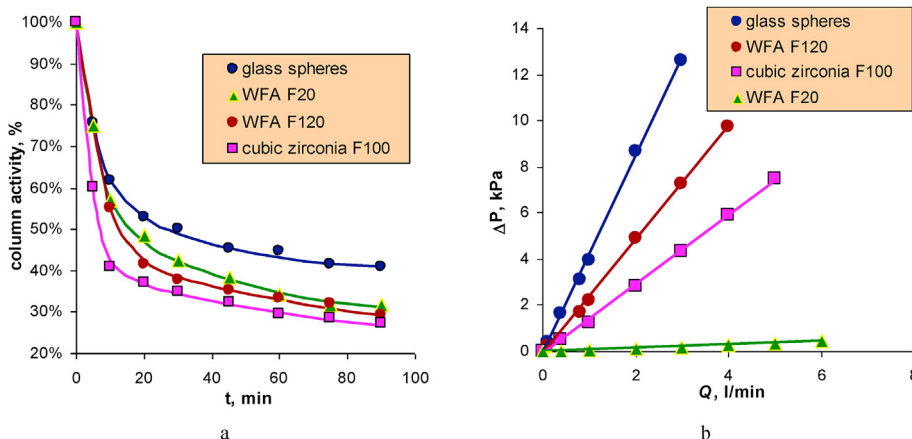

a

b

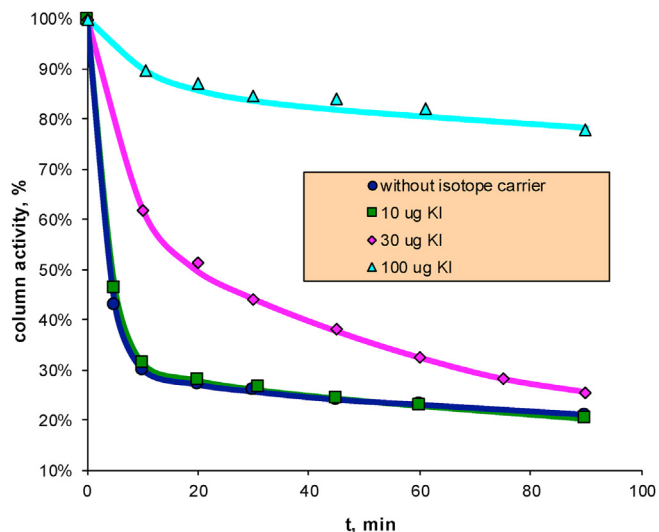**Fig. 4.** The isotopic exchange kinetics (a) and the hydraulic resistance (b) for non-porous materials.

Fig. 6. The isotopic exchange kinetics with the amount of a stable iodine isotope carrier for WFA F20.

Fig. 7. The isotopic exchange efficiency at different temperatures of the "reagent" column operation.

a small (up to 10 μg) amount of isotope carrier into the "reagent" does not affect the kinetic curves nature (Fig. 6), while more significant amounts of KI (30 and 100 μg) in the "reagent" lead to a noticeable decrease in the isotopic exchange efficiency, probably due to the isotopic dilution of iodine-131.

To study the methyliodide concentration effect in the gas stream and the gas flow rate on the isotopic exchange efficiency, a series of samples of WFA F20 labeled with iodine-131 without an isotope carrier was prepared. The drying time of the samples was 1.0 h at 100 °C. The air flow rate with CH$_3$I vapors through the column was 0.1–0.4 l/min; the column temperature was 120 °C; the methyliodide concentration in the gas stream was ~30–250 mg/l.

The maximum isotopic exchange efficiency per hour of testing was achieved at methyliodide concentration in the gas stream of 130–250 mg/l (Table 4). At low radioiodine concentrations (~30 mg/l), the exchange efficiency decreases abruptly. Reducing the phase contact time with the same methyliodide amount in the gas does not lead to a significant decrease in the isotopic exchange efficiency.

During 1 h of testing under the most favorable conditions (c = 130–250 mg/l; Q = 0.2 l/min), 85% of stable iodine exchange rate for radioactive isotope I-131 was achieved.

In the final series of experiments, the optimal column temperature during isotopic exchange was found out. The experimental conditions were as follows: the air flow rate with CH$_3$I vapor through the column was 0.2 l/min; the column temperature varied from 70 to 170 °C; the methyliodide concentration in the gas stream was ~55 mg/l. Carrying agent for the "reagent" − WFA F20.

The obtained data allowed us to establish that temperature change from 70 to 100 °C leads to significant increase in the isotopic exchange efficiency (Fig. 7). A further temperature increase up to

170 °C slightly affects it. In general, we can conclude that to achieve the maximum isotopic exchange efficiency (75–85%), it is necessary to heat the "reagent" up to 150–170 °C.

4. Conclusion

As a result of the experiments, the optimal isotopic exchange process parameters between the labeled I-131 "reagent" and the methyliodide that does not contain radioactive isotopes were selected. The non-porous material WFA F20 (white fused alumina), which has a relatively low hydraulic resistance, can serve as a material for "reagent" production of a labeled methyliodide vapor generator. It was found that porous inert carrying agents used in chromatography are less suitable due to their tendency to dust, as well as the need to observe the conditions for their preparation and control the humidity of the gas stream during isotopic exchange strictly.

The experiments made it possible to formulate a simple method for obtaining vapors of labeled I-131 methyliodide using a heterophase isotopic exchange.

"Reagent" for isotopic exchange is prepared on WFA F20 basis with a water-ethanol solution of Na^{131}I in a volume ratio of 2:5 by mixing in evaporating pan made of PTFE and dried for 1 h at a temperature of 100 °C. The isotopic exchange is carried out at the gas flow rate through the column with the "reagent" 0.1–0.2 l/min, which corresponds to the gas contact time with the carrier 5.1–2.6 s. The optimal methyliodide concentration range in the gas flow is 60–250 mg/l. The recommended temperature range of the "reagent" column is 150–170 °C. At the same time, the isotopic exchange efficiency reaches 85% in 1 h of testing.

As a result, the main data necessary for the organization process for obtaining gaseous methyliodide labeled with the isotope iodine-131 for testing the iodine filters at the nuclear power plant "in-situ" were obtained.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Table 4
The kinetic conditions effect on iodine isotopic exchange efficiency (carrying agent −WFA F20).

No	Q = 0.2 l/min		m(CH$_3$I) ≈ 1000 mg	
	c, mg/l	E, %	Q, l/min	E, %
1	30	55 ± 2	0.1	77 ± 3
2	55	77 ± 3	0.2	77 ± 3
3	130	85 ± 3	0.4	70 ± 3
4	250	86 ± 3	—	—

References

[1] Brian J. Riley, et al., Materials and processes for the effective capture and immobilization of radioiodine: a review, J. Nucl. Mater. 470 (2016) 307—326, https://doi.org/10.1016/j.jnucmat.2015.11.038.

[2] Joffrey Huve, et al., Porous sorbents for the capture of radioactive iodine compounds: a review, RSC Adv. 8 (2018) 29248—29273, https://doi.org/10.1039/C8RA04775H.

[3] ISO 18417 Iodine Charcoal Sorbents for Nuclear Facilities — Method for Defining Sorption Capacity Index, 2017.

[4] E.P. Magomedbekov, A.V. Obruchikov, A method for properties evaluation of activated charcoal sorbents in iodine capture under dynamic conditions, Nucl. Eng. Technol. 51 (2019) 641—645, https://doi.org/10.1016/j.net.2018.10.018.

[5] H. Deuber, Investigations on the retention of elemental radioiodine by activated carbons at high temperatures, Nucl. Technol. 72 (1986) 44—48, https://doi.org/10.13182/NT86-A33751.

[6] H. Deuber, J.G. Wilhelm, Retention of elemental radioiodine by deep bed carbon filters under accident conditions, in: 17th DOE Nuclear Air Cleaning Conference, Denver, CO, USA, 1 Aug, 1982.

[7] N.I. Ampelogova, et al., Carbon-fiber adsorbent materials for removing radioactive iodine from gases, At. Energy. 92 (2002) 336—340, https://doi.org/10.1023/A:1016558127710.

[8] Jungsook Clara Wren, et al., Methyl iodide trapping efficiency of aged charcoal samples from bruce-A emergency filtered air discharge systems, Nucl. Technol. 125 (1999) 28—39, https://doi.org/10.13182/NT99-A2930.

[9] C.M. González-García, J.F. González, S. Román, Removal efficiency of radioactive methyl iodide on TEDA-impregnated activated carbons, Fuel Process. Technol. 92 (2011) 247—252, https://doi.org/10.1016/j.fuproc.2010.04.014.

[10] International Atomic Energy Agency, Testing and Monitoring of Off-Gas Cleanup Systems at Nuclear Facilities, Technical Reports Series No. 243, IAEA, Vienna, 1984.

[11] International Atomic Energy Agency, Comparison of High Efficiency Particulate Filter Testing Methods, IAEA-TECDOC-355, Vienna, 1985.

[12] S.A. Kulyukhin, Fundamental and applied aspects of the chemistry of radioactive iodine in gas and aqueous media, Russ. Chem. Rev. 81 (2012) 960—982, https://doi.org/10.1070/RC2012v081n10ABEH004269.

[13] Ki Bang Sung, et al., Method and device for synthesizing radioactive methyl iodide tracer, 8 Apr. 2014. United States Patent No. 8,692,039.

[14] S.A. Mamedov, et al., Method of Obtaining Methyl Iodide, Soviet Union Patent No. 611900, 25 Jun. 1978.

[15] A.V. Obruchikov, S.M. Lebedev, Study on adsorption removal of radioactive methyl iodide by modified Busofit carbon fibers, Inorg. Mater. Appl. Res. 3 (2012) 398—400, https://doi.org/10.1134/S2075113312050127.

[16] A.V. Obruchikov, et al., Method for obtaining radioactive methyliodide vapors under dynamic conditions, J. Radioanal. Nucl. Chem. 326 (2020) 1895—1900, https://doi.org/10.1007/s10967-020-07434-9.