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## **Title page**

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# **Preparation of a radon-free thoron source for a thoron calibration chamber**

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## **Abstract**

During long-term radon/thoron surveys, solid-state nuclear track detectors (SSNTDs) are commonly used. For the application of these integral devices, it is important to solve the commensurate calibration. At the calibration process, radon can be interfering with thoron; therefore, radon-free thoron atmosphere is required for the accurate calibration. In this study, radon-free thoron source with a high emanation capability was prepared by chemical separation of Ac-228. Based on the results of this and the previously performed experiments, a method combines precipitation with  $\text{FeCl}_3$  and embedding into ceramic matrix containing low feldspar content and heat treatment on 200 °C has been proposed.

## **Keywords**

thoron source; calibration; Ac-228 separation

## **Introduction**

Previously performed surveys have indicated that the accurate determination of thoron concentration is important for several reasons [1-6]. During protracted campaigns, the application of active measuring devices is difficult or not possible. In response, integral devices, such as SSNTDs, are commonly used [7-11]. For the application of track detectors, a well-defined calibration method is needed. As technical difficulties

concerning measurement occur due to the short half-life, the development of a calibration chamber and a validation process is complicated. Recently, a thoron calibration chamber has been developed at the Institute of Radiochemistry and Radioecology at the University of Pannonia; however, examinations performed until now have shown that its development is necessary for a more accurate operation [12].

Various techniques can be found in the literature for thoron source preparation [13-15]. In one of the latest works in this field made by Cardellini et al., natural thorium in equilibrium state was used as thoron source. In this case, the source contained thoron and radon gas as well; therefore, different measurement techniques were applied combined with Monte Carlo simulation for radon/thoron measurements. In this research, it was found that the emanation of the source strongly decreased below 30 % relative humidity.

At the Institute of Radiochemistry and Radioecology, three types of ceramic sources made by heat treatment of ceramic spheres containing natural thorium nitrate were prepared [16]; however, for the accurate operation of the calibration chamber the optimization of the source's properties was needed. For this purpose, 27 thoron sources were made with the application of ceramics with different chemical composition, thorium nitrate content and firing temperature [17]. The aim of that study was to describe the function between the morphological properties of the source's material and the thoron flux that is produced. Based on the results, it was found that an increase in firing temperature causes a decrease in emanation for all cases; therefore, heat treatment at lower temperatures is advantageous. Furthermore, higher emanation rates are observed in cases of ceramics with lower feldspar content. The effect of the relevant environmental parameters (temperature, humidity) on the emanation was also examined. No correlation was found between the humidity and the emanation, probably due to morphological properties of the applied ceramic material.

However, in the above mentioned experiments, natural thorium nitrate was used. A problem with natural thorium nitrate-based sources is that the chemical also contains Th-230, from which Rn-222 is formed. Different studies showed that the presence of radon increases the detection limit of thoron measurements, since the background is increased

[18, 19]; therefore, the elimination of radon from thoron source is proposed. This can be solved by the separation of an element of the Th-232 decay series by a chemical separation method, along with the preparation of an isotope generator from it. With this technique a radon-free thoron source can be prepared.

The first step is to decide which element would be the most appropriate for separation. Looking at the decay series, it seems obvious that the separation of radium is not expedient, since the source will contain the disturbing Ra-226 isotope later on. For the same reason, the separation of Th-228 is also not directly possible. In the Th-232 series, the only element that is not present in the U-238 series is the actinium. Based on this, the task involves the chemical separation of actinium and the preparation of the source from it.

Several methods were found in the literature, which can facilitate the selective separation of actinium. The following techniques were chosen for experimental applications:

1. Separation by DIPHONIX resin and HEDPA solution [20];
2. Bonding radium and actinium on DOWEX resin, eluting actinium [21]:
  - a. Application of  $\text{HClO}_4$  in the second step;
  - b. Application of  $\text{HNO}_3$  in the second step;
  - c. Application of  $\text{HNO}_3$  and  $\text{HCl}$  in the second step;
3. Separation of actinium by precipitation with  $\text{FeCl}_3$  [22].

In this work the above mentioned actinium separation techniques have been examined and compared, in focus of thoron source preparation. Based on the results, the steps of an exact method are given.

## **Experimental**

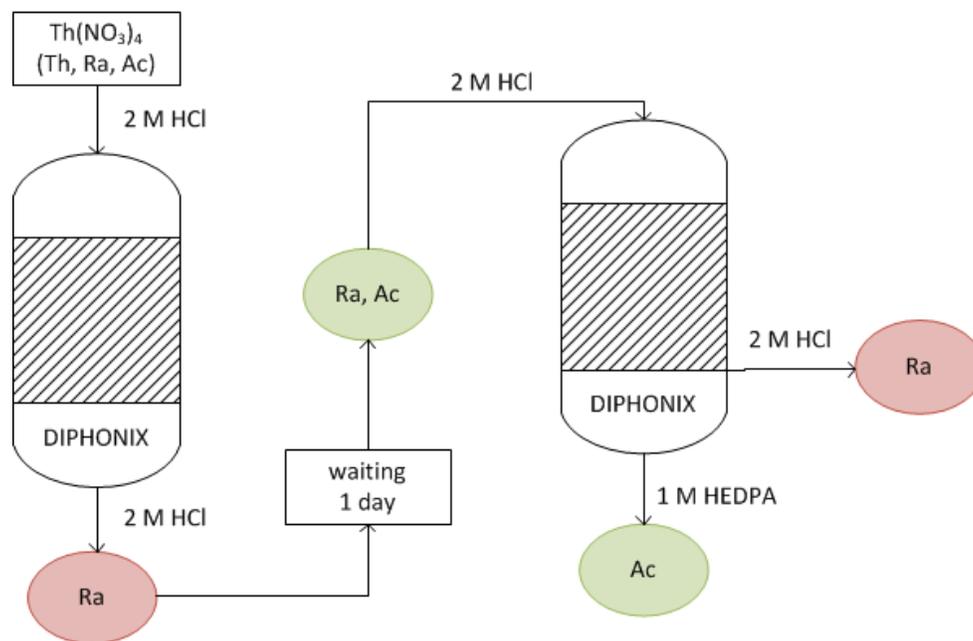
Stock solution was made from solid natural thorium nitrate in equilibrium state, with 1 mL of Ba-133 tracer added in all cases. In the first step of the methods, the separation of radium occurs, while the generated actinium is separated from radium in the second step, which takes about a few minutes only. Due to this, the Ac-228 loss during the separation is insignificant. (The half-life of Ac-228 is 6.13 hours.) The Ra-228 solution can be used as an isotope generator for further separations.

A gamma spectrometer with an HPGe detector was applied to follow the process. Taking advantage of the similarity in the chemical behaviour between barium and radium, the intensity of the 356 keV energy gamma line of Ba-133 is suitable when determining the radium activity of the sample, as well as the efficiency of the separation.

### **1. Separation by DIPHONIX resin and HEDPA solution**

100 mL of a 2 M HCl-based stock solution was prepared, from which 10 mL was added to a column with 0.7 cm diameter and 2.5 cm height, filled with 100-200 mesh DIPHONIX resin, preconditioned with 10 mL of a 2 M HCl. The radium and the barium were eluted with 15 mL of a 2 M HCl. After one day Ac-228 was formed from Ra-228 and the solution was filled to another column, then the radium and the barium were eluted with 15 mL of a 2 M HCl. The actinium remained on the resin, from which it was eluted with 5 mL of a 1 M 1-hydroxyethan-1,1-diphosphate (HEDPA) solution. The method is presented on Fig. 1.

The separation of Ac-228 according to this method was not efficient (see “Results and discussion” section below).



**Fig. 1** Separation by DIPHONIX resin and HEDPA solution

## 2. Bonding radium and actinium on DOWEX resin, eluting actinium

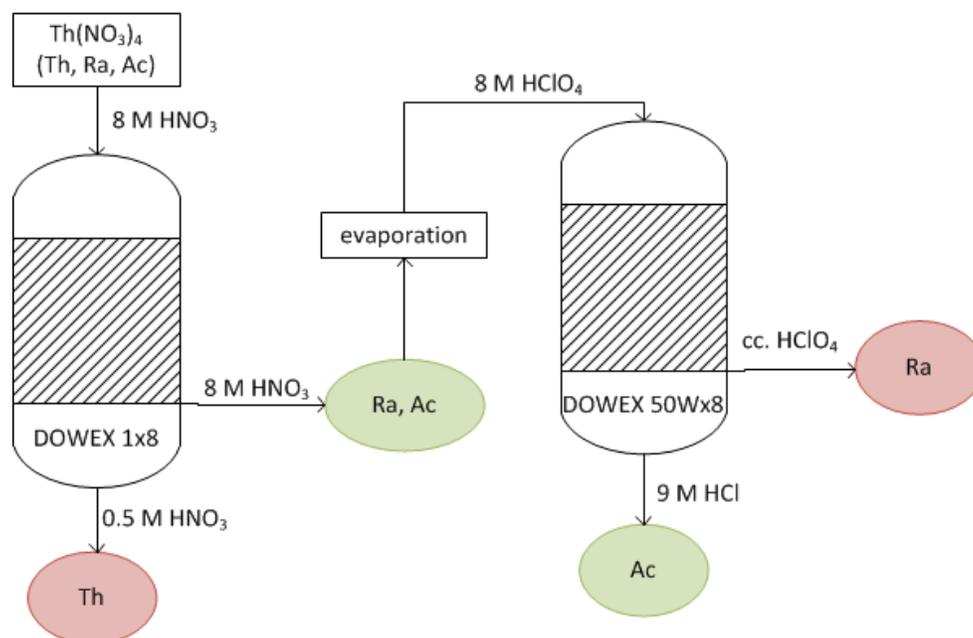
5 mL of a 8 M  $\text{HNO}_3$ -based stock solution was added to a column with 1 cm diameter and 5 cm height, filled with 200-400 mesh DOWEX 1x8 resin, preconditioned with 20 mL 8 M  $\text{HNO}_3$ . The radium (barium) and actinium were eluted with 20 mL of an 8 M  $\text{HNO}_3$  and the solution was evaporated to the point of dryness. After that, the cation exchange followed on a column with 0.7 cm diameter and 2.5 cm height, filled with 100-200 mesh DOWEX 50Wx8 resin. The cation exchange was carried out on three different ways described below.

The separation of  $\text{Ac-228}$  according to this method was not efficient (see “Results and discussion” section below).

### *Variant “A”: Application of $\text{HClO}_4$ in the second step*

The residue was dissolved in 5 mL of an 8 M  $\text{HClO}_4$  and added to the column, preconditioned with 15 mL of an 8 M  $\text{HClO}_4$ . The radium was eluted with 15 mL of cc.

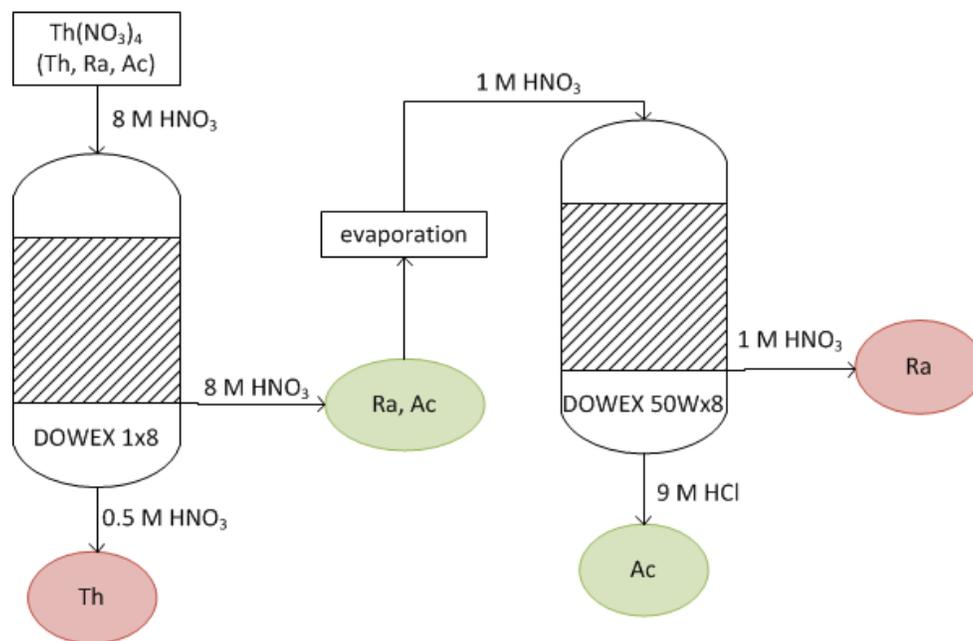
HClO<sub>4</sub> and the actinium was eluted with 15 mL of a 9 M HCl. The method is presented on Fig. 2.



**Fig. 2** Bonding radium and actinium on DOWEX resin, eluting actinium (variant “A”)

*Variant “B”: Application of HNO<sub>3</sub> in the second step*

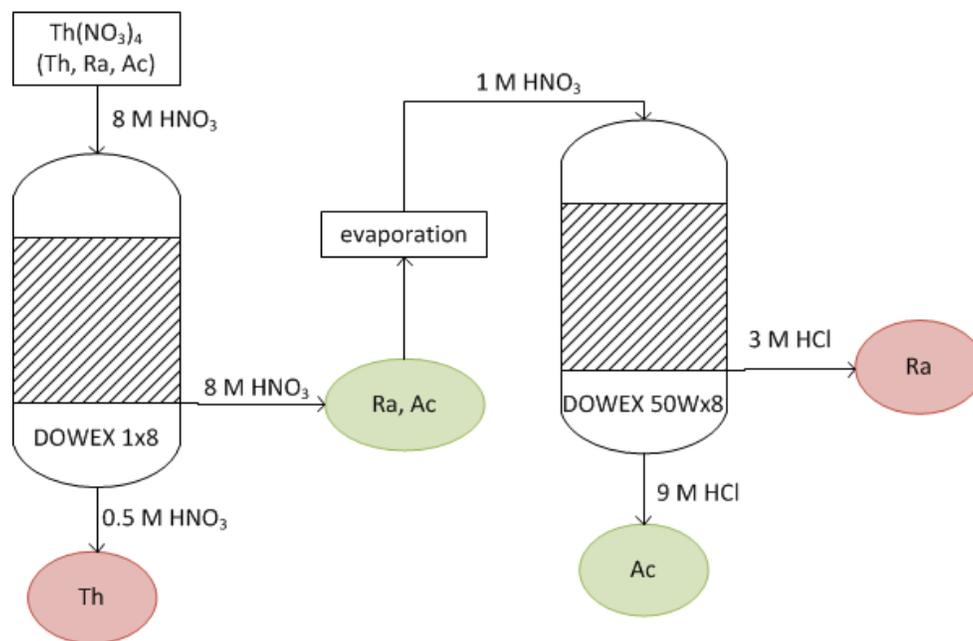
The residue was dissolved in 5 mL of a 1 M HNO<sub>3</sub> and added to the column, preconditioned with 15 mL of a 1 M HNO<sub>3</sub>. The radium was eluted with 15 mL of a 1 M HNO<sub>3</sub> and the actinium was eluted with 15 mL of a 9 M HCl. The method is presented on Fig. 3.



**Fig. 3** Bonding radium and actinium on DOWEX resin, eluting actinium (variant “B”)

*Variant “C”: Application of  $\text{HNO}_3$  and  $\text{HCl}$  in the second step*

The residue was dissolved in 5 mL of a 1 M  $\text{HNO}_3$  and added to the column, preconditioned with 15 mL of a 1 M  $\text{HNO}_3$ . The radium was eluted with 15 mL of a 3 M  $\text{HCl}$  and the actinium was eluted with 15 mL of a 9 M  $\text{HCl}$ . The method is presented on Fig. 4.

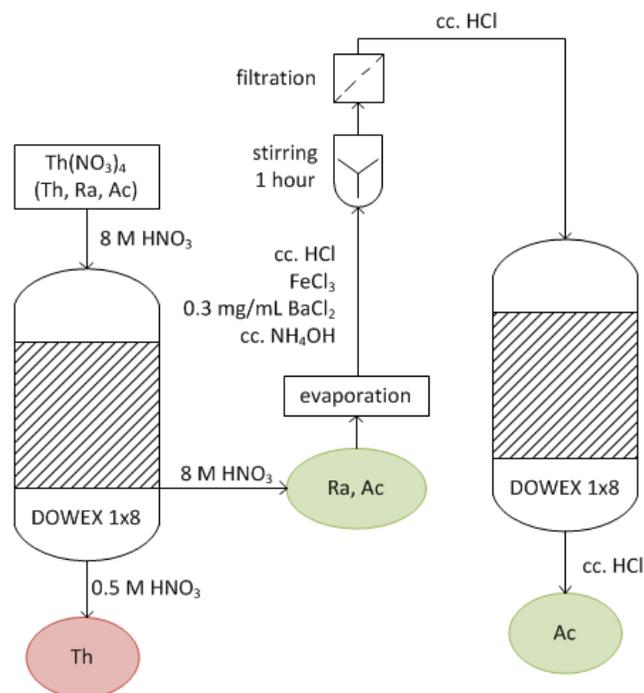


**Fig. 4** Bonding radium and actinium on DOWEX resin, eluting actinium (variant “C”)

### 3. Separation of actinium by precipitation with $\text{FeCl}_3$

The anion exchange step was carried out on DOWEX 1x8 resin according to Alhassanieh et al. as previously described [21]. The residue was dissolved in 5 mL of cc.  $\text{HCl}$ , then 1 mg of solid  $\text{FeCl}_3$ , 0.25 mL of a 0.3 mg/mL  $\text{BaCl}_2$  solution and 10 mL of cc.  $\text{NH}_4\text{OH}$  were added. The solution was stirred with a magnetic stirrer for one hour and filtered on a Millipore AA 0.8  $\mu\text{m}$  filter paper. The precipitate was dissolved with 5 mL of cc.  $\text{HCl}$  and it was cleaned with a DOWEX 1x8 resin. The actinium was eluted with cc.  $\text{HCl}$ . The method is presented on Fig. 5.

The separation of  $\text{Ac-228}$  according to this method was efficient (see “Results and discussion” section below).



**Fig. 5** Separation of actinium by precipitation with FeCl<sub>3</sub>

## Results and discussion

During the test involving different methods, the gamma spectra of solutions obtained from the separation steps were registered and compared to the gamma spectrum of the stock solution. Efficiency of the separation can be calculated from the intensity of the 338 keV gamma line of Ac-228 and the 356 keV gamma line of Ba-133 in the separated and stock solution (Eq. (1)). Efficiency of the detector can be neglected due to the proximity of energies.

$$\eta_{sep} = \frac{I_{Ac-228}^S / I_{Ba-133}^S - I_{Ac-228}^0 / I_{Ba-133}^0}{I_{Ac-228}^0 / I_{Ba-133}^0} \quad (1)$$

where  $\eta_{sep}$  is the efficiency of the separation,  $I_{Ac-228}^S$  is the intensity of the 338 keV gamma line of Ac-228 in the sample solution (after separation),  $I_{Ba-133}^S$  is the intensity of the 356 keV gamma line of Ba-133 in the sample solution (after separation),  $I_{Ac-228}^0$  is the intensity of the 338 keV gamma line of Ac-228 in the stock solution (before separation),

$I_{\text{Ba-133}}^0$  is the intensity of the 356 keV gamma line of Ba-133 in the stock solution (before separation).

### 1. Separation by DIPHONIX resin and HEDPA solution

Neither Ac-228, nor Ba-133 peaks was identified in the sample solution; therefore, the separation with this technique was unsuccessful. The separation efficiency could not be calculated.

### 2. Bonding radium and actinium on DOWEX resin, eluting actinium

Problems occurred during variant “A”, since the cc.  $\text{HClO}_4$  partially destroyed the resin; therefore, the separation was unsuccessful. In case of variant “B” the Ac-228 and Ba-133 gamma lines could be identified in the sample solution; however, based on the intensities, the amount of the actinium decreased; therefore the separation was unsuccessful. In case of variant “C”, the amount of the actinium only slightly increased, the separation efficiency is 2 %; therefore, the separation was unsuccessful.

### 3. Separation of actinium by precipitation with $\text{FeCl}_3$

In this case, the Ac-228 and Ba-133 gamma lines could be identified in the sample solution. Based on the intensities, the actinium content increased relatively largely, the efficiency of the separation is 74 %; therefore, the separation was successful.

### The proposed method

The results are summarized in Table 1.

**Table 1** Results of the tested separation methods

	$I_{\text{Ac-228}}$	$I_{\text{Ba-133}}$	$I_{\text{Ac-228}}/I_{\text{Ba-133}}$	Efficiency (%)
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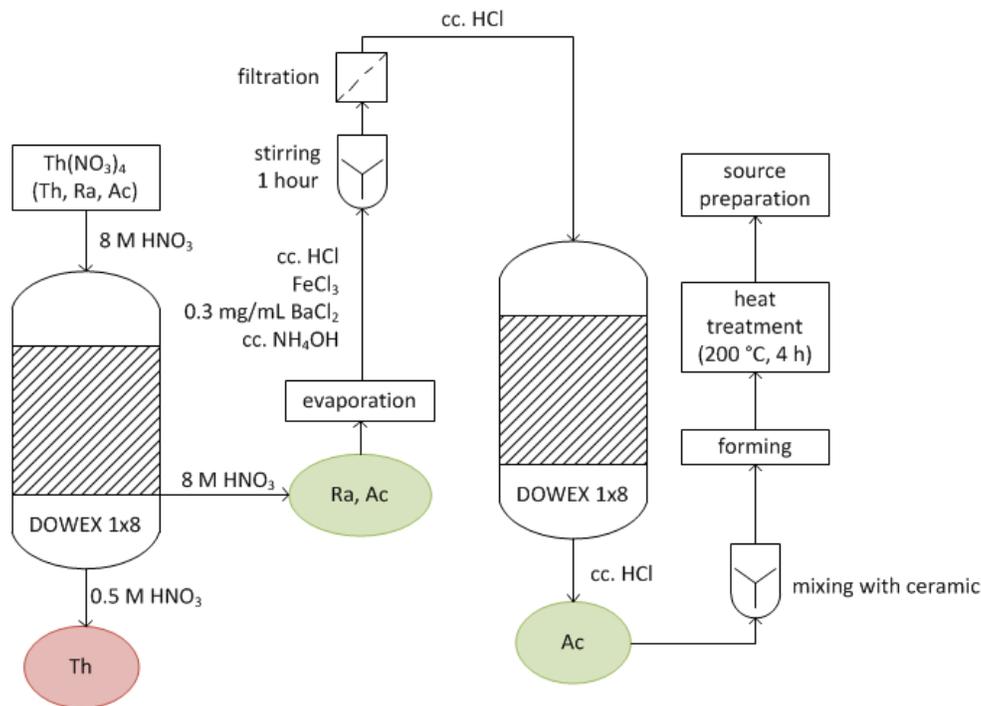
Stock solution	2258	2844	0.79	–
Method 1	–	–	–	–
Method 2 variant “A”	–	–	–	–
Method 2 variant “B”	152	215	0.71	–
Method 2 variant “C”	455	564	0.81	2
Method 3	90	65	1.38	74

Based on the results, the Ac-228 separation by precipitation with  $\text{FeCl}_3$  (method 3) is suitable for radon-free thoron source preparation. Considering the results of the previously performed experiments as well [17], ceramic sources made from “clean” Ac-228 (Ra-224) solution, which is produced by this technique, is proposed for source preparation. Different thoron concentrations are needed for calibration measurements; therefore, several sources with different Ra-224 content should be prepared. Three sources are proposed for calibration on three thoron levels. The steps of the method are as follows:

1. 100 mL of a 0.05 M stock solution is made from solid  $\text{Th}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$  on the basis of 8 M  $\text{HNO}_3$ .
2. The solution is added to an ion exchange column filled with 200-400 mesh DOWEX anion exchange resin preconditioned with 8 M  $\text{HNO}_3$  and washed with 400 mL of 8 M  $\text{HNO}_3$ . The eluate is evaporated to the point of dryness.
3. The residue is dissolved in 100 mL of concentrated HCl, then 20 mg of solid  $\text{FeCl}_3$ , 5 mL of a 0.3 mg/mL  $\text{BaCl}_2$  solution and 200 mL of cc.  $\text{NH}_4\text{OH}$  are added. The solution is mixed with a magnetic stirrer for one hour.
4. The solution is filtered through a Millipore AA 0.8  $\mu\text{m}$  filter and washed with distilled water. The filtered precipitate is dissolved in 10 mL of cc. HCl.
5. The solution is cleaned with a DOWEX 1x8 anion exchange resin. The actinium is washed with 100 mL of cc. HCl.

6. The solution containing actinium is diluted by two and five times the amount, such that three solutions are made with different actinium concentrations.
7. 40-40 mL of the three solutions is mixed with 250 g ceramic powder containing low feldspar content. Spheres with a 2 mm diameter are formed from the dollop.
8. Spheres are treated at 200 °C for four hours.
9. After heat treatment, the ceramic spheres are placed into a plastic cylinder bearing with valves.

The method is presented on Fig. 6.



**Fig. 6** Proposed method for preparation of radon-free thoron source

## Conclusions

During this work, various chemical separation techniques were tested to separate Ac-228 for thoron source preparation. Based on the results, precipitation by  $\text{FeCl}_3$  was found to

be the most efficient from the selected methods. As such, an isotope generator can be prepared by Ac-228 separated in this way, from which Ra-224 can be obtained daily. With this technique, radon-free thoron source can be prepared; however, a quite complicated separation process is needed. Based on the results of this and the previously performed experiments, a method combining precipitation with FeCl<sub>3</sub> and embedding into ceramic matrix containing low feldspar content and heat treatment on 200 °C is proposed.

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