A NEW STRONTIUM-82/RUBIDIUM-82 GENERATOR

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Due to similarity of rubidium and potassium cations, the radionuclide ^{82}Rb, a positron emitter, has been used in nuclear medicine to characterize myocardial perfusion with high sensitivity and specificity [1-3]. The advantage of ^{82}Rb positron emission tomography (PET) *vs.* classical SPECT with ^{201}Tl is the short half-life of ^{82}Rb ($T_{1/2}$=75 s) which allows one to scanning of the patients every 10 minutes and to reduce the exposure of patient to radiation. Additionally, ^{82}Rb is a generator produced from the longer lived parent radionuclide ^{82}Sr ($T_{1/2}$=25.55 days), which permits clinical PET studies also in hospitals which do not have expensive on-site cyclotrons. Numerous methods for manufacturing the ^{82}Sr/^{82}Rb generator have been already described [4,5]. All these procedures, however, suffer from various limitations, *e.g.* a complicated multi-step separation of ^{82}Sr from a rubidium target, insignificant radiation resistance of the organic extractans and ion exchange resins, *etc*. To avoid these disadvantages, we used for the separation an inorganic ion exchanger – cryptomelane MnO_2. Cryptomelane MnO_2 has a tunnel-framed structure with exchangeable alkali or alkali earth cations. The average tunnel diameter is 280 pm, therefore the sorbent is selective for the cations with crystal ionic radii of 130-150 pm, *e.g.* K^+, Rb^+, Ba^{2+} and Ra^{2+}. To find optimum conditions for Rb^+-Sr^{2+} separations, the distribution coefficients (K_d) of Rb^+ and Sr^{2+} on cryptomelane MnO_2 were determined as a function of HNO_3 concentration. The influence of the HNO_3 concentration on the K_d for Sr^{2+} and Rb^+ on cryptomelane MnO_2 is shown in Fig.1. It can be seen that K_d for Rb^+ is very high even at 1 M HNO_3. This confirms high affinity of
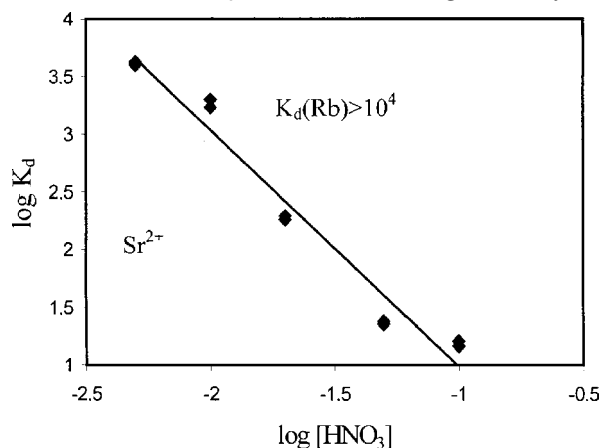
Table. Radionuclides detected in the ^{nat}RbCl target after irradiation with 48 MeV proton beam.

Radionuclide	$T_{1/2}$ [days]	Activity [MBq]	Nuclear reaction
^{82}Sr	25.5	6.49	^{85}Rb(p,4n)^{82}Sr
^{83}Sr	1.35	4.45	^{85}Rb(p,3n)^{83}Sr
^{85}Sr	64.8	8.55	^{85}Rb(p,n)^{85}Sr ^{87}Rb(p,3n)^{85}Sr
^{83}Rb	86.2	18.60	^{83}Sr(EC,β$^+$)→^{83}Rb
^{84}Rb	32.9	14.29	^{85}Rb(p,pn)^{84}Rb
^{86}Rb	18.7	18.66	^{85}Rb(n,γ)^{86}Rb

while for Sr^{2+} it is close to 1. This allows one to perform a simple and quantitative separation of ^{82}Sr from the irradiated rubidium target.

The isotope ^{82}Sr was produced on an AIC-144 cyclotron located at the Institute of Nuclear Physics (Kraków, Poland). In the pilot experiment, a target of 0.133 g RbCl of natural isotopic abundance (72.17% ^{85}Rb, 27.83% ^{87}Rb) was irradiated with an internal proton beam of 48 MeV, 0.5 μA, during 4 hours. At this energy, proton activation of the natural rubidium target leads to direct or indirect formation of ^{82,83,85}Sr and ^{82,83,84,86}Rb isotopes. These radionuclides detected by gamma spectrometry in the irradiated target are presented in Table.

After 8 days of waiting period, which is enough for the decay of ^{83}Sr, the RbCl target was dissolved in 0.5 M HNO_3 solution. The solution was then passed through a cryptomelane MnO_2 column (d=3 mm, h=30 mm). The inactive rubidium (target material) and ^{83,84,86}Rb were quantitatively adsorbed on cryptomelane MnO_2. The effluent from the column was alkalized by 1 M NaOH to pH=6-8. Afterward, the strontium radionuclides from the neutralized solution were loaded on the top of a SnO_2
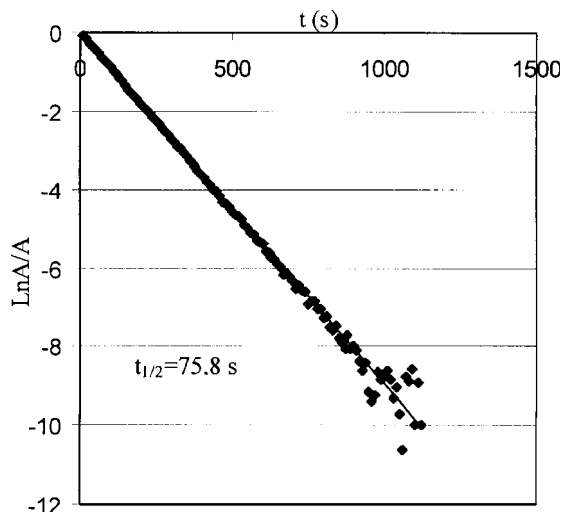

Fig.1. Dependence of Sr^{2+} and Rb^+ distribution coefficients on HNO_3 concentration.

cryptomelane MnO_2 for cations with ionic radii close to 150 pm. For Sr^{2+}, whose ionic radius is lower (118 pm), K_d decreases with increasing concentration of H^+ ions. For the efficient separation of the Rb^+-Sr^{2+} pair, 0.5 mol dm^{-3} HNO_3 was chosen as optimal solution. In this system, the K_d for Rb^+ on cryptomelane MnO_2 is greater than 10^4,

Fig.2. Decay curve of ^{82}Rb fraction.

aq. column. The inorganic ion exchanger – tin oxide was prepared by acidification of sodium stannate solution according to the procedure described in [6]. The ^{82}Rb formed from the decay of ^{82}Sr was eluted from the column by 0.9% NaCl (physiological saline). The elution was repeated every 10 minutes. The radionuclide purity of the effluent was measured by gamma spectrometry after the decay of ^{82}Rb. Additionally, we measured also the decay curves of the effluent fractions (Fig.2). The ^{82}Sr and ^{85}Sr breakthroughs measured by gamma spectrometry were lower than the established limits. After passing 1 liter of 0.9% NaCl through the column, no significant breakthrough was observed either by gamma spectrometry or by analyzing the decay

curves. The half-life of the eluted ^{82}Rb, determined from the decay curve measured for more than 6 expected half-lives, is identical with the literature value.

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APPROACHES TO ESTIMATE THE IONIC RADIUS OF Po²⁺

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Due to the relativistic stabilisation of $6p_{1/2}$ electrons, polonium – usually present in the 4+ oxidation state – can be reduced to the 2+ oxidation state. This cation has outside its filled [Xe]$4f^{14}5d^{10}$ electron shells – two electron pairs: $6s^2$ and $6p_{1/2}^2$. No information is available about the ionic radius of Po²⁺ and about the coordination number of Po²⁺ in aqueous solutions. The measurement of the ionic radius could be the first step towards a better understanding of the contribution of Po²⁺ electron orbitals to the chemical bonding.

The goal of our studies was to estimate the ionic radius of hydrated Po²⁺ from a comparison of the distribution coefficients (K_d) for Po²⁺ with K_d values of divalent metal cations of the second group of the Periodic Table (Ca²⁺, Sr²⁺ and Ba²⁺). This is based upon a well established linear correlation between ionic radii (known for Ca²⁺, Sr²⁺ and Ba²⁺) and the K_d values. This correlation is valid for ions with similar coordination numbers. K_d values can be obtained from the maxima of elution peaks in liquid chromatography experiments. Earlier a cation exchange study of Po⁴⁺ in acid solutions (HClO₄, H₂SO₄, H₃PO₄, CH₃COOH and oxalic acid) was reported [1].

We eluted polonium from the cation exchange resin Dowex 50W-X8, 200-400 mesh, with 3 M HClO₄ and 3.3 M CF₃SO₃H (triflic acid), both in SO₂ water solution. Perchloric and triflic acids were used because of their non-complexing properties for metal cations [2]. In order to reduce Po(IV) to Po(II), sulfur dioxide was applied. It is commonly known that sulfur dioxide and hydrazine reduce polonium to oxidation state +2 in acidic solution [3]. As we were using low-level radioactive tracer solutions of ^{210}Po, the measurement of α-activity from this samples was mandatory. Therefore, we were only able to use sulfur dioxide as the reducing agent. The use of hydrazine was impossible due to white salt residues which appeared during the evaporation step for α-sample preparation.

The used radiotracers ^{47}Ca (40 Bq/mg) and ^{85}Sr (3.3 kBq/mg) were produced at the Mainz TRIGA

reactor. While the calcium tracer had a very low specific activity, the commercially available ^{133}Ba was carrier free. The tracer solutions were prepared by dissolving the irradiated oxides in perchloric acid or trifluoromethanesulphonic acid and aliquots were loaded onto the column: 46 mm length and 3.2 mm inner diameter. Elutions were performed at a rate of about 3.3 ml min⁻¹.

From the maxima of the elution position in 3 M HClO₄, we determined K_d values equal to 2, 7 and 24 for ^{47}Ca²⁺, ^{85}Sr²⁺, and ^{133}Ba²⁺, respectively. The corresponding literature [4] values are 10.4, 13.4 and 25.1. Presumably, the lower K_d values for calcium and strontium in comparison with the literature values from [4] result from the use of relatively large amounts of carrier material in our experiment. It should also be noted here that our calcium and strontium elution curves were rather wide and exhibited considerable tailings. For the elution with 3.3 M CF₃SO₃H, the K_d values were 11 for strontium and 37 for barium.

Then we studied the behaviour of polonium during the elution using 3 M HClO₄ both with and without SO₂. The elution curves for both solutions were similar. Peaks were very broad with maxima appearing only after 65-75 ml giving incomprehensibly large K_d values (~450-550). As an additional surprise, we measured a large elution maximum at about 25 ml, corresponding to a K_d of ~150, with 3.3 M CF₃SO₃H in SO₂ water. One would not expect such a large, if any, difference in the elution of Po²⁺ with 3.3 M CF₃SO₃H and 3 M HClO₄.

Therefore, we interpret the large K_d values for polonium observed in both systems in terms of incomplete reduction of polonium to the +2 oxidation state by sulfur dioxide. The observation of the different elution position in the two acids can possibly be explained by the oxidizing properties of HClO₄. In the perchloric acid solution we most likely could not reduce Po(IV) to the lower oxidation state at all.

The next step in these experiments will be the application of hydrazine as a reductant when using