Investigation of the kinetic of In^{3+}- DOTA complexation by a γγ-perturbed angular correlation one detector method (1-PAC)

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To evaluate the capacity of the method of perturbed angular γ-γ-correlation measurements using one HPGe detector only (1-PAC) to study the kinetics of chemical reactions in solutions, the complex formation of In(III) with DOTA have been investigated.
The underlying physical phenomena of the PAC methods are (i) an angular correlation between two cascades γ-quanta in the decay of the probe-nucleus and (ii) the perturbation of this correlation caused by interaction of the nucleus with its environment (hyperfine interaction). The time-integrated angular correlation of cascade γ-rays is given by:

$$W(\theta,T)=1+A_{22}G_2(\infty)Q_2P_2(\cos(\theta))+.....$$

where A_{ii} are the angular correlation coefficients, $P_i(\cos\theta)$ are the Legendre polynomials, Q_i corresponds to a geometry coefficient that includes influence of finite sizes of both the detector and the sample and $G_i(\infty)$ are the time-integrated angular correlation perturbation factor. The relative probability to detect the cascade γ-rays γ_n, γ_m ($R_{\gamma n+\gamma m}$) at an angle θ, at the individual A_{ii}, $G_i(\infty)$ and Q_i values is equal to $W(\theta,\infty)$:

$$R_{\gamma n+\gamma m}={}^{\gamma n,\gamma m}W_{Aii,\ Gi,\ Qi}(\theta,\ \infty)$$

The possibility to use only one detector (1-PAC method) was described in detail elsewhere [1]. The characteristic parameter is the relative probability $R_{\gamma1+\gamma2}$ at an angle of 0°. Non-carrier-added ^{111}In ($T_{1/2}$ = 2.81 d) was purchased from Mallinckrodt in 0.1 M HCl stock solution. The specific activity of the solution was 370 MBq/ml.
The background chloride solution with an overall ionic strength μ = 0.1 and pH-value of 3.3(1) of the electrolytes media $Na^+/H^+/Cl^-$ were prepared using p.a. chemicals (Merck) and analytical grade water. The concentration of DOTA was 10^{-6} M.

1-PAC measurements were performed using polyethylene vials of 2 ml volume. The activity of the samples was 40-50 kBq. The volume of each sample was 0.5 ml.
It was shown elsewhere that the $R_{\gamma1+\gamma2}$ –value depends on the radionuclide chemical form and increases with its molecular weight [2]. The measured magnitudes for $In[H_2O]^{3+}$ and its complex with DOTA as In[DOTA] in chloride solution versus time are given in Figure 1 (see description). The difference of $R_{\gamma1+\gamma2}$ –values between these two indium formations is about 4%. Each measurement was performed for 4500 seconds with appropriation of the value to the half of this period.

The measured $R_{\gamma1+\gamma2}$ value is a weighted sum of individual values over all species of indium in the studied system. It allows to investigate the chemical equilibrea [3]. The transition of the radionuclide form from the partial hydrolysed indium to the DOTA-complex formation at room temperature is illustrated in Figure 2. The DOTA was added to the system after first measurement. The subsequent measurements at 4500 sec – intervals indicate an increase of $R_{\gamma1+\gamma2}$. The constant value of $R_{\gamma1+\gamma2}$ = 0.912(3), which represent the complete transfer of $In[H_2O]^{3+}$ to In[DOTA] is reached after eight hours.
The method allows to study the kinetics of some In^{3+} complexations. This scheme is limited by the velocity of the reaction. Decreasing the length of the measurement leads to an increasing of the statistic error. This fact makes this method suitable only for investigation of systems with sufficiently slow velocity of complexation.

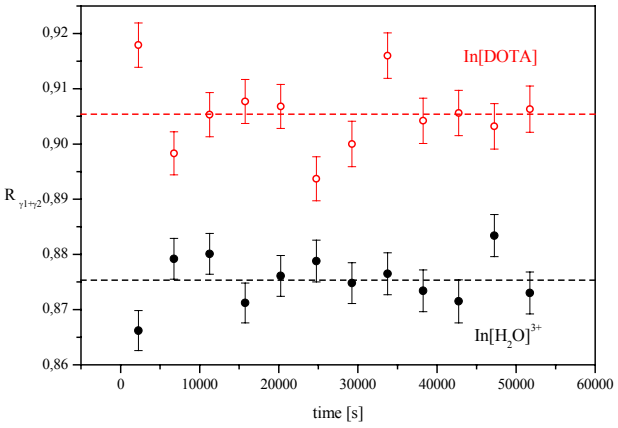

Figure 1. $R_{\gamma1+\gamma2}$ versus time: ^{111}In in NaCl and NaCl-DOTA systems - black and red points, respectively, pH = 3.3(1), μ = 0.1, room temperature (the $Na^+/H^+/Cl^-$/DOTA system was heated with radionuclide for 45 minutes at 100° C before the measurements). Dotted lines represent the means values.

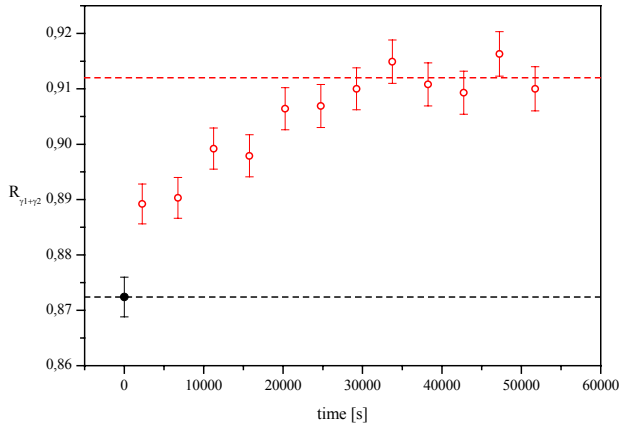

Figure 2. $R_{\gamma1+\gamma2}$ versus time: ^{111}In in NaCl-DOTA system, pH = 3.3(1), μ = 0.1, room temperature. The DOTA was added to the system after first measurement

[1] D. V. Filossofov et. al, Appl. Rad. and Isot. **57**, 437 (2002). [2] D. V. Filossofov et. al. P6-2001-112 JINR Dubna, 2001. [3] Zhernosekov et. al., this report.