

1-PAC: A one-detector gamma-gamma perturbed angular correlation technique for the determination of physical-chemical properties of radioelements: DTPA complex formations of ^{111}In

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Introduction: As shown in [1], the ratio of sum peaks (SP) intensities S compared to intensities of photopeak and roentgen emissions may be used to determine gamma-gamma perturbed angular correlations using one detector only. It is assumed that the relative probability of recording of cascade γ -rays $R_{\gamma_n+\gamma_m}$ in TSP at the individual values of A_{ii} , $\overline{G}_i(\infty)$ and Q_i is equal to TIAC $\overline{W}(\theta, \infty)$, where A_{ii} is the angular correlation coefficients depending on spins and multipolarities of transitions; $P_i(\cos\theta)$ are the Legendre polynomials; Q_i are the solid angle correction factors taking into account the detector and source finite sizes; and $\overline{G}_i(\infty)$ is the TIAC perturbation factor which yields information on hyperfine interactions. The following calculations were applied.

$$R_{\gamma_1+\gamma_2} = N_{K_{\alpha,\beta+\gamma_1}} \cdot \frac{S_{\gamma_1+\gamma_2} \cdot S_{K_{\alpha,\beta}}}{S_{\gamma_2} \cdot S_{\gamma_1+K_{\alpha,\beta}}} \text{ or } R_{\gamma_1+\gamma_2} = N_{K_{\alpha,\beta+\gamma_2}} \cdot \frac{S_{\gamma_1+\gamma_2} \cdot S_{K_{\alpha,\beta}}}{S_{\gamma_1} \cdot S_{\gamma_2+K_{\alpha,\beta}}}$$

with $N_{K_{\alpha,\beta+\gamma_1}} = 0.9176$ and $N_{K_{\alpha,\beta+\gamma_2}} = 0.9507$.

The first observations of the sum peak intensity change due to chemical environment was reported for ^{181}Hf compounds by De Bruin et al [2] and for ^{111}In compounds by Yoshihara et al [3,4]. However, proposed methods had not received practical applications. In the present work it is proposed to utilize the SP in the γ -spectrum from the radionuclide ^{111}In obtained with one detector to define the physico-chemical state of the complex formation of $\text{In}^{(III)}$ with DTPA.

Experiments: Measurements have been carried out with a coaxial HPGe detector of a volume of 200 cm^3 . The radioactivity of the samples amounted to $\approx 40 \text{ kBq}$ resulting in a count rate of ≈ 8000 pulses/s at the selected distance of 37 mm from the surface of the detector. Within the time of 30 min of registration, the events accumulated in TSP were in the order of $\sim 10^5$.

No-carrier-added ^{111}In was purchased from Amersham. Samples were prepared from high-grade pure chemicals (HNO_3 , NaOH , NaNO_3 , $\text{In}(\text{NO}_3)_3$, DTPA, deionised water). Carrier concentrations of 10^{-5} M for In were added to the samples. DTPA was added in concentration of $1.3 \cdot 10^{-5} \text{ M}$, the pH ranging from 1 to 13.8. The ionic strength was kept constant ($\mu=0.1$), except for measurements at $\text{pH}=13.88$ and $\text{pH}=0.2$. The volume of the samples was $500 \mu\text{l}$ using polyethylene Eppendorf vials. The measurements were carried out at room temperature. The obtained data are summarized in Fig. 1.

In the absence of DTPA the shift corresponds to the hydrolysis equilibrium of indium [5]. The difference of $R_{\gamma_1+\gamma_2}$ values in the acidic and alkaline media is due to the differences of $\overline{G}_2(\infty)$ for the $[\text{In}(\text{H}_2\text{O})_6]^{3+}$ ("liquid" state, $\overline{G}_2(\infty)=1$) and $\text{In}(\text{OH})_{3(\text{solid})}$ ("solid" state, $\overline{G}_2(\infty)=0.2$).

In the presence of DTPA at $\text{pH}<1$ the DTPA ligand is almost completely protonated, i.e. the InDTPA complex cannot be formed and $R_{\gamma_1+\gamma_2}$ becomes close to that of the solutions without DTPA. The $R_{\gamma_1+\gamma_2}$ value is almost constant in solutions of $\text{pH} 4$ to 11 , explained by the fact that $\text{In}^{(III)}$ is forming complexes of the type InDTPA . This complex has a greater size compared to that of the In aqua-

complex $[\text{In}(\text{H}_2\text{O})_6]^{3+}$, therefore $\overline{G}_2(\infty)$ for the InDTPA complex is smaller ($R_{\gamma_1+\gamma_2}$ is greater) compared to the values of $[\text{In}(\text{H}_2\text{O})_6]^{3+}$. At $\text{pH}>10$ the InDTPA complex disappears in favour of the formation of the hydroxide $\text{In}(\text{OH})_3$. Consequently, $\overline{G}_2(\infty)$ starts to approach 0.2, i.e. $R_{\gamma_1+\gamma_2}$ increases. At $\text{pH}>12.5$ the dissolution of the precipitate is observed while formation of $\text{In}(\text{OH})_4^-$ and $\overline{G}_2(\infty)$ again becomes 1 with decreasing values of $R_{\gamma_1+\gamma_2}$.

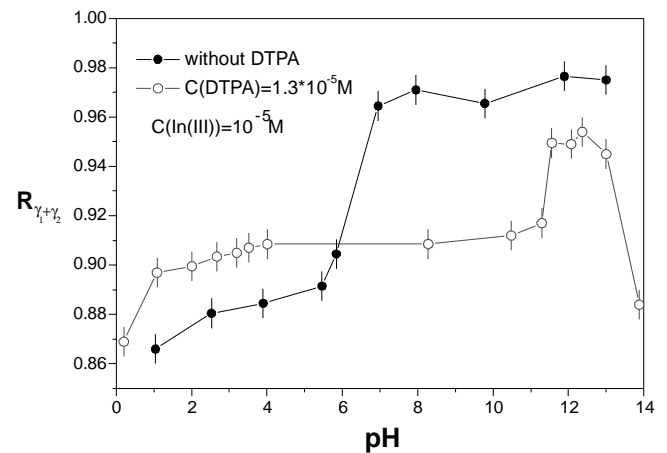


Fig. 1. The $R_{\gamma_1+\gamma_2(\text{exp})}$ dependencies for ^{111}In in aqueous solutions of different pH at as measured by means of 1-PAC method.

Conclusion: The 1-PAC method allows to study properties of the condensed matter at submicro-level concentration using a simple and widespread instrumentation. On the basis of defined $R_{\gamma_n+\gamma_m}$ values and of the dependence of perturbation of an angular correlation on an electronic constitution of matter, parameters of an elements chemical equilibrium can be determined. This allows to apply the 1-PAC method even for investigation of biological samples and objects "in vitro" and "in vivo".

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