



Speciation of U and Th in natural waters after specific extraction with ionic liquid and ICP-MS/Gamma spectrometry measurement

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Abstract

Uranium is a widespread natural radionuclide causing adverse physiological effects after entering the human body. In nature it can be found both in geological and aqueous environment. Because of its radiotoxicity the determination of its total concentration in natural water resources has been studied extensively.

Although the knowledge of uranium speciation in natural waters is essential for predicting the migration and health effects, this question has not been studied in detail. Furthermore, the daughter radioisotopes of ²³⁸U - e.g. ²³⁴Th, have very different environmental migration properties which needs to be considered.

The chemistry of U and Th in natural waters can be very complicated and is mainly controlled by pH, redox potential, and type of available complexing agents, such as carbonates, phosphates, and sulfates, etc.

Therefore, the aim of this research is to study the formation of different U and Th chemical species in water samples in dependence on pH, the presence of complexing agents and/or buffer solution. Applying HYDRA calculation software possible chemical species of the two radionuclides in accordance to experimental conditions were generated.

The obtained theoretical models were used as a basis for optimization and development of an analytical procedure for extraction of specific chemical species of U and Th with the ionic liquids (IL) 1-methyl-3-octylimidazolium saccharinate from water solutions. After quantitative analysis with ICP-MS/Gamma spectrometry measurements, the extraction efficiency was determined and assumptions about the mechanisms of exchange of specific species under varying experimental conditions have been made.

Results and Discussion

For the experiments liquid-liquid extractions were performed with the IL 1-methyl-3-octylimidazolium saccharinate as an organic phase and standard solutions of ^{238}U and ^{234}Th , mixed with universal buffer solution (Na_2HPO_3 , H_3BO_3 , citric acid, NaOH , HCl) and/or NaHCO_3 ($C=0.385\text{ M}$), as an aqueous phase. The selected extraction time was 1 hour, after which the samples were centrifuged for 3 minutes at 3000 rpm. At the end, the two phases were gently separated and aliquote samples (100 μl) were taken for ICP-MS and GAMMA-Spectrometry analysis.

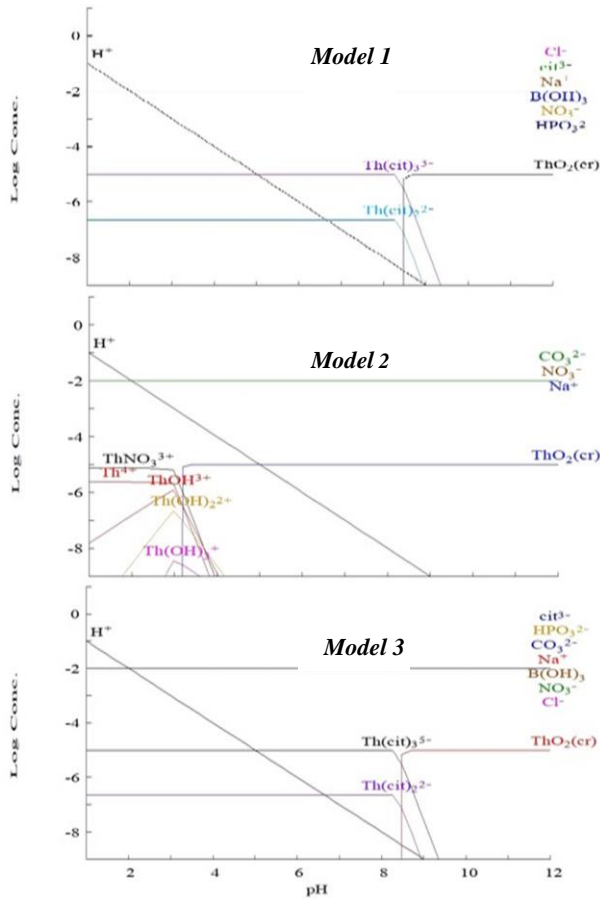


Figure 1. HYDRA-diagrams showing the chemical species of ^{234}Th appearing in the presence of a universal buffer solution (model 1), NaHCO_3 (model 2) and a combination of both (model 3)

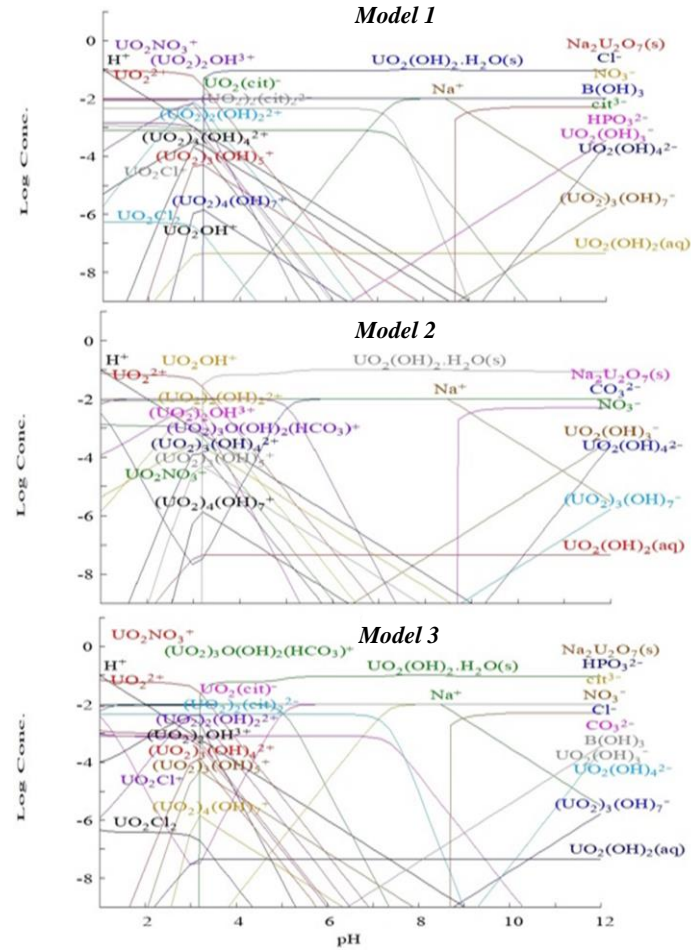


Figure 2. HYDRA-diagrams showing the chemical species of ^{238}U appearing in the presence of a universal buffer solution (model 1), NaHCO_3 (model 2) and a combination of both (model 3)

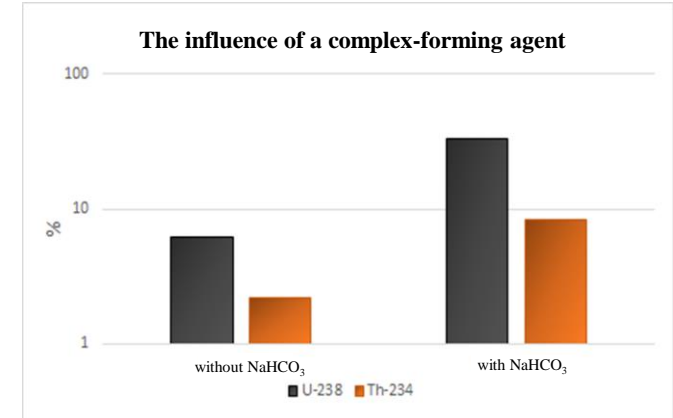


Figure 3. Extraction efficiency [E%] of ^{238}U u ^{234}Th in the presence of a universal buffer solution with and without NaHCO_3 .

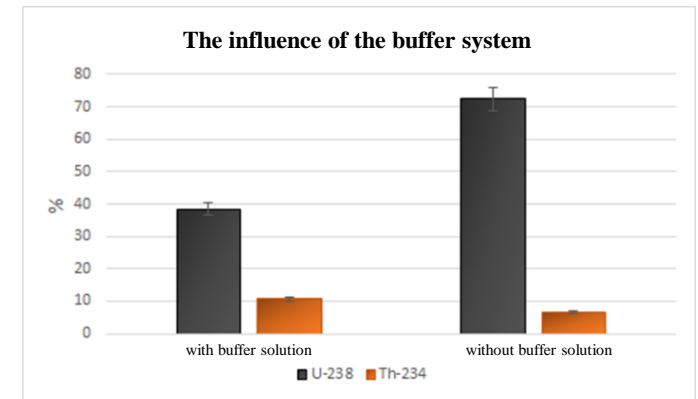


Figure 4. Extraction efficiency [E%] of ^{238}U u ^{234}Th in the presence of NaHCO_3 with and without a universal buffer solution.

Conclusions

After performing series of experiments, the following conclusions were made:

- NaHCO_3 increases the extraction efficiency values of ^{238}U up to $72,24 \pm 1,13$ % because of the formation of the complex ion - $(\text{UO}_2)_3\text{O}(\text{OH})_2(\text{HCO}_3)^+$, while $(\text{UO}_2)(\text{cit})^-$, $(\text{UO}_2)_2(\text{cit})_2^{3-}$, UO_2Cl decrease E % of U to $13,24 \pm 1,2\%$. This results lead to the conclusion that ^{238}U is included in cation exchange with the used ionic liquid.
- NaHCO_3 , hydroxy (ThOH^{3+} , $\text{Th}(\text{OH})_2^{2+}$, $\text{Th}(\text{OH})_3^{3+}$) or nitric cations (ThNO_3^{3+}) do not change the extraction efficiency of Th. The citric complex anions ($\text{Th}(\text{cit})_3^{5-}$, $\text{Th}(\text{cit})_2^{2-}$) however increase E% of ^{234}Th , which shows a big possibility for Th to take part in anion exchange mechanism with 1-methyl-3-octylimidazolium saccharinate
- The highest separation factor (SF) between the two radioisotopes ^{238}U and ^{234}Th equals to 12 and is reached after providing the following conditions: ratio between IL : aqueous phase = 1 : 3; pH = 3; T = 35°; and in the presence of NaHCO_3 .

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