Chemical studies on separation and determination of thorium element and its application on differant rock samples

Mohamed Abdullah Sedik Elsayed

This thesis is mainly concerned with studies related to the extraction and determination of thorium from its standard solution to obtain the best factors controlling the extraction process. The second is concerned with the application of the obtained parameters on certified reference samples and geologic samples collected from South Eastern Desert, Egypt.This work carried out is given in three main chapters:Chapter I: The introduction includes the main aspects related to chemistry of thorium, nature, discovery and origin of name, methods of thorium separation, factors controlling thorium extraction, methods for thorium determination. It includes also a reasented scientific literature for these aspects.Chapter II: The experimental, contains the different chemicals and reagents used in this study as well as the methods utilized for extraction and determination of thorium. It includes also the experimental techniques used during this work and the methods of preparation of the selected extractant used.Chapter III: The results and discussion, is directed into two parts, the first part covers the extraction of thorium element from its mineral solutions and study the different variables affecting the extraction and determination processes. The second part applies the obtained parameters affecting extraction and determination of thorium in both certain certified samples and geologic samples; collected from South Eastern Desert, Egypt. Also thorium was separated in a laboratory scale from a representative sample of the geologic materials comprised six samples (1M-2M) in a pure state as thorium oxide.Different solvents include: benzene, carbon tetrachloride, chloroform, cyclohexane, kerosene, toluene, and o-xylene, were used as diluents for preparing certain concentrations of the extractant TOPO. It was found that cyclohexane and toluene are the best diluents ones, where the extraction of thorium gave its high efficiency (99.99%), but in the differentiation between both solvents it was found that cyclohexane is the best one for preparing the extractant solution due to its lower dielectric constant and also to its availability.The effect of aqueous phase to organic phase TOPO ratio (A/O) was studied using different volumes of the organic extractant to reach the maximum extraction percent. It was found that, the best aqueous to organic phase ratio is 1:2 (A/O).The effect of extractant concentration was studied using different concentrations of the organic extractant (0.02, 0.04, 0.06, 0.08, 1, and 2M). It was found that the best extraction concentration is from 0.08 to 2M so 0.08M was

selected for the purpose which gave the best extraction efficiency (99.9%). It was found that, 0.08M TOPO in cyclohexane with 1:2 aqueous to organic phase ratio gave 99.99% of thorium extraction per one cycle.The effect of temperature was studied at different temperatures from 22 to 100°C under fixed conditions of the other parameter. It was found that the ambient laboratory temperature 22±1°C is the best temperature degree which gave 99.99% of thorium extraction per one cycle.The effect of pH was studied by varying the pH values from 1 to 10. It was found that with the increase in pH values, the thorium extraction decreases. The best thorium extraction (99.99%) was reached at pH 1. This pH value was chosen as the best value for the pH.The effect of shaking time was studied on fixing the other controlling parameters. The time periods applied during the experiments were 1 to 10min. The thorium extraction was evaluated at each time period of shaking. It was found that, the shaking time required to produce a thorium extraction of 99.99% is from 4 to 10min. Therefore, the best time of shaking was chosen 4min which produced the maximum 99.99% of thorium extraction.Different stripping agents were tried for back extraction of thorium from the organic phase. This was conducted using the stripping agents with the different aqueous/organic phase ratio: 4/1, 3/1, 2/1 and 1/1. Certain solutions of: hydrochloric, sulfuric and nitric acid with different molarities as well as water with different pH values were used as stripping agents. The maximum stripping values of thorium were 95.16 for HNO_3, 94.91 for HCl, 99.82 for H_2SO_4, and 96.39 for H_2O, respectively. So, sulfuric acid of 2M was chosen as the best for back extraction of thorium.Many interfering ions affect the extraction of thorium by enhancing or decreasing the extraction efficiency. So the extraction of thorium was performed at first without the presence of any interfering ions to observe any changes which might be occurred by interfering ions. Different concentrations from 10 to 100 ppm for the cations (Si^{4+}, Al^{3+}, Fe^{3+}, Na^{+}, K^{+}, Ca^{2+}, Mg^{2+}, and Ti^{4+}) were prepared.It was found that most cations do not interfere with the extraction process by the extractant TOPO, while the trace elements like U^{6+}, Zr^{4+}, Co^{2+}, and Ni^{2+} cause the interferences. In order to reduce the effect of interfering ions some masking agents: oxalic and citric acids as well as sodium potassium tartarate, potassium cyanide and meso tartaric acid were used to inhibit the effect of these interfering ions. The preparation of masking agents was done by taking weights ranged from 5 to 10% of the material that acts as a masking agent where 3 ml were added in each sample. The obtained results showed that meso-tartaric acid is the best one for the extraction when compared to the other masking agents used.Several methods for digestion of the samples were used to facilitate the analysis and choose the best one which reduces the effect of interfering ions that affect thorium extraction and determination: complete attack, nitric acid, mixture of nitric and hydrofluoric acids and the proposed procedure (0.2g of sample was mixed with 20 ml HF, evaporated till dryness, diluted with 15 ml HF (1:1) was then filtrated and treated the precipitate with 10 ml conc. $HClO_4$ and 5 ml conc. HNO_3 and heated till dryness. 15 ml 1:1 HCl was added to the residue and completed to the required volume). The data obtained showed that the proposed procedure is the best one used for digestion not only for removing the effect of most of interfering ions but also it gave the maximum extraction efficiency of thorium (99%).The proposed method of

digestion was applied for both certified reference samples and geologic samples; collected from South Eastern Desert, Egypt, Then, the obtained controlling factors affecting extraction and determination of thorium were applied. These factors are, 0.08M TOPO in cyclohexane, pH 1 of aqueous solution, 3 ml of 5% meso tartaric acid as a masking agent, 1:2 aqueous/organic phase ratio, shaking time 4 min. at 22± 1°C. 2M H_2SO_4 was used for stripping the eluted solution with 4:1 aqueous/organic phase ratio, shaking time 4min. at 22± 1°C.In order to separate thorium from the representative sample comprised from six samples (1M to 6M), three steps were carried out. These steps are leaching, extraction & stripping and precipitation.The XRD and scan electron microscope examination were used to confirm that the final product is ThO_2Statistical calculations indicated that the error percent in certified reference samples and geologic samples ranges from 0.084 to 1.195%. The accuracy (Δ) of certified reference samples and geologic samples are ranges between ± 0.121 and ± 1.563, this mean that the error percent and accuracy values is less than ± 2, which indicates high accuracy and precision for the method