

Application of Electrochemically Synthesized Ferrates (VI) for the Removal of Th(IV) From Natural Water Samples¹

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Received December 17, 2015

Revised April 24, 2018

Accepted December 25, 2018

Abstract—The efficiency of the application of electrochemically generated Na₂FeO₄, for the purpose of the elimination of Th(IV) ions from water samples as coagulating agent was investigated. Th is a radioactive element often used as a fuel for nuclear reactors. The continuous exposure to Th(IV) may cause cancer of the pancreas, bone or lung. Analyzed natural water samples spiked with Th(IV) were treated with solution of ferrates (VI) under recommended conditions of electrochemically synthesized ferrates solution and Th(IV) was quantified by established kinetic method. Removal of Th(IV) ions by ferrates (VI) was successfully confirmed by comparison of the concentration of Th(IV) before and after ferrates (VI) treatment of spiked analyzed water samples. A simple kinetic-spectrophotometric method was successfully applied to determine Th(IV) concentration, indicating the decrease in the concentration of Th(IV) in water samples applying ferrate (VI).

DOI: 10.3103/S1063455X19020061

Keywords: Th(IV), ferrates (VI), kinetic method, natural waters.

INTRODUCTION

Th together with the other long-living nuclides such as ⁴⁰K, ¹⁸⁷Re, ²²²Rn, ²³⁵U, ²³⁸U, and its products such as ²²⁶Ra, ¹⁷⁶Lu, remain present in nature for billions of years. The development of new methods and application of tandem-techniques are topics in numerous scientific papers because of the application of Th as a nuclear fuel, and from the point of its environmental impact as a chemical and radiological contaminant in different samples. Nuclear accidents have also released a large amount of radionuclides into the environment. Many of radioactive elements are found in the Earth's crust, sediments, minerals, rocks, and can be found dissolved in water or even in the air. The concentration of radionuclides in natural water varies and depends on the concentration of the minerals and rocks in the Earth's crust [1]. The appearance of radionuclides in nature is the result of their crystal-chemical and physico-chemical properties. Physico-chemical properties of the isotope of heavy elements are slightly different and become insignificant for lead, Th and uranium. High concentrations of radionuclides are harmful to nature and humans. For the radiation protection purpose, the level of these radionuclides in various environmental and biological samples needs to be determined. Th(IV) ion is extremely mobile and once entered living bodies will provoke inner irradiation (due to γ -active decay products). The continuous exposure to Th may cause an increased chance of developing cancer of the pancreas, lung or bones, and changes in genetic material of body cells. Recently, many sensitive and simple, low-cost spectrophotometric methods for the determination of Th have been published [2–9] and kinetic-spectrophotometric determination of Th(IV) was also reported [10]. Frequently used techniques for the determination of radionuclides are gamma and alpha spectrometry with sufficiently low limit of detection, in environmental samples with fast sample preparation and good accuracy [11]. Nowadays, mass-spectrometry as fast, sensitive

¹ The text was submitted by the authors in English.

method is the most frequently used in trace element analysis [12, 13]. Generally, trace analysis is more likely to be contaminated by interfering species from reagents or labware and these disadvantages are overcome by improved quadrupole mass spectrometers [14]. Kinetic method applied in this study is less expensive, sensitive and accurate method for the determination of Th.

This method was based on catalytic effect of Th(IV) ions on applied indicator reaction oxidation of 4-hydroxycoumarin by KMnO_4 , and allows determination of its concentration [10], before and after treatment with ferrate(VI) solution, in order to remove Th(IV) by coagulation effect of ferrate(VI).

Ferrate(VI) is termed a “Green-Chemical” because of its unique multifunctional properties related to “green nature”. It is widely used as one of the chemicals of the next generation for the remediation of the aquatic environment [15]. Because of its strong oxidizing capacity, ferrate(VI) is employed as potential chemical for the degradation of numerous inorganic, organic and radioactive pollutants in aqueous solutions. Ferrate(VI) was used as a potential chemical to remove several metal cations/anions including Mn^{2+} , Cu^{2+} , Pb^{2+} , Cd^{2+} , As^{3+} , Cr^{3+} , Hg^{2+} , SCN^- and CN^- from aqueous solutions via oxidation/coagulation/adsorption processes using lower dose of Fe(VI) (10–100 mg/L) [16]. It is particularly interesting that ferrates(VI) reduce the concentration of radionuclides such as americium and plutonium [17], giving the idea for the possibility of its application for the removal of Th from different samples (in this study from natural water samples). The application is based on the assumption that radionuclides are coagulated with reduced Fe(III). The efficiency of the process of water treatment using ferrate(VI) can be explained by high oxidation-reduction potential in acidic and neutral media, the formation of iron(III)-hydroxide (product of the reduction of ferrate(VI)), which is extremely good coagulation resource, and oxygen generation by water oxidation. Reduction of ferrate(VI) in acidic medium is shown by equation



The ferrate salts are dissolved in water, oxygen is evolved and ferric hydroxide is precipitated [16]:



In this study Na_2FeO_4 electrochemically generated by trans-passive anodic oxidation of electrical steel in 10 M NaOH solution was applied to remove Th(IV) from spiked water samples [18, 19]. The stability of ferrate(VI) aqueous solutions depends on several factors such as ferrate(VI) concentration, temperature of the solution, presence of other ions, and pH. The spontaneous decomposition of ferrate(VI) in aqueous solutions was reported to be increased significantly with decreasing of pH of the solution. Ferrates(VI) because of their characteristics, as well as strong oxidizing properties, are quite unstable in aqueous solutions, due to the oxidation of water, so it is necessary to perform qualitative and quantitative analyses immediately after the completion of the synthesis process in order to obtain reliable data. The aqueous solution of ferrate(VI) prepared in alkaline media (10 M NaOH) is stable, and it is of red-purple color.

Ferrates(VI) are relatively stable and easy to synthesize electrochemically. This method is based on the principle of the dissolution of iron anode in a strongly alkaline media, in an electrolysis cell, and having electric current in order to oxidize the dissolved iron to Fe(VI) ion [16]. Beside this method, there are methods of dry oxidation of iron on high temperature and method of wet oxidation by chemical oxidizing agents [16]. Ferrates(VI) act as a coagulant, disinfectant and oxidant. In scientific literature a large number of papers has been published that deal with issues of development and application of ferrates(VI) for water and wastewater treatments [20–28]. Challenges occurred for the implementation of ferrate(VI) technology in practice due to instability of ferrate(VI) solution or high cost of ferrate(VI) products.

In addition, ferrate(VI) is effectively used to remove metals such as Cr, As, Fe, and Mn from drinking and groundwater. Many of the research studies indicate that ferrates(VI) are more effective coagulants than other inorganic coagulants (aluminum, ferric, ferrous salts, etc.) [16]. Ferrate(VI) has advantages as coagulating agent comparing to the iron salts and aluminum due to the combination of its coagulating and a strong oxidizing effect wherein the degradable organic compounds bind heavy metals and there is no way for coagulation. New approaches have been explored to obtain ferrates(VI) focusing on high yield and stability, not only low-cost, which is substantially achieved by the method applied in this study.

By careful review of the published scientific literature it was not found application of ferrates(VI) for the removal of Th. The goal of this work was to assay possibility of application of electrochemically generated Na_2FeO_4 to reduce the concentration of Th(IV) ions in spiked natural water samples. Simple and effective kinetic-spectrometric method for Th(IV) quantitative determination was applied in this work.

EXPERIMENTAL

Analytical grade reagents (Merck®) and deionised water (MicroMed high purity water system, TKA Wasseraufbereitungssysteme GmbH) were used for the preparation of all solutions. Spectrophotometric measurements were performed on Perkin-Elmer Lambda 15 UV-Vis spectrophotometer. pH measurements were carried out using Hanna Instruments pH-meter. Potentiostat-galvanostat PAR EGG connected to a computer with built-in data recording system ED 2000 Electronic design with the use of LABVIEW program for recording the results of measurements was used. For heating and mixing of the electrolyte solution laboratory magnetic stirrer with heating was used. Angular velocity of mixing the electrolyte was in all measurements $\omega \approx 2 \text{ s}^{-1}$. The anodic dissolution of electrical steel M120 in 10 M NaOH at a constant current density of 0.046 cm^{-2} for a period of 3 h was performed. A work solution of KMnO_4 ($1 \times 10^{-3} \text{ mol/L}$) was prepared by diluting a standard solution of KMnO_4 ($2 \times 10^{-2} \text{ mol/L}$) which was prepared from an ampoule. $1 \times 10^{-3} \text{ mol/L}$ solution of 4-hydroxycoumarin was prepared by dissolving 0.16414 g of the solid in 10 mL of 0.1 mol/L NaOH, to improve the solubility of 4-hydroxycoumarin, and diluted with deionized water to 1 dm^3 in calibrated volumetric flask. Standard stock solution of Th(IV) ($1 \times 10^{-3} \text{ mol/L}$) was prepared by dissolving appropriate amounts of $\text{Th}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$ in calibrated volumetric flask with deionized water.

A solution of Cr (III) chloride is prepared by the addition of 25 g $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ in 150 mL of deionized water. Solution of sulfuric acid and phosphoric acid, in 240 mL of deionized water were added to 60 mL (conc.) sulfuric acid and 150 mL of 85% phosphoric acid. A solution of sodium diphenylamine sulfonate is made by dissolving 0.32 g in 100 mL deionized water.

Water samples (spring, lake, ground, spa) were collected randomly in sufficiently clean polyethylene tubes. After sampling, the water samples were filtered through a cellulose membrane filter ("Millipore") with a $0.45 \mu\text{m}$ pore size. The working pH value was adjusted prior to use. Randomly sampled water samples were spiked with a known amount of Th(IV) and collected in polyethylene containers. An appropriate aliquot of the sample was placed in volumetric flasks following previously proposed and published procedure for kinetic-spectrophotometric determination of Th(IV) [10]. The linearity of the used kinetic method is $0.2\text{--}2 \mu\text{g/mL}$. The limit of quantification and limit of detection of the mentioned kinetic method was 0.056 and $0.017 \mu\text{g/mL}$, respectively. Regarding the selectivity of the kinetic method obtained results showed that method was successfully applied for Th(IV) determination in analyzed water samples.

A volume of 1.0 mL of 0.1 mol/L of Cl^- was added in reagents mixture, as a complexing and masking agent-in order to eliminate the main interference effects from the presence of Fe^{3+} and Mn^{2+} as main present interfering ions in natural water [29]. After treatment with ferrate(VI), an appropriate volume of spiked natural water samples prepared in this way, was analyzed by kinetic procedure [10], at 25°C and 525 nm, in order to determine the concentration of Th(IV).

This procedure was performed before and after treatment of water samples with ferrates(VI) solution in order to determine influence of ferrate(VI) treatment on the concentration of Th(IV) ions.

RESULTS AND DISCUSSION

In this work spring, lake, ground and thermo mineral/spa water samples were collected, treated and spiked with appropriate amount of Th(IV), in working concentration range of the applied kinetic-spectrophotometric method (Table). Concentration of Th(IV) was determined, after sample preparation according to recommended procedure, previously proposed and validated [10]. Analytical parameters of applied procedure [10] allow measurements of Th(IV) concentration under these working parameters, regarding limit of detection (LOD), limit of quantification (LOQ) and selectivity of the method. After that a volume of 100 mL of analyzed samples in working range of proposed kinetic method was treated at 20°C with a total of 400 mL of solution of $1 \text{ mg} \cdot \text{dm}^{-3} \text{ Na}_2\text{FeO}_4$ in 10 M NaOH in a glass ceramic spinal beaker with magnetic stirring. Th occurs in solutions exclusively in the positive tetravalent oxidation state. Analyzed water samples were treated with vigorous stirring until the disappearance of the characteristic color of ferrate(VI), and then carried out with gentle mixing and coagulation and flocculation of the resulting iron (III)-hydroxide for 10 min. Filtering was performed on Buchner funnel under reduced pressure through a quantitative filter (black bars). pH of the treated solution, was carried out adjusting the acidity of the filtrate to pH 4. After these treatments, concentration of Th was measured again in working samples, in order to compare its concentration before and after treatments with ferrates(VI). Obtained results of kinetic measurements of Th(IV) concentration before and after ferrate(VI) treatment were summarized and they are shown in table. As can be seen from table the concentration of Th(IV) significantly decreased in analyzed samples after ferrate(VI) treatment.

Th (IV) determination before (a) and after (b) treatment water samples by ferrate(VI)

Water samples	Th(IV) added, $\mu\text{g/mL}$	Th(IV) found, $\mu\text{g/mL}$		Th(IV) added, $\mu\text{g/mL}$	Th(IV) found, $\mu\text{g/mL}$	
		<i>a</i>	<i>b</i>		<i>a</i>	<i>b</i>
Spring	1.0	1.12 ± 0.12	0.15 ± 0.02	2.0	2.04 ± 0.22	0.40 ± 0.07
Lake	1.0	1.10 ± 0.09	0.10 ± 0.01	2.0	2.07 ± 0.18	0.56 ± 0.03
Ground	1.0	1.13 ± 0.11	0.13 ± 0.02	2.0	2.09 ± 0.10	0.22 ± 0.04
Spa	1.0	1.11 ± 0.10	0.11 ± 0.03	2.0	2.13 ± 0.19	0.30 ± 0.05

CONCLUSIONS

The coagulation efficiency of Na_2FeO_4 solution, electrochemically generated by trans-passive anodic oxidation of electrical steel in 10 M NaOH solution, was confirmed in the process of removal of Th(IV) ions from natural waters samples. The removal efficiency of traces of this radionuclide was evaluated by comparing the values obtained after and before treatment of spiked water samples with ferrates(VI) solution. On the basis of this study it was successfully confirmed previously observed purification effect of ferrates(VI) in many different samples regarding radioactive pollutants, which examined in this study on Th(IV) presence. Results were obtained applying simple kinetic-spectrophotometric procedure.

FUNDING

This work was supported by the Ministry of Education, Science and Technological Development, Republic of Serbia, Project No. TR34025 and Project No 174007.

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