Talanta 87 (2011) 80–84

Contents lists available at SciVerse ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

In vitro monitoring of natural thorium in urine using fluorimeter

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ARTICLE INFO

Article history:
Received 18 June 2011
Received in revised form
15 September 2011
Accepted 16 September 2011
Available online 1 October 2011

Keywords:
Bioassay
Thorium
Solvent extraction
Fluorimetry

ABSTRACT

A relatively less expensive and less time consuming radio analytical technique for quantitative determination of Th_{nat} in urine at mBq level is developed and reported in this paper. Th in urine is co-precipitated with $Ca_3(PO_4)_2$ from wet oxidized urine matrix and the precipitate is dissolved in HNO_3 and evaporated to dryness. The residue is dissolved in 3 M HCl and 200 mg of Na-EDTA is added to mask Ca^{2+}, Mg^{2+} and Fe^{3+} ions. Th^{4+} is extracted into 0.01 M PC-88A (2-ethyl hexyl phosphonic acid mono-2-ethylhexyl ester), dissolved in toluene from the experimentally optimized pH 2.5 ± 0.3 in aqueous phase. Th^{4+} is stripped into 8.0 M HCl and evaporated to dryness. The content of the beaker is dissolved in pH 1.8 HCl and complexed with 3-hydroxy flavone. The sample is excited at 397 nm and fluorescence intensity is measured at 462 nm. The detailed study of the method is presented in this paper. Interference study on elements that are normally present in urine and other actinides (if present) is also given.

1. Introduction

Radiation workers who handle thorium are routinely monitored at predetermined intervals. After the intake, the majority of thorium that enters the body is excreted through the feces in the first 48 h and a small amount through the urine. Urine containing thorium undergoes systemic excretion whereas feces containing thorium undergoes both systemic and non-systemic excretions. Therefore, urinalysis is preferred for dose assessment. In addition, the body also has a retention factor for thorium which drops rapidly [1]. Hence, sensitive and fast method is required to estimate thorium in urine. Sensitive techniques like ICPMS method with MDA 1.0 ng/l [2] and Neutron Activation Analysis (NAA) with MDA 0.01 ng/l [3] are very much suitable for low level estimation of natural thorium but are expensive. It is reported that alpha spectrometric technique involving anion exchange separation requires seven days for completion of analysis with MDA 0.1 mBq/l [4]. Hence, an attempt is made to develop a sensitive and fast method for estimation of intake of thorium and the same is given in detail in this paper. This is a solvent extraction method of using PC-88A as extractant [5–7] and estimation of quantity using fluorimeter. Thorium is extracted into 2-ethyl hexyl phosphonic acid mono-2-ethyl hexyl ester (PC-88A) dissolved in toluene. In addition, fluorescent technique is also optimized to determine thorium at sub microgram level by complexing with 3-hydroxy flavone dissolved in different polar solvents.

2. Experimental

2.1. Chemicals

All chemicals used in the experiments including $Th(NO_3)_4{\cdot}4H_2O$ were of analytical reagent grade.

2.2. Instrument

Fluorolog-3 Jobin Yvon–Spex Spectrofluorimeter, New Jersey is used. Its spectral resolution is 0.2 nm.

2.3. Method

The separation scheme for thorium from urine matrix is given with flow chart format in Fig. 1. The scheme essentially consists of three steps viz: (a) pre concentration, (b) solvent extraction separation and (c) fluorimetric estimation.

2.3.1. Pre-concentration

To 1000 ml of each pooled urine sample, a known amount of Th at microgram level was spiked, stirred and heated with 50 ml of conc. HNO_3, 25 ml of conc. HCl and 1 ml of H_2O_2 until the solution turns into pale yellow. Thorium is then co-precipitated with $Ca_3(PO_4)_2$ by adjusting the pH of the sample to 9 using ammonia. The precipitate is centrifuged and dissolved in 10 ml of 8 M

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doi:10.1016/j.talanta.2011.09.044

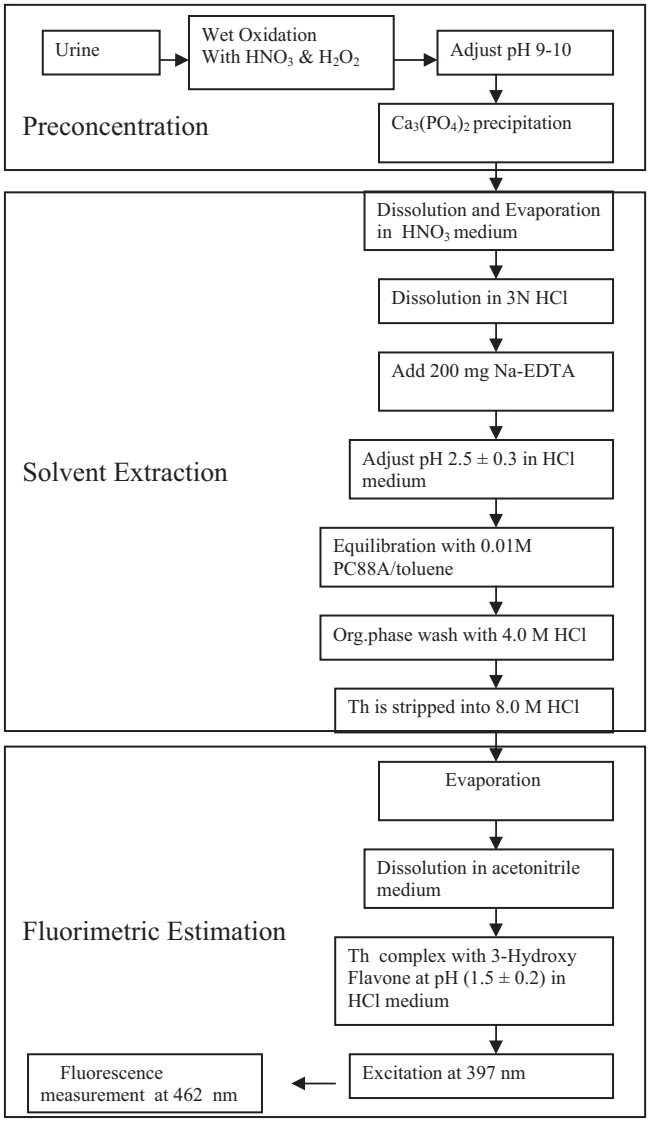

Fig. 1. Flow chart of separation schemes for Th in urine matrix.

HNO_3 followed by evaporation to destruct organic matter. Finally, the residue is dissolved in 10 ml of 3 M HCl and the solution is covered with a watch glass and boiled for 30 min to hydrolyse the pyrophosphate and to get homogeneous solution.

2.3.2. Solvent extraction separation

To the pre-concentrated solution, 200 mg Na-EDTA is added and the pH is adjusted to 2.5 ± 0.3 using 10% ammonia and 6 M HCl. The sample solution is filtered and the filtrate is equilibrated with 15 ml of 0.01 M PC-88A/toluene for 10 min. This step is repeated with fresh PC-88A for quantitative extraction of Th. Then the organic phase is collectively washed with 4 M HCl to remove U [7]. Finally, the organic phase is equilibrated with 15 ml of 8.0 M HCl for 10 min. This step is repeated with fresh 8 M HCl solution for quantitative elution of Th into HCl solution [7] and evaporated to dryness.

2.3.3. Fluorimetric estimation

The residue content in the beaker is dissolved in 1.5 ml volume of HCl solution (pH 1.8), transferred to 10 ml standard flask, added 1 ml of 0.01% 3-hydroxy flavone (prepared in acetonitrile solvent) and the rest of the volume is made up with acetonitrile solvent. The pH of the resultant solution is 1.5 ± 0.2. The solution is taken in the cell and kept in the sample holder of the fluorimeter. The sample excited at 397 nm and fluorescence intensity is measured at 462 nm.

3. Results and discussion

3.1. Optimization of the conditions for fluorimetric estimation of Th

The complex of thorium with morin, quercetin and 3-hydroxy flavone (3-HF) gives fluorescence when they are excited at 420 nm, 425 nm and 390 nm respectively. The Minimum Detectable Activity (MDA) for Th when complexes with Morin and Quercetin is 20 μg/l [8,9] and for 3-hydroxy flavone, it is 10 μg/l [10]. It is also given in the literature that the fluorescence of flavone complexes with metals are higher in polar solvents than in apolar solvents. Therefore, to arrive at maximum fluorescence intensity for a given amount of Th, the complex of thorium-3-hydroxy flavone was investigated using different polar solvents like ethanol, methanol, acetonitrile, dioxane, isopropanol and in tetrahydrofuran.

The stability of the complex depends essentially on pH. Hence, optimization studies on the pH value for thorium-3-hydroxy flavone complex for given solvents were undertaken. The pH value of thorium-3-hydroxy flavone complex was varied between 0 and 3.5 in different polar solvents and the fluorescence intensity of the complex was measured for a known amount of Th (i.e. 9.45 μg/ml). The complex was excited at 397 nm and the emission peak was observed between 461 and 467 nm for different polar solvents as shown in Table 1. It is found that among various solvents, the ratio of the average fluorescence intensity due to Th with respect to average fluorescence intensity due to blank is the highest (i.e. 892) in acetonitrile solvent. The relative fluorescence intensity of the complex in different polar solvents is given in Fig. 2. The optimum pH value of the complex for maximum fluorescence efficiency was observed between 1.5 and 1.8. Among different polar solvents, maximum fluorescence intensity was observed in methanol and ethanol solvents when the concentration of Th is 9.45 μg/ml and no fluorescence is observed in both the solvents when Th concentration is decreased to 0.5 μg/ml. However, in acetonitrile solvent, fluorescence is observed at this concentration of Th.

3.2. Calibration of fluorimeter

To estimate the percent chemical recovery of Th from the above established method, fluorimeter needs to be calibrated. To calibrate fluorimeter, fluorescence intensity of Th-3-hydroxy flavone was measured for different amounts of Th_{nat} ranging from 0.4 to 4.8 μg spiked in each 10 ml volume. Measurements were taken in both right-angle and front-face modes. From the data obtained as given in Table 2, it was observed that the best fitted line could be obtained in the right angle mode with slit width 2.0 nm both for excitation and emission monochromator (Fig. 3). A typical fluorescence spectrum obtained in comparison with blank (zero amount of Th) is shown in Fig. 4. From this, it can be inferred that low level of thorium can quantitatively be estimated which is the objective of developing this method.

3.3. Optimizing the conditions for extraction of Th into PC-88A

It is reported in the literature that Th can be quantitatively extracted from dilute $HClO_4$ solution in the pH range 2.3–3.8 with 0.01 M PC-88A dissolved in toluene [7]. But the presence of Ca^{2+} and Mg^{2+} ions each at 100 mg and PO_4^{3-} ions at 500 mg in the aqueous phase gave undesirable precipitate during equilibration with PC-88A. Therefore, experiments were repeated with different acidity of aqueous phase using dil. HCl from pH 0 to 5.0 and found that Th could quantitatively be extracted between pH 2.5 and 3.5.