Contribution to validation of spectrophotometric determination of thorium using Arsenazo III

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Abstract

The paper is devoted to the evaluation of important validation descriptors concerning the spectrophotometric determination of thorium using Arsenazo III. In diluted hydrochloric acid the relevant complex is formed instantly and remains stable for 25 minutes with constant absorbance. Beer's law is obeyed in the range from 0.70 to 11.64 $mol \cdot L^{-1}$. The molar absorptivity at 660 nm is equal to $9.74 \ (\pm 0.09) \cdot 104 \ cm^{-1} \cdot mol^{-1} \cdot L$ (data in parentheses stands for standard deviation). LOD and LOQ values were established applying three approaches - the 3-σ, the ULA2 and the Hubaux-Vos ones. The precision was tested at three concentrations, namely at $3.88 \ mol \cdot L^{-1}$, $1.30 \ mol \cdot L^{-1}$ and $7.76 \ mol \cdot L^{-1}$. The relevant relative standard deviations (RSD) reached $\pm 1.48\%$, $\pm 4.34\%$ and $\pm 3.07\%$, respectively. The trueness did not exceed 3%. Stoichiometry of complex formation was examined by the mole ratio method and the method of continuous variation. The ratio found was 1:2. Foreign ions interference by thorium determination has been checked as well. The cations Cu(II), Zn(II), Co(II), Mn(II), La(III),U(VI), Eu(III), Ce(IV) were tested in the range of 10- to 100-fold molar excess of thorium. U(VI), Co(II) and Ce(IV) caused significant interference.

Keywords: *thorium, spectrophotometry, Arsenazo III, foreign ions*

1 Introduction

Thorium is a naturally occurring radioactive element of extraordinary long lifetime. The most reliable sources of elemental concentrations in earth crust report values representing approx. 6 ppm of thorium in average. Thorium is first of all a worthwhile potential raw material for fissile nuclear fuel production. Taking in account chemical and geochemical determinateness of thorium, the quantification of its concentration in different matrices requires in addition to high accuracy also satisfactory detection limits. The mentioned element can be determined by many instrumental techniques based on different principles including mass spectrometry with inductively coupled plasma [40, 11], electrochemical methods [22, 14, 19, 12], atomic emission spectrometry with inductively coupled plasma [10, 35], atomic absorption spectrometry [7], chromatography [2, 16, 9, 32, 18, 36] and others. A necessary part of most analytical determinations of elements in real matrices is separation and preconcentration. To achieve this goal a number of effective procedures have been developed, for example [4, 17, 3, 38, 8, 30, 28, 24, 5, 6, 34]. Concerning spectrophotometric determination of Th a specific group of methods has been studied. To the most promising ones belong the disodium Arsenazo III method [21] which has been successfully applied for determination of thorium at $\mu g \cdot g^{-1}$ level in ore samples with a precision of $\pm 0.04\%$, the Eriochrome Cyanine R method [1] proposed for determination of Th(IV), La(III) and Y(III) in natural water samples and in some ore samples; the 2,4-dihydroxybenzaldehyde isonicotinoylhydrazone method [33]. To the less frequently cited reagents proposed for spectrophotometric determination of thorium belong 2-(2,5-disulfonic-4-methoxyphenylazo)-7-(2-hydroxyl-5-carboxylphenylazo)-1,8dihydroxynaphthalene-3,6 disulfonic acid [26], DCB-Arsenazo [39] and Arsenazo III [20], however none of them became a generally accepted one. Arsenazo III has been applied for spectrophotometric determination of thorium in early sixties and in this paper were decribed some basic parameters as optimal concentration of HCl, optimal volume of chelating reagent and stoichiometry of relevant complex [31]. But some validation parameters as limit of detection, limit of quantification, trueness, precision and time stability of formed complex have not been studied yet. The presented work is devoted to quantification of important validation parameters for spectrophotometric determination of thorium in $\mu mol \cdot L^{-1}$ concentration range utilizing Arsenazo III in presence of hydrochloric acid including the study of presumable interferences.

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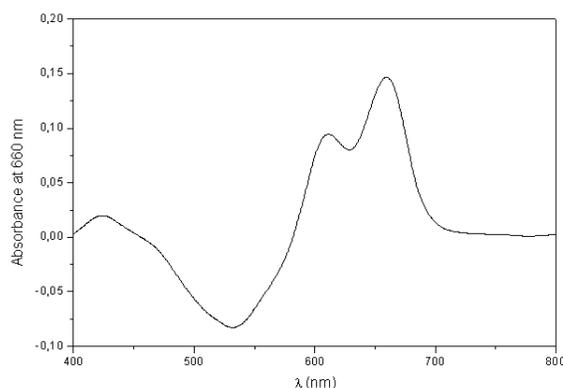
Figure 1: Absorption spectra of thorium - Arsenazo III complex (Th $= 4.31$ mol $\cdot$ L^{-1}) against a reagent blank
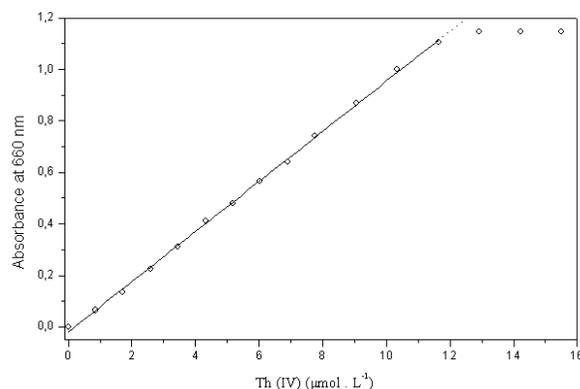

Figure 2: Absorbance of thorium-Arsenazo III complex at 660 nm as a function of thorium concentration against a reagent blank

2 Experimental

All reagents used were of analytical grade and all the solutions were prepared in deionised water. Thorium stock solution (Department of Nuclear Chemistry, Faculty of Natural Sciences, Comenius University in Bratislava) containing 43.1 μmol $\cdot$ L^{-1} was used. The concentration of Arsenazo III water solution (Fluka Analytical) was $2.58 \cdot 10^{-4}$ mol $\cdot$ L^{-1}. The medium of measured solutions has been adjusted by addition of dilute hydrochloric acid (Mikrochem) 1:1 (vol./vol.). Foreign ions stock solutions with concentration of 25.9 mmol $\cdot$ L^{-1} were prepared by dilution of standard solutions (Fluka Analytical, Merck). All measurements were performed using Cary WinUV 50 (Varian Inc.) spectrophotometer. We performed all measurements using the Cary WinUV 50 (Varian Inc.) spectrophotometer. We used three replicate samples for each absorbance determination and we utilized the average value of the signal versus blank in next computations. All calculations were performed using Microsoft Excel 2003 (Microsoft Corporation., v.11.5612.5606). Processing of readings from the spectrophotometer Cary 50 WinUV was made by Cary WinUV Analysis Software Pack (Varian Inc., ver. 4.10). Program Origin Pro8 Professional (OriginLab Corporation., V. 80724, 1991-2007) was used for adjustment of the measured data and for graphical presentations concerning the relevant dependencies.

Procedure

We transferred thorium stock solution containing up to 11.64 μmol $\cdot$ L^{-1} of Th(IV) into 10 mL volumetric flask, then we added 4 mL of diluted hydrochloric acid (1:1) and 2 mL of Arsenazo III solution. The mixture was filled up to the mark with deionised water (0.054 μS $\cdot$ cm^{-1}). After thorough mixing, the absorbance at 660 nm against a reagent blank was measured.

Table 1: LOD and LOQ computed by using three different approaches

3-σ approach			ULA2 approach		
$s_{y/x}$	LOD [μmol $\cdot$ L^{-1}]	0.34	LOD ($\alpha = 0.05$) [μmol $\cdot$ L^{-1}]	0.23	
	LOD [μmol $\cdot$ L^{-1}]	1.12	LOD ($\alpha = 0.05$) [μmol $\cdot$ L^{-1}]	0.68	
s_b	LOD [μmol $\cdot$ L^{-1}]	0.17	LOD ($\alpha = 0.05$) [μmol $\cdot$ L^{-1}]	0.34	
	LOD [μmol $\cdot$ L^{-1}]	0.57	LOD ($\alpha = 0.05$) [μmol $\cdot$ L^{-1}]	1.03	
Hubaux-Vos approach					
LOD ($\alpha = 0.05$) [μmol $\cdot$ L^{-1}]					0.22
LOD ($\alpha = 0.05$) [μmol $\cdot$ L^{-1}]					0.65
LOD ($\alpha = 0.05$) [μmol $\cdot$ L^{-1}]					0.31
LOD ($\alpha = 0.05$) [μmol $\cdot$ L^{-1}]					0.93

Table 2: LOD and LOQ computed by using three different approaches

c Th(IV) [μmol $\cdot$ L^{-1}]	relative error [%]	RSD [%]
1.30	-3.09	± 4.34
3.88	-0.72	± 1.48
7.76	-2.1	± 3.07

3 Results and discussion

Thorium-Arsenazo III complex in diluted hydrochloric acid showed two absorption peaks, namely at 610 nm and 660 nm (Figure 1). While both of the mentioned peaks were sufficiently separated, the latter one was used for the determination.

The upper limit of the linear range was established by application of QC parameter [37]. The Beer's law was obeyed from 0.70 to 11.64 mol$\cdot$L^{-1} (Figure 2). The molar absorptivity was established to be $\varepsilon_{660} = 9.74(\pm 0.09) \cdot 10^{-4} \cdot 104$ cm$^{-1} \cdot$ mol$^{-1} \cdot$ L (data in parentheses represents standard deviation). The coefficient of determination reached the value $R^2 = 0.9991$. The computed Sandell's sensitivity had the value of $0.050(\pm 0.006)$ μg $\cdot$ cm^{-2}. The limit of detection (LOD) and the limit of quantification (LOQ) were calculated by 3-σ [15], *ULA2* [27] and *Hubaux-Vos* [13] approaches as well. The results are given in Table 1. In the case of computation of LOD a LOQ by 3-σ approach was used in calculations residual standard deviation ($s_{y/x}$) and standard deviation of y-intercept (s_b) [23, 25]. The experimentally verified limit of detection and limit of quantification reached the following values: LOD = 0.22 μmol $\cdot$ L^{-1} and LOQ = 0.70 μmol $\cdot$ L^{-1}. The best agreement between theoretically computed and practically verified values of LOD and LOQ was observed using *ULA2* and *Hubaux-Vos* approaches namely at significance level $\alpha = 0.05$. The results were satisfactory even in the case of 3-σ approach application, where sb was implemented into the calculation.

The precision and trueness of the method was examined by six replicate solutions. The relevant conclusions are shown in Table 2. Examination of trueness was carried out by spike/recovery procedure.

The optical density was found constant for 25 minutes under normal laboratory conditions. A significant decrease in the absorbance was observed only for thorium concentration exceeding 6.90 μmol $\cdot$ L^{-1} (Figure 3).

The thorium - Arsenazo III complex stoichiometry has been established by two methods, namely the method of continuous variation (Figure 4) and the mole ratio method. Concentration of diluted HCl in measured solutions was maintained at 2.33 mol $\cdot$ L^{-1}. Our experimental results at the above mentioned conditions led to formation of a 1:2 complex utilizing both relevant methods, while in 6 mol $\cdot$ L^{-1} HCl [29] proved two different complex
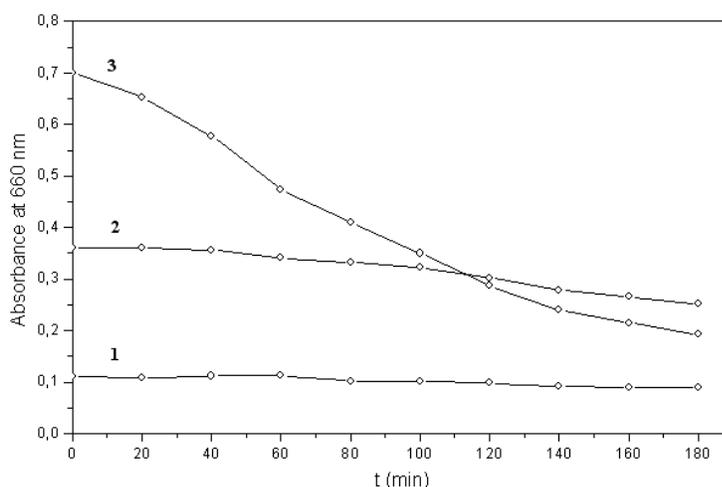
Figure 3: Time dependance of absorbance for Th concentrations: $1.08\ \mu\text{mol} \cdot \text{L}^{-1}$ (line 1), $3.45\ \mu\text{mol} \cdot \text{L}^{-1}$ (line 2) and $6.90\ \mu\text{mol} \cdot \text{L}^{-1}$ (line 3)

Table 3: Effect of chosen ions on thorium determination with Arsenazo III in hydrochloric acid, Th(IV) concentration $4.31\ \mu\text{mol} \cdot \text{L}^{-1}$

Foreign ion	Deviation [%]	Foreign ion	Deviation [%]
Cu(II)†	+3.74	La(III)‡	+13.25
Zn(II)†	+0.37	U(VI)†	+57.50
Co(II)†	+49.63	Eu(III)†	+7.37
Mn(II)†	+5.03	Ce(IV)†	+36.99

stoichiometries, namely the 1:1 and 1:2 ones. In the next step the influence of potentially interfering ions was checked. The impact of 60- fold excess of chosen ions is summarized in Table 3. Our results indicated that U(VI), Co(II) and Ce(IV) caused significant interference.

We checked the repeatability of thorium determination influenced by 90- and 50-fold excess of La(III), Eu(III) and Ce(IV) as well. The obtained results applying six replicate measurements are shown in Table 4.

4 Conclusions

The studied spectrophotometric method for determination of Th(IV) in water solutions using Arsenazo III in hydrochloric acid enables the quantification of the analyte in concentration range $0.70 - 11.64\ \mu\text{mol} \cdot \text{L}^{-1}$ with RSD not exceeding 4.5%. The maximal time stability of the measured Th-Arsenazo III complex for the investigated method stood for 25 minutes. The experimentally verified limit of detection and limit of quantification reached 0.22 and $0.70\ \mu\text{mol} \cdot \text{L}^{-1}$, respectively. This values were in good agreement with our computational results obtained by application of that of ULA2 as well as Hubaux-Vos approach (at significance level $\alpha = 0.05$). While Cu(II), Zn(II) and Mn(II) in 60-fold excess (comparing the investigated Th concentration) caused acceptable in-

Table 4: Results of repeatability for chosen interfering cations (data in parentheses represent standard deviations)

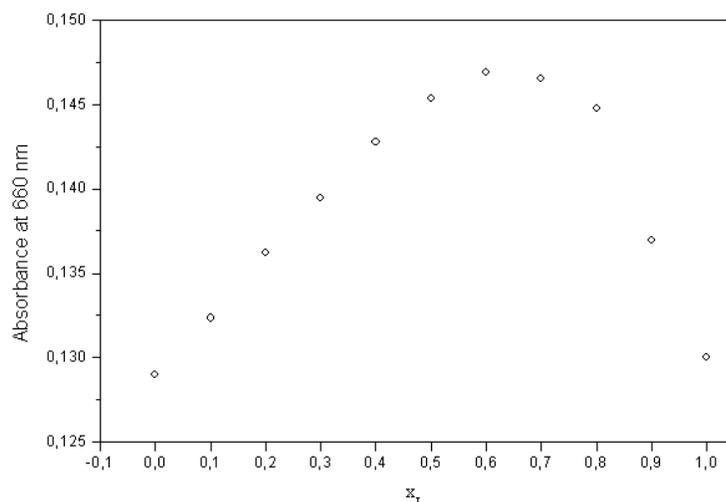| Foreign ion	Molar excess	Deviation [%]
La(III)	90-fold	$+22.03(\pm1.59)\%$
Eu(III)	50-fold	$+7.50(\pm1.32)\%$
Ce(IV)	50-fold	$+30.01(\pm2.37)\%$

Figure 4: Method of continuous variation. x_L - mole fraction of ligand (Arsenazo III), $c\,(HCl) = 2.33\,\mathrm{mol}\cdot\mathrm{L}^{-1}$

terferences (deviations in absorbance not exceeding 5%), the influences of 60-fold excess of U(VI), Co(II) and Ce(IV) led to deviations reaching $35-57.5\%$.

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