



ADVANTAGES AND DISADVANTAGES OF ARSENAZO III AND CHLOROPHOSPONAZO III UTILIZATION FOR SPECTROPHOTOMETRIC THORIUM DETERMINATION

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The presented work is devoted to the evaluation of important validation descriptors concerning the spectrophotometric determination of thorium using Arsenazo III and Chlorophosponazo III. In diluted hydrochloric acid the complex between Th(IV) and Arsenazo III 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 $\mu\text{mol} \cdot \text{L}^{-1}$. The molar absorptivity at 660 nm is equal to $9.74(\pm 0.09) \cdot 10^4 \text{ cm}^{-1} \text{ mol}^{-1} \text{ L}$ (data in parentheses stands for standard deviation). The relevant relative standard deviations (RSD) reached $\pm 1.48 \%$, $\pm 4.34 \%$ and ± 3.07 , respectively. Thorium concentration can be quantified using Chlorophosponazo III in media of diluted nitric acid. The linear range of the proposed method was from 1.59 to 18.10 $\mu\text{mol L}^{-1}$ of thorium(IV). The experimentally determined values of molar absorptivity reached $\epsilon_{691} = 3.76(\pm 0.05) \cdot 10^4 \text{ cm}^{-1} \text{ mol}^{-1} \text{ L}$. The repeatability and trueness of determination in the linear range did not exceed $\pm 2.2\%$ and 3.3% , respectively. Color stability of the Th(IV)-Chlorophosponazo III complex maintained a constant value for at least two hours. LOD and LOQ values for both methods were established applying three approaches – the 3- σ , the ULA2 and the Hubaux-Vos ones.

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of partial hydrolysis of metal ions to be determined. They are complexing reagents suggested primarily for spectrophotometric determination of lanthanides, actinides and alkaline earth metals.²⁷

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 plasma¹⁻², electrochemical methods³⁻⁶, atomic emission spectrometry with inductively coupled plasma,⁷⁻⁸ atomic absorption spectrometry⁹, chromatography¹⁰⁻¹³ 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 developed¹⁴⁻¹⁸. There are many spectrophotometric methods for thorium determination in environmental samples.¹⁹⁻²⁶

The application of organic reagents for spectrophotometric determination of thorium is well known and continues to be interesting. Chlorophosponazo III and Arsenazo III belong to azo-dyes based on chromotropic acids. The reagents have ability to form stable chelates and can work in strongly acidic medium eliminating the chances

Russian scientists Fadeeva and Alimarin²⁸ have published the first use of complexing agent Chlorophosponazo III for spectrophotometric determination of thorium(IV) in diluted hydrochloric acid media. Extraction of Th(IV)-Chlorophosponazo III complex into organic solvent led to an increase of selectivity and sensitivity of the relevant determination.²⁹⁻³⁰ In monazite sand samples, the spectrophotometric determination of thorium using Chlorophosponazo III in presence of diluted phosphoric acid was carried out as well. The relative error of the determination did not exceed 1%.³¹ While the successful applicability of Chlorophosponazo III for spectrophotometric quantification of thorium(IV) in different matrices is indisputable, the number of works dealing with detailed evaluation of particular determinations is surprisingly limited. The use of Arsenazo III for spectrophotometric determination of thorium(IV) was described in work of soviet scientist Savvin. Measurements were carried out in presence of diluted hydrochloric acid at the 665 nm. Molar absorptivity reached the value $1.3 \cdot 10^5 \text{ L mol}^{-1} \text{ cm}^{-1}$. This method proved to be suitable for the determination of microgram amounts of Th in minerals and natural waters. The relative error of the determination does not exceed 4%.³² A rapid and sensitive spectrophotometric method has been developed for the determination of thorium(IV) using 0.04% Arsenazo-III in a 2M perchloric acid solution.³³ The complex is formed instantly in perchloric acid and remains stable for 45 minutes with constant absorbance. Beer's law is obeyed in the range 1 – 60 $\mu\text{g g}^{-1}$ of thorium(IV) concentration with a molar absorptivity at 654 nm = $3.07 \cdot 10^5 \text{ M}^{-1} \cdot \text{cm}^{-1}$. The foreign ions interference in thorium determination have been

checked. The cations were tested at > 60-fold excess of thorium(IV), Mn(II), Fe(III), Co(II) and Ni(II) interfere negatively, whereas only Ce(III) has increased the absorbance. Among the anions, cyanide, phosphate, thiocyanate and acetate at 150-fold excess of thorium(IV) cause significant interference. However, thorium can be determined in the presence of nitrate, chloride, oxalate, tartrate, ascorbate, thiosulphate and citrate. The method has been applied on certified reference material for thorium determination after extractive separation and the result was found in good agreement with the certified value.³³

The utilization of mentioned complexing agents in question has valuable advantages such as an excellent time stability of the absorbance and a relatively wide linear range, etc. Chlorophosphonazo III and Arsenazo III still have a justified place among the complexing agents utilized in trace analysis and the interest in their analytical applications significantly grows in recent years.

The presented study is focused on the evaluation and comparison of important validation parameters for spectrophotometric determination of thorium in $\mu\text{mol L}^{-1}$ concentration range using abovementioned reagents.

Material and methods

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. The value of the specific conductivity of the deionized water used in experiments was $0.054 \mu\text{S cm}^{-1}$. All reagents used were of analytical grade and all the solutions were prepared in deionized water. Thorium(IV) stock solution (Fluka Analytical) containing $43.1 \mu\text{mol L}^{-1}$ was used. The concentration of solution of the Chlorophosphonazo III (Dojindo Laboratories) was 0.04% (w./v.) and Arsenazo III (Fluka Analytical) was 0.02% (w./v.). The medium of measured solutions has been adjusted by addition of diluted nitric acid or hydrochloric acid (Mikrochem) with concentration 10 mol L^{-1} . The foreign ions stock solutions were prepared by dilution of standard solutions (Fluka Analytical, Merck).

Results and discussion

Arsenazo III method

Thorium stock solution containing up to $11.64 \mu\text{mol L}^{-1}$ of Th (IV) was transferred into 10 mL volumetric flask, then 2.3 mL of diluted hydrochloric acid and 2 mL of Arsenazo III solution have been added. The mixture was filled up to the mark with distilled water. After thorough mixing the absorbance at 660 nm against a reagent blank was measured. The upper limit of the linear range was established by application of QC parameter³⁴ and application of F-test of significance of quadratic parameter.³⁵ The Beer's law was obeyed from 0.7 to $11.64 \mu\text{mol L}^{-1}$ (Figure 1). Beyond this value, a significant deviation from the linearity was observed. The molar absorptivity reached value $\epsilon_{660} = 9.74(\pm 0.09) \cdot 10^4 \text{ cm}^{-1} \text{ mol}^{-1} \text{ L}$ (data in parentheses represents standard deviation).

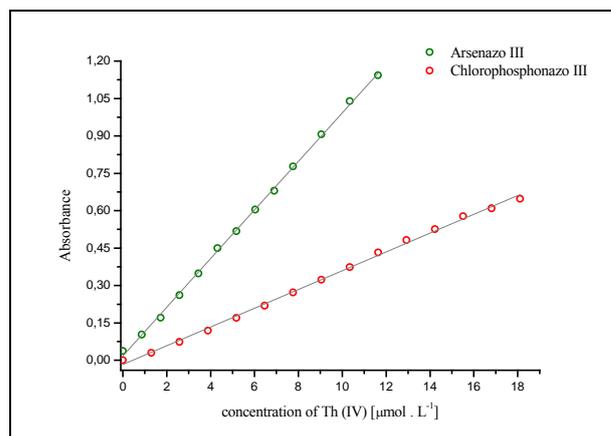


Figure 1 Absorbance of thorium(IV)-Arsenazo III (Chlorophosphonazo III) complex as a function of thorium concentration against a reagent blank.

The optical density was found constant only 25 minutes under normal laboratory conditions. A significant decrease in the absorbance was observed only for thorium(IV) concentration exceeding $6.90 \mu\text{mol L}^{-1}$ (data not shown). The values of limit of detection (LOD) and limit of quantification (LOQ) were calculated by $3\text{-}\sigma$,³⁶ ULA2³⁷ and Hubaux-Vos³⁸ approaches as well. In the case of computation by $3\text{-}\sigma$ approach residual standard deviation ($s_{y/x}$), standard deviation of y-intercept (s_b) and standard deviation of blank (s_{blank}) were applied. Results of these theoretical computations are summarized in Table 1.

Table 1 LOD and LOQ computed by using three different approaches. †10 replicate determinations of blank.

3- σ		
s_{blank}^\dagger	LOD [$\mu\text{mol L}^{-1}$]	0.63
	LOQ [$\mu\text{mol L}^{-1}$]	2.07
$s_{y/x}$	LOD [$\mu\text{mol L}^{-1}$]	0.34
	LOQ [$\mu\text{mol L}^{-1}$]	1.12
s_b	LOD [$\mu\text{mol L}^{-1}$]	0.17
	LOQ [$\mu\text{mol L}^{-1}$]	0.57
ULA2		
	LOD ($\alpha = 0.05$) [$\mu\text{mol L}^{-1}$]	0.23
	LOQ ($\alpha = 0.05$) [$\mu\text{mol L}^{-1}$]	0.68
	LOD ($\alpha = 0.01$) [$\mu\text{mol L}^{-1}$]	0.34
	LOQ ($\alpha = 0.01$) [$\mu\text{mol L}^{-1}$]	1.03
Hubaux-Vos		
	LOD ($\alpha = 0.05$) [$\mu\text{mol L}^{-1}$]	0.22
	LOQ ($\alpha = 0.05$) [$\mu\text{mol L}^{-1}$]	0.65
	LOD ($\alpha = 0.01$) [$\mu\text{mol L}^{-1}$]	0.31
	LOQ ($\alpha = 0.01$) [$\mu\text{mol L}^{-1}$]	0.93

The experimentally verified limit of detection and limit of quantification reached the following values: LOD = $0.22 \mu\text{mol L}^{-1}$ and LOQ = $0.70 \mu\text{mol L}^{-1}$. 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 $3\text{-}\sigma$ approach application, where s_b was implemented into the calculation. The precision and trueness of the method was examined using 7 replicate solutions and conclusions are in Table 2.

Table 2 Obtained data for precision and trueness appraisal concerning the studied method.

Th (IV) concentration [$\mu\text{mol L}^{-1}$]	Relative error [%]	RSD [%]
1.30	-3.09	± 4.34
3.88	-0.72	± 1.48
7.76	-2.11	± 3.07

Influence of potentially interfering ions has been checked. The impact of 60-fold foreign ions excess (Th(IV) concentration $4.31 \mu\text{mol L}^{-1}$) is summarized in Table 3. Our results indicated that U(VI), Co(II) and Ce(IV) caused significant interference.

Table 3 Effect of chosen ions on thorium(IV) determination with Arsenazo III in hydrochloric acid.

Foreign ion	Relative error [%]	Foreign ion	Relative error [%]
Cu(II) ^a	+3.74	La(III) ^b	+13.25
Zn(II) ^a	+0.37	U(VI) ^a	+57.50
Co(II) ^a	+49.63	Eu(III) ^a	+7.37
Mn(II) ^a	+5.03	Ce(IV) ^a	+36.99

(a) as nitrate (b) as chloride

Chlorophosphonazo III method

Thorium stock solution containing up to $18.10 \mu\text{mol L}^{-1}$ of Th(IV) was transferred into 10 mL volumetric flask, then we added 1.5 mL of diluted nitric acid and 0.7 mL of Chlorophosphonazo III solution. The mixture was filled up to the mark with deionized water. After thorough mixing, the absorbance at 691 nm against a reagent blank was measured. The upper limit of the linear range was established by application of QC parameter and application of F-test of significance of quadratic parameter as in previous method. The Beer's law was obeyed from 1.59 to $18.10 \mu\text{mol L}^{-1}$ (Figure 1). Beyond this value, a significant deviation from the linearity was observed. The molar absorptivity was established to be $\epsilon_{691} = 3.76(\pm 0.05) \cdot 10^4 \text{ cm}^{-1} \text{ mol}^{-1} \text{ L}$ (data in parentheses represents standard deviation). The optical density was found constant at least for 2 hours under normal laboratory conditions within the linear range.

The values of LOD and of LOQ were calculated by $3\text{-}\sigma$, ULA2 and Hubaux-Vos approaches as well. Results of these theoretical computations are summarized in Table 4. The experimentally verified limit of detection and limit of quantification reached the following values: $\text{LOD} = 0.55 \mu\text{mol L}^{-1}$ and $\text{LOQ} = 1.59 \mu\text{mol L}^{-1}$. 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 $\alpha = 0.05$. This is due to the fact that the mentioned statistical models take into account the uncertainty of the regression line and multiplying factors are not fixed (as in $3\text{-}\sigma$ approach), but their values depend on the design of the experiment.

Table 4. LOD and LOQ computed by using three different approaches. [†]10 replicate determinations of blank.

3- σ		
$s_{\text{blank}}^{\dagger}$	LOD [$\mu\text{mol} \cdot \text{L}^{-1}$]	0.12
	LOQ [$\mu\text{mol} \cdot \text{L}^{-1}$]	0.40
	LOD [$\mu\text{mol} \cdot \text{L}^{-1}$]	0.71
$s_{y/x}$	LOQ [$\mu\text{mol} \cdot \text{L}^{-1}$]	0.37
	LOD [$\mu\text{mol} \cdot \text{L}^{-1}$]	0.40
s_b	LOQ [$\mu\text{mol} \cdot \text{L}^{-1}$]	1.34
	ULA2	
	LOD ($\alpha = 0.05$) [$\mu\text{mol} \cdot \text{L}^{-1}$]	0.53
	LOQ ($\alpha = 0.05$) [$\mu\text{mol} \cdot \text{L}^{-1}$]	1.61
	LOD ($\alpha = 0.01$) [$\mu\text{mol} \cdot \text{L}^{-1}$]	0.80
	LOQ ($\alpha = 0.01$) [$\mu\text{mol} \cdot \text{L}^{-1}$]	2.41
Hubaux-Vos		
	LOD ($\alpha = 0.05$) [$\mu\text{mol} \cdot \text{L}^{-1}$]	0.52
	LOQ ($\alpha = 0.05$) [$\mu\text{mol} \cdot \text{L}^{-1}$]	1.57
	LOD ($\alpha = 0.01$) [$\mu\text{mol} \cdot \text{L}^{-1}$]	0.75
	LOQ ($\alpha = 0.01$) [$\mu\text{mol} \cdot \text{L}^{-1}$]	2.25

The precision and trueness of the method was examined by 7 replicate solutions. The relevant conclusions are shown in Table 5.

Table 5 Obtained data for precision and trueness appraisal for the studied method.

Th (IV) concentration, $\mu\text{mol L}^{-1}$	Relative error [%]	RSD [%]
6.03	+0.11	± 2.15
10.78	+3.32	± 1.14
16.38	-2.27	± 0.95

The influence of potentially interfering ions was checked. The impact of 50-fold foreign ions excess (Th(IV) concentration $6.47 \mu\text{mol} \cdot \text{L}^{-1}$) is summarized in Table 6.

It was carried out five replicate determinations for each interfering ion. The average value of three replicate Th-Chlorophosphonazo III absorbances (not containing foreign ions) was taken into account as a reference value. Results indicated that all the studied cations except of Ca(II) caused significant interferences.

Table 6 Effect of chosen ions on thorium determination with Chlorophosphonazo III in nitric acid.

Foreign ion	Relative error [%]
Cerium(IV) ^a	+26.6(± 1.8)
Lanthanum(III) ^b	+78.1(± 3.8)
Europium(III) ^a	+22.2(± 1.6)
Calcium(II) ^b	-0.4(± 1.2)
Uranium(VI) ^a	+38.8(± 2.9)

(a) as nitrate (b) as chloride

Conclusions

The studied spectrophotometric methods for determination of Th (IV) in water solutions using Arsenazo III or Chlorophosphonazo III in hydrochloric (nitric) acid enable the quantification of the analyte in wide concentration range.

Both reagents are characterized by excellent repeatability of the results expressed by the relative standard deviation, whose value does not exceed the limit of $\pm 4.4\%$ and also favorable value relative errors ($<3\%$). Some differences between these two methods can be observed in the time stability of absorbance. Using Arsenazo III method the time stability of absorbance is limited to 25 minutes and the concentration limits $6.90 \mu\text{mol L}^{-1}$ Th(IV), in contrast use of Chlorophosphonazo III method extended stability up to two hours within whole linear range. Influence of selected foreign ions for accuracy determination of thorium is not negligible, but after their removal, or masking it would be possible to obtain relevant information about the concentration of Th in some types of real samples. As mentioned before - these complexing agents react with many other elements, and because the content of thorium in environmental samples is very low, it is not possible to use the method described for the direct determination of this element without appropriate separation and preconcentration procedures.

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