

POSSIBILITY OF THE SPECTROPHOTOMETRIC DETERMINATION OF EUROPIUM BY MEANS OF ARSENAZO III

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Abstract: The concentration of Eu(III) cations in model aqueous solutions can be quantified by means of Arsenazo III reagent. Absorbance of the solution was measured at the wavelength $\lambda_{\max} = 655$ nm. Molar absorptivity reached the value $\epsilon_{655} = 5.5 \pm 0.2 \cdot 10^4 \text{ cm}^{-1} \cdot \text{mol}^{-1} \cdot \text{dm}^3$. Beer's law was obeyed in the range from 0 to $2 \text{ mg} \cdot \text{dm}^{-3}$ Eu(III). The value of limit of detection was established by application of 3σ approach and reached the value of $20.9 \mu\text{g} \cdot \text{dm}^{-3}$. Repeatability of analysis expressed by relative standard deviation does not exceed the value of $\pm 8\%$ and apparent recovery lay in acceptable range from 91 to 106 %. Stoichiometry between Eu(III) and Arsenazo III in media of relevant solution was 1:1. The absorbance of the solutions within the linear range of the proposed method maintained a constant value for 60 minutes. Described procedure can be utilized to determination of Eu(III) concentration in real samples, but it is necessary eliminate interfering ions. Cations like La(III), Sm(III), Th(IV), U(VI) and complexing agent EDTA cause significant error at the determination of Eu(III) in model solution. Presented spectrophotometric method could be applied for the determination of europium in the minerals and water samples, however after a suitable separation and preconcentration of target analyte.

Key words: europium, Arsenazo III, spectrophotometry, limit of detection.

1. Introduction

Europium is a soft silvery white metal which belongs to the lanthanide family. It was discovered in 1896 and isolated in 1901 by Eugène-Anatole Demarçay (HEISERMAN, 1992); its atomic number is 63 and atomic weight is 151.96. Europium can exist in two oxidation states, namely Eu(II) and Eu(III) and the latter represents its most stable oxidation form. Majority of europium is obtained from monazite sand, which is a mixture of phosphates of calcium, thorium, cerium and most of the other rare earth metals. Europium can be separated from the rare earth metals first of all by precipitation (BLAZEJAK-DITGES, 1970). The result of this process is formation of europium oxide, Eu_2O_3 . Europium in metal state can be prepared by mixing with powdered lanthanum metal in a tantalum crucible. Various methods have been developed for the determination of rare earth metals including europium. They include spectrofluorimetry (TAKATATSU and SATO, 1979; YAMADA *et al.*, 1982), polarography (FU *et al.*, 1993), voltammetry (MLAKAR and BRANICA, 1991), atomic emission spectroscopy with inductively coupled plasma (DASKALOVA *et al.*, 1996) and mass spectrometry with inductively coupled plasma (ZANG *et al.*, 1995). However, all these procedures are troublesome or the instruments are not readily available. Therefore, there is the need for suitable laboratories equipped with inexpensive instrumentation, which allows the determination of europium to be carried

out in a fast and cheap way without sacrificing precision. Spectrophotometric method is an alternative that satisfies these requirements and can be afforded by most laboratories. In the present time exists some spectrophotometric methods suggested for the determination of traces of europium in different types of samples, for example (FANG *et al.*, 1999; POLUEKTOV *et al.*, 1971; STOYANOV *et al.*, 2011).

Arsenazo III is reported to be suitable primarily for the photometric determination of lanthanides and actinides (SAVVIN, 1961; SAVVIN 1964). It is commercially available and soluble in water and diluted acids. The reagent has ability to form stable chelates and can work in strongly acidic medium eliminating the chances of partial hydrolysis of metal ions to be determined. Its sensitivity due to color reaction is quite high (0.05–0.01 $\mu\text{g cm}^{-3}$ of the element). The high sensitivity and stability is coupled with a well-defined contrast in color transition from pinkish (reagent) to blue-green or raspberry-red (complex with Arsenazo III) (BASARGIN *et al.*, 2000). In this paper is described the spectrophotometric method for determination of europium using Arsenazo III as chromogenic reagent in buffer medium.

2. Material and methods

2.1 Chemicals and reagents

All used reagents were of analytical grade and were prepared in deionized water. Stock solution of Eu(III) with mass concentration $\underline{m} = 10.0 \pm 0.1 \text{ mg} \cdot \text{dm}^{-3}$ was prepared by appropriate dilution of standard solution (Fluka Analytical, Austria). 100 cm^3 of given solution was stabilized by addition of 0.5 cm^3 concentrated nitric acid (Merck, Germany). Stock solution of Arsenazo III (Fluka Analytical, Austria) with concentration 0.05% (w./v) was prepared by weighting and dissolution of appropriate amount of complexing agent in deionized water. Buffer solutions in the pH range from 2.20 to 4.00 were prepared by suitable mixing of diluted hydrochloric acid with molar concentration $c = 1 \text{ mol} \cdot \text{dm}^{-3}$ (Mikrochem, Slovakia) and solution of potassium hydrogen phthalate with molar concentration $c = 0.1 \text{ mol} \cdot \text{dm}^{-3}$ (Merck Millipore, Germany). Stock solutions of interfering cations and anions with given mass concentrations were prepared by appropriate dilution of their standard solutions (Merck, Germany).

2.2 Apparatus

A double wavelength/double beam spectrophotometer Cary WinUV 50 with 10 mm quartz rectangular cuvette (Varian Inc., Australia) was employed for the absorbance measurements. The pH of studied solutions and buffer solutions was measured and adjusted by pH-meter InoLab 730 (WTW GmbH, Germany). For the production of deionized water with specific conductivity $< 0.054 \mu\text{S} \cdot \text{cm}^{-1}$ was used ultrapure water system Simplicity 185 (Millipore, Germany).

2.3 Recommended procedure

Place the appropriate amount of pretreated sample containing $< 20 \mu\text{g}$ Eu(III) into 10 cm^3 volumetric flask, add 2 cm^3 of buffer solution with pH = 2.60 and 0.8 cm^3

of Arsenazo III solution; then fill with deionized water to mark and mix thoroughly. Measure the absorbance of this solution against the reagent blank at the wavelength 655 nm. Obtain the europium quantity from a calibration curve, which has been prepared with known amounts (0-20 μg) of europium. It is necessary to use technique of standard additions or technique of external calibration with matrix-matched standards in the case of existence of matrix effect.

3. Results and discussion

The absorption maximum of the complex between Eu(III) and Arsenazo III was observed at the wavelength 610 and 655 nm, respectively. The latter wavelength was used for the determination due to the lower absorbance of background and higher value of analytical signal of formed complex. The position of measured peak ($\lambda = 655 \text{ nm}$) was not affected by the value of pH in the range from 2.20 to 4.00 as shown in Fig. 1.

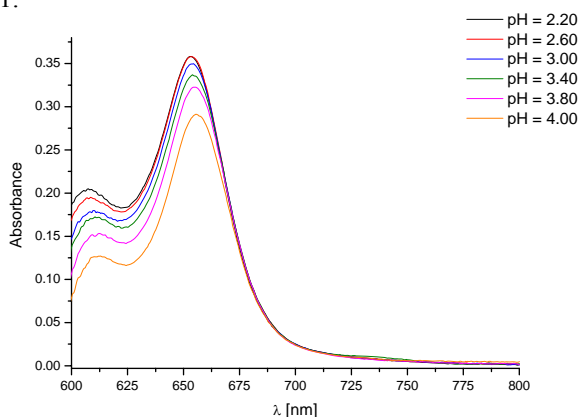


Fig. 1. Absorption spectra of Eu(III)-Arsenazo III complex at the pH value of solutions; blank corrected. $c \text{ Eu(III)} = 1 \text{ mg} \cdot \text{dm}^{-3}$; buffer solution $V = 2 \text{ cm}^3$, Arsenazo III solution $V = 1 \text{ cm}^3$.

The effect of buffer solution pH on the absorbance of relevant complex in the range from 2.20 to 4.00 has been investigated. It has been found out that the maximum absorbance for Eu(III)-Arsenazo III complex was occurred at pH = 2.60. On the basis of this finding, pH of measured solutions was adjusted to this value and used for subsequent measurements. The optimum volume of Arsenazo III, necessary for maximum absorbance, is represented by 0.8 cm^3 . The raspberry-red colour of formed complex develops instantaneously.

The validity of Beer's law was verified in the concentration range from 0 to 2 mg dm^{-3} Eu(III) (Fig. 2). However, beyond that, a deviation from the linearity was observed.

The molar extinction coefficient and Sandell's sensitivity of the complex were calculated from the regression equation and reached the value $\epsilon_{655} = 5.5 \pm 0.2 \cdot 10^4 \text{ cm}^{-1} \cdot \text{mol}^{-1} \cdot \text{dm}^3$ and $0.02 \mu\text{g cm}^{-2}$, respectively. Coefficient of determination R^2 was equal to 0.9952. Upper boundary of Beer's law validity was

established by application of QC parameter (VAN LOCO *et al.*, 2002). Results for determination of repeatability of measurement and trueness of measurement are given in Table 1. Trueness of measurement was verified by spike-recovery procedure.

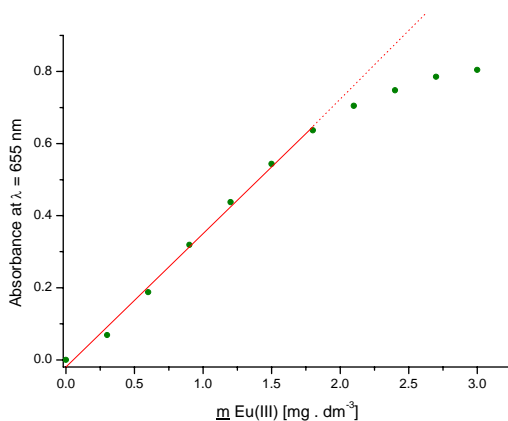


Fig. 2. Absorbance of Eu(III)-Arsenazo III complex as a function of europium mass concentration; blank corrected.

Table 1. Determination of repeatability and trueness for studied analytical procedure (n = 10).

\underline{m} Eu(III) [$\text{mg} \cdot \text{dm}^{-3}$]	apparent recovery [%]	relative standard deviation [%]
0.5	91.1	± 7.8
1.0	100.7	± 3.0
1.5	106.1	± 2.3

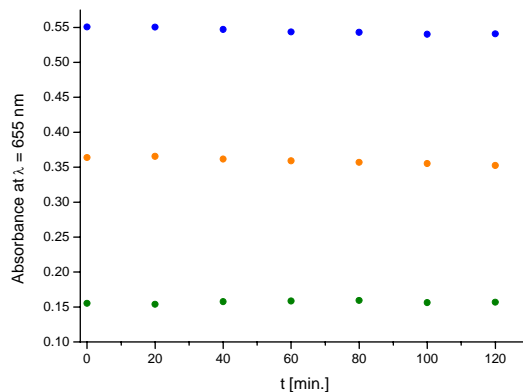


Fig. 2. Time dependence of absorbance for Eu(III)-Arsenazo III complex; blank corrected. (●) – 0.5 mg dm^{-3} ; (●) – 1.0 mg dm^{-3} ; (●) – 1.5 mg dm^{-3} .

The intercept of calibration line has proven to be statistically negligible against the hypothetical value 0 (significance level $\alpha = 0.05$). The Student *t*-test was used for this

purpose. Limit of detection calculated according to 3σ criterion reached the value $20.9 \mu\text{g} \cdot \text{dm}^{-3}$. The optical density was found constant within the linear range for 60 minutes under normal laboratory conditions (Fig. 2). A gradual decrease in the absorbance was then observed.

Composition of Eu(III)-Arsenazo III complex under presented experimental design, equal to 1:1, was established by mole ratio method (Fig. 3). Same results gained ROHWER and HOSTEN (1997).

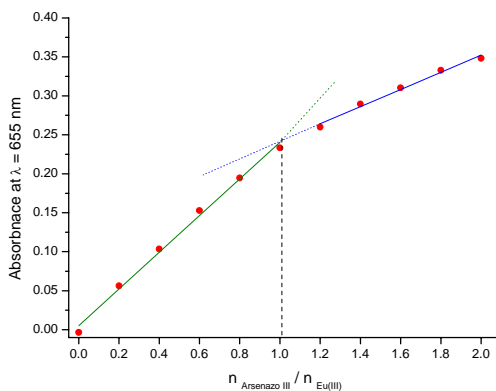


Fig. 3. Determination of Eu(III)-Arsenazo III composition by mole ratio method; blank corrected. $c_{\text{Eu(III)}} = 6.85 \mu\text{mol} \cdot \text{dm}^{-3}$.

The effect of selected ions on europium determination has been checked. The results are listed in Table 2. The mass concentration of Eu(III) was maintained at the level $\underline{m} = 1 \text{ mg} \cdot \text{dm}^{-3}$. The mass ratio between Eu(III) and studied cations and anions is given in relevant table. A $\pm 5\%$ variation in the absorbance is taken as tolerable limit within experimental error.

Table 2. Impact of selected cations and anions on the Eu(III) determination in model solutions.

anion	mass ratio	deviation [%]	cation	mass ratio	deviation [%]	cation	mass ratio	deviation [%]
EDTA ^c	1:15	-21.9	Ca(II) ^a	10:1	+0.1	Sr(III) ^b	10:1	+0.2
fluoride ^c	1:10	+0.8	Cu(II) ^b	10:1	+0.8	Th(IV) ^b	2:1	+26.0
phosphate ^c	1:10	+2.0	Fe(III) ^a	10:1	+2.5	U(VI) ^b	2:1	+24.1
sulphate ^c	1:10	+2.2	La(III) ^b	10:1	+13.2			
oxalate ^e	1:10	-2.7	Mg(II) ^a	2:1	+1.1			
tartrate ^d	1:10	+1.4	Sm(III) ^a	10:1	+11.0			

^a as chloride, ^b as nitrate, ^c as sodium salt, ^d as acid, ^e as ammonium salt.

Results indicate that La(III), Sm(III), Th(IV), U(VI) cations and EDTA anion interfere seriously. All interfering ions, except EDTA, have increased the absorbance. Cation-exchange resin, for example AG50W-X8 (STRELOW, 1980) should be applied for removal of above mentioned interfering ions from matrix of real sample containing analyte of interest.

4. Conclusions

Simple, sensitive and fast spectrophotometric procedure has been developed for determining Eu(III) using Arsenazo III as chromogenic reagent. A calibration curve was linear over the range up to $2.0 \text{ mg} \cdot \text{dm}^{-3}$ Eu(III) and the limit of detection reached the value $20.9 \text{ } \mu\text{g} \cdot \text{dm}^{-3}$. Elements from the lanthanide and actinide family interfere seriously and should be removed. The method is applicable for europium determination in ores and water with reasonable accuracy, but it is necessary to use proper type of cation-exchange resins or another type of separation technique.

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