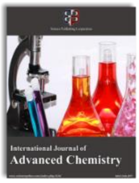
International Journal of Advanced Chemistry, 7 (1) (2019) 26-34

International Journal of Advanced Chemistry

Website: www.sciencepubco.com/index.php/IJAC

Research paper



Estimation of samarium in nuclear fuel reprocessing streams by fiber optic aided spectrophotometry

S.Ganesh[1]*, N.K.Pandey[1]

[1]Reprocessing Group, Indira Gandhi centre for Atomic Research, Kalpakkam 603102
**Corresponding author E-mail:nkpandey@igcar.gov.in*

Abstract

A simple analytical procedure is developed and validated for the estimation of traces amount of samarium in aqueous streams of nuclear waste. In this method, the formation of chelation of samarium ion with 3, 6-bis [(2-Arsonophenyl) azo]-4,5dihydroxy-2,7-naphtalene disulphonic acid (Arsenazo III) to produce a reddish purple colour complex which has maximum absorption at 654 nm at pH 2.6-2.8. The intensity of the colour is proportional to the amount of Sm(III). Linear calibration graphs were obtained for 0.31 to 2.78 µg/mL of Sm(III) with a relative standard deviation (RSD) of 1.32 % and correlation coefficient of R2 = 0.999 (n=10). Its molar absorptivity and Sandell's sensitivity are found to be 4.88x104 L.Mol-1.cm-1 and 2.05x10-5 µg/cm2 respectively. The stoichiometric composition of the chelate is 1:1. The reaction is instantaneous, and absorbance remains stable for over 24 hrs. The system allowed for the determination of samarium with a limit of detection (LOD) (3.3σ/S) of 0.314 µg/mL, the limit of quantitation (LOQ) (10σ/S) of 0.952 µg/mL. A systematic study of the influence of different parameters like pH, the concentration of the complexing agent, the stability of the colour, the volume of the buffer and interference of other competing metal ions. Results of the present method are in good agreement with those obtained by the standard procedure. It is directly applicable for the determination of samarium in environmental, industrial, water and waste streams of the nuclear plant.

Keywords: *Samarium; Arsenazo III; Spectrophotometry; Molar Absorptivity.*

1. Introduction

Trivalent lanthanides and actinides exhibit similar chemical behaviour are the same in solid and aqueous phase under PUREX process conditions. The lanthanides particularly Nd, Sm and Eu have almost identical ionic radii with actinides such as Am and Cm in the M(III) oxidation state. The significant advantages of the lanthanides are non-radioactive and can handle without special safety precautions even at higher concentrations. Samarium has familiar in the nuclear industry (soluble neutron poison and control rod) [1], and its oxide is used mainly as shielding and fluxing devices. Criticality is a significant challenging issue to be addressed at each stage of the reprocessing of high plutonium content spent fuel from the Fast Breeder Reactor [2]. Generally, the criticality safety precautions are taken by either controlling the geometry of equipment, mass or concentration of plutonium or combination of both may use. It is found to be the best possible choice as soluble neutron poison due to its high neutron absorption cross-section, adequately high solubility in nitric acid and chemical compatibility in the PUREX solvent extraction process conditions. For the determination of Sm(III), inductively coupled plasma mass spectrometry [3], inductively coupled plasma mass and atomic emission spectrometry [4], polarography [5], radiochemical [6], voltammetry [7], neutron activation analysis [8], potentiometry [9] and spectrophotometry [10-22] are available in the literature. Most of the methods required costly equipment and needs special care during the analysis. Therefore, a simple, fast and reliable based on the colour formation of Arsenazo III and samarium, describes the development of an analytical procedure for the determination of samarium without sacrificing precision. It is adaptable for on-site or at-line monitoring.

2. Experimental

2.1. Instrumentation

Indigenously developed fibre optic aided spectrophotometer coupled with the dip type probe has 1 cm path length was employed for measurement of absorbance. pH/mV meter coupled with the glass electrode was used for pH measurements of studied solutions and buffer solutions from Chemlabs, Bangalore, make Micro-07. For the production of deionised water with specific conductivity < 0.054 μScm^{-1} was used pure water system from MilliQ, India.

2.2. Chemicals and reagents

All the chemical and reagents used in the present study were of analytical grade. Stock solution of samarium (III) nitrate of 99.9% purity (obtained from M/s Alfa Aesar Chemicals) were prepared and standardised by EDTA titration using xylenol orange as an indicator [16]. From this stock solution, different concentrations of samarium standards are made with proper dilution. Prepared the buffer solution of pH 2.6-2.8 by dissolving 28.5 g of mono chloroacetic acid and 12.3 g of sodium acetate together in 500 mL of double distilled water. 0.05% of Arsenazo (III) (obtained from Merck, India) solution is prepared in distilled water. EDTA stock solution (0.01W/v) made by 10 mg of ACS grade of disodium dihydrogen ethylenediamine tetraacetate dehydrate in 100 mL of distilled water.

2.3. Developed procedure

To suitable aliquots of Sm(III) (0.1-3.0 µg) solution, 0.5 mL of 0.2% Arsenazo III solution and 1.0 mL of the buffer solution with pH 2.8 was added to each flask and made up to 10 mL standard flasks with double distilled water and the absorption spectrum was recorded from 700-380 nm against a reagent blank prepared.

3. Results and discussion

Free Arsenazo III molecule (Fig. 1a), is symmetrical and both the chromophore systems are identical resulting in only one absorption band due to coincident absorption spectra. The appearance of two absorption bands in the complex of Arsenazo III with Sm(III) ions is indicative of a symmetry breakdown in the complex molecule (Fig. 1b). The fact that these two peaks correspond to two electronic transitions in the same molecule is indicated by their simultaneous decrease upon successive additions of samarium in the solution. The absorption band in the curve at 538 nm due to free Arsenazo III disappears on the adding up of Sm(III) solution, and two sharp peaks at 610 nm and 654 nm appear, which are characteristic of Arsenazo III–Sm(III) complex is represented in Table 1.

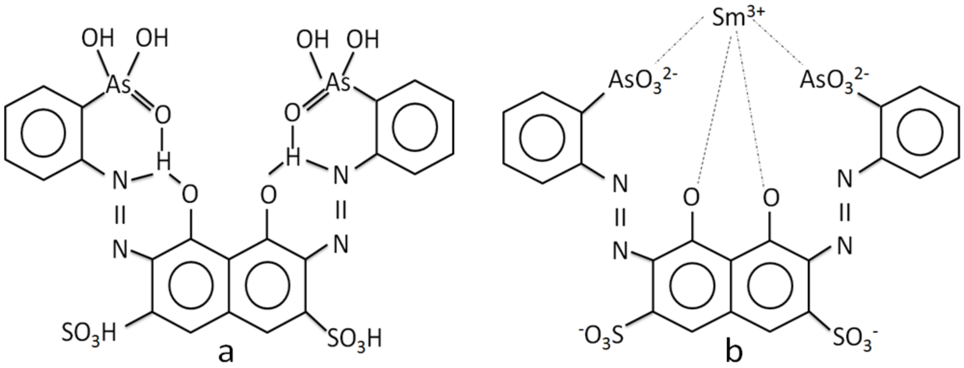


Fig. 1: Structure of Arsenazo III in (A) Uncomplexed and (B) Complexed with Sm^{3+} [22].

Table 1: Spectral Characteristics of Sm-AR III Complex

Parameter	Sm-Arsenazo III complex	
λ max, (nm)	654	610
Beer's law limit ((µg/mL)	0.31-2.768	0.53-4.76
Molar absorptivity, ($L.Mol^{-1}.cm^{-1}$)	$4.88x 10^4$	$2.84x 10^4$
Sandell's sensitivity ($µg/cm^2$)	2.05×10^{-5}	3.52×10^{-5}
Detection Limit (µg/mL)	0.314	0.393
Quantitation Limit (µg/mL)	0.952	1.192
Regression equation	Y=0.327x	Y=0.193x
Correlation coefficient (r)	0.9993	0.996
Linear Range (µg/mL)	0.31-2.78	0.52-4.76
Stability formation region (pH)	2.6-2.8	2.6-2.8
Monochloro acetic acid & sodium acetate buffer (mL)	1	1
Arsenazo III (0.05%) (mL)	0.5	0.5

3.1. Spectral characteristics

Arsenazo III forms a stable reddish purple colour complex with Sm(III) in the aqueous medium at pH 2.6-2.8. The complex is stable for 24 hours. Fig. 2, which shows the typical absorption spectrum is a symmetric curve with maximum absorbance at λmax = 654 nm against a reagent blank.

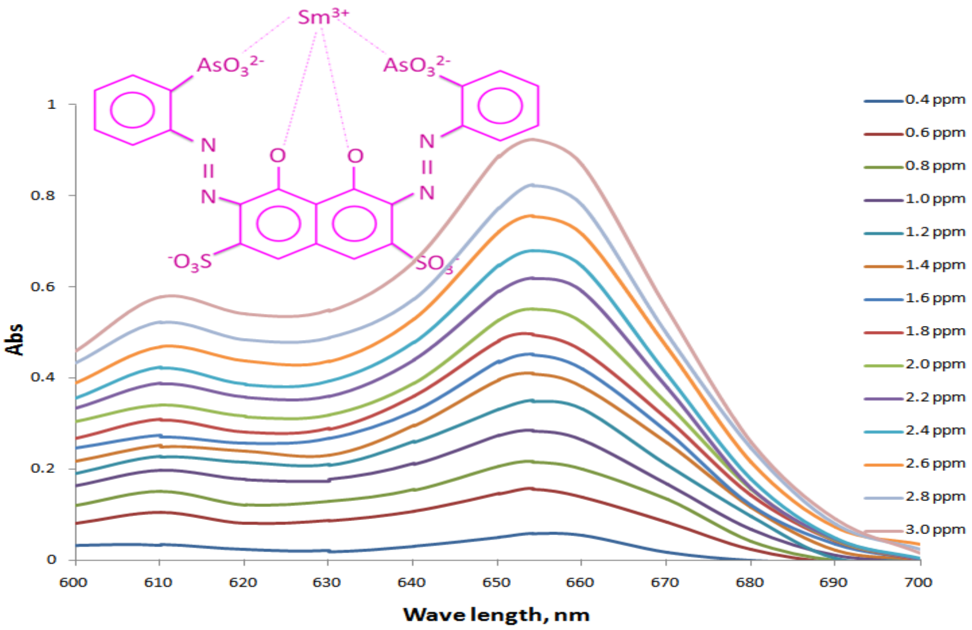


Fig. 2: Typical Absorption Spectrum of Sm(III)-Arsenazo III Complex at the Ph 2.6-2.8 Solutions; Blank Corrected. Buffer Solution V = 1 Ml, Arsenazo III Solution V = 0.5 Ml, [Sm(III)] = 0.2-3 µg/Ml.

3.2. Calibration graph, beer's law and sensitivity

A calibration curve is made with fixed concentrations of Arsenazo III (0.5 mL, 0.2%) and variable concentrations of Sm(III) (0.31-2.78 µg/mL) (in presence of buffer pH = 2.8, 1 mL) at 654 and 610 nm and given in Fig.3. At these wavelengths, the system obeys Lambert-Beer's law in the concentration range of 0.31-2.78 µg/mL for 654 nm and 0.53-4.76 µg/mL for 610 nm. Fitting of the obtained data gives a linear regression equation at 654±0.5 nm obtained was: A = 0.327 x C, Sm (µg/mL), with a good correlation coefficient (R^2) equals 0.999. The slope of the relation verifies Beer's law in the equation mentioned above and gives the molar absorptivity (ε). Since the sensitivity of the spectrophotometric method is often expressed in terms of the expression 'sensitivity index' given by Sandell [23], the sensitivity of the present method for determining samarium (atomic mass: 150.36 g.mole^{-1}, λ_{max} of 654±0.5 nm)in the aqueous medium. The molar absorptivity and Sandell's sensitivity (concentration for 0.001 absorbance unit) are found to equal $4.88\pm0.2\times10^4$ L.Mole^{-1}.cm^{-1} and 2.05x10^{-5} µg.cm^{-2} respectively. To detect the optimum concentration ranges for maximum precision employ the Ringbom's plot [24]. The transmittance plotted against the logarithm of metal concentration. The linear portion of the curve indicates that the range was 0.1 to 0.5 ppm of Sm(III) (Fig.4) and slope of Ringbom's plot was 0.483.

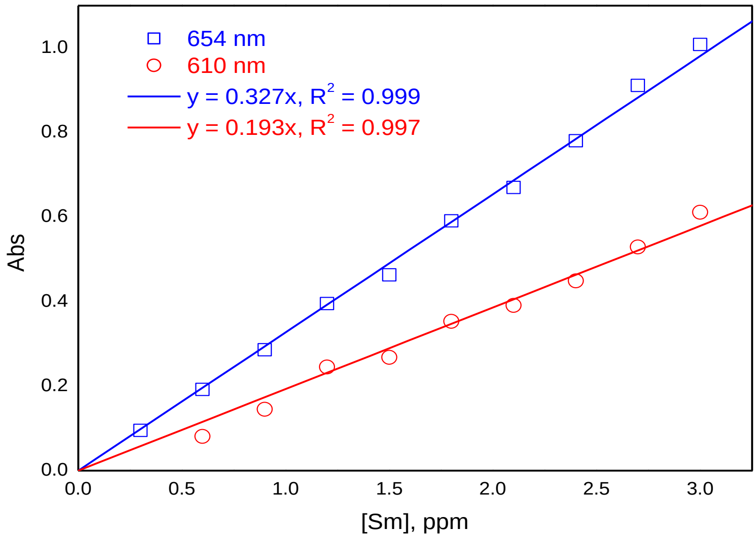


Fig. 3: Typical Calibration Graph For Determination of Sm (III) Nitrate with Arsenazo III at 654 and 610 Nm, Blank Corrected. Buffer Solution V = 1 Ml, Arsenazo III Solution V = 0.5 Ml, [Sm (III)] = 0.2-3 µg/Ml.

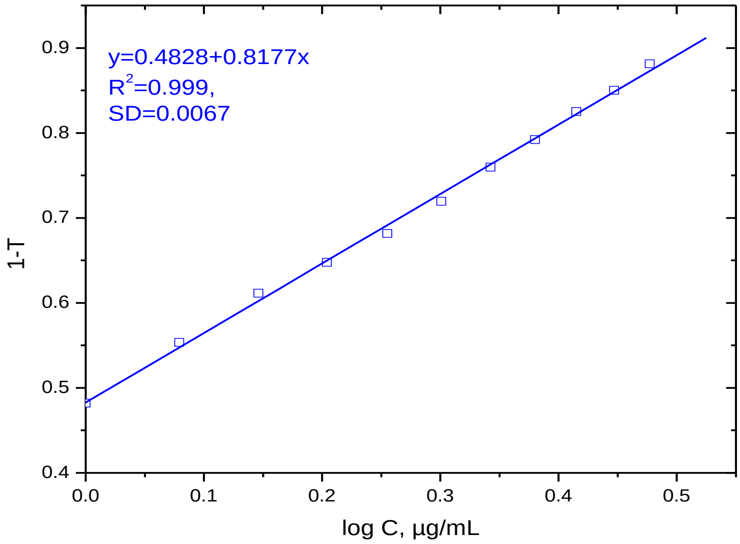


Fig. 4: Ringbom'sPlot for Determination of Sm(III) Nitrate with Arsenazo III at 654, Blank Corrected. Buffer Solution V = 1 Ml, Arsenazo III Solution V = 0.5 Ml, [Sm(III)] = 0.2-3 µg/Ml.

3.3. Effect of buffer solutions

Fig 5 shows the influence of the concentration of the buffer solution on the absorbance of Sm(III)-Arsenazo III complex. And there is a considerable effect of the buffer solution on the system. 1 mL of a buffer solution is sufficient for maximum absorbance. No significant change observed if more than one mL. Thus, 1 mL of buffer solution is adequate for all studies.

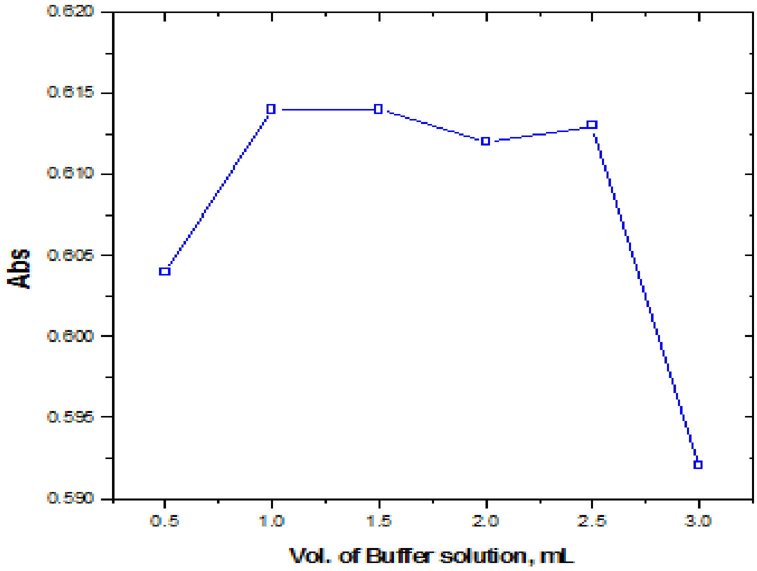


Fig. 5: Effect of Volume of Buffer Solution on the Absorbance of Samarium Estimation at 654 Nm, Blank Corrected. Buffer Solution V = 1 Ml, Arsenazo III Solution V = 0.5-3 Ml, [Sm(III)] = 2 µg/Ml.

3.4. Effect of pH solution

The pH of the solution has a significant influence on the absorbance of the Sm (III)-Arsenazo III Complex. To vary the pH of the reaction mixture was varied from 2 to 12 and the absorbance was found to be maximum, in the pH range 2.8 (Fig.6). Hence pH 2.8 was found to be most suitable for maintaining pH and mono chloroacetic acid /sodium acetate buffer solution employed as optimum for all subsequent work.

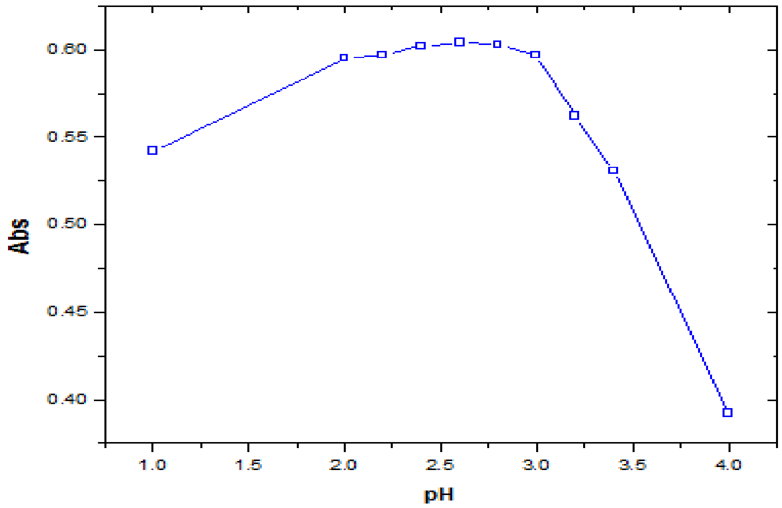


Fig. 6: Effect of Volume of Ph Solution on the Absorbance of Samarium Estimation at 654 Nm, Blank Corrected. Buffer Solution V = 1 Ml, Arsenazo III Solution V = 0.5-3 Ml, [Sm(III)] = 2 µg/Ml.

3.5. Effect of arsenazo III dye concentration

The study of Arsenazo III dye concentration was essential for the optimum complex formation and its stability. In general dye concentration, less or higher than the required amount, would cause deviation from Beer’s law and overlapping of dye spectra with other ion-dye complexes. To optimise the 0.2% Arsenazo III, a series of the solution containing fixed Sm(III) concentration, fixed buffer solution and different volume of Arsenazo III from 0.1 to 1 mL to form Sm(III)-Arsenazo III complex at pH 2.8. From Fig. 7, it indicates that the maximum absorbance was the most obvious when adding one mL dye at 654 nm, once it exceeds this volume, absorbance would remain constant. So one mL of Arsenazo III is favourable and used in subsequent experiments.

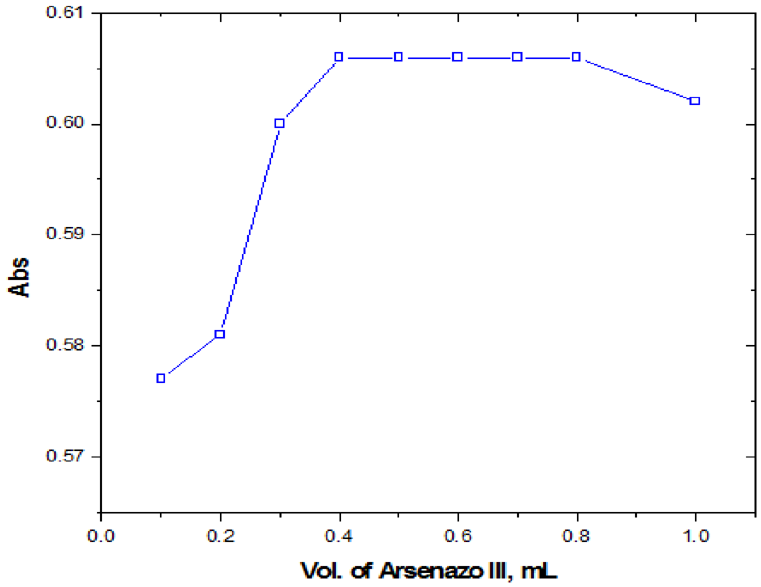


Fig. 7: Effect of Arsenazo III on the Absorbance of Samarium Estimation at 654 Nm, Blank Corrected. Buffer Solution V = 1 Ml, Arsenazo III Solution V = 0.5-3 Ml, [Sm (III)] = 2 µg/Ml.

3.6. Stability

The formation of the coloured complex of Sm(III) with Arsenazo III was instantaneous. Measurement of the absorbance was carried out immediately after mixing the Sm(III) and Arsenazo III, and the complex was found to be stable for 24 hours (Fig. 8). Freshly prepared buffer solution used for the measurement of absorbance.

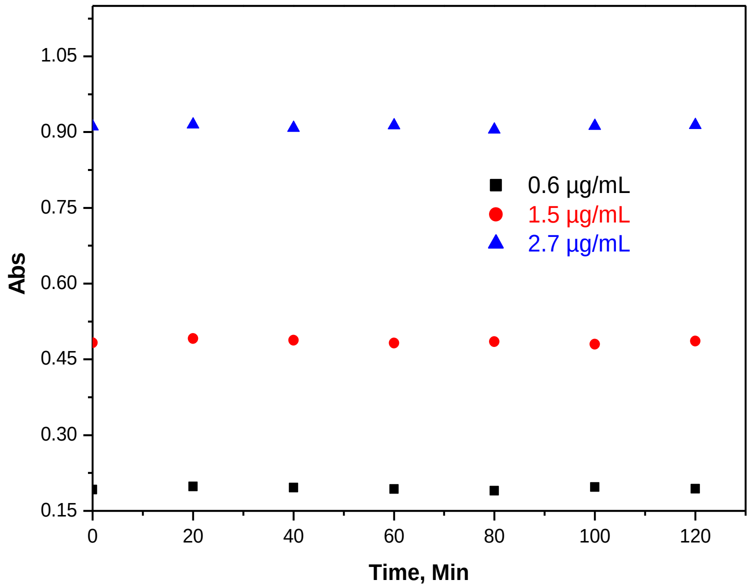


Fig. 8: Time Dependence of Absorbance for Sm(III)-Arsenazo III Complex; Blank Corrected. (●) – 0.6 µg/Ml; (●) – 1.0 µg/Ml; (●) – 2.7 µg/Ml.

3.7. Composition of the complex

To investigate the composition of Sm(III)-Arsenazo (III) using the mole ratio method [25] and Job's method of continuous variation [26]. In the mole ratio method (Fig.9) a break was observed when the Sm(III)-Arsenazo(III) ratio was 1:1, indicating an ML type complex formation. The plot of Job's method also confirms the same pattern of an ML type composition of the complex which represented in Fig. 10.

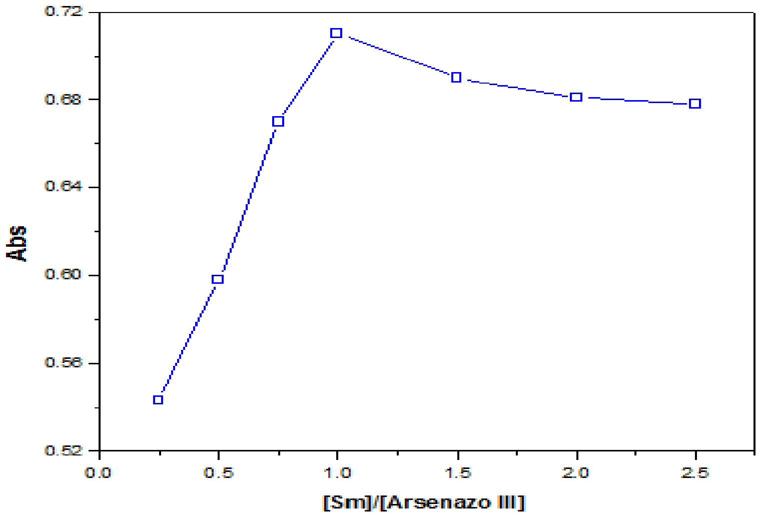


Fig. 9: Mole Ratio Method.

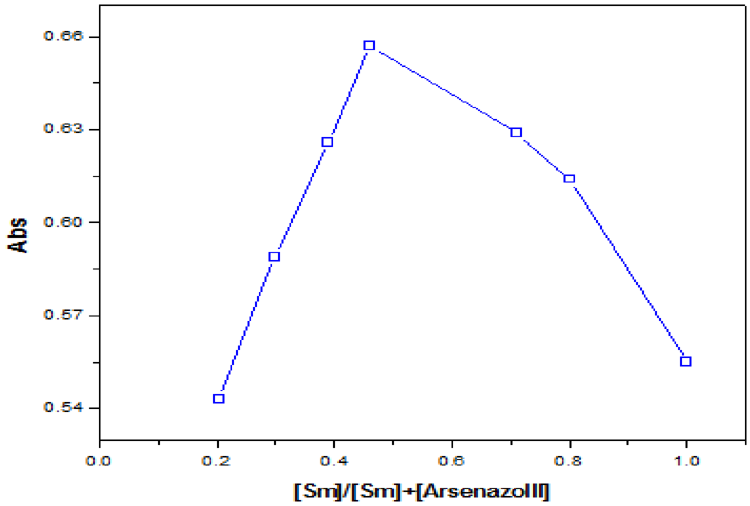


Fig. 10: Job's Continuous Variation Method.

3.8. Effect of foreign ions

To investigate the influence of various metal ions in the present method by complexation or ion exchange separation process. It is no selective, but minimum interference leading to improved selectivity using complexation and results compiled in Table 2. The most severe interferences were from Nd(III) ions. Interference from those ions is probably due to complex with arsenazo (III). To achieve the higher tolerance limits of trivalent metal ions by using several masking agents such as 1% tartaric acid, 1% citric acid, 0.5% EDTA, 1% thiocyanate and thiourea. During the interference studies, any precipitate formed was removed by centrifugation. Interference from these metal ions Eu(III), La(III), Nd(III), Y(III) and U(VI) have been removed by a short single-step ion-exchange separation process using cation-exchange resin (ex) AG50 W-X8 [27].

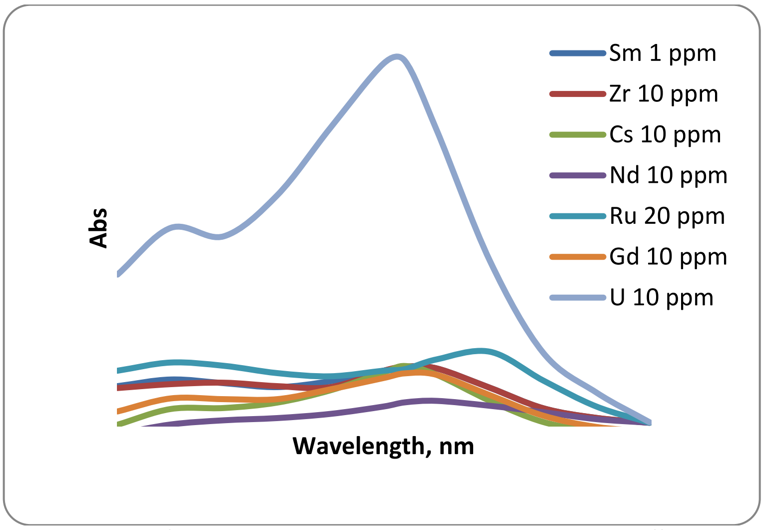


Fig. 10: Effect of Arsenazo III on the Absorbance of Samarium Estimation at 654 Nm, Blank Corrected. Buffer Solution V = 1 Ml, Arsenazo III Solution V = 0.5-3 Ml, [Sm(III)] = 2 µg/Ml.

Table 2: Interference of Metal Ions during the Determination of Samarium

Interference of metal ions		Concentration of Samarium (µg/mL)		% error
Metal	Conc. Taken (µg/mL)	Taken	Obtained	
$CsNO_3$	10	0.725	9.398	1.34
$Zr(NO_3)_4$	10	0.725	9.351	0.130
$UO_2(NO_3)_2$	10	0.725	9.378	514.01
$Gd(NO_3)_3$	10	0.725	8.744	11.45
$Nd(NO_3)_3$	10	0.725	8.492	61.48
Ru(III)	10	0.725	Peak shifted	-
$Y(NO_3)_3$	10	0.725	7.834	17.3

Masked with 1 mL 1% aqueous thiocyanate solution, Anions are effectively masked by the addition of 0.3 mL 0.5% EDTA, ii. Eu(III), La(III), U(VI) interfering ions are effectively separated by convenient type cation -exchange resin (ex) AG50 W-X8.

3.9. Removal of arsenazo III

Chromogenic reagents create the main problems associated with the treatment of chemical and radiochemical laboratories. So disposal of waste required special treatment. Arsenazo III is hazardous and contains arsenic, which is a very toxic element. It was used in acidic medium and widely applicable for the determination of many metal ions. Arsenazo based analytical waste generated during the estimation of samarium, which introduced a new toxic metal ion like arsenic and acidic medium. After analysis, the waste solution was passed through the activated charcoal column for removal of arsenazo III from the waste solution [28].

4. Validation of the proposed procedure

To validate the developed procedure under the experimental conditions by the guidelines from the international conference for Harmonization (ICH) [29] like linearity, accuracy, precision and specificity.

4.1. Precision and accuracy

To evaluate the accuracy and precision of the present method by determining different concentration levels of samarium (each analysis replicate at least five times). The relative standard deviation (n = 5) was 1.32% for 0.5 to 500 µg of samarium in 10 mL, indicating that this method is highly precise and reproducible. Five sample solutions of each concentration were analyzed under the same experimental conditions within one day (intra day precision) and in five consecutive days (inter day precision). The % RSD and data summarised in Table.3. Hence, the precision and accuracy of the method were found to be excellent.

Table 3: Accuracy and Precision of Proposed Method

Parameters	Intraday assay			Inter day assay		
[Sm] taken, ppm	1	1.5	2.8	1	1.5	2.8
[Sm] found, ppm	0.991	1.499	2.808	1.008	1.509	2.746
Standard deviation* (SD), ppm	0.006	0.008	0.037	0.158	0.195	0.271

RSD (%)	0.604	0.532	1.315	1.06	0.898	0.46
Standard analytical error (%)	0.084	0.078	0.12	0.105	0.071	0.121
Confidence limit#						0.333

*Mean for five independent determinations.

Confidence limit at 95% confidence level and four degree of freedom (t=2.776).

4.2. Detection limit and quantitation limit

The detection limit has been calculated as ($3.3\sigma/S$), where σ denotes the standard deviation for blank (n=10) and S stands for the slope of the analytical curve from the calibration graph. The limit of detection (LOD) was found to be 0.314 µg/mL, whereas the limit of quantitation (LOQ) ($10\sigma/S$) was 0.952 µg/mL with precision (was evaluated by determination of the different concentration of samarium) expressed as relative standard deviation (RSD) of 1.32%. The obtained results indicate that this method is highly precise and reproducible. Calculations were made the recommendations by IUPAC [30]. The best agreement between theoretically computed and practically verified values of LOD and LOQ was approached namely at significance level $\alpha = 0.05$.

4.3. Robustness and ruggedness

To examine the robustness of the developed procedure by the influence of a small variation like the concentration of analytical reagent and the pH of the solution. It showed that a slight difference in these variables did not affect the procedure significantly. The ruggedness was tested by applying the proposed method of analysis of samarium under the same experimental conditions by two different analysts. Results obtained from inter-day RSD and within-day RSD were found to be reproducible and between 0.45 and 1.32% (Table.4).

Table 4: Reproducibility of the Method by Two Different Analysts

	[Sm], ppm		% RSD
	Taken	Obtained	
Analyst 1	1.2	1.216	0.85
Analyst 2	1.2	1.197	
Analyst 1	0.44	0.447	0.45
Analyst 2	0.44	0.413	

4.4. Range and linearity

The precision and accuracy of the method were tested by taking known two different trace amounts of samarium. As shown in table 5, mean values were obtained with Student's t-values at 95% confidence level and the variance ratio F-values calculated (p=0.05) for 5 degrees of freedom. The results showed comparable accuracy (t-test) and precision (F-test) and did not exceed the theoretical values, indicating that there was no significant difference in accuracy and precision. The performance of the proposed method was verified with other existing UV-Vis spectrophotometric method using Chrome azurol S as chromogenic reagent reported in the literature [13].It is clear from table 5 that the calculated t value is less than the tabulated t value at the 95% confidence level for four degrees of freedom is 2.776. Therefore, $t_{cal} < t_{table}$, and there is no significant difference between the two methods at this confidence level. The proposed method is simple and requires less time to complete the analysis. The proposed procedure is simple, fast, less time, versatile, accurate and useful due to high tolerance limits from cations and anions.

Table 5: Evaluation Data of Accuracy and Precision Calculation for Sm-Arsenazo III Complex

	Variable 1		Variable 2	
	Present Method	Reference Method[13]	Present Method	Reference Method[13]
Mean	1.852	1.848	2.402	2.406
Standard Deviation	0.0193	0.022	0.0192	0.0358
Variance	0.00037	0.0004	0.0004	0.0013
RSD	1.041	1.164	0.8008	1.488
Degree of freedom	4	4	4	4
f-Test cal	1.256		1.661	
f-Test table	2.298			
p (Probability)	0.05		0.05	
$f_{cal} < f_{table}$	No significant different		No significant different	
Confidence level	95%		95%	
t-Test cal	0.99		1.859	
t-Test table	2.228		2.228	
$t_{cal} < t_{table}$	No significant different		No significant different	

5. Applications

To utilize the proposed method for the determination of samarium concentration during the solvent extraction behaviour of it with the TBP-HNO_3 system at conditions prevalent in FBR fuel reprocessing. Figure 11 is the schematic diagram of at-line monitoring setup. A suitable aliquot of Sm(III) sample was put into the reactor, which is mixed thoroughly with the continuous flow of buffer and arsenazo III solutions. Both solutions were allowed continuously through the isocratic pump with a flow rate of 0.5 ml/min. A dip type probe inserted into the column and consistently run the spectrum of the colour complex of Sm-Arsenazo III. During this exercise, the arsenazo III based analytical waste generated. This waste processed separately passed through the activated carbon and removed the arsenazo based complex and sent back to the process streams.

6. Conclusions

The developed method for the determination of Sm(III) ions in the aqueous medium is simple, sensitive, selective and applicable for all the range of nitric acid and heavy metal ion concentration relevant to PUREX process for continuous monitoring. The accuracy and selectivity concerning relative standard deviation of the present method are reliable for the determination of samarium in real samples to microgram levels in the aqueous medium at room temperature (25 ± 5)^{oC}. The obtained results by the developed procedure compared with those derived from neutron activation analysis method [8] and one more spectrophotometry [13]. The results are found to be a good agreement. The removal of arsenazo (III) is 98%. It also applicable for at-line monitoring of samarium

References

[1] Natarajan, R., (2017), Reprocessing of spent nuclear fuel in India: Present challenges and future programme, *Progress in Nucl. Energy*, 101, pp. 118-132. https://doi.org/10.1016/j.pnucene.2017.03.001.

[2] Ganesh, S., Desigan, N., Pandey, N.K., Mallika, C., KamachiMudali, U., (2017), Extraction studies of gadolinium relevant to its use as neutron poison in the PUREX process, *Progress in Nucl. Energy*, 98, pp 234-238. https://doi.org/10.1016/j.pnucene.2017.03.027.

[3] Li, B., Sun, Y., Yin, J., (1996), Determination of cerium, neodymium and samarium in biological materials at low levels by isotope dilution inductively coupled plasma mass spectrometry, *J. Anal. Atomic Spectrometry*, 14(12), pp1843-1848. https://doi.org/10.1039/a905346h.

[4] Paama, L., Pamoja, E., Must, M., Peramaki, P., (2001), Optimal conditions for europium and samarium determination in cathodoluminophors by inductively coupled plasma atomic emission spectrometry, *J. Anal. Atomic Spectrometry*, 16(11), pp1333-1336.

[5] T.M. Florence, L.E. Smythe, (1960), Polarographic determination of lanthanides by means of azo dye stuffs, U. S. At. Energy Comm, TID-7606, p. 14.

[6] R.G. Monk, J. Herrington, (1961), Microchemical methods in radiochemical analysis, *Anal. Chim. Acta*, 24, pp. 481. https://doi.org/10.1016/0003-2670(61)80100-1.

[7] M. Servigne, Detection and micro chemical determination of rare elements by luminescence, (1940), *Bull. Soc. Chim. Biol*, 7, pp. 121

[8] Orvini, E., Speziali, M., Salvini, A., Herbog, C. (2000), *Microchem. J*, 67, pp.97-104. https://doi.org/10.1016/S0026-265X(00)00104-1.

[9] Gupta, V.K., Goyal, R.N., Sharma, R.A. (2009), *Anal.Chimica Acta*, 647, pp 66-71. https://doi.org/10.1016/j.aca.2009.05.031.

[10] Pushpa Ratre, P., Devendra Kumar, (2001), Spectrophotoemtric determination of trace amounts of samarium in environmental samples, *Am. Int. J. Res. In formal, applied & Natural Science*, 3(1), pp 110-118.

[11] Mathew, A.V., Kumar, K., Rao, I.M., Satyanarayana A, and Shyamala, P., (2012) Spectrophotometric determination of neodymium (III), Samarium (III) in micellar medium - An alternative to solvent extraction procedures., *Indian J. Chem. Tech*, 19, pp. 331-336.

[12] Dey, A.K., and Munshi, N.K., (1971), Spectrophotometric determination of lanthanides using 4-(2-Pyridyl azo) resorcinol, *Microchimica acta*, 59, pp 751-756. https://doi.org/10.1007/BF01217100.

[13] Soyalk, M., Orhan, T., (2000), Spectrophotometric determination of samarium (III) with chrome azurol s in the presence of cetylpyridinium chloride, *Talanta*, 53, pp 125-129. https://doi.org/10.1016/S0039-9140(00)00386-6.

[14] Ujrovcik, J., and Leny, J. (2014), Extractive spectrophotometric determination of samarium with chlorophosphonaso III, *Acta TechnicaJourinensis*, 7(1), pp 62-70. https://doi.org/10.14513/actatechjaur.v7.n1.218.

[15] Mohammed, M.T., Hafezand and Zaki, M, (1986) Application of 8-hydroxyquinoline sulfonic acid in the spectrophotometric determination of some lanthanides, *Microchem, J*., 34, pp.258-261. https://doi.org/10.1016/0026-265X(86)90118-9.

[16] Agrawal, Y.K., and Thomaskutty, P.T., (1987), Separation and micro determination of rare earth metals with N-phenylbenzohydroxamic acid and xylenol orange", *J. Radioanal. Nu. Chem*., 116, pp.365-374. https://doi.org/10.1007/BF02035781.

[17] Alaa, A., and Ibrahim, A.S., (2010), Complexation and spectrophotometric study of samarium (III) using pyrimidine azo derivatives in the presence of cetyltrimethyl ammonium bromide, *Anal.Lett*. 43, pp2598-2608. https://doi.org/10.1080/00032711003726910.

[18] Gadzhieva, S.R., Chyragov, F.M., and Guseinov, F.E., (2005), Spectrophotometric study of the complexation of samarium (III) with disodium 2-(2-hydroxy-3-sulpho-5-nitrophenylazo)naphthalene-1,8-dihydroxy-3-6-disulphonate in the presence of cetyltrimethylammonium bromide, *J.Anal.Chem*, 60, pp 819-821. https://doi.org/10.1007/s10809-005-0188-5.

[19] Dik, T.A., Kostyuk, N.N., and Trebnikov, A.G., (2003), Spectrophotometric determination of Sm(III) content in hydrochloric acid solution, *J. Appl. Spectro*., 70, pp 729-732. https://doi.org/10.1023/B:JAPS.0000008870.62153.93.

[20] Shah, V.L., and Sancal, S.P., (1969), A spectrophotometric study of the chelates of chromotrope 2R with praseodymium, neodymium, samarium and europium, *Microchem. J*., 14, pp 261-270. https://doi.org/10.1016/0026-265X(69)90041-1.

[21] Bhagavathy V., Prasada Rao, T., Dhamodaran, A.D., (1988), Third order derivate molecular absorption spectrophotometric determination of traces of samarium with methyl thymol blue-CTAB or CPB, *Anal Letters*., vol. 21(5), pp.901-920. https://doi.org/10.1080/00032718808070868.

[22] Savvin, B., (1964), Analytical applications of arsenazo III-the mechanism of complex formation between arsenazo III and certain elements, *Talanta*, 11, pp.7-13. https://doi.org/10.1016/0039-9140(64)80004-7.

[23] Sandell, E.B., (1950), Colorimetric determination of traces of metal. Chapter III, 2nd Edition, Interscience publishers, New York.

[24] Ringbom, A.Z., (1938), *Anal Chem*., 115, 332. https://doi.org/10.1007/BF01753937.

[25] Yoe, J.H., Jones, A.L., (1994), *Ind.Eng.Chem.Anal.Ed*. 16, pp. 111

[26] Job, P., Job plot, (1928), *Ann Chim*., 9, pp 113-203.

[27] Strelow, F.W.E., (1980), *Anal. Chim. Acta*, 120, pp.249-254. https://doi.org/10.1016/S0003-2670(01)84368-3.

[28] Ahmed, I.M., Aglan, R.F., Hamed, M.M., (2017), Removal of Arsenazo III and thorin from radioactive waste solutions by adsorption onto low-cost adsorbent, *J.Radioanal.Nucl.Chem*. 314, pp 2253-2262. https://doi.org/10.1007/s10967-017-5586-2.

[29] Currie, L.A., (1995), Nomenclature in evaluation of analytical methods including detection and quantification capabilities, IUPAC recommendations, *Pure and applied chem*. 67(10), pp 1699-1723. https://doi.org/10.1351/pac199567101699.

[30] IUPAC: Analytical chemistry Division, (1978), *Spectrochimica Acta*. 33, pp. 242.