# Spectrophotometric Determination of Cerium (III) with Arsenazo III: Application to Sea Water and Synthetic Alloys

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#### **ABSTRACT**

The detailed investigation of a sensitive and selective spectrophotometric method for the determination of trace amounts of cerium is described. The method is based on the reaction of cerium(III) with arsenazo III in the presence of sodium dodecyl sulphate surfactant at pH 3.0 to form a blue-greenish coloured chelate absorbing maximum at 653 nm. Beer's law is obeyed over the range  $(5-70) \mu g/25 ml$ , with a molar absorptivity of  $(4.99\times10^4) l.mol^{-1}.cm^{-1}$  and the coefficient of determination  $(r^2)$  is 0.9994, Sandell's sensitivity index is  $(28.08\times10^{-4}) \mu g.cm^{-2}$ , a relative error of (0.0-0.2%) and a relative standard deviation of (0.0) to +2.1%, depending on the concentration levels in the calibration curve. The method has been applied successfully to determine cerium in sea water and some synthetic alloys.

**Keywords**: Ce(III) determination; Arsenazo III reagent; Sodium dodecyl sulphate; Spectrophotometry.

3.0

653

%(+2.1-0)

#### INTRODUCTION

Cerium is the most abundant rare earth element, and is a silvery metal, belonging to the lanthanide group. Cerium is especially interesting because of its variable electronic structure. It tarnishes slowly in air and burns readily at 150°C to form cerium oxide. Cerium is quite electropositive and reacts slowly with cold water and quite quickly with hot water to form cerium hydroxide (Internet, 2009).

Cerium (III) chloride is used to facilitate reactions of carbonyl groups in organic chemistry. The metal itself was too electropositive to be isolated by the current smelting technology, a characteristic of rare earth metal in general. Cerium alloys are used in permanent magnets and in tungsten electrodes for gas tungsten arc welding. Cerium is used in carbon-arc lighting, especially in the motion picture industry (Hammond, 2000).

Cerium is a strong reducing agent, workers exposed to cerium have experienced itching, sensitivity to heat and skin lesions. Animals injected with large doses of cerium have died due to cardiovascular collapse (Alessandro, 2002). Therefore, determination of cerium is of considerable importance.

Sodium triphosphate acts as specific reagent for enhancing the fluorescence intensity of Ce(III). The excitation and emission wavelengths are 303.5 nm and 353 nm, respectively. The fluorescence varies linearly with the concentration of cerium(III) in the range (0.001-45)  $\mu$ g ml<sup>-1</sup>, the detection limit is (9.4×10<sup>-4</sup>)  $\mu$ g ml<sup>-1</sup>. The relative standard deviations for 30  $\mu$ g ml<sup>-1</sup> and 0.05  $\mu$ g ml<sup>-1</sup> are 1.1% and 0.72%, respectively, (Ayglgek and Rakicioglu,1996).

A new ion-selective electrode for cerium(III) ions based on a new ligand, N-[(Z)-2-chloro-2-(1-hydroxy-1,1,1-triphenylphosphoranyl)-1-ethenyl]-4-ethyl-1-benzene sulphonamide, as ionophore was prepared. The electrode has a wide linear dynamic range  $(6.6\times10^{-7}\text{ to }6.2\times10^{-2}\text{M})$ , with a low detection limit  $(2.3\times10^{-7}\text{ M})$ . This sensor was applied to determination of fluoride ion in pharmaceutical samples and of cerium content in stainless steel samples (Karami, 2003). Trace amounts of cerium were analyzed by flow injection-kinetic spectrophotometry. The determination of Ce (IV) in the range 0-8.0 µg ml<sup>-1</sup>, with a correlation coefficient (r) of 0.9982 was obtained. The proposed method was applied to analyze Ce in soil successfully (Zhu *et al.*, 2008). Colorimetric method for the determination of cerium (IV) ions with ampicillin and amoxicillin has been worked out. Beer's Law is obeyed in the concentration range from 2.5 to 25 µg and from 2 to 10 µg in 25 ml for ampicillin and amoxicillin, respecitively. The absorbance was measured at  $\lambda_{\text{max}} = 655$  nm at pH 3.2-3.6. The molar absorptivity was found to be  $2.7\times10^5$  l. mol<sup>-1</sup> cm<sup>-1</sup> for ampicillin and  $5.2\times10^5$  l. mol<sup>-1</sup> cm<sup>-1</sup> for amoxicillin (Franciszek *et al.*, 2001).

The determination of Ce (III) ions using octadecyl-bonded silica membrane discs modified with 1,3,5-trithiacyclohexane (TTCH) and spectrophotometry with arsenazo III was accomplished (Shamsipur *et al.*, 2002).

The present article is devoted to develop a spectrophotometric method to determination of cerium (III) ion using arsenazo III (scheme 1) as a chromo-genic reagent [arsenazo III is 2,7-bis(arsenophenylazo)-1,8-dihydroxy-3,6-naphthalenedisulfonic acid] in the presence of sodium dodecyl sulphate as surfactant.

#### Scheme 1. Arsenazo III structure

#### **EXPERIMENTAL**

#### **Apparatus**

Spectral and absorbance measurements were carried out using Shimazu UV-160 spectrophotometer with 1-cm matched quartz cells while the pH measurements were carried out using HANNA pH-211 pH meter.

### Reagents

All chemicals used are of the highest purity available.

### Stock cerium(III) (100 µg/ml) solution.

This solution was prepared by dissolving 0.0266 g of cerium chloride heptahydrate (Hopkin and Williams) in distilled water and the volume was completed to 100 ml with distilled water in a volumetric flask.

## Working cerium(ш) (50 μg/ml) solution.

This solution was prepared by diluting 50 ml of the above stock cerium(III) solution to 100 ml in a volumetric flask with distilled water.

# Arsenazo ш reagent (Az ш) (1×10<sup>-4</sup>M) solution.

It was prepared by dissolving 0.0194~g of arsenazo m (Fluka) in distilled water and the solution was diluted to 250 ml in a volumetric flask and then transferred to a dark bottle, where it is stable for at least five days.

### **Buffer solution (pH3).**

This solution was prepared by mixing 50 ml of 0.1 *M* glycine solution and 5.7 ml of 0.2 *M* HCl and the volume was completed to 100 ml with distilled water in a volumetric flask (Perrin and Dempsey, 1974).

# Sodium dodecyl sulphate (SDS) $(1 \times 10^{-3} M)$ solution.

This solution was prepared by dissolving 0.0288 g of sodium dodecyl sulphate (BDH) in distilled water and the volume is completed to 100 ml in a volumetric flask.

## Interfering ion solutions.

A100 µg/ml solution of each ion tested was prepared in distilled water.

## Synthetic sea water.

It was prepared as described (Herkinson, 1965) by dissolving 2.2 g NaCl, 9.7 g MgCl<sub>2</sub>.6H<sub>2</sub>O, 3.7 g Na<sub>2</sub>SO<sub>4</sub>, 1 g CaCl<sub>2</sub>, 0.65 g KCl, 0.17 g NaHCO<sub>3</sub> and 0.023 g H<sub>3</sub>BO<sub>3</sub> in about 500 ml of distilled water, then the resulted solution diluted to 1 L with distilled water in a volumetric flask.

#### RESULTS AND DISCUSSION

For subsequent experiments, 50  $\mu g$  of Ce(III) ion were taken and final volumes were 25 ml.

#### **Preliminary investigations**

The visible spectra of the blue-greenish coloured chelate were measured immediately after mixing 50 µg of cerium (III) solution (M), 3ml of  $(1\times10^{-4}M)$  arsenazo III (R) and 1ml of 0.01 M HCl and showed an absorption band at 653 nm, which indicates a definite reaction between Ce (III) and Az III reagent in contrast with the reagent blank which shows maximum absorption at 537 nm. The reaction shows good colour contrast ( $\Delta\lambda$ =116 nm). The wavelength at 653 nm has been selected for the subsequent experiments because: (a) the absorbance is higher, (b) the absorbance of the blank is lower.

## Study of the optimum reaction conditions

The effect of various parameters on the absorption intensity of the coloured complex as studied and the optimum conditions have been selected for determination of cerium (III) with arsenazo III.

## Effect of pH

The influence of pH on the colour intensity of the complex formed has been studied by transferring 50  $\mu$ g of cerium (III) ion solution, 5 ml of  $1\times10^{-4}M$  solution of arsenazo III reagent and different volumes of 0.01 M HCl and 0.01 M NaOH, separately. The volumes are then completed to 25 ml, in volumetric flasks, with distilled water. The absorbance was measured at 653 nm for each solution and the final pH is taken. The results obtained are presented in Table 1.

Table 1	: Effect of	f pH on	absor	bance
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ml of acid	Absorbance/ml of acid or base added						
or base	HCl (0	0.01M)	NaOH	(0.01M)			
solution added	A	рН	A	рН			
0.0	0.407	5.2	0.407	5.2			
1	0.693	3.5	0.245	10.2			
2	0.717	3.2	0.186	10.6			
3	0.712	3.0	0.137	10.9			
4	0.665	2.9	0.110	11.1			
5	0.648	2.8	0.093	11.3			
6	0.623	2.7	0.045	11.4			
7	0.612	2.7	0.015	11.4			
8	0.605	2.6	0.013	11.5			
9	0.537	2.6	0.012	11.6			
10	0.522	2.6	0.009	11.7			

From Table (1), the higher absorbance is observed in acidic medium at pH 3.2-3.0. In basic medium, the sensitivity has been lowered and accompanied by a weak contrast. In the subsequent experiments, pH 3 has been selected as optimum and therefore, different buffers

(Perrin and Dempsey, 1974) corresponding to the above optimum pH have been sought for their greater capacity as well. The experimental results are represented in Table (2).

The following buffers were made (100 ml in volumetric flasks).

B1(pH 2.8): (44.2 ml of 2*M* formic acid and 5ml of 2*M* NaOH).

B1(pH 3.0): (29.4 ml of 2*M* formic acid and 5ml of 2*M* NaOH).

B2(pH 3.0): (50 ml of 0.1*M* KHP and 22.3 ml of 0.1 *M* of HCl).

B3(pH 3.0): (10 ml of 2M tartaric acid and 7ml of 2M NaOH).

B4(pH 3.0): (10 ml of 2M citric acid and 6ml of 2M NaOH).

B5(pH 2.8): (50 ml of 0.1 M glycine and 8.4 ml of 0.2 M HCl).

B5(pH 3.0): (50 ml of 0.1 *M* glycine and 5.7 ml of 0.2 *M* HCl).

B5(pH 3.2): (50 ml of 0.1 *M* glycine and 4.1 ml of 0.2 *M* HCl).

Table 2: Effect of different buffers on absorbance

ml of						Abs	orban	ce/ ml	of buf	fer ad	lded					
buffer solution	$B_1$ (pH	[ 2.8)	B <sub>1</sub> (pl	H 3)	$B_2(p)$	H3)	B <sub>3</sub> (pl	H 3)	B <sub>4</sub> (pl	H 3)	B <sub>5</sub> (pH	I 2.8)	B <sub>5</sub> (pl	H 3)	B <sub>5</sub> (pF	H 3.2)
	A	pН	A	pН	A	pН	A	pН	A	pН	A	pН	A	pН	A	pН
0	0.41	5.2	0.41	5.2	0.41	5.2	0.41	5.2	0.41	5.2	0.41	5.2	0.41	5.2	0.41	5.2
1	0.65	3.2	0.61	3.3	0.63	3.3	0.55	3.5	0.51	3.3	0.68	3.3	0.69	3.3	0.66	3.5
2	0.63	3.2	0.60	3.3	0.64	3.3	0.54	3.5	0.43	3.3	0.69	3.3	0.72	3.2	0.67	3.4
3	0.63	3.2	0.59	3.3	0.65	3.2	0.51	3.5	0.38	3.3	0.69	3.2	0.73	3.2	0.66	3.5
4	0.63	3.2	0.56	3.2	0.65	3.2	0.48	3.5	0.33	3.3	0.66	3.2	0.70	3.2	0.65	3.5
5	0.59	3.2	0.55	3.2	0.61	3.2	0.45	3.5	0.33	3.2	0.66	3.2	0.68	3.3	0.64	3.5

From the results in Table (2), 3 ml of glycine-HCl (B5) (pH 3.0) buffer solution was chosen for the subsequent work, since it gives a good absorbance for the standard and lower blank value.

#### Effect of reagent amount:

The effect of arsenazo  $\coprod$  reagent amount on maximum formation of the coloured complex is investigated. A 7 ml of  $1 \times 10^{-4} M$  arsenazo  $\coprod$  reagent is recommended as optimal value for the following experiments because of its highest sensitivity and relatively lower blank value as shown in Table (3).

Table 3: Effect of the reagent amount on absorbance

ml of 1×10 <sup>-4</sup> M Az ııı reagent	A <sup>s</sup> <sub>B</sub>	$\mathbf{A^B_W}$
solution		
1	0.155	0.003
3	0.438	0.008
4	0.569	0.009
5	0.693	0.010
7	0.801	0.015
10	0.702	0.026

#### **Effect of surfactants**

The effect addition of different types of surfactants on the optical properties of the coloured chelated complex was studied. The experimental data reveal that only 1.5 ml of  $1 \times 10^{-3} M$  of sodium dodecyl sulphate (SDS) solution was useful when added before buffer (Cerium(III) ion + Arsenazo III reagent + SDS + pH3 glycine buffer) and diluted to the mark (Fig.1).

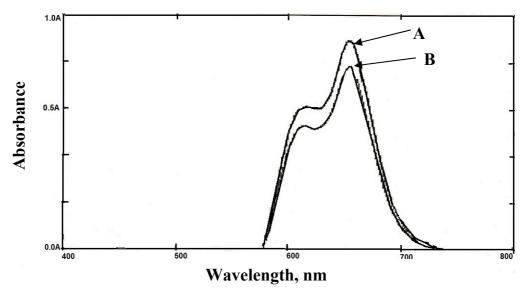


Fig. 1: Absorption spectra of Ce(ш)-Az ш complex. (A): in the presence of SDS, (B): in the absence of SDS.

The enhancing effect (Fig. 1) of the SDS surfactant may indicate that the formed chelate has acquired a positive charge. The cationic surfactants destroy the chelate due to charge repulsion.

#### **Effect of time**

The effect of time on the colour intensity of the Ce(III)-Az III chelate complex produced from different amounts of cerium(III) ion has been explored. The results are shown in Table (4).

Table	4.	<b>Effect</b>	of time	on ahe	sorbance.
IADIC	-		OI HILLE	UII AIDS	wii Daille.

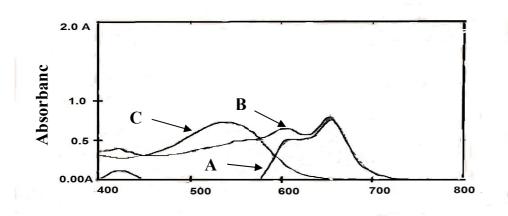
Time	Absorbance/ µg Се(ш) added						
(min)	5	10	30	50	70	100	
5	0.065	0.119	0.427	0.726	0.992	0.995	
10	0.072	0.118	0.432	0.732	0.996	0.994	
20	0.082	0.120	0.430	0.728	0.992	0.994	
30	0.087	0.121	0.430	0.725	0.990	0.991	
50	0.098	0.120	0.427	0.723	0.987	0.991	
60	0.093	0.132	0.342	0.706	0.914	0.991	

The last results show that the coloured chelate develops after 5min and with maximum intensity, which remains so for at least 1 hour, and is independent of cerium(III)

concentration. This may reflect the higher strength of the chelate formed while in the absence of SDS, lower absorbancies are observed and less efficient stability is attained.

# Final absorption spectra

The absorption spectra of the coloured complex and it's corresponding reagent blank are shown in (Fig. 2). The formed complex shows maximum absorption at 653 nm, while the reagent blank gives maximum absorption at 537 nm. The wavelength 653 nm of maximum absorption was still retained for subsequent work.

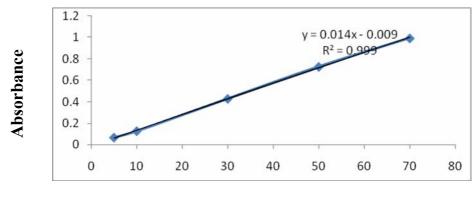


Wavelength, nm

Fig. 2: Absorption spectra of 50 μg Ce(ш) treated as under optimum experimental conditions and measured (A) against blank, (B) against distilled water and (C) blank measured against distilled water.

## Recommended procedure and calibration graph:

By establishing the optimum reaction conditions, calibration graph is constructed by transferring increasing volumes of 50 µg/ml of Ce(III) solution into 25-ml volumetric flasks to cover the range (5-100) µg / 25 ml. Then 7 ml of (1×10<sup>-4</sup>) M arsenazo III reagent and 1.5 ml of (1×10<sup>-3</sup>) M SDS and 3 ml of glycine buffer pH 3 and volumes are completed to the mark with distilled water. The absorbances at 653 nm are measured for reaction mixtures against the reagent blank prepared in the same manner but without cerium(III). Beer's law is obeyed over the range of (5-70) III Ce(III) (Fig. 3).



Concentration µg/ 25ml

Fig. 3: Calibration graph for cerium(III) determination with arsenazo III reagent.

The average molar absorptivity of the coloured complex is calculated from the calibration graph and found to be  $(4.99 \times 10^4)\,\mathrm{l.\,mol^{-1}}$ . cm<sup>-1</sup>, while limit of detection (LOD), limit of quantitation (LOQ) (Valcarcel, 2000) are found to be  $(66.7\times10^{-3})\,\mu\mathrm{g/ml}$  and  $(92.7\times10^{-3})\,\mu\mathrm{g/ml}$ , respectively. The results are given in Table (6). At higher concentration (> 70  $\mu\mathrm{g/25ml}$ ) of Ce(III), a negative deviation was observed. Fig. 6 shows the absorption spectra for different amounts of Cerium(III) ion: (A)  $5\mu\mathrm{g}$ , (B)  $10\,\mu\mathrm{g}$ , (C)  $30\,\mu\mathrm{g}$ , (D)  $50\,\mu\mathrm{g}$ , (E)  $70\,\mu\mathrm{g}$  and (F)  $100\,\mu\mathrm{g}$ .

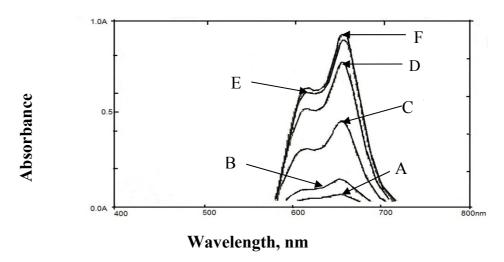


Fig. 4: Absorption spectra of different amounts (μg) of cerium(ш) when complexed with Az III reagent: (A) 5 μg, (B) 10 μg, (C) 30 μg (D) 50 μg, (E) 70 μg, (F) 100 μg.

#### **Accuracy and precision**

To check the accuracy and precision of the calibration graph, cerium(III) was determined at six different concentrations.

Table 5: Accuracy and precision.

Ce(III) taken, (µg)	Recovery, %*	Relative Standard Deviation,%
10	100.0	0.0
30	102.1	±2.1
50	99.8	±0.2

<sup>\*</sup>For six determinations

The results given in Table (5) show that the accuracy and precision of the calibration graph are very satisfactory.

#### **Nature of the complex**

Job's method of continuous variations and mole-ratio method (Hargis, 1988) are used to evaluate the combining ratio between Ce(III) ion and Az III chelating agent. The results

indicated that Az III reagent has reacted with Ce(III) in a 2:1 ratio, and the SDS ratio to complex is 2:1 (mole - ratio method).

Therefore, the structural formula of the chelate may be postulated as follows:

Scheme 2: Ce(III) –Az III chelate

The constant stability of the postulated chelated complex is  $2.153 \times 10^{12} M^{-2}$ 

#### **Effect of organic solvents**

Different organic solvents have been examined to evaluate their effects on the spectrum of the coloured chelate formed by mixing 50  $\mu$ g of Ce( $\mu$ ) solution with 7ml of (1×10<sup>-4</sup>M) arsenazo  $\mu$ , 1.5 ml of SDS and 3 ml of glycine buffer pH 3 and diluted to the mark with different organic solvents in 25-ml volumetric flasks.

The results illustrated in Table (6) and Fig. (5), show that there is no significant change in the spectral position (with reference to water) but a decrease in intensity of absorbance is observed in formic acid, so water is still recommended for dilution in the proposed method because of availability and low cost.

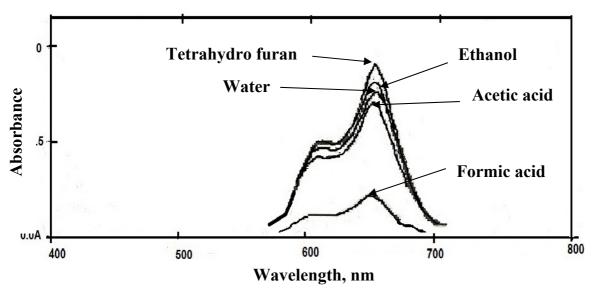


Fig. 5: Effect of solvents on spectral properties of Az ш-Се(ш) chelated complex

Table 6: Effect of organic solvents.

Solvents	גmax, nm	$A^{S}_{B}$	$A^{B}_{w}$	ε l.mol <sup>-1</sup> cm <sup>-1</sup>
Ethanol	653	0.834	0.109	$5.87x10^4$
Tetra hydro furan	653	0.913	0.049	$6.43x10^4$
Formic acid	652	0.229	0.039	$1.61 \times 10^4$
Acetic acid	652	0.718	0.049	$5.06 \text{x} 10^4$
Water	653	0.728	0.022	$5.13x10^4$

## **Study of Interferences**

The recommended procedure was applied to test the selectivity for the spectrophotometric determination of Ce(III) using arsenazo III reagent by the study of interfering effects of foreign species in the determination of 50  $\mu$ g of Ce(III) in presence of each interfering ion. The results are shown in Table (7).

**Table 7: Study of interferences** 

$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Foreign ion	Form added as	Amount added, μg	Interferences,%
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	A1 <sup>3+</sup>	AlCl <sub>3</sub> .6H <sub>2</sub> O	50	+18.40
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$			100	+17.63
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$			500	+22.01
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$			1000	+27.16
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Te <sup>4+</sup>	TeO <sub>2</sub>	50	+1.97
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		_	100	+3.42
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$			1000	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$			2500	-23.65
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Bi <sup>3+</sup>	Bi(NO <sub>3</sub> ) <sub>3</sub>	50	+1.80
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		3,3	100	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$				
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$			1000	-15.90
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$\mathrm{Be}^{2+}$	BeSO <sub>4</sub>		
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		·	100	-10.50
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$				
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Ni <sup>2+</sup>	NiCl <sub>2</sub> .6H <sub>2</sub> O	50	+1.30
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$			100	+2.50
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$				
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$				
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$			2500	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Th <sup>4+</sup>	Th(NO <sub>3</sub> ) <sub>4</sub> .6H <sub>2</sub> O		
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		371 2		
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Cr <sup>3+</sup>	CrCl <sub>3</sub>		
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$				
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$				
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$V^{+5}$	NH <sub>4</sub> VO <sub>3</sub>		
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	·	43		
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	Sn <sup>2+</sup>	SnCl2		
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$				
$Cd^{2+}$ $Cd(CH_3COO)_2.2H_2O$ 50 +0.77 100 -1.30				
100 -1.30	$Cd^{2+}$	Cd(CH <sub>2</sub> COO) <sub>2</sub> 2H <sub>2</sub> O		
	Cu	Cu(C113COO)2.2112O		
500 +0.39			500	+0.39

Fe <sup>3+</sup>	Fe(NO <sub>3</sub> ) <sub>3</sub> .9H <sub>2</sub> O	50	-74
	, 3,3 2	100	-76
2+		500	-80
Fe <sup>2+</sup>	$Fe(NH_4)_2(SO_4)_2.6H_2O$	50	-3.43
		100	-8.94
Pb <sup>2+</sup>	Pb(NO <sub>3</sub> ) <sub>2</sub>	500 50	-3.70 -7.80
FU	F0(NO <sub>3</sub> ) <sub>2</sub>	100	-15.10
Hg <sup>2+</sup>	Hg(NO <sub>3</sub> ) <sub>2</sub>	50	4.55
	3,72	100	1.04
		500	3.50
$Mg^{2+}$	MgSO <sub>4</sub> .7H <sub>2</sub> O	50	3.64
		100	2.73
G 2+	g alo ) di o	500	-1.17
Co <sup>2+</sup>	Co(NO <sub>3</sub> ) <sub>2.</sub> 6H <sub>2</sub> O	50	+13.25
		100	4.20
Ca <sup>2+</sup>	CaCl <sub>2</sub>	500 50	2.60 3.15
Ca	CaC <sub>12</sub>	100	5.52
		500	3.93
Li <sup>+</sup>	Li <sub>2</sub> SO <sub>4</sub> .H <sub>2</sub> O	50	0.66
Li Li	212504.1120	100	0.66
		500	-5.60
Cu <sup>2+</sup>	CuSO <sub>4</sub>	50	+5. 28
	·	100	10.30
		500	-21.90
$W^{6+}$	Na <sub>2</sub> WO <sub>4</sub> .2H <sub>2</sub> O	50	-4.63
		100	-6.56
_ 2+		500	+5. 66
Ba <sup>2+</sup>	BaCl <sub>2</sub> .2H <sub>2</sub> O	50	+3.35
		100	-0.128
Mn <sup>2+</sup>	MnCl <sub>2</sub> .4H <sub>2</sub> O	500 50	+2.06 -6.95
Min	MINC1 <sub>2</sub> .4H <sub>2</sub> O	100	-6.95 -5.41
		500	-4.38
Na <sup>+</sup>	NaCl	50	+0.13
1.00	T.WET	100	+3.91
		500	+0.63
K <sup>+</sup>	KI	50	+0.89
		100	+10.97
<u> </u>		500	+5.99
$Zn^{2+}$	Zn(OOCCH <sub>3</sub> ) <sub>2.</sub> 2H <sub>2</sub> O	50	-3.94
g 4+	9.0	100	-3.08
Se <sup>4+</sup>	$\mathrm{SeO}_2$	50	+1.79
		100 500	-0.77 +2.68
Zr <sup>4+</sup>	ZrOCl <sub>2</sub> .6H <sub>2</sub> O	500	+2.68 -12.60
Sr <sup>2+</sup>	SrCl <sub>2</sub>	100	-5.99
31	S1C1 <sub>2</sub>	500	-3.99 +4.72
Mo <sup>6+</sup>	(NH <sub>4</sub> ) <sub>6</sub> .Mo <sub>7</sub> O <sub>24</sub> .4H <sub>2</sub> O	50	+1.66
1410	(1.114/0.1110/0.24.71120	100	-3.95
SCN <sup>-</sup>	KSCN	50	+5.04
		100	+1.01
		500	-0.88
Br <sup>-</sup>	KBr	50	5.63
		100	-0.86
		500	0.0
HCO <sub>3</sub>	NaHCO <sub>3</sub>	100	-1.96

		500	-1.84
$S_2O_3^{-2}$	$Na_2S_2O_3.5H_2O$	50	-4.28
		100	-1.84
BrO <sub>3</sub>	NaBrO <sub>3</sub>	50	1.22
		100	-0.73
		500	-0.43
$SO_3^{-2}$	$Na_2SO_3$	50	-0.39
		100	+0.26
		500	-0.66
$\mathrm{BO_3}^{-3}$	$H_3BO_3$	50	-2.94
		100	-8.45
		500	-5.39
$SO_4^{-2}$	$CdSO_4$	50	+3.94
		100	0.74
		500	-5.42
$CO_3^{-2}$	Na <sub>2</sub> CO <sub>3</sub>	50	-30.70

The results in the above table indicate that a high error is observed in the case of Al<sup>+3</sup>, Te<sup>+4</sup>, Th<sup>4+</sup>, Be<sup>2+</sup>, Cr<sup>3+</sup>, Fe<sup>3+</sup>, Pb<sup>2+</sup> and Zr<sup>4+</sup> due to the competition of these ions with Ce<sup>3+</sup> for the reagent (appearance of blue- violet colour) there by depleting the reagent available for the Ce<sup>3+</sup>ion

# **Application of the method**

This method has been applied to the determination of cerium ion in synthetic composite mixture firstly and in sea water secondly. The results are listed below:

# 1. Determination of cerium(III) in synthetic composite mixture

Mixtures containing cations and anions and 50  $\mu g$  of cerium (III) have been prepared and analyzed for cerium. The results are given in Table (8).

Table 8 :Recovery of Cerium(ш) in synthetic composite mixture.

Ion added	Amount added, μg	Ce(ш) added, µg	Recovery, %
Se <sup>4+</sup> ,Te <sup>4+</sup> ,Mg <sup>2+</sup> , Br <sup>-</sup> ,	50	50	100
$SO_3^{2}$ -(I)	100	50	100.7
Ni <sup>2+</sup> ,Bi <sup>3+</sup> ,Li <sup>+</sup> ,SO <sub>4</sub> <sup>2-</sup>	50	50	91.4
(II)	100	50	85.6
Na <sup>+</sup> ,Mg <sup>2+</sup> ,SCN <sup>-</sup> ,SO <sub>3</sub> <sup>2-</sup>	50	50	119.6
(III)	100	50	100
Ni <sup>2</sup> ,Ca <sup>2+</sup> ,SO <sub>4</sub> <sup>2-</sup> ,Br <sup>-</sup> (IV)	50	50	98.4
	100	50	103.6

Other composite mixtures are tried but with unsuccessful results. It can be observed that the method gives fair recovery of cerium (III), and applicable for case (I) and (IV).

# 2. Determination of cerium (III) in sea water

Table (9) shows the results obtained for the determination of Ce(III) in sea water which is prepared in the laboratory (Henriksen, 1965).

ml of sample	Ce(ш) added, µg	Recovery, *%
0.5	10	152.680
	30	147.198
	50	92.127
1.0	10	125.168
	30	108.500
	50	89.519
1.5	10	118.120
	30	108.400
	50	87 299

Table 9: Determination of cerium(III) in sea water samples.

The results in Table (9) indicate that the method should be preceded by a separation step for cerium (III) before determination.

# **Comparison of the methods**

The comparison between the analytical variables of the present method with those of another method. The data were given in Table (10).

Table 10: Comparison of the method.

Analytical parameters	Present method	Literature method (Marczenko, 2000)
рН	3.00	2.3-2.7
Molar absorptivity (L.mol <sup>-1</sup> .cm <sup>-1</sup> )	4.99×10 <sup>4</sup>	5.6×10 <sup>4</sup>
Effect of surfactant	1.5 ml of $1 \times 10^{-3} M$ SDS	
Beer's law range (ppm)	0.2-2.8	
Determination coefficient (r <sup>2</sup> )	0.9994	
K (L.mol <sup>-1</sup> )	$0.2153 \times 10^{13}$	
Amount of reagent	7ml of $1 \times 10^{-4} M$	
$\lambda_{max}$ (nm)	653	650
Sandell's index(µg.cm <sup>-2</sup> )	28.08×10 <sup>-4</sup>	

Various analytical parameters are missed from the literature method.

The present method differs from the literature method in two main things:

- (a) the fantastic introduction of SDS surfactant.
- (b) the detailed optimization of experimental conditions that has not been established yet.

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<sup>\*</sup>Average of three determinations.

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