SPECTROPHOTOMETRIC DETERMINATION OF CERIUM – A REVIEW

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CONTENTS

REVIEW

A survey of literature reported for the spectrophotometric determination of cerium from 1972 to 1993 has been made. To save space the available information has been reported in tabular form. The information is presented under the different headings like "name of the reagent", "λ_{max}", "pH", "ε", "remarks" and "references". Under "remarks" information regarding composition of the complex, details of the method, interferences, application of the method, etc. is reported.

Reagent	pH	λ max nm	ε	Remarks	Ref.
H_2O_2	10.5	335-364	4000	To 4 ml of ammonical 0.05 M EDTA of pH 10.5 add 0.5 ml of 1.5% aq. H_2O_2 and Ce solution (50 µg as chloride or perchlorate) dilute to 25 ml and measure the extinction at the given wavelength. If sufficient EDTA is added to mask any Mn(II) present, MnO is formed and interferes with the determination of Ce The method can be used for analysing binary mixtures of Ce wtih Ca, Zn, Pb, La and Mn.	1
3- (2 Carboxyphenyl azo)-6-(4-nitro phenyl azo) chromotropic acid.	1.8 - 3.1	730	1,60,000	In acidic medium, rare earth metals apart from U, Yb, Er Ho and Dy give complex with the reagent at the given wavelength.. The optimium pH range are as follows La (2-3.5), Ce (1.8-3.1), Pr (2.2-3.5), Nd (2.2.-3.5), Sm (2.7 to 4.2), Eu (3-4.5). Maximum colour intensity occurs at room temperature after 30 min with Ce, La, Pr, Nd and after 1-2 hrs. with remaining metals. Increase of temp or addition of an organic solvent reduces the intensity. Ce group metals can be determined in the presence of 40 fold amount of metals of Y sub-group with 18 ug of La in 25ml of solution of pH 2.8 to 3.2. There is no interference by 4000-fold amount of tartaric acid, ascorbic acid thiourea, or hydroxyamine 250-fold of Mo(VI), 150-fold of Cd, 10-fold U VI) or B, 70- fold of Zr or Co, 30-fold of Mg, Zn, or Pb, 10-fold of Cu or Ni.	2

Solochrome Azurine BS (Mordant Blue I)	4.92	505	11,200	pH of Ce is adjusted to 4.92 and 5.5 for Al & U by sodium acetate buffer. Excess of dye (3-fold Al, 2-fold for Ce or U) is added and measured the extinction. Beers law range is obeyed 0-5 ppm of Al(ε=8880 at 560nm), 1-15 ppm of U(ε = 2250 at 600nm) and2.8-11.0 ppm of Ce. Mean sensitivities for Al, U, and Ce complex are 0.03, 0.297, and 0.071 per sq cem per 0.005 extinction unit respectively. Serious interfrence is caused by many ions but some can be eliminated by masking agents	3
Arsenazo III and its analogue [3-(2-carboxyphenylazo)-6-(4-nitrophenylazo chromotropic acid]	1.8-4.3	730	116000 163000	The reagent reacts with La, Ce, Pr, Nd, Sm, Eu and Gd but does not react with Tb, Dy, Ho, Er, Yb or Y. La can be determined with the reagent in the presence of 40-fold excess of Yb.	4
Methyl xylenol blue	9.0-9.7	568-576 In presence of CTAB 630-650	–	Except Pm and Tb other lanthanoids react with reagent to form bluish violet water soluble complex with Sandell sensitivity in the range 0.0037 to 0.0054 ug/sq. cm. In the presence of CTAB water soluble blue complex formed with Sandell sensitivity equal to 0.0017 to 0.0032 ug/sq. cm. Beers law is obeyed for complex of La, Ce(III), Pr and Nd at metal concentration upto 10ug/ml and for other upto 20ug/ml for Pr, Gd and Lu complex. The mole ratio of the complex is 1:2:3 for metal :reagent:CTAB.	5
Antipyrine S [3. 6-bis antipyrinylazo chromotropic acid] and its analogue	-	-	–	La(1-25 ug in 25 ml of HCl solution of pH 2.5) has been determined by this reagent at 735 nm. It is found that there is a possibility to determine La, Ce, Pr or Nd in presence of Er, Ho, Dy or Gd.	6

Reagent	pH	λ max nm	ε	Remarks	Ref.
Beryllon II	7.6	610	21500	Ce(III) reacts with the reagent in the ratio of 1:1. The reagent absorbs at 555 nm. 0.1 to 1.2 mg of Ce 50 ml is determined. No interference from large excess of K, Na NH_4, Mg, Ba, Ca, Sr, Al, Cd, SCN^-, NO_3^-, I^-, $S_2O_3^{2-}$ and thiourea. Tolerable amount of other species related to Ce are Cu(3), Ga(1), Tl(5.7), P^-(8), tartaric acid(30), sulphosalicyclic acid (40), ascorbic acid (80). In, Zn, Be, Fe, As O_4^{3-} PO_4^{3-}, BO_3^{3-} interferes.	7
By formation of molybdocerophosphoric acid	0.4 M HNO_3	318	–	i) The three methods described are based on the formation of molybdocerophosphoric acid (I)by reaction with Ce(IV), Mo O_4^{2-}, PO_4^{2-} in 0.4-molar nitric acid. Ce is then determined directly be measuring the absorbance. Beers law range is 1.6-10 ug of Ce/ml of final solution. ii) Indirectly by selective extraction to $CHCl_3$-butanol (4:1). Excess of molybdophosphoric acid(II) form simultaneously decompose the (I) in aqueous phase at approximately 550°C, adding more MoO_4^{2-} and thus extracting (II) in isobutly alcohol (10ml) measure at 318 nm. Analytical range is 25-250 ug of Ce and only those ions that suppress the formation of I interferes.	8

				iii) By AAS at 313.2 nm in No_2 acetylene flame of Mo in isobutly acetate extract obtained in ii. Analytical ranges 40-400 ug of Ce and the senstivities ~ 900 times better than that attained by direct AAS for 200 µg of Ce. The coefficient of variations are 1.36% for (i), 3.6% for (ii) and 4.7% for (iii).	
2-thenoyl tri-fluoro acetone	4.30 and 6.5	440	–	The use of this reagent is discussed for Ce previously and is modified so that Ce and Mn can be extracted at the given pH. The test solution is mixed with sodium acetate buffer at 4.3 and shaken with 0.5M reagent solution in xylene. Ce can be extracted from organic phase by shaking it with molar nitric acid. The original aqueous phase containing Mn is adjusted to pH 6.5 with aqueous ammonia and shaken with 0.15M reagent solution in acetone and the combine organic phases are shaken with molar HNO_3 to extract Mn. The acid extract containing the two metals are evaporated and digested with $HClO_4$, HNO_3 and Ce and Mn determined at 440 nm with (I). A detailed scheme of extraction with a different necessary washing stage is given. Upto 0.5ng of iron can be present and various anionic species donot interfere when present in 0.05-1 mM amount of mixture containing each of Ce and Mn. Co-efficient of variation lies between 1 to 3.7% respectively.	9

Reagent	pH	λ max nm	ε	Remarks	Ref.
Carboxy nitrazo [3-(2-carboxy phenylazo)-6-(4-nitro phenylazo) chromotropic acid (I)]	2 2.3	730	–	The selectivity of the reaction of this reagent for individual rare-earth metals has been studied in the presence of EDTA or of EDTA + iron (III) and method for determining La or Ce in steel not containing Pr or Nd are described. With unalloyed steel the sample (0.125gr) is dissolved in 10-15ml of HCl (1:1), Fe(II) is oxidised with HNO_3. The solution is evaporated nearly to dryness, the residue is dissolved in 10 ml of 0.1 M HCl and the solution is diluted to 100 ml with water. An aliquot (2-5 ml) is treated with EDTA (Fe(II)):EDTA should be 1:1 or 1:2) then diluted with water upto 12 to 15 ml and adjusted to pH 2-2.3 with 0.2 M HCl or NaOHl. 1.5 ml of 0.06% reagent solution and water added to 25 ml. Measure the colour at 730 nm, after 30-40 minutes against water. The calibration graph based on solution of similar weight of steel + added La or Ce covers amount of 1.25 to 20 µg in final solution. With alloyed steel the solution of the sample is first oxidised with $(NH_4)_2 S_2O_8$ and $AgNO_3$ and Fe, Mn, Cr are precipitated as hydroxides.	10
Ortho anilic β[3-phenylazo)-6-(2-sulphophenylazo) chromotropic acid.	4.0	730	–	Ortho anilic β forms 2:1 (L:M) complex with Ce, Pr and Nd in the presence of a protective colloid (gelatin) at an optimum pH of 4. The complex shows max absorbance at 730 nm and the lower levels of determination (µg/ml) are La 0.15, Ce=0.5, Pr=0.5 and Nd=0.75. Sr, Sn (II), Ba, B acetate, phosphate, sulphate, Fe(III), Al(III) Pb(II),	11

				Th(IV) and Cr(III) and 10-fold amounts of other lanthanoids (Eu-Lu) do not interfere. A spectrophometric method based on these findings has been used for the determination of La (20-73%) in binary mixtures with Lu. Relative errors were less than ± 3.4% (10results)	
Crystal violet	1M-HCL	460	–	In molar HCl Ce(IV) and the dye forms a yellow 1:2 complex that can be used for the determination of 3-35 ppm of Ce and the absorbance was measured at the given wavelength after 30 min. At the 10 ppm of Ce level there is interference at the levels given (ppm) by Bi(4), Fe(8), Cr(III)(10), Zn, Cu, Te or Zr(20), In or La (30), Tl(I) and Hg(II)(50). Pr(III) interferes at all the concentrations.	12
Di ethylene triamine penta acetic acid and benzylthiouranium (I)	3-10	298	600	This reagent (I) forms 2:1 complex with Ce(III) at the given pH. Beer's law for Ce followed in concentration range of 0.8-580 µg/ml. In the prerence of an approxmately 100-fold molar excess (relative to Ce) of (I) and an approximately 2500-fold amount benzoyl thio uranium. A ternaray complex is formed at pH 8. This complex is extractable and has max absorbance at the given pH and the Beer's law is obeyed over the same range as for the binary complex. An extraction spectrophotometric method based on these findings has been used for the determination of Ce(III) inmixture of rare earth metals. A 10-fold excess (with respect to Ce) of Eu interferes. But 50-fold excess of other rare earth metals do not. For 5 µg/ml of Ce in the presence of 50-fold amount of diverse ions, the coefficient of variation was 7%.	13

Reagent	pH	λ max nm	ε	Remarks	Ref.
4-(4-dimethl aminophenylazo) benzene arsonic acid (I)	1.09-2.50	490	–	The rose coloured reagent (I) (as an aqueous solution) is bleached to pale yellow by oxidation with Ce(IV). Optimum pH for determination is 1.09-2.50. 1ml (10-450 µg Ce) of sample solution with 20 ml of sod acetate-HCl buffer solution (1.09 pH) and 3 ml of I solution (0.1 g reagent dissolved in 20 ml hot M HCl) and diluted to 1 lit with molar HCl. Dilute the mixture to 50 ml and measure at the given wavelength. Interference form I can be avoided by precipitating $Ce(OH)_4$ with aqueous ammonia. Dissolve the precipitate in H_2SO_4 and proceed as above.	14
Carboxy nitrazo [3-2 carboxy phenylazo)-6-(4-nitrophenylazo) chromotropic acid]	2.1-2.6	730	–	Ce, La, Pr, and Nd (approximately 0.1 to 1.0 µg of each) can be determined spectrophotometrically in the presence of approximately 650 fold amounts of Fe(III) (masked by EDTA) by using carboxy nitrozo as reagent. The extinction is measured at the given wavelenth at given pH. The method has been used for determining 0.005-0.01% of Ce, La, in steels. Prior sepration of iron is unnecessary if the sample contains greater than 0.08% of La or Ce. The coefficient of variation (8-13 results) was less than 7.7%.	15
3 4-dihydroxy benzoic acid	-	-	–	A red-violet 1:3 Ce(IV) : Reagent complex is formed in ammonia solution. The reaction conditions were investigated spectrophotometrically. The ions and the amount that may interfere with the determination are listed.	16
O-anilic [3-(2-carboxy phenylazo)-6-(2-sulphophenylazo) chromotropic acid].	4-4.5	660-670	27000–18300	At the given pH rareearth forms 1:2 complex with the reagent at the given λ max. values of the complex decreases with increasing Z. Example from 27 000 to 18,300 for La,	17

				Ce, Pr and Nd and from 3400 to 2700 for Tn, Yb and Lu and that for Y is about 3000. Beer's law is obeyed for 0.23 to 3.5 μg/ml of La, and 3.5-15 μg/ml of Y. The sensitivity is better by an order of magnitude for La, Ce and Pr than for Ho, Er, Tn, Yb, Lu or Y. The reagent is thus recommended for estimating La, Ce, Pr or Nd in binary mixtures with Tm, Yb, Lu or Y. Interference is caused by equal amounts of Ba, Bi, Sr, or acetate (relative to the rare earth metal) by 2-fold amounts of SO_4^{2-}, PO_4^{3-}, Fe(III), Al, Pb(II), Th, Ca, or Mg and by 5-fold amounts U(VI), Fe(II) or Zn.	
Quinalizarin (I) and 8-hydroxyquinoline (II).	6 7 5	6(0-62 0	~15000-22000	These metals form 1:2:2 (M:I:II) complex that can be extracted from aqueous medium of pH 6.5 into iso pentyl alcohol. I is used as its complex with B. The lanthanoid complex shows maximum aborbance at 520-550 nm but measurements are made in the given range. If a competing ligand and is added to the aqueous phare before extraction some complexes are decomposed and some remain uneffected. Thus Lu (0.17-0.77μg/ml) can be determined in the presence of La, Ce, Pr, Nd or Sn. If the aquous phase is made 0.06 M in sorbitol Ce (0.28-1.35 μg/ml) can be determined in the presence of an equal amount of Lu. If the aqueous phase is made 4mM in NaF, Tm, Lu (0.34-0.95 μg/ml) can be determined in the presence of 2-fold amounts of Ce, La or Pr. If the aqueous phase is made 60mM Na_2 EDTA or Er, Tm, Lu (0.23-0.93 μg/ml) can be determined in the presence of an equal amount of La, Sm, Pr or Nd. the aqueous phase is made 0.12 mM in nitrilotriacetic acid. The coefficient of variation was less than 1% (4-6 results) for all the determinations cited.	18

Reagent	pH	λ max nm	ε	Remarks	Ref.
N-(p-tolyl)-2-flurohydroxamic acid	8.5-9.0	465	4000	This compound was used as a 0.1% solution in $CHCl_3$ selectively extracts Ce(IV) from aqueous solution at the given pH. The complex is stable and shows λmax at the given wavelength. Beer's law is obeyed from 0.05-40 ppm of Ce. Many cations and anions do not interfere. The nature of the extracted species is discussed.	19
N-P(tolyl)benzohydroxamicacid.	8.5	465	-	Sample solution (10ml) was extracted at pH 8.5 with 1% solution of reagent in $CHCl_3$ (10,3,3 ml) combined extract was dried over Na_2SO_4 and made upto 25 ml with $CHCl_3$. It was measured at the given wave length against $CHCl_3$. Beer's law was in the range of 0.03-40 μg/ml of Ce. No interference from approximately 1000-fold amounts of 30 anions and 26 cations was listed. Ce is determined in sea water.	20
p-ansidine	2.0	510	1366	In the medium of pH 2.0 (KCl-HCl buffer) Ce(IV) forms with the reagent reddish violet complex extracted into iso-amylalcohol. The extinction of the extract was measured at the given wavelength. Beer's law was followed between 0.5-20 ppm of Ce. Sandell sensitivity 0.1 $\mu g/cm^2$. No interference from 10-fold amount (with respect to Ce) of other lanthanoids Cu, Pd, Ni, Mg, Mn, Cl^-, Br^- and NO_3^-.	21

Xylenol orange ethyl trioctyl ammonium bromide.	-	-	–	Complex formed between metal, reagent and ethyl trioctyl ammonium bromide are extractable in xylene and other aromatic solvents (not in polar solvents). For La, Pr, Ce, Gd, Dy the optimum values of pH for extraction of the complex and the values of wavelength and ε are reported. Beer's law is obeyed upto 4.5 μg of metal in 5 ml of xylene. Some interfering ions are listed.	22
l-Naphthyl amine	-	465	–	Zh.Khim. 19GD 1977(12) Abstr No. 12G122.	23
3-Nitro N-m-tolyl benzo hydroxamic acid.	8.0	492	4000	Micro amounts of Ce were determined spectrophotometrically by reaction at pH 8.0, with this reagent to form a 1:4 (Ce:L) complex which was extracted into $CHCl_3$ and the extinction was measured at the given wavelength. Beer's law was obeyed from 0.3-3.0 μg/ml of Ce. Interfering ions are reported. The standard deviation was 0.01-0.3 μg in determination of 2.4 μg of Ce in 25 ml.	24
8-Hydroxy quinaline	10		–	Cast iron steel sample was dessolved in HCl-H_2O_2 and the solution is evaporated. The residue was dissolved in HCl and diluted with acetone and applied on Dowex 50 ω -X8 resin. Column was washed with 2N HCcl (for steel containing Zr also with lN H_2SO_4). Ce was eluted with 5N HCl. The eluant was treated with citric acid made alkaline with ammonia boiled with $Na_2S_2O_8$ and KCN. pH was adjusted to 10 and the solution was shaken with 3% of the reagent in $CHCl_3$ and measured at the given wavelength. Standard deviation was 8 ppm with determining 944 ppm of Ce. Large amount of Zr interfered. Detection limit was 2-8 ppm.	25

Reagent	pH	λ max nm	ε	Remarks	Ref.
2 m-ethoxy N-p tolyl benzo hydroxamic acid.	7.9 8 2	460	3250	Orange red Ce ligand complex was extracted at the given pH in $CHCl_3$ and measured at the given wavelength. Beer's law was followed from 2.17-3.45 µg/ml of Ce in the presence of 3M $(NH_4)_2SO_4$ as salting out agent. Sensitivity was 0 04 µg cm^{-2} and error ± 1.85% for micro amount of Ce. Tolerance limits and interference of diverse ions was given.	26
Fe(III) resacetophenone oximate complex.	5.0	450	2000	A portion of Ce(IV) mixed with 0.1 M of $(NH_4)_2SO_4$-$FeSO_4$ (1ml) acetate buffer solution of pH 5 0 (4 ml) and 0.1 M reagent (1 ml) mixture was diluted to 25 ml and measured at the given wavelength against blank. Sandell sensitivity is 0 07 µg cm^{-2} of Ce(IV). Beer's law is obeyed in the range of 2.8-40 ppm. Interference of common metal ions are reported Zr greater than 9 ppm thorium in excess, but F and oxalate do not interfere if Al^{+3} is added.	27
Methyl green	-	470	–	Mix the solution of $Ce(SO_4)_2$ in M H_2SO_4 with 0 5 ml of 2% reagent solution in H_2SO_4. Dilute to 10 ml with acid and measure at the given wave length in 1 cm against water. Beer s law is obeyed in the range of 1-11 µg/ml.	28
P-anisidine	2.0	510	–	Solution upto 20µg Ce(III) was treated with 5ml of ethanolic 1% reagent at the given pH KCl-HCl buffer and dilute it to 25 ml. Violet complex is extracted in 10 ml of iso-amylalcohol and measured at the given wavelength. Sandell sensitivity was 0.1µg cm^{-2}, Fe(III), MnO_4^-, $Cr_2O_7^{-2}$ interferes but Cu(II), Ni, Co, Mg, CN^- Br and NO_3^- do not interfere. This method can be used to separate Ce(IV) from other lanthanoids.	29

N p-tolylbenzohydroxamic acid	8.4-9.8	465	–	Adjust the pH of the aqueous layer of a mixture of 10 ml of mM Ce(IV) and 10ml of a solution of the reagent in $CHCl_3$ to 8.4 to 9.8 (with aq. ammonia) and shake for 10 min. Dry the aqueous phase with Na_2SO_4 re-extract the aqueous phase twice with 3 ml of reagent solution and then combine the dry organic phase and dilute to 25 ml with $CHCl_3$. Measure the absorbance at the given wavelength against the reagent blank. Many common anions and cations do not interfere.	30
Phthalexon S [3,3'-[bis(carboxymethyl) amino methyl] phenol sulphonaphthalein].	6.0	610	–	This reagent (I) and cetrimonium (II) ions forms 1:2:2 (M:I:II) complex with lanthaniods in the medium of pH 6 i.e., 0.1 mM in I and 0.5 mM in II. Maximum absorption and ε values are given for La, Ce, Pr, Nd, Sm and Eu (the Ce sub-group) and less than 8000 for Ho, Er, Tm, Yb and Lu (Y-subgroup). Beer's law is obeyed for 0.05-3.8 μg/ml of Ce sub-group elements. A method based on these facts has been used for determining the Ce sub-group elements in the presence of Y sub-group elements ex. greater than 15% of La_2O_3 can be determined in the mixture Er_2O_3.	31
Promethazine hydrochloride	4.4 M H_3PO_4	518	10060	The method for Ce(IV) (1.6-15 ppm) is based on the oxidation of the reagent (I) in 4.4M H_3PO_4 medium to a red product having the given maxium absorption. In the determination of 8 ppm of Ce(IV) othe lanthanoids are tolerated at the concentration of 4000 ppm. Tolerable concenration (ppm) for some other species are Au(III) (0.25), $S_2O_3^{-2}$ (0.5), I or EDTA (0.8). The indirect determination of As(III) 0.15-2.4 are NO_2 (0.05-1.72) ppm involves the oxidation of the test species by Ce(IV) (in the presence of Os (VIII) as a catalyst for As(III)) in 0.5M Hcl medium and the determination of unconsumed Ce(IV) with (I) after adding H_3PO_4. The method has been used to determine Ce in MISH metal.	32

Reagent	pH	λ max nm	ε	Remarks	Ref.
EDTA and oxalate	-	287	490	Mixed ligand complexes containing rare earth metal EDTA and oxalate in the ratio 1:1:1 are formed. If a precipitate of the oxalate of Ce, Pr, Nd, Sm, Eu and Gd is dissolved in aqueous Na_2 EDTA (the solution produced should be 15mM in oxalate and 30mM in EDTA) at pH 6.5-11.0. Spectrophotometric properties of these complexes (metal, λmax, ε, lower levels of determination μg/ml) are Ce, 286, 490, 0.8; Pr, 449 10.4, 3.3; Nd 579, 15, 2.5; Sm, 405, 5.2, 8.7; Eu, 396, 3.4, 8.8 and bd, 272, 4.9, 63.5. Individual rare earth metals can thus be determined in the oxlate precipitate but correction must be made for the effects of the absorption of the Eu, Sm, Pr, and Ce complexes and that of the Ce, Pr, Nd and Gd complexes respectively. To determine the La the sum of all the named lanthanoids is determined by complexometric titrations and the content of La is found from the difference between the results of the spectrophotometric and titimetric determinations. Contents (μg/ml) of La_2O_3 (65), Ce_2O_3(16), Pr_2O_3(55),Nd_2O_3(44), Sm_2O_3(110), Eu_2O_3(63), Gd_2O_3(180) were determined in a suspension of rare earth metal oxalate isolated from industrial solution. The coefficient of variation were < 11% (5-10 results).	33
N-p-tolyl benzo hydroxamic acid(1)	–	460	–	This reagent was used as a reagent for Ce(IV) in phosphorite sample solution extracted into 0.1% reagent solution in $CHCl_3$ as red-complex. Extraction was quantitative and the extract obeyed Beer's law from 0.03-30 μg/ml of Ce. This method is claimed to be selective.	34

Chromotrope B	1.09-5.2	510	–	This dye used as an aqueous 0.1% solution is oxidised by Ce(IV) in the given pH range (Na acetate-HCl) buffer. The extent of the reaction is being monitered by the decrease in absorption at the given wavelength. The calibration graph is rectilinear upto 8 µg/ml of Ce. Many common cations (including those of other lantanoids) and anions do not interfere. But Cr(VI), Mn(III), Mn(VII), Co(III) do.	35
Trifluprom azine hydrochloride.	acidic range	503	–	This compound used as an aqueous 0.2% solution is oxidised by Ce(IV) in a medium of 2.5-4 M H_3PO_4. The resulting red species exibits maximum absorption at the given wavelength. The optimum analytical range is 1.2-13.7 ppm of Ce and the Sandell sensitivity is 20 ng/cm^{-2}. Large amounts of other lanthanoids do not interfere. Tolerance levels for several other elements and anions are listed.	36
8-hydroxy-7-iodoquinoline 5-sulphonic acid.	4-6	370	–	The named reagent (I) forms a 2:1 (L:M) chelate with Ce(III) at the given pH (acetate buffer) and I equal to 0.1. The maximum absorption is at 370 nm, at pH 5.7 with the use of 1mM of I the measurement at 25°C in 1cm cell. The calibration graph was rectilinear over the range 25-125 ppm of Ce(III). Determination of trace concentration of Ce should thus be possible with a sensitivity of 56ng/cm^2.	37

Reagent	pH	λ max nm	ε	Remarks	Ref.
N-(N-chloro phenyl)-3-methoxy benzo hydroxamic acid.	8-10	450	–	Of 26 such hydro oxamic acids studied the cited one (used as a 0.2% solution in ethanol) I is recommended as a spectrophotometric reagent for Ce. In NH_4NO_3 medium at a given pH this compound forms a complex that can be extracted into $CHCl_3$ for the measurement at the given pH. Optimum analytical range 4-20 ppm of Ce. Bivalent Cu, Ni, Co, Fe(III), Pb(II) Al, Ti(IV), Zr(iv), Th and U(VI) interfere with the extraction process and the result is low if La, Pr, Sm Dy, Nd and Gd are present. Tartrate, citrate, oxalate, fluoride and phosphate interfere.	38
O-tolidine	0.5 to 1N H_2SO_4	437		The photometric method decribed is suitable for the determination of 0.03-0.2% in steel. The reaction between Ce((IV) and the reagent in 0.5-0 1N H_2SO_4 medium gives a coloured complex the absorbance of which is measured at the given wavelength. Complex is stable and the interfereing elements can be removed by preliminary co-precipitation of Ce(La) as oxalate. Full experimental details are given.	39
4-chloro-N-P tolylbenzo hydroxamic acid.	8 5-9.0	460	–	lml aliquot of 0.1 mM Cr(IV) is diluted with 10ml of 1% reagent solution in $CHCl_3$, pH is adjusted with aqueous 0 5 M ammonia. Mixture is shaken for 5-10 min in $CHCl_3$, $KHCl_3$ layer is reparated and dried over Na_2SO_4 and diluted to 25 ml with $CHCl_3$ and the absorption is measured at given wavelength against reagent blank. Effect of pH, solvent, temperature, shaking time reagent concentration and presence of other ions are discussed Beer's law range lies between 0.5-28 ppm of Ce. In determination 3-36 µg of Ce standard deviation was ± (.01 µg (8 determinations).	40

Solochrome black 6 B	2.0	530	–	Absorbance of the reagent (I) at 530 nm is diminished by the addition of Ce(IV). The extent of effect being directly proportional to the amount of Ce(IV) present. To 2.0 ml of I add 12 ml of sodium acetate-HCl buffer of the desired pH, and various volumes of Ce IV) and dilute to 25 ml with water after 10 min measure the absorbance at the given wavelength. This method allow the determination of 1-20 µg/ml of Ce(IV). Tolerable concentrations of 34 ionic species are listed	41
Sulphonazo III and antipyrine	3.5-6.0	660	36600	The cited reagent formed mixed ligand complex with La, Ce(III), Pr and Nd in aqueous medium of pH 3.5-5 that are 30 µM is sulphanazo III and 0.5 M in antipyrine. These complex exhibit maximum absorbance at the given wavelength. Beer's law obtayed for 0.(5-50 µg/ml of each of the named element Other lanthanoids Y, Sc do not interfere with the given values.	42
Gallocyanine methyl ester	6.5-7.8	-	–	This reagent reacted with La, Ce III), Pr, Nd, Gd, Tb, Dy, Ho, Er, Yb in aqueous 10, 2) and 30% ethanol medium in the given pH range to form 1:3 (M:L) complex with well defined absorption maximum. Stability contans are calculated and it was used for spectrophotometric determination of rare-earths	43

Reagent	pH	λ max nm	ε	Remarks	Ref.
Chlorogallein methyl ester and oxime [8-hydroxy quinoline]	-	660	–	The cited ternary complex has slightly higher absorbance than do the corresponding complex with chlorogaline methyl ester (I) above and the ternary complex are stable and soluble in water containing poly (vinyl pyrrolidone). The reaction have been used for semi quanitiative determination of Ce(III) and Pb(II). The calibration graph are rectilinear upto 40μg of Ce(III) or upto 60μg of Pb(II) in 10 ml of final solution. The corresponding Sandell sensitivity at 660 nm are 5.5 and 1-0 ng cm^2 A solution of I can be used as the spray reagent for the determination of Pb(II), Cu(II), Ni(II), Cd(II), Zn(II), Sn(II) or Sn(IV) on paper chromatography.	44
N, N'-ethylenebis (salicylidene-mine)	-	-	–	Complex formed between Th(IV), U(VI), Ce(III) and the named reagent in the ethanolic solution was monitored by spectral and conductance measurements and the effect of ligand and metal ion concentraton was investigated. M:L ratio was found to be 1:1. Beer's law was followed in the range 2.3-11.52, 2.38-16.66 and 1.40-6.30 μg/ml for Th(IV), U(VI), and Ce(III) respectively. The coresponding limits of determination were 2.3, 2.4 and 1.4 μg.	45

4-Chloro substituted cinnmohydroxamic acid	9.0	470	–	To Ce(IV) samples add 2 ml of 2% ethanolic solution of the reagent and 6 ml of buffer solution at the given pH and is and combined dried extract are diluted to 25 ml with extracted with $CHCl_3$ and measured at the given wavelength against reagent blank. The effect of pH, reagent concentration, nature of solvent, extraction time and presence of other ions, stability and stochio metry of the complex were studied. Beer's law liesin the range of 0.2-30 ppm of Ce. Method is precise and accurate and many metal ions and anions do not interfere.	46
Tetra sulphonato-metal-phthalocyanine complex	5-8 N with H_3PO_4	630 618 or 608	–	Determination of Ce-5-100 µg of Ce(IV) (for the tetra sodium salt (I) of CO_2, 4, 11, 18, 25 tetrasulpho thalocyanine-2-hydride)6 are 5-195 µg of Ce(IV) (for the tetra sodium salt (II or III) respectively of Ni(II), 3,10, 17, 24 or Ni(II), 4, 11, 18, 25-tetrasulpho thalocyanine) was added sufficient 25N H_3PO_4 was added to make the concentration 5N (for I or III) or 8 N (for I or II) or 8N (for II) followed by 1.5 ml of aqueous 0.05% I,II or III. The resulting solution was diluted to 25 ml with water and the absorbance was measured at the given wavelength for I, II and III respectively. Beer's law was obeyed over the cited range. A similar discription for the As determination is also given.	47

Reagent	pH	λ max nm	ε	Remarks	Ref.
Solochrome black	2.0	530	-	The proposed method involves measurement at 530 nm and the decrease in absorbance of red-violet reagent solution when treated with Ce(IV) at pH 2.0. Beer's law is obeyed for 1-10 ppm of Ce. Tolerance limits for ions are given.	48
Chlorophosphonazo-m-NO_2 [6-(4-chloro-2-phosphono phenylazo)-3-(3-nitrophenylazo) chromotropic acid.	2.0	666	–	An aliqot of the sample containing about 12 µg of La or Ce is adjusted to pH 2.0, and mixed with 1 ml of 1 M HCl, 10 ml of 3% oxalic acid and 3 ml of an aqueous 0.02% solution of the cited reagent. After dilution to 25 ml with water, the absorbance is measured at the given wavelength against a reagent blank. The coefficient of variation at the 10µg level are 0.37% for La and 0.92% for Ce. No interference is caused by 10-40 fold amounts of the Y sub-group elements or by 1.5 mg of U(VI) but Th, Zr, Ca, and Ba interferes. The preparation of the reagent is discussed.	49
Salicylic arylidene hydrazide	-	-	–	Complexes formed by the salicylidene, vanillylidene and methoxy benzylidene hydrazides of salicyclic acid with Ce have been studied spectrophotometrically and conductometrically. Complexes with metal to ligand have the ratio of 1:1 and 1:2 and their stability constants and their molar absorption coefficients were determined. These compounds were satisfactory reagents for the spectrophotometric determination of 0.5-2.5 µg/ml of U, Th, or Ce and 1.5-5 µg/ml of La or Y.	50

N-4-chlorophenyl 2-furo hydroxamic acid.	7.8 to 10	460	–	A solution containing 4-40 μg of Ce(IV) was adjusted to pH 7.8-10 then 5 ml of 0.5% (w/v) solution of the named reagent (I) in ethanol was added. The resulting precipitate was extracted into $CHCl_3$ (2 x 5 ml, 2 x 2 ml) combined extract was diluted to 25 ml and the absorbance was measured at the given wavelength. Beer's law was obeyed over the range of 2-20 ppm of Ce(IV). Interference by tartrate, oxalate and citrate was prevented by addition of HNO_3 before the precipitation of Ce(IV) and the V(V), Ti(IV), Fe(III), Cu(II), Ni(II), Co(II), and U(VI) which all interferes were extracted form 4-8 ml of HCl solution into 0.1 M of the reagent in $CHCl_3$. This method was applied to the determination of Ce in lanthanum oxide.	51
Methyl thymol blue	-	600	–	A study has been made of complex formation between the cited species in both presence and absence of various bases (NH_3 and 12 amines were tested). In the absence of amines a 1:1 complex is formed, and Beer's law is obeyed over 0.5-7 ppm of Ce(IV) with measurement at 600 nm. The complex formed in the presence of amines depends on the order of addition. A 2:1 (M:L) complex is formed, if amine is present. When the methyl thymol blue is added, this complex obeys Beess law from 1.4-13 ppm of Ce(IV) with the measurement at 540 nm. The 1:1 complex formed when the amine is added after methyl thymol blue has maximum absorbance at 590 nm and Beer's law is obyed for 1.4-7 ppm of Ce(IV).	52

Reagent	pH	λ max nm	ε	Remarks	Ref.
PAR and antipyrine.	–	520-530	–	To the slightly acidic sample solution are added 5 ml of 3 mM PAR (Na salt), 2 ml of 1 M antipyrine and 1 ml of 2 M $NaClO_4$. The pH is adjusted to 6.5 with aqueous NaOH and $HClO_4$ and the solution is diluted to 15 ml and shaken with 15 ml of nitrobenzene for 1 minute. The separated organic phase is dried with Na_2SO_4 and absorbance is measured at the given wavelength against the reagent blank. The colour remains stable for atleast 6 h. The optimum pH range, λmax and the upper limit (3.7-5.8 ppm) of the range over which Beer's law obyed are tabulated for La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu. A 1000-fold excess of Cl^-, Br^-, NO_3^-, and SO_4^{-2}, acetate, SCN^- or CN^- and 100-fold excess of F-, $P_2O_7^{-4}$, $S_2O_3^{-2}$, citrate, tartrate or oxalat does not interfere. But EDTA and PO_4^{3-} do. Al, Be, Mo, Ca, Mg and Tl do not interfere in 100-fold excess. Zn, Co, Ni, Cd, Cu, U and Fe(III) must be removed by extracting their diethyl thiocarbonate complex into $CHCl_3$-acetone (5:2).	53
Methyl thymol blue	6.5	515	–	Complex between Ce III, methyl thymol blue and various aliphatic amine, cyclic amines and azo group containing amines have been studied by spectrophotometry with the use of hexamine as the ligand. Beer's law is obyed for 0.02-0.8 ppm of Ce(III).	54

N-phenyl-2-naphtha hydroxamic acid in $CHCl_3$	8.5–9.0	470	5500	Ce(IV) is extracted from aqueous solution at a given pH into a 1% solution of the reagent in $CHCl_3$ and the extract is dried over Na_2SO_4. The absorbance of the 1:4 (M:L) complex is measured at the given wavelength. A rectilinear graph is obtained in the range 0.05–3.0 µg/ml of Ce in $CHCl_3$. There is no interfere in the determination 200 µg of Ce from 30-100 mg of a wide range of ions commonly associated with Ce. The method has been applied to the determination of Ce in rock minerals and sea waters.	55
Arsenazo I	-	-	–	Ce(III), Dy, Eu, Gd, and La were determined in Co and its ferro magnetic alloys by measuring the absorbance of the rare earth and the reagent complex in tri ethanol amine buffer solution of pH 8.1. The parameters of the rectilinear calibration graphare given. Co, Cd, Cu, Fe, Ni, Zn, Ag, Sc, and P were masked with KCN and Al was masked with potassium sulpho salicy. The limits of determination was 0.04 µg/ml of the rare earth metal.	56
4-benzoyl 2, 4-di hydro-5-methyl 2-???phynyl-3-4-phyrazol-3-one	4.8	455	–	A 1:4 (M:L) complex formed between Ce(IV) and the cited reagent can be extracted from the aqueous medium at the optimum pH 4.8 (acetate buffer) into C_6H_6. The extracted complex exhibits maximum absorbance at the given wavelength and obeys Beer's law in the effective photometric range 5-35 µg/ml of Ce(IV). The possible use of the method to determine Ce in monazite sand has been studied. Of the other elements commonly present in monazite sands, UI(VI), Th, Zr, La and Pr are tolerated but Fe(III) interferes. So do citrate, tartrate and EDTA. Errors in determining 45-300 µg of Ce(IV) in pure solution range from -3.0 to + 3.3 %.	57

Reagent	pH	λ max nm	ε	Remarks	Ref.
Xylenol orange and poly-(1-dodecyl 4-vinyl pyridinium bromide)-a surfactant.	-	-	–	The enhancement property of the named surfactant were studied with reference of the spectrophotometric analysis of La(III)-methyl thymol blue. Lanthanoid ions [Ce(III), Sn(III), Eu(III) or Gd(III)] are xylenol orange, Be(II)-chrome azuro and Be-eriochrome cyanine R systems. For the first system quoted there was a marked increase in the absorbance with a shift of the absorption maximum for 603 to 650 nm indicating the formation of the ternary complex> Enhancement and bathochromic shift of absorption maximum were also recorded for the two Be systems. For the xylenol orange systems maximum absorbance was at 611 nm (Ce and Eu) or 613 nm with ε of 1.58, 1.26, 1.06 and 1.03 (each x 10^5) for Ce, Sm, Eu, Gd respectively.	58
Phthalexon S (3, 3'-bis [bis (carboxymethyl) amino methyl] phenol sulpho naphthalein)	8	605-610	20000–25000	Lanthanum forms a La-reagent-hexadecyl pyridinium (1:2:2) complex in an aqueous medium of pH 8(phosphate buffer)i.e., 0.1 mM in reagent and 1 mM in hexadecyl pyridinium bromide. The complex exhibits maximum absorbance at 605 nm (ε = 28400) and Beer's law is obeyed for 0.05-5 µg/ml of La, Pr, Ce, Nd, Sm, Eu, and Gd but Dy, Ho, Er, Tm, Yb, La and Y do not form such complex. Method based on these findings can be used for determining lanthaniods from La to Gd in the presence of Y and the lanthanoids from Dy to Lu. The coefficient of variation was 1.1% (5 results) when determining $La_2O_3 + Gd_2O_3$ (60.2%) in a standard sample containing also 24% of Y_2O_3, 4.5% Dy_2O_3, 10% Er_2O_3, and 1% Yb_2O_3.	59

Stilbazo and CTAB	6.8	580	–	Formation of ternary complex of light rare-earth metals (particularly La, Pr, Nd) at the given pH is prevented at high concentration of CTAB (I). Formation of complex of Ce, Tm, Yb and Lu is uneffected by high concentration of I and formation of complex of other rare earth metals, ex Y, is partially effected. The complexes exhibit maximum absorption at 570 nm (580 nm for that of Ce). In a method for the determination of traces of Ce in lanthanum oxide, use of 1.6 mM of I effectively suppresses complex formation by La.	60
4, 4'-bis (3-methyl-1-phenyl pyrazolin-5-one) (I)	-	580	–	A study of the optical properties of the cited reagent (I) is reported. For the determination of Ce(IV) a solution containing 70-700 µg of Ce(IV) is mixed with 2.5 M H_2SO_4 (25 ml) and 0.01 M of I (5 ml) and extracted with $CHCl_3$ (15 ml) and the absorbance of the extract is measured at the given wavelength vs. a blank. Alternatively the acidified test solution is titrated potentionmetrically with 0.01 M of I with the use of a Pt electrode vs. the SCE. Limits of detection are 6.9 and 12.3 µg/ml respectively. To determine H_2O_2 a solution containing 0.1 to 10 mM H_2O_2 is mixed with 6 M HCl (30 ml) and 0.5% I solution (5 ml) after 3 hrs. The mixture is extracted with $CHCl_3$ (15 ml) and the absorbance of the extract is measured at 580 nm vs. a blank. Detection limts is 9.5 µm.	61

Reagent	pH	λ max nm	ε	Remarks	Ref.
Quinalizarin	5.0	560	–	To determine Ce(III) (2-20 ppm) the solution is treated with an aqueous solution of the reagent in a buffer mixture of pH 5.0. The mixture is diluted to 100 ml with water and the absorbance of the resulting solution is measured at the given wavelength. Many ions interfere. The reagent-Ce(III) complex can also be used to determine F(76-1134 ppb) in aqueous 30% DMF at pH 4.1 by heating the solution at 100°C for 45 min. After cooling measure the absorbance at 660 nm.	62
m-formylchloro phosphonazo [6(4-chloro-2-phosphono phenylazo)3-(3-formyl phenyl azo)-chromotropic acid] (I)	-	680	156000–170000	In 0.1 M HCl rare earth metals react with the cited reagent (I) and CTAB (II) to produce purple 1:4:8 ion association complex having the given λmax. The test solution is treated with 2.5 ml each of 1 M HCl and 95% ethanol and 2 ml each of aqueous 0.4% II and aqueous 0.05% I, then water is added to produce 25 ml. Beer's alw is obeyed for $\leq$ 20 µg of rare earth metal in 25 ml and the colour is stable for 90 min. The error in the determination of 10 µg is $\leq$ 10% in the presence of 40 ml Mn(II) 5 ml of Fe(II) , or F-, 4 ml Ni, Cu, Zn or Cd, 3 ml of Cr(III), 2 ml of Fe(III), Pb or V(V), 1 ml of Mg or Co, 0.5 mg of Ca or Al, 0.2 mg of Ti(IV), 20 µg of W(VI) and 5 µg of Zr. To determine Ce in alloy steel the sample is dissolved as described earlier. Hydroxides are precipitated from the clear solution in the presence of 10 drcps of 1% $MnCl_2$ solution and some papu pulp. The mixture is filtered and the precipitate is washed several times with 2% NaOH solution and once with water. The precipitate is then dessolved in the original beaker in 25 ml of HCl (1:1).	63

				The solution is evaporated to drigness, the residus is dissolved in HCl (1:1) and the solution is diluted to known volume with water. An aliquot is treated with 1% oxalic acid solution to mask Co, Fe, Al, Zr and other metals and Ce is determined as described above. Results of the sample containing 14-210 ppm of Cu were satisfactory.	
Purpurin	8	450-600	–	The reactivity of 44 cations with purpurin (80 µm) solution in aqueous 40% ethanol is examined at a given pH in the MIBK-H_2O system. The chelates of Ni, Co, Zn, La, Y, Ce and Pr have been prepared and extracted. The absorption spectra have been recorded. The stoichiometry indicated are 1:1 and 2:1 with bivalent and tervalnt ions, respectively.	64
PAN	10.2	545	39 50	A sensitive procedure has been developed for the spectrophotometric determination of Ce(III). At the given pH Ce racts with PAN in 40% ethanol medium to form a red complex having the given λmax. The complex is most stable in pure ethanol. The stoichiometry and the structures of chelates were studied by conductometric titration. Ir and vis spectrophotometry. The mode of co-ordination was identified.	65
2, (5-bromo-2-pyridyl azo) 5-diethyl amino phenol	10.4	605	-	The cited reagent forms stable complex with Y, Ce(III) and La The absorbance is measured at a given λmax for Y and Ce and for La at 610 nm. Beer's law is obeyed for up o 15 µg/ml of each metal The best sensitivity is obtained at pH 9 9 10.4 and 11.0 for Y, Ce and La respectively. Sensitivity for each element is considerably better than that of previous spectrophotometric method. Alkali and alkalin earths, and many anions do not interfere in upto 500fold excess, but some cations ex Zn^{2+}, Hg^{2+}, Cu^{2+}, Sb^{3+}, Cu^{2+} interfere.	66

Reagent	pH	λ max nm	ε	Remarks	Ref.
PAR	6.5	480	–	Mixtures containing La, Ce, Pr, Nd each at a concentration of approximately 10 μM can be analysed for the componenets spectrophotometrically by measuring the absorbance of lanthaniods-PAR complexes at 490 nm (or 480 nm) and 550 nm at pH 6.1, 6.5, 7.1 and 7.5 in aqueous solution containing ≥ 20-fold molar excess of the reagent relative to the sum of the lanthanoids. From the 8 absorbance values (and from previously determined ε values of the individual complexes) the concentration of each component can be computed. The method was used for determining La, Ce and the sum of Pr and Nd in monozite sand. The lanthanoids were initially separated as oxalates and then Th was removed by precipitation with N-phenyl benzo hydroxamic acid.	67
Oxidation with persulphate and Ag^+	–	330	–	Ce is separated by precipitation with oxalic acid at pH 1.0 ± 0.1 in presence of La(III) as carrier oxidant with persulphate catalysed by Ag^+ is used and the absorbance of Ce(IV) is measured at the given λmax. The same solution after selective production of Ce(IV) with azide is used as the blank. Addition of H_3PO_3 prevents the precipitation of the oxidised Mn. The présent method gives good results in the determination of 0.001-0.2% of Ce. Optimization of the method is discussed.	68

N-(4-chloro phenyl) cinnamo hydroxamic acid.	8–9	460	–	A portion of test solution containing 0.05-0 5 Mg of Ce(IV) was diluted to 20 ml and treated with an ethanolic 0.2% solution of the cited reagent. The pH was adjusted to 8.9 with aqueous ammonia or dil HCl, the solution was diluted to 50 ml and 1:4 (Ce:R) complex was extracted with $CHCl_3$. The extract was diluted to 50 ml with $CHCl_3$ and dried over Na_2SO_4 and its absorbance was measured at the given wavelength vs. $CHCl_3$. Beer's law was obeyed for 2-18 ppm of Ce and the co-efficient of variation can be avoided by initial extraction at pH 3.0 or below, the Ce remained in the aqueous layer.	69
Phenathiazines	-	510	–	Promathezine hydrochloride, promazine hydrochoride, chloropromazine and thio-promazine mesylate each forms a 1:7 complex with Ce(IV) in dil H_3PO_4 medium. The complexes exhibit maximum absorbance at the given λmax. optimum analytical range, ε values and Sandell sensitivity for each complex are tabulated. Bivalent Fe(II), Sn(II), As(III), V(V), NO_2^-, $FeCN_6^{-}$, SCN^-, $S_2O_8^{2-}$, SO_3^{2-}, and BrO_3^- interferes seriously.	70
Substituted hydroxamic acid	9.0	465	–	The sample (1 ml) was mixed with 3 ml of ethanolic 0.2% N-(4-chorphenyl)-3,4,5-trimethoxy cinnamohydroxanic acid(I) solution. The pH was adjusted to 9.0 by the addition of borate buffer solution and the volume was made upto 25 ml. The solution was extracted with 10 ml of $CHCl_3$. A further 2 ml of I solution was added to the aqueous phase and the extraction was repeated with 2x5 ml of $CHCl_3$. The combined extracts were diluted to 25 ml with $CHCl_3$ and the absorbance of the resulting solution was measured at the given wavelength. Beer's law was obeyed in the range 0.3 to 15 ppm of Ce(IV) in the final solution. The method was applied to monazite ore or sea water.	71

Reagent	pH	λ max nm	ε	Remarks	Ref.
Tetraethylene pentamine hepta acetic acid TPhA.	5.5	304	45000	A solution containing 10-100 µg Ce (III), was mixed with 2.5 ml of a 0.2 M solution of the cited reagent and made upto 100 ml with water and after 10 minutes the absorbance of the intensely yellow chelate was measured at the given wavelength. Beer's law was obeyed over the range 0.05 to 0.5 ppm of Ce only Fe(III) ($\geq$ 100 ppm) caused slight interference. Various ions were tested for their effects under the conditon of this procedure.	72
Ferrion [tris-(phenanthroline) iron III].	-	530	–	The method was based on the oxidation of Ce(III) to Ce(IV) by this reagent, in the presence of $Na_2H_2P_2O_7$ and determination of the purple-red Fe(II) complex formed by absorbance measurements at the given λmax upto 400 µg Ce(III) could thus be indirectly determined (in 50 ml of solution) with a relative error of $\pm$ 3.5%. The method was applied to the determination of Ce(III) in commercial preparation of ceria and of ceric sulphate.	73
Prochloroperazine bismuthane sulphonate (I).	-	526-530	9160	The cited reagnet (I) instantaneously forms a red complex with Ce(IV) in 4-6 M H_3PO_4. At least a 15 fold excess of I over Ce is needed for full colour development. Beer's law is obeyed from 0.2 to 16.0 µg ml^{-1}. Tolerance limit (µg ml^{-1}) for various ions in the determination of 6 ppm of Ce are La, Pr, Nd, Gd, Dy, Ho, Eu, Er, Yb, Y, Tb and Sm (4500); Fe (3600); Mg (1400); Zn (1500); Mo (1200); U (1300); Cd (1500); Pb (300); Co (250); Cu (280); Ni (400) and F , Br, SO_4^{2-}acetate, citrate, tartrate NO_3^- between 1000-10000 The relative error is $\pm$ 0.2%; $S_2O_3^{2-}$. I, EDTA and Pt group metals are poorly tolerated. Synthetic misch metals have been analysed by this method.	74

p-acetylarsenazo	2.2	670 & 542	–	In an acid medium of pH 2.2 (after dissolution in 5% HCl & 7% NaCl solution) La, Ce, Pr, Nd and Sm form 1:2 complex with the cited reagent with which they can be determined by dual wavelength spectrophotometry at a given wavelength. Oxalic acid (0.2%) is used to mask heavy rare earth metals, Al and Fe. Recoveries were 82 to 115%. The method compares favourably with the use of chlorophosphonazo III and phospho nazo III.	75
Bromo phospono bis azo-derivative of chromotropic acid	-	-	–	The synthesis of 14 of the cited reagents is discribed. The substitution of Br for Cl produced improved sensitivity, contrast and stablity in the complexes with the rare earth elements. Particularly good results were obtained for the complexes of elements of Ce and Y sub groups. In the pH range 0.8 - 1.5 and 0.8 - 1.2, the complex absorbs at 670 - 685 nm and 663 - 730 nm, with ε values of 82000 to 112000 and 45000 - 102000 for Ce, Y respectively. The effect of addition of surfactants to the complexes has also been studied.	76
Chrome Azurols	7.4 - 8.4	610	18000	Complex formation of Al, Ga, In, Sc, Y La and Ce (III) with purefied chrome Azurola (I) was studied spectrophotometrically and the analytical properties of the metal chelates produced were established. The Al-I (1:1) complex was formed at optimum pH of 5.4 - 6.2 and it exhibt maximum absorption at 546 nm (ε- = 64000). Analogous values for the other metal complexes of I (1:1) were Ga, pH 4.8 - 5.2, 560, 57000; In, pH 5.8-6.2, 560,13000; Sc, pH 6.0 - 6.3, 550 nm, 30000; Y pH 7.6 - 8.6, 560, 22000 La pH 7.6 - 8.6, 610, ε = 165000 and Ce as given.	77

Reagent	pH	λ max nm	ε	Remarks	Ref.
Nitro phospho nazo - mN [6- (3-nitropheyl azo)-3-(4-nitro-2-phosphono phenylazo) chromotropic acid].	-	660	81000	The cited reagent prepared by an azo coupling reaction in LiOH solution forms stable blue complex with rare earth metals in strong acidic medium (8ml of HNO_3 and 50 ml of H_2SO_4 dilute to 1 lit). At the given λmax against blank 0-12.5 µg of Ce is 25 ml solution could be determined. Recovery of 10 µg of Ce in 97.9 to 100%. Coefficiant of varation is 0.87% (n = 10). This reagent is used for the spectrophotometric determination of Ce sub group element in the presence of Y sub group elements masked by oxalic acid.	78
P(m)sulphamoy sch orophospho n a z o [3 - [4 - c h l o r o - 2 - phosphophenyl azo)-6-(4 (cr 3) sulphamoyl phenylazo chromotropic acid]	-	668	9600	The preparation of reagent is discussed. This reagent forms complex with Ce is 0.1 to 0.2 M HNO_3 with given ε at the given λmax. This reagent is used for the colorimetric determination of rare earth metals in Al alloys.	79
3(4-chloro-2-phosphono-3-tri fluoro methyl phenylazo chromotropic acid.	0.6 to 1.6	670	79500	Upto 30 µg Ce (or La, Pr, Nd) treated with 2.5 ml of 1M HCl 3 ml aq .05% reagent and H_2O to 25ml and measured against reagent blank. Beer's law is obeyed for ≤ 1.2 µg ml^{-1} of analyte. Serious interference caused by Zr, Sc, Fe, Ti or W is masked by 25 ml of oxalic acid. In iron based alloy sample is dissoved in 30 ml acid mixture of 5% H_2SO_4 8%. HNO_3 and 2 ml of 3% $(NH_4)_2 S_2O_8$ and cooled. The	80

				solution is diluted and filtered 5 ml of it is treated with 10 ml of 5% oxalic acid and 5 ml of 0.05% reagent. Al based alloys dissolved in 6 M HCl and add H_2O_2, boil to dryness, and again boil in 6 M HCl and treat with 5.2 ml of 5% oxalic acid and 0.05% of reagent. Satisfactory results were obtained.	
Pyrogallol red-I	5.0	507	–	The oxidation of pyrogallol red (I) by Ce(IV) in acetate buffer solution at pH 5.0 at 25°C was studied by monitaring the absorbance at the given λmax. For 63 µM I calibration graph based on absorbance measurements taken 5 min. after mixing the reactants were rectilinear for 0-15 ppm of Ce(IV). For the determenation of 2-15 ppm of Ce(IV), the coefficient of variation was 3.1 to 0.3% (n, 5). A study on the effects of 26 foreign species on the oxidation of 64 bM I by 6 ppm of Ce (iv) showed that there was serious interference.	81
Trichloro phosphonazo	-	641-644	108000 117000 108000 86000	The cited reagent reacts with rare earth metals in 0.2 to 1.2 M HCl medium to give complexes that absorbs at the given wavelength. The reagents absorbs at 548 nm. ε vlues are given for Ce, Gd, Y, Yb respectively. The effect of foreign ions on the determination of 10 µg of Ce are reported. Beer's law is obeyed for upto 1-2 µg ml^{-1} of Ce.	82

Reagent	pH	λ max nm	ε	Remarks	Ref.
Perphenazine	-	516	8600	10-500 µg Ce is mixed with 11.25 of 10 M H_3PO_4, 2 ml of 0.2% reagent and diluted to 25 cc. Absorbance is measured at a given λ max with the given ε. Beer's law is followed between 0.4-20 ppm of Ce (IV) with an optimum working range of 1-19 ppm. The relative errors and standard deviation (10 determinations, 5 samples) ranged from + 0.55% to -0.53% and 0.01 - 0.02 respectively. Many foreign ions do not interfere in the determination of 7 ppm of Ce(IV) but vanadate, $Cr_2O_3^-$, IO_3^- and MnO_4^- interfered at all concentrations. Indirect determination of As(III) was done byoxidation to As (IV) with a known excess (20 - 100%) of $Ce(SO_4)_2$ in 0.25 - 0.5 M H_2SO_4 medium containing 1.2 µg of Os (VIII) as catalyst. Nitrite was also determined indirectly by its oxidation to NO_3^- in 0.5 - 1 M H_2SO_4 by a similar known excess of $Ce(SO_4)_2$. The un reacted Ce(IV) was then determined by the proposed method. Suitable range of determinations were 0.5 - 3.1 µg/ml of As (III) and 0.04 - 1.5 µg/ml of NO_2^-. The method for Ce(IV) was used successfully for its determination in synthetic mixture corresponding to mish metal.	83
3-methoxy and 3,4,5-trimethoxy derative of Dibenzoyl methane (I & II respectively).	8.5-9.3 (I) 7.2-8.0 (II)	390 I 394 II	–	The cited reagents were synthesized and were used in the spectrophotometric determination of Ce(III). I forms yellow complex at the given pH and λmax and II forms yellow complex at given pH and measured at given λmax with either reagent. Metal:ligand ratio is 1:2 and the respective Sandell sensitivities are 18.7 and 25.7 ng cm^{-2}.	84

DBC-arsenazo [3-(2-Arsono phenylazo) 6-(2, 6-dibromids-4-chlorophenyl azo) chromotropic.	1.7 M HCl	630	129000	The cited reagent forms 3:1 (L:M) complex with rare earth metals in 1.7 M HCl. I can be used as a colour reagent for direct spectrophotometric determination of Ce in high temperature alloys. The sample (0.1 to 0.2 g) is dissolved in aqua regia and treated with 7.5 ml of H_3PO_4. The mixture is heated to fuming then 10 ml of 6 M HCl is added and the solution is boiled cooled and diluted to 50 ml with H_2O. For the preparation of the reference solution a 5 ml portion of the sample solution is treated with 5 ml of 10% of $Na_4P_2O_7$ solution, 2 ml of 10% sodium hexameta phosphate solution and 2.5 ml of 0.5%. I solution and diluted to 25 ml with H_2O. For the production of a coloured solution the other portion of the sample solution is treated with 5 ml of 6 M HCl and 2.5 ml of 0.05% I solution and diluted to 25ml with H_2O. The absorbance is measured at given λmax with gives ε-Beer's law is obeyed upto 0.8 μg ml^{-1} of Ce. Upto 50 mg of Ni(III) and 8.5 mg of Cr(III) do not interfere.	85
Sulphanilic acid	-	495	–	Combined ion exchange-spectrophotometric study of Ce(IV) and reagent were done. The mixture of Ce(IV) and reagent was passed through the column (15 cm x 1 cm) of vionit CS-3 (H^+ or NH_4^+) or vionit AT-1 (Chloride form). The percolate was diluted and measured at a given λmax with the removal of all interferences.	86
4-sulpho-2-aminobenzenethiol [3-amino-4-mercaplo benzene sulphonic acid.	-	560	8060	To a portion of the test solution was addded 7 ml of aq 1 % reagent and the mixture was made 1.9 M in HCl. After 45 min the solution was diluted to 25 ml with H_2O and the absorbance was measured at the given wavelength vs water. Beer's law was obeyed for 0.4 - 18 ppm of Ce and Sandell sensitivity was 17.2 ng cm^{-2}. There was no interference from Zr, Th, Ti(IV), Mo(VI), U(VI), Zn, Pb(II), Cr(III), Cd, Ni(II) Co(II) or Cu(II) or from 17 anions tested.	87

Reagent	pH	λ max nm	ε	Remarks	Ref.
Catechol violet	–	–	–	Reference only.	88
Molybdate and pyrocatechol violet, I	0.6–1.8	614	10100	Molybdate reacts with catechol violet (I) in the given pH range to form blue complex having the given λmax. The molar ratio of Mo(VI):I is 1:1. The colour of the complex is discharged by oxidation of Ce(IV). The extent of decolourisation being proportional to the Ce concentration. The oxidation reaction has been applied in the spectrophotometric determination of Ce in mixtures of rare earth metals. The optimum pH of the reaction is 1.05-1.35 and no interference is caused by 1000 fold amounts of La, Sm or Pr.	89
Tiron	-	500	14131	Ce(IV) is determined as its purple red complex with the reagent by measuring the absorbance of the stable soluble complex at at the given λmax. Beer's law is obeyed for upto 40 µg /ml of Ce(IV). Ce(III) did not form a complex with the reagent. Foreign ions did not interfere except for iron. The method was used to determine Ce(IV) in rare earth metal mixtures with satisfactory results without previous separation and oxidation of Ce.	90
4-(2-thiazolylazo) resorcinol (TAR) and 1-(2-thiazolylazo)-2-naphthol (TAN).	8.0 6.8	550 610	-	An acidic solution containing less than 80 µg of Ce(III) was mixed with 10 ml of borate buffer and 1 ml of either TAR and TAN together with 5 ml of propanol to dissolve	91

				the sparingly soluble complex formed with TAN). The mixture was diluted to 25 ml and the absorbance was measured at 550 or 620 for TAR and TAN respectively. Beer's law was obeyed for 0.6-2.2 and 0.08-2μg/ml of Ce(III) respectively. The tolerance limits of 50 interfering ions were studied. Both methods allowed determination of Ce(IV) after reduction to Ce(III).	
P-nitrochlorophosphonazo	-	672-674	-	The mineral sample fused with Na_2O_2 and interferent impurities were extracted with 4-benzoyl-3-methyl-1-phenyl-pyrazolin-5-one before reaction of the rare earth metals with the reagent in HCl medium. The Ce sub-group element (La, Ce, Pr, Nd Sm) formed complexes with the given λmax and yittrium sub-group (Tb, Dy, Ho, Er, Tm, Yb, Lu, Y) complex showed λmax at 727-731, each sub-group could be determined with little interference by the other one.	92
Chlorphosphar azo III	-	660-665	15500–17300	The proposed method is suitable for the determination of lanthanoids in organic extracts of 30% bis-(2-ethyl hexyl) hydrogen phosphate in kerosine or 0.2 M trioctyl amine in toluene. A portion of the organic extract containing ≥25 μg of lanthanoids is mixed with butanol until a homogenous solution is obtained. The 5 ml of 0.04% of the reagent in butanol is added. The mixture is diluted to 25 ml with butanol and the absorbance in measured against a reagent blank. For La, Ce, Pr and Nd the λmax occurs in the given range and the given ε values. Beers law is obeyed for upto 1μg/ml of lantanoids. The reagent is sensitive to other metal ions ex. Th(iv), Fe(III), Cu(II), and Co(II). The envisaged use of the method is in the measurement of extraction constant and distribution coefficient of individual lanthanoids.	93

Reagent	pH	λ max nm	ε	Remarks	Ref.
DBN Chlorophosphonazo	-	640-648	106000	The reagent forms complex with Ce sub-group elements in 0.5M HCl in the presence of oxalic acid and H_3O_4. These complexes are stable and have the given λmax and ε values. Beers law is obeyed for 0-10 µg of Ce in 25 ml. The method was applied to determine Ce sub-group elements in steel and cast iron.	94
Arsenazo III-Cu-1, 10-Phenanthroline-Rare earth system	3-4 5	665	132000	Analysis was based on the fact that in the mentioned pH range the greatest absorbance of the complex (1:2:2 of Ce La, Ho or Eu with the given reagent at their given λmax, but their λmax of the reagent blank was at 550 nm. ε values were 13700, 11000, 9500 and 8400 respectively in the absence of masking agents. Beer's law was obeyed upto 0 8 µg/ml of rare earth metals The following species (mg) did not interfere V and Cr (0.02) Sb, Ba, Ca, Mo and W (0 1) and Al, Mn (0 5) when excess of I was present Zn. Co, and Ni did not interfere Small amounts of Fe(III) Pb, and Sn could be masked with Zn acetate-Na_2 EDTA The standard deviation (n=6) for the determination of 5 µg fo Ce - La (1:1) in the copper based alloys containing Al, Mn and Fe was 0.13.	95
2-(p-sulfophenylazo)-1, 8-dihydroxynaphtho'3,6-disulfonic acid [SPADNS].	4.5-5.0	585	2300	The 1 1 complexes of Be (II) (λmax; 585 nm; ε = 1000) and Ce with the cited reagent have been used for the spectrophotometric determination of the metals in acetate buffer at the given pH. Beer's law ranges are 0.5 to 3 00 and 25-500 µg in 25 ml of solution for Be and Ce respectively	96

				Sandell's sensitivities are 0.03 and 1.25 μg cm-2 respectively. Non interfering ions are listed Cu, Zn, Cd, Sn(II), Fe(III), Al, Zr(IV), Th(IV) rare earth metals (except Lu(III) and Yb (III) with Ce) F^-, PO_4^{3-} copraate and tartrate interfere. Upto 5mg of Fe and Cu can be masked with mercaptoacetic acid and $S_2O_3^{2-}$ respectively.	
4-Chlorophosphonazo (4-CPA)	1.4	706	133000	Such derivatives of the form 3(6)-(4-chloro-2-phosphono phenylazo)-6(3)-(x) chromotropic acid were prepared in which x was 4-bomo phenylazo (I), 4-nitrophenylazo, 2, 4, 6 tribromo phenyl azo. The usefulness of the compound as spectrophotometric reagent for Y and Ce was tested and the dervative I was shown to form complexes with the λmax at 174, ε = 66700 for Y and 706 nm, ε= 133000 for Ce. Beer's law was obeyedin the range 3-20 μg of Y and 5-22.5 big of Ce in 25 ml of final solution. Optimum pH values for complex formation were 4-6 for Y and 1.4 for Ce.	97
3-(2-arsonophenyl azo)-6-(2- 6-dibromo 4-chlorophenylazo)-4,5-dihydroxynaphthalene 2, 7 di sulphonic acid.	-	640	120000	The reagent forms 3.1 (L:H) complex with Ce-group metal in HCl medium. The complexes exhibit the given λmax. Reagent was used as a colour reagent for direct spectrophotometric determination of Ce in tap water or well water. A 2.5 l sample was evaporated to 40 ml and filled immediately. The filter paper and insoluble residue were washed with H_2O and the combined filtrate and washing were diluted to 50 ml. A 10 ml portion of the solution was treated with 7 ml of 6 M HCl, 1 ml of 1% ascorbic acid solution and 3 ml of 0.041, reagent solutions and diluted to 25 ml of H_2O. The absorbance of the solution was measured at the given λmax. Beer's law was obeyed upt 0.8 μg ml^{-1} of Ce.	98

Reagent	pH	λ max nm	ε	Remarks	Ref.
Chlorophosphonazo p-benzoyl glycine.	16-32 Mol/dm³ HCl	681	–	Rare earth-reagent-cetyl pyridinium bromide in the presence of alcohol have been studied. Blue complex is formed. The apparent molar absorbance coefficient for Ce is $1.65 \cdot 10^5$ L mol^{-1} Cm^{-1} at the given λmax Ce:Reagent: CPB ratio in 1:3:4. Beer's law is obeyed between 0-15 μg/25 cm^3 with oxalic acid as masking agent many ions donot interfere. This method is used to determine Ce-group metals in Mg alloys and cast silver samples.	99
Dibromo p-nitro chloro phoshonazo (DBNCPA)	5.5	642	104000	A 0.1 g sample was digested with a mixture of H_2O, HF and $HClO_4$ and the digest was treated with 1 ml of H_2O and 1 ml of 30% H_2O_2 and evaporated to dryness. The residue was dissolved in 7 ml of cone HCl and the solution was diluted to 50 ml with H_2O. A portion of the solution (contg > 10 big of Ce) was mixed with 1 drop of 0.03% methyl orange indicator 2 ml of 10% K. Na. tartrate. cone. aqueous NH_3 to a yellow colouration 4 ml of Na acetate buffer (pH 5.5) and H_2O to 10 ml. The mixture was extracted for 1min. with 10 ml of 0.01 M reagent in light petroleum and 0.5 ml of 180 amyl alcohol. The organic layer was back extracted with 10 ml of 1 M HCl for i min. and 2 ml of 5% oxalic acid, 5 ml of .02% reagent were added to ag phase. The absorbance was measured at the given λmax vs reagent blank. Beer's law was obeyed upto 10 μg of Ce in 25 ml of solution. Recovery was > 95% the coefficent of variation (n = 3 to 5) was ≤ 2%. Little interference was observed	100

N-(4-Chloro phenyl)-2 furyle acrylo hydroxamic acid	9.0	470	8500	Sample solution containing 4-40 µg of Ce(IV) was adjusted to the given pH with 1M HCl and NaOH and 5 ml of ethanolic 5% reagent was added with stirring. The precipitate was extracted with $CHCl_3$ (2 + 5 ml) and the combined extract was diluted 2-25 ml with $CHCl_3$ and absorbance was measured at the given λmax. The binary complex could be converted to ternary complex for increased sensitivity. The $CHCl_3$ extract was mixed with 10 ml of aq. 0.01% PAN amd 0.02% tartaric acid at pH 6.4 and shaken for 5 min. Organic phase was separated and diluted to 25 ml with $CHCl_3$ and absorbance was measuredat 515 nm (ε = 18000). Ce is determined in organic biological tissue plant and water.	101
Arsenazo	-	610	-	A sample typically silico manganese was decomposed incompletely with HNO_3 and HCl and the mixture was evaporated to dryness. The residue was dissovled HCl and solution was filtered and diluted. Masking agent (Ascrobic acid and ammonium oxalate) and buffer solution containing HCl and KCl were added. The solution was acidified with 0.1M HCl. Ce concentration was determined with 0.01% reagent by measuring absorbance at the given λmax vs. reagent blank. Calibration graph was rectilinear upto 2 µg/ml.	102
Dibromo-p-nitro chlorophosphonezo (DBNCPA)	-	642	104000-110000	The cited reagent forms complex with La, Ce Pr, Nd and Sm in aq HCl medium. The absorbance of the colour is measured at the λmax given. Yttrium sub-group metals and other interfering ions can be masked with oxalic acid. Reagent was used to determine Ce in Ni alloys.	103

Reagent	pH	λ max nm	ε	Remarks	Ref.
3-(2-arseno phenyl azo)-6-(2, 4, dibromo -6-carboxyphenylazo) chromotropic acid benzoyl metaone	-	634	122000 132000	This reagent has been used to determine Ce sub group rare earth metals in soil. 1 gm sample was treated with 30 ml of aqua regia overnight and then digested for 3 hr by heating nearly to dryness. The residue was mixed with 5 ml of $HClO_4$ heated to expel white fumes and dissolved in hot HCl (1:1) and the solution was filtered. The residue was washed with ~ 1% HCl and the filtrate was diluted to 100 ml with H_2O. A 3 ml portion was mixed with 12 ml of 6 M HCl, 5 ml of 5% oxalic acid, 3 ml portion of 1% reagent solution and H_2O to 25 ml absorbance is measured at 634 nm vs reagent blank. Beer's law obeyed upto 1 μg ml^{-1} of Ce. Revoeries of 2-6 μg of Ce ranges from a 95.8-99.3%. Effect of 26 common ions on the diterminations of Ce twere investigated. Y sub-group rare earth metals and other foreign ions could be masked with oxalic acid	104
3, 4, 5 - Trimethoxy 4'-methyl di benzoyl methane	6.9-7.5	410	17000	A brownishe yellow complex was formed between Ce(III) and the cited reagent at the given pH and the absorbance was measured at λmax. The Beer's law ranged from 0.1 to 0.6 mM of Ce(III). Sandell sensitivits was 8.2 ng cm^{-2} and coefficent of variation was < 1% (n = 10).	105

15 C.own 5 with picrate	6-8	655	–	Ce(III) was quantitatively extracted from solution also ccntaining U(VI), Sc, Y, Th, Sr and Ca with 5 mm 15 crown-5 at the given pH with 10 mM. Pcericacid as the counter ion and shaking for 10 min. The orgnic layer was then extracted with 1 M $HClO_4$ for 10 min. and Ce(III) was determined in the aq. layer as its arsenazo (IV) complex at the given pH. The optimum concentration of Ce(III) for quantitate determination was 0.5 to 4 µg ml-1. Extraction with other crown ethes was less effictive. This method is applied in the analysis of monozoilt sand.	105
3-(4 ace yl)-2- arsenophenylazo chromo rc p c acid.	3.2	670	–	Mixed rare earth oxide sample (0.1 gr) was dissolved in little H_2O and 6 M HCl. To 2 ml of solution were added 5 ml of chloroacetic acid, 0.1 M NaOH buffer of pH 3.2, 2 ml of aq. 0.2 M EDTA and 1 ml of aq. 0.2M Zn-0.2M EDTA followed by adjustment to pH 3.2 with HCl (1:1) or aq. NH_3 and addition of 3 ml of aq. 0.1% reagent and H_2O to a known volume. After 10 min. absorbance is measued at the given λmax vs. reagent blank. Beer's law was obeyed between 1-35 µg of La and Ce in 25 ml solution for analysis of 14 µg of La_2O_3 and CeO_2. Coefficent of variation (n = 5) was <5%. Interference from 28 coexisting ions as well as large amount of heavy and light rare earth metal was masked by EDTA and Zn-EDTA. No pre treament was needed and the results was satisfactory.	107

Reagent	pH	λ max nm	ε	Remarks	Ref.
P-acetyl arsenazo		670	–	The sample is treated with 10 ml of chloroacetic acid - Na acetate buffer solution of pH 3.2, 1 ml of aq. 0.02M Zn-0.2M-EDTA, HCl or aq. NH_3 to pH 3.2, 3 ml of 0.1% p-acetyl arsenazo solution and H_2O to 25 ml and after 10 min. the absorbance was measured at given λmax vs. reagent blank. Measurement is than repeated with 2 ml of Zn-EDTA solution in the presence of 1 or 2 ml of this solution. Absorbance of La and Ce differ sufficently and their indvidual concentration can be calculated by simultaneous equations. The coefficient of variation were < 5%. There is little interference from foregn elements. This method is applied to the synthetic samples and Al alloy with satisfactory results.	108
Di-bromo carboxy arsenazo	–	632	140000	Synthesis of the reagent (I) from 2 amino-3,5-di bromo benzoic acid and arsenazo (I) is discussed. To determine Ce 10 ml of CeO_2 is dissolved in 6 ml of 6 M HCl before mixing with 5 ml of 0.05% I solution diluted with H_2O. Absorbance is measured at the given λ max vs. reagent blank. The solution is stable for 24 hrs. Beer's law is obeyed in the range of 0-20 μg of Ce in 25 ml of solution. Most foreign ions in mg amount do not interfere. The method was compared favourable with methods using chloro phosphonazo (III) and arsenazo DBS.	109

Pyridine-2-6, diol	-	410	71000	0.4-2.8 µg of Ce(III) was treated with 5-fold excess of the reagent and 2 ml H_2SO_4. Mixture is heated on a water bath for 15 min. cooled and diluted to 10 ml and the absorbance is measured at the λmax. Among foreign tested only the lanthanoids interfere.	110
Tribromo arsenazo	-	630	136000	La and Ce in 1-2 M HCl were reacted with the given reagent to form 1:3 complex and the absorbance of the solution was measured at its λmax. A Rosenbrack algorithm routin based on BASIC is presented for the determination of the composition, molar absorptivity and apparent stability coefficient of the complex and the concentration of the complexing agent.	111
$(INH_4)_2$ S_2O_8 and Ag^+		380	1200	Ce was determined in HNO_3-H_2SO_4 with the given compounds at the given λmax. Beer's law was obeyed for 100-1000µg 25 ml^{-1} of Ce and recoveries were 94-108%.	112
Calix [4] arene-5, 11, 17, 23-tetra-sulphonate.		417	–	The solution (5ml) containing 0-400 µg of Ce(III) and 500µg of La(III) was mixed with 0.025 M of the reagent (5ml) and 1M NH_3-NH_4Cl buffer. After dilution to 25 ml the abosorbance was measured at the given λmax. The calibration graph was rectiliner. Other lanthanoids did not interfere and their presence was necessary in concentration >20ppm to maintain a constant colour intensity. Therefore the measurement was carried out in the presence of La.	113

Reagent	pH	λ max nm	ε	Remarks	Ref.
Resorcylaldehyde quanyl hydrazone.	-	425	6500	Sample solution containing 100 µg of Ce(IV) was heated for 30 mn. with 4.2 ml of aq. 1 mM. Resorcylaldehyde quanyl hydrazone and 2 ml of borax-NaOH buffer of pH 12.5. The cooled mixture was adjusted to pH 12.5 with buffer solution and diluted to 10 ml with water. The absorbance of the resulting yellow complex was mesured at the given λmax vs. reagent blank. Beer's law obeyed for $\leq$ 5ppm of Ce(IV). The effect of diverse ions is discussed. The method was used for the analysis of the Mg based Ce alloy.	114
P nitrochlorophosphonazo	-	680	-	Sample (0.5-1 g) and 20 mg of Fe was dissolved by heating in 30 ml of HNO_3 (1:2) and then boiled to remove any oxides after cooling 10 ml of H_2O and 5 gr. of NH_4Cl were added before heating at 70 to 80°C and the solution was neutralized with amononium hydroxide to precipitate $Fe(OH)_3$ Ce and Ce group metals. The solution was filtered, the precipitate was dissolved in 20 ml of hot HCl(1:1) and the solution was evaporated to fumes with 8 ml of H_2SO_4 (1:1). The residue was dissolved and diluted with H_2O 100 ml and portion (10 ml) of the solution was treated 4 ml Fe, 5 ml of oxalic acid (100g/lit), 5 ml of reagent and H_2O to 25 ml. The absorbance of the mixture was measured at the λmax vs. a reagent blank containing 1.6 ml of H_2SO_4 (1:3). After pretreatment and masking little interference was obsorved. Results were compared with those obtained by the chloro phosphonazo method.	115

4-Bromoarsenazo	4.5	-	–	La, Ce, Pr, Nd were determined in Al by treating the sample with the reagent in buffer (pH 4.5) to form blue complex followed by simultaneous spectrophotometric determination with Kalman filtering.	116
Methyl orange	-	510	11000	Methyl orange in 1.2 to 2.2 M H_2SO_4 was oxidised and decolourized by Ce(IV) in mixedrare earths and absorbance was mesured at the given λmax. The amount of Ce(IV) present was inversely proportional to the absorbance and Beer's law was obeyed from 0-25 µg/ml of Ce(IV).	117
4, 5-dibromopyrocatechin	9.5	540	–	Sample was decomposed with 50% HCl and 30% H_2O_2 treated with ethanolic 0.1 M reagent at pH 9.5 and any Fe present was removed by extraction into butanol. The aq. layer was mixed with ethanolic 0.2 M tetrabromo pyrocatechin adjusted to pH 11.5 and extracted with $CHCl_3$. The absorbance of the extract was measured at its λmax vs. reagent blank.	118
1, 8-Dihydroxy-3, 6-naphtha arsenazo III.	-	650	-	Alloy was dissolved in hot 50% HNO_3 and after evaporation and dilution. The solution was mixed with 10% $Na_2S_2O_3$ and pH was adjusted to 3.5. 0.05% reagent was added and the absorbance was measured at given λmax. Calibration graph was rectilinear upto 2.5 mg/l or in presence of Pb, Al, Ni and Fe up to 1.6 mg/l	119

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