A Systematic Approach for the Determination of Individual Lanthanides using Inexpensive Conductometric Technique

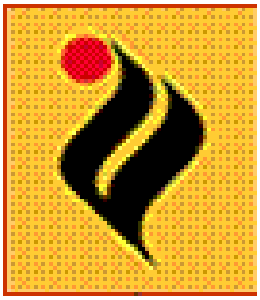
A

Thesis Submitted

In partial fulfillment of the requirements for the

Degree of

Master of Science in Chemistry



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Shilpa Pandey

CANDIDATE'S DECLERATION

I here by declare that the work being presented in the dissertation entitled "**A Systematic Approach for the Determination of Individual Lanthanides using Inexpensive Conductometric Technique**" in partial fulfillment of the requirement for the award of degree of Master of Science in chemistry in the school and Biochemistry, Thapar University, Patiala, is my own work during the period of January 2010 to June 2010 under the supervision of Dr. Ashok Kumar S.K., Lecturer, School of Chemistry and Biochemistry, Thapar University, Patiala. I have not submitted the matter embodied in this dissertation for the award of any other degree.

Patiala

Date: 7th July 10

Shilpa Pandey

This is to certify that the above statement made by the candidate is correct and true to the best of knowledge.

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CERTIFICATE

This is certify that the project "**A Systematic Approach for the Determination of Individual Lanthanides using Inexpensive Conductometric Technique**" being submitted by Ms. Shilpa Pandey in partial fulfillment of requirements for the award of degree of Master of Science in Chemistry in the School of Chemistry and Biochemistry, Thapar University Patiala, is a bonifide work carried out under the supervision of Dr. Ashok Kumar S.K. and that no part of this project has been submitted for the award of any other degree.

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THESIS ABSTRACT

A new conductometric titration method is established to determine quantitatively lanthanide (Lns) ions using ethylenediaminetetraacetic acid (EDTA) as a ligand. The detection limit of Ln(III) ions was found to be $1x10^{-5}M$ using cell constant: 1.0, 0.45 and $0.1cm^{-1}$. The proposed method is tested for selective determination of individual lanthanides in the presence of interfering ions like selected alkali, alkaline earth, and transition metal ions.

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LIST OF ABBRIVATIONS

AHA	α- Hydroxycarboxylic acid
CE	Capillary Electrophoresis
Ce	Cerium
CPE	Carbon paste electrode
DTPA	Diethylene triamine pentaacetic acid
EDTA	Ethylene diaminetetra acetate
EDXRF	Energy dispersive X-ray fluorescence
FFT-CCV	Fast Fourier Transform Continuous Cyclic Voltammetery
HIBA	α-Hydroxyisobutyric acid
HPLC	High liquid performance chromatography
ICP-AES	Inductively coupled plasma-atomic emission spectrometry
ICP-MS	Inductively coupled plasma-mass spectroscopy
ICP-OES	Inductively coupled plasma-optical emission spectrometry
ISE	Ion selective electrode
Ln	Lanthanides
NAA	Neutron activation analysis
PCR	Post-column reaction
PAN	1-(2-pyridylazo)-2-napthol
PLSR	Partial least-square regression
REE	Rare earth elements
TTA	Thenoyltrifluroacetone
XRF	X-ray fluorescence

Chapter-1

INTRODUCTION

The nature of molecular motion can be obtained by studying the motion of ions in solution, for ions can be dragged through the solvent by the application of a potential difference between two electrodes immersed in the sample solution. By studying the transport of charge through electrolyte solutions it is possible to build up a picture of the events that occur in them. Electrolytic conductance serve as a usual signal of the electrical conductivity of mainly aqueous electrolyte solution and conductometery has been developed into an electrochemical analytical method based on measuring the conductance in electrolyte solutions (1 - 5).

Two types of methods are based upon the measurement of the electrical conductance of solutions, namely direct conductance method and conductometeric titrations. The principal advantage of these methods is their simplicity and relatively good sensitivity (6 – 8). Two platinum electrodes are immersed into the solution of an electrolyte and connected to the source of electricity, the current (I), which flows are determined both by applied voltage (E) and by the electrical resistance (R) of that portion of the solution between the electrodes. This relationship is expressed mathematically by Ohm's law.

$$I = E/ R \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1.1)$$

Where, 'I' is in amperes, E in volts and R in ohms. All the ionic species in a solution contribute to the ability of that solution to conduct electricity, both intrinsic mobility and concentration of anions deciding the extent of participation of each individual species. This property of the electrolytic solution is known as conductance or conductivity.

1.1 How do we Measure Conductivity?

We know that a solution will conduct electricity if it contains ions that are free to move. If we want to study the way ions conduct, then electrolysis can be a nuisance, largely because the ions are constantly being removed from the solution. Electrolysis can be avoided if, instead of keeping the electrodes permanently positively and negatively charged, we reportedly change the charge on them. This achieved by using an alternating voltage. A conductivity cell contains two platinum electrodes bonded into the glass walls of the cell. In use, the cell is placed into the solution and the electrodes are connected to the conductivity meter. The electronics in the meter is designed to connect an alternating voltage to the cell, and at the same time to measure the

resistance of the solution between the electrodes. The higher the resistance, the lower the conductivity and vice versa, in other words, the conductivity is inversely proportional to the resistance. If there is greater length of the solution between the electrodes, then the resistance will increase. On the other hand, if we keep the distance between the electrodes fixed, but increase their area, then the resistance should decrease. (This is exactly the same behavior that we find with metals. If we increase the length of a metal wire, its resistance increases, but a wire of greater cross section area will have lower resistance than one with smaller area (9)).
Now we can define the conductivity (κ) Kappa as:

$$\kappa = (1/R) \times (L/A) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1.2)$$

Thus, if we know the dimensions of the cell (L and A) and we take the reading from the conductivity meter, we can calculate the conductivity. We now know how to measure the conductivity of the solution; if we have to compare conductivities we should compare like with like. For this reason we make use of molar conductivities or equivalent conductivity.

Equivalent conductance (Λ_{eq}) is defined as the conductivity power of all the ions produced by one gram equivalent of an electrolyte in a given solution.

$$\Lambda_{eq} = 1000\ \kappa / \text{Normality} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1.3)$$

Molar Conductance (Λ_m) is defined as the conductivity power of all the ions produced by one mole of the electrolyte in a given solution.

$$\Lambda_m = 1000\ \kappa / \text{Molarity} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1.4)$$

The conductance of an electrolyte solution depends upon the number of ions in a solution, their charge, and the rate of measurement under the influence of an electromotive force (10). The ability of a solute to conduct electricity is expressed in terms of its equivalent conductance or molar conductance.

1.2. How Individual Ions Contribute To Conductivities?

In 1874 the German Chemist Friedrich Kohlrausch (11) pointed out that there was good evidence to suggest that: the conductivity of a solution is the sum of the individual contributions from the positive and the negative ions. Thus,

‘‘The ionic equivalent conductivity of an electrolyte at infinite dilution ($/\!\backslash_o$) is the sum of two parts one due to cation, and other due to anion ”

$$/\!\backslash_o = \lambda^o_+ + \lambda^o_- \quad \text{.....(1.5)}$$

In terms of molar conductivities the Kohlarusch law may be stated as:

$$\Lambda^\infty_m = V_+\lambda^\infty_+ + V_-\lambda^\infty_- \quad \text{.....(1.6)}$$

Where, V_+ and V_- are respectively the number of cations and anions obtained from one molecule of the electrolyte on dissociation.

Table 1: Equivalent conductivity of ions at infinite dilution at 298 K (12-13).

Cation	**/\ (S cm^2 mol^{-1})**	**Anion**	**/\ (S cm^2 mol^{-1})**
H_3O^+	349.8	OH^-	198.5
Na^+	50.1	Cl^-	76.3
K^+	73.5	NO_3^-	71.5
Dy^{3+}	62.9	NO_3^-	71.5

A conductivity measurement responds to any and all ions present in a solution. A solution cannot be identified or its concentration known, from conductivity alone. In certain cases, the concentration of an electrolyte in solution can be determined by the conductivity if the composition and the solution are known.

Even though it is non-specific (14) but if follows necessary measurement conditions, the composition of the solution shall be measured.

i. There must be a measurable change in the conductivity over the desired concentration range.
ii. Conductivity must either strictly increase or decrease with increasing concentration. If a maximum (hump) and a minimum (valley) are present in the desired concentration range, then the concentration cannot be measured accurately.

1.3 Complexometeric Titration

The conductance method can be employed to follow the course of a titration, provided that there is a significant difference in specific conductance between the original solution and the reagent or the product of reaction. Thus, conductometeric titration is applicable to any titration in which there is a sharp change in the conductivity at the end point. Complexing agents have found long use in analytical chemistry and their role has been enhanced by the application of organic reagents. Some principal analytical use of complexing agents may be summarized as:

i. The complexing agent may act as precipitant.
ii. The complexing agent may act as chromogenic and flourogenic agent.
iii. The complexing agent may make an extraction possible.
iv. The complexing agent may serve as a titrant.
v. The complexing agent through complex formation may alter redox process and may stabilize an oxidation state.
vi. The complexing agent may serve as masking agents.

So, the complex formation, although often of benefit in chemical analysis, may also be a source of difficulty. A titration based on the reaction of a metal ion with a ligand to form a soluble complex and in which one of these two reactants serve as the titrant is called a complexometeric titration (15 – 21).

The reaction between the cation of the metal, M^{m-1} and ligand Z^{z-}, to form mono nuclear normal complex may be expressed by the general equation.

$$M^{m+} + n\,Z^{z-} \rightleftharpoons MZ_n^{\,m-nz}$$

The stability constant of the resulting complex is given by:

$$K = [MZ_n^{\,m-nz}] / [M^{m+}]\,[Z^{z-}]^n \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(1.7)$$

The charge on the ligand, z, may be zero or an integer.

In the present case the complexation of the metal ion by EDTA, the fully deprotonated anion of which may be represented by Y^{4-}.

The complexation reaction for the selected

$$M^{m+} + Y^{4-} \rightleftharpoons MY^{m-4}.$$

Most anionic and neutral ligands undergo protonation as a consequence the metal ion must compete with the hydrogen ion for possession of the ligand. In the case of EDTA, below about pH =11 it will be present not only as Y^{4-} but also in the various protonated forms HY^{3-}, H_2Y^{2-}, H_3Y^- and H_4Y. In a strongly acidic solution the forms H_5Y^+ and H_6Y^{2+} also exists, but usually at too small a concentration to affect the evaluation of practical situations.

The formation of a metal complex in aqueous medium actually involves the displacement of water from the aqua complex of the metal ion by a ligand and the ligand act as chelating agent, each molecule of the multidentate ligand displaces two or more molecules of water from the single metal ion. Consequently the number of mobile ions in the system is increased and therefore also the entropy. This entropic effect accounts largely for the so called chelate effect. For a ligand to act as chelating ligand, not only must it have to two or more ligand atoms, but the structural relation of these atoms must be such that the formation of one or more stable, usually five or six membered, rings with the metal ion is possible.

One of the advantages of complexometeric titration is that a solution of a single chelating agent, such as EDTA, can be used for the titration of many metal ions and by indirect procedure for the determination of many other species. Such versatility, however, corresponds to low selectivity. In the application of complexometeric titrations to the analytical resolution of mixtures of metal ions, close attention is required to measure that may improve the selectivity. If the complexes formed by two metal ions with ligands are sufficiently stable to permit both metals to be titrated with the ligand. If the complexes differ sufficiently in stability, a selective titration of the metal forming the more stable complex is still possible by lowering the pH of the solution. The EDTA complexes of common metal ions can be divided into four groups with regards to stability:

i. log K > 20, tri- and tetra positive cations, including Bi^{3+}, Fe^{3+}, In^{3+}, Ga^{3+}, Tl^{3+}, Th^{4+}, Zr^{4+} and Hg^{2+}.
ii. log K = 12 – 20, dipositive transition metals, rare earths and Al^{3+}.
iii. log K = 7.5 – 12; alkaline earths and.
iv. log K < 7.5 alkali metals, Ag^+, and Tl^+.

Cations of the first group can be titrated with EDTA at pH 1-3 without interference from cations of the 3rd and 4th group and with no or slightly interference from those of the second group. Cations of the second group can be titrated at pH 4 – 6 with EDTA without interference from the

alkaline earths, which in turn can only be titrated in alkaline solution. The alkali metals, Ag^{+} and Tl^{+} cannot be titrated directly with EDTA.

Improved selectivity can often be achieved by the application of a method of end point detection that avoids the use of complex forming indicator, notably the employment of a redox indicator or of certain instrumental methods of indication**.** it can be demonstrate that in order to obtain two useful breaks in the titration curve of a complexometeric titration involving 1:1 complexes a differences of at least 4-5 logarithmic unit in the value of the apparent Stability constants is required. However, where a complex forming indicator is used, this difference must be considerably larger and is critically dependent on the stability of the indicator. This is explained by the fact that a complexometeric titration is not pertained to an end point where the P^{m} values of the indicator equilibrium is equal to or close to the P^{m} values of the equivalence points, but rather to a point where all the metals is taken from the indicator complex. The location of this will depend on the stability of this complex.

For titrimetery, instrumental methods were formally favored only when a visual titration either was unsatisfactorily or failed or when many similar samples were to be analyzed. Instrument assemblies with varying degrees of automation and sophistication are now becoming progressively available for titration purposes. In complexometeric titrations, an instrumental method of end point detection will be of value when no fully satisfactory indicator is available; whenever the solution to be titrated is turbid or strongly turbid or when extreme dilutions would either obviate a visual titration or require special measures. Beyond these relatively important advantages, instrumental methods often have possibility of increased selectivity. As mentioned above, for a selective titration of one metal ion in the presence of another, the difference required in the apparent stability constant is less if the method of indication does not involve formation of a conditional metal complex. In an instrumental titration, slow complexation with the titrant or sluggish reaction of a metal indicator system has less effect on the titration result.

1.4. Research Problem

Lanthanides (III) ions are of great interest because of their specific characteristics in several areas, such as material science (22), heterogeneous and homogenous catalysis (23), diagnosis and therapy in medicine (24) and in the nuclear fuel cycle (25). As a result of their usage, more and more Ln(III) ions are getting into the environment, accumulating in organisms and entering

into the food chain. Thus, determination of Ln (III) in various matrixes becomes increasingly significant and several techniques have been used. Moreover, problem is no specific reagents for the Ln(III) ions of the individual elements are known. However, under certain conditions the selectivity of group reagents can be improved by binding the interfering ions as stable complexes. Because of the poor selectivity of the various reagents employed in the analytical chemistry of Ln(III) ions, separation methods based on differences in the properties of their compounds acquire special importance. The quick determination of lanthanides by simple methods is of great importance in Analytical Chemistry. In the today's world, determination of lanthanides (Lns) without any preliminary separation becomes a higher priority on the scientific agenda of the world's industrialized nations.

Trivalent metal ions have high charge to radius ratio and thus on account of this they are highly solvated. On complexation, EDTA replaces the solvent sheath around the metal ion and as a result, moving entirely becomes too bulky.

Chapter - 2

LITERATURE REVIEW

As most of the lanthnaides elements appear in solution as particularly stable 3+ ions, few classical methods are available for the determination of individual elements. However, both volumetric and gravimetric procedures are applicable to cerium, and there is a volumetric method for europium. Volumetric and gravimetric procedures are also available for assessing the total lanthanide content and for ascertaining the mean equivalent. Usually, it is necessary to rely upon physical methods for the determination of individual lanthanides.

Table 2: The principal quantitative analytical methods for lanthanides determination

<table>
<tr><td colspan="6">Quantitative Technique</td></tr>
<tr><td>Classical Technique</td><td colspan="5">Instrumental method of analysis</td></tr>
<tr><td rowspan="2">Gravimetric method

Volumetric method</td><td>Electro analytical Method</td><td colspan="2">Spectroscopic Method</td><td>Chromatographic Method</td><td>Radiation Chemistry Method</td></tr>
<tr><td>Voltammeteric

Potentiometeric

Conductometeric</td><td>Atomic Absorption

ICP-AES

ICP-MS</td><td>UV-Vis Spectroscopy

Fluorescence Spectroscopy</td><td>Gas Chromatography

HPLC

Capillary Electrophoresis</td><td>Neutron Activation Analysis</td></tr>
</table>

2.1 Gravimetric Method

The methods are based on the law of conservation of total mass in a chemical reaction. Determination of cerium depends upon the quantitative precipitation of ceric iodate, Ce $(IO_3)_4$, which is finally weighed as ceric oxide (26). Total lanthanide by oxalate precipitation is probably the best procedure available for the quantitative isolation of the elements (27). Oxalate precipitation is probably the best procedure available for the quantitative isolation of the elements (28)

2.2 Volumetric Method

The ceric ion is reduced to the 3+ state by titration with a reducing agent, usually a standard ferrous iron solution, in the presence of an indicator of the phenanthroline type (29). Europium is reduced quantitatively to the bipositive state by passing an acidified solution pH 3-4 of salt through a Jones redactor. The europium ion in the effluent is oxidized quantitatively to the 3+ state by a standard solution of either iodine or potassium dichromate (30). The Ln (III) elements all form negatively charged complex anions with EDTA and by using xylenol orange indicator total lanthanides or individual lanthanides (if it contains single ion in the mixture) can be quantitatively determined (31).

2.3 UV-Visible Method

A spectrophotometer is employed to measure the amount of light that a sample absorbs. The instrument operates by passing a beam of light through a sample and measuring the intensity of light reaching a detector. The basic principle of UV/Vis spectrophotometery is described by well known Beer-Lambert law which can be used to determine the concentration of a specific analyte in a sample at a specific wavelength:

$$A = \varepsilon b C \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (2.1)$$

Where, A is the measured absorbance, ε is the molar absorbtivity or extinction coefficient ($M^{-1}cm^2$), b is the path length (cm), and C is the molar analyte concentration (M).Provided that the sample is measured at a level at which the absorbance of the analyte or its derived chromophore varies linearly with concentration, the Beer-Lambert law can be reliably applied in practice. There are many parameters that can be determined using simple application of Beer-Lambert in UV/Vis spectrophotometery.

Jingwan et al (32) described the determination of Ln (III) ions by using a flotation-spectrophotometric method. In this a ternary ion-association complex of Ln (III) coordinated by thiocyanate (SCN^-) and diantipyryl methane (DA) is separated by a mixed solvent containing benzene and chloroform at pH 3.1- 4.2, a third phase is observed between the aqueous and organic phases. This solid ternary complex dissolved in acetone that contains thenoyltrifluoroacetone (TTA) and then individual Ln (III) ion determined by using the 4th derivative spectra directly. **Ski *et al*** (33) describes method of simultaneous determination of

heavy and light lanthanides. In the first stage, the total amount of rare earth elements is determined (complexometrically with EDTA as a titrant and methylthymol blue as an indicator, pH = 5.5). The applicability of the method is limited by REE concentration equal to 3×10^{-5} M. In the case when the content of one of the metals amounts to at least 15% of their sum, the relative error of determination does not exceed 2%. **Citron *et al*** (34) describes an analytical method for the quantitative determination of total lanthanide concentration in aqueous solution by absorbance at 240 nm in the ultraviolet followed by quantitative determination of individual lanthanide ion concentrations by the use of concentration (independent of ligand used) responsive absorption peaks in the 190-235 nm region. Ligands ultimately selected for complexation were citrate for La^{+3}, Nd^{+3}, and Ho^{+3}, and DTPA for Eu^{+3}, Ho^{+3}, and Yb^{+3}. When large amounts of heavy metal ions were present, a modified method was developed with citrate as complexing ligand for all five lanthanides. The method permits the analyses of lanthanide ions in aqueous solution without prior separation. **Zamora *et al*** (35) describes the simultaneous determination of lanthanide family elements, due to the close similarity of their chemical properties. Spectrophotometric methods are not of great importance because of various mutual spectral interferences so multivariate calibration methods (partial least-squares regression, PLSR) used. **Shkrob *et al*** (36) describes several methods for rapid sequestration, fluorometric detection, and the subsequent mass spectroscopic analysis of lanthanide ions using surface modified polystyrene magnetic microspheres. **Hassan *et al*** (37) describes the sensitive and reasonably selective methods for the spectrophotometric, potentiometric, and gravimetric determination of lanthanides using peri-dihydroxynaphthindenone as a novel chromogenic and precipitating reagent. Many foreign Ions naturally occurring or frequently associated with lanthanides do not interfere or can be tolerated.

2.4 Atomic Absorption Spectroscopic Method

This technique makes use of absorption spectrometry to assess the concentration of an analyte in a sample. Beer-Lambert law relationship is applicable to calculate analyte concentration. In this, the electrons of the atoms in the atomizer can be promoted to higher orbitals for a short amount of time by absorbing a set quantity of energy (i.e. light of a given wavelength). This amount of energy (or wavelength) is specific to a particular electron transition in a particular element, and in general, each wavelength corresponds to only one element. This gives the technique its elemental selectivity.

Arrebola *et al* (38) noted that the elements La, Y, Pr, Nd, Sm and Ce form with Mg (II) and purpurin (1,2,4-trihydroxyanthraquinone) mixed-metal complexes which can be extracted into isobutyl methyl ketone at pH 7.5. The total content of these metals can be determined by measuring the magnesium absorbance by AAS. This method permits the determination of concentrations at ppb levels, and applied to the analysis of synthetic samples.

2.5 Inductively Coupled Plasma Spectroscopic Method

Inductively coupled plasma mass spectrometry (ICP-MS) is a type of mass spectrometry that is highly sensitive and capable of the determination of a range of metals and several non-metals at concentrations below one part in 10^{12} (part per trillion). It is based on coupling together inductively coupled plasma as a method of producing ions (ionization) with a mass spectrometer as a method of separating and detecting the ions. ICP-MS is also capable of monitoring isotopic speciation for the ions of choice. **Rajendran *et al*** (39) described the performance of ICP-AES for the determination of fourteen lanthanides and yttrium in monazite, in comparison with inductively coupled plasma-mass spectrometry (ICP-MS) analysis. Monazite was separated by gravity and magnetic separations from the mineral black sands and effective dissolution of the rare earth elements was carried out and then collectively separated from concomitant matrix elements by ion-exchange chromatographic separation using the resin Dowex 50X-8. **Dressler *et al* (40)** describes the mass spectrometric method for the determination of lanthanides (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu) at ng / g levels in small amounts of biological specimens by inductively coupled plasma-mass spectrometry (ICP-MS) after microwave digestion. **Bentlin *et al*** (41) describes low concentrations determination of the fourteen naturally occurring lanthanides (ng/g or ng/ L) by inductively coupled plasma optical emission spectrometry (ICP OES).

2.6. X-ray Fluorescence Spectroscopy

X-ray Fluorescence Spectrometry is a non- destructive analytical technique used to identify and determine the concentration of elements present in solid, powdered and liquid samples.XRF is capable of measuring elements from beryllium (Be) to uranium (U) and beyond at trace levels often below one part per million and up to 100%. The XRF spectrometer measures the individual component wavelengths of the fluorescent emission produced by a sample when irradiated with

X-rays. **Bhagavathy *et al*** (42) describes a method for the simultaneous multi-element determination of yttrium and lanthanides at microgram level. This is based on the pre-concentration of these lanthanides on to 1-(2-pyridylazo)-2-naphthol (PAN) modified naphthalene.

2.7. Neutron Activation Analysis

Neutron activation analysis (NAA) stands at the forefront of techniques for the quantitative multi-element analysis of major, minor, trace and rare elements. NAA begins with neutron bombardment of a sample to convert stable isotopes to radioactive isotopes (e.g., natural sodium [^{23}Na] is converted to radioactive sodium [^{24}Na]). The usual procedure involves placing the samples to be analyzed plus a number of suitable standards into the neutron field produced by a neutron source. Radioisotopes created during the irradiation will decay with time. A portion of the energy released during decay is often in the form of gamma radiation, which is capable of traveling out of the sample. The gamma rays possess unique energies that are characteristic of the radioisotope undergoing decay. Gamma rays detected at a particular energy are usually indicative of a specific radionuclide's presence. **Ozaki *et al* (43)** analyzed about 70 kinds of fem samples by means of neutron activation analysis in order to deduce characteristics and mechanisms of accumulation of rare earth elements. **Koeberl *et al* (44)** reports the determinations of rare earth element (REE) contents in biological (especially human) samples.

2.8. Chromatographic Technique

Chromatography is an analytical technique used for separating a mixture of chemical substances into its components so that these can be identified or analyzed. **Srinivasan *et al* (45)** describes a novel HPLC based separation technique using Bis-2-ethylhexyl succinamic acid (BEHSA) modified reversed phase support for the isolation and quantitative determination of lanthanides as a group in uranium matrix. **Subramanian *et al*** (46) describes the simultaneous ion chromatographic determination of trace-levels of lanthanides (or lanthanides) by using either direct non-suppressed conductivity detection or UV/VIS detection after post-column reaction (PCR) with arsenazo III at 655 nm. Conductivity detection under isocratic conditions resulted in an overall analysis time of approx. 70 minutes while, the determination of the lanthanides via gradient elution and subsequent spectrophotometric detection of the arsenazo III-lanthanide(III) complexes was 22 minutes. Besides the outstanding analysis time, UV/VIS detection did not

suffer from interferences by non-lanthanide impurities such as iron (III) or other transition metals. **Burgett *et al*** (47) reported a gas chromatographic method for the separation and subsequent quantitative determination of the yttrium group lanthanides. The lanthanides are synergistically extracted from aqueous solution with the polyfluorinated p-diketone 1,1,1,2,2,6,6,7,7,7-decafluoro-3,5-heptanedione, as ligand, and di-nbutylsulfoxide (DBSO) as neutral donor. Individual lanthanides were determined with 97.5% and mixtures of lanthanides were determined with 97.1% recovery.

2.9. Capillary Electrophoresis

Capillary electrophoresis (CE), also known as capillary zone electrophoresis (CZE), can be used to separate ionic species by their charge and frictional forces and hydrodynamic radius. In traditional electrophoresis, electrically charged analytes move in a conductive liquid medium under the influence of an electric field. **Foret *et al*** (48) describes the separation of 14 lanthanides by capillary zone electrophoresis using electrolyte hydroxyisobutyric acid as complexing counter ion and creatinine as a UV absorbing co-ion for indirect detection of lanthanide zones. A complete separation was achieved in less than 5 min and the applicability of the method for the analysis of real samples. **Stern *et al*** (49) describes CE coupled with ICP-MS (CE-ICP-MS) method is used to separate and detect metal species at trace-element concentrations by partitioning of the rare earth elements (REE) between HS (humic substance) and a competing ligand (EDTA) under near environmental conditions (pH 6–10, 0.1 mol L^{-1} $NaNO_3$, 100 nmol L^{-1} REE, 10 mg L^{-1} HS).

2.10. Potentiometeric Method

Potentiometer is a type of bridge circuit for measuring voltages below 1.5 volts. In this circuit, the unknown voltage is connected across a section of resistance wire the ends of which are connected to a standard electrochemical cell that provides a constant current through the wire, the unknown emf, in series with a galvanometer, is then connected across a variable-length section of the resistance wire using a sliding contact(s). The sliding contact is moved until no current flows into or out of the standard cell, as indicated by a galvanometer in series with the unknown emf. The voltage across the selected section of wire is then equal to the unknown voltage. All that remains is to calculate the unknown voltage from the current and the fraction of the length of the resistance wire that was connected to the unknown emf. The galvanometer does

not need to be calibrated, as its only function is to read zero. When the galvanometer reads zero, no current is drawn from the unknown electro motive force and so the reading is independent of the source's internal resistance. **Rahayu *et al*** *(*50*)* prepared lanthanum (III) ion selective electrode based on ionophore 1,10-diaza-4,7,13,16-tetraoxacyclooctadecane-N,N'-diacetic acid. **Karami *et al*** (51) prepared a membrane ion-selective electrode (ISE) for cerium (III) ions based on a new ligand *N*-[(*Z*)-2-chloro-2-(1-hydroxy-1,1,1-triphenyl phosphoranyl)-1-ethenyl]-4-ethyl-1-benzene sulfonamide, as ionophore. The electrode has a wide linear dynamic range ($6.6x10^{-7}$ to $6.2x10^{-2}$ M; $n = 10$; $r = 0.9994$), with a Nernstian slope of 19.5 ± 0.3 mV/decade, a low detection limit ($2.3x10^{-7}$ M) and a fast response time (<10 s). **Zamani *et al*** (52) describes a new PVC membrane potentiometric sensor that is highly selective to Tb(III) ions, prepared by using 4-amino-3-{2-[4-amino-6-methyl-5-oxo-4,5-dihydro-1,2,4-triazin-3(2H)-yliden]hydrazono}-6-methyl-3,4-dihydro-1,2,4-triazin-5(2H)-one (ATO) as a suitable carrier. The sensor works satisfactorily in the concentration range of $1.0x10^{-6}$ to $1.0x10^{-1}$ mol L^{-1} (detection limit 8.6×10^{-7} mol L^{-1}) with a Nernstian slope of 19.4 ± 0.5 mV/decade of activity. **Prasad *et al*** (53) prepared ion-selective electrode (ISE) by dispersing the dysprosium (III) IIP particles in 2-nitrophenyloctyl ether plasticizer and then embedded in polyvinyl chloride matrix. The ISE shows Nernstian response for dysprosium(III) over concentration range (8.0×10^{-6} to 1.0×10^{-1} M) with a slope of 21.7 mV/decade and detection limit of 2×10^{-6} M. **Gupta *et al*** (54) describes Lanthanum(III)-selective sensors, fabricated from poly(vinyl chloride) (PVC) matrix membranes containing neutral carrier, monoaza-12-crown-4 as ionophore with the composition crown:PVC:NaTPB:DBBP in the ratio 7:48:8:37 (w/w). This membrane works well over a wide concentration range of 3.16×10^{-5} to 1.00×10^{-1} M of La^{3+} with a Nernstian slope of 20.5±1.0 mV per decade of La^{3+} activity and response time <15 s. **Shamsipur *et al*** (55) describes a novel Ce^{3+} ion-selective electrode based on 1,3,5-trithiane. The electrode exhibits a Nernstian slope of 19.2±0.1mV/ decade over a wide concentration range (4.7×10^{-4} - 2.5×10^{-8} M) with a limit of detection of 2.0×10^{-8} M and response time ~10 s. It was used as an indicator electrode in determination of F^- ion in some mouth wash preparations with Ce^{3+} ion.

2.11. Voltammeteric Method

The basis of voltammetry is that the electro active species is either oxidized or reduced at the sensor surface by an applied potential. The measured faradaic current is then proportional to the concentration of chemical in the region of the sensor. Several characteristics make voltammetry

attractive for chemical monitoring. **Pourjavid *et al*** (56) published three reports on lanthanide determination in 2009, first report describes the cation-exchange separations of the light lanthanides (La^{3+}, Ce^{3+}, Pr^{3+} and Nd^{3+}) on Nucleosil 100-5-SA ion-exchange column with use of α-hydroxyisobutyricacid (HIBA) as elution agent and fast Fourier transform continuous cyclic voltammetry (FFT-CCV) was used for detection and identification. The best performance obtained at pH value of 4.0, scan rate value of 30 V/s, accumulation potential of -300 mV, and accumulation time of 0.3 s. The proposed method displays a linear dynamic range between 250 and 21000 ppb and a detection limit of 90 ppb. Second report (57) describes the separation of medium lanthanides (Sm^{3+}, Eu^{3+}, Gd^{3+}, Tb^{3+} and Dy^{3+}) on Nucleosil 100-5-SA (an ion exchange column) in the presence of α-hydroxyisobutyric acid (HIBA) as an elution agent and then determinations are performed by Fast Fourier Transform Continuous Cyclic Voltammetry (FFT-CCV) in a flowing solution. The best performance obtained was at; pH 4.0, scan rate 30V $s^{-1,}$ accumulation potential -300 mV, and accumulation time 0.3 s. The proposed method displays a linear dynamic range between 0.26-23 mg L^{-1} and a detection limit of 0.08 mg L^{-1}. Third report (58) describes the separation of heavy lanthanides (Ho^{3+}, Er^{3+}, Tm^{3+}, Yb^{3+}, and Lu^{3+}) separation on Nucleosil 100-5-SA, an ion-exchange column, using an isocratic program of α-hydroxyisobutyric acid (HIBA) eluent. The best performance of the method was obtained at pH of 4.0, scan rate of 30 V s^{-1}, accumulation potential of −300 mV, and accumulation time of 0.3 s, a linear dynamic range of 140 and 18,000 μg L^{-1} and a detection limit of 50 μg L^{-1}. **Li *et al*** (59) describes the determination of trace rare earths in the presence of alizarin complexon (ALC) at a carbon paste electrode (CPE). A sensitive adsorptive oxidation peak was found for the complexes of middle and heavy rare earths(III) with ALC in a supporting electrolyte of 0.12 M HAc + NaAc and 0.03 M potassium biphthalate (pH 5.0) for linear-scanning from −0.2 to 0.8 V at 100 mV s^{-1}. The sensitivity of the heavy rare earths (Dy, Ho, Er, Tm, Yb, and Lu) is higher than that of other rare earths.

A comprehensive literature survey report shows that there are no reports available on the conductometeric determination of lanthanides using EDTA as a ligand.

Chapter – 3

METHODOLOGY

3.1 Reagents and Solution

Solutions of metal ions were prepared by direct weighing of AnalaR grade (99.9%) metal chlorides supplied by Chengdu beyond Chemicals, China in double distilled de-ionised water having conductivity less than $5\mu Sm^{-1}$. Ethylenediaminetetraacetic acid (EDTA) and HEDTA were obtained as sodium salts Na_4EDTA (L) from (Aldrich, USA) and used as received.

3.2 Instrumentation

All measurements were done at 25±0.1°C by using conductivity meter of Indegenious make i.e., ELICO using cell constant 0.1, 0.45 and $1.0cm^{-1}$.

3.3 Procedure for Specific Conductance Measurement

a. Firstly the conductivity cell is standardized with 0.1N KCl at 25 ^oC to minimize the errors and then wash the electrode thoroughly with de-ionized water.
b. Then the Ln (III) solution (50 mL of $1x10^{-3}$ M) is placed in a titration flask and conductivity is measured using the conductivity meter.
c. Fill the burette with Na_4EDTA solution ($1x10^{-2}$ M) and is added to the titration flask in 0.5mL increments and measured the conductivity until EDTA is sufficiently larger than the 1:2 metal: EDTA stiochmetery.
d. Then plot the graph of conductivity versus volume of EDTA used and the equivalence point is measured as the sharp inflexion point of the titration curves.

Chapter – 4

RESULTS & DISCUSSION

4.1 EDTA as Analytical Reagent

G. Schwarzenbach first recognized the potential of EDTA as an analytical reagent in 1969 (60). Since this original work, investigators throughout the world have described applications of these polyaminocarboxylic acids to the volumetric analysis. Using these, more than forty-five elements can be determined by direct and back-titration procedures to a visual end point. The EDTA complexes of common metal ions can be divided into four groups with regard to stability (Table 3): (a) log K> 20: di, tri- and tetrapositive cations, including Fe^{3+}, In^{3+}, Bi^{3+}, Ga^{3+}, Tl^{3+}, Th^{4+}, Zr^{4+} and Hg^{2+} (b) log K=12-20: dipositive transition metals, lanthanides and Al^{3+} (c) log K=7.5-12: alkaline earths and (d) log K< 7.5: alkali metals, Ag^{+} and Tl^{+}. The study shows that cations in the first group can be titrated with EDTA at pH 1-3 without interference from cations of the third and fourth groups with no or only slight interference from those of the second group. Cations of the second group can be titrated at pH 4-6 with EDTA without interference from the alkaline earths, which in turn can only be titrated in alkaline solution.

Table 3: Stability constant (logK) values of EDTA-Ln(III) (60)

Metal ion(III)	EDTA-Ln(III)	Interfering ions (B)	EDTA-B
Lanthanum	15.5	Magensium	8.69
Cerium	15.98	Calcium	10.96
Praseodymium	16.40	Stronsium	8.63
Neodymium	16.61	Barium	7.76
Promethium	16.75	Cobalt (II)	16.31
Samarium	16.70	Nickel	18.62
Europium	17.35	Iron, Fe(III)	25.10
Gadolinium	17	Copper	18.8
Terbium	17.81	Zinc	16.5
Dysprosium	18.30	Silver	7.32
Holmium	18.05	Mercury	21.80
Erbium	18.38	Lead	18.04
Thulium	18.62	Thorium	23.20
Ytterbium	18.88		
Lutetium	19.65		

4.2 Measuring Range and Detection limit

The conductivity is measured over a concentration range from $1x10^{-8}$M to $1x10^{-1}$M of Ln(III) ions. Conductivity values ranged from 10 to 16000μScm^{-1}. The conductivity values were plotted against square root of concentration to conform to the Kohlrausch's Law and Onsager equation for strong electrolytes (61). The plots between Λ_m and √C show that the law is applicable over a wide concentration range of 10^{-5}M to 10^{-1}M. In order to plot these wide ranges we used log Λ_m and logC plots**.** Curves were drawn between logΛ_m and logC to find the detection limit of the proposed analytical method (**Figure1 and Figure 2**). The point of intersection of two straight-line portions of the calibration cur ve was taken as the detection limit. The detection limit for Ln(III) ions is found to be $1x10^{-5}$M. Further, the detection limit was evaluated by conductometric titration of different concentrations of Ce(III) ions against L solution. During each titration the concentration of L is about 10-fold to Ce(III) ions. The plots between conductivity *vs* volume of titration is half sigmoid. Beyond concentration $1x10^{-5}$M (lower than $1x10^{-5}$M) the sigmoid curve becomes parallel to the volume axis.

4.3 Effect of pH

Conductivity measurements for the titration of Ce(III) with EDTA were also done in the presence of buffer (sodium acetate-acetic acid buffer solution, pH= 4), but no effect of the buffer was noticed on the equivalence point because the initial pH of the lanthanide solution (pH = 4.5) is just suitable for a stable complex formation with EDTA and all along the titration, pH changes only up to 4.0 due the release of H^+ ions on complex formation with EDTA. However, there is a change in the magnitude of conductivity values that did not cause any significant difference in the equivalence point.. Hence, buffer solution was not used in subsequent studies.

4.4 Curve Evolutions and Shape of Titration Curves

To study actual conductometric titration behavior of Ln(III)-EDTA complexes with Na_4EDTA (L). Curves for titration with L (**Figure 3**) shows two distinct features; a small variation or constant conductivity of the solution up to the equivalence point followed by a regular increase in conductivity. The shape of the titration curve depends on all the species present during the titration and also factors such as viscosity, dielectric constant, solvation, ion-pair association and proton transfer change the shape of the curve (62).

Ln(III) ions with L_3 in aqueous medium (Figure 5)

Species present before addition of L : $Ln^{3+} + 3Cl^-$

$\downarrow$ L **(Y^{4-})**

Species present at E.P.: $4Na^+ + [Ln\text{-}EDTA]^- + 3Cl^-$

$\downarrow$ L **(Y^{4-})**

Species present after the E.P.: $3Cl^- + 4Na^+ + [Ln\text{-}EDTA]^- + L$

4.5 Criteria for Selection of Cell Constant and EDTA

The electrical conductivity 'K' of a solution is defined as the conductance (G) of electrolyte between two electrodes, each with an area 'A', separated by a distance 'L' the conductivity is given

$$K = G \times L/A \quad \ldots\ldots\ldots\ldots\ldots\ldots (4.1)$$

The traditional units of electrolytic conductivity, Siemens per centimeter (S/cm), the quotient L/A (cm^{-1}) depends on the geometry of the cell. The electric field is never homogeneous over the cross section of a real cell, so it is not possible to calculate actual conductivity that is polarization effects at the electrode / electrolyte interface and electrolyte decomposition. For this reason, the cell constant is infact constant only over a limited conductivity range. Suitable value for the cell constant, depends on the anticipated level of conductivity titration system, 0.45 cm^{-1} cell constant can be used for titration 10^{-3} and 10^{-4} M Ln^{3+} against EDTA with high accuracy while 0.1cm^{-1} cell constant is better for 10^{-5} M concentration Ln(III) vs EDTA Accordingly further studies done by choosing proper cell constant. From the **Table 4** and **Figure 3** shows that L can be used for the determination of Ln (III) ions. The behavior of L follows linear titration, that is, the titration curve consists of two straight line segments are sufficiently well developed to permit extra plotation to their intersection, which is taken as the end point Hence, L is used in subsequent studies.

4.6 Titrations of Lanthanides and their Binary Mixtures with Cerium (III)

Conductometric titration of each metal ion was done against L to study their complexation behavior as shown. When two lanthanides are titrated against EDTA, no separate end points corresponding to each of the metal ions were observed (Table 5, and Figure 4). The stability constant values (logK: Ce(III)-EDTA= 15.98 and La(III)-EDTA=15.50) difference between two adjacent lanthanides is very small and this small difference does not make a noticeable change in

conductivity value. Hence, equivalence point is obtained for total Ln(III) ions present in the system.

4.7 Determination of Ce (III) in the Prescence of Interfering Ions using L as Ligand

Selectivity is one of the most important characteristics of any analytical system, as it often determines whether a selective measurement is possible or not. There is no selectivity coefficient determination method available in the literature for such system as conductometric titrations. Hence, a ratio of conductivity of pure Ln (III) solution to that of the mixture contain interfering ion should indicate the degree of the interference to the proposed method. Results show that Th^{4+}, Fe^{3+}, Ni^{2+}, Cu^{2+}, Co^{2+} Ca^{2+} and Mg^{2+} metal do not interfere at all in the determination of Ln(III) ion, which itself is the first proposed report of its kind.

Conductometric titrations of a binary mixture of Ce^{3+} solution (20 mL, $1x10^{-3}$ M) and an equal concentration of each of the interfering ions; Th^{4+}, Fe^{3+}, Pb^{2+}, Al^{3+},Sr^{2+}, Ni^{2+}, Cu^{2+}, Co^{2+}, Ca^{2+} and Mg^{2+} (20 mL, $1x10^{-3}$ M) were titrated against L ($1x10^{-2}$ M) (Table 5). In case of (Cu^{2+} + Ce^{3+}) titration against EDTA gives two equivalent points one at 2.3ml and another at 4.4ml (Figure 5), against the calculated value of 2.0ml and 4.0ml. These equivalence points shows that there is 1:1 complex formation of Cu^{2+}-EDTA till first equivalence point and further addition of EDTA results in second equivalence point with Ce^{3+}-EDTA complex formation. Similar trend follow in the case of $Ca^{2+}$and Ce^{3+} (Figure 6) & $Mg^{2+}$and Ce^{3+} mixture (Figure7).

Similarly in case of (Th^{4+} + Ce^{3+}) titration against EDTA (L) (Figure 8) conductivity decreases gradually till first equivalence point which corresponds to 1:1 complex formation of Th^{4+}-EDTA. Further addition of L results in the formation of Ce^{3+}-EDTA complex and the conductivity remains same till second equivalence point, where 1:1 complex formation of Ce (III)-EDTA is obtained. By using this method, both Th^{4+} and Ce^{3+} contents could be determined quantitatively and similar trend followed in case of Fe^{3+} and Ce^{3+} mixture (Figure 9).

The presence of Fe^{3+}, Co^{2+} (Figure 10) and Pb^{2+} (Figure 11) does not cause so much of interference in the determination of Ce (III) ions. The interfering ions like Ni^{2+}, Sr^{2+}, Cu^{2+}, Ca^{2+} and Th^{4+} shows little interference in the determination of Ce (III) ions, while Al^{3+} is shown in Figure 12, interfering to the maximum extent.

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Table 4: **Conductometric titration of La (III) *Vs* L using cell constants 1.0, 0.45 and 0.1cm^{-1}**

Composition of the titration	**Actual end point**	**E.P. using cell constant (1.0cm^{-1}) (n=3)**	**E.P. using cell constant (0.45cm^{-1}) (n=3)**	**E.P. using cell constant (0.1cm^{-1}) (n=3)**
30 mL of 1x10^{-3} M La(III) vs 1x10^{-2} M Na_4EDTA **(Figure 3)**	3.0 ml	3.0 ± 0.2ml	**3.0± 0.1ml**	3.0 ±0.2ml
30 mL of 1x10^{-4} M La(III) vs 1x10^{-3} M Na_4EDTA	3.0 ml	2.8 ±0.2ml	**3.0 ± 0.2ml**	3.2± 0.2ml
30 mL of 1x10^{-5} M La(III) vs 1x10^{-4} M Na_4EDTA	3.0 ml	2.5± 0.3ml	**2.8± 0.2ml**	3.2 ±0.3ml
30 mL of 1x10^{-6} M La(III) vs 1x10^{-5} M Na_4EDTA	3.0 ml	No changes in conductivity	No changes in conductivity	No changes in conductivity

Table 5: **Conductometric titration of binary mixtures of Ce(III) and interfering ions *Vs* L_1 (ligand) Using cell constant 0.45cm^{-1}**

Composition of titration system	**Actual endpoint (mL)**	**Obtained endpoint (mL)**
25 mL of 1x10^{-3} M [(La (III) + Ce(III)] vs 1x10^{-2} **L** (**Figure 4)**	One E.P. at 2.5 mL and another at 5.0 mL	One E.P. at 5.01± 0.2 mL
20 mL of 1x10^{-3} M [Ce(III) + Cu(II))] vs 1x10^{-2} L (**Figure-5)**	E.P at 2.0 and 4.0 mL	E.P at 2.3 mL
20 mL of 1x10^{-3} M [Ce(III) + Ca(II)] vs 1x10^{-2} L (**Figure-6)**	E.P at 2.0 and 4.0 mL	E.P at 2.3 and 4.4 mL
20 mL of 1x10^{-3} M [(Ce(III) + Mg(II))] vs 1x10^{-2} L **(Figure-7**)	E.P at 2.0 and 4.0 mL	E.P at 2.7 and 6.0mL
20 mL of 1x10^{-3} M [Ce(III) + Th(IV)] vs 1x10^{-2} L (**Figure-8**)	E.P at 2.0 and 4.0 mL	E.P at 3.0 and 5.5 mL
20 mL of 1x10^{-3} M [Ce(III) + Fe(III)] vs 1x10^{-2} L (**Figure-9**)	E.P at 2.0 and 4.0 mL	E.P at 2.3 and 5.2 mL
20 mL of 1x10^{-3} M [Ce(III) + Co(II)] vs 1x10^{-2} L (**Figure-10**)	E.P at 2.0 and 4.0 mL	E.P at 4.0 mL

20 mL of $1x10^{-3}$ M [Ce(III) + Pb(II)]vs $1x10^{-2}$ L (**Figure-11**)	E.P at 2.0 and 4.0 mL	E.P at 2.0 and 5.5 mL
20 mL of $1x10^{-3}$ M [(Ce(III) + Al(III))] vs $1x10^{-2}$ L (**Figure-12**)	E.P at 2.0 and 4.0 mL	E.P at 5.0 mL
20 mL of $1x10^{-3}$ M [(Ce(III) + Sr(II))] vs $1x10^{-2}$ L	E.P at 2.0 and 4.0 mL	E.P at 2.5 and 6.0 mL
20 mL of $1x10^{-3}$ M [Ce(III) + Ni(II)] vs $1x10^{-2}$ L_3	E.P at 2.0 and 4.0 mL	E.P at 3.0 and 6.0 mL

LIST OF FIGURES

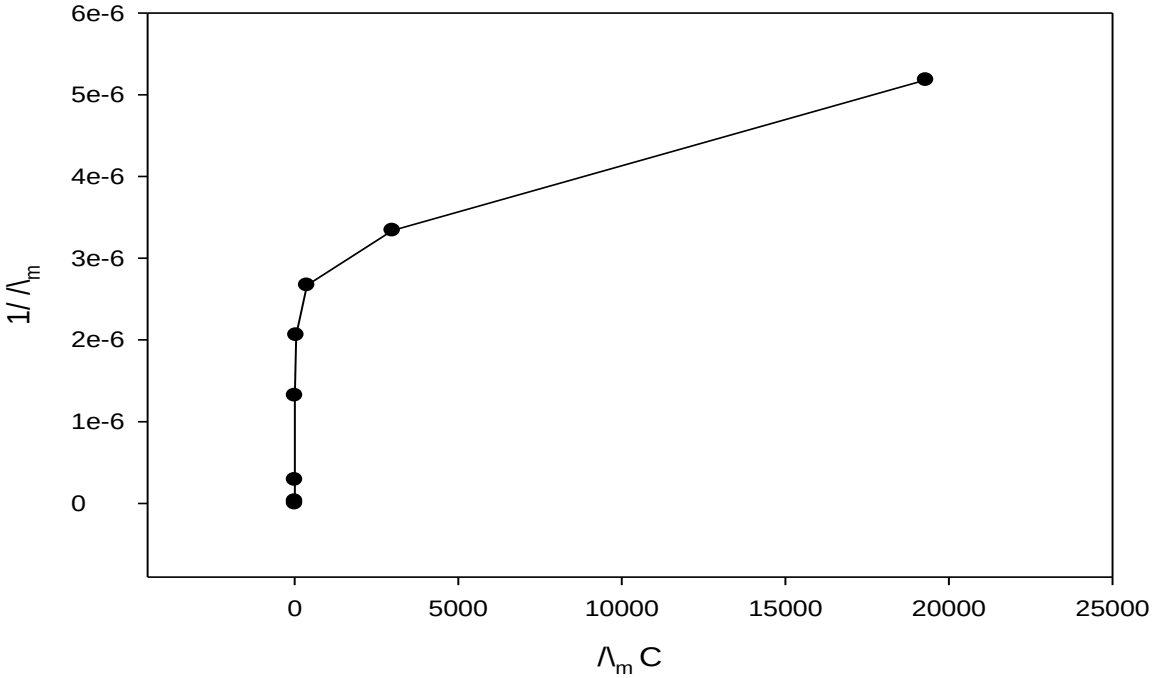

Fig.1: Verification of Onsagar Equation

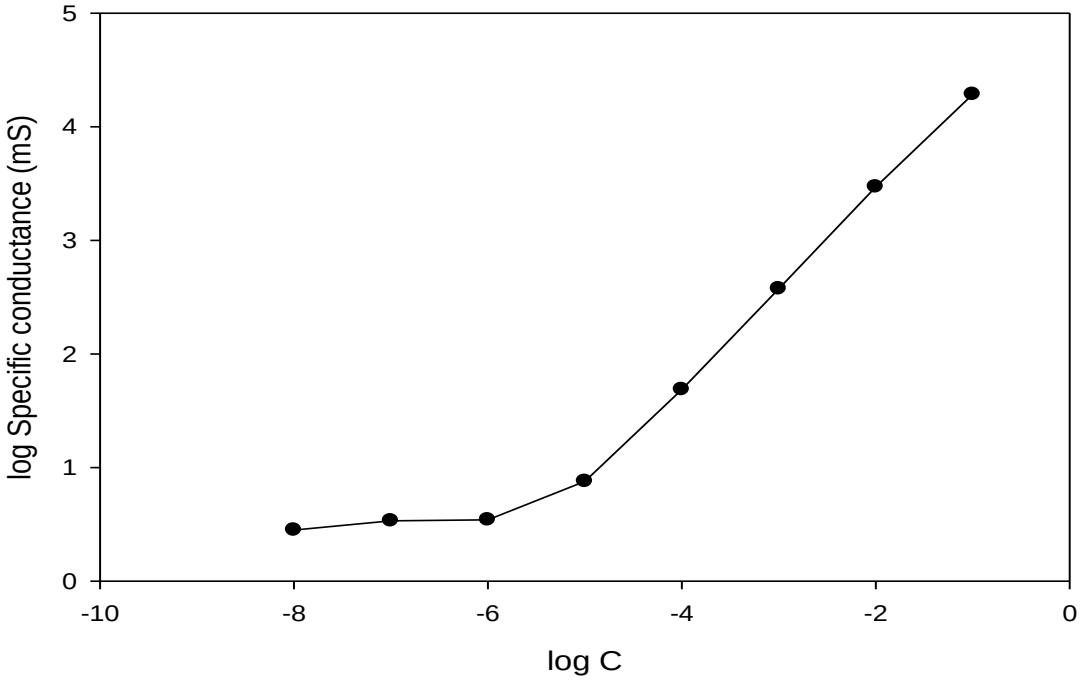

Fig.2: Calibration curve between log κ and log C for La(III)

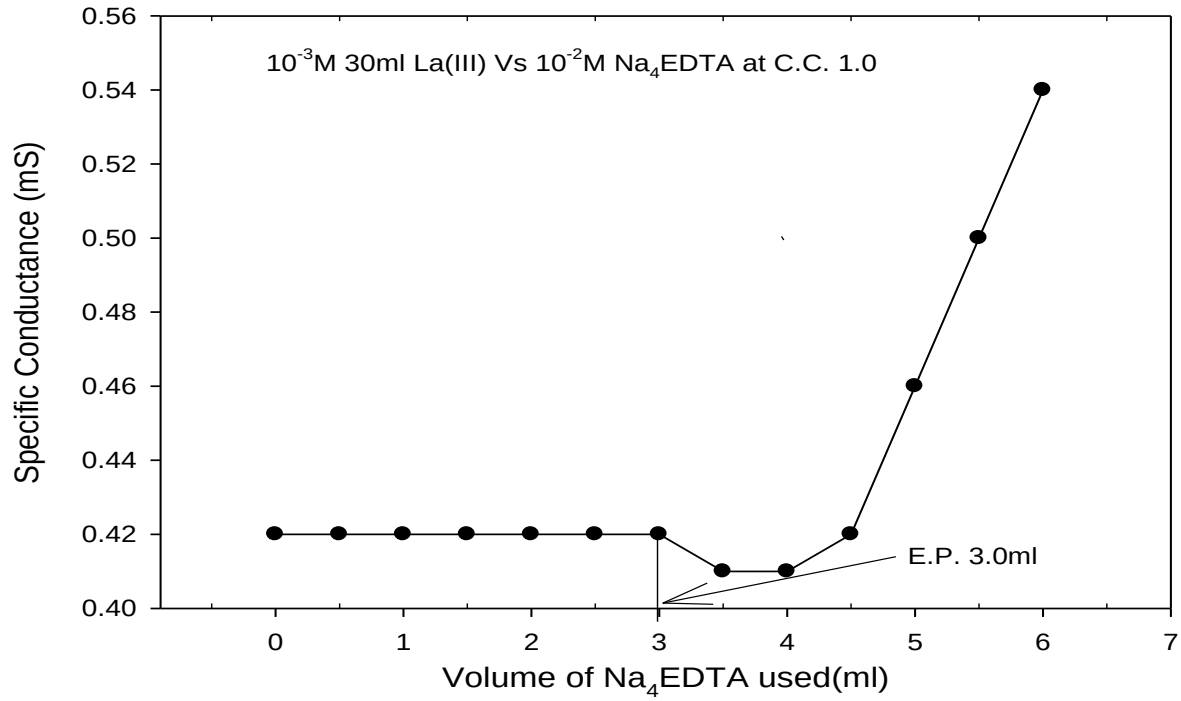

Fig.3: Conductometric titration curve for 30mL of La(III) ($1x10^{-3}$M) *Vs* L ($1x10^{-2}$ M)

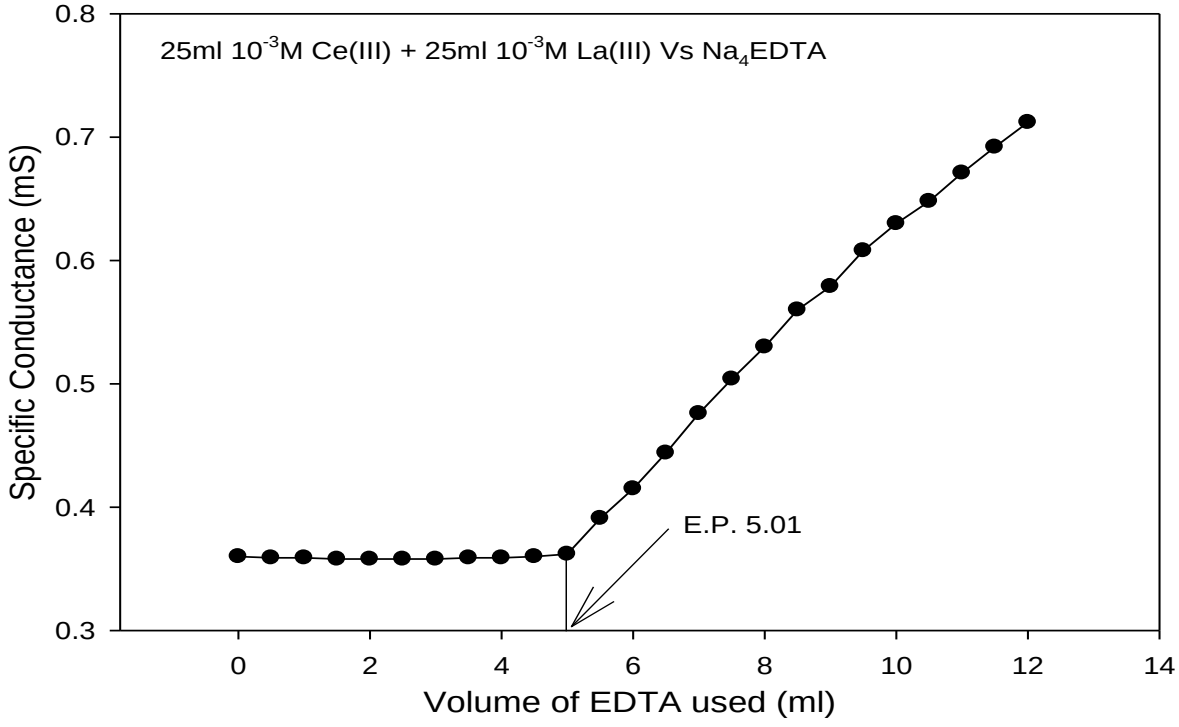

Fig.4: Conductometric titration curve for 25 mL of $1x10^{-3}$M [La(III)+Ce(III)] *Vs* $1x10^{-2}$ **L**

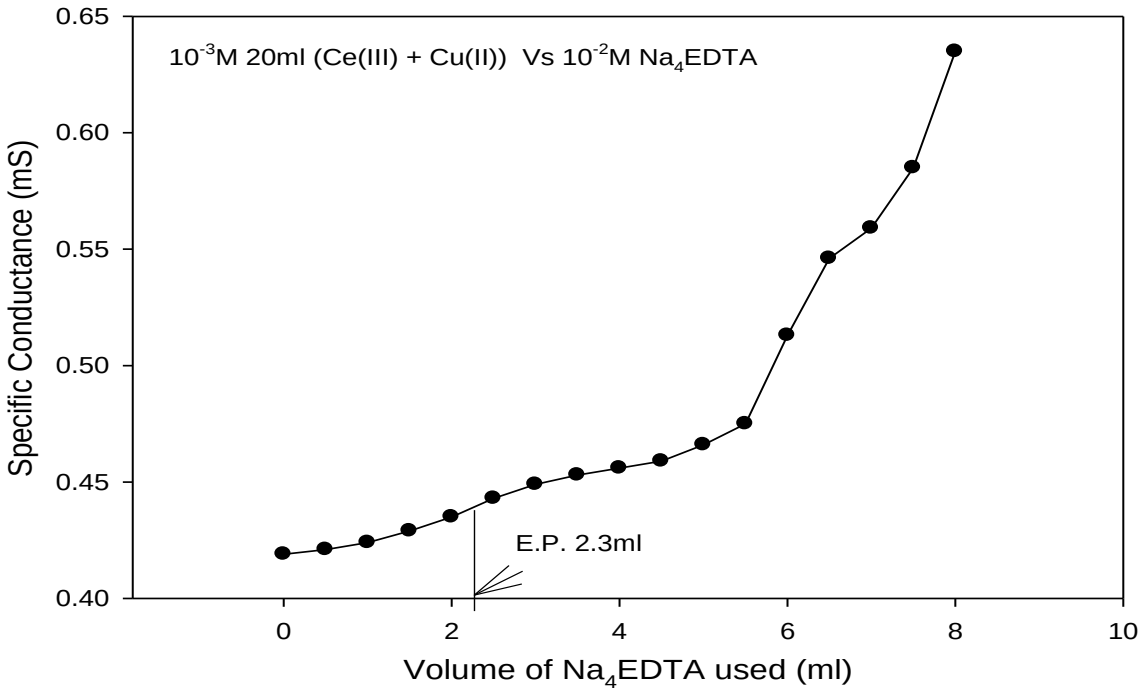

Fig.5: Conductometric titration curve for20 mL of 1x10^{-3} M [Ce(III)+Cu(II)] *Vs* 1x10^{-2} L

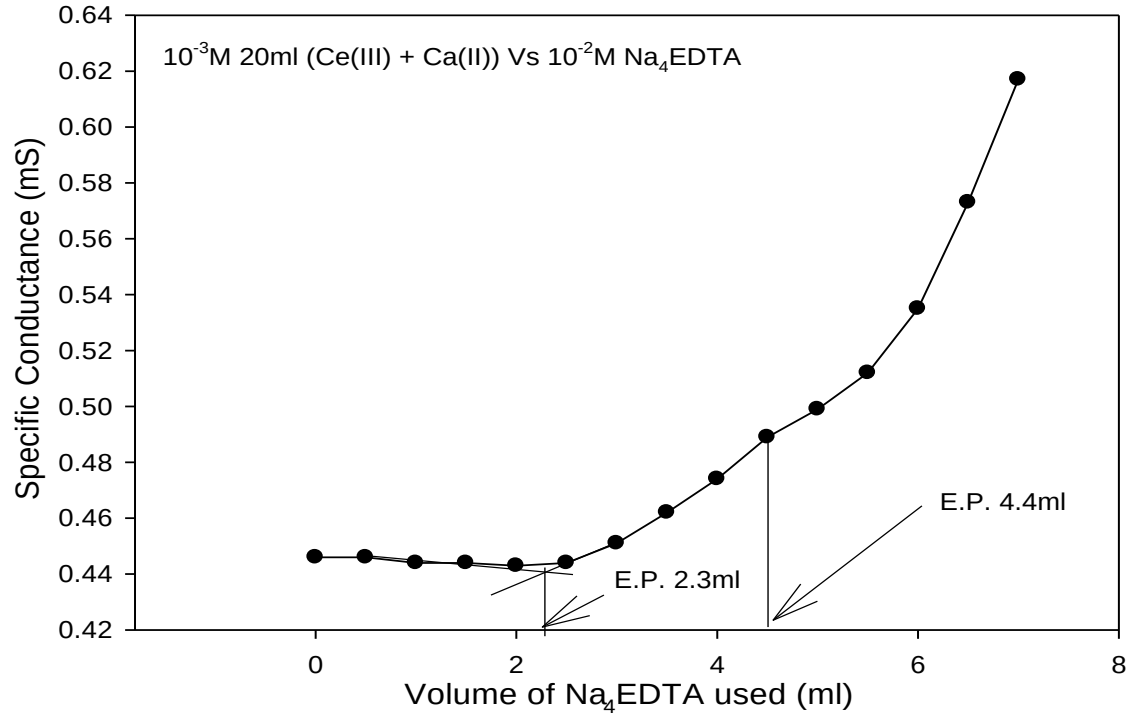

Fig.6: Conductometric titration curve for20 mL of 1x10^{-3} M [Ce(III)+Ca(II)] *Vs* 1x10^{-2} L

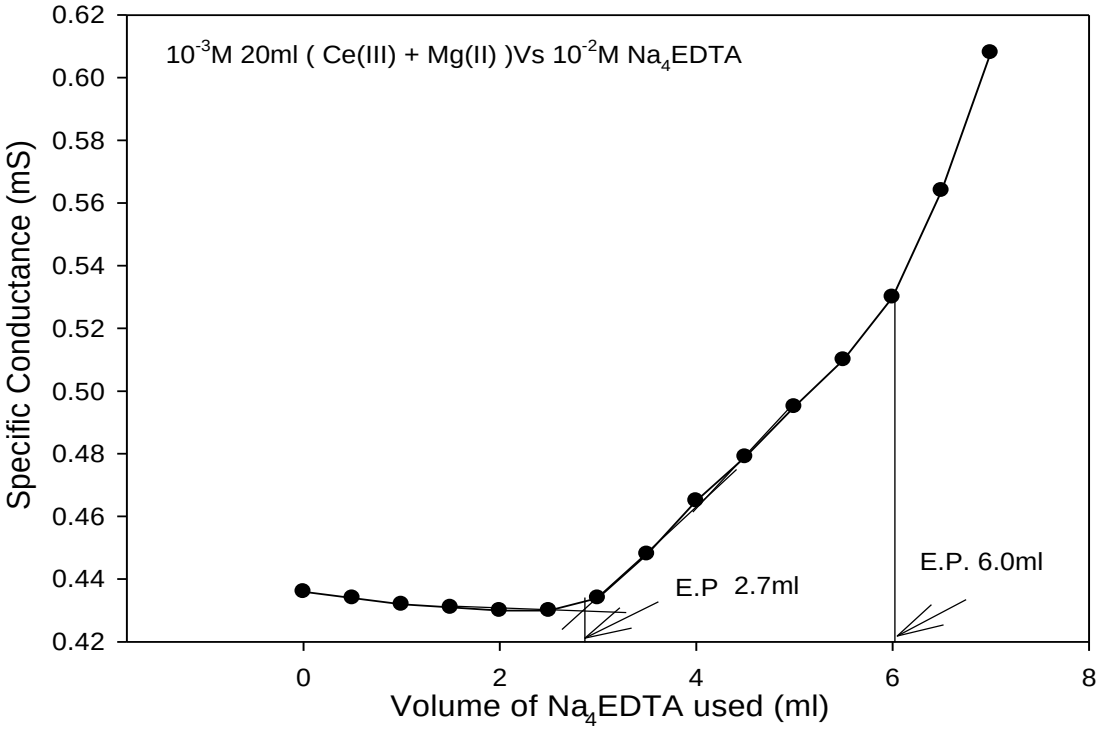

Fig.7: Conductometric titration curve for 20 mL of $1x10^{-3}$ M [Ce(III)+Mg(II)] *Vs* $1x10^{-}$

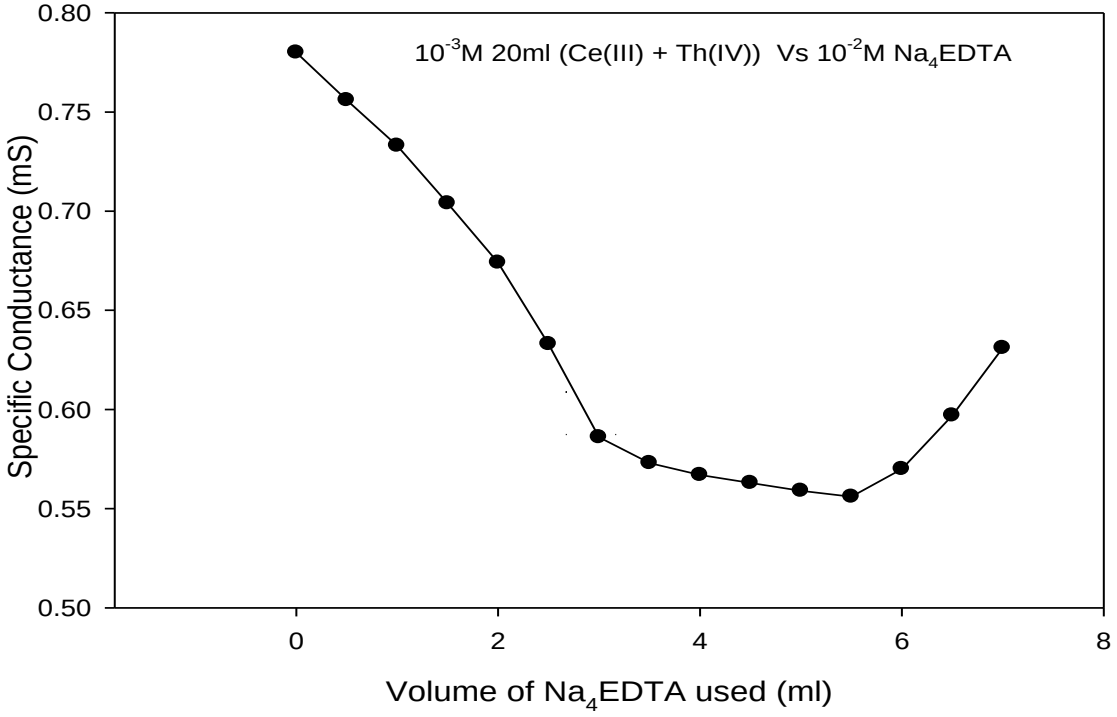

Fig.8: Conductometric titration curve for 20 mL of $1x10^{-3}$ M [Ce(III)+Th(IV)] *Vs* $1x10^{-2}$ L

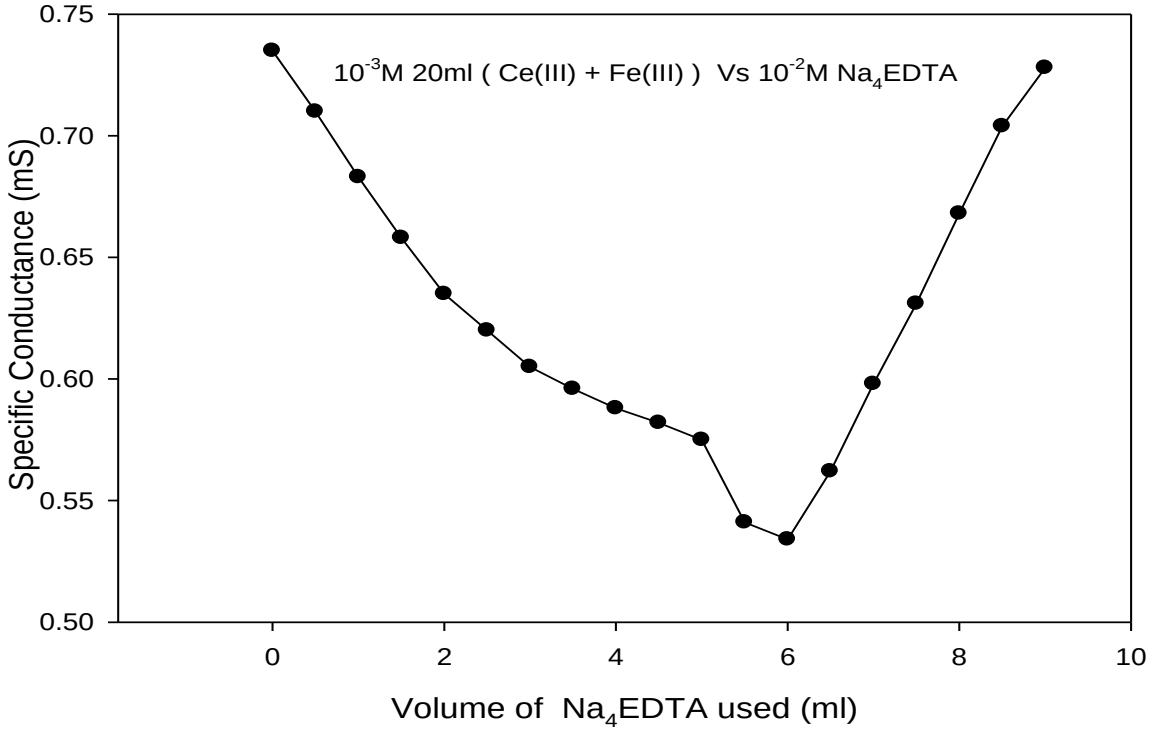

Fig. 9: Conductometric titration curve for 20 mL of 1x10^{-3} M [Ce(III) + Fe(III)] *Vs* 1x10^{-2} L

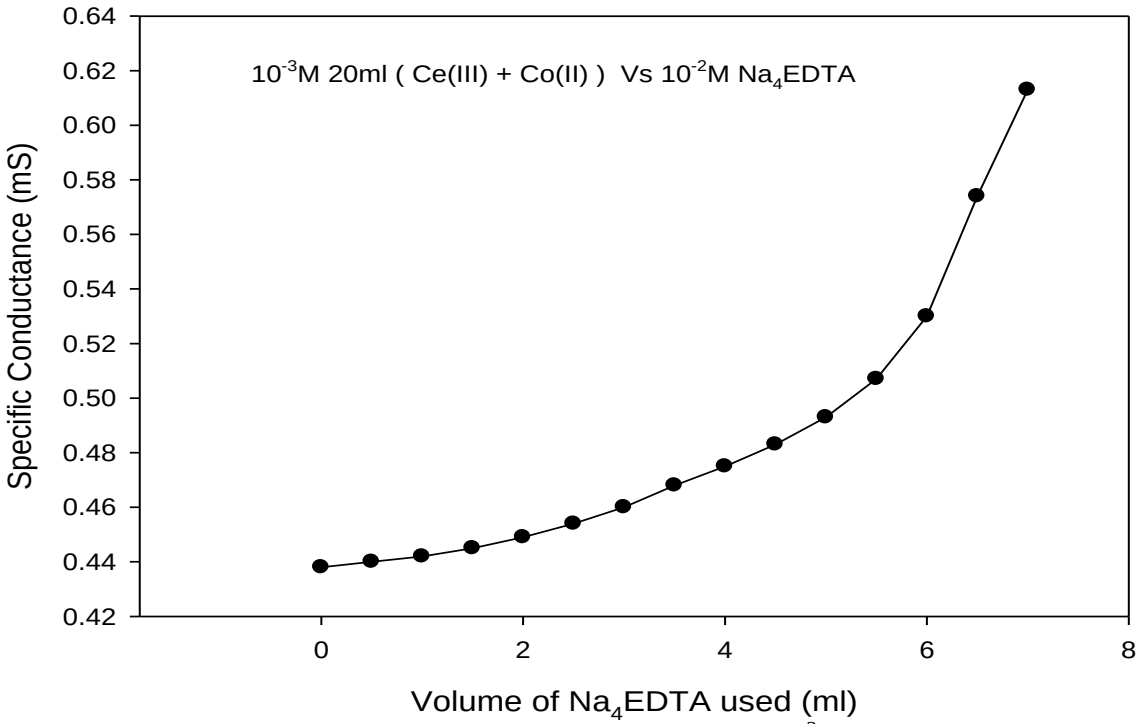

Fig.10. Conductometric titration curve for 20 mL of 1x10^{-3} M [Ce(III)+ Co(II)] *Vs* 1x10^{-2} L

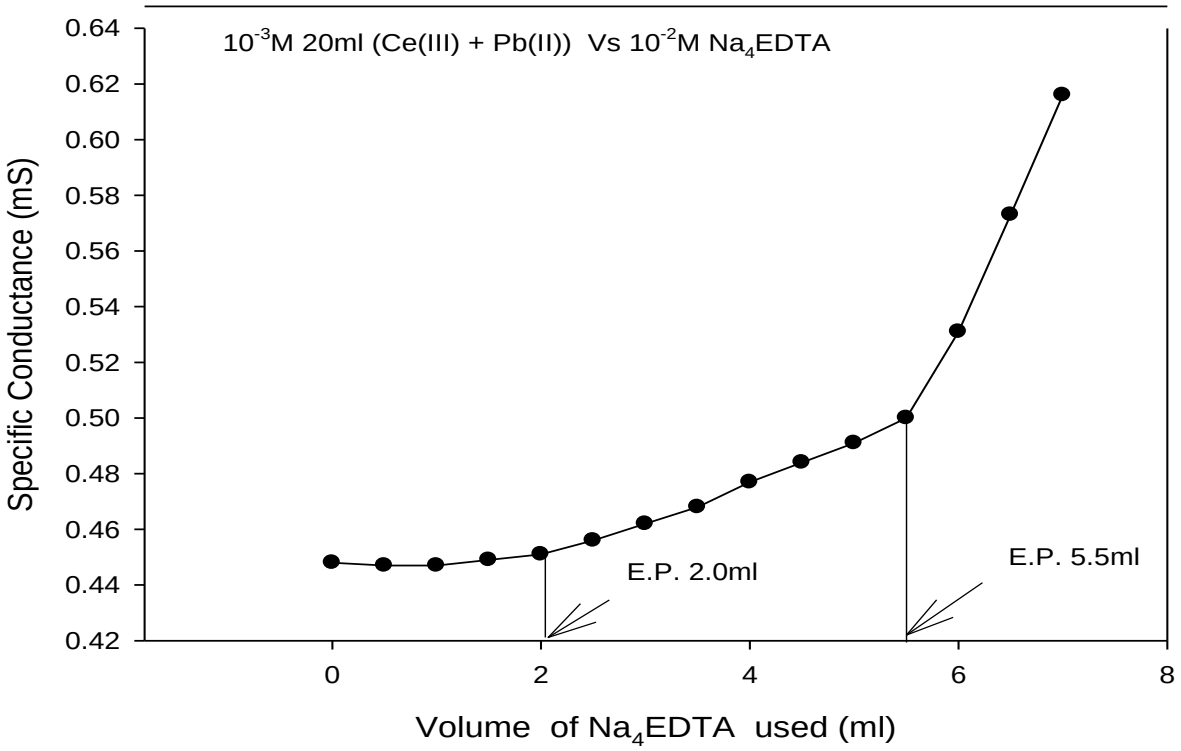

Fig.11: Conductometric titration curve for 20 mL of 1x10^{-3} M [Ce(III) + Pb(II)] *Vs* 1x10^{-2} L

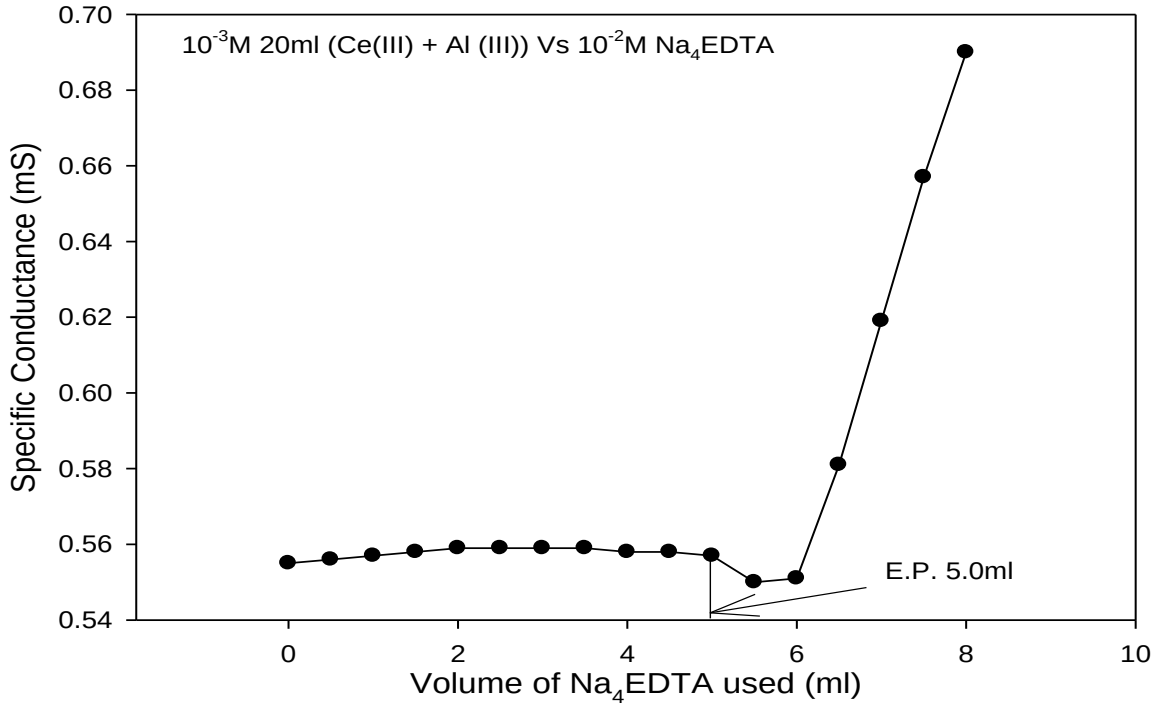

Fig.12: Conductometric titration curve for 20 mL of 1x10^{-3} M [(Ce (III) + Al(III))] *Vs* 1x10^{-2} L

Conclusions and Future Scope of the Work

A new analytical method is established for the quantitative determination of lanthanides by simple and rapid conductometric method. The results obtained in the form of changes in conductivity followed during complexometric titration against EDTA are completely explained. The proposed method is tested for selective determination of individual lanthanides in the presence of interfering ions like selected alkali, alkaline earth, and transition metal ions. The future scope of this work is to get individual end points corresponding to Ln(III) ions without separation. This can be conducted by using EDTA as ligand and weak complexing medium (HIBA) as a co-ligand.

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