# PRECONCENTRATION AND DETERMINATION OF TRACE AMOUNTS OF NEODYMIUM AND SAMARIUM

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## CERTIFICATE

This is to certify that the thesis bound herewith is an authentic record of the research work carried out by **Bhagavathy V., M.Sc.** under my supervision in partial fulfilment of the requirements for the **Degree of Doctor of Philosophy in Chemistry** of the University of Kerala and further that no part thereof has been presented before for any other degree.

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# DECLARATION

I hereby declare that this thesis is a bonafide record of the research work done by me and that no part of the thesis has been presented earlier for any degree, diploma or similar title of any other University.

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# CONTENTS

# CHAPTER I

# INTRODUCTION

Rare earths exhibit close similarity in their chemical properties due to identical outer electronic configuration of their atoms. The quantification of individual rare earth elements assume added significance in view of their widespread use in lasers, magnets and superconducting materials[1] and in development of a model to predict mobilization of thorium from a laterite material[2] and formation of lateritic material deposit highly enriched in rare earth elements, niobium and thorium[3]. The increasing awareness of the role of rare earth elements in wide areas has been the stimulant for the development of new methods and refinement of the existing methods and their extension to the determination of these metals in various matrices. This has led to the growth of a voluminous literature on the analytical chemistry of rare earth metals in general and also to the determination of individual rare earth elements.

## 1.1 DISCOVERY, OCCURRENCE AND USES

### 1.1.1 Discovery

In 1787 Arrhenius[4] discovered a new dark coloured mineral in the ytterby Felspar quarry near Stockholm, Sweden. Gadolin[5] analysed the mineral in 1794, found an unknown substance in it and the name 'yttria' was given. Gadolin's observation was only the introduction. The isolation and identification of sixteen chemical elements of the rare earths were completed only in 1945. In 1803, Klaproth[6] discovered another substance that was similar to, yet different from yttria. This was named as ceria. Berzelius and other chemists[7] examined these substances and found that neither yttria nor ceria was a pure substance. In 1839, Mosander[8] proved this fact by resolving ceria into two dissimilar oxides, the one being readily soluble in dilute nitric acid and the other being very resistant to this reagent. Mosander named the readily soluble substance as lanthanum oxide and the other one as cerium oxide. In 1842 Mosander[9] succeeded in detecting another new element from lanthanum and named as didymium. Fractional crystallisation or fractional precipitation of various compounds of these oxides exhibited divergent properties indicating that they were mixtures of materials. The individual elements, were separated one after another as follows. In 1843 Mosander[10] separated Gadolin's yttria into yttria, erbia and terbia. In 1878 Galissard de Marignac[11,12] separated ytterbia from Mosander's erbia and impure gadolinia from samarskite. In 1879 Boisbaudran[13,14] isolated samaria from Mosander's didymia and in the same year Fredrik[15] isolated scandia from euxenite while Cleve[16] further resolved erbia into holmia, erbia and thulia. Later in 1885 Welsbach[17] resolved didymia into praseodymia and neodymia. In 1886 Boisbaudran[18] resolved Cleve's holmia into dysprosia and holmia. In 1901 Demarcay[19] discovered europium in samarium fractions and in 1907 Urbain[20,21] separated ytterbia into ytterbia and lutetia. Moseley's[22] determination of atomic numbers provided positive knowledge of the number of elements in the rare earth series and Bohr's new theory of atomic structure provided a satisfactory explanation of the periodic arrangement and the importance of the rare earths. One element, with atomic number 61 was not reported by any separation study. In 1945, Marinsky and Glendenin[23] isolated promethium from fission products. The discovery of this element was delayed because of its instability due to its radioactive nature. Finally, it was concluded that the rare earths consist of the sixteen elements viz. yttrium (atomic number, 39) and lanthanum to lutetium (atomic number, 57 to 71). Out of these promethium (61) does not occur in nature.

### 1.1.2 Occurrence

Natural occurrence[4]

The rare earths as a group constitute $8 \times 10^{-3}$ % by weight of the earth's crust. They occur in a variety of minerals chiefly in pegmatite dikes associated with igneous rocks and in deposits derived from the weathering of pegmatites. The chief commercial sources of rare earth minerals are monazite, xenotime, bastnaesite and gadolinite. These rare earth minerals in general find thorium as the principal accompanying metallic element. Some other elements which accompany less frequently are uranium, zirconium, hafnium, titanium, tantalum, niobium, beryllium, aluminium, iron and very rarely scandium. The usual anionic species are phosphate, silicate, carbonate and fluoride.

### Industrial occurrence[4]

Rare earths as impurities are of concern chiefly in materials for atomic energy use. The rare earths occur in all uranium and thorium materials and must be removed to a level of a few parts per billion to minimize their effects as neutron absorbers. Rare earths are products of the fissioning of reactor fuels and become highly detrimental as their concentration builds up. It is this occurrence that is responsible for the surge of interest that produced the great advances in chemistry and technology of the rare earths during the past two decades.

### 1.1.3 Uses[4]

Rare earths are used industrially chiefly as the naturally occurring mixture derived from monazite. Cerium, lanthanum and a partially separated low cerium mixture known as didymium have attained the status of tonnage production. Samarium, gadolinium, europium, dysprosium and erbium are of interest in atomic energy development as control and shut down materials because of their neutron absorption characteristics. Europium has been the first to be used in operating plants. Yttrium which has a low neutron cross section is receiving attention as a possible structural metal and as a fuel matrix material. Electronic materials are emerging as consumers of rare earths. Didymium has been used for the manufacture of ceramic capacitors having low temperature dependance. The recent development of yttrium-iron garnets as low loss magnetic components for microwave circuitry has been of great importance. Gadolinium is also used in garnet manufacture. Compounds such as cerium sulphide and gadolinium selenide are useful for thermoelectric power generation. Cerium is used in the manufacture of photosensitive glass, and in radiation resistant glass, as an optical coating and as a catalyst. Neodymium and praseodymium are used for colouring glass and enamels. Very highly purified lanthanum is used for the manufacture of glass for instrument and camera lenses. This glass has a high index of refraction but low dispersion which facilitates the design of lens system having low chromatic aberration.

The mixture of rare earth chlorides is used for the manufacture of misch metal which is alloyed with iron for the manufacture of lighter flints. Rare earth fluorides and oxides are used as core materials in carbon electrodes for arc illumination, as the rare earth mixture provides very high light intensity and a stable use. Rare earths (as their oxides, phosphates, sulphates etc.) are widely used as polishing agents in particular, for ophthalmic precision lenses. A magnesium alloy containing several percent of rare earths has superior high temperature properties. The addition of yttrium to alloys help them for high temperature service and increase their service life. The addition of misch metal to stainless steel[24] and aluminium metal[25] changes the microstructure of the alloys and thereby improves their mechanical properties.

Recently, rare earth oxides have been used widely in the manufacture of superconducting materials. Samarium-cobalt alloy has been used as magnets. Rare earths have been employed for lasers[26] especially as optically pumped solid state lasers. Rare earth lasers provide pulsed or continuous monochromatic radiation of high intensity, coherence and directionality. Their applications include laboratory use and research (optical spectroscopy, holography, laser fusion), materials processing (cutting, drilling, welding) communications (integrated optics, high data rate transmission, satellite communication system) and military (range finders, target designers). $Nd^{3+}$ is the most extensively studied laser ion. The most widely used solid state laser is Nd : YAG (neodymium : yttrium aluminium garnet). In view of the important uses of neodymium and samarium, these elements were chosen for detailed study.

## 1.2 ANALYTICAL CHEMISTRY

Most of the interest in the analytical chemistry[27] of the rare earths, in particular neodymium and samarium lies in their determination as minor or trace additives or contaminants in a large variety of materials. They are added to steels, cast irons, aluminium and magnesium to impart specific properties. They are of interest geologically in trace concentrations and in nuclear materials as contaminants. Many of the existing classical methods[28] were superseded by physical techniques including spectroscopic techniques for the individual quantitation of rare earth elements. For concentration levels greater than 0.1%, conventional wavelength dispersive x-ray fluorescence is still considered to be the most versatile technique. Atomic absorption spectrometry, flame emission, d.c. arc and more recently plasma spectrometry have been used for the simultaneous multielement determination of lanthanides at lower concentrations. Molecular absorption spectrophotometry using various chromogenic reagents have also been used for the determination of traces of rare earth elements. Activation by neutrons coupled with low energy photon detectors would probably be the technique of choice if it does not depend on a high neutron flux resulting in a costly and sometimes tedious and time consuming procedure. As each technique provides a different and unique approach for the determination of rare earth elements at trace levels, it was felt desirable to compare the performance of various techniques available for the rare earth determination. A brief description of the principles of the techniques with a few applications to the determination of rare earth elements in general are described.

## 1.3 ANALYTICAL TECHNIQUES

### 1.3.1 Molecular absorption spectrophotometry (MAS)

Molecular absorption spectrophotometry [29] is a rapid, reliable and routine analytical technique and is widely employed in view of its simplicity and very low cost. The technique involves the development of colour by reacting the analyte with a suitable chromogenic reagent. Deuterium and tungsten lamps are used as sources in ultraviolet and visible regions respectively. The absorption of the metal-reagent solution is measured against a reagent blank at appropriate wavelength where the absorption due to metal-reagent is maximum and the reagent is less. Most of the inorganic and organic analytes can be analysed by proper selection of reagents and reaction conditions. The various chromogenic reagents used for the determination of traces of neodymium and samarium with experimental conditions are described in Table I.

## Table I

| Reagent | Experimental conditions (pH/acidity; $\lambda_{max(nm)}$; $\epsilon$ (l $mole^{-1}$ $cm^{-1}$); Beer's law range; interferences) | Materials analysed |
|---|---|---|
| 1 | 2 | 3 |
| **A. REAGENTS FOR NEODYMIUM** | | |
| 1. Arsenazo III[30] | 3.8 (1:1 HCl); 676;<br>upto 10 ppm;<br>Al, Fe, Ni, Co, Cu, V & W do not interfere | Molybdenum alloys |
| 2. 4-benzoyl-3-methyl 1-phenyl pyrozolin-5-one [31] | 3-4 (0.01 to 0.1 M acetate buffer); extraction into $CHCl_3$ | - |
| 3. 4-benzoyl 3-methyl 1-phenyl pyrozolin-5-one[32] | Extraction into tributyl phosphate, piperidine or 1,10 phenanthroline in $CHCl_3$, $CCl_4$ or cyclohexane | - |
| 4. Beryllon II [3-(8 hydroxy-3,6 – disulpho 1-naphthyl azo) chromotropic acid][33] | 2; 610; 20750 | - |
| 5. Boron disulpho phenyl fluorone [4-(2,6,7 trihydroxy 3-oxo xanthen-9-yl) benzene 1,3-disulphonic acid][34] | 7.7 to 8.3; 515; 35200;<br>4-28 $\mu g\ l^{-1}$ | - |

| 1 | 2 | 3 |
|---|---|---|
| 6. Bromo pyrogallol red-nitrilo triacetic acid[35] | Hexamine buffer; 664 | 0.25 to 20% of $Nd_2O_3$ in $Y_2O_3$ |
| 7. Carboxy arsenazo 2-[7-(2-carboxy phenylazo)-1,8 dihydroxy-3,6-disulpho-2-naphthyl azo] benzene arsonic acid (disodium salt) [36] | 2.5 - 4.8; 665; 50800; 2 µg-30 µg per 25 ml; Mg, Ca, Zn, Mn, Co, Cu, Fe, Al, $F^-$ $H_2PO_4^-$, oxalate, tartrate, citrate or EDTA masked by suitable reagents | - |
| 8. Chlorosulpho phenol S [3,6 bis (5-chloro-2-hydroxy-3-sulphophenylazo) chromotropic acid][37] | 4.3 - 5.8; 645; 24,000; 0-100 µg Nd in 25 ml | - |
| 9. Chromotrope 2 R[38] | 6; 550 | - |
| 10. Chromotropic acid[39] | 3.8 - 8.05 (5.07); 525; 0.3 m M - 3 m M | - |
| 11. 1',3'-dihydro 8-methoxy-1',3',3' trimethyl 6-nitrospiro [2 H-1-benzo pyran-2,2' (2H) indole] [40] | 0.3 µm HCl, 487, 4100 | - |
| 12. Ethylene diamine tetraacetic acid - catechol or pyrogallol[41] | 2 M NaOH; 16000-18000 | - |

| 1 | 2 | 3 |
|---|---|---|
| 13. 2,2'-bipyridyl-eosin[42] | 5.9 - 6.2; 520; 13000 | 1-25% $Nd_2O_3$ in $La_2O_3$ |
| 14. Eriochrome blue black B[43] | 8-10 | - |
| 15. m-formyl chlorophosphonazo [6-(4-chloro-2-phosphone phenylazo) 3-(3-formyl phenylazo)-chromotropic acid] - hexadecyl trimethyl ammonium bromide[44] | 0.1 M HCl; 680<br>170000<br>(B.L.) $\leq$ 20 µg in 25 ml | Alloy steel |
| 16. Gallein-cetyl trimethyl ammonium bromide[45] | 7 (hexamine buffer)<br>630; 25000;<br>1-40% $Nd_2O_3$,<br>Ni, Co, Hg, Pb, Cu, Sc, Ga, In, $U^{VI}$ and Ge interfere, 4-6 µg of Be, Sr(II), Cr(III), Al or Th per ml of the sample can be tolerated | 1 to 30% $Nd_2O_3$ in $Y_2O_3$ |
| 17. Gallocyanine methyl ester[46] | 6.5 - 7.8 | - |
| 18. 8-hydroxy 5,7 dinitro Quinoline-Rhodamine B[47] | 6-8 (acetate buffer); 553;<br>Extraction into benzene;<br>Co(II), Ni(II), Mn(II), Fe(II), Fe(III), Zn, Cd, Hg(II), Y, In, Pb, La and Th interfere | - |

| 1 | 2 | 3 |
|---|---|---|
| 19. Methyl xylenol blue - hexadecyl trimethyl ammonium bromide[48] | 7-9; 640<br>upto 1.6 $\mu g\ ml^{-1}$ | - |
| 20. 2[N-(2-hydroxy phenyl)-forminidoyl] quinolin-8-ol-cupferron[49] | 8.5 (aq. ammoniacal buffer); 480; 5000<br>0.1 to 20 $\mu g\ ml^{-1}$; extraction into $CHCl_3$ | 5.5% Nd in Mg based alloys containing Al, Mn, Cd or Zr |
| 21. Phthalexon S {3,3'-[bis (carboxymethyl) amino methyl] phenolsulphon-phthalein} - cetrimmonium bromide[50] | 6; 610; 55000;<br>0.05 - 3.8 $\mu g\ ml^{-1}$ | - |
| 22. 4(2-pyridylazo) resorcinol[51] | 7 - 7.5; 550 | Pr with Nd in monazite sand |
| 23. Salicylic acid - rhodamine B[52] | Extraction into $CHCl_3$ | - |
| 24. Sodium p-(1,3 dioxo-3-phenyl propyl) benzene-sulphonate[53] | 9.1 - 9.2; 530<br>0.6 m M to 5 m M | - |
| 25. Sulphonazo III - antipyrine[54] | 3.5 - 6; 660; 22800;<br>0.05 - 50 $\mu g\ ml^{-1}$ | - |
| 26. Sulphonazo III - caprolactam[55] | 3.5 - 6.0; 660;<br>Upto 15 $\mu g\ l^{-1}$; La, Ce, Pr, Sm or Eu interfere, 2 fold amounts of Y or rare earth metals of Y group can be tolerated | - |

| | 1 | 2 | 3 |
|---|---|---|---|
| **B.** | **REAGENTS FOR SAMARIUM** | | |
| 1. | Alizarin red S-phenazone[56] | 5 ; 536; Extraction into isobutyl alcohol 20 fold amounts of Sr or Ca do not interfere | Sm-Ga-Te and Sm-Se alloys |
| 2. | Arsenazo I[57] | 7 - 7.9; 575 | Sm in zirconium dioxide refractory materials |
| 3. | Arsenazo III[58] | Methanolic 0.1 M HCl; 650 | Phlogosam-ointment (sodium dihydrogen bis(5-sulpho salicylato) samarate) |
| 4. | Arsenazo III[59] | 3; 650 | Samarium cobalt magnet |
| 5. | Arsenazo-p-nitro reagent [3-(2-arsonophenylazo)-6-(4-nitrophenylazo) chromotropic acid][60] | 3.6 - 3.8; 660;<br>1 - 10 µm | - |
| 6. | Chlorophosphonazo III [3,6-bis-(4-chloro-2-phosphonophenyl azo) chromotropic acid][61] | 1.1 - 1.5; 668; Extraction into butanol; $UO_2^{2+}$, $Th^{IV}$, Sc, Fe interfere | - |
| 7. | Hydroxy naphthol blue [3-hydroxy-4-(2-hydroxy-4-sulpho-1-naphthylazo) naphthalene 2,7 disulphonic acid]-ethylene diamine tetra acetic acid[62] | 6 (phosphate or acetate buffer); Detection limit = 1.6 µg $ml^{-1}$ | - |

| | 1 | 2 | 3 |
|---|---|---|---|
| 8. | N-phenyl benzohydroxamic acid - bromopyrogallol red[63] | 602; Extraction into isobutyl alcohol | Sm in lanthanum |
| 9. | Xylenol orange-poly(1-dodecyl-4-vinyl-pyridinium bromide)[64] | 6-8; 613; 126000 | - |
| 10. | 1-(2-pyridylazo) 2-naphthol[65] | 9; 552; Extraction into ethyl ether | Sm in lead chloride |
| 11. | 3,5 diiodosalicylic acid - Rhodamine B[66] | 5-6; 548; 100000; 0.03 - 6 μg ml $^{-1}$ | - |
| C. | **REAGENTS FOR NEODYMIUM AND SAMARIUM** | | |
| 1. | Arsenazo I-nitron[67] | 4.95 (Ammonium acetate buffer); 560-570; Extraction into nitromethane-dichloromethane (1:1) | - |
| 2. | Carboxy nitrazo [3-(2-carboxy phenylazo)-6-(4-nitro phenylazo-) chromotropic acid][68] | 1.8 - 4.8; 730; 139000 | |
| 3. | Bromopyrogallol red[69] | 6.5; 685; 20 min. heating | |

| 1 | 2 | 3 |
|---|---|---|
| 4. Carboxy nitrazo [3-(2-carboxy phenylazo)-6-(4-nitrophenylazo) chromotropic acid][70] | 2.2 - 4.3; 730<br>colour intensity occurs after 30 min. for Nd<br>1-2 h for Sm<br>160000 Nd, 120000 Sm | - |
| 5. Chrome azurol S-2,2' bipyridyl dodecyl pyridinium chloride[71] | 9.5 - 11.5; 640;<br>150000;<br>0.1 - 1 μg $ml^{-1}$ | - |
| 6. Chrome azurol S-Cetyl pyridinium bromide (I) or cetriimide (II)[72] | 5.4; 540 to 620;<br>0.7 - 2 ppm | - |
| 7. Chrome azurol S - Quinolin-8-ol[73] | 6 - 6.8 (ammonium acetate buffer);<br>610;<br>18300-20000;<br>0.1 - 2.8 μg $ml^{-1}$ | $Cu_8Sm$<br>$Sm_2Se_3$ |
| 8. Chrome azurol S - 5-nitro 1,10-phenanthroline-hexadecyl ammonium bromide[74] | 9.5;<br>20 μg in 25 ml | - |
| 9. Chromotrope 2 R[75,76] | 6; 590;<br>0.57 - 8.10 (Nd);<br>0.60 - 8.42 (Sm) | - |
| 10. EDTA-acetyl acetone[77] | 575 ( ϵ = 15.3) for Nd,<br>402 ( ϵ = 2.4) for Sm,<br>0.01 - 1 mg $ml^{-1}$ | - |

| 1 | 2 | 3 |
|---|---|---|
| 11. Eriochrome azurol B-hexadecyl trimethyl ammonium bromide[78] | 6; 650;<br>0.45 - 1.2 | - |
| 12. Eriochrome cyanine RC[79] | 6.5; 530 (Nd),<br>540 (Sm) | - |
| 13. Ethyl trioctyl ammonium bromide - xylenol orange[80] | Extraction into xylene;<br>0-4.5 μg per 5 ml of xylene | - |
| 14. $HClO_4$ medium[81] | 575; 7.15 (Nd)<br>402; 3.23 (Sm) | Electronic industry |
| 15. Quinolin-8-ol[82] | 8 .5 - 9.5; 375;<br>Extraction into $CHCl_3$;<br>10-100 μ M | - |
| 16. Peri-dihydroxy naphthondenone (2,3 dihydroxy-1H-phenalen-1-one)[83] | 2-7; 580; Cd(II), Pb(II), Fe(III), Bi(III), Th(IV) and U(IV) interfere | - |
| 17. Phthalexon S {3,3' - [bis (carboxy methyl) amino methyl] phenol sulphon phthalein} - hexadecyl pyridinium bromide[84] | 8 (phosphate buffer);<br>605; 26400;<br>0.05 - 5 μg $ml^{-1}$ | - |
| 18. 4(2-pyridyl azo) resorcinol - antipyrine[85] | 6.5; 525; Extraction into nitrobenzene;<br>3.7 - 5.8 ppm | - |

| 1 | 2 | 3 |
|---|---|---|
| 19. Semiphthalexon S {3,[ bis (carboxy methyl) amino methyl] phenol-sulphone phthalein} - hexadecyl trimethyl ammonium bromide[86] | 6-8; 610; 20000<br>0-3 μg $ml^{-1}$ | - |
| 20. Solochrome cyanine R-Cetyl trimethyl ammonium bromide[87] | 5-6; 610;<br>30-80 μg per 25 ml;<br>Be, $U^{VI}$, In, $PO_4^{3-}$ $SO_4^{2-}$ and $NO_3^-$ interfere | - |
| 21. Xylenol orange[88] | 5.5; 570 | - |

### 1.3.2 Atomic absorption spectrometry (AAS)

Atomic absorption spectrometry[89] is an analytical method for the determination of elements based upon the absorption of radiation by free atoms. It is a versatile laboratory technique especially for trace analysis. It is superior in sensitivity to atomic emission because the proportion of ground state atoms is higher. For multielement analysis, AAS provides best excitation conditions for all elements simultaneously and offers excellent precision and accuracy. The concentration range where AAS may be applied is from picogrammes and fractions of a part per billion of many cations in solutions upto tens of percent of metallic constituents in solid samples. Flame atomic methods require only one dissolution of the sample, since it is a multielement analytical technique.

Atomic absorption spectroscopic techniques[90] provide several of the most useful and specific means for the determination of the rare earth elements at the trace, minor, and major constituent levels. Eventhough the chemical properties of the elements may be remarkably similar, the energy states within such atomic system are just as uniquely different for the individual rare earth elements as they are for other elements. As a consequence, the spectra produced by energy transition between these states are also highly specific. In a systematic study on the absorption spectra of the rare earth elements in a fuel rich, oxy acetylene flame fed with ethanolic solutions of these elements, Fassel and Mossotti[91] and Mossotti and Fassel[92] identified over 1000 absorption lines in the 2500 to 6500 A$^{0}$ region. Many of these lines were of sufficient intensity to be useful for analytical purposes. It has also been reported that when higher temperature flames (fuel rich nitrous oxide - acetylene) were used, the detection limits were also improved.

Europium in rare earths of Baotou ores[93] was determined by AAS using nitrous oxide-acetylene flame at a wavelength of 457.4 nm. Erbium and holmium[94] in yttrium earth oxides and yttrium in nickel base alloy[95] have been determined by flame AAS. Electrothermal AAS was used for the determination of microgram amounts of ytterbium[96, 97]. Here the sample solution was applied to a tantalum-tungsten lined pyrolytic graphite coated tube and atomized at 2770 C after ashing. Dittrich et al[98] determined traces of rare earths in other rare earth metals by AAS with electrothermal atomization. Youwei et al[99] determined 15 rare earth elements in ores by atomic absorption using a graphite oven. A graphite furnace was used for the determination of rare earths[100] after preconcentration by extraction using pyrophosphates into chloroform and back extraction into nitric acid. Neodymium in neodymium doped yttrium-aluminium garnet crystals was determined[101] by AAS. A fuel rich acetylene-nitrous oxide flame was used and measurements were made at 489.7 nm. Except praseodymium other lanthanides do not interfere with the more sensitive neodymium line. In the presence of praseodymium, neodymium can be determined using less sensitive neodymium line or praseodymium has to be removed by some other method.

### 1.3.3 Emission spectrometry (ES)

In emission spectrometry[102], radiation is emitted by atoms which are in excited states. Flame emission and absorption are complementary techniques. Some elements can be detected at lower concentrations by emission measurements and some by absorption, but absorption measurements are less prone to interelement interference effects. In both techniques, sample molecules are dissociated into their atoms. In principle, the same equipment can be used for both emission and absorption, although a separate radiation source is required for absorption measurements. Generally, the absorption should be virtually independent of temperature, whereas in emission, the emission intensity varies exponentially with temperature. Similarly, within certain limits, emission intensity varies linearly with concentration whereas absorption follows beer's law.

Emission spectrometry is a good method for the determination of microamounts of rare earths[103]. Europium in rocks[104] was rapidly, cheaply and reliably determined by emission spectrometry at 459.4, 462.72 and 466.19 nm. Acetylene-nitrous oxide flame was used for excitation and the results were found to be in good agreement with those obtained by inductively coupled plasma spectrometry and neutron activation analysis. The neodymium present in neodymium doped yttrium garnet was determined[105] by flame emission spectrometry. Determination of rare earth elements in yttrium oxide[106] was done directly by emission spectrometry and also after extraction chromatography[107] using tributyl phosphate-ammonium thiocyanate to enhance sensitivity.

Osumi et al[108] reported the sensitivity enhancement of using caesium chloride - graphite buffer on the d.c. arc emission spectrometric analysis of neodymium oxide. The emission spectrometric determination of fourteen rare earth elements in high purity europium oxide[109] was effected by an a.c. arc in a silica gas cell containing argon-oxygen in the ratio 3:2. The determination of traces of europium, samarium, gadolinium and yttrium in oxides of yttrium, samarium and gadolinium[110] was done by emission spectrometry in a.c. arc. Direct current plasma atomic emission spectrometry[111] was used for the determination of cerium, europium and terbium in rare earth phosphors. The emissions were measured at 418.66 for cerium, 282.08 for europium and 332.44 nm for terbium respectively.

### 1.3.4 Spectrography

Analytical applications of emission spectrography[112] have been developed by extending and amplifying the principles inherent in the qualitative flame test. Thus more powerful methods of excitation such as electric spark, or electric arc are used and the spectra are recorded photographically by means of a spectrograph. Since the characteristic spectra of many elements occur in the ultra violet, the optical system used to disperse the radiation is generally made of quartz. The applications of emission spectrography include the examination of a single metal or an alloy for impurities, the analysis of an alloy for its general composition including a search for minor components and traces of impurities, the analysis of ash of organic substances and other materials (e.g. natural waters) amenable to similar treatment and the detection of contaminants in food. This procedure is specific for the element being determined, the method is time saving and it does not require any preliminary treatment for quantitative determination of traces of the elements in a sample.

A number of methods were reported for the determination of microamounts of rare earths using a.c. arc and d.c. arc emission spectrography. The spectrographic determination of fourteen rare earths in highly pure praseodymium oxide[113] was done using a d.c. arc in an oxygen-argon atmosphere. The detection limit for each metal was 9 ppm when concentrated using a column of CL-P 507 resin [114]. Traces of cerium, praseodymium, neodymium and terbium in lanthanum oxide[115] were determined by emission spectrography in d.c. arc in the atmosphere of air or argon-oxygen-nitrogen. 40 ppm of cerium, 25 ppm of praseodymium, 25 ppm of neodymium and 42 ppm of terbium in 20 mg of lanthanum oxide were determined by this method. By properly choosing the analytical line, matrix effect can be reduced. Thus europium in gadolinium oxide[116] was determined spectrographically at 459.4 nm since the other lines at 390.7, 393.1 and 397.2 nm were subjected to interference by the presence of gadolinium. The determination of lanthanum, cerium, praseodymium, neodymium, gadolinium, dysprosium, holmium, erbium, thulium, ytterbium and lutetium in magnesium-yttrium alloys[117] was done by spectrographically. Here, carbon powder was used as the buffering agent, barium chloride as carrier and scandium as internal standard. Fourteen trace rare earth impurities were determined in high purity gadolinium oxide[118] by a solution-dry residue technique involving a.c. arc excitation in oxygen-argon for spectrographic measurement. The coefficient of variation was $< 5\%$ and recoveries were satisfactory.

### 1.3.5 X-ray fluorescence spectrometry (XRFS)

X-ray fluorescence spectrometry[119] also known as X-ray secondary emission spectrometry is a nondestructive instrumental method used for both qualitative and quantitative chemical analysis. The basis of the x-ray fluorescence[120] technique lies in the relationship between the wavelengths of the x-ray photons emitted by an irradiated sample element and the atomic number of that element. When an atom is excited by removal of an electron from an inner shell, it usually returns to its normal state by transferring an electron from some outer shell to the inner shell with consequent emission of energy as x-rays. X-ray fluorescence spectrometers use either the diffracting power of a single crystal to isolate narrow wavelength bands, or a proportional detector to isolate narrow energy bands from the polychromatic beam, corresponding to the characteristic radiation excited in the sample. The first of these methods is called wavelength-dispersive x-ray fluorecence (WDXRF) spectrometry and the second, energy dispersive x-ray fluorescence (EDXRF) spectrometry. Because of the known relationship between emission wavelength (in WDXRF) or emission energy (in EDXRF) and atomic number, isolation of individual characteristic line allows the unique identification of an element to be made and elemental concentrations can be estimated from characteristic line intensities. Thus this technique is a means of materials characterisation in terms of chemical composition. In WDXRF, usually primary x-radiation from x-ray tubes and in EDXRF x-ray or $\gamma$-ray emission from radioactive sources is used for excitation of the elements. Multielement analysis in one sample without separation is the main advantage of XRF spectrometry. WDXRF spectrometry is found to be more sensitive than EDXRF spectrometry.

XRF spectrometry is a widely used analytical technique for the determination of rare earths[90]. Most of the works reported for the determination of rare earths were done using WDXRF spectrometry. In almost all, the rare earth metals were converted into oxalate and the oxalate was made into pellet with boric acid as binder. L x-rays were used for quantitation since conventional x-ray tube excitation system did not sufficiently excite K x-rays. A detailed report of some of the common procedures using XRF spectrometry are described in Table II.

The determination of rare earth elements in presence of low atomic number elements like iron, titanium etc. can be done by EDXRF spectrometry since the K x-rays of rare earth elements do not interfere with those of the mentioned elements[140]. Thus barium, lanthanum, cerium and neodymium in lateritic materials[141] were determined using energy dispersive x-ray fluorescence spectrometry. In this method, three procedures were described, (i) a sample was mixed with $Al_2O_3$ and $SiO_2$ in the ratio 1:2:1 and then pelletized with methocel and irradiated using $^{57}Co$ annular source for K x-rays, (ii) a ground and dried sample was pressed into a 1 cm disc and a $^{241}Am$ source was used to excite K x-rays, (iii) a ground sample was agitated with water, the slurry was transferred onto mylar foil in a sample cup and air dried. The intensity of the K x-rays were measured as counts. The determination of traces of lanthanides of the neodymium oxide in neodymium doped yttrium-aluminium garnet[142] were done using EDXRF spectrometry via their characteristic K x-rays. In general, EDXRF spectrometric technique has been used for the determination of rare earth elements in minerals[143,144], rare earth concentrates [145,146] and magnetic materials[147,148].

## Table II

| Sl.No. | Analytes | Material analysed | Details of the method | Detection limit/(precision) coefficient of variation/ limit of determination |
|---|---|---|---|---|
| 1 | 2 | 3 | 4 | 5 |
| 1. | Rare earth impurities[121] | High purity yttrium oxide | Converted into oxalate, mixed with boric acid and pressed as a double layer onto $H_3BO_3$ pellet | 15 ppm for Eu and Gd to 68 ppm for Yb.<br>20% to 0.3% for 0.005 to 1% impurities |
| 2. | Rare earth impurities[122] | High purity yttrium oxide | Converted into oxalate, mixed with boric acid and pressed as a double layer onto $H_3BO_3$ pellet | 0.005% except for Yb (0.01%)<br>0.005 to 1% for 4.9% |
| 3. | Yttrium, cerium, praseodymium, neodymium, europium and gadolinium[123] | High purity samarium oxide | Converted into oxalate, mixed with boric acid and made into pellet | 0.002% for Y, Ce, Nd and Gd.<br>0.006% for Eu and 0.009% for Pr.<br>$\simeq$ 0.5% at 1% level to 20 to 40% at 0.005% level |
| 4. | Ce, Pr, Sm, Eu and Gd[124] | High purity neodymium oxide | Converted into oxalate, mixed with boric acid and made into pellet | 100 ppm for all the cited rare earth elements except Eu (for which it is 50 ppm) |

| 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|
| 5. | Tb, Dy, Ho, Tm, Yb, Lu, and Y oxides[125] . | Erbium oxide | Converted into oxalate, mixed with boric acid and made into pellet over a supporting pellet of boric acid | 50 ppm for all impurities except Yb (100 ppm) |
| 6. | Nd[126] | Aluminium yttrium garnet doped with 0.2 to 6% of Nd | Compressed into disc (standard prepared by sintering) | 10 ppm of Nd for $L\alpha_1$ line<br>80 ppm of Nd for $K\alpha$ line<br>$< 1\%$ |
| 7. | Gd, Tb, Dy, Er, Tm and Yb[127] | Holmium oxide | Converted into oxalate, mixed with boric acid and made into pellet over a supporting pellet of boric acid | - |
| 8. | Y, Eu, Gd, Tb, Ho and Er[128] | High purity dysprosium oxide | Converted into oxalate, mixed with boric acid and made into pellet over a supporting pellet of boric acid | 15 $\mu g\ g^{-1}$ for Gd to 2.6 $\mu g\ g^{-1}$ for Er<br>$\simeq$ 20% for 5 $\mu g\ g^{-1}$ and 0.5% or less for 500 $\mu g\ g^{-1}$ |

| 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|
| 9. | Rare earth impurities[129] | Praseodymium oxide | Converted into oxalate, mixed with boric acid and made into pellet over a supporting boric acid pellet | 21 to 36 ppm,<br>42% for 0.01% of La<br>0.016% for 1.0% of Sm |
| 10. | Sm, Eu, Tb, Dy, Ho, and Yb[130] | High purity gadolinium oxide | Converted into oxalate, mixed with boric acid and made into pellet over a supporting boric acid pellet | 10 to 80 ppm, limit of determination - 50 ppm, 5 to 14% |
| 11. | Ce, Pr, Sm, Eu and Gd[131] | Neodymium oxide | Converted into oxalate and made into pellet with 50% of its weight of boric acid | Analytical range -<br>0.005 to 1% for Eu,<br>0.01 to 1% for other elements |
| 12. | La, Ce, Pr, Nd, Sm, Eu and Gd[132] | Rare earth metal concentrates | Mixed with resin and pressed into a tablet | - |
| 13. | La, Ce, Pr, Nd and Sm[133] | Rare earth metal aluminium alloys | Filtered and collected over a filter paper | $< 1\ \mu g\ cm^{-2}$,<br>3.59% - 12.61% |

| 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|
| 14. | Y, Er, Tm and Yb[134] | High purity lutetium oxide | Converted into oxalate and pelletized with boric acid | 20-10000 ppm for Tm, 0.002% to 1% of Y, Er, Tm and Yb in $Lu_2O_3$ |
| 15. | Rare earth impurities[135] | Erbium oxide | Converted into oxalate, mixed with boric acid in the ratio 3:1 and compressed to form a pellet with a backing of boric acid | < 4% for a concentration of 1% |
| 16. | Y and Ce[136] | Ceria-yttria mixtures | Fused with $Li_2B_4O_7$ at $1000^oC$ for 20 to 40 min, cooled, bottom surfaces of the disc were ground and polished | Relative error for (12 to 85%) of $Y_2O_3$ and (15 to 88%) of $CeO_2$ $< \pm$ 1% |
| 17. | Ho, Er, Tm and La[137] | Ytterbium oxide | Converted into oxalate and made into pellet | 50-10000 ppm of Ho, Er, Tm or Y<br>100 to 10000 ppm of Lu |

| 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|
| 18. | La, Pr, Nd and $Sm^{138}$ | Cerium dioxide | Converted into oxalate, mixed with equal amount of boric acid, and pressed to form a double layer disc over a backing disc of boric acid | 50 to 100 ppm, $\simeq$ 1 to $\simeq$40% |
| 19. | Sm. Eu, Gd, Dy, Ho and $Y^{139}$ | Terbium oxide | Converted into oxalate, mixed with half the amount of $H_3BO_3$ and compressed at 20 tons into a pellet over a $H_3BO_3$ backing pellet | Limits of determination 0.01% for rare earth oxides and 0.005% for $Y_2O_3$<br>0.7 to 3.5% at the 0.5% level,<br>9.2 to 51.4% at the 0.02% level |

### 1.3.6 Inductively coupled plasma spectrometry

A highly sensitive and most promising analytical technique emerged during the eighties is the inductively coupled plasma spectrometry[149]. An inductively coupled plasma is a high energy, optically thin excitation source. Power from a radio frequency generator is coupled to a flow of ionised argon gas inside a quartz tube encircled by an induction coil. To initiate the plasma, argon is ionized by a momentary high voltage discharge. The ionized gas passing through the high frequency magnetic field absorbs energy. This causes further local heating and ionization to form a ball of electrically conducting gas of plasma. This electrical flames or electrically generated "flame like" plasmas possess physical and spectroscopic properties that convert the analyte into free atoms and ions which emit characteristic spectra. This forms the basis of inductively coupled plasma-atomic emission spectrometry (ICP-AES). Further, when the ions in plasma are collected and analysed by mass spectrometer, it resulted in a much more powerful technique viz. inductively coupled plasma-mass spectrometry (ICP-MS).

Many wavelengths of varied sensitivity are available for the determination of any one element, so that inductively coupled plasma is suitable for all concentrations, from ultratrace levels to major components. A complete multielement analysis can be undertaken in a period as short as 30 seconds and with the consumption of only 0.5 ml of sample solution. More than seventy of the elements in the periodic table are capable of being determined by inductively coupled plasma spectrometry.

In more recent years, ICP-AES has been used for rare earth analysis because of the small effect of matrix and low detection limits[103]. This method has been applied to determine trace amounts of fourteen rare earth elements in high purity yttrium oxide[150]. The detection limits of quantitative determination for most rare earth elements were 0.3 - 3.0 ppm except cerium and praseodymium. The relative standard deviation was 2.3 - 7.3%[151]. Walsh et al[152] developed a method for the determination of rare earth elements present in six standard rocks with a coefficient of variation of 1 to 2%. First, they isolated the rare earth elements present in rock samples by using ion exchange chromatography on Dowex AG 50 W - X8. ICP-AES has been successfully utilized for the determination of trace rare earth elements in lanthanum oxide[153], in high purity yttrium oxide[154] and in high purity cerium dioxide[155]. Simultaneous determination of fifteen rare earth metal impurities in oxides of lanthanum, cerium, praseodymium, neodymium, samarium and yttrium was achieved by this technique[156]. Rare earth impurities present in highly pure gadolinium oxide[157] were separated by extraction chromatography with bis(1-methyl heptyl) hydrogen phosphate and eluted with hydrochloric acid. The eluates were analysed by ICP-AES. Recovery and precision were good and the method could be applied to $Gd_2O_3$ of purity $\geq$ 99.999%. Wenfan[158] proposed the application of ICP-AES with direct powder introduction technique to simultaneous spectroscopic determinations of 32 elements in silicate samples. The measuring range is 1-1000 ppm for lanthanum and scandium, 0.1 - 1000 ppm for yttrium and ytterbium respectively. The method is characterised by rapidity in analysis, higher sensitivity, better reproducibility, less memory effect and wide measuring range. Ge Weibao et al[159] used this method to determine the detection limit for 67 elements (containing 16 rare earth elements).

ICP-MS[160] yields simpler spectra and better detection limits for rare earth elements. The detection limits follow the trend of isotopic abundances i.e. detection limits are best for the monoisotopic elements. It is easy to select atleast one useful m/z value for each rare earth element irrespective of their abundance and also without prohibitive interference. Lichte et al[161] determined values for rare earth concentrations in several standard reference materials such as Basalt BCR-1 and coal NBS 1632 a. The agreement with the reference values is very good even in those cases where corrections for overlap from oxide ions were necessary. The whole rare earth group could be determined by ICP-MS without a separation and preconcentration step. Hutton[162] reported analytical results for the determination of rare earth elements in an oil standard reference material. Some precautions are necessary for determination of elements of low m/z values because of additional background ions observed when organic solvents are nebulized. However at high m/z values corresponding to rare earth ions, the spectrum is not much different from that observed during nebulization of aqueous solutions. Thus Hutton analysed the rare earth elements in fuel oil (NBS 1634 a) by ICP-MS Sample dissolution has been eliminated by introducing solids directly into ICPMS. Mass spectra for rare earth analytes have been carried out by arc nebulization of the sample. Because of the rapid scanning possible with the mass spectrometer, virtually all the elements can be identified and determined quickly by ICP-MS. ICP-MS is particularly attractive because of the high and fairly uniform sensitivity for most elements, the simple, readily interpreted spectra and the ability to follow a transient sample introduction pulse. The combination of a solid sampling technique with ICP-MS would be very valuable if a variety of solids could be analysed without standards that closely mimic the sample matrix as preparation of matched, homogeneous solid standards is very difficult and expensive.

In ICP-MS suppression of oxide ions, improvements in precision and alleviation of matrix interference effects are desirable. The main problems in ICP-AES for rare earths are spectral interferences and detection limits that are not quite good enough for many applications.

### 1.3.7 Spark source mass spectrometry (SSMS)

More recently, spark source mass spectrometry[102] has provided the analytical chemist with the ability to cover the full range of elements in any sample in a single determination and the ability to detect these elements at the parts per billion (ppb) level. A radiofrequency (about one megahertz) voltage of several tens of kilovolts is applied in pulses across a small gap (a few thousandths of a centimeter) between the two sample electrodes in the source under high vacuum. The breakdown that occurs in this gap initiates an electrical vacuum discharge. The positive ions from this discharge, which are representative of the sample under study are then accelerated through the electrostatic analyser and finally separated according to their m/e ratios. A monitor collector placed between the electrostatic and magnetic analysers intercepts a small portion of the ion current and provides a measure of the intensity of the ion beam. The product of this ion current and the time of measurement gives the exposure for that particular run (in nanocoulombs).

The application of SSMS to the analysis of rare earth matrices was first reported by Guthrie[163-166] who showed that in spite of difficulties due to inhomogeneities, SSMS was applicable to the analysis of rare earth elements. Now rare earth matrices are considered to be ideal for SSMS analytical technique[167]. Later SSMS[168] has been used for the analysis of approximately 1600 rare earth samples. These samples were mainly rare earth metals (580), oxides (830), and fluorides (150). SSMS was used for the determination of 0.1 ppm levels of rare earth impurities in high purity yttrium oxide[169,170]. Wang et al[171,172] reported that the trace amounts of rare earth elements in the mantle and moon rocks have been determined by SSMS.

### 1.3.8 Luminescence spectrometry [29]

When a quantity of radiant energy is absorbed from a beam of radiation by a chemical species, the species is promoted to an excited state. The excited state has a limited life time and would prefer to rid itself of this extra energy and return to the ground state. To attain this state of tranquility, an excited chemical species must dispose of a quantity of energy equal to the difference in energy between the excited state and the ground state. This energy can be released in several ways. It can be transferred to other species, it can be converted into other forms of energy (thermal or electrical) or it can be emitted in the form of electromagnetic radiation. When the energy gained by a chemical species during absorption is emitted in the form of radiation, the process is called luminescence. The radiant power of luminescence will depend both on the concentration of the luminescing chemical species and on the frequency of the incident radiation. Thus the frequency of the luminescence spectra characterises the chemical species and the intensity depends on the concentration of the chemical species.

Luminescence spectrometry is based on the formation of crystalline phosphors and measuring the resulting luminescence intensity. This procedure facilitates the determination of gadolinium, europium, dysprosium, samarium and terbium in yttrium oxide[173], terbium, dysprosium and holmium in lanthanum oxide[174], samarium and europium in gadolinium oxide[175], europium[176] in oxides of lanthanum, gadolinium, terbium and yttrium, neodymium, samarium and europium in lanthanum oxide[177] and samarium, europium and dysprosium in gadolinium oxide[178]. For the determination of 0.1 ppm to 0.06% of neodymium and 0.04 ppm to 0.1% of dysprosium in gadolinium oxide[179], the sample was mixed with calculated quantity of ammonium fluoride and the mixture was fused at 750$^oC$ for 45 min. to produce a crystalline phosphor based on gadolinium fluoride oxide. This phosphor exhibits maximum luminescence at 885 nm for neodymium and 576 nm for dysprosium. The coefficient of variation was $< 8\%$ (10 results) when determining 2.5 to 7 ppm of neodymium or 1.7 to 30 ppm of dysprosium. Fluoride oxide phosphor preparation and subsequent determination via luminescence intensity were reported for terbium in yttrium fluoride oxide[180] and dysprosium in ytterbium oxide[181]. Europium[182] was determined by measuring the luminescence of its 1:1:1 complex with EDTA and 1,10-phenanthroline. The detection limit was 0.014 $\mu g\ ml^{-1}$ of europium. The method was used for determining europium in oxides of rare earth metals such as lanthanum, neodymium, gadolinium and yttrium. Traces of rare earth impurities in yttrium, gadolinium and lutetium matrix[183] were determined by converting into orthophosphates (as crystalline phosphors) and measuring the luminescence intensity of all rare earth elements.

### 1.3.9 Neutron activation analysis (NAA)

Nuclear transitions are free from the effects of chemical bonding and can be utilised for elemental analysis. Naturally occurring radioactive elements undergo distinctive nuclear transitions resulting in the emission of alpha particles, beta particles, and gamma rays. The energy spectra of these radiations can be used to identify and determine the elements. This procedure provides the basis for radiotracer experiments in biology, biochemistry and medicine. For non radioactive elements, a technique called NAA can be employed to yield similar results. In NAA, the sample to be analysed is bombarded with slow (thermal) neutrons, some of which are captured by the atomic nuclei to produce radioactive isotopes. Since these artificially activated nuclei emit characteristic radiation just as the naturally occuring radioactive elements do, the energy spectra of these radiations can be utilised for their determination. NAA is an extremely sensitive technique and can detect as little as $10^{-15}$ g of an element. However its use requires the availability of source of slow neutrons, so that it is somewhat restricted in its application.

NAA offers a highly sensitive technique for the quantitative determination of the rare earth elements. The rare earth elements in meteorites, rocks, soils, river waters, biological materials, high purity silicone materials[184] and environmental samples[185] have been determined by NAA. Twelve geological standard materials[186] were analysed for samarium by NAA. For the determination of europium, holmium and terbium in thulium oxide[187] , 10 mg of the sample (thulium oxide) wrapped in polyethylene was irradiated for 15 minutes in a flux of $\simeq$ 2.9 x $10^{13}$ thermal neutrons per sq. cm per sec, after 15 hours the activity due to $^{152m}$Eu was measured at 0.8 to 0.9 meV by $\gamma$-ray spectrometry [NaI (T1) detector]. In the determination of holmium and terbium, the sample wrapped in aluminium was irradiated under the same conditions for 5 hours, after 2 days $^{166m}$Ho was counted from the 1.37 meV $\gamma$-ray peak. After a further 4 days $^{160m}$Tb was counted at 0.837 to 0.961 meV. The sensitivity was found to be 0.05 ppm for europium and 2 ppm for holmium and terbium. NAA was used to determine lanthanum, europium, terbium, dysprosium and thorium[188] in cerium dioxide. A high resolution Ge(Li) detector was used. The detection limits for lanthanum, europium, terbium and thorium when 23 mg of cerium dioxide was irradiated in a flux of 9 x $10^{12}$ neutrons cm$^{-2}$ s$^{-1}$ for 10 hrs were 25, 1.9, 4.2 and 9.3 ppm respectively. Irradiation of 22 mg of sample for 5 min. with the same flux, allowed the detection of 0.32 ppm of dysprosium.

### 1.3.10 Electroanalytical techniques

Electrical methods of analysis[189] involve the measurement of current, voltage and resistance in relation to the concentration of a certain species in solution. Some of the techniques which are used for the analysis of rare earth elements are polarography, voltammetry, coulometry and amperometry.

Polarography

Polarography[29] derives its analytical importance from characteristic current-potential curves or polarograms obtained with a dropping mercury electrode. A current potential curve consists of a plot of the current (which flows as reactions occur at a working electrode) versus the potential of that electrode (measured against an appropriate reference electrode). In polarography, the position of a polarogram along the potential axis indicates the identity of the substance which undergoes electron transfer. Under experimental conditions that are easily achieved, a polarogram exhibits a diffusion controlled limiting current whose magnitude is governed by the concentration of the electroactive substance.

For routine determination, the optimum concentration range for polarography is $10^{-5}$ to $10^{-2}$ M and analytical results accurate to within ± 2 percent are usually attainable. With special care, the uncertainity of a polarographic analysis may be as small as few tenths of 1%. Solution containing two or more electroactive substances can be analysed polarographically if the half wave potentials for the various species differ by atleast 0.2 volt.

Europium in bastnaesite[190] mineral was determined by differential pulse polarography. In this method, the height of the peak at $\sim$ -0.7 volt versus the SCE was measured. The limit of determination was found to be 60 nm europium(III). Sheaushya et al[191] presented an adsorption complex wave of lanthanum-oxine-maleic acid in potassium chloride solution. The complex has the composition of lanthanum-oxine-maleic acid equal to 1:3:1. The concentration of lanthanum(III) in the range from $5 \times 10^{-7}$ to $5 \times 10^{-6}$ M is proportional to the decrease of the wave heights which has been used for the determination of lanthanum in the rare earths phosphor $(LaGd)_2 O_2 S$. The polarographic adsorptive complex wave of terbium-oxine-sodium perchlorate has also been studied[192]. The concentration of samarium in the range $3 \times 10^{-7}$ to $2 \times 10^{-6}$ M has been determined by taking advantage of the decreases of waveheights[193] in samarium-rhodamine B - diphenylguanidine system. Juiquin et al[194] found that a sensitive polarographic catalytic wave appeared at -1.45 volt vs saturated calomel electrode (SCE) in ytterbium-ammonium chloride - potassium (sodium) nitrate system. The detection limit was found to be $5.0 \times 10^{-7}$ M. The method has been used to determine microamounts of ytterbium in ores.

## Voltammetry

Voltammetry[195] is concerned with the study of voltage - current - time relationships during electrolysis carried out in a cell where the working electrode has a very small surface area and is often referred to as a microelectrode and the other electrode is of relatively large surface area referred as counter electrode. The technique commonly involves studying the influence of voltage changes between working and reference electrode on the current flowing in the cell. The microelectrode is usually constructed of some inert, conducting material such as gold, platinium, or glassy carbon. Anodic stripping voltammetry is the most commonly used technique wherein the metal is preconcentrated at a suitable negative potential and stripped subsequently during anodic scan. The current flowing between working and counter electrode was measured and this forms analytical signal. The determination of cerium in rare earth metal oxides and yttrium[196] has been done by stripping voltammetry with graphite electrode. After dissolution of the sample, the cerium was deposited on a graphite electrode by electrolysis for 20 min. at + 1.4 volt vs the SCE. The cathodic polarisation was recorded with a potential scan at 50 mV $s^{-1}$ and the maximum current occured at + 0.6 volt. 25 g $l^{-1}$ of lanthanum, praseodymium, neodymium, samarium or europium, 10 g $l^{-1}$ of holmium, dysprosium, erbium or terbium and 2 g $l^{-1}$ of terbium, thulium or lutetium did not interfere in the determination of cerium.

### Coulometry

Coulometry[197] is a method of quantitative determination of species that will undergo a reaction at an electrode with 100% efficiency by measuring the quantity of electricity necessary to effect complete reaction. This quantity is proportional to the amount of material present in the solution. Thus terbium[198] in a mixture of light rare earth elements was determined coulometrically after separation by high speed cation exchange chromatography at 70 °C followed by elution with 0.2 M 2-hydroxy butyric acid of pH 5.2.

### Amperometry[189]

In an amperometric titration the current passing through a polarography cell at a fixed potential is plotted against the volume of titrant added. The plot consists of two straight lines of different slope on either side of the equivalence point. The interaction of the two lines on extrapolation gives the equivalence point. The determination of terbium[199] in the presence of other rare earth elements was done by amperometric titration with $(NH_4)_2SO_4.FeSO_4$.

### 1.3.11 Laser spectrometry[200]

A laser beam that passes through the sample whose spectrum is desired is tuned over the selected wavelength interval. For the visible and near UV portions of the spectrum, tunable dye lasers have been used as the light source. Lasers offer narrow spectral line width and high brightness. Absorption of laser energy can excite one specific energy level in a molecule. The laser is tuned so that its wavelength matches an absorption of the molecule of interest. Laser intracavity absorption spectrometry of neodymium [201] has been used for the determination of neodymium in cerium earths. Europium and samarium[202] in the range 0.04 and 0.3 parts per trillion respectively, present in geological samples were determined by laser liquid fluorimetry. The mentioned elements were allowed to react with 0.3 ml of ethanolic 0.2% 2-thenoyl trifluoroacetone, 0.3 ml of 0.3% 1,10 phenanthroline in 50% ethanol and 1 ml of 30% ammonium acetate solution and extracted into benzene. The fluorescence of the complexes in benzene was measured by the standard addition method with a UA-3 laser source uranium analyser. Similarly the tiron complexes of terbium, dysprosium and samarium[203] were used for laser liquid fluorimetric determination using radiation from a shielded nitrogen laser in a UA-3 uranium analyser. The detection limits for terbium, dysprosium and samarium were 0.04, 0.4 and 0.9 parts per trillion respectively.

# CHAPTER II

# EXTRACTION - SPECTROPHOTOMETRIC DETERMINATION OF NEODYMIUM WITH 5,7-DICHLOROOXINE AND RHODAMINE 6G

A number of metallochromic indicators[43,51,69,75,78] have been described for the determination of trace amounts of neodymium, but most of these as evident from Table I in Chapter I leave much to be desired in terms of sensitivity, selectivity and reliability. Almost all methods were based on the formation of binary complexes and among these Nd-beryllon II [3-(8-hydroxy-3,6-disulpho-1-naphthylazo) chromotropic acid][33] was found to have an $\epsilon$ value of $\sim$20750. The binary system consisting of neodymium-carboxyarsenazo {2-[7-(2-carboxy phenylazo)-1,8 dihydroxy-3,6 —disulpho-2-naphthylazo] benzene arsonic acid}[36] was more sensitive with an $\epsilon$ value of 50800. However the binary complex formed with Arsenazo III[68] gave the best sensitivity compared to other reagents. ( $\epsilon$ value is between 1,16,000 and 1,63,000 for lanthanides).

Systems involving extraction of the binary complex using immiscible organic solvents were also described for the determination of traces of neodymium. Usually this technique has been chosen when the colour difference between the sample and blank was indistinguishable in aqueous phase. The extraction of the binary complex formed with 4-benzoyl 3-methyl 1-phenyl pyrazoline 5-one[31] into chloroform was reported for the trace determination of neodymium.

The colour reactions based on ternary complexes can be classified into three categories, viz. mixed ligand, surfactant sensitized and ion association. Among the mixed ligand systems, the extraction of the complex of neodymium with 4-benzoyl-3-methyl-1-phenyl pyrazoline-5-one into 10 mM solution of tributyl phosphate, piperidine or 1,10-phenanthroline in chloroform, carbon tetrachloride or cyclohexane[32] . was found to be more sensitive compared to other similar systems. The sensitization of binary neodymium-m-formyl chlorophosphonazo using hexadecyl trimethyl ammonium bromide[44] and neodymium-gallein with cetrimide[45] were reported.

Formation of ion associate system in aqueous phase or the extraction of the ion associate into organic solvents were also investigated for the rapid determination of neodymium because of the higher sensitivity and reliability offered by this type of methods over conventional methods involving the formation of binary complex. The ion association systems in a more general way resulted from the interaction of charged binary complexes with oppositely charged ions i.e. the charged complex was allowed to react with the oppositely charged dye molecule. In cases where there is no difference in the aqueous phase between the blank and sample, then they can be extracted into suitable organic solvents for spectrophotometric determination.

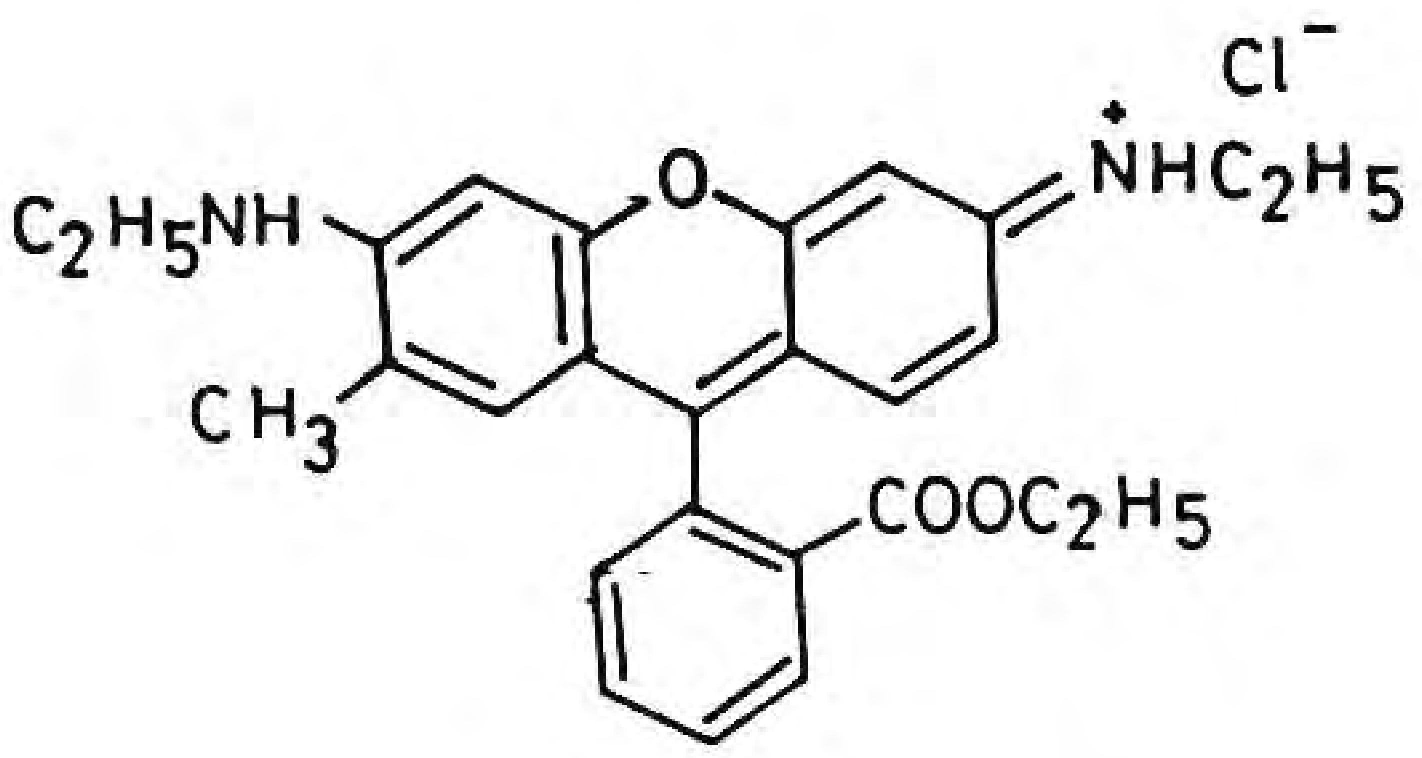
Usually the derivatives of 8-hydroxy quinoline and salicylic acid were used for the formation of anionic complexes of neodymium . These complexes were allowed to associate with cationic dyes like rhodamine 6G or rhodamine B and subsequently extracted into organic solvents. Toe, Kyoji and Kazumasa[47] had studied the extraction of ternary complex of neodymium ion with 8-hydroxy 5,7-dinitroquinoline and rhodamine B into benzene. Tselik and Poluektov[52] have reported the stability of ion associates of lanthanides with the derivatives of salicylic acid or quinolin-8-ol and rhodamine B. Under these circumstances, it is advisable to have some procedure for the determination of traces of neodymium based on the formation of ion association system. It has been found that rhodamine 6G is little more sensitive than rhodamine B. The investigations described in this Chapter concern with such an examination that led to the development of a simple and reliable procedure for the extractive separation and determination of traces of neodymium. The application of the developed procedure for the determination of traces of neodymium present in neodymium doped aluminium is also described.

## PRELIMINARY INVESTIGATIONS

Preliminary examination on the extraction of neodymium(III) in presence of 5,7-dichloro oxine with rhodamine 6G into toluene showed that the intensity of colour is more pronounced when the reaction is carried out in alkaline medium. It was observed that the ion pair formation proceeds rapidly when the metal solutions containing 5,7-dichloro oxine was treated with the dye solution. But the colour change was distinct only by extraction into organic solvents.

Preliminary studies on the liquid-liquid extraction of the ternary complex, neodymium-5,7-dichloro oxine-rhodamine 6G from neutral to weakly alkaline media into various solvents indicated that toluene is the better extractant than other solvents. After extraction, the organic layer was filtered through Whatman No.1 filter paper plug and centrifuged and subjected to spectrophotometric determination. It was decided to use a 0.05% solution of 5,7-dichloro oxine and 0.01% solution of rhodamine 6G.

Rhodamine 6G is a dull red cationic dye stuff soluble in water to give a fluorescent solution and has its absorption maximum at 530 nm in aqueous phase.



Rhodamine 6G

In preliminary studies, the ternary ion association complex was formed by reacting 1 ml of 10 ppm solution of neodymium with 1 ml of 0.05% 5,7-dichloro oxine, 1.0 ml of 0.25 M ammonia-ammonium chloride buffer (pH 8.5) and 2.5 ml of 0.01% rhodamine 6G. The solution was diluted to 25 ml with water in a 60 ml separating funnel and equilibrated with 10 ml of toluene. A reagent blank was run concurrently following the same procedure. The aqueous layer was discarded and the organic layer was drained through fresh filter paper and centrifuged. The spectra of the solutions were recorded over the wavelength range 400 to 700 nm. The complex was found to absorb maximally at 535 nm and it was decided to optimise the various parameters that influence the formation and extraction of the ternary complex.

## 2.1 EFFECT OF pH

The optimum pH range for the liquid-liquid extraction of the ternary complex and subsequent determination by spectrophotometry was studied in the pH range 7.0 to 10.0. In this study, 1 ml of 10 ppm solution of neodymium, 1 ml of 0.05% 5,7-dichlorooxine and 2.5 ml of 0.01% rhodamine 6G were present in each instance. After diluting to about 25 ml, the solutions were adjusted to a desired pH using a pH meter. A reagent blank was also prepared for each pH. The solutions were transferred quantitatively into 60 ml separating funnels and equilibrated with 10 ml of toluene for 3 minutes. The aqueous layer was discarded and the organic layer was drained through the fresh filter paper and centrifuged. The absorbance was measured at 535 nm against the respective reagent blank. The results are shown in Fig. 2.1. At both higher and lower pH values, the extraction was incomplete and hence all further extractions were carried out at pH 8.5 ± 0.5. It was decided to maintain the pH at 8.5 ± 0.5 using 0.25 M ammonia-ammonium chloride buffer.

## 2.2 EFFECT OF SOLVENT

The influence of other solvents for the extraction of neodymium-5,7-dichlorooxine-rhodamine 6G ternary ion association complex was next investigated. Using 10 µg of neodymium, 1 ml of 0.05% 5,7-dichlorooxine, 1 ml of 0.25 M ammonia-ammonium chloride buffer (pH 8.5) and 2.5 ml of 0.01% rhodamine 6G in a

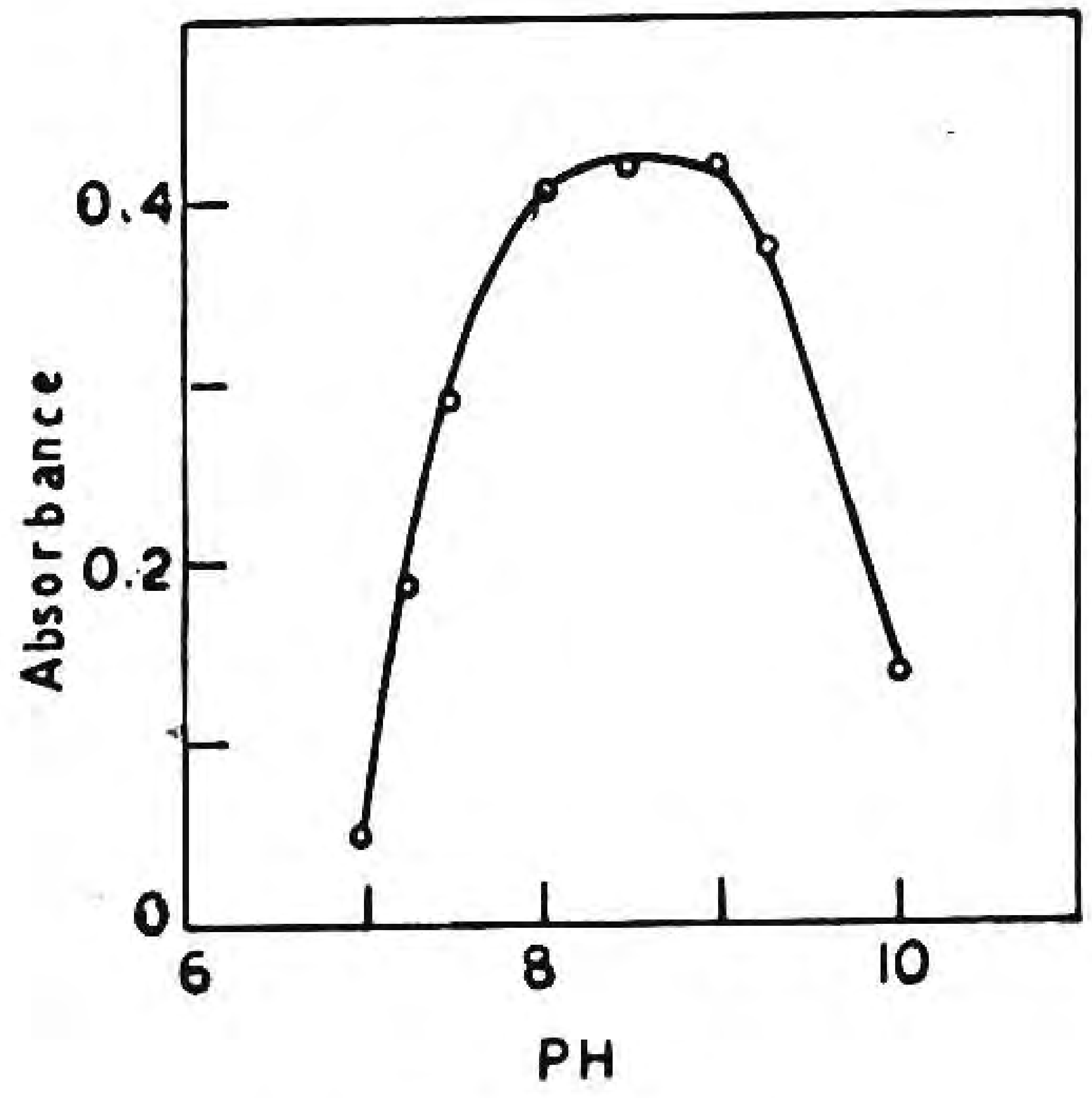


Fig. 2.1 Effect of pH

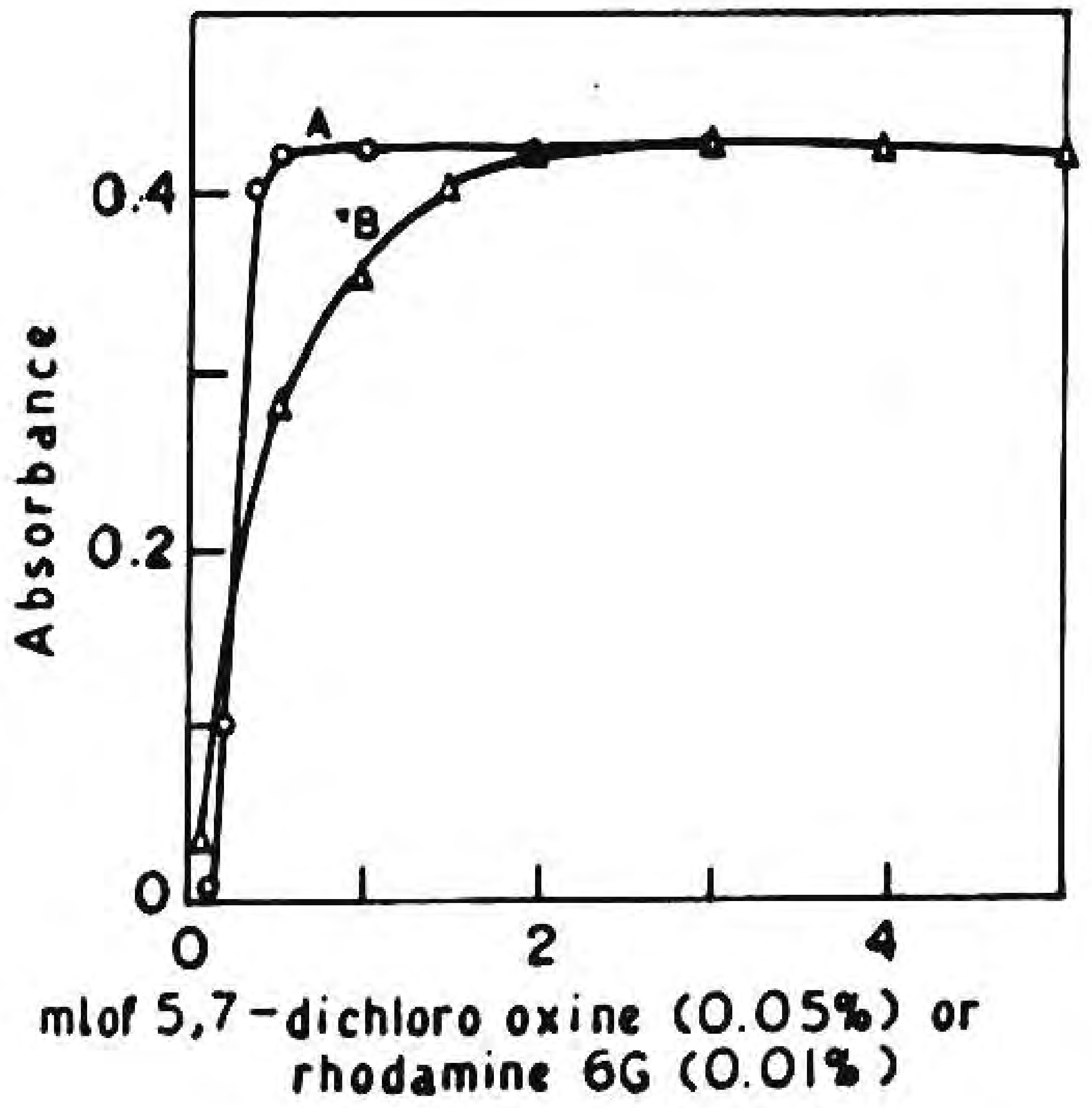


Fig. 2.2 Effect of 5,7- dichloro oxine or rhodamine 6G

final volume of 25 ml, the extractability into 10 ml of various solvents was examined. Blanks were also carried out for each solvent. The absorbances were measured at 535 nm against the respective reagent blanks for each solvent. The results thus obtained are shown in Table I.

**Table I**

**Choice of solvent (10 μg neodymium)**

| Solvent | Absorbance |
|---|---|
| Toluene | 0.420 |
| Benzene | 0.387 |
| Xylene | 0.267 |
| Ethyl acetate | 0.372 |
| Butanol | 0.187 |
| Dichloroethane | 0.146 |
| Carbon tetrachloride | 0 |
| Nitrobenzene | 0 |

## 2.3 EFFECT OF 5,7-DICHLOROOXINE

The optimum concentration of 5,7-dichlorooxine required for the quantitative extraction of the neodymium as its ternary ion association complex, neodymium-5,7-dichlorooxine-rhodamine 6G into toluene was established using solutions containing 10 μg of neodymium, varying volumes of 0.05% solution of 5,7-dichlorooxine in methanol from 0.1 ml to 3 ml, 1 ml of 0.25 M ammonia-ammonium chloride buffer (pH 8.5) and 2.5 ml of 0.01% rhodamine 6G. The solutions were diluted to 25 ml and transferred to 60 ml separating funnels. These solutions were equilibrated with 10 ml of toluene for 3 minutes. Blanks were also prepared under the same conditions. Then the absorbances of solutions were measured at 535 nm against the respective reagent blanks. The results are shown in curve A of Fig. 2.2. It was found that maximum and constant absorbance was obtained in the range 0.5 to 3 ml of 0.05% 5,7-dichlorooxine solution. Hence 1 ml of 0.05% 5,7-dichlorooxine solution was used for further extractions.

## 2.4 EFFECT OF RHODAMINE 6G

The optimum concentration of rhodamine 6G required for the quantitative extraction of the neodymium as its ternary ion association complex, neodymium-5,7-dichlorooxine-rhodamine 6G into toluene was established using solutions containing 10 μg of neodymium, 1 ml of 0.05% 5-7-dichlorooxine, 1 ml of 0.25 M ammonia-ammonium chloride buffer and varying volumes of 0.01% rhodamine 6G from 1 ml to 5 ml in a final volume of 25 ml. Blanks were also prepared under the same conditions. The solutions were quantitatively transferred to 60 ml separating funnels and equilibrated with 10 ml of toluene by shaking for 3 minutes. The absorbances of the solutions were measured at 535 nm against respective reagent blanks. The results are shown in curve B of Fig. 2.2. It has been found that the maximum absorbance was obtained from 2 to 5 ml of 0.01% rhodamine 6G. Hence 2.5 ml of 0.01% rhodamine 6G was used for further studies.

## 2.5 EFFECT OF EQUILIBRATION TIME

A series of extractions were carried out using 10 µg of neodymium, 1 ml of 0.05% 5-7-dichlorooxine, 1 ml of 0.25 M ammonia-ammonium chloride buffer (pH 8.5) and 2.5 ml of 0.01% rhodamine 6G in a total volume of 25 ml and equilibrating it with 10 ml of toluene for varying lengths of times, viz. from 10 seconds to 10 minutes. The results are depicted in Table II which indicate that 2 minutes of equilibration is sufficient for quantitative extraction of the neodymium-5,7-dichlorooxine-rhodamine 6G complex. However, it was decided to equilibrate r 3 minutes to ensure complete extraction in all further investigations.

**Table II**

**Time of equilibration**

| Time | Absorbance |
|---|---|
| 10 seconds | 0.077 |
| 30 seconds | 0.160 |
| 1 minute | 0.242 |
| 2 minutes | 0.420 |
| 3 minutes | 0.418 |
| 5 minutes | 0.419 |
| 10 minutes | 0.420 |

## 2.6 VARIATION OF AQUEOUS PHASE VOLUME

The effect of varying the aqueous phase volume on the extraction of the neodymium-5,7-dichlorooxine-rhodamine 6G ternary ion association complex was next investigated. The aqueous phase volume was varied from 5 to 30 ml. In these experiments, 10 μg of neodymium, 1 ml of 0.05% 5,7-dichlorooxine, 1 ml of 0.25 M ammonia-ammonium chloride buffer (pH 8.5) and 2.5 ml of 0.01% rhodamine 6G were present in each instance. After adjusting to various volumes ranging from 5 to 30 ml, the solutions were equilibrated with 10 ml of toluene for 3 minutes. Blanks were also prepared under the same conditions. The absorbances of the solutions were measured at 535 nm against respective reagent blanks. The results thus obtained are shown in Table III from which it is clear that the maximum absorbance was obtained by maintaining an aqueous phase volume between 15 and 30 ml. 25 ml of aqueous phase volume was chosen for further studies.

**Table III**

**Variation of aqueous phase volume**

| Volume of the aqueous phase (ml) | Absorbance |
|---|---|
| 5 | 0.370 |
| 10 | 0.383 |
| 15 | 0.419 |
| 20 | 0.418 |
| 30 | 0.415 |
| 50 | 0.397 |

## 2.7 ORDER OF ADDITION OF REAGENTS

Using 10 μg of neodymium and optimum concentration of the reagent solutions, the order of addition of 5,7-dichlorooxine, rhodamine 6G, and ammonia-ammonium chloride buffer on the formation and extraction of the ternary ion association complex was next investigated. The results are shown in Table IV from which it is clear that order of addition is not critical provided ammonia-ammonium chloride buffer is added after the addition of 5,7-dichlorooxine. But the prior addition of buffer directly to neodymium solution results in the partial precipitation of neodymium as hydroxide resulting in a low absorbance value. Hence the buffer was added after the addition of 5,7-dichlorooxine.

**Table IV**

**Order of addition of reagents**

| Sl. No. | Order of addition | Absorbance |
|---|---|---|
| 1 | Nd + buffer + 5,7-dichlorooxine + rhodamine 6G | 0.400 |
| 2 | Nd + buffer + rhodamine 6G + 5,7-dichlorooxine | 0.352 |
| 3 | Nd + 5,7-dichlorooxine + buffer + rhodamine 6G | 0.419 |
| 4 | 5,7-dichlorooxine + buffer + rhodamine 6G + Nd | 0.418 |
| 5 | Nd + rhodamine 6G + 5,7-dichlorooxine + buffer | 0.418 |

## 2.8 OPTIMUM TIME FOR COLOUR DEVELOPMENT AND STABILITY

Under optimal conditions, the formation of the ternary ion association complex was instantaneous and the extraction requires minimum 2 minutes shaking. The stability of the ternary system was established by measuring the absorbance of the colour system at 535 nm in 10 mm cuvettes at regular intervals of 10 minutes from the time the organic layer was drained and collected in a test tube. It was found from Table V that the colour system remains stable for 1 hour.

**Table V**

**Stability of the ternary ion associate: neodymium-5,7-dichlorooxine-rhodamine 6G**

| Time of standing (min) | Absorbance |
|---|---|
| 10 | 0.420 |
| 20 | 0.418 |
| 30 | 0.419 |
| 40 | 0.415 |
| 50 | 0.420 |
| 60 | 0.419 |
| 120 | 0.362 |

## 2.9 ABSORPTION SPECTRA

The absorption spectra of the reagent blank and that of the neodymium-5,7-dichlorooxine-rhodamine 6G complex were recorded in the range 400 to 700 nm. In these studies 0, 5, 10 and 20 µg of neodymium (III) were mixed with 1 ml of 0.05% 5,7-dichlorooxine, 1 ml of 0.25 M ammonia-ammonium chloride buffer, adjusted the pH to 8.5 and added 2.5 ml of 0.01% rhodamine 6G and diluted to 25 ml. The solutions were transferred into 60 ml separating funnels and the ternary ion association complex was extracted into toluene by shaking for 3 minutes. The aqueous layer was discarded and the organic layer was drained through the filter paper and centrifuged. Curve A in Fig. 2.3 represents the absorption spectra of the reagent blank against pure toluene while B, C and D represent the spectra of the ternary complex with 5, 10 and 20 µg of neodymium respectively against reagent blank. The complex has maximum absorption at 535 nm.

## 2.10 CALIBRATION GRAPH

Calibration graph was obtained using 0-20 µg of neodymium (III). To each, 1 ml of 0.05% 5,7-dichlorooxine, 1 ml of 0.25 M ammonia-ammonium chloride buffer of pH 8.5 and 2.5 ml of 0.01% rhodamine 6G were added and diluted to 25 ml. The solutions were transferred to 60 ml separating funnels and equilibrated with 10 ml of toluene by shaking for 3 minutes. The organic layers were separated from the aqueous layers and drained through filter paper and centrifuged. Absorbance of each solution was measured in 10 mm cuvettes at 535 nm against the reagent blank. Fig. 2.4 represents the plot of absorbance versus the concentration of neodymium (III). The plot is a straight line in the range 0-12 µg of

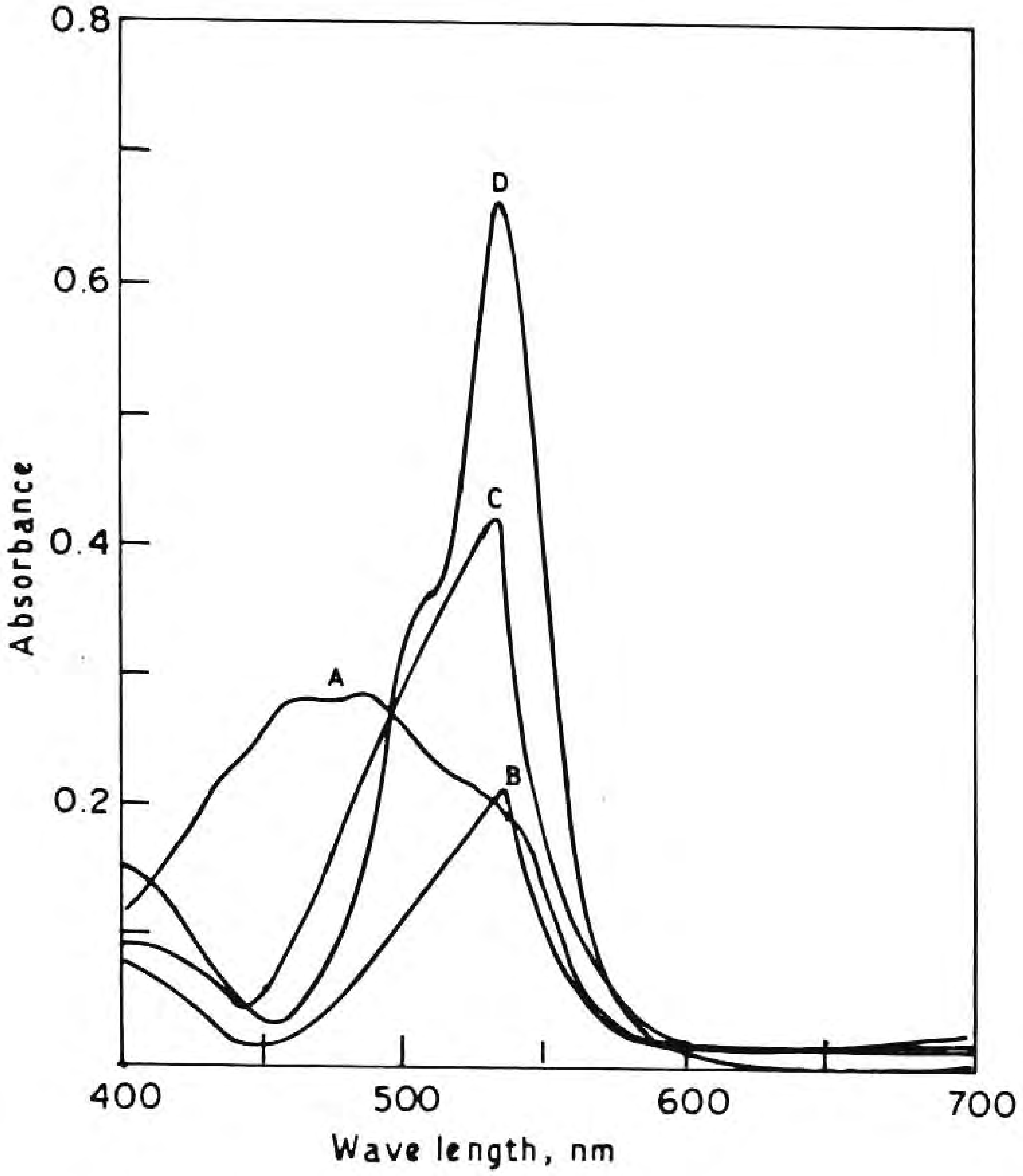


Fig. 2.3 Absorption spectra

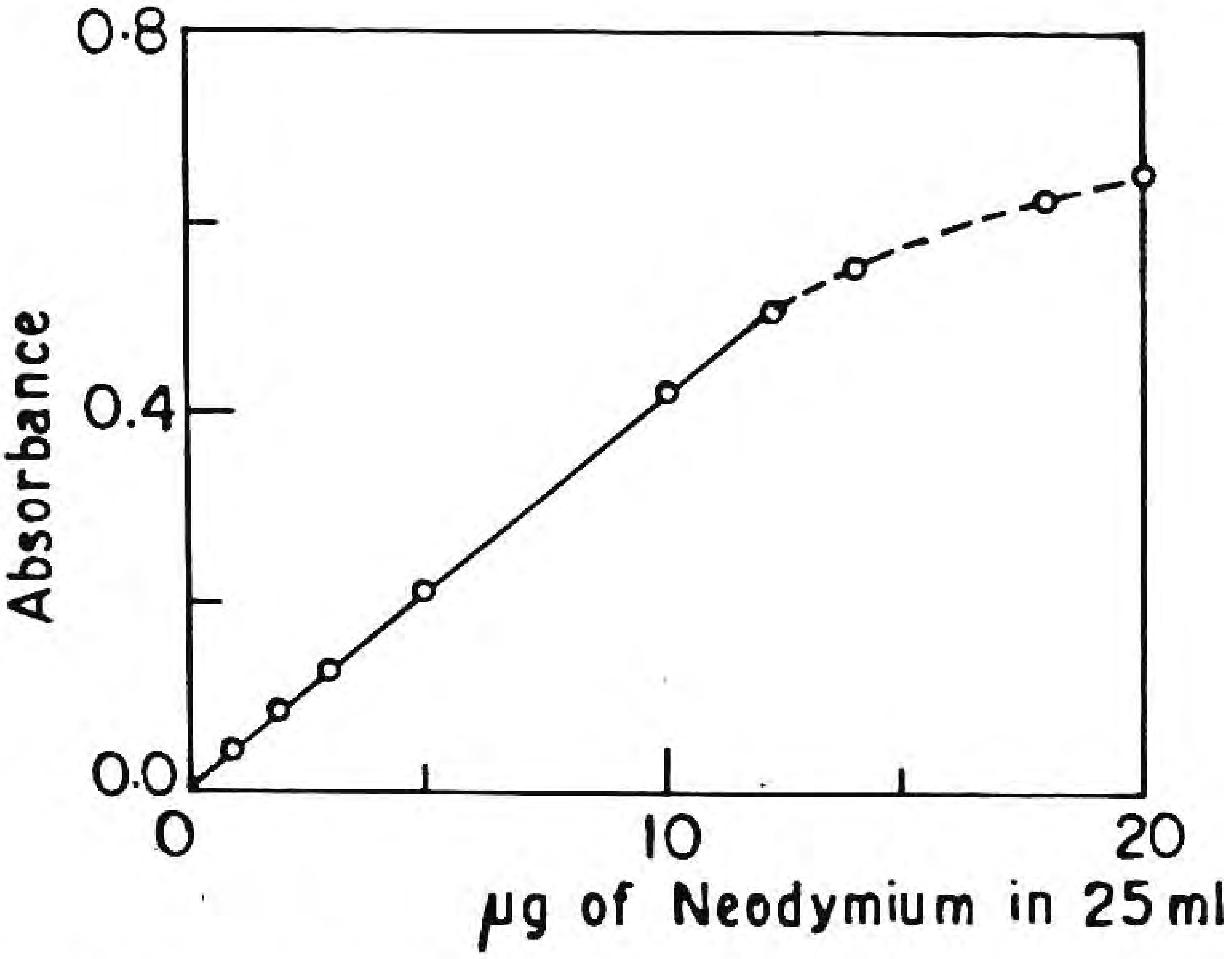


Fig.2.4 Calibration graph

neodymium passing through the origin. The detection limit corresponding to a SNR (signal to noise ratio) of 2 was found to be 1 μg of neodymium present in 25 ml of the aqueous phase.

## 2.11 SENSITIVITY AND PRECISION

The apparent molar absorptivity and Sandell sensitivity were calculated to be $1.36 \times 10^5$ $1\ mole^{-1}\ cm^{-1}$ and $9.523 \times 10^{-4}\ \mu g\, cm^{-2}$ for neodymium (III).

The standard deviation of the developed method was established by carrying out ten separate determinations using 10 μg of neodymium by following the procedure described under calibration graph. Calculations were made using the formula

$$\sigma = \sqrt{\frac{\sum (x_n - \bar{x})^2}{n-1}}$$

where .

$\sigma$ = standard deviation

$x_n$ = result obtained for nth determination

$\bar{x}$ = average of n determination

The relative standard deviation of the method was calculated to be 2.11%. The results are shown in Table VI.

## Table VI

### Precision studies

| Sl.No. | $x_n$ Nd found ( μg) | $(x_n - \bar{x})$ | $(x_n - \bar{x})^2$ |
|---|---|---|---|
| 1 | 10 | -0.07 | 0.0049 |
| 2 | 10.4 | +0.33 | 0.1089 |
| 3 | 10.1 | 0.03 | 0.0009 |
| 4 | 10.4 | 0.33 | 0.1089 |
| 5 | 9.8 | -0.27 | 0.0729 |
| 6 | 10 | -0.07 | 0.0049 |
| 7 | 10.2 | 0.13 | 0.0169 |
| 8 | 10 | -0.07 | 0.0049 |
| 9 | 10 | -0.07 | 0.0049 |
| 10 | 9.8 | -0.27 | 0.0729 |

$$\bar{x} = 10.07$$

$$\sum (x_n - \bar{x})^2 = 0.401$$

$$\sigma = \sqrt{\frac{\sum (x_n - \bar{x})^2}{n-1}}$$

$$\sigma = \sqrt{\frac{0.401}{9}} = 0.21108$$

Relative standard deviation $\sigma_{(rel)} = \frac{0.21108 \times 100}{10} = 2.11\%$

## 2.12 COMPOSITION STUDIES

The composition of the ternary complex viz. neodymium-5,7-dichlorooxine-rhodamine 6G was established spectrophotometrically using mole ratio and equilibrium shift methods.

### 2.12.1 Neodymium to 5,7-dichlorooxine ratio

Equilibrium shift method[204]

Considering the equilibrium for the formation of the complex $ML_n$,

$$M + nL \overset{k}{\rightleftharpoons} mL_n$$

where $n \geq 1$, according to the law of mass action,

$$k = \frac{[ML]}{[M]\ [L]^n}$$

where k is the formation constant

Hence,

$$\frac{[ML_n]}{[M]} = k\ [L]^n.$$

$$\text{or} \quad \log \frac{[ML_n]}{[M]} = \log k + n \log [L]$$

If $A_x$ is the absorbance of the complex $ML_n$ at a particular concentration of the ligand and $A_o$ is the absorbance when the ligand is present in large excess, then

$$[ML_n] = A_x$$

$$[M] = A_o - A_x$$

and hence

$$\log \left[\frac{A_x}{A_o - A_x}\right] = \log k + n \log [L]$$

which is of the general form

$$y = c + m x$$

Therefore the plot of $\log \left[\frac{A_x}{A_o - A_x}\right]$ against log [L] will be a straight line. The formation constant of the complex can be obtained from the intercept while the slope of the line directly gives the combining ratio of the metal to ligand. Depending upon the range of $A_x$ chosen, Sanchez, Leyva and Ceba[204] suggested two criteria, A (0.1 to 0.9 $A_o$) and B (0.8 to 0.9 $A_o$). Here criterion A was used to establish the combining ratio of neodymium to 5,7-dichlorooxine.

Fig., 2.5 shows the plot of $\log \left[\frac{A_x}{A_o - A_x}\right]$ against log [5,7-dichlorooxine] obtained for solutions containing 10 $\mu$g of

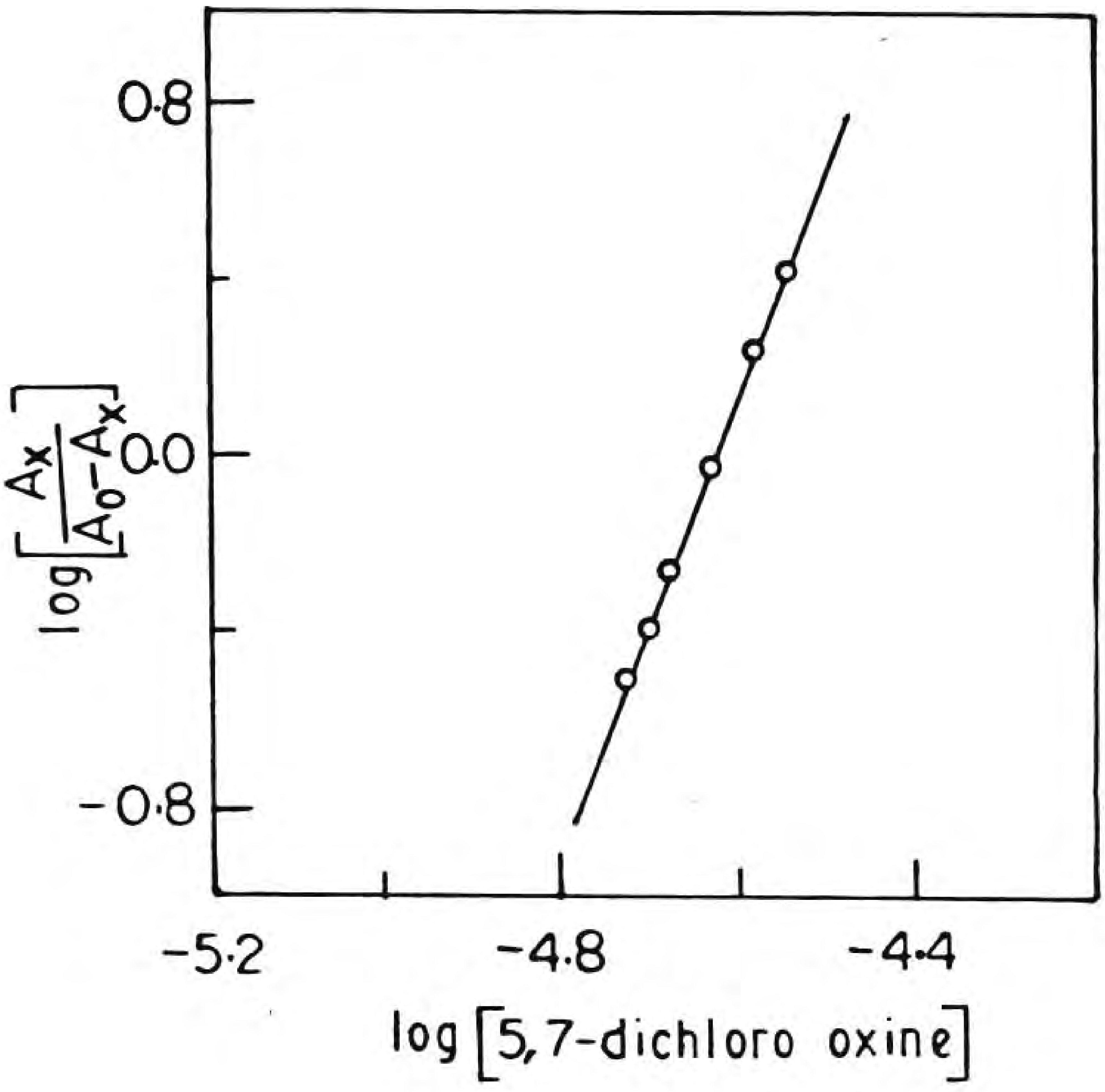


Fig.2.5 Equilibrium shift method

neodymium (III) that were treated with varying volumes of (0.2 ml to 0.35 ml) 0.05% 5,7-dichlorooxine, 1 ml of 0.25 M ammonia-ammonium chloride buffer of pH 8.5, and 2.5 ml of 0.01% rhodamine 6G. The solutions were diluted to 25 ml, transferred to 60 ml separating funnels and equilibrated with 10 ml of toluene by shaking for 3 minutes. The aqueous layers were discarded and the organic layers were drained through filter paper and centrifuged. The absorbances were measured at 535 nm against corresponding reagent blanks. The slope of the straight line thus obtained is 5 indicating that the combining ratio of neodymium to 5,7-dichlorooxine is 1:5.

### 2.12.2 Neodymium to rhodamine 6G

Mole ratio method

Yoe and Jones[205] found that for a stable binary complex AB, a plot of absorbance against mole ratio of the component B to component A with A as constant, rose from origin as a straight line and broke sharply at an absorbance corresponding to the mole ratio of the components. This procedure was used to investigate the ratio of neodymium to rhodamine 6G in the ternary complex by converting it into a pseudo binary one. This was accomplished by using large excess of 5,7-dichlorooxine for a fixed concentration of neodymium and then varying the concentration of rhodamine 6G.

To a series of solutions containing $6.9328 \times 10^{-5}$ M solution of neodymium, 1 ml of 0.05% 5,7-dichlorooxine, 1 ml of 0.25 M ammonia-ammonium chloride buffer of pH 8.5 and varying volumes of (1 ml to 8 ml) of 0.0016% (3.4664 x $10^{-5}$ M) rhodamine 6G were added and made upto 25 ml. The solutions were transferred to 60 ml separating funnels, equilibrated with 10 ml of toluene by shaking for 3 minutes. The aqueous layers were discarded, the organic layers were drained through filter paper and centrifuged. The absorbances of the solutions were measured at 535 nm against respective reagent blanks. The results obtained are shown in Fig. 2.6 from which it is clear that the ratio of neodymium to rhodamine 6G is 1:2.

Equilibrium shift method

The ratio of neodymium to rhodamine 6G was also established by the equilibrium shift method as described in page 61. In these studies, 10 µg of neodymium (III) was treated with 1 ml of 0.05% 5,7-dichlorooxine, 1 ml of 0.25 M ammonia-ammonium chloride buffer of pH 8.5 and varying volumes of (0.05 ml to 0.5 ml) 0.01% rhodamine 6G and diluted to 25 ml. The solutions were transferred to 60 ml separating funnels and equilibrated with 10 ml of toluene by shaking for 3 minutes. The aqueous layers were discarded and the organic layers were drained through filter paper and centrifuged. The absorbances of the solutions were measured at 535 nm against respective reagent blanks. The plot of log $\left[\frac{A_x}{A_o - A_x}\right]$ versus log [rhodamine 6G] as shown in Fig. 2.7 is a straight line.

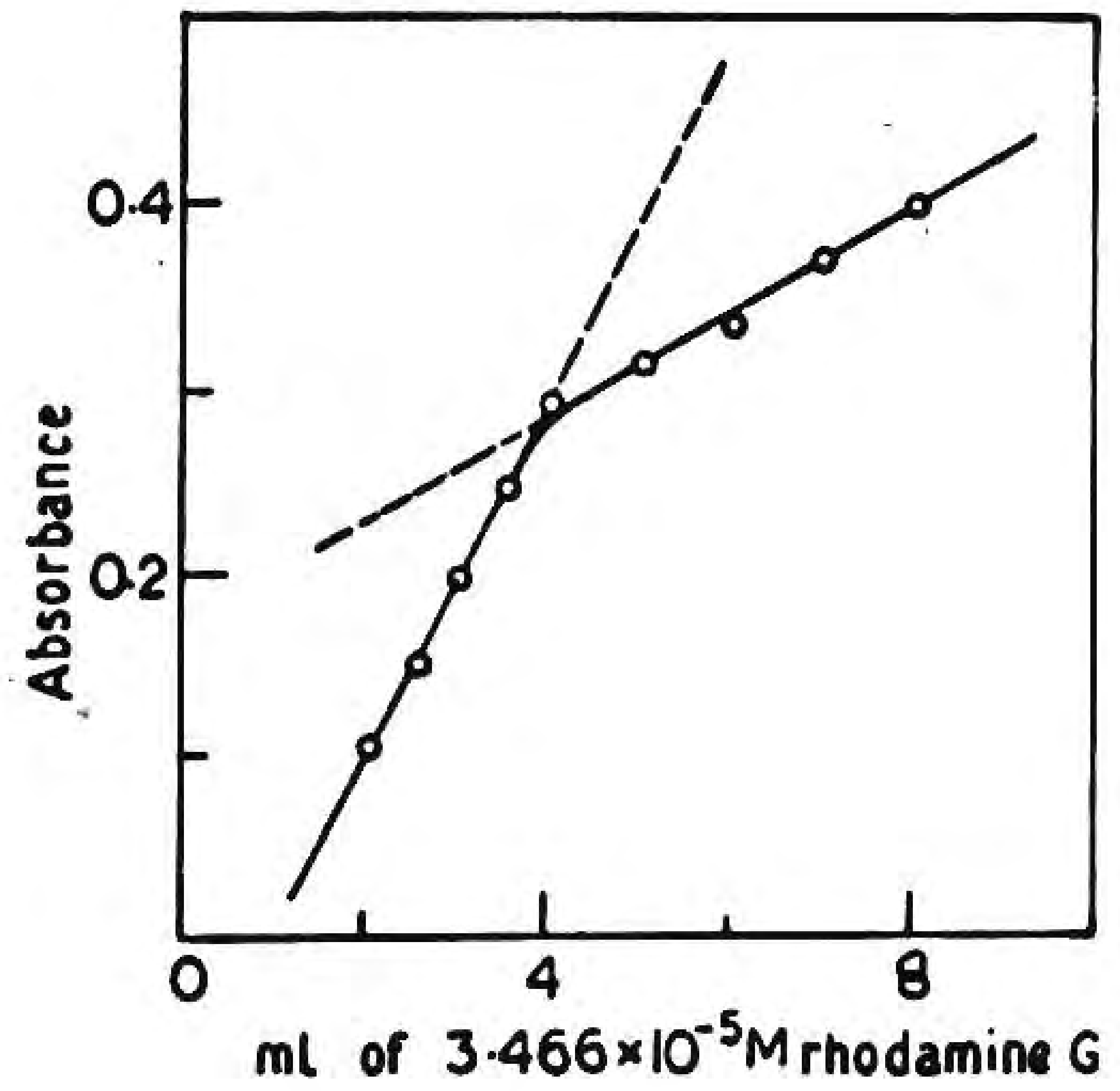


Fig 2·6 Mole ratio method

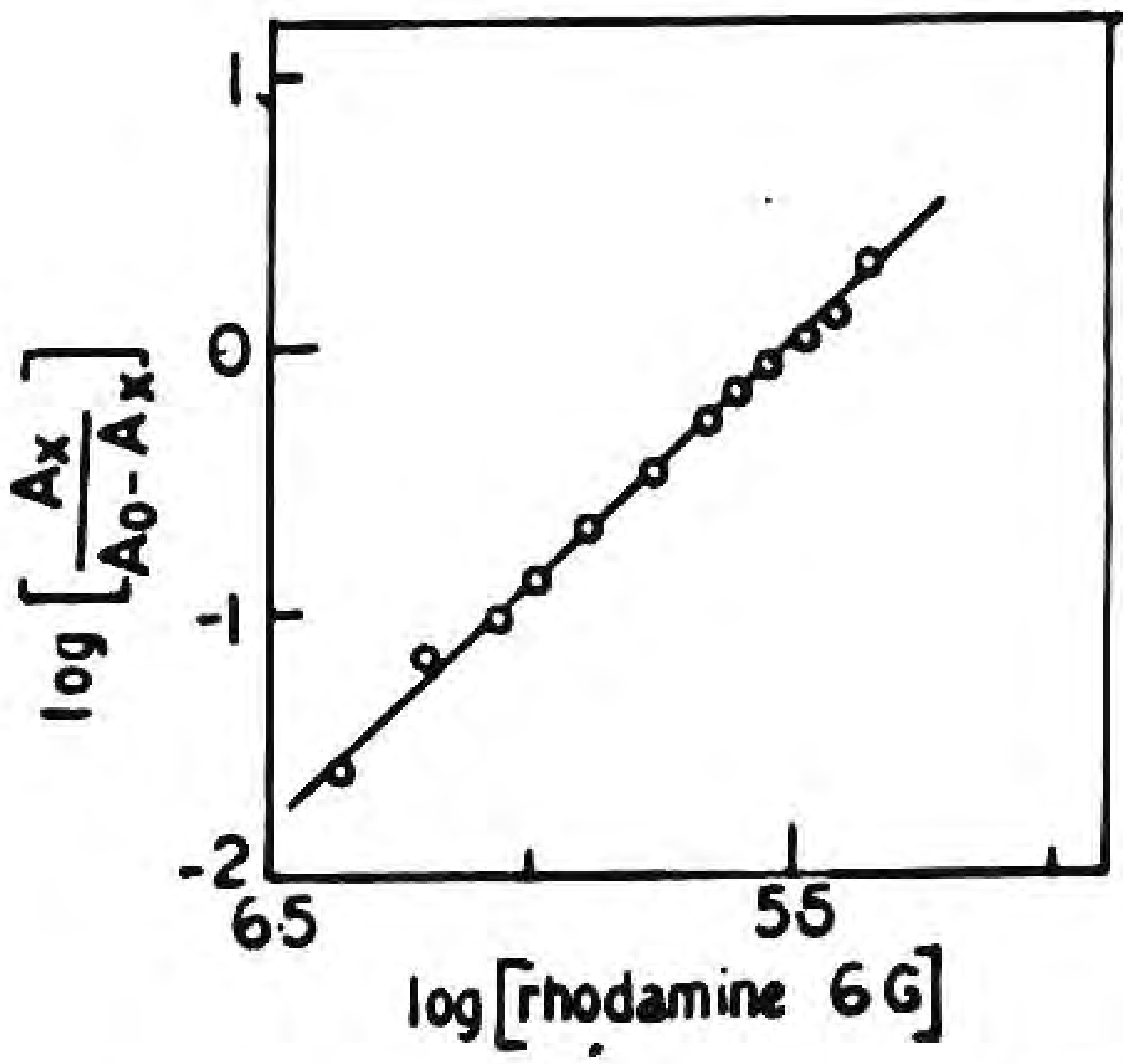


Fig 2·7 Equilibrium shift method

The slope is found to be 2 which indicates that the combining ratio of neodymium to rhodamine 6G is 1:2.

On the basis of these evidences, it was concluded that the combining ratio of the metal, 5,7-dichlorooxine and rhodamine 6G is 1:5:2.

From the foregoing studies and the fact that the product readily extracted into nonpolar solvents like toluene, it was concluded that neodymium forms electrically neutral ternary ion associate in presence of 5,7-dichlorooxine and rhodamine 6G. Thus neodymium reacts with five molecules of 5,7-dichlorooxine resulting in the formation of an anionic complex $[\mathrm{Nd}\ (5,7\text{-dichlorooxine})_5]^{2-}$. This associates with 2 molecules of rhodamine 6G cation and gives a neutral ternary ion associate. Accordingly the empirical formula of the ternary ion associate may be represented as $[\mathrm{Nd}\ (5,7\text{-dichlorooxine})_5]\mathrm{R}_2$ where R represents the rhodamine 6G cation.

## 2.13 INTERFERENCE STUDIES

The effect of the presence of foreign ions on the determination of 10 μg neodymium (III) was next examined. The ions studied included 1 mg amounts of Fe(III), As(V), Al, Ba, Cu(II), Ni, Mo(VI), Cr(VI), Mg, Hg(II), U(VI), Ti(IV), Co(II), Bi(III), Be, Zn, Zr(IV), W(VI), Mn(II), Te(IV), Pt(IV), $S_2O_3^{2-}$, $CNS^-$, $ClO_4^-$, $Br^-$, $SO_4^{2-}$, $F^-$ and $PO_4^{3-}$. The effect of these ions were studied individually by adding them to the neodymium solution prior to the addition of other reagents. The determinations were completed by following the procedure described under calibration graph. A deviation of ± 0.01 from the absorbance obtained in the absence of interfering ion was taken as the sign of interference. The results are summarised in Table VII.

**Table VII**

**Interference studies**

| Interferents | Mode of interference |
|---|---|
| As(V), Ba, Cr(VI), Be, W(VI), $S_2O_3^{2-}$, $CNS^-$, $ClO_4^-$ thiourea | No interference |
| Mo(VI), Te(IV), Mn(II) | Interfered by enhancing the absorbance |
| Fe(III), Al, Ni, Cu(II), Mg, Hg(II), U(VI), Ti(IV), Co(II), Bi(III), Zn, $PO_4^{3-}$, Pt(IV) | Interfered by decreasing the absorbance |

Attempts to overcome the interference due to milligram amounts of various ions revealed that 2 ml of 5% thiourea eliminates the interference from 1 mg amount of Hg(II). The addition of 2 ml of 5% sodium tartarate eliminates the interference from 1 mg amounts of Bi(III), Mo(VI) and Zr(IV). Further, interference due to 1 mg amounts of Cu(II) and Pt(IV) can be overcome by adding 2 ml of 5% thioglycollic acid.

## 2.14 ANALYSIS OF SYNTHETIC SAMPLES

The applicability of the developed procedure was tested by analysing the neodymium content of various synthetic samples. Various metals like iron, aluminium, chromium, and nickel were interfered in the developed procedure for the determination of traces of neodymium. Common masking agents failed to overcome the effect of these metal ions. So an ion exchange separation procedure was developed for the separation of neodymium from various other metal ions.

The procedure was based on the retention of trace amounts of neodymium (used as a solution in 1 M HCl) on Dowex 50 W - X8 ($H^+$) cation exchange resin. Other cations like iron, aluminium, chromium and nickel were eluted with 1 M hydrochloric acid. This method resulted in the quantitative recovery of neodymium. This can be explained by the analysis of the synthetic mixtures containing mg amounts of $Fe^{3+}$, $Cr^{3+}$ and $Ni^{2+}$ along with neodymium (100 µg). The mixture was passed through the Dowex W - X8 ($H^+$)

column in 1 M HCl. All the other cations were eluted, only the neodymium was found to be retained in the column. The column was washed with water until it was free from acid. Then it was eluted with 0.5 M ammonium chloride solution. The quantitative recovery of neodymium obtained in the above experiment was shown in Table VIII.

**Table VIII**

**Analysis of trace amounts of neodymium in a mixture containing iron, chromium, nickel**

| Sl.No. | Sample (mg) | Neodymium added ( μg) | Neodymium found ( μg) | Recovery (%) |
|---|---|---|---|---|
| 1 | $Fe^{3+}$ (5)<br>$Cr^{3+}$ (3)<br>$Ni^{2}$ (2) | 100 | 98.8 | 98.8 |
| 2 | $Fe^{3+}$ (5)<br>$Cr^{3+}$ (3)<br>$Ni^{2+}$ (3) | 50 | 49 | 98 |
| 3 | $Fe^{3+}$ (5)<br>$Cr^{3+}$ (3)<br>$Ni^{2+}$ (1) | 10 | 9.7 | 97 |

## 2.15 ANALYSIS OF ALUMINIUM METAL SAMPLES

Neodymium doped aluminium metal samples are widely used in solar collectors[206]. As real samples are not available, the applicability of the procedure to the determination of neodymium in aluminium salts and metal samples was tested by adding known amounts of neodymium prior to sample dissolution. The sample solution in 1 M - HCl was passed through Dowex 50 W - X8 ($H^+$) resin. Neodymium was separated from bulk of aluminium as described in 2.14 and determined by the developed procedure. The results obtained are given in Table IX from which it can be seen that the recoveries are satisfactory.

Table IX

**Analysis of aluminium metal and aluminium chloride samples**

| Sample (g) | Neodymium added ( μg) | Neodymium found ( μg) | Recovery % |
|---|---|---|---|
| Aluminium metal | | | |
| 0.1 | 10 | 9.98 | 99.8 |
| 0.25 | 50 | 49.0 | 98.0 |
| 1.0 | 100 | 98.0 | 98.0 |
| Aluminium chloride | | | |
| 0.5 | 10 | 9.95 | 99.5 |
| 1.0 | 50 | 49.5 | 99.0 |
| 2.0 | 100 | 98.6 | 98.6 |

## 2.16 EXPERIMENTAL

### 2.16.1 Apparatus

A microcomputer based spectrophotometer system was used. This consists of a Hitachi Model 220 double beam spectrophotometer with an extended programme. The instrument has a scan speed range of 15-480 nm $min^{-1}$.

A pair of 10 mm matched quartz cuvettes which were periodically cleaned with $H_2SO_4$ + $HNO_3$ mixture and thoroughly washed with conductivity water was used in this study. ELICO digital pH meter was used for adjusting the pH.

### 2.16.2 Reagents

All the chemicals used were of Analar reagent grade.

**1. Neodymium (III) stock solution, 1000 ppm**

Dissolve 0.2916 g of neodymium oxide (99.99% purity, IRE, Alwaye) in minimum amount of hot 1:1 HCl and diluting to 250 ml with double distilled water. Standardize this neodymium solution by titration with EDTA and dilute suitably to obtain 10 ppm solution.

**2. 5,7-dichlorooxine solution (0.05%)**

Dissolve 0.05 g of 5,7-dichlorooxine in 100 ml methanol daily.

**3. Rhodamine 6G solution (0.01%)**

Dissolve 0.025 g of rhodamine 6G in water and make upto 250 ml.

**4. Ammonia-ammonium chloride buffer (pH 8.5) 0.25 M**

Dissolve 1.8 g of $NH_4Cl$, add 2.5 ml of $NH_3$ (25%) solution and dilute to almost 250 ml. Adjust the pH to 8.50 and make upto 250 ml.

### 2.16.3 Procedure

To an aliquot of neodymium solution containing 0-12 µg in in 20 ml, add 1 ml of 5,7-dichlorooxine solution, 1.0 ml of $NH_3$ - $NH_4Cl$ buffer adjust the pH to 8.5, and add 2.5 ml of rhodamine 6G and dilute to 25 ml. Transfer the solution into 60 ml separating funnel and extract the ternary ion association complex into toluene by shaking for 3 minutes. Discard the aqueous layer, drain the organic layer through the fresh filter and centrifuge. Measure the absorbance at 535 nm against reagent blank.

## CHAPTER III

# THIRD ORDER DERIVATIVE SPECTROPHOTOMETRIC DETERMINATION OF TRACES OF SAMARIUM WITH METHYL THYMOL BLUE-CTAB/CPB

The identical properties of rare earth elements towards reaction with various chromogenic reagents in molecular absorption spectrophotometry (MAS) lead to a requirement for the development of procedures with greater selectivity. The wavelength of maximum absorption ( $\lambda$ max) may vary in the range 1 to 10 nm among the rare earth elements. This small shift in $\lambda$ max do not allow the determination of one rare earth element in the presence of other. One way of solving this problem is by utilising derivative spectroscopy wherein the composite spectrum is transformed to first or higher order derivative in the wavelength domain.

Derivative techniques have been employed in instrumental methods of analysis for many decades[195, 207-210]. In particular, first order derivative techniques are used in location of equivalence point in titrimetry and potentiometry[195] and in isolating the analytical noise signal in polarography[208] and in thermal analysis. The technique for second and higher order derivative spectroscopy was patented as early as 1950[209]. Buttlers and Hopkins[210] utilised these techniques during their UV-visible studies on the fine structure of plant pigments. The renaissance of interest in derivative techniques, is mainly due to the rapid evolution of micro computers and advent of low noise operational amplifiers[207]. Application of higher order derivative techniques in biochemical, clinical, forensic and pharmaceutical analysis was reviewed recently by Fell[211]. Even order derivative especially second order derivative was employed in all these studies.

Higher order derivatives in MAS for inorganic analysis was described only in 1985[212,213]. The first one concerns with the second and fourth order derivative spectrophotometric determination of neodymium, holmium and erbium by reacting with 4-benzoyl-3-methyl-1-phenyl pyrazoline-5-one.[212] In the second procedure, third order derivative MAS method was described for the determination of neodymium, holmium, erbium and thulium by employing thenoyl trifluoroacetone as chromogenic reagent[213]. A higher order derivative procedure was recently described by Rao and Sukumar[214] for the simultaneous determination of trace amounts of lanthanum and europium with bromopyrogallol red as chromogenic reagent.

A number of metallochromic reagents have been proposed for the molecular absorption spectrophotometric determination of samarium at trace levels. Most of the procedures described for the determination of samarium involves the utilization of binary complex i.e. metal reacting with chromogenic reagent. Amongst these, the most sensitive procedure for determination of samarium is based on its reaction with carboxy nitrazo[68] ( $\epsilon = 1.16 \times 10$ l mole$^{-1}$ cm$^{-1}$ ).

Superior selectivity and sensitivity in addition to high stability and reproducibility are offered by ternary complexes. The survey of various ternary systems proposed for the determination of samarium indicated the use of ion association systems (metal-ligand-cationic dye), surfactant sensitized systems and mixed ligand systems.

Derivative spectrophotometric procedure hitherto described for the determination of rare earths are based on binary complex formation i.e. metal reacting with chromogenic reagent. The details pertaining to the development of a higher order derivative MAS procedure for the determination of samarium based on ternary complex formation are given below.

Of the various ternary ion-association systems, the extraction of samarium with rhodamine B in presence of 3,5-diiodosalicylic acid[66] into toluene is most sensitive ( $\epsilon = 1 \times 10^5$ l mole$^{-1}$ cm$^{-1}$ ). Similarly, amongst the surfactant sensitized systems the sensitization of samarium-xylenol orange[64] with a cationic surfactant poly(1-dodecyl-4-vinyl pyridinium) bromide is most sensitive ( $\epsilon = 1.26 \times 10^5$ l mole$^{-1}$ cm$^{-1}$ ).

## PRELIMINARY STUDIES

Preliminary studies of the reaction of samarium with various metallochromic reagents were carried out. It has been shown that the binary samarium - methyl thymol blue system can be sensitized by using cationic surfactants like cetyl trimethyl ammonium bromide (CTAB) or cetyl pyridinium bromide (CPB). On the other hand, the addition of anionic surfactant like sodium lauryl sulphate was found to be not useful. This type of sensitization was found in other colour systems like chromeazurol S [71,72], phthalexon S[84] and solochrome cyanine R [87].

Among the above mentioned surfactant sensitized systems, only the samarium - methyl thymol blue - CPB/CTAB system was found to have difference in $\lambda_{max}$ between ternary complexes of samarium and other rare earth elements. Hence, a higher order derivative spectrophotometric procedure was developed for the determination of samarium in presence of other rare earths. The details of development of such a procedure are given below.

### 3.1 PRELIMINARY ABSORPTION SPECTRA

Figure 3.1 shows $^{0}D$ or normal absorption spectra of 0.8 ppm each of samarium, dysprosium, thulium and lutetium (curves A, B, C and D respectively) against the reagent blank after reacting with 3 ml of 0.02% methyl thymol blue, 2.5 ml of buffer (0.1 M ammonium acetate) solution and 1 ml of 1% CTAB

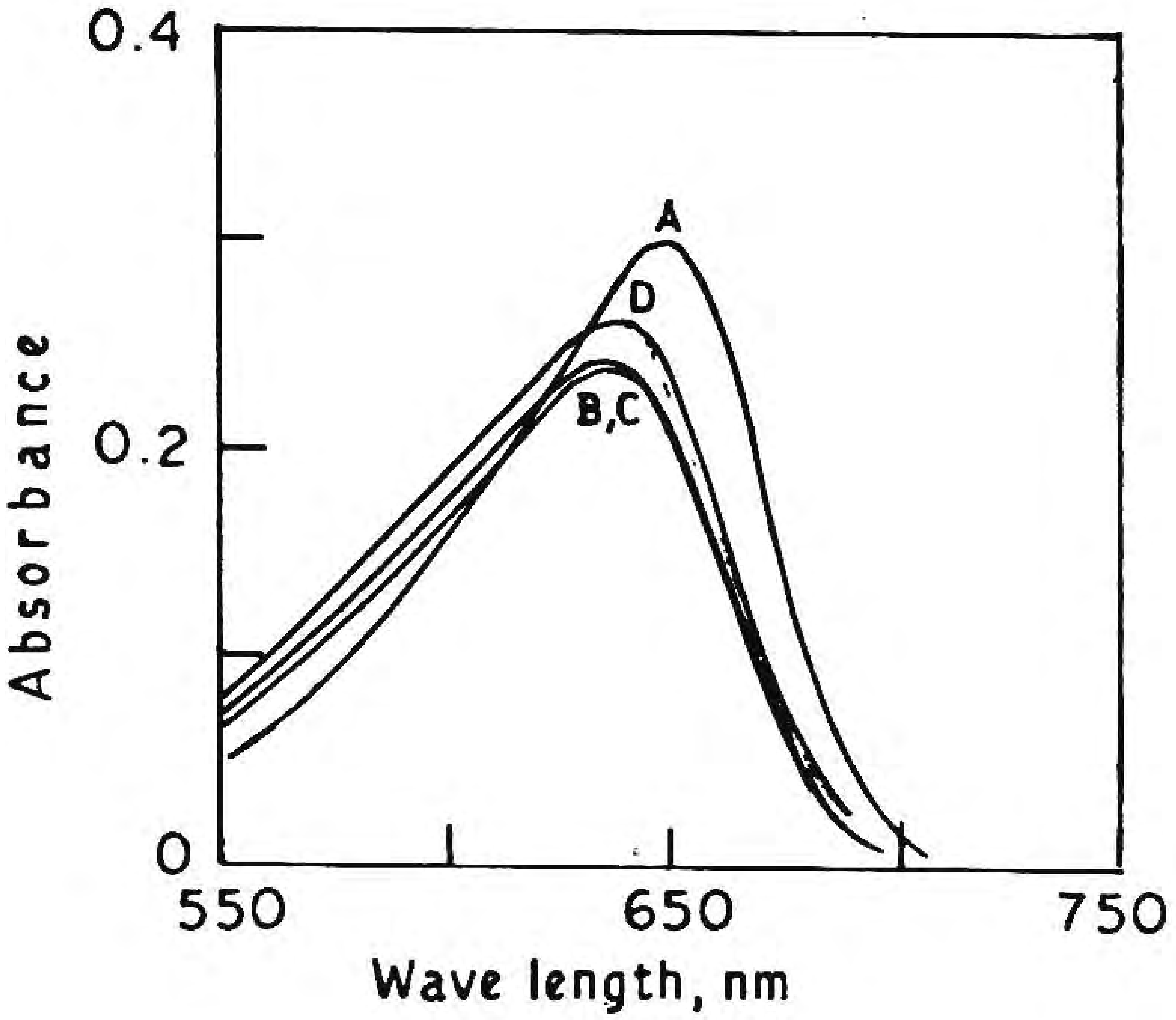


Fig. 3.1 Zeroth order derivative absorption spectra

solution and making upto 25 ml. The wavelength of maximum absorption of samarium ternary complex is 645 nm while the other elements have maximum absorption at 638 nm (cf Fig. 3.1). Eventhough the absorption maximum of samarium is different from that of dysprosium, thulium and lutetium, it is impossible to determine samarium in presence of these elements even at equal amounts. Other rare earth elements also have similar spectral characteristics and hence the selective determination of samarium at trace levels in the presence of other rare earths is an arduous task by employing molecular absorption spectrophotometry.

Figure 3.2 shows the $^{1}D$ absorption spectra of the solutions mentioned in Fig. 3.1. As clear from the curves A, B, C and D of Figure 3.2, the $^{1}D$ absorption spectra have maximum amplitudes at 614 nm (for samarium) and 602 nm (for dysprosium, thulium and lutetium). The $^{1}D$ absorption spectra are better than $^{0}D$ but are insufficiently resolved to be amenable for the selective determination of samarium in presence of other rare earths. The $^{2}D$ absorption spectra of samarium and other rare earth elements viz. dysprosium, thulium and lutetium have identical spectral characteristics (cf. Fig. 3.3) and hence are not considered. On the other hand, Fig. 3.4 shows $^{3}D$ absorption spectra which clearly depict the deconvolution of overlapping absorption spectra of samarium and other rare earths. The amplitude for samarium in the wavelength range 670 to 680 nm is quite significant and is negligible for dysprosium, thulium and lutetium.

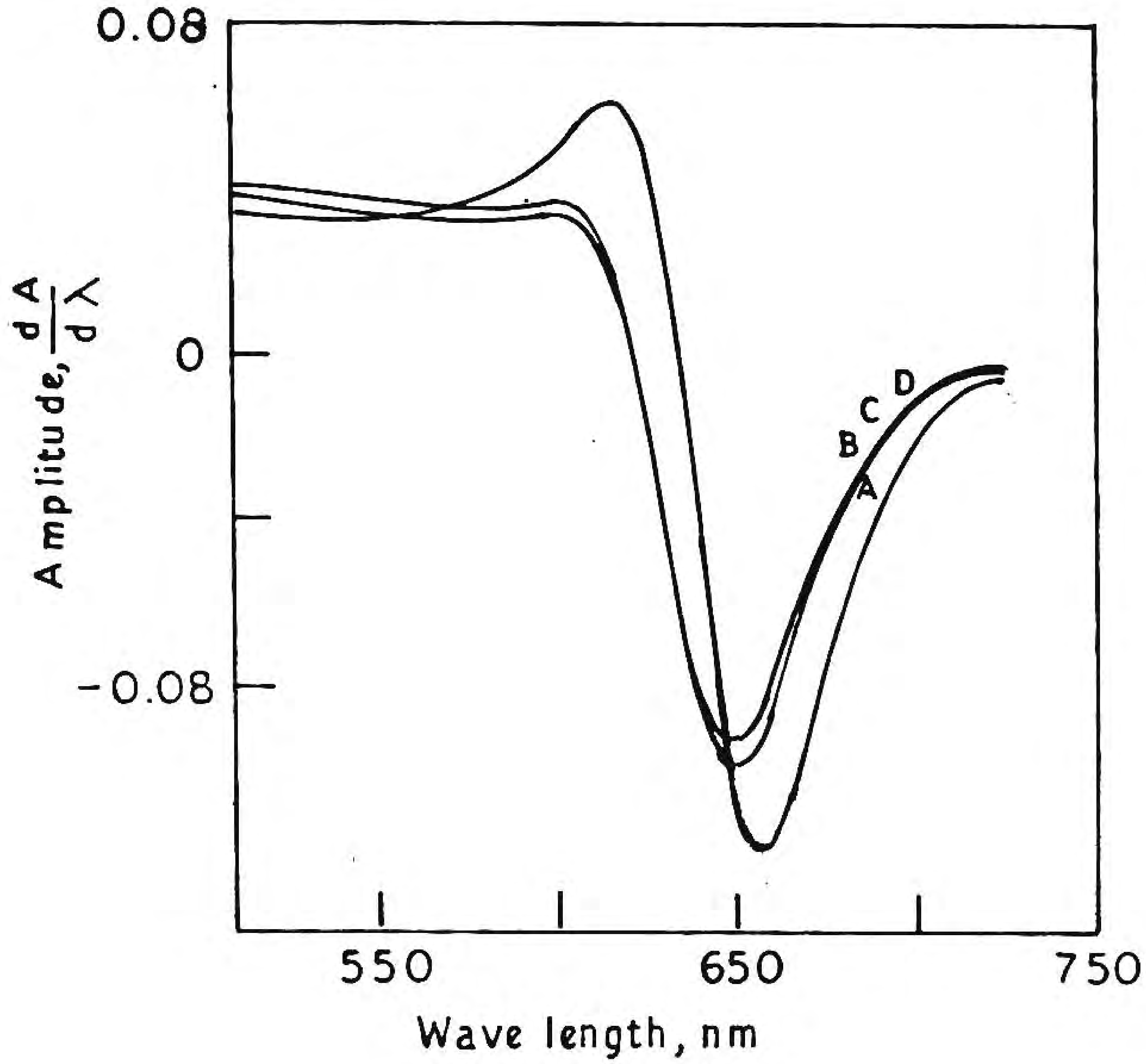


Fig. 3.2 First order derivative absorption spectra

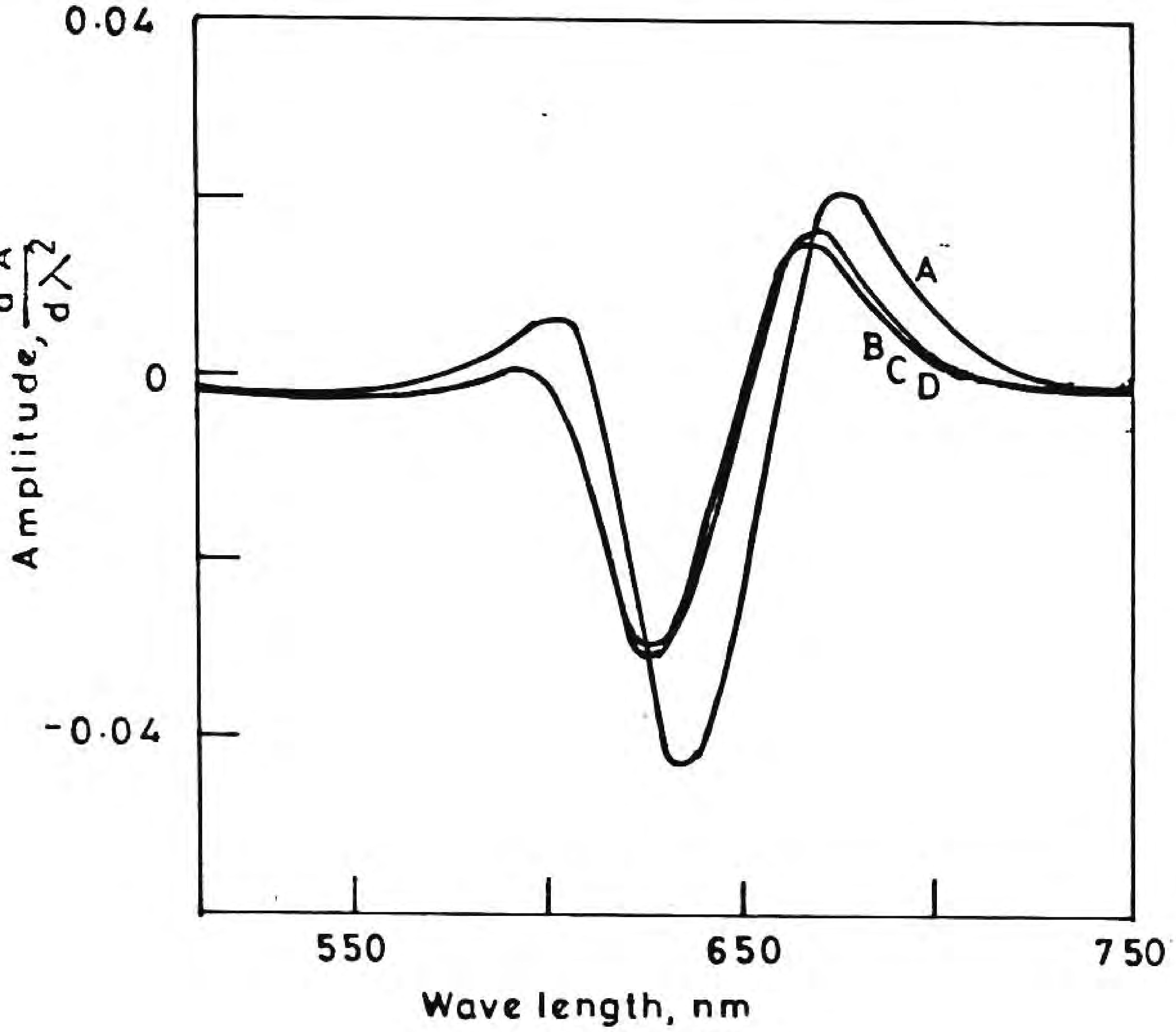


Fig. 3.3 Second order derivative absorption spectra

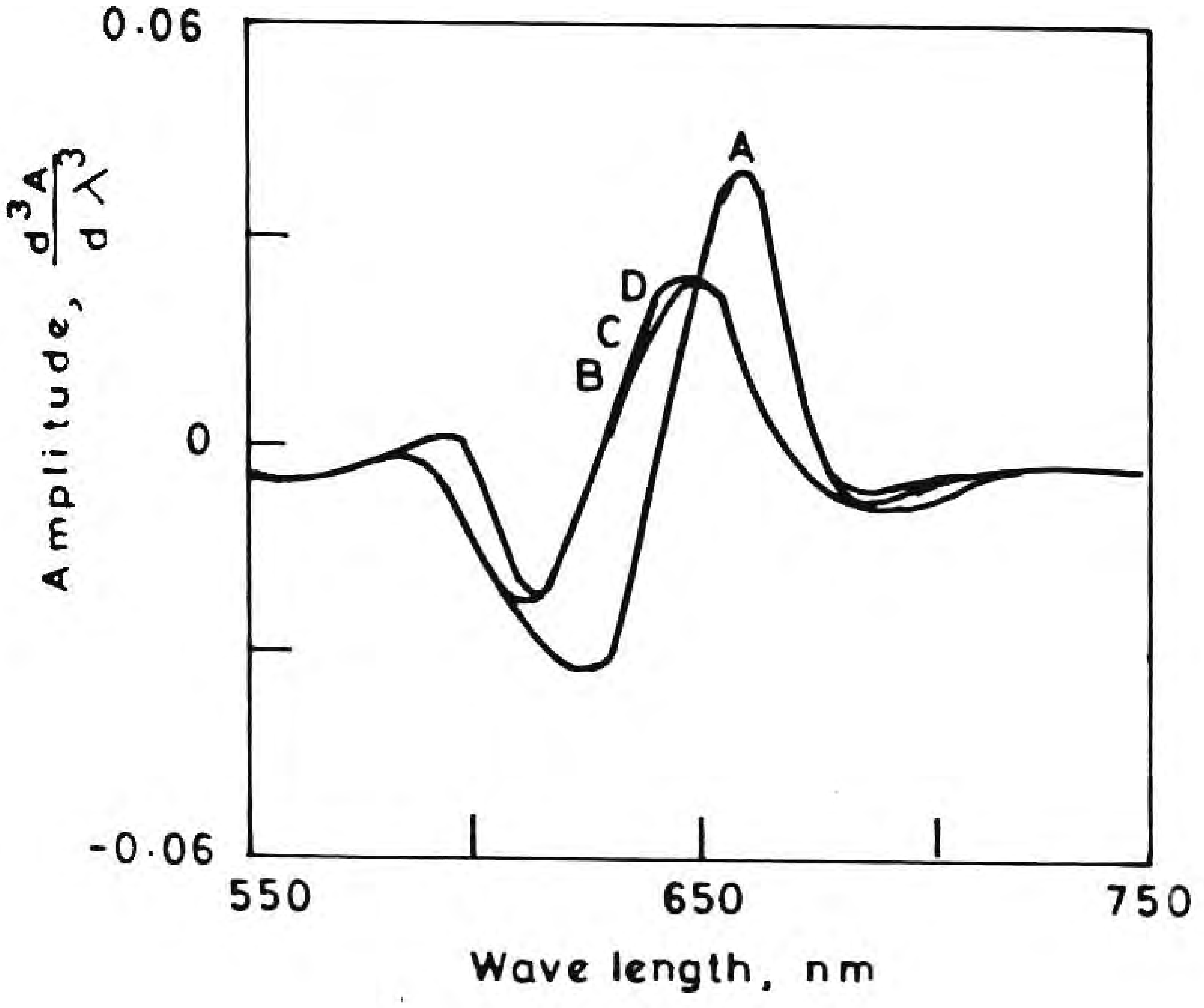


Fig. 3.4 Third order derivative absorption spectra

Fourth order derivative absorption spectra are recorded for 0.8 ppm of samarium, dysprosium, thulium and lutetium. The amplitudes obtained are very less compared to third order derivative mode and are not considered. Hence third order derivative mode is chosen for further studies.

Various factors that influence amplitude measurements in $^3D$ mode include (i) instrumental parameters, and (ii) reaction conditions for maximum colour development. These were studied systematically and the results obtained are discussed below.

## OPTIMIZATION OF INSTRUMENTAL PARAMETERS FOR $^3D$ DETERMINATION OF SAMARIUM

### 3.2 CHOICE OF $\Delta\lambda$

The appropriate $\Delta\lambda$ value was chosen by carrying out the experiments at $\Delta\lambda$ values ranging from 1 to 10 nm at a constant scan speed of 60 nm $min^{-1}$ and with a slit width of 2 nm. Further an appropriate full scale expansion was selected to permit satisfactory measurement of noise level. Figure 3.5 shows the $^3D$ absorption spectra scanned in the wavelength range 750 to 550 nm with $\Delta\lambda$ values of 1, 5 and 9 nm (curves A, B and C respectively) for 0.8 ppm of samarium after treating with 3 ml of 0.02% methyl thymol blue, 2.5 ml of ammonium acetate (pH 7.0) buffer and 1 ml of 1% CTAB against reagent blank. The mean amplitudes thus obtained in the wavelength range 670 to 680 nm are listed in Table I. The more appropriate $\Delta\lambda$ value was chosen by

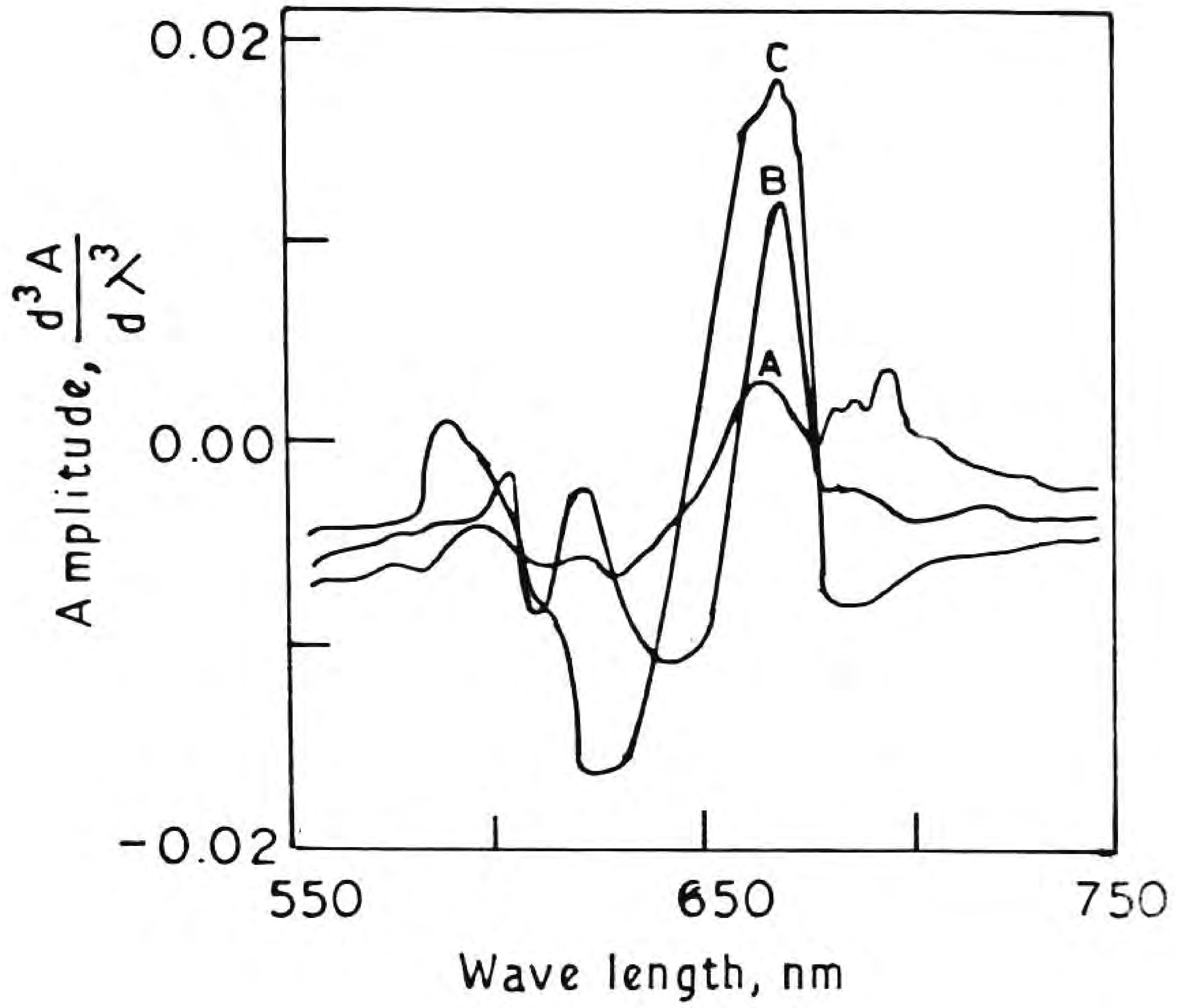


Fig. 3.5 Choice of $\Delta\lambda$

comparing the signal to noise ratio (SNR) at various values of $\Delta\lambda$. It is clear from Table I that the mean amplitude and SNR increases nonlinearly over the range listed. The $\Delta\lambda$ values in the range 1 to 4 nm were not considered because of very low SNR values. The percentage change of SNR values on change of $\Delta\lambda$ from 8 to 9 nm was the lowest and hence 9 nm was chosen as the most reasonable value for the determination.

**Table I**

**Choice of $\Delta\lambda$**

| nm | Mean amplitude at $^3D$ 670, 680 | Relative amplitude at $^3D$ 670, 680 | Attenuation % | Mean SNR |
|---|---|---|---|---|
| 1 | 0.003 | 9.4 | 90.6 | 3.4 |
| 2 | 0.005 | 14.1 | 85.9 | 4.5 |
| 4 | 0.006 | 17.2 | 82.8 | 5.5 |
| 5 | 0.011 | 34.4 | 65.6 | 27.5 |
| 6 | 0.012 | 37.5 | 62.5 | 40.0 |
| 8 | 0.025 | 78.1 | 21.9 | 50.0 |
| 9 | 0.026 | 81.3 | 18.8 | 52.0 |
| 10 | 0.032 | 100 | 0 | 64.0 |

N = 5

Relative amplitudes were calculated as a percentage of that for $\Delta\lambda$ = 10

Attenuation was expressed as the percentage of amplitude at $\Delta\lambda$= 10.

## 3.3 CHOICE OF SLIT WIDTH

The optimal slit width was established by measuring the mean amplitudes of five successive determinations of 0.8 ppm of samarium. In these experiments the slit width was varied in the range 0.1 to 4.0 nm. These spectral measurements were carried out at a $\Delta\lambda$ value of 9 nm and with identical scan speed of 60 nm/min and full scale response setting. The mean amplitudes obtained for 5 individual determinations of 0.8 ppm of samarium at ${}^{3}D_{670,680}$ are shown in Table II. The increase of slit width from 0.1 to 1.0 nm enhances the SNR value and remain constant in the range 1.0 to 4 nm; hence it was decided to employ a slit width of 2 nm in subsequent studies.

**Table II**

**Effect of slit width on peak amplitude and SNR of samarium-methyl thymol blue - CTAB system at ${}^{3}D_{670,680}$**

| Slit width nm | Mean amplitude* | Noise** | SNR |
|---|---|---|---|
| 0.1 | 0.04 | 0.02 | 2.0 |
| 0.2 | 0.026 | 0.013 | 2.0 |
| 0.5 | 0.026 | 0.004 | 6.5 |
| 1.0 | 0.026 | 0.0005 | 52.0 |
| 2.0 | 0.026 | 0.0005 | 52.0 |
| 4.0 | 0.026 | 0.0005 | 52.0 |

* N = 5

** Noise was measured as the peak to peak amplitude on the same scale of expansion as the signal.

## 3.4 CHOICE OF SCAN SPEED

The influence of scan speed on the mean amplitude of 5 successive determinations of 0.8 ppm of samarium at $^3D_{670,680}$ was next studied in the range 15-480 nm/minute, by recording the $^3D$ absorption spectra in the wavelength range 750-550 nm. Fig. 3.6 shows the $^3D$ absorption spectra obtained by using scan speeds of 15, 120, 240 and 480 nm per minute (curves A, B, C and D respectively). The mean amplitudes and the peak positions measured from the $^3D$ absorption spectra recorded at varying scan speeds are shown in Table III. As seen from Table III the peak amplitudes were attenuated only at higher speeds, i.e. 20 and 40% for 240 and 480 nm $\text{min}^{-1}$ of scan speed respectively. The position of the peak also moves in the direction of the scan (i.e. from long to short wavelengths) at scan speeds $>$ 120 nm $\text{min}^{-1}$ as seen from Table III. Since the wavelength drift is dependent on scan speed, 60 nm/min. was chosen in subsequent experiments where the attenuation was negligible and provides reasonably short analysis times.

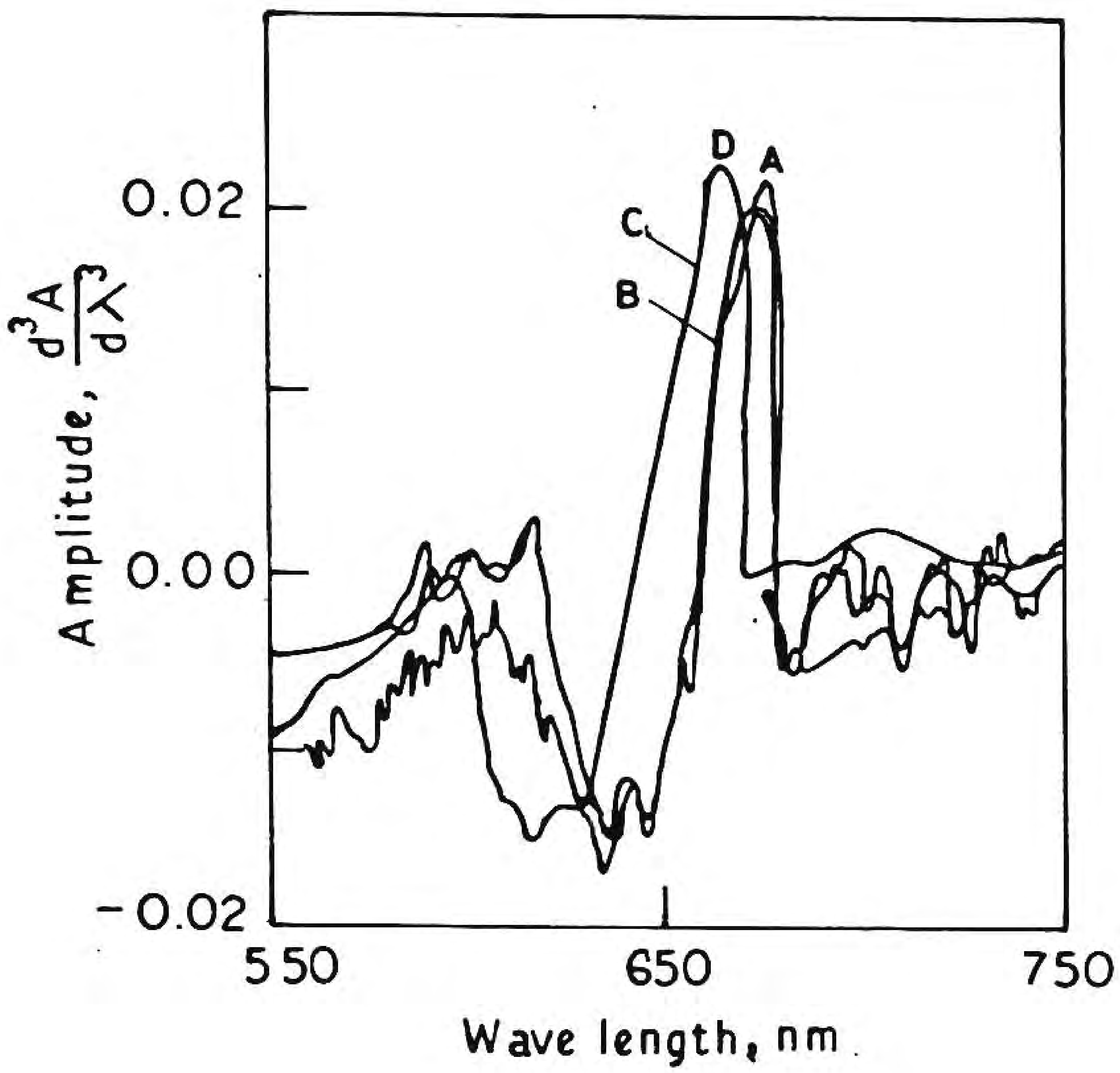


Fig. 3.6 Choice of scan speed

## Table III

**Variation of peak amplitudes and peak positions of samarium-methyl thymol blue - CTAB complex as a function of scan speed**

| Scan speed nm $min^{-1}$ | Mean amplitude* | Actual wavelength of measurement nm | Wavelength drift, nm |
|---|---|---|---|
| 15 | 0.026 | 670, 680 | 0, 0 |
| 30 | 0.026 | 670, 680 | 0, 0 |
| 60 | 0.026 | 670, 680 | 0, 0 |
| 120 | 0.026 | 666, 680 | -4, 0 |
| 240 | 0.021 | 664, 678 | -6, -2 |
| 480 | 0.016 | 662, 676 | -8, -4 |

* Mean amplitude was expressed on an arbitrary scale (N = 5)

## OPTIMAL REACTION CONDITIONS FOR THE FORMATION OF THE TERNARY COMPLEX: SAMARIUM-METHYL THYMOL BLUE - CTAB/CPB

### 3.5 EFFECT OF pH

The optimum pH range for the formation of samarium-methyl thymol blue - CTAB/CPB complex and the subsequent determination by $^3D_{MAS}$ was studied by adjusting the pH of the solution in the range 4-10 in steps of 1. In these studies 20 $\mu$g of samarium was allowed to react with 3 ml of 0.02% methyl thymol blue, 2.5 ml of 0.1 M ammonium acetate buffer and 1 ml of 1% CTAB or 0.25% CPB and after adjusting the pH to desired value the solutions were made upto 25 ml. A reagent blank was also prepared for each pH. The mean amplitudes were measured at $^3D_{670,680}$ after recording $^3D$ absorption spectra in the wavelength range of 700 to 650 nm against respective reagent blanks. The results are shown in Fig. 3.7 from which it is clear that the optimal pH range for the formation of samarium-methyl thymol blue-CTAB (or CPB) complex is 6 to 8. Hence pH 7 ammonium acetate (0.1 M) buffer was chosen in subsequent studies.

### 3.6 EFFECT OF METHYL THYMOL BLUE (MTB) CONCENTRATION

The influence of methyl tnymol blue concentration on the formation of samarium-methyl thymol blue - CTAB/CPB complex was established by reacting 20 $\mu$g of samarium with 0.5 to 5 ml of 0.02% methyl thymol blue. The pH of the above solutions were adjusted to 7 after the addition of 2.5 ml of 0.1 M ammonium

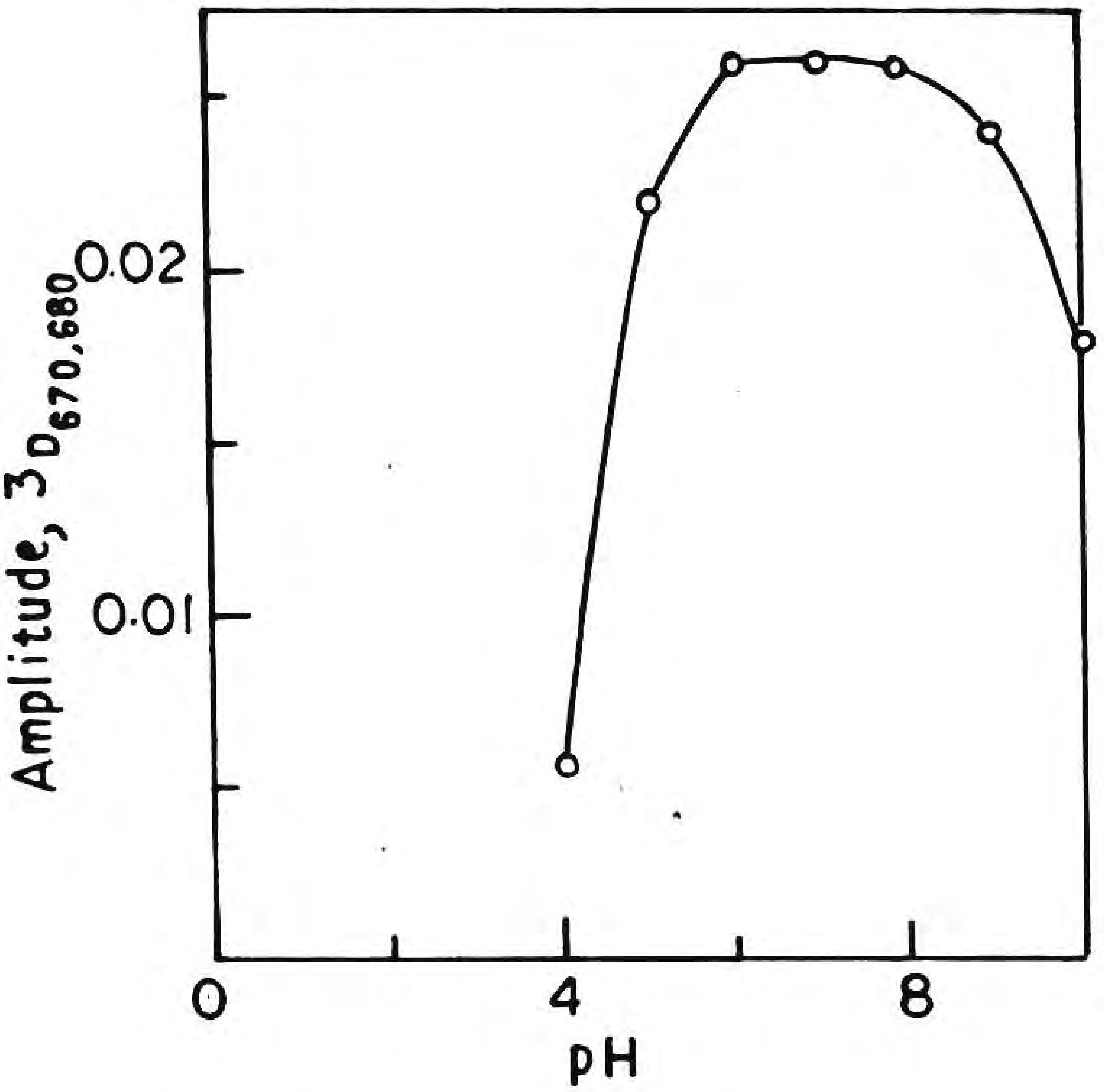


Fig 3.7 Effect of pH

acetate buffer and 1 ml of 1% CTAB or 0.25% CPB. The solutions were then diluted to 25 ml with water. The mean amplitudes were measured at $^3D_{670,680}$ after recording $^3D$ absorption spectra in the wavelength range of 700 to 650 nm against respective reagent blanks. The results are shown in Fig. 3.8.

It is evident from the figure that the mean amplitudes were found to increase with increase in methyl thymol blue concentration upto 2.5 ml of 0.02% and remained constant on further increase. Hence it was decided to maintain the methyl thymol blue concentration as 3 ml of 0.02% in subsequent studies.

## 3.7 EFFECT OF CTAB/CPB CONCENTRATION

A similar experiment to ascertain the optimum concentration of CTAB/CPB required for maximum colour development was carried out by varying the volume of CTAB/CPB from 1 to 9 ml of 0.2% CTAB/0.1% CPB after adjusting the pH of the solution to 7. In these studies 20 µg of samarium, 2.5 ml of ammonium acetate (0.1 M) buffer and 3 ml of 0.02% methyl thymol blue were present in each instance. The mean amplitude of these solutions were measured at $^3D_{670,680}$ after recording $^3D$ absorption spectra in the wavelength range 700 to 650 nm against corresponding reagent blank. The results are shown in Fig. 3.9 from which it is evident that the mean amplitude reaches a maximum at 4 ml of CTAB (curve A) or 2 ml of CPB (curve B) and remain constant with further increase of CTAB/CPB. Therefore, it was

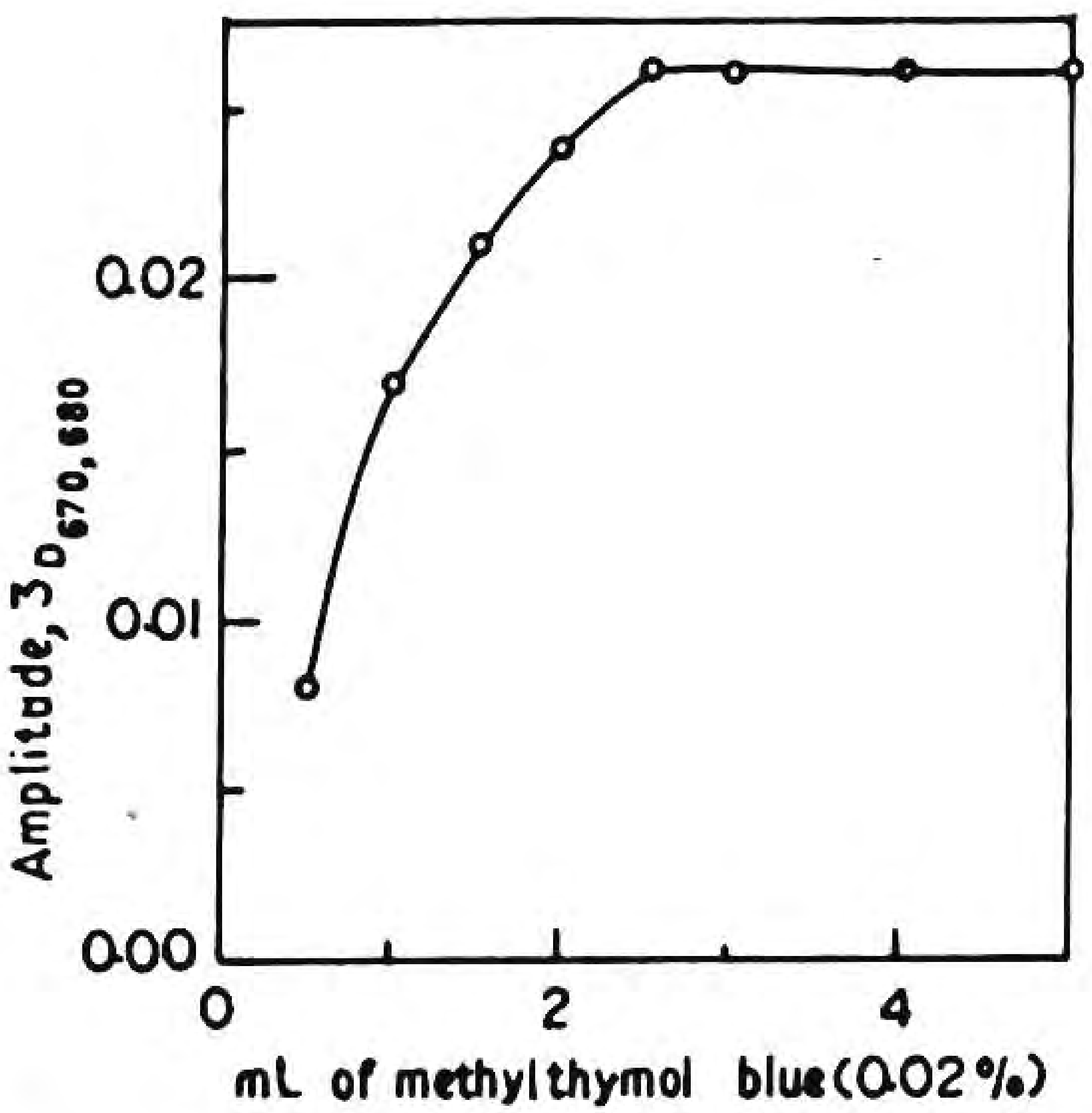


Fig 3.8 Effect of methyl thymol blue concentration.

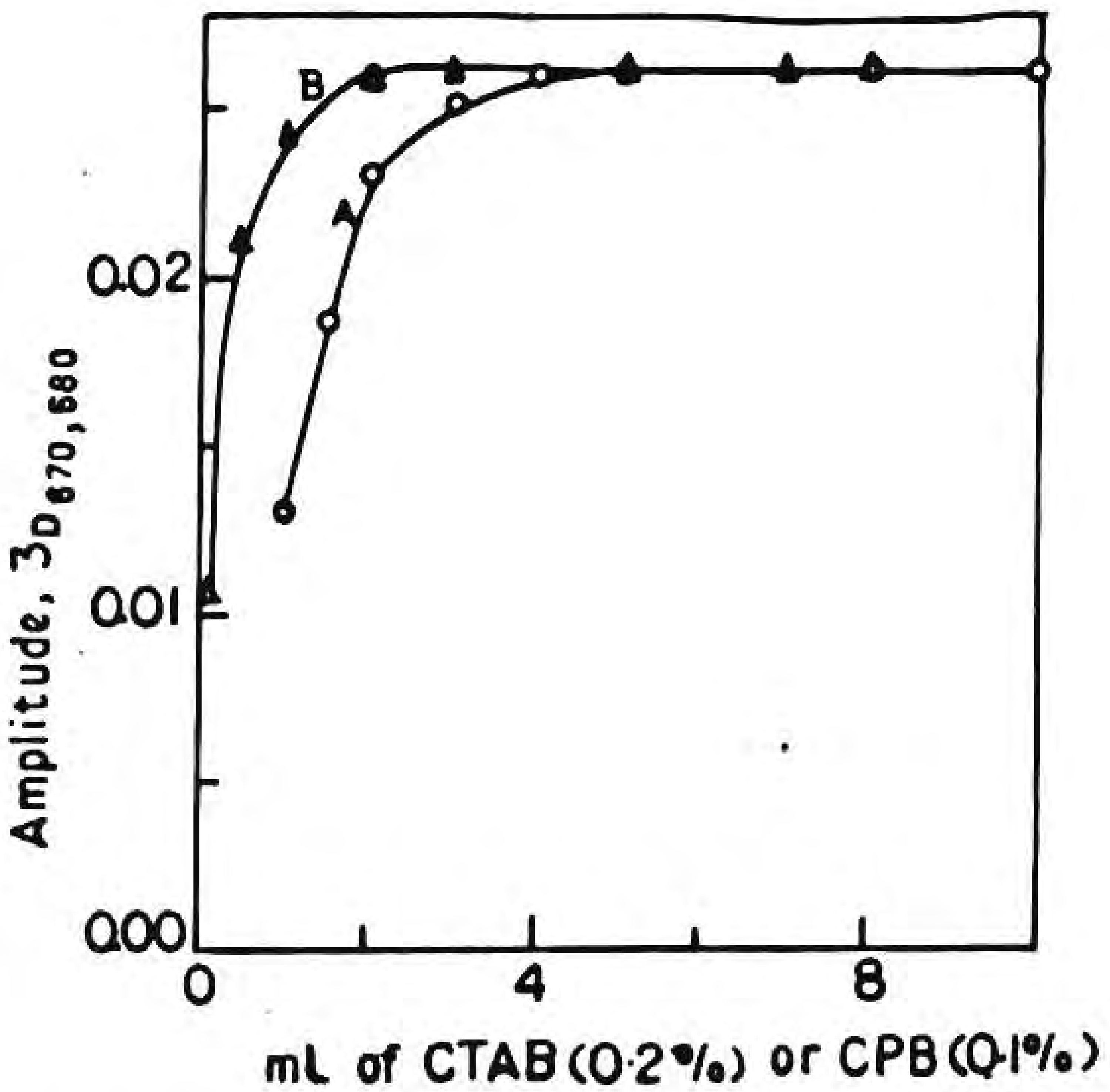


Fig 3.9 Effect of CTAB or CPB concentration

decided to add 1 ml of 1% CTAB or 1 ml of 0.25% CPB in all subsequent studies.

## 3.8 ORDER OF ADDITION OF REAGENTS

Using 20 μg of samarium and optimum concentrations of the reagent solutions, the order of addition of ammonium acetate buffer, methyl thymol blue and CTAB/CPB on the formation of ternary complex was next investigated. The results are shown in Table IV which indicated that the order of addition is not critical.

**Table IV**

**Order of addition of reagents**

| Sl. No. | Order of addition | Mean amplitude at $^3D_{670,680}$ |
|---|---|---|
| 1 | Sm + Ammonium acetate buffer + MTB + CTAB/CPB | 0.026 |
| 2 | Sm + CTAB/CPB + Ammonium acetate buffer + MTB | 0.026 |
| 3 | Sm + CTAB/CPB + MTB + Ammonium acetate buffer | 0.026 |
| 4 | MTB + CTAB/CPB + Ammonium acetate buffer + Sm | 0.026 |

## 3.9 OPTIMUM TIME FOR COLOUR DEVELOPMENT AND STABILITY

Under optimal conditions, the formation of ternary complex was instantaneous. The stability of the ternary system was established by measuring the mean amplitude of the colour system at $^{3}D_{670,680}$ in 10 mm cuvettes at regular intervals from the time the solutions were made upto the mark. It was found that the colour system remains stable for more than 24 hours.

## 3.10 ABSORPTION SPECTRA

The $^{3}D$ absorption spectra of 0.2, 0.6 and 0.8 ppm of samarium (curves A, B and C respectively) after forming the ternary complex with methyl thymol blue and CTAB/CPB under optimized conditions against reagent blank is shown in Fig. 3.10. The amplitude for other rare earth elements viz. dysprosium, thulium and lutetium in the wavelength range 670-680 nm is negligible as seen from Fig. 3.4. Hence $^{3}D_{670,680}$ was chosen in subsequent studies for the determination of samarium.

## 3.11 CALIBRATION GRAPH

The adherence of the colour system to Beer's law in $^{0}D$ mode was next studied. To 0-30 µg of samarium, 3 ml of 0.02% methyl thymol blue solution, 2.5 ml of 0.1 M ammonium acetate were added and the pH was adjusted to 7. Then 1 ml of 1% CTAB or 0.25% CPB was added and the solution was made upto 25 ml in a volumetric flask. The absorbance of these solutions were

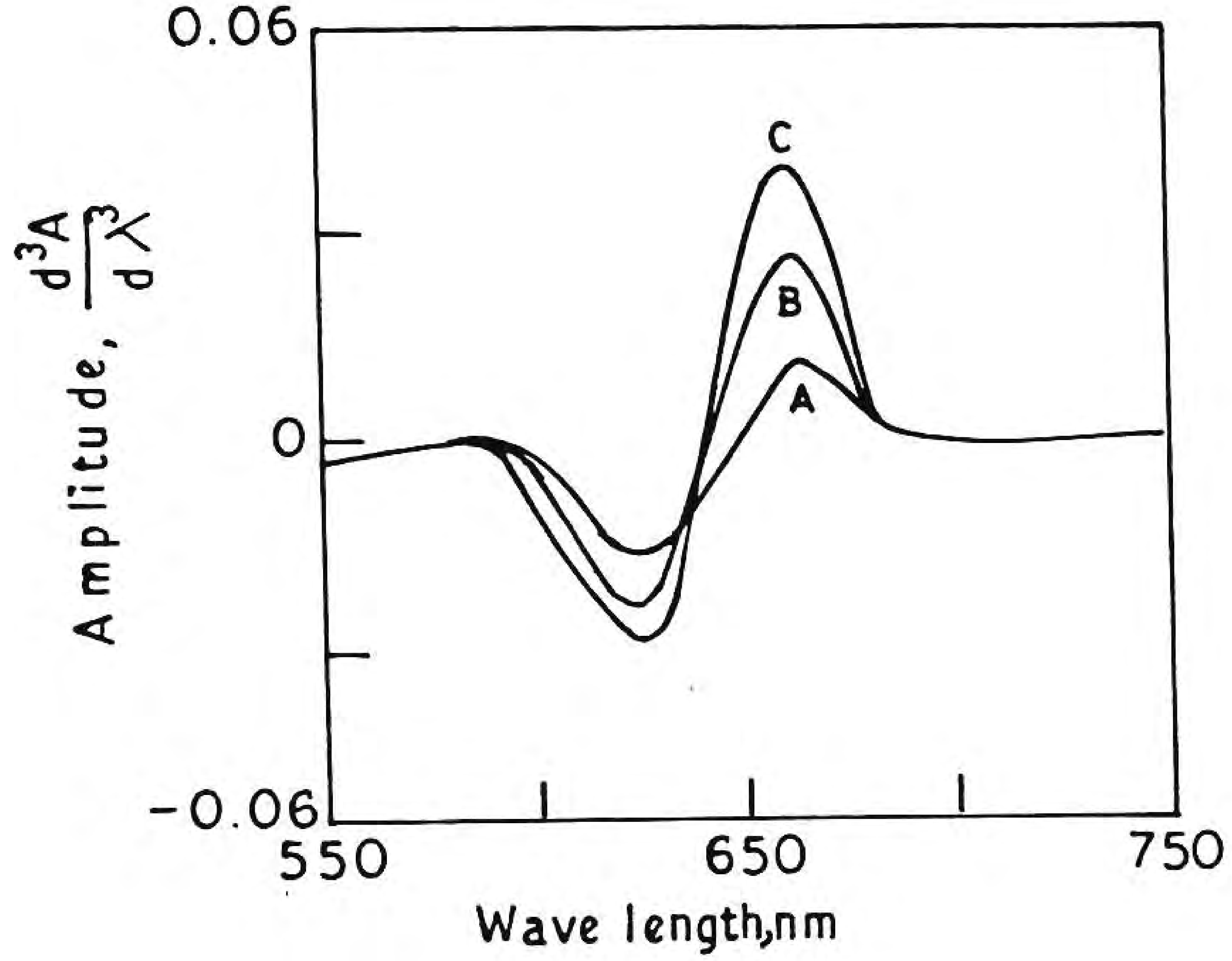


Fig. 3.10 Absorption spectra

measured at 645 nm in 10 mm cuvettes. The plot of the absorbance against concentration of samarium is shown in Fig. 3.11 (CPB system) and in Fig. 3.12 (CTAB system). The calibration graph thus obtained is a straight line in the range 0 to 30 µg of samarium present in 25 ml of aqueous phase.

Fig. 3.13 shows the calibration plot obtained under similar conditions for different amounts of samarium in $^{3}D$ mode of measurements. The amplitude at different concentrations for samarium were measured at $^{3}D_{670,680}$ after recording the respective absorption spectra in the wavelength range 700-650 nm against a reagent blank.

## 3.12 SENSITIVITY AND PRECISION

The molar absorptivity and Sandell's sensitivity were found to be $7 \times 10^{4}$ l $mole^{-1}$ $cm^{-1}$ and $2.162 \times 10^{-3}$ µg $cm^{-2}$ respectively for $^{0}D$ absorption measurements.

The standard deviation of the method developed was established by carrying out ten separate determinations using 20 µg of samarium by following the procedure described under calibration graph in $^{3}D$ mode. Calculations were made using the formula described in Chapter II.

The standard deviation of the method was calculated to be 1.62%. The results are shown in Table V.

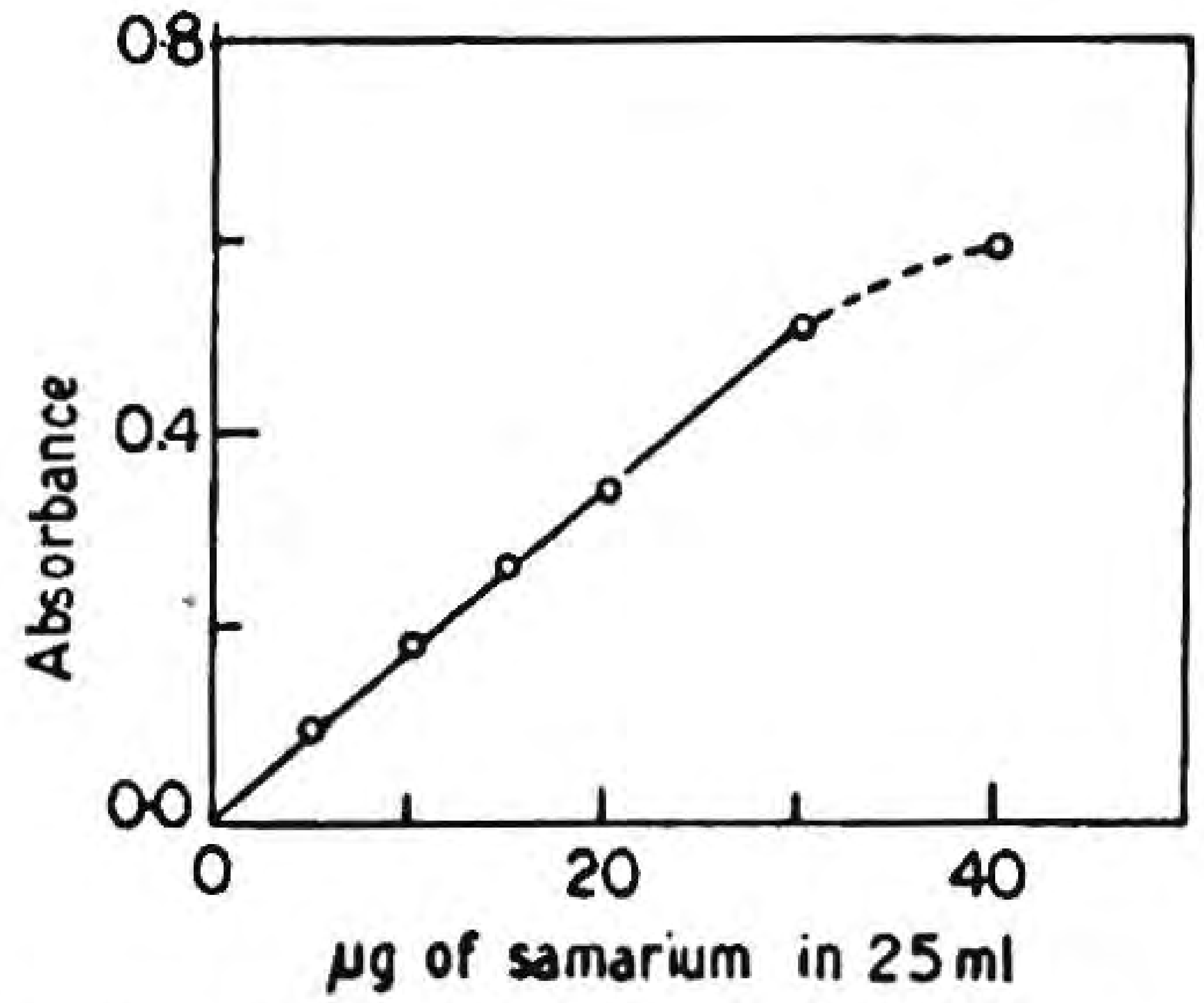


Fig 3.11 Calibration graph (CPB system)

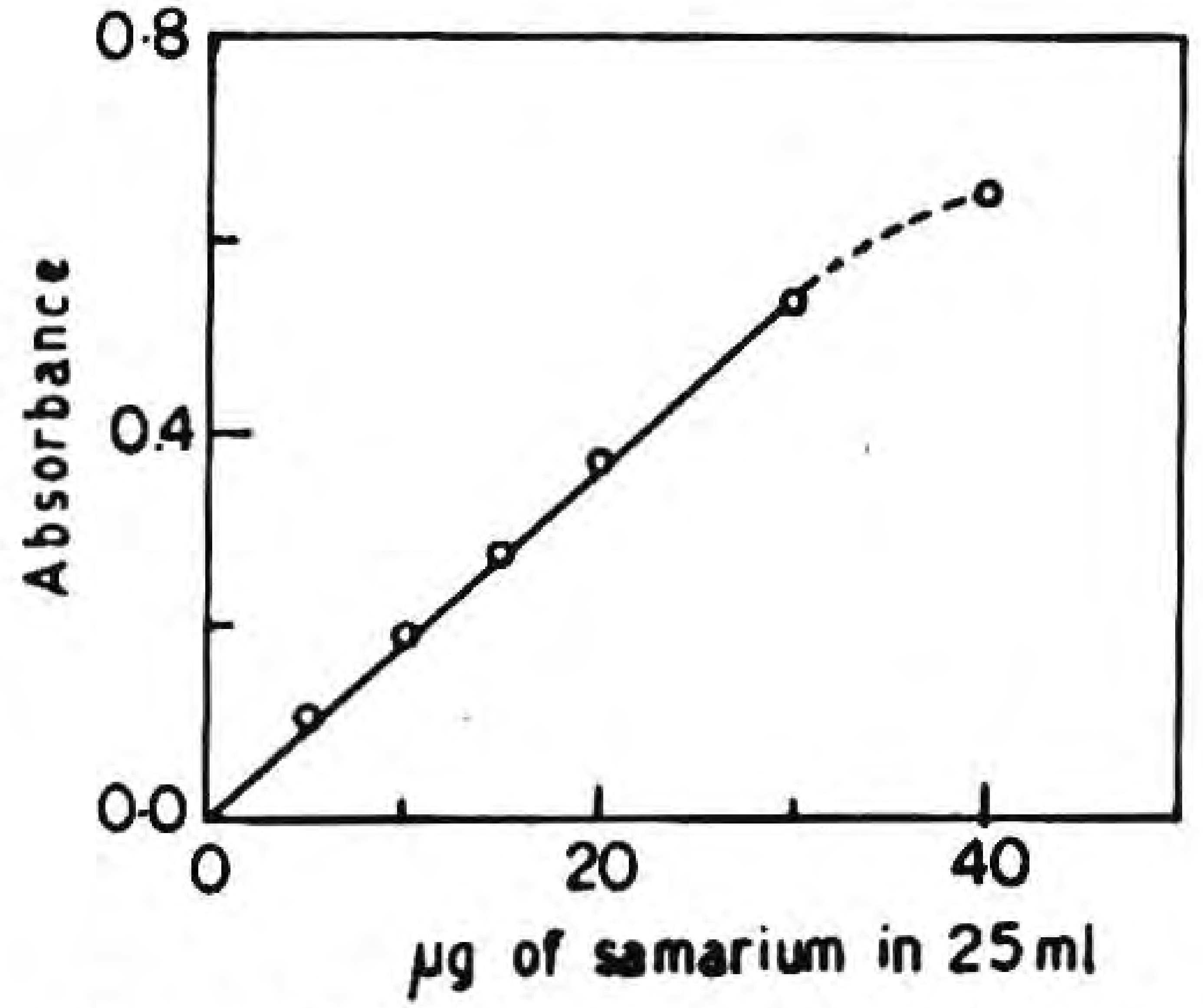


Fig 3.12 Calibration graph (CTAB system)

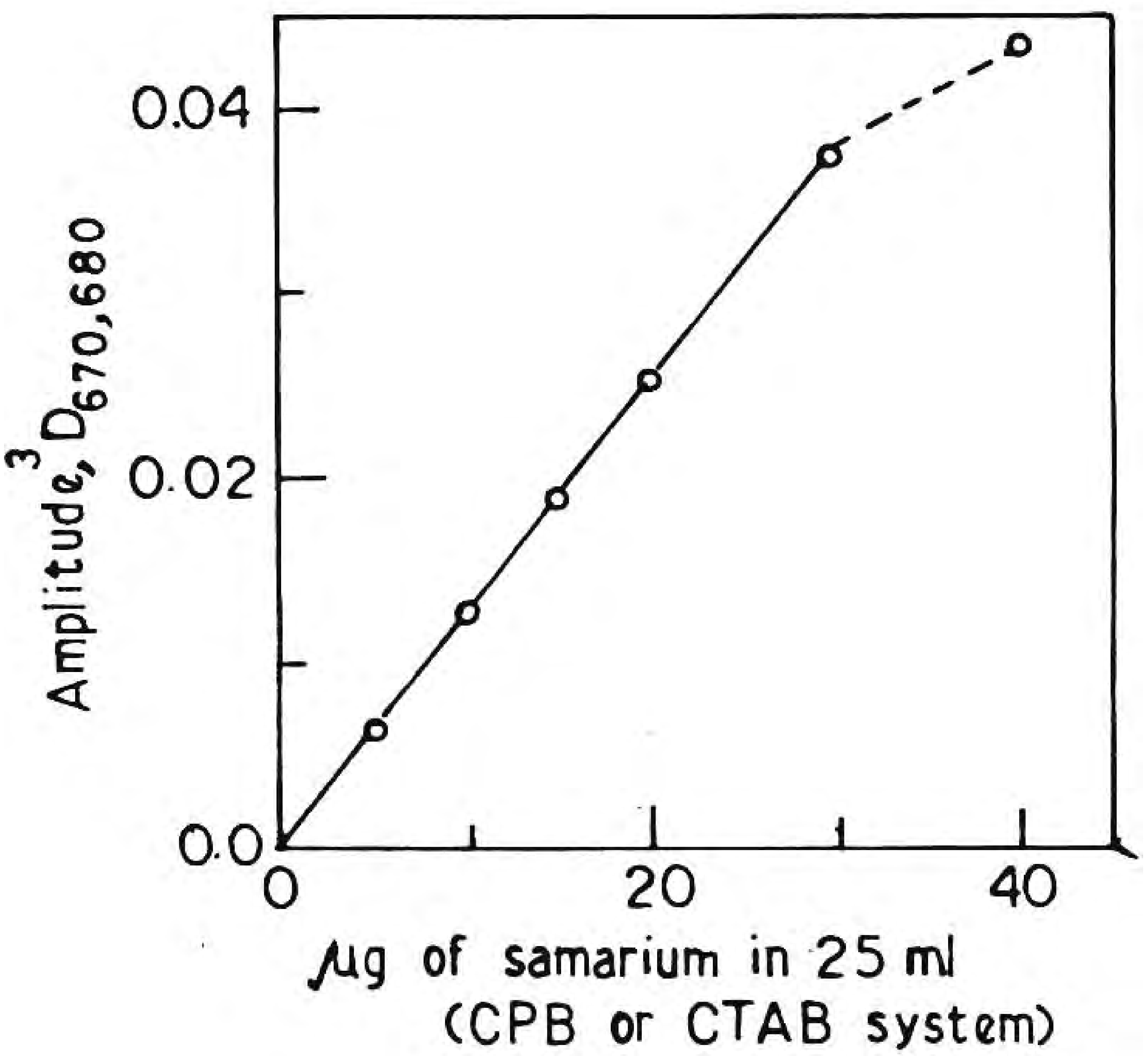


Fig 3.13 Calibration graph.

## Table V

## Precision studies

| Sl. No. | Xn Sm found ( $\mu g$) | $(Xn - \bar{X})$ | $(Xn - \bar{X})^2$ |
|---|---|---|---|
| 1 | 20 | 0.08 | 0.0064 |
| 2 | 19.75 | 0.17 | 0. 0289 |
| 3 | 19.55 | 0.37 | 0.1369 |
| 4 | 20.35 | 0.43 | 0.1849 |
| 5 | 20.20 | 0.28 | 0.0784 |
| 6 | 19.70 | 0.22 | 0.0484 |
| 7 | 20.20 | 0.28 | 0.0784 |
| 8 | 19.55 | 0.37 | 0.1369 |
| 9 | 20.30 | 0.38 | 0.1444 |
| 10 | 19.60 | 0.32 | 0.1024 |

$\bar{X} = 19.92$ $\sum(Xn - \bar{X})^2 = 0.946$

$$\sigma = \sqrt{\frac{\sum(Xn - \bar{X})^2}{n - 1}}$$

$$\sigma = 0.3242$$

Relative standard deviation ( $\sigma_{rel}$) $= \frac{0.3242 \times 100}{20} = 1.62\%$

## 3.13 COMPOSITION STUDIES

The composition of the ternary complex viz. samarium-methyl thymol blue - CPB/CTAB was established spectrophotometrically using mole ratio and continuous variation methods.

### 3.13.1 Samarium to methyl thymol blue ratio

Mole ratio method

Yoe and Jones[205] found that for a stable binary complex AB, a plot of absorbance against mole ratio of the component B to component A with A as constant, rose from origin as a straight line and broke sharply at an absorbance corresponding to the mole ratio of the components. This procedure was used to investigate the ratio of samarium to methyl thymol blue in the ternary complex by converting it into a pseudo binary one. This was accomplished by using large excess of CPB/CTAB for a fixed concentration of samarium and then varying the concentration of methyl thymol blue.

To a series of solutions containing 1 ml of $1.33 \times 10^{-4}$ M solution of samarium, 2.5 ml of 0.1 M ammonium acetate was added followed by 1 to 10 ml of $1.33 \times 10^{-4}$ M solution of methyl thymol blue. The solutions were made upto 25 ml after the addition of 1 ml of 0.25 or 1.0% CPB/CTAB. The absorbances of these solutions were measured at 645 nm in 10 mm cells against the respective reagent blanks. The results obtained are shown in Fig. 3.14 and 3.15 from which it is clear that the ratio of samarium to methyl

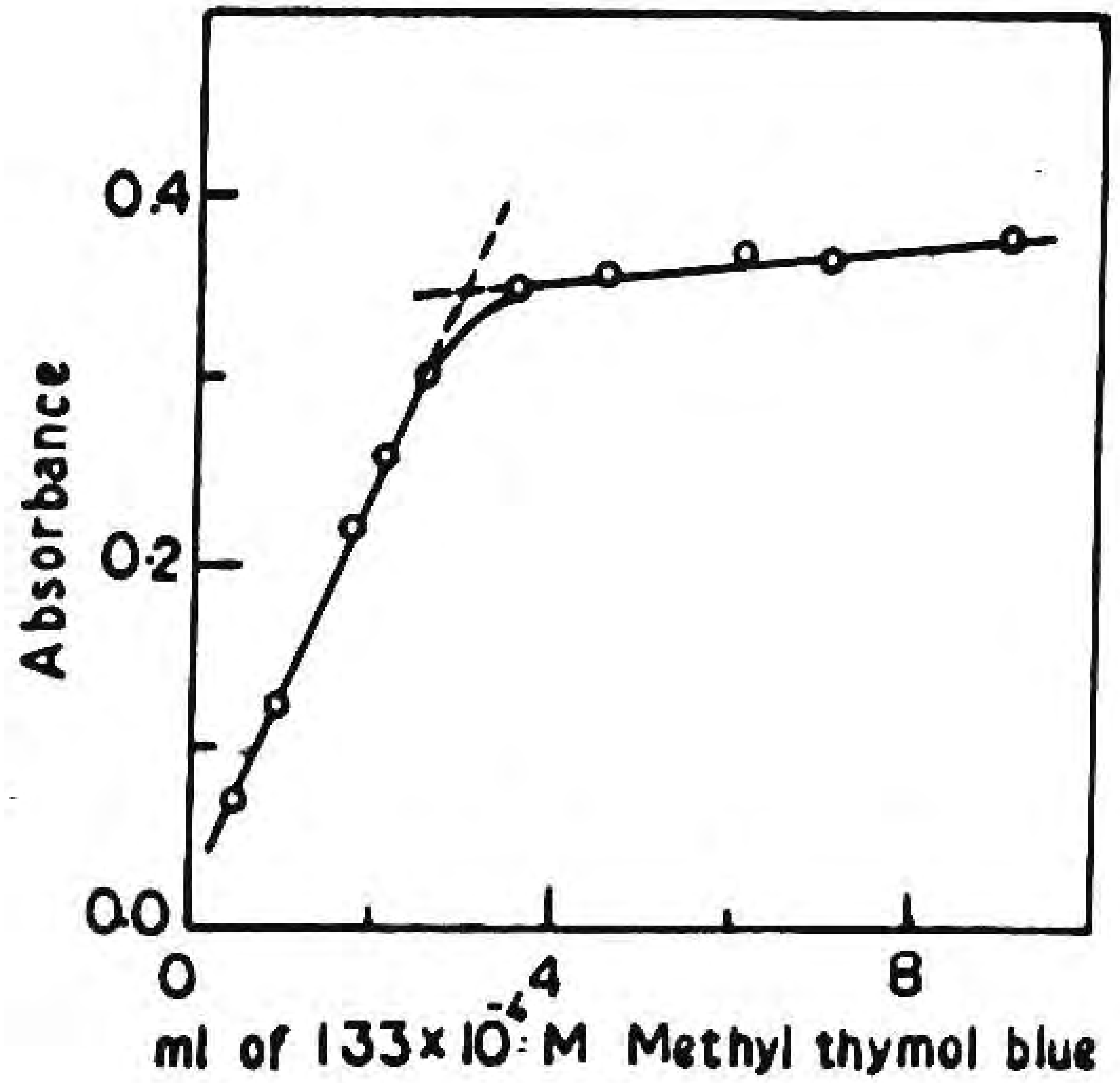


Fig. 3.1.4 Mole ratio method (CPB) system

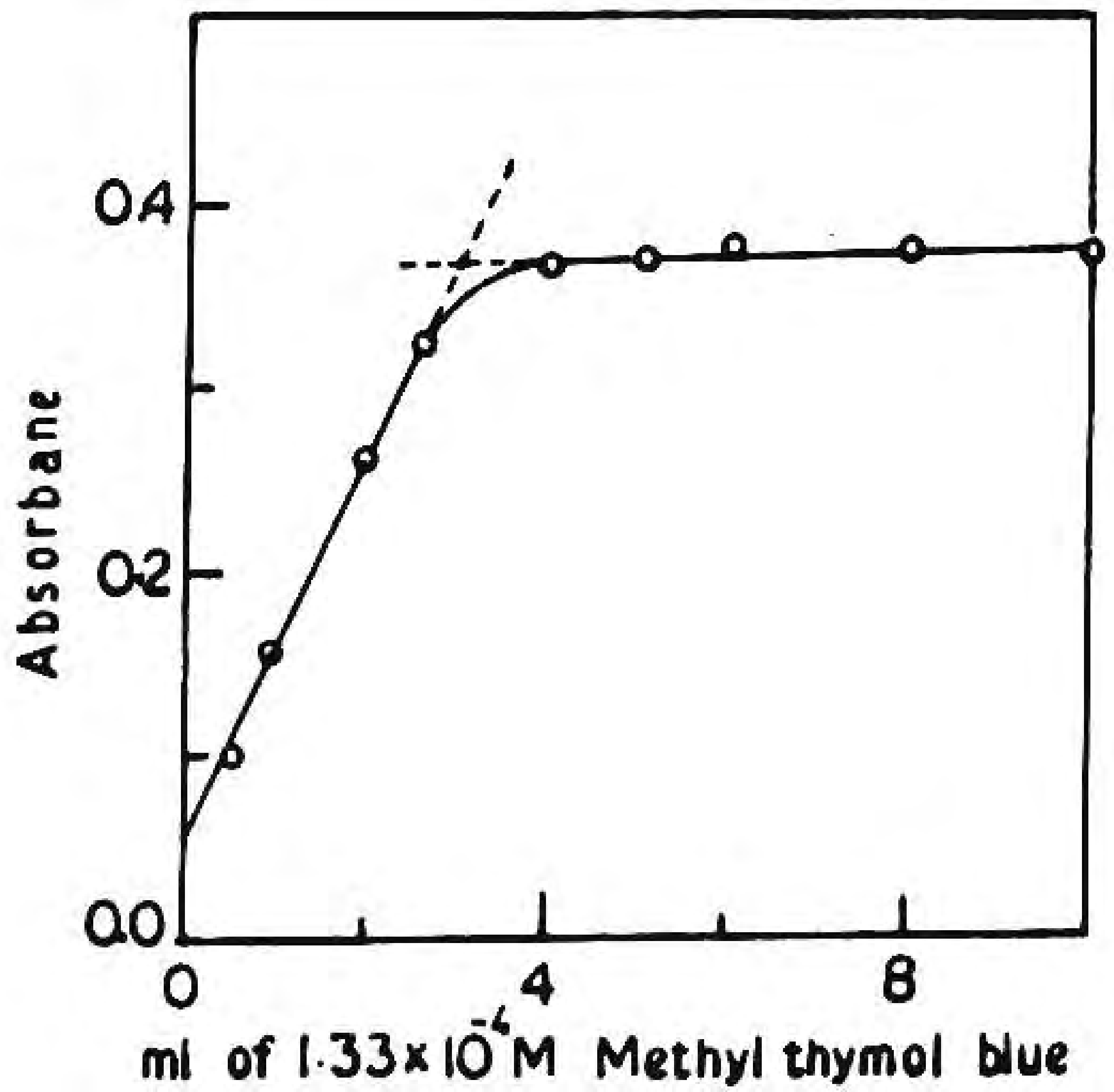


Fig .3.15 Mole ratio method (CTA B) system.

thymol blue is 1:3.

Continuous variation method[215]

This method, proposed by Job, is based on the principle that the absorbance due to the complex $ML_n$, formed by the interaction of metal ion M with a ligand L according to the equilibrium

$$M + nL \rightleftharpoons [ML_n]$$

will attain maximum at

$$\frac{[M]}{[M]+[L]} = \frac{1}{n+1}$$

provided the variation of the metal and ligand concentration is done by keeping their combined concentration i.e. [M] + [L] a constant. Here again the ratio of samarium to methyl thymol blue was established by converting the ternary complex into a pseudo-binary complex by keeping the concentration of CTAB/CPB in large excess.

To a series of solutions containing 1 to 9 ml of $6.6 \times 10^{-5}$ M solution of samarium, varying volumes of $6.6 \times 10^{-5}$ M solution of methyl thymol blue were added so that the total concentration of samarium and methyl thymol blue in each instance was 10 ml of $6.6 \times 10^{-5}$ M. The solutions were diluted to 25 ml after the addition of 2.5 ml of 0.1 M ammonium acetate buffer (pH 7) and

1 ml of 0.25% CPB or 1 ml of 1% CTAB and absorbance measurements were made against respective reagent blanks at 645 nm in 10 mm cells. The plot of absorbance against mole fraction of samarium is shown in Figs. 3.16 and 3.17 (CPB and CTAB systems). The results confirmed that the ratio of samarium to methyl thymol blue in the ternary complex is 1:3.

### 3.13.2 Samarium to CPB and CTAB ratio

Mole ratio method

This method was used to investigate the ratio of samarium to CPB and CTAB in the ternary complex by converting it into a pseudo binary one. This was accomplished by using large excess of methyl thymol blue for a fixed concentration of samarium and then varying the concentrations of CPB/CTAB.

To a series of solutions containing 1 ml of $1.33 \times 10^{-4}$ M solution of samarium, 3 ml of 0.02% methyl thymol blue, and 2.5 ml of 0.1 M ammonium acetate buffer were added and then adjusted the pH to 7. Then 1-10 ml of $1.33 \times 10^{-4}$ M solution of CPB/CTAB were added.

Blanks were also prepared for each reagent concentration. The absorbance of the solutions were measured at 645 nm in 10 mm cuvettes against the respective reagent blanks. The results obtained are shown in Figs. 3.18 and 3.19 (CPB/CTAB) from which it is clear that a sharp break occurs at 3 ml in the case of CPB

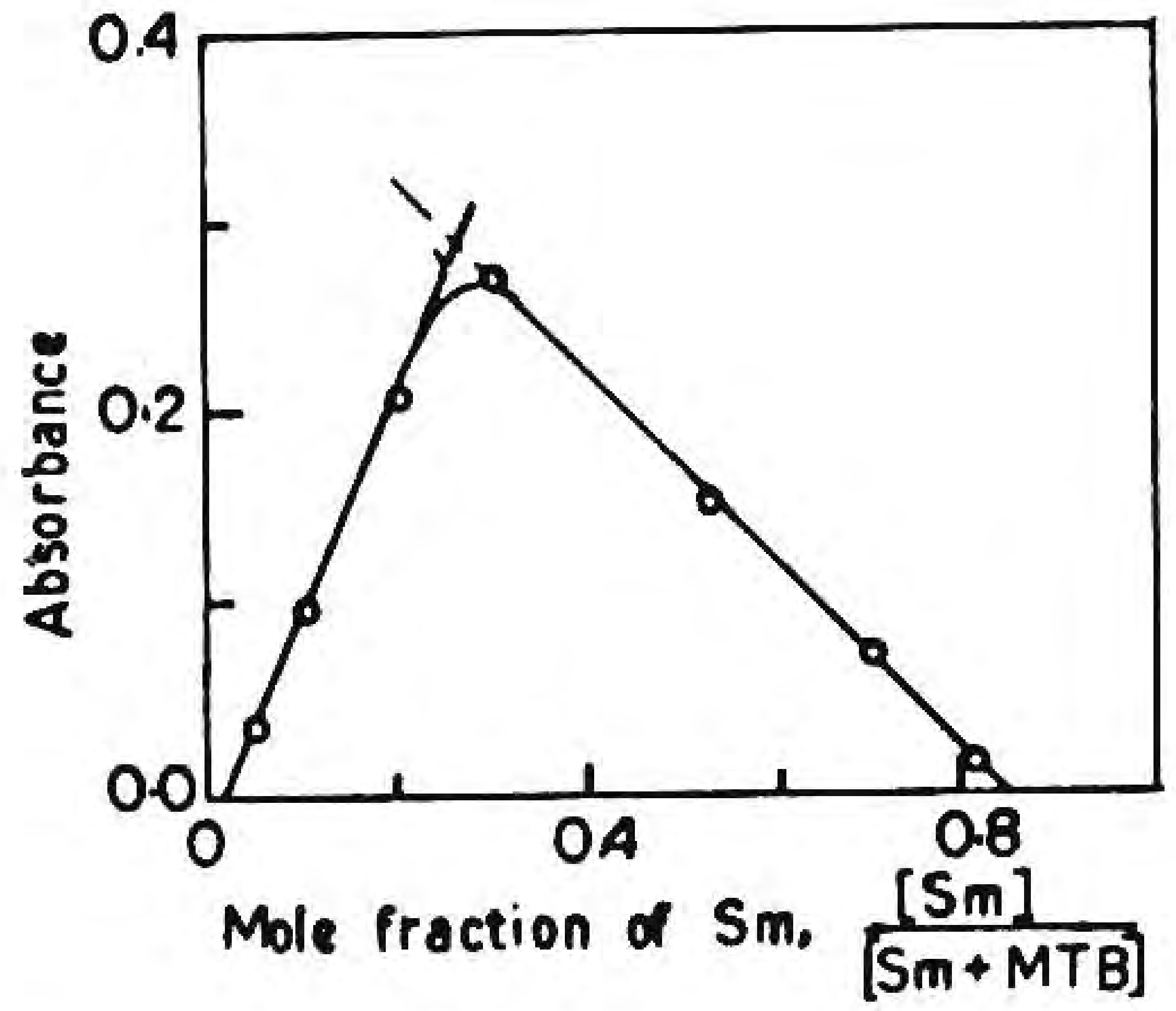


Fig. 3·16 Continuous variation method (CPB system)

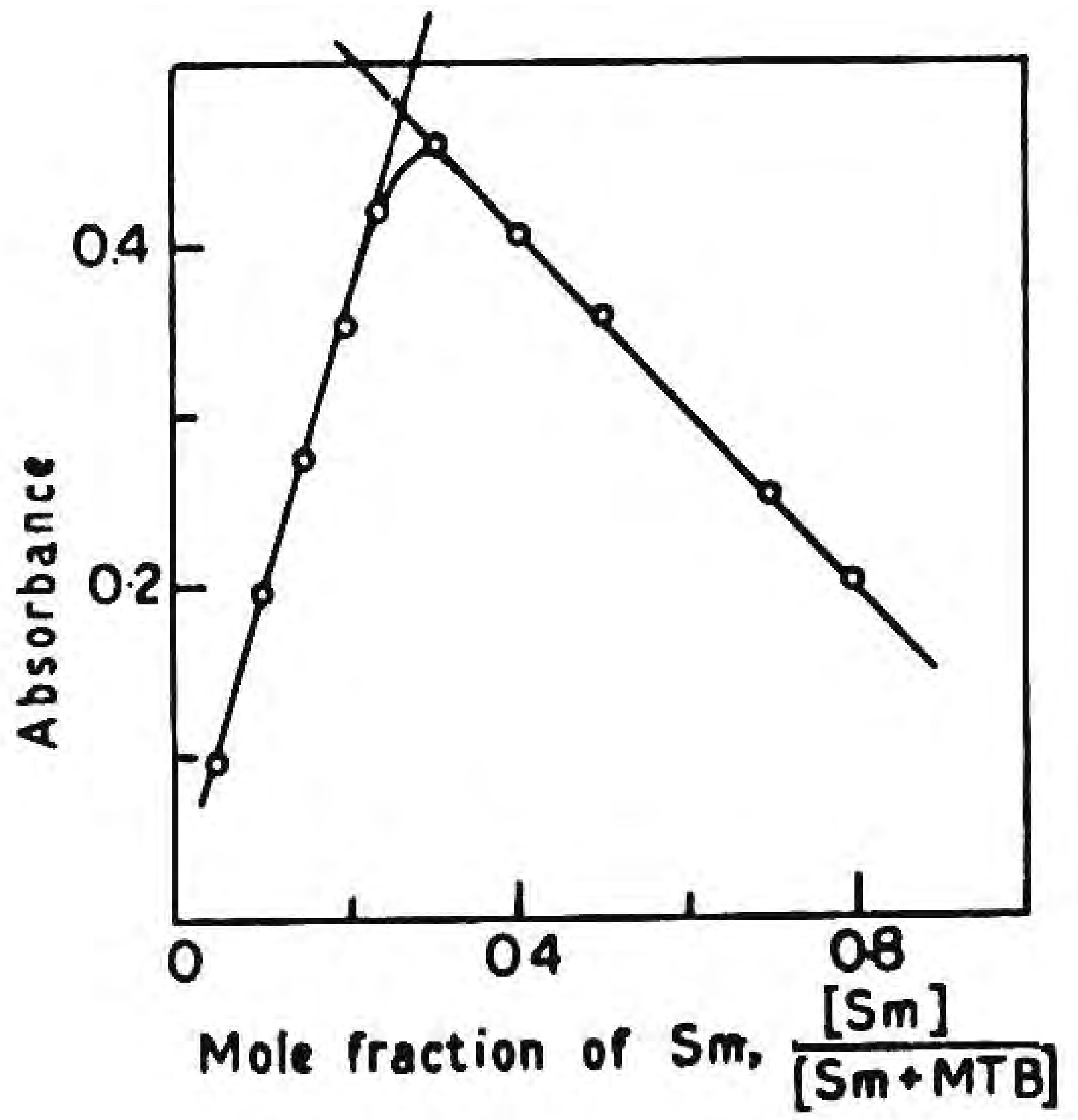


Fig. 3.17 Continuous variation method (CTAB system)

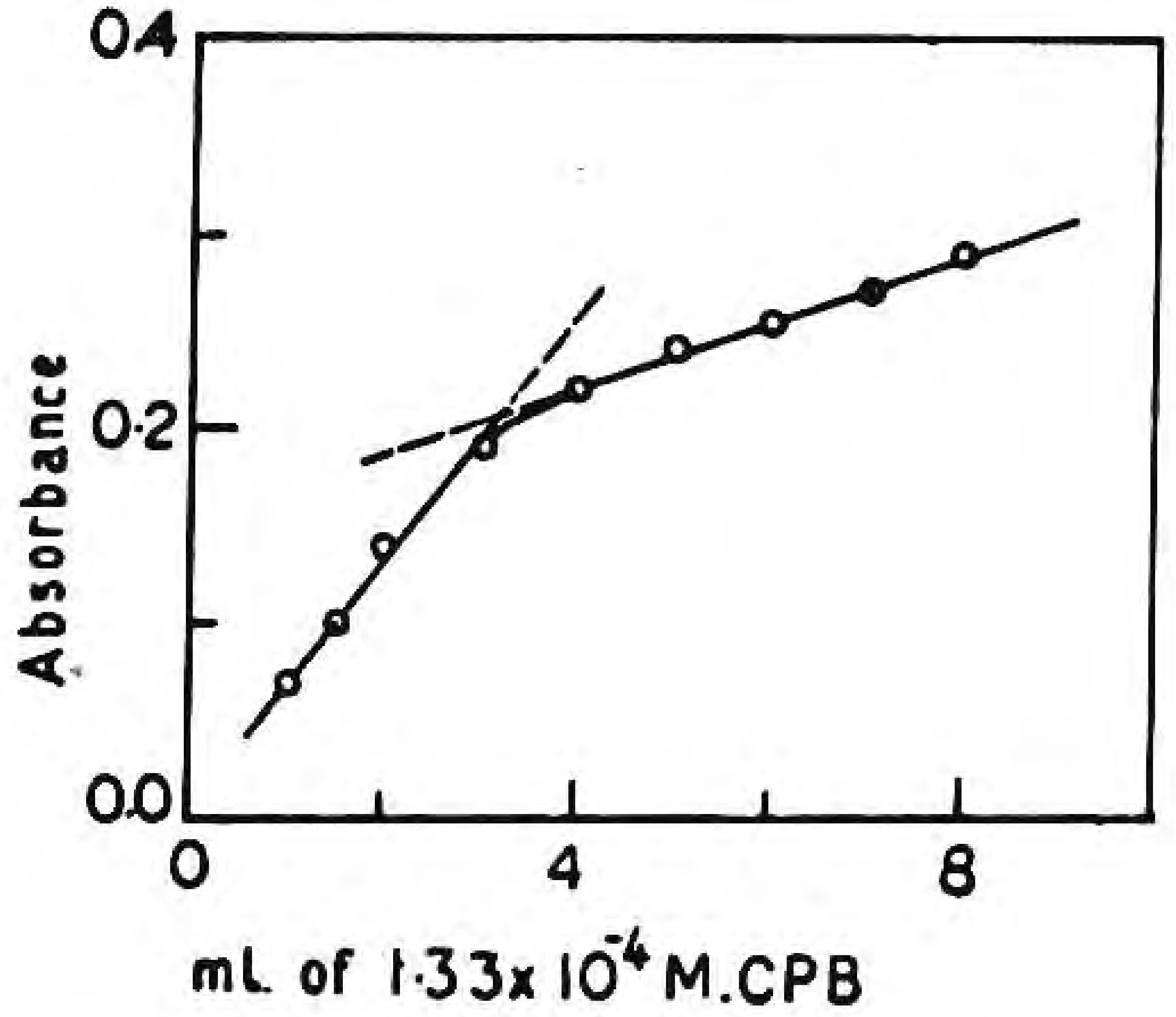


Fig.3.18 Mole ratio method

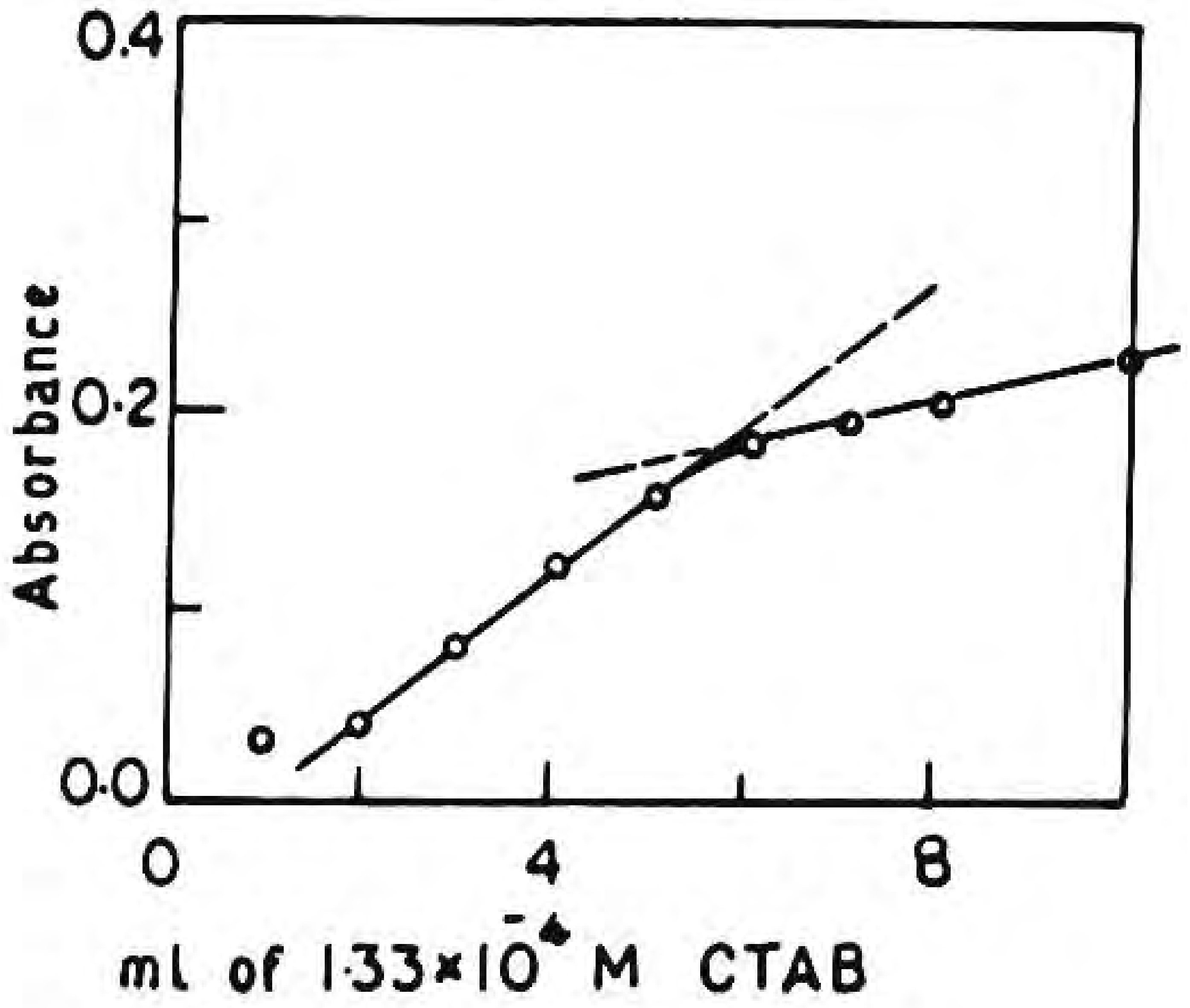


Fig. 3.19 Mole ratio method

and 6 ml in the case of CTAB, indicating that the ratio of samarium to CPB is 1:3 and that of samarium to CTAB is 1:6.

### Continuous variation method

Further evidence for the 1:3 ratio of samarium to CPB and 1:6 ratio of samarium to CTAB was obtained by the continuous variation method.

Here again the ratio of samarium to CPB/CTAB was established by converting the ternary complex into a pseudo-binary complex by keeping the concentration of methyl thymol blue in large excess over samarium.

The ratio of samarium to CPB/CTAB was established by maintaining the total concentration at 10 ml of 6.66 x $10^{-5}$ M by using solutions containing 1 to 9 ml of 6.66 x $10^{-5}$ M solutions of samarium with varying volume of 6.66 x $10^{-5}$ M CPB/CTAB. In each instance, 3 ml of 0.02% methyl thymol blue, and 2.5 ml of ammonium acetate were added and the pH was adjusted to 7. After diluting to 25 ml, the absorbance measurements were done against respective blanks at 645 nm in 10 mm cuvettes. The plot of absorbance against mole fraction of samarium is shown in Figs. 3.20 and 3.21 for CPB/CTAB systems. It is clear from the figures that the combining ratio of samarium to CPB is 1:3 and samarium to CTAB is 1:6. This difference in the surprising behaviour of CPB and CTAB is due to the inability of the former to deprotonate the phenolic group since the electrophilic nature of $CP^+$ is less compared to that of $CTA^+$ [216] .

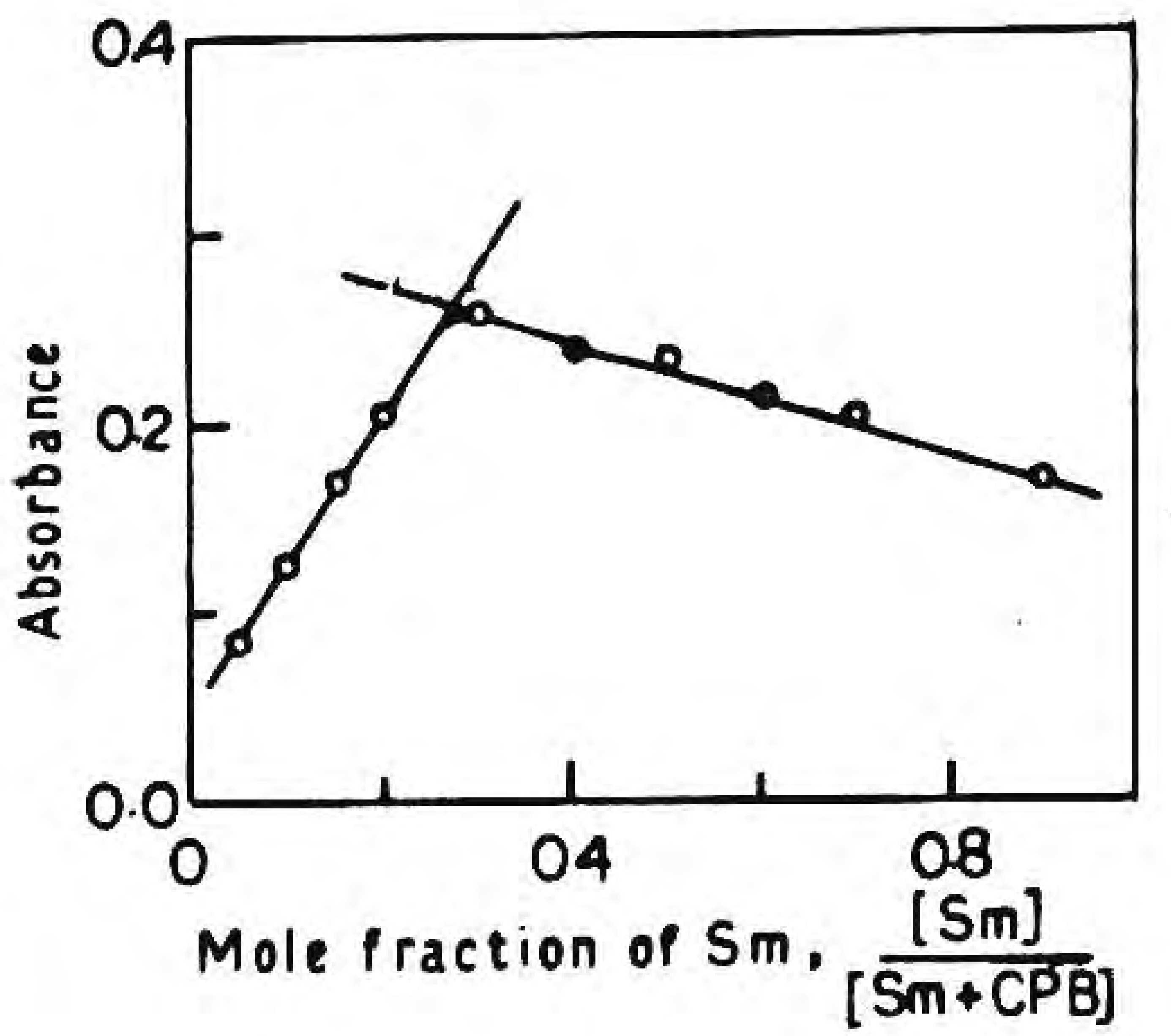


Fig. 3.20 Continuous variation method.

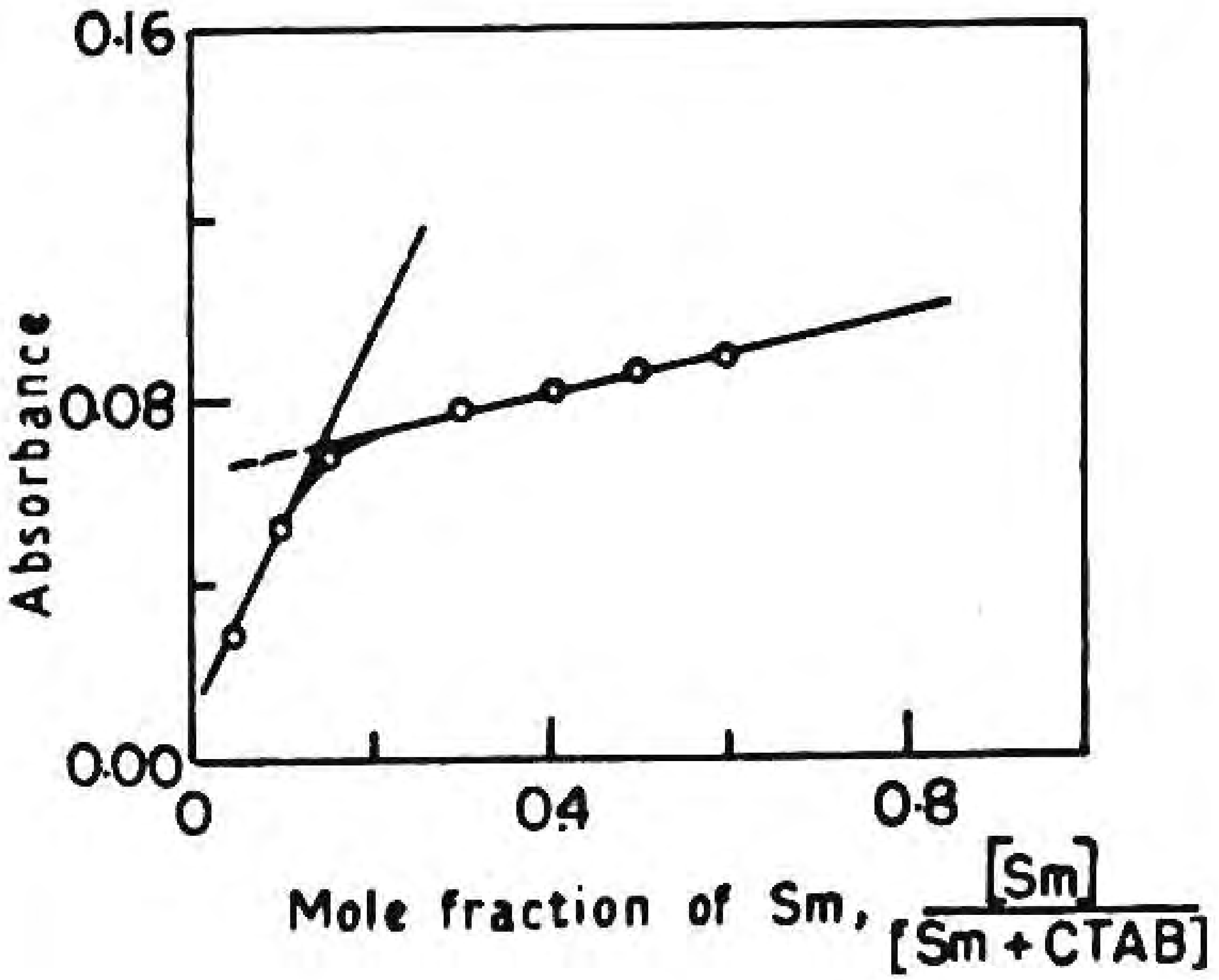


Fig. 3.21 Continuous variation method

## 3.15 INTERFERENCE STUDIES

A systematic study of the influence of a number of cations and anions on the determination of samarium was next examined. Interference was examined by adding 1 mg of interferent to 10 $\mu$g of samarium prior to the addition of other reagent solutions. The determinations were then carried out as described under "Calibration Graph". A 3 percent deviation in the amplitude obtained with samarium without any interfering ion was taken as an indication of interference. The results are summarized in Table VI.

Attempts to overcome the interference due to 1 mg amounts of various ions revealed that 2 ml of 5% sodium tartrate overcome the deleterious effects of $Bi^{3+}$, $Cu^{2+}$, $Mn^{2+}$ and $CrO_4^{2-}$. The addition of 2 ml of 5% thiourea eliminated the interference due to $Hg^{2+}$ and $Zn^{2+}$. The interference due to $Fe^{3+}$ was overcome by the addition of 2,2'-bipyridyl after the reduction of $Fe^{3+}$ to $Fe^{2+}$ by using hydroxylamine hydrochloride. Further, $UO_2^{2+}$ and $Pb^{2+}$ were masked by adding 2 ml of 5% sodium carbonate and thus eliminating their interference effect.

## Table VI

### Interference studies

| Interferents | Remarks |
|---|---|
| $Li^+$, $Ba^{2+}$, $Ca^{2+}$, $Sr^{2+}$, $Mg^{2+}$, $NH_4^+$, $MoO_4^{2-}$, $WO_4^{2-}$, $AsO_2^-$, $NO_3^-$, $S_2O_3^{2-}$, $SO_4^{2-}$, $Br^-$, $Cl^-$, $I^-$, $ClO_4^-$, $SCN^-$, tartrate, thiourea, thioglycollic acid, sulphosalicylic acid, 1,10 - phenanthroline, 2,2'-bipyridyl, hydrazine sulphate, hydroxylamine hydrochloride and ascorbic acid | No interference |
| $Al^{3+}$, $Cu^{2+}$, $Zr^{4+}$, $Hg^{2+}$, $Ti^{4+}$, $Fe^{3+}$ | Interfered by precipitation |
| $Bi^{3+}$, $Cd^{2+}$, $Co^{2+}$, $Ni^{2+}$, $UO_2^{2+}$, $Mn^{2+}$, $Pb^{2+}$, $Zn^{2+}$ | Interfered by enhancing the absorbance |
| $Be^{2+}$, $CrO_4^{2-}$ | Interfered by lowering the absorbance |

Interference of other rare earth elements

A systematic study of the influence of other rare earth elements was carried out in the determination of samarium by the third order derivative molecular absorption spectrophotometric procedure based on the sensitization of samarium - methyl thymol blue binary complex with cationic surfactants. $Gd^{3+}$, $Tb^{3+}$, $Dy^{3+}$, $Ho^{3+}$, $Tm^{3+}$ and $Lu^{3+}$ did not find to interfere in the trace determination of samarium by the developed procedure. However, $Y^{3+}$, $La^{3+}$ and $Nd^{3+}$ were found to interfere even at equal amounts to that of samarium. Hence the developed procedure can be reliably used for the trace determination of samarium only in presence of middle and heavier rare earth elements.

## 3.15 EXPERIMENTAL

### 3.15.1 Apparatus

A microcomputer based spectrophotometer system was used. This consists of a Hitachi Model 220 double beam spectrophotometer with an extended programme. This instrument has a scan speed range of 15-480 nm min$^{-1}$.

A pair of 10 mm matched quartz cuvettes which were periodically cleaned with $H_2SO_4$ + $HNO_3$ mixture and thoroughly washed with conductivity water was used in this study. ELICO digital pH meter was used for adjusting the pH.

### 3.15.2 Reagents

All reagents used were of analytical reagents grade.

**1. Samarium (III) stock solution (1000 ppm)**

Dissolve 0.2899 g of samarium oxide (99.99% purity, IRE, Alwaye, India) in minimum amount of hot 1:1 HCl and diluting to 250 ml with double distilled water. Standardize this samarium solution by titration with EDTA and dilute suitably to obtain 10 ppm solution.

**2. Methyl thymol blue solution (0.02%)**

Dissolve 0.2 g of methyl thymol blue (E. Merck, Darmstadt) in double distilled water and dilute to 1 L.

**3. CTAB solution (1%)**

Dissolve 1.0 g of cetyl trimethyl ammonium bromide (CTAB) in double distilled water and dilute to 100 ml.

**4. CPB solution (0.25%)**

Dissolve 0.25 g of cetyl pyridinium bromide (CPB) in double distilled water and dilute to 100 ml.

**5. Ammonium acetate buffer (pH 7), 0.1 M**

Dissolve 3.85 g of ammonium acetate in 450 ml of water and adjust the pH to 7 using a pH meter and then dilute to 500 ml with water.

### 3.15.3 Notation of amplitude measurements

The notation for amplitude measurements is essentially the one recommended by Fasanmade and Fell[211] and described elsewhere also[214].

The letter D is used to indicate that an amplitude of a peak has been measured in the derivative domain. The order of derivative (e.g. 1, 2, 3 or 4) is specified by a leading superscript to the letter D, e.g. $^{1}D$, $^{2}D$, $^{3}D$ or $^{4}D$. The wavelengths between which the derivative peak is measured are specified by subscripts separated by a comma. The first wavelength corresponds to the more positive amplitude while the second defines the position of the more negative value. Hence, $^{3}D_{670,680}$ describes the peak amplitude (usually in arbitrary units) that has been measured between the more positive displacement of the peak at 670 nm and the more negative displacement at 680 nm in the third order derivative spectrum.

### 3.15.4 Procedure

Transfer a suitable aliquat (15 ml) of sample solution containing 1-30 μg of samarium into a 25 ml volumetric flask. Add with mixing 3 ml of methyl thymol blue, 2.5 ml of ammonium acetate buffer (pH 7) and 1 ml of CTAB or CPB solution. Dilute the solution to mark with double distilled water and record the third order derivative spectra in the wavelength range 700 to 650 nm. Prepare a calibration graph by measuring the amplitudes at $^{3}D_{670,680}$.

# CHAPTER IV

# PRECONCENTRATION

According to IUPAC [217], 'Preconcentration' is defined as an operation (process) as a result of which the ratio of the concentration or the amount of microcomponents (trace constituents) or macrocomponents (matrix) increases. Preconcentration improves the analytical detection limit, increases the sensitivity by several orders of magnitude, enhances the accuracy of the results and facilitates calibration. In addition, preconcentration allows the sample volume taken to be increased and so improves the representative nature of the results. Preconcentration, is carried out when sufficiently large samples are available. In general, it can be referred to as the enrichment process consisting of either stripping the major components from the minor ones or extraction of the analyte into a second phase of less volume than original.

In trace analysis, a preconcentration procedure is not simply an alternative to the use of sophisticated instrumentation, but is often an integral stage in the sample treatment before the final measurement. When the species of interest have to be determined at or below the detection limit of the instrumental method, preconcentration is essential to raise the analyte concentrations to measurable levels. Sometimes the preconcentration enables simpler instruments to be used in the final measurements which can simplify automation.

In principle, any preconcentration method can be coupled with almost all analytical techniques to get the above advantages. However, preconcentration increases the time required for analyses, complicates the analyses and may involve risks of contamination and losses of trace elements or of certain species in some cases. The merits and demerits of more commonly used preconcentration procedures with some examples are discussed in this Chapter[218].

## 4.1 EVAPORATION

The most obvious and straight forward method for preconcentrating ions from solution is evaporation of the solvent. Evaporation collects quantitatively all nonvolatile elements irrespective of their specificity; it requires little attention or manpower. The problem of contamination which is inherent in most preconcentration techniques is minimised, in evaporation technique. Compared with inorganic chemistry, evaporation is more versatile in organic chemistry.

This technique has some drawbacks; the evaporation step is time consuming. If the sample is highly saline, or hard, then the preconcentration may not be efficient and sensitive. Incomplete recovery of the evaporation residue from the containers can lead to errors. This type of errors can be minimized by using internal standard. In addition, the variability of the residue from various types of samples implies variable matrix effects unless sophisticated matrix correction procedures are applied or unless a diluter is used at the expense of lowering the detection limits.

Preconcentration of trace elements in water had been carried out by evaporation in a rotary evaporator and subsequent determination using inductively coupled plasma atomic emission spectrometry (ICPAES) was developed by Nishikawa et al[219]. Meier et al[220] and Cornil and Ledent[221] mixed the evaporation residue of water sample with an organic binder to reduce matrix effects for x-ray fluorescence (XRF) spectrometric determination.

Trace amounts of cadmium in various biological matrices and cobalt, chromium, copper, iron, manganese and nickel in light conducting glassy materials[222] were determined using atomic absorption spectrometry (AAS) after preconcentration by volatilisation of large volume of sample. The vapour filtration procedure[223] offers an interesting approach atleast for similar samples with low salinity. The cellophane bottom of a container was permeable to water vapour but not to water or dissolved material. The bottom surface was exposed to vacuum, the water vapour was pumped away and all the dissolved materials were left behind on the membrane. In combination with proton induced x-ray emission spectrometry (PIXES), typical detection limits of 0.1 - 3 $\mu g\ l^{-1}$ have been achieved[224].

'Freeze-drying' of 80 ml of waste water on 1.2 g of cellulose followed by grinding and pelletizing of the residue for energy dispersive x-ray fluorescence (EDXRF) spectrometry led to 0.1 $mg\,l^{-1}$ detection limits for many elements[225]. Spotting of sample to a thin Formvar or Mylar carrier and subsequent evaporation for preconcentration had also been reported[226-231]. The detection limit obtained in such type of concentration for PIXES technique was 10 $\mu g\ l^{-1}$. Pfeiffer and Zemany[232] described the method of impregnating a filter paper along with the sample solution and evaporating the solution in the presence of filter paper. The constituents of sample solution were concentrated on the filter paper which could be used for wavelength dispersive x-ray fluorescence (WDXRF) spectrometric determination. The sensitivity of the procedure had thereby improved. The ring oven technique recommended by Ackermann et al[233] improved the sensitivity of the procedure.

Johnson and Nagel[234] proposed spotting the sample within a controlled area which was obtained by applying a hydrophobic wax ring on the filter paper. The hydrophobic wax ring reduced the spreading of the solution in the filter and any differential chromatographic effects, increased the sensitivity and reduced errors arising from heterogeneous analyte distribution.

The preconcentration by evaporation seems to be a very simple technique eventhough time consuming since it does not depend on any external factors. This is suitable for simple screening of samples when extreme sensitivity, accuracy and versatility are not required and when the trace metal speciation is complex or variable.

## 4.2 ION EXCHANGERS

Materials with ion exchange properties have extensively been used for preconcentration in both the batch and the column mode. The effect of the ion exchange resin particle size is also important for selective preconcentration.

The preconcentration of fifteen trace elements from aqueous solution as their complexes with six organic compounds on amberlite XAD-4 had been reported. The resin could be used for selective trace separation by appropriate choice of complexing agent and pH. The metals were eluted readily from the resin with 1 M-$HNO_3$ in acetone and determined by flame or graphite tube AAS[235]. However, ordinary cation and anion exchangers are of limited use for concentrating trace elements from natural water because of their inability to exclude major ions selectively. This can be applied if limited amount of alkali and alkaline earth ions are present. Tanaka et al[236] described a method for the determination of trace amounts of iron(III) in environmental waters by using Dionex cation exchange column (20 cm x 3 mm). Then the metal was eluted with 5 mM ethylene diamine tetraacetic acid (EDTA) of pH 3.2 at 1.0 ml $min^{-1}$ and the absorbance of the Fe(III)-EDTA complex in the eluate was measured at 260 nm and a temperature of $40^{o}C$ was used. The coefficient of variation was found to be approximately 3% for a concentration of 10 ppb.

Chelating ion exchange resins are more promising, i.e. Dowex A1 or chelex 100 with iminodiacetate functional groups are more popular. Generally it offers very high distribution ratios for transition metal ions, mercury and lead, but not for alkali ions. The potential of chelex 100 resin for the preconcentrations in the analysis of ground water and rain water showed that9000 mg $l^{-1}$ sodium ion and 200 mg $l^{-1}$ calcium ion[237] could be tolerated. In XRF spectrometry after the collection of trace metals, the resin with metals is used to pelletize for subsequent determination. An ion exchanger "SRAFION NMRR" had been used for the enrichment and separation of traces of molybdenum, uranium, silver, chromium, copper, iron, manganese, nickel, lead and zinc from sea water[238]. Leyden et al[239] used 100 mg of polyamine-polyurea resin columns to preconcentrate nickel, copper and zinc quantitatively from 1 litre of sea water of natural pH and to determine these trace metals by WDXRF spectrometry down to 0.1 - 0.3 μg $l^{-1}$

concentration. (Inspite of the 16 g $l^{-1}$ of $Na^+$, 1300 mg $l^{-1}$ of $Mg^{2+}$ and 500 mg $l^{-1}$ of $Ca^{2+}$ normally present in sea water).

Ion exchangers are used to recover hydrated ions, charged complexes and ions complexed by labile ligands. The recovery depends on the distribution ratio of the ion on the resin, the stability constants of the complexes in the solution, the exchange kinetics and the presence of other competing ions. The ion exchange resins efficiently collect trace amounts of transition metals as their stable complexes or after adsorption on colloids. The use of chelex 100 for trace metal preconcentration had been criticized by Florence and Batley[240]. Abdullah et al[241] found that the metals in colloidal form or adsorbed on particulates which could be separated from the sample by centrifugation were not retained by chelex 100, while only the dissolved and electroreducible species of copper, zinc, lead and cadmium corresponded to the fraction taken up by the resin. This resulted in poor recoveries of colloidal and adsorbed species of metals.

Ion exchange method for the preconcentration using resins show some drawbacks. The sensitivity is not optimal because the preconcentration factor (ratio of original to final sample weight) is around 5000 only (eg. 100 mg of ion exchanger per 500 ml of sample usually). The eluting agent, pH and the collection of different fractions require greater skill in almost all techniques except XRF. In XRF spectrometry, after column preconcentration, the ion exchanger should be homogenized and pelletized.

## 4.3 ION COLLECTING FILTERS

Ion collecting filters can be used for preconcentration if quantitative recovery is obtained by a single filtration step at natural pH. Ion collecting filters are more attractive for combination with XRF spectrometry than with any other analytical technique. The advantage is that the loaded filter is a thin homogeneous target which can be used directly to the XRF determination without any sample preparation. Thin targets offer optimal sensitivity and accuracy because the absorption enhancement corrections remain small and the background of exciting radiation is limited. Ideally, particulate and dissolved trace metals in tap water can be determined by plugging a filter holder with both a common filter and an ion collecting membrane on to the tap, running a certain volume of water through it and subjecting both loaded filters to XRF spectrometry.

Campbell and coworkers[242-244] used Reeve - Angel cation-exchange papers, SA-2 for the preconcentration and quantitative recovery of a dozen cations at pH 2 and also reported good collections on Reeve-Angel anion-exchange papers, SB-2 with quaternary ammonium groups. The detection limits were just below 1 µg for WDXRF spectrometry.

The SA-2 filters with sulphonic acid functional groups containing approximately 50% amberlite IR-120 resin and 50% cellulose were also used. Some preliminary studies[245-256] showed that they were having an exchange capacity of 2 meq $g^{-1}$. The usual sample volume was 10–100 ml and number of passes were 6-10. The reported detection limits were between 10 and 400 $\mu g\ l^{-1}$. Later studies showed that the exchange capacity had decreased to 0.25 meq/filter in the presence of large amounts of alkali and alkaline earth ions. Since the collection of transition metal ions was not quantitative for large sample volumes of natural water in which alkali and alkaline earth ions were abundant, the applicable sample volume was limited to a great extent. The preconcentration factor was too low and relevant detection limit became very poor. SA-2 filters were not ideal for direct XRF spectrometric determination of waters. Ulrich and Hopka[257] used the SB-2 anion exchange filters for trace metal collection from natural waters after a complexation step at pH 12 with 0.01 - 0.2 mM cyanide or with 0.02 mM BPPM-S [2-(3'-sulphobenzoyl)-pyridine-2-pyridyl hydrazone]. Kingston and Pella[258] used SA-2 filters for the determination of nickel, manganese, zinc, copper and lead in sea water at the 2-4 $\mu g\ l^{-1}$ level with a standard deviation of only 0.2 $\mu g\ l^{-1}$ by EDXRF spectrometry. The sea water was first processed for the separation of the trace elements from sodium, potassium, calcium and magnesium on a chelex-100 column and the eluate was evaporated, heated to sublime ammonium salts, taken up in acid and then only passed through SA-2 filters.

Acropor CH filters[259] with chelex 100 or iminodiacetate groups were found to be better than SA-2 filters especially due to the less affinity towards alkaline earth ions. Cellulose powder films with immobilized chromotropic acid functional groups[260] were also used, but it suffered from the interferences of $Na^+$ and $Ca^{2+}$. Hyphan filters were prepared by immobilizing 1-2(-hydroxyphenylazo)-2-naphthol on short fibred cellulose powder which had a 0.05 meq exchange capacity. High recoveries of trace metals were possible from 3 litre of fresh water and 0.5 M sodium chloride solutions at a flow rate upto 18 ml $min^{-1}$ $cm^{-2}$ at pH 7 and the detection limits for EDXRF were around 1 $\mu g\ l^{-1}$[261-263].

Smits and Van Grieken[264] immobilized cellulose filters with 2,2'- diaminodiethylamine (DEN) functional groups for trace anion preconcentration from aqueous solution with subsequent XRF spectrometric measurement. For most oxoanions, quantitative collection was obtained at a pH 3-6 with a filtration rate upto 0.5 ml $min^{-1}$ $cm^{-2}$ from a sample volume upto 100 ml $cm^{-2}$. The DEN filter exhibited some selectivity towards oxoanions with a central metal atom. These filters were shown to preconcentrate trace cations at a pH above 5-6 with satisfactory efficiency and capacity, independent of the usually abundant alkali and alkaline earth ions in solution. Leyden et al[265-269] had observed that ethylenediamine functional groups immobilized on silica gel also collected oxoanions with a central metal ion selectively. Accuracy and precision were both around 10% for higher concentration levels. The main drawback of the DEN filters is that they are not commercially available while their synthesis is not trivial but requires some precautions.

An ideal complexing molecule for preconcentrating filters should fulfil the following requirements. (1) No affinity for alkali and alkaline earth ions, (2) High stability constants for heavy metal ions, (3) Formation of a stable molecular structure, (4) Easy immobilization onto cellulose. 2.2' diaminodiethylamine often called diethylenetriamine (DEN) satisfy these requirements very well.

## 4.4 COPRECIPITATION AND PRECIPITATION

A large number of preconcentration methods were reported using precipitation or coprecipitation coupling with various analytical technique. In analytical chemistry, the selection of specific precipitant or coprecipitant is important. These are more useful if the subsequent analytical technique requires solid samples. The simplicity of the procedure, the completeness of the precipitation and the inherent capacities available will be the most important features. For a technique like XRF spectrometry, solid samples are appropriate and due to a high inherent selectivity of the instrument; instead of selective precipitation, nonspecific multielement reagents are more attractive.

Coprecipitation is used to concentrate microconstituents of solutions to useful levels. Here concentration is accomplished by the formation of a primary precipitate in the solution which acts as a carrier or collector, for the entraminent of the microconstituents. The requirements of a precipitate to act as a collector in coprecipitation are: it should have large surface area, gelatinous character and ability to coagulate. It should not help peptization or dissolution of the precipitate formed in the solution.

Various reagents are used for coprecipitation and almost all techniques are used for the subsequent determination of elements.

The determination of trace amounts of metals in mineral water is difficult due to matrix effect and the inadequate detection limits. The traces were separated from the macrocomponents by the precipitation of their tetramethylene dithiocarbamates with iron(III) as collector or by coprecipitation on iron(III) hydroxide. By this procedure trace amounts of cadmium, cobalt, chromium, copper, nickel and lead were preconcentrated and determined using AAS by electrothermal atomization[268]. The detection limits were 0.005, 0.30, 0.08, 0.10, 2 and 0.10 $\mu g\ l^{-1}$ for cadmium, cobalt, chromium, copper, nickel and lead respectively. The results were satisfactory. The precision was 2-7%. The presence of high concentration of alkali metal, alkaline earth metal, sulphate, chloride and bicarbonate ions created unspecific absorption signals during evaporation in the atomization step. The prior separation of the metals by coprecipitation was advisable to avoid this problem. Since most mineral waters contained iron in comparatively large quantities, the suitability of iron(III) hydroxide and of iron(III) tetramethylene dithiocarbamate (TMDTC) for the coprecipitation of the above elements was examined.

When the trace elements were coprecipitated, the precipitate also adsorbed ions of the main constituents i.e. alkali and alkaline earth metals, aluminium, and other ions. It had been found that the adsorption of these elements on the precipitate of iron - tetramethylenedithiocarbamate was much lower than that on Fe(III) hydroxide and thereby the interferences were also reduced.

Sub ppb levels of cadmium, cobalt, copper, iron, manganese, lead and zinc in water samples (10 to 350 ml) containing 0.1% nitric acid were coprecipitated with 4 mg of nickel by adding 1 ml of an ethanolic solution containing 1.75% of dimethyl glyoxime and 0.2% of 1-(2-pyridylazo)2-naphthol, adjusting the pH to 10 with concentrated aqueous ammonia and keeping the solution for 1 hour at 60°. The precipitates were collected by filtration, dried and analyzed by graphite cup AAS. Calibration graphs were rectilinear in the nanogram range (upto 50 ng of Mn). The coefficient of variation was 1.1 to 4.7% (n = 4 or 5). The detection limits in 100 g samples ranged from 0.6 ng of cadmium to 10 ng of iron. The method was used to determine cadmium, copper, manganese, lead and zinc in lake water and copper, manganese and lead in coastal sea water[269]. The determination of trace impurities in high purity aluminium was determined after coprecipitation with $Ni(OH)_2$ using AAS[270]. Jackwerth et al[271] developed a method for the preconcentration of trace impurities viz. silver, bismuth, chromium, copper, iron, indium, nickel and lead from high purity cadmium. The acidic cadmium sample solution containing these impurities was treated with aqueous ammonia followed by the addition of aqueous potassium permanganate. The resulting solution was heated to 80°C and thioacetamide was added to coprecipitate partially cadmium sulphide (CdS), $MnO_2$ and the trace metals. The addition of benzil $\alpha$-dioxime to the mixture improved the recovery of nickel. The precipitate was collected and digested with nitric acid and analysed using AAS. Traces of lanthanides[272] were selectively coprecipitated with strontium sulphate and separated from milligram amounts of manganese(II) and iron(III). The determination of iron in foods of high sodium chloride concentration[273] was carried out by coprecipitating with zirconium hydroxide ($ZrOCl_2$+NaOH) and analysed using AAS after dissolving in hydrochloric acid.

Coprecipitation with gallium hydroxide[274] was studied for the preconcentration of trace metals in sea water before multielement analysis by ICPAES. **Gallium** precipitated at pH 9 only when magnesium was present. This method was free from contamination because of the use of highly pure gallium metal and a small amount of sodium hydroxide for pH adjustment. A concentration factor of more than 200 could be obtained. Detection limits ranged from a few ng $l^{-1}$ to 150 ng $l^{-1}$ for aluminium, cobalt, chromium, iron, lanthanum, manganese, nickel, titanium, uranium, zinc, yttrium and lead. Trace heavy metals[275] were quantitatively coprecipitated with indium hydroxide and floated with sodium oleate and nitrogen bubbles. Indium and the surfactant were removed by solvent extraction. Cadmium at ng $l^{-1}$ level in 20 litre of water was concentrated 2000 fold with recovery of 93%. AAS, ICP-AES and XRF spectrometry are not directly applicable to the determination of trace heavy metals at the nanogram per litre level in aqueous solutions. Because of lack of intrinsic detectability, preconcentration is always necessary in such cases. The trace amounts of copper, iron, cobalt, nickel, manganese, zinc, vanadium and chromium in high purity barium chloride and barium carbonate[276] were determined after coprecipitation with cadmium sulphide using spectrographic analysis in a 10 A d.c. arc.

The rare earth elements in the range 10-600 µg was separated from large amounts of iron, zirconium, uranium, beryllium and aluminium by coprecipitation with manganese dioxide[277]. The precipitate was filtered off and the residue was dissolved in hot $HCl-H_2O_2$ solution. The solution was evaporated and residue was dissolved in 0.01 M HCl. The rare earth elements were determined spectrophotometrically with arsenazo III. The iron in medical mud baths was determined[278] by coprecipitation with $Zr(OH)_4$ and analysed using sulphosalicylate photometry.

Rare earth elements were coprecipitated with double alkali metal - alkaline earth metal sulphates and determined by AAS, XRF spectrometry and neutron activation analysis[279]. Interference from iron(III), indium, chromium(III), titanium(IV) and zirconium were reduced by this method.

Direct XRF methods are not successful if standard samples are not available and are difficult to apply to low metal concentrations because the method lacks sensitivity. In such cases a preliminary coprecipitation is often preferred for the concentration and separation of trace elements from complex matrices. Thus the determination of vanadium in steel samples[280] was done by coprecipitation with 4-caprinoyl-3-methyl-1-phenyl 5-pyrazolone at pH 1. The precipitate was collected as a film on a membrane for XRF spectrometric analysis. The limit of detection was 2 μg of vanadium. This procedure gave satisfactory results on standard steels containing 0.003 - 0.091% of vanadium. 4-benzoyl-3-methyl 1-phenyl 5-pyrazolone (BMPP) had also been used. Similarly vanadium was coprecipitated [281] from filtered sea water with a cobalt-pyrolidine dithiocarbamate carrier complex at pH 4.0. The precipitate was collected as a thin film on a membrane filter (0.4 μm pore size) and the precipitate was analysed for vanadium by XRF spectrometry. The detection limit for 100 ml water samples and a counting time of 100 seconds was 0.02 μg vanadium $1^{-1}$. The coprecipitation efficiency in the 0-5 μg $1^{-1}$ range was 95% for V(IV) or V(V). Similarly uranium in natural waters[282] was determined after coprecipitation using an iron dibenzyl dithiocarbamate carrier complex. The precipitate was collected as a thin film and measured by WDXRF spectrometry. UV-radiation was utilized prior to coprecipitation to alleviate the effect of filter clogging colloids. The solubility and particle size of the precipitate are very important factors for quantitative recovery of the precipitate.

Supersaturation may also affect the quantitative recovery of many metals at parts per trillion concentration level. Quantitative precipitation may be achieved by the addition of a carrier ion or coprecipitant which will precipitate itself and aid in the recovery of the ion or ions of interest. Luke[283] reported the coprecipitation of uranium(VI) as hydroxide with 100 µg of iron(II) to coprecipitate at pH 9 and the coprecipitation of uranium(IV) with cupferron or phenyl fluorone at pH 4 with titanium(IV) as the coprecipitant.

Luke's well known "coprex"[283] technique involves adding diethyl dithiocarbamate (DDTC) and a spike of a suitable metal ion as a coprecipitating agent and as an internal standard, adjusting the pH and filtering for XRF spectrometric measurements. Luke recommended[283] the use of 50-200 µg of an appropriate coprecipitating element but emphasised the fact that reasonably good results could still be achieved, if the loss was not more than 10%. If this loss is constant, it gets compensated in the calibration.

Leyden[284] developed a method for the determination of traces of silver, arsenic, cadmium, cobalt, chromium, copper, iron, manganese, mercury, nickel, lead, antimony, selenium, thallium and zinc by coprecipitation with sodium dibenzyl dithiocarbamate and subsequent EDXRF quantitation. Van Grieken et al [285,286] observed that $Fe(OH)_3$ can be used as a good coprecipitant for the quantitative collection of traces of cadmium, cobalt, copper, nickel, zinc and lead. By using XRF, the detection limits were found to be $< 1$ $\mu g\ l^{-1}$. The two valence states of arsenic(III/V) and chromium(III/VI) were separated[287] by precipitation with dibenzyldithiocarbamate followed by filtration and the filtrate was coprecipitated with iron(III) hydroxide. Then the two precipitates were determined separately using XRF spectrometry. Similarly Leyden et al[288] developed a method for the separation and determination of vanadium(IV) and vanadium(V) by coprecipitation with diethyl dithiocarbamate (DDTC) at pH 4 and 1.8 respectively.

## 4.5 LIQUID-LIQUID EXTRACTION

Liquid-liquid extraction is the most popular separation-cum-preconcentration method in AAS. Extraction procedures are simple and rapid and they may be automated fairly easily. A large number of monographs and reviews on this technique are available. An excellent general survey by Bachmann[289] refers to much of the work. This separation technique is possible and is often desirable in AAS than any other technique. The choice of complexing reagent is not limited as in colorimetry where colour development by reaction with metal is essential. This is not commonly applied in XRF spectrometry mainly because subsequent evaporation is necessary and the preconcentration coefficients are quite low.

The extraction of ammonium pyrrolidine – dithiocarbamate (APDC) metal complexes into a suitable organic phase is very advantageous since the metal may be concentrated by 100 fold or more and subsequently analysed by AAS. Methyl isobutyl ketone (MIBK) is a recommended solvent for AAS. Jan and Young[290] investigated an APDC-MIBK extraction of trace metals (silver, cadmium, chromium, iron, nickel, lead and zinc) followed by back extraction with 4 N nitric acid and analysed them by flameless AAS. They also compared their results with those obtained by the chelex 100 cation exchange[291] and APDC-MIBK single extraction methods. The method proposed by Jan and Young offered the advantage in consumption of small sample volumes, better recovery and stability of the metal complexes in the acid extracts over the (i) ion exchange, and (ii) APDC-MIBK single extraction methods. A method[292] was reported for the enrichment of europium from a mixed rare earth chloride solution by liquid-liquid extraction with bis(2-ethyl hexyl) phosphonic acid in kerosine, where a three stage extraction followed by scrubbing and stripping was used. A 20 fold enrichment of europium was achieved.

Marcie[293] extracted the transition metals as their ammonium pyrrolidine dithiocarbamate complexes into chloroform. This chloroform layer was carefully evaporated on a filter paper carrier for XRF spectrometric measurement. The capacity was 300 μeq of divalent transition metals. Kuroha and Shibuya[294] extracted the metals with diethyl - dithiocarbamate from pH 5-9 medium into carbon tetrachloride, added polystyrene and an internal standard to the extract and dried it under i.r. radiation on a mylar foil to obtain a very thin film for WDXRF spectrometry. The detection limits of 0.03 - 1 µg were achieved for 15 elements with a coefficient of variation 3-5% at the 20 µg level. Another work was reported[295] where extraction was carried out with 8-quinolinol into chloroform or with trioctylamine into xylene. The radioisotope excited XRF spectrometric measurement on these water samples showed detection limits in the range 1-5 mg $l^{-1}$ level.

Magyar and Lobanov[296] extracted the trace metals into molten quinolin-8-ol and subsequently dried, remelted, cooled, ground and pelletized the organic phase for EDXRF spectrometric measurement. Such a method avoids the problems inherent in separating a small volume of organic phase from the aqueous sample and in adhesion of the organic solvent to the wall of the vessel.

Eventhough liquid-liquid extraction as a preconcentration technique is more appropriate for AAS, it can be coupled to any analytical technique with utmost care.

## 4.6 CHELATION AND SUBSEQUENT SORPTION IMMOBILIZATION

Inspite of liquid-liquid extraction, reversed phase technique with organic solvents adsorbed on the surface of a small particle support seemed to be more attractive. In these processes quantitative yields can be expected by repeating the extraction even if the distribution constants are low. In their original work, Knapp et al[297] formed the transition metal chelates with sodium diethyl dithiocarbamate and subsequently adsorbed the chelates onto chromosorb W-DMCS columns. The sorption of iron, cobalt, nickel, copper, zinc, cadmium, mercury and lead was found to be complete at pH 4 or 5. Then the carbamates were eluted with 2 ml of chloroform onto a filter paper in a special teflon container for WDXRF spectrometric measurement. For 100 ml samples the detection limits were 0.01 - 1.1 μg.

Quinolin-8-ol immobilized or crosslinked poly(vinyl pyrrolidone), a macrorecticular styrene - divinyl benzene (XE-305) or methylated polystyrene substrate was used[298] for the preconcentration of ions of cadmium, zinc, lead, copper, iron, manganese, nickel, cobalt and chromium from sea water. Then these elements were determined by electrothermal AAS. Chelating resins containing the functional groups, Ar(OH)N(OH)R had been prepared and found to retain a number of metal cations at different pH. These chelating resins were useful for separation and concentration of a variety of metal ions. In some cases the complex was so strong that rapid quantitative elution of the metal ion became a problem. Usually hydroxamic acid[299] had been used as a complexing agent and metal complexes were sorbed on a small resin column. The sorbed complexes were eluted from the column by an organic solvent. The above procedure had also been used with quinolin-8-ol[299] as the complexing agent. The sequence of complexation, sorption and elution has several advantages over the complexation and solvent extraction procedures that are widely used for concentration prior to measurement of metal ions by AAS. Sorption can provide larger concentration factors than those by liquid-liquid extraction. Also manipulation is reduced and water miscible organic solvents can be used in the complexation and sorption procedure.

Microgram amounts of lanthanides and yttrium were preconcentrated[300] by passing a 0.5 to 2 litre sample (pH 6), 0.5 M in sodium chloride at 10 ml $min^{-1}$ through a bed (diameter 2 cm, height 7 mm) of poly(arsenazo-N) fibrous chelating sorbent previously used for the preconcentration of uranium(VI). The retained analytes were eluted with $\geq$ 30 ml of 6 M-HCl or 5 M-$H_2SO_4$. If the analysis is in natural water, fulvic acids if present do not interfere. Uranium, thorium, zirconium, hafnium, niobium, tantalum, protoactinium, americium and curium were preconcentrated together with the rare earth elements. A column of chelax 100 chelating ion exchanger[301] was used to preconcentrate traces of cadmium, copper, lead and zinc present in drinking water. These elements were eluted with $HNO_3$ and determined by AAS.

Water soluble polymeric chelating agents poly(vinylamines ), poly(acrylic acid), poly(ethylenimine) and some copolymers and their derivatives of molecular weight 20000 to 200000 can be used for the separation of metal ions[302].

2,2'-dipyridyl-4-amino-3-hydrazino -5-mercapto-1,2,4-triazole-hydrazone (DPTH) was prepared[303] and immobilized on silica gel. This material was used to preconcentrate traces of copper, zinc, lead, nickel, cadmium and cobalt. After sorption, copper, zinc, cadmium, nickel and lead were quantitatively eluted with 0.1 M ethylenediamine tetraacetic acid solution, while cobalt remained on the silica gel. It was also observed that copper, zinc, cadmium and nickel were quantitatively eluted with 0.1 M potassium cyanide. About 85% of the cobalt was eluted with this cyanide solution, but lead remained on the column. Cobalt was quantitatively eluted from the column by $\geq 1.5$ M perchloric acid but elution of DPTH from the gel was also observed. The eluted metal ions were analysed by AAS.

Acid washed native cellulose crosslinked with formaldehyde, acetyl cellulose or Baker RP-$C_6H_5$ was used in batch or column procedures[304] to retain trace metals from aqueous solution as their complexes with ammonium pyrrolidine-1-carbodithioate, dibenzyl ammonium dibenzyl dithiocarbamate or hexahydroazepium hexahydroazepine-1-carbodithioate. This sorption method was used to determine trace metals in aluminium samples, in water and in biological materials. Preconcentration of HMDC complexes on acetyl cellulose in batch mode took $\sim$ 30 minutes at $\mu g\ l^{-1}$ concentration. Determination was done by AAS or ICP-AES The method was used to determine calcium, cadmium, cobalt, copper, nickel and lead in urine, these metals and iron in bovine liver and 10 elements in high purity aluminium and in water.

Use of the bonded glass beads as adsorbent was preferred to that of amberlite XAD-2 or XAD-7 resin since the latter required more eluent to desorb the complex from XAD-2 and the complex cannot be eluted at all from XAD-7. Thus for the determination of bivalent iron it was treated with bathophenanthroline at pH 3 and the solution was passed through a column packed with $C_{18}$ bonded glass beads[305]. The adsorbed complex was eluted with a mixture of ethanol and dimethyl sulphoxide, an aliquot of the eluate was made upto 25 ml with ethanol and the absorbance was measured at 534 nm. A column of trioctyl-ammonium chloride supported on poly(tetrafluoroethylene) was used to preconcentrate trace impurities of sodium, potassium, calcium, manganese, iron and copper present in high purity molybdenum and its compounds[306]. The analytes were eluted and subjected to polarographic method for determination.

Silylated controlled pore glass was used as a preconcentration material[307,308] prior to XRF spectrometric determination of trace elements. The silylated controlled pore glass acted as an immobilized chelating agent removing trace metals from aqueous solutions. These materials were found to have capacities similar to chelating resins, yet equilibrated much faster with metal ions in solution. Controlling pore glass support for the silanes offered low flow resistance and relatively large surface area. These properties which made the silylated controlled pore glass ideal for use as a preconcentration agent suggested that it could be used as a stationary phase in ligand exchange chromatography. N- $\beta$ -amino ethyl - $\gamma$ -amino propyl silane (Dow Corning Z-6020) immobilized on a silica substrate filled in a column was used[309] to preconcentrate traces of tungstate and molybdate from aqueous concentrated sodium chloride solution.

A very popular and promising procedure consists of chelation followed by immobilization on activated carbon, the most traditional of all adsorbents. Activated carbon is a good adsorber for organic colloidal material and for trace metals that are bound to organic or colloidal matter. Free ions are not quantitatively adsorbed onto activated carbon, but addition of a chelating agent will convert them to an adsorbable form. The addition of chelating agent and subsequent adsorption on activated carbon is a very powerful technique for collecting both originally free and colloidal organic trace metal species. Jackwerth et al[310] were the first to exploit this idea for preconcentrations in AAS. For chelation and immobilization quinolin-8-ol is a suitable multielement chelating agent because the chelates exhibit high stability constants at nearly natural pH levels for many transition metal ions; further the quinolin-8-olates can be adsorbed onto activated carbon very efficiently and straightforwardly. Koshima and Onishi[311] studied the adsorption of 20 metal species by activated carbon from aqueous solutions of pH 1-13. The determination of selenium[312] at mg $g^{-1}$ to $\mu$g $g^{-1}$ in biological and environmental samples was carried out by reducing selenium using 4 N HCl-ascorbic acid and adsorbing on activated carbon. The analysis was done using EDXRF spectrometry.

## 4.7 ELECTRODEPOSITION

Electrodeposition is more sophisticated and has a very different approach as a preconcentration technique.

Electrochemical preconcentration techniques[313] could be used in atomic absorption analysis of trace metals in the presence of high concentration of salts which would otherwise give rise to unspecific light losses. In one version of the technique[314] the metal in question was deposited electrolytically onto a thin metal wire and was then atomized by electrical heating of the wire. This method had been successfully applied to the determination of cadmium in water[315] and urine[316]. In another approach the metals were preconcentrated on a graphite rod, which was dried and ground and a portion of the graphite powder was finally analysed in a graphite furnace. These techniques utilized flameless atomization of the metals after the preconcentration step. The metals like platinum, iridium, tungsten and tantalum had all been used as filament materials in AAS. The purity of the wire was very important.

The choice of deposition potential depends on the metal which is of interest. The more negative the potential, the more elements are deposited onto the filament. The solution should be well buffered; otherwise may lead to precipitation of metal hydroxides.

Cathodic deposition has been applied for preconcentrations from sample solutions. Vassos et al[317] determined 2-40 μg of chromium, cobalt, copper, mercury, nickel or zinc by constant current electrodeposition on 1 cm diameter graphite rod electrodes in 15 ml of solution containing low concentrations of supporting electrolyte to stimulate natural waters. The electrodeposition of anionic complexes[318] from mixed organic aqueous media in a high potential electric field was also reported. In this study, detection limits around 1 μg $l^{-1}$ were claimed for cobalt, nickel, copper, zinc and cadmium.

Various other techniques which are recently used for preconcentration purposes are osmosis, transport on supported liquid membrane etc. The transport of divalent copper across a liquid membrane consisting of LIX-64 N (mixed oximes) in kerosine on a celgard 2400 microporous polypropylene support was reported. The copper transported was determined by AAS[319] . Preconcentration of traces of cadmium, copper, manganese, nickel and zinc in the range 20 μg $l^{-1}$ to 20 mg $l^{-1}$ with or without EDTA chelation was obtained by osmosis[320] . A two block plexiglas cell into which four channels were cut, had been used for upto nine fold concentration of aqueous solution by osmotic extraction of water into concentrated sodium chloride solution, via a cellulose acetate membrane. The concentrated sodium chloride solution obtained as extractant enriched in analytes was analysed by ICP-AES Recoveries were within the range 90 to 95%.

The preconcentration techniques described in this Chapter have their own merits and demerits. However, these factors depend to a greater extent on the instrument to be used for further analysis. Some instruments are capable of doing multielement analysis like XRF spectrometry, ICPAES, neutron activation analysis etc. Indeed no method is simultaneously extremely sensitive, applicable over an infinite concentration range, free of interference and matrix effects and capable of determining all elements in their different oxidation states. Hence, a suitable preconcentration technique together with analytical instrument can be selected depending on the type and variability of samples, number and concentration of elements to be assayed and on the relative importance that one attributes to speed, quality and cost of the analysis.

# CHAPTER V

# COPRECIPITATIVE PRECONCENTRATION AND EDXRF DETERMINATION OF RARE EARTHS

A number of methods were developed[321-323] for the determination of rare earth elements using wavelength dispersive x-ray fluorescence (WDXRF) where low energy L x-rays are used. Almost all methods consist of the direct determination of the rare earth elements present in the sample without any sample pretreatment. Some methods[121,131] consist of the conversion of the rare earth elements of the sample into oxalate and oxalate was pelletized with boric acid for x-ray fluorescence analysis. The conventional x-ray tube excitation of the WDXRF did not sufficiently excite K x-rays. The major limitation of using L x-rays for the determination of rare earth elements was that they are strongly overlapped by the K x-rays of elements with low atomic numbers. This is important in the analysis of rare earth elements in lateritic and xenotime samples due to the presence of varying amounts of iron and titanium. This problem was only partially overcome because of high spectral resolution in WDXRF while it is compensated in energy dispersive x-ray fluorescence (EDXRF) by computer programmes[324-326]. Recently Madanlal et al[327] have improved the detection limits in the determination of rare earth elements obtainable with EDXRF by employing close coupled side source geometry instead of conventional uncollimated annular geometry.

The energy dispersive x-ray fluorescence gives low sensitivity which is inherent in the technique compared to WDXRF. Preconcentration is an adequate step especially for the determination of traces of elements with good detection limits. Here, preconcentration increases the amount of metal which can be measured by the EDXRF. Many preconcentration procedures were described in Chapter IV. Among them, coprecipitation is one of the most widely used techniques for preconcentration as explained in Chapter IV.

Jackwerth et al[328] developed a method for the determination of traces of silver, bismuth, cadmium, cobalt, copper, mercury, indium, molybdenum, nickel, lead, selenium and zinc present in soil and sediment samples by precipitation with hexahydroazepine-1-carbodithioate with some of the iron as coprecipitant. This was subjected to atomic absorption spectrometric determination after dissolving in nitric acid. The limit of detection obtained was in the range 0.1 to 1.0 ppm with ~ 3% coefficient of variation. Cerium, europium, holmium and lutetium were separated by coprecipitation with strontium sulphate[272]. The trace elements present in water were preconcentrated[285] by coprecipitation with iron hydroxide and subsequently determined by XRF. High recovery of nickel, copper, zinc and lead was obtained in this study. The water sample was treated with 2 mg of iron(III) and the pH was adjusted to 9 with sodium hydroxide and after one hour the solution was filtered through a nucleopore membrane. The precipitate was dried and subjected to XRF analysis. Submicrogram amounts[277] of rare earth metals (10 to 600 $\mu$g) were separated from large amounts of iron, zirconium, uranium, beryllium and aluminium by coprecipitation with manganese dioxide in solutions of ammonium fluoride in alkaline medium. The mixture was boiled and the precipitate was filtered and dissolved in hot hydrochloric acid - hydrogen peroxide solution. The solution was evaporated and the residue was dissolved in dilute hydrochloric acid and rare earth metals were determined spectrophotometrically with arsenazo III. Leyden[284] developed a method for the preconcentrative determination of traces of silver, arsenic, cadmium, cobalt, chromium, copper, iron, manganese, mercury, nickel, lead, antimony, selenium, thallium and zinc by coprecipitation using sodium dibenzyl dithiocarbamate. The coprecipitated mixture was subjected to EDXRF analysis. The iron content of food materials[273] of high sodium chloride concentration was determined by coprecipitation with zirconium hydroxide and subsequently analysed by atomic absorption spectrometry. Around 90% recovery of rare earth elements[279] was obtained by coprecipitation with alkali metal-alkaline earth metal sulphates. The determination can be done by atomic absorption spectrometry, XRF or neutron activation analysis. Cadmium, cobalt and europium were coprecipitated[286] from synthetic sea water with $Fe(OH)_3$ by the addition of $FeCl_3$ and aqueous ammonia. The precipitate was allowed to settle for one hour and was collected on a nucleopore membrane for radiochemical studies.

Similarly, as coprecipitants, cobalt pyrolidine dithiocarbamate [281] and 4-caprinoyl-3-methyl 4-phenyl 5-pyrazolone[280] for vanadium, dibenzyl dithiocarbamate[287] for chromium and aresenic, iron dibenzyl dithiocarbamate[282] as carrier complex for uranium, gallium hydroxide[274] for aluminium, cobalt, chromium, iron, lanthanum, manganese, nickel, titanium, uranium, zinc, yttrium and lead, iron tetramethylene dithiocarbamate[268] for cadmium, cobalt, chromium, copper, nickel and lead were also reported. The use of iron(III) hydroxide as coprecipitant for rare earth elements and subsequent determination using EDXRF in derivative mode are described in detail in this Chapter.

## PRELIMINARY STUDIES

Preliminary studies indicated the quantitative coprecipitation of rare earth elements onto iron(III) hydroxide from weakly to strongly alkaline solutions. This was evidenced by the absence of these elements in centrifugate as determined by titrimetrically using xylenol orange[4] and spectrophotometrically using arsenazo 1 [4].
The feasibility of iron(III) hydroxide as collector for rare earth elements from liquid samples and subsequent quantitation by EDXRF was investigated systematically.

The EDXRF spectrum obtained with ethyl cellulose (0.5 g) pellet when irradiated for 10 minutes with 50 mci Am-241 annular source with a Si(Li) detector and the EDXRF spectrum obtained under identical conditions for ethyl cellulose pellet consisting of 10 mg of Fe(III) have exactly identical features at the energies corresponding to the characteristic K x-rays of all rare earth elements. The spectral characteristics of EDXRF spectra obtained with 100 µg each of neodymium and samarium in ethyl cellulose matrix remain unchanged even by the addition of 5-20 mg of iron(III) to ethyl cellulose matrix.

The above observations clearly indicate the possibility of determining trace amounts of rare earth elements present in liquid samples by EDXRF, if the coprecipitation of rare earth elements onto iron(III) hydroxide is precise and quantitative.

Initial experiments showed that the traces of rare earth elements were coprecipitated along with iron(III) hydroxide in alkaline medium. The coprecipitated mixture was digested on a steam bath. After cooling, the iron(III) hydroxide along with the coprecipitated rare earth elements was vacuum filtered through ethyl cellulose powder supported on a Whatman No.41 filter paper. The filter paper containing ethyl cellulose and coprecipitated iron(III) hydroxide was dried in hot air oven ( $\sim 100^{o}C$) for one hour. The contents from the dried filter was scraped and transferred to an agate mortar. The contents were homogeneously powdered and pressed in the form of pellets in a 1 inch die by applying a pressure of 5 tons per square inch in a carvar press.

The EDXRF system consisted of a Si(Li) detector mounted inside a cryostat situated at a distance of 5 mm from window. The window was made of beryllium of thickness 1 mil. The characteristic K x-rays of rare earth elements were produced by radioisotope excitation. An annular source holder containing the annular source Am-241, 50 mci, 59.57 Kev, 1 inch active dia provides x-rays for excitation.

The pressed powder pellets were analysed by irradiating with 50 mci Am-241 source for 10 minutes in a mylar based sample holder (1 inch diameter). Each element was counted thrice by using multichannel analyser. The background obtained by average of low and high backgrounds was subtracted from the measured peak intensity to give the net peak intensity. The average of three net peak intensities was then calculated from three individual measurements. The average of average values obtained in three sets of samples was then used to obtain the calibration graphs. Various parameters that influence the coprecipitation of rare earth elements with iron(III) hydroxide was investigated systematically. Since all rare earth elements behave identically, the results obtained with a key element viz. samarium alone was described in detail for unambiguity.

## 5.1 EFFECT OF pH

The effect of pH on the collection of rare earth elements was examined over the range 4 to 12 in steps of 1. The trace amounts of rare earth elements were coprecipitated with iron(III) hydroxide. In this study, 50 µg each of rare earth elements present in a total volume of 500 ml was treated with 5 mg of iron(III). Then the pH of the solution was adjusted in the above range one after another, using sodium hydroxide and hydrochloric acid. A blank for each pH was also made. The resulting solution was digested for 10 minutes on a steam bath.

The coprecipitated rare earth hydroxide with $Fe(OH)_3$ was vacuum filtered through 0.25 g ethyl cellulose powder (200 mesh) supported on Whatman No.41 filter paper. The filter paper containing ethyl cellulose and iron(III) hydroxide was dried in hot air oven at $100^{o}C$ for 1 hour. The contents from the dried filter was transferred by scraping and homogeneously powdered in an agate mortar and pressed into pellets by applying a pressure of 5 tons giving pellets of diameter of 2.5 cm and about 0.07 cm thick.

Three sets of samples were prepared and pressed powder pellets were subjected to EDXRF quantitation via their K x-rays. Each element was counted thrice by using multichannel analyser. The background obtained by average of low and high backgrounds was subtracted from the measured peak intensity to give the net peak intensity. The average of three net peak intensities was then calculated from three individual measurements. The average of the average values obtained in three sets of samples was taken as true net peak intensity. The recovery of rare earth elements was found to be quantitative in the pH range 9 to 12 and pH 10 was chosen in subsequent experiments. A typical influence of pH on coprecipitation of rare earth elements on iron(III) hydroxide is shown in Fig. 5.1 (for samarium).

## 5.2 EFFECT OF CONCENTRATION OF COPRECIPITANT

The minimum amount of coprecipitant required for the quantitative collection of rare earth elements was next investigated. In this experiment 50 μg each of rare earth elements present in 500 ml was coprecipitated by varying the iron(III) amount from 0.5 to 10 mg. The pH of the solution was adjusted to 10 and digested for 10 minutes. The blanks were also run for the varying amounts of iron(III). Three sets of samples were prepared as

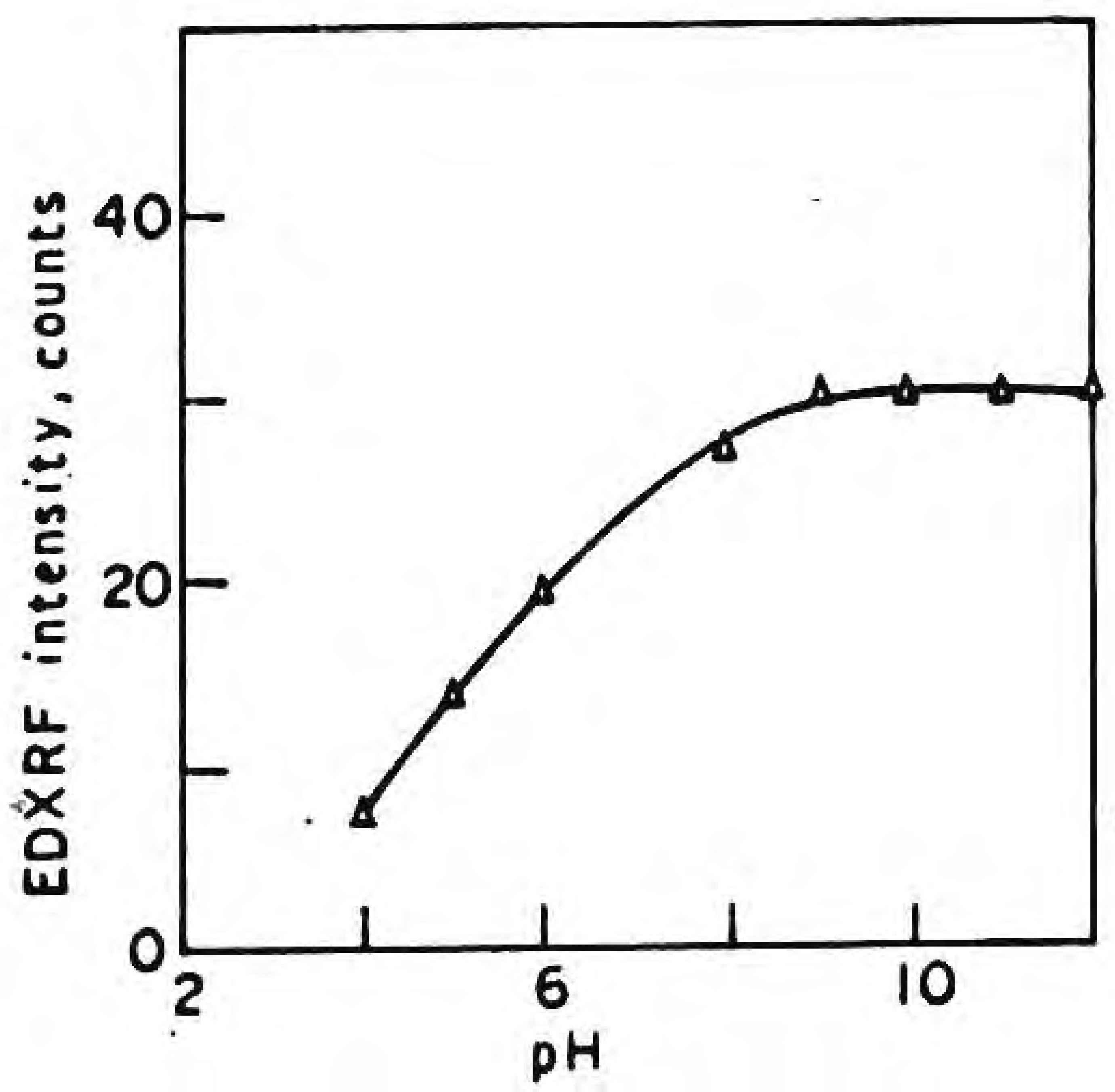


Fig. 5.1 Effect of pH

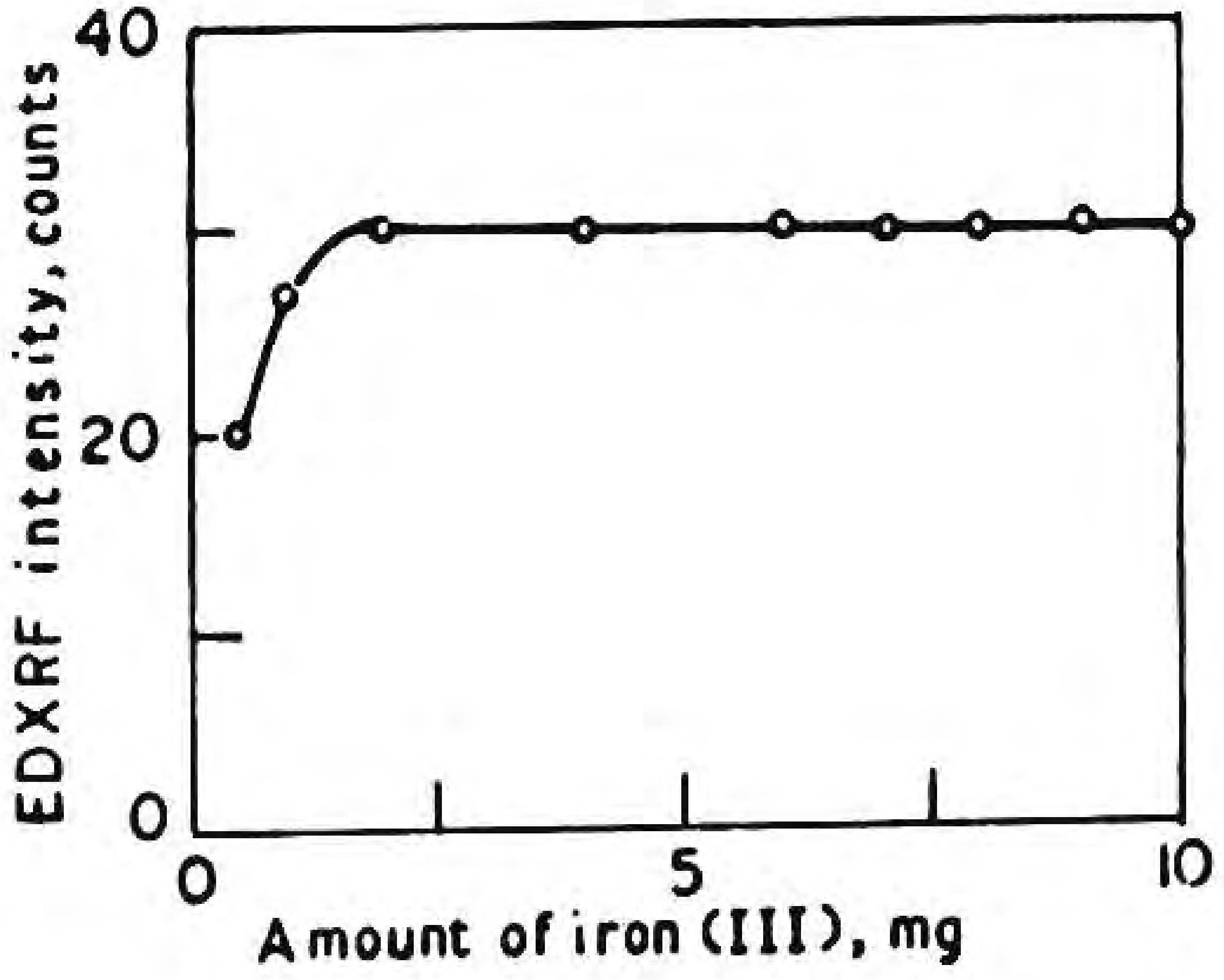


Fig. 5.2 Effect of concentration of coprecipitant

described in para 2 of 5.1.

The pressed powder pellets were subjected to EDXRF quantitation via their K x-rays. Each element was counted thrice by using multichannel analyser. The background obtained by average of low and high backgrounds was subtracted from the measured peak intensity to give the net peak intensity. The average of three net peak intensities was then calculated from three individual measurements. The average of the average values obtained in three sets of samples was taken as the true net peak intensity. It has been founnd that the collection of rare earth elements was quantitative in presence of as low as 2 mg of iron(III) and remains unaffected at higher amounts. Fig. 5.2 shows the effect of concentration of coprecipitant on the collection of samarium. In order to provide sufficient excess of coprecipitant, 5 mg of iron(III) was used in subsequent studies.

## 5.3 EFFECT OF DIGESTION TIME

The influence of digestion time for the collection efficiency of iron(III) hydroxide as coprecipitant was studied. In the present study 50 μg each of rare earth elements present in 500 ml of solution was taken. 5 mg of Fe(III) was added to the rare earth solution and pH was adjusted to 10. The solutions were digested over a period of 5 to 30 minutes one after another and corresponding blanks were also made . The samples were prepared as described in para 2 of 5.1.

The pressed powder pellets were subjected to EDXRF quantitation by irradiating with 50 mci Am-241 source for 10 minutes in a mylar based sample holder of 1 inch diameter. Three sets of samples were prepared. Each element was counted thrice by using multichannel analyser. The background obtained by average of low and high backgrounds was subtracted from the measured peak intensity to give net peak intensity. The average value obtained for three countings was then taken. Finally, the average value of three sets of samples carried out by same procedure was taken as the net intensity of the signal. As low as 5 minutes of digestion on steam bath was required for quantitative collection as shown in Fig. 5.3. Ten minutes digestion time was chosen in order to provide sufficient excess in subsequent studies.

## 5.4 EFFECT OF SAMPLE VOLUME

The effect of sample volume for the quantitative recovery of rare earth elements was next investigated. 50 $\mu$g each of rare earth elements was taken in sample volumes ranging from 25 to 1000 ml. The pH of the solutions were adjusted to 10 after the addition of 5 mg of Fe(III). Then the solutions were digested for 10 minutes on a steam bath. The coprecipitated rare earth hydroxide along with Fe(III) hydroxide was made into pellets for EDXRF quantitation as described in para 2 of 5.1.

The pressed powder pellets were subjected to EDXRF

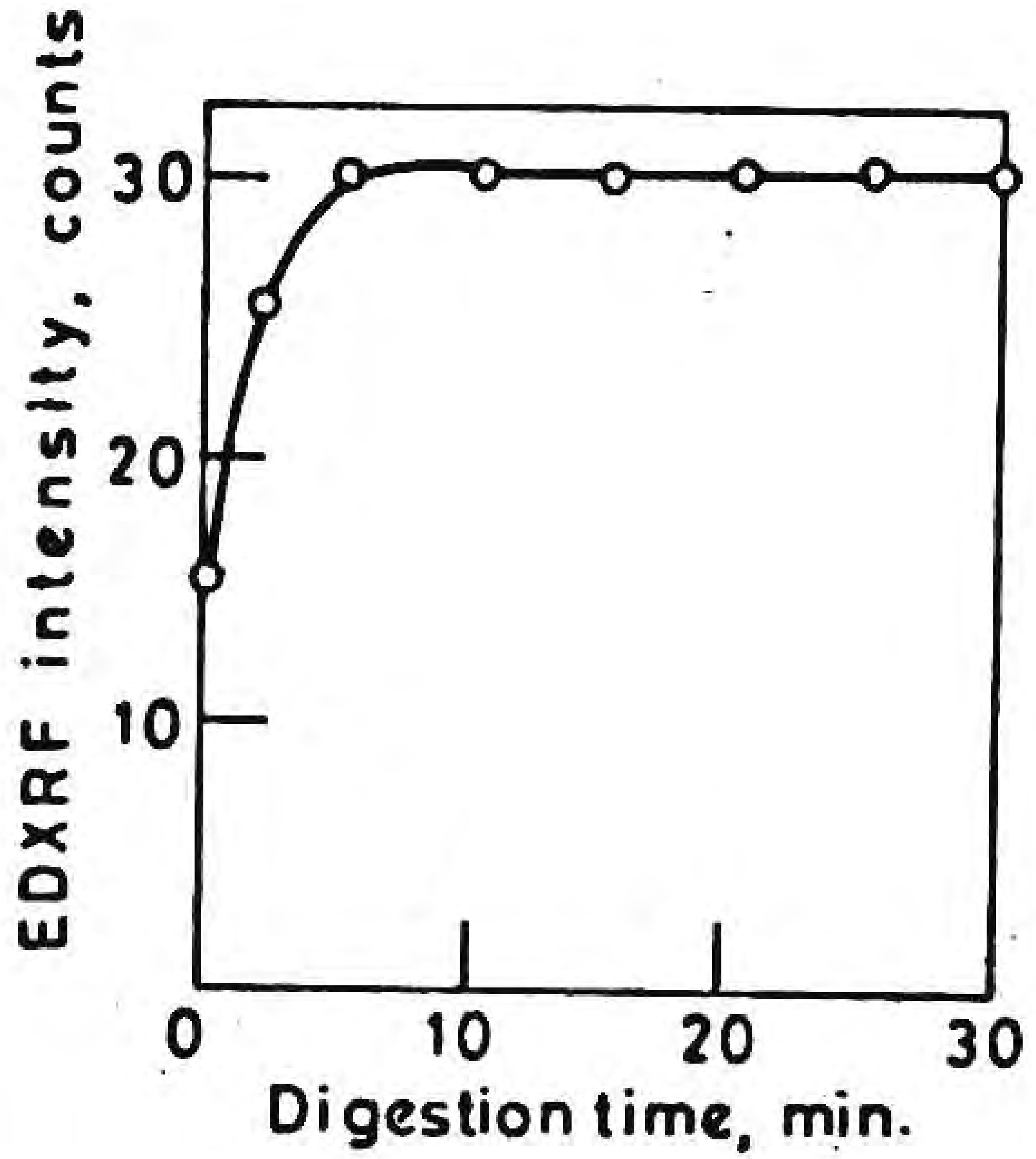


Fig. 5.3 Effect of digestion time

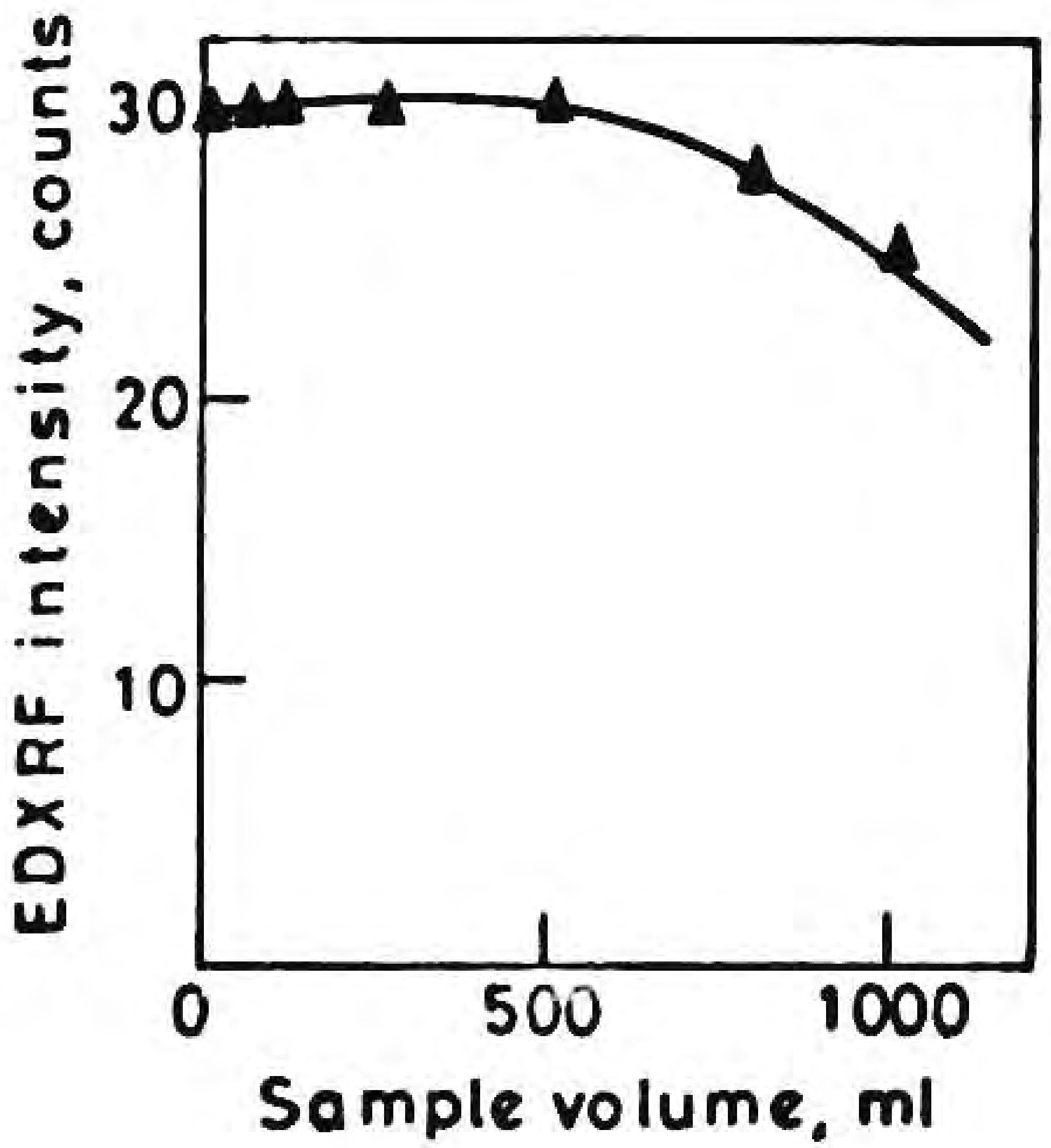


Fig. 5.4 Effect of sample volume

quantitation via their K x-rays. Each element was counted thrice. The background was obtained as the average of low and high backgrounds. This was then subtracted from the measured peak intensity to give the net peak intensity. The average of three net peak intensities was then calculated from three individual measurements. The average of the average values obtained in three sets of samples was taken as true net peak intensity. It has been found that quantitative recoveries were obtained for sample volumes in the range 25 to 500 ml as shown in Fig. 5.4.

## 5.5 CALIBRATION GRAPH

After establishing the optimum conditions for the quantitative coprecipitation of rare earth hydroxide on iron(III) hydroxide, single element and multielement calibration curves for rare earth elements were obtained. Then the linearity of the calibration graphs were tested. To 0.0-400 $\mu$g of rare earth element present in 500 ml of solution, 5 mg of iron(III) was added. The pH of the resulting solutions was adjusted to $\sim$10 using sodium hydroxide solution. The solutions were digested for 10 minutes on a steam bath. After cooling, the iron(III) hydroxide along with the coprecipitated rare earth elements was vacuum filtered through ethyl cellulose powder (200 mesh) supported on Whatman No.41 filter paper. The filter paper containing ethyl cellulose and coprecipitated iron(III) hydroxide was dried in hot air oven at 100$^{o}$C for one hour. The contents from the dried filter paper were scraped and homogeneously powdered in an agate mortar and pressed into pellets by applying a pressure of 5 tons per square inch giving pellets of diameter 2.5 cm and about 0.07 cm thick.

The pressed powder pellets were subjected to EDXRF quantitation by irradiating with 50 mci Am-241 source for 10 minutes in a mylar based sample holder of 1 inch diameter. Three sets of samples were prepared. Each element was counted thrice for 10 minutes by using multichannel analyser. The average of low and high backgrounds was subtracted from the measured peak intensity to give the net peak intensity. The average of three net peak intensities was then calculated from three individual measurements. The average of the average values obtained in three sets of samples was taken as true net peak intensity. These values were taken for drawing calibration graph. A plot of the net peak counts against the concentration of rare earth elements expressed in micrograms is a straight line passing through the origin as shown in Fig. 5.5.

## 5.6 DETECTION LIMIT AND PRECISION

The theoretical detection limit (TDL) calculated for samarium according to the formula[329]

$$\text{TDL} = (3 \times I_p^{1/2} \times \text{concentration})/\text{Net counts}$$

(where $I_p$ = mean background count for 15 determinations) was

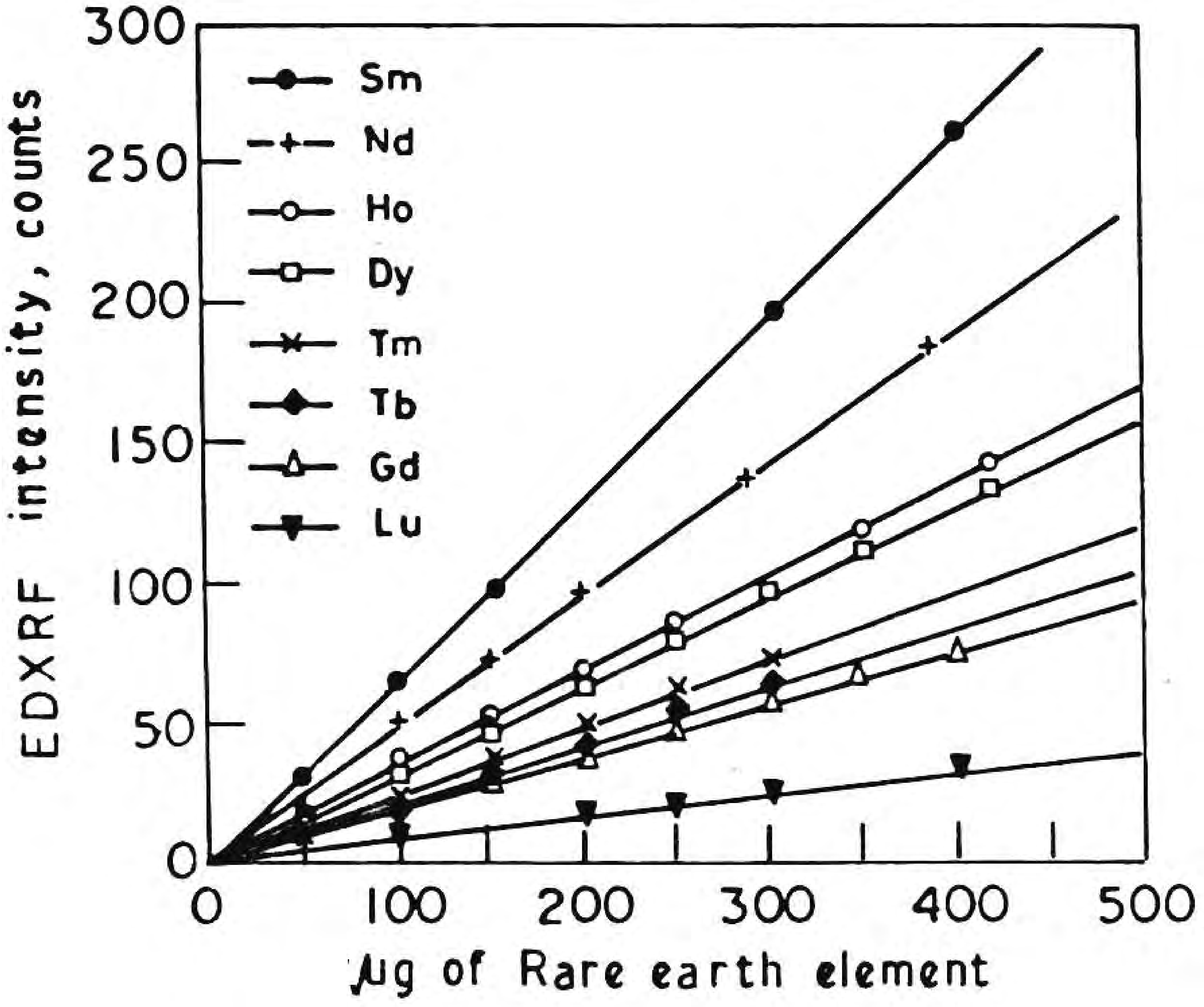


Fig. 5.5 Calibration graph (in °D mode)

found to be 60 ppb. The TDL values for various rare earth elements lie in the range 50 to 100 ppb.

The precision of the developed procedure was deduced from the relative standard deviation (RSD) values obtained from 15 values each of peak counts and background counts using the formula[329]

$$\% \text{ SD (RSD)} = [(\sigma N_p^2 + \sigma N_b^2)^{1/2} / (I_p - I_b)] \times 100$$

where

$$\sigma N_p^2 = \Sigma d_p^2 / n-1$$

$$\sigma N_b^2 = \Sigma d_p^2 / n-1$$

$\Sigma d_p^2$ = sum of the squares of differences of individual peak counts from mean total peak count ($I_p$)

$\Sigma d_b^2$ = sum of the squares of differences of individual background counts from mean background count ($I_b$)

The relative standard deviation for rare earth element was found to be concentration dependent and precision was better at higher concentrations. The RSD values were calculated for the key element, samarium. It has been found that the RSD values were 4.53 and 7.89% for 300 and 100 ppb respectively.

The detection limits and RSD values are quite high because of the constant Compton background arising from the source itself in view of the annular geometry[140] employed. Several methods have been tried for the elimination of the Compton background in order to improve the detection limit. Madanlal et al[327] used side source geometry instead of annular source geometry which improved the detection limit. Another approach would probably be the use of numerical methods of familiar operations as a prelude to further treatment of data. Numerical counterparts of analog devices that perform operations of differentiation and filtering such as RC filters etc. are often used.

Among the various numerical methods available, method of least squares was used without additional computational complexity and with considerable improvement in the information to be obtained[330]. The least squares calculations were being carried out in the computer by convolution of the data points with properly chosen sets of integers. These sets of integers and their normalising factors were described[330] and it was applied for the data obtained in the present study. The computer programs required were relatively simple i.e. subroutines in the FORTRAN language. In this method the sole function of computer was to act as a filter to smooth the noise fluctuations and at the same time not unduly degrading the underlying information[331] and with the simple evaluation of the first few derivatives of the information with respect to the graph abscissa.

The points of the two parameters must be at a fixed, uniform interval in the chosen abscissa and the curves formed by graphing the points must be continuous and more or less smooth. In the present study the two parameters (variables) were energy values characteristic of the elements and the peak counts corresponding to the intensity. One of the simplest ways to smooth fluctuating data was by a moving average method. In this procedure a fixed number of points were taken, their ordinates were added together and divided by the number of points to obtain the average ordinate at the centre abscissa of the group. Next, the point at one end of the group was dropped, the next point at the other end was added and the process was repeated. There is a much simpler way to compute the moving average than the particular one described. This is based on the concept of a convolute and of a convolution function. To perform the convolution of the ordinate numbers with a set of convoluting integers, each number was multiplied by the corresponding convoluting integer, the resulting products were added and this sum was divided by a number corresponding to the number of integers taken. The number was known as the normalizing factor. The next point in the moving average was obtained by repeating the same process after sliding down the center block one line.

The concept of convolution could be generalized beyond the simple moving average. In the general case the c's represent any set of convoluting integers. There was an associated normalizing or scaling factor. The procedure was to multiply $C_{-2}$ times the number opposite to it, then $C_{-1}$ by its number etc., summed the results, divided by the normalizing factor if appropriate, and the result was the desired function evaluated at the point indicated by $C_0$. For the next point, we moved the set of convoluting integers down and repeated etc. The mathematical description of this process is

$$Y_j = \frac{\sum_{i=-m}^{i=m} C_i \, Y_{j+1}}{N}$$

The index j represents the running index of the ordinate data in the original data table.

For the moving average each $C_i$ was equal to one and N was the number of convoluting integers. However for many types of data the set of all 1's which yielded the average, was not particularly useful. Then these integers were used for drawing the curve.

The convoluting functions discussed so far were rather simple and did not extract as much information as is possible. The experimenter, if presented with a plot of the data points, would tend to draw through these points a line which best fits them. Numerically this could also be done, provided one can adequately define what was meant by best fit. The most common criterion was that of least squares which might be stated as follows:

A set of points was to be fitted to some curve, for example, the curve $a_3x^3 + a_2x^2 + a_1x + a_0 = y$. The a's were to be selected such that when each abscissa point was substituted into this equation, the square of the differences between the computed numbers, y, and the observed numbers was a minimum for the total of the observations used in determining the coefficients. All of the error was assumed to be in the ordinate and none in the abscissa.

The utility of simple averaging of a large number of runs enhanced the signal to noise ratio[332] . The use of combined smoothing and averaging could considerably reduce the instrument time required, throwing the burden onto the computer which operated in a wholly different time domain. A characteristic of the procedure was that the noise was reduced approximately as the square root of the number of points used. The value which was obtained by this procedure was the best value at that point based on the least squares criterion i.e. on the function which was chosen and on the group of points examined.

In the present work the 'digitization' and averaging of EDXRF data of rare earth elements was carried out with MC 35 plus multichannel analyser and printer. The data thus obtained was subjected to smoothing and differentiation by the above described least square method.

A set of nine consecutive values for the determination of the best mean square fit through these values of a polynomial of degree five and of the form

$$F_i = b_o + b_i\, i + b_2\, i^2 + b_3\, i^3 + b_4\, i^4 + b_5\, i^5$$

were selected. The letters $b_o$, $b_1$, $b_2$, $b_3$, $b_4$ and $b_5$ were constants of the polynomial. The value of $i$ ranged from -4 to 4 and that $i = 0$ at the central point of the set of the values considered. The function i.e. the difference between the observed value and the calculated value was differentiated with respect to the constants of the polynomial resulting in the following six normal equations:

$$S_0 b_0 + S_2 b_2 + S_4 b_4 = F_0 \qquad (1)$$

$$S_2 b_0 + S_4 b_2 + S_6 b_4 = F_2 \qquad (2)$$

$$S_4 b_0 + S_6 b_2 + S_8 b_4 = F_4 \qquad (3)$$

$$S_2 b_1 + S_4 b_3 + S_6 b_5 = F_1 \qquad (4)$$

$$S_4 b_1 + S_6 b_3 + S_8 b_5 = F_3 \qquad (5)$$

$$S_6 b_1 + S_8 b_3 + S_{10} b_5 = F_5 \qquad (6)$$

Equations 1, 2 and 3 were used to solve for $b_0$, $b_2$ and $b_4$ while equations 4, 5 and 6 were used to solve for $b_1$, $b_3$ and $b_5$. The constants $S_0 - S_{10}$ were estimated using the equation

$$S_{r+k} = \sum_{i=-4}^{i=4} i^{r+k}$$

and the F's were calculated with the formula

$$F_k = \sum_{i=-4}^{i=4} i^k y_i$$

$b_0$ then represented the smoothness value and also the $0^{th}$ derivative.

In addition to simple curve fitting, a variety of least squares were used for determining the first order derivative and higher order derivatives. The derivatives were calculated using the formula

$$D_s = S! . b_s / \Delta x^s$$

where $\Delta x$ is the sampling interval (=0.03 kev in the present study) and s is the order of the derivative. The procedure was repeated for the other values by droping the point at one end of the group and adding next point at the other end. The computations were done using HCL Work Horse II computer and the plots were obtained using 1-2-3 lotus facility.

Fig. 5.6 shows the EDXRF data obtained for 0 and 50 $\mu$g of samarium with and without smoothening by using the algorithm described above. Higher order derivatives i.e. from 0th to 4th order derivatives were calculated for 0 and 50 $\mu$g of samarium after subtracting the blank. Figures 5.7, 5.8, 5.9, 5,10 and 5.11 show the resulting spectra of $^0D$, $^1D$, $^2D$, $^3D$ and $^4D$.

## 5:7 CHOICE OF DERIVATIVE ORDER

The best derivative order was chosen by calculating the SNR (signal to noise ratio) values. As shown in Table I the SNR value of 2.5 was obtained for first order derivative for 10 $\mu$g of samarium present in 500 ml of the solution. The sample preparation for EDXRF quantitation was same as described earlier. Hence $^1D$ was chosen as it offered a good detection limit of 10 ppb of samarium.

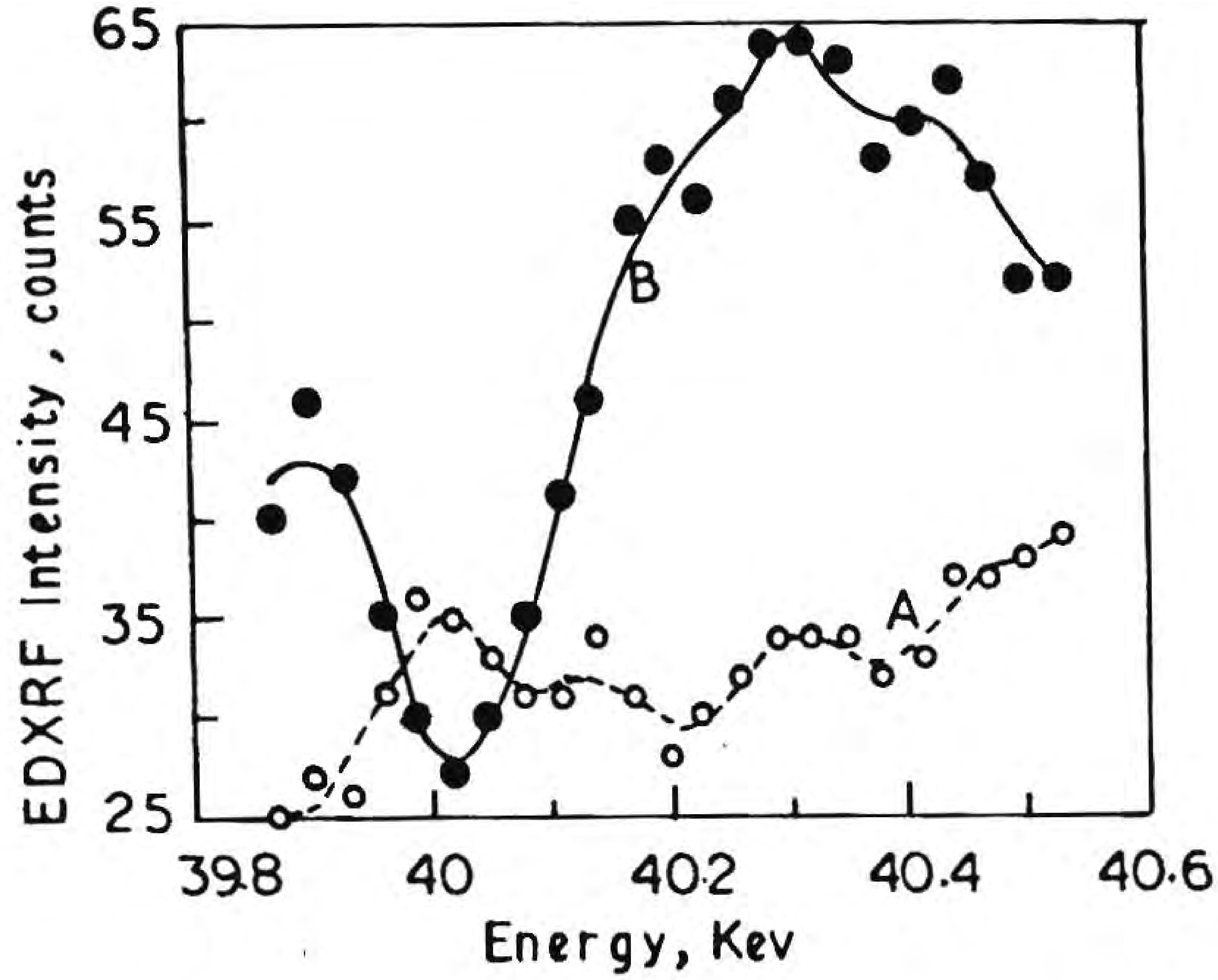


Fig 5.6 EDXRF spectra obtained for O (curve A) and 50 μg (curve B) of samarium with and without smoothening by using the described algorithm

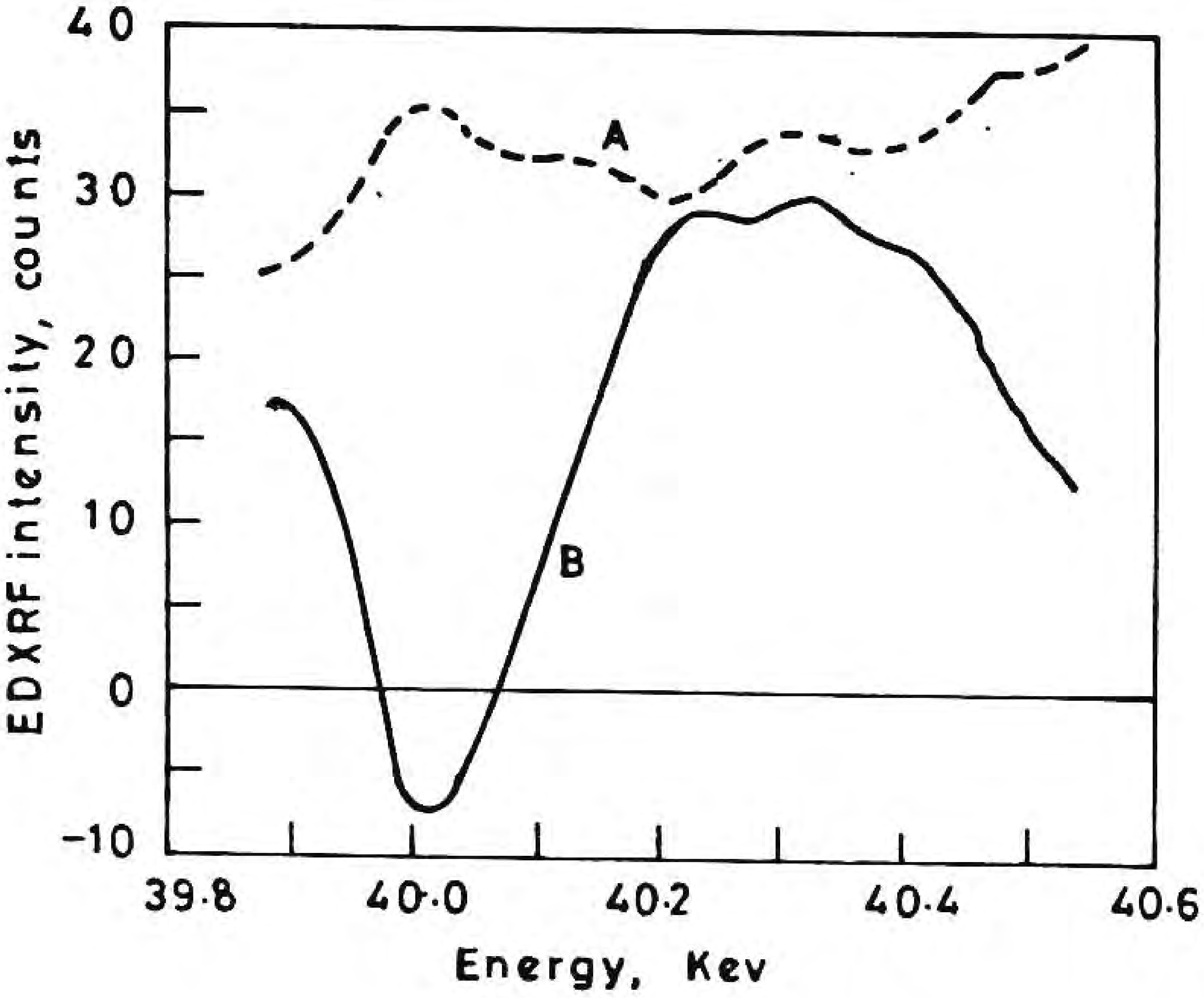


Fig. 5·7 Zero order derivative EDXRF spectra of 0 (curve A) and 50 $\mu$g (curve B) of samarium (after subtracting blank) under optimal conditions

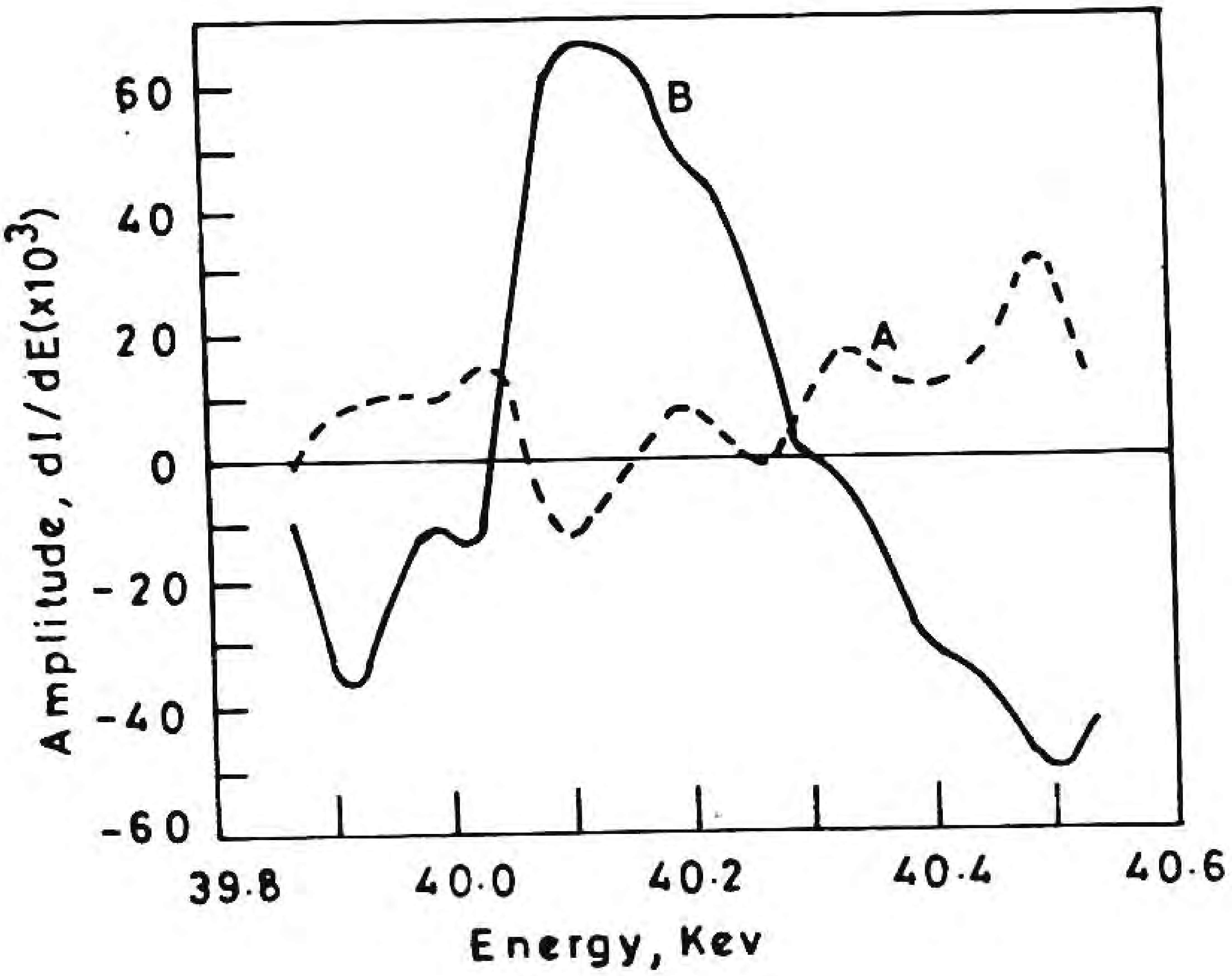


Fig. 5.8 First order derivative EDXRF spectra 0 (curve A) and 50 µg (curve B) of samarium (after subtracting blank) under optimal conditions

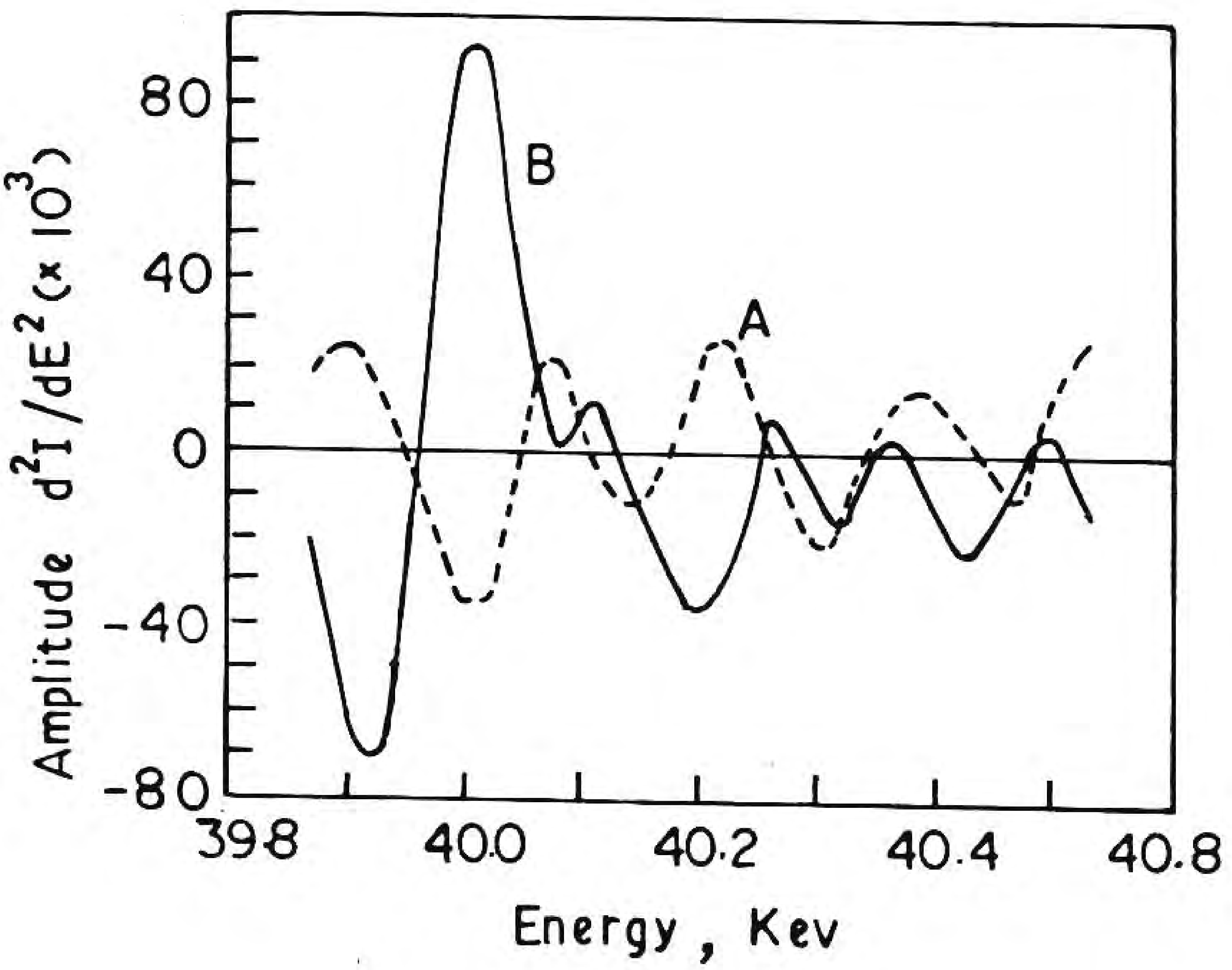


Fig .5.9 Second order derivative EDXRF spectra of 0 (curve A) and 50 μg (curve B) of samarium after subtracting blank under optimal conditions.

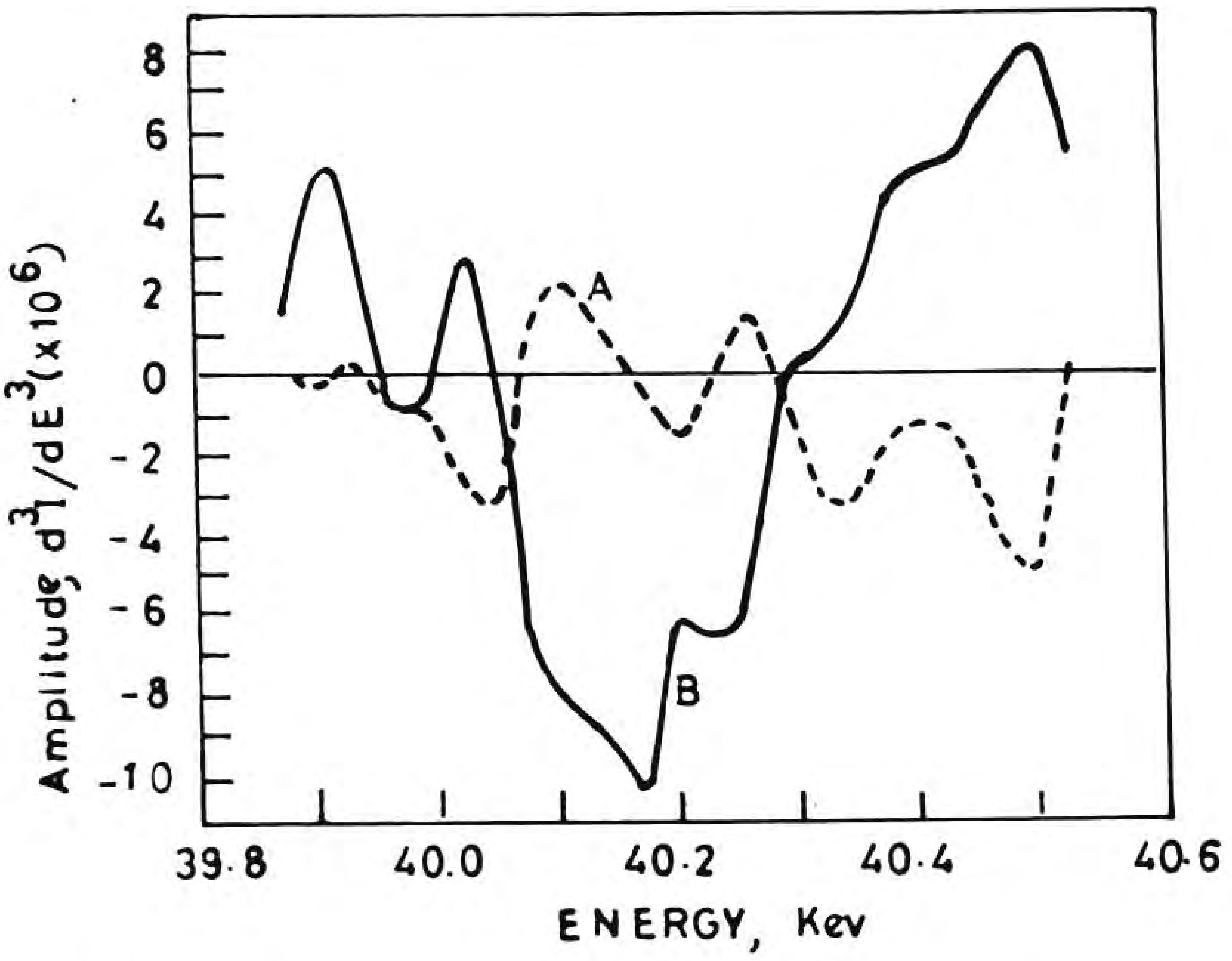


Fig. 5.10 Third order derivative spectra of 0 (curve A) and 50 μg (curve B) of samarium (after subtracting blank) under optimal conditions.

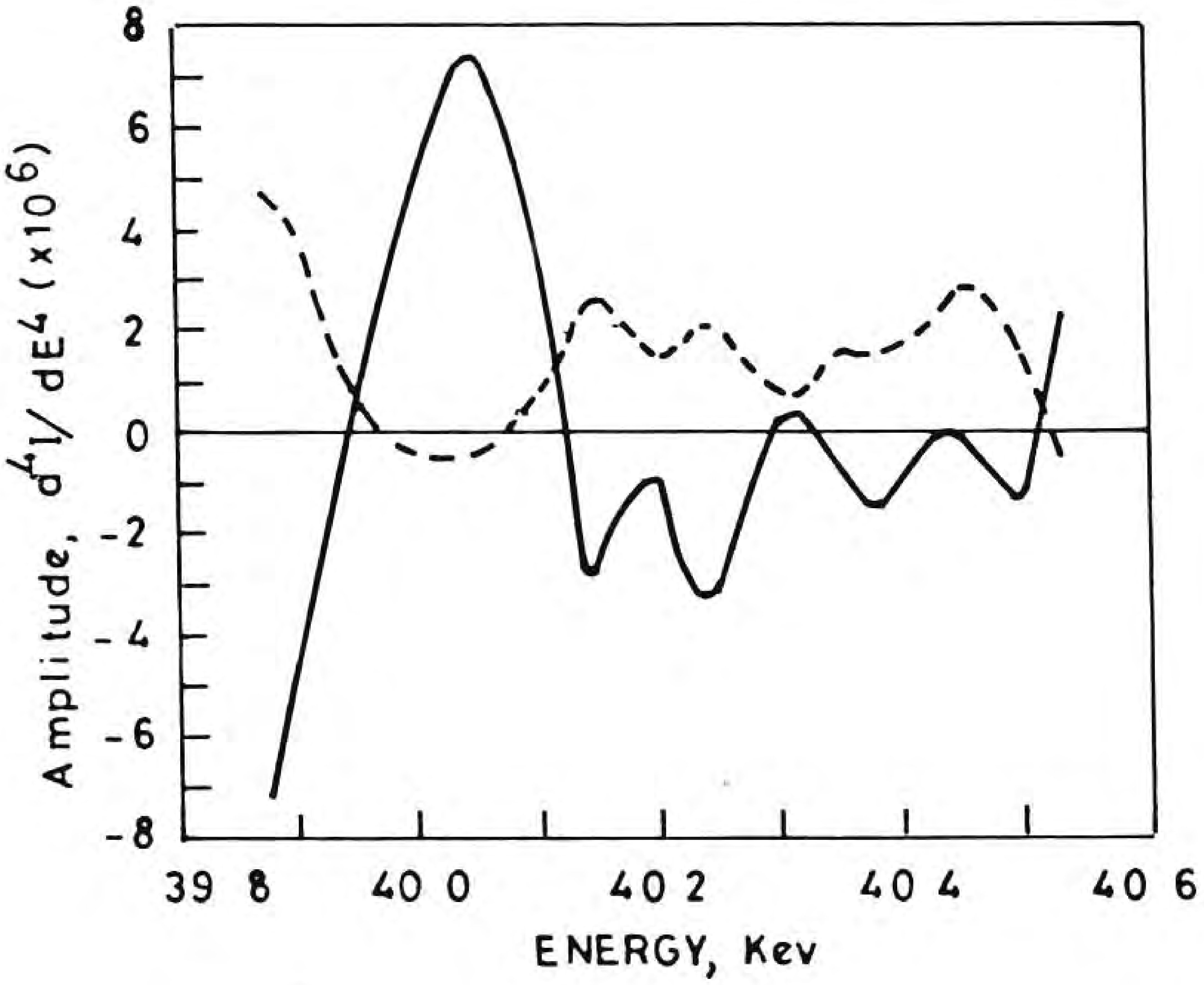


Fig. 5·11 Fourth order derivative spectra of 0 (curve A) and 50 μg (curve B) of samarium (after subtracting blank) under optimal conditions.

**Table I**

| No. | Order of derivative mode | SNR |
|---|---|---|
| 1 | $^{0}D$ | 0.25 |
| 2 | $^{1}D$ | 2.5 |
| 3 | $^{2}D$ | 2.25 |
| 4 | $^{3}D$ | 2.20 |
| 5 | $^{4}D$ | 1.5 |

Single element and multielement calibration graphs were drawn as shown in Fig. 5.12 by plotting the amplitudes of $^{1}D$ mode obtained after collection of 0-400 µg of rare earth elements present in 500 ml of the solution into 5 mg of iron(III) and analysing by EDXRF in conjunction with least square procedure. The amplitudes were proportional to the concentration of rare earth elements and can reliably be used for the determination of as low as 10 ppb of either individual or mixture of rare earth elements.

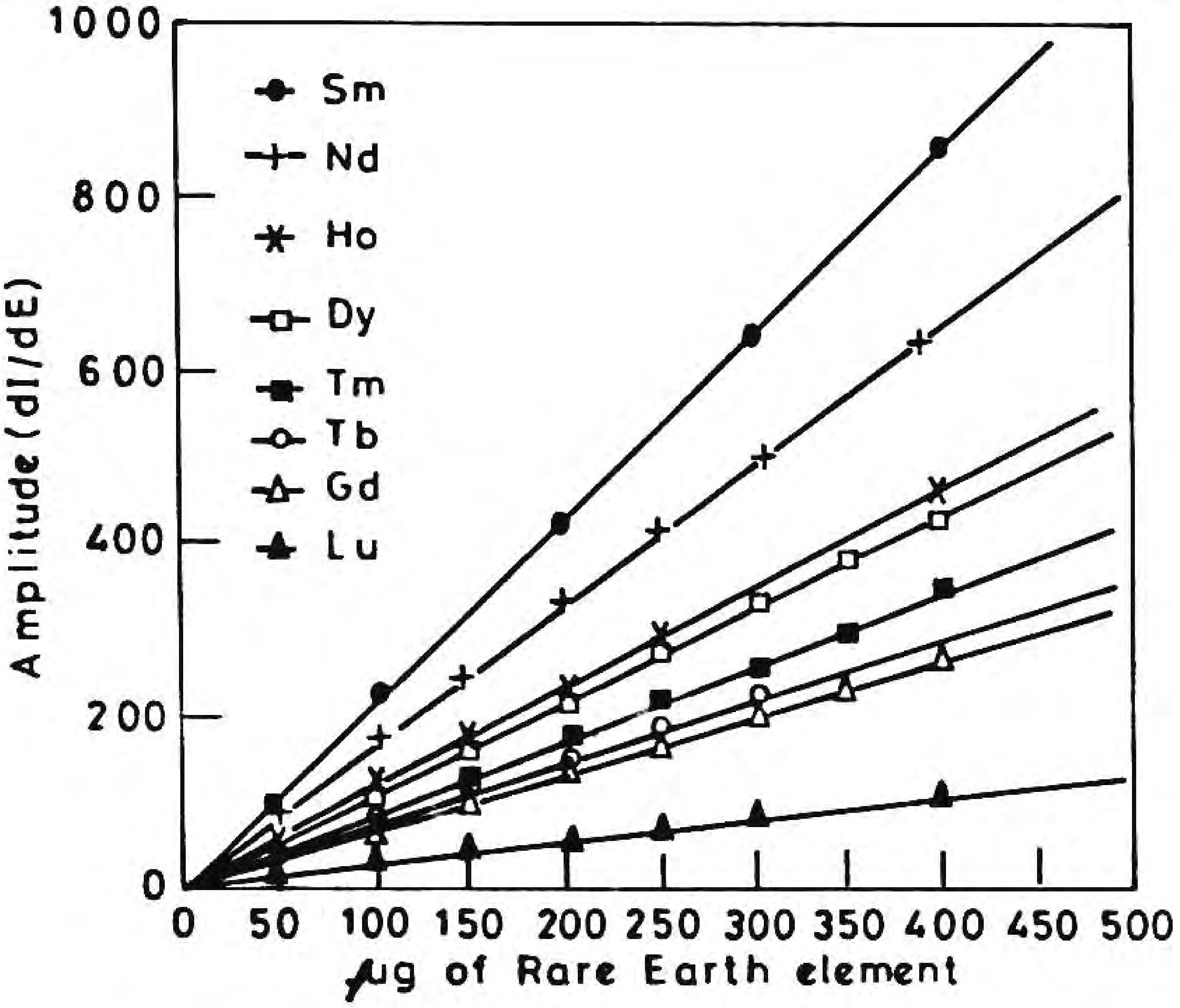


Fig. 5.12 Calibration graph (in $^1$D mode)

## 5.8 ANALYSIS OF SYNTHETIC SAMPLES

The applicability of the developed procedure was tested by analysing the rare earth content of various synthetic samples. The results of the analysis of samples with varying amounts of different rare earth elements are shown in Table II. The results clearly show that the method can find use in the analysis of trace levels of rare earth elements since the recoveries are good.

## Table II

## Recovery studies

| Sl. No. | Composition of mixture ( µg/0.5 litre) | | | | | | | | Recovery* (%) | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Nd | Sm | Gd | Tb | Dy | Hb | Tm | Lu | Nd | Sm | Gd | Tb | Dy | Ho | Tm | Lu |
| 1 | 50 | 50 | 100 | 100 | 200 | 200 | 300 | 300 | 95.5 | 96.5 | 98.0 | 98.0 | 98.5 | 98.5 | 100.5 | 102.2 |
| 2 | 100 | 100 | 200 | 200 | 300 | 300 | 50 | 50 | 96.0 | 95.5 | 97.3 | 98.4 | 96.2 | 101.4 | 95.8 | 96.8 |
| 3 | 200 | 200 | 300 | 300 | 50 | 50 | 100 | 100 | 101.2 | 99.1 | 98.0 | 97.4 | 96.3 | 96.5 | 95.8 | 97.6 |
| 4 | 300 | 300 | 50 | 50 | 100 | 100 | 200 | 200 | 99.3 | 98.7 | 97.6 | 102.4 | 96.2 | 97.4 | 95.8 | 98.3 |

* Average of 3 determinations

## 5.9 EXPERIMENTAL

### 5.9.1 Apparatus

Canberra-Energy dispersive x-ray fluorescence analyser.

The radioisotope system consisted of a Canberra Si(Li) detector (30 $mm^2$ x 3 mm) mounted inside a cryostat (liquid nitrogen) situated at a distance of 5 mm from window. The window was made up of beryllium of thickness 1 mil. An annular source holder containing the annular source Am-241, 50 mci, 59.57 keV, 1 inch active dia provided x-rays for excitation. The spectrometer was coupled to a Canberra MC series 35 plus multichannel analyser and printer.

Elico digital pH meter was used for adjusting the pH.

### 5.9.2 Reagents

All reagents were of analytical grade.

1. Standard rare earth element solutions:

Prepare individual rare earth element stock solutions (Rare Earth Products, Chehire) by dissolving respective rare earth oxides in 1:1 hydrochloric acid and standardize with EDTA.

2. Iron(III) solution (1000 ppm):

Dissolve 0.370 g of ferric oxide (J.T. Baker, New Jersey) in a minimum amount of hydrochloric acid and dilute to 250 ml.

3. Ethyl cellulose (Loba Chemie, Bombay).

### 5.9.3 Procedure

Take an aliquot of solution containing ≥ 5 μg of any single rare earth element or admixture containing a minimum of 5 μg each of rare earth elements. Transfer to 1 litre beaker containing 5 mg of Fe(III) in 500 ml of solution. Adjust the pH of the solution to ~ 10 with sodium hydroxide. Digest the resulting solution for 10 minutes on a steam bath. Cool, and filter the iron(III) hydroxide along with the coprecipitated rare earth elements through ethyl cellulose powder (200 mesh) supported on Whatman No.41 filter paper.

### 5.9.4 Sample preparation

Dry the filter paper containing ethyl cellulose and coprecipitated iron(III) hydroxide in hot air oven at $100^{\circ}C$ for 1 hour. Scrap the contents from the dried filter paper and powder homogeneously in an agate mortar and press into pellets by applying a pressure of 5 tons per square inch giving pellets of diameter of 2.5 cm and about 0.07 cm thick. Analyse all samples using pressed powder pellets and irradiate for 10 minutes in a mylar based sample holder (1 inch diameter). Count each element thrice and subtract the background (average of low and high backgrounds) from the measured peak intensity to give net peak intensity. Calculate the average of three net peak intensities from three individual measurements. Take the average of the average values obtained in three sets of samples as true net peak intensity. Obtain the calibration graphs using these average values.

### 5.9.5 Derivative procedure

Proceed as described above, then convert the counts of each rare earth element into amplitude in first derivative mode by using the formula described in page No.144 after subjecting to simplified least square procedure.

## CHAPTER VI

# PRECONCENTRATION OF RARE EARTH-QUINOLIN-8-OL COMPLEXES ONTO ACTIVATED CARBON AND FIRST ORDER DERIVATIVE EDXRF DETERMINAION

Koshima and Onishi[311] have studied the adsorption behaviour of 20 metal species by activated carbon from aqueous solutions of pH 1-13. Adsorption of metal chelates on activated carbon has also been used for separation and concentration of metal ions[333]. Such experiments involve formation (precipitation) of the chelates and their subsequent adsorption (filtration) with activated carbon. The adsorption behaviour of many metals in the absence of chelating agents have been described by Sigworth and Smith[334] and Jackwerth et al[335].

A reported work [336] described the preconcentration of silver, gold, copper, cobalt, nickel, iron, zinc, calcium and silicon by adsorption on activated carbon and subsequent analysis by x-ray fluorescence spectrometry and inductively coupled plasma spectrometry.

Robberecht and Van Grieken[312] developed a method for determination of traces of selenium present in biological materials. In this work, selenium at mg $g^{-1}$ to µg $g^{-1}$ level was reduced by 4 M hydrochloric acid - ascorbic acid. The colloidal selenium thus obtained was adsorbed on activated carbon and filtered through a nucleopore membrane and subjected to energy dispersive x-ray fluorescence determination. Quantitative recovery with a detection limit of 20 ng was achieved. Microgram amounts of iron(III), gallium(III), thallium(III), antimony(V) and antimony(III) were adsorbed[337] on activated carbon from hydrochloric acid solution. Rapid determination of gold[338] was also done by adsorption on activated carbon and then determined by x-ray fluorescence spectrometry.

Potassium xanthogenate forms complex compounds with a number of metals which accompany the manganese during its production process. Thus the traces of bismuth, cadmium, copper, cobalt, iron, indium, nickel, lead, thallium and zinc from pure manganese and manganese compounds were separated [339] after complexation with potassium xanthogenate in acidic medium. The solution was filtered through a filter paper covered with activated carbon whereby complex compounds were separated from the matrix. When the carbon was treated with acid, a trace element concentrate was obtained which was nearly free of manganese. The determination was carried out by flame atomic absorption spectrophotometry and the detection limits for the analysis of 10 g samples of manganese metal were $< 0.5$ ppm and for 30 g samples of $MnCl_2 \cdot 4 H_2O$ were $\leq 0.1$ ppm. Diethyl phosphorodithioate[340] was one of the reagents used in conjunction with adsorption on activated carbon for bismuth, cadmium, copper, indium and thallium. Enrichment of trace metals like copper, zinc, lead and iron was done[341] by complexation with L-ascorbic acid and then adsorbed on activated carbon. The resulting material was analysed by x-ray fluorescence spectrometry. A number[342] of ferroin type ligands and adsorption of such metal chelates on activated carbon for applications in reagent purification and trace metal enrichment were investigated. One of the reagent largely used in this type is 2,2'-dipyridyl ketone-2-pyridyl hydrazone (DPPH). Ammonium diethyl phosphorodithioate[343] was used as a complexing agent for iron and concentrated on activated carbon. Iron thus collected was determined by atomic absorption spectrometry.

A suspension of the ion exchange resin on activated carbon in water or water-glycerol (4:1) was prepared by grinding. This suspension was used for the enrichment of gold and silver and subsequently determined by atomic absorption spectrometry[344].

Quinolin-8-ol was a promising chelating agent for most of the elements. The preconcentration and separation[345] of copper, cadmium and nickel was done by the collection of their quinolin-8-olates on phenolphthalein or 2-naphthol. Octadecylamine was used as surfactant for flotation in this study. Willie et al[298] compared quinolin-8-ol bonded polymer supports for the preconcentration of trace metals from sea water. Quinolin-8-ol immobilized on cross-linked poly(vinyl pyrrolidone) or macroreticular styrene - divinyl benzene (XE-305) or methylated polystyrene substrates was used for the preconcentration of traces of cadmium, zinc, lead, copper, iron, manganese, nickel, cobalt and chromium from sea water prior to their measurement by electrothermal atomic absorption spectrometry. Optimal results were obtained with XE-305 substrate. Silica immobilized quinolin-8-ol[346] was used for enrichment of cadmium, lead, zinc, copper, iron, manganese, nickel and cobalt from sea water.. The metals were eluted with 2 M hydrochloric acid and determined by atomic absorption spectrometry. Studies[235] were carried out for the preconcentration of 15 trace elements from aqueous solution as their complexes with organic compounds, for e.g. 1,10-phenanthroline, or quinolin-8-ol on amberlite XAD-4. The resin could be used for selective trace separation by appropriate choice of complexing agent and pH. The metals were eluted from the resin with 1 M nitric acid in acetone and determined by flame or graphite tube atomic absorption spectrometry.

Leyden et al[347] developed a method for the preconcentration of metal ions like cobalt(II), chromium(III), copper(II) o. iron(III) as their quinolin-8-ol complexes and adsorption on activated carbon.

Vanderborght and Van Grieken developed methods for preconcentration of traces of selenium[348] and rare earth elements[333] by adsorption on activated carbon. However, the adsorption of rare earth elements as their quinolin-8-ol complexes on activated carbon have not been carried out so far. The details of the complete investigations in this line is described in this Chapter.

## PRELIMINARY STUDIES

Initial experiments showed that the adsorption of rare earth elements on activated carbon from acidic or alkaline solutions was not quantitative. This was confirmed by the presence of rare earth elements in the sample solution obtained after adsorption as determined by Arsenazo I.[4] However, it has been found that the addition of quinolin-8-ol to weakly alkaline solution and the adsorption of rare earth element - quinolin-8-ol complexes on activated carbon was quantitative. The reliability and practicability of this determination procedure were studied systematically.

The EDXRF spectra obtained with 1 g ethyl cellulose and 1 g ethyl cellulose with 0.6 g activated carbon when irradiated for 10 minutes with 50 mci Am-241 annular source with a Si(Li) detector are identical. The rare earth element spectrum is also found to be not affected by the presence of varying amounts of activated carbon matrix. These studies throw light on the possibility of using activated carbon as adsorbent without interference in the determination of traces of rare earth elements present in liquid samples after the formation of quinolin-8-ol complexes.

It was observed that the traces of rare earth elements as their quinolin-8-ol complexes were adsorbed on activated carbon from weakly alkaline medium. The sample solution containing rare earth element, activated carbon and quinolin-8-ol was stirred using a magnetic stirrer to effect quantitative collection. Then the activated carbon with adsorbed rare earth element - quinolin-8-ol complexes was vacuum filtered through ethyl cellulose powder supported on a Whatman No.41 filter paper. The filter paper containing adsorbed material was dried in hot air oven at 100°C for 1 hour. The contents from the dried filter were scraped and transferred to an agate mortar. The contents were homogeneously powdered and pressed in the form of pellets by applying a pressure of 5 tons per square inch using a 1 inch die in a carvar press.

An annular source holder containing the annular source Am-241 (50 mci, 59.57 Kev, 1 inch active dia) provided x-rays for excitation. This radioisotopic excitation produced the characteristic K x-ray of rare earth elements.

The pressed powder pellets were analysed by irradiating for 10 minutes with Am-241 source in a mylar based sample holder. Each element was counted thrice by using multichannel analyser. The background obtained by average of low and high backgrounds was subtracted from the measured peak intensity to give net peak intensity. The average of three net peak intensities were then calculated from three individual measurements. The average of average values obtained in three sets of samples was then used to obtain the calibration graphs. Various parameters that influence the adsorption of rare earth elements as their quinolin-8-ol complexes on activated carbon were investigated systematically.

The identical behaviour of rare earth elements preclude their individual description and hence the results obtained for a key element viz. neodymium is discussed in detail.

## 6.1 EFFECT OF pH

The effect of pH on the adsorption of rare earth element-quinolin-8-ol complexes on activated carbon was investigated. The pH was varied in the range 2 to 12 in steps of 1. In this study, 100 µg each of rare earth elements present in a total volume of 500 ml was taken, 0.3 g of activated carbon was added followed by 0.1 g of quinolin-8-ol in the minimum volume of acetic acid. Then the pH of the solution was adjusted in the above range one after another using sodium hydroxide and 1 M hydrochloric acid. A blank for each pH was also made. The resulting solution was stirred for 20 minutes using a magnetic stirrer.

The adsorbed rare earth element - quinolin-8-ol complexes along with activated carbon were vacuum filtered through 1.4 g of ethyl cellulose powder (200 mesh) supported on Whatman No.41 filter paper. The filter paper with contents was dried in hot air oven at 100° C for 1 hour. The contents from the dried filter were quantitatively transferred by scraping and homogeneously powdered in an agate mortar. 1 g of the sample was taken and pressed into pellets by applying a pressure of 5 tons giving pellets of diameter 2.5 cm and about 0.18 cm thick.

Three sets of samples were prepared and pressed powder pellets were subjected to EDXRF quantitation via their K x-rays. Each element was counted thrice by using multichannel analyser. The background obtained by average of low and high backgrounds was subtracted from the measured peak intensity to give net peak intensity. The average of three net peak intensities was then calculated from three individual measurements. The average of the average values obtained in three sets of samples was taken. The recovery of rare earth elements was found to be quantitative in the pH range 8-12 and pH 9 was chosen in subsequent studies. A typical influence of pH on adsorption of neodymium on activated carbon as its quinolin-8-ol complex is shown in Fig. 6.1.

## 6.2 EFFECT OF AMOUNT OF ACTIVATED CARBON

The minimum amount of activated carbon required for the quantitative collection of rare earth element was next investigated. 100 µg each of rare earth element in 500 ml was taken. The amount of activated carbon was varied in the range 0.1 g to 0.8 g. 0.1 g of quinolin-8-ol dissolved in minimum amount of acetic acid was added. The pH of the solution was adjusted to 9 and stirred for 20 minutes. The blanks were also carried out under the identical conditions. Three sets of samples were prepared as described in para 2 of 6.1. The pressed powder pellets were subjected to EDXRF quantitation via their K x-rays. Each element was counted thrice by using multichannel analyser. The background obtained by average of low and high backgrounds was subtracted

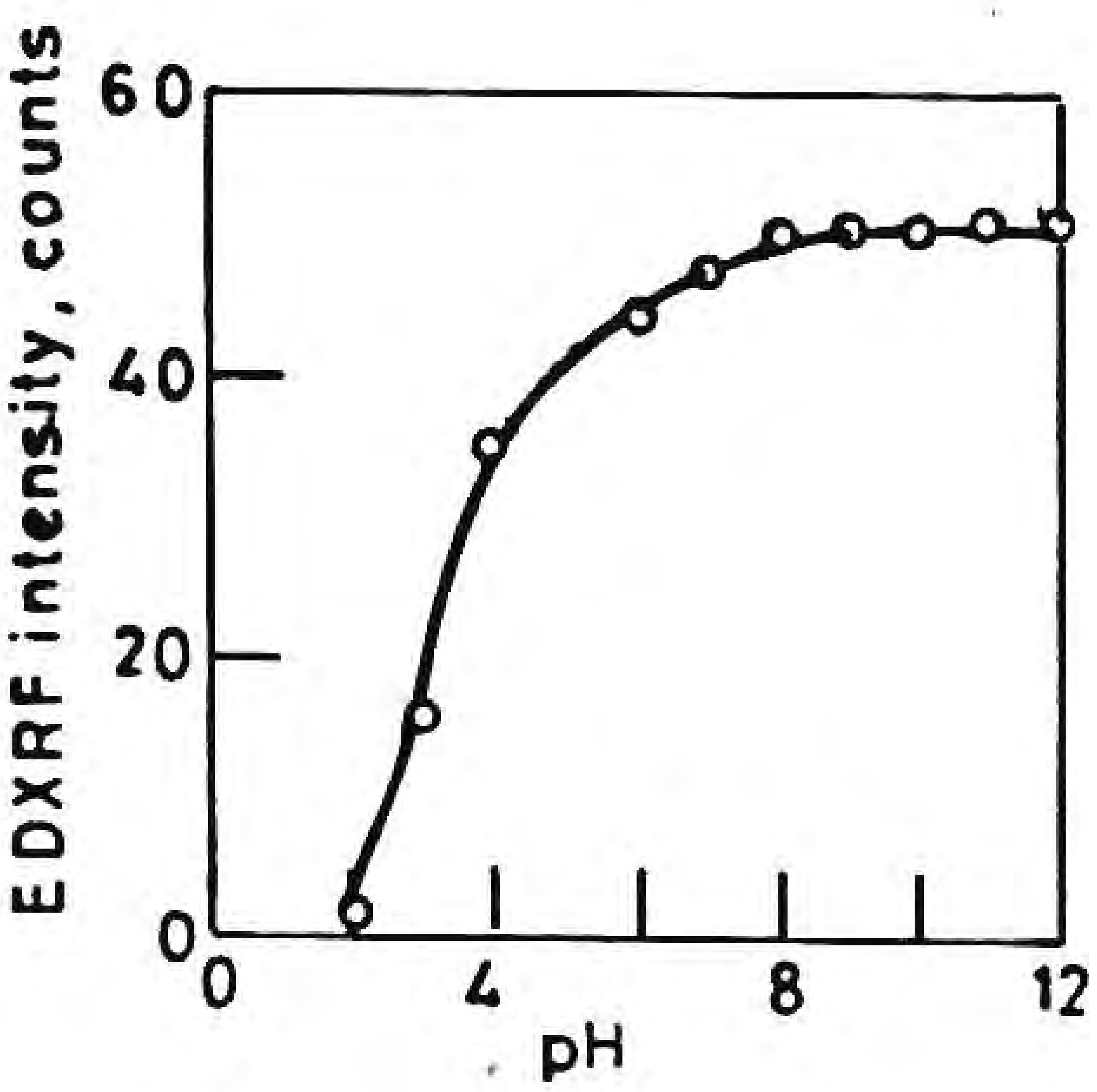


Fig. 6.1 Effect of pH

from the measured peak intensity to give net peak intensity. The average of three net peak intensities was then calculated from three individual measurements. The average of average value obtained in three sets of samples was taken.

It has been found that the collection of rare earth elements was quantitative from 0.25 g onwards as shown in Fig. 6.2. 0.3 g of activated carbon was used in subsequent studies.

## 6.3 EFFECT OF AMOUNT OF QUINOLIN-8-OL

The amount of quinolin-8-ol required for the quantitative collection of 100 $\mu$g of each of rare earth elements present in 500 ml was next investigated. 0.3 g of activated carbon was added. The amount of quinolin-8-ol was varied from 1 to 20 ml of 1% quinolin-8-ol in minimum amount of acetic acid. The pH of the solutions was adjusted to 9 and stirred the solutions for 20 minutes using a magnetic stirrer. The corresponding blanks were also carried out for the varying amounts of quinolin-8-ol. Three sets of samples were prepared as described and the quantitation of rare earth elements was made as described in 6.1. The average of three net peak intensities was then calculated from three individual measurements. The average of these average values obtained for three sets of samples was taken. It can be seen from Fig. 6.3 that a minimum of 5 ml of 1% quinolin-8-ol is essential and in order to provide sufficient excess of reagent, 10 ml of 1% was used for further studies.

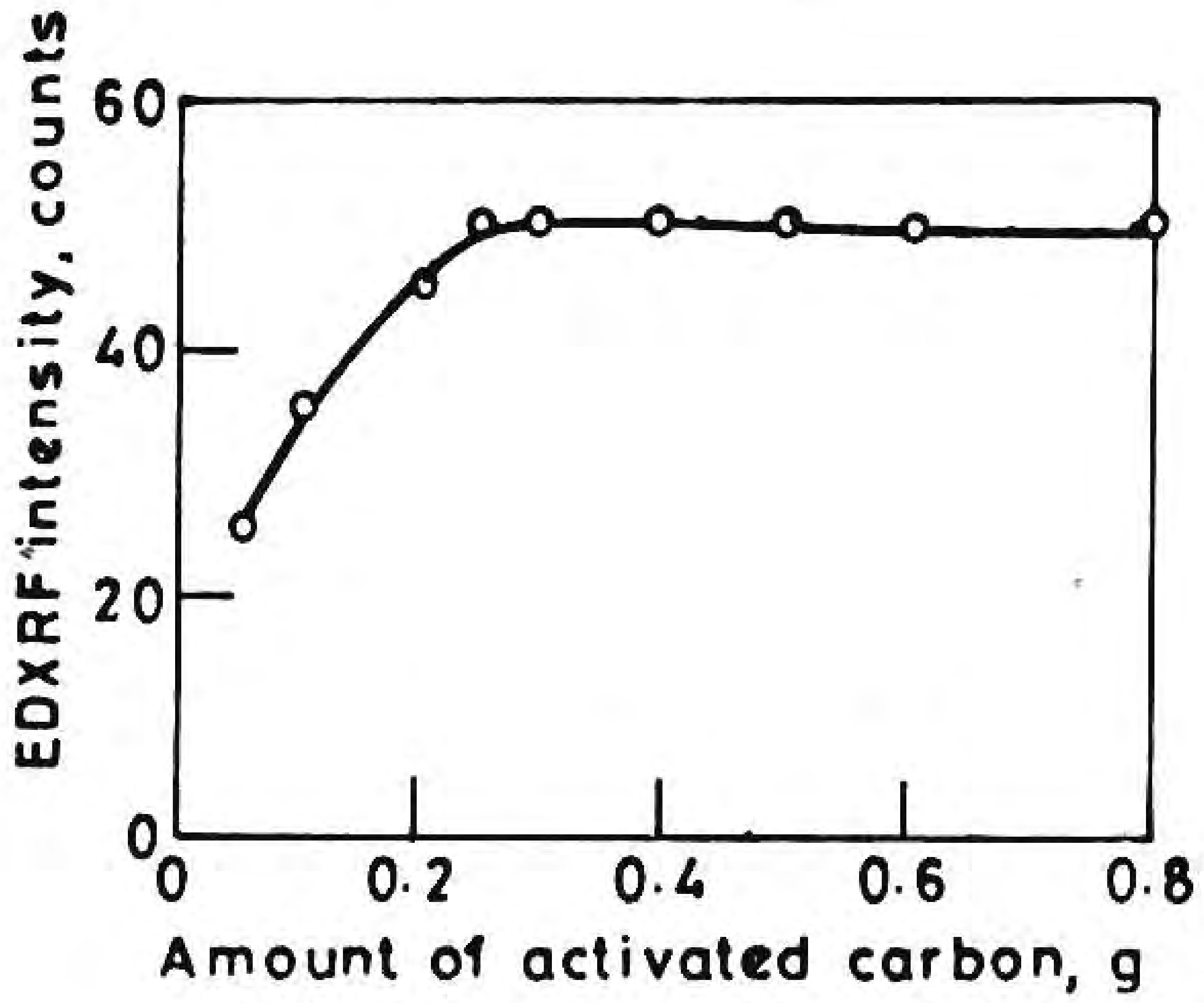


Fig. 6·2 Effect of amount of activated carbon

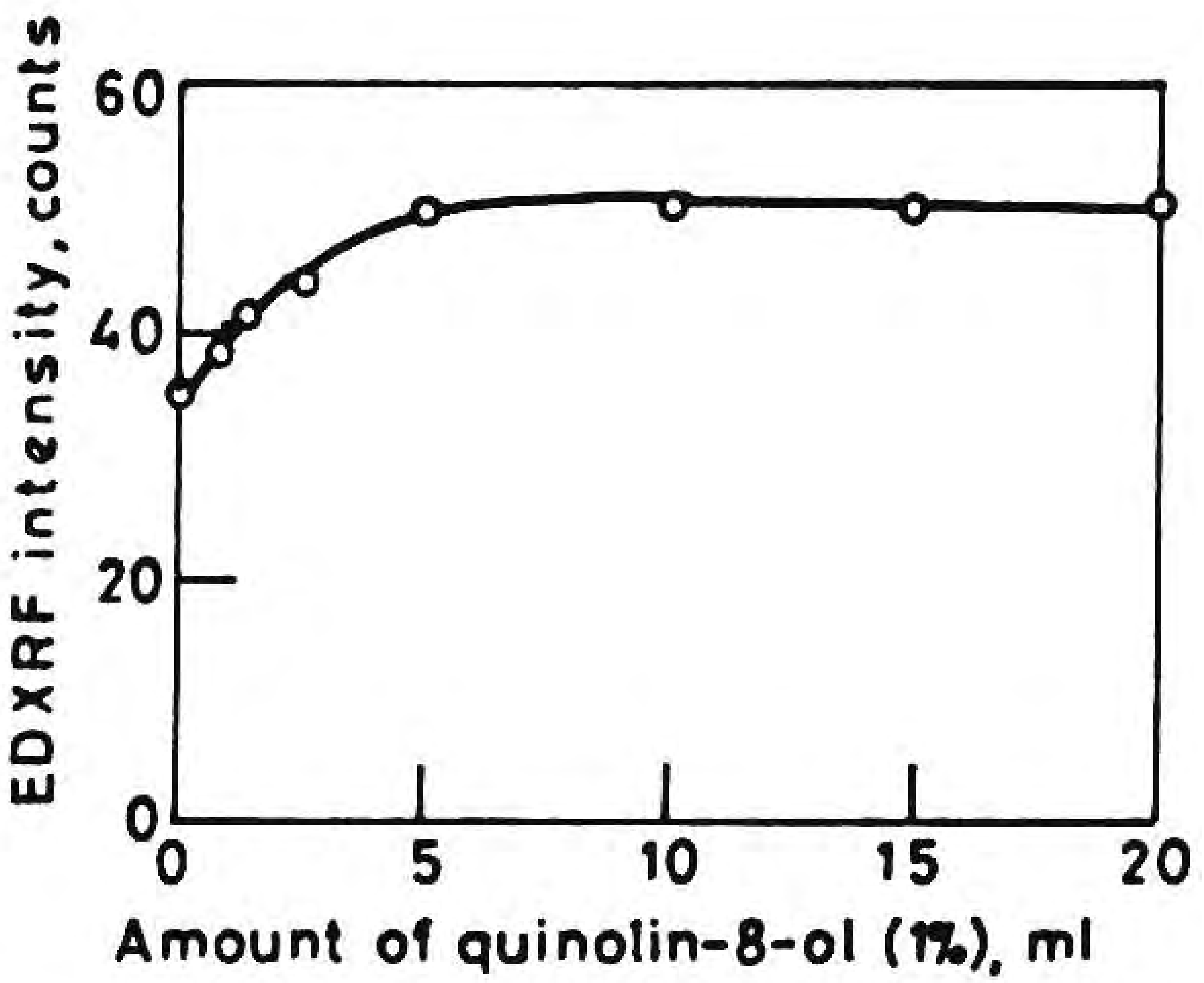


Fig 6·3 Effect of amount of quinolin-8-ol

## 6.4 EFFECT OF STIRRING TIME

The influence of stirring time for the collection of rare earth elements on activated carbon was studied. In the present study, 100 µg each of rare earth elements present in 500 ml was taken. 0.3 g of activated carbon and 10 ml of 1% quinolin-8-ol were added. The pH of the solution was adjusted to 9. The stirring time was varied over a period of 5 minutes to 60 minutes using a magnetic stirrer. The corresponding blanks were also made. Three sets of samples were prepared as described in para 2 of 6.1. The pressed powder pellets were subjected to EDXRF quantitation via. their K x-rays. Each element was counted thrice by using a multichannel analyser. The background obtained by average of low and high backgrounds was subtracted from the measured peak intensity to give net peak intensity. The average value of the three net peak intensities was then calculated from three individual measurements. The average of the average values obtained in three sets of samples was taken. Fig. 6.4 shows that the quantitative recovery of rare earth elements was obtained in the range 15 to 60 minutes. 20 minutes stirring time was chosen in subsequent studies.

## 6.5 EFFECT OF SAMPLE VOLUME

The effect of sample volume for the quantitative recovery of each of rare earth elements was next investigated. 100 µg each of rare earth elements was taken in sample volumes ranging

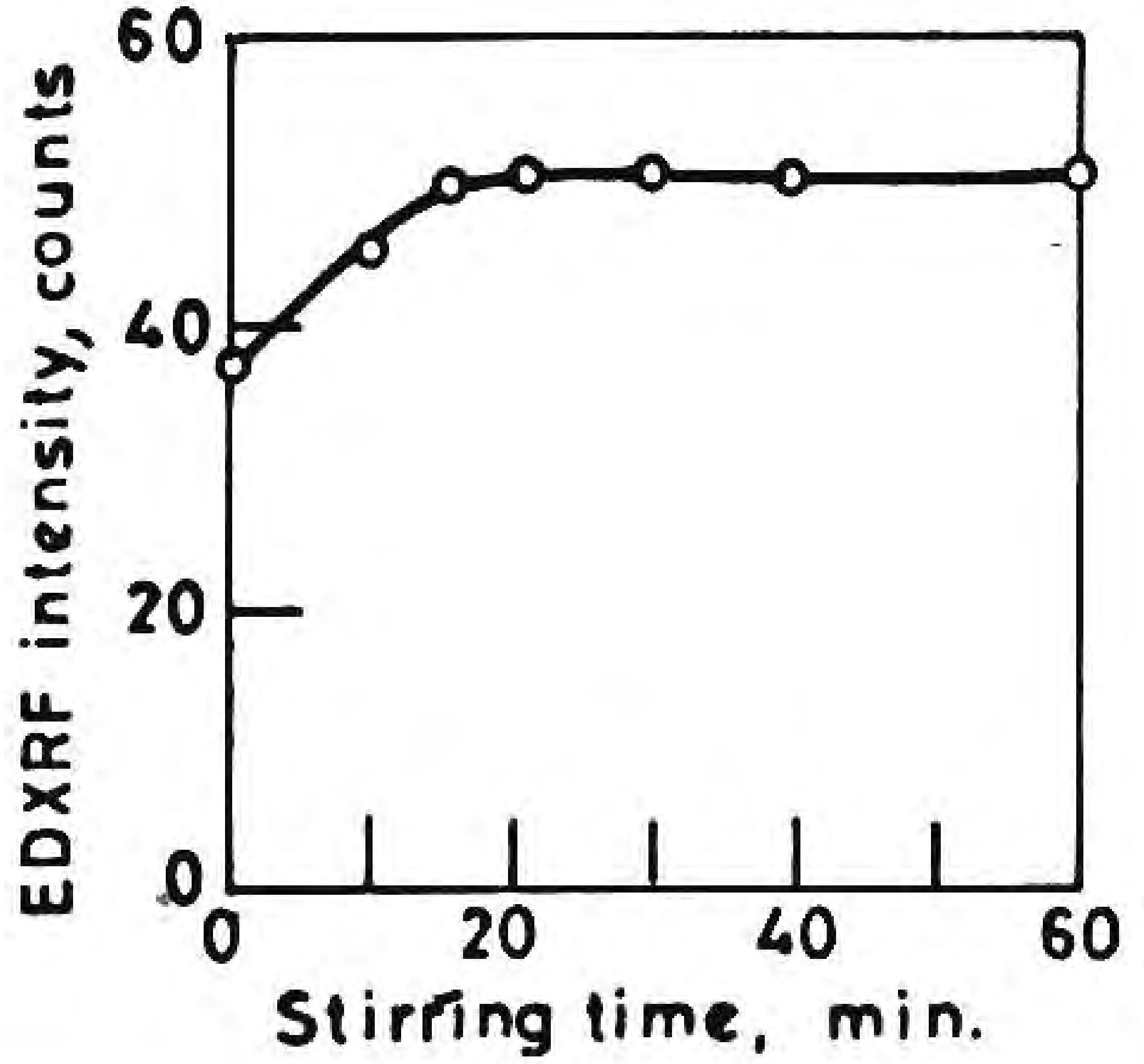


Fig. 6.4 Effect of stirring time

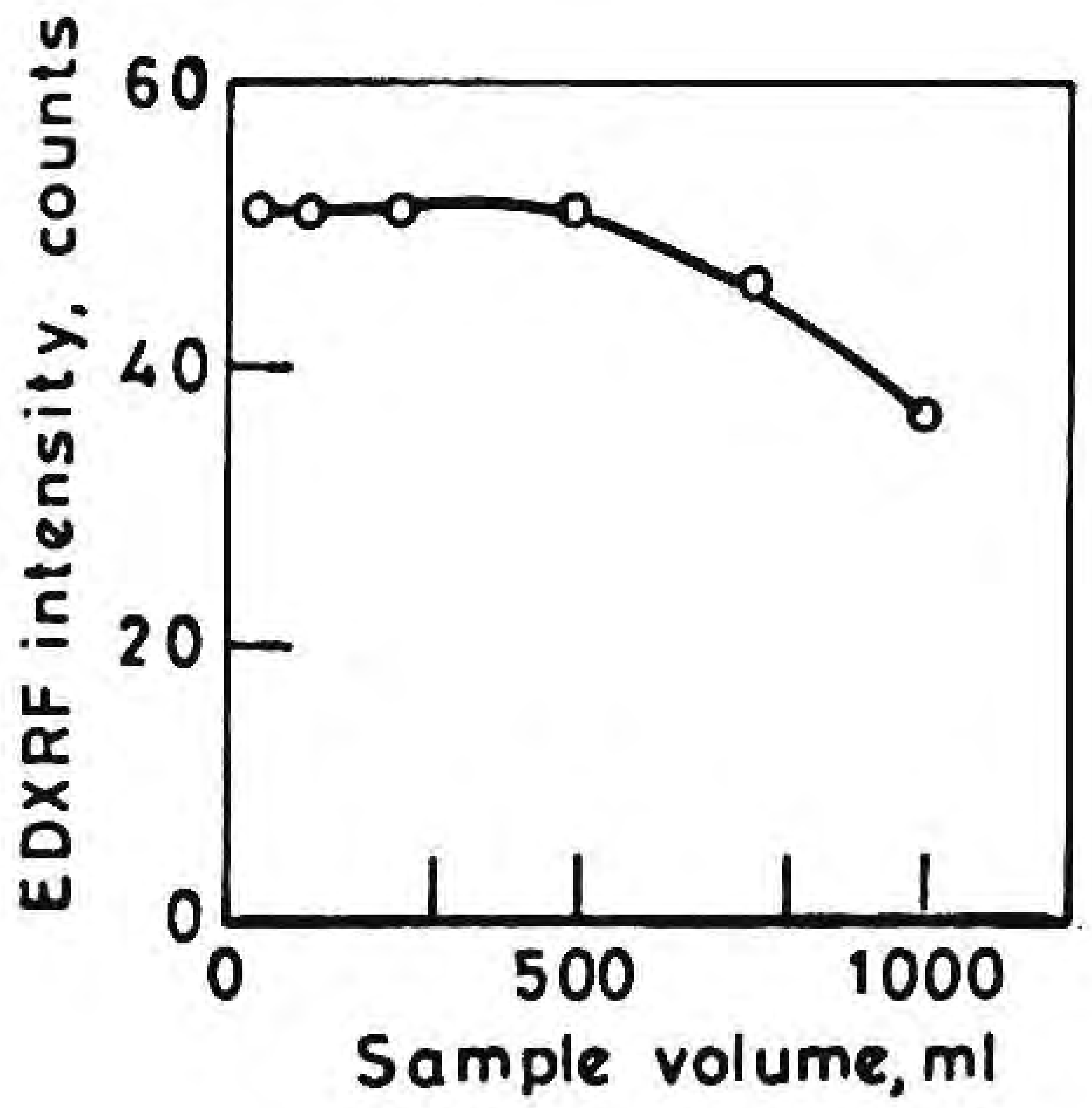


Fig. 6.5 Effect of sample volume

from 25 to 1000 ml. 0.3 g of activated carbon and 10 ml of 1% quinolin-8-ol were added. The resulting solutions were stirred for 20 minutes. Blanks were also run in each case. The adsorbed rare earth element - quinolin-8-ol complexes on activated carbon were made into pellets and quantitation was done as described in 6.1. It has been found that quantitative recoveries were obtained in the range 25 to 500 ml as shown in Fig. 6.5.

## 6.6 CALIBRATION GRAPH

Under the optimal conditions for the quantitative collection of rare earth elements as their quinolin-8-ol complexes on activated carbon, single and multielement calibration graphs for rare earth elements were obtained. Then the linearity of the calibration graphs were tested. To 0-400 µg of rare earth elements present in 500 ml of solution, 0.3 g of activated carbon followed by 10 ml of 1% quinolin-8-ol were added. The pH of the solutions was adjusted to 9 and stirred for 20 minutes using a magnetic stirrer. The activated carbon with rare earth element - quinolin-8-ol complex was vacuum filtered through 1.4 g ethyl cellulose supported on Whatman No.41 filter paper. The filter paper with contents was dried in hot air oven at $100^{o}$ C for 1 hour. The contents from the dried filter paper were scraped and homogeneously powdered in an agate mortar. 1 g of substance was taken and pressed into pellets by applying a pressure of 5 tons per square inch giving pellets of diameter 2.5 cm and about 0.18 cm thick.

The pressed powder pellets were subjected to EDXRF quantitation by irradiating with 50 mci Am-241 source for 10 minutes in a mylar based sample holder of 1 inch diameter. Three sets of samples were prepared. Each rare earth element was counted thrice for 10 minutes by using multichannel analyser. The average of low and high backgrounds was subtracted from the measured peak intensity to give net peak intensity. The average of three net peak intensities was then calculated from three individual measurements. The average of these average values obtained for three sets of samples was taken for calibration. A plot of the net peak counts against the concentration of rare earth elements expressed in microgram is a straight line passing through the origin as shown in Fig. 6.6(a) and 6.6(b)).

## 6.7 PRECISION

The precision of the developed procedure was deduced from the relative standard deviation (RSD) values calculated using the formula[329]

$$\mathrm{RSD} = ( \sigma N_p^2 + \sigma N_b^2)^{1/2} / (I_p - I_b) \times 100 \qquad (1)$$

where

$$\sigma N_p^2 = \Sigma d_p^2 / n-1 \quad \text{where} \quad n = 15 \qquad (2)$$

and

$$\sigma N_b^2 = \Sigma d_b^2 / n-1 \quad \text{where} \quad n = 15 \qquad (3)$$

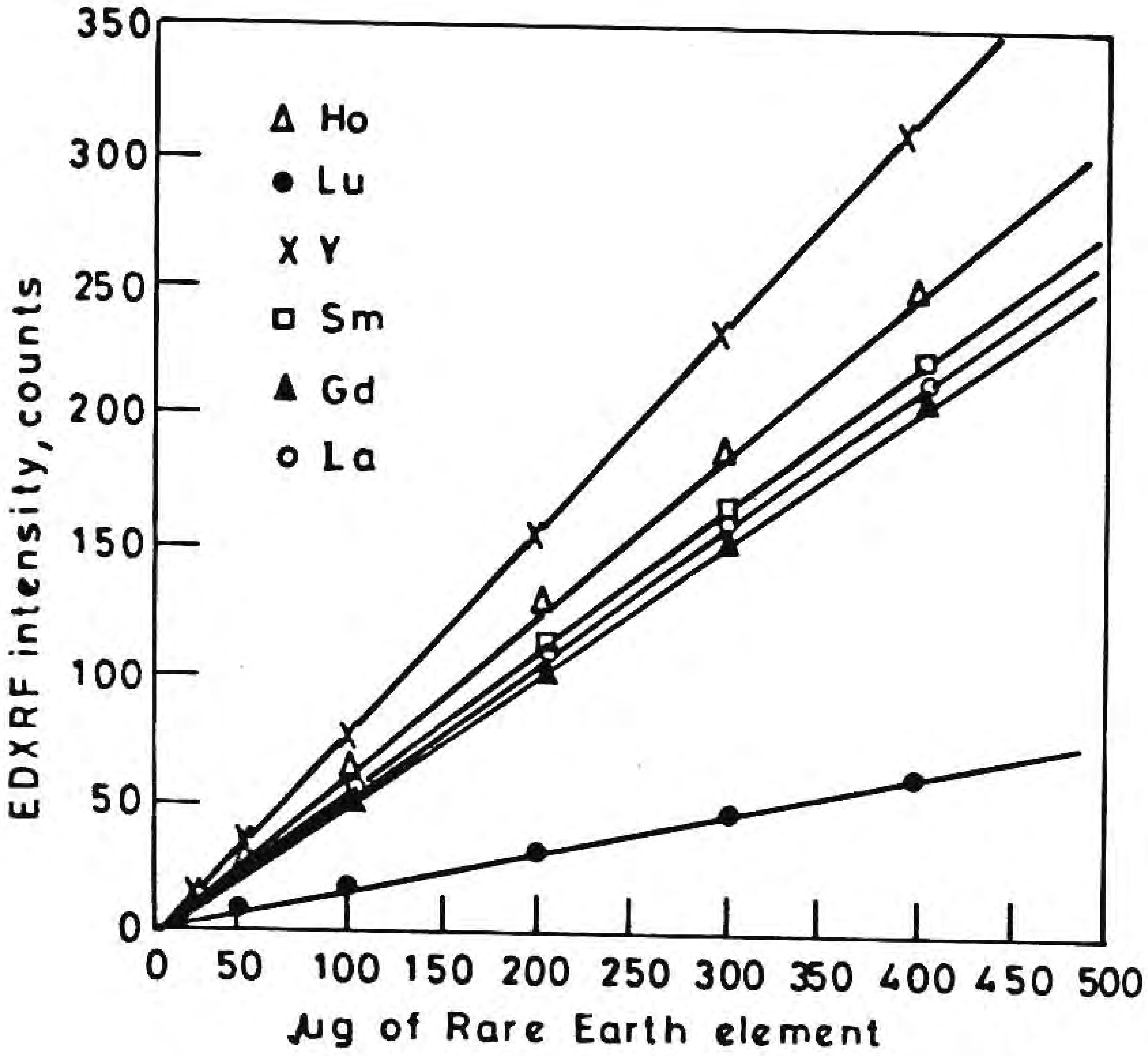


Fig. 6.6 (a) Calibration graph

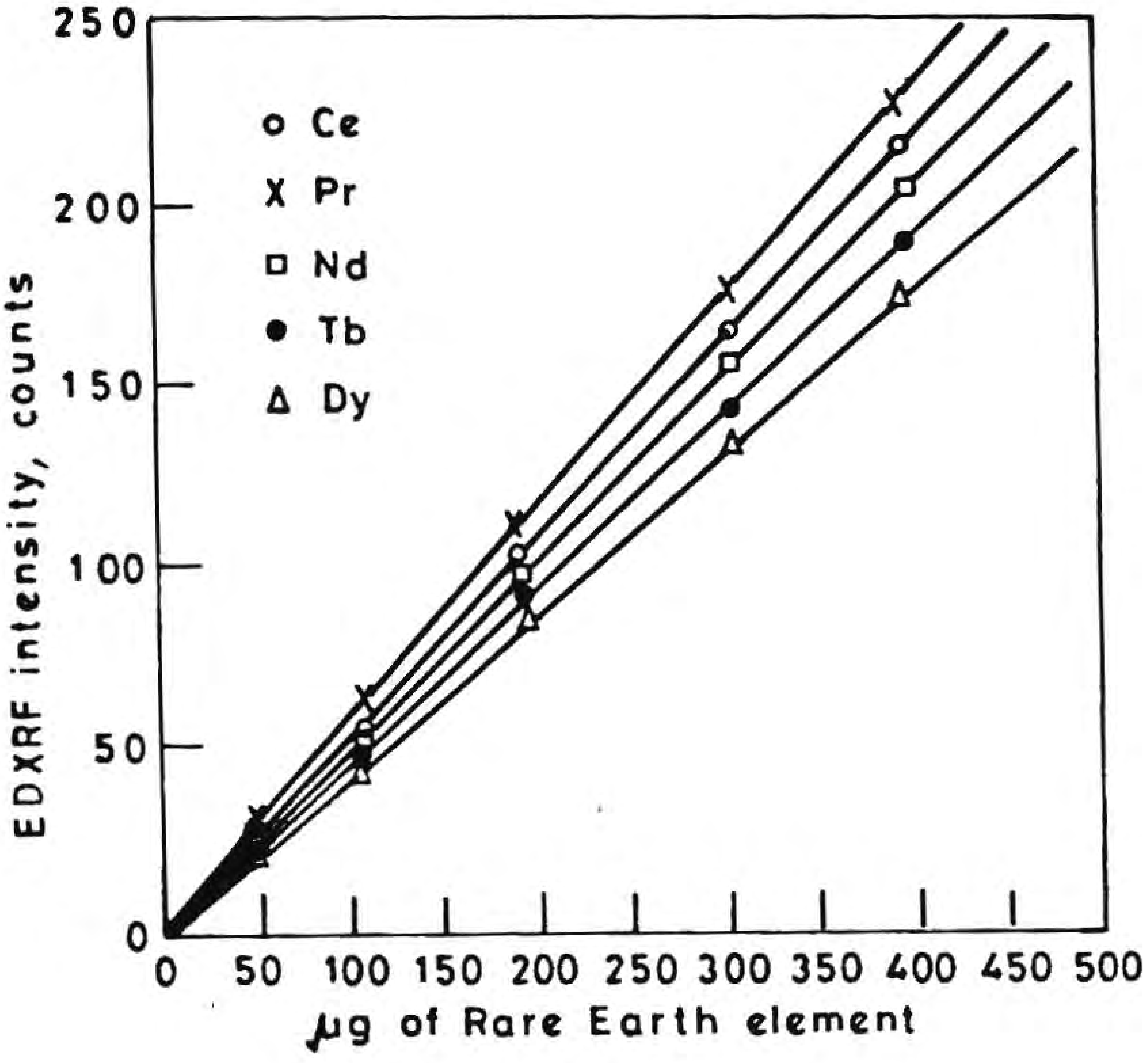


Fig. 6.6 (b) Calibration graph

$\Sigma d_p^2$ = sum of the squares of differences of individual peak counts from mean total peak count ($I_p$)

$\Sigma d_b^2$ = sum of the squares of differences of individual background counts from mean background count ($I_b$)

The relative standard deviation values for various rare earth elements lie in the range 5 to 10% for 100 μg each of individual rare earth elements present in 500 ml of solution. These values are concentration dependent and precision was better at higher concentrations.

The RSD and signal to noise ratio were quite high mainly because of the constant compton background arising from the source itself in view of the annular geometry employed[140].

One way of eliminating this compton background was by the use of analog device that perform operations of differentiation and filtering such as RC filters. Among the various numerical methods, method of least squares performed these operations without additional computational complexity unaffected by the practical restrictions of real circuitry and serve loops resulting in considerable improvement in the information to be obtained as described in previous Chapter. The least square calculations were carried out using fifth order polynomial with 25 consecutive values on computer by the convolution of the previously digitized and averaged data points with properly chosen integers. Instead of nine consecutive values in Chapter V twenty five consecutive values were chosen as it gave a better representative curve corresponding to actual points. After simple curve fitting as described above, a variety of least squares were used for determining the first order derivative and higher order derivatives. The derivatives were obtained from the formula

$$D_S = S! \cdot b_S / \Delta x^S$$

where $\Delta x$ is the sampling interval (=0.03 Kev in the present study and S is the order of the derivative. The procedure was repeated for the other values by droping the point at one end of the group and adding next point at the other end. The computations were done using HCL Work Horse II computer and the plots were obtained using 1-2-3 lotus facility. The best derivative was chosen by calculating the SNR values. As shown in Table I, the SNR value of 2.7 was obtained for first order derivative for 10 μg of neodymium present in 500 ml of the solution. Hence $^1D$ was chosen as it offers a good detection limit of 10 ppb of neodymium.

Fig. 6.7 shows the typical spectra obtained for 0 and 100 μg of neodymium present in 500 ml of solution with and without smoothening by using the algorithm described above. Figures 6.8 and 6.9 show zeroth and first order derivative obtained for 0 and 100 μg (after subtracting blank) of $Nd^{3+}$ present in 500 ml of solution. First order derivative was chosen

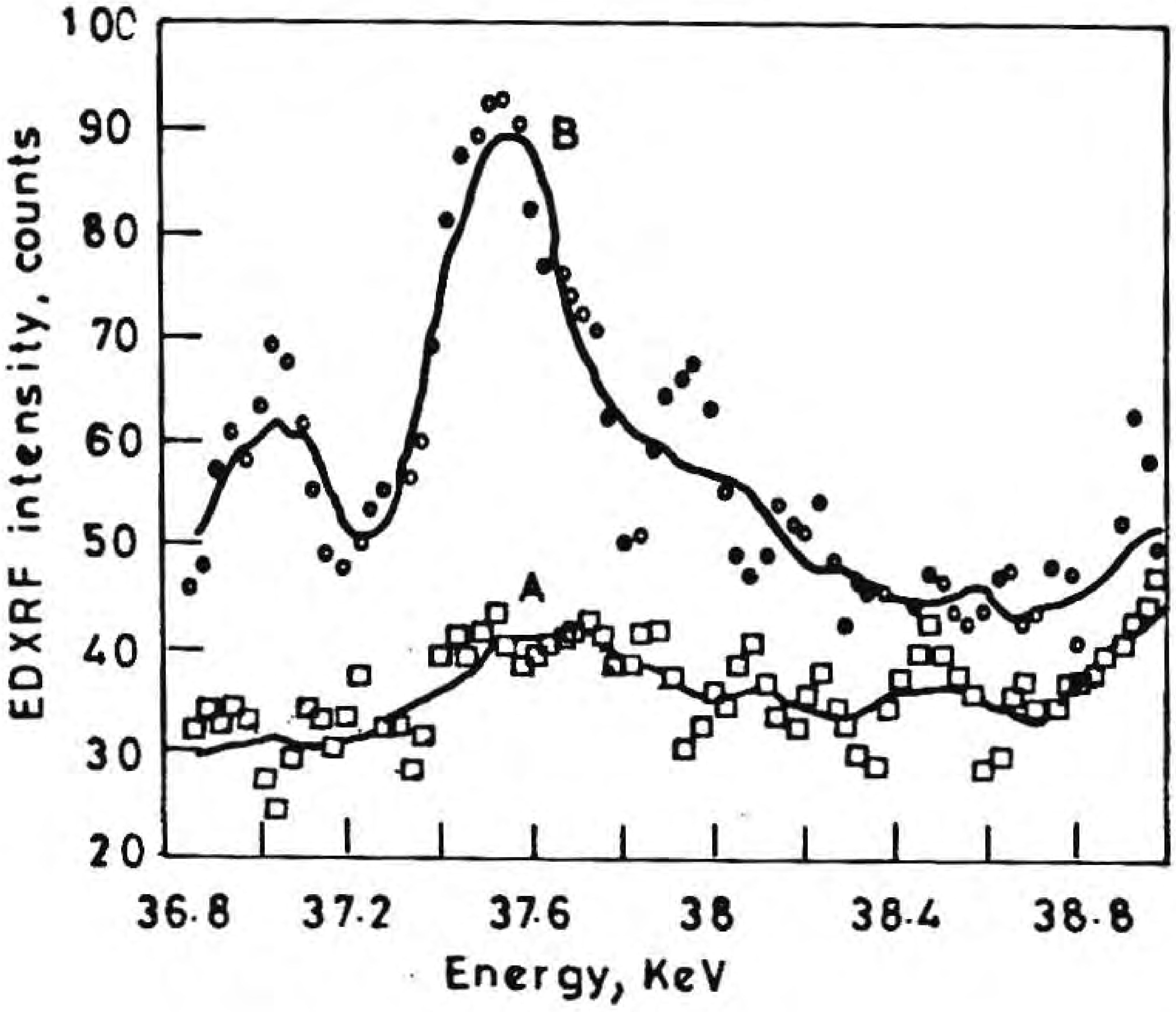


Fig. 6.7 EDXRF spectra obtained for 0 (curve A) and 100 µg (curve B) of neodymium with and without smoothening by using the described algorithm

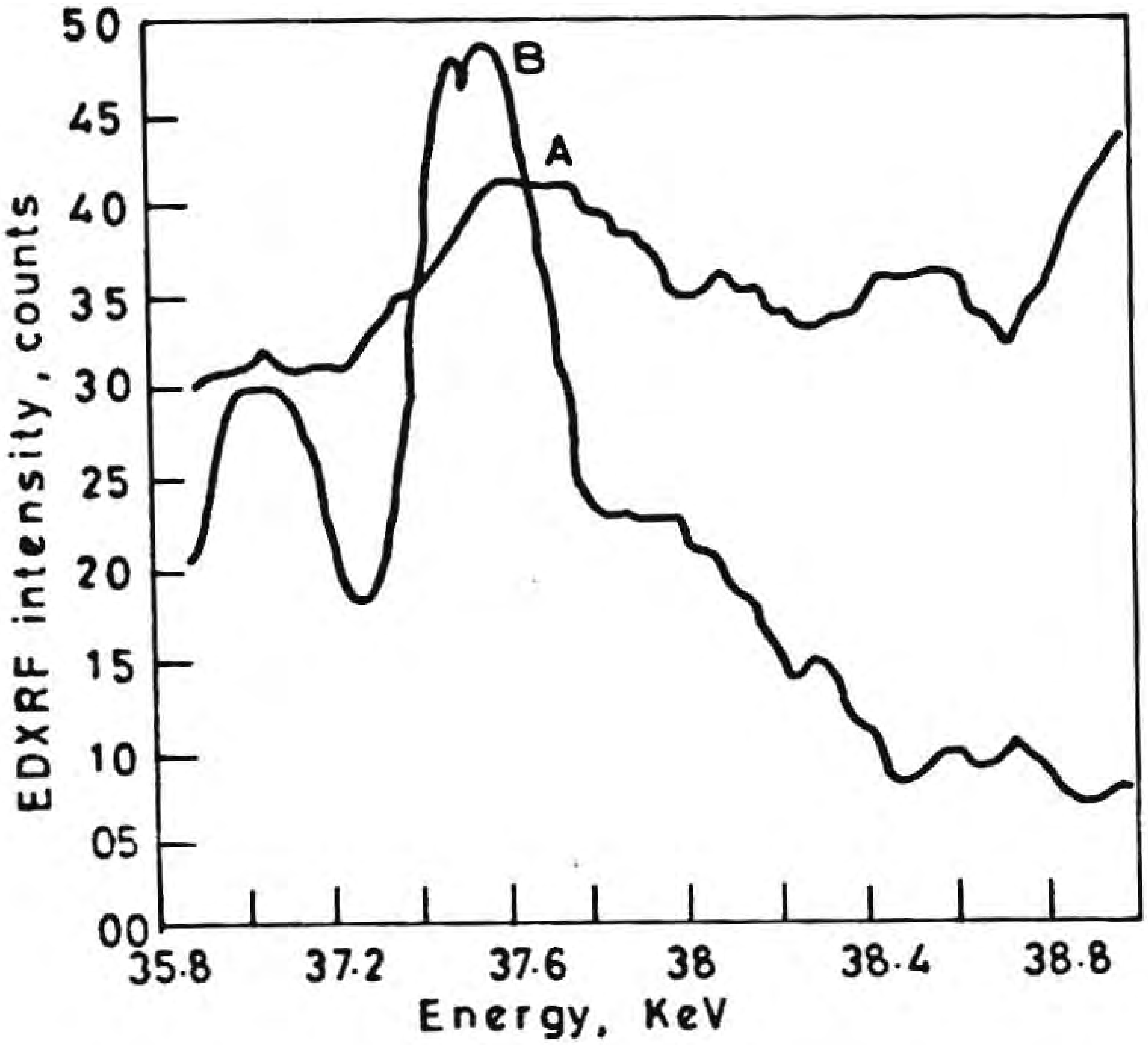


Fig. 6.8 Zero order derivative EDXRF spectra of 0 (curve A) and 100 µg (curve B) of neodymium (after subtracting blank under optimal conditions

as it offered higher sensitivity(i.e. higher signal to noise ratio) as shown in Table I.

Table I

| No. | Order of derivative mode | SNR value |
|---|---|---|
| 1 | $^{0}D$ | 0.30 |
| 2 | $^{1}D$ | 2.7 |
| 3 | $^{2}D$ | 2.20 |
| 4 | $^{3}D$ | 2.00 |
| 5 | $^{4}D$ | 1.70 |

Single and multi element calibration graphs were drawn. The rare earth elements present in 500 ml of solution was treated with 0.3 g of activated carbon. Then 10 ml of 1% solution of quinolin-8-ol in minimum amount of acetic acid was added. Then the resulting solutions were stirred for 20 minutes, so as to ensure quantitative collection using a magnetic stirrer.

The samples were prepared as described earlier and subjected to EDXRF quantitation.' Then the data for first order derivative were calculated using computer. The calibration graphs were drawn for each element by plotting the amplitudes against concentration of rare earth element expressed in micrograms. As shown in Fig. 6.10 (a and b), it has been found that linear calibration graphs passing through the origin were obtained for 0 to 400 μg of rare earth elements present in 500 ml of solution.

## 6.8 ANALYSIS OF SYNTHETIC SAMPLES

The usefulness of the developed method was tested by analysing the rare earth element content of various synthetic samples. The results are summarised in Table II. It is clear from the table that the recoveries were good and therefore the method can be used for the reliable determination of rare earth elements present in unknown samples of similar composition.

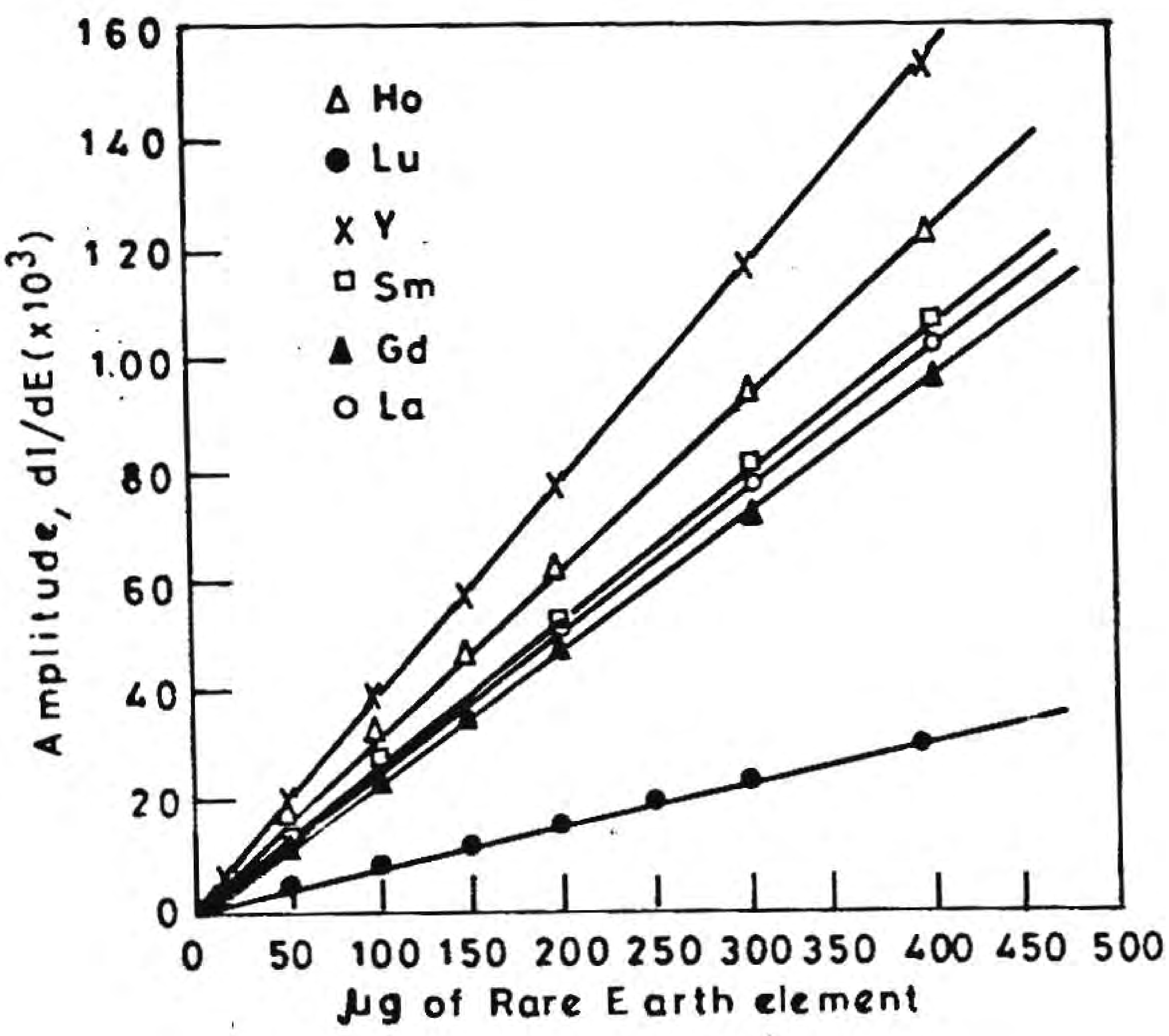


Fig. 6.10 (a) Calibration graph (in $^1$D mode)

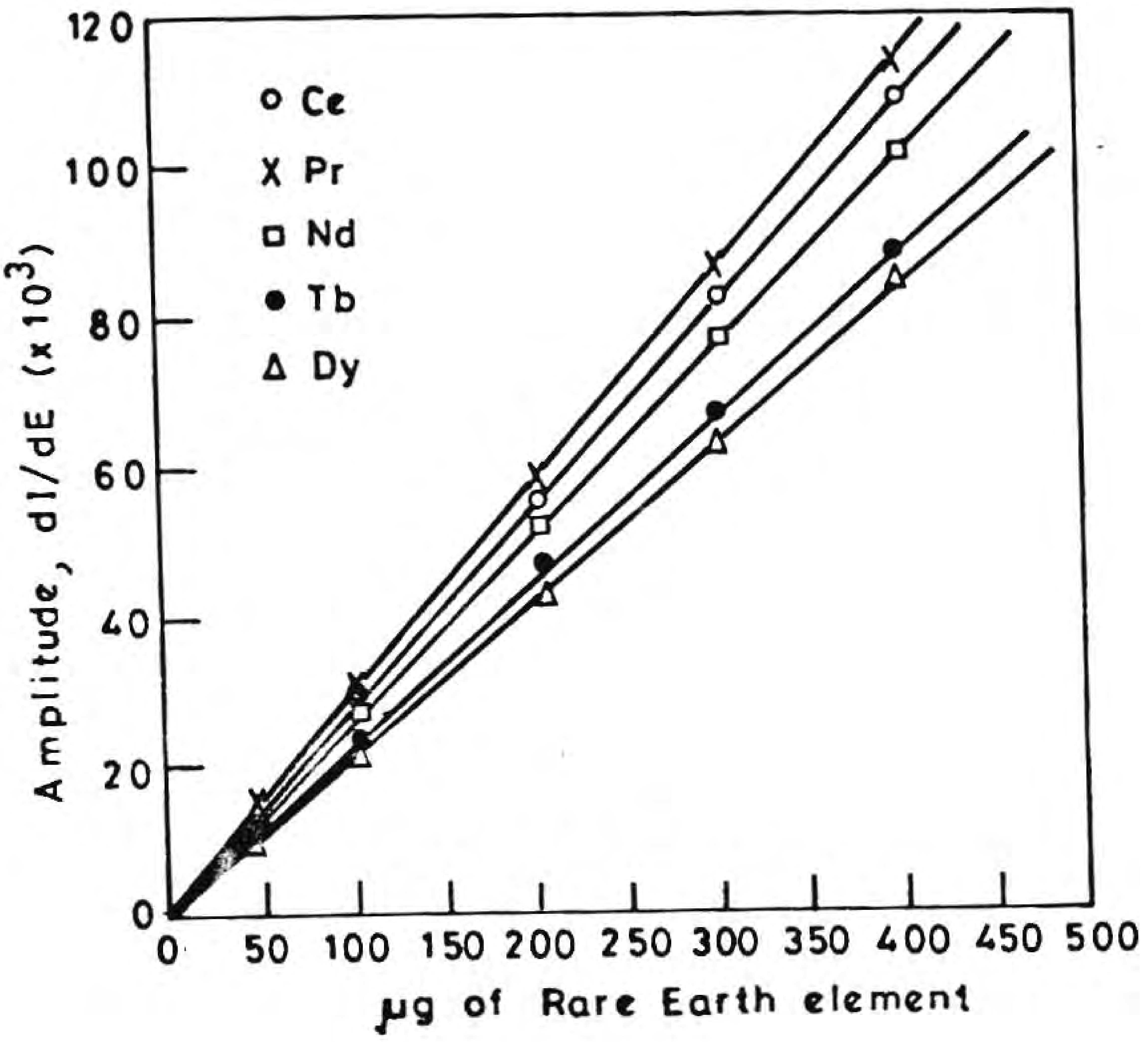


Fig. 6.10 (b) Calibration graph (in $^1$D mode)

## Table II

## Recovery studies

| Sample No. | Composition of mixture, µg/0.5 litre | | | | | | | | Recovery*, % | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Nd | Sm | Gd | Tb | Dy | Ho | Tm | Lu | Nd | Sm | Gd | Tb | Dy | Ho | Tm | Lu |
| 1 | 50 | 50 | 100 | 100 | 200 | 200 | 300 | 300 | 100 | 100 | 99.2 | 99.0 | 99.4 | 98 | 98.5 | 98 |
| 2 | 100 | 100 | 200 | 200 | 300 | 300 | 50 | 50 | 100 | 100 | 98.6 | 99.2 | 99.3 | 98.9 | 99 | 99.6 |
| 3 | 200 | 200 | 300 | 300 | 50 | 50 | 100 | 100 | 99.4 | 99.5 | 99.1 | 98.8 | 99.8 | 99.5 | 99.3 | 98.8 |
| 4 | 300 | 300 | 50 | 50 | 100 | 100 | 200 | 200 | 99.2 | 99.4 | 99.2 | 99.3 | 98.7 | 98.9 | 98.6 | 99.2 |

* Average of 3 determinations

## 6.9 EXPERIMENTAL

### 6.9.1 Apparatus

The details of energy dispersive x-ray fluorescence spectrometer were same as described in Chapter V.

### 6.9.2 Reagents

All reagents used were of analytical grade.

1. Standard rare earth element solutions:

Prepare individual rare earth element stock solutions (Rare Earth Products, Cheshire) by dissolving respective rare earth oxides in 1:1 hydrochloric acid and standardize with EDTA.

2. Activated carbon (Riedel-de-Haen):

3. Quinolin-8-ol (Merck, 1%):

Dissolve 10 g of quinolin-8-ol in minimum amount of glacial acetic acid and dilute with water to 1 L.

4. Ethyl cellulose (Loba Chemie, Bombay)

### 6.9.3 Procedure

Transfer an aliquot of solution containing $\geq 5$ $\mu$g of any single rare earth element or admixture containing a minimum of 5 $\mu$g of each rare earth element to a 1 L beaker. Add 0.3 g of activated carbon and 10 ml of 1% quinolin-8-ol. Adjust the pH of the solution to 9 with 2% sodium hydroxide. Stir the resulting solution for 20 minutes for quantitative collection of trace amounts of rare earth elements.

Filter activated carbon along with rare earth element - quinolin-8-ol complex through 1.4 g ethyl cellulose (200 mesh) supported on Whatman No.41 filter paper. Dry the filter paper with contents in hot air oven at 100$^{\circ}$C for 1 hour. Scrap the contents from the dried filter paper. Powder homogeneously in an agate mortar. Take 1 g of substance and press into pellets by applying a pressure of 5 tons per square inch giving pellets of diameter 2.5 cm and about 0.18 cm thick.

Irradiate the pressed powder pellets with 30 mci Am-241 source for 10 minutes in a mylar based sample holder of 1 inch diameter. Prepare three sets of samples. Count each rare earth element thrice for 10 minutes by using multichannel analyser. Subtract the average of low and high backgrounds from the measured peak intensity to give net peak intensity. Calculate the average of three net peak intensities from three individual measurements. Take the average of these average values obtained for three sets of samples for calibration.

### 6.9.4 Derivative procedure

Proceed as described above. Convert the counts of each rare earth element into amplitude in first derivative mode by using a fifth order polynomial with 25 consecutive values for smoothing and differentiation. Take these amplitudes for each concentration while drawing calibration graph.

# CHAPTER VII

# EDXRF DETERMINATION OF RARE EARTHS AFTER PRECONCENTRATION ON PAN MODIFIED NAPHTHALENE

The growing interest in the development of good preconcentration technique for the determination of traces of inogranics led to the introduction of new substances and in some cases modification of such substances by appropriate chelating groups as collectors.

Naphthalene in the molten state was found to be a good collector for the collection of traces of almost all elements. Sataka and Fujinaga [349-351] used molten naphthalene for preconcentration of all elements irrespective of their nature. A large number of studies were reported for the preconcentration of iron by the extraction of various iron complexes, binary or ternary into molten naphthalene and subsequent spectrophotometric determination of the extracted complexes. Ternary complex of iron(II) with 2,2'- bipyridyl[352] (1,10-phenanthroline) and tetraphenyl borate was an example of this type. Bismuth[354], cobalt[349], nickel[349], ruthenium[355], rhodium[355], copper[356], palladium[357], uranium[357] and molybdenum[351] were preconcentrated after forming the complexes with chromogenic reagents such as 2-mercaptobenzothiazole, phenanthrenequinone monoxime, nioxime (cyclohexane-1,2,diene dioxime), 9,10-phenanthrenequinone monoxime, pyrrolidene carbodithioate and oxine and extraction of the respective complexes into molten naphthalene. Then the extracted complexes were separated and determined by spectrophotometry. Thus molten naphthalene in presence of a variety of chelating agents was proved to be a good collector as described above.

Some reports were available where microcrystalline naphthalene was used together with adsorbed chromogenic reagents. The reagents used in the molten naphthalene procedures were also used along with microcrystalline naphthalene. Zinc, cadmium and lead in an admixture[358] was concentrated after coprecipitation of their morpholine-4-carbodithioate with microcrystalline naphthalene and subsequent determination by atomic absorption spectrometry. Oxine was used for collecting magnesium[359] and zinc[360] and these are subsequently determined by spectrophotometry.

Fujinaga et al[361] had developed a method for the rapid x-ray fluorescence analysis of trace metals after collecting over naphthalene powder doped with 1-(2-thiozolylazo)-2-naphthol.

Puschel [362] introduced the use of 1-(2-pyridylazo)2-naphthol (PAN) for preconcentration purposes. Watanabe et al [363] applied PAN in combination with wavelength dispersive x-ray spectrometry. The reported works were mainly connected with the trace analysis of transition metals. Sub ppb levels of cadmium, cobalt, copper, iron, manganese, lead and zinc [269] in water samples were preconcentrated via their complexation with 1-(2-pyridylazo)2-naphthol and determined by atomic absorption spectrometry. Fang et al [364] studied the separation of osmium and ruthenium in a high performance liquid chromatographic column as PAN chelates. A procedure [365] was described for the preconcentration of cadmium, cobalt, chromium, copper, manganese, uranium and zinc from sea water samples by coprecipitation with PAN prior to neutron activation analysis. Preconcentration with 30 mg of PAN was most effective at pH 9 with final recoveries of 76-91% for six elements and 50% for uranium. Among different organic collectors, PAN seems to be the most promising for neutron activation analysis of many heavy metals [366,367]. Further, it has been applied for preconcentration of heavy metals from natural water and artificial sea water in conjunction with x-ray fluorescence spectrometry [362,363,368].

The feasibility of using PAN - polyether and polyester-polyurethane foam in batch and column operations had been examined [369]. The uptake of cobalt and manganese on PAN-polyester foam column was found to be quantitative. Braun et al [370] developed a spectrophotometric method for the determination of traces of cobalt in water after preconcentration on polyurethane foam loaded with 1-(2-pyridylazo)2-naphthol. The preconcentration of traces of cobalt from water at the ppb level with a preconcentration factor of 1000 or more was achieved. Satake et al[371] used 5,7-dichlorooxine for the formation of iron complex. This complex was shaken with naphthalene in acetone. The precipitate was filtered, washed and dissolved in dimethyl formamide and determined by spectrophotometry at 476 nm.

Based on all these reports the possibility of using PAN modified naphthalene as a collector for the preconcentration of traces of rare earth elements is checked and the procedure is described in detail. The application of this procedure to the analysis of xenotime sample is also described.

## PRELIMINARY STUDIES

Preliminary investigations indicated the quantitative preconcentration of rare earth elements onto PAN modified naphthalene as evidenced by the absence of these elements in the solution as determined by Arsenazo I[4] procedure by using spectrophotometry. The possibility of using pure naphthalene for the preconcentration of rare earth elements was checked. It was found that preconcentration did not occur onto unmodified naphthalene as proved by the presence of these elements in the sample after treating with naphthalene. Eventhough molten naphthalene was a good collector for trace metals [351-353], solid naphthalene requires an additional chelating agent to complex the trace metal ions.

The EDXRF spectrum obtained with naphthalene (0.5 g) pellet when irradiated for 10 minutes with 50 mci Am-241 annular source with Si(Li) detector and the EDXRF spectrum obtained with PAN modified naphthalene under the same conditions had exactly identical features and did not produce high background at the energies corresponding to the characteristic K x-rays of all rare earth elements. This shows the suitability of the PAN modified naphthalene being used as a collector for rare earth elements.

Initial experiments showed that the collection of rare earth elements on PAN modified naphthalene was not possible in acidic medium and it was not quantitative in neutral medium. But it became quantitative in weakly alkaline medium of pH around 9 which is the optimum pH for the spectrophotometric determination of samarium[65] using 1-(2-pyridylazo)2-naphthol as chromogenic reagent. The advantage of the use of PAN modified naphthalene is that it does not require any external binder for pellet preparation for EDXRF quantitation while the other two procedures described in Chapters V and VI required ethyl cellulose as external binder. Here naphthalene itself serves as a binder. Again it was found that stirring of the solution is essential to get the quantitative collection.

Traces of rare earth elements were taken up by the PAN present in the PAN modified naphthalene in alkaline medium. The PAN modified naphthalene with rare earth elements in aqueous solution was stirred using magnetic stirrer. Then the sample was filtered through a Whatman No.41 filter paper and air dried. The contents from dried filter paper was scraped and transferred to an agate mortar. The contents were homogeneously powdered and pressed in the form of pellets of 1 inch diameter by applying a pressure of 5 tons per square inch in a carvar press.

The characteristic K x-rays of rare earth elements were produced by radioisotope excitation. An annular source holder containing the annular source Am-241, 50 mci, 59.57 Kev, 1 inch active dia. provided x-rays for excitation. The characteristic secondary K x-rays were detected by the Si(Li) detector.

The pressed powder pellets were analysed by irradiating with Am-241 source for 10 minutes in a mylar based sample holder (1 inch diameter). Three sets of samples were prepared. Each element was counted thrice for 10 minutes by using multichannel analyser. The average of low and high backgrounds was subtracted from the measured peak intensity to give net peak intensity. The average of three net peak intensities were then calculated from three individual measurements. The average of the average values obtained for three sets of samples was considered as correct peak count and used to draw the calibration graphs.

Various parameters that influence the collection of rare earth elements on PAN modified naphthalene was investigated systematically. The results obtained with a key element viz. neodymium alone is described in detail since all rare earth elements behave similarly. The applicability of the developed procedure for the analysis of xenotime sample is also described.

## 7.1 EFFECT OF PERCENTAGE OF PAN IN PAN MODIFIED NAPHTHALENE

The percentage of PAN in naphthalene for the preparation of PAN modified naphthalene was varied in the range 1-50%. Naphthalene and PAN were mixed in the required proportions and dissolved in minimum amount of acetone. This acetone solution was poured as a fine stream into a 1 litre beaker containing water and stirred for 30 minutes using magnetic stirrer. The PAN modified naphthalene was filtered and air dried.

From each composition, 0.5 g of PAN modified naphthalene was taken and 100 µg each of rare earth elements present in 500 ml of solution was transferred to 1000 ml beaker. The solution was maintained at 0.1 M in $NH_3$-$NH_4Cl$ by adding 50 ml of 1 M ammonia-ammonium chloride buffer. The pH of the solution was adjusted to 9. The resulting solution was stirred for about 20 minutes for quantitative collection.

The PAN modified naphthalene along with the rare earth elements was filtered through Whatman No.41 filter paper, air dried and ground in an agate mortar. The resulting sample was pressed into solid thin targets of diameter 2.5 cm and about 0.07 cm thick.

Corresponding blanks were also prepared for each composition of PAN modified naphthalene. Three sets of samples were prepared and pressed powder pellets were subjected to EDXRF quantitation via. their characteristic k-radiation. Each element was counted thrice by using multichannel analyser. The background obtained by average of low and high backgrounds was subtracted from the measured peak intensity to give net peak intensity. The average of three net peak intensities was calculated from three individual measurements. The average of the average values obtained for three sets of samples was considered as the correct peak count. It has been found that at percentages $\geq$ 6% of PAN in naphthalene, collection is quantitative as shown in Fig. 7.1. 0.5 g of 10% PAN modified naphthalene was used in subsequent studies.

## 7.2 EFFECT OF pH

The solution containing 100 μg each of rare earth elements present in a total volume of 500 ml was treated with 0.5 g of 10% PAN modified naphthalene. Then the pH of the solutions was adjusted in the range 2 to 12 one after another. Corresponding blanks were also run. The resulting solutions were stirred for 20 minutes using a magnetic stirrer. The PAN modified naphthalene along with the rare earth elements was filtered through Whatman No.41 filter paper. The samples were air dried and ground in an agate mortar and pressed into pellets for EDXRF quantitation. Three sets of samples were prepared. Each element was counted thrice using multichannel analyser. The background obtained by average of low and high backgrounds was subtracted from the measured peak intensity to give net peak intensity. The average of three net peak intensities was calculated from three individual measurements. The average of the average values obtained for three sets of samples was considered as the correct peak count. The results obtained are shown in Fig. 7.2. It is clear from the figure that quantitative collection of rare earth elements was obtained in the pH range 8-12 and pH ~ 9 was maintained in subsequent studies.

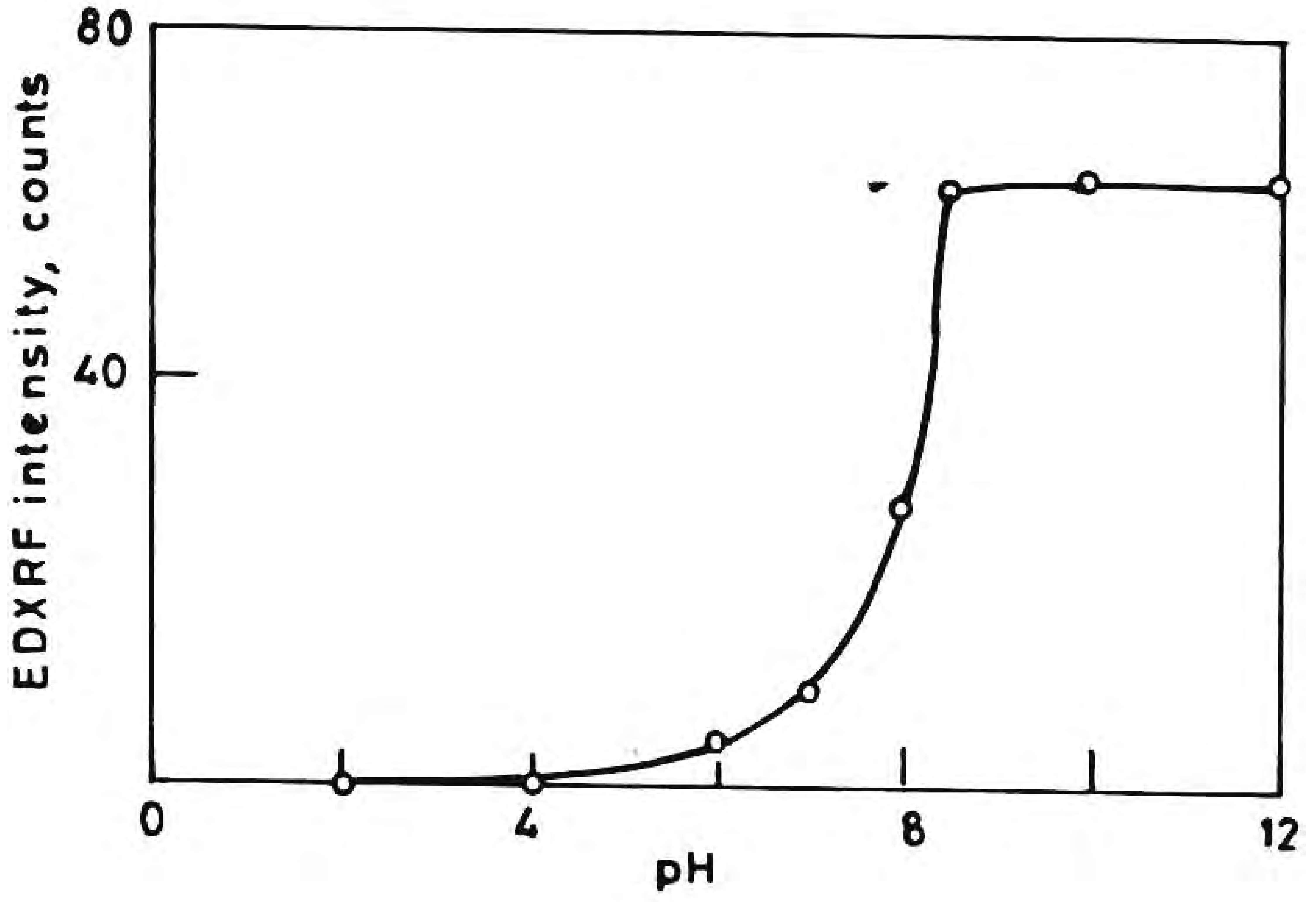


Fig. 7.2 Effect of pH

## 7.3 EFFECT OF STIRRING TIME

0.5 g of 10% PAN modified naphthalene was added to a solution containing 100 μg each of rare earth elements present in 500 ml. The resulting solution was maintained at 0.1 M in $NH_3$-$NH_4Cl$ by adding 50 ml of 1 M $NH_3$ -$NH_4$ Cl buffer. Then the pH of the solution was adjusted to 9. Similarly prepared solutions were stirred in the range 5-60 minutes using a magnetic stirrer. Blanks were also run in the same range.

The PAN modified naphthalene along with collected rare earth elements was filtered through Whatman No.41 filter paper. The precipitate was filtered, air dried and made into pellets and subjected to EDXRF quantitation. Three sets of samples were prepared. Each element was counted thrice by using multichannel analyser. The background obtained by average of low and high backgrounds was subtracted from the measured peak intensity to give net peak intensity. The average of three net peak intensities was calculated from three individual measurements. The average of the average values obtained for three sets of samples was considered as the correct peak count.

A minimum of 10 minutes stirring time was enough for quantitative collection of rare earth elements as seen from Fig.7.3. A stirring time of 20 minutes was chosen in subsequent experiments.

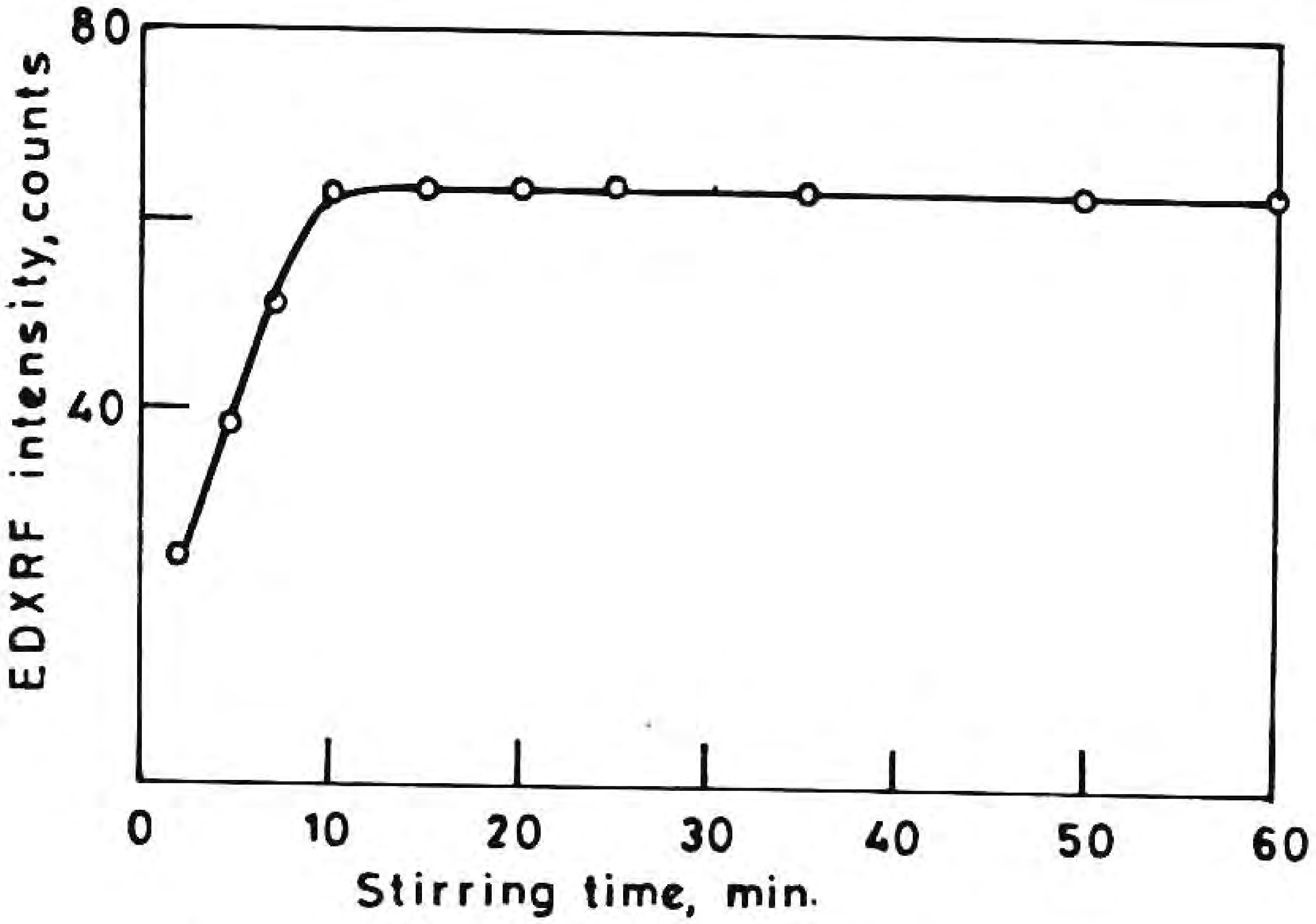


Fig. 7.3 Effect of stirring time

## 7.4 EFFECT OF SAMPLE VOLUME

100 μg each of rare earth elements present in aqueous solution was treated with 0.5 g of 10% PAN modified naphthalene. The sample volume was varied in the range 25 to 1000 ml. The solutions were maintained at 0.1 M in $NH_3$-$NH_4Cl$ and adjusted the pH to 9. The resulting solutions were stirred for 20 minutes using a magnetic stirrer. Corresponding blanks were also run. The PAN modified naphthalene with rare earth elements was filtered through Whatman No.41 filter paper. Then the precipitates were air dried and made into pellets. Three sets of samples were prepared for each sample volume. Each element was counted thrice by using multichannel analyser. The background obtained by average of low and high backgrounds was subtracted from the measured peak intensity to give net peak intensity. The average of three net peak intensities was calculated from three individual measurements. The average of the average values obtained for three sets of samples was considered as the correct peak count. The results obtained are shown in Fig. 7.4. It has been found that the collection was quantitative in the sample volume ranging from 25 to 500 ml.

## 7.5 CALIBRATION GRAPH

Single and multielement calibration graphs were drawn.

500 ml solutions containing 0-400 μg of rare earth elements

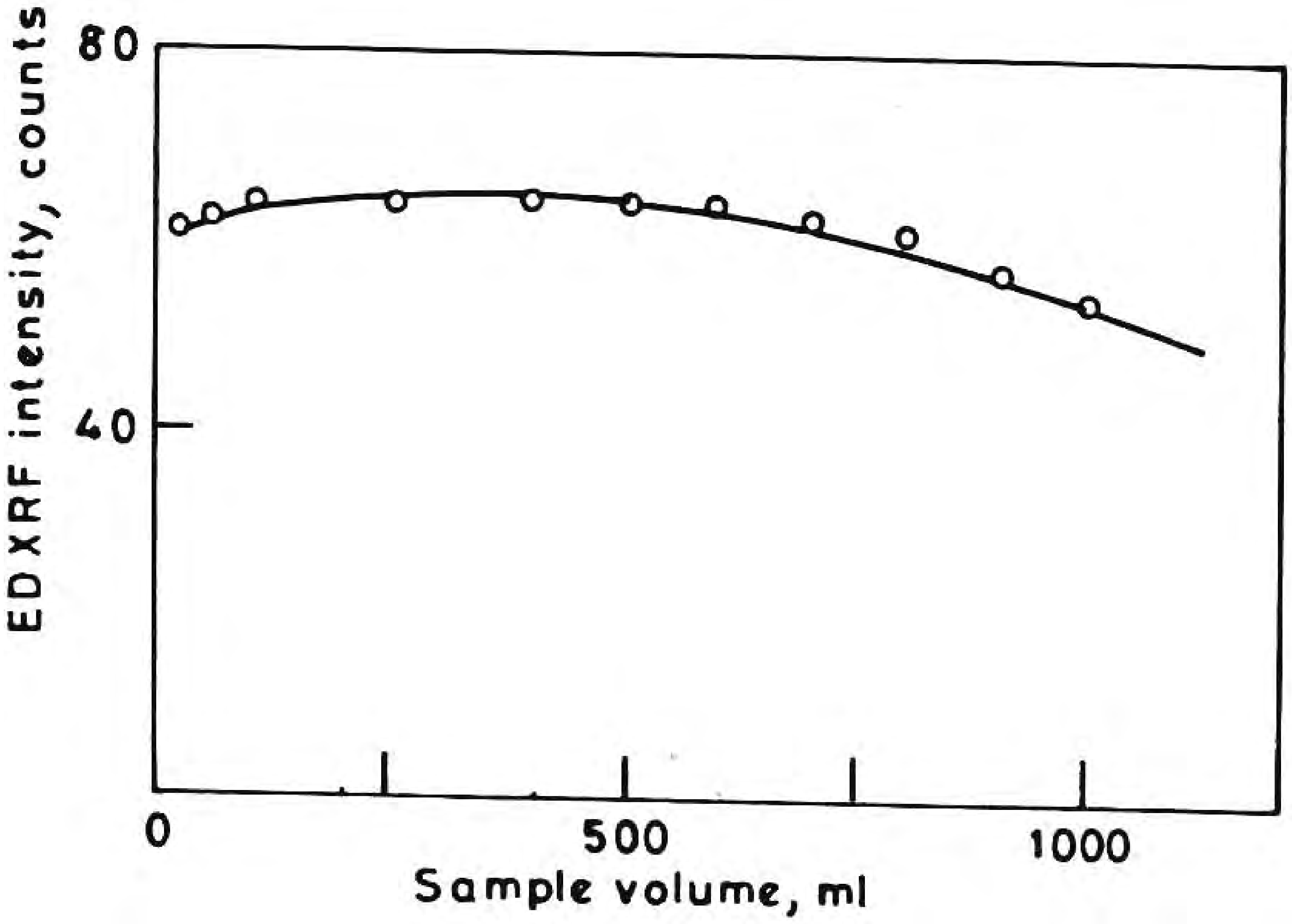


Fig. 7.4 Effect of sample volume

were treated with 0.5 g of 10% PAN modified naphthalene. The overall concentration of the solution was maintained at 0.1 M in $NH_3$ -$NH_4$ Cl. The pH of the solutions was adjusted to 9. The resulting solutions were stirred for 20 minutes using magnetic stirrer. A blank was also run under the identical conditions.

The PAN modified naphthalene along with different amounts of rare earth elements were filtered through Whatman No.41 filter paper and air dried. The contents from the dried filter paper were scraped and transferred to an agate mortar. The contents were homogeneously powdered and pressed in the form of pellets of 1 inch diameter by applying a pressure of 5 tons per square inch in a carvar press.

Three sets of samples were prepared for each concentration. The characteristic K x-rays of rare earth elements were produced by radioisotope excitation. An annular source holder containing the annular source Am-241, 50 mci, 59.57 Kev, 1 inch active dia provided x-rays for excitation. The characteristic secondary x-rays were produced by irradiating for 10 minutes in a mylar based sample holder and detected by the Si(Li) detector. Each element was counted thrice for 10 minutes by using multichannel analyser. The average of low and high backgrounds was subtracted from the measured peak intensity to give net peak intensity. The average of three net peak intensities were then calculated from three individual measurements. The average of the average values obtained for three sets of samples was considered as the correct peak count. The correct peak counts were plotted against the concentration of rare earth elements expressed in micrograms. Linear calibration graphs passing through the origin were obtained for all rare earth elements in the range 0-400 μg present in 500 ml as shown in Fig. 7.5.

## 7.6 PRECISION

The precision of the developed procedure for various rare earth elements was deduced from relative standard deviation (RSD) values obtained on 15 different samples using the formula[329] as described in Chapter V and VI.

$$\% \text{ SD (RSD)} = \frac{[\,\sigma N_p^2 + \sigma N_b^2)^{1/2}\,] \times 100}{(I_p - I_b)}$$

where

$\sigma N_p^2 = \Sigma d_p^2/(n-1)$ where $n = 15$

$\sigma N_b^2 = \Sigma d_b^2/(n-1)$ where $n = 15$

$\Sigma d_p^2$ = sum of the squares of differences of individual peak counts from mean total peak count $(I_p)$

$\Sigma d_b^2$ = sum of the squares of differences of individual background counts from mean background

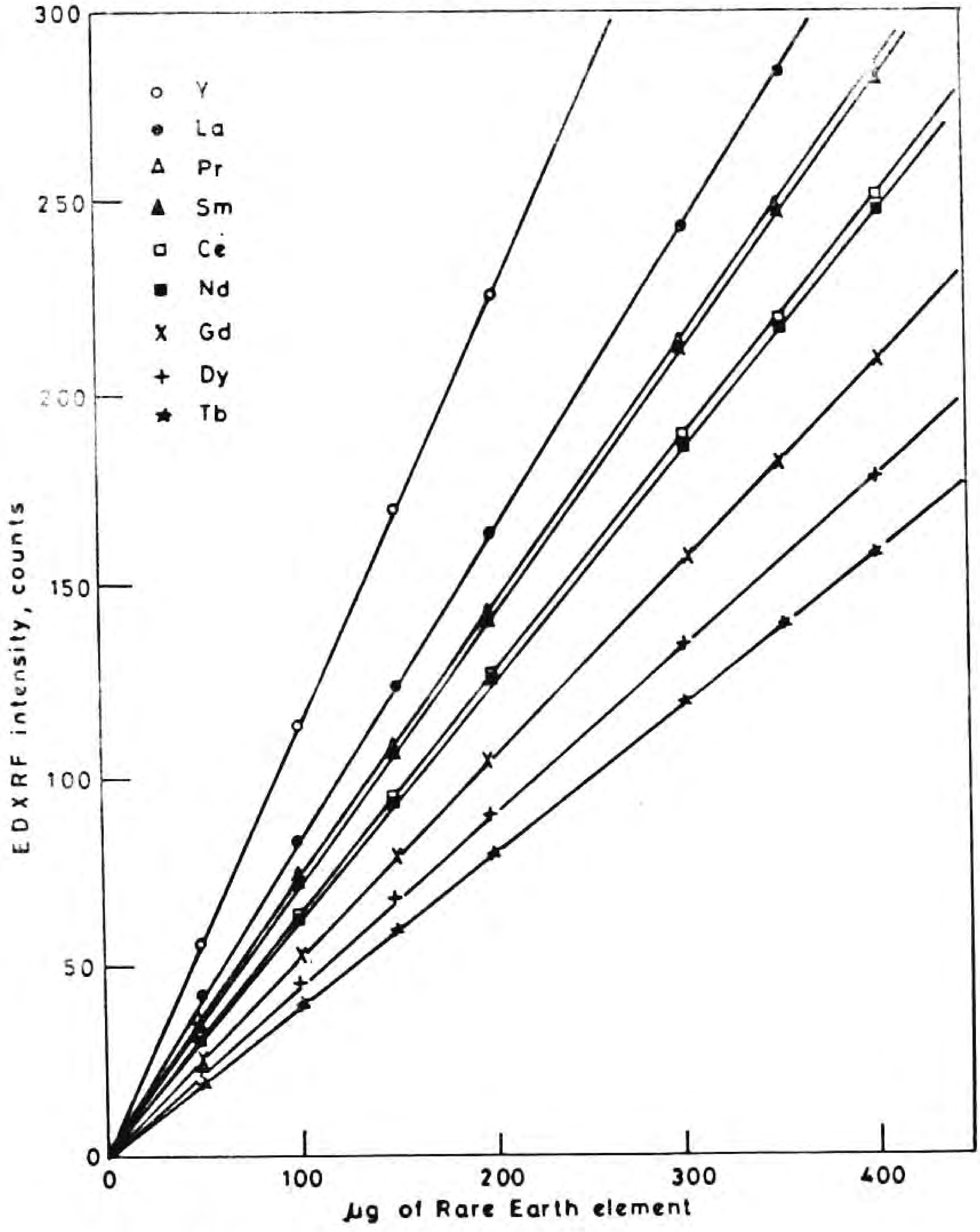


Fig. 7.5 Calibration graph

The relative standard deviation for different rare earth elements was calculated to be $\sim$5%.

## 7.7 ANALYSIS OF SYNTHETIC SAMPLES

The applicability of the developed procedure was tested by analysing the rare earth content of various synthetic samples. The results of the analysis of solutions with varying concentrations are shown in Table I. The results clearly show that the method can find use in the analysis of rare earth elements at trace levels in practical samples like xenotime.

## 7.8 APPLICATION

### 7.8.1 Analysis of xenotime sample

The developed procedure had been tested for its applicability to the analysis of xenotime samples. This analysis involved two steps.

Dissolution of the xenotime sample:

0.5246 g of finely ground mineral was fused with 15 g of potassium pyrosulphate in a covered silica crucible at a dull red heat. The melt was cooled periodically, a few drops of sulphuric acid were added and heating was continued. The procedure was continued for two hours. The pyrosulphate melt was dissolved in 200 ml of water. Excess of ammonium hydroxide was added to precipitate rare earth elements as their hydroxides.

## Table I

## Recovery studies

| Sample No. | Composition of mixture, µg/0.5 litre | | | | | | | | Recovery*, % | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Nd | Sm | Gd | Tb | Dy | Ho | Tm | Lu | Nd | Sm | Gd | Tb | Dy | Ho | Tm | Lu |
| 1 | 300 | 300 | 50 | 50 | 100 | 100 | 200 | 200 | 99.2 | 99.0 | 98.8 | 97.9 | 101.2 | 98.2 | 95.8 | 99.3 |
| 2 | 200 | 200 | 300 | 300 | 50 | 50 | 100 | 100 | 101.2 | 99.5 | 99.6 | 98.7 | 100.5 | 99.6 | 101.8 | 98.6 |
| 3 | 100 | 100 | 200 | 200 | 300 | 300 | 50 | 50 | 97.6 | 98.0 | 99.0 | 98.2 | 97.5 | 98.9 | 97.4 | 99.2 |
| 4 | 50 | 50 | 100 | 100 | 200 | 200 | 300 | 300 | 98.8 | 100.0 | 99.9 | 101.5 | 98.8 | 99.3 | 97.5 | 98.4 |

* Average of 3 determinations

The precipitate was filtered and washed thoroughly with 2% ammonia to remove sodium and potassium salts. The paper and precipitate were placed in a platinum dish, dried and ashed the paper at a low temperature. After cooling, 10 ml of 48% HF was added and heating was continued until the silica present in the sample had been completely removed. The resulting sample was dissolved in hydrochloric acid and made upto 100 ml.

An aliquot of 5 ml was taken from the sample solution. 0.5 g of 10% PAN modified naphthalene was added. The sample was diluted to 500 ml. The solution was maintained at 0.1 M in $NH_3$-$NH_4Cl$ and adjusted the pH to 9. The resulting solution was stirred for about 20 minutes for quantitative collection.

The PAN modified naphthalene along with the rare earth elements was filtered through Whatman No.41 filter paper and air dried. The contents from the dried filter paper were scraped, transferred to an agate mortar, and homogeneously powdered. The precipitate was pressed into pellets of diameter 2.5 cm, and about 0.07 cm thick. Corresponding blank was also prepared. Three sets of pellets were prepared. Each element was counted thrice for 10 minutes by using multichannel analyser. The average of the low and high backgrounds was subtracted from the measured peak intensity to give net peak intensity. The average of three net peak intensities was then calculated from three individual measurements. The average of the average values obtained for three sets of samples was considered as the correct peak count. This quantitation was carried out for each rare earth element. The percentages of each rare earth element in the xenotime was calculated and the results are shown in Table II.

**Table II**

**Analysis of xenotime**

| Element | Percentage obtained by | |
|---|---|---|
| | Present procedure | Standard procedure |
| Y | 25.2 | 25.9 |
| La | 0.27 | 0.25 |
| Ce | 0.40 | 0.40 |
| Pr | 0.044 | 0.05 |
| Nd | 0.44 | 0.48 |
| Sm | 0.44 | 0.50 |
| Gd | 0.91 | 1.2 |
| Tb | 0.44 | 0.48 |
| Dy | 3.93 | 4.5 |
| Er | 0.48 | 0.40 |
| Ho | 2.91 | 2.80 |
| Lu | 1.02 | 1.10 |

An aliquot of 5 ml was taken from the same sample solution. The rare earth elements present in the solution were precipitated as their oxalate[121]. Then the mixed oxalate was made into pellet with boric acid as binder. Three sets of samples were made and one blank was also made. Then the pellets were subjected to EDXRF quantitation by irradiating with 50 mci Am-241 source for 10 minutes in a mylar based sample holder of 1 inch diameter. Each element was counted thrice for 10 minutes using multichannel analyser. The average of the low and high background counts was subtracted from the measured peak intensity to give net peak intensity. The average of three net peak intensities was then calculated from three individual measurements. The average of the average values of three sets of samples was considered as the correct peak count. Then the percentage of the rare earth elements present in the xenotime sample was calculated and the results are shown in Table II.

The results obtained by the present method and a standardised procedure are found to be same. This shows that the developed method is good and can be used for reliable determination of rare earth elements.

## 7.9 EXPERIMENTAL

### 7.9.1 Apparatus

The instrumental details of energy dispersive x-ray fluorescence analyser were same as described in Chapter V.

### 7.9.2 Reagents

All reagents were of analytical grade.

1. Standard rare earth element solutions:

Prepare individual rare earth element stock solutions (Rare Earth Products, Cheshire) by dissolving respective rare earth oxides in 1:1 hydrochloric acid and standardize with EDTA.

2. Naphthalene (Loba Chemie, Bombay):

3. 1-(2-pyridylazo)2-naphthol (PAN) (Fluka):

4. Ammonia-ammonium chloride solution (1 M):

Mix 27 g of ammonium chloride and 34 ml of 25% ammonia and make upto 1000 ml.

Procedure

The preconcentration of rare earth elements onto PAN modified naphthalene involves three steps.

## 1. Preparation of PAN modified naphthalene

Dissolve PAN and naphthalene in the weight ratio of 1:9 in minimum amount of acetone. Pour this acetone solution as a fine stream into a 1 litre beaker containing water which was stirred using a magnetic stirrer. Continue the stirring for half an hour more after the addition of acetone solution. Filter PAN modified naphthalene, dry in air and store in a polythene bottle.

## 2. Preconcentration procedure

Transfer an aliquot of solution containing $\geq 50$ µg of a particular rare earth element or in a mixture to a 1 litre beaker. Add 0.5 g of 10% PAN modified naphthalene. Add 50 ml of 1 M ammonia-ammonium chloride and adjust the pH to 9. Stir the resulting solution using magnetic stirrer for 20 minutes.

## 3. Sample preparation for EDXRF analysis

Filter the PAN modified naphthalene along with the rare earth elements through Whatman No.41 filter paper, dry and grind in an agate mortar. Press the precipitate into solid thin targets of diameter 2.5 cm and about 0.07 cm thick by applying a pressure of 5 tons per square inch in a carvar press. Use these solid thin targets for subsequent quantitation by EDXRF via. their characteristic K-radiation using Am-241 source.

Analyse the pressed powder pellets by irradiating with 50 mci Am-241 source for 10 minutes in a mylar based sample holder of 1 inch diameter. Prepare three sets of samples. Count each rare earth element thrice for 10 minutes using multichannel analyser. Subtract the average of low and high backgrounds from the measured peak intensity to give net peak intensity. Calculate the average of three net peak intensities from three individual measurements. Calculate the average of these average values obtained with three sets of samples for all rare earth elements and obtain calibration graphs.

# CHAPTER VIII

# CONCLUSIONS AND SUGGESTIONS FOR FUTURE WORK

The investigations carried out during the course of this work have clearly demonstrated the methods which can be used for the determination of traces of neodymium and samarium. In the present study, molecular absorption spectrophotometry (MAS) and energy dispersive x-ray fluorescence (EDXRF) spectrometry were used for the development of new methods.

A simple and sensitive method was developed for the determination of trace amounts of neodymium by spectrophotometry. The method was based on the extraction of ternary ion association complex formed by reacting neodymium with rhodomine 6G in presence of 5,7-dichlorooxine and extracting into toluene. The colour reaction was sensitive ( $\epsilon = 1.36 \times 10^5$ ) and was useful for the determination of 0 to 20 μg of neodymium present in 25 ml. Neodymium was separated from aluminium and other elements by passing the sample solution through Dowex 50 W - X8 in 1 M HCl. Neodymium thus retained on ion exchange column was eluted using ammonium chloride and subsequently determined by the above determination procedure. The developed procedure in conjunction with ion exchange separation was successfully applied for the determination of traces of neodymium in high purity aluminium metal samples which are used for the manufacture of solar collector cells.

During the investigations on the extractability of the ion-associate into various solvents, it was found that this ion associate readily separated out from the aqueous phase and adsorbed onto the walls of the separating funnels when equilibrated with hexane. This adsorbed complex upon treatment with acetone readily released the strongly fluorescent rhodamine 6G. A more detailed study may pave the way for specctrophotometric/spectrofluorimetric determination of neodymium and also of other rare earth elements.

A third order derivative molecular absorption spectrophotometric procedure was developed for the determination of traces of samarium. The method was based on the formation of a stable, blue coloured water soluble ternary complex (metal-chromogenic reagent-surfactant) which was formed when cetyl trimethyl ammonium bromide or cetyl pyridinium bromide was added to binary samarium-methyl thymol blue system. Linear calibration graphs were obtained for 0-30 µg of samarium present in 25 ml. Third order derivative spectrum of the described complex eliminated the interference due to gadolinium, terbium, dysprosium, holmium, thulium and lutetium in the determination of samarium. This was achieved by the deconvolution of the overlapping spectra of samarium from middle and heavier rare earth elements. By suitably selecting the more sensitive chromogenic reagents and higher order derivative, it may be possible to determine traces of one rare earth element in presence of other and also it can be extended to heavy metals.

Energy dispersive x-ray fluorescence spectrometry has been successfully used for the determination of rare earth elements present in an admixture. In order to improve the detection limit and possibility of handling liquid samples, preconcentration procedures were adopted. Merits and demerits of various preconcentration procedures together with various analytical techniques were reviewed in Chapter IV.

A method was described for the determination of rare earth elements at ppb level by coprecipitative preconcentration using iron(III) hydroxide as collector and subsequent characterisation by EDXRF. The procedure by EDXRF with Am-241 radioisotope showed that iron and titanium did not interfere in the determination of rare earth elements when their characteristic K x-rays were used for characterisation and at the same time iron(III) hydroxide enabled to collect even the trace amounts of rare earth elements quantitatively. In addition, a numerical method based on simple least square procedure was developed for smoothing and differentiation of the EDXRF data which had been previously digitized and averaged. By carrying out the least square calculations on a computer via convolution of the EDXRF data obtained after coprecipitative preconcentration, with properly chosen integers facilitated the determination of as low as 10 ppb each of rare earth elements. A set of nine consecutive values for the determination of the best mean square fit through these values of polynomial of degree five was used for the above numerical calculation. First order derivative was chosen since it offered better SNR value and low RSD and blank values and thereby enhancing the detection limit.

Single and multielement calibration graphs were obtained in the range 0-400 $\mu$g of rare earth elements present in 500 ml of solution. The developed procedure was applied to the analysis of synthetic samples and recoveries were found to be good. So the method can be applied to the analysis of real samples and also the similar coprecipitative preconcentration method can be developed for other elements using either iron(III) hydroxide or some other coprecipitant. Likewise, the simple least square method can be modified in such a way so as to get better detection limit.

Another preconcentration method based on the adsorption of rare earth - quinolin-8-ol complexes onto activated carbon was developed for EDXRF quantitation. Eventhough the activated carbon is a good collector, the adsorption of rare earth elements onto activated carbon was found to be not quantitative. However, by the addition of quinolin-8-ol to weakly alkaline solutions containing traces of rare earth elements, the collection of rare earth elements as their quinolin-8-ol complexes was quantitative. A simple least square procedure using fifth order polynomial with 25 consecutive values was developed for smoothing and differentiation of EDXRF data which was previously digitised and averaged. Instead of nine consecutive values in Chapter V, twenty five consecutive values were chosen as it gave a better representative curve corresponding to actual points. First order derivative EDXRF in conjunction with adsorptive preconcentration on activated carbon enabled to determine as low as 10 ppb of each of individual rare earth elements. The developed method was successfully applied to the analysis of synthetic samples and the recoveries were found to be good indicating that the method can be used for reliable determination of rare earth element. The usefulness of other chelating ligands in the place of quinolin-8-ol can be tried in order to find out whether these will improve the selectivity of the procedure.

The individual determination of rare earth elements at microgram levels was possible by preconcentrating the rare earth elements over 1-(2-pyridylazo) 2-naphthol modified naphthalene and subsequent determination by EDXRF via their characteristic K x-ray lines. 1-(2-pyridylazo)2-naphthol and crystalline naphthalene were mixed in the ratio 1:9 and dissolved in minimum amount of acetone. This acetone solution was poured into water as a fine stream while stirring using a magnetic stirrer for 30 minutes. The crystalline PAN-naphthalene was filtered, dried and stored for subsequent use. Rare earth elements were adsorbed on the PAN-modified naphthalene and pressed into pellet for subsequent EDXRF quantitation. Use of naphthalene eliminated the requirement of external binder for making pellet. Linear calibration graphs were obtained in the range 0-400 $\mu$g of the rare earth elements. Synthetic samples were successfully analysed by the developed procedure. Further, the results obtained on analysing xenotime samples agrees well with the standard procedure. The same method can be applied to the analysis of rare earth elements present in rare earth concentrates, rocks and minerals. The PAN modified naphthalene can be used as a collector for preconcentration for the analysis of other elements by suitably selecting the reaction conditions. After collection, in addition to EDXRF other analytical techniques can also be used for characterisation.

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