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THE DETERMINATION OF RARE EARTH ELEMENTS BY FLAME EMISSION SPECTROSCOPY

by

J. A. ROTHERAM

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THE DETERMINATION OF RARE EARTH ELEMENTS IN STEEL BY FLAME EMISSION SPECTROSCOPY

BY J.A. ROTHERAM

ABSTRACT

Rare earth elements are added to high quality steels to improve certain physical properties. This has led to increased interest in rare earth chemistry and particularly in the development of methods to determine trace levels of these elements in steel. Flame emission spectroscopy can provide a useful method for rare earth element analysis being concerned with lower energy levels than the conventional arc or spark emission system and preferred to the classical methods which have been criticised on grounds of sensitivity, selectivity or speed of analysis. The light lanthanoid elements Ce (primarily), La, Nd and Pr, were investigated using a reducing nitrous oxide/acetylene flame in a conventional atomic absorption spectrometer switched to an emission mode. Useful analytical lines and bands were determined and recorded for each element. The importance of flame temperature and flame chemistry for the efficient production of free atoms of these highly refractory rare earth elements was confirmed. The usefulness of an ionisation suppressor, e.g. K or Cs, and organic media to enhance the emission signal was also confirmed. The 2σ detection limits were obtained for the four elements. The interference effects of typical elements found in specialised steels and the extent of mutual rare earth interference were investigated in detail and spectral interference found to be severe for some elements. The requirement for separation of the lanthanoids due to spectral interference and the desirability of lowering the available detection limit led to the investigation of a number of methods, e.g. ion exchange; solvent extraction and precipitation, to remove and concentrate the rare earth elements from the steel matrix. Two useful analytical methods have been developed involving solvent extraction, precipitation and flame emission spectroscopy for the determination of single rare earth additions to steel (involving hydroxide precipitation) and cerium in the presence of rare earth mixtures in steel (involving oxalate precipitation).

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CHAPTER I

INTRODUCTION

The rare earths, or lanthanoids, are a group of 15 metals ranging from atomic number 57 to 71 in group 3B of the periodic table of elements. Table I classifies these elements (1, 2). The discovery of the first rare earths is reported to have been in 1887 by C.A. Arrhenium who discovered yttrium in an unusual mineral specimen (1). The main rare earth group was subsequently discovered between 1803 and 1907. The misnomer "rare earth" was so initiated by Gadolin, a Finnish chemist, because at the time, the term for oxide was "earth" and these particular oxides were thought to be extremely rare. Today it is known that the rare earths are relatively abundant, being widely scattered through more than one hundred known minerals with estimated world reserves of ten million tons, but the term "rare earth" is retained as a common term for this group of elements.

The physical, chemical and spectral properties of the rare earths can be logically summarised from an understanding of the electronic configurations. The ground state configurations are given in Table I. The majority of the lanthanoids have the form $4f^{n+1}6s^2$ with the exceptions La, Ce, Gd and Lu, having $4f^n5d6s^2$. The trivalent ion configurations are important in the determination of many of the physical and chemical properties of these metals and represent the 'normal' configuration of this group. Other configurations are, however, possible for certain elements and these account for the alternate oxidation states of Ce, Pr and Tb (tetravalent) and for Sm, Eu and Yb (divalent). The rare earths are quite electropositive, exceeded in the eletrochemical series only by the alkali and alkaline earth metals, and also have large metallic radii. These two factors play a considerable role in their chemical and metallurgical behaviour, e.g. the rare earths form stable compounds with halides and oxides and, because of their size, are essentially insoluble in the solid state of most of the major industrial metals. The rare earth oxides are amongst the most refractory oxides formed by any of the elements, which is evident when comparing the energy conditions required for atomisation in flame or plasma spectroscopy with those of many other metallic oxides.

TABLE I

THE RARE EARTH METALS

Atomic No.	Element/Symbol		Classification	Electronic Configuration		
				+2	+3	+4
57	lanthanum	La	light sub-group		$4f^{o}$	
58	cerium	Ce		$4f^{2}$	$4f^{1}$	$4f^{o}$
59	praseodymium	Pr			$4f^{2}$	$4f^{1}$
60	neodymium	Nd		$4f^{4}$	$4f^{3}$	$4f^{2}$
61	promethium	Pm			$4f^{4}$	
62	samarium	Sm		$4f^{6}$	$4f^{5}$	
63	europium	Eu		$4f^{7}$	$4f^{6}$	
64	gadolinium	Gd	heavy sub-group		$4f^{7}$	
65	terbium	Tb			$4f^{8}$	$4f^{7}$
66	dysprosium	Dy			$4f^{9}$	$4f^{8}$
67	holmium	Ho			$4f^{10}$	
68	erbium	Er			$4f^{11}$	
69	thulium	Tm		4f	4f	
70	ytterbium	Yb		4f	4f	
71	lutetium	Lu				
39*	yttrium	Y				

* Yttrium is usually included in this group due to its chemical similarities and common co-existence with rare earths although its atomic number is only 39.

The rare earth elements of interest in this research project are the light sub group Ce, La, Nd and Pr. These elements react readily with oxygen and moisture and need careful handling, whereas the remaining rare earth metals are less reactive. These rare earths readily dissolve in mineral acids (except hydrofluoric acid) and can easily be converted to the stable R_2O_3 oxide (except Ce and Pr which form CeO_2 and Pr_6O_{11}) by heating in air at 800°C - 1000°C. This is important in wet chemistry and spectrophotometric methods when preparing samples for spectroscopic analysis in which the oxide is the preferred chemical species. The rare earth metals also form essentially insoluble hydroxides, fluorides and oxalates in aqueous solutions, with the oxalate being the preferred precipitate for quantitative analytical measurements.

The spectral properties are based on the inner electron energy levels and transitions between them. The complexity of the spectra of most of the individual rare earth elements has been known for many years and even today a catalogue to identify and index the rare earth spectra still remains uncompleted. The partially filled 4f level is a major factor in the production of such complex spectra. The spectra consist of transitions between energy levels and so there are many more lines in a spectrum than there are energy levels. Dieke and Crosswhite (3) noted that for Sm^{3+} the four lowest energy levels ($4f^5$, $4f^45d$, $4f^46s$ and $4f^46p$) give rise to a total of 1994 levels, giving rise to a possible 306,604 allowed transitions. The spectroscopic methods currently available for the analysis of the rare earths do not use the complete spectra. Some techniques, such as solution spectrophotometric analysis, rely on selected absorption bands of a given element. Others, such as emission spectroscopy, make use of one of a large number of resolved lines (electronic transitions). X-ray excited optical fluorescence uses one, or a few, of the electronic transitions.

A metallurgical interest in the development of the rare earth elements was initiated by the discovery that a small addition of cerium could nodulize graphite to produce nodular cast iron. This development has been reviewed by Ross (2). The exact physical or chemical mechanism by which the phenomena occurred has been the subject of detailed investigation, resulting in increased use of the rare earths in the production of high quality steels. Rare earth metals basically improve steel by reducing the oxygen and sulphur to low levels.

Modern steel development has led to the necessity for greater impact strength, weldability and isotropy. All these properties are severely affected by the manganese sulphide inclusions in steel which are plastic and elongate at rolling temperatures (4). Pipelines laid in Arctic zones, which may be at very low temperatures, require high shelf energies to resist rupture. The new high strength low alloy steels used in highly configured car parts must have extra resistance to fracture when bent or stretched in the transverse direction (5).

The manganese sulphide may be precipitated from molten steel in any of three different morphologies, type 1 - randomly dispersed globular, type 2 - interdendritic or type 3 - randomly dispersed angular (6,7). The degree of deoxidation of the liquid steel determines which will form. Rare earth alloys are generally used in two forms - as 'mischmetal' or 'rare earth silicide'. Typical compositions of these alloys are given in Table II (6).

TABLE II

Type of Rare Earth Alloy	Typical Compositions - W/W %				
	Fe	Ce	La	Nd	Pr
Mischmetal	3.0(max.)	45-51	23-26	15-19	4-6
Rare earth silicide	3 0-3 5	48-50	32-34	13-14	4-5

An appropriate amount of aluminium is usually first added to the steel to lower the oxygen level and improve the rare earth recovery and then the rare earth addition made. This breaks down the manganese sulphide stringers and globular rare earth inclusions form (8). When the rare earth (R.E.) content in steel ranges between 0.008% and 0.20%, the inclusion comprises two types of rare earth aluminium - oxide and a modified manganese sulphide. At lower levels of rare earth, 0.0008% rare earth, most inclusions are of the type $R.E.AI_{11}O_{18}$. These inclusions then affect the plasticity so that during hot rolling the sulphides do not elongate to the same extent. Wilson and Wells (9) have shown a rare earth inclusion showing a central core of rare earth oxy-sulphide, which is the first to precipitate, surrounded by a rare earth silicide. Rare earth levels between 0.020% and 0.070% produce

the maximum improvement in steel properties as a result of elimination of all traces of manganese sulphide (6). The affect of rare earth additions to steel can be summarised as below. Rare earth elements are extremely strong deoxidants and so can desulphurise steel. The inclusions formed as a result of adding the rare earth metals to steel are initially oxides, then oxysulphides and then sulphides. No rare earth carbides or nitrides form and the rare earth sulphide inclusions only form at high rare earth levels. Laboratory experiments have confirmed all these effects and have shown them to be in accordance with thermodynamic data. It has been demonstrated that the effect of the rare earths on steels can improve the transverse impact properties of steel to levels almost equal to the longitudinal properties, improve the through thickness ductility and improve the bend performance of light gauge, hot rolled materials. This leads to a substantial increase in the overheating temperature of low sulphur steel, elimination of lead embrittlement in high strength steels and a reduction in the incidence under-bead cracking in the HAZ of weldments. There is, therefore, a requirement for analytical methods to quantitatively determine the levels of the elements Ce, La, Nd and Pr in steels. This, in turn, will lead to greater knowledge of this inclusion phenomen in this currently important field of steel production.

The earliest rare earth determinations involved basic gravimetric techniques of precipitation usually by the hydroxide or oxalate ion or reaction to form a coloured solution. Redox titrations were later applied. The identification of individual rare earths was attempted, with difficulty, using their absorption spectra in solution. Quantitative analysis in the steel industry today is almost entirely instrumental in nature and, in fact, it was only by the development of instrumentation that quantitative analysis for rare earths could be carried out effectively. Wet chemical analysis is still a very necessary and important method. The steel industry, for example, requires standards or reference results for comparison with instrumental results. The elements in such steel standards (e.g. British Chemical Standards) are always analysed by various chemical techniques to provide a selection of reference samples.

Vickery (10) outlines several gravimetric procedures for the rare earths using hydroxide, oxalate, bromate or iodate precipitations. Eremin and Martyshova (11) have comprehensively reviewed methods of chemical analysis for determining small amounts of cerium, including redox titrimetric, gravimetric and colorimetric methods. Many other

papers have been published utilising basic gravimetric or volumetric techniques (12-18). Masin and Dolezal (19) have recently published a paper for the determination of cerium in a gravimetric procedure using cerium IV phosphate for the separation and determination of cerium in a rare earth concentrate.

Two classes of spectrophotometric analysis are available. One utilises the band absorption spectra of the coloured rare earth ions and the other method is based upon the absorption spectra of coloured complexes with dyes. The absorption of the lanthanoid ions can be enhanced by the formation of inorganic complexes. The most common techniques are co-precipitation and liquid/liquid extraction.

J. Korkisch (20) has reviewed both of these techniques. The most important extractants are tributyl phosphate, 4 methyl pentan-2-one and di (2-ethyl hexyl) phosphoric acid. The trivalent rare earths behave nearly identically but tetravalent cerium has a far greater extraction co-efficient and so useful separation can be achieved.

Several papers have been written outlining methods for determining cerium in cast iron or steel using a spectrophotometric finish. Iordanov et al (21) used tetron, (NNN^1N^1 - tetra methyl-o-tolidine) to extract cerium with measurement at 470nm, and detection limits as low as 0.05%. Blazejak-Ditges (22) determined cerium in alloy steel using methanolic-o-tolidine after separating cerium from the steel media. Other workers used ethanolic-o-dianisidine, 8-hydroxyquinoline (in chloroform) or alizarin red S with ammonia (23 - 26). In general these methods are not suited for the determination of individual rare earths in the presence of each other and little detail is given with respect to individual rare earth interferences.

The more recent application of ion exchange for the mutual separation of the lanthanoids has proved very popular and useful. The cation exchange technique is based on the steady decrease in size with atomic number of the rare earth group and the corresponding increase in binding energy of the ligands. The presence of organic complexing agents, e.g. citrate, malate or E.D.T.A. is necessary since the affinities of the various lanthanoids for the resin are similar. Korkisch (27) gives a good summary of cation exchange based on alpha-hydroxy isobutyric acid (A.H.I.B.) showing that cation exchange has proved a powerful method for the mutual separation of dilute solutions of the lanthanoids.

The application of anion exchangers for the mutual separation of the rare earths, and for their separation from steels, uses the fact that the absorption of the rare earths on an anion exchanger increases rapidly when a miscible organic solvent is added to the liquid phase to form anionic complexes with the rare earths. The resins used are based on very basic quaternary ammonium salts which trap and retain the rare earth ions from the organic based media but allow other elements, e.g. Mn, Cr, V, Ni etc. in steel to pass through. Cerium IV is strongly retained by anion exchangers but the other rare earths absorbed to a lesser extent. Korkisch (28) and Faris (29) demonstrated the application of anion exchangers to rare earth mixtures.

Analytically, the use of anion exchangers is not favoured for the mutual separation of the rare earth ions compared to cation exchange but research work to separate cerium from steel by this application has provided a useful method in this field. Korkisch and Ahluwalia (30) determined cerium in ferrous alloys using an anion resin, Dowex 10, in a methanolic/nitric acid media. Willis (31) determined cerium in plain carbon and low alloy steels by anion exchange, finishing with a colorimetric measurement. This was an extension of the method outlined by Green (32) who separated cerium in steel using a basic quaternary ammonium salt anion exchanger, and again using a colorimetric finish. Other methods involving a combination of ion exchange and spectrophotometric techniques have been reported (33). Ahluwalia et al (34) used a titrimetric finish to an anion exchange technique. Tomlinson (35) determined cerium by an ion exchange/photometric determination. It was also found that the elements lead and bismuth, if present in the steel sample, were similarly absorbed and eluted with cerium but all the other typical elements found in steel were successfully separated. Rare earth determinations in steels or related alloys by ion exchange has not been extended with any success to the elements La, Nd or Pr.

The behaviour of interferences of the other rare earth elements La, Pr and Nd in the mischmetal mixture is not known in detail. The use of an ion exchange system is, therefore, useful for determining trace quantities of cerium in steel but the method used is both time consuming and not necessarily selective and so the development of a faster and more comprehensive method for determining Ce, La, Nd and Pr in steel could prove useful for future steel analysis.

All the classical methods, discussed above, can be criticised on grounds of sensitivity, selectivity between rare earth elements or speed of analysis. There is, therefore, a need for a reasonably rapid, selective and sensitive method. X-ray fluorescence is becoming an increasingly popular technique for rare earth analysis in solids, particularly for low level determinations. This leads to a requirement for solid standards and, therefore, a new approach to the determination of rare earths at trace levels using only aqueous solutions as standards would be a significant advance. The emission spectra of these elements contain many lines at high wavelength (i.e. low excitation energy), suggesting from the Boltzmann criteria that atomic emission spectroscopy might offer a sensitive alternative.

The conventional arc or spark emission spectra of most of the rare earth elements are very complex, possessing thousands of lines of rather uniform intensity and lacking the characteristically intense lines found in the spectra of other elements. Even under high dispersion the probability of line interference is high and difficulties are frequently encountered in locating interference-free lines. The use of a flame or electrothermal atom cell produces fewer lines and so greater analytical utility may be achieved. Additionally, these techniques may conventionally be simply standardised using aqueous solutions.

Some of the first analytical applications of flame emission spectroscopy to the lanthanoids used observations on the rare earth monoxide band systems. Piccardi (36) described the principal features of the oxyhydrogen flame spectra of most of the rare earth elements. He introduced the rare earths into the flames as aerosols of aqueous solutions and, under these moderate excitation conditions, observed that most of the spectra were devoid of any atomic lines. It was noted, however, that there was a tendency to form stable diatomic monoxide (MO.) molecules in the flame. This was indicated by the presence of a characteristic diatomic band emission spectra in oxyhydrogen flames. The overlap of the individual spectra greatly restricted the general analytical utility of these band systems and so research at this stage was limited.

Later work was concentrated on using the several components of these band systems which occur relatively free of interference. The most prominent of these are the LaO bands at 437.2, 441.8, 740.3 and

791.0nm. Menis et al (37) and Ishida (38) found that these bands were subject to various degrees of interference by other cations present in the solution but under certain conditions the LaO line at 791.0nm did not exhibit significant interelement effects or spectral interference from other rare earth elements. Later work by Rains et al (39) showed the NdO bands at 660.6 and 712.0nm and the Yb atom line at 398.8nm to be useful for the determination of the parent atom in rare earth mixtures. The high incidence of spectral interference generally among rare earth monoxide band systems, lead many workers to believe that the analytical utility of the band spectra could not be significantly extended.

The presence of atomic line spectra being emitted in flames was found to be rare and to give rise to only weak intensities. In most flame types the predominant features were those of monoxide band systems. The relatively high temperatures in stoichiometric oxyacetylene flames were insufficient to effectively dissociate these molecules. Collaborative thermodynamic data can be found in the relatively high dissociation energies of these molecules. The high stability of these monoxide molecules greatly reduces the free atom concentration in the flame and, therefore, the atomic line emission will be weak or non-existent. Fassel, Curry and Kniseley (40) found that flame chemistry rather than flame temperature, was the important consideration in the production of free atoms of the rare earth elements. The increase in the free atom population was found to be a direct result of the high concentration of carbon containing species prevalent in high temperature hydrocarbon flames. The emission and absorption enhancement factors observed in a fuel-rich flame vary considerably, with the greatest enhancements observed for the rare earth elements which have the most stable monoxides. Very fuel-rich flames are found necessary for the efficient production of free atoms of those elements that form stable monoxides (e.g. Ce and La), whereas near stoichiometric flames produce maximal absorption or emission for Eu and Yb, whose monoxide dissociation energies are relatively low.

The atomic absorption spectra of these elements were first studied in flames by Mossotti and Fassel (41 - 42). Later observations were made on free atoms formed in turbulent, fuel-rich oxyacetylene and premixed oxyacetylene or nitrous oxide acetylene flames burning on slot burners. At the present time little useful work has been published on flame atomic absorption methods for the light rare earths due to poor

detection limits and the difficulty in obtaining adequate hollow cathode lamps with the pure rare earth metals being so reactive. In general, the powers of detection reported were inferior to those found in flame emission.

Ooghe and Verbeek (43) have outlined a method for the determination of the lanthanoids in mineral ores by atomic absorption. They used a Perkin Elmer 303 atomic absorption spectrophotometer with a nitrousoxide/acetylene flame in a 5cm slot burner. Intensitron hollow cathode lamps were used as the line source for each element. To improve sensitivity, the use of ionisation buffers - e.g. potassium chloride or sodium chloride and organic solvents were investigated and found to be successful for improving the absorption signal. Detection limits were listed for La, Nd and Pr, but no results were obtained for Ce. Chemical and matrix interferences were overcome by the standard addition technique.

Van Loon, Galbraith and Aarden (44) determined several of the rare earth elements in minerals by atomic absorption using a nitrous oxide/acetylene flame. The method is described for determining Yt, Eu, Tb, Dy, Ho, Er, Tm, Yb and Lu in zirconium and calcium rare earth silicates and involves the use of a lanthanum suppressor. Sensitivities and detection limits are listed for each element.

Gupta (45) determined the certain lanthanoids in rocks and minerals by atomic absorption. He showed that an ethanol solution of the pechlorate of the metal, rather than an aqueous solution, improved the sensitivity of rare earths in the nitrous oxide/acetylene flame. It was also shown that the use of spectroscopic buffers (e.g. Na or La) gave improved signals. In general, several workers found that the use of an organic media improved the lanthanoid signal by increasing the nebulisation efficiency and that sensitivity was also increased by the use of an ionisation buffer to reduce the degree of ionisation in the flame.

Johnson, Kirkbright and Whitehouse (46) used the formation of molybdocerophosphoric acid to determine cerium by measuring molybdenum atomic absorption after solvent extraction.

Grobenski (47) has reported the determination of cerium with difficulty by atomic absorption due to hollow cathode lamp problems but has, with more success, determined other rare earths by atomic absorption using a graphite furnace atomiser. To our knowledge, no useful work has been published on the determination of rare earths in steel by atomic absorption.

The recent development of the inductively coupled plasma (I.C.P.) as an excitation source for optical emission spectroscopy, has also created a possible atom cell for rare earth atomisation. The overriding advantage of the inductively coupled plasma is claimed to be the high temperature attainable ca.8000K. This enables easier atomisation of highly refractory elements, e.g. all the rare earths, which prove so difficult in lower energy systems. Additional claims are made that, using this source, simultaneous multi-element analysis is possible at ultra trace level and without serious chemical interferences. Fassel and Kniseley (48) outlined the inductively coupled plasma as a promising excitation source for simultaneous multi-element analysis and have reported experimentally determined detection limits for many elements including the rare earths. Greenfield, McGeachin and Smith (49) have determined many of the rare earths including Ce, La, Nd and Pr with the inductively coupled plasma.
Recently the rare earth elements in mischmetal Ce, La, Nd and Pr, have been determined in a steel matrix using the inductively coupled plasma source. Newland (50) used the induction coupled plasma excitation source, with an ultra-sonic nebuliser and large quartz spectrograph to determine cerium (0.02 - 1.3%), lanthanum (0.01 - 0.5%), neodymium (0.01 - 0.4%) and praseodymium (0.003 - 0.14%) in plain carbon and low alloy steels. Iron was used as an internal standard for the spectrographic determination instead of another rare earth element as trace quantities of any rare earth element could have been present in the steel samples. Calibration graphs for all these lanthanoid elements were given and the analytical data obtained showed useful agreement with results obtained from X-ray fluorescence and neutron activation analysis. The sample treatment involved a dissolution procedure, followed by a solvent extraction process using butyl acetate to separate the rare earths from the bulk of the steel matrix. This paper currently provides the most useful information for the determination of rare earth mixtures in low alloy and carbon steels.
Broekaert, Leis and Lagua (51) determined certain rare earth elements, including Ce, La, Nd and Pr. in mineralogical samples by means of inductively coupled plasma, optical emission spectroscopy. They report, however, that the detection limits obtained were generally lower than those obtained with atomic absorption spectroscopic techniques using a nitrous oxide/acetylene flame or d.c. plasma jet emission spectro-

scopy. Reference to the rare earth group of elements is also given in other papers with regard to line selection in difficult matrices (52) and the use of ultrasonic nebulisers with the plasma torch.
The high temperature and nature of the plasma, however, unfortunately create problems of spectral interference and ionisation effects. Spectral interference at typical rare earth wavelengths may be severe due to the complex spectra obtained under these high excitation conditions. An improved signal, therefore, may also be matched with increased spectral interference problems. There is also evidence to suggest that the formation of ionic species, as a result of the high temperature in the inductively coupled plasma could produce additional problems. The rare earths, therefore, may produce complex ion line spectra in the inductively coupled plasma. This is a problem which is not realised in conventional flames, where ionisation may be simply suppressed by the use of an ionization buffer. The cost and flexibility of the inductively coupled plasma compared to other systems is another factor to be considered. The inductively coupled plasma coupled to a fixed wavelength, multi-element, direct readout attachment, may be most useful on a routine basis. This instrument is, however, very expensive compared to other emission sources and lacks flexibility when required for analysis of the less common elements, e.g. the rare earths on a non-routine scale.
The introduction of another novel source, the heated carbon furnace, as an alternative atom cell to conventional flame and the inductively coupled plasma, may prove to be a useful system. The reduced background and spectral interferences compared to the inductively coupled plasma, are possible advantages of the heated carbon furnace. The potential advantages expected of this method for atomic emission, compared to flame atomisation are improved sensitivity largely through using smaller sample volumes, closer control over the chemical environment of the analyte atoms and a considerable reduction of the background radiation from such species as C_2, CH, CN and OH. Disadvantages include, however, reduced precision, lack of speed and the necessity for greater experimental skill which are all important factors in the routine analytical laboratory. It is expected that some of these problems will be overcome by automatic sample introduction in the future.
Many useful techniques have been developed using the atomic absorption technique and recently the potential for development in the emission

field has been demonstrated.

Fuller has detailed the basic principles and uses of the heated graphite tube in atomic absorption in his monograph (54). Ottaway and Shaw (55) have made a preliminary appraisal of the heated graphite furnace for atomic emission work using easily atomised elements, e.g. Na, K or Li. Littlejohn and Ottaway (56) investigated the background emission effect in carbon furnace emission spectrometry and discussed methods for further reducing the continuous background signal. Massmann and Gucer (57) have described the emission spectra of some rare earth elements using a graphite tube furnace coupled to a 3.5 metre spectrograph to obtain a photographed spectrum. They comment on the complexity of the spectrum and outline the difficulties of carrying out quantitative analysis under such conditions. Grobenski (58) determined the lanthanoids in the graphite furnace by atomic absorption using graphite tubes coated with pyrolytic graphite, with the exception of Ce and Pm. Two mechanisms for the atomisation of this rare earth group were proposed - one for the 'light' group of lower atomic number and another for the 'heavy' group of higher atomic number - and the presence of molecular emission was measured at certain molecular bands, e.g. LaO at 441.7nm and NdO at 597.5nm.

In conclusion it can be realised that the analysis of rare earth mixtures can be most usefully carried out using analytical applications of atomic spectra, since classical chemical methods are generally not applicable. Flame atomic or molecular emission spectra possess several advantages over the other spectra used for the analysis of rare earth mixtures. Firstly, the flame spectra are striking in their simplicity compared to arc, spark or inductively coupled plasma sources. It is, therefore, possible to achieve adequate spectral resolution with small table model spectrometers, whereas large high dispersion spectrometers are required when arcs or sparks are observed. Similarly, expensive inductively coupled plasma systems coupled to direct readout instruments may prove unsatisfactory for the non-routine analysis of rare earths. Secondly, all the rare earths exhibit line spectra of sufficient intensity to possess analytical utility. In addition, there is no evidence of interelement effects, which contrasts sharply with selective enhancements and absorption effects observed in X-ray fluorescent spectrometric measurements. Thirdly, flame atomic emission generally exhibits greater powers of detection than atomic absorption measurements by factors ranging from 2 - 80 for rare earth elements.

As a consequence, flame emission spectroscopic techniques have found a wider application to the analysis of rare earth mixtures and to the determination of low concentrations of the rare earth elements. The requirement for more knowledge in the area of flame emission spectroscopy and particularly for highly refractory rare earth element determinations provides a potential field for increasingly useful research work. The techniques of flame and carbon furnace emission spectroscopy could be used for the investigation of spectra and atomisation studies of the rare earth elements. Such techniques could also be used on a routine basis in any analytical laboratory and to provide the necessary standards for X-ray fluorescence analysis.

CHAPTER II

EXPERIMENTAL

2.1 Instrumentation and Reagents

Instrumentation

A Perkin Elmer, model 360 Atomic Absorption Spectrophotometer (Perkin Elmer Corporation, Norwalk, Connecticut, U.S.A.), was used.

The instrument comprises a grating monochromator blazed at 250nm and of reciprocal linear dispersion 1.6nm/mm. The burner system includes a 5cm premixed slot type burner for the N_2O/C_2H_2 flame and a 10cm burner for the air/C_2H_2 flame. The readout involves a needle galvanometer scale for absorbance and emission readings and an integrate mode can be used for three or ten second periods. Emission signals can be expanded using the expansion mode, whereas absorption signals can also be read using the concentration mode where an expansion facility operates. A push button automatic zero is used to reset the zero with the blank under aspiration. An additional feature is the automatic wavelength scan facility which is useful, particularly for reading emission spectra over a wavelength range; a chart recorder can be coupled to the instrument for use in conjunction with wavelength scanning. The chart recorder used for this research project was a Honeywell model (model Electronik 194, Honeywell Controls Ltd., Greenford, Middlesex, England).

The lanthanum and neodymium hollow cathode lamps used were made by Perkin Elmer (intensitron models, Perkin Elmer Corporation, Norwalk, Connecticut, U.S.A.), and operated under continuous d.c. with recommended maximum operating currents of 30mA. All emission and absorption readings were taken after spraying a blank sample and resetting the zero if necessary. A control sample (e.g. a standard at the higher concentration range of each set of readings) was also used and resprayed frequently to check the consistency of the results. An average of at least three readings was always used.

Reagents

The following standard solutions were prepared using deionised water and diluted as required - Cerium 1000mg.dm^{-3} (3.91g dm^{-3} analar ammonium ceric nitrate A.R. B.D.H. Poole, Dorset); lanthanum 1000mg dm^{-3} (3.24g dm^{-3} lanthanum nitrate - atomic absorption reagent, Hopkins and Williams, Chadwell Heath, Essex, England); neodymium 1000mg dm^{-3} (2.90g dm^{-3} neodymium nitrate, 99.9% pure, Koch Light Laboratories Ltd., Colnbrook, Bucks, England); and praseodymium 1000mg dm^{-3} (2.96g dm^{-3} praseodymium nitrate, 99.9% pure, Koch Light Laboratories Ltd., Colnbrook, Bucks., England).

Acids, Alkalis and Salts

These were prepared as required from Analar grade reagents.

Steel Samples

British Chemical Standards (B.C.S., Bureau of Analysed Samples Ltd., Newhall Hall, Middlesborough, Teeside, England), were used throughout with the main samples being B.C.S. 404, B.C.S. 402 (low alloy steels), B.C.S. 329 (mild steel) and an 'iron sponge' sample (spec pure iron, Johnson Matthey Chemicals Ltd., Orchard Road, Royston, Herts, England). Steels containing rare earth mixtures were obtained with the courtesy of the M.Q.A.D. Bragg Laboratory, Sheffield, and consisted of low alloy or mild steels with up to 0.2% mischmetal additions. Additional steel samples containing cerium were obtained from B.S.C. Grangetown Laboratories, Teeside, England.

Steel Dissolution Procedures

The steel samples, which currently contain lanthanoid additions, are all mild or low alloy steels. These, therefore, contain low levels of carbon and silicon and so a dissolution method using aqua regia was found to be suitable. The method is outlined below:-

> Weigh out 1g steel into a clean, dry 300cm^3 beaker. Add 30cm^3 1:1 hydrochloric acid and 5cm^3 concentrated nitric acid. Cover with a watch glass and allow to stand for 5 - 10 minutes until the initial vigorous reaction evolving nitrogen dioxide fumes has ceased. Then warm the steel mixture and gently bring to the boil, checking that all the steel particles have dissolved to form an orange/yellow solution. Boil

and fume down slowly to a syrupy state (almost dry) without allowing the solution to overheat and spit on the glass sides. Cool and redissolve in about $10cm^3$ hydrochloric acid (the strength depending on the method requirements).

This method was compared with other dissolution methods (e.g. with hydrofluoric acid) and was found to be completely satisfactory for total dissolving of all the rare earth content in the steel samples (see Chapter IV).

2.2 The Flame as an Atom Cell in Atomic Spectroscopy

Classification of flames

A basic classification of flame types can be made in terms of the state of flow which may be described as either laminar or turbulent. In a turbulent flow of gas, it is possible to identify specific regions in which all flow is in a particular direction, but the regions themselves have random velocities and may collide with each other and sometimes mix. In laminar flow, transport phenomena within the gas may be described in terms of molecular motion, where all volume elements move parallel to each other. Flame types are further divided according to whether the gases are premixed before leaving the burner or whether the gases are allowed to mix only on reaching the point of ignition, the latter type being referred to as unpremixed flames. An example of this latter type is the diffusion flame, in which only the fuel gas leaves the burner, subsequently mixing with the surrounding air which acts as an oxidant to support a flame. Unpremixed flames are, by definition, always turbulent.

The structure of premixed flames (e.g. nitrous oxide/acetylene) can be divided into three main regions or zones. The gases leaving the top of the burner tube enter a preheating zone where they are raised to their ignition temperature by the heat of the existing flame. Surrounding this zone is the bright luminous primary reaction zone whose outer surface forms the flame front. In flames burning at atmospheric pressure, the primary reaction zone is extremely thin and the residence time of the gases too short for a thermodynamic equilibrium to be established. This results in high noise levels and intense background radiation.

The flame radicals and partially combusted gases pass from the reaction zone into a region known as the interconal zone. This is a broader area and its nature varies considerably with the fuel/oxidant combination, as this will affect the composition of gases passing from the primary reaction zone. In typical hydrocarbon flames, the gases will be made up of molecules such as CO, H_2, O_2, N_2, and radicals such as CN, CH and OH. Equilibrium is established fairly quickly with recombination of radicals and dissociation of the combustion products. The hot, partly combusted gases of the interconal zone come into contact with oxygen from the surrounding air and further reactions occur, giving rise to a secondary reaction zone. The participation of the atmospheric air is complex with both diffusion and entrainment of the air occurring due to the upward motion of the hot gases.

The most intense radiation from the flame originates in the primary reaction zone and is mainly due to molecular band spectra. Atomic lines and a continuum background however, are also observed. The species producing the molecular species are commonly C_2, CH, CHO, OH, CN, NO, and NH. Radiation from the interconal zone is less intense owing to the existence of lower populations in this region of the flame of many of the species giving strong band spectra. The interconal zone of the fuel rich nitrous oxide/acetylene flame exhibits a bright red emission owing to the presence of a high concentration of CN radicals. The secondary reaction zone also gives much less intense radiation than the primary zone with the main emission observed as being from OH radicals which is most intense in this region.

Burner Design

Burner design is an important factor when considering the use of premixed flames. Any burner to be used in analytical spectroscopy with premixed laminar flames, must meet certain requirements. There must be complete mixing of the fuel and oxidant gases. The gas flow must be laminar on leaving the burner top. Burner ports must be designed to give a stable flame with suitable gas flow rate, and to prevent flash-back of the flame into the burner; any flash-back must also be contained within the burner. The burner should be able to be

run for long periods without overheating or clogging. Finally, the flame should be of convenient size and shape, quiet and usable over a wide range of mixture strengths. In practice the design of the burner head and its port is the most critical, while the construction of the main body is usually straightforward.

Many early analytical flame spectroscopic experiments were made using the large circular burner port (the Bunsen burner type). A form of safety device was then added, composed of a jet (for fuel gas) and venturi (for the total gas mixture). The burner port was composed of a set of small holed (meker type) or a narrow slit (slot burner). These two types of ports are the most commonly used today. The nitrous oxide/acetylene flame is usually used in conjunction with a slot type burner with a slit of commonly 5cm for maximum efficiency and safety.

The nitrous oxide/acetylene flame

The nitrous oxide/acetylene flame was introduced by Willis in 1965 (59) as a possible atom cell for atomic absorption spectroscopy. It is now widely used for routine analysis and is essential for the determination of some elements, particularly refractory elements, by atomic absorption and emission techniques. The elimination of many of the chemical interferences, previously encountered in the air/acetylene flame, shows the additional advantages of this flame. The nitrous oxide/acetylene combination was originally chosen for its ability to give a flame as hot as oxygen/acetylene, but with a much lower burning velocity. The combustion characteristics of the nitrous oxide/acetylene flame are given below in Table III (60).

TABLE III

Combustion characteristics of the nitrous oxide/acetylene flame

Fuel	Oxidant	Energy released (Kcal)	Maximum burning velocity (cms^{-1})	Maximum flame temperature (experimental) (K)
C_2H_2	N_2O	401.5	160	2990

The stoichiometric reaction is:-

$$C_2H_2 + \frac{5}{2}N_2O \longrightarrow 2CO_2 + H_2O + 5N_2$$

The characteristic red, interconal zone obtained under slightly fuel rich conditions is extremely effective for the atomisation of elements that form stable, refractory oxides (e.g. the lanthanoids). The reducing nature of this zone appears to result from the presence of a substantial concentration of gaseous carbon containing species (e.g. C, CN, CH and HCN) and very low concentrations of oxidising species. With careful optimisation of flame and burner conditions the interconal zone extends over a relatively large volume and allows sensitive emission and absorption measurements even for elements forming stable oxides while low noise levels can be retained.

Experimental procedure for the nitrous oxide/acetylene flame

The cylinder pressures of the acetylene and nitrousoxide gases were set to 8 psi. and 40 psi. (from a constant reducing valve) respectively. The cylinder pressures were always re-checked before use to ensure that the gas levels were not too low. The nitrous oxide gas was fed into the burner through a two-way valve, which normally was used to control air flow. A 5cm slot type burner was introduced into the chamber head and always restrained by means of a thin wire safety chain in case of a flash-back.

In operation an air/acetylene mixture was lit first and then the acetylene flow increased to produce a highly luminous flame. The nitrous oxide was then fed into the flame by switching over the two-way valve from air to nitrous oxide, producing the characteristic nitrous oxide/acetylene flame in a fuel rich state, and then the acetylene flow rate reduced to produce the required flame stoichiometry.

The nitrous oxide/acetylene flame consists of three main zones, as stated previously -

(a) the primary reaction zone - a 2-3mm high blue/grey layer just above the burner

(b) the interconal zone - a 10-25mm red area called the 'red feather' which can be increased or reduced in height by altering the fuel flow rate, and

(c) the secondary diffusion zone - the bluish area above the red feather.

In extinguishing the flame the nitrous oxide gas was always turned over to air by the two-way valve and then the acetylene flow rate reduced until incomplete combustion occurred. The drain tube was bent to form a loop (of approximately 20cm diameter) filled with water as a precaution against the operating pressure of gas in the spray chamber in case of a blow-back of gases.

The fuel flow rates are given in Table IV showing the acetylene rates to produce various red feather heights. A flame with an excess of acetylene produces a large red feather and is described as fuel rich or reducing whereas one deficient in acetylene as lean or oxidising.

TABLE IV

Fuel flow rates

Acetylene flow rate	Red feather height mm
58	5
60	10
62	20
64	30
65	40

The acetylene flow rate figures given are as read from the P.E.360 instruments with the oxidant flow rate maintained at a constant reading of 40.

CHAPTER III

INVESTIGATION OF RARE EARTH EMISSION SPECTRA USING THE NITROUS OXIDE/ACETYLENE FLAME

3.1 Atomisation Problems Associated with the Lanthanoid Elements

The similarity in the chemical properties of the lanthanoid group of elements precludes the simple use of the classical techniques for the quantitative analysis of most rare earth mixtures. The measurement, therefore, of physical properties of these elements is valuable in order to obtain analytical data on lanthanoid mixtures. The most useful analytical information has been obtained from intensity measurements of various characteristic spectra of these elements. The arc or spark emission spectra of most of the rare earth elements are very complex, possessing thousands of lines of rather uniform intensity and lacking characteristically intense lines found in the spectra of other elements. The promise that a simpler spectra can be obtained under less energetic excitation conditions has led to an interest in the use of spectra excited in conventional flames.

Under these moderate excitation conditions, introducing the rare earths into the flames as aerosols of aqueous solutions, the early workers observed that most of the spectra (61) were remarkedly devoid of any atomic lines. Piccardi noted that most of the rare earth elements had a tendency to form diatomic molecules in the oxyhydrogen flame. The relative stability of these molecules in this flame, compared to atoms, was noted. Pinta (62) extended his observations to air/acetylene flames and made a thorough study of the analytical utility of these spectra. Most of the monoxide band systems were found to be concentrated in the wavelength region 480 - 600nm, but the band overlap of the individual spectra was found to greatly restrict the general analytical utility of these molecular systems. The strong experimental evidence and corroborative thermodynamic data suggested that stable diatomic rare earth monoxide molecule formation was the major controlling factor which limits the production of line spectra in oxygen supported flames. This

conclusion is supported by the exceptionally high dissociation energies exhibited by these molecules (Table V) (63).

TABLE V

Atomisation Problems

Element	Dissociation Energy (LnO/eV)
La	8.2
Ce	8.3
Nd	7.4
Pr	7.9

These high dissociation energies explain the lack of atomic lines in spectra observed in oxygen containing flames. The number of free atoms present in a flame depends on the degree of dissociation of the parent monoxide molecules. The rare earth monoxides are not dissociated to any appreciable extent at the temperature of the air/acetylene flame but hotter flames, e.g. oxyacetylene or nitrous oxide/acetylene proved to be more useful in the production of free atoms.

The degree of ionisation of the rare earth atoms at the temperature of the flame is significant. The ionisation potentials for the relevant rare earths are given in Table VI (63).

TABLE VI

Ionisation Problems

Element	Ionisation Potential (eV)
La	5.61
Ce	5.60
Nd	5.48
Pr	5.45

The flame conditions necessary to produce free rare earth atoms are, therefore, suitable also for the formation of rare earth ions. Once the ions are formed, the lower excited states can be

populated by a thermal excitation mechanism, thus producing ion lines.

Premixed high temperature flames (ca. 2900°C) may be produced by burning acetylene with nitrous oxide or oxygen nitrogen mixtures. The performance of both types of flame in the atomisation of metals is fairly similar, though the nitrous oxide/acetylene mixture is more convenient and can be burned with greater velocity at a long burner. This flame has been reviewed in Chapter II. The chief problem in working with high temperature premixed flames is that they usually have high burning velocities. This means that to prevent flash-back, a high rate of gas flow through the burner port must be maintained, which, in turn, requires that the total area of the burner port must be small. Table VII (64) shows the characteristics of the high temperature flames nitrous oxide/acetylene, oxygen/acetylene and nitric oxide/acetylene compared to the widely used low temperature flame air/acetylene.

TABLE VII

Characteristics of flames suitable for flame atomic spectroscopy

Gas Mixture	Maximum Flame Speed (cm sec^{-1})	Maximum Temperature (°C)
air/C_2H_2	160	2300
N_2O/C_2H_2	180	2955
No/C_2H_2	90	3095
O_2/C_2H_2	1130	3065

The early workers experimented with various gas mixtures and various burner designs which unfortunately produced various laboratory explosions (65 - 68). Eventually the use of premixed flames in a slot burner system with calculated slit widths and lengths produced a safe and useful system and the direct injection burners were then superseded to a large extent. Thermodynamically the combustion process in the stoichiometric nitrous oxide/acetylene flame may be considered to be:-

$$5N_2O \longrightarrow 5N_2 + \frac{5}{2}\,O_2$$

$$C_2H_2 + \frac{5}{2}\,O_2 \longrightarrow 2CO_2 + H_2O_{(g)}$$

The nitrous oxide decomposes to give a mixture of 33.3% oxygen and 66.7% nitrogen, with which the acetylene burns, the temperature of the flame being increased by absorption of the energy liberated by this decomposition.
After the introduction of the nitrous oxide/acetylene to analytical atomic absorption spectroscopy, Willis and Amos (64) extended this work determining some additional 25 elements by this flame, such as Ca, Sr, Ba and Mo, which were only partially atomised in cooler flames, were found to be determined with sensitivity and greater freedom from chemical interference by the nitrous oxide/acetylene flame. At the same time Pickett and Koirtyohann (69) have shown that fuel rich nitrous oxide/acetylene flames effectively produce free atoms of the rare earth elements. Atomic absorption and emission in this flame was found to be comparable to that observed in the premixed oxy acetylene flame.
Fassel, Curry and Kniseley (70) found that flame chemistry, rather than flame temperature, was an important consideration in the production of free atoms of the rare earth elements. Their studies have shown that the increase in the free atom population is a direct result of the high concentration of carbon containing species prevalent in high temperature hydrocarbon flames. A fuel rich flame thus offered sufficient reducing character to shift the dissociation equilibrium of the rare earth oxides towards the production of free atoms. The original work on the flame excitation of the line spectra of the rare earth elements was done with the total consumption burner (Beckmann type) that produced a highly turbulent flame. For most of the subsequent investigations in both emission and absorption premixed nitrous oxide/acetylene and oxygen/acetylene flames were employed using slot burners of the type normally used in atomic absorption instruments. The emission and absorption enhancement factors observed in the fuel rich flame were found to vary considerably with the greatest enhancements observed for the rare earths which have the most stable monoxides (e.g. La and Ce).

It was noted that for both the flame absorption and emission determinations of the rare earths, flame stoichiometry was a critical variable.

3.2 A Comparison of Flame Emission Spectroscopy with Flame Atomic Absorption Spectroscopy

Flame emission spectroscopy was expected to prove a better method than flame atomic absorption spectroscopy for the lanthanoid group of elements. For certain groups of elements both methods can be regarded as of equivalent sensitivity, but for other elements absorption spectroscopy may provide the most sensitive method of analysis (or vice versa). In different situations the instrumental advantages or disadvantages of one technique may favour its use as opposed to the other. The probability of the superimposition of resonance lines of different elements is extremely small even compared to the probability that in emission methods an emission line will be superimposed on the resonance line. Where spectral interference is found to occur, such interferences are easily overcome by use of another resonance line. This possibility was expected when considering the rare earth group due to the complex spectra of these elements. The intensity of radiation in the atomic emission technique depends on the population of the excited level. Small variations in flame temperature (e.g. by fluctuations in the fuel flow rate) have a great effect on the population of excited atoms, as determined by the Boltzmann distribution (given in the equation below) and hence on the analytical signal

$$N_j = No \frac{gj}{go} e^{-\left(\frac{Ej}{KT}\right)} \qquad \text{Boltzmann distribution Law}$$

where No is the number of atoms in ground unexcited state, Nj is number of atoms in excited state and Ej energy of atoms in the excited state - gj and go are the statistical weights of the jth and ground (zero) states respectively. T is the absolute temperature and K a constant.

Atomic absorption spectroscopy measures the intensity of radiation of atoms in the unexcited (ground) state. Temperature variations do not alter the number of ground-state atoms present and so flame fluctuations are not important in atomic absorption which can provide an analytical advantage. An increase in sensitivity, however, cannot be achieved in atomic absorption

spectroscopy by altering the flame conditions but in atomic emission spectroscopy this can readily be achieved by using a hotter flame as the number of excited atoms is related to flame temperature from the Boltzmann distribution. Many studies have been made comparing the signal strengths and detection levels theoretically obtainable from atomic emission spectroscopy and atomic absorption spectroscopy. Atomic emission, in general, was found to be most sensitive at higher wavelengths (>350nm) as the shorter wavelengths correspond to higher energy transitions and high temperature flames such as the nitrous oxide/acetylene flame do not possess enough thermal energy to produce sufficient atomic populations of higher excited states. The lanthanoid group of elements are, therefore, expected to prove to be more sensitively determined by atomic emission compared to atomic absorption.

Atomic absorption measures the ratio of the unabsorbed signal to the absorbed signal. This removes the possibility of systematic errors arising from small shifts in the monochromator setting, or small variations in the sensitivity of the detection system between optimisation and the completion of analysis. This is an advantage of the atomic absorption technique but also places a practical limit on the sensitivity of the absorption technique as it is experimentally difficult to measure a small difference in two large quantities. The sensitivity can be increased by the use of higher temperatures and expansion modes available on atomic emission/absorption instruments.

Finally, the atomic emission technique does not require a spectral source, i.e. a hollow cathode lamp. This is an important advantage for the lanthanoid elements, particularly cerium. Due to the difficulty in obtaining these elements in the pure state for use as cathodes, the hollow cathode lamps available for the lanthanoid group are generally unsatisfactory, giving poor and inadequate detection limits in atomic absorption. Flame emission spectroscopy can, additionally, use molecular species, whereas absorption techniques apply only to atomic species. This is an important factor for the highly refractory lanthanoid group of elements where there is a predominance of molecular species even in the hotter nitrous oxide/acetylene flame.

Overall, therefore, the advantages of atomic emission spectroscopy outweigh those of atomic absorption spectroscopy when applied to the rare earth element group.
In conclusion, for an analytical determination of the lanthanoids, an atomic emission method, using a high temperature flame, the presence of reducing species and the addition of an ionisation suppressor, was considered desirable. Research plans were then listed with these important factors being taken into account.

3.3 Wavelength Selection and Instrument Optimisation

Initial research work was started using the nitrous oxide/acetylene flame and a 5cm slot type burner, and primary investigations were made with 1000 $mg.dm^{-3}$ lanthanoid solutions. The experimental details of instrumentation and reagents are given in Chapter II. The first experimental work was concerned with obtaining satisfactory emission signals of these rare earth elements using the nitrous oxide/acetylene flame under reducing conditions. Spectral scans of the four lanthanoids of interest Ce, La, Nd and Pr were recorded in the range 350nm to 700nm. This was carried out by continuous spraying of -

(a) pure water
(b) potassium solution (see 3.4)
(c) rare earth stock solution

into a fuel-rich nitrous oxide/acetylene flame with the automatic wavelength scan in operation. The emission readings were displayed visually on the needle galvanometer scale and also recorded by connection to a chart recorder at a slow speed. In this way a detailed chart of each rare earth spectra was obtained from which rare earth emission was observed predominantly in the region 450nm to 580nm. The spectra produced were complex patterns and so it was necessary to label the key lines and bands resulting from the flame spectra in order to isolate the residual spectra due to the required lanthanoid emission. The Ce scan is given in Figure I with important lines and bands labelled for identification.
Overall it was observed that the rare earth elements produced very complex band patterns with some evidence of atomic emission but predominantly emission due to molecular bands. With the use of spectral tables (71 - 73) the most intense lines and bands

were checked. Initial observations showed that mutual rare earth spectral interference was evident and so investigations were made to seek wavelengths for each element with sufficient sensitivity to measure low levels but with minimum spectral interference from the other rare earths. Table VIII shows the wavelengths, selected from spectral tables, which are listed as the most sensitive lines or bands for these particular lanthanoids. The wavelengths which were observed from the experimental scans are denoted in this table. In conjunction with this table, spectral scans of these four elements at selected wavelengths are also shown in Figure 2.

Rains (74) commented that the LaO band systems at 791.0nm should be useful for the determination of the parent elements in rare earth mixtures. These bands were investigated but no emission was observed at the LaO band in the nitrous oxide/acetylene or air/acetylene flames using the instrumentation available, but the NdO band at 660.6nm was found to be sufficiently intense and also spectrally free from emission from the other rare earths present. The bands and lines selected for each element, with sufficient intensity to measure concentrations in the mg dm^{-3} range but with minimum interference from other rare earths, are shown in Table IX. The presence of band systems rather than solely line spectra, at the cerium wavelength 468.4nm and neodymium wavelength 660.6nm, indicate the presence of molecular species rather than atoms in the flame. The possibility of an atomic line lying above a broad molecular band in the same region was also considered. The praseodymium wavelength 493.9nm showed rather unusual behaviour. A continuous signal over a span of $\sim$ 10nm existed which was not characteristically typical of either an atomic line or band. This may have been due to the poor resolution of the instrument at this wavelength.

Complex lines, however, may appear like band structure and the available instrumentation may not have been capable of resolving such lines. The lanthanum wavelength 593.0nm is listed as an atomic line but the scan showed this to possess band character rather than purely an atomic line structure.

The instrument conditions for the determination of the

Figure 1. Wavelength Scan for Cerium (range 300 → 700 nm)

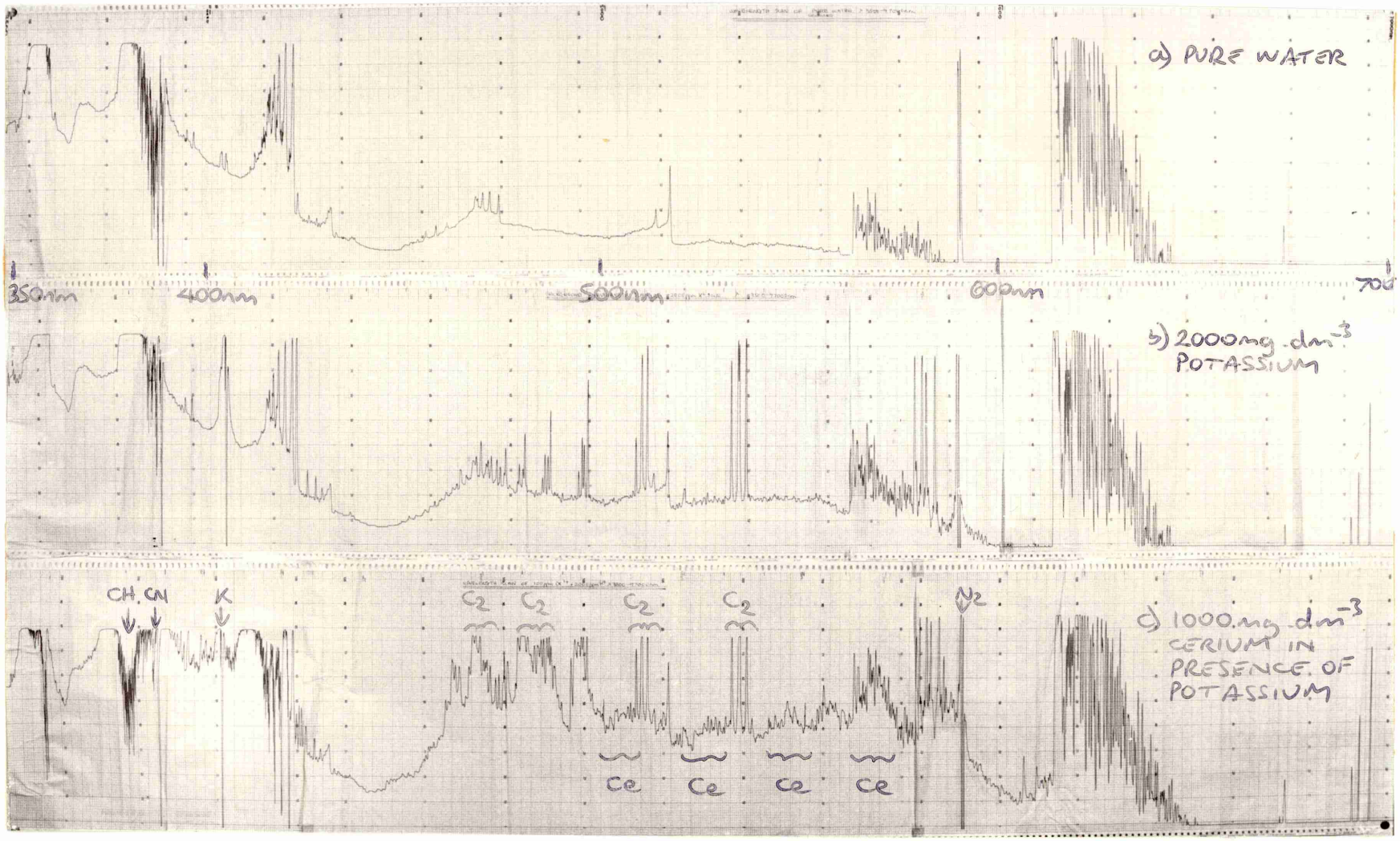
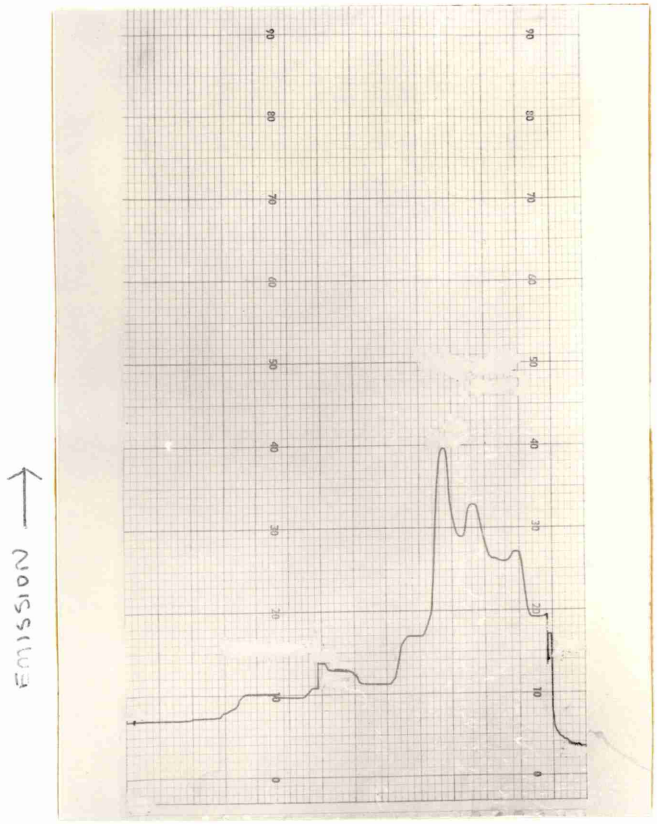


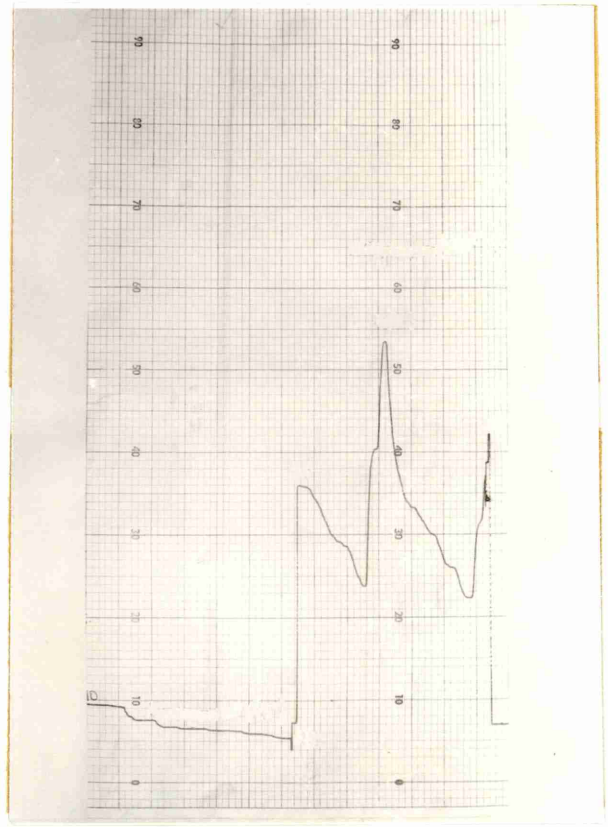
TABLE VIII

WAVELENGTH SELECTION

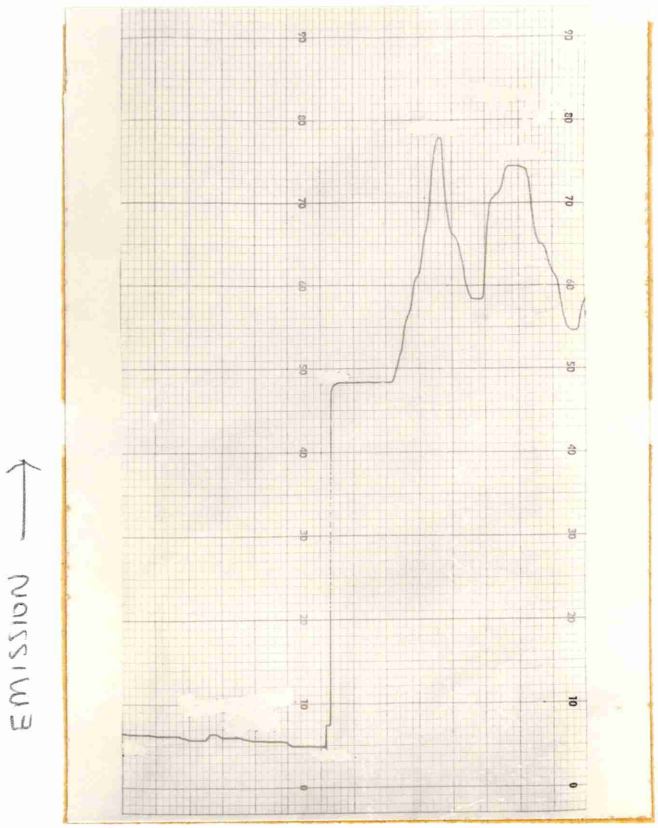
	ATOMIC LINES (nm)	MOLECULAR BANDS (nm)
CERIUM	569.9	468.4
	522.3	479.7
LANTHANUM	579.1	791.0
	550.1	794.0
	593.0	
NEODYMIUM	488.3	
	492.4	660.6
	486.4	
PRASEODYMIUM	493.9	576.3
	495.1	569.1
	501.8	709.5
		849.5
		559.6



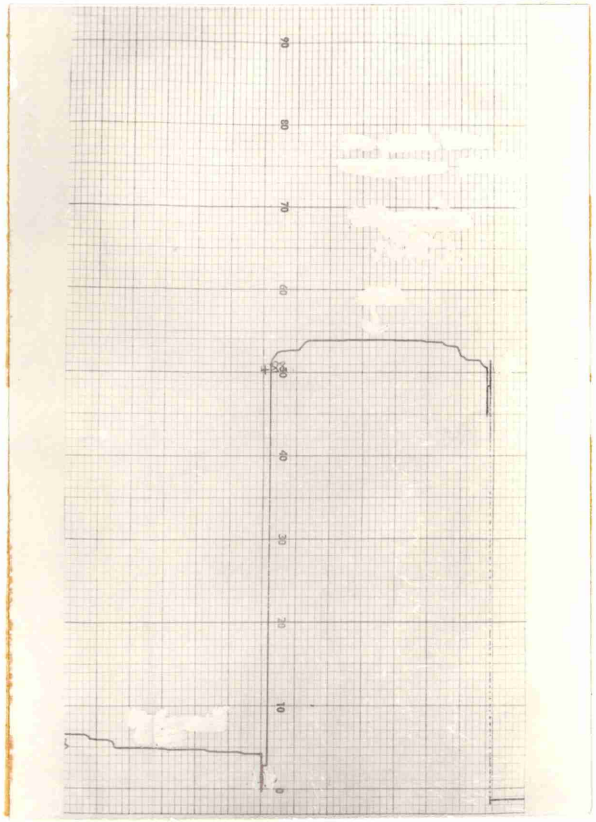
1) Ce. 467.5nm



2) La. 592.1nm



3) Nd. 660.1nm



4) Pr. 493.9nm

lanthanoids Ce, La, Nd and Pr by flame emission spectroscopy were then rigorously assessed. The parameters of -

(a) slit width

(b) sample uptake rate (nebuliser flow rate)

(c) fuel/oxidant ratio (degree of reducing character inflame)

(d) burner position (observation height)

were all investigated to provide the appropriate conditions for the determination of the detection limits of these four elements.

Only fixed slit widths with nominal spectral band pass of 0.2nm, 0.7nm and 2.0nm were available. The smallest slit width, 0.2nm, was found to be the most useful, giving a satisfactory signal for all elements with 50mg dm^{-3} solutions. The larger slits gave very noisy signals requiring maximum damping to give readable results. A wide slit will obviously allow a large intensity (emission signal) to be received but increased noise levels and poor resolution may also occur particularly with the instrumentation in question. A small slit improved the signal to noise ratio, but the actual signal passing through will be reduced under these narrow conditions. The smallest slit of 0.2nm was found to give the most useful signal for the lanthanoids suggesting that the signal to noise ratio was an important factor under the expanded instrumental conditions required for these difficult elements.

The sample uptake rate through the nebuliser was then investigated. The spray or mist created inside the nebuliser chamber can be increased or reduced by alteration of the orifice dimension (a simple screw device achieves this). The flow rate of liquid into the nebuliser was calculated by measuring the amount of liquid sucked from a $10cm^3$ measuring cylinder in one minute. A minimum flow rate of ca. $1.2cm^2$ min^{-1} and a maximum of ca. $8.0cm^3$ min^{-1} was obtained. Graph I shows the effect of flow rate on the emission signal for Ce at 468.4nm. Similar results were also obtained for the other rare earths at their respective wavelengths. The emission signal was observed to increase rapidly with a nebuliser flow rate increase from ca. 1.4cm min^{-1} to ca. $3cm^3$ min. A plateau region was then obtained with increase in the flow rate with a small degree of tailing at high flow rates. The small nebuliser device

TABLE IX

WAVELENGTH TABLE

ELEMENT	WAVELENGTH (nm)
Ce	468.4 mu 569.9 a
La	579.1 a 593.0 au
Nd	660.6 mu
Pr	493.9 au

a = atomic line

m = molecular band

u = currently in use

Instrument conditions:- slit width -.2nm
flame N_2O/C_2H_2 reducing
observation height - in primary reaction zone

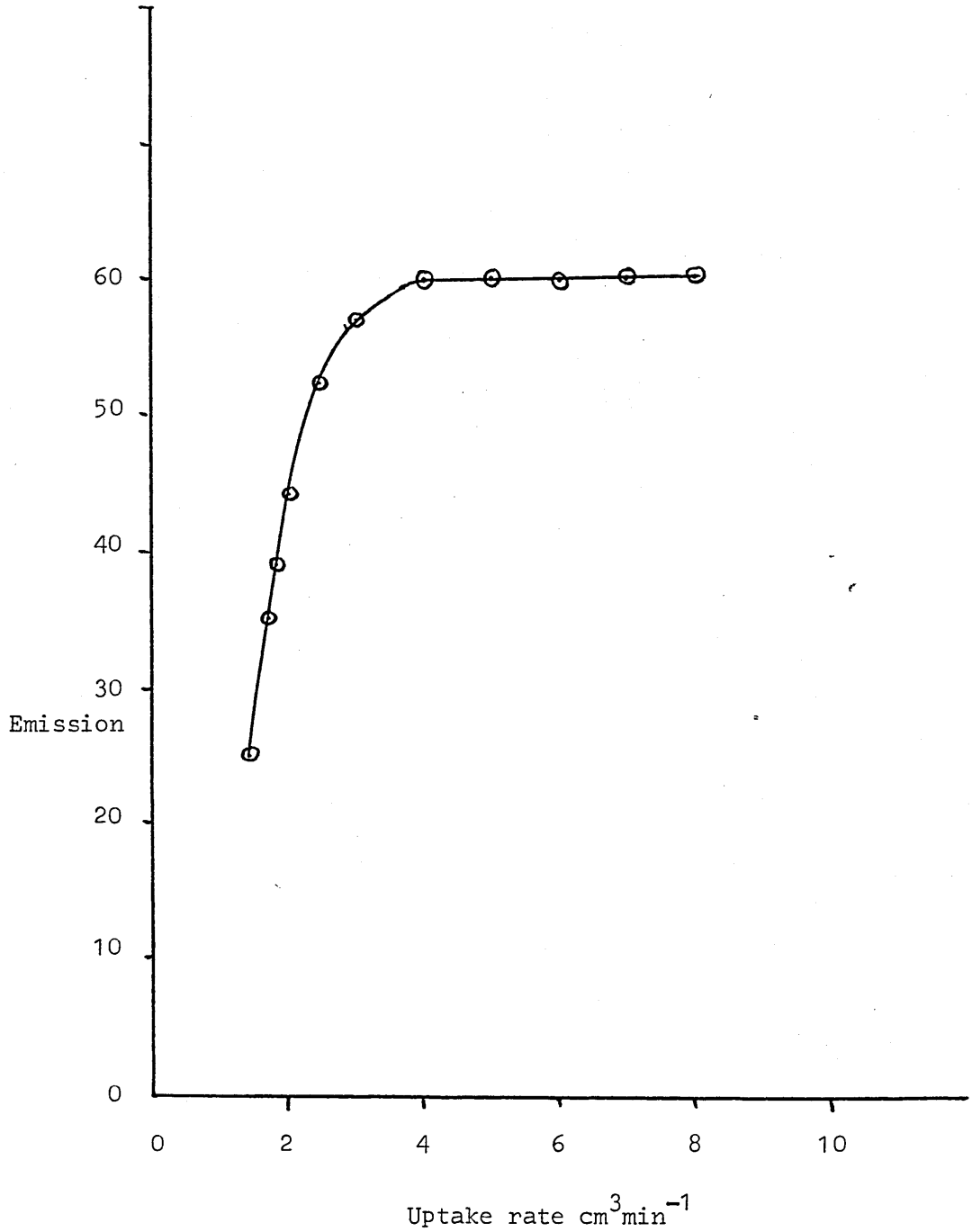
basically converts the liquid flow into a fine mist of droplets which are then carried by the gas flow through the nebuliser chamber and finally into the flame. A baffle within the chamber stops the movement of large droplets which condense on the walls and flow out through the drain tap. The smaller droplets are carried into the flame and evaporation of the solvent first occurs to form clots of solid rare earth element. These then fuse or sublime directly to give a molecule of solid, in this case a rare earth oxide species. Dissociation of this molecule into atoms will then occur in the high temperature flame if sufficient enthalpy is present to break down the particular banding.

Considering Graph I, the rapid increase in emission is due to the increase in the number of available molecules or atoms within the flame. At high flow rates this increase slows down and levels off to a maximum as saturation of the flame occurs. A balance between saturation of the species and the efficiency of nebulisation may occur. At high flow rates the efficiency may decrease as the droplets produced may be larger and so a greater number are lost by the baffle system than at low rates. The increase in the number of drops entering the flame means that more energy is required for desolvation and dissociation. This causes a possible cooling effect of the flame and so no increase in the number of free atoms occurs beyond a certain flow rate. Graph I shows this occurring at about $3.5cm^3\ min^{-1}$. The slight decrease in emission at very high flow rates gives some evidence of this cooling effect resulting in a slight reduction in the number of free atoms available. A flow rate into the nebuliser of $3.5 - 4.5cm^3\ min^{-1}$ was considered optimum producing a large emission signal without excessive use of sample. This factor was an important one if it was considered necessary to confine a finished steel sample to a small volume (e.g. $10 - 20cm^2$), in order to concentrate any low levels of rare earth elements.

The flame conditions were then investigated for each element at each respective wavelength. Very interesting results were obtained in this section of work. It was evident from the wavelength scans that band emission, rather than purely atomic emission, was present. This was expected as the rare earth

GRAPH I

Optimisation of solution flow rate



molecules, being highly refractory, tend to form stable diatomic monoxides in the flame. The dissociation energy values for the rare earths are given in Table V. These high energy values indicate that high temperature conditions in the flame are required to produce significant atomisation. The temperatures of the air/acetylene and nitrous oxide/acetylene flames are ca. 2300°C and ca. 2950°C respectively (see Table VI) and it is thought that these temperatures are, in themselves, insufficient to break down the strong oxides to form stable atoms in the flame. The conditions of the nitrous oxide/acetylene flame are sufficient to produce a small percentage of free atoms but the greater percentage apparently remain as oxide molecules in the flame and creates the band emission over a relatively wide spectral region, as seen from the wavelength scans.

The parameters of the fuel/oxidant ratio and the observation height of the burner were investigated in conjunction with each other. The flame mixture was altered to give increasing reducing character (by increasing the acetylene flow rate) to see if an improved signal could be obtained in the presence of an oxidising flame or a lean flame. Increase in the fuel rates could be seen visually by the enlargement of the characteristic 'red feather' within the flame. The fuel rates corresponding to measured 'red feather' heights are given in Chapter II - Table IV. The observation height (the position of the burner slit lip from the centre of the slit) was altered to investigate where maximum emission was occurring in the flame. The three main zones of the flame, the primary, interconal, and secondary diffusion areas of the flame, could be systematically observed.

The effect of these two parameters were investigated at the most sensitive lines and bands for each lanthanoid element. In this way the conditions for maximum emission could be optimised and, additionally, the extent of atomisation of these highly refractory elements could be clarified. Graphs 2, 3, 4 and 5 show the results of this work. The emission signal was plotted for each element Ce, La, Nd and Pr, with varying flame conditions by increasing gradually the reducing character of the flame. Curves were then constructed for the emission signal received for each

zone in the flame. Dramatic differences in the emission signal were observed under varying conditions and, although the four rare earths did not behave identically, a general trend was observed. The use of a highly reducing flame increased the atomic emission signal for all the lanthanoids under investigation; the active reducing agent in the reducing flame is usually regarded as the cyanogen radical, which gives rise to the intense emission in the 'red feather'. At a near stoichiometric flame an atomic emission signal was obtained but this increased to a maximum with increase in acetylene flow rate. In conjunction with the Graphs 2, 3, 4 and 5, this effect can be seen from scans taken at the cerium 569.7nm line shown in Figure III.

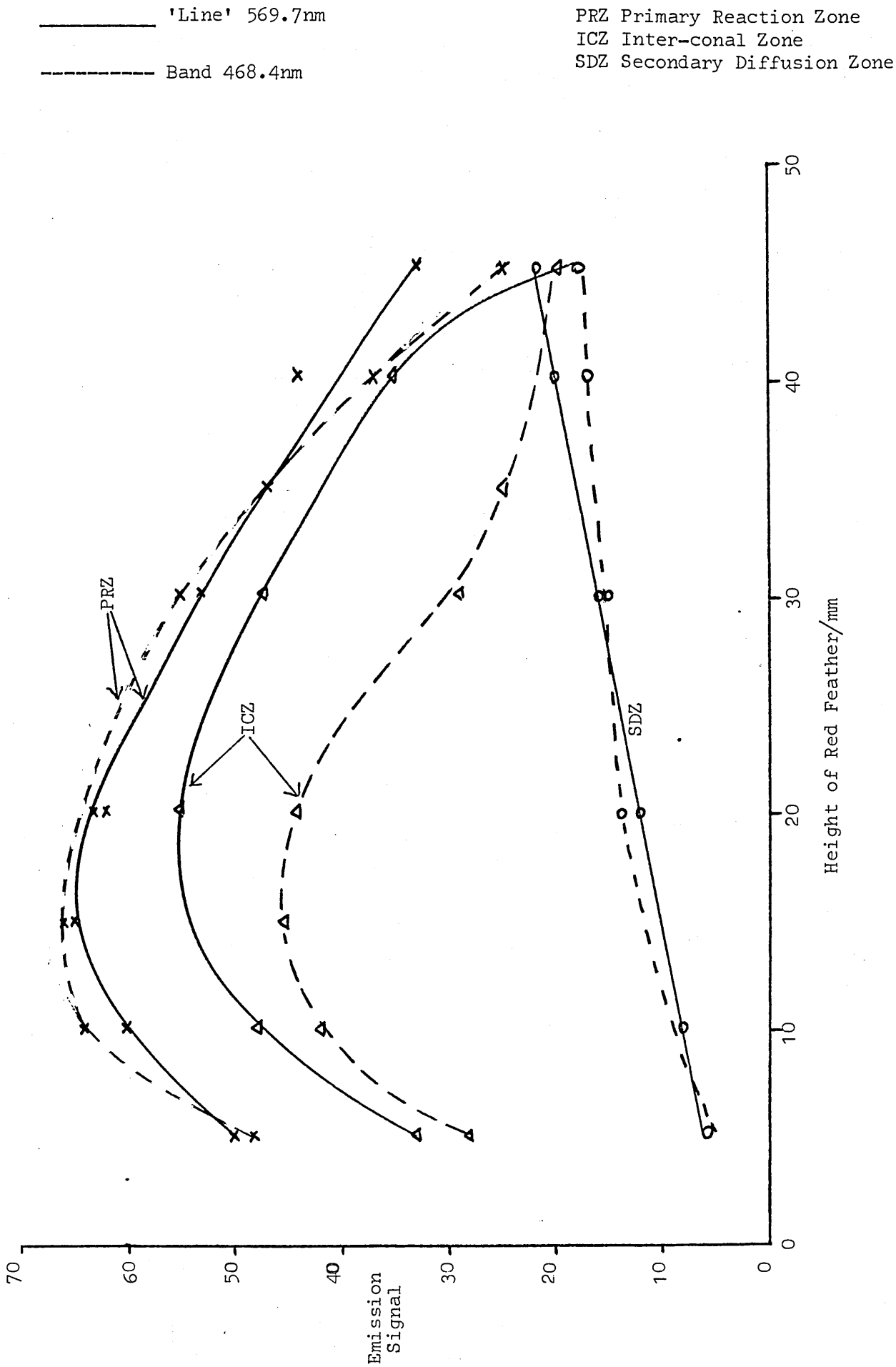
At higher acetylene flow rates, a decrease in signal was observed probably due to the cooling of the flame by excess fuel. This shows that the flame chemistry rather than just flame temperatures is an important consideration in the production of free atoms. At a near stoichiometric flame, the flame temperature is at a maximum but the number of cyanogen radicals is not. At the peak signal the combined effect of temperature and reducing nature is at a maximum; the temperature of the flame will be slightly lower than at a stoichiometric flame but the presence of sufficient cyanogen radicals produces many more free atoms. At high acetylene flow rates the temperature of the flame is reduced due to the cooling effect of excess fuel in the system. This causes a reduction in the signal because the number of excited atoms is exponentially related to the temperature by the Boltzmann distribution (see page 26). Although more free atoms may be formed under these cooler, but more reducing, conditions the operation of the Boltzmann criteria more than offsets this gain. It is instructive to compare this behaviour with the more reducing conditions widely used in atomic absorption spectroscopy where ground state atoms are involved and the Boltzmann distribution may be largely ignored.

The effect of flame conditions on the emission signals for Nd and Pr, shown in Graphs 4 and 5, were very similar, and being more clearly defined, can be used to explain the trend of behaviour of the four lanthanoids of interest. Lanthanum also

exhibited similar general behaviour, but cerium, although providing some areas of agreement, produced rather more complex results to interpret. In general, therefore, considering the primary and interconal zone of the flame, the molecular bands gave maximum emission signal for lower fuel flow rates (or lean flame) conditions). The signal significantly decreased with increase in acetylene flow rates dropping to near zero levels of emission at high values. The secondary diffusion zone was not adversely affected by increase in the fuel flow and, in all cases, gave poor emission signals. Conversely, the atomic lines showed low emission under leaner flame conditions, but a rapid increase with increased acetylene flow rates reaching a maximum signal before a sharp drop with very high fuel levels. Again the primary and interconal zones gave higher and dramatic emission variations with acetylene increase, while the secondary diffusion zone remained almost constant over a wide range, rising slightly at high fuel levels. Graph 2 shows the effect of flame conditions on cerium. In this case the difference between the atomic and molecular wavelengths was not apparent, as in the other graphs. The two wavelengths show similar behaviour, rising to a maximum signal for medium reducing flame conditions (15mm red feather) and then a sharp drop with increased fuel levels. The primary reaction zone gave higher emission levels than the interconal zone, whereas for the other elements, the primary reaction zone was only marginally favoured over the interconal zone. The behaviour in the secondary zone conformed to the other rare earth elements, giving a poor signal, not affected adversely by acetylene increase, but rising slightly at high levels of fuel. It would appear, therefore, that the atomic line for cerium may not be exhibiting truely atomic character under the conditions of the experiment. The behaviour at the line was more in agreement with the band behaviour of the other rare earths. Considering the results of all four graphs, a gradual increase in the ease of atom forming ability was apparent from Ce$\longrightarrow$La$\longrightarrow$Pr$\longrightarrow$Nd. This is partly in agreement with the dissociation energy values which are high for Ce, the first member of the group, decreasing to the element Pr.

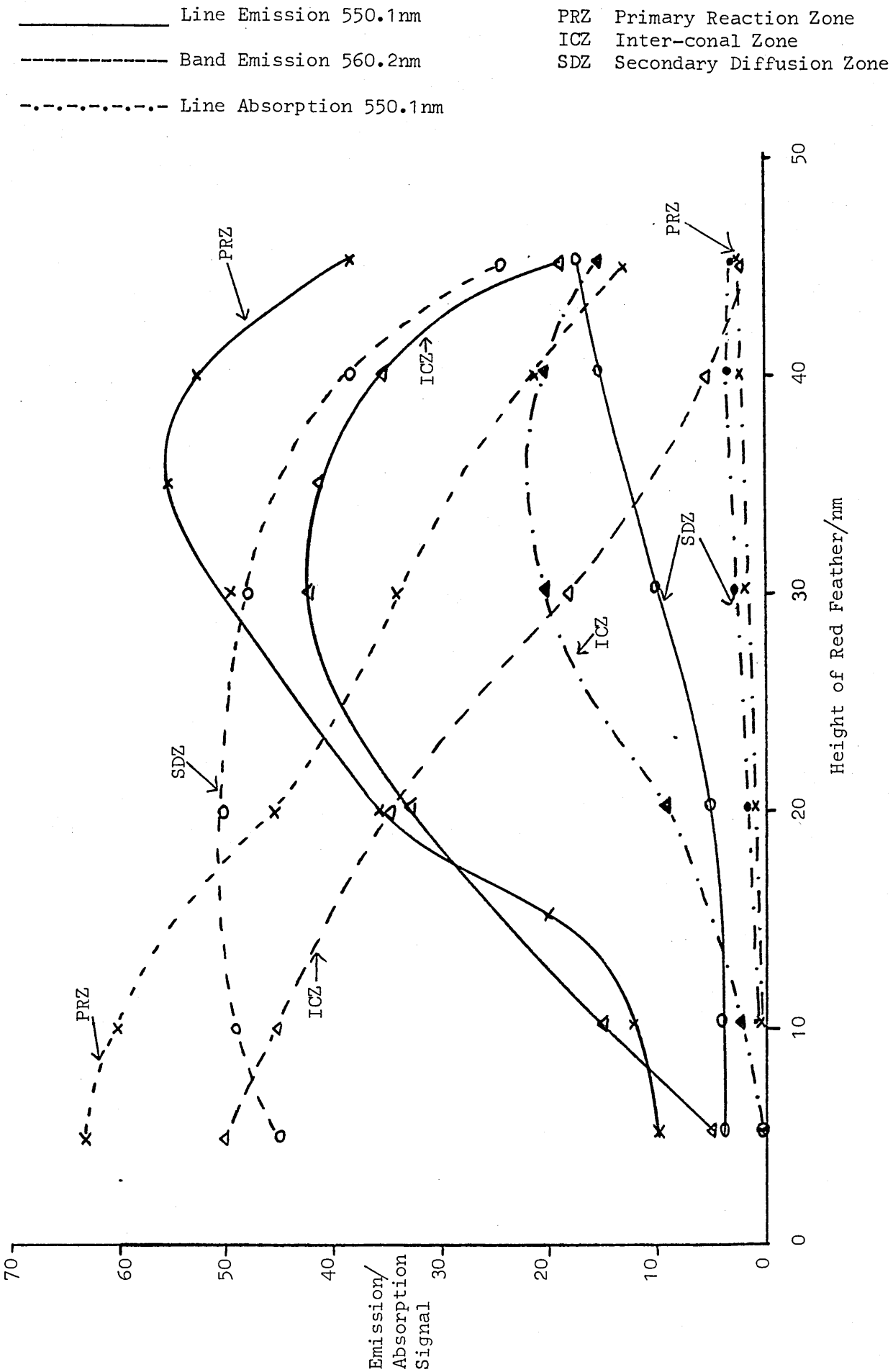
GRAPH 2

Effect of Flame Conditions on Ce and CeO Emission Signals



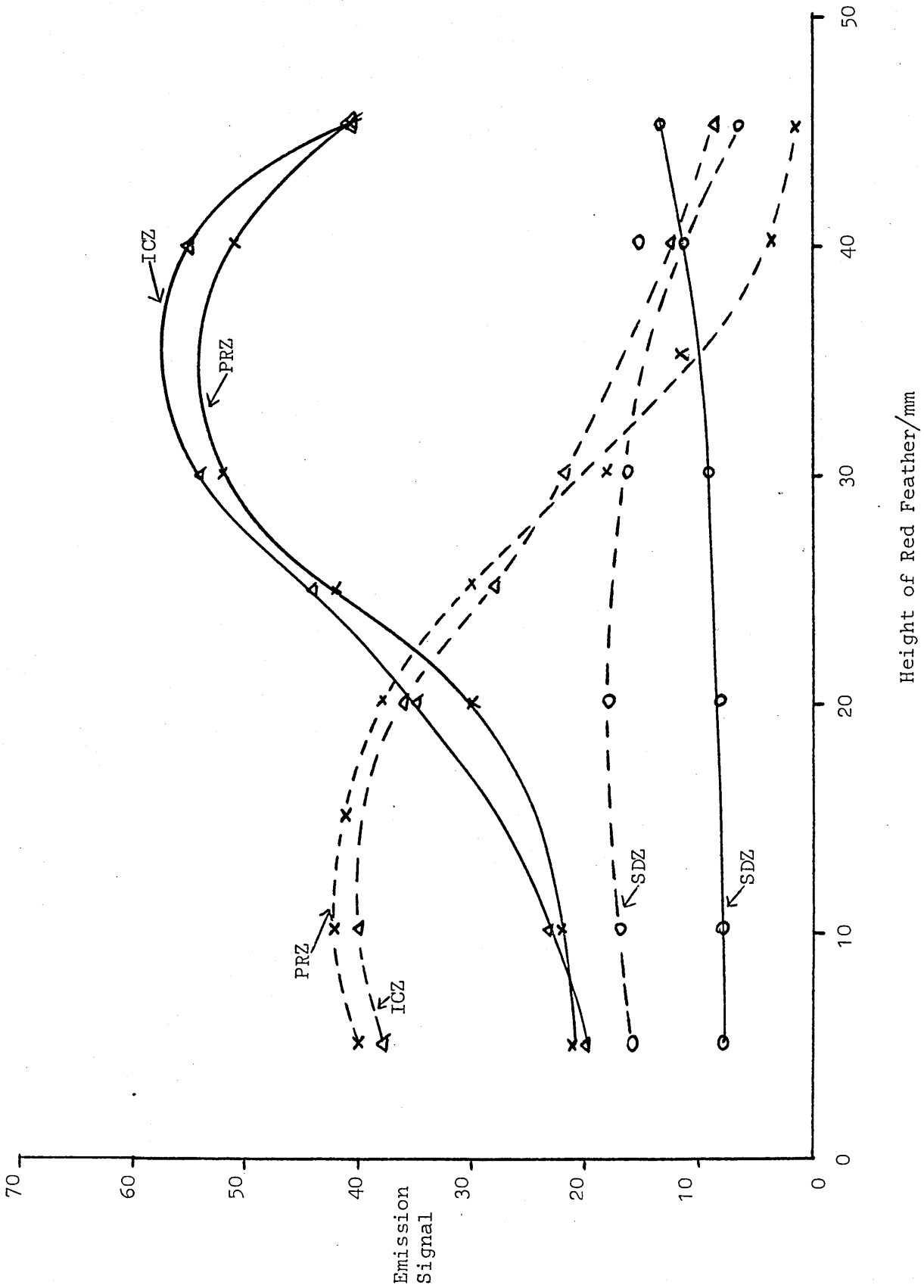
GRAPH 3

Effect of Flame Conditions on La and LaO Signals



GRAPH 4

Effect of Flame Conditions on Nd and NdO Emission Signals



GRAPH 3

Effect of Flame Conditions on Pr and PrO Emission Signals

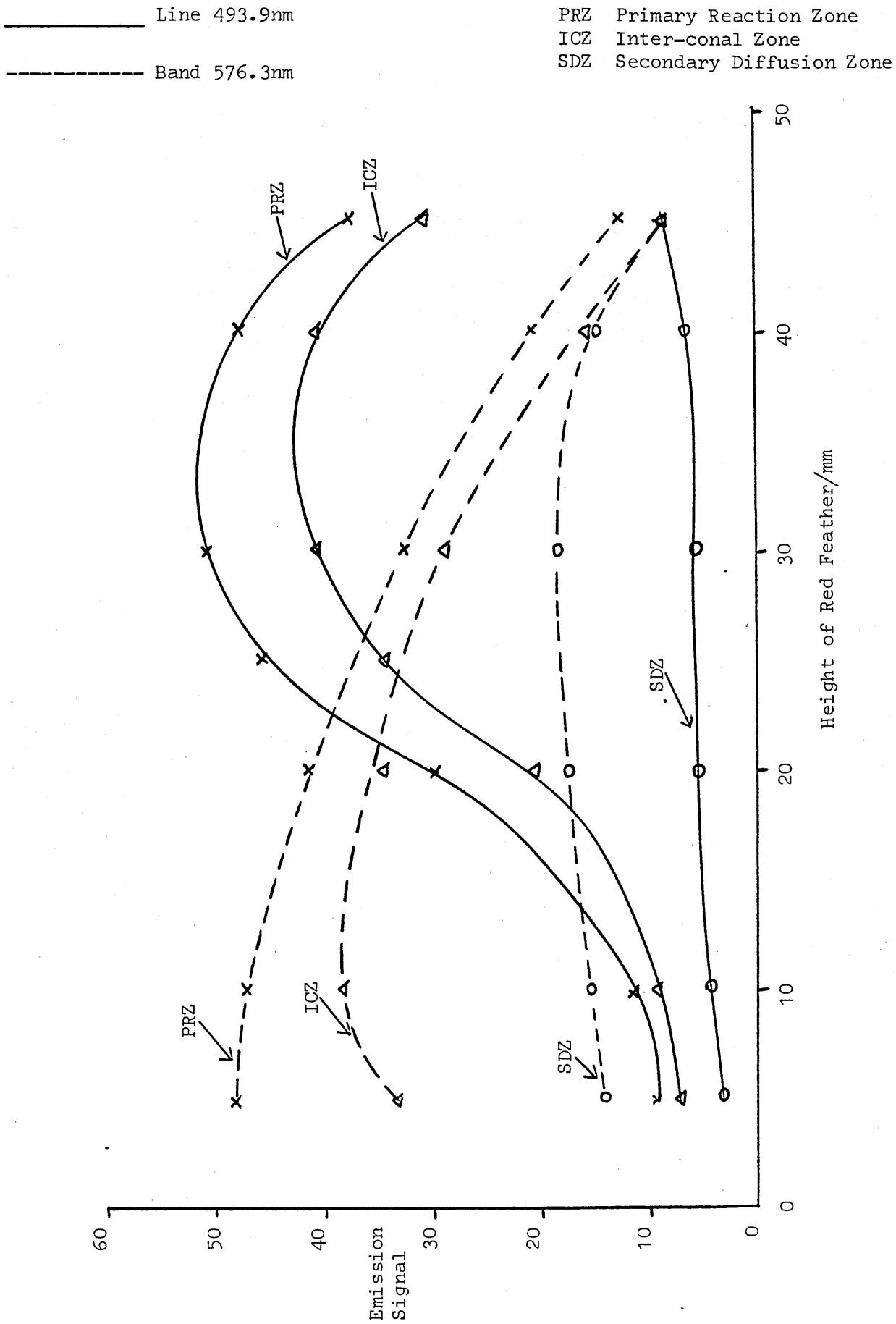
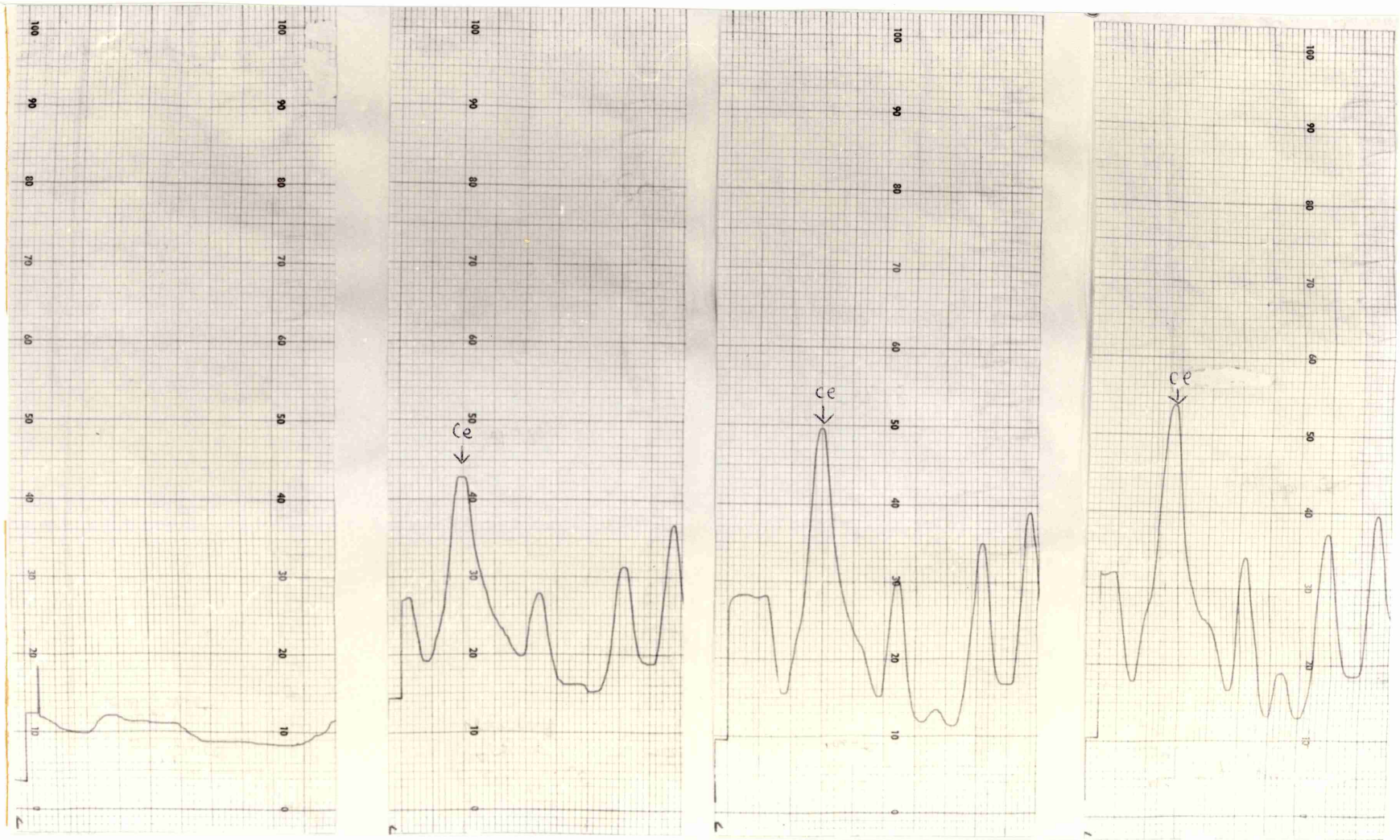


Figure 3 Effect of Flame Conditions on the Cerium Wavelength 569.7 nm using 500mg.dm^{-3} Ce solution



lean flame → highly reducing flame

The effects of flame conditions on the emission readings for atomic lines and molecular bands of the lanthanoids Ce, La, Nd and Pr can be summarised. In general, with the exception of Ce, the effect of flame conditions was more pronounced when atomic lines were being observed and can be explained if the percentage of atoms is very low, typically less than 10%. A doubling of the number of free atoms by increasing the reducing conditions would, therefore, give a great and abrupt effect in the emission signal at the atomic line but a smaller effect at a molecular band where the percentage of oxide species would only be slightly reduced. This explains to some extent the decrease in signal at the molecular bands. This decrease will also be affected by the cooling effect of excess fuel in the flame having a more dramatic effect at the molecular band as there would be no compensatory increase from the increase reducing conditions which apply only to atomic lines. The increased emission at the atomic lines is due to the increased presence of reducing species (regarded as cyanogen radicals) in the flame with higher fuel levels. The reducing action creates more free atoms in the flame and this more than offsets the cooling effect within the flame.

In conclusion, the emission signals obtained at both atomic and molecular wavelengths were at a maximum in the primary reaction zone of the flame and at a minimum in the secondary reaction zone. The interconal zone generally gave high emission, and, in some cases comparable to the primary reaction zone. The high emission signals in the primary reaction zone can be attributed to the phenomenon called chemiluminescence or over-excitation.

At this stage in the research work it was considered instructive to compare the above results obtained by flame emission spectroscopy with the complementary method of flame atomic absorption spectroscopy. As previously stated, limited work has been published on the lanthanoid group of elements by atomic absorption techniques and the main problem associated with this is the non availability of useful hollow cathode lamps for the rare earths. It was not possible to obtain a usable lamp for cerium, but hollow cathode lamps for lanthanum and neodymium were available.

These two elements were then investigated by an atomic absorption technique. Weak absorption signals were initially obtained using 2500mg dm^{-3} solutions at the Nd 463.4nm and La 550.13nm absorption lines. The instrument parameters of slit width, nebuliser flow rate, fuel/oxidant ratio and observation height were optimised in a similar way to the emission technique. A slit width of 0.7nm and nebuliser flow rate of 3.6cm sec^{-1} were found to be optimum. The reducing character of the nitrous oxide/acetylene flame was altered from a near stoichiometric flame to a very reducing flame by increasing the fuel flow. This was initially done without altering the height of observation of the flame compared to the lamp and then repeated with the flame being positioned so that the light passed through - firstly the primary reaction zone, secondly through the interconal zone and finally through the secondary diffusion zone. This corresponded to observation heights of 0.25cm (primary zone), 0.75 - 3.0cm (interconal zone) and 3.5cm (secondary zone). The results showed that the largest absorption signals were found to be in the interconal zone with a reducing flame for both elements, La and Nd. Insignificant signals were obtained in the primary reaction zone and the secondary diffusion zone of the flame, even under highly reducing conditions where instrument noise was an obvious problem. The effect of flame conditions and height of observation for these elements can be seen in Graph 3 for lanthanum and can be compared with results obtained by flame emission spectroscopy.

It was concluded that alteration of flame conditions had a far greater effect on emission signals than on absorption signals. The absorption signals, unlike emission signals, were not critically dependent on small variations in fuel/oxidant ratio or the height of observation. Instead it can be seen that there is only one specific position and flame condition to produce any detectable absorption signal for La or Nd. The requirements for atomic absorption for the rare earths are a highly reducing flame and observation being made in the interconal zone. At near stoichiometric conditions and in the primary or secondary zones of the flame, no significant absorption was detected.

These results are in agreement with the mode of excitement of atomic species by atomic absorption spectroscopy and Graph 3 is useful in outlining the different patterns of behaviour in emission and absorption techniques. Since atomic absorption spectroscopy is concerned with ground state atoms, it was not expected that small flame temperature variations (obtained by altering the fuel/oxidant ratio) would offset the absorption signal. Emission excitement is based, however, on non-ground state electrons and so flame temperature is critical as outlined previously by the Boltzmann distribution. The interconal zone of the nitrous oxide/acetylene flame was the only region in the flame to create any atomic absorption. This zone is the region of premixed flame in which most useful atomic absorption measurements are frequently made. It is a much broader zone than the primary reaction zone and its nature varies considerably with alteration fuel/oxidant ratios but presents an area where equilibrium is fairly quickly established via recombination of radicals and dissociation of the combustion products. This provides a hot temperature environment and, in the case of a reducing nitrous oxide/acetylene flame, an important predominance of cyanogen radicals. This provides a suitable environment for the reduction of the highly refractory lanthanoid oxide bond to produce free atoms in the flame. This cannot occur in the secondary diffusion zone where there is a minimal number of reducing species. The primary zone is in a state of non-thermal equilibrium and so, although useful for emission measurements, where the phenomena of chemiluminescence can occur is not suitable for the production of free atoms in the ground state for absorption measurements. It is clear, therefore, that a condition of non-thermal equilibrium in flames is of greater concern and interest in measurements of emission spectra than in absorption work.

The decrease in the absorption signal in the interconal zone at very high fuel flows, may be due to the cooling effect in the flame by excess fuel which could cause a significant temperature drop at these levels and of dissociation relative to temperature. This would affect the thermal equilibrium within the flame and create a tendency towards a non-thermal

equilibrium. A balance, therefore, between flame temperature and the degree of reducing species in the flame is necessary to produce atomic absorption measurements. The importance of flame chemistry, together with flame temperature is noted with regard to lanthanoid investigation by atomic absorption.

The absorption signals obtained under all of the appropriate optimum instrument parameters were still poor in comparison to the emission measurements. Increasing the lamp currents to high levels did not improve the signals and the problem of noise within the instrument created difficulties in obtaining useful signal noise ratios. It was evident that improved results for the determination of rare earth elements would be obtained by a flame emission technique. These results were expected, as noted previously, and until improved hollow cathode lamps can be made for the rare earth elements, the flame emission technique will be the preferred method for lanthanoid analysis by flame spectroscopy. Research work was then confined to the emission, rather than the absorption, technique.

Radiation in flames may be separated into two categories, thermal and non-thermal. Thermal excitation occurs when a species is raised to its excited state by virtue of the high temperature of its surroundings before emitting radiation. Energy is transferred between flame species and converted to electronic excitation by collision processes. The most common source of non-thermal radiation is referred to as chemiluminescence. This arises when the emitting species is formed directly in an excited state as a result of a chemical reaction. Chemiluminescence may result from reaction of the flame gases themselves or a similar process may be obtained with elements added to the flame.

In many cases it is not clear whether the non-thermal emission from a flame is due to chemiluminescence, induced chemiluminescence or energy transfer and then it is more satisfactory to term the radiation as over-excitation.

Over-excitation in flames originates from the primary reaction zone where there is the greatest release of energy and an absence of local thermal equilibrium conditions.

Radicals such as OH, CH, C_2 and HCO are well known for their non thermal emission in this region of the flame. Since the maximum emission signals for the lanthanoids were obtained in this zone it is reasonable to propose that the mechanism of energy formation is due to chemiluminescence or over-excitation as given above. The interconal zone also creates some non-thermal radiation; the extent and height to which it is observed will vary from flame to flame and with the species considered. The nitrous oxide/acetylene fuel rich flame will cause CN, C_2 and CH chemiluminescence to persist to a greater height and so the high emission signals obtained in the interconal zone can be considered to be due also to the chemiluminescence phenomena creating reduction of the refractory rare earth oxide species. The secondary reaction zone is in a state of thermal equilibrium and so no chemiluminescence occurs in this region. This explains why only small emission signals for the lanthanoids were obtained in this zone.

The mechanism of over-excitation of the nitrous oxide/acetylene flame has never been fully described but Kirkbright et al (75) thought that the CN and NH radicals present in the reaction zone might account for the excessive atomisation (dissociation of oxides), and that slow recombination could enable atomic concentrations to persist above the reaction zone. Many examples of chemiluminescence in the reaction zone of hydrocarbon flames are known. Chemiluminescence of the rare earths has also been observed by flame emission (78). The mechanism of chemiluminescence or over-excitation can, therefore, be adequately used to describe the emission signals obtained by the lanthanoids Ce, La, Nd and Pr in the fuel rich nitrous oxide/acetylene flame.

3.4 Investigation of Ionisation Interference

The next stage in the research work was to investigate ways of improving the emission signals of the four lanthanoids obtained in the nitrous oxide/acetylene flame. Firstly, the presence and suppression of any ionisation of the rare earth atomic species was considered. It can be shown from the Boltzmann distribution (see p.26) that the proportion of excited atoms is critically dependent on temperature and that the

number of atoms remaining in the ground state is almost unaffected. If the temperature of the flame is sufficiently high, it is obvious that a proportion of the atoms present will be ionised, thus removing atoms from the unionised or excited ground states and hence reducing the emission. This effect is particularly noticeable with the alkali and some alkaline earth metals that have low ionisation potentials and so are significantly ionised in hot flames. A table of ionisation potentials for Cs, K, Nd, is given below (76).

TABLE X

Element	First Order Ionisation Potential (eV)
Cs	3.89
K	4.34
Nd	5.14

Various workers have investigated the ionisation effects in flames. Baker and Garton (77) investigated the determination of potassium by emission and absorption in the oxy/propane flame and showed that the presence of Li, Cs or Na increased the potassium signal. The increase was related to the ionisation potential of the added elements; caesium with the lowest potential, giving the maximum enhancement. Trent and Slavin (78) used an air/acetylene flame and an atomic ground state line to investigate the determination of strontium and showed that an increase in absorption occurred when an alkali metal was added to the solution. When an ionic ground state line was used the reverse occurred, a decrease in the signal. These observations showed that there is a shift in the equilibrium between atoms and ions due to a form of mass action effect; as the amount of an easily ionised element in the flame is increased, the proportion of ionised to unionised atoms is decreased, with a corresponding rise in the number of atoms in the atomic ground state. This explanation was substantiated by tests made with a cooler air/coal gas flame where no enhancement was observed in either emission or absorption.

Rare earth elements can be expected to ionise in the hot nitrous oxide/acetylene flame as their ionisation potentials are sufficiently low for this to occur (see Table VI). The addition of an excess of a readily ionisable salt, e.g. potassium chloride or caesium chloride, to various elements analysed by atomic absorption or emission techniques is known to improve the signal by reducing the degree of ionisation of that particular element.

Barnett (79) used an atomic absorption spectrophotometer for flame emission analysis and showed that detection limits for cerium were poor in the nitrous oxide/acetylene flame, but were improved substantially by the addition of an ionisation suppressor. Ooghe and Verbeck (80) used an organic media of 80% methanol and an ionisation suppressor, e.g. potassium chloride, to determine the optimum conditions and sensitivities for various lanthanoids including Ce, La, Pr and Nd in the nitrous oxide/acetylene flame by atomic absorption.

Experiments were carried out with cerium . To a 1000 $mg.dm^{-3}$ cerium solution excess potassium chloride solution were added to form 250, 500, 1000, 2000, 3000, 4000 and 5000 $mg.dm^{-3}$. The emission was read for each solution at 569.7nm and blank solutions of potassium chloride were also taken to obtain a true background reading. Graph 6 shows this effect for cerium. From this graph it can be concluded that cerium ionic species were present in the nitrous oxide/acetylene flame and, by suppression of these ions to reform atoms, an increase in the atomic emission signal was obtained. The equations relating to this effect are given below:

$$KCI \rightleftharpoons K^{+} + CI^{-}$$ (excess here) — almost completely ionised in nitrous oxide/acetylene flame

$$Ce \rightleftharpoons Ce^{+} + e$$ — partially ionised in nitrous oxide/acetylene flame

the excess of potassium ions pushes the cerium equilibrium to the left (atomic form)

When all the ions have been suppressed then further additions of potassium had no increased effect as shown from the plateau region obtained. The addition of 2000 $mg.dm^{-3}$ potassium to

1000 $mg.dm^{-3}$ Ce solution created the maximum effect. This effect can also be shown by scanning the cerium peak at 569.7nm, firstly without the presence of potassium and then repeated with added ionisation suppressor. The signal increase can be seen in Figure 4.

The use of sodium or caesium gave similar results, but the background from sodium was higher and so this element was not thought to be as suitable for general use where spectral interference over a wavelength range could occur. The emission wavelengths for potassium and caesium were at much higher wavelengths and so the possibility of high backgrounds is reduced.

A calibration curve for cerium was then constructed. For cerium solutions 10 $\longrightarrow$ 100 $mg.dm^{-3}$ containing 2000 $mg.dm^{-3}$ potassium a straight line graph was obtained (see Graph 7). Without the addition of potassium a gentle curve was noted showing that the effect of ionisation was more pronounced at low levels. This curve away from the concentration axis is very characteristic of ionisation effects and the tendency towards the straight line at high $mg.dm^{-3}$ levels is explained by self suppression of cerium; cerium here can act as its own ionisation suppressor, whereas at low levels this effect cannot occur due to the small population of ions. The addition of potassium successfully reduced the ionisation effect and so a straight line calibration was produced. A similar effect was noted for the other elements La, Nd and Pr at the atomic lines for these elements.

3.5 Organic Enhancement Effect

Several workers have used an organic solution rather than an aqueous media to increase the sensitivity of various elements analysed by atomic absorption or emission. The efficiency of atomisation of a liquid is dependent on the characteristics of the atomiser and also on the physical properties of the solution, e.g. viscosity, surface tension and saturated vapour pressure. A change in solute concentration, or the use of an alternative solvent, could influence the physical properties of a solution sufficiently to cause a change in the rate of atomisation which, in turn, will alter the recorded absorption or emission signal. It is generally found that when a miscible organic solvent is present in an aqueous solution, an increase in absorption or emission is observed for a fixed concentration of the particular element.

GRAPH 6

Ionisation suppression effect by potassium on cerium at 569.7nm

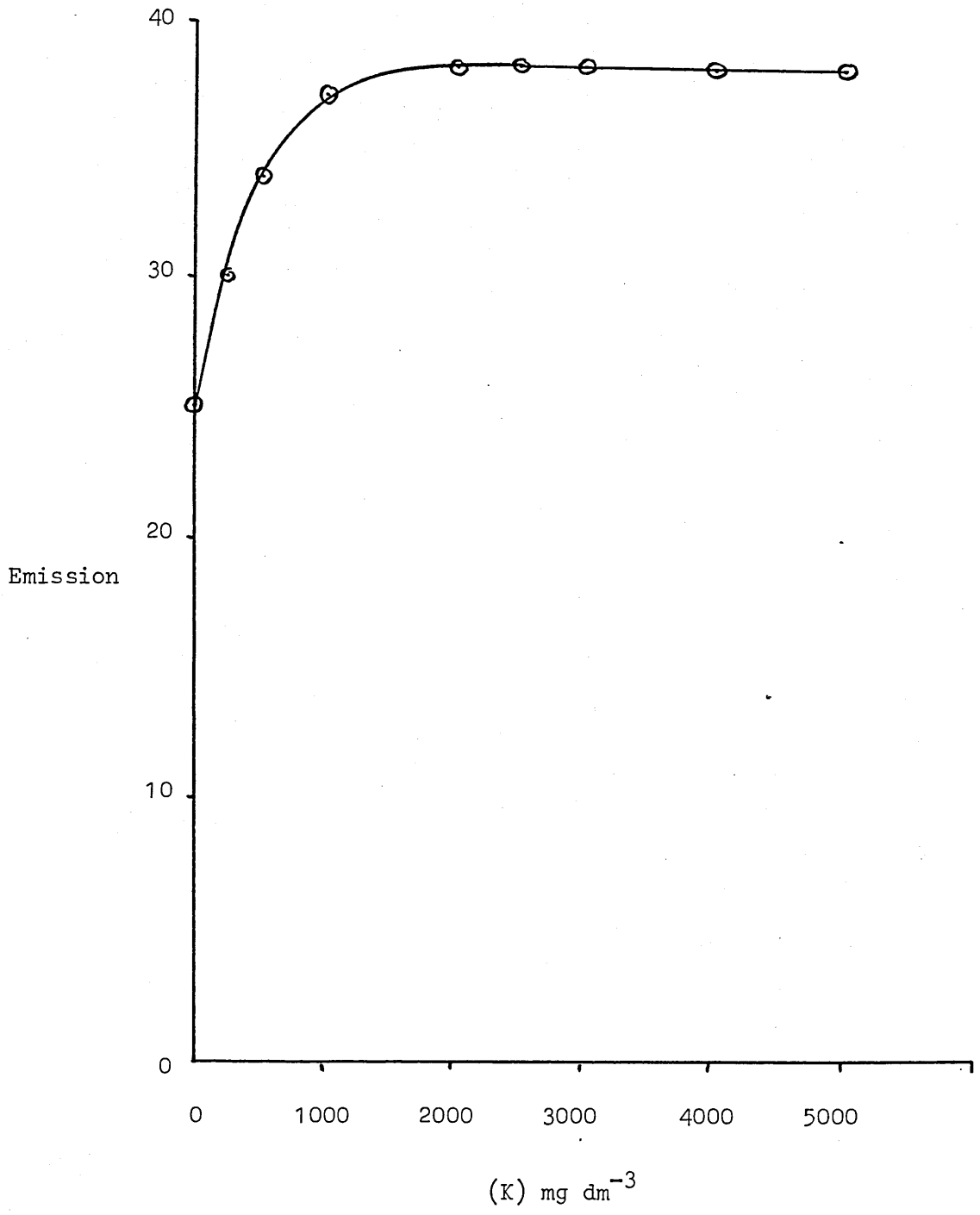
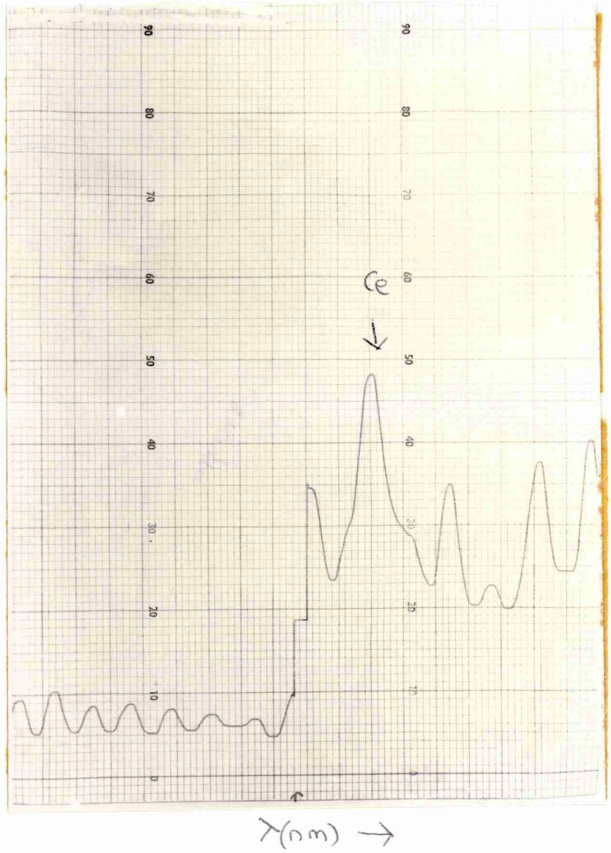
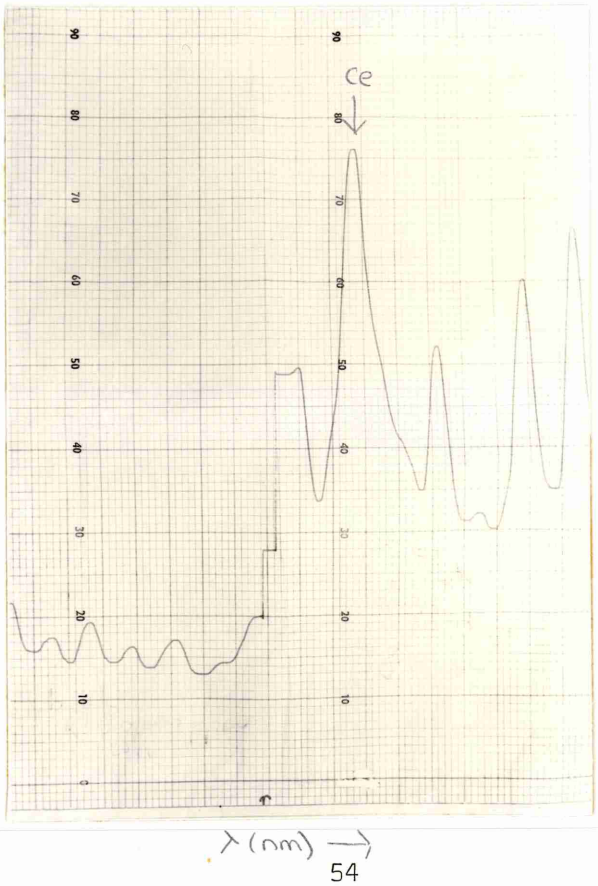


Figure 4 Ionisation Effect of Potassium at the Cerium Wavelength 569.7 nm



1) emission signal for 500mg.dm^{-3} Ce in a highly reducing N_2O/C_2H_2 flame



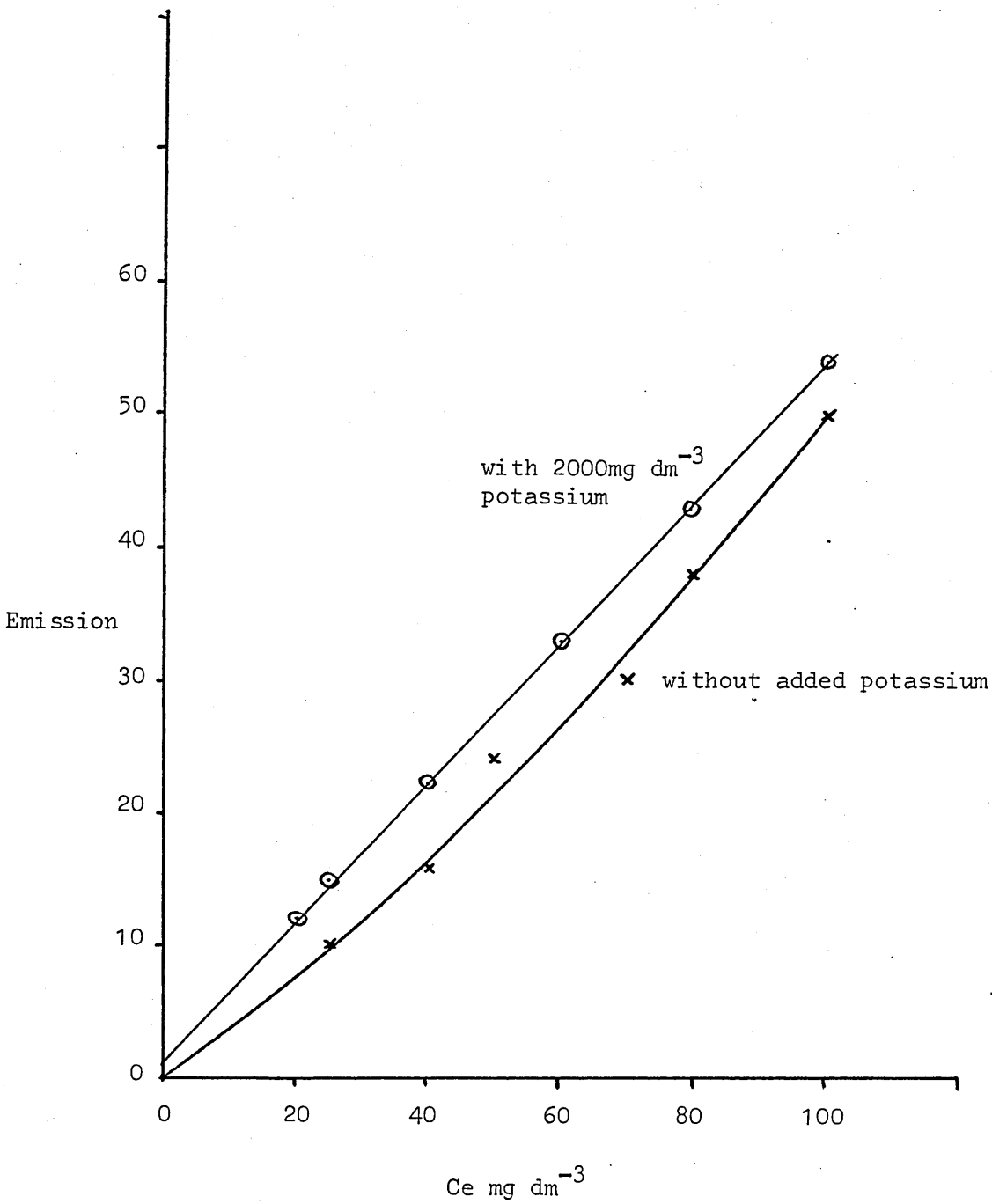
2) emission signal for 500mg.dm^{-3} Ce plus 500mg.dm^{-3} potassium in the same highly reducing N_2O/C_2H_2 flame

GRAPH 7

Calibration curves for cerium in water -

(a) without ionisation suppressor

(b) with ionisation suppressor



Experiments indicated that the main cause of this increase is due to the increase in the rate of production of fine spray (81). The nebuliser efficiency of aqueous solutions is normally less than 10% with most of the solution being lost within the nebuliser chamber. The additions of organics to the system increases the nebuliser efficiency mainly because of the greater volatility of the organic solvent. In analytical procedures a method of concentrating an element may involve an organic solvent extraction step and so advantage can be taken of this means of improving nebulisation efficiency if the organic phase can be sprayed directly into the flame. In this way the two factors of element concentration and atomiser efficiency improve the detection limit attainable. Christian (82) compared the absorption and emission methods for several rare earth elements La, Pr, Sm, Tb, Yb, Nd and Tm. He showed that, by using an organic media of 80% acetone, emission measurements of these elements in the nitrous oxide/acetylene flame offered improved sensitivity over atomic absorption measurements. Ooghe and Verbeck (80) used an organic media of 80% methanol to determine the best conditions and sensitivities of various rare earths including Ce, La, Pr and Nd, by atomic absorption.

Various organic media were investigated with the cerium. Solutions of 100 $mg.dm^{-3}$ Ce in 25, 50, 75% acetone, methanol and propanol, were made up and the emission intensities read at 569.7nm. Potassium was also added to act as an ionisation suppressor. Increased emission was observed in all cases compared to an aqueous media but a noisy signal was obtained in all cases and, even with maximum damping, very unsteady signals remained. It was known that increased background emission usually accompanies such hydrocarbon solvents but scanning over a wavelength range did not provide conditions which avoided the problem of noise. Reduction of the fuel flow rate (acetylene flow rate) in the presence of the organic solution helped to reduce the background emission but this created practical complications as this flow rate varied from one organic solvent to another and care had to be taken to ensure that no blow-back resulted in the burner by reducing

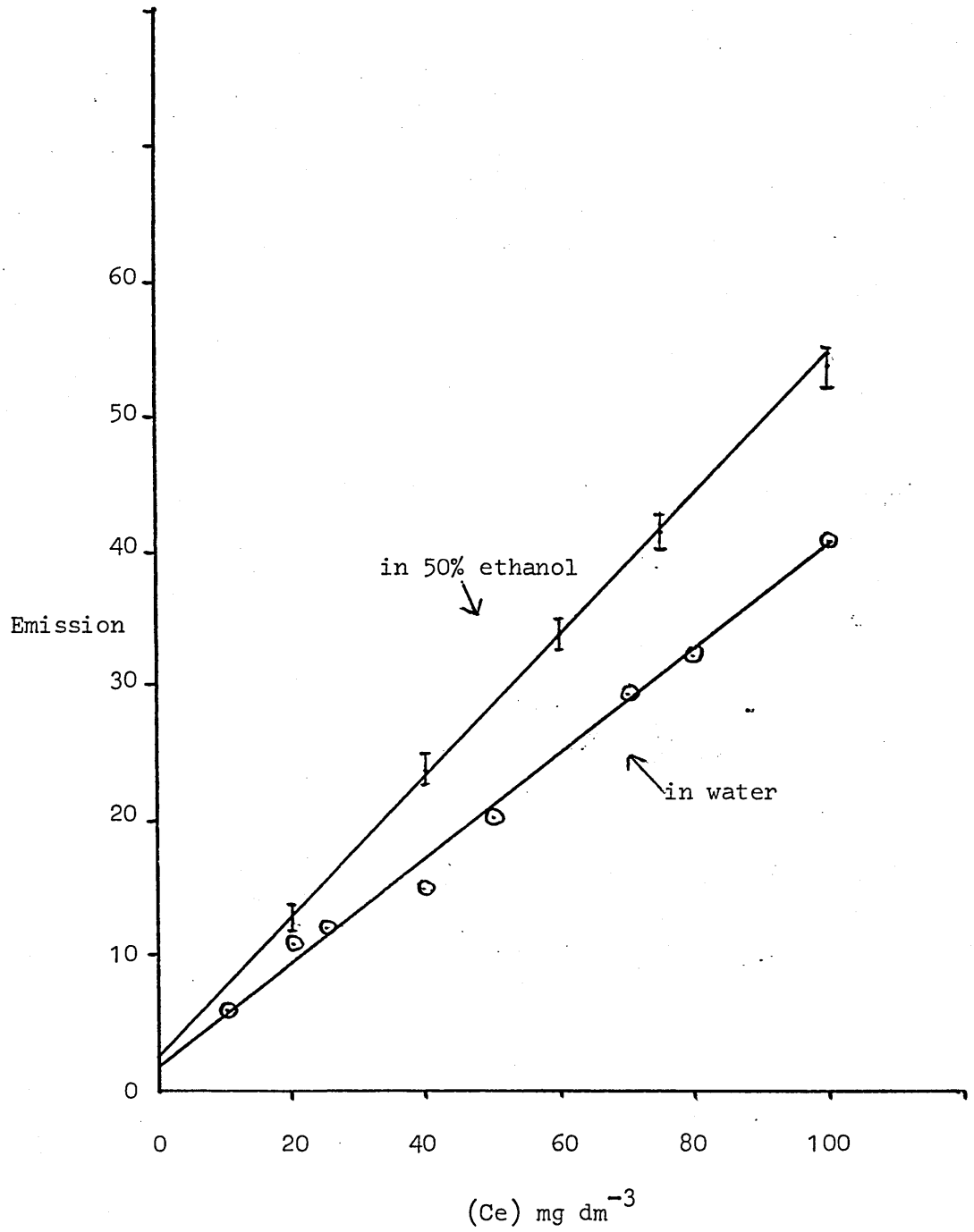
the acetylene flow below the stoichiometric value for the nitrous oxide/acetylene flame while the organic solvent was present in the flame. Cerium was also extracted into tributyl phosphate (T.B.P.) and 4-methyl pentan-2-one (M.I.B.K.) under specific conditions (used typically for concentrating rare earths by a solvent extraction technique). Increased sensitivity was obtained but at the expense of difficult operation conditions and resulting in very noisy signals which were slightly improved by scanning across the wavelength. Graph 8 shows the effect of a 50% ethanol solution compared to an aqueous media for 100 $mg.dm^{-3}$ Ce solutions at 569.7nm. It was considered, at this stage in the research work, more useful to continue working in purely aqueous solutions of the lanthanoids due to the difficulty in the operating conditions when using organic solvents. The use of organics, however, to possibly improve detection limits, was not ruled out in any further research work.

In conclusion, the detection limits of the four rare earth elements Ce, La, Nd and Pr were determined in aqueous media in the presence of an ionisation suppressor and using the flame conditions and instrument parameters found to be optimum. The limit of detection is defined as the minimum concentration or amount of an element which can be detected with a 95% certainty assuming a normal distribution of errors. This is that quantity of the element which gives a reading equal to twice the standard deviation of a series of at least ten determinations at or near the blank level (a 2σ result). The term, detection limit, is considered the most useful for comparing various elements. The detection limit is dependent, not only on sensitivity (useful only for comparing relative performances of differing equipment) but also on other factors that affect the stability of the optical signal, e.g. light intensity fluctuations or photomultiplier noise.

5 $mg.dm^{-3}$ La, Nd and Pr and 10 $mg.dm^{-3}$ Ce stock solutions were used to determine the detection units. At each respective wavelength a blank reading (using a 1000 $mg.dm^{-3}$ K solution) was taken followed by a sample reading. This was repeated twenty times using the three second integrate mode. From the results

GRAPH 8

Comparison of emission signal for cerium at 569.7nm in aqueous media and organic media



obtained the standard deviation was calculated and subsequently the detection limit based on a 2σ result determined.

The Table below shows the detection limits obtained for Ce, La, Nd and Pr, under the optimum instrument conditions.

DETECTION LIMITS

ELEMENT	WAVELENGTH (nm)	2σ l.o.d.* $mg.dm^{-3}$
Ce	468.4 mu 569.9 a	2.5 1.2
La	579.1 a 593.0 au	0.2 0.9
Nd	660.6 mu	0.8
Pr	493.9 au	1.0

* = with ionization suppressor

a = atomic line

m = molecular band

u = currently in use

Instrument conditions:- slit width -.2nm
flame N_2O/C_2H_2 reducing
observation height - in primary reaction zone

CHAPTER IV

INVESTIGATION OF THE POSSIBLE INTERFERENCE EFFECTS IN STEEL ANALYSIS

4.1 The Source of Possible Errors in Flame Emission Spectroscopy

Attention was next directed to the investigation and determination of lanthanoids in a steel matrix with emphasis on the possible interference effects at the rare earth emission wavelengths in the nitrous oxide/acetylene flame. The sources of possible inaccuracy can be broadly divided into the following sections:-

(a) instrumental errors

(b) spectral or radiation interferences

(c) ionisation interferences

(d) chemical interferences.

Instrumental errors are derived from physical characteristics, flame characteristics or instrument design. A variation in the aspiration flow can affect the atomisation efficiency which creates a physical interference. An example of this is when organic solvents are used in place of a matching aqueous media (see Chapter III) resulting in increased atomisation efficiency and subsequent enhancement of the emission signal. The flame temperature must be kept constant for emission spectroscopy as the number of excited atoms is proportional exponentially to temperature. The effect of reduced gas pressure can alter the gas flow rates and a temperature variation may occur so it is important to maintain accurate control of the flame. Instrument design interferences include detector and wavelength drift. Detector drift can occur from the photomultiplier tubes with time and so the emission radiation reacting the detector may vary. Wavelength drift occurs when the optical path length changes fractionally with thermal expansion of the instrument if there is insufficient insulation from the flame. This is important in atomic emission spectroscopy. The use of a ratio method, involving spraying a strong stock solution periodically into the flame along-side the actual samples, is applied to this problem.

Spectral, or radiation, interferences are also important in emission spectroscopy where line emission and band emission can overlap from the same or different elements. A line source is used in atomic absorption spectroscopy and so this type of interference is usually negligible. In emission work all the lines must be separated in the band pass of the monochromator. The use of a good monochromator with narrow band pass can minimise spectral interference. Examples of lines which can cause spectral problems are potassium at 404.414nm and manganese at 404.076nm. A mixture of these elements could create obvious problems in flame emission analysis. The problem of a band being confused with a line is an important factor; the chromium line at 425.4nm and calcium at 422.7nm could be difficult to separate from the hydroxide band at 425nm. The problem of severe spectral interference is usually solved by moving to another wavelength free from the specific interference but if this is not possible for molecular emission problems background readings are taken along with sample emission readings, as determined from a short wavelength scan over the region of interest. An average background reading is then taken from the average signal reading. This method was used, where necessary, when taking emission readings for the lanthanoids. Since the rare earths all exhibit complex spectra rather than characteristic lines, the possibility of mutual spectra interference is high as one lanthanoid line or band may easily overlap that of another element. The elements typically found in steel, e.g. Fe, Cr, Mn, Ni, Mo, Co, and V, may also have intense lines or bands within the same wavelength range as the lanthanoid group so spectral interference from these elements may occur, particularly when considering the relative amounts of these elements compared to the low rare earth percent within the steel matrix.

Ionisation interferences can occur in atomic absorption or atomic emission spectroscopy and this had already been observed with the lanthanoids in the nitrous oxide/acetylene flame (see Chapter III). The use of potassium or caesium was used to act as an ionisation suppressor and was found to create an enhancement effect for the rare earth elements of interest Ce, La, Nd and Pr.

Ionisation interference should never result in error, however, as its effect can always be corrected.

Chemical interference is an important type of interference in atomic absorption and atomic emission spectroscopy. It usually involves the formation of refractory compounds which are less easily dissociated and can be termed as condensed phase or solute vaporisation interferences. Examples of known chemical interferences include the effect of phosphate on calcium, strontium and barium emission intensities. Yofe et al (83) showed that calcium, strontium and barium orthophosphates were converted to pyrophosphates at 1000°C and were only partially decomposed in the air/acetylene flame. An addition of lanthanum produced less soluble lanthanum phosphate and this released the elements calcium, strontium and barium from this refractory compound formation creating an enhancement effect. In this case lanthanum acts as a releasing agent. Baker and Garton (84) noted a suppression of the calcium signal due to calcium phosphate in the air/acetylene flame. This suppression was found to be reduced by dilution of sample, more efficient atomisation, or more favourable position in the flame. In fact by changing the air/acetylene flame to the nitrous oxide/acetylene flame the hotter temperature is enough to break down the calcium phosphate bonding to produce free calcium atoms and so an enhancement in the flame is obtained.

4.2 Dissolution Methods for Steels Containing Lanthanoid Elements

The possibility of chemical or spectral interference from the solution matrix of steels containing rare earth elements had to be considered and investigated. Additionally the effect of any reagents, e.g. acids, alkalis or salts used in the steel dissolution procedures had to be noted.

The first experiments under this section were to investigate the most suitable dissolution procedure for steel samples containing rare earth mixtures (or mischmetal) additions. Lanthanoids are currently added to mild or low alloy steels to produce specialised steels and so dissolution methods were considered with a view to low alloy and steels (with small amounts of added carbon or silicon) rather than high alloy type steels which would require different and more difficult analytical procedures to produce complete dissolution.

Two methods were investigated:

(a) to create complete dissolution of the steel including the elements silicon and carbon etc.

(b) to quickly dissolve most of the steel with the exception of silicon or carbon, if present.

The two methods used are outlined below.

Method I

Weight out 1g steel into a P.T.F.E. beaker, add $15cm^3$ HF (40%), $5cm^3$ conc. HNO_3 and $20cm^3$ conc. $HClO_4$ (60%). Fume with the lid on until white fumes of $HClO_4$ are evolved and then continue to fume for five minutes, cool, dilute with H_2O ($25-30cm^3$) and make up to volume.

Method II

Weigh out 1g steel into $400cm^3$ glass beaker, add $30cm^3$ 1:1 HCl, $5-10cm^3$ conc. HNO_3, fume slowly to digest steel until all the NO_2 is evolved and then fume down to near dryness slowly. Redissolve in $10cm^3$ conc. HCl to give deep orange solution and make up to volume ($100cm^3$) with c.a. $2000mg\ dm^{-3}$ potassium solution.

Method I requires more time and care but complete dissolution of mild or low alloy steels is achieved. The addition of caesium or porassium as an ionisation suppressor is impossible due to the formation of a potassium chlorate precipitate forming. Also the presence of perchloric acid may be undesirable if subsequent organic addition, e.g. a solvent extraction procedure, is required. The use of hydrofluoric and perchloric acid requires careful handling for maximum safety. Method II is easy to perform, safe, and readily suitable for potassium addition and/or organic addition or solvent extraction. In some cases silicon or carbon present in the steel sample, however, remained undissolved and so the possibility of co-precipitation or occlusion of the rare earth elements must be checked. Several steels given in the Table below were dissolved by both of the above methods.

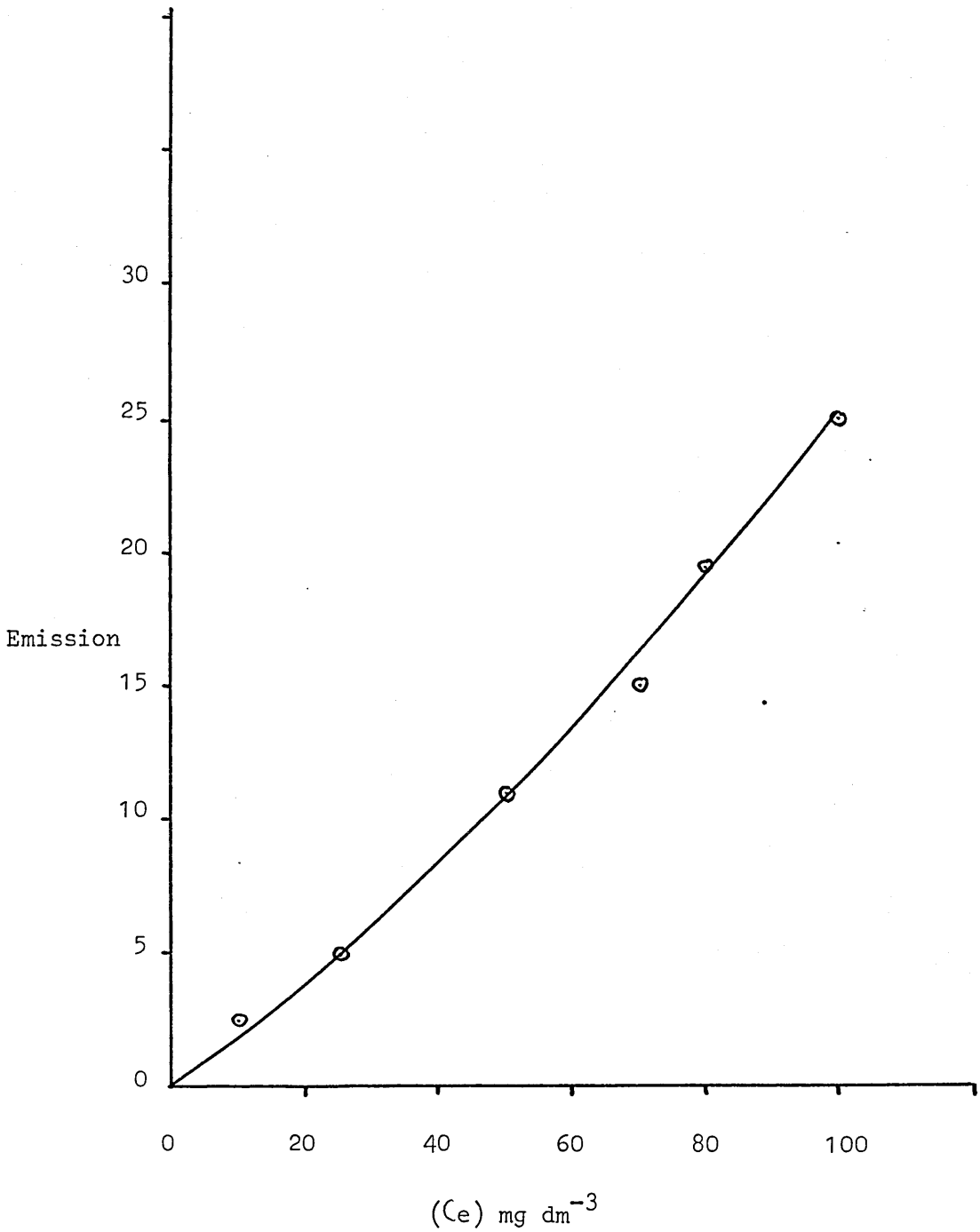
Table XI

Steel	Type	Lanthanoid additions
B.C.S. 329	Mild	doped with 0.2% Ce
B.C.S. 402	Low alloy	" " 0.1% Ce
B.C.S. 404	Low alloy	" " 0.15% Ce
Spec. pure iron	-	" " 0.122% Ce
Special Steel DI/I348	Low alloy	1.39% Ce

Using spec. pure iron as a synthetic steel and adding aliquots of cerium to the sample before the dissolution method, a range of steels made up to $100cm^3$ were made containing $20 \longrightarrow 100mg\ dm^{-3}$ Ce. These were used for calibration purposes. A mild steel B.C.S. 329 was also used in the same way, and blank solutions (without cerium) were also made by the same methods. Calibration graphs of emission signals for cerium at 569.7nm against cerium concentration, were drawn (see graphs 9 and 10). The calibration graph for cerium in steel by Method I was a slight curve; this was probably due to the ionisation of cerium in the flame as no potassium or caesium could be added in this method. The calibration graph by Method 2 was a good straight line. In both cases the blank sample gave a high background signal which had to be subtracted from all readings. This implied the presence of spectral interference at this wavelength. Other steel samples e.g. B.C.S. 402 and B.C.S. 404, were read for emission and the percentage of cerium calculated with the aid of graph 10 using Method 2 dissolution. The calculated result agreed with the known value for cerium showing that no cerium was lost in Method 2 by co-precipitation or occlusion to any element left undissolved. The other lanthanoid elements La, Nd and Pr were similarly investigated and Method 2 found to be a satisfactory procedure. It was concluded that a dissolution procedure for the steels containing lanthanoid additions, based on Method 2, would be entirely satisfactory for subsequent analysis being a quick, easy and safe method and readily suitable for ionisation suppression additions, e.g. potassium and solvent extraction. It was realised that for the low levels of Ce, La, Nd and Pr, expected in steels a concentration and/or a separation technique such as solvent extraction would be necessary to obtain

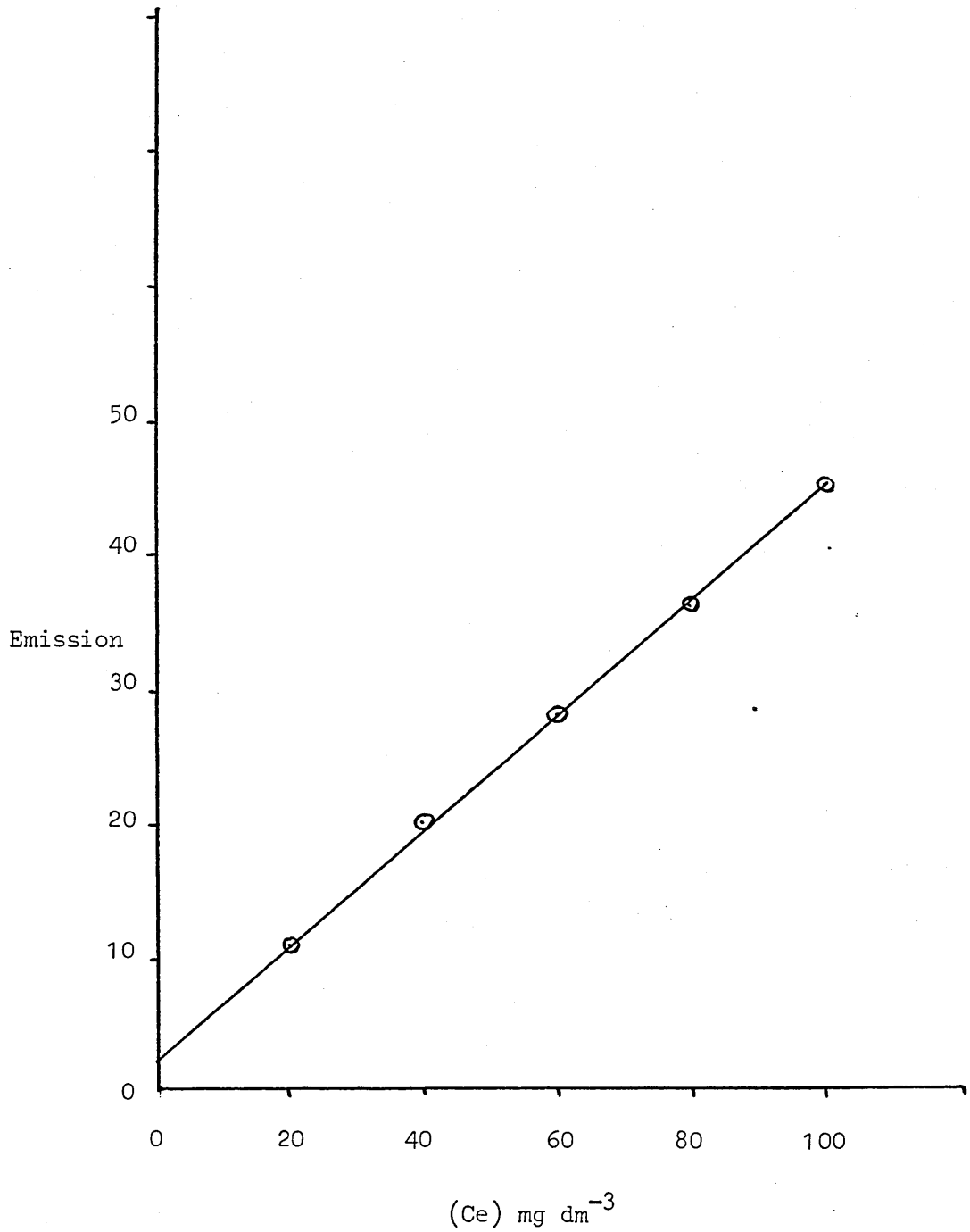
GRAPH 9

Calibration curve for cerium in steel (Method I)



GRAPH 10

Calibration curve for cerium in steel (Method 2)



suitable strength solutions to be easily detected at each rare earth wavelength.

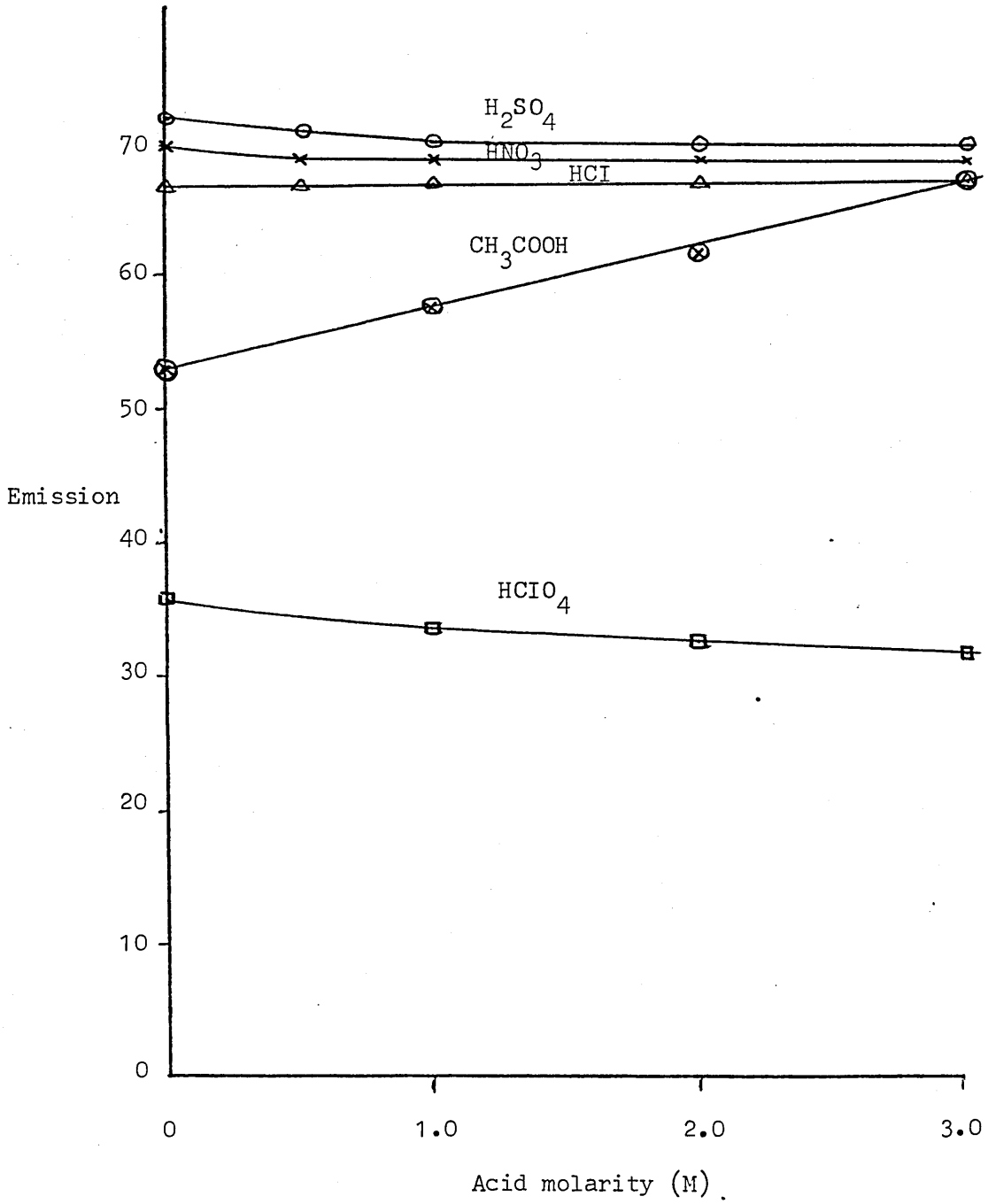
4.3 Investigation of Chemical and Spectral Interferences

The aspect of chemical interference was then considered. From a knowledge of the basic inorganic chemistry of the lanthanoid group of elements, possible chemical compound formation could be predicted. The effect of typical acids and radicals used in the dissolution procedure, or of possible future interest, were investigated in case any spurious effects were discovered. The acids hydrochloric, nitric and sulphuric (up to 3M concentration) did not affect the emission signal of any of the four lanthanoids of interest. Perchloric acid gave a slight decrease in signal, while phosphoric acid rendered a white precipitate and hence no signal. Acetic acid increased the emission signal for all the rare earths in question. This was possibly due to the increased organic nature of the sample and follows the enhancement observed with ethanol rather than any chemical interference. The ions - bromide, iodide, ammonium, carbonate, sulphite - gave no interference but fluoride/hydroxide and the oxalate ion gave precipitates and hence no signal again. Fluoride, hydroxide and oxalate precipitates are commonly used for the gravimetric separation of the rare earths from rocks and minerals etc. A graph of emission signal against acid concentration is given (see Graph 11) for cerium, showing some of these effects. In general, where solutions were formed, no chemical interference effects in the flame were noted from the above reagents and the results were in agreement with expected known data.

The blank readings obtained from steel solutions (without rare earth additions) were found to be high at all rare earth wavelengths. The difference in the blank readings compared to steel solutions doped with rare earths, were consistent with the increasing rare earth additions, giving good straight line calibrations. This indicated initially that no chemical interference was present but rather a simple spectral interference as different steels gave different background reading, e.g. B.C.S. 329 reading was much lower than B.S.C. 404 blank reading. The interference effect of each typical element found in steel was then investigated to obtain a more comprehensive picture.

GRAPH 11

Effect of acids on cerium emission signal at 569.7nm



The elements commonly found in mild or low alloy, or specialised (rare earth added) steels are listed below:

Element	% Range
Ni	0.02 - 4.60
Mn	0.15 - 2.00
Cr	0.04 - 3.00
Cu	0.02 - 0.70
Co	0.006 - 0.17
Pb	0.003 - 0.05
Sn	0.003 - 0.06
Al	0.02 - 0.09
W	0.05 - 0.17
V	0.004 - 0.50
Mo	0.02 - 1.20
Ce, La, Nd, Pr	mixtures of 0.001 - 1.0%

The total percentage of rare earths is considerably lower than any of the other typical alloy elements and so it can be seen that any relative spectral interference effect will be amplified under the necessary operating conditions for flame emission in the nitrous oxide/acetylene flame for the lanthanoid group of elements. The mutual spectral interference of the rare earth elements was investigated also. Interference within the lanthanoid group was expected as all the elements have complex spectra with their most sensitive lines or bands in the same broad wave-length region and so suitable selection of wave-length must be a compromise between sensitivity and mutual rare earth interference when considering analysis of rare earth mixtures. The lines and bands of useful sensitivity for the lanthanoids Ce, La, Nd and Pr are listed in Table XII. The mutual spectral interference of one lanthanoid on another was then investigated and the percentage enhancement at 100mg.dm^{-3} level from 100mg.dm^{-3} of the other rare earths, were recorded and listed in Table XIII. This showed that severe mutual rare

TABLE XII

Analytical Wavelengths	
Element	Wavelength (nm)
Ce	468.4 a
La	593.0 b
Nd	660.6 a
Pr	493.9, 576.3 b

a denotes molecular band

b denotes atomic line

TABLE XIII

MUTUAL SPECTRAL INTERFERENCE OF RARE EARTH ELEMENTS

	% Enhancement at 100 $mg.dm^{-3}$ level from 100 $mg.dm^{-3}$			
Interferent	La 593.0 nm	Ce 468.4 nm	Nd 660.6 nm	Pr 493.9 nm
La	-	n.s.	n.s.	n.s.
Ce	11	-	5	100
Nd	35	61	-	117
Pr	46	47	26	-

TABLE XIV

SPECTRAL INTERFERENCE-EFFECTS OF TYPICAL ALLOYING ELEMENTS AT RARE EARTH ELEMENT WAVELENGTHS

	% ENHANCEMENT OBSERVED FROM 10 FOLD EXCESS AT 100 $mg.dm^{-3}$ LEVEL			
ELEMENT	La 593.0 nm	Ce 468.4 nm	Nd 660.6 nm	Pr 493.9 nm
Cr	91	58	11	216
Mn	n.s.	n.s.	n.s.	n.s.
Ni	n.s.	n.s.	n.s.	n.s.
Fe	109	n.s.	n.s.	n.s.
Cu	n.s.	n.s.	n.s.	n.s.
Pb	n.s.	n.s.	n.s.	n.s.
Mo	26	145	10	166
W	26	50	11	84
Co	n.s.	n.s.	n.s.	50
Ag	22	n.s.	n.s.	42
Bi	n.s.	n.s.	n.s.	n.s.
V	130	52	155	166

earth interference occurred at many of the sensitive wavelengths and so a choice of suitable wavelengths for these rare earth elements had to be made with a view to minimum spectral interference but sufficient sensitivity. There was evidence of chemical interference within the rare earth group. The analytical wavelengths selected on this basis are given in Table XII and the mutual rare earth interferences of the rare earth elements at these wavelengths are given in Table XIII. Lanthanum is notable in that it does not interfere, spectrally, at any of the other rare earth wavelengths. This element is first in the lanthanoid group, and so has a slightly less complex spectra by having no 4f electrons in its electronic arrangement resulting in less available transitions.

The spectral interference effects of typical alloying elements at rare earth element wavelengths, was then investigated. A ten-fold excess of added alloying element to 100mg dm^{-3} lanthanoid was used and the emission signal read, compared to the blank at the selected analytical lanthanoid wavelengths. The results are listed in Table XIV. Chromium gave large spectral interference at all wavelengths and posed a serious problem for future analysis. Chromium is present in very significant quantities, compared to the small rare earth percentage, in most metal and low alloy steels and would have to be removed from the steel matrix to prevent interference when analysing lanthanoid elements. Vanadium, Molybdenum and tungsten, also strongly interfered at all lanthanoid wavelengths and so, if present in the steel sample, would create problems in the analysis of rare earths. At the listed sensitive wavelengths in Table XIV other elements also strongly interfered and chromium continued to show spectral interference at almost all of these other wavelengths.

In conclusion, it was noted that elements in the steel matrix gave rise to significant spectral interference at the rare earth wavelengths. It was considered necessary, therefore, to seek a method to isolate the rare earth elements efficiently from the steel matrix prior to an emission measurement in the nitrous oxide/acetylene flame. The possibility of either separating each individual rare earth element from each other or correcting for the mutual rare earth interference was researched in detail.

CHAPTER V

DEVELOPMENT OF A METHOD TO DETERMINE TRACE RARE EARTH ELEMENTS IN STEEL

5.1 Comparison of Available Methods

The development of a method to determine the rare earth elements Ce, La, Nd and Pr in steel at trace level was planned with consideration for three main factors. Firstly, given the severe nature of some of the spectral interferences in mild or low alloy steel samples (see Chapter IV), it was deemed necessary to separate the lanthanoids from certain elements, e.g. iron, chromium and vanadium. Secondly, the detection limits obtained (see Chapter III), indicated that concentration of the sample, with respect to the rare earth content, was required before aspiration into the flame. Finally, the extent of mutual rare earth interference at the selected analytical wavelengths was significant. A requirement, therefore, for individual rare earth separation could prove necessary if ideas, based on correction factors for mutual rare earth interference, gave poor results. Three main methods for the separation of lanthanoid elements, based on precipitation, ion exchange and solvent extraction, were considered.

Gravimetric procedures for the rare earths usually involve the formation of fluoride, hydroxide or oxalate precipitates (10). The oxalate precipitate is generally preferred as being more specific and usually the rare earth is converted and weighed as the oxide, e.g. CeO_2.

Ion exchange separation procedures for the lanthanoids involve both cation and anion exchange techniques (84).

The mutual separation of the lanthanoids is usually based on cation exchange procedures. This method is based upon the steady decrease in size with atomic number and the corresponding increase in binding energy of ligands. Exchange resins in the form NH_4^+ or H^+ are commonly used but other mixtures of ions, e.g. Ni^{2+} and VO^{2+} can increase the efficiency of separation by an ionic barrier effect. The presence of organic complexing agents is necessary, e.g. EDTA, HDEHP, TBP or TOPO, since the affinity of the various

lanthanoids for the resin are very similar. Cation exchange, however, cannot be very successfully applied to the separation of the rare earths from a steel media due to the interference from the other elements in the steel matrix. Stepwise separation procedures then need to be applied which produces a tedious and time-consuming method.

Anion exchange has been shown to possess greater selectivity for the separation of the lanthanoids, particularly cerium, from steels (31, 32, 35). Strongly basic anion exchangers (usually in NO_3^- form) are used. Lanthanoids are not absorbed on strongly basic resins from nitric acid alone (except tervalent cerium) but the use of miscible organic solvents added to the liquid phase considerably increase the absorption of the rare earths by the formation of larger oxyanion molecules. Other elements present in steel, e.g. Mn, Ni, Al, Mo. etc. pass into the effluent and, therefore, are quantitatively separated. Elution by acid, e.g. hydrochloric acid, removes the desired rare earth ion. The experimental conditions of any rare earth ion exchange system are not simple and usually involve complex, precise mixtures of solvents and acids to produce a useful method.

Solvent extraction procedures can be basically subdivided into two main areas -

(a) ion association systems, and

(b) chelate systems.

An example of an ion association system is the use of a nitric acid media containing rare earths, e.g. solvent extraction of cerium IV with tributyl phosphate (TBP), diethyl ether or 4 methyl pent-2-one (MIBK) (85).

A chelate system could involve the use of 8-hydroxyl-2-methyl quinoline in carbon tetrachloride. This extracts cerium IV at pHIO in the presence of malic acid (20).

Solvent extraction systems are often dependent on critical pH conditions but generally are not so experimentally complex as ion exchange techniques for lanthanoid elements. A combination of these three main methods can be used to separate the rare earths, and particularly cerium, from steels.

An ideal procedure would have been the removal and concentration of trace quantities of rare earths from the bulk of the steel

sample in one single, quick and efficient step, e.g. by a highly selective solvent extraction system. An initial literature search, with this in mind, showed that no problem - free method to fit this ideal could be found. The possibility of the separation of cerium from the other lanthanoids was also researched utilising the differing chemical behaviour of this element. Cerium can exist in the Ce IV oxidation state, whereas La, Nd and Pr, can only react in the La III, Nd III or Pr III state and so the possibility of separation, based on an oxidation/reduction reaction was considered. Several methods were attempted to separate cerium from the steel media and these are described below, but none were completely successful as either the efficiency of extraction or the presence of contaminants undermined the usefulness of the extraction.

Khopkar and Anil (86) outlined a method for the determination of cerium IV using 2-thenoylfluoroacetone in benzene or xylene with 100% extraction being achieved at pH 5.4. Eremin, Raevskaya and Romanou (90) separated microamounts of cerium from steel media and from other rare earths present. The methods described above were attempted for determining cerium in mild or low alloy steels but were not found to be totally specific for cerium IV as the other rare earths La, Nd and Pr, were extracted to some extent. The use of benzene and 0.IM trifluoroacetone proved difficult; good separation was achieved for pH 1-3.5 but in the range pH 4-6 an emulsion formed due to the presence of other elements in the steel media interacting (separation was clear when a simple rare earth solution was used). The need to carry out the extraction from a nitrate media, rather than a chloride media, also proved troublesome in terms of dissolving the steels completely in nitric acid only. 0.IM trifluoroacetone in xylene gave good, clear separation over the pH range, but, as in the case of benzene an unacceptably high level of background emission was obtained in the flame.

The use of 0.IM trifluoroacetone in 4 methyl pentan-2-one gave fast separation and c a. 50% extraction efficiency was obtained for the rare earths, but interference from chromium was observed with up to 30% chromium being co-extracted. The idea of using a blank to compensate for this problem was considered unsuitable as the steel samples under analysis contain varying amounts of

chromium. The presence of iron in the sample inhibited the extraction of the rare earths using this system; with samples containing no iron greater than 80% efficiency of extraction was obtained.

Experiments with tributyl phosphate gave better results but were again not entirely satisfactory. Fast and clear separation of the rare earths from a steel solution was achieved and the efficiency of extraction was increased by saturating the tributyl phosphate with nitric acid prior to shaking the steel. Nickel, chromium and iron were co-extracted and, although the levels of these elements were reduced by a back extraction into 6N hydrochloric acid, they were not eliminated. In all these experiments the presence or absence of the elements of interest in solution were determined by accurate spot tests (88) and the extraction efficiencies were determined approximately in the aqueous layers by comparing the emission readings with synthetic standards using a nitrous oxide/acetylene flame. The necessity, however, to ensure an absolute minimum of interference from other elements, e.g. chromium and vanadium, due to their spectral interference at the lanthanoid wavelengths, made it necessary to seek an alternative method. A single step extraction was apparently not available for selective efficient extraction of the lanthanoids from steel and it was realised that a more detailed method must be envisaged.

An ion exchange system was then considered. It was known that the use of a basic anion exchange resin in the chloride or nitrate form could be used to separate the actinides and lanthanides from other elements (89 - 93).

Typically sorption occurs from hydrochloric or nitric acid in 70% - 90% methanol and elution is carried out with aqueous hydrochloric or nitric acid. Methods for determining cerium in steel by such a method have been outlined by Green (32), so experiments were carried out to evaluate the feasibility of employing this method of separation.

A method based on Green's paper was carried out using 1g and 2.5g steel samples to produce final rare earth solutions within the required detection limits for the nitrous oxide/acetylene flame. A doped steel sample was made by adding appropriate amounts of

1000mg dm^{-3} stock cerium solution to a B.C.S. 402 steel to produce a low alloy steel containing 0.1% cerium. Additionally, other steels containing mischmetal (obtained from the Bragg Laboratory, M.Q.A.D., Sheffield) were tested by this method. The steels were heated in sufficient nitric acid and dissolved in the methanol/acetic acid/nitric acid mixture, as outlined in Green's paper, making a total volume of one litre. Various experimental parameters were compared to create the most suitable conditions for efficient cerium separation;

(a) column lengths of 10, 20, 50 and 100cm were used

(b) Dowex - X10 resin (mesh sizes 100 - 200 and 50 - 100) were tested and

(c) the solution flow rate through the column was varied from 2 to $20cm^3min^{-1}$

A column length of 30cm, mesh size of 50 - 100 mesh and flow rate of $5cm^3min^{-1}$ were found to be optimum.

The method successfully separated most of the cerium and some of the other rare earths, but residual iron remained in the final solution and extensive washing of the column was required for a 2.5g sample to remove all of the chromium, manganese and nickel in the steel sample (spot tests were carried out periodically to test for the presence of all these elements). The volume of eluted solution, required to obtain all of the cerium present, was large c.a. $250cm^3$ and, therefore, this had to be carefully reduced by slow evaporation to about $25cm^3$ to concentrate the cerium to a useful level. This step was considered unacceptable, both analytically and in terms of the time required, for the development of a useful and practical laboratory method. The presence of other ions eluted from the Dowex resin, created a high emission background in the flame, and so a blank sample had to be run alongside the steel samples to compensate for this reading. The steels containing mischmetal produced final solutions which contained varying amounts of the other rare earths neodymium and praseodymium (detected from experimental readings in the nitrous oxide/acetylene flame), but lanthanum was detected only in much lower levels. This ion exchange method proved to be experimentally selective for cerium in steels, but practically, was a time-consuming method, taking one and a half days for a 2.5g steel sample. The problems of

column washing to ensure complete removal of iron and the necessity to concentrate the final solution, were disadvantages of this method. Results also showed that total separation of cerium from the other rare earths could not have been achieved by this method.

5.2 The Determination of the Rare Earths in Steel by a Hydroxide Precipitation Method

It was evident at this stage in the research that a single selective extraction step could not be found to separate the lanthanoids from the steel matrix. A method was then developed to solve the problems associated with the interference of the multi-element steel matrix. The iron content of a mild or low alloy steel is usually greater than 97%, whereas the total rare earth content may only be as high as 0.2% and so it was considered appropriate to remove the bulk of the iron, which could inhibit completion of a lanthanoid reaction from the steel sample prior to any selective rare earth separation. Additionally, the severe spectral interference problems associated with certain elements commonly found in steel, e.g. chromium and vanadium, made it necessary to seek a method to totally separate these elements from the lanthanoid group. A method was then devised using a step-wise procedure involving solvent extraction and precipitation techniques. The method is outlined on page 84.

The solvent extraction step to remove iron from the steel sample was developed using an ion-association system. The steel must be completely dissolved prior to any successive treatment to ensure that the total lanthanoid content was contained in the aqueous media. The solvent extraction techniques available, were, therefore, restricted to the media involved in creating such dissolution, e.g. an acidic environment of chloride, nitrate or sulphate. The steel dissolution method given in Chapter IV was used providing a chloride media for subsequent solvent extraction. Typical solvent extraction systems for this media include diethyl ether or M.I.B.K. for iron chloro-complex extraction (85), both being quick and efficient extractions commonly used in steel analysis. Both reagents were tested and diethyl ether selected, giving a slightly higher extraction efficiency (c.a. 98%) and rapid separation of the aqueous and

organic phase. The use of ether, however, in the laboratory, necessitated obvious safety precautions to ensure no fire risks were created by the volatile nature of this organic reagent. Experiments showed that 2 - 3 extractions of $100cm^3$ diethyl ether with $25cm^3$ steel solution removed almost all trace of iron (spot tests with potassium ferrocyanide were carried out to check for the presence of iron (III)). The next step was to separate the interfering elements, e.g. chromium and vanadium from the rare earth elements. Precipitation methods were investigated using the hydroxide, oxalate an and fluoride ions. Fluoride precipitates are generally difficult to redissolve but the oxalate and hydroxide ions were both found to give useful results. Using ammonium hydroxide, all the rare earths gave immediate white flocculent hydroxide precipitates at pH values greater than 7 at room temperature. Boiling for five minutes produced almost 100% precipitation (tested by spraying the residual solution into the nitrous oxide/acetylene flame to detect any remaining rare earth emission). The hydroxide precipitate could be easily redissolved in concentrated mineral acid. Oxalate precipitation was also very efficient but the rare earths varied in their reactivity. Lanthanum oxalate would form immediately at pH values greater than four, whereas cerium would only slowly precipitate increasing with pH increase. Neodymium and praseodymium formed oxalate precipitates at pH values above five or six. To produce efficient precipitation (e.g. 95%) the oxalate precipitate, in all cases, had to be developed by warming on a steam bath gently for about one hour, with boiling reducing the precipitation by about 10%. At this stage the hydroxide method was chosen, being quicker and of equal reactivity to all the lanthanoids. Considering the steel matrix, the rare earth separation could not be simply achieved by addition of ammonium hydroxide to the residual steel solution as other elements also reacted with the hydroxide ion, e.g. Cr^{3+} and VO^{2+}. These elements, however, did not precipitate in their oxidised states, e.g. Cr^{6+} and V^{5+} and so selective separation could be achieved from these elements by oxidation prior to precipitation.

The classical oxidation method for chromium and vanadium (94) involving the use of ammonium persulphate and silver nitrate catalyst, was compared with the simple use of perchloric acid to effect the oxidation. The classical persulphate method has been widely used and gives 100% oxidation but is a longer process as the conditions for oxidation require a sulphate media and so the steel solution had to be fumed with sulphuric acid to remove chloride ions from solution (the presence of chloride was tested by addition of silver nitrate, the presence of a white silver chloride precipitate indicated chloride to be present). The use of perchloric acid, however, was a single step process requiring boiling of the solution until the orange oxidised chromium state was observed. The perchloric method, though, may not have achieved total oxidation and so this had to be investigated as a small amount of reduced chromium or vanadium could have seriously affected the final reading in the nitrous oxide/acetylene flame (giving high results by spectral interference). Care had also to be taken with perchloric acid to ensure that no organic reagents, e.g. diethyl ether were in the solution which, when in concentrated form with perchloric acid, could lead to explosive results. The oxidation reactions which occur are given below, and it was shown that the Cr^{3+} and V^{2+} were successfully converted to the higher Cr^{6+} and V^{5+} states. The presence of Cr^{6+} was detected with diphenylcarbazide at pH7:

(a) <u>persulphate oxidation</u>

$$2Cr^{3+} + S_2O_8^{2-} + 7H_2O \longrightarrow Cr_2O_7^{2-} + 14H^+ + 2SO_4^{2-}$$

$$2VO^{2+} + S_2O_8^{2-} + 6H_2O \longrightarrow 2VO_4^{3-} + 12H^+ + 2SO_4^{2-}$$

$$2Mn^{2+} + 8H_2O + 5S_2O_8^{2-} \longrightarrow 2MnO_4^- + 16H^+ + 10SO_4^{2-}$$

(b) <u>perchloric oxidation</u>

$$3ClO_4^- + 8Cr^{3+} + 20H_2O \longrightarrow 3Cl^- + 40H^+ + 8CrO_4^{2-}$$

$$5ClO_4^- + 8Mn^{2+} + 12H_2O \longrightarrow 5Cl^- + 8MnO_4^- + 24H^+$$

$$ClO_4^- + 8VO^{2+} + 20H_2O \longrightarrow Cl^- + 8VO_4^{3-} + 40H^+$$

The oxidation of manganese by persulphate can be observed visually. As the reaction proceeds the steel solution turns purple indicating the presence of Mn^{7+}; this shows that the oxidation

reaction is proceeding correctly. The silver nitrate acts as a catalyst in this reaction.

Experiments showed that the perchloric acid method gave similar results to the persulphate method. As one of the objects of method development is to combine efficiency of reaction with speed of analysis, the perchloric acid scheme was used to cut down on the time required. This was important as the complexity of the extraction of the lanthanoids from steel was inevitably going to involve a rather detailed procedure.

After oxidation of the steel sample, the precipitation step was adopted using just sufficient concentrated ammonium hydroxide to produce the white rare earth precipitate and then adding $10cm^3$ ammonia in excess. The solution was carefully boiled, to avoid spitting, for five minutes, cooled and either filtered through a number 42 Whatmann type filter paper, or centrifuged at 2000 revs min^{-1} for five minutes to separate the precipitate from the supernatant liquid.

The centrifuge method proved to be the quicker way. The precipitate was washed three times with distilled water and then redissolved in a minimum of concentrated hydrochloric acid and made up to $10cm^3$ or $25cm^3$ (depending on the level of rare earth content) with sufficient caesium chloride to produce a solution containing 2000mg dm^{-3} caesium to act as an ionisation suppressor in the nitrous oxide/acetylene flame.

Practical errors in this method could occur from several steps in the procedure. The steel sample must initially be completely dissolved to ensure the lanthanoid content is in the aqueous layer. No error should have resulted from the solvent extraction step if sufficient extractions were carried out to ensure that, with each extraction, none of the aqueous layer was removed with the organic layer (the diethyl ether was previously saturated with 9M hydrochloric acid prior to use, to reduce any absorption effects in the organic layer. An error in the final emission reading would occur if incomplete oxidation of chromium or vanadium occurred. Any Cr^{3+} present would precipitate as the hydroxide and then be carried into the final solution and sprayed into the flame giving high results. Prolonged treatment with perchloric acid cut this factor down to a minimum. Incomplete

precipitation of the rare earth hydroxides could lead to an error and give lower results than expected but initial experiments to achieve maximum precipitation showed that the procedure given in the scheme should ensure almost 100% precipitation, but spillage by spitting or over-boiling had to be carefully avoided.

This method was then carried out with a range of steel samples (1g or 2g) including -

(a) B.C.S. 402 and 404 (low alloy steels) containing individual amounts of Ce, La, Nd and Pr (0 ⟶ 0.15%) to act as calibration standards.

(b) a selection of mild and low alloy steels B.C.S. 329, 402 and 404 doped with single lanthanoid and mixed lanthanoid additions (0 ⟶ 0.1%) and

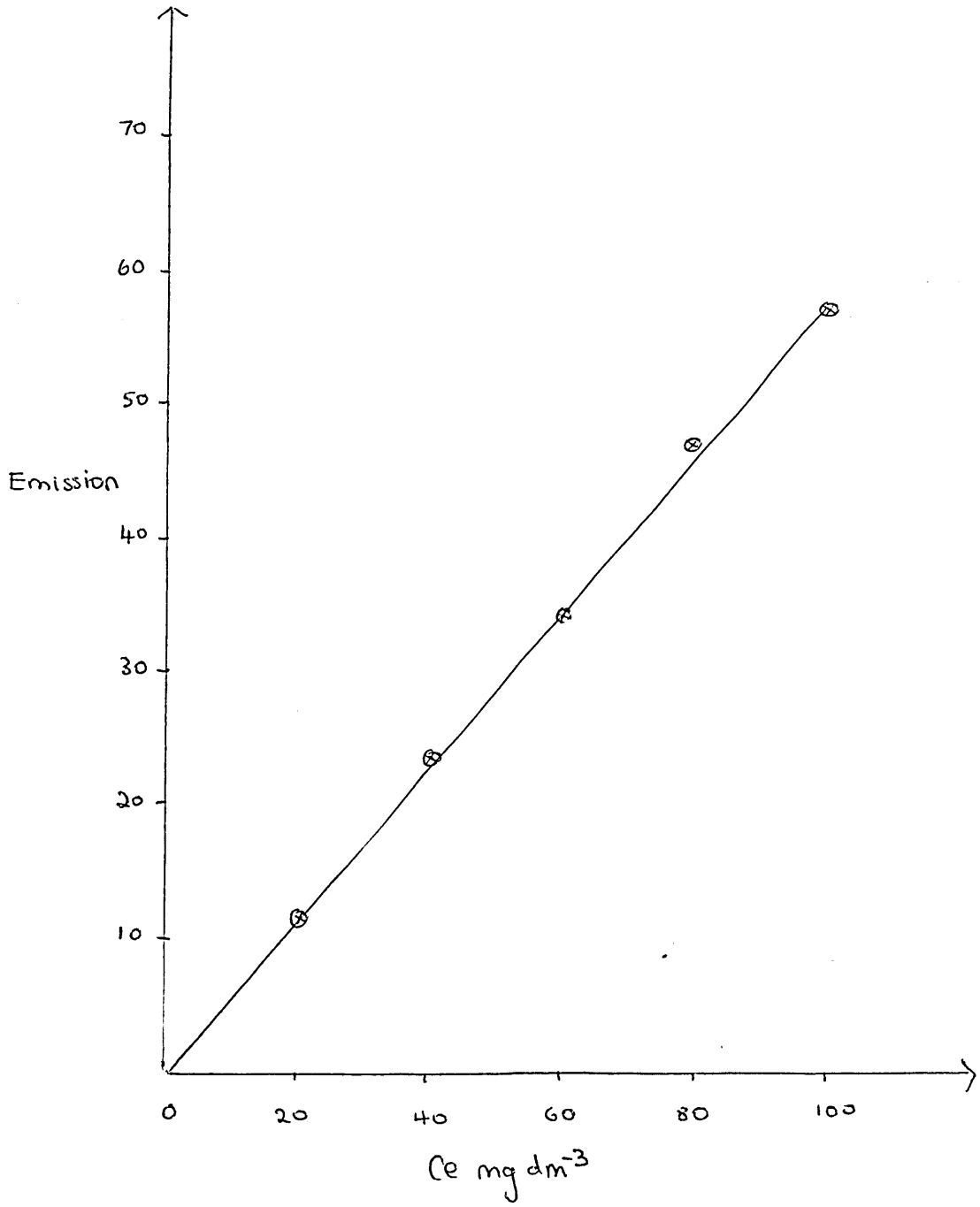
(c) steel samples containing 'mischmetal' additions (obtained from M.Q.A.D. Sheffield 0.047 ⟶ 0.122%)

Lanthanoid additions were made using the prepared stock solutions for each element. The standard steels B.C.S. 402 and 404 were chosen for calibration purposes as these steels resembled the steel samples containing mischmetal in their Cr, Mn, Ni and V content. The use of two, slightly different, standards was employed to check that the calibration line obtained was not affected by variations in the steel matrix.

This method was successful for steels containing single rare earth element additions, but high results, in some cases, were obtained for steels containing mischmetal. The calibration line for cerium is shown in Graph 13 giving a good straight line in the presence of an ionisation suppressor. Similar straight lines were obtained for La, Nd and Pr. Samples containing mischmetal and doped rare earth additions were then sprayed into the flame and emission readings taken at each lanthanoid wavelength. Care had to be taken with the mischmetal steel samples to ensure that four correct readings were taken for each rare earth element as a total volume of $25cm^3$ did not allow scope for more than one duplicate emission reading. The calibration graphs were then used to calculate the percentage of each lanthanoid element in these unknown steel samples. The results obtained are given in Tables, XV, XVI and XVII.

GRAPH XIII

Calibration curve for cerium at wavelength 468.4nm.



METHOD I

Determination of the rare earths Ce, La, Nd and Pr in mild or low alloy steels by solvent extraction and hydroxide precipitation

1/2g steel

↓ conc. HCl/HNO_3 (3:1) (Method I / Chapter II)

solution in 9M HCl

SOLVENT EXTRACTION STEP

↓ 9M HCl/diethyl ether 2 - 3 extractions

iron free solution

1) add $20cm^3$ conc. H_2SO_4 fume to remove chloride ions
2) make up to $200cm^3$ oxidise with $(NH_4)_2S_2O_8$ using silver nitrate catalyst

1) add $15cm^3$ 40% $HClO_4$ fume to orange solution of Cr^{6+}

↓

oxidised solution (Cr^{6+} V^{5+} Mn^{7+})

PRECIPITATION STEP

↓ addition of conc. NH_3 to precipitate the rare earths as hydroxides. Boil for five minutes.

$Ln(OH)_3$

rare earth hydroxide precipitate

↓ filter, wash and redissolve in a minimum conc. HCl, make up to volume with caesium solution to give 2000 $mg.dm^{-3}$ Cs. solution

$25cm^3$ solution

take emission readings in N_2O/C_2H_2 flame at each wavelength

Ce	La	Nd	Pr
468.4nm	593.0nm	660.6nm	493.9nm

TABLE XV

The Determination of the Rare Earths Ce, La, Nd and Pr in Low and Mild Alloy Steels by Method 1

Results for single lanthanoid additions

Identification	% Ln added	% Ln found
	1) % Ce added	1) % Ce found
A BCS 402	0.040	0.040
B BCS 402	0.100	0.098
C BCS 402	0.060	0.049
D BCS 404	0.050	0.050
E BCS 404	0.080	0.075
F BCS 404	0.020	0.018
G BCS 329	0.100	0.100
H BCS 329	0.050	0.045
	2) % La added	2) % La found
A BCS 402	0.100	0.096
B BCS 402	0.080	0.081
C BCS 402	0.050	0.046
D BCS 404	0.080	0.068
E BCS 404	0.060	0.056
F BCS 404	0.040	0.040
G BCS 329	0.050	0.042
H BCS 329	0.020	0.016
	3) % Nd added	3) % Nd found
A BCS 402	0.060	0.060
B BCS 402	0.050	0.052
C BCS 402	0.040	0.038
D BCS 404	0.080	0.076
E BCS 404	0.060	0.062
F BCS 404	0.020	0.019
G BCS 329	0.020	0.018
H BCS 329	0.040	0.038

TABLE XV (continued)

Identification	% Ln added	% Ln found
	4) % Pr added	4) % Pr found
A BCS 402	0.050	0.047
B BCS 402	0.040	0.035
C BCS 402	0.010	0.011
D BCS 404	0.060	0.052
E BCS 404	0.040	0.036
F BCS 404	0.020	0.012
G BCS 329	0.050	0.043
H BCS 329	0.010	0.011

TABLE XVI

Recovery of Rare Earth Mixture Additions to Mild and Low Alloy Steels

Sample Identification

A, B, C, D :- BCS 402 steel sample

E, F, G :- BCS 404 steel sample

Each steel sample was doped with a rare earth mixture according to the table given below.

Identification	% R.E. added	% R.E. found
A	0.100% Ce 0.050% La	0.097% Ce
B	0.100% Ce 0.050% La 0.020% Nd	0.108% Ce 0.078% La 0.027% Nd
C	0.080% Ce 0.040% La 0.020% Nd 0.010% Pr	0.095% Ce 0.066% La 0.031% Nd 0.100% Pr
D	0.060% Ce 0.040% La 0.020% Nd 0.020% Pr	0.086% Ce 0.060% La 0.030% Nd 0.108% Pr
E	0.100% Ce 0.080% La 0.040% Nd 0.010% Pr	0.110% Ce 0.107% La 0.050% Nd 0.140% Pr
F	0.050% Ce 0.030% La 0.010% Nd 0.010% Pr	0.061% Ce 0.045% La 0.019% Nd 0.072% Pr

TABLE XVI (continued)

Identification	% R.E. added	% R.E. found
G	0.050% Ce 0.020% La	0.050% Ce 0.028% La

TABLE XVII

Determination of the Rare Earths in Mild or Low Alloy Steels

Sample Identification

D1/1346 - D1/1348 :- from Bragg Laboratory, Sheffield.

8590 :- from B.S.C., Teeside.

Only the cerium figure has been reported by other workers using X-ray fluorescence, or ion exchange techniques.

Identification	% Ce reported by other workers	% R.E. found
D1/1346	0.047% Ce	0.052% Ce 0.028% La 0.021% Nd 0.063% Pr
D1/1347	0.080% Ce	0.098% Ce 0.061% La. 0.040% Nd 0.092% Pr
D1/1348	0.122% Ce	0.122% Ce 0.061% La 0.008% Nd 0.105% Pr
8590	0.063% Ce	0.081% Ce 0.051% La 0.032% Nd 0.091% Pr

Good agreement between '% rare earth added' and '% rare earth found' can be seen for single lanthanoid additions from the table of results. The method is, therefore, suitable where only one lanthanoid element is present. The results for steels containing mischmetal are generally high for each rare earth element under consideration. The mutual rare earth spectral interference effect results in a higher emission reading at each wavelength than expected and so this problem is significant even at the low rare earth levels under consideration. The high results, however, did not occur for all steel samples containing mischmetal but did occur for all steel samples purposely doped with the mischmetal ratio of lanthanoids.

Considering samples 'A' and 'G' (Table XVI) it can be seen that lanthanum does not interfere at the cerium wavelength giving an accurate result for cerium. Cerium interferes with the lanthanum wavelength, giving a higher result than expected. Samples 'B' to 'F', containing three or four rare earth additions, show the effect of further spectral interference giving high results. The cerium result is affected mainly by the neodymium level in the sample (this being higher in the mischmetal ratio than praseodymium) whereas the neodymium result is only really affected by cerium, as it is in relatively high levels, although not a strong spectral problem. The praseodymium results show dramatically high values. This is due to the severe spectral interference of Ce and Nd on the Pr line and, additionally, the fact that Pr will be present in the smallest quantities and so the interference of cerium particularly, will swamp the tiny Pr emission signal. These results are in agreement with the mutual rare earth interference values given in Table IX (Chapter III). The low level of praseodymium expected in a steel sample and the extent of mutual rare earth interference lead to the realisation that the Pr 493.9nm, although selected as the best analytical line for rare earth mixtures, possibly may not be usefully employed for this type of analysis.

The percentage recoveries of the rare earths from the melt, after the desulphurisation modification process (see Chapter I) are assumed to be in the same ratio as the mischmetal addition. This may not be correct as each rare earth element may modify the steel by dissimilar inclusion formation and rates of recovery can vary

from one element to another. Higher results may be due to the presence of larger quantities of the other rare earths, Nd and Pr, than in the expected mischmetal composition. This may create a small but significant increase at the other rare earth wavelength, e.g. cerium wavelength. The emission signal received would, therefore, be a summation of the total cerium emission plus a contribution from the other rare earths. The method, therefore, must be extended to correct for mutual rare earth interference where high results are obtained. Additionally, it may then be possible to determine all of the four rare earth elements present from one solution by measuring the total emission at all of the four rare earth wavelengths followed by a correction for the extent of mutual rare earth interference at each wavelength. A series of simultaneous equations can then be used to compute the individual percentage rare earth content. This method may then be superior to may colo rimetric, gravimetric or ion exchange methods in that four rare earth elements can be determined from one prepared solution simultaneously. This idea was investigated to, hopefully, provide closer results to the known lanthanoid values. The steel preparation method was followed as given in schematic diagram 1. The same mild steels - B.C.S. 402 and 404 - were prepared with doped additions of rare earth mixtures as shown in Table XVI. A 2.5g steel sample was used, in duplicate, for this investigation to provide a final solution of 10 - 25cm^3 (depending on the level of lanthanoid addition) which would provide rare earth concentrations between 10 and 100mg dm^{-3}, these being suitable levels for obtaining emission readings in the nitrous oxide/acetylene flame. The removal of iron from a 2.5g steel sample required at least three extractions to ensure almost 100% removal. Calibration solutions were made up for the four lanthanoid elements with added ionisation suppressor from stock solutions in the range 10 - 100mg dm^{-3} and then the four sets of standards measured simultaneously at each lanthanoid wavelength in a reducing nitrous oxide/acetylene flame, optimised to produce the most suitable flame conditions for rare earth analysis (as outlined in Chapter III). Emission readings were taken over a three second count and checked periodically against a concentrated

standard for each element. The steel samples were read under similar conditions at each respective wavelength. Steel blanks were also run alongside the actual samples to ensure no high background readings occurred. Steel samples containing the mischmetal additions were treated in a similar manner and emission readings similarly taken at each wavelength.
A series of calibration graphs of emission against rare earth concentration were plotted at each lanthanoid wavelength. Various combinations of two, three or four rare earths in one solution were also tested at each wavelength to show that, in the presence of excess ionisation suppressor, no extraneous increases or depressions in the emission signal were obtained as a result of unknown chemical or physical interactions in the flame between any of the rare earth species. From the graphs obtained the matrix for solution of the linear equations could be calculated, from the gradient of each line. An example of the standard set of four equations is given below.

$$a_{11}x_1 + a_{12}x_2 + a_{13}x_3 + a_{14}x_4 = C_1$$

$$a_{21}x_1 + a_{22}x_2 + a_{23}x_3 + a_{24}x_4 = C_2$$

$$a_{31}x_1 + a_{32}x_2 + a_{33}x_3 + a_{34}x_4 = C_3$$

$$a_{41}x_1 + a_{42}x_2 + a_{43}x_3 + a_{44}x_4 = C_4$$

where, in this case

x_1 = Ce concentration/mg dm^{-3}

x_2 = La concentration/mg dm^{-3}

x_3 = Nd concentration/mg dm^{-3}

x_4 = Pr concentration/mg dm^{-3}

and

C_1 = total emission at Ce wavelength 468.4nm

C_2 = total emission at La wavelength 593.0nm

C_3 = total emission at Nd wavelength 660.1nm

C_4 = total emission at Pr wavelength 493.9nm

and a_{14} - a_{44} are the matrix values for the spectral interference factors of each element at each wavelength, e.g. a_{12} is the interference factor of lanthanum at the cerium wavelength; a_{43} is the interference factor of neodymium at the praseodymium

wavelength. Each 'a' value can be calculated from the graphs (14, 15, 16, 17) 'a' being the gradient of each interference line, e.g. a_{12} is the gradient of the lanthanum line at the cerium wavelength. This series of linear equations can be solved by the Gauss Jordan reduction (95).

New results, with these spectral corrections applied, were then obtained using a standard computer programme for solving simultaneous equations. An example of typical computer results are shown in Figure 2 using a sample containing 60mg dm^{-3} Ce, 30mg dm^{-3} La, 20mg dm^{-3} Nd and 10mg dm^{-3} Pr. The gradients were calculated from the graphs (14, 15, 16, 17) and the C_1 to C_4 values measured and fed into the computer. The results are printed out and show that agreement is quite good for Ce and La, reduced for Nd, but very poor for Pr. In this example the result for praseodymium is unacceptably low. In other examples, some hypothetical, however, high results and even negative results were calculated for praseodymium.

Sample 'A' (Table XVI) was used to see the effect of using two, three and four simultaneous equations to calculate values for Ce and La. The results are shown in Figure 3. The computer print-out shows the effect when the number of simultaneous equations for correction is increased from two to three to four. The values X(1), X(2), X(3) and X(4) refer to the Ce, La, Nd and Pr values in mg dm^{-3}. The concentration of rare earth added to the sample formed a concentration of 80mg dm^{-3} Ce and 40mg dm^{-3} La. With the use of two equations for La and Ce the results show good agreement for Ce but high results for La. With three equations to include the neodymium correction, the results are similar with a small, but not significant, value being given for Nd. With four equations, however, a small negative result is given for Nd, slightly reduced results for Ce and La, but a significant and relatively high result for Pr. The summation of errors in this correction calculation are, therefore, more significant at the Pr line. A practical error introduced initially into the computer (i.e. the high La reading) caused a summation of errors in the calculation which has the most dramatic effect at the Pr line which corresponds to a low Pr content and high levels of spectral interference from the other rare earths.

Correction calculations from other samples containing all four rare earths showed varying results, but it was realised that small practical errors in the initial values created a dramatic summation of errors effect on the Pr corrected value (sometimes giving negative results) and to a lesser extent on the Nd value.

Typical results are shown in Table XVIII comparing the original results (in Table XVII) with corrected results from computer reading. For samples with only two rare earths present, e.g. La and Ce, the corrected values give improved results but in all other cases the Ce value was still too high and the other rare earth values were not satisfactory, giving lower, but negative, values at the Pr line but high results at the Nd and La lines. Any initial practical error appeared, therefore, magnified by the correction calculation. This can be expected when dealing with four simultaneous equations. Analytical methods involving such correction techniques, commonly use a two equation correction but the use of four equations is not a generally accepted practice due to the problem of summation of errors.

The method involving correction factors, was, therefore, not successful at this stage in providing improved results for the mischmetal content in mild and low alloy steels. Mixtures of the four rare earths Ce, La, Nd and Pr were too complex to analyse in the nitrous oxide/acetylene flame by an emission technique. It was concluded that if one element could be determined with more certainty, then the errors involved in this method could be reduced. The separation and isolation of cerium was considered to be the logical choice, being present in the largest quantity, and being capable of separation by virtue of its differing chemical behaviour.

FIGURE 2

COMPUTER PRINTOUT EXAMPLE

This program solves sets of simultaneous equations with up to 10 equations per set.

Enter the matrix of your equations, a row at a time, include the right hand sides.

E.g. to solve:

```
X(1) + X(2) = X(3)    =  6
2*X(1) + 5*X(3)       =  2
2*X(1) + X(2) - X(3)  =  0
```

Enter your data after the question marks, thus:

```
? 1, 1, 1, 6
?? 2, 0, 5, 2
?? 2, 1, -1, 0
```

Pressing X off after each line.

How many equations are there in your set?

Enter zero if you have finished.

```
?
4
```

Now enter your matrix.

```
?
0.57, 0.0, 0.35, 0.27, 45
??
0.07, 0.63, 0.22, 0.29, 30
??
0.04, 0.0, 0.72, 0.19, 20
??
0.4, 0.0, 0.38, 0.33, 35
X( 1)  =  63.57678
X( 2)  =  31.51775
X( 3)  =  23.83685
X( 4)  =  1.549362
```

FIGURE 3

This program solves sets of simultaneous equations
with up to 10 equations per set.
Enter the matrix of your equations, a row at a time, including
the right hand sides.
E.g. to solve:

```
X(1) + X(2) + X(3)   =  6
2*X(1) + 5*X(3)      =  2
2*X(1) + X(2) - X(3) =  0
```

Enter your data after the question marks, thus:

```
? 1, 1, 1, 6
?? 2, 0, 5, 2
?? 2, 1, -1, 0
```

Pressing X off after each line.
Now enter your matrix.

```
?
0.57, 0.0, 45
??
0.07, 0.63, 35
X( 1)  =  78.94736 mg dm^-3   =  Ce concentration
X( 2)  =  46.78362 mg dm^-3   =  La concentration
```

How many equations are there in your set?
Enter zero if you have finished.

```
?
3
```

Now enter your matrix.

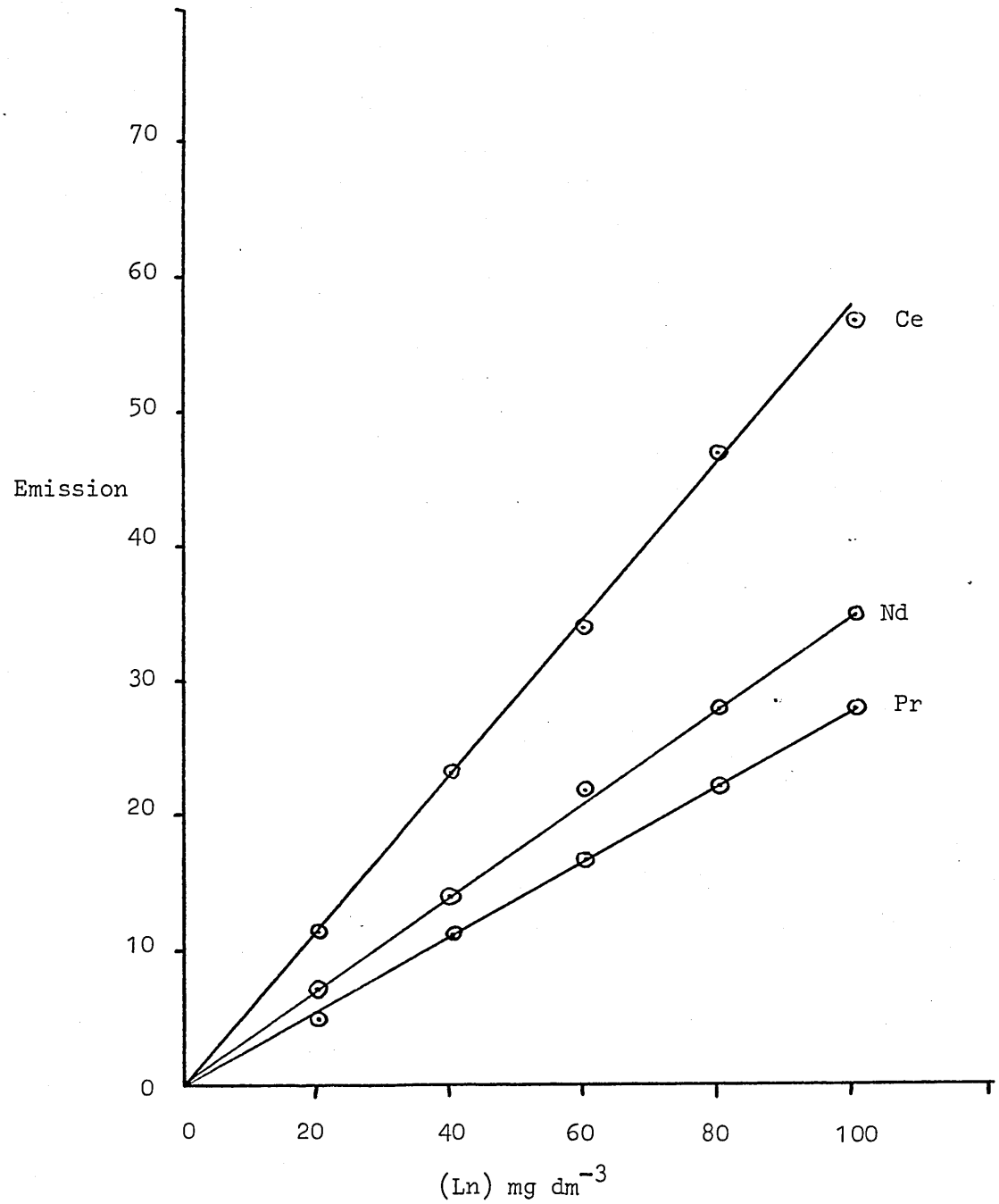
```
?
0.57, 0.0, 0.35, 50
??
0.07, 0.63, 0.22, 41
??
0.04, 0.0, 0.72, 24
X( 1)  =  69.62662
X( 2)  =  47.05362
X( 3)  =  29.46518
```

FIGURE 3 (continued)

```
How many equations are there in your set?
Enter zero if you have finished.
?
4
Now enter your matrix.
?
0.57, 0.0, 0.35, 0.27, 45
??
0.07, 0.63, 0.22, 0.29, 30
??
0.04, 0.0, 0.72, 0.19, 18
??
0.4, 0.0, 0.38, 0.33, 28
X( 1)  =  85.19778
X( 2)  =  53.16072
X( 3)  =  36.09685
X( 4)  = -59.98766
```

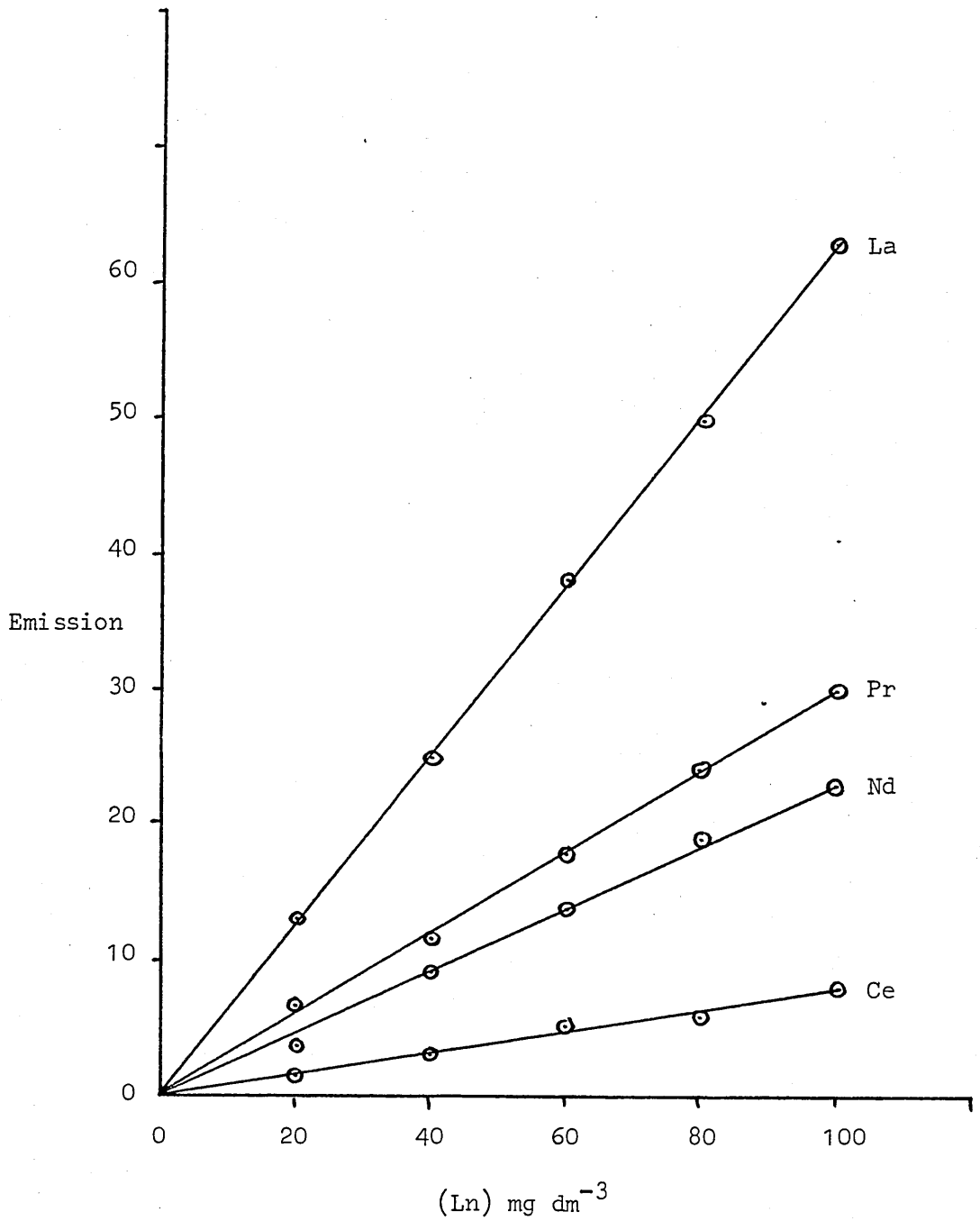
GRAPH 14

Calibration curves at cerium wavelength 468.4nm



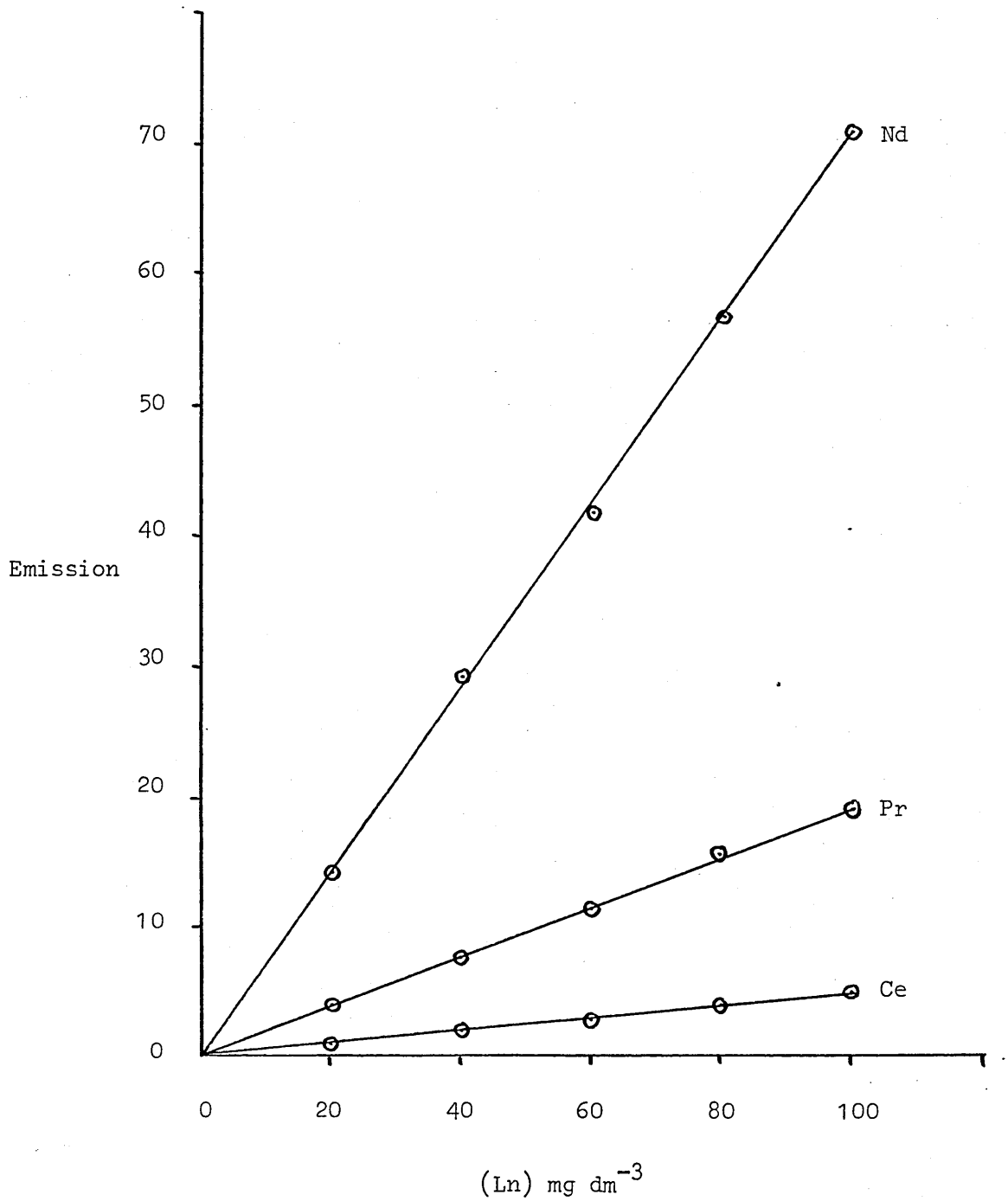
GRAPH 15

Calibration curves at lanthanum wavelength 593.0nm



GRAPH 16

Calibration curves at neodymium wavelength 660.1nm



GRAPH 17

Calibration curves at praseodymium wavelength 493.9nm

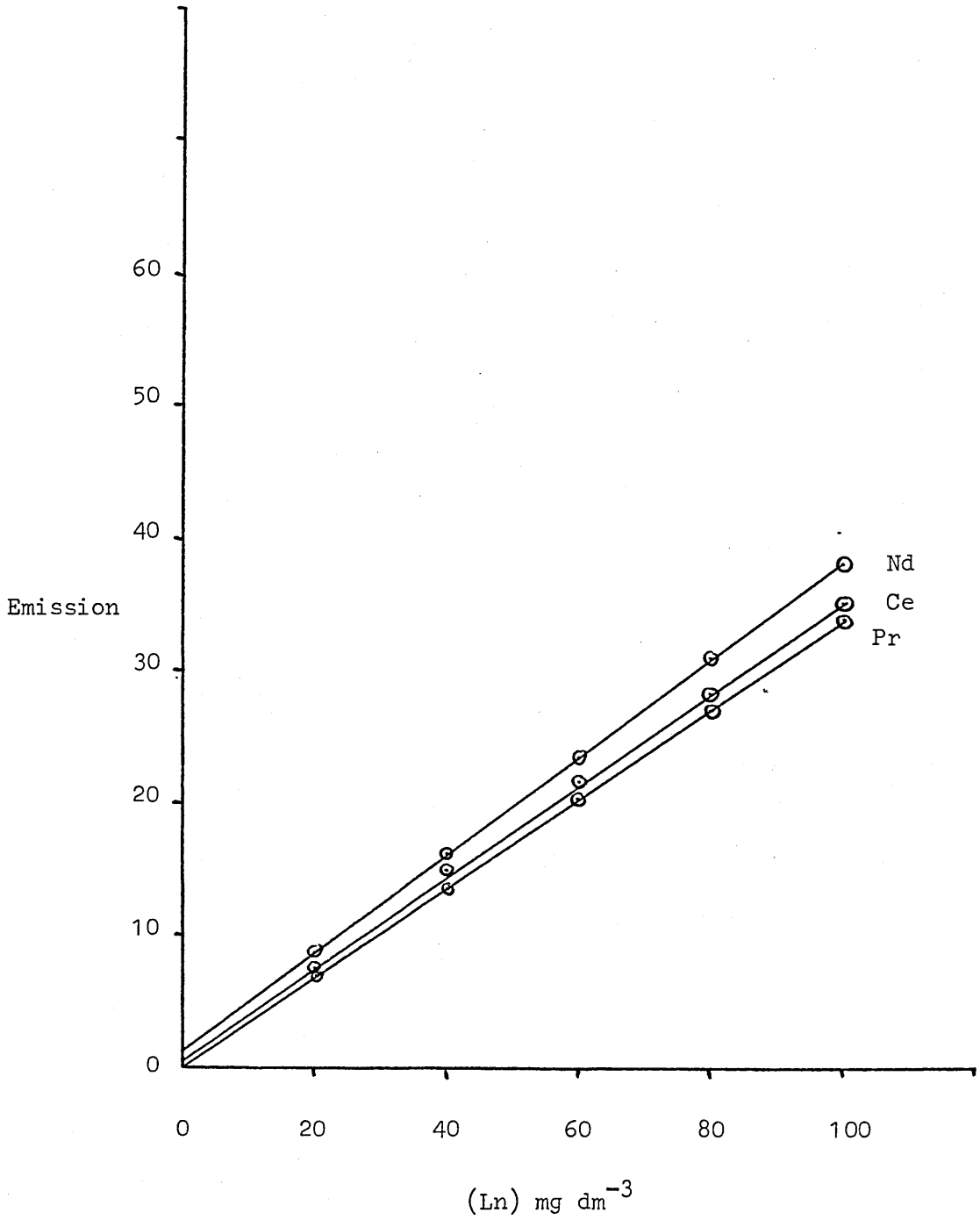


TABLE XVIII

Table of Lanthanoid Results to Show Comparison Between Experimental Values and Corrected Values (using Simultaneous Equations)

Identification	% R.E. found (experimental)	% R.E. found (corrected)
A 0.100% Ce	0.097% Ce	0.103% Ce
0.050% La	0.065% La	0.062% La
B 0.100% Ce	0.108% Ce	0.104% Ce
0.050% La	0.078% La	0.063% La
0.020% Nd	0.027% Nd	0.023% Nd
C 0.080% Ce	0.095% Ce	0.121% Ce
0.040% La	0.066% La	0.089% La
0.020% Nd	0.031% Nd	0.017% Nd
0.010% Pr	0.100% Pr	-0.078% Pr
D 0.060% Ce	0.086% Ce	0.087% Ce
0.040% La	0.060% La	0.056% La
0.020% Nd	0.030% Nd	0.038% Nd
0.020% Pr	0.108% Pr	-0.043% Pr
E 0.100% Ce	0.110% Ce	0.085% Ce
0.080% La	0.107% La	0.090% La
0.040% Nd	0.050% Nd	0.049% Nd
0.010% Pr	0.140% Pr	-0.012% Pr
F 0.050% Ce	0.061% Ce	0.060% Ce
0.030% La	0.045% La	0.048% La
0.010% Nd	0.019% Nd	0.025% Nd
0.010% Pr	0.072% Pr	-0.030% Pr
G. 0.050% Ce	0.050% Ce	0.050% Ce
0.020% La	0.028% La	0.024% La

TABLE XVIII (continued)

Identification	% R.E. found (experimental)	% R.E. found (corrected)
D1/1346		
0.047% Ce	0.052% Ce	0.044% Ce
	0.028% La	0.024% La
	0.021% Nd	0.051% Nd
	0.063% Pr	-0.013% Pr
D1/1347		
0.080% Ce	0.098% Ce	0.120% Ce
	0.061% La	0.079% La
	0.040% Nd	0.065% Nd
	0.092% Pr	-0.121% Pr
D1/1348		
0.122% Ce	0.122% Ce	0.155% Ce
	0.061% La	0.086% La
	0.008% Nd	0.034% Nd
	0.105% Pr	-0.120% Pr
8590		
0.063% Ce	0.081% Ce	0.072% Ce
	0.051% La	0.056% La
	0.032% Nd	0.075% Nd
	0.091% Pr	-0.083% Pr

5.3 The Determination of Cerium in Mild and Low Alloy Steels by Oxalate Precipitation

The method comprising total rare earth precipitation and application of correction factors for mutual rare earth interference in the nitrous oxide/acetylene flame was not satisfactory in obtaining an accurate analysis for lanthanoid mixtures. Considering that cerium constitutes the major fraction of the mischmetal addition, and, that metallurgical interest is primarily concerned with this element in terms of inclusion modifications in steels, a method was investigated to determine cerium in mild and low alloy steels. Additionally, the determination of cerium separately might enable a revised correction method to be applied to the original precipitation scheme. In this way only three elements would then be under consideration and the summation of errors in the correction calculation might be greatly reduced.

Cerium has certain chemical properties which differ fundamentally from the other light rare earths and so a separation method, based on different chemical behaviour was considered. Cerium is the second member of the lanthanoid series and its electronic arrangement enables two stable oxidation states to occur, Ce^{3+} and Ce^{4+}. The other light lanthanoids can only exist in the 3+ state in solution. Separation of cerium from mischmetal can, therefore, be achieved by an oxidation reaction from a lanthanoid mixture.

Various methods were investigated. The reactions of CeIV in solvent extraction systems are adequately summarised by Korkisch (88) and Morrison and Freiser (87).

Chelate and ion association systems are suitable for CeIV separation but the use of an ion-association system, using a nitric acid media, was more appropriate for using in a flame emission technique. Typical systems include the use of tributyl phosphate (T.B.P.), 4 methyl-pentan-2-one (M.I.B.K.) diethyl ether or (2-ethyl hexyl)-orthophosphoric acid (HDEH P) saturated with 9M nitric acid prior to treatment with rare earths to facilitate the transfer of ions from the aqueous to the organic layer.

Oxidation of Ce^{3+} can be achieved by boiling with potassium bromate (a strong oxidising agent); a vigorous redox reaction occurs giving off bromine fumes and converting Ce^{3+} to Ce^{4+}.

Preliminary investigations were carried out to selectively solvent extract Ce^{4+} from trivalent lanthanides (Ln^{3+}) using T.B.P., M.I.B.K. and HDEHP. The extraction of any trace quantities of lanthanum into the organic layer would not pose a problem as this element did not spectrally interfere at the cerium wavelength, but the virtual absence of neodymium and praseodymium was desired as these elements would create a positive error. Experiments were carried out initially with single lanthanoid solutions, and then mixtures were used. The presence or absence of a rare earth element in the aqueous or organic layer was detected by measuring the lanthanoid emission in the nitrous oxide/acetylene flame in the aqueous before and after extraction. Tributyl phosphate gave good, clear, quick separation of aqueous and organic layers but the presence of low levels of Nd were also detected in the organic layer. The use of M.I.B.K. gave satisfactory results. Although the extraction efficiency was lower for one single extraction compared to the other organics, no trace of Nd or Pr was found in the organic layer. It was anticipated that the extraction efficiency would be increased by repeating the extraction two or three times. Elements in the steel matrix were also tested individually and then in mixtures to see their effect on the organic layer and on the efficiency of cerium extraction. A series of stepwise experiments were carried out to build up the overall pattern of reaction and interaction in the steel matrix. Significant levels of Cr, Mn, Ni and V were found in the organic layer although a greater percentage remained in the aqueous layer. The presence of other elements also reduced the extraction of the cerium IV ion by up to ca. 30%. Iron was not included in these tests as it was decided to remove it from steel by an ether extraction prior to the selective separation of Ce IV. Experiments showed that the presence of large amounts of iron would seriously reduce the extraction of Ce IV.

The extraction efficiency of cerium was considered carefully. Cerium was added to a typical steel matrix (e.g. B.C.S. 402) and after dissolution, the iron removed by an ether extraction as given in Method I. The resulting aqueous solution was then fumed with concentrated nitric acid to convert the solution to

a nitric medium and the cerium was then oxidised by boiling in excess potassium bromate. Solvent extraction with M.I.B.K. (previously saturated with nitric acid) was carried out and the extraction efficiency of a single extraction of $25cm^3$ organic with $15cm^3$ steel solution roughly calculated by testing the residual amount of cerium in the aqueous layer. The efficiency was found to be as low as 30% and so investigations were made to see if this figure could be improved by using multiple extractors. Considering $25cm^3$ organic and $25cm^3$ aqueous solution, the percentage extraction after three extractions, was calculated to be ca. 75% but with $25cm^3$ organic and $15cm^3$ aqueous solution, the percentage efficiency after three extractions was calculated to be higher at Ca. 95%. The solvent extraction was then repeated with the latter volume values and an experimental efficiency of 86% found, which was considered satisfactory at this stage. The molarity of the nitric acid was varied to see if an increased efficiency could be achieved but maximum extraction was found to occur at 10M nitric acid; at lower molarities of 2M, 5M and 7M poor extraction occurred.

Back extraction of the cerium from the organic layer was achieved using water or dilute hydrogen peroxide (to reduce Ce^{4+} to Ce^{3+}). The use of hydrogen peroxide was preferred as less volume was required to effect the same result as water. Again, three extractions were required to obtain almost 100% back extraction. Small levels of chromium, vanadium, manganese and nickel were recovered in the back extraction.

In the development of this method the use of the oxalate ion rather than the hydroxide or fluoride was investigated to remove and concentrate the cerium from the residual matrix. Oxalate precipitation is generally considered to be more selective and, as noted from initial research work, the best conditions of rare earth oxalate precipitation were found to vary from element to element. Favourable conditions for cerium could, therefore, be used which may, at the same time, be non-optimum for the other rare earths, particularly Nd and Pr, and also for the elements in the steel matrix, e.g. chromium and vanadium.

The precipitation step was, therefore, investigated to produce

maximum precipitation of the rare earth oxalate and minimum interference from reaction or co-precipitation of other elements present in the steel media. The use of a collector in such trace level precipitation techniques is often desirable, with calcium or lanthanum being widely used for oxalate formation. Since lanthanum did not interfere at the cerium wavelength, this element was used as a collector for cerium.

Preliminary results showed that the presence of a tenfold excess of lanthanum enhanced the cerium emission signal at 468.4nm in the nitrous oxide/acetylene flame by greater than 200% (see Graph 18 & Fig. 5). The shape of this graph is similar to that produced by the ionisation suppression effect of potassium or caesium. The addition of 2000mg dm^{-3} potassium or caesium to a solution containing 100mg dm^{-3} Ce and 1000mg dm^{-3} La did not further enhance the cerium emission signal and so it was concluded that excess lanthanum acted as an ionisation suppressor for cerium (the ionisation energy for La is slightly lower than for Ce - see Table III). Lanthanum was found to readily precipitate as the oxalate in acidic or alkaline conditions and so was useful as a collector to ensure maximum precipitation at trace levels. The use of lanthanum was concluded, therefore, to have a dual purpose -

(a) to act as a collector for cerium and

(b) to act as an enhancing agent in the flame.

Preliminary tests showed that oxalic acid would precipitate lanthanum completely in acidic conditions $>$ pH4, but cerium would only partially precipitate at this stage, giving an orange precipitate and only reach maximum precipitation at pH $>$ 7 where hydroxide precipitation can also occur. A graph of emission signal for cerium at 468.4nm against pH at the precipitation stage (see graph 19), shows these results. The use of alkaline conditions was found, however, to be undesirable as this produced interference from vanadium and chromium hydroxide precipitation which, due to spectral interference, would lead to high results for cerium. The use of an oxidation step, e.g. use of 40% perchloric acid, prior to the precipitation step, was considered (as described in schematic Method I) to selectively oxidise vanadium

GRAPH 18

Enhancement effect of lanthanum on cerium emission at 468.4nm

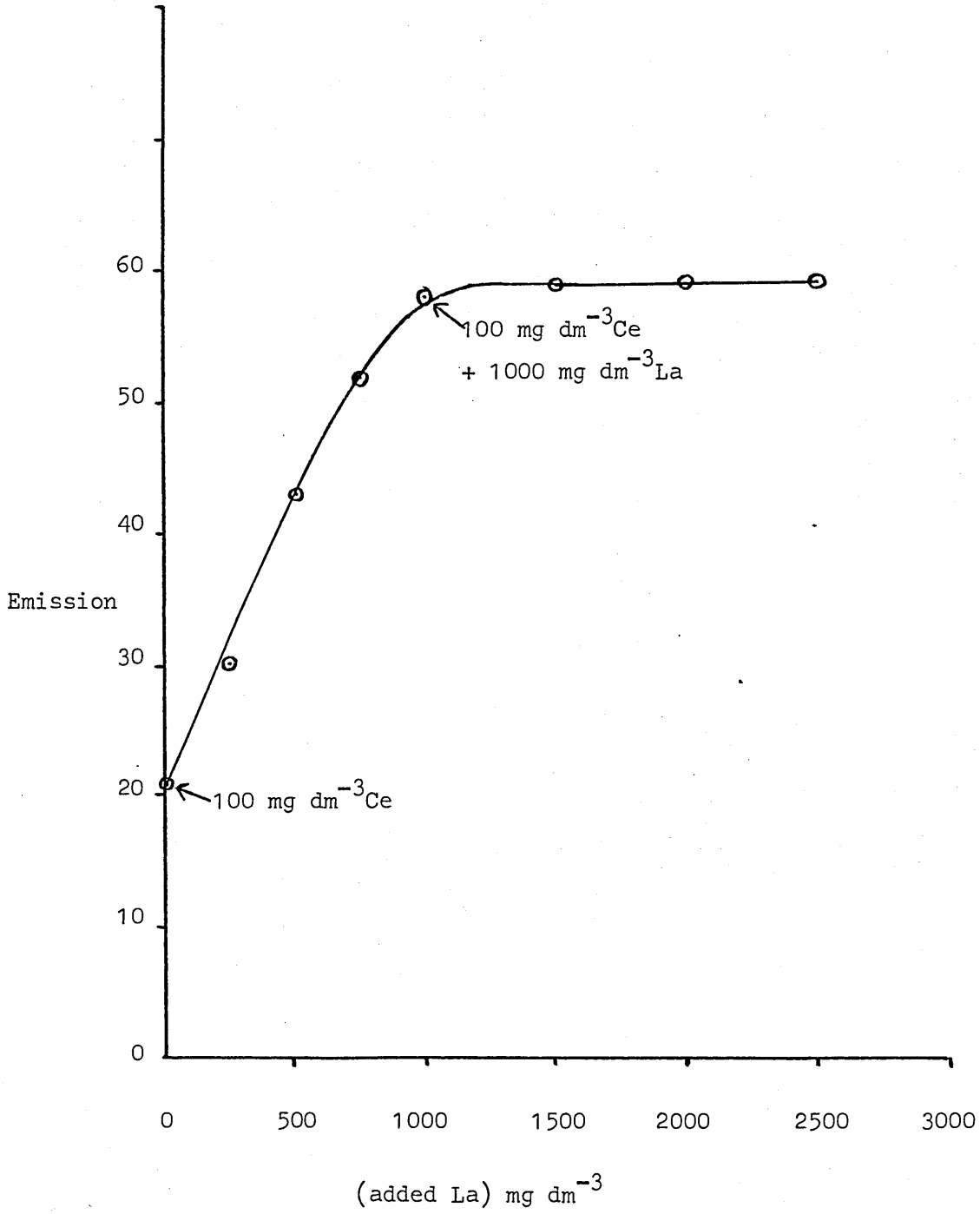
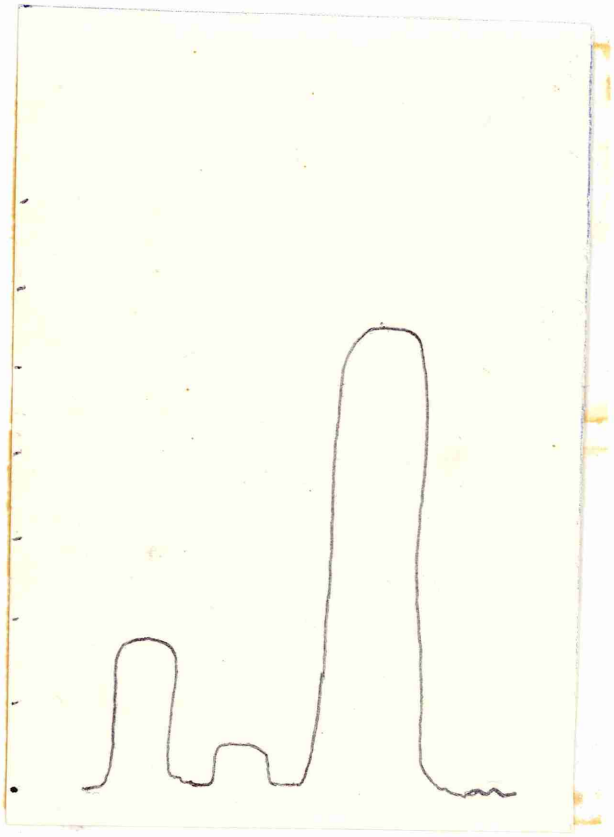


Figure 5 Enhancement Effect of Lanthanum on Cerium at 468.4nm



1 2 3

1. 90mg.dm^{-3}, Ce
2. 900mg.dm^{-3}, La
3. 90mg.dm^{-3} Ce + 900mg.dm^{-3} La

and chromium. Oxalic acid is, however, a reducing agent and so the oxidation step would not be useful. Experiments using chromium and vanadium solutions, were carried out to prove that reduction did, in fact, happen.

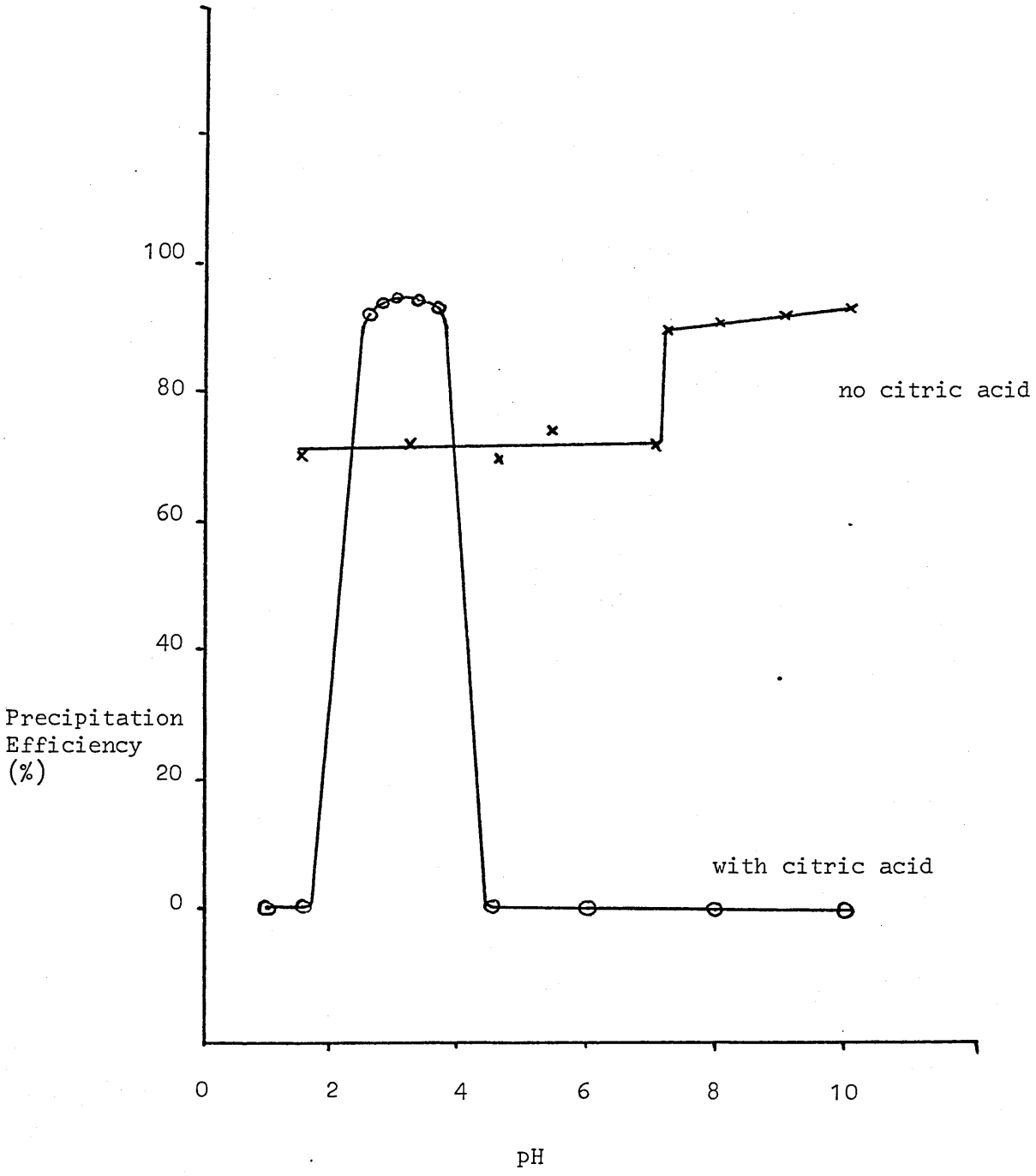
All other possible elements in the steel matrix, e.g. Mn, Ni, Al, W, Co, were tested for oxalate formation under various pH conditions to see if any unfavourable reaction occurred in the presence of cerium. The presence of Mn^{2+} in the steel media was found to produce additional problems in alkaline conditions by forming a precipitate of basic manganese IV oxide in the presence of oxalic acid. This reaction enhances the reduction of any Cr^{6+} to Cr^{3+} resulting again in the chromic hydroxide precipitate. Other elements in the steel matrix did not interfere with the formation of the cerium oxalate.

The method had to be modified to solve the problem of co-precipitation of undesirable elements with cerium at the oxalate formation stage. Masking agents are commonly used in analytical techniques for this purpose and a suitable selection for a steel media and oxalate precipitation was made including citric acid and tartaric acid (dicarboxylic acids), E.D.T.A. and sulfosalicyclic acid. The addition of citric or tartaric acid to the steel solution successfully eliminated the problems of co-precipitation and created the conditions whereby only rare earth oxalate precipitation occurred.

Citric acid, being readily available, was used and test results showed that this reagent prevented the reducing effect of oxalic acid by acting as a masking agent. In the absence of citric acid, cerium oxalate would only readily precipitate from a steel solution at pH values greater than 7, but in the presence of citric acid a green solution formed at pH >7 with no precipitate developing. At pH values 6-7, a brown/green solution formed and for pH 2-4 the maximum formation of an orange/brown precipitate formed. For pH values <1.4 only trace precipitation occurred. Graph 20 shows that maximum precipitation of cerium occurs in the pH range 2.5 - 3.5. Graph 19 compares the change in precipitation efficiency in the presence and absence of citric acid. The precipitation efficiency was measured as a function of the cerium

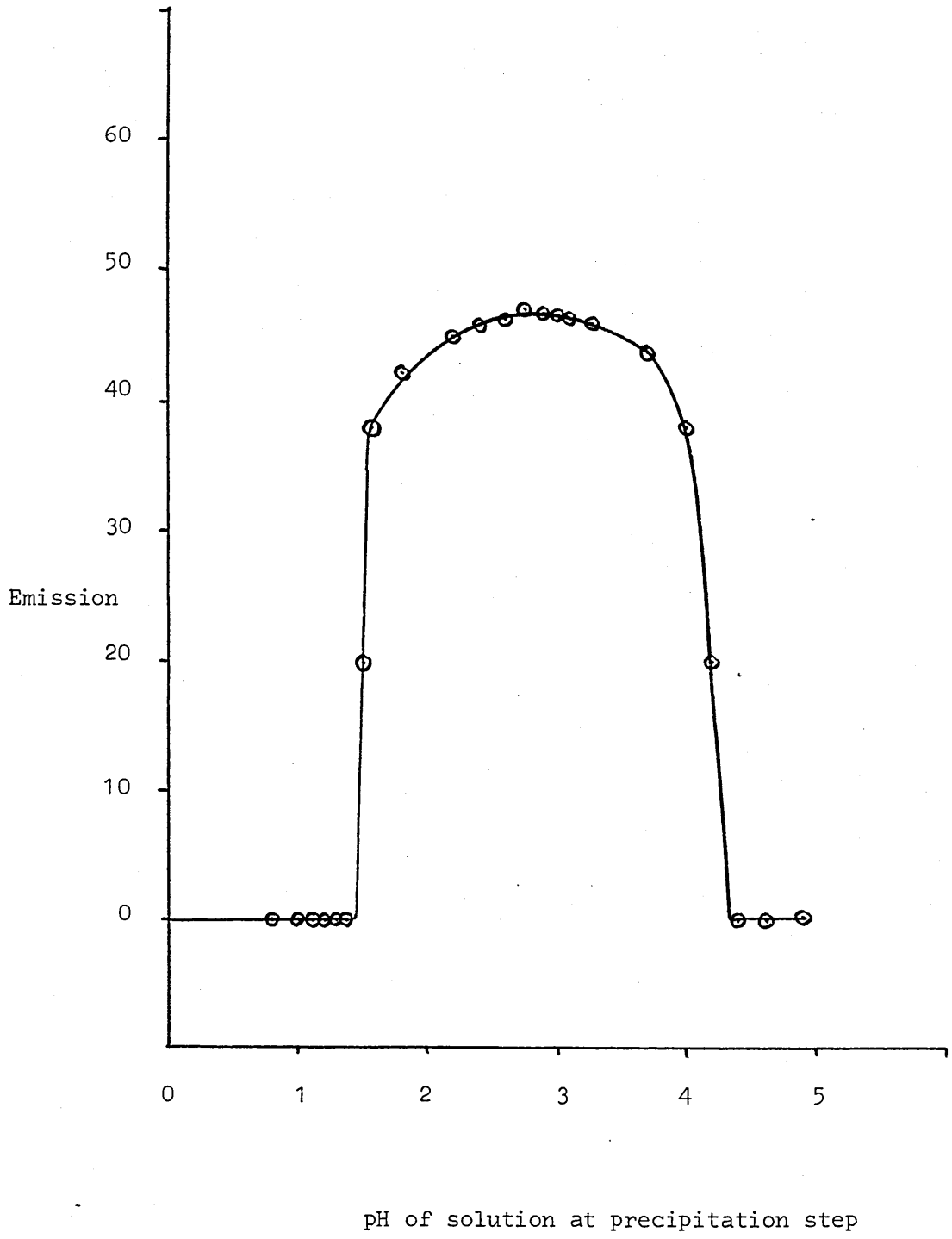
GRAPH 19

Graph to show effect of citric acid on the precipitation of cerium oxalates



GRAPH 20

Effect of pH on oxalate precipitate in citrate media



emission signal at 468.4nm in the nitrous oxide/acetylene flame. $25cm^3$ of 100mg dm^{-3} cerium stock solution was taken and for each pH value (adjusted by addition of ammonium hydroxide) the precipitate collected, redissolved in nitric acid and made up to $25cm^3$ again. The emission signal of this solution was compared with the standard of 100mg dm^{-3} Ce. Citric acid or oxalic acid did not give a blank reading which could have affected the results obtained. At pH 2.8, results showed that an efficiency of precipitation of cerium oxalate of ca. 95% was achieved. this was considered acceptable for the development of an analytical method. Under these conditions no chromium, vanadium, nickel or manganese ions were found present in the final solution and so a useful and efficient separation method for cerium was achieved without the need for an additional oxidation step. This was important from the aspect of the development of a practically useful laboratory method as a desirable technique should ideally be selective, accurate and quick.

The procedure for the determination of cerium in steels was then outlined as given in Method 2. The steel sample was dissolved in a nitric/hydrochloric mixture by the method given in detail in Chapter IV. Iron was then removed from the steel media by selective solvent extraction with 9M hydrochloric acid/diethyl ether (2-3 extractions required). The remaining aqueous solution was then fumed with concentrated nitric (ca. $50cm^3$) to boil off the chloride ions and render the solution into a nitric acid medium. Dry potassium bromate (ca.1g) was then added to the cooled solution and gently heated after the initial vigorous redox reaction to convert all of the Ce^{3+} to Ce^{4+}, bromine was given off at this stage so it was important to carry out this step in a fume cupboard. The solution was then cooled and a second solvent extraction made using M.I.B.K. The steel solution was adjusted to 9M nitric acid and the M.I.B.K. solution shaken with 9M nitric acid just before required. This solvent absorbed fairly large quantities of acid and so it was essential to saturate the media with nitric acid to increase the efficiency of cerium extraction and to prevent the extraction of any other elements in steel by an aqueous absorption effect. Stock solutions of the saturated M.I.B.K. solution were not stored as this solution was known to

METHOD 2

The Determination of Cerium in Low and Mild Alloy Steels

	2g steel	
	↓	digest with $30cm^3$ 1:1 HCI and $4cm^3$ conc. HNO_3. Boil to syrupy state and redissolve in 9M HCI.
	solution	
SOLVENT EXTRACTION STEP	↓	removal of iron by shaking with diethyl ether (1 extraction of $100cm^3$ suffices).
	iron free solution	
	↓	addition of $50cm^3$ 10M HNO_3 fume down to remove CI^- ions (test with Ag NO_3 solution).
	solution in nitric media	
SOLVENT EXTRACTION STEP	↓	addition of $KBrO_3$ (Ig), boil to oxidise all cerium to CeIV state. solvent extraction with 10M HNO_3 M.I.B.K. (3 extractions of $25cm^3$ each suffices). Back extraction with dilute H_2O_2 solution (3 extractions of $25cm^3$ required.
	solution containing Ce separation of CeIV from Ln III ions	
PRECIPITATION STEP	↓	addition of a) $15cm^3$ sat. citric acid b) $25cm^3$ $100mg.dm^{-3}$ lanthanum c) $10cm^3$ sat. oxalic acid adjust to pH 2.7 - 3.0 with conc. ammonium hydroxide. Warm ppt. for 1 hour.
	rare earth oxalate ppt.	
	↓	
AT 468.4nm	read for Ce with N_2O/C_2H_2 flame	filter, wash with H_2O, redissolve in minimum conc. HNO_3. Make up to required volume ($25cm^3$).

be potentially unstable, fresh M.I.B.K. solutions were saturated just prior to use. Three extractions were made using 3 x 25cm^3 of M.I.B.K. with 15cm^3 steel solution. The three fractions were added together and a back extraction made using 3 x 25cm^3 ca. 5% hydrogen peroxide solution. This reduced the Ce^{4+} to Ce^{3+} which was back-extracted into the aqueous media.

The cerium was then collected and concentrated from the 75cm^3 volume of diluted hydrogen peroxide by addition of -

(a) 15cm^3 saturated citric acid

(b) 25cm^3 1000mg dm^{-3} lanthanum solution, and

(c) 10cm^3 saturated oxalic acid specifically in that order specifically in that order. The solution was then adjusted to pH 2.7 - 3.0 with concentrated ammonia and the resulting precipitate warmed on a steam bath for about one hour. After cooling the precipitate was filtered through a Whatman No. 42 filter paper or centrifuged and redissolved in a minimum of concentrated nitric acid, made up to the required volume (10 - 25cm^3 depending on the cerium concentration) and the emission signal read in the nitrous oxide/acetylene flame under optimum conditions. This method did not require the addition of an ionisation suppressor as the lanthanum acted in this capacity.

Practical errors could arise from any one of the individual stages in this method but good results were obtained by careful laboratory procedure :

(a) by consistent measurement of all volumes of additions at each stage

(b) by efficient and sufficient shaking during each solvent extraction procedure with correct pH control

(c) control of, and care of, any heating stage to prevent spitting or spillage of solution (use of watch glasses etc.), and

(d) use of analar reagents and very clean glassware to prevent contamination.

The method took between 8 and 10 hours to complete.

A range of standards for calibration purposes was investigated. A selection of mild and low alloy steels, e.g. B.C.S. 329, 402 and 404 were taken and cerium (in the form of a stock solution

of ammonium ceric nitrate) added to produce samples in the range 0 ⟶ 0.1% Ce, e.g. 0, 0.025, 0.050, 0.075 and 0.10% Ce. 2g (duplicate) steel samples were weighed out, appropriate volumes of cerium solution added, and the procedure given in schematic diagram 2 carried out. A calibration graph 'see graph 21) was obtained producing a good straight line from a range of steel standards. A range of cerium steels were then analysed in triplicate and the % Ce calculated. The results are shown in Tables XIX and XX. Good results were obtained showing close agreement between % Ce added and % Ce recovered by method 2 in Table XX. A small percentage of cerium was lost by this method but was considered acceptable within the limits of experimental error. The results in Table XIX showed close agreement with results obtained by other workers and improved values compared to Method 1. It was concluded that the recovery of cerium from mild and low alloy steels by an oxalate precipitation and a flame emission technique in the nitrous oxide/acetylene flame provided a satisfactory method which could be used routinely in an analytical laboratory.

GRAPH 21

Calibration curve for cerium in mild and low alloy steels

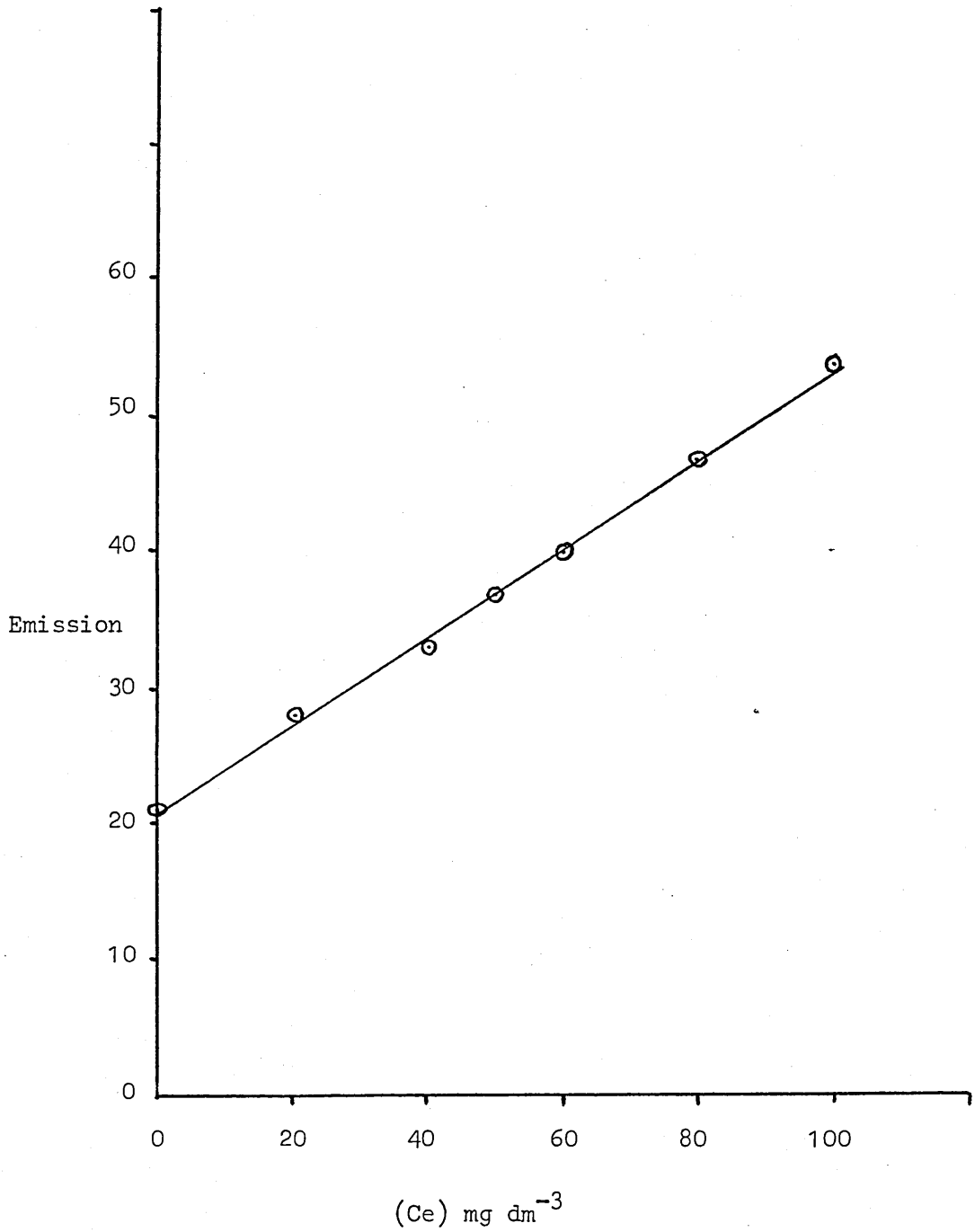


TABLE XIX

DETERMINATION OF CERIUM IN MILD OR LOW ALLOY STEELS

Identification	% Ce (w/w) found		% Ce (w/w) Reported by other workers
	Method 1	Method 2	
D1/1346	0.046	0.043	0.047
D1/1347	0.100	0.090	0.080
D1/1348	0.122	0.120	0.122
8590	0.076	0.068	0.063

TABLE XX

RECOVERY OF Ce FROM MILD AND LOW ALLOY STEELS

by

(a) HYDROXIDE PPT IN PRESENCE OF OTHER RARE EARTHS - METHOD I

and

(b) OXALATE PPT BY METHOD 2

Identification % Ce added	% Ce found Method I	% Ce found Method 2
A 0.100% Ce	0.097% Ce	0.095% Ce
B 0.100% Ce	0.108% Ce	0.092% Ce
C 0.080% Ce	0.095% Ce	0.076% Ce
D 0.060% Ce	0.086% Ce	0.060% Ce
E 0.100% Ce	0.110% Ce	0.091% Ce
F 0.050% Ce	0.061% Ce	0.044% Ce
G 0.050% Ce	0.050% Ce	0.047% Ce

5.4 Evaluation of Results

Two useful methods have been developed for the determination of the light rare earth elements in mild and low alloy steels by flame emission spectroscopy. Method 1, involving hydroxide precipitation, can be used for the determination of single lanthanoid additions, i.e. Ce, La, Nd or Pr in mild and low alloy steels. Method 2, involving oxalate precipitation, can be used to determine cerium, in the presence of other rare earth elements, in low and mild alloy steels. The results show good recoveries from doped samples and excellent agreement with results reported by other workers using X-ray fluorescence, ion exchange and spectrophotometric methods.

The percentage recovery of cerium by both methods was compared using Table II and the results are given in Table XXI. Method 2 shows efficient recovery of cerium ranging from 75% - 95% (with an average value of 90% for seven samples) confirms that a useful analytical technique has been developed. Method 1 gives results greater than 100% due to the spectral interference effect of the other lanthanoid and the errors involved in correction for this. The results for Method 1, where single lanthanoid additions only were considered, showed much better agreement and the percentage recoveries excellent. The percentage recovery results for some samples by Method 1 are given in Table XXI, showing efficient rare earth recovery in most cases ranging from 75% - 120%, with average recoveries for five samples of (a) cerium 93%; (b) lanthanum 93%; (c) neodymium 99%; (d) praseodymium 98%. Each steel sample analysed by either Method 1 or Method 2 was carried out in triplicate. The range of results for a selection of these samples for cerium is shown in Table XXIII and can be compared favourably, in most cases, with the mean value obtained. Experiments were not, however, carried out on more than a triplicate basis since the available quantity of each steel was limited.

The determination of cerium by Method 2 in the presence of other rare earths presented a possibility of determining the other rare earth elements La, Nd and Pr by Method 1 using a set of three simultaneous equations. The isolation and determination of cerium by a separate method should reduce

the extent of errors involved in this calculation by reducing the number of "unknowns" from four to three. The cerium results obtained by oxalate precipitation and flame emission spectroscopy were substituted into the series of simultaneous equations and new results for La, Nd and Pr calculated. A selection of results is shown in Table XXIV. These results can be compared with the corrected results given in Table XVIII. An improvement in the percentage rare earth content was noted in general, but negative results were still obtained in some cases for Nd and Pr. Generally lower results were obtained and in slightly closer agreement to the known value than in Table XVIII, but the results for La, Nd or Pr did not show as close agreement as is analytically desirable. The extent of summation of errors even in a series of three simultaneous equations, is important. Future research could usefully involve more detailed work in this area of the project to attempt to find an accurate method for determining rare earth mixtures in mild and low alloy steels.

TABLE XXI

Comparison of Percentage Recoveries of Cerium by Method 1 and Method 2

Sample Identification	% Ce found Method 1	% Recovery Method 1	% Ce found Method 2	% Recovery Method 2
A 0.100% Ce	0.097	97	0.095	95
B 0.100% Ce	0.108	108	0.092	92
C 0.080% Ce	0.095	119	0.076	95
D 0.060% Ce	0.086	143	0.060	75
E 0.100% Ce	0.110	110	0.091	91
F 0.050% Ce	0.061	122	0.044	88
G 0.050% Ce	0.050	100	0.047	94

TABLE XXII

Percentage Recoveries of Single Lanthanoid Additions to Steel by Method 1

Identification & lanthanoid element added		% R.E. added	% R.E. found	% recovery
A	Ce	0.040	0.040	100
B	Ce	0.100	0.098	98
C	Ce	0.060	0.049	82
E	Ce	0.080	0.075	94
H	Ce	0.050	0.045	90
A	La	0.100	0.096	96
B	La	0.080	0.081	101
C	La	0.050	0.046	92
E	La	0.060	0.056	93
G	La	0.050	0.042	84
A	Nd	0.060	0.060	100
B	Nd	0.050	0.052	104
C	Nd	0.040	0.038	95
E	Nd	0.060	0.062	103
H	Nd	0.040	0.038	95
A	Pr	0.050	0.047	94
B	Pr	0.040	0.035	88
C	Pr	0.010	0.012	120
E	Pr	0.040	0.036	90
H	Pr	0.010	0.012	120

TABLE XXIII

Range of Results for Cerium by Method 1 and Method 2

Percentage Cerium (in triplicate)	Mean Value for Cerium
Method 1	
1) 0.039	
0.040	0.040
0.041	
2) 0.097	
0.098	0.098
0.098	
3) 0.053	
0.047	0.049
0.047	
4) 0.075	
0.075	0.075
0.076	
5) 0.041	
0.047	0.045
0.048	
Method 2	
1) 0.095	
0.094	0.095
0.096	
2) 0.090	
0.094	0.092
0.092	
3) 0.073	
0.078	0.076
0.077	
4) 0.070	
0.058	0.060
0.052	
5) 0.096	
0.088	0.091
0.089	

TABLE XXIV

Determination of La, Nd and Pr in Steel by Method 1
(with Ce as known value)

Sample Identification		% Ce found Method 2	% Rare Earth (with correction) Method 1
A	0.100% Ce	0.095	0.062 La
	0.050% La		
B	0.100% Ce	0.092	0.060 La
	0.050% La		-0.016 Nd
	0.020% Nd		
C	0.080% Ce	0.076	0.065 La
	0.040% La		-0.033 Nd
	0.020% Nd		0.010 Pr
	0.010% Pr		
D	0.060% Ce	0.060	0.042 La
	0.040% La		0.025 Nd
	0.020% Nd		0.004 Pr
	0.020% Pr		
E	0.100% Ce	0.091	0.057 La
	0.080% La		0.049 Nd
	0.040% Nd		-0.017 Pr
	0.010% Pr		

CHAPTER VI

CONCLUSION AND FUTURE WORK

6.1 Conclusion

The experimental results obtained in Chapters III, IV and V, lead to the following conclusions concerning the determination of the light rare earths in mild and low alloy steels by flame emission spectroscopy.

1) The relatively moderate excitation conditions of the nitrous oxide/acetylene flame produced complex wavelength spectra for the light lanthanoid group. A complex emission spectrum was observed, devoid of lines of outstanding intensity. Emission was observed predominantly in the region 450nm to 580nm. Overall it was concluded that the rare earth elements produced very complex band patterns with some evidence of atomic emission but predominantly emission due to molecular bands. This observation was in agreement with the highly refractory nature of these elements which have high dissociation energies and explains why cooler flames, e.g. air/acetylene, gave very poor line emission signals.

2) Flame chemistry, in addition to flame temperature, was an important factor in the production of free atoms in the nitrous oxide/acetylene flame. The temperature of the nitrous oxide/acetylene flame ca. 2950°C was obviously insufficient in itself to break down the strong lanthanoid oxides to form stable atoms in the flame. Results showed that the use of a highly reducing flame increased the lanthanoid atomic emission signal in the primary and interconal zones of the flame. This was concluded to be due to the increased presence of reducing species, regarded as the cynanogen radical, which gives rise to the visible intense emission (red feather) in the flame. The high emission signals in the primary reaction zone can be attributed to the phenomenon called chemiluminescence or over-excitation.

3) A comparison between the two techniques - atomic absorption spectrometry and flame emission spectrometry - was made. Results showed that the latter technique gives superior detection limits and is to be generally preferred. Atomic absorption measurements for neodymium and lanthanum gave poor results and showed a less critical dependence than flame emission on fuel/oxidant ratios in the flames. The requirements for maximum atomic absorption were to use a highly reducing flame with observations being made in the interconal zone. These results are in agreement with the mechanism of atomic absorption compared to atomic emission spectroscopy. Atomic absorption measurements are based on ground state atoms, whereas emission measurements are concerned with excited states. The phenomenon of chemilumine scence occurring in the non-thermal equilibrium of the primary reaction zone of the flame is not suitable for the production of ground state atoms and so is not applicable to absorption measurements. A future development of better light sources for the lanthanoids may significantly improve atomic absorption detection limits for these elements.

4) Analytical signals were improved significantly by the use of ionisation suppressors, e.g. potassium, caesium or sodium, which successfully reduced the number of lanthanoid ionic species in the flame. An addition of 2000mg dm^{-3} of rare earth solution created the maximum effect. Detection limits (2σ) at the most suitable analytical wavelengths for light lanthanoid mixtures in the presence of potassium are calculated as :

(a) cerium (468.4nm) 2.5mg dm^{-3}
(b) lanthanum (593.0nm) 0.9mg dm^{-3}
(c) neodymium (660.6nm) 0.8mg dm^{-3}
(d) praseodymium (493.9nm) 1.0mg dm^{-3}

5) The use of an organic, rather than an aqueous, media increased the lanthanoid emission signal but, with the instrumentation available, produced noisy unstable signals. The use of organic reagents, however, in the appropriate

conditions, was concluded to be useful in any further research work to possible improve detection limits and to concentrate trace lanthanoid mixtures in a single step.

6) The determination of cerium, lanthanum, neodymium and praseodymium is mild and low alloy steels cannot be simply carried out by the use of a flame emission technique using a dissolved steel sample. The steel matrix, consisting of typical elements, e.g. iron, chromium and vanadium, gave rise to severe spectral interference problems at the lanthanoid analytical wavelengths. Results showed that the rare earth content in a steel sample must be separated from the steel matrix prior to analysis in the nitrous oxide/acetylene flame by an emission technique. Additionally, this separation step can be used to concentrate the rare earth content to levels above the calculated detection limits for these elements.

7) Two useful analytical methods have been developed to determine the light rare earths in mild and low alloy steels by flame emission spectroscopy in the nitrous oxide/acetylene flame. Method I, based on solvent extraction and hydroxide precipitation, was very satisfactory for determining single lanthanoid elements, e.g. Ce, La, Nd or Pr (range 0.02 - 0.1%). Lower lanthanoid levels can be determined by increasing the initial weight of steel sample taken (1g). This method was not suitable for rare earth mixtures as the mutual rare earth spectral interference at the selected wavelengths gave rise to errors.
Method 2, involving solvent extraction and oxalate precipitation, was a useful method for determining cerium in a rare earth mixture (or mischmetal) in mild or low alloy steels. This method utilised the specific property of cerium to form an oxidised CeIV state and so effective separation of this element from the other light rare earths was achieved by oxidation and solvent extraction. Good results were obtained for cerium (range 0.02 - 0.1%) and again lower levels can easily be analysed by doubling the starting weight sample. These two methods, described in Chapter V, involve a stepwise procedure but can be carried

out usefully in an analytical laboratory in a normal laboratory day schedule.

Method I

Determination of Ce, La, Nd or Pr in mild or low alloy steels

Weigh out 1g steel into a $400cm^3$ glass beaker, add $30cm^3$ 1:1 HCl, 5 cm^3 conc. HNO_3, and allow the solution to fume slowly in the cold. When the first initial reaction evolving nitrogen dioxide fumes has ceased, warm gently and check that all the steel has dissolved. Bring to the boil and then fume down carefully to near dryness, covering the beaker with a watch glass. Cool and then add $10cm^3$ 9M HCl and warm gently to redissolve all the steel sample to give an orange/yellow solution.

Transfer the steel solution into a $250cm^3$ separating funnel and add $50cm^3$ of diethyl ether (previously saturated with 9M HCl) using a small volume to wash out the $400cm^3$ beaker. Shake these two solutions gently in a fume cupboard, releasing the contained pressure frequently, for three minutes. Allow the two layers to settle, which gives quick, clear separation, and discard the ether layer. Repeat this solvent extraction process twice to remove almost 100% of the iron in the steel sample. Transfer the aqueous layer to a $250cm^3$ clean glass beaker. Cover with a watch glass, warm gently on a steam bath to remove any trace of diethyl ether from the solution. Cool, add $15cm^3$, 40% $HClO_4$ and fume gently for 15 - 20 minutes until an orange coloured solution develops (of Cr^{6+}) and dense white perchloric fumes form within the beaker. Cool, add conc. ammonia dropwise to form a white rare earth hydroxide precipitate and then add $10cm^3$ in excess. Boil gently for five minutes, cool and either filter through a No. 42 Whatmann filter paper or centrifuge to separate the white precipitate. Wash this precipitate three times with water and then redissolve it in a minimum of conc. HCl. Add caesium chloride solution and make up to $10cm^3$ or $25cm^3$ (depending on mg dm^{-3} desired) with water to produce a solution of caesium concentration 2000mg dm^{-3}. Take

emission readings in a reducing nitrous oxide/acetylene flame at the rare earth wavelengths - Ce 468.4nm, La 593.0nm, Nd 660.6nm and Pr 493.9nm - using a 2000mg dm^{-3} caesium solution as a blank sample. Make up calibration solutions for each lanthanoid element in the range 0 - 100mg dm^{-3} by appropriate dilution of stock solutions and add sufficient caesium chloride solution to form concentrations of 2000mg dm^{-3}. Take emission readings for these calibration solutions under the same flame conditions as the steel samples and construct calibration lines for each rare earth element. The emission readings of the steel samples can then be read on these graphs and the corresponding rare earth concentration calculated.

Method 2

Determination of cerium in mild and low alloy steels

Weigh out 1g steel into a $400cm^3$ glass beaker and proceed as in Method 1 for steel dissolution and solvent extraction of iron.

To the iron-free solution add $50cm^3$, 10M HNO_3 acid and fume down for about 20 - 30 minutes to remove chloride ions present in the solution (test for the presence of any Cl^- ions by testing a drop of the steel solution with $AgNO_3$ solution. No precipitate should form when all of the chloride ions have been expelled). Add 1g (approximately) of dry $KBrO_3$ and allow the vigorous redox reaction to proceed in the cold. Gently bring to the boil and maintain boiling for a few minutes to ensure complete oxidation of CeIII to CeIV. Transfer the oxidised solution to a separating funnel and solvent extract with $25cm^3$ of analar 4 methyl pent-an-2-one (M.I.B.K.) (freshly saturated with 10M HNO_3 as M.I.B.K. absorbs substantial volumes of nitric acid), washing out the beaker containing the oxidised solution with the M.I.B.K. sample. Shake the two layers for a few minutes and allow the two solutions to separate. Retain the organic extract and do two repeat extractions with the aqueous layer, each time retaining the organic layer. Carry out a back extraction on the organic layer using 3 x $25cm^3$ dilute H_2O_2 solution, and retain the aqueous layer. To this aqueous layer add,

in the following order, 15cm^3 saturated citric acid, 25cm^3 100mg dm^{-3} lanthanum solution (use lanthanum nitrate) and 10cm^3 saturated oxalic acid. Adjust to pH 2.7 - 3.0 by adding conc. ammonia dropwise

measuring the pH of the solution after each addition. Care at this stage avoids over-running the correct pH value. Warm the white precipitate so formed on a steam bath for one hour, covering the beaker with a watch glass. Cool and filter through a No. 42 Whatman paper or centrifuge to separate the precipitate. Wash three times with water and then redissolve the precipitate in minimum of conc. HNO_3. Make up to 25cm^3 in a graduated flask with distilled water and take emission readings in a reducing nitrous oxide/acetylene flame at 468.4nm. Prepare calibration solutions of cerium (0 - 100mg dm^{-3}) by taking appropriate volumes of stock cerium solution (use ammonium cerium nitrate A.R.) and add 15cm^3 saturated citric acid, 25cm^3 100mg dm^{-3} lanthanum solution and 10cm^3 saturated oxalic acid. Adjust to pH 2.7 - 3.0 and carry on similar to the steel sample treatment. As in Method 1, take emission readings of these cerium calibration solutions under the same flame conditions as the steel samples and construct calibration lines from which the cerium concentration in the unknown samples can be calculated. In this method the added lanthanum acts as an ionisation suppressor.

6.2 Future Work

The current metallurgical interest in the behaviour of the light lanthanoids (single rare earth or mischmetal addition) in specialised steels creates requirements for more knowledge in the field of lanthanoid chemistry. The need for the development of more specific and faster methods for the determination of rare earth elements in mild and low alloy steels is apparent. Research work in this thesis could be very usefully extended to give improved techniques for their determination. The use of an improved flame emission system, or a non-flame system (e.g. a heated graphite furnace or an inductively coupled plasma), and the development of a more selective and analytically easier lanthanoid separation technique (i.e. a single step solvent extraction or ion exchange system) would significantly improve

efficiency of the method.

Future research ideas can be summarised below.

(a) The series of chemical steps required in Methods 1 and 2 to usefully separate the lanthanoids as a group or cerium as a single element, might be replaced by a highly specific but quicker procedure. Research into the fields of solvent extraction or ion exchange could lead to the development of suitable methods to separate and isolate single rare earth elements, at trace level, from the steel matrix and from the rare earth mixture. Cationic ion exchangers are currently used to separate single lanthanoid elements from mixtures by the variation in the atomic size of these elements in the group. The smaller the difference in size between two lanthanoid ions, however, the more difficult the separation. Research into the area of anion exchange or chelating ion exchange which promises to be more specific, could be useful when considering the analysis of rare earths in steels.

The currently used organic reagents for solvent extraction of the rare earths from various matrices are, in the main, not as specific as desirable for trace analysis; the other matrix elements hamper certain instrumental techniques. Further research into the development of more selective reagents for extraction may provide fruitful results.

(b) One of the potential advantages of an atomic spectroscopic emission technique is the ability, in certain circumstances, to provide a multi element analysis from a single matrix sample. This idea was investigated in Chapter V with a view to developing a method to determine Ce, La, Nd and Pr from a single solution sample. The complex lanthanoid spectra, coupled with the resolution limitation of the available instrumentation, posed considerable difficulties. The use of a mathematical programme involving simultaneous equations to correct for the problem of mutual spectral interference of the rare earths was not, given the limitations of time and instrumentation, successful. The summation of errors involved in such a system proved

troublesome. Research work into this area to determine the relationships of such errors and their potential elimination would be very useful and the possibility of a suitable lanthanoid, multi-element method, may then be in sight. Alternatively, the use of an improved instrumental system to provide better resolution and detection would potentially enable interference-free lines or bands to be used for this type of analysis and then no correction method need be applied.

(c) Further research ideas include the use of the more recently developed instrumental techniques in the field of atomic emission spectroscopy, i.e. the inductively coupled plasma and the heated graphite furnace. The use of the inductively coupled plasma as a possible excitation source for rare earth atomisation, has been reviewed in Chapter I. The obvious advantages of this atom cell for lanthanoid analysis is the high temperatures attainable which would enable the easier atomisation of these highly refractory elements which prove so difficult in lower energy systems. This would enable significantly lower detection limits to be obtained for rare earths, which is very desirable when considering the micro amounts of rare earth mixtures commonly added to specialised steels. The problems of spectral interference and increased levels of complex ion lines produced in the inductively coupled plasma must not, however, be overlooked. Detailed research into the use of the inductively coupled plasma for lanthanoid analysis should prove very useful in providing alternative methods for the determination of lanthanoids in steels and for potentially providing increased knowledge on the understanding of the atomisation process of these refractory elements. Newland and Mostyn (50) have already demonstrated that the inductively coupled plasma provides a useful technique for the determination of rare earths in specialised steels, but the spectral interference problems remained and their method involved the use of spectrographic plates for the determination which made the method rather involved.

The introduction of another novel emission source, the heated carbon furnace, as an alternative to the conventional flame

and the inductively coupled plasma may prove to be a useful system. The three main advantages generally claimed for electrothermal atomisation, compared with flame atomisation, are greater sensitivity; capability to analyse small quantities of sample, and ability to carry out sample treatment in situ. Fuller (54) has given a comparison of detection limits for flame and electrothermal atomisation. He shows that, although considerable improvement in detection limits is obtained by electrothermal atomisation, the levels of improvement are well below the theoretical value. He concludes that the results are lower than expected due to the atomisation process being considerably less efficient in electrothermal atomisers than flames or that the production of atoms in the atomiser is slow compared to their rate of removal. More detailed knowledge about the important factors involved in atomisation from graphite furnaces is, therefore, required and a study of these factors for rare earth elements could form a major research topic for future work. Pyrolytic coatings of the graphite tube have already proved favourable with respect to sensitivity and detection limits for some refractory elements, e.g. Cu, Al and Sn, and so this could be further investigated. Sturgeon and Chakrabarti (96) have suggested that this improvement is due to the lower porosity of the pyrolytic-graphite coating resulting in reduced soaking of these elements into the pores of the surface at high temperatures. This technique could be assessed for its applicability to the rare earth elements and other approaches based on the introduction of a film to the tube surface evaluated. The present use of N_2 of Ar to sheath the graphite tube could be investigated and compared to other gases, e.g. C_2H_2 or H_2. The use of C_2H_2 may introduce increased reducing conditions favourable for rare earth analysis. Research work into this field could lead to a greater understanding of the total atomisation process, in general, and particularly for the rare earth elements. Flame spectroscopy has shown that analytically useful emission signals may be obtained from rare earth oxide species as well as atoms. The use of these emission signals for the successful determination of cerium in steel has been described in Chapter V. Massman (97) has

observed emission oxide spectra and Ottaway and co-workers (98), more recently, have studied the emission of calcium oxide species from a similar furnace. This offers the possibility that rare earth oxide and perhaps other molecular emission spectra may be observed at analytically favourable levels. This might enable both a greater understanding of atomisation mechanisms and analytical data for steels to be obtained. This would then further emphasise the theoretical and practical value of versatility of emission spectroscopy already shown in this thesis with the nitrous oxide/acetylene flame.

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POST - GRADUATE STUDIES AND MEETINGS ATTENDED

Post-graduate Courses

Selected lectures from the M.Sc. Instrumental Analysis Course held at the Chemistry department, Sheffield City Polytechnic, including -

(a) atomic spectroscopy - 28 lectures, and

(b) separation techniques (solvent extraction and ion exchange methods) - 4 lectures.

Meetings

1. Selected lectures held by the 'Modern Methods of Analysis Group' of the Sheffield Metallurgical and Engineering Association.
2. Two meetings of the 'Annual Symposium of the Annual Reports of Analytical Atomic Spectroscopy', (6/1/77 and 5/1/78) at Sheffield.
3. 'Plasma Emission Spectrometry' - Atomic Spectroscopy Group of the Chemical Society (17/5/78) at Salford.
4. 'Instrumental Aspects of Atomic Spectroscopy' - Atomic Spectroscopy Group of the Chemical Society (18/5/77) at Coventry.
5. 'Analytical Techniques in the Steel Industry' - North East Region of the Analytical Division of the Chemical Society, (19/5/77) at the Teeside Laboratory of the British Steel Corporation.
6. 'Safety and Spectroscopy' - Atomic Spectroscopy Group of the Chemical Society (27/6/78 - 28/6/78) at Kings College, Cambridge.
7. 'Analytical Instrumentation' - Atomic Spectroscopy Group of the Chemical Society (15/11/77) at Sheffield.