CONDITION MONITORING

USING

STABLE ISOTOPES

by

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ABSTRACT.

The aim of this project is to assess the feasibility of using rare stable isotopes in a condition monitoring method for detecting excessive damage to key transmission components on a single helicopter / aircraft basis in the field.

Condition monitoring techniques currently available are reviewed and examples given of industrial applications. One technique, termed thin layer activation, involves labelling the component with a radioisotope and determining its state by monitoring the level of radiation. However, this technique has not been used 'in the field' but only for development applications because of the problems associated with radiation. In order to overcome this a method is investigated based upon the detection of certain stable, rare isotopes namely nitrogen-15 and carbon-13.

This project has three clearly defined stages : the incorporation of the stable isotope into the steel components; the generation of wear debris; and finally the detection of the isotope by analysis of the debris. There are several possibile ways of achieving each of these, and at each stage these are considered before selecting the most

suitable method.

The development of a monitoring method based on the detection of nitrogen-15 is described. Plasma nitriding is used to incorporate the isotope into a steel surface, a cone-on-roller wear machine is used to generate wear debris from the nitrided surface in preparation for nitrogen analysis. Finally the isotope contained in the debris is detected by infrared spectroscopy with secondary ion mass spectrometry investigated as an alternative. Experimental details and results for each stage in the development are given.

A method is proposed for the detection of carbon-13 but no experimental back-up has been carried out.

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LIST OF CONTENTS.

LIST OF FIGURES.

PAGE

PAGE

LIST OF TABLES.

LIST OF PLATES.

CHAPTER 1 INTRODUCTION.

Industrial breakdowns are expensive in terms of loss of production, maintenance and repair costs and in certain situations, such as in the aerospace industry, can cause loss of human life. When such a breakdown occurs it is therefore vital to establish its cause. This allows for remedial action to be taken to prevent a similar situation from arising again, thereby increasing the life, reliability and performance of the engineering system. Several failure analysis techniques are available to achieve this but in recent years it has been recognised that it is preferable to prevent failure by predicting its onset rather than to have to cure it. With this in mind monitoring methods have been developed, some based on failure analysis techniques, to determine the condition of tribological components in engineering systems.

A review of currently available monitoring methods is given in Chapter 2 together with their application to Industry. Each of the different techniques have certain advantages and limitations and therefore when selecting a technique it is necessary to consider many aspects such as the engineering system, the type of information required,

the volume and type of sample available and the time and cost involved. Certain techniques are complimentary and often it may be necessary to use two or more techniques to fully assess the situation. A review of the literature outlined in the next chapter reveals a need by industry for a monitoring system which is simple, quick, on-line and has the ability to determine which of a number of tribological components is suffering damage. One technique which comes close to fulfilling these requirements is thin layer activation. However, because of the safety problems associated with radiography and widespread public prejudice against radioactivity its major disadvantage is one of acceptance. Thin layer activation is currently confined to use in laboratory development applications.

In certain applications, such as clinical and environmental work where there is a high risk to health caused by radiation, radioisotopes are often complemented by stable but rare isotopes. With this in mind the aim of this project is to investigate whether it is possible to monitor the progression of wear of steel components labelled with stable isotopes as opposed to radioactive ones. The stable isotopes under consideration are carbon-13 (C-13) and nitrogen-15 (N-15) whose more abundant isotopes, C-12 and N-14, are used in case-hardening gear steel. In order to assess the feasibility of this concept the project has been subdivided into three sections:

(i) incorporation of the stable isotope into the surface of steel component;

(ii) generation of wear debris, thereby removing the isotope from the component;

(iii) detection of the stable isotope.

There are several possible ways of achieving the above and these are discussed in Chapter 3. After selecting the optimum methods for each of the three categories these were then evaluated by laboratory experiments as detailed in Chapters 4, 5 and 6 respectively.

Finally, in Chapter 7 the practicability of using stable, rare isotopes in monitoring is critically assessed in the light of work carried out.

CHAPTER 2. LITERATURE SURVEY.

Several methods have been developed to monitor the condition of engineering systems in order to enable them to be operated and maintained with safety and economy. A review of such methods is given in the first section of this chapter together with their application to Industry.

The second section deals with stable isotopes and describes their function in the research and development environment.

2.1. Condition Monitoring.

In 1966, a survey of the application of tribology to British Industry revealed that savings in the order of £500m per annum were plausible, with the greatest benefits arising from savings in maintenance and replacement costs and the prevention of breakdowns (1). The cost of a breakdown in terms of loss of production and repair costs is considerable in an economic sense but can be catastrophic in situations where loss of life may result as , for example, in the aero- space industry. Therefore, when a failure does occur it is important to establish the cause. This enables remedial action to be taken which may also lead to improvements in the design of a system, thereby increasing its life, reliability and performance (2).

Various investigative techniques are available for failure analysis such as optical examination of component surfaces, metallographic examination of sub-surfaces and the examination of debris and lubricant contamination. However, from an economic point of view it is preferable to be able to prevent a failure by predicting its onset. Benefits obtained by industry on applying a condition monitoring programme include (3) :

- increased machine availability, thereby improving production
- reduced maintenance costs

- improved operator (and passenger) safety
- more efficient plant operation and more consistent quality
- better customer relations by avoiding inconvenient breakdowns
- design improvements.

With this in mind several techniques have been developed for monitoring the tribological condition of engineering systems, which can be categorised into four basic methods, namely visual, performance, vibration and wear debris monitoring (3) :

(i) Visual monitoring.

Visual inspection is usually applied to stationary components but is limited by direct eye access. Methods are available to assist the inspection such as light probes, boroscopes, dye penetrants and infra red thermography.

(ii) Performance monitoring.

The performance monitoring of machinery involves measuring the quantity or quality of output or the relationship between input and output, for example in terms of fuel or power consumption, flow/pressure ratios. This method tends to be insensitive in terms of detecting incipient machine failure because many serious component defects become quite advanced before they produce a measurable effect on the machine performance.

(iii) Vibration monitoring.

Vibrations (and noise) arise from cyclic excitation forces within a machine which are inherent in its design or can arise from the propagation of some defect, and therefore a study of the nature and magnitude of the vibrations or noise can indicate its mechanical condition. Analysis of the spectrum of frequencies of the vibration waveform provide a warning of machine deterioration and help to diagnose the nature of the defect. Vibration and noise monitoring techniques are generally applied to rotating machinery rather than to reciprocating machinery.

(iv) Wear debris monitoring.

Wear debris monitoring methods are normally applied to monitor components lubricated by a circulatory oil system. They involve monitoring machine lubricants for the presence of wear debris generated by wear processes at the relatively moving surfaces of load carrying components such as bearings, gears, pistons, to provide advance warning for the many failures of lubricated surfaces which are progressive in nature, rather than sudden.

The choice of monitoring technique for a given application is dependent upon the engineering system, the type of information required, the volume and type of sample available, the time involved and the cost involved (4,5).

Programmes can be developed to monitor a complete plant, key machines only, or a few critical components of key machines. Only the latter two are generally applicable to industry (3).

A detailed description of those methods developed for lubricated systems is given in the next few sections. Other methods, such as performance and vibration monitoring, which are generally applied to machines as opposed to individual components within the machine, were considered to be outside the scope of the aim of this study. This aim is to develop a technique to assess the condition of key tribological components based on the detection of stable isotopes.

Those monitoring techniques reviewed in this survey can be sub-divided into two major types namely analysis of the lubricant and analysis of the state of the solid surfaces.

2.1.1. Lubricant Chemical Analysis.

Lubricant analysis can be used to provide two types of information. Firstly it can indicate whether a lubricant change or readjustment is required by monitoring its quantity and quality (6). The quantity of oil can easily be measured by physical means such as a dip stick or float system and oil pressure gauges and oil flow meters are available to ensure that sufficient oil is reaching the components.

A lubricant is selected for the required application on the basis of its physical and chemical properties, but during service these properties can deteriorate to such an extent that the lubricant no longer performs its intended function. The Institute of Petroleum have published standardised tests to measure the lubricant properties which can be used to monitor the extent of the deterioration of the lubricant (7). Such tests include the measurements of viscosity, degree of oxidation (from the Total Acid Number (TAN) or Total Base Number (TBN)), water content, flash point, insoluble materials content and additive derived metals content.

It is clearly very important in such tests to ensure that the lubricant sample is representative of the system and not drawn from stagnant or non-typical regions.

A second, and equally important use of lubricant analysis is to monitor solid surface damage by measuring the quantity and nature of metal originating from the surfaces in the form of wear debris particles. This analysis is generally carried out spectrographically as will be described in the next section.

2.1.1.1. Spectrographic Oil Analysis.

Spectrographic oil analysis is primarily concerned with the elemental analysis of the metallic wear products suspended in oil. It is possible to detect metal concentrations of the order of 1 ppm by this means. The selection of the metals to be analysed is dependent on the system being monitored, typical examples include iron, chromium, aluminium, magnesium, copper, zinc, sodium, silicon (5,6). An assessment of the metal concentration in the lubricant, combined with a knowledge of the chemical composition of the lubricated components, assists the analyst in monitoring the wear of a component such as a bearing, gear, cam, tappet, cylinder or shaft. An example of this is given in table 2.1 which summarises the possible sources of the wear materials present in the circulating

lubricant of a diesel engine which are detected by spectroscopy (8). A sudden rise in the concentration of a wear element could be indicative of a possible impending failure.

TABLE 2.1 : Sources of Wear Material Detected by Spectroscopy(8).

Metal	Sources
Aluminium (Al)	Pistons, bearings, turbo charger casing
Copper (Cu)	Bearings
Chromium (Cr)	Piston rings, cylinder liners
Iron (Fe)	Cylinder liners, crank shaft, auxiliary drive, piston rings, camshaft
Lead (Pb)	Bearings
Molybdenum (Mo)	Piston rings
Nickel (Ni)	Valves
Silver (Ag)	Bearings
Tin (Sn)	Bearings
Silicon (Si)	Ingested dirt, core sand

For most applications, iron is the most important element and the choice of instrumentation used for the analysis of the oil depends upon the amount of iron present. Generally, atomic emission spectroscopy is preferred for relatively dirty systems where the iron content is greater than about 20 ppm whereas atomic absorption spectroscopy is used for cleaner systems (9). This has the advantage of cheaper, less complicated apparatus and is more sensitive than the emission spectrograph. The semi-automatic spectrographs generally used for oil analysis can detect and measure the concentration of ten or more wear metals both quickly and cheaply. During spectrographic oil analysis on British Rail diesel engines oils, twelve metals are normally determined simultaneously; four of these being present in oil additives (Zn, Ba, Ca, P) and eight arising from wear, corrosion and extraneous contamination of the oil (Fe, Pb, Si, Cr, Al, Na, Cu, Sn) (9).

A major limitation of spectrographic oil analysis is the upper limit of the particle size that can be detected. Particles greater than 2 μm in size are not atomised and therefore not detected. Consequently the results are dependent upon the particle size distribution which changes during the progression of wear (10). Generally, the ratio of large to small wear particles increases with time. Consistent results are only obtained if the increase of wear

product concentration in the oil samples is proportional to the component wear rate. Also false variations in the measurements of the contamination levels can occur if a standard sampling procedure is not followed (6). Whilst an indication of the rate of wear and possibly what is wearing is given by spectrographic oil analysis, it offers no information on the mode of wear, nor any warning for those wear mechanisms that produce very little wear debris before rapid failure, such as rolling contact fatigue (5).

Recent advances in spectrographic oil analysis have led to the development of automatic systems. An inductively coupled plasma (ICP) emission spectrometer system has been designed and basically consists of two major sub-systems : an automatic injection and dilution system which provides for the unattended introduction of the untreated oil samples into the plasma excitation source; and a specialised operating package, PlasmaComp II, which executes any combination of optical alignment, calibration, standardisation, analysis, storage, data transmission and statistical analysis (11,12). The instrument is capable of automatically analysing eighty samples per hour for up to sixty elements (4800 elemental determinations). A sophisticated laboratory system has been developed by Spectron (13a,b). Atomic emission spectroscopy, infrared spectroscopy and viscosity measurements of the lubricant are taken under the control of a network of small computers.

Other computers with network access to central files assess this data in terms of equipment and lubricant characteristics and prior equipment history. The system claims to be "able to diagnose nearly all lubricant-related causes of abnormal wear and to make maintenance recommendations to allow for remedial action to be taken".

2.1.1.2. Chemical Microsensors.

The Naval Research Laborotories in Washington are currently developing chemical microsensors which are small, rugged, inexpensive and yet sensitive enough to detect trace quantities of specific chemicals in ship and aircraft environments (14). These microsensors have many potential applications including the analysis of engine lubricants and could possibly be used in situ to monitor such parameters as additive depletion rates, appearance of lubricant degradation products and the outgassing of low molecular weight volatile products. All of these can be related to engine performance. The microsensors make use of the recent techniques in electronic microfabrication, integrated circuitry, micro computer process control and data analysis in order to detect and monitor the chemicals, but are not yet commercially available.

2.1.2. Analysis of the State of the Surfaces.

In order to analyse the state of the solid surfaces directly in a complex machine it is usually necessary to dismantle it. However, this procedure is time consuming, expensive and involves a danger of failure during run-in after re-assembly. Such routine maintenance is generally carried out on a fixed-time basis and is therefore sometimes unnecessary, but the monitoring of the condition of the machine allows for essential rather than periodic maintenance (4,5).

Many different types of monitoring techniques have been developed to examine the state of the tribological components 'in-situ'. These include vibration analysis (15), sonic emission measurements (16), neutron activation analysis (17), thin layer activation analysis (18), wear debris analysis (19).

Detailed literature on all the different techniques is available. However, for the purposes of this study only those techniques developed specifically for lubricant-based systems have been reviewed, in particular wear debris analysis techniques and radioactive isotope tracer techniques.

2.1.2.1. Wear Debris Analysis.

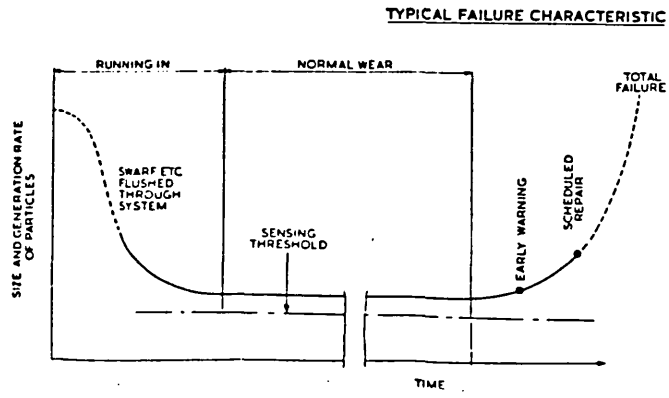
Wear is defined as "the progressive loss of substance from the operating surface of a body occurring as a result of relative motion at the surface" (20). The wear processes encountered in an engineering system are usually sub-divided into five main types : abrasive wear, adhesive wear, erosion and cavitation, and chemical wear. However, in most practical situations more than one wear process will be in operation at any given time. Fretting for instance can exhibit adhesive, abrasive, fatigue and chemical aspects of damage, either operating consecutively or simultaneously. The mechanisms of the different wear processes such as they are understood are described in detail in the literature (20,21,22).

Wear occurs by surface interactions at asperities and results in the generation of wear debris for the majority of wear mechanisms. The wear debris particles exhibit certain characteristics identifiable with those mechanisms (19,23). Rubbing wear particles have the form of platelets and indicate normal permissible wear. However, the presence of miniature spirals, loops and bent wires is indicative of a severe, abrasive wear process. A sudden increase in the

concentration of such particles signals the imminent failure of the machine. Spherical steel particles are associated with fatigue crack propagation in rolling contacts. A rapid increase in the quantity of particles and particularly the ratio of large to small particles indicates the initiation of a more severe wear process.

The size distribution of the wear particles ranges from sub-micron to hundreds of microns in plane dimension. Determining the concentration of small particles which remain in fluid suspension provides a measure of the progression on a cumulative basis. Figure 2.1 illustrates a typical characteristic curve of the size and generation rate of particles leading to a failure (24). The final stages of failure of a system are generally signalled by some increase in both the size and production rate of debris particles.

FIGURE 2.1 : Wear Debris Characteristic, Bath-Tub Curve.



Thus, sampling from a lubricant system provides reliable indications of the build-up of the small size particle conentration and this readily permits monitoring of the wear condition with time. It should be noted that larger particles (greater than 1 μm) do not remain in suspension, so analysis of a sample of lubricant on this basis tends to reflect an instantaneous (not cumulative) wear state.

Position, method and time of sampling represent important aspects in determining the true wear condition and its progress. Samples should preferably be taken during machine operation or immediately after shutdown to ensure that they are representative of the lubricant circulating system.

A number of different methods have been used to examine and measure wear debris particles. These are now briefly described followed by examples of their application to industrial situations.

2.1.2.1.1. Microscopic Techniques.

Contaminant particles can be separated from the lubricant using a centrifuge and then examined by optical and electron microscopy. The number and size distribution of the particles can be determined using a quantitative television microscope and their composition may be determined by electron diffraction, X-ray diffraction and electron probe X-ray microanalysis techniques (19).

Electron optical microscopy has also been used to study the degradation of polymeric fibres contained in the lubricant due to the lubricant additives and the interaction between the lubricant and the solid surfaces (2).

A simple, qualitative device has recently been evaluated, by the Fluid Power Research Centre at Oklahoma State University, termed the Conpar system (25). It provides a method for the rapid on-site evaluation of particulate contamination levels in fluid and lubrication systems. A fluid sample (100 ml) is passed through a filter membrane which is then 'sandwiched' between two glass slides. The membrane is rendered transparent by a mountant solution present on one of the slides and this sample slide

is then compared to master slides which are contaminated to a known level thus enabling a qualitative and semi-quantitative assessment of the particle density to be made. Further, more detailed evaluations of particle shape, size and colour are possible to provide information concerning the source and material of the particles as well as the wear mechanisms taking place which resulted in their formation.

One of the major problems with microscopic examination is the agglomeration of particles which could give rise to a false impression of the particle size and number, and could cause some particles to be obscured by others. This problem has been overcome by the development of Ferrography.

2.1.2.1.2. Ferrography.

An investigation to find an improved method of analysing the lubricating oil of jet engines resulted in the development of the Ferrograph (26). The object of the investigation was to develop a method which would require

less apparatus than existing spectrographic systems and produce a system that would provide earlier warning of an impending failure. Generally the standard, simple methods were not sensitive enough and the sensitive methods were not simple enough.

The principle of Ferrography involves separating ferrous wear debris from the lubricant according to its particle size by means of a high gradient magnetic field (26,27). Two types of Ferrograph analysers are available : the Direct Reading (DR) Ferrograph and the Analytical Ferrograph.

DR Ferrography simply measures the optical densities of deposits in selected particle size ranges thereby enabling the severity of wear index, I_S, to be calculated. I_S is defined as

$$I_S = (A_L - A_S).A_L$$

where A_L is the area % coverage of large particles in the 20 to 30 μm size range and A_S is the area % coverage of particles in the 1 to 2 μm size range. As the operating wear modes become severe, the ratio of large to small

particles increases and therefore I_S increases.

Analytical Ferography produces ferrograms, whereby the debris is arranged according to its size distribution onto a transparent substrate, with particles larger than 5 μm being deposited at the entry point on the slide and the remaining particles down to 1 μm being deposited according to particle size. Optical density readings can be taken at selected size ranges to determine the concentration and size distribution of the particles. Morphological information is obtained with the aid of a bichromatic microscope which uses simultaneous reflected red light and transmitted green light. Metal particles reflect red light and block green light and therefore appear red, whereas particles such as sand allow much of the green light to pass and appear green or, if they are relatively thick, yellow or pink. Examination of ferrograms using a scanning electron microscope can reveal specific characteristic details of wear particles which can be identified with the specific wear mechanisms as described earlier. X-ray energy analysis in the scanning electron microscope and electron probe X-ray microanalysis provide a means of determining the material of the wearing component. It is possible to differentiate between certain metallic materials by observing the colour

changes due to the progressive heating of the ferrogram (8). At 320 °C low carbon alloy steel changes to blue, cast iron is straw coloured whilst even after heating to 500 °C chromium, aluminium, lead and molybdenum remain white.

Ferrography has been used in research on lubricants, in the study of wear mechanisms and as a means of monitoring the condition of systems as diverse as gas turbines, hydraulic and geared systems and in the medical field for the separation of cartilage in synovial fluid. Generally, the less expensive DR Ferrograph is used for on-site machinery condition monitoring and when required a more comprehensive ferrographic analysis can be carried out to determine more detailed information.

There are certain problems involved with ferrography which can only be resolved by time-consuming and costly procedures. Such problems include a lack of repeatability of ferrograms due to variation in the pumping action of the peristaltic pump and also the difficulties in obtaining reproducible dilutions of the oil sample. The squeezing action of the pump on the tubing may cause the mechanical degradation of the particles. Blockage of the tubing due to large particles can also occur. Other problems encountered

include particle 'pile-up' in the entry region, deposition of unwanted 'foreign residue' deposits and fluid breaking through the mechanical barrier.

Whilst the time and expense of a ferrographic analysis is justifiable in a research and development application, for industrial condition monitoring purposes a technique which is rapid, simple and relatively cheap would be preferable. This has led to the development of the Rotary Particle Depositor (RPD), which is described in the next section, as an alternative procedure for depositing particles onto a substrate (28).

2.1.2.1.3. Rotary Particle Depositor.

The RPD consists of a magnet / slide arrangement which can be rotated by means of a variable drive unit such that the deposited sample fluid flows radially outward and the particulate content is deposited on the slide as a series of concentric rings. Sample dilutions are not necessary, but for samples containing only a low concentration of debris it is sometimes necessary to increase the quantity of sample.

The whole sequence of operations, namely deposition, washing and drying, takes approximately 5 to 10 minutes (28).

Price and Yardley have evaluated the RPD in the monitoring of gear transmissions used for mining (29). They have shown that this technique is superior to ferrography in this application where a large amount of debris is produced.

2.1.2.1.4. Magnetic Plugs.

Magnetic plugs rely upon the attraction of ferromagnetic debris to a highly magnetised probe inserted in an oil-way. Regular examination of the plug by visual and magnetic means enables a trend to be plotted relating the mass of the total debris to the wear condition of the system being monitored. Individual pieces of debris can later be examined by the microscopic techniques described earlier and the region from which they originated can be identified by their shape and mechanical constituents. The major drawbacks of this relatively simple on-line technique are the catch efficiency of the collecting devices and the 100 μm lower limit particle size (24). Only ferrous particles are collected but by using special filters in conjunction with the magnetic plugs all other particles down

to the mesh size of the filter can also be collected and retained for further analysis (3).

2.1.2.1.5. Quantitative Debris Monitoring Systems.

Tranducers can be positioned on the head of probes to provide a continuously variable electronic signal proportional to the mass of the captured wear debris. Requirements for the on-line wear debris transducers include (30) :

- on-line mode of use
- low cost
- simple to install
- maintenance free and reliable
- response to a wide range of particle sizes
- good environmental performance
- collection of debris for subsequent off-line analysis if required.

Various systems have been developed including the optical oil turbidity monitor, an electrically conducting filter, inductive detection methods and capacitative detection

methods (31), though they are not yet generally available on a commercial basis (3). Measurement errors can arise due to the detection of air bubbles and extraneous particles other than the critical wear particles.

The optical oil turbidity monitor uses the principle of light scattering to detect all particulate debris and light attenuation for chemical / thermal degradation of the lubricant. Whereas an electrically conducting filter traps and indicates any debris in the oil that is electrically conducting. The filter mesh screen is usually designed to be insensitive to normal wear debris, and therefore indicates the generation of abnormally large particles only. An inductive detection transducer relies upon the attraction of ferromagnetic debris into an 'air' gap in a magnetic circuit, resulting in a change in the circuit reluctance and a change in an induced electrical voltage which is proportional to the quantity of metal particles present in the gap. Capacitative debris sensors operate on the principle that any metal particles between the plates of a capacitor will alter its AC capacatative coupling.

Tauber and Howard (32) report on a quantitative debris monitoring (QDM) system based on the inductive detection of ferrous wear particles. It is composed of a sensor mounting chamber, a debris sensor, a sensor signal preamplifier (integral with the sensor for applications where lubricant

temperature is below 125 °C) and a signal conditioner and data processor (dp) unit. It monitors the rate of debris generation and the total amount of accumulated debris and is able to discriminate between different particle sizes.

This QDM sensor consists of a permanent magnet and coil assembly and performs two functions : the capture of ferrous debris and the generation of an output signal proportional to the mass of the captured particle. The output signal is a measure of the magnetic flux changes due to variations of magnetic field which is caused by the captured debris. Incoming pulses are classified into two categories representing particles larger than 5 µg (which is equivalent to a 200 µm size bearing spall flake) and particles larger than 40 µg (which is equivalent to 1000 µm). The sensor is unaffected by air entrained in the lubricant or by flow rate variations and it also retains the ferrous debris for subsequent analysis. This allows for off-line determination of the source of the particles and the verification of the severity of the impending failure.

This QDM system has been evaluated on numerous airborne and ground based turbine engines and gearbox monitoring applications. One such system is currently in operation on an off-shore gas pumping rig to monitor the industrial turbine engine used to provide the hot gas required to drive a turbine and pump assembly and pump the natural gas

on-shore (32). The purpose of this installation is to obtain data on the initiation and progression rate of turbine engine bearing failures and to provide advance warning of impending engine failures in time to permit scheduled maintenance action and eliminate unplanned pumping interuptions. Other QDM diagnostic systems are in production for the Westland W-30 helicopter.

2.1.3. Radioactive Isotope Techniques.

The first recorded information on the application of radioisotopes for evaluating wear was by Ferris in 1943 (33), where radioactive phosphorus was added to a melt of steel and the piston rings made from the steel were installed in a test engine.

In 1947, Stanley reported work involving radioactive carbon which was designed to test current theories about the mechanism of carburisation and the action of energisers using the pack carburising technique (34). The test confirmed the mechanism of carburising in the presence of the energiser, barium carbonate $BaCO_3$, as shown below (where *C = 'labelled' C):

$$Ba^*CO_3 + C \longrightarrow BaO + 2^*CO$$

$$2^*CO + \text{iron} \longrightarrow {}^*CO + {}^*C_{(\text{in iron})}$$

$$BaO + {}^*CO \longrightarrow Ba^*CO_3$$

The initial research into the use of radioisotopes in studies of friction, lubrication and wear has been extensively reviewed by Lancaster (35) and Kohl et al (36). More recent research developments in tribology have involved studies in a wide range of applications including :

- wear rate measurements of rubber by neutron activation analysis (37)
- wear in the friction cutting of cast iron using thin layer activation (38)
- the measurement of cam follower wear (39)
- the effect of .gamma. irradiation on the friction and wear of ultrahigh molecular weight polyethylene (40)
- the measurement of tool flank wear (41)
- monitoring internal combustion engines (42)
- investigations into the effects of additives upon layering, friction and wear (43)
- the effect of gamma-irradiated polyethylene powder as lubricant additive (44).

The use of radioisotopes in condition monitoring has been developed in response to a need by industry to detect very small amounts of wear and corrosion without dismantling apparatus and machinery (45,46). A component is made radioactive which then undergoes radioactive decay to produce gamma rays which can be detected through material layers which may be several inches (iron equivalent) in thickness. Wear measurements of activated samples can be carried out by two different methods. Radioactive material can be monitored as it appears in the lubricant in the form of wear debris as a result of wear and corrosion. Conlon

claims that the sensitivity for wear measurements by this method can be as high as 0.025 μm (45). Alternatively the rate of wear of a component can be monitored by the loss of radioactivity of its surface as a result of the formation of wear debris with time. A sensitivity of 0.2 μm is claimed.

Radioactive samples can be generated either by neutron activation analysis (NAA) or thin layer activation analysis (TLA).

2.1.3.1. Neutron Activation Analysis.

The component is exposed to neutrons which interact with its nuclei. The activated nuclei then undergo various nuclear reactions of which the (n,γ) type are considered the most important in NAA. Emitted radiation is detected by gamma spectrometry (47).

The total radioactivity of the activated sample is high and special precautions must be taken in its handling and also in its disposal after use.

In recent years the TLA method has superceded NAA.

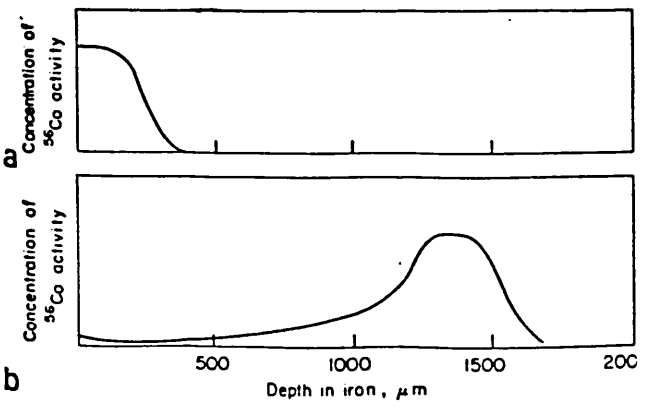
2.1.3.2. Thin Layer Activation.

This technique has been developed by a team of research workers led by Conlon at AERE Harwell (45,46). The component of interest is bombarded by a high energy ion beam, thus producing a thin layer of radioactive atoms. For example, if iron is irradiated with a 13 MeV proton beam radioactive cobalt is produced :

$$^{56}Fe + p \longrightarrow {}^{56}Co + n$$

The penetration of the beam is dependent upon its energy and the type of ion used as illustrated in figure 2.2 (45).

FIGURE 2.2 : (a) Surface Activation by 13 MeV Protons. (b) Sub-Surface Activation by 30 MeV Protons.



Total depth of activation of the component can be chosen to be comparable to the anticipated wear range. Also it is possible to focus the ion beam into a small surface area so only small amounts of radioactive material need be produced (typically 1 to 10 microcurie). Both of these factors ensure that the radiation level is kept low.

The detection system consists of a gamma ray probe (for example, a NaI scintillation crystal) and a shelf of electronics which is portable.

(i) Advantages of TLA.

- This technique is sensitive enough to detect low levels of wear and corrosion.

- Penetration of the ion beam into material is comparable to depth of wear tolerated in many situations before replacement of a component becomes essential.

- It is possible to measure the wear or corrosion of inaccessible components under operating conditions without having to dismantle the machine.

- The absolute amount of radioactivity involved (1 to 10

microcurie) is relatively small.

(ii) Limitations of TLA.

- This method is not used to continuously monitor wear over the full working life of a component. It involves testing over relatively short periods (about one year), then making large extrapolations to the full working life.

- The activation process can only be carried out by high energy particle accelerators (for example, the Tandem accelerator at Harwell) which are relatively costly and therefore favour batch processing.

- By activating the surface layer of a component, its chemistry is altered. Consequently, the doped material may behave differently under operating conditions and therefore it is important to determine experimentally whether there are any significant changes (40).

- Only a small proportion of the surface area is irradiated so that any wear occuring outside this area will go undetected.

- Removal of material from the surface by wear or corrosion can only be accurately measured if it is

uniform over the active area. This is not always the case. However it may be possible to overcome this using the double layer activation technique which is described below (48).

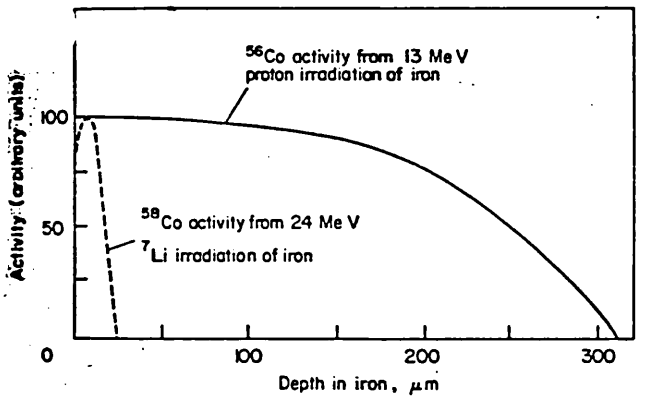
(iii) Double Layer Activation.

This technique was developed as a means of detecting non-uniform wear or corrosion, such as the formation of deep pits. The sample is labelled with two (or possibly more) radionuclides to different depths by ion beam activation. This can be achieved either by two different ion beams or by a single beam which will undergo two relevant reactions. An example of the latter is the action of a 12.5 MeV deuteron beam on iron resulting in the two following reactions :

$$^{56}Fe + d \longrightarrow {}^{57}Co + n$$
$$^{56}Fe + d \longrightarrow {}^{56}Co + 2n$$

The activity-depth profiles for ^{56}Co and ^{57}Co are shown in figure 2.3 (48). Determining the ratio of emitted radiation due to ^{57}Co and ^{56}Co provides an indication of the extent of wear.

FIGURE 2.3 : Comparison of the Activity Depth Distribution for ^{58}Co Produced by 24 MeV ^{7}Li Irradiation of Iron and ^{56}Co Produced by 13 MeV Proton Irradiation of Iron.



2.1.4. Examples of the Application of Condition Monitoring Techniques in Industry.

2.1.4.1. British Rail.

British Rail (BR) have been using lubricant analysis techniques to monitor the state of their fleet of diesel engines for many years (49). Typical diesel engine lubricant contaminants include wear debris, ingested dirt, carbon from a combustion process, polymers / fibres from filter and gasket materials, diesel fuel and coolant. The lubricant analysis is divided into two categories : determination of the physical properties of the oil; and elemental determination by spectrographic analysis.

BR policy is to apply spectrographic analysis when a new type of engine is introduced in to service in order to establish the wear rates and overhaul periods and also to highlight specific problem areas. Remedial action can then be taken, possibly by the introduction of design changes, in order to overcome any problems. This can result in the termination of the spectrographic oil analysis programme for that particular type of engine as is the case with the majority of the main line locomotive fleet.

The use of spectrographic oil analysis on high speed

train (HST) engines has resulted in an approximate annual saving in excess of £1.5 m on repair costs (49), the annual cost of an analysis for one engine is £500 and for the fleet £100,000.

BR investigated the technique of ferrography as an alternative to spectrographic oil analysis in the condition monitoring of HST engines in service by analysing crankcase oil samples (9). Results of the investigation revealed that ferrography was of no benefit whatsoever in this application, largely due to the fact that problem areas in the diesel engine are often caused by soluble compounds (such as coolant salts or products of corrosion) which ferography can not detect. Therefore, spectrographic oil analysis will continue to be a valuable technique for monitoring diesel engines despite its drawbacks, namely that it will not detect failures which do not generate metallic elements (for example, fatigue cracks) and that it does not provide direct information on the location of the problem. A careful appraisal of the situation is necessary to ensure that action is taken before catastrophic failure but that early abortive examinations are minimised. This could possibly be achieved using ferrography as a complementary technique by carrying out a full analytical ferrographic analysis when the spectrographic trend analysis indicates a problem (8).

2.1.4.2. British Coal.

The Mining Research and Development Establishment (MRDE) division of British Coal carried out a test programme to assess the use of ferrography and spectrographic oil analysis to monitor the condition of fairly large and relatively unsophisticated industrial machinery, such as a 90 kW conveyor gearbox, as an alternative to its periodic stripping and inspection (50). Although spectrographic oil analysis was found to be more successful than ferrography in detecting and predicting failure it was considered that the sensitivity of the ferrograph could be improved. Results from this investigation were considered sufficiently encouraging to allow for a more detailed comparitive evaluation of a number of machine health monitoring tests to be carried out with a view to providing a practical health monitoring package for the coal board type gearboxes. The parameters under evaluation were temperature, vibration, oil condition, power and torque and the results, which have been reported by Lewis (51), indicated that vibraton and oil condition analysis held the greatest potential. Field experience of vibration analysis is much less advanced than oil debris analysis due to the complexity of the analysis. Therefore, further development work involved using wear debris analysis, namely ferrography, as a means of monitoring underground gear transmissions.

The level of wear debris and other contaminant particles in underground transmissions is very high, and even after a dilution factor of 100 : 1, the examination of ferrograms was found to be difficult due to the overlapping of particles and the deposition of rock and coal particles. Also, the ferrograph was considered too complex for use at colliery level and therefore expensive centralised laboratory facilities would be needed. Despite these shortcomings, ferrography was still considered the best pre-emptive technique so far developed for this application.

To overcome these problems the MRDE developed a technique called the Debris Tester which quantifies the amount of ferrous wear debris in oil samples, and is sufficiently rapid and simple for use at collieries. It is based on an instrument developed to quantify the amount of material collected on magnetic chip detectors and operates on an eddy current principle. This technique is described in detail by Moreton and Yardley (52) and has been undergoing service trials at a colliery in the North Nottinghamshire Area since 1983.

2.1.4.3. Central Electricity Generating Board.

The Central Electricity Generating Board (CEGB) criteria for condition monitoring include (53):

- the monitored equipment / machine is critical to the operation of the industry and the cost of plant failure is high.
- the equipment or machine will normally have a long life-span with little change in its working environment or condition.
- it has unimpeded access for monitoring with sophisticated systems.
- often the condition monitoring facility is shared between a large number of machines.

To ensure the safe and efficient operation of turbine generator sets several monitoring techniques are applied to specific components such as the white-metalled journal bearings and seals. Such techniques include vibration monitoring and clearance monitoring which are very effective in indicating an imminent catastrophic failure. The type of failure arising in this situation is often rapid and is generally caused by either the persistent overloading of a bearing or the interuption of the oil supply resulting in a breakdown of the oil film. The bearing can tolerate a substantial amount of damage if it continues to be fed with

a copious supply of lubricant as might arise if it is transiently overloaded. Hence the primary concern has been to monitor the pressure and temperature of the lubricating oil feed.

Nevertheless, wear debris analysis techniques might be of use in predicting certain potentially damaging situations which might arise in turbine generator sets. These situations include the so-called 'wire-wool' failures associated with high chromium shafts, electrical discharging or cavitation at bearing surfaces, fatigue cracking of the white metal, excessive corrosion of the system and the presence of abrasive matter in the oil.

Lloyd and Cox have reported on the wear debris analysis work carried out by the CEGB to establish the 'normal' lubricant conditions of operational turbine generators (53). Examination of the debris has shown that monitoring the level of tin (or white metal) by spectrographic analysis can reveal damage to the bearings and hydrogen seals, thus allowing for remedial action. Several on-line techniques to automatically monitor tin in oil were investigated (such as X-ray fluorescence and capacitative transducers) and were found to be inadequate. Based on these findings, the monitoring procedure favoured by the CEGB is a simple on-line filtration technique which allows for variations in the amount of debris to be monitored in order to draw

attention to changes in condition, followed by off-line techniques using centralised, sophisticated analytical equipment to diagnose the significance of any change and long-term trends.

Bogue reports on a new wear debris transducer which has been developed in close collaboration with the CEGB (30). The transducer head is attached to a magnetic plug and is designed to operate on-line to capture and quantify metallic wear particles in power generation plant. Results of the development test work indicate that the majority of the criteria identified in section 2.1.2.1.5 may be satisfied.

2.1.4.4. Royal Navy.

The Naval Aircraft Material Laboratory provides a condition monitoring service for Royal Naval aircraft assemblies (54). A variety of techniques are regularly used including :

- Spectrographic oil analysis (SOA) techniques, namely atomic absorption, atomic emission and an inductively coupled plasma spectrometer, have been in use since 1968.
- Analytical ferrography has been used since 1975 in conjunction with SOA for monitoring some gas turbine and helicopter gearboxes.
- Magnetic plug and filter debris is evaluated by microscopic techniques and electron probe X-ray microanalysis.
- Vibration analysis is used for the monitoring of helicopter rotors, transmission gearboxes and gas turbine engines.

DR-ferrography is currently under evaluation as part of a package to provide in-field monitoring for specific high-risk components. It is necessary to ensure that suitable representative lubricant samples can be obtained.

Factors such as oil filtration and particle settling which preferentially remove the larger particles affect this technique considerably.

2.1.4.5. United States Air Force.

Under current United States Air Force (USAF) operational procedure SOAP is used to detect abnormal wear in gas turbine engines. However, the use of a continuous 'in-flight' monitoring system would eliminate the problems encountered by SOAP namely the analysis of lubricant samples during aircraft operation and the production of wear metal data in 'real-time', thereby improving the probability of detecting abnormal wear conditions prior to engine failure.

Packer reports on a laboratory assessment of an X-ray fluorescent (XRF) wear metal monitoring system capable of continuously measuring the concentrations of iron, copper, silver and titanium in the lubricant (55). The system developed can be made compatible with aircraft propulsion and instrument systems and with flight operations.

Though the level of radiation from the XRF radioisotope excitation sources is within the limits set under existing

radiological safety regulations and procedures, actual approval for its use as an in-flight wear metal monitoring system "will most likely be contingent on the operational payoff of the device" (55). Further work is necessary to overcome the thermal instability in the XRF sensor preamplifier which was revealed during the initial test measurements. Then a comparison between SOAP and the XRF flowing oil monitoring system must be investigated to determine the suitability of that system.

2.1.4.6. Unmanned Operation of Lighthouses and Lightships.

Lansdown reports on a series of tests with diesel generator sets, at the Trinity House Lighthouse Service Experimental Station, Dungeness, designed to establish the optimum operating conditions for diesel engines (56). The aim of the project was to obtain the highest reliability with the least amount of maintenance with the view to reduced manning of lighthouses and lightships. The Swansea Tribology Centre cooperated in the lubricant aspects of the project. Routine tests performed on the oil samples included water content, viscosity, pentane insoluble material, flash point, total acid number, total base number, metal contents by emission spectroscopy. The results of the engine tests revealed that as the system approaches failure, most of the lubricant parameters deteriorated together, but prior to the failure only one or two tests showed any indication of its onset. However, no one test in particular indicated the onset of the several different failures that occurred during the test programme. This shows the importance of carrying out a variety of different tests. In this project no fault was detected by wear debris monitoring.

2.1.5. Summary.

A variety of techniques are available to assess the condition of lubricated engineering systems during operation and hence provide a means of pre-empting failure. Limitations of these techniques can be categorised into five areas : mode of use; cost; particle size response; information provided; and environmental performance. Whilst off-line systems provide reliable diagnostic information they generally require centralised laboratory facilities and skilled operators and therefore the operating costs are high. Also there is a time delay in obtaining the results. Care must be taken to ensure that lubricant samples represent the true operating conditions of the system or the results could be misleading. It is possible to miss rapidly deteriorating fault conditions when using the sampling techniques. Ideally they should be supported by an on-line fault detection system.

The different condition monitoring methods described in the earlier sections are summarised in table 2.2.

TABLE 2.2 : Summary of Condition Monitoring Methods for Lubricant - Based Systems.

METHOD	ADVANTAGES	LIMITATIONS	FURTHER COMMENTS
Physical Analyses	Simple, quick, on - line, inexpensive.	Provide limited information.	Engine performance monitored by measuring the quantity of oil and ensuring that sufficient oil is reaching components.
Chemical analyses	On - site	Sampling technique, lab. facilities required.	Monitor the deterioration of the lubricant by determining its properties.
Spectrographic Oil Analysis Programme	Indicates wear rate, semi-differentiating, measure 10 wear metals simultaneously detection limit is approx. 1 ppm.	Sampling technique, central lab, Upper limit particle size is 2 μm, elemental analysis.	Results are dependent upon the particle size distribution which changes during the progression of wear. No information on the mode of wear. No warning of those mechanisms that produce very little wear debris.
Chemical Microsensors	Trace quantities detected, on - line small, rugged, inexpensive.	Only specific detected.	Monitor additive depletion rates and appearance of lubricant degradation products which can be related performance. Not yet available commercially.

.....TABLE 2.2 cont.

METHOD	ADVANTAGES	LIMITATIONS	FURTHER COMMENTS
Microscopic examination methods	Determine conc., size distribution and particle composition. Morphological info. Semi-differentiating.	Centralised lab. facilities, sampling particle agglomeration.	Well established, standard techniques including optical and electron microscopy, X.R.F., X.R.D., electron probe X-ray microanalysis, particle counters.
Analytical Ferrography, (R.P.D.)	Production of ferrograms, determine the particle size distribution.	Centralised lab. facilities, sampling, particle size range 1 - 5 μm.	Developed to eliminate the problem of particle agglomeration. Usually used in conjunction with microscopic examination methods to provide quantitative information.
DR - Ferrography	On - site, determine particle size distribution.	Sampling, Particle size range 1 - 30 μm.	Severity of wear index determined
Magnetic plugs	on - line, simple, inexpensive.	Catch efficiency of collecting device, 100 μm lower limit particle size, only ferrous particles collected.	System is monitored by relating mass of total debris to its wear condition. Debris can be removed for analysis by microscopic examination methods.

.....TABLE 2.2 cont.

METHOD	ADVANTAGES	LIMITATIONS	FURTHER COMMENTS
Quant. debris monitoring	on - line, rugged, inexpensive.	Measurement errors due to air bubbles and extraneous particles, catch efficiency, lower limit particle size of 100 μm.	Variety of methods developed include optical oil turbidity monitor, electrically conducting filter, inductive and capacitative detection methods. Not yet available commercially. Collection of debris for subsequent off - line analysis.
Thin layer Activation	On - line, sensitive, differentiating, indicates wear rate	Expensive activation process, only a small proportion of surface is irradiated, health hazard due to radiation.	Used in development applications and not as a monitoring method.

In selecting which method to apply to a particular engineering system several factors need to be considered namely :

- the system itself
- the mode of wear in operation
- the kind of information required
- the volume and type of sample available
- the time involved
- the cost involved.

For example, spectrographic oil analysis is expensive in terms of equipment and analysis and therefore only those organisations involved with a large number of high capital cost machines can afford to operate such a programme. It has been widely applied to locomotive diesel engines, pipeline compressor engines and aircraft gas turbines. Wear debris analysis techniques are well established in the avaiation field particularly for monitoring rolling element bearings and gears where progressive failure usually occurs.

Recent advances in the field of condition monitoring for lubricated systems have been in two clearly defined areas. One has been in the development of techniques to provide specific information for a particular application such as the Wear Debris Tester, the Conpar system and chemical microsensors. These techniques are relatively simple and are designed to provide information in 'real-time'. At the other extreme, highly sophisticated

computerised systems are being developed in an attempt to quantify monitoring analyses, thereby eliminating the subjective nature of machinery diagnostics.

The techniques currently available can be categorised in two important ways, namely mode of use and the ability to differentiate between tribological components (tables 2.3 and 2.4). It can be seen from these tables that a major category of monitoring technique is currently not available commercially, namely one that is both on-line or on-site and is also differentiating with respect to which units in a tribological system are undergoing damage. The only method which potentially satisfies both criteria is thin layer activation, however, there is no evidence to date of this method being applied to a real monitoring situation, probably due to the safety and health hazard implications of using radioisotopes.

TABLE 2.3 : Classification of Condition Monitoring Techniques : Mode of Use.

MODE	TECHNIQUE
On-line	Magnetic plugs Abrasivity meter Chemical microsensor Physical methods (i.e. dip stick, flow meter) Detection of radioisotopes
On-site	DR-Ferrography Conpar Wear Debris Tester Detection of radioisotopes in wear debris Chemical methods
Laboratory	S.O.A.(Computerised systems) Analytical Ferrography RPD Microscopic examination methods

TABLE 2.4 : Classification of Condition Monitoring Techniques : The Ability to Differentiate Between Tribological Components.

CLASSIFICATION	TECHNIQUE
Non-differentiating	Chemical / physical analyses Magnetic plugs Abrasivity meter DR-Ferrography Wear Debris Tester Conpar
Semi-differentiating	S.O.A. Analytical Ferrography / R.P.D. (in conjunction with microscopic methods)
Differentiating	Detection of radioisotopes

As well as radioactive isotopes there exist rare, stable isotopes. These occur in nature only in very small concentrations, as shown in table 2.5 which gives the natural abundance levels of carbon-13 and nitrogen-15 (108). However, many rare, stable isotopes can be purchased in concentrated form.

TABLE 2.5 : Natural Abundance Levels of Stable Isotopes.

Isotope	Natural abundance (%)
C	98.89
C	1.11
N	99.63
N	0.366

Most of the elements in the periodic table have stable isotope counterparts but only carbon-13 and nitrogen-15 are of interest to this study. A brief review of stable isotopes is given in the next section. Often the use of stable isotopes and radioisotopes is complementary but for certain applications such as in clinical and environmental studies radioisotopes can not be used because of the health and safety risks resulting from the emitted radiation. Also for nitrogen studies there is no suitable radioactive counterpart available.

With this in mind it was decided to investigate the possibility of monitoring the progression of wear of steel components doped with stable isotopes as opposed to radioactive ones, to see whether the potentially available differentiation and on-site capability of radiotracing could be obtained by using stable, rare isotopes.

A review on the properties and use of stable isotopes is described in the following section.

2.2. Stable Isotopes.

2.2.1. History.

During the period 1927-1932 the stable isotopes hydrogen-2, carbon-13, nitrogen-15, oxygen-17, oxygen-18, sulphur-33 and sulphur-34 were discovered. The importance of stable isotopes, especially carbon-13, in the study of biochemistry was rapidly recognised. This work was reviewed by Clarke et al at a symposium in 1947 (57). However, by 1945 the radioactive isotope carbon-14 was readily available and considerably simpler to detect than the stable isotopes. Consequently, there was a decline in the use of stable isotopes.

In 1957, Rudiger reported that the isotope nitrogen-15 had been considered as a means of analysing for nitrogen in steels (58). However, this idea was not taken any further because the detection methods were considered too complicated.

Since the development of new detection techniques in the 1960's stable isotopes have been widely applied to many scientific areas. Such techniques include gas chromatography interfaced with mass spectrometry and Fourier transform nuclear magnetic resonance spectroscopy.

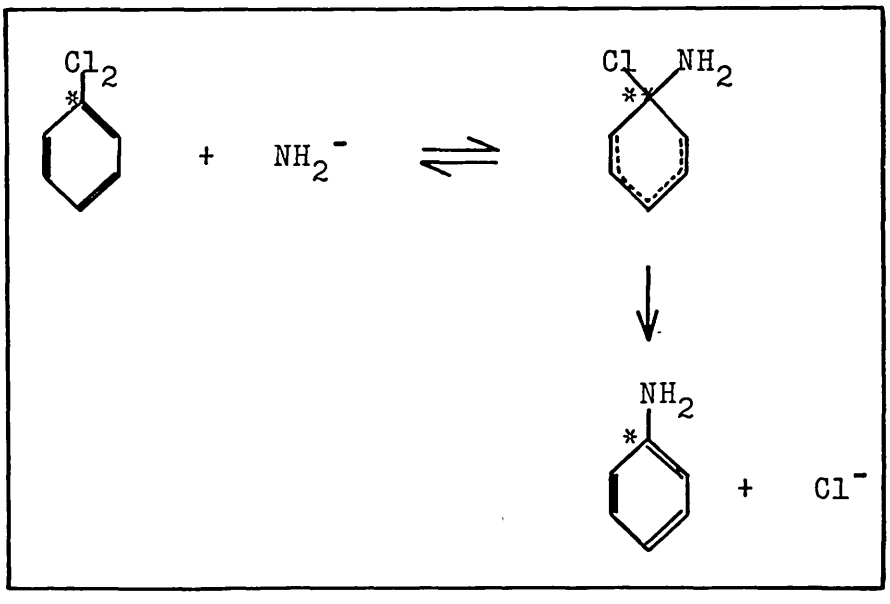
2.2.2. Applications of Stable Isotopes.

The stable isotopes of the main bioelements C-13, N-15 and O-18 have been applied to biochemical, environmental, clinical and pharmocological research (59,60,61,62). More recent applications involve isotope abundance variations in the fields of geochemistry, cosmochemistry and agriculture.

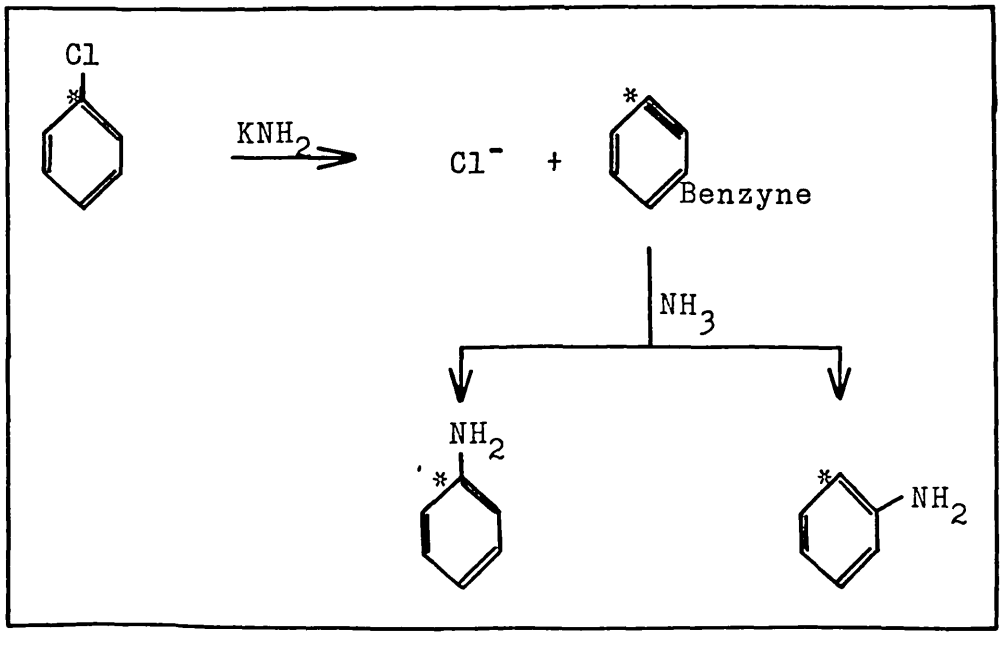
A typical example of the use of an isotopic label is in the determination of one of the mechanisms of nucleophilic aromatic substitution. For the aminolysis of chlorobenzene with potassium amide in liquid ammonia it was thought that the reaction proceeded by one of two possible mechanisms as illustrated in figure 2.4; namely an addition-elimination mechanism (reaction scheme 1) and a mechanism involving the benzyne intermediate (reaction scheme 2). The correct mechanism was identified by using a reactant in which one carbon atom (marked *) was labelled with C-14 (63). The position of the label was determined by degradation of the product aniline and almost equal amounts were found at two carbon atoms. Therefore, the results show that the reaction proceeds via the second mechanism.

FIGURE 2.4 : Possible Mechanisms for the Aminolysis of Chlorobenzene.

REACTION SCHEME 1 : Addition - Elimination Mechanism.



REACTION SCHEME 2 : Via Benzyne Intermediate Formation.



2.2.3. Analysis Techniques.

Only those techniques which are influenced by the effects of the mass of an atom (or molecule) can be applied to stable isotope studies in order to be able to differentiate between the atom and its stable counterpart. The four most important techniques for the detection and assay of stable isotopes are mass spectrometry, nuclear magnetic resonance-, optical emission- and infrared spectroscopy (64,65). These techniques are described briefly below.

2.2.3.1. Mass Spectrometry.

Mass spectrometry is the most widely applied method employed for isotopic studies (66,67,68). Two types of instrument are used : an isotope mass spectrometer and an organic mass spectrometer. The isotope mass spectrometer measures the abundance of an isotope in a gas sample compared with a known reference gas. Therefore, it is essential to convert the sample to a gaseous form. The preparation of N-15 samples is normally achieved either by a Dumas direct combustion technique to produce nitrogen or by a Kjeldahl conversion to ammonia followed by oxidation with

hypobromite. C-13 is usually assayed as carbon dioxide produced by combustion of the sample. Matthews and Hayes have reported on the simultaneous determination of the isotopic ratios of carbon and nitrogen by placing a combustion tube between a gas chromatograph and an isotope mass spectrometer and monitoring the ions at masses 28 and 29 for nitrogen (N_2, $N^{15}N$) and at 44 and 45 for carbon (CO_2, $^{13}CO_2$) (69). By using a computer controlled mass spectrometer, enrichments as low as 0.004 atom % excess were detected. Typically, isotope mass spectrometers cover the range m:e 2 to 100.

The organic mass spectrometer is a more sophisticated instrument than the isotope mass spectrometer. With a gas inlet system it can be used for the analysis of labelled gases and gas mixtures and for the analysis of compounds that can be readily converted to an appropriate gaseous form. When linked to a gas chromatograph, complex mixtures can be fractionated and structural information obtained as well as the location of the label in the compounds.

Mass spectrometry is very versatile in that it can be applied to many different stable isotopes and can be used in the natural range of isotope abundances and quantitative detection of specific labelled ions can be made at the sub-nanogram level. One disadvantage of this technique is that samples need to be volatile and therefore chemical

treatment of N-15 and C-13 samples are necessary prior to analysis as described above. This makes this technique inappropriate to the direct study of wear debris though it is possible to analyse solid samples by secondary ion mass spectrometry (SIMS). This process involves bombarding the sample by an energetic primary ion beam in an ultra high vacuum analysis chamber which causes sputtering of the target atoms (98). A small fraction of this material carries a charge and these 'secondary ions' can be analysed in a mass spectrometer.

2.2.3.2. Nuclear Magnetic Resonance.

Nuclear Magnetic Resonance (NMR) spectroscopy is based on the absorption of photons of very low energies whose frequencies are typically of the order of 60 MHz. For nuclei which possess a magnetic moment, it is possible to induce transitions between the different energy levels with an alternating magnetic field of the correct orientation and frequency. The exact resonance frequency of a nucleus depends on the chemical structure of the molecule or grouping containing the nucleus. Therefore, NMR will provide information on the precise location of the nucleus in a complex molecule, as well as acting as a non-specific

detection method. This is important for chemical mechanism studies.

Since the development of Fourier transform NMR, this technique has been applied to stable isotope studies, particularly to those employing carbon-13 (69,70). By using a short pulse radiofrequency all the C-13 nuclei in a sample can be excited simultaneously. The absorptions of the individual frequency components by each nucleus are then detected by the receiver and abstracted by Fourier transformations using data acquisition and processing equipment. The use of N-14 NMR and N-15 NMR have been reviewed (71). N-15 spectra display good resolution but its use has been resticted by poor signal to noise ratios.

2.2.3.3. Vibrational and Rotational Spectroscopic Techniques.

There are several analytical spectroscopic techniques available for determining molecular structure which measure the specific energy changes in an excited molecule caused by incident radiation. Energy changes are brought about by the molecular adjustments of the vibrational and rotational states and the electronic transitions between the molecular orbitals. Spectra can be obtained experimentally in one of three ways : emission spectroscopy, absorption spectroscopy

and Raman scattering spectroscopy. Detailed literature on spectroscopy is available in abundance and therefore only those techniques which have been used in stable isotope studies are described briefly below. Such techniques include optical emission spectroscopy (72), infrared spectroscopy (73) and Raman scattering spectroscopy (74). The substitution of a stable isotope into a molecule, thereby labelling that molecule, results in isotopic shifts in the wavelengths of those observed frequency bands due to the labelled atom. Spectral differences observed for isotopically labelled compounds are larger the higher the respective m^i/m ratio, where m^i is the mass of the labelled atom and m is the mass of the normal atom.

Optical emission spectroscopy is used for the determination of nitrogen in areas such as agricultural studies. The technique relies upon converting the nitrogen present in the sample to nitrogen gas, which is then excited by a radiofrequency in a flow discharge tube and the wavelengths of the emitted radiation due to the three species N_2, $N^{15}N$, $^{15}N_2$ measured. However, the accuracy of this method is not as high for mass spectrometry and it does not provide direct information on the molecular environment of the isotope.

The effect of labelled compounds in infrared absorption spectroscopy has been reviewed in great detail by Pinchas

and Laulicht (75). For the majority of carbon-13 infrared studies, the various molecular absorption frequencies of specific CX groups (where X = H,O,N) are measured. The isotopic shift for the stretching frequency of carbon-13 monoxide ^{13}CO is of the order of 48 cm^{-1}.

Raman scattering has not found widespread use in isotopic studies but it has been investigated as a means of determining isotopic ratios, as in the case of the analysis of ^{14}N, ^{15}N using an argon laser (76).

2.2.3.4. Activation Analysis.

Activation analysis has been used for isotopic analysis, particularly for elements of medium atomic weight such as chromium-56, ^{56}Cr. The whole process can be expressed as follows :

$$\underset{\text{target nucleus}}{X} + \underset{\text{neutron}}{n} \longrightarrow \underset{\text{composed nucleus}}{[X + n]^{*}} \xrightarrow{\text{decomposition of}} \underset{\text{composed nucleus}}{\longrightarrow}$$

On exposure to neutrons, the target sample nuclei undergo nuclear reactions resulting in the formation of new nuclei which are often radioactive (i.e. 'activation' has

occurred). The most important nuclear reations for activation analysis are (n,gamma) transformations in which the excited nucleus passes to a lower energy state by the emission of a gamma ray. Analysis of the different types and energy of radiation allows for differentiation of the elements present in the sample.

This method, however, is relatively expensive, time-consuming and not readily applicable to isotopes of the light elements, such as C-13 and N-15.

CHAPTER 3 DEVELOPMENT OF THE EXPERIMENTAL PLAN.

The purpose of this work is to assess the potential for monitoring excessive wear of key tribological components in an engineering system by the detection of stable isotopes. Three distinct points need to be considered in order to assess the feasibility of this concept. Firstly how can the stable isotopes nitrogen-15 and carbon-13 be incorporated into the surface of steel components; secondly how can wear debris be produced and separated in forms containing the labelled isotope and quantities appropriate for measurement; and finally how can the stable isotopes be detected? The options available for each of the above stages are discussed in this chapter.

3.1. Incorporation of Stable Isotopes into Steel Components.

Surface hardening treatments have been widely used throughout the engineering industry to improve the wear resistance, corrosion resistance and fatigue strength of steel components. The literature contains many references outlining the principles, limitations and applications of the different techniques (78-85). Such treatments are usually carried out for reasons of economy to avoid the necessity of an expensive, bulk hardened steel, and because the surface and subsurface requirements of a component may be incompatible. Generally, surface hardening treatments can be divided into thermal treatments and thermochemical treatments.

Thermal treatments rely solely on heat to bring about changes in the metallurgical structure which result in a hardened surface, thereby improving wear resistance. There are several methods of thermal hardening including induction, flame, electron beam, spark and laser hardening.

A thermochemical heat treatment has been defined as "A heat treatment in which the chemical composition of an object or material is intentionally changed by the diffusion of one or more elements into or out of the surface" (82). This definition allows for those treatments which involve

the diffusion of both metals and non-metals. However, for the purpose of this study, only those treatments involving the latter, in particular carbon and nitrogen, have been considered. These can be divided into two groups : austenitic and ferritic. Austenitic treatments, carburisation and carbonitridation, involve the diffusion of carbon or carbon and nitrogen respectively into the austenite phase of the steel component whilst ferritic treatments, namely nitridation and nitrocarburisation, involve the diffusion of nitrogen or nitrogen and carbon respectively into the ferrite phase.

The choice of a surface hardening technique is dependent upon the design requirements of the steel component. Table 3.1 outlines the characteristics of the hardened surfaces produced by some of the different techniques (80).

As an alternative to thermochemical heat treatments, ion implantation has been investigated as a means of improving the tribological properties of engineering components (86-91). Improvements in the wear and fatigue properties of steel have been achieved by the implantation of nitrogen.

TABLE 3.1 : Characteristics of Hardened Surfaces (80).

Thermal Hardening	Hard,highly wear-resistant surface (deep case depths); good capacity for contact load; good bending fatigue strength; fair resistance to seizure; fair dimensional control possible; fair freedom from quench cracks; low-cost steels usually satisfactory; medium capital investment required for induction hardening; low capital investment required for flame hardening.
Carburising	Hard, highly wear-resistant surface (medium case depths); excellent capacity for contact load; good bending fatigue strength; good resistance to seizure; excellent freedom from quench cracking; low- to medium- cost steels required; high capital investment required
Carbonitriding	Hard, highly wear-resistant surface (shallow case depths); fair capacity for contact load; good bending fatigue strength; good resistance to seizure; good dimensional control possible excellent freedom from quench cracking; low-cost steels usually satisfactory; medium capital investment required.
Nitriding and Nitrocarburising	Hard, highly wear-resistant surface (shallow case depths); fair capacity for contact load; good bending fatigue strength; excellent dimensional control possible; good freedom from quench cracking (in the pretreatment); medium- to high cost steels required; medium capital investment required.

It is thus clear that techniques are available whereby carbon and nitrogen are introduced into the steel surface and the substitution of 'ordinary' carbon-12 and nitrogen-14 with the stable isotopes carbon-13 and nitrogen-15 should provide the means of introducing the isotopes into the surface. The different techniques are discussed below with a view to selecting the most suitable for stable isotope substitution.

3.1.1. Carburisation.

Generally, carburising treatments involve heating a steel component (usually a low-carbon steel) in the presence of a carbon-rich material in the temperature range 850 to 950 ^{o}C which results in the diffusion of carbon into the austenite phase. The transport of carbon from the carburising medium always takes place via a gaseous phase, usually carbon monoxide, CO. Transformation of the austenite to martensite then ensues via a quenching treatment, thus producing the hardened surface. The whole treatment is termed 'case-hardening.'

Carburisation can be effected in either a solid, liquid or gaseous medium, usually termed pack, salt-bath or gas

carburisng respectively. Each method has its own intrinsic charecteristics which produce different case-hardening results. Detailed information on the different methods and their applications is available in the literature (78,79,80).

Pack carburising is a dirty and labour intensive process, over which the operator has very little control. In order to carburise steel components uniformly extreme care is necessary in loading the furnace. Basically, the components are packed in a carburising compound typically composed of a charcoal and barium carbonate mixture. The reaction proceeds via the following mechanism :

$$BaCO_3 \longrightarrow BaO + CO_2$$
$$CO_2 + C \longrightarrow 2CO$$
$$2CO \longrightarrow CO_2 + C$$

whereby the nascent carbon, thus produced, is readily dissolved by the austenite phase of the steel and diffuses into the surface. This mechanism was confirmed by radioactive isotopic substitution experiments as reported by Stanley in 1947.

The active carburising agent in a salt bath is usually sodium cyanide or potassium cyanide. Carburisation is believed to proceed via the following reaction path :

$$2NaCN + O_2 \longrightarrow 2NaCNO$$

$$4NaCNO \longrightarrow 2NaCN + Na_2CO_3 + CO + 2N$$

$$3Fe + 2CO \longrightarrow Fe_3C + CO_2$$

Some of the nitrogen liberated in the second reaction is also taken up by the steel. Carbon and nitrogen pick-up is controlled by the cyanide content of the bath and its temperature. Salt bath carburising is more controllable than pack carburising though it is as labour intensive. Health and safety problems encountered when using cyanide salts can be overcome by skilled handling of the toxic waste, but disposal of waste causes difficulties.

Nowadays, the gas carburising process is the most popular method of case hardening and has largely superceded the two aforementioned processes. A hydrocarbon gas and air mixture is generally used and the process proceeds by the following typical reactions :

$$2CO \longrightarrow C + CO_2$$

$$CH_4 \longrightarrow C + 2H_2$$

$$CO + H_2 \longrightarrow C + H_2O$$

Although the furnaces are very expensive they are economic in operation. The 'sealed quench furnace', which is perhaps the most popular, consists of both heating and quenching

chambers. Once the furnace is loaded the process proceeds automatically. As the carburising potential is proportional to both the water content and the carbon dioxide content of the gas mixture in the furnace, control of the process can be achieved by analysis of these gaseous products, by means of a dew point meter or an infra red carbon dioxide analyser respectively. Thermocouples are used as a means of controlling the temperature of the gas mixture and the temperature uniformity of the furnace.

Recent advances in surface heat treatments have been in the experimental development of the plasma carburising process (92). The principles of the plasma treatment are described later in section 3.1.3, when dealing with the plasma nitriding process. Plasma carburising is not yet available commercially.

3.1.2. Carbonitridation.

Carbonitridation can be thought of in terms of a carburising process with simultaneous nitrogen pick-up. Only simple modifications to the carburising processes, described in the previous section, are necessary. For example in gaseous carbonitridation ammonia is added to the carburising gas mixture. Slight variations in the cyanide

content and the temperature of the salt bath enables carbonitridation to proceed as opposed to carburisation. The treatment temperature is usually in the range 800 to 900 ^{o}C and as for carburising, the treated components are hardened by quenching.

The presence of nitrogen in the heat treated layer increases its hardness compared to a 'plain' carburised layer, thereby increasing the component's hardenability and wear resistance.

3.1.3. Nitridation.

Nitridation is a hardening process which involves diffusing nitrogen into the surface of fully heat-treated steel components in the temperature range 500 to 590 ^{o}C. It is a ferritic thermochemical process and consequently no phase transformation occurs on cooling to room temperature. This offers an important advantage over carburising and carbonitriding where distortion of the treated components may occur as a result of the thermal shock and phase transformations involved during hardening.

Generally, nitriding steels contain nitride-forming

elements such as aluminium, chromium, molybdenum and vanadium which are necessary to produce the surface hardness of the nitrided layer (greater than 1000 HV) caused by the high level of compressive stresses in the layer due to finely dispersed metal nitrides and carbonitrides distorting the ferrite lattice. The main factors governing the case depth are treatment time, temperature and steel composition.

The main methods of nitriding are gas nitriding and salt-bath nitriding, though many variations within these methods exist. Plasma nitriding (also termed glow-discharge nitriding and ion-nitriding) is the most recent development in this field (94,95). More detailed information can be found in the literature (78,79,80).

In gas nitriding the nascent nitrogen is obtained by the dissociation of ammonia gas :

$$2NH_3 \longrightarrow 2(N)_{iron} + 3H_2$$

Control of the process is achieved by monitoring the dissociation by means of a dissociation burette and varying the gas flow. The treatment cycle is very long, typically in the range 10 to 100 hours.

An obvious advantage of the salt-bath process over gas nitriding is the considerable reduction in treatment time,

which is of the order of 1 to 4 hours. The salt bath contains a mixture of salts, namely cyanides, carbonates and cyanates, and the process is controlled by regulating the composition of the bath. One of the main methods of salt-bath nitriding is called the Tufftride process (93) and a popular variation to this is the Sulfinuz treatment, whereby sodium sulphide is added to the salt mixture. Salt-bath nitriding is a form of liquid nitrocarburising in that both nitrogen and carbon diffuse into the steel surface.

The most recently developed method of nitriding uses a plasma to generate atomic nitrogen and is termed 'plasma nitriding'. This also has a time advantage over the conventional gas process and has a further advantage in that of all the methods it is the most controllable. Although the necessary equipment is very expensive the operating costs in terms of energy and gas are considerably reduced compared to gas nitriding. More detailed information on this process is given later in Chapter 4.

3.1.4. Nitrocarburisation.

The process of salt-bath nitriding is basically a form of liquid nitrocarburising in that both nitrogen and carbon diffuse into the steel surface simultaneously. This process

has been discussed earlier in section 3.1.3. Gaseous nitrocarburising has been developed as an alternative to the salt bath method, mainly because of economic and ecological pressures.

3.1.5. Ion Implantation.

Ion implantation was originally developed as an effective and controllable method of fabricating semiconductor devices. The process involves injecting atomic species into the surface of a solid by using an accelerated beam of ions in a relatively high vacuum.

Since the early seventies, research work has been studied in the effects of ion implantation on metals and alloys with a view to improving the tribological properties of engineering components (86-91). The penetration depth of the implanted atom is usually less than 1 μm which is extremely small in engineering but not tribological terms. Improvements in the wear and fatigue properties of steel have been achieved from the implantation of nitrogen.

The advantages and disadvantages of ion implantation have been summarised in table 3.2 (88).

TABLE 3.2 : Advantages and Disadvantages of Ion Implantation as a Treatment Process for Metals and Carbides (88).

ADVANTAGES	DISADVANTAGES
Versatility as regards ion species and substrate Controllability Low temperature process No build-up Clean vacuum process Applied to finished components Monitored electrically throughout Low power consumption Conserves materials No toxicity	High capital cost Shallow treatment Line-of-sight process Ion sources need development Unfamiliar process Requires in vacuo manipulation

3.1.6. Conclusions.

After considering the limitations of the various thermochemical heat treatments briefly described in the earlier sections it was decided that the plasma process was the most appropriate means of introducing the stable isotopes into the steel surface. The reason for this choice is that this process is the most controllable and there is a considerable reduction, compared to the gaseous methods, in the operating costs in terms of energy and especially gas. A 95 % reduction in gas consumption has been reported (92) which is very important when considering the very high price of stable isotopes.

Ion implantation compares favourably to the plasma process as many of the advantages listed in table 3.2 could be applied to both techniques. However, because the penetration depth of the implanted atom is very shallow and because plasma nitriding has already been developed commercially, the plasma process was considered more suitable than ion implantation. Development of the plasma carburising process on an industrial level is currently under consideration (92).

The initial experimental work to investigate the feasibility of the project will therefore involve using the plasma nitriding technique as a means of incorporating the

stable isotope, nitrogen-15, into the steel surface.

3.2. Removal of the Isotope from Steel Surfaces.

Having introduced the stable isotope into the surface of the steel component, the next stage in this feasibility study is to remove it by generation of wear debris. There are numerous types of machines available for wear testing though generally it is the friction and temperatue recordings and the wear scar on the components that are of interest and not the collection and subsequent analysis of the wear debris. A brief assessment of some of these wear machines is given below in order to select the most suitable one for this stage of the study.

3.2.1. Wear Testing Machines.(96,97).

The most common type of wear testing machine is the pin-on-disc. Basically the pin, which has a lower wear resistance than the disc, is loaded against the disc which is then rotated. Wear measurements on the pin can be carried out in a variety of ways the most common of which is to measure the area of the wear scar on a hemispherical or conically ended pin. Shortening of the pin may be measured with a displacement transducer.

Disc machines can also be used to study wear, where two or more discs rotate in contact at the speed required to give the desired amount of sliding. The advantage of these machines is that the geometry of the contact does not alter as wear proceeds so that the load and contact pressure can be kept constant during a wear test. However, disc machines require a large amount of lubricant and relatively expensive test specimens.

The standard 4-ball machine consists of three balls clamped together to prevent movement and the fourth ball rotated in contact with them. In order to measure wear the system has to be completely dismantled and the wear scars measured. As, in practice, it is impossible to reassemble the system in exactly the original pattern only one measurement can be obtained from each test.

Variations on the 4-ball machine have been developed (96). In the ball-on-triplane machine the three lower balls have been replaced by the flat ends of the three rollers such that three different wear tracks are produced on the fourth ball. The cone-on-roller machine consists of three rollers positioned in a cup such that a cone can be rotated in contact with their cylindrical sides. The main advantage of this system is that it is possible to use materials which are not available as balls.

3.2.2. Requirements of the Wear Experiments.

The three requirements of the experimental wear tests are :

generation of wear debris in sufficient quantity for analysis;

retention of the debris in the lubricant;

and the removal of the debris from the lubricant.

After considering the different types of wear test machines, described briefly in section 3.2.1, it was decided to employ the cone-on-roller machine because this best satisfies the requirements listed aboveand also because it was available for use. A more detailed description of this machine is given later in section 5.1.

3.3. Detection of the Stable Isotope in Wear Debris.

Consideration of three different areas is necessary in order to develop the experimental outline for the detection of the stable isotopes carbon-13 and nitrogen-15 in wear debris. These areas are : stable isotope detection techniques; carbon analysis in steel; and nitrogen analysis in steel.

3.3.1. Techniques for the Detection of Stable Isotopes.

The most important techniques for the analysis of stable isotopes are mass spectrometry, nuclear magnetic resonance spectrometry, optical emission spectroscopy and infrared spectroscopy. These have been discussed previously in some detail (see section 2.2.3.).

3.3.2. Carbon Determination.

Detection of carbon in metals and alloys is determined by heating the sample to a temperature of about 1200 ^{o}C in the presence of a stream of oxygen which results in the oxidation of carbon to carbon dioxide (99,100) :

$$C + O_2 \longrightarrow CO_2$$

Carbon dioxide may then be measured gravimetrically, volumetrically, conductiometrically, or by low pressure combustion, thermal conductivity, or infrared methods.

By 1966, several commercial analysers were available for determining carbon in steel which were entirely automatic. These analysers can be classified into three groups according to the technique used for the measurement of the carbon dioxide evolved during the high temperature combustion of the steel samples, namely electrochemical, thermal conductivity, and infrared absorption. The majority of the analysers incorporated a static measurement system whereby the combustion gas was collected before analysis. Therefore, precautions had to be taken to ensure that combustion was complete before measurement took place.

Improvements in the analysers, in terms of maximum speed and efficiency, resulted from the development of

dynamic analysers to continuously monitor the carbon dioxide content of the combustion gas. White and Scholes developed one such system in 1966 using a specially designed infrared gas analyser and integration system (101). When this is used in conjunction with a conventional resistance-tube furnace, the speed of the determination varies from 40 to 55 seconds for mild and low alloy steels and slightly longer for highly alloyed materials.

Koch and Lemm (102) developed a high-speed process for the rapid and simultaneous determination of the carbon and sulphur contents of steel in 1970. A new combustion furnace was designed and the analysis of the combustion gases carried out by means of infrared absorption equipment. The reproducibility and accuracy of the results using this technique was found to be comparable with those of other procedures.

In 1970 Scholes (103) reports some of the more significant developments in physico-chemical techniques for analytical quality control with emphasis on the determination of carbon and other elements present in small amounts outside the normal range of physical techniques of analysis. Particular reference is made to atomic absorption and automated spectrophotometric analysis. Scholes also reports on the findings of the performance of various combustion techniques for carbon detection. The objectives

were to compare analytical performance and to recommend one or more techniques which might replace the outdated gravimetric method as a British Standard. The techniques examined were : coulometry; low pressure gasometry; non-aqueous titration; infra-red absorption; thermal conductivity; gravimetric; and electrical conductivity. From the results of this study group, the different techniques were ranked in order of suitability for carbon dioxide analysis in the order given above whereby coulometry was found to be the most suitable.

On considering the different techniques applied to both carbon determination and the detection of stable isotopes, it can be seen that the one method most suited for their combined application is infra-red absorption spectrophotometry.

3.3.3. Nitrogen Determination.

In 1958, the Iron and Steel Institute (ISI) published a special report entitled "The Determination of Nitrogen in Steel". The report group investigated and compared the two major areas for nitrogen determination, namely chemical methods and the vacuum-fusion method (104). A report published in 1970 by Healy and Parker (105) on the chemical determination of nitrogen in various alloy metal nitrides investigated what they considered to be the more suitable chemical methods in terms of their precision, accuracy, speed and simplicity of operation, with a view to recommending an optimum method for each one.

Based largely on the findings of these reports a method was selected by the author to be the most suitable choice for the experimental work to assess the feasibility of this project.

3.3.3.1. Chemical Methods.

(i) Kjeldahl Method.

Many nitrogen-containing compounds (inorganic or organic) when treated with an acid solution at a high temperature in the presence of suitable catalysts, are decomposed with the formation of ammonia which is immediately fixed by the acid as an ammonium salt. This mixture is then made strongly alkaline to release the ammonia which is distilled into an excess of standard acid. Nitrogen content of the distillate is determined either by back titration with standard alkali, which is the usual method, or colourimetrically. Therefore, the Kjeldahl method involves three stages : digestion, distillation and titration.

The most important step in this process is considered to be the dissolution of the sample. Several different procedures have been developed in an attempt to minimise the amount of insoluble residue. Various acids and acid mixtures have been tried : dilute sulphuric; dilute hydrochloric; mixtures of sulphuric with phosphoric or perchloric or both; mixtures of hydrochloric and hydrofluoric acids; fuming sulphuric acid, sometimes with the addition of an alkali sulphate; selenium or mercury additions to the acid solution to act as catalysts. The ISI

group reports that (104):

> "With the exception of steels containing silicon nitride and possibly some boron steels where the evidence is inconclusive, the Group has found that a fuming treatment, provided it is sufficiently severe, will give full recovery of nitrogen in all steels. The use of complex mixtures of acids or catalysts offers no advantage, and is not recommended as an alternative to a fuming treatment."

This finding is supported by Healy and Parker (105) who recommend the use of a concentrated sulphuric acid / sodium sulphate mixture. The addition of the alkali metal salt is beneficial in that it raises the temperature which the acid attains.

A modification to the Kjeldahl dissolution was developed which involved dissolution under pressure in a closed system in an attempt to decrease the reaction time. Parker and Healy have described this technique and the development of the steel reaction vessel lined with P.T.F.E. (106). The initial experiments with sulphuric acid were unsuccessful but by using a 50:50 mixture (by volume) of hydrofluoric and hydrochloric acid complete dissolution of the nitrides of titanium, boron, silicon and zirconium was

obtained though it was necessary to heat the mixture overnight. Therefore, the acid dissolution reaction time was not considerably reduced compared to the original Kjeldahl method.

(ii) The Dumas Method.

This method is normally used for the determination of nitrogen in organic compounds but it can be applied to the analysis of nitrides. It involves heating the nitride in a stream of carbon dioxide to a temperature of between 1000 and 1200 ^{o}C usually in the presence of copper oxide which acts as an oxidising agent. The nitride is oxidised to nitrogen and the volume of nitrogen produced can be measured in a nitrometer which is an inverted burette filled with 50 % potassium hydroxide solution, KOH. Other gases, usually carbon dioxide and water, also released with the nitrogen are trapped by the KOH and, therefore, the volume of gas obtained is that of nitrogen.

(iii) Alkaline Fusion Method.

The alkaline fusion method involves the fusion of the nitride sample with a large excess of alkali (sodium hydroxide is usually used) in a stream of inert gas at a

temperature of 700 ± 20 °C. This results in the formation of ammonia which can be trapped in a known quantity of standard acid, then analysed by titration.

3.3.3.2. The Vacuum-Fusion Method.

The vacuum-fusion method has been widely used for the determination of nitrogen, oxygen and hydrogen in steel. Full descriptions of the equipment and methods of operation are given in the reports of the Oxygen Sub-Committee (107). Nitrogen determination by this method may be divided into two equally important stages : the extraction of nitrogen from the sample; and the analysis of the evolved gas.

Nitrogen is separated by fusion of the sample in a vacuum in the presence of carbon. All oxides present are reduced to carbon monoxide, and nitrogen and hydrogen are liberated. Carbon monoxide is converted to carbon dioxide and frozen out in liquid nitrogen. Hydrogen is oxidised to water and absorbed in anhydrous magnesium perchlorate. The residual gas is nitrogen.

3.3.3.3. Comparison of the Different Nitrogen Analysis Techniques.

The ISI Group compared the results for nitrogen analyses by the Kjeldahl dissolution method and the vacuum-fusion technique. Nitrogen values determined by the latter technique were found by some investigators to be 0.01 to 0.02 % lower than those obtained by the chemical procedure.

On comparing the results for the various chemical methods investigated by Healy and Parker, it was found that the Kjeldahl dissolution method and the Dumas method both gave accepable results which also agreed satisfactorily with each other. The acid dissolution under pressure modification could not be applied to all the metal nitrides investigated and the coefficient of variation obtained from the results was found to be approximately three times greater than that for the Kjeldahl method. The alkaline-fusion results tended to be slightly lower than those obtained by the acid dissolution and Dumas methods, though the technique is reasonably quick and comparatively simple.

Based on the above findings, the choice of analysis techniques for the detection of nitrogen was limited to the Kjeldahl method and the Dumas method. The Kjeldahl method

was selected because it results in the production of ammonia, which is active in the infrared region, whereas the nitrogen produced by the Dumas method is infrared inactive. This is important when considering substituting nitrogen by its stable counterpart, N-15.

3.4. Summary.

As a result on the findings of this survey, two similar monitoring methods are proposed. One involves the detection of the stable isotope nitrogen-15, whilst the other is based on carbon-13 detection. In order to assess the feasibility of the concept of monitoring wear by stable isotope detection it was decided that the experimental work will involve using nitrogen-15. Plasma nitriding was chosen as the means of incorporating the isotope into the steel surface. The plasma processing unit at the Wolfson Institute for Surface Engineering, University of Birmingham was employed to carry out nitriding treatments.

It was decided to use the cone-on-roller wear machine to generate wear debris from the nitrided specimens.

This wear debris would be treated using a modified version of the Kjeldahl method, with any resultant ammonia being analysed by infrared spectroscopy. Alternative methods of analysis, such as mass spectrometry and SIMS, may be considered after the initial experimental work.

Details of the experimental development of the next three stages prior to stable isotope substitution are described in the following three chapters.

CHAPTER 4. PLASMA NITRIDING EXPERIMENTAL WORK.

It was essential to use ordinary nitrogen-14 (N-14) gas in order to optimise the plasma nitriding conditions prior to the isotopic work with costly labelled gas containing the stable isotope, nitrogen-15 (N-15). This chapter contains an outline of the plasma process followed by preliminary experimental work on nitriding using N-14.

4.1. Details of the Plasma Nitriding Process.

A schematic representation of a plasma processing unit is given in figure 4.1 (94). A typical treatment cycle can be sub-divided into :

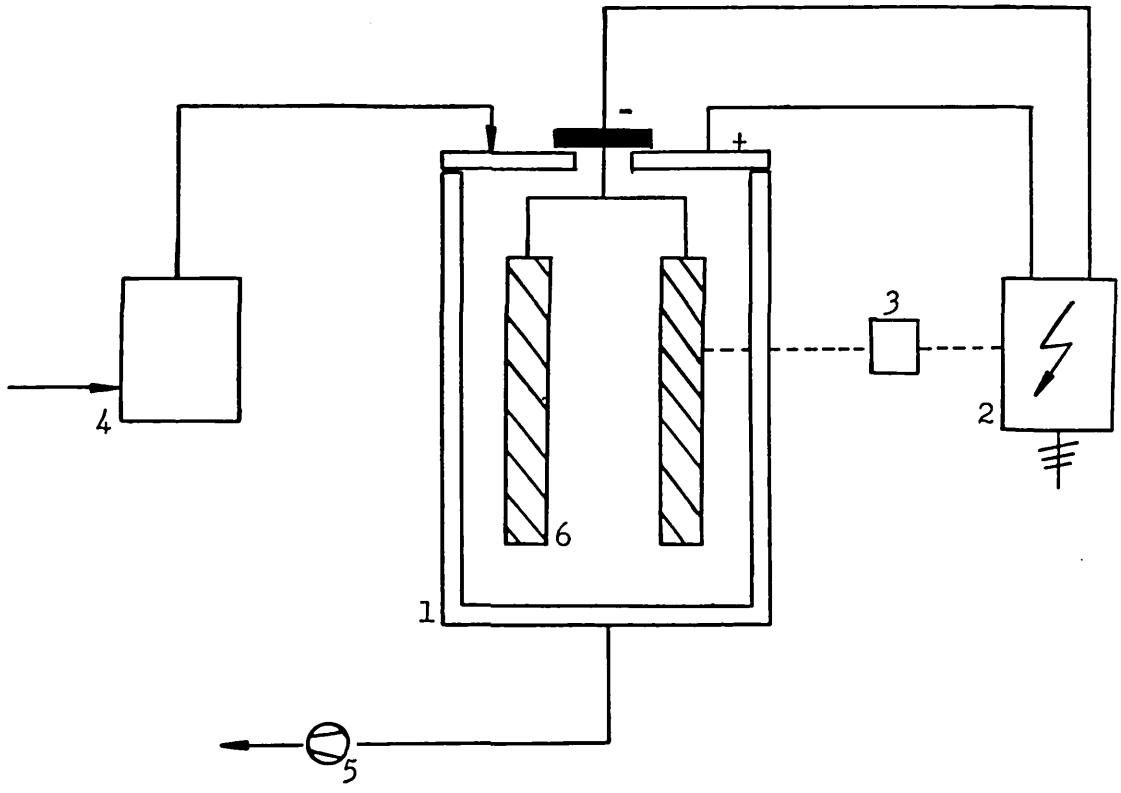
(i) evacuation,

(ii) heating-up period

(iii) nitriding treatment.

Prior to evacuation, the steel components are carefully degreased in trichloroethane then placed in the vacuum chamber. After evacuating, the chamber is filled with the appropriate gas and maintained at the required vacuum, of typically 0.1 mbar. An electric potential of several hundred volts is then applied between the components (the cathode) and the wall of the furnace (the anode) resulting in the formation of the 'glow discharge' (also termed the plasma) due to the excitation and ionisation of the molecules and atoms of the gas. The positive ions of the treatment gas accelerate towards the negatively connected component and hit its surface with very high kinetic energy which is released in the form of heat. This results in both the components being heated and the ions being occluded into the steel surface. When the required temperature is reached this is regulated by means of a controller which varies the power output of the electric unit.

FIGURE 4.1 : Schematic Representation of a Plasma Processing Unit.



1	Vacuum furnace
2	Electrical unit
3	Regulating unit
4	Gas distribution
5	Vacuum pump
6	Workpiece

The nitriding treatment is then allowed to proceed for the desired time, after which the process is stopped and the treated samples allowed to cool before being removed from the chamber.

It is common for the treatment gas to be used during the heating-up period but this is not essential and alternatives can be used at this stage.

4.2 Treatment Conditions.

When selecting nitriding conditions it is necessary initially to consider the design requirements of the steel components. Then by applying a combination of available information, experience and experimental 'trial and error' optimisation of the conditions is possible. Experimentally generated graphs which relate metallurgical properties of nitrided surfaces to plasma nitriding conditions are available in the literature as shown in figures 4.2 (94), 4.3 (95) and 4.4 (95). Factors governing the nature of the nitrided case are treament time, temperature, nitrogen activity and steel composition.

FIGURE 4.2 : Hardness Profiles Achieved on En40 B Steel for Various Processing Temperatures (Plasma Nitrided for 20h at 2.7mbar; gas, 20% N_2- 80% H_2).

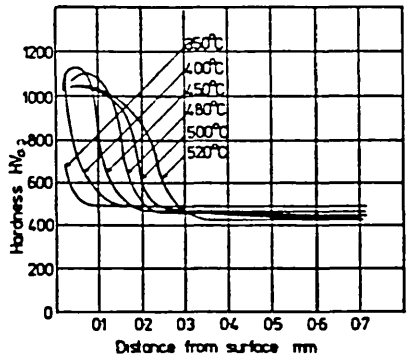


FIGURE 4.3 : Microhardness Profiles Obtained on Samples Plasma Nitrided at 480°C for 40h in one pct, 2.5 pct and 25 pct Nitrogen / Hydrogen Gas Mixtures.

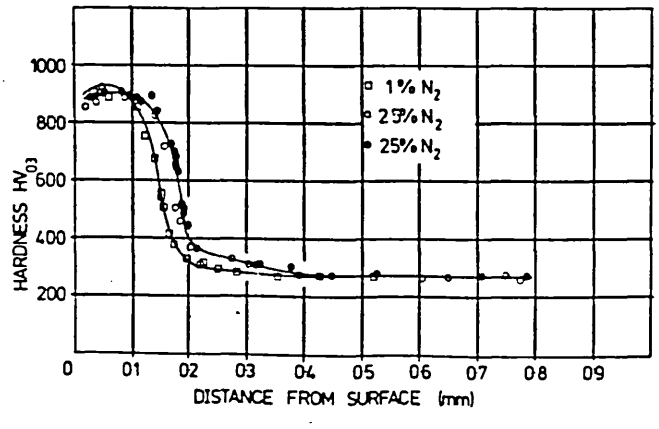
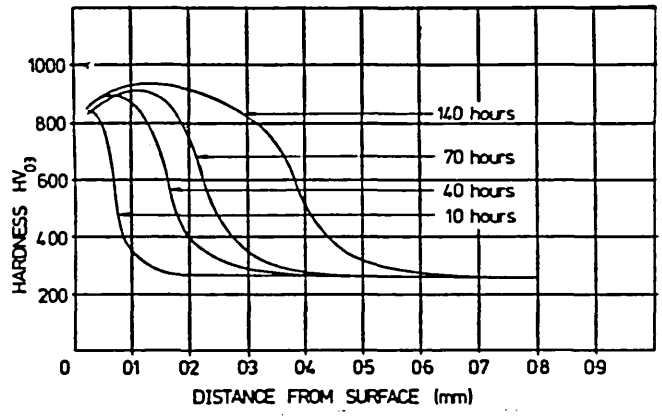


FIGURE 4.4 : Microhardness Profiles of Specimens Bright Nitrided at 480°C for 10, 40, 70 and 140h Respectively.



The basic requirement of this work was to produce a nitrided surface with no compound layer. A nitrided surface consists of two distinct regions namely the 'compound layer' (also termed the 'white layer') and the 'nitrided zone'. The former contains a much higher concentration of nitrogen than the latter. Plates 4.1. 4.2 and 4.3 show typical nitrided surfaces. It is possible that the presence of the compound layer might mask the nitrogen from the nitrided zone in the subsequent nitrogen analysis. This would of course depend upon the sensitivity of the analysis. As the ultimate aim of this work is to incorporate nitrogen-15 into the nitrided zone, it was decided to carry out several exploratory treatments to produce a nitrided surface with a minimum compound layer thickness.

4.3. Experimental Work.

The plasma nitriding test specimens were provided by Westland Helicopters Ltd. and were rollers, the dimensions of which are given later in figure 5.3. They were made from En41B steel, a typical nitriding gear steel,(0.388 %C / 3.13 %Cr / 0.87 %Mo / 0.50 %Mn / 0.23 %Si / 0.19 %V / 0.12 %Ni) and had been hardened initially at 950 ^{o}C for 1 hour, then at 620 ^{o}C for 1 hour before undergoing an annealing treatment at 500 ^{o}C for 24 hours, resulting in their overall hardness being 415 HB. Finally the samples were ground finished.

Plasma nitriding was carried out at the Wolfson Institute for Surface Engineering at Birmingham University using a 25 kW plasma processing unit. Details of the treatments are given in table 4.1.

TABLE 4.1 : Details of the Plasma Nitriding Treatments.

Batch No.	Time/hrs.	Temp./ ^{o}C	Gas Composition
A	24	520	25 %N_2 / 75 %H_2
B	24	520 - 530	Cracked NH_3
C	2x20	500 - 510	2.5 %N_2 / 97.5 %H_2

Polished and tapered sections from each of the plasma treatments were prepared from nitrided roller samples for analysis by optical microscopy and microhardness testing. Results of these analyses are given in the following section. The remainder of the rollers were used in the experimental wear tests described later in Chapter 5.

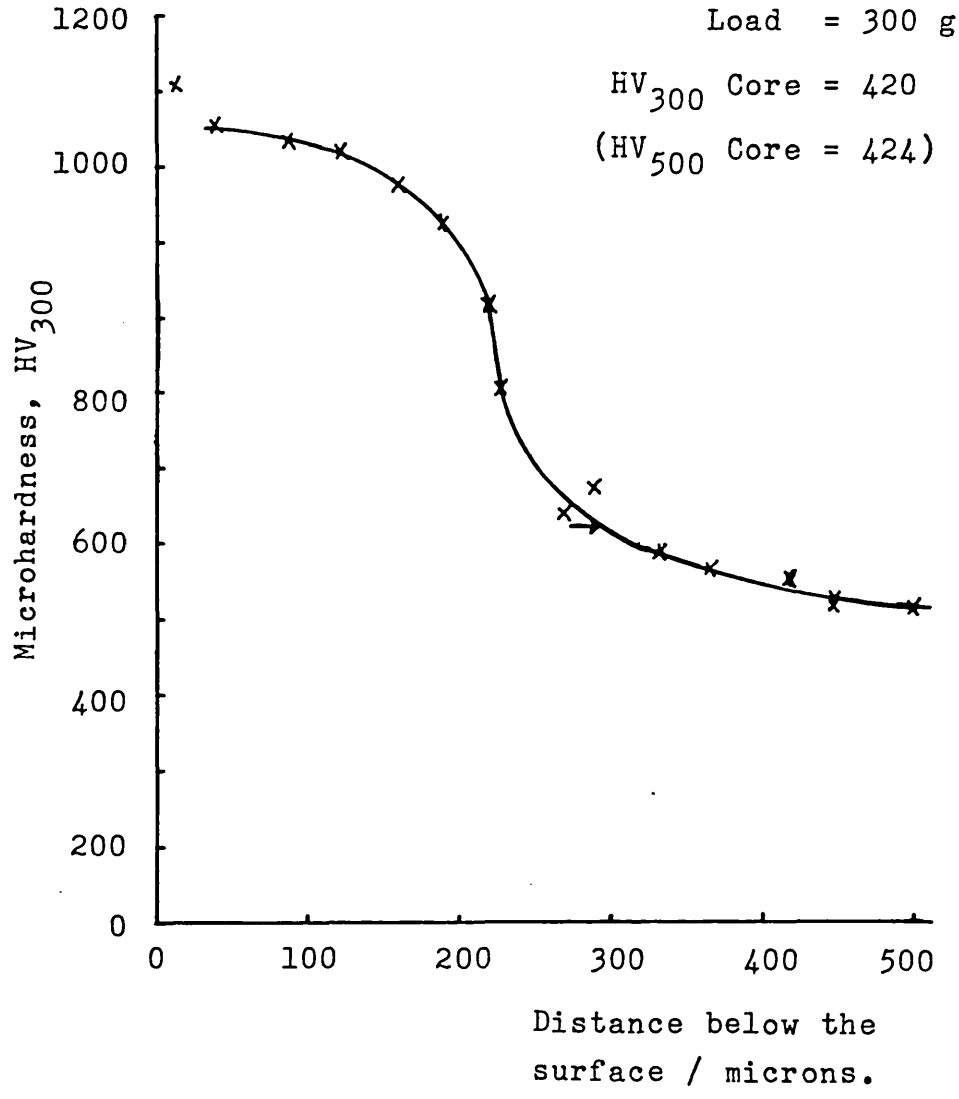
4.4 Results.

Polished sections of samples from each of the plasma nitriding treatments detailed in table 4.1 were analysed by optical microscopy, thereby enabling the thickness of the compound layer to be determined. Plates 4.1 (a), (b) and (c) show examples of these nitrided surfaces and plate 4.2 shows the surface prior to treatment. Microhardness profiles through the nitrided layers were measured from tapered sections in order to determine the case depth which is defined as that depth at which the microhardness value is 100 HV in excess of the core hardness. Figures 4.5, 4.6 and 4.7 show the microhardness profile for each of the treatments and the measured results are summarised in table 4.2.

TABLE 4.2 : Results of Nitriding Treatments.

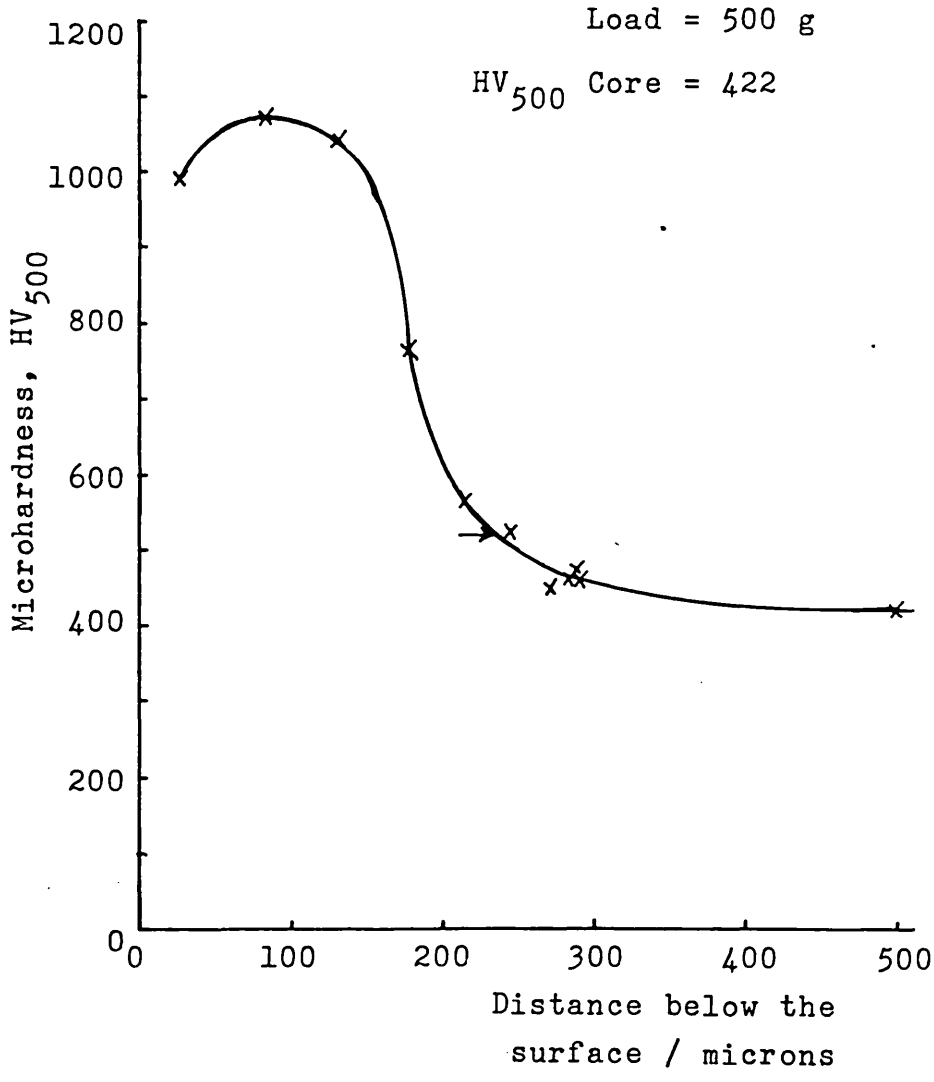
Treatment Batch No.	Case Depth (μms)	White layer thickness (μms)
A	300	4.75
B	234	12
C	200	0

FIGURE 4.5 : Microhardness Profile of a Plasma Nitrided Sample Treated Under Conditions A.



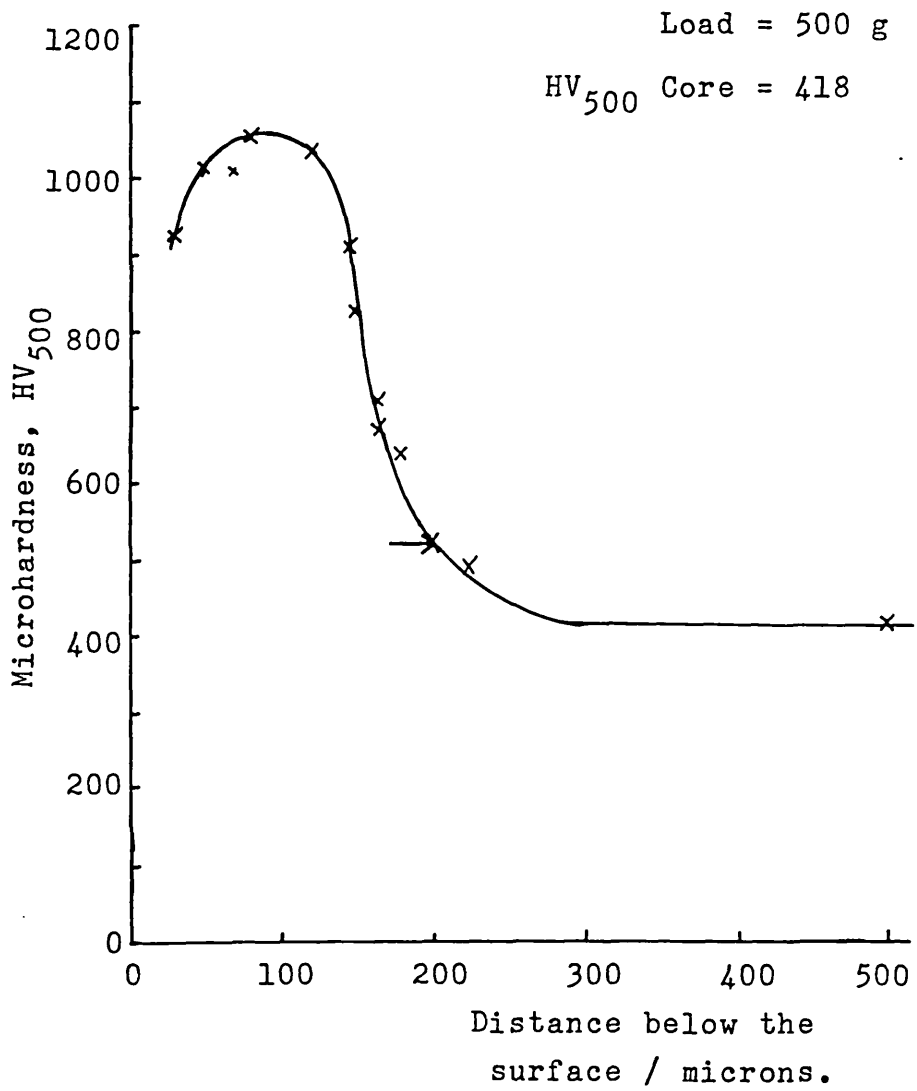
Case depth = 300 microns

FIGURE 4.6 : Microhardness Profile Obtained on a Sample from Treatment Conditions B.



Case depth = 234 microns

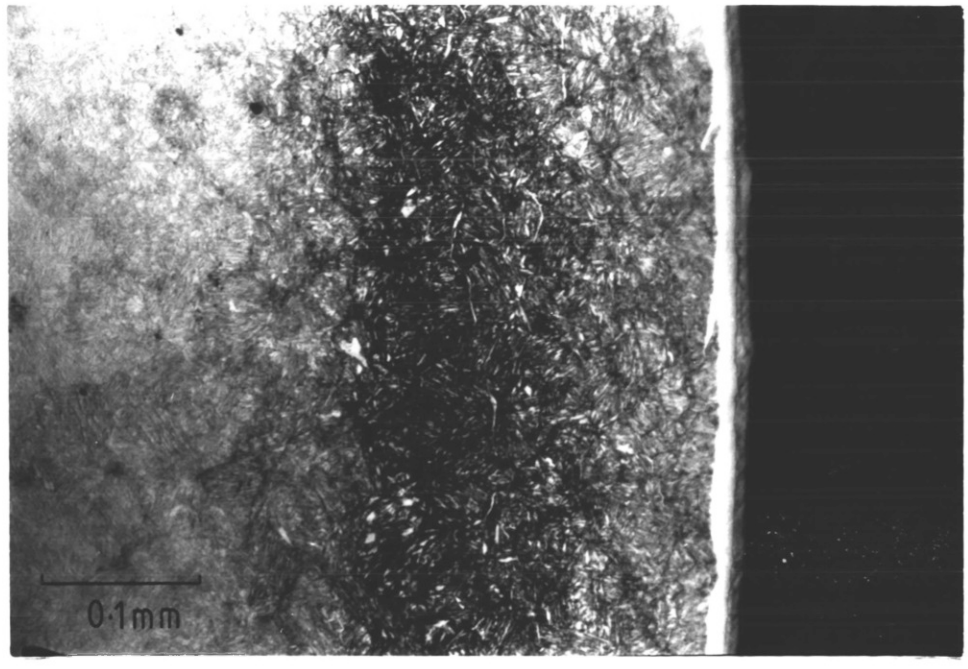
FIGURE 4.7 : Microhardness Profile of a Nitrided Sample After Treatment C.



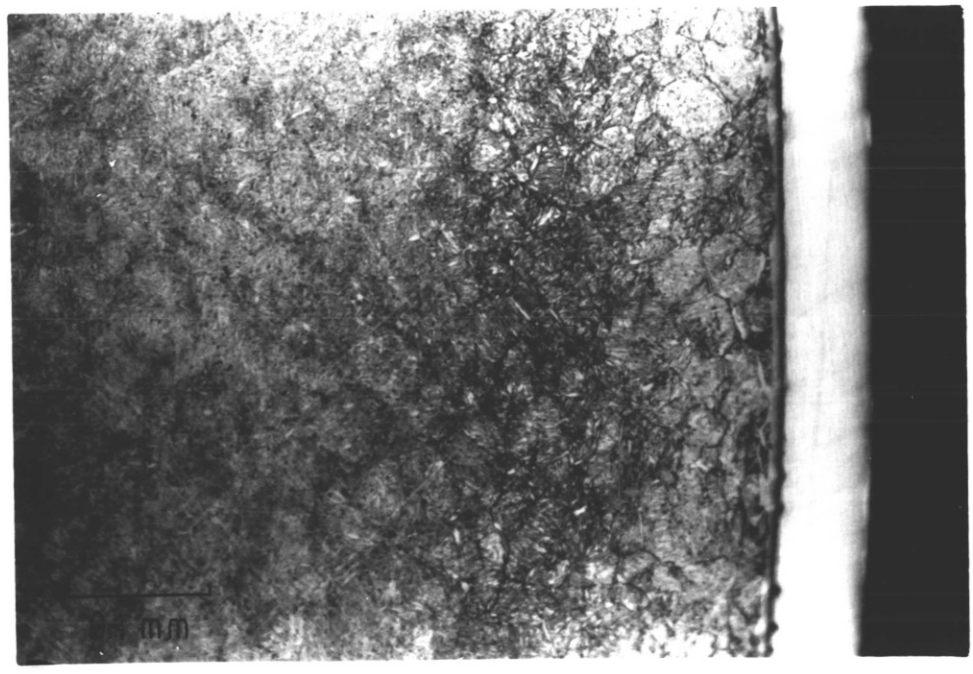
Case depth = 200 microns

PLATE 4.1 : Microstructure of Nitrided Surfaces. (Etched in 5% Nital.)

(a) Treatment A. 210 x.



(b) Treatment B. 210 x.



(c) Treatment C. 375 x.

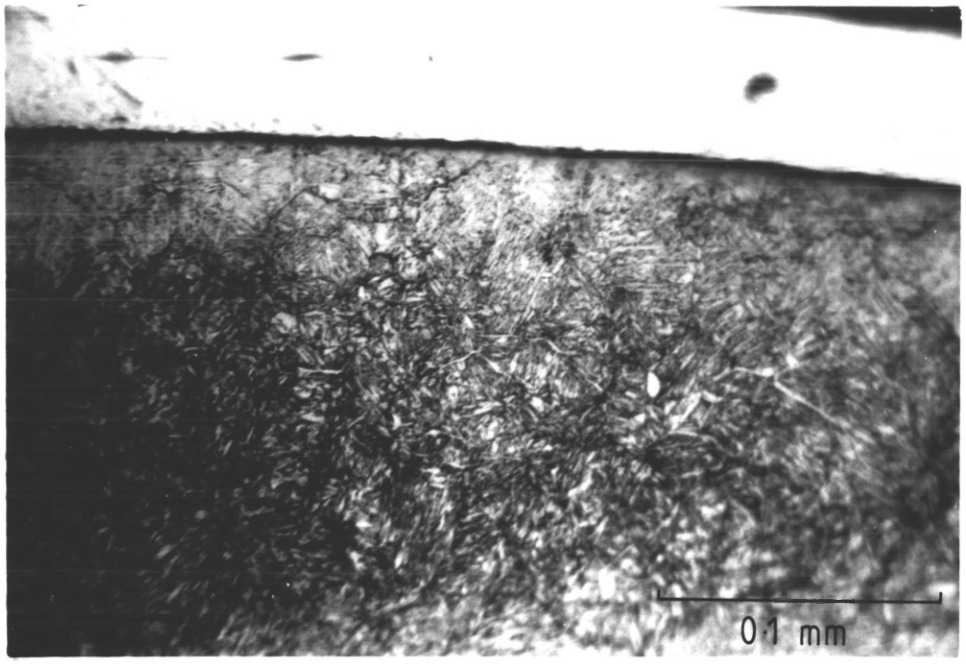
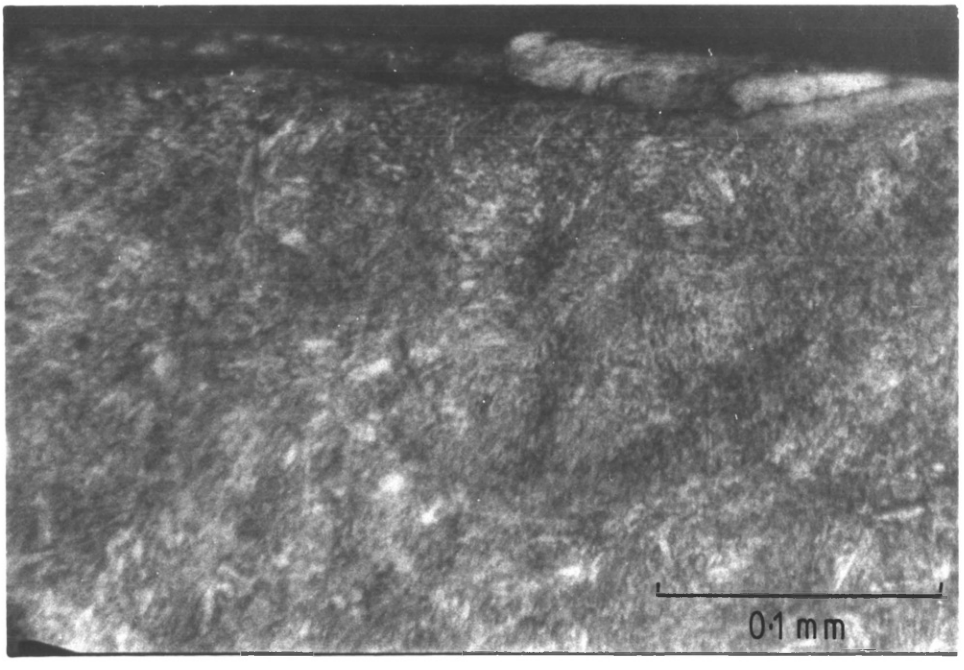


PLATE 4·2 : Microstructure of En40B Steel Surface. Etched in 5% Nital. 375x.



4.5 Summary.

Several plasma nitriding experiments were carried out to determine the treatment parameters required to produce a nitrided layer with a minimum compound layer thickness. The parameters controlling the final nitrided surface include steel composition, gas composition, time and temperature. A set of conditions were obtained which were considered suitable to produce the desired surface as listed in table 4.3.

TABLE 4.3 : Summary of Nitriding Parameters.

Control Parameters	Set Values
Steel composition	En41B
Gas composition	2.5% N_2 / 97.5% H_2
Time	40 hours
Temperature	510 /520 ^{o}C

These conditions appeared appropriate for the nitriding experiment using the stable isotope, nitrogen-15, where at a suitable stage in the plasma treatment the 'ordinary' gas would be substituted by a $^{15}N_2$ / H_2 mixture.

Details of the stable isotope experimental studies are described later in chapter 7.

CHAPTER 5. WEAR DEBRIS GENERATION.

After introducing nitrogen into the surface of the steel rollers the cone-on-roller- wear machine was used to generate and collect wear debris for analysis as discussed earlier in chapter 3. This chapter describes the cone-on-roller machine, then the experimental details and results obtained in preliminary work using N-14 treated surfaces.

5.1. Cone-on-Roller Wear Machine.

The cone-on-roller wear machine, illustrated in figure 5.1 and plate 5.1, was originally designed and developed by Bailey to enable wear experiments similar to 4-ball wear tests to be carried out on materials which were not available as balls (96). The top ball of the 4-ball machine has been replaced by a cone and the three lower ones by cylindrical rollers. Figure 5.2 and plate 5.2 show a section of the stainless steel cup in which the three rollers are mounted so as to be constrained from all movement. The inside of the cup is a 45^{o} cone which parallels the test cone. A lubricant-shield is threaded onto the cup to retain lubricant in the fully-flooded contacts. The cup is located on three pins on top of a torque tube and the whole lower assembly is mounted on a lever arm so that it can be loaded upwards against the cone using a spring balance. Plate 5.3 shows the whole assembly loaded in preparation for a test run. The cone is held in a chuck via a grub screw at the rim of the chuck and contacts the curved sides of the three rollers such that each roller supports an equal load. An electric motor drives the cone / chuck assembly about the vertical axis at a constant speed of 1,000 rpm via a toothed belt and gearbox. Rotation of the cup is constrained by the torque tube and a slipping clutch prevents the torque exceeding a pre-set value.

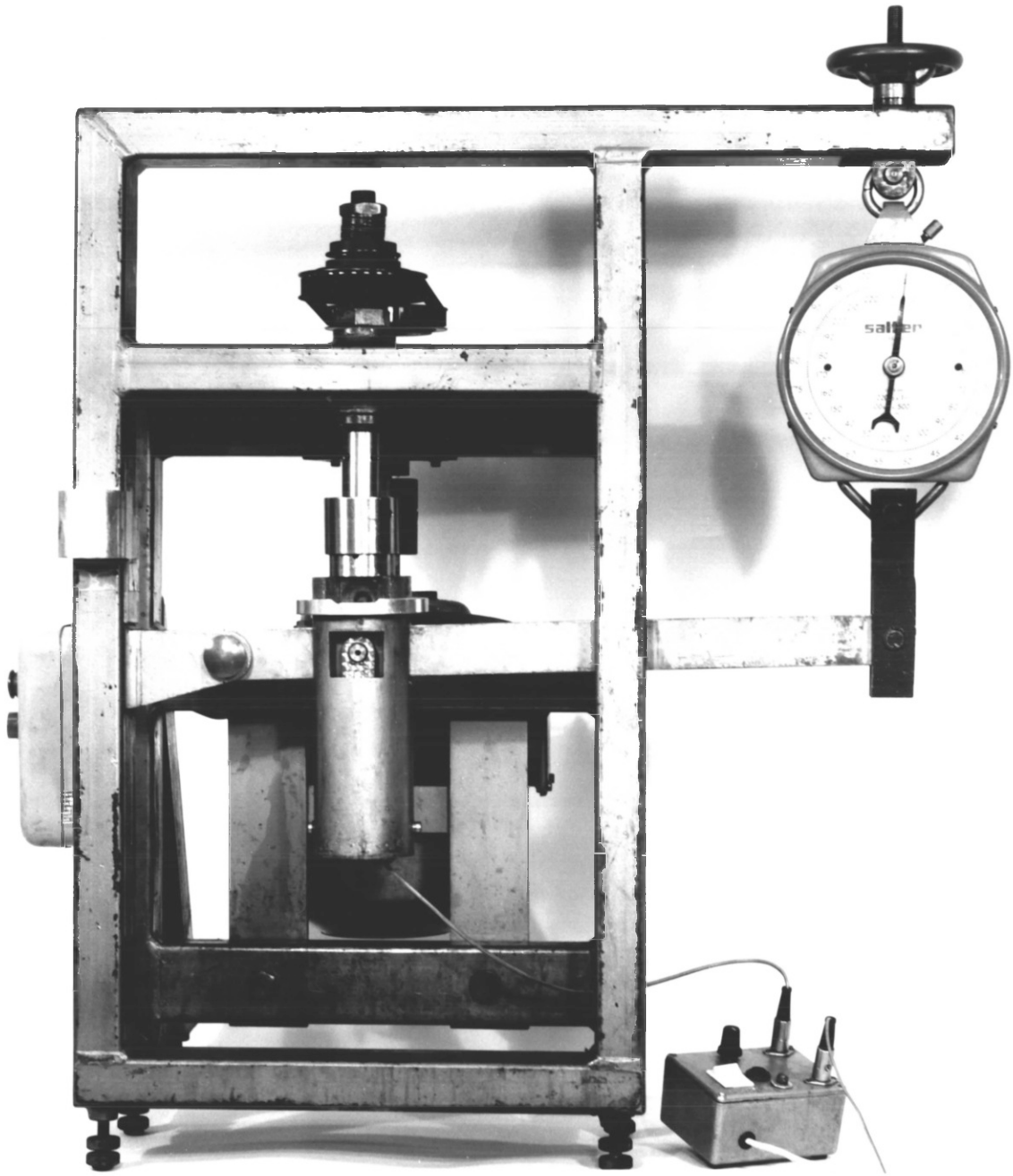


PLATE 5·1 : The Cone-on-Roller Wear Machine.

FIGURE 5.1 : Diagrammatic View of the Cone-on-Roller Wear Machine.

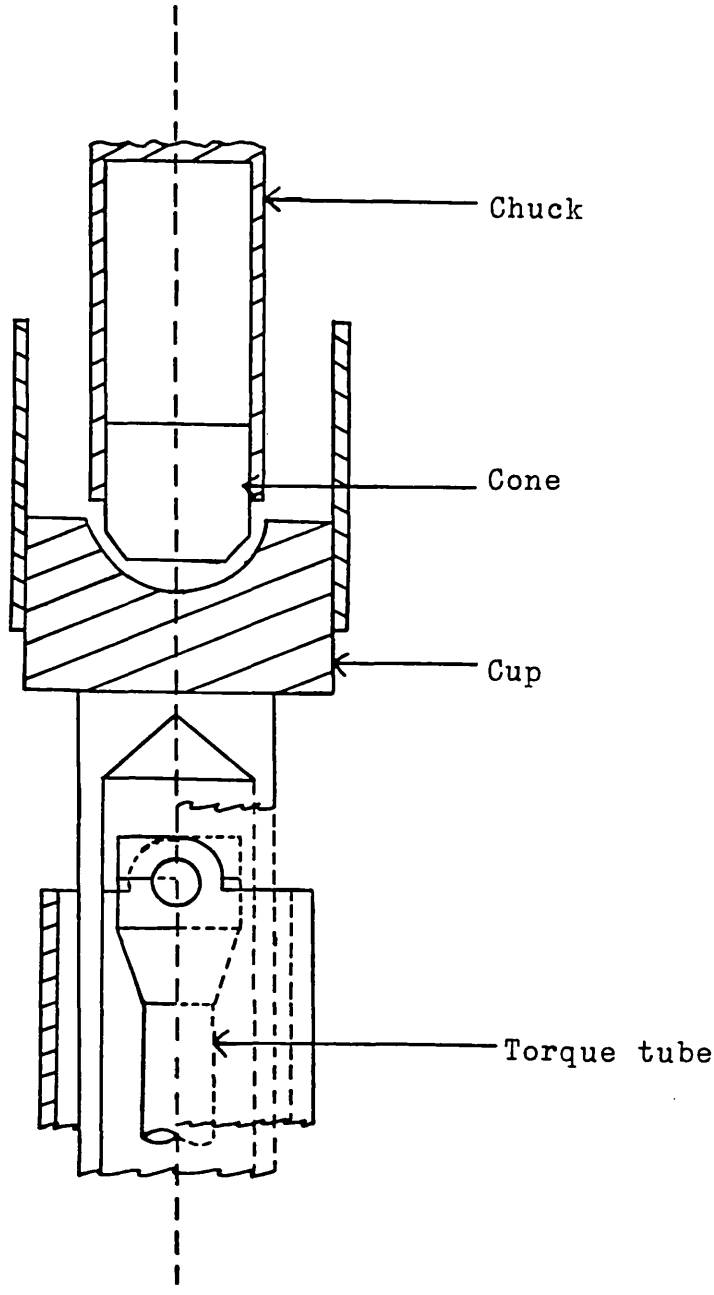
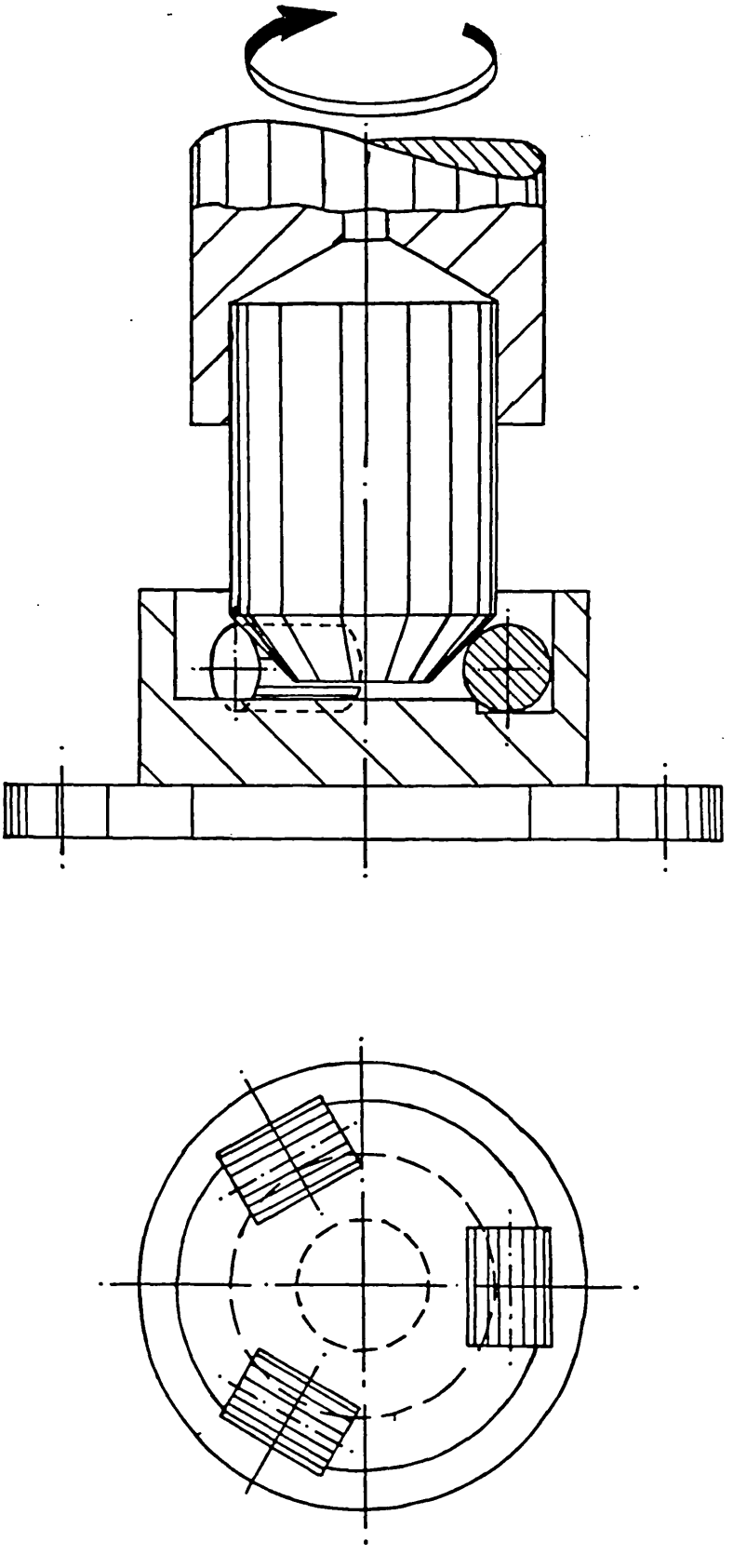


PLATE 5·2 : Cone and Rollers Prior to Loading.

PLATE 5·3 : The Loaded Assembly.

FIGURE 5.2 : Schematic Representation of a Cone Loaded Against Three Rollers Mounted in a Cup.

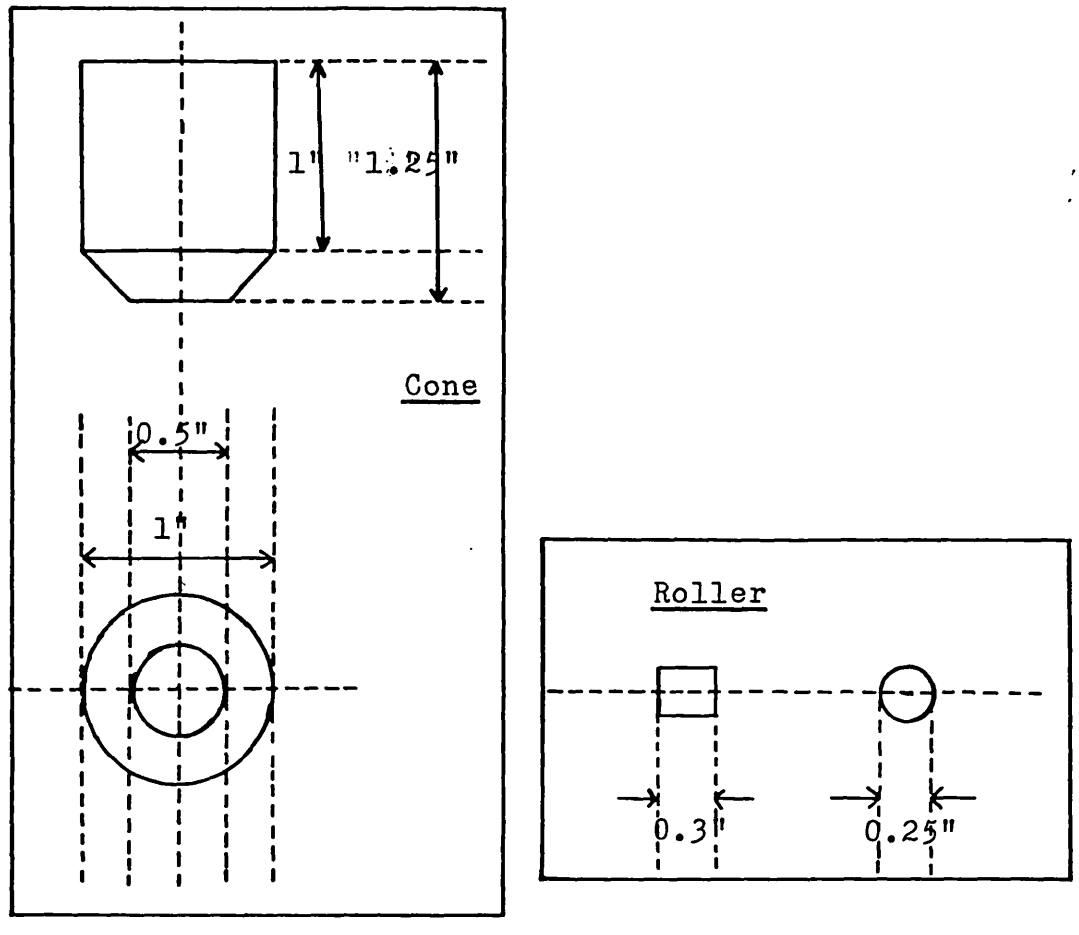


Strain gauges are fitted to the torque tube, thereby enabling the frictional torque developed by the rotation of the cone against the stationary rollers to be measured. Also the system allows for temperature measurements using thermocouples, but for the purpose of this work neither measurement was considered necessary.

Dimensions of the cone and roller test specimens are given in figure 5.3. The rollers were made from En41B steel and subjected to the heat treatments and plasma nitriding treatments described earlier in section 4.3. The cones, which were provided by Neale Components, Coventry, U.K., were made from EN32B steel and were carburised and heat treated.

A new cone and set of three rollers were used for each test run.

FIGURE 5.3 : Cone and Roller Dimensions.



5.2. Experimental Details.

Prior to each experiment, the cup and lubricant shield were degreased with toluene for five minutes using an ultrasonic cleaning bath followed by a further five minute period in acetone in order to remove all traces of toluene. A Soxhlet apparatus was used for cleaning the cone and rollers whereby they were continuously washed in refluxing toluene for two hours, then rinsed in acetone in the ultrasonic bath. All the cleaned parts were allowed to dry in air before assembly.

Immediately after the three rollers were positioned in the cup they were completely covered by the lubricant. A cone was then mounted in the chuck, the whole system assembled as described in the previous section and an initial load of 5 lb. applied. Details of the individual experiments are given in table 5.1. For experiments B2 to C2 the lubricant used was ETO 25 , an aviation gas turbine oil meeting specification MIL-L-23699 (marked * in the table), and for the remainder an ester base oil Mobil 2948 was used (marked **). As each experiment progressed the load was increased by 5 lbs. at 1 minute intervals without it affecting the sliding unless otherwise stated. The frictional torque was continuously recorded via a chart recorder.

TABLE 5.1 : Details of the Wear Experiments.

TEST NO.	TIME/MINS.	COMMENTS
*B2	4.25	Initial seizure after 2 mins. Test stopped because lubricant was leaking from the cup
*B3	8.75	Seizure occurred at 45 lb.load
*B4	8.00	Initial seizure after load was increased to 15 lb.
*B5	6.00	Test stopped after seizure occurred at 30 lb. load
*C1	29.00	Wear machine not working properly. Experiment stopped and rollers reloaded 6 times. Total time was 29 mins. Load was increased in 10 lb increments. Maximum load was 40 lb.
*C2	31.00	Experiment stopped and cylinders reloaded 6 times. Load increased in 10 lb increments, maximum load was 45 lbs. Problem due to shaft seizure because of the slip clutch
**C3	4.25	Initial seizure after 1 min. 2nd. seizure occurred after 2 mins. when load increased to 15 lbs. Maintained at 15 lbs for 2.25 mins. Test stopped due to excessive noise.
**C4	2.10	Initial seizure after 1 min. 2nd. seizure after 2 mins. Test stopped because of noise level.
**C5	3.8	Seizure after 1 min. and 2 mins. Maintained at 15 lb. load for 1.8 mins. Stopped because of noise
**C6	2.2	Seizure after 1 min. and 2 mins. Stopped because of noise.

The letters B and C in the wear test numbers shown in table 5.1 link the rollers to the relevant plasma treatment detailed in table 4.1. Rollers from the A treatment were used solely in preliminary experiments to establish the experimental method.

After each test the lubricant containing the wear debris was collected and the cup rinsed out with toluene. A centrifuge was used to assist in the separation of the debris from the lubricant / toluene mixture. Any remaining adsorbed lubricant was dissolved away by rinsing in acetone and finally the debris was dried in air.

5.3. Results.

Results of the cone-on-roller experiments are summarised in table 5.2. The wear scar parameters, a and b, are defined by figure 5.4 and are measured using a travelling microscope. Plate 5.4 shows a typical wear scar obtained from a wear experiment and the shape and size distribution of the wear debris obtained in this work can be seen in plate 5.5.

FIGURE 5.4 : Diagrammatic Representation of a Worn Roller.

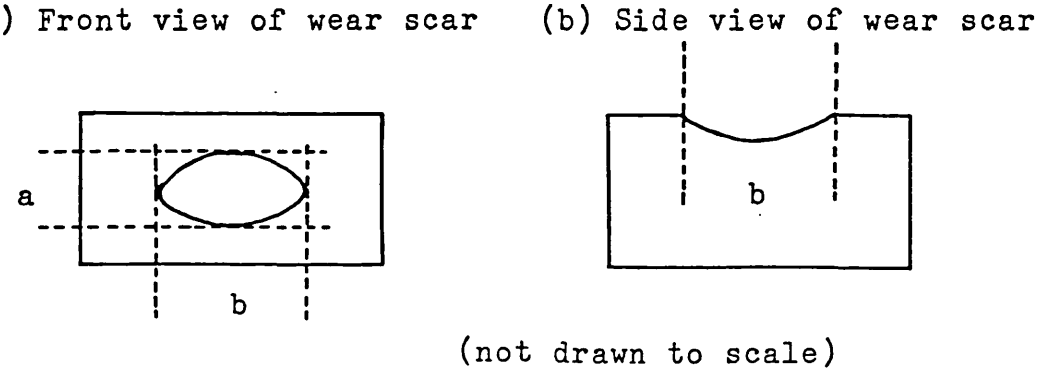


TABLE 5.2 : Results of the Wear Experiments.

Wear Test No.	Wt. loss of cylinders / mg	Wear scar measurements a / mm	b /mm	Wt.debris collected / mg
B2	6.63	1.6	6.3	-
B3	35.96	2.7	5.7	10.02
B4	10.88	2.0	4.2	
		1.6	3.5	23.81
B5	40.49	1.4	3.0	
		1.4	3.0	
C1	2.74	2.5	5.7	13.65
C2	5.98	1.9	4.1	
		1.4	2.8	
C3	-	2.6	5.8	20.67
C4	14.07	2.0	4.2	
C5	81.28	3.2	6.3	32.49
C6	11.93	2.0	4.3	

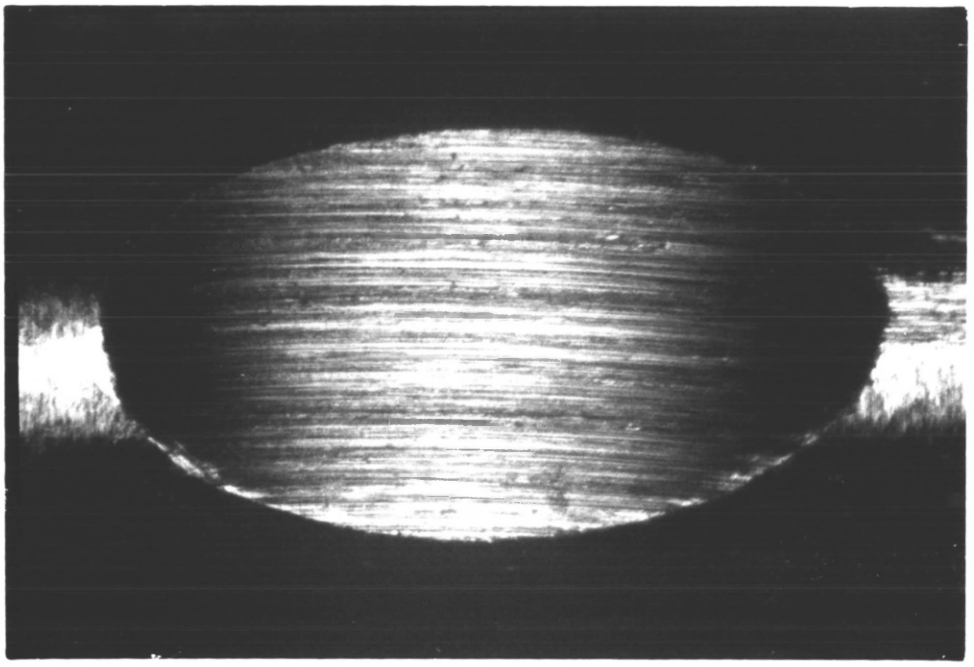
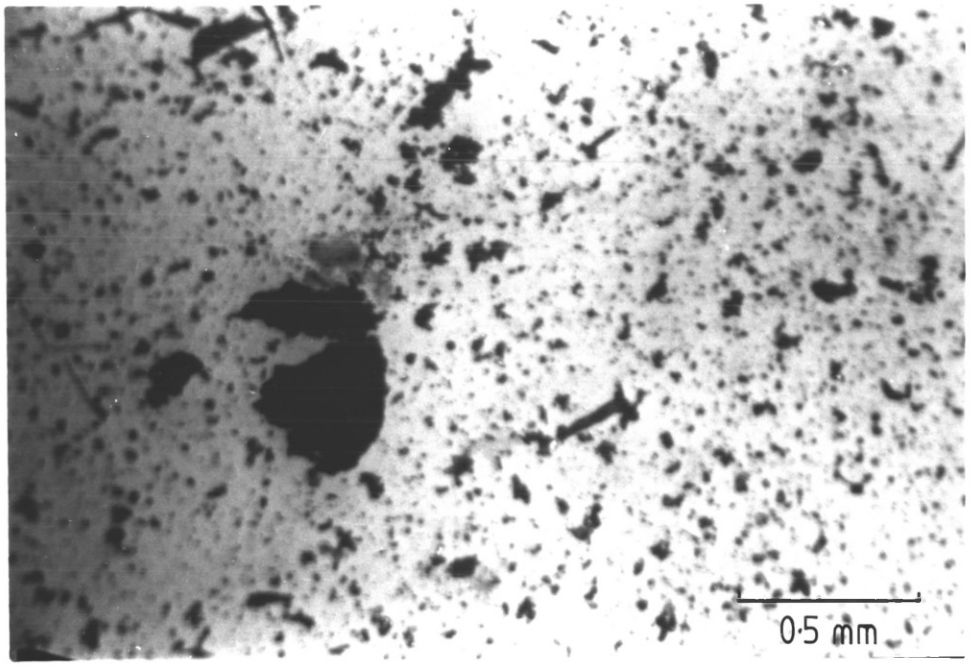


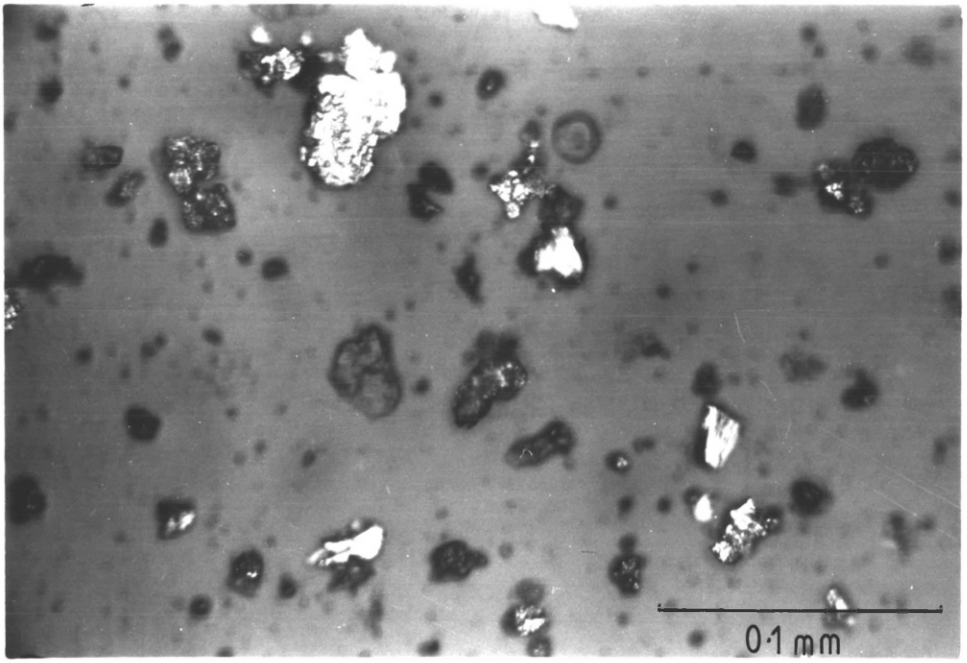
PLATE 5·4 : A Typical Wear Scar.

PLATE 5·5 : Wear Debris Particles Generated During A Wear Experiment.

(a) 48 x.



(b) 375 x.



5.4. Discussion.

The size distribution of the wear debris particles ranged from sub-micron up to about 200 μms, with the lower size range containing the larger proportion of particles as can clearly be seen in plate 5.5. This accounts for the low recovery of debris after the wear experiments because the very fine particles remain in suspension in the lubricant and are not seperated either by filtration or by centrifuge.

However, the cone-on-roller wear machine was still considered suitable for the purposes of this study which was to generate wear debris from nitrided surfaces in preparation for nitrogen analyses investigations.

CHAPTER 6. NITROGEN ANALYSIS PRELIMINARY EXPERIMENTS.

Nitrogen in nitrided steel debris is in the form of metal nitrides. Healy and Parker (105) have carried out exhaustive research on the chemical determination of metal nitrides and the results of this form the basis of an experimental method adopted in this study for the detection of nitrogen ,N-14, and its stable counterpart N-15. As concluded in chapter 3 the most suitable means of detecting this nitrogen is using a modification of the Kjeldahl method of nitrogen analysis.

This chapter describes the development of the apparatus and analysis procedure using 'ordinary' nitrogen (N-14) along with the calibration of the ratios NH_3 / $^{15}NH_3$ to the ratios of the infrared bands.

6.1. Analytical Procedure.

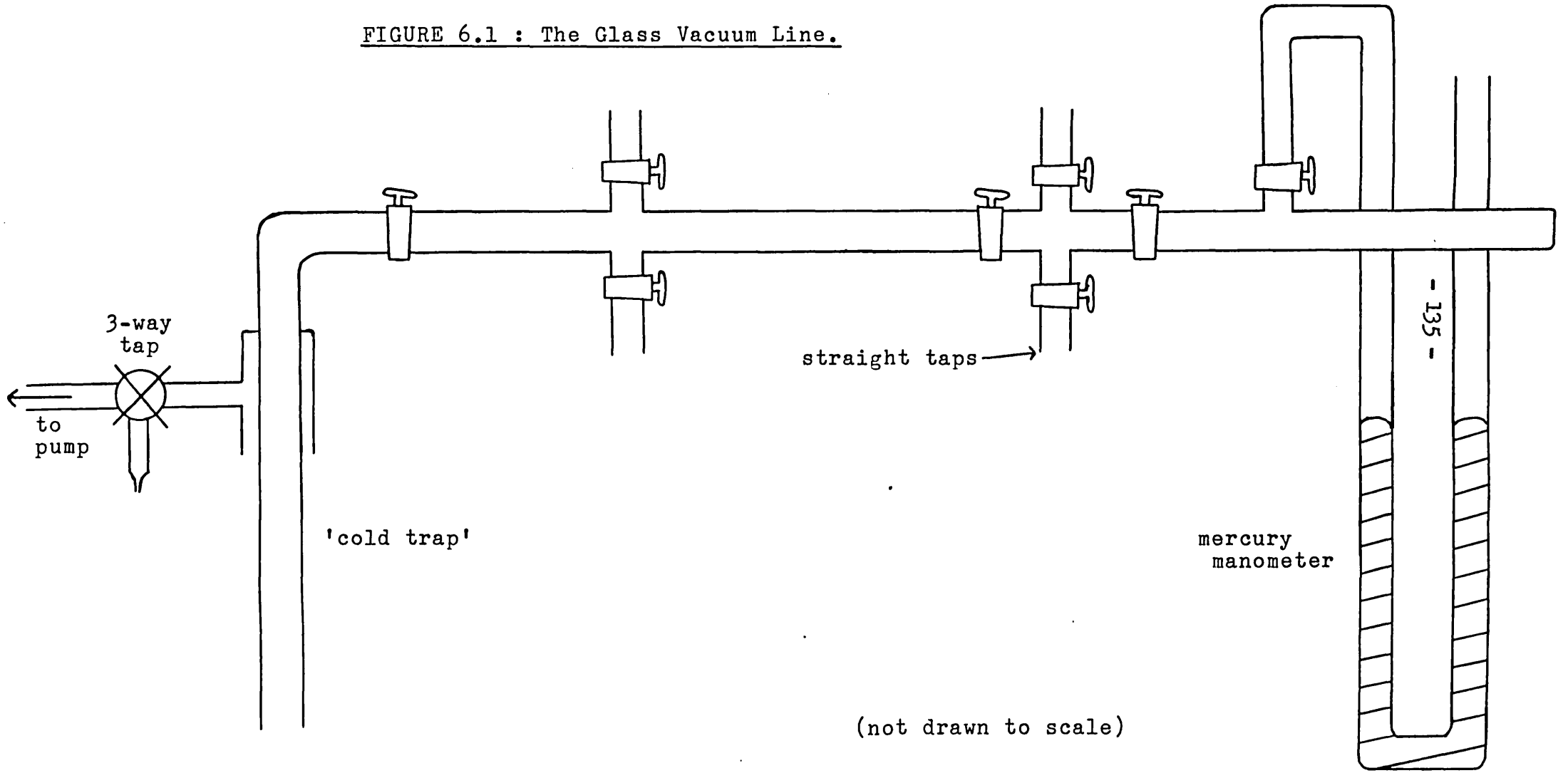
An outline of the experimental procedure is as follows :

Initially anhydrous sodium sulphate, $Na_2 SO_4$, (10 g) is dissolved in concentrated sulphuric acid, $H_2 SO_4$, (10 cm^3) prior to the addition of the nitrided debris (approximately 30 mg). This acid mixture is then refluxed vigorously until dissolution is complete. After cooling, 40 % sodium hydroxide solution, NaOH, (40 cm^3) is added and finally the mixture is distilled and the resulting gas analysed by infrared (IR) transmission spectroscopy.

6.2. The Apparatus.

The standard chemical method of handling gaseous materials in the laboratory is to use a glass vacuum line (98). This line is often designed for a specific purpose as it is preferable to minimise the number of joints and taps thereby reducing the possibility of leaks. Figure 6.1 shows the vacuum line designed for nitrogen analysis of the debris. It was constructed by the glassblower in the Chemical Engineering department, Imperial College.

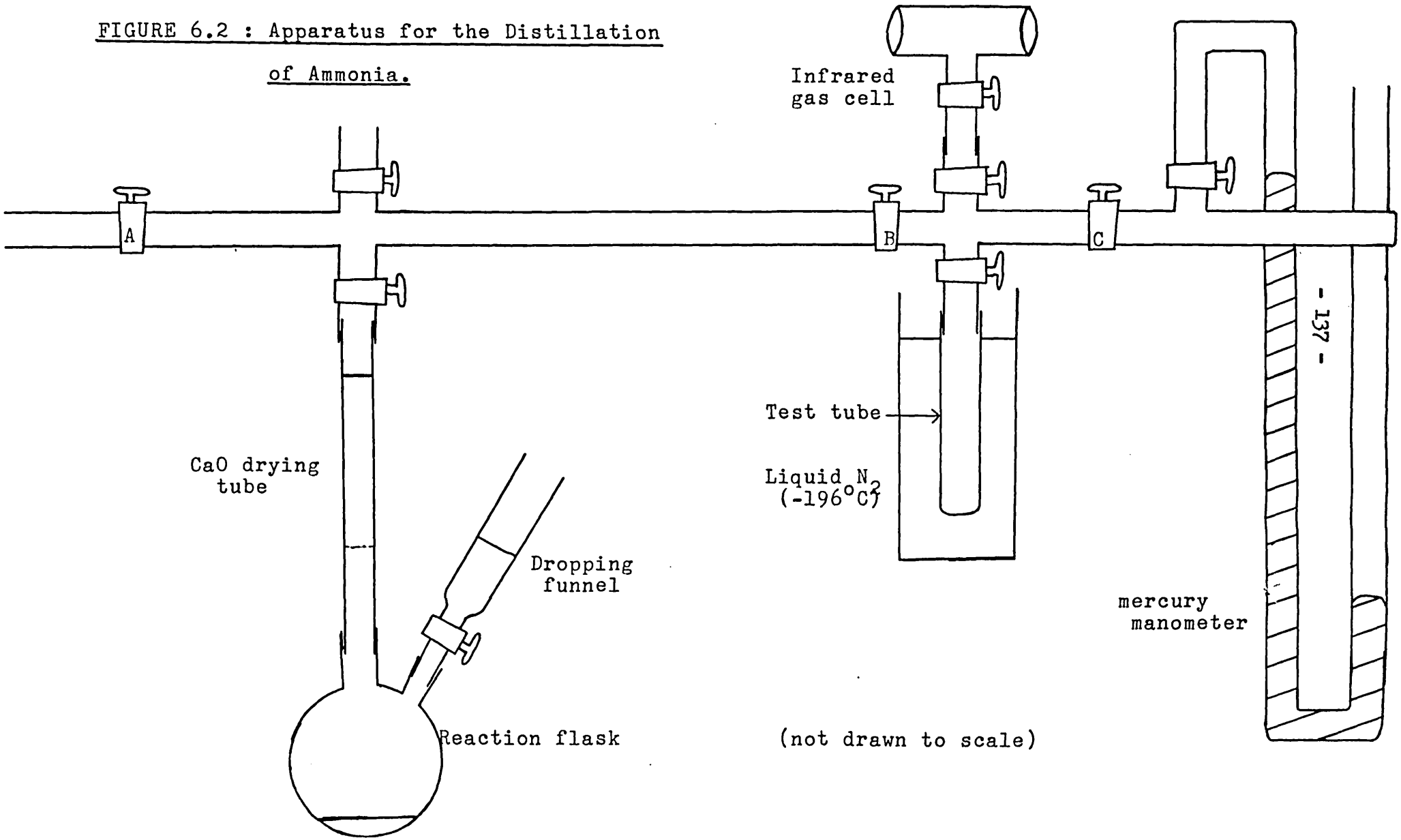
FIGURE 6.1 : The Glass Vacuum Line.



In order to explain the technique , the system is considered as a whole (that is with the apparatus assembled on to the line) as illustrated in figure 6.2.

After the acid digestion stage the apparatus is assembled on to the vacuum line and the whole system evacuated using a vacuum pump. It is tested for leaks by isolating the line from the pump (i.e. tap A is closed) and watching for an increase in pressure as indicated by the mercury manometer. When the system is free from leaks it is isolated and the test-tube immersed in liquid nitrogen, N_2. On addition of the alkali any gas produced will diffuse into all available space. However, with time it will concentrate in the test-tube (known as the 'cold finger') and solidify due to the extreme temperature of liquid N_2, -196 ^{o}C. When the reaction is complete taps B and C are closed and the test-tube is opened to the IR gas cell. The Dewar flask containing the liquid N_2 is then removed. As the 'cold finger' warms up the gas diffuses into all the available space, of which approximately 60 % is accounted for by the IR cell. The cell can then be removed to the spectrometer for analysis of the gas.

FIGURE 6.2 : Apparatus for the Distillation of Ammonia.



6.2.1. Precautions.

Special precautions are necessary when working with vacuum lines. It is important to ensure that the liquid N_2 level in the Dewar flask is maintained throughout the experiment in order to prevent a build-up of the gas pressure. Care must be taken not to allow air into the line when the cold trap is immersed in liquid N_2 in order to prevent condensation of liquid oxygen which is explosive. Apiezon-M grease was used on all the taps and ground-glass joints but it is important not to over-grease them as this could result in blockage of the tap barrels.

6.3. Ammonium Sulphate Studies.

Preliminary chemical experiments were necessary to :

(i) develop and test the apparatus described in section 6.2;

(ii) determine whether it was possible to detect ammonia from the acidic mixture;

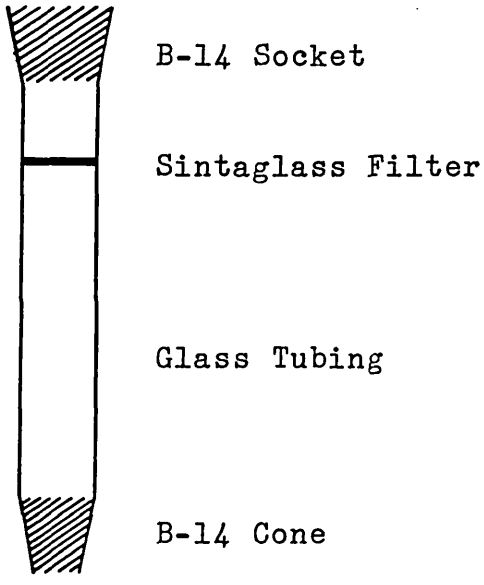
(iii) determine whether it was possible to distinguish between N-14 and N-15, and if so calibrate the ratios of NH_3 / $^{15}NH_3$ to the ratios of the absorption bands in the infrared spectra.

To investigate these aims, experiments were carried out using the ammonium sulphate salts $(NH_4)_2SO_4$ and $(^{15}NH_4)_2SO_4$ dissolved in sulphuric acid in preference to digested steel debris. The justification for this was that during the digestion process the nitrogen in the steel is oxidised to ammonia which is fixed as ammonium sulphate by sulphuric acid. On making the solution alkaline ammonia is formed :

$$(NH_4)_2SO_4 + H_2SO_4 + 4NaOH \longrightarrow 2NH_3 + 2Na_2SO_4 + 4H_2O$$

Initially the chemical apparatus used was standard Quickfit glassware with the exception of the vacuum line described in section 6.2 and the drying tube which consisted of a cone, a socket and a sintaglass filter as can be seen in figure 6.3.

FIGURE 6.3 : Drying Tube.



Acidic salt mixtures were prepared by dissolving known quantities of the salts $(^{14}NH_4)_2SO_4$ and $(^{15}NH_4)_2SO_4$, approximately 0.1 g in total, in concentrated H_2SO_4 (10 cm^3). This mixture was then treated in the same way as the acid digest which is described in section 6.1, namely alkali addition, distillation and infrared analyses of the resultant gas. Results of the infrared analyses are discussed later in section 6.5.

6.4. Wear Debris Analyses.

Debris obtained from the wear experiments described in section 5.2 was analysed using the method described earlier in section 6.1. One experiment involved digesting 32.49 mg of nitrided debris and another 68.15 mg. The infrared spectra obtained from these experiments are given and discussed later in section 6.6.

6.5. Results of the Ammonium Sulphate Studies.

"May her rest be long and placid,
She added water to the acid.
But praise the girl who did as taught 'er
-She added acid to the water." (anon)

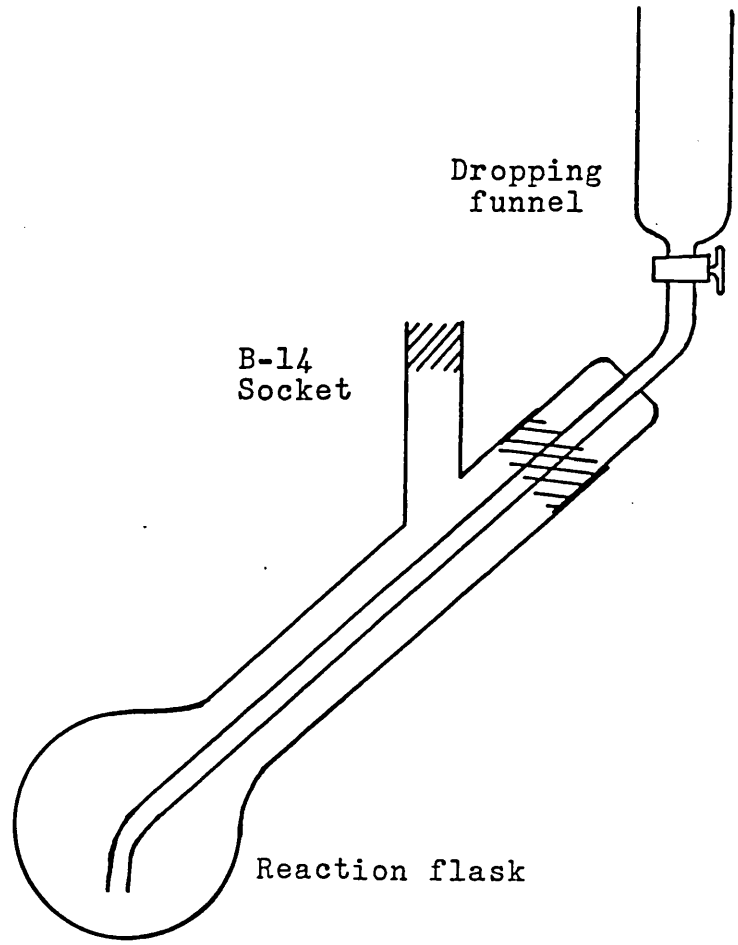
Problems were encountered in the initial experiments as a result of using standard Quickfit glassware. These were finally overcome by the development of a set of apparatus designed specifically for this work. The addition of alkali to an acid is a highly exothermic, 'violent' reaction, resulting in temperatures in the order of 500 ^{o}C which caused the grease in the ground-glass joints to melt, thereby weakening the vacuum seal. This, together with the build-up of gas pressure due to the rapid evolution of gases, resulted in sometimes dramatic 'explosions' at one of the weakened joints. Control of this reaction was possible by the careful addition of the alkali over a period of approximately one hour. However, this was considered unsuitable in terms of time, labour and safety.

In order to overcome this problem a set of apparatus was designed based on the standard Kjeldahl apparatus, which was adapted to fit on to the vacuum line. It consisted of a Kjeldahl flask, a B-14 socket, a B-24 cone, a B-24 socket and a dropping funnel, all joined as shown in figure 6.4.

Advantages of this system include :

- the long neck of the Kjeldahl flask serves as both an air condenser and a means of separating the ground-glass joints from the reaction vessel;
- the alkali can be added rapidly to the acid mixture via the lengthened dropping funnel.

FIGURE 6.4 : Modified Kjeldahl Apparatus.



This modified Kjeldahl apparatus replaced the round-bottomed flask and dropping funnel illustrated in figure 6.2.

Figure 6.5(a),(b),(c) shows the infrared transmittance spectrum from 2,000 - 700 cm^{-1} of the gas collected from the reaction of the alkali addition to the ammonium (N-14) sulphate solution. Assignment of the major bands observed in figure 6.5 has been summarised in table 6.1 (109). The other peaks observed in the spectrum are the hyperfine structure due to molecular rotations, typical in infrared spectra of gaseous samples. Table 6.2 contains the fundamental wavenumbers of the absorption bands due to ammonia (NH_3 and $^{15}NH_3$) given by Pinchas and Laulicht (75).

FIGURE 6.5 : Infrared Transmittance Spectrum of the Gas Obtianed from $(NH_4)_2SO_4$.

(a) 2000 - 1550 cm^{-1}

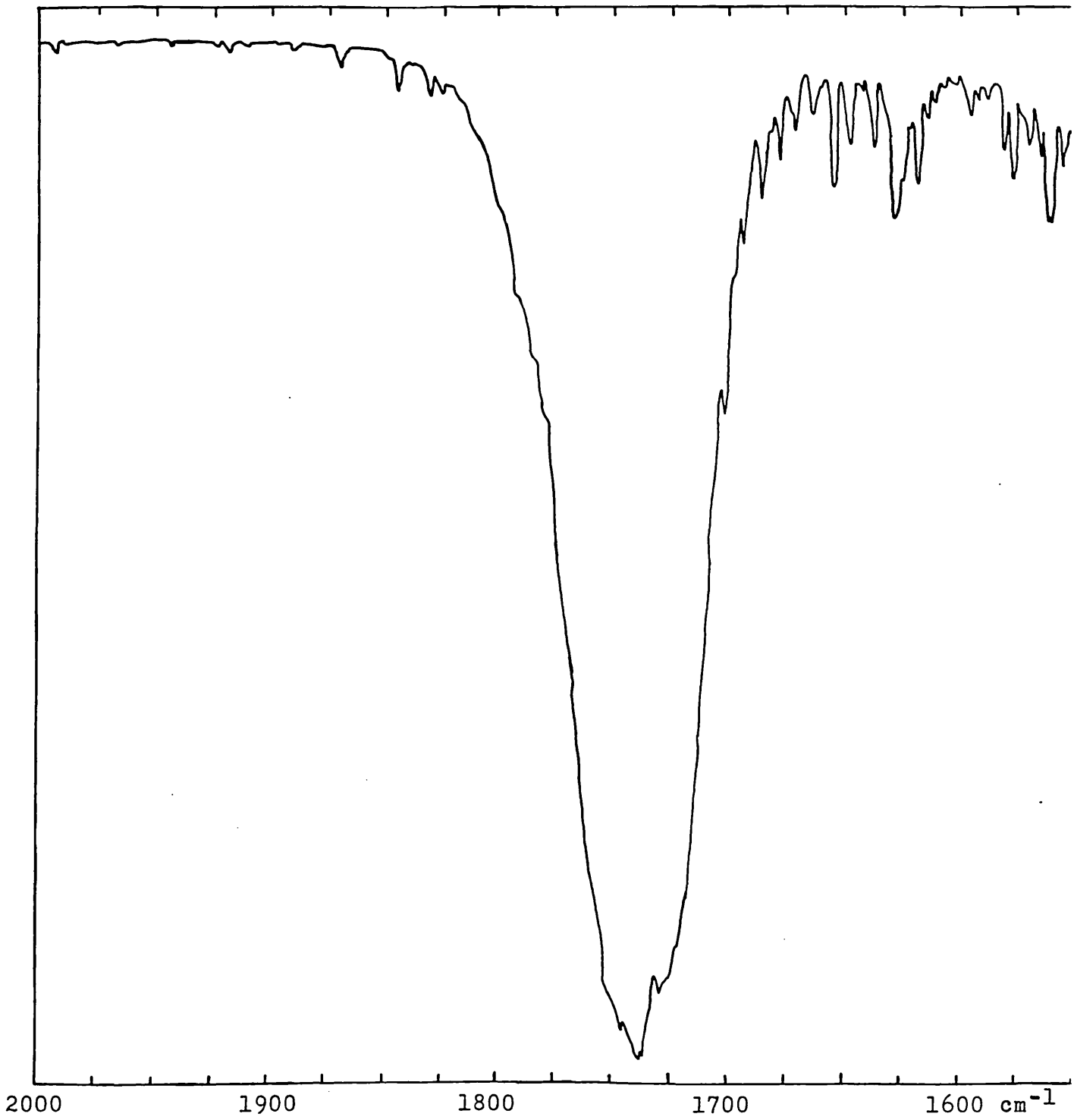


FIGURE 6.5 (b) : 1550 - 1100 cm^{-1}

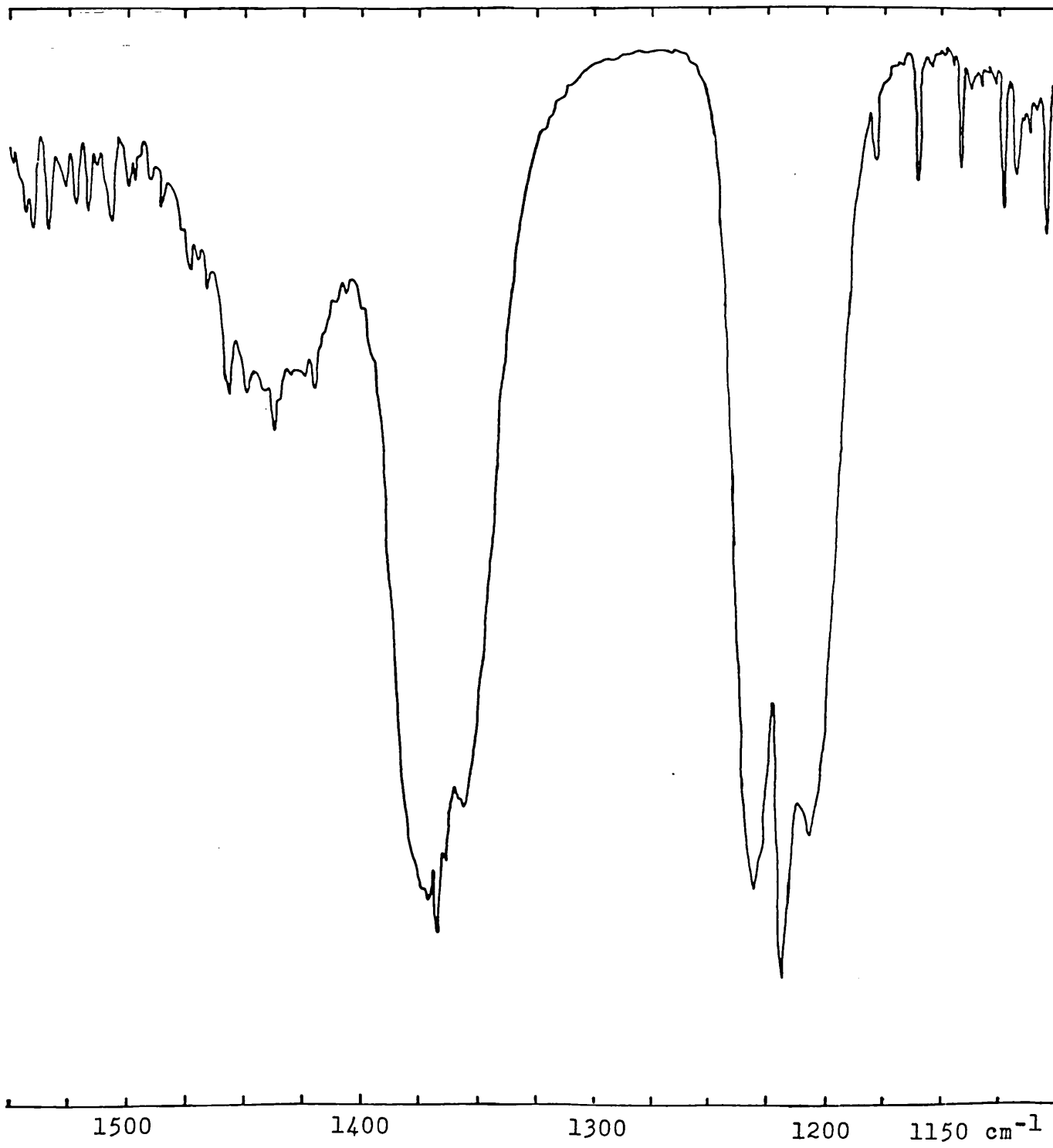


FIGURE 6.5 (c) 1100 - 700 cm^{-1}.

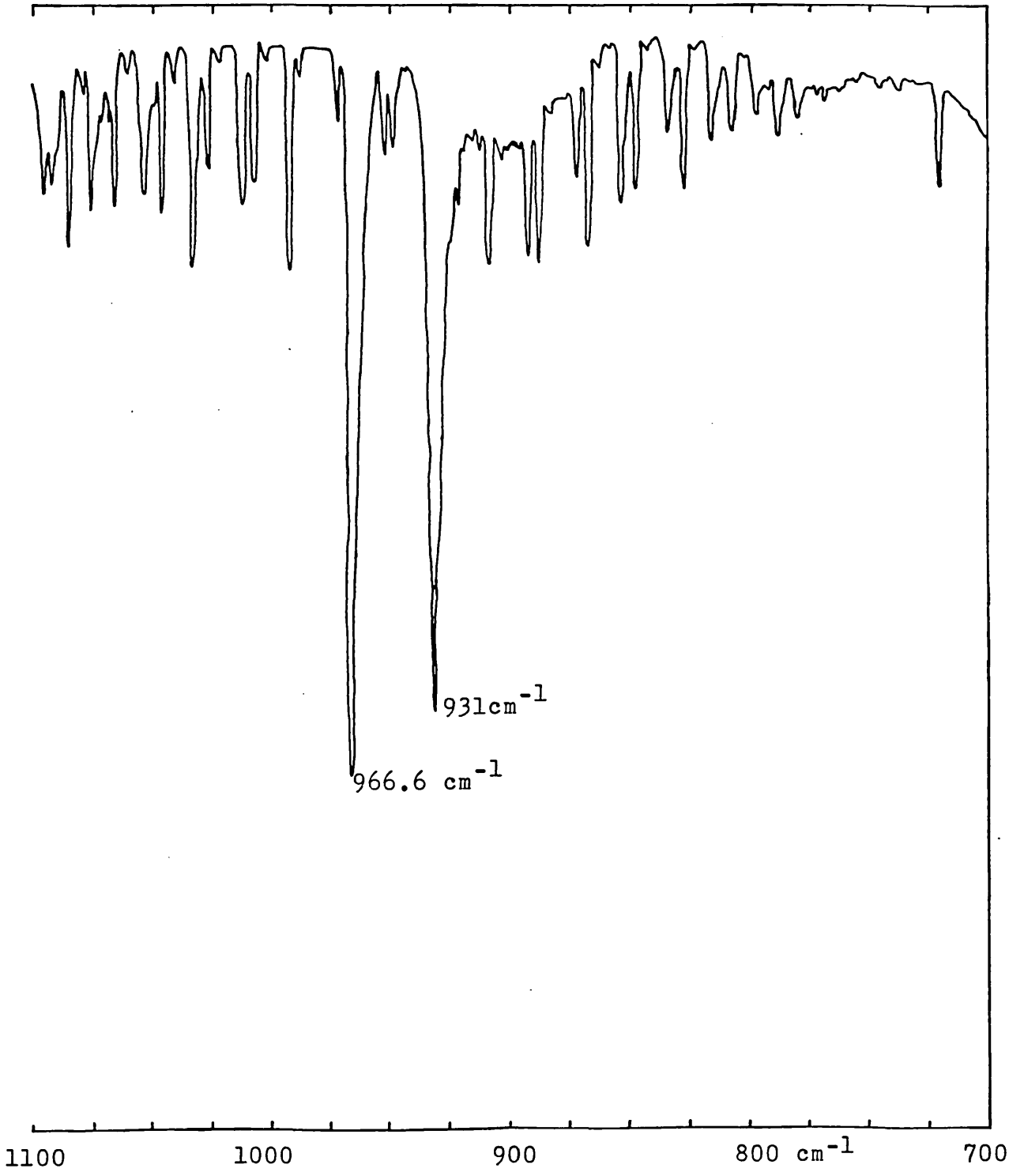


TABLE 6.1 : Observed Spectral Bands of Gas Obtained on Analysis of $(NH_4)_2SO_4$.

Wavenumbers (cm^{-1})	Assignment
1825 - 1690	Primary Amides?
1427 - 1420	NH_4^+
1420 - 1325	SO_2
1235	
1220 - 1175	Covalent Sulphates
967	NH_3, ν_2 fundamental
931	NH_3, ν_2 fundamental

TABLE 6.2 : Fundamental Wavenumbers of the Absorption Bands of NH_3 and $^{15}NH_3$.

NH_3 (cm^{-1})	$^{15}NH_3$ (cm^{-1})	Frequency shift (cm^{-1})	Assignment
931	926.3	4.3	2 ν_2 symmetrical bending
966.6	961	5.6	
1627.5	1625	2.5	asymmetrical deformation
3337	3335	2.0	unresolved symmetrical stretching doublet

The two ν_2 symmetrical bending absorption bands at 966.6 cm^{-1} and 931 cm^{-1} are much stronger in intensity than the other fundamental band at 1627.5 cm^{-1}. For this reason and because they have the highest frequency shift, the band at 966.6 cm^{-1} and 961 cm^{-1} for $^{14}NH_3$ and $^{15}NH_3$ respectively were selected for calibrating the ratio of the infrared absorption bands of $^{14}NH_3$ / $^{15}NH_3$ to the ratio of N-14 / N-15 as calculated from the mol % of the salts.

The infrared spectrum of $^{14}NH_3$ obtained from $(^{14}NH_4)_2SO_4$ in the region of 1000 - 900 cm^{-1} is shown in figure 6.6. However, on analysing the gas produced from $(^{15}NH_4)_2SO_4$ its spectrum revealed the presence of both $^{14}NH_3$ and $^{15}NH_3$ as can be seen in figure 6.7.

FIGURE 6.6 : Infrared Transmittance Spectrum of NH_3 (N-14).

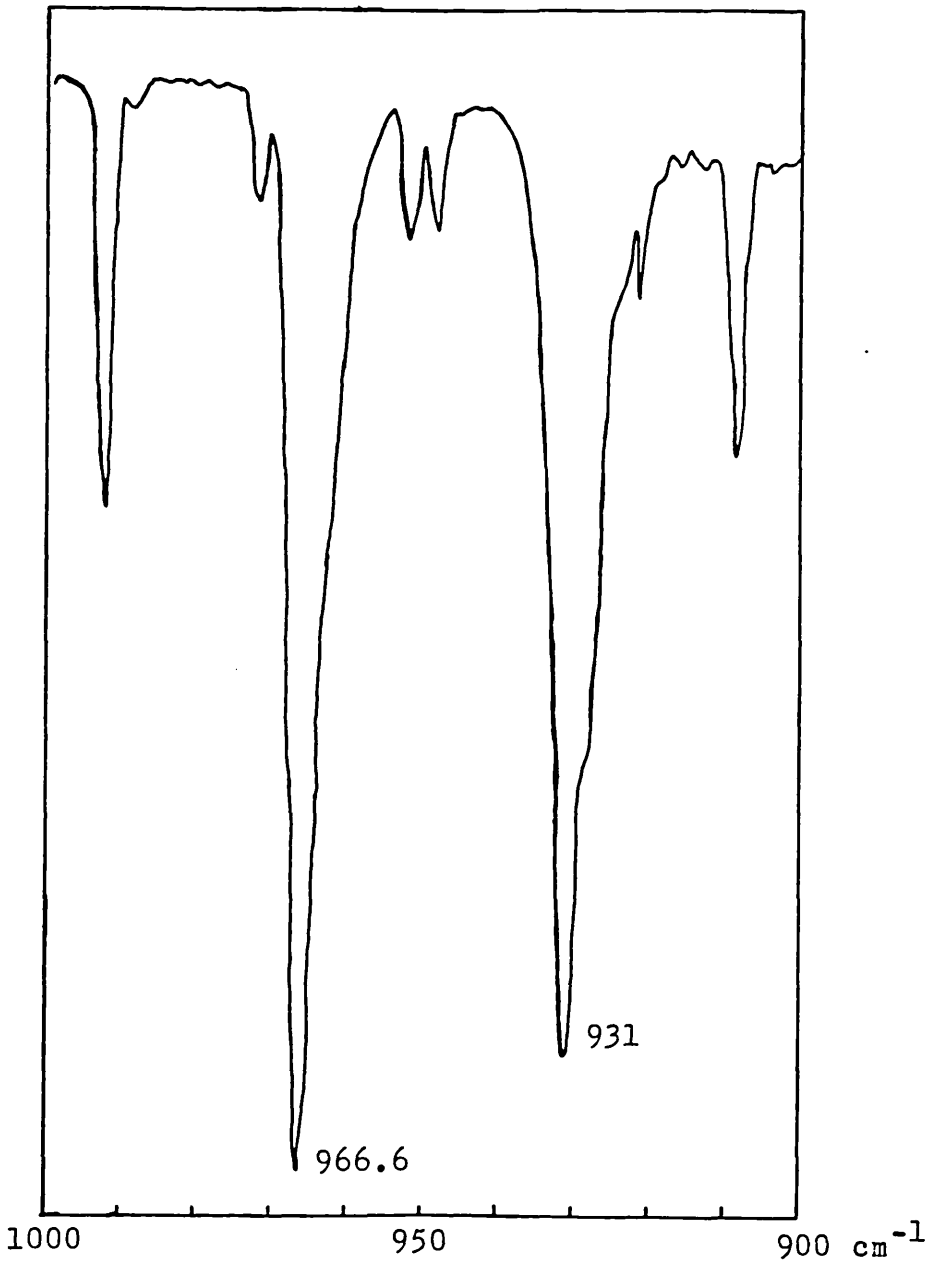
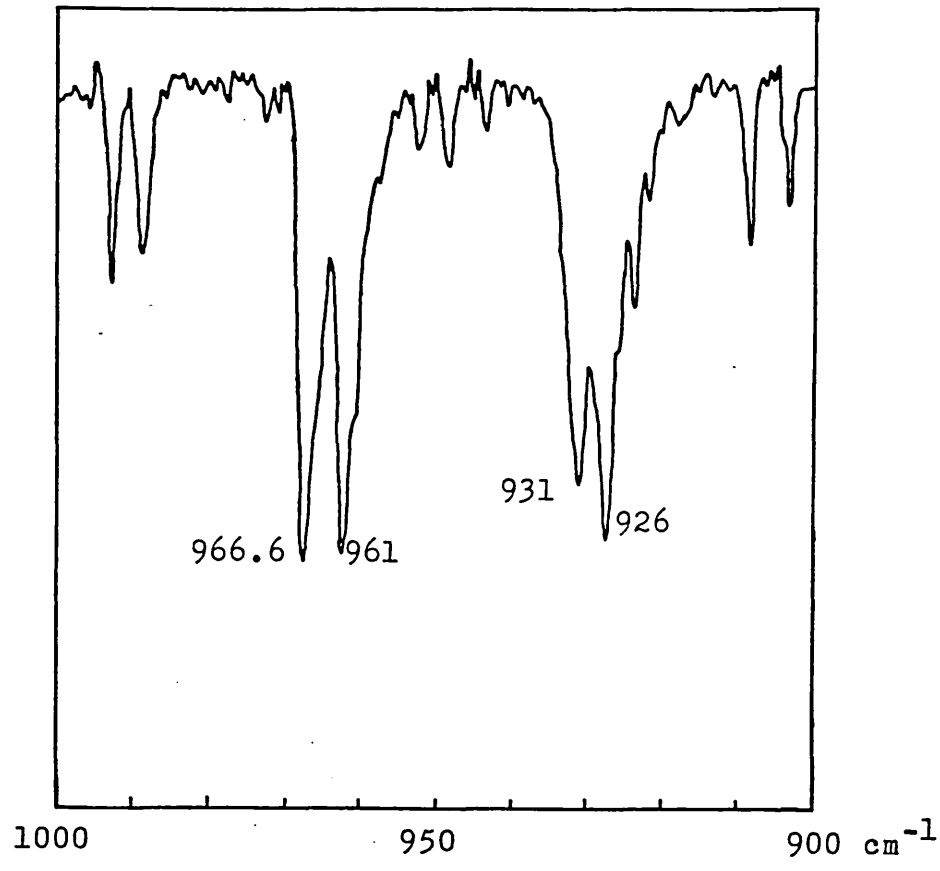


FIGURE 6.7 : Infrared Transmittance Spectrum of 'Pure' $^{15}NH_3$.

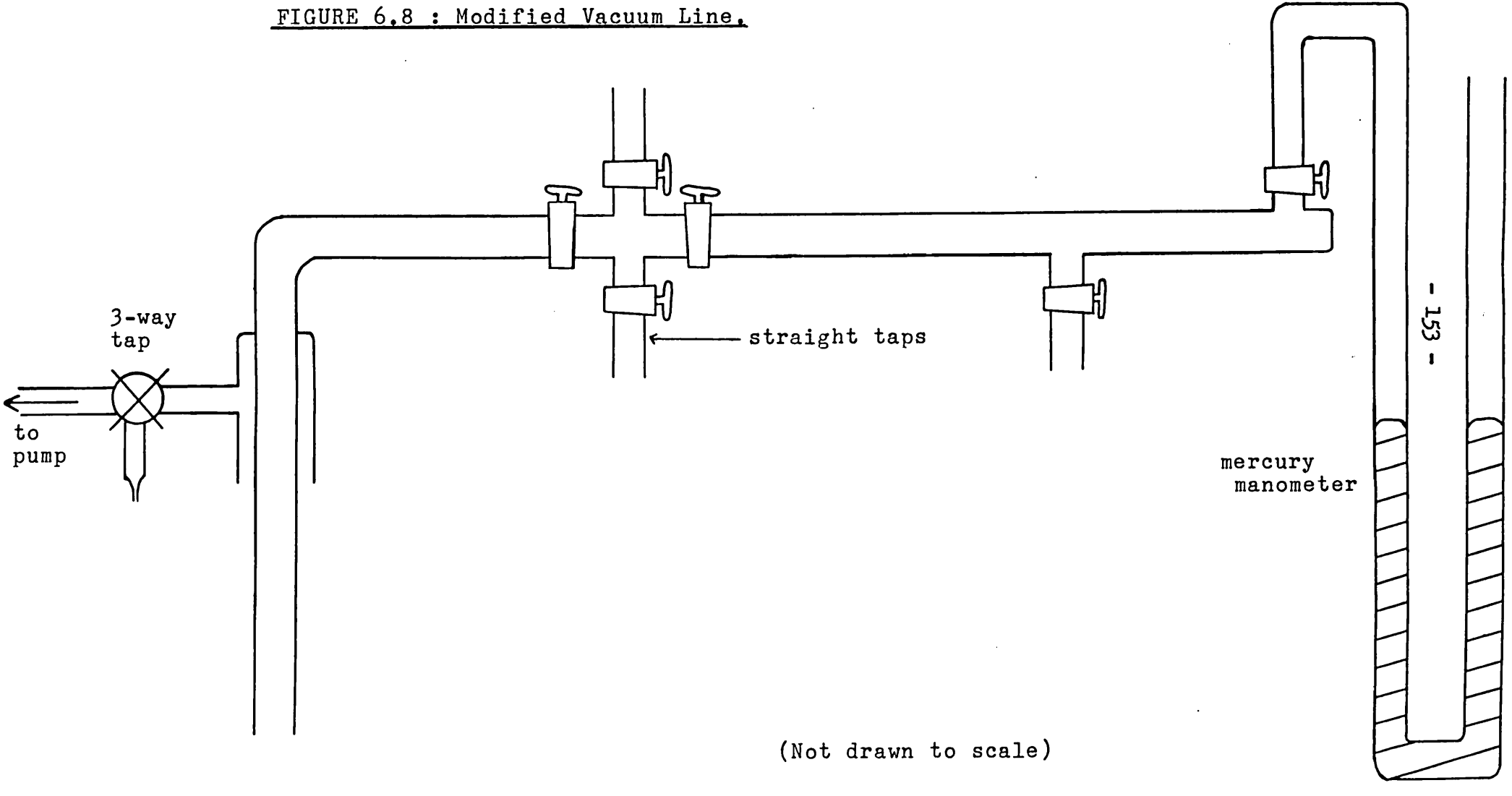


After repeating the experiment it was discovered that gas from previous experiments was being physically adsorbed on to the glass walls of the vacuum line and the infrared gas call. Initially it was thought possible to 'clean' the line simply by evacuating it for a suficient period of time, but as revealed in figure 6.7 this is not the case.

In order to overcome this problem a cleaning procedure was developed whereby the vacuum line was washed with water followed by ethanol, toluene and acetone. It was necessary to ensure that the line was dried thoroughly because of the very high solubility of ammonia in water. The infrared cell was dismantled and the glass parts cleaned as above and the cell windows rinsed in heptane. This cleaning procedure was used after each experiment.

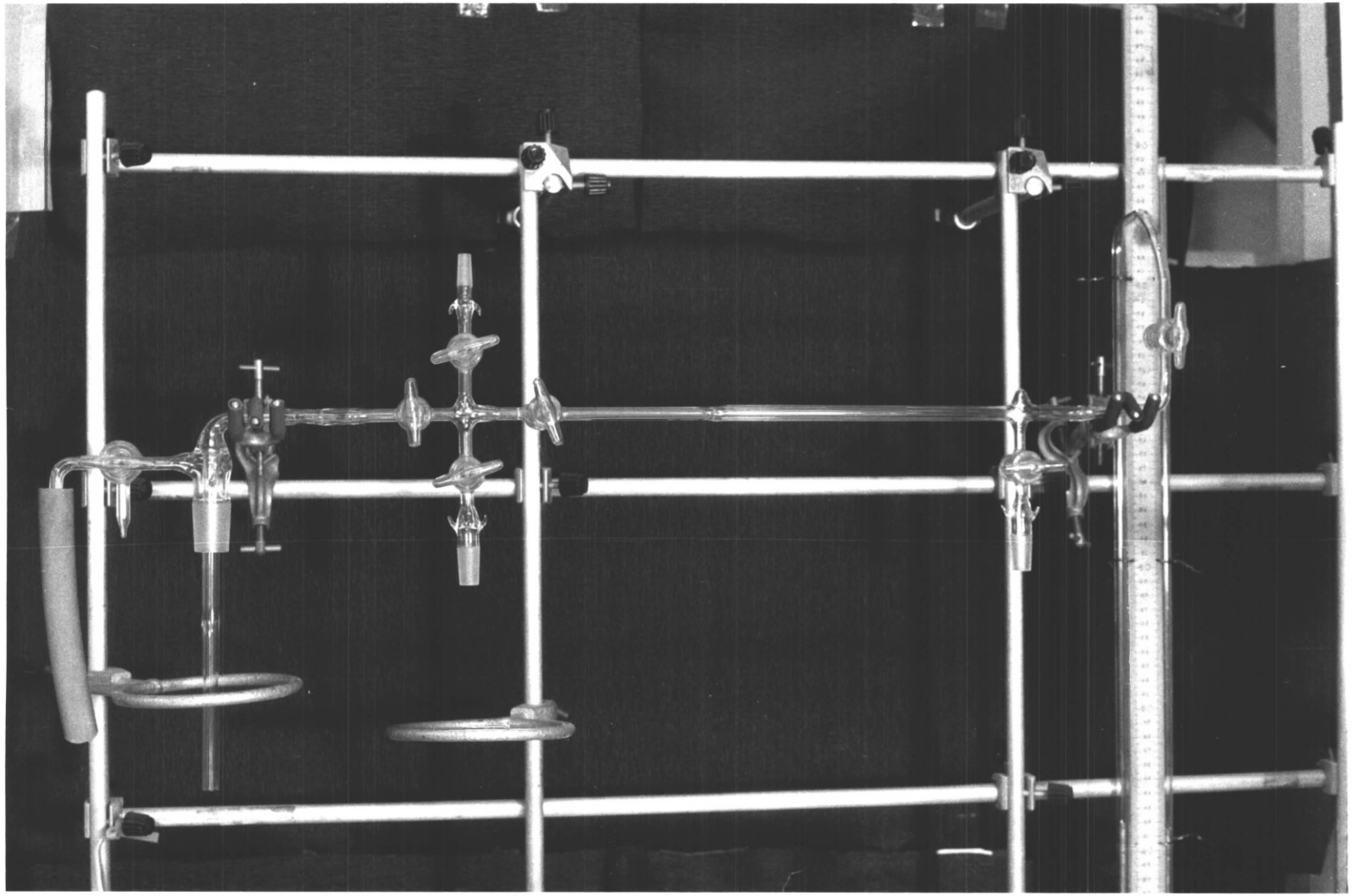
In an attempt to reduce the time taken in allowing the gas to diffuse into the 'cold finger' and also to improve the handling of the gas , the vacuum line was modified by the glassblower as shown in figure 6.8 and plate 6.1, thereby enabling the generated gas to be pumped into the 'cold finger'. Plate 6.2 shows the apparatus assembled on to the vacuum line.

FIGURE 6.8 : Modified Vacuum Line.



(Not drawn to scale)

PLATE 6·1 : The Glass Vacuum Line.



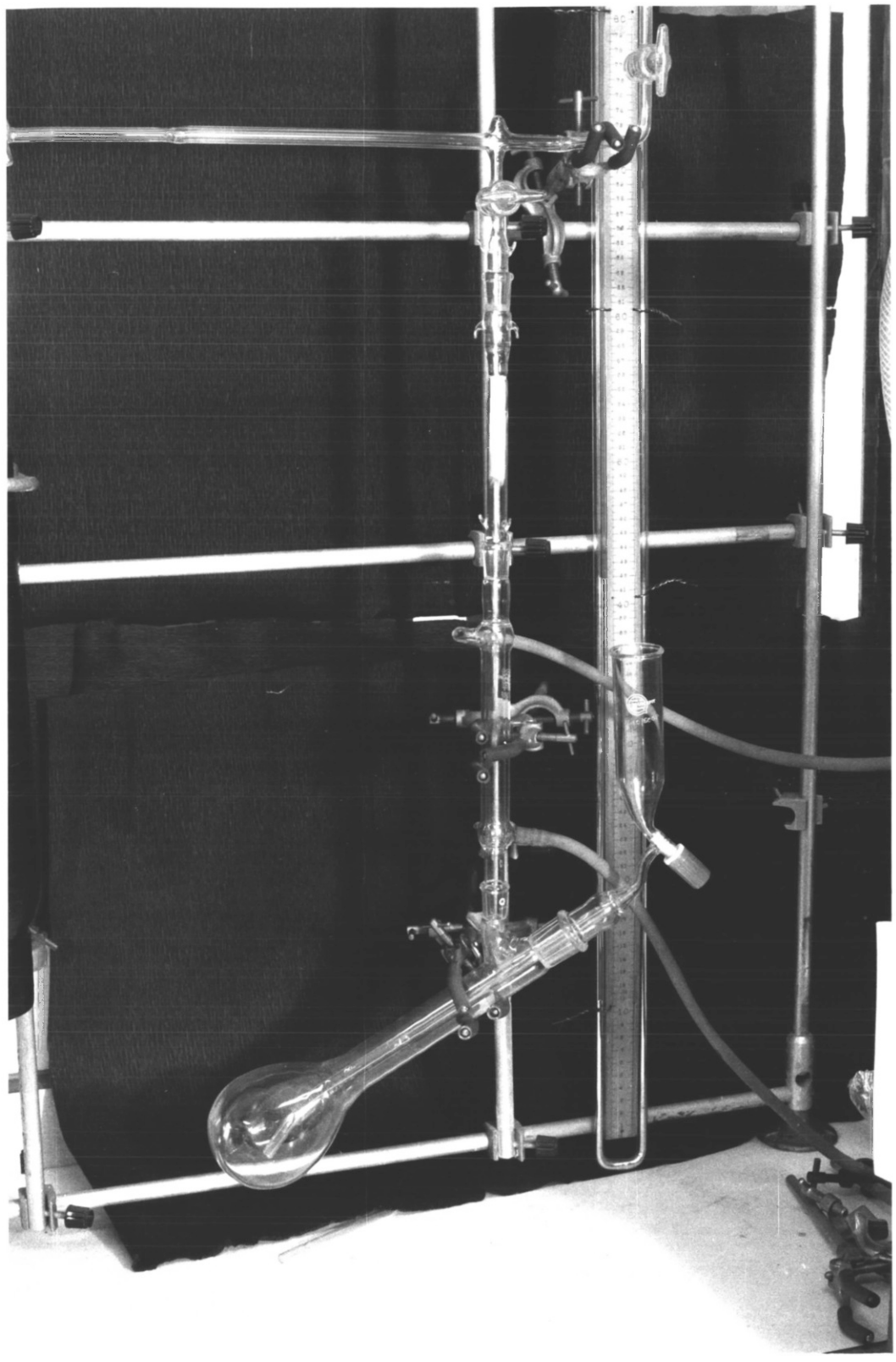
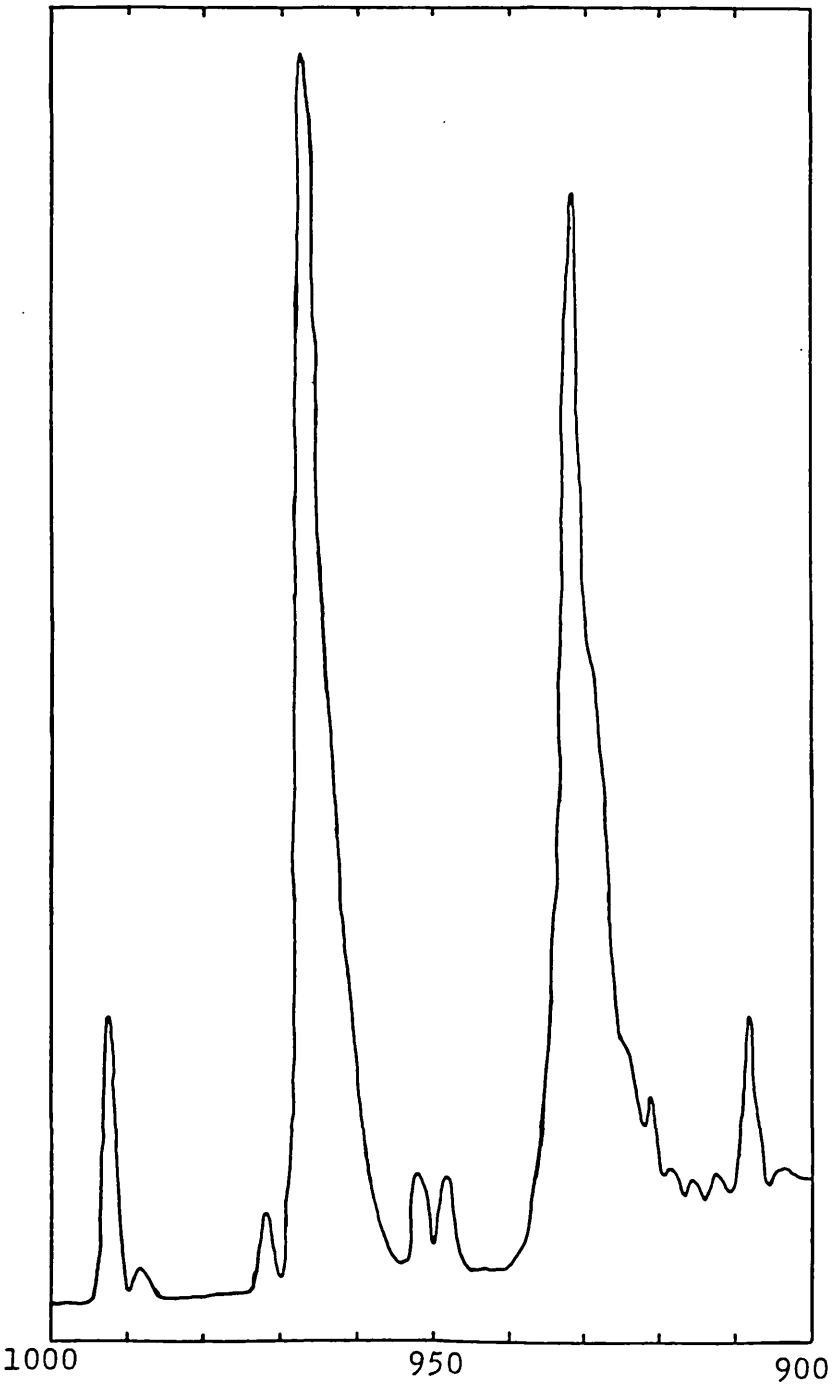


PLATE 6·2 : Apparatus Assembled onto the Vacuum Line.

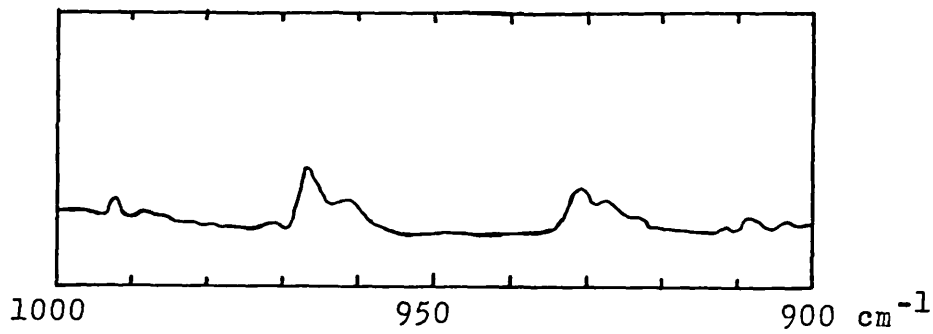
The infrared absorbance spectra obtained from the analyses of different ammonium sulphate (N-14 and N-15) salt mixtures are shown in figure 6.9 a to m. Figure 6.10 illustrates how the absorbance ratio, N-15 / N-14, was determined by measuring the height of the respective absorption bands b/a from the spectra, and appendix 1 shows a typical calculation to determine the mol % $(^{15}NH_4)_2SO_4$. These results are presented in table 6.3 and the calibration graph of the absorbance ratio N-15 /N-14 to the mol % $(^{15}NH_4)_2SO_4$ is given in figure 6.11. The shape of this graph obeys the Beer-Lambert law, as is explained in appendix 2, when the mol % $(^{15}NH_4)_2SO_4$ is greater than 30%. However, those samples containing less than 30 % $(^{15}NH_4)_2SO_4$ deviate considerably from the theory. This might be due to interaction of the 961 cm^{-1} $^{15}NH_3$ absorption band with the $^{14}NH_3$ band. As can be seen in figure 6.9a the $^{14}NH_3$ absorption band covers the range 970 - 954 cm^{-1} at its base, the peak being at 966.6 cm^{-1}. Therefore interaction with the 961 cm^{-1} $^{15}NH_3$ band is highly likely, though this effect appears to be negligible for those mixtures containing greater than 30 % $(^{15}NH_4)_2SO_4$.

FIGURE 6.9 : Infrared Absorbance Spectra of Gas Obtained from Ammonium Sulphate Salt Mixtures.

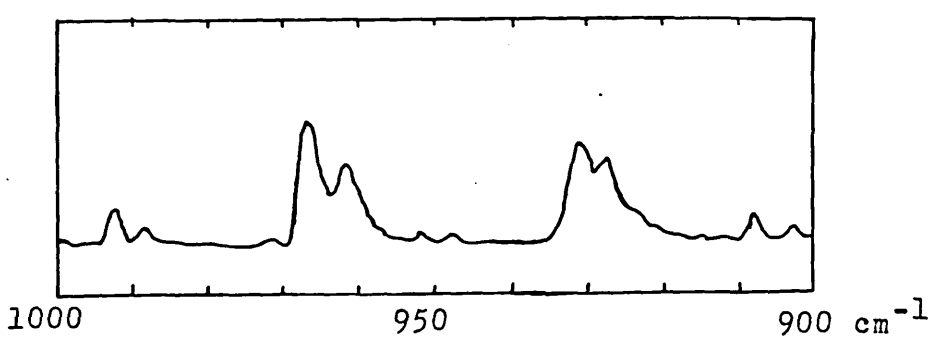
(a) 100 % $(^{14}NH_4)_2SO_4$.



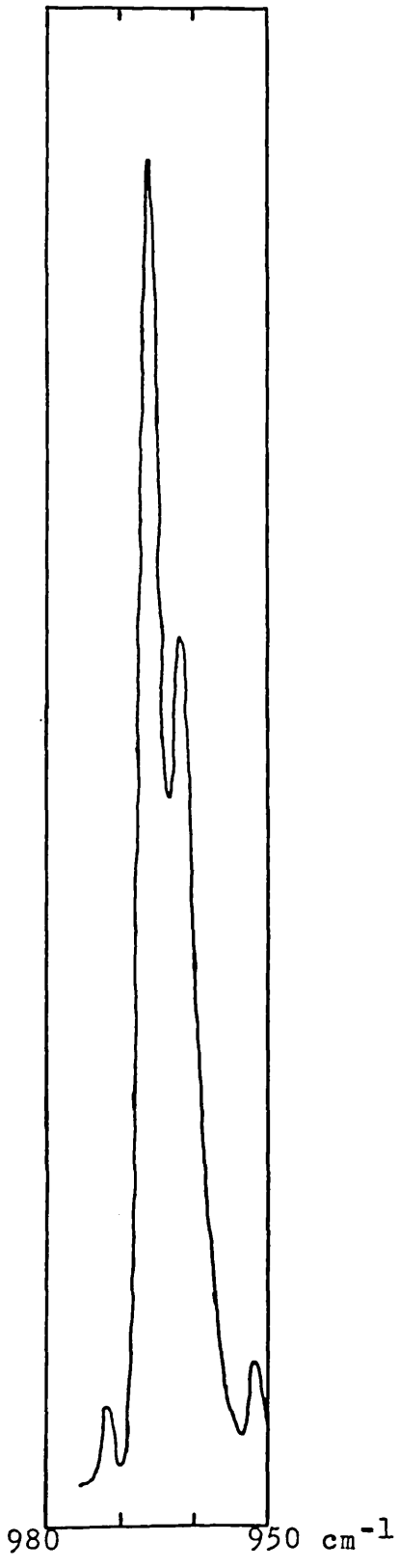
(b) 13.56 mol % N-15.



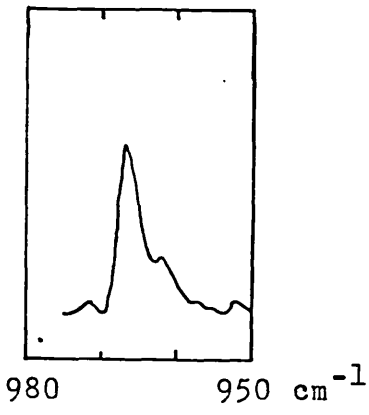
(c) 19.68 mol % N-15.



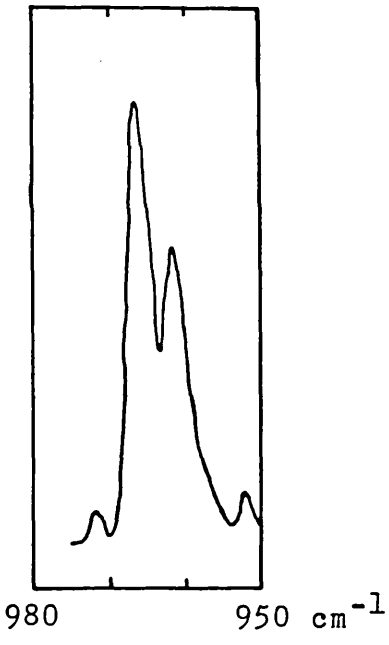
(d) 19.99 mol % N-15.



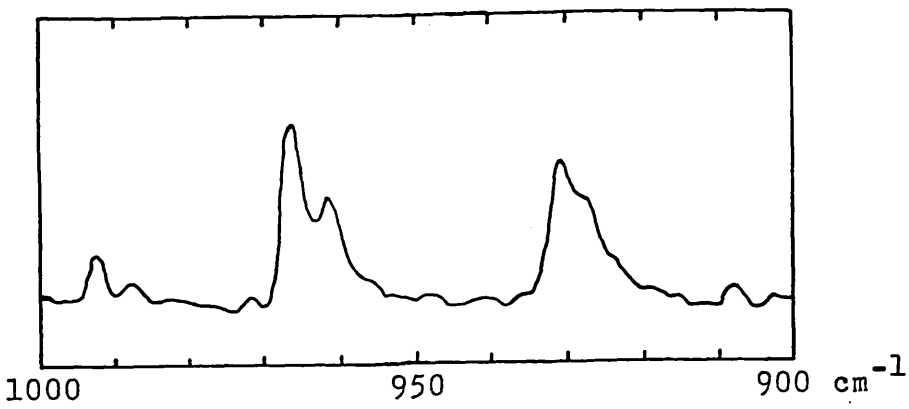
(e) 20.73 mol % N-15.



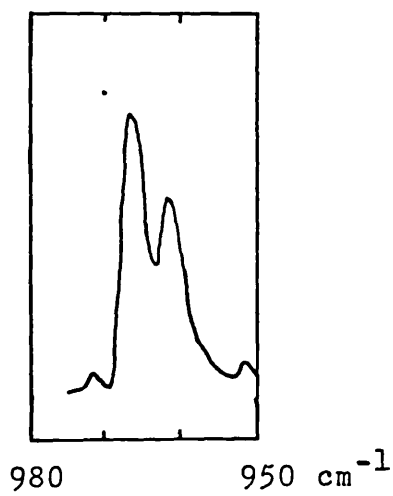
(f) 29.08 mol % N-15.



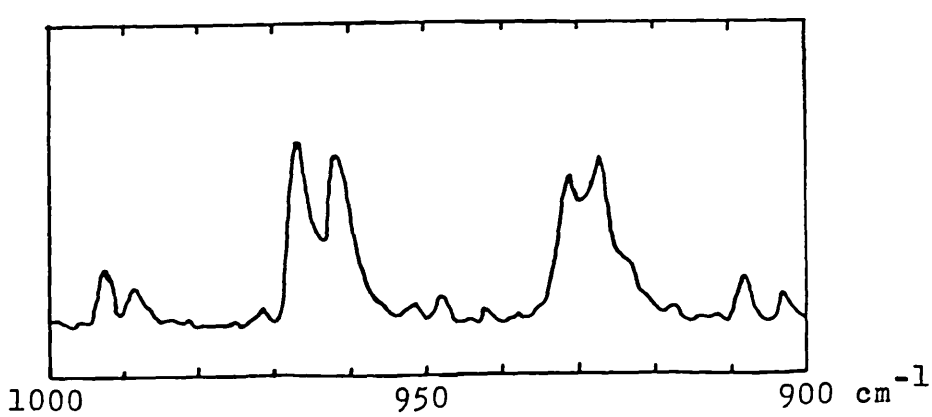
(g) 32.89 mol % N-15.



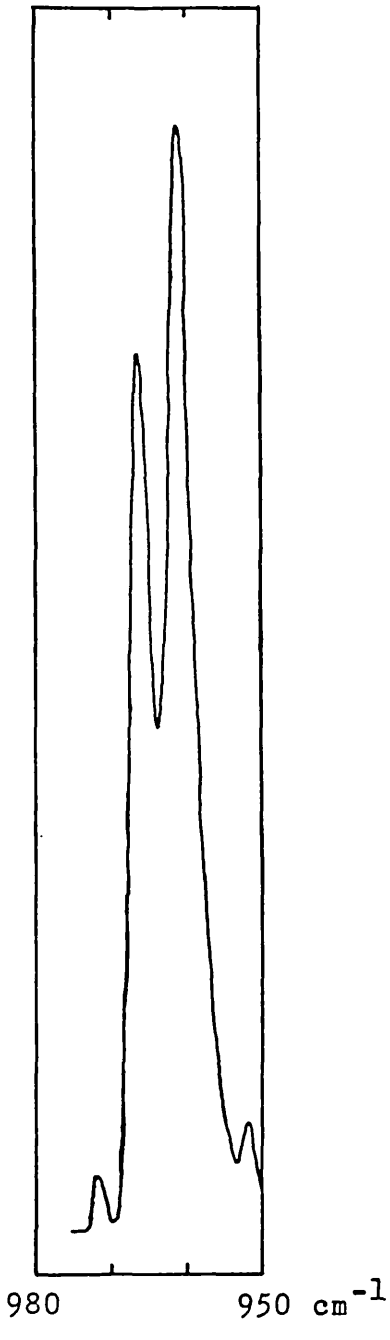
(h) 39.10 mol % N-15.



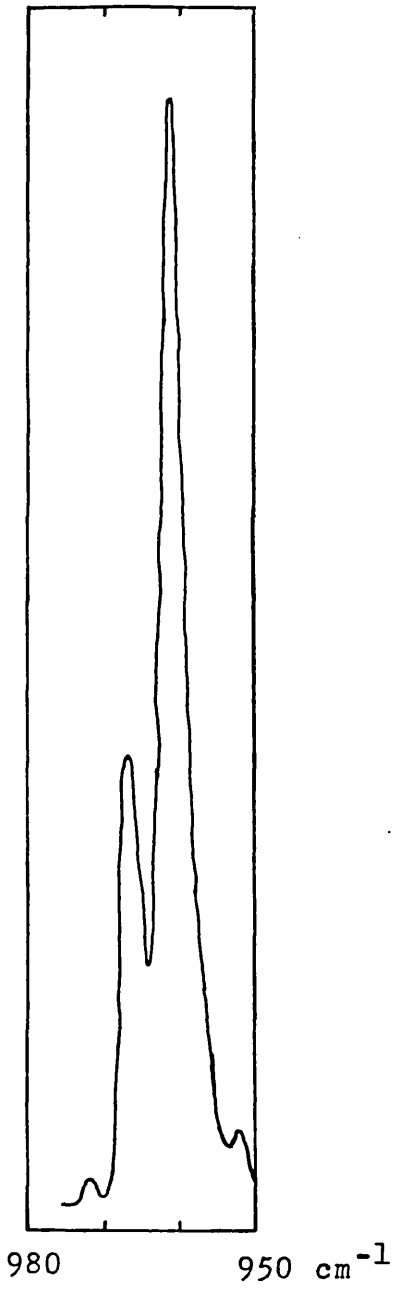
(i) 48.26 mol % N-15.



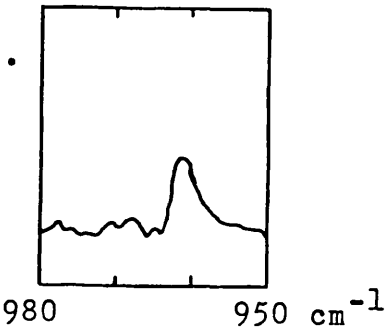
(j) 59.52 mol % N-15.



(l) 79.66 mol % N-15.



(m) 100 mol % N-15.



(k) 69.09 mol % N-15.

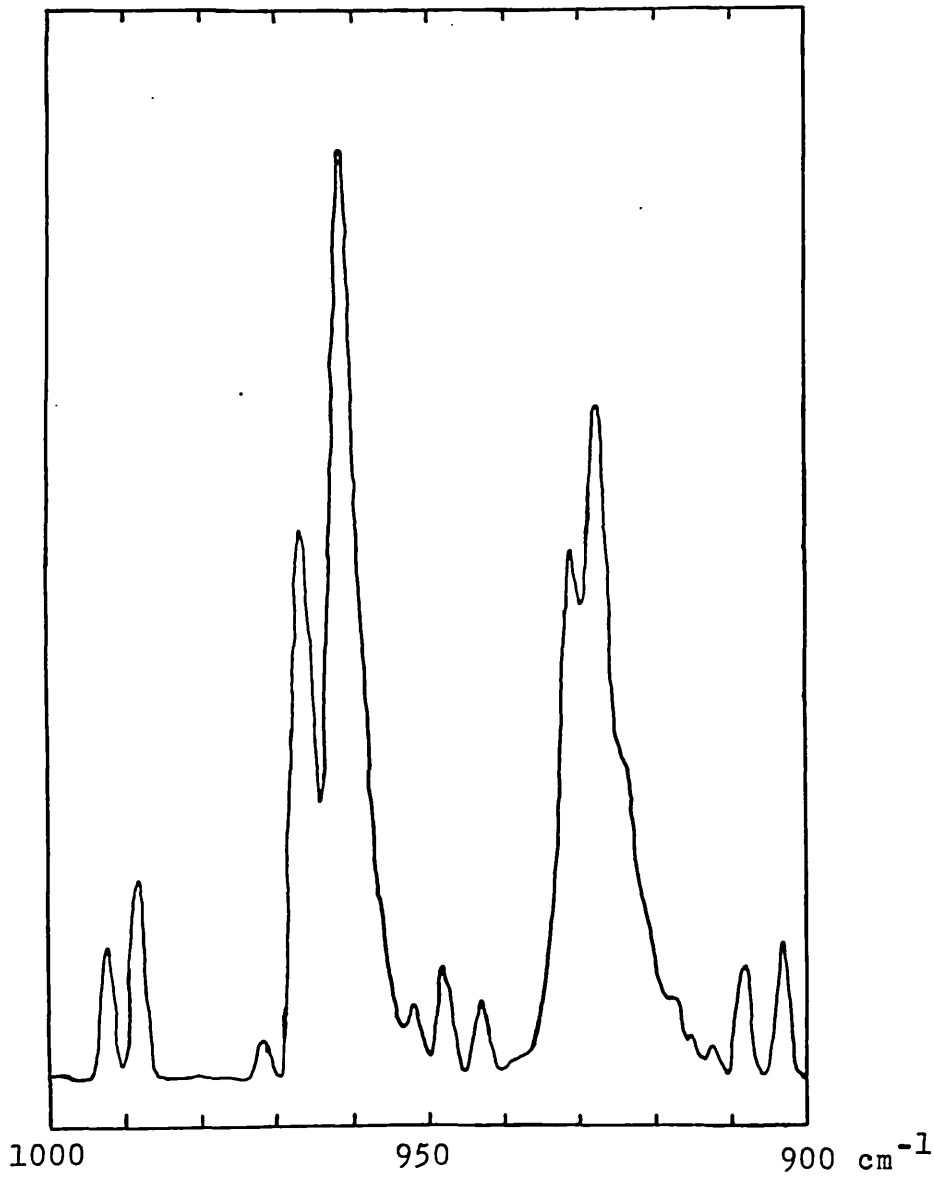


FIGURE 6.10 : Measurement of Absorbance Ratio (N-15 / N-14).

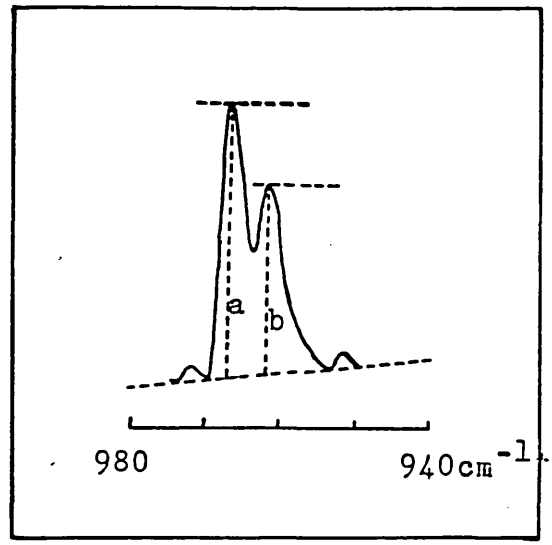
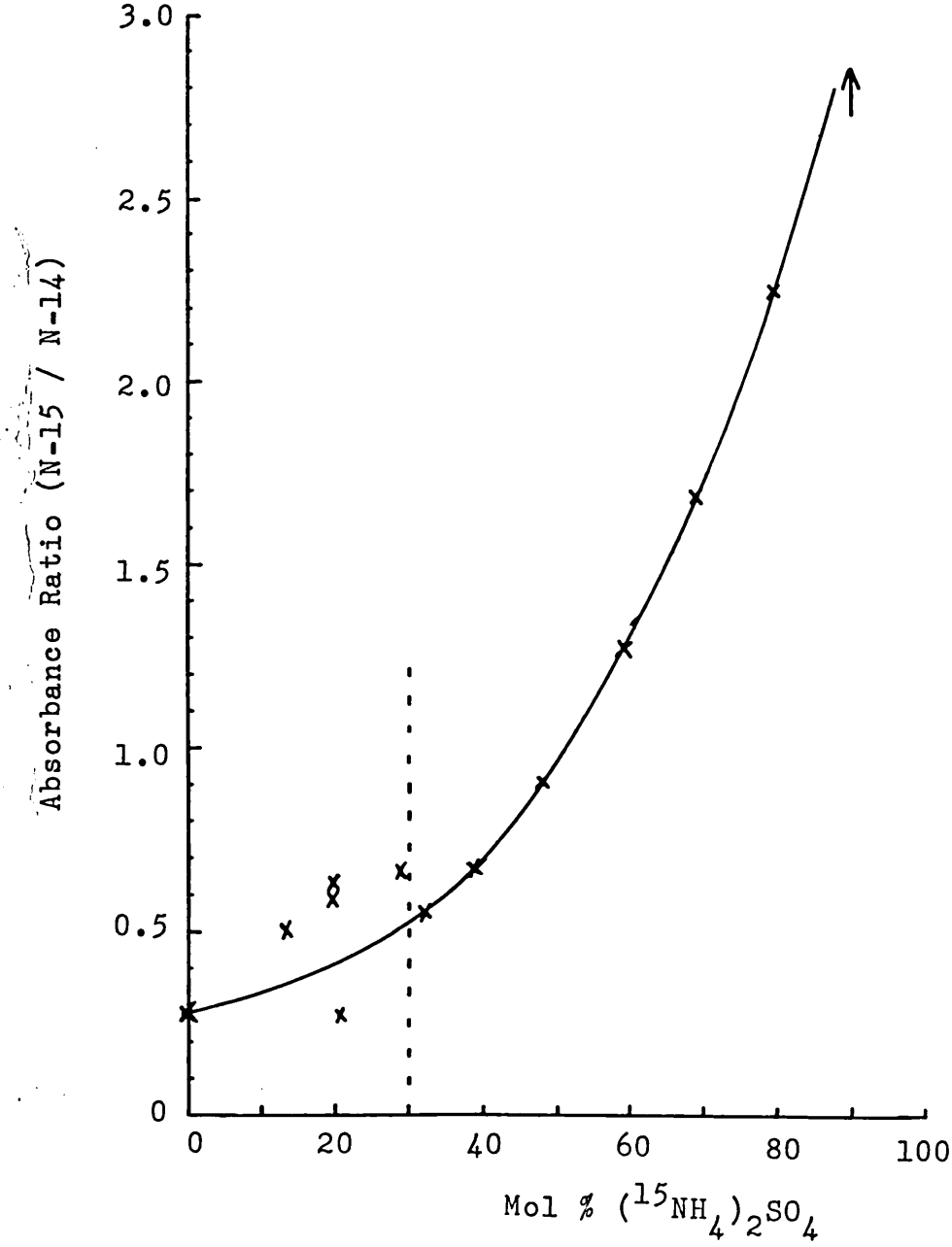


TABLE 6.3 : Calibration of Absorbance Ratio (N-15 / N-14) to the mol % of $(^{15}NH_4)_2SO_4$.

Wt. ammonium salts (g) N-14	N-15	Mol % $(^{15}NH_4)_2SO_4$	Abs. band height (mm) N-14	N-15	Ratio N-15 / N-14
0.123	-	0	160	39	0.244
0.125	0.02	13.56	8	4	0.5
0.08	0.02	19.68	16	9.5	0.594
0.0824	0.021	19.99	177	111	0.627
0.0877	0.0234	20.73	22	6	0.273
0.076	0.0318	29.08	56	37	0.661
0.06	0.03	32.89	24	13	0.542
0.0635	0.0416	39.10	36	24	0.667
0.056	0.0533	48.26	23	21	0.913
0.0412	0.0618	59.52	111	138	0.804
0.036	0.0821	69.09	70	118	1.686
0.0213	0.0851	79.66	56	139	2.482
-	0.09686	100	-	10	

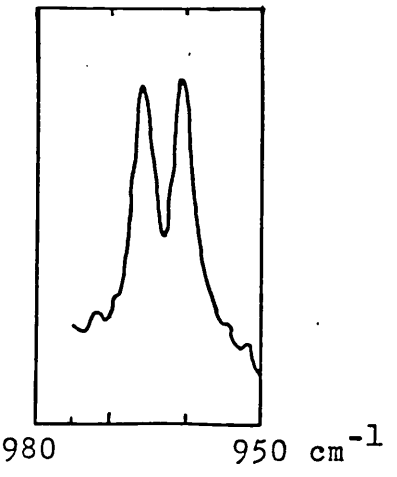
FIGURE 6.11 : Calibration Graph of Absorbance Ratio (N-15 / N-14) to the Mol % $(^{15}NH_4)_2SO_4$.



6.6 Results of Wear Debris Studies.

Figure 6.12 shows the infrared absorbance spectrum of the gas collected during the analysis of 32.49 mg of N-14 nitrided debris. Two absorption bands were observed indicating the presence of both NH_3 and $^{15}NH_3$ even though the sample contained only nitrogen-14. These bands were traced to the presence of residual gas on the infrared cell windows. The windows were repolished and the experiment repeated with 68.15 mg of debris. Unfortunately no ammonia was detected.

FIGURE 6.12 : Infrared Spectrum Obtained from the Wear Debris Analysis. (X50)



6.7. Discussion.

Ammonium sulphate salt studies were carried out for two reasons. Firstly the development and testing of both the apparatus and the final stage of the nitrogen analysis procedure, namely the production and measurement of ammonia, and secondly to calibrate the ratio of N-15 / N-14 to the absorbance ratios of the infrared bands. The early experiments highlighted several problems which were overcome by modifying the glassware and developing a cleaning procedure. At this stage the analytical procedure appeared to be successful although a quantitative analysis of the gas produced during the experiments was not possible. Even though attempts were made to standardise the test procedure the actual amount of gas collected after each experiment varied considerably. The proportion of N-14 to N-15, however, did not appear to be affected by this and the calibration of N-15 / N-14 in the gas sample to the ratio of the observed absorbance bands in the IR spectra was possible, though it was found to be sensitive enough only when the mol % $(^{15}NH_4)_2SO_4$ was greater than 30 %.

Nitrogen analysis of the wear debris proved to be unsuccessful. Assuming the percentage of nitrogen present in the debris is 1 % the quantity of nitrogen is approximately 0.3 mg which is of the same order as that for the salt studies, where the elemental amount of nitrogen

present is approximately 0.2 mg. However, the overall elemental percentage of nitrogen in steel debris is considerably less than 1 %, the actual amount present being below the detection limit of the spectrometer. It should be possible to overcome this either by using a Fourier transform infrared spectrometer or a gas cell with a path length of 1 - 10 m. Studies have been carried out on gas samples of 'ordinary' carbon dioxide (CO_2) whereby $^{13}CO_2$ has been detected even though it was present at the natural abundance level (1.11 %) using an infrared gas cell with a 10 m path length ( ).

At this stage, however, it was decided not to proceed with infrared spectroscopy as the means of detecting the nitrogen in steel debris. This was because the ultimate purpose behind this study is to develop a monitoring technique to compare favourably with the currently available radioisotope technique. The infrared analysis procedure proved to be relatively time-consuming as well as requiring sophisticated laboratory apparatus and therefore central laboratory facilities, as opposed to 'on-site', would have to be used.

Therefore, it was decided to investigate alternative means of detecting the stable isotope. Secondary ion mass spectrometry was selected. This will be discussed further in chapter 7.

CHAPTER 7. STABLE ISOTOPE STUDIES.

This chapter describes the N-15 isotopic experimental studies carried out, namely the incorporation of N-15 into steel surfaces and its subsequent detection by secondary ion mass spectrometry.

7.1. Incorporation of Nitrogen-15 into Steel Surfaces.

7.1.1. Experimental Details.

The plasma nitriding process has been detailed in chapter 4. Experiments were conducted using the plasma processing unit at Birmingham University, whereby N-14 was substituted with N-15 at some stage during the nitriding process. The choice of treatment parameters used was based on the preliminary experiments described earlier (see chapter 4). Details of the different treatments carried out are summarised in table 7.1, and table 7.2 explains how steel roller samples were nitrided by a combination of those treatments. N-15 was introduced at the end of the nitriding cycle for samples IB and at the beginning for samples IC. No isotope was introduced into samples IA in order to provide a control.

Polished and tapered sections of samples from each of the different batches were prepared for metallographic examination and microhardness profiles through the treated surfaces were determined.

TABLE 7.1 : Plasma Nitriding Treatments.

Number	Time	Temp./ ^{o}C	Gas Composition
i	20 hours	510	2.5% N_2 / 97.5% H_2
ii	30 mins. 5 mins.	510 510	2.5% N_2 / 97.5% H_2 2.5% $^{15}N_2$ / 97.5% H_2
iii	20 hours	510	2.5% N_2 / 97.5% H_2

TABLE 7.2 : Details of the Treatments on Batches of Samples.

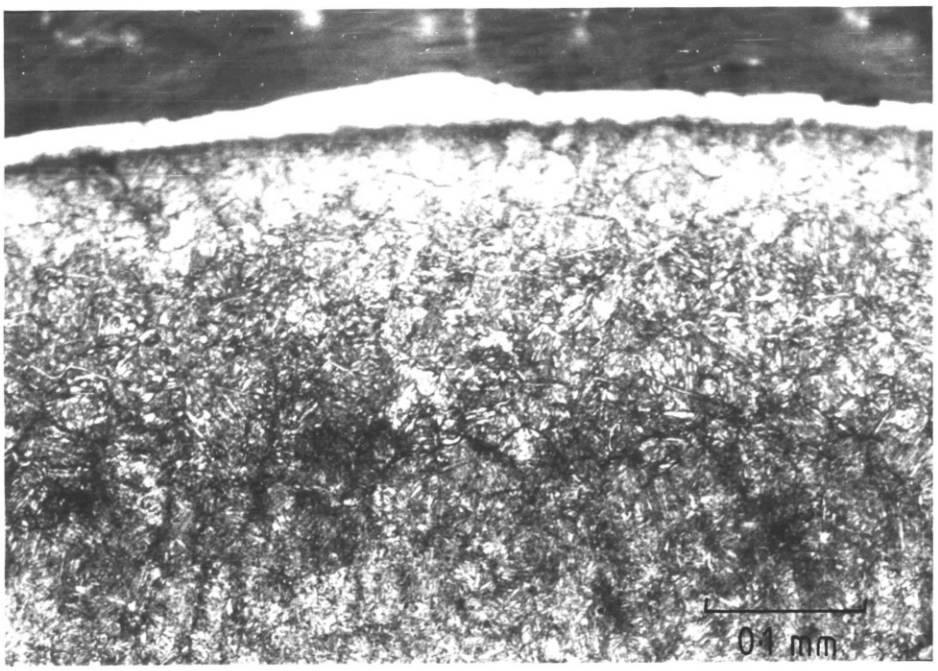
Batch No.	Treatments
IA	i
IB	i followed by ii
IC	ii followed by iii

7.1.2. Results.

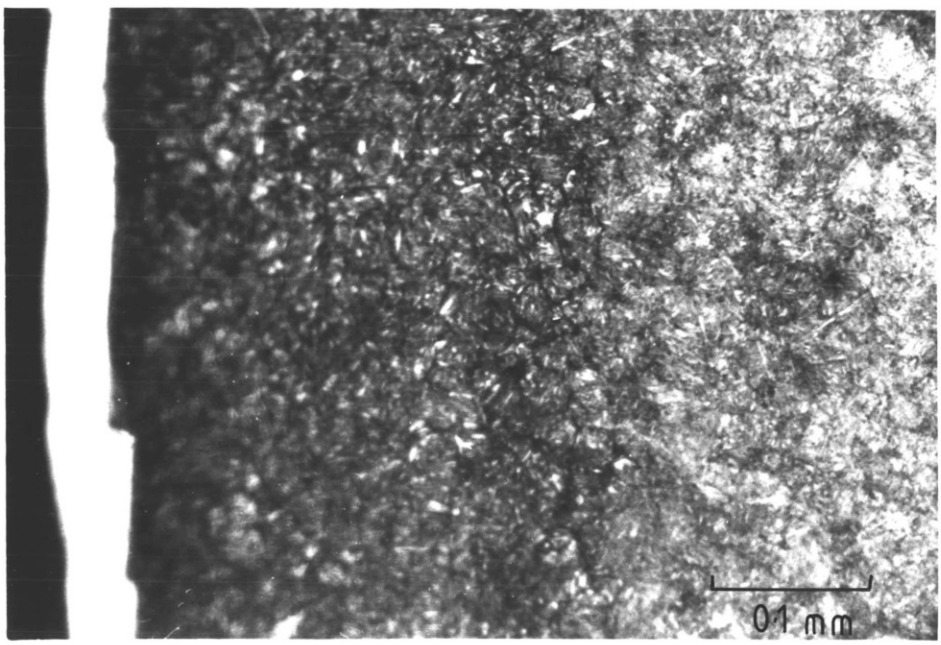
Results of the metallographic examination can be seen in plate 7.1. No adverse effects due to the substitution by N-15 are apparent except for changes in the observed microstructure close to the edge of the steel rollers. Sample IC has a slightly shallower nitrided layer compared to IA and IB. This observation is supported by the case depths determined from the microhardness profiles shown in figures 7.1, 7.2 and 7.3, namely 210 μms for IA and IB compared to 200 μms for sample IC. No white layer is in evidence at any of the surfaces, as expected from the preliminary investigations described earlier in chapter 4.

PLATE 7·1 : Microstructure of Plasma Nitrided Surfaces. Etched in 5% Nital.

(a) Sample IA. 210 x.



(b) Sample IB. 210x.



(c) Sample IC. 210x.

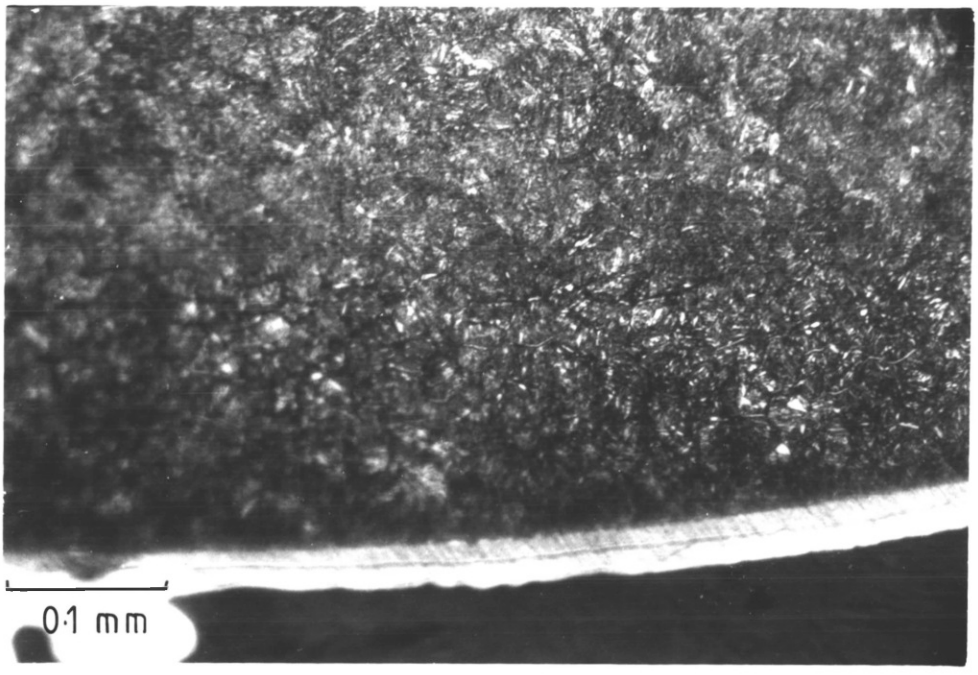
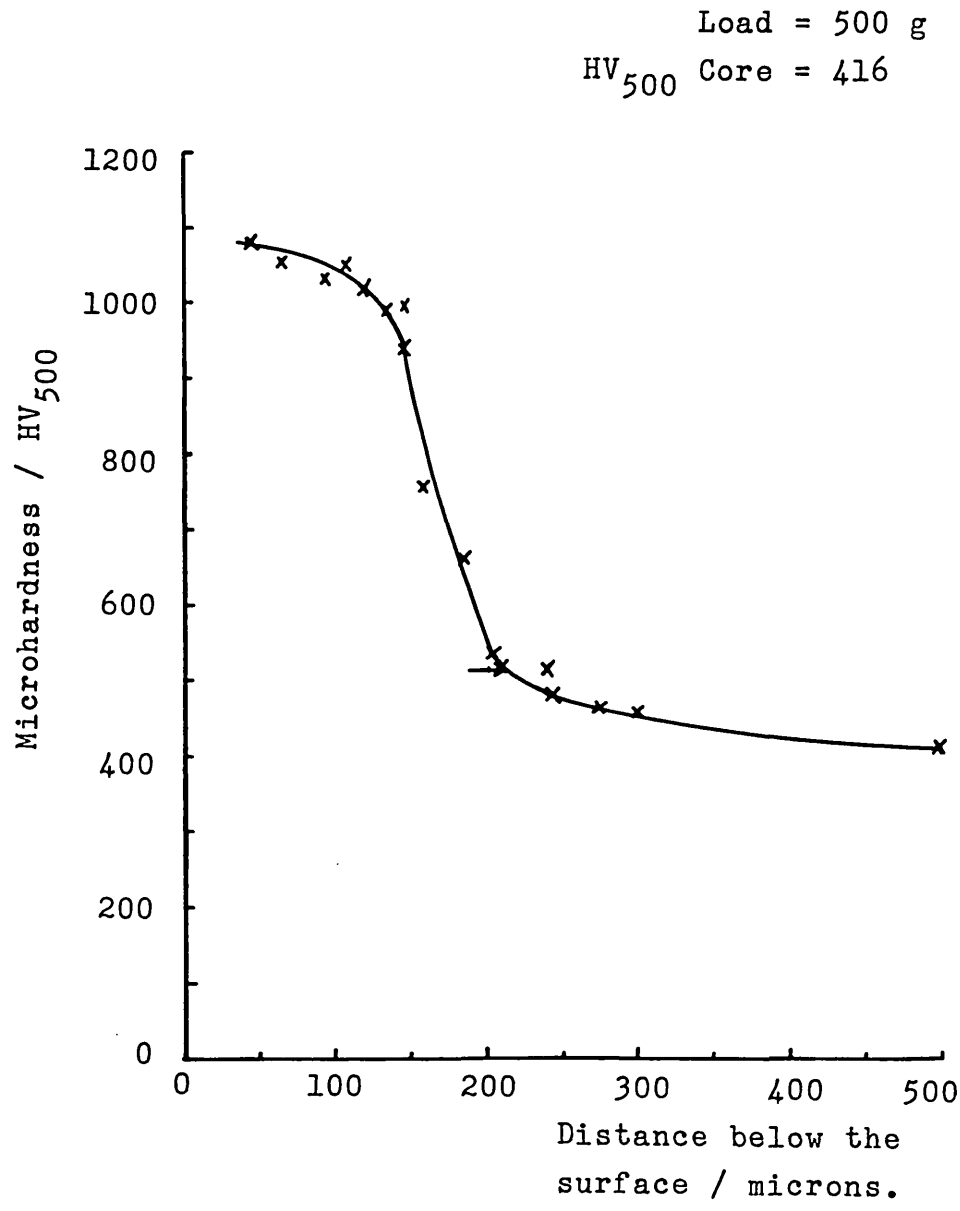
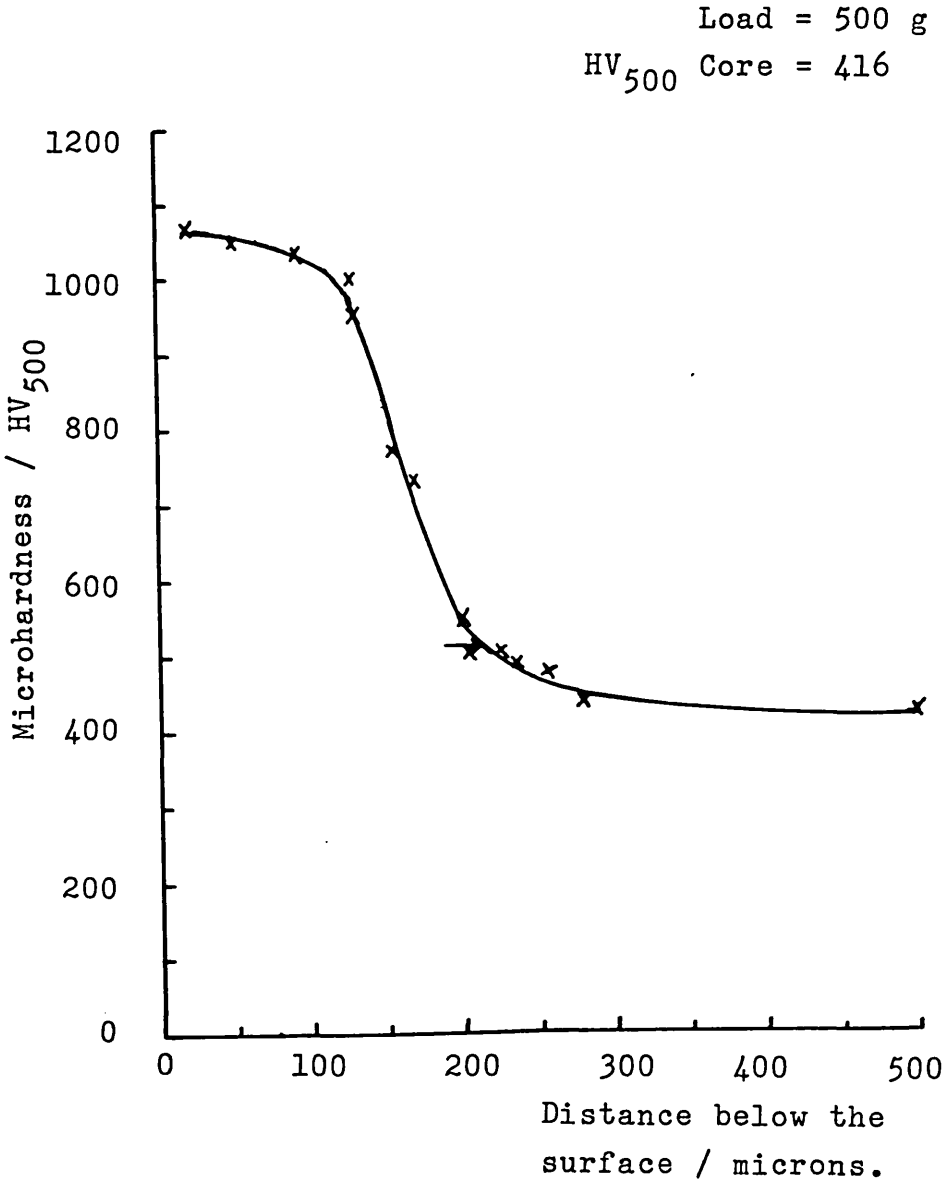


FIGURE 7.1 : Microhardness Profile of Sample IA.



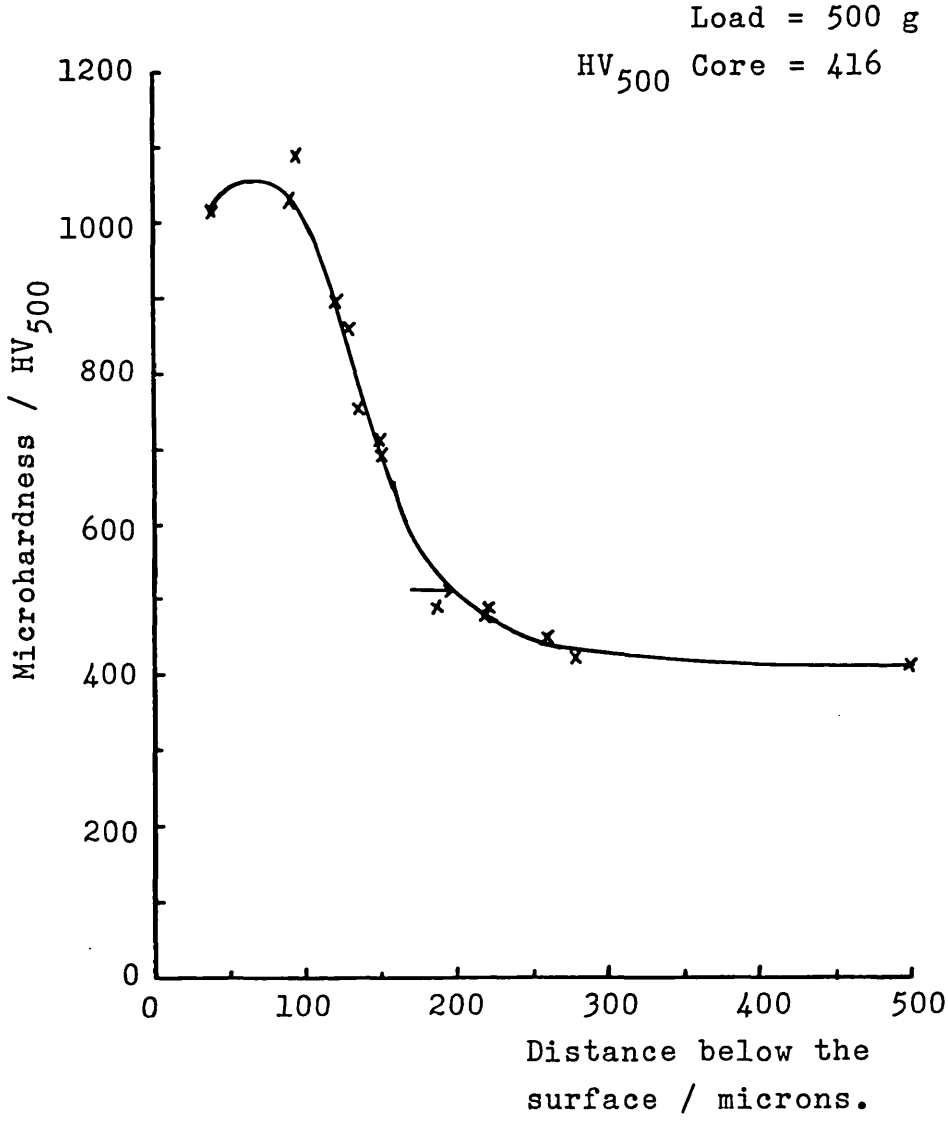
Case depth = 210 microns

FIGURE 7.2 : Microhardness Profile of Sample IB.



Case depth = 210 microns

FIGURE 7.3 : Microhardness Profile of Sample IC.



Case depth = 200 microns

7.2. Detection of Nitrogen-15.

Results of previous work conducted on rollers nitrided with 'ordinary' nitrogen (as reported in chapter 6) revealed the difficulties encountered in detecting the nitrogen present in the nitrided layer by means of infrared spectroscopy. Nitrogen concentration through this layer is very low, typically less than 1%. The previous attempts at detecting this level of nitrogen involved a multistage process which is likely to introduce experimental errors at each stage, thereby reducing the sensitivity of the experiment. Therefore, at this point it was considered that a means of directly detecting nitrogen, N-14 and N-15, in the steel samples would be of considerable benefit in two ways :

- in determining whether it is possible to introduce a layer of N-15 concentrated deep within the diffusion zone as opposed to being spread evenly throughout this region,
- and subsequently whether it would be possible to detect the nitrogen directly from the steel debris.

Secondary ion mass spectrometry, SIMS, was investigated as a possible means of meeting these requirements.

7.2.1. Experimental Details.

In SIMS the sample is bombarded by an energetic primary ion beam in an ultra high vacuum chamber which results in sputtering of the target material thereby removing the surface atoms. A small fraction of the sputtered material carries a charge and these so called secondary ions are analysed in a mass spectrometer (hence SIMS). Both positive and negative secondary ions can be produced but generally electropositive elements preferentially form positive ions while electronegative species favour the formation of negative ions. It is possible to analyse all the elements of the periodic table by SIMS though sensitivity varies considerably.

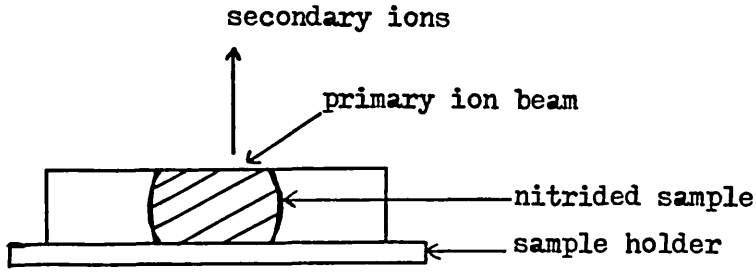
Tapered sections of samples from each of the plasma nitriding treatments detailed in table 7.2 were prepared for analysis by SIMS. It was necessary to cut the mounted rollers in half to enable electrical contact to be made and in order to avoid charging effects when the ion beam was positioned close to or on the edge of the sample. The adjacent area of the mount was coated with silver contact paint. Details of the sample preparation are illustrated in figure 7.4.

The primary beam used was a 4.5 kV argon ion (Ar^+) beam set at a current of 20 nA and the analysed spot size was

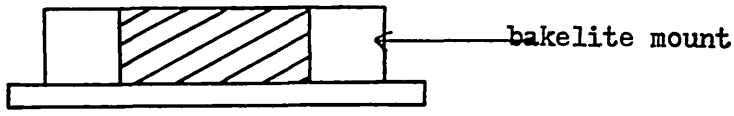
approximately 80 μms. This original work was conducted at AWRE Aldermaston. An initial experiment was carried out on a polished section of a sample from the nitriding treatment C by recording both the positive ion and the negative ion spectra at two locations : one at the centre of the sample (the un-nitrided zone) and the other at the edge (the nitrided region). Further experiments involved line scan measurements which were obtained by moving the sample under the ion beam using a linear motion drive as illustated in figure 7.4(iii). In an attempt to overcome surface contamination problems each position analysed was etched (by the primary ion beam) and a reading taken when the signal became constant. The results obtained are outlined in the following section.

FIGURE 7.4 : Sample Preparation for SIMS Analysis.

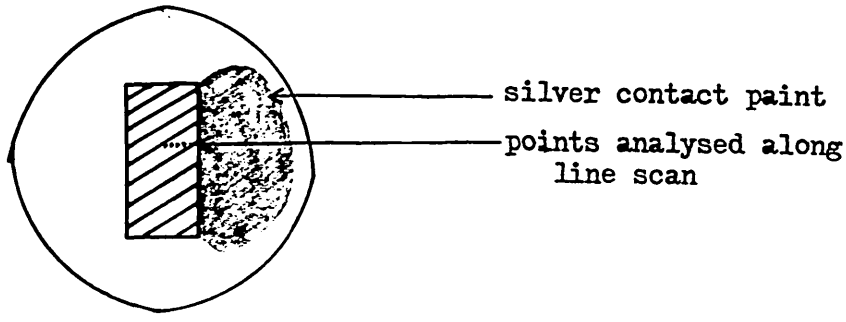
(i) Cross-section through the sample.



(ii) Cross-section along the length of sample.



(iii) Top view of tapered section.



7.2.2. Results and Discussion.

Preliminary analyses were carried out on sample C to assess which mass peaks might be suitable to characterise the nitrogen distribution through the nitrided layer. A complete mass spectrum over the range 0 - 100 amu was recorded at two areas of the sample, one in the nitrided layer and the other in the untreated core. Figures 7.5 and 7.6 show the results of the positive ion analysis of the non-nitrided and nitrided zones respectively and figures 7.7 and 7.8 show the spectra obtained from the negative ion analysis.

Assignment of the major peaks is given in the figures. Those peaks observed in figures 7.5 and 7.6 due to Na^+, K^+, Ca^+ and Al^+ arise from contaminants at the surface and are always observed due to the high sensitivity of these species to the SIMS method. The major effect observed that can be attributed to the nitriding treatment is the reduction in the ratio of peak heights of Cr^+ / Fe^+. One apparent effect that could be significant was the slight increase at 66 amu in figure 7.6 possibly due to the formation of CrN^+.

FIGURE 7.5 : Positive Ion Spectrum from the Centre of the Sample (the Un-nitrided Region).

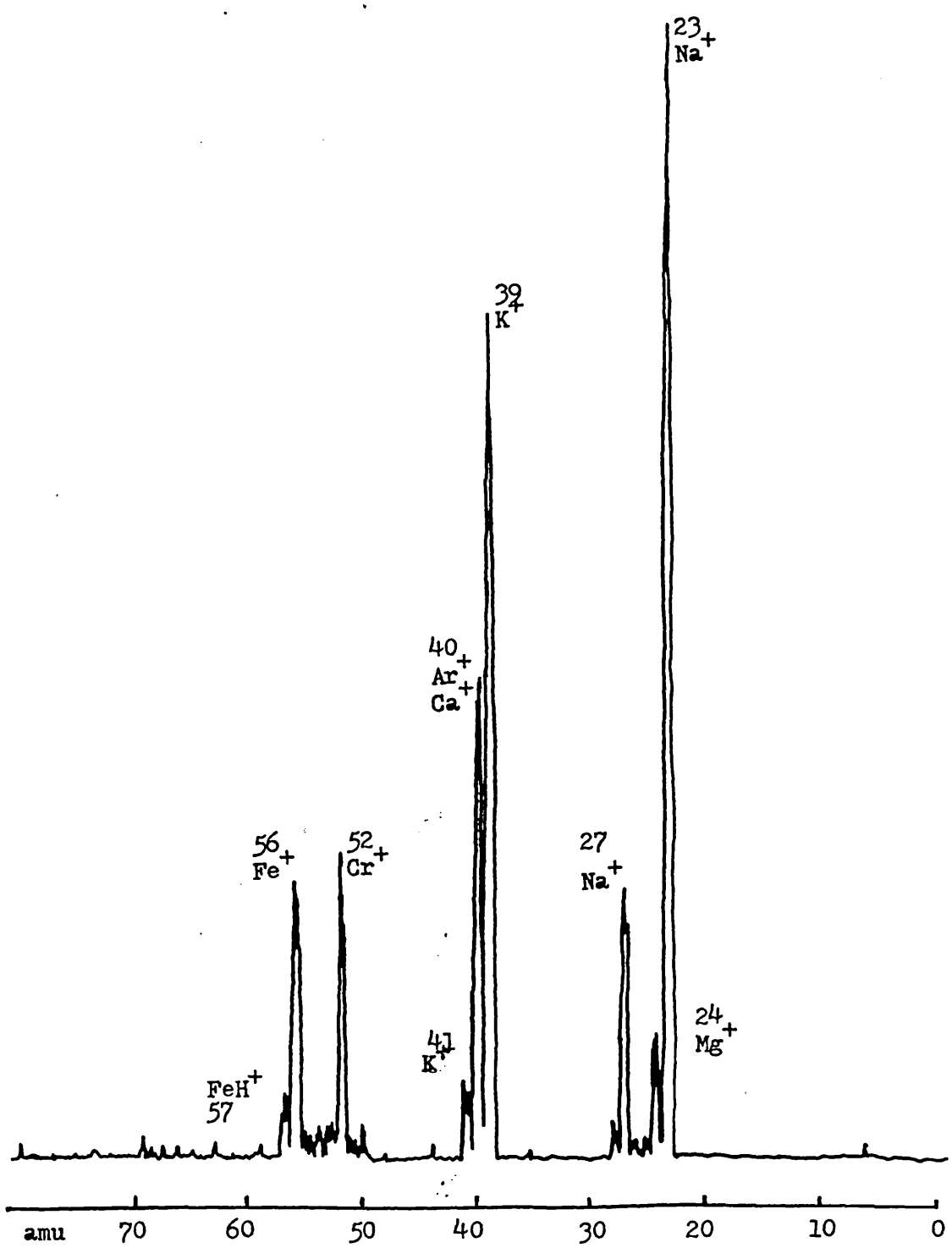
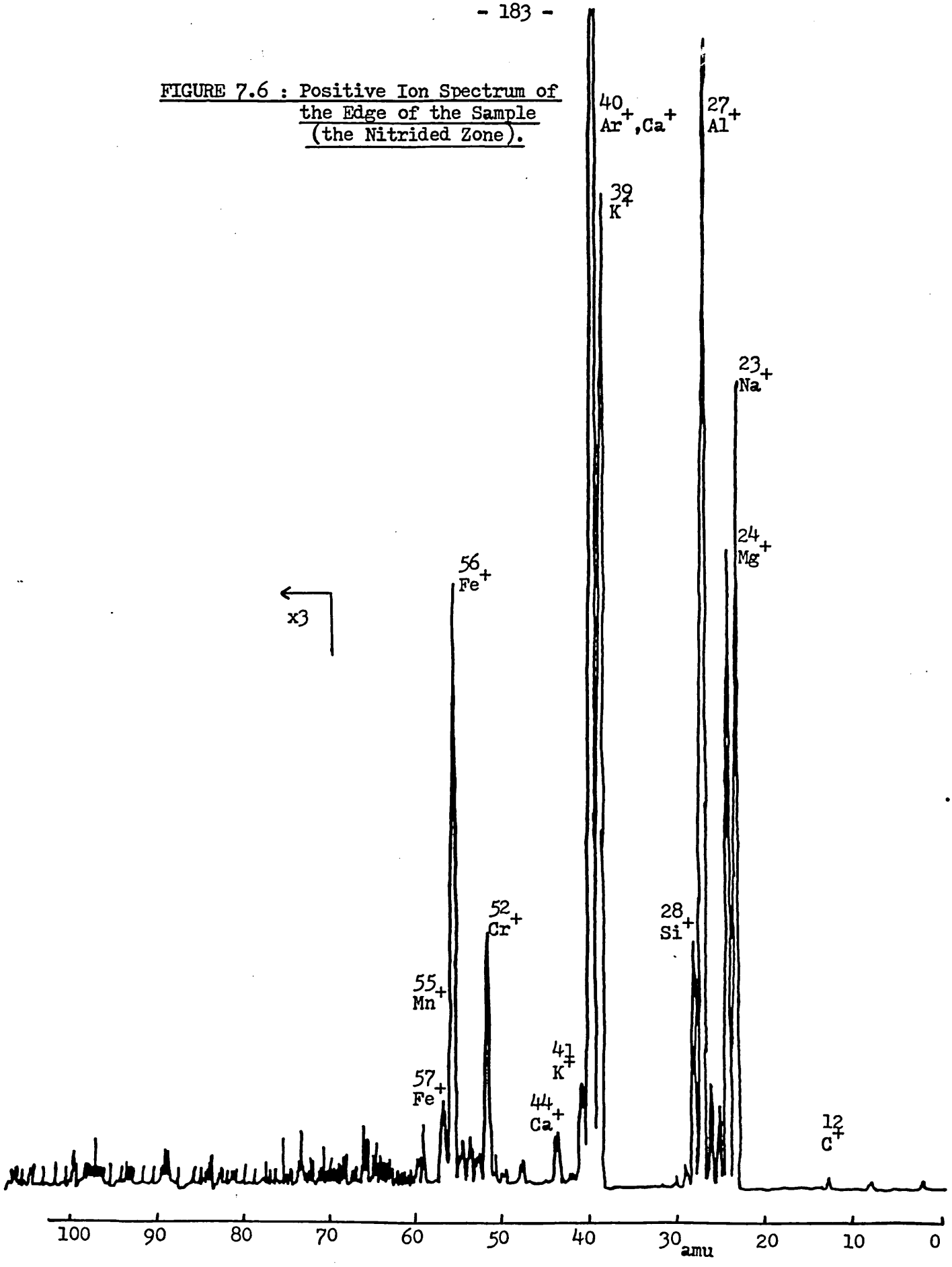


FIGURE 7.6 : Positive Ion Spectrum of the Edge of the Sample (the Nitrided Zone).



Direct comparison of figures 7.7 and 7.8 reveals an increase in intensity of the CN^- peak at 26 amu which is attributed to the effects of the nitriding treatment. It is tentatively suggested that this difference is a result of CN compounds at the surface or a carbon - nitrogen interaction in the ion beam. The other major peaks observed namely C^-, CH^-, F^-, Cl^-, C_2^-, C_2H^-, CN^- and Cl^- are probably due to contaminants and O^- is thought to arise from both surface oxides and residual gas in the analysis chamber.

Due to the uncertainty in the origin of the CN^- peak, it was decided at this stage to concentrate further efforts on the positive ion peaks observed at selected masses namely 14(N^+ ,CH_2^+), 52(Cr^+), 56(Fe^+), 66$(Cr+14)^+$, 67$(Cr+15)^+$, 70$(Fe+14)^+$ and 71$(Fe+15)^+$.

FIGURE 7.7 : Negative Ion Spectrum from the Un-nitrided Region.

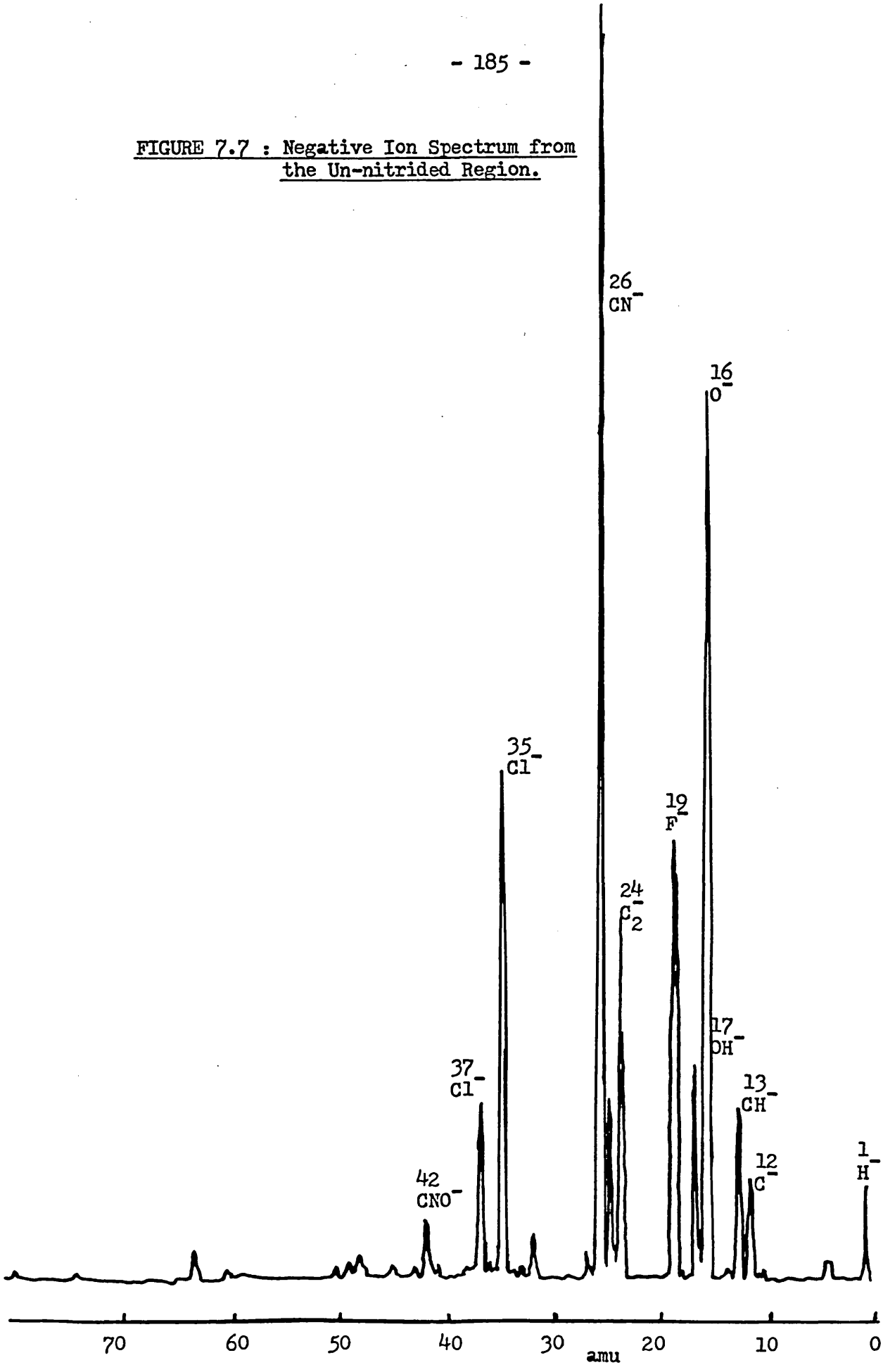


FIGURE 7.8 : Negative Ion Spectrum from the Nitrided Zone.

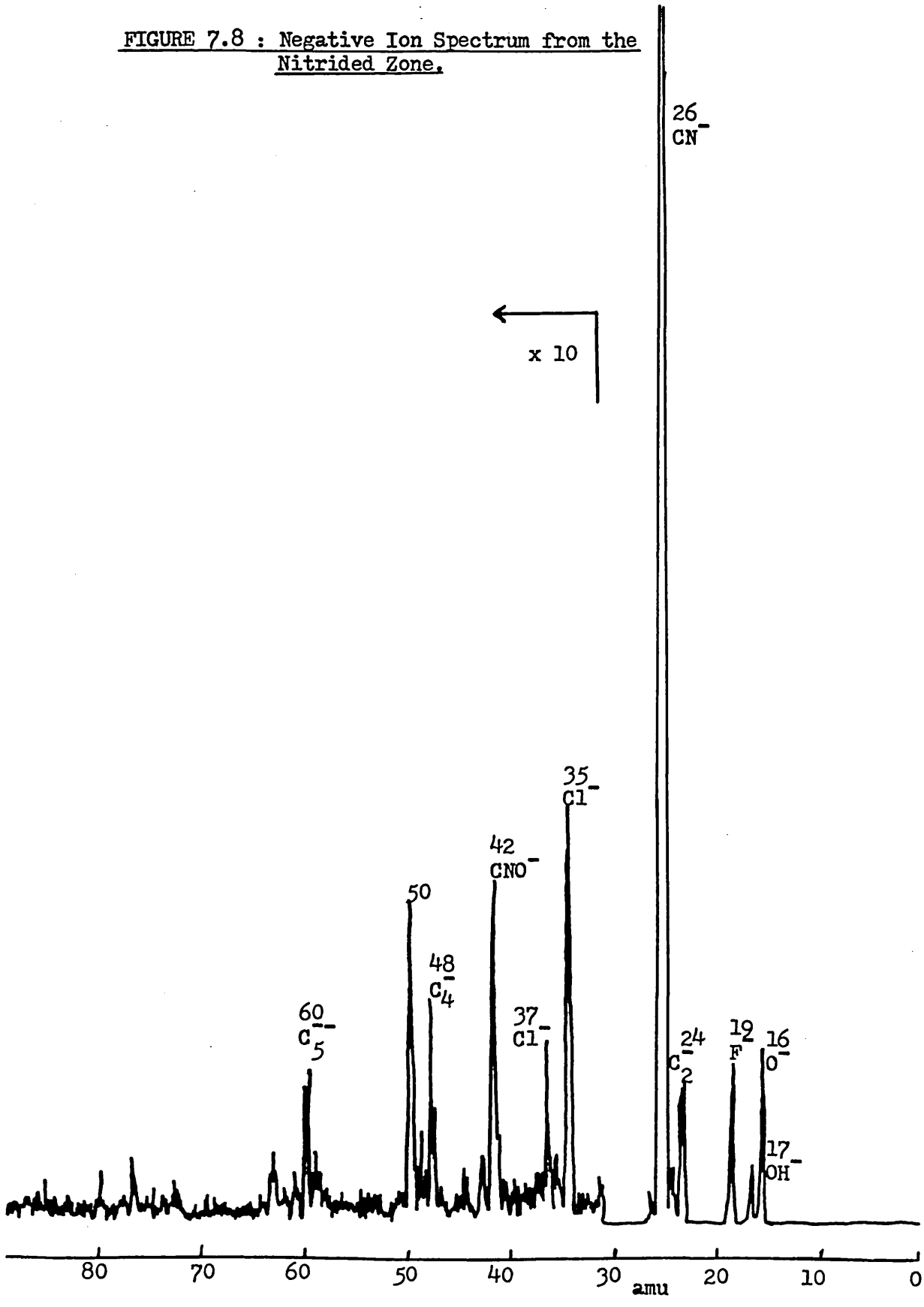
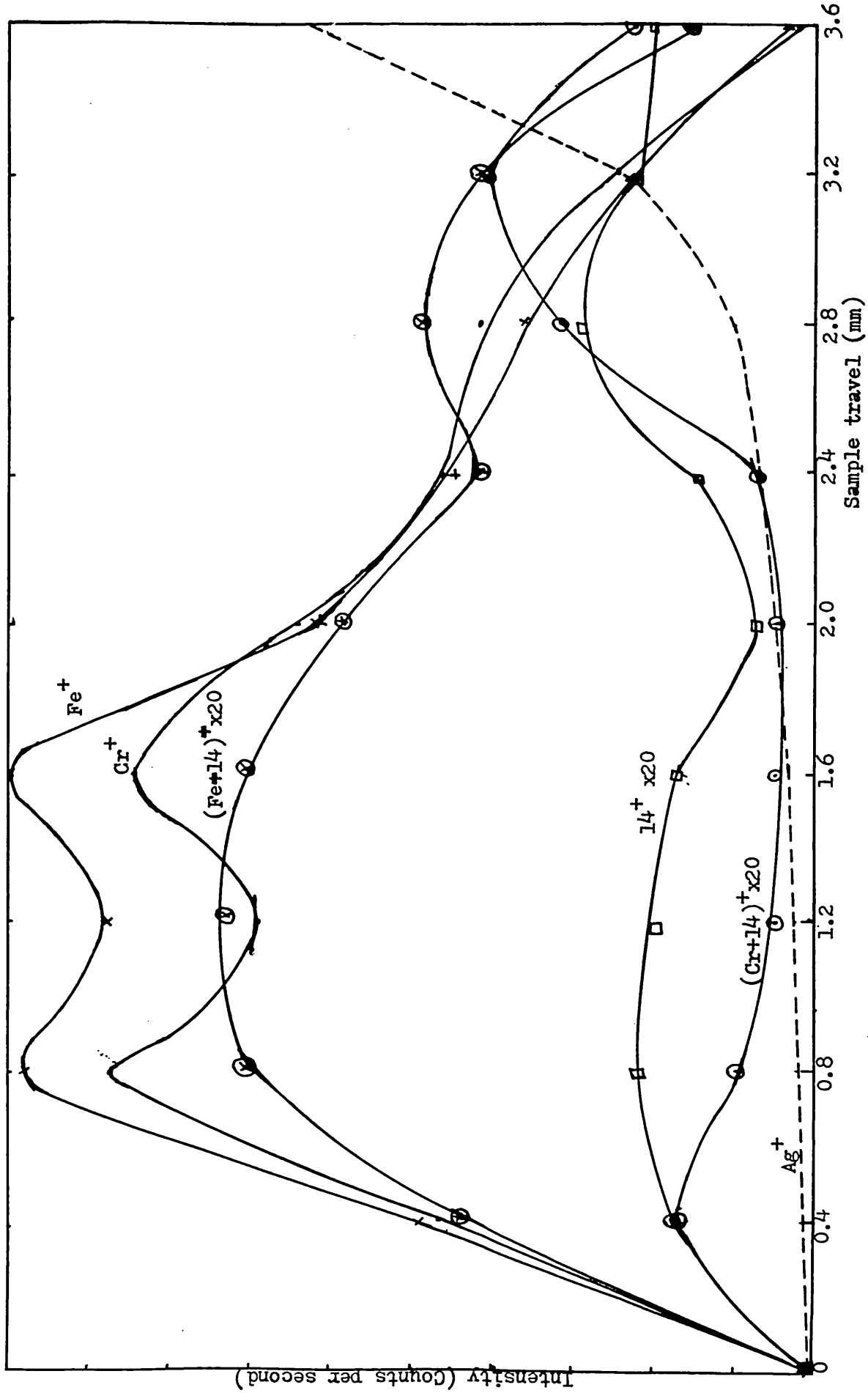


Figure 7.9 shows the results of a line scan of sample IA with measurements being recorded at 0.4 mm intervals. The intensity of the peaks of masses 14, 52, 56, 66, 70 and 107(Ag^+) is plotted as a function of the distance the sample was moved. It is important to note that the zero on the x-scale is purely arbitrary and only represents the start of the scan and not the edge of the nitrided roller.

The Fe^+ and Cr^+ peaks arise from the major constituents of the steel and show a significant increase in signal intensity which occurs roughly in the centre of the sample. Maxima were observed in the peak heights of the $(M+14)^+$ ionic species (where M = Fe,Cr) close to the edge of the sample as expected, though the relatively high signal intensity in the core region for masses 66 and 70 is not as expected.

FIGURE 7.9 : Preliminary Line Scan Analysis.



Based on these findings further investigations concentrated on the signal at the pre-selected masses 52(Cr^+), 56(Fe^+), 66($Cr^{14}N^+$?), 67($Cr^{15}N^+$?), 70($Fe^{14}N^+$?) and 71($Fe^{15}N^+$?). Measurements were recorded with greater accuracy by analysing at points every 0.2 mm along the line scan and by scanning the spectrometer to each mass peak in turn and counting for 10 secs. The results obtained for samples IA, IB and IC are given in tables 7.3, 7.4 and 7.5 and figures 7.10 to 7.14.

The actual depth of each analysed point below the surface has not been calculated because of uncertainty in the position of the edge of the sample. However, the distance along the line scan from the edge of the roller samples to the boundary between the nitrided layer and the core has been estimated based upon the case depth measurements determined from the microhardness profile (see Appendix 3). Consequently, an approximation of how much of the exposed surface is the core of the sample (length EG in Appendix 3) has been determined as 0.58 mm for sample IA, 0.76 mm for IB and 0.64 mm for IC.

TABLE 7.3 : Line Scan Results for Sample IA.

Travel mm	Signal Intensity (counts per second) Cr	Fe	$Cr+14^+$	$Fe+14^+$
0.0	34	105	7	7
0.2	39	343	12	27
0.4	598	1412	21	71
0.6	1877	3393	28	111
0.8	2616	4321	25	54
1.0	2000	3262	13	38
1.2	3271	3814	17	43
1.4	2163	3377	11	38
1.6	2120	3610	11	41
1.8	2001	3413	12	38

TABLE 7.4 : Line Scan Results for Sample IB.

Travel mm	Signal Intensity (counts per second) Cr	Fe	$Cr+14^+$	$Fe+14^+$	$Cr+15^+$	$Fe+15^+$
0.0	124	137	12	13	31	23
0.2	250	1059	13	12	38	17
0.4	1681	9833	42	55	92	30
0.6	4044	18,644	57	88	123	52
0.8	6475	17,241	69	101	307	99
1.0	8825	18,668	116	149	292	92
1.2	10,748	19,434	130	154	116	122
1.4	11,507	18,161	124	151	78	86
1.6	12,664	19,337	178	140	60	104
1.8	13,442	19,870	149	122	68	168
2.0	14,653	20,900	175	131	233	90
2.2	16,130	22,244	200	108	150	68
2.4	18,448	23,020	200	157	72	124

TABLE 7.5 : Line Scan Results for Sample IC.

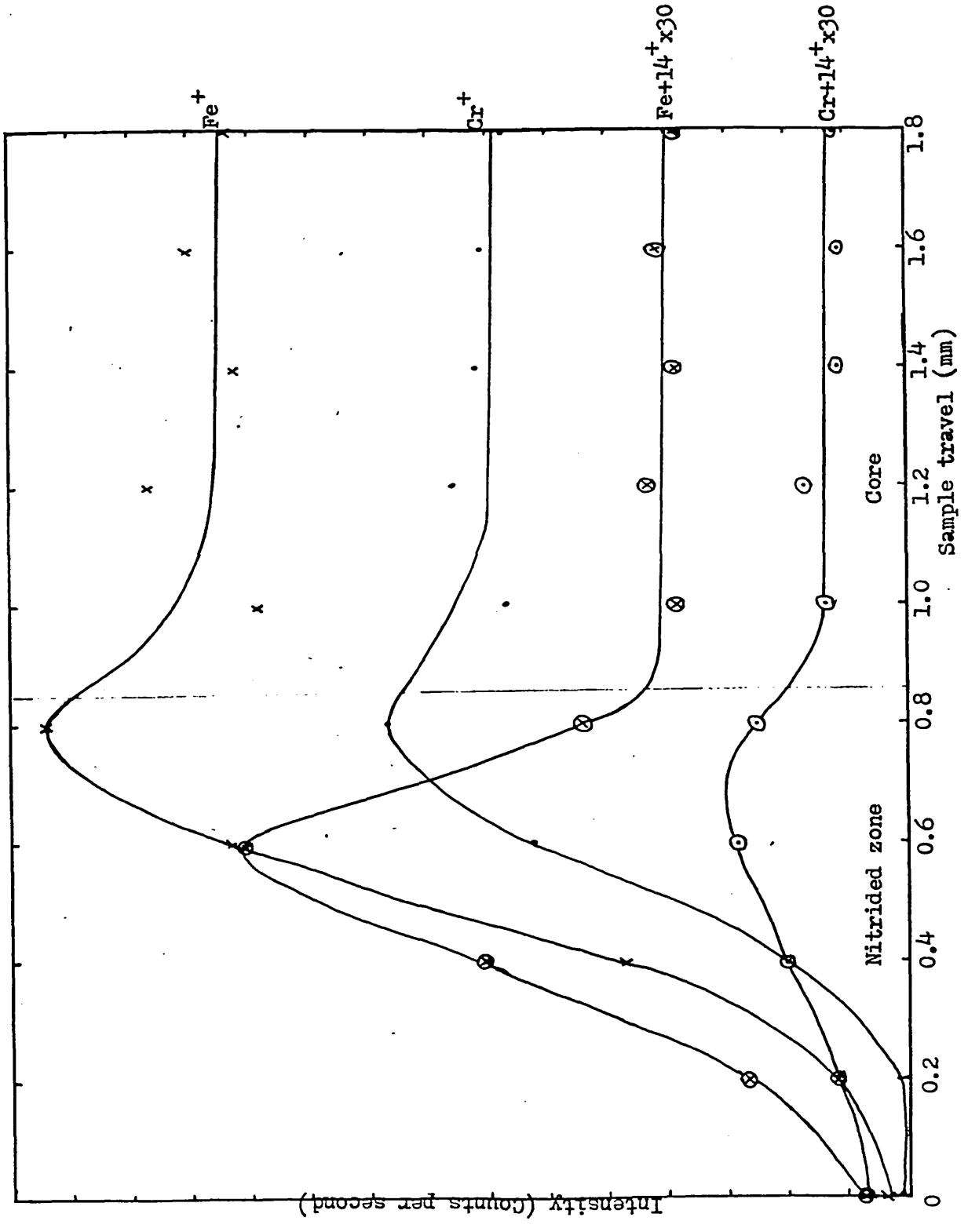
Travel mm	Signal Intensity (counts per second) Cr	Fe	Cr^{+14}	Fe^{+14}	Cr^{+15}	Fe^{+15}
0.0	773	2,235	23	112	49	30
0.2	5,683	22,631	13	522	72	4
0.4	15,945	39,950	108	1091	508	303
0.6	24,399	51,648	274	830	831	296
0.8	24,849	41,187	281	339	779	81
1.0	30,557	39,031	336	288	541	21
1.2	22,802	38,675	352	96	576	8
1.4	20,842	35,646	286	99	332	119
1.6	22,063	38,719	324	82	380	26
1.8	19,561	35,649	324	93	300	119
2.0	19,211	36,461	324	73	360	101

Figure 7.10 shows the results obtained for samples IA. Note that the sensitivity of the M^+ ions is 30 times the $(M+14)^+$ ions. The boundary between the core and the nitrided zone has been estimated as can be seen in the figure.

Based upon theoretical considerations the intensities of the Fe^+ and Cr^+ profiles are expected to be maximum in the core region with a sharp decrease to 'zero' through the nitrided layer as the metal ion concentration is reduced due to the formation of metal nitrides. The reverse is expected for the $(M+14)^+$ ions in that the profile should pass through a maximum in the nitrided region through to zero in the untreated core.

On the whole this effect is observed for sample IA, though the reason for the Fe^+ and Cr^+ profiles passing through a maximum peak at the transition boundary is not known. The $(Fe+14)^+$ and $(Cr+14)^+$ profiles are indeed maximum in the nitrided layer though their signal is higher than expected in the core. One possible explanation for this is that the (+14) species does not arise from nitrogen-14 alone. It is known from previous experiments that hydrocarbon contamination gives rise to a prominent peak due to CH_2 (110) and this could possibly account for the observed effect, which is also seen in figure 7.9 for the $(14)^+$ signal.

FIGURE 7.10 : Line Scan of Sample IA.



With the possible exception of the $(Cr+15)^+$ profile, the results obtained for sample IB do not appear to be consistent with the theory (see figures 7.11 and 7.12). These results suggest that this sample has not been nitrided, though from the metallographic examinations and the microhardness profiles it is known that this is not the case. One plausible explanation is that the line scan was not taken through the nitrided layer and the profiles represent those of the core. It is possible that the region 0 to 0.6 mm in the figures is that part of the sample coated with the silver paint thereby masking the nitrided layer. This would then account for the location of the $(Cr+15)^+$ maximum peak which, based on the mechanism of nitriding and the treatment conditions undertaken for sample IB, would be expected at the transition boundary between the nitrided layer and the core.

FIGURE 7.11 : Line Scan of Iron Species for Sample IB.

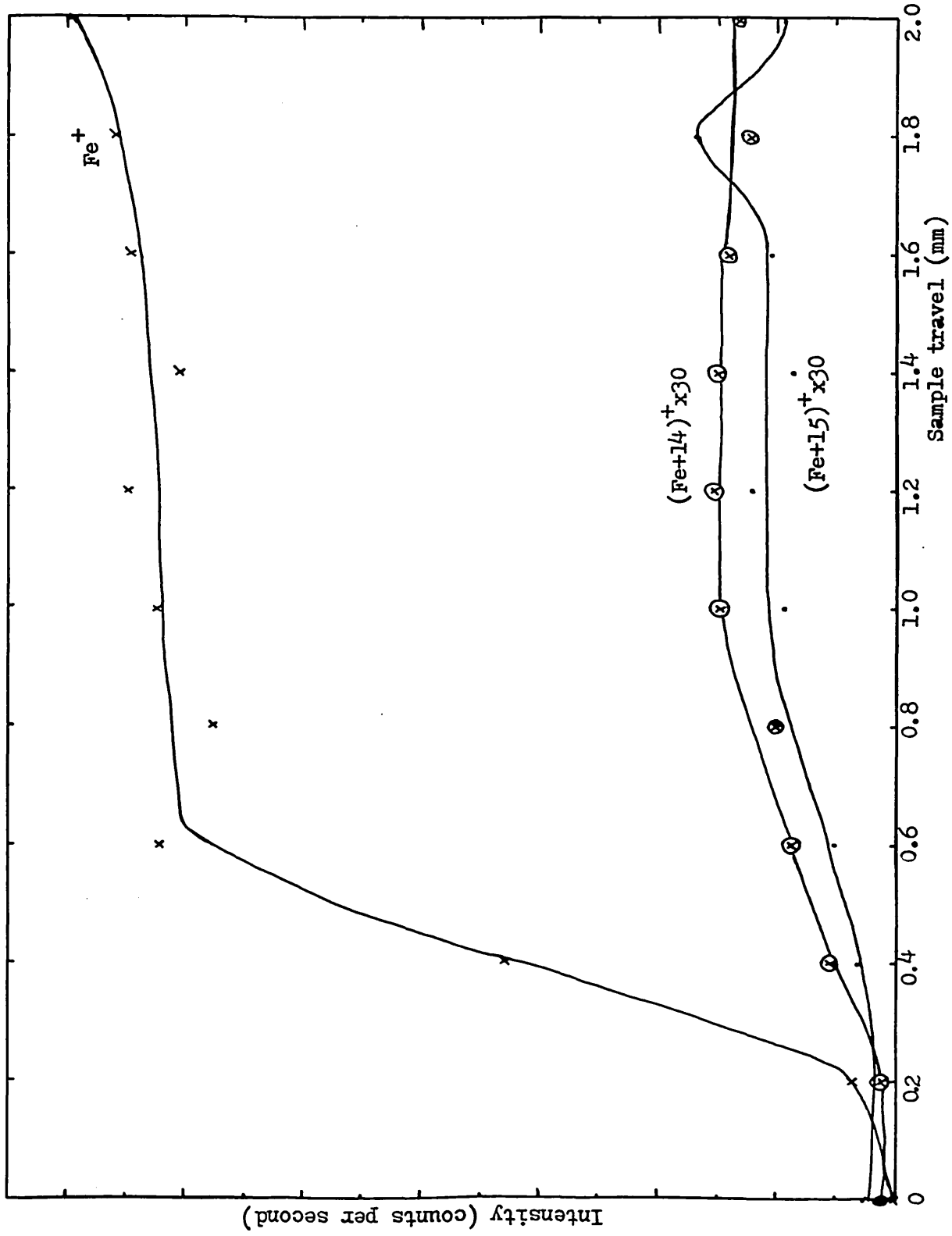
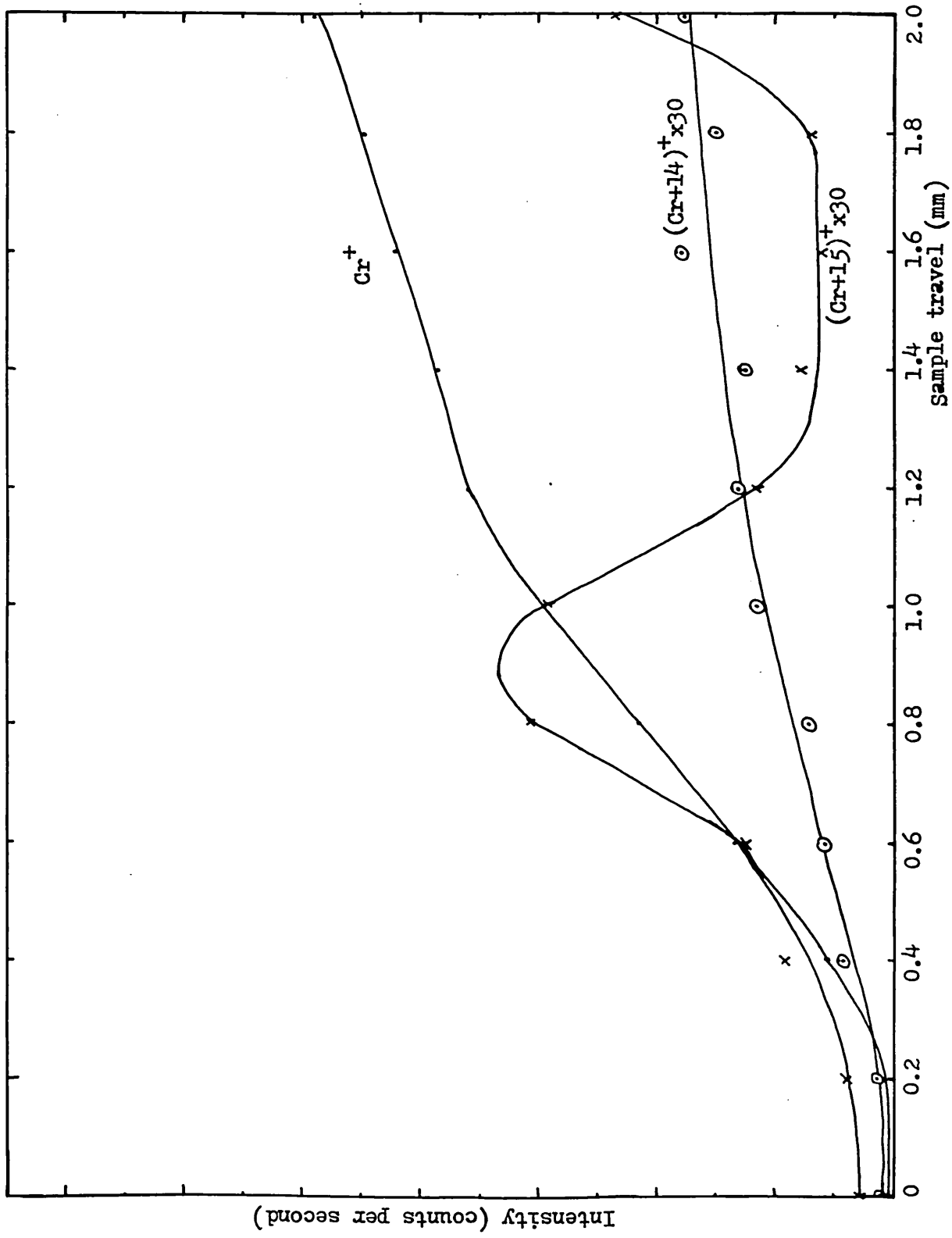


FIGURE 7.12 : Line Scan of the Chromium Species of Sample IB.



The treatment conditions for IC differ from those for IB in that the isotope was introduced at the start of the treatment as opposed to the end. Consequently, the isotope is expected to be situated at the edge of the IC rollers.

Figures 7.13 and 7.14 illustrate the results obtained on SIMS analysis of sample IC. In this case the isotope nitrogen-15 appears to have reacted predominantly with the Cr alloy throughout the nitrided layer and to a lesser degree with the Fe. It is not concentrated at the outer edge as was initially expected. Another interesting point to note is the absence of a $(Cr+14)^+$ maximum peak in this nitrided region though the $(Fe+14)^+$ ion peak is particularly strong. Also this is in good agreement with the results observed for sample IA namely a strong $(Fe+14)^+$ peak compared to a much weaker $(Cr+14)^+$ peak in the nitrided zone.

In order to explain these results it is again necessary to consider the nitriding mechanism.

FIGURE 7.13 : Line Scan of the Iron Species of Sample IC.

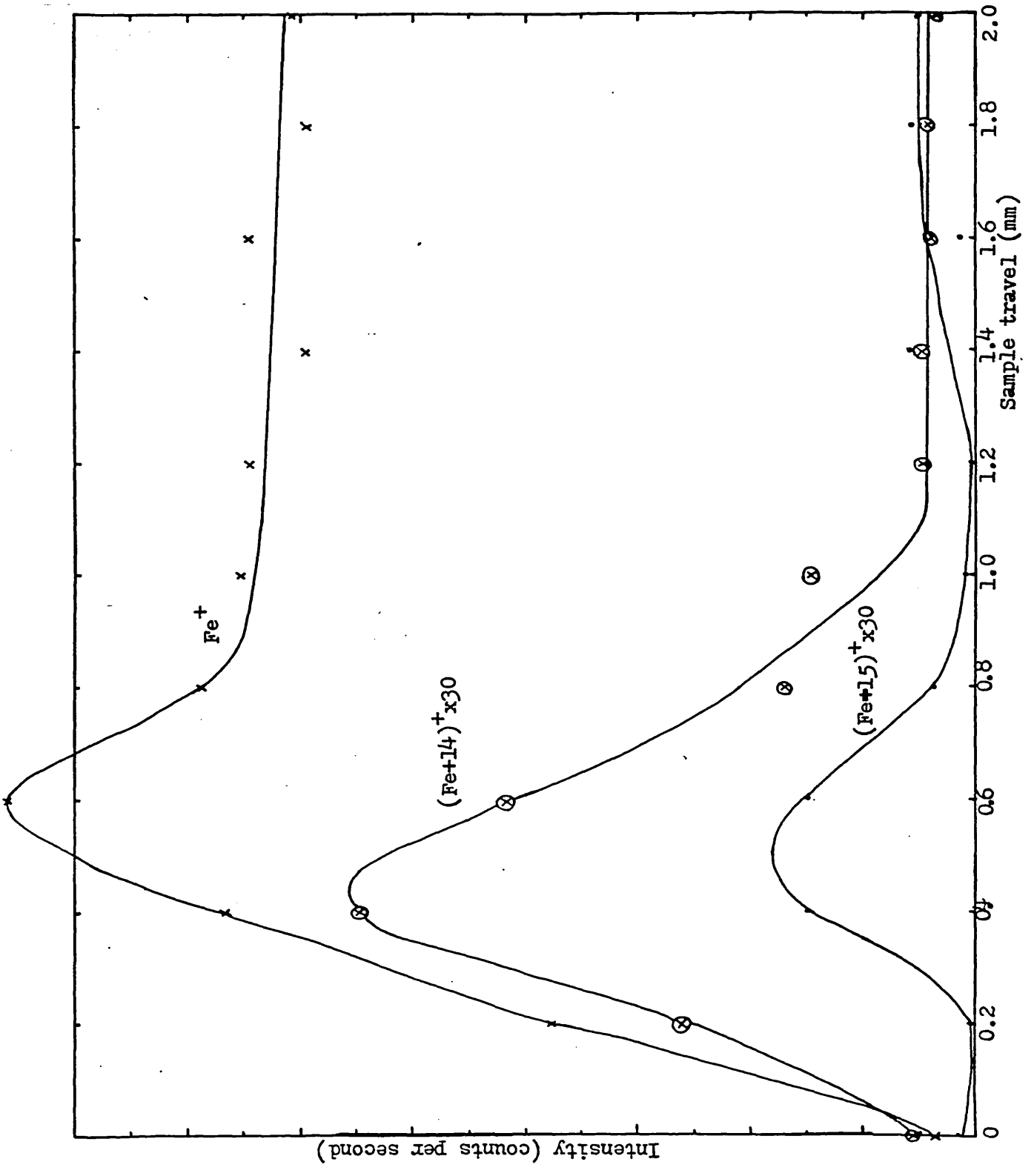
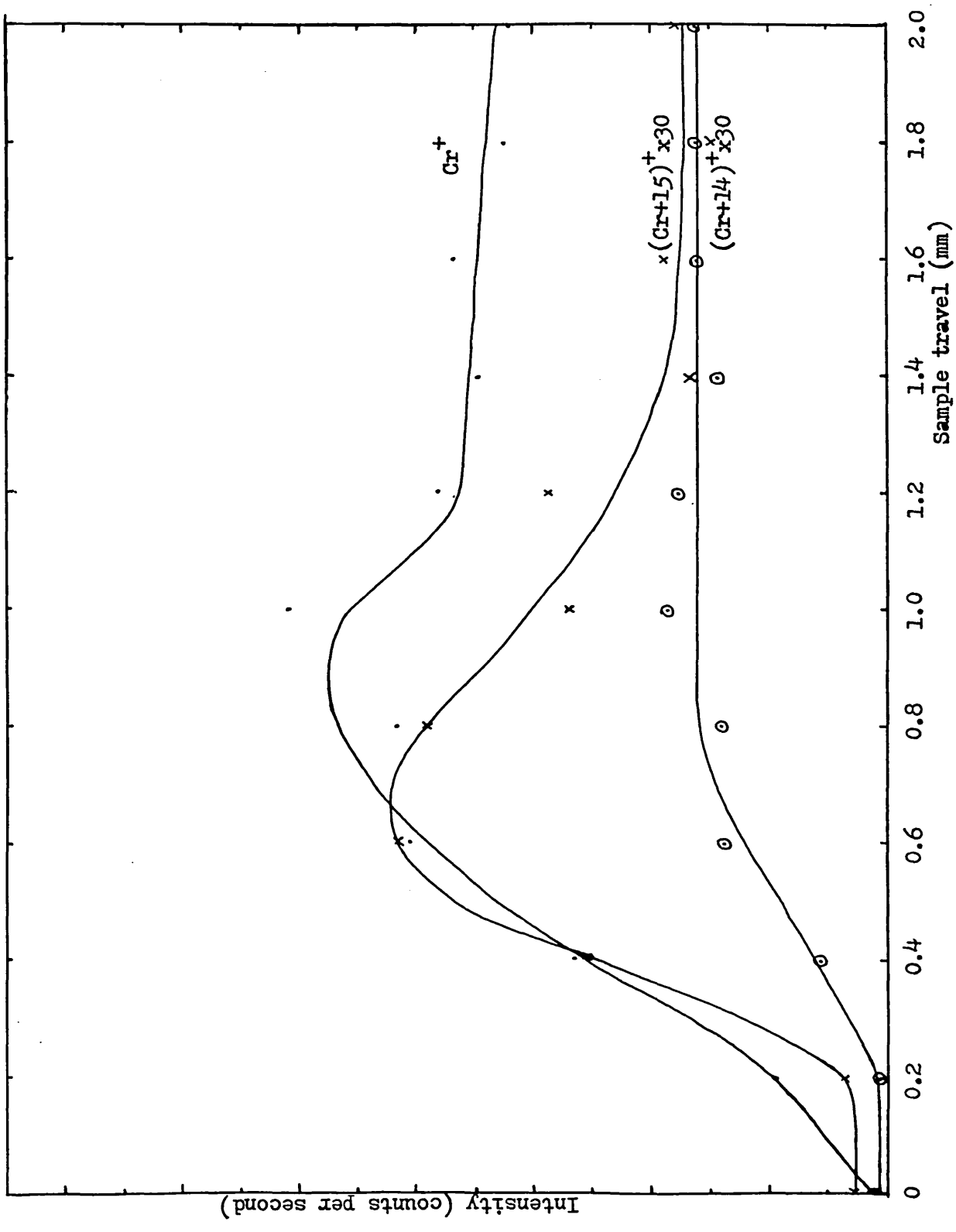


FIGURE 7.14 : Line Scan of the Chromium Species of Sample IC.



After the introduction of the nascent nitrogen to the steel surface, two different processes come into effect, namely the rate of diffusion of the nitrogen atoms into the steel and the rate of formation of the metal nitrides. Chromium nitride is a highly stable compound compared to iron nitride, FeN, which is known to decompose under the treatment conditions to form iron nitride compounds Fe_xN (where x = 2,3,4) with the release of nascent nitrogen. There is considerable evidence for this decomposition reaction occurring at the steel surface during nitriding resulting in the formation of the compound layer (80). This could possibly account for the presence of the $(M+15)^+$ ions throughout the treated layer.

Initially the isotope N-15 would react at the edge of the steel surface forming both stable $Cr^{15}N$ and the relatively unstable $Fe^{15}N$. The subsequent decomposition of this iron compound would result in the release of N-15 which would be free to return either to the plasma, and consequently be available for further treatment, or to diffuse further into the steel surface. Therefore, it is possible that N-15 would be present throughout the nitrided layer and its apparent preference for Cr as opposed to Fe can be explained by the relative stabilities of these metal nitrides.

If this is indeed the case, the presence of N-15 in

sample IB where the isotope was introduced at the end of the process, would be expected to be situated deep within the layer. A repeat analysis of the nitrided region of sample IB would be desirable to confirm this.

7.2.3. Repeat Analyses Using SIMS.

Further tapered sections of samples from each of the plasma nitriding treatments IA, IB and IC, coded A-2, B-2 and C-2 respectively, were prepared for SIMS analysis as described earlier and submitted to Surface Analysis Technology plc, Department of Materials, Imperial College. Experimental conditions differed slightly from the previous work in that a primary oxygen ion beam was used and not argon. The elements at masses 52, 56, 66, 67, 70 and 71 were monitored along a line scan at a resolution of 10 μm in 10 μm steps and the results obtained are presented in figures 7.15 to 7.20.

FIGURE 7.15 : Line Scan of the Iron Species of Sample A-2.

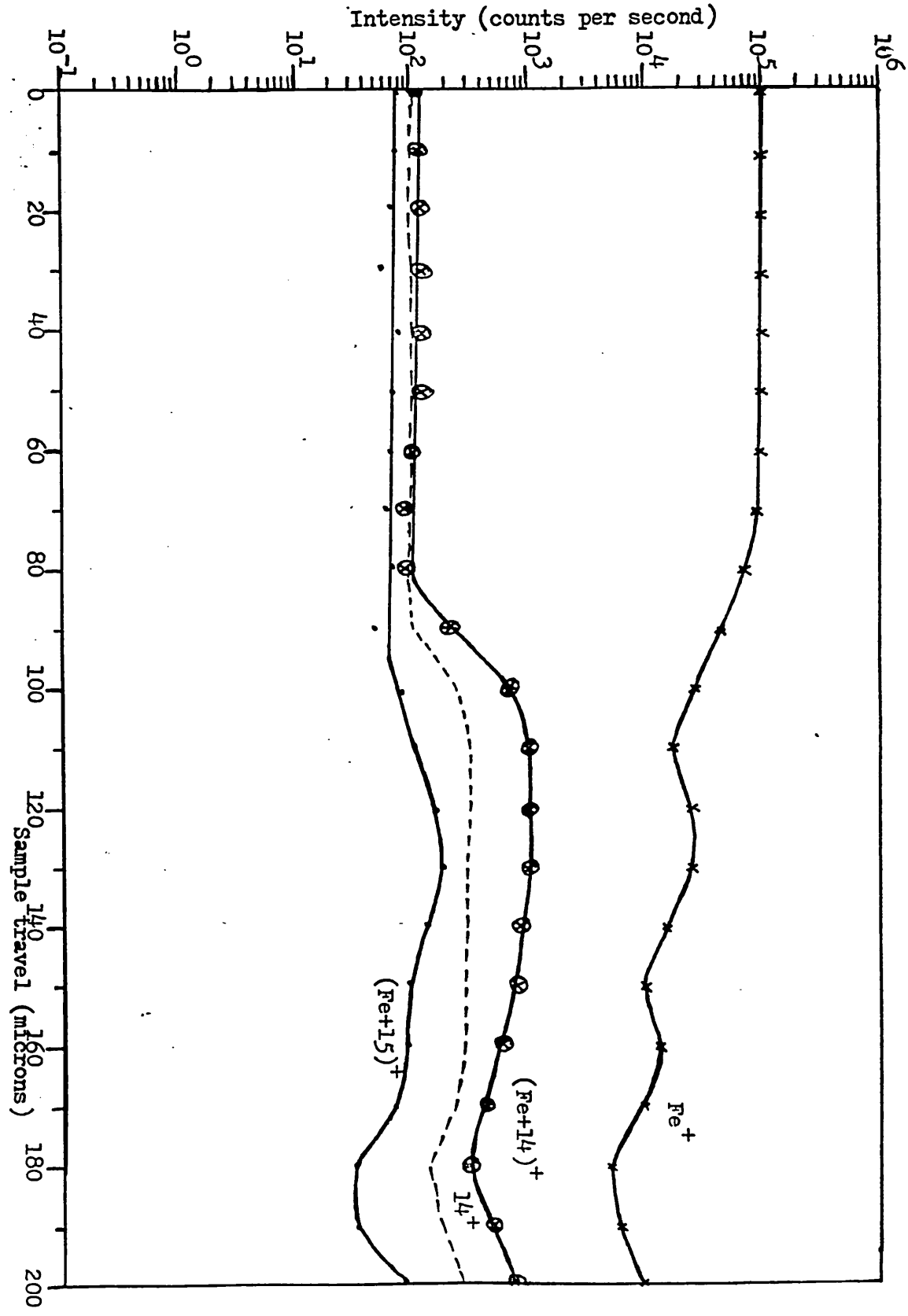


FIGURE 7.16 : Line Scan of the Chromium Species in Sample A-2.

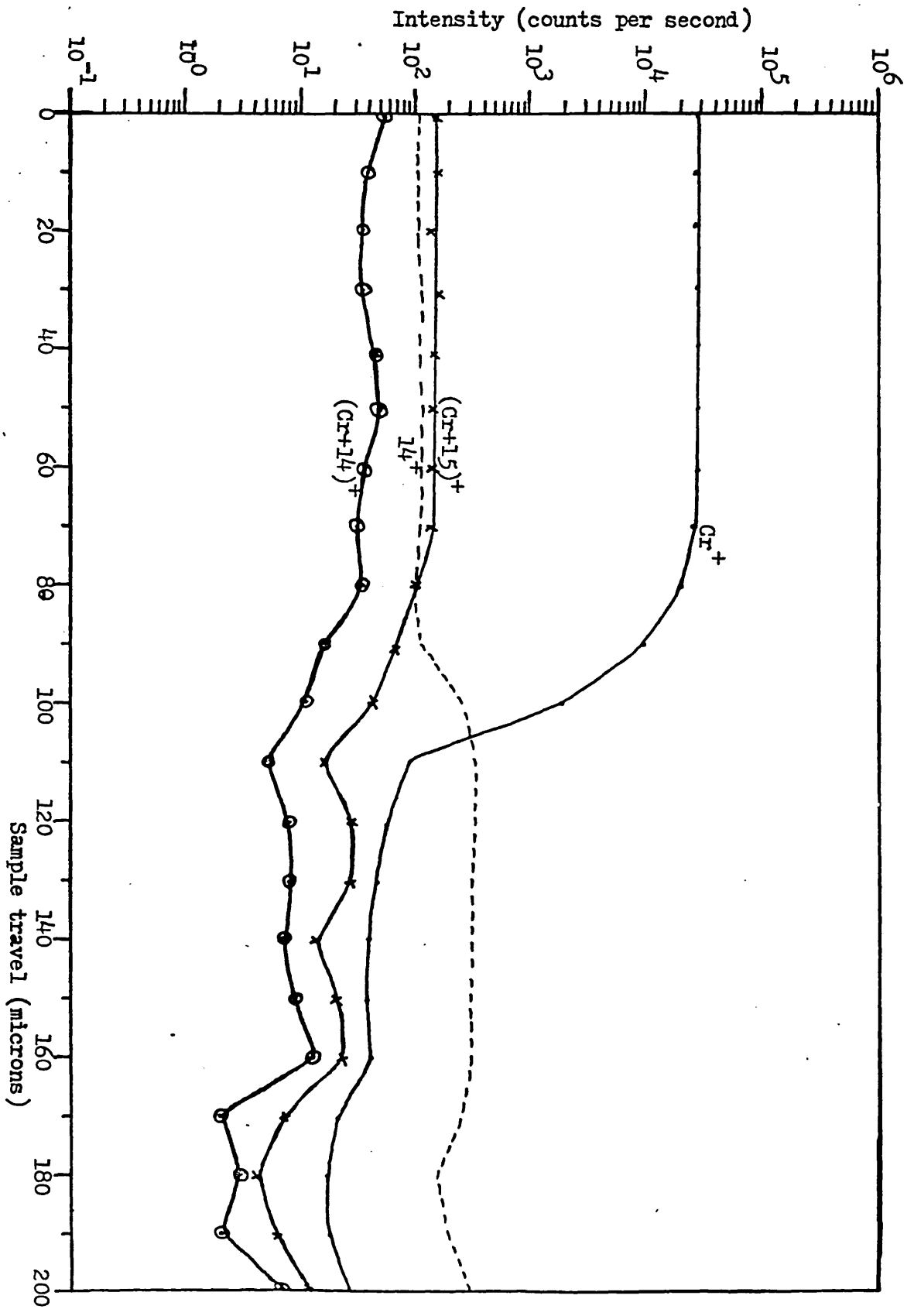


FIGURE 7.17 : Line Scan of the Iron Species in Sample B-2.

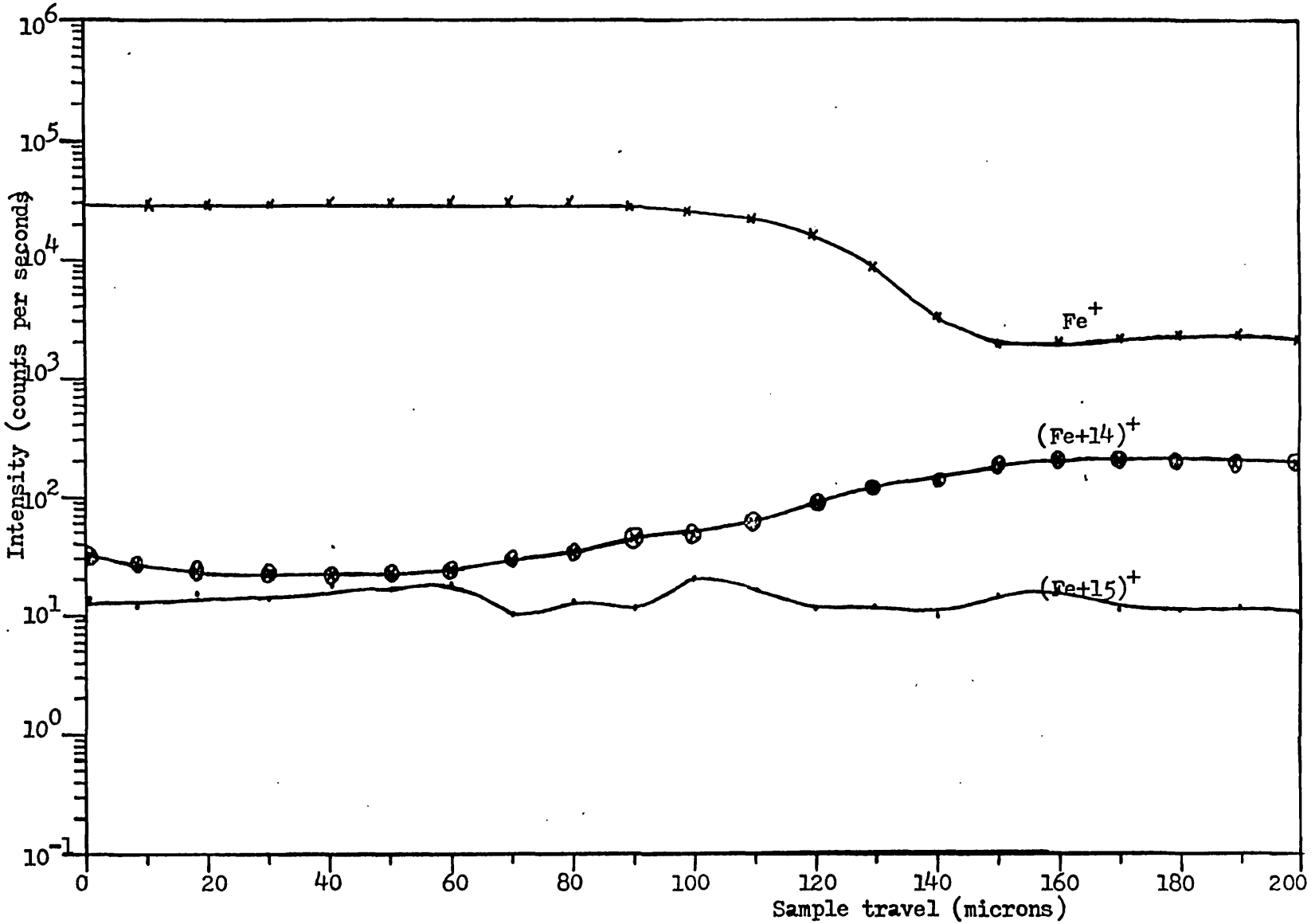


FIGURE 7.18 : Line Scan of the Chromium Species in Sample B-2.

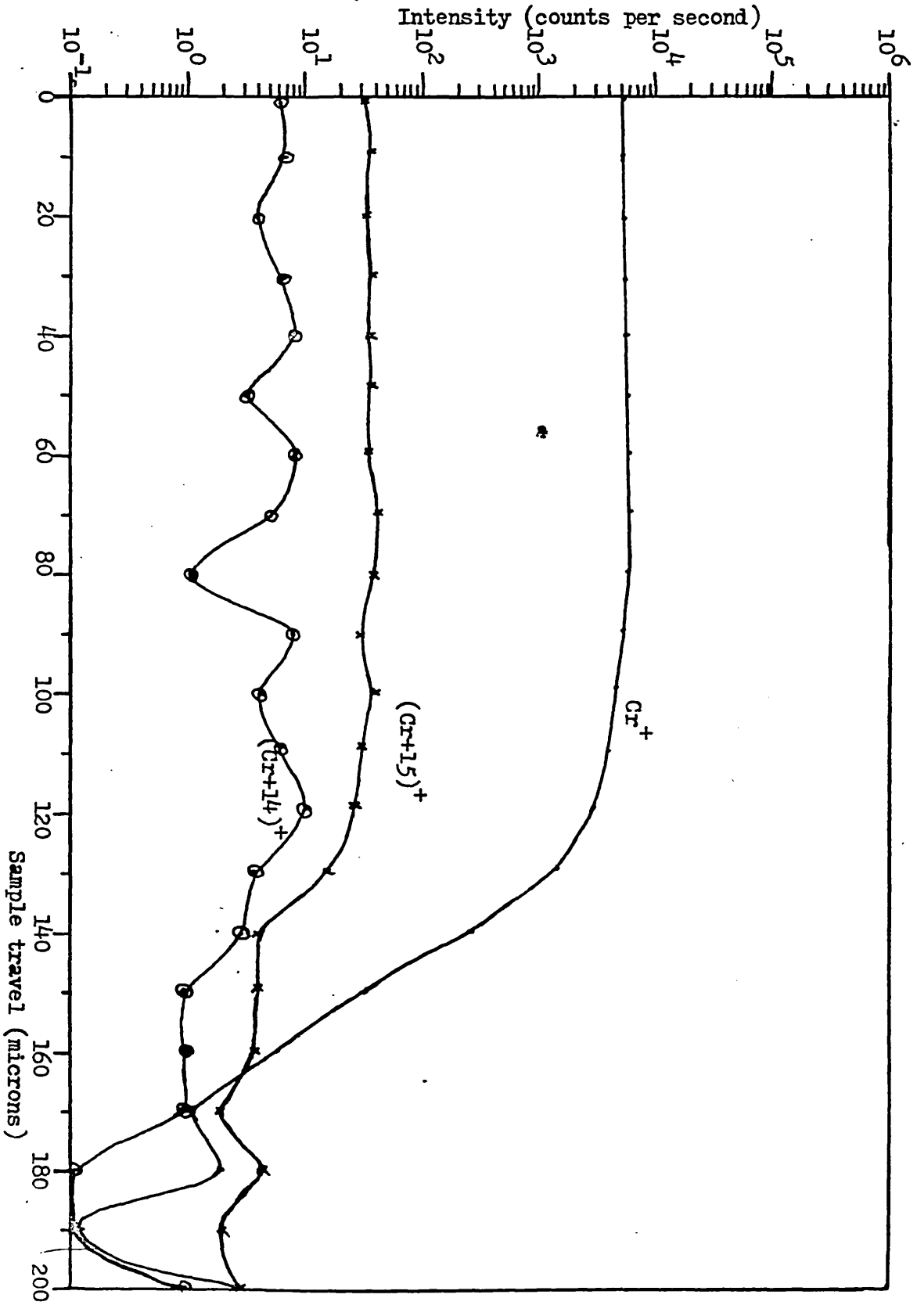


FIGURE 7.19 : Line Scan of the Iron Species in Sample C-2.

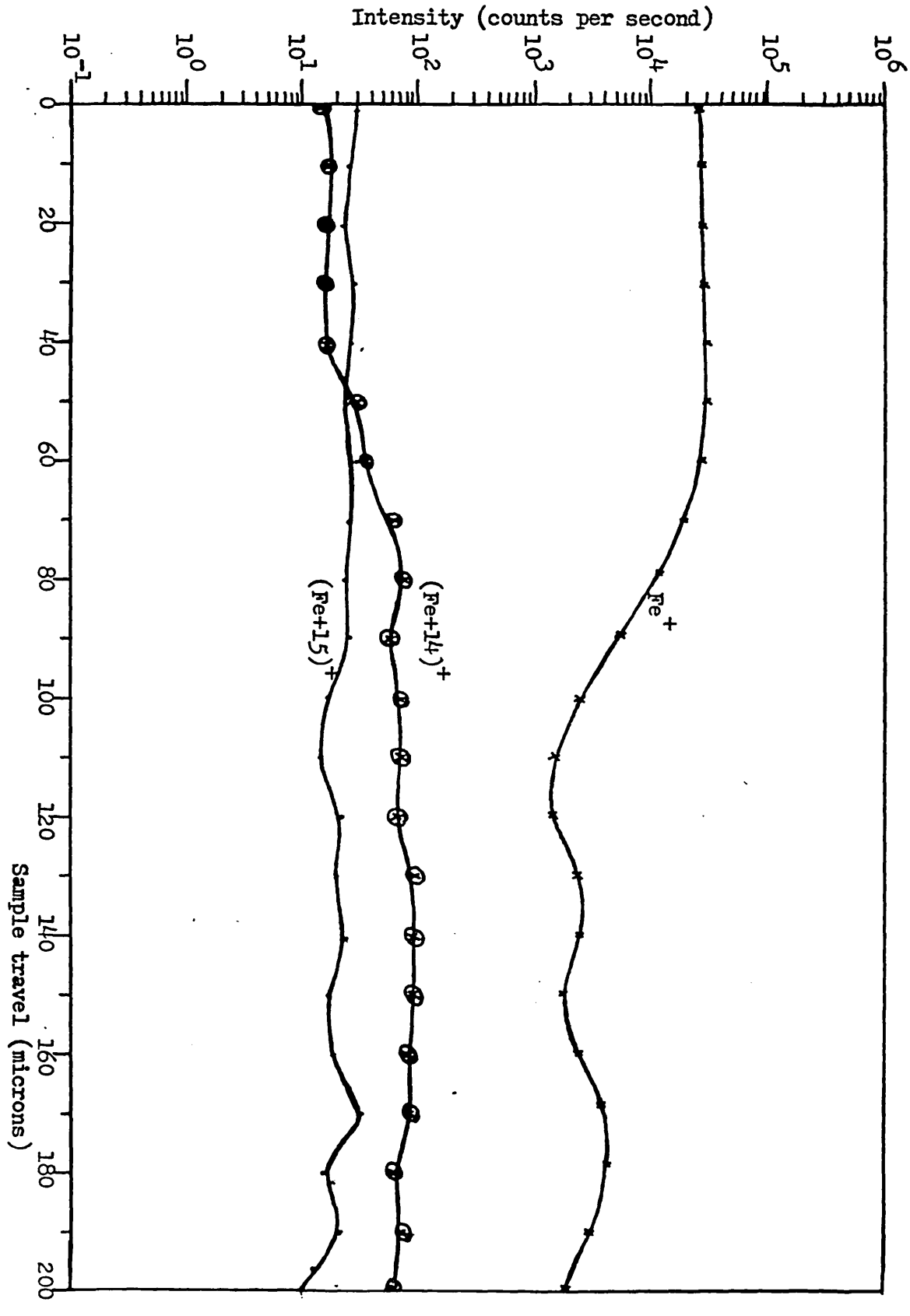
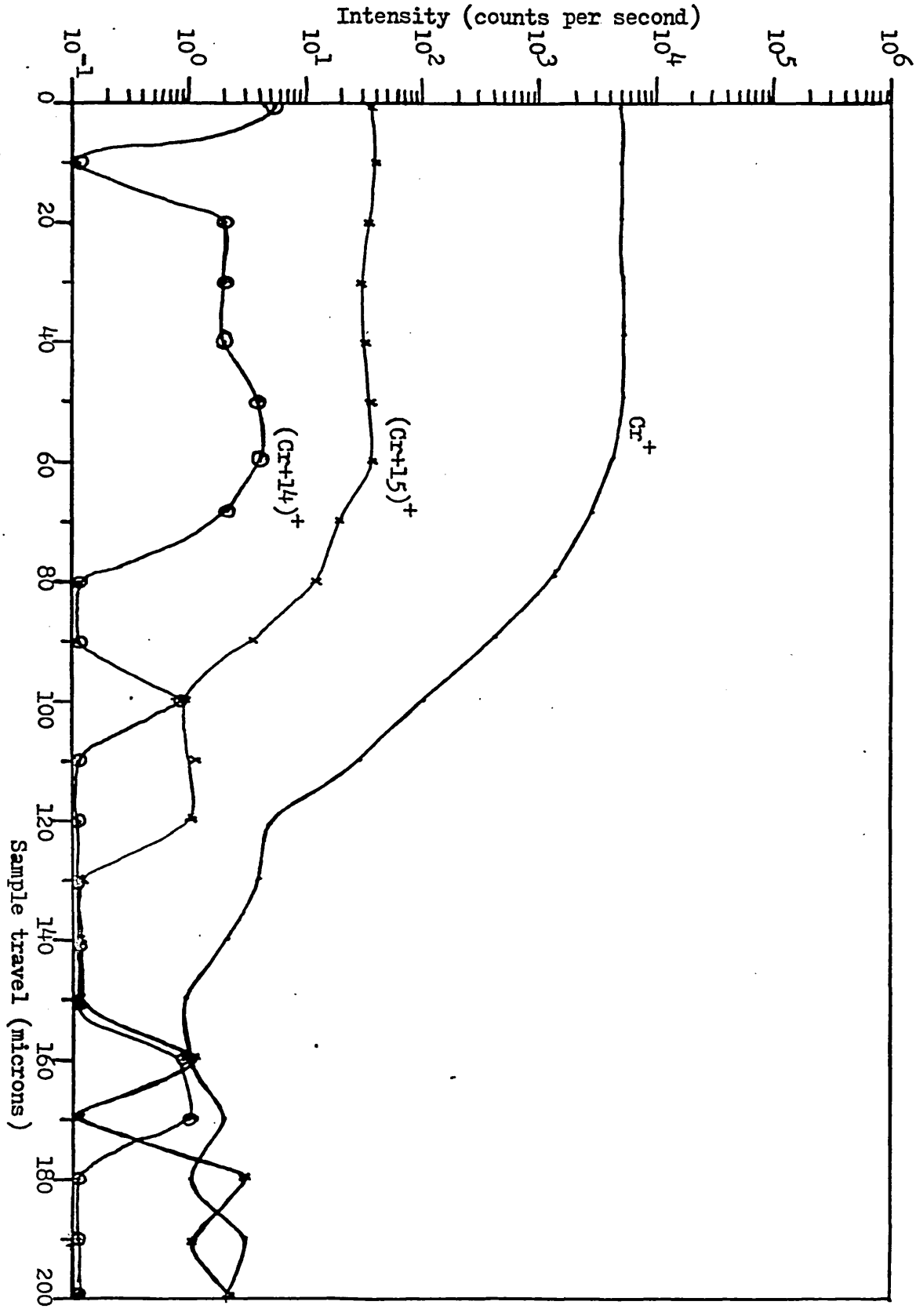


FIGURE 7.20 : Line Scan of the Chromium Species in Sample C-2.



With the exception of the 67 amu signal all three samples are expected to show similar profiles. This is indeed the case as several features in common are observed for all three samples :

- the intensities of the core signals are of the same order
- there is a significant reduction in both the Fe^+ and Cr^+ signals from the core to the nitriding zone as a result of the formation of the metal nitrides
- there is an increase in intensity of the 70 amu peak attributed to $(Fe+14)^+$ in the nitrided zone, which is indicative of the formation of iron nitride
- conversely, there is a decrease in the $(Cr+14)^+$ signal in the nitrided zone
- there is also a decrease in the $(Cr+15)^+$ signal on moving into the nitrided layer
- no noteable changes are seen for $(Fe+15)^+$ along the line scan as expected as the concentration of nitrogen-15 introduced into the surface was very low and would be expected to react with chromium (and the other alloy metals present) in preference to iron.

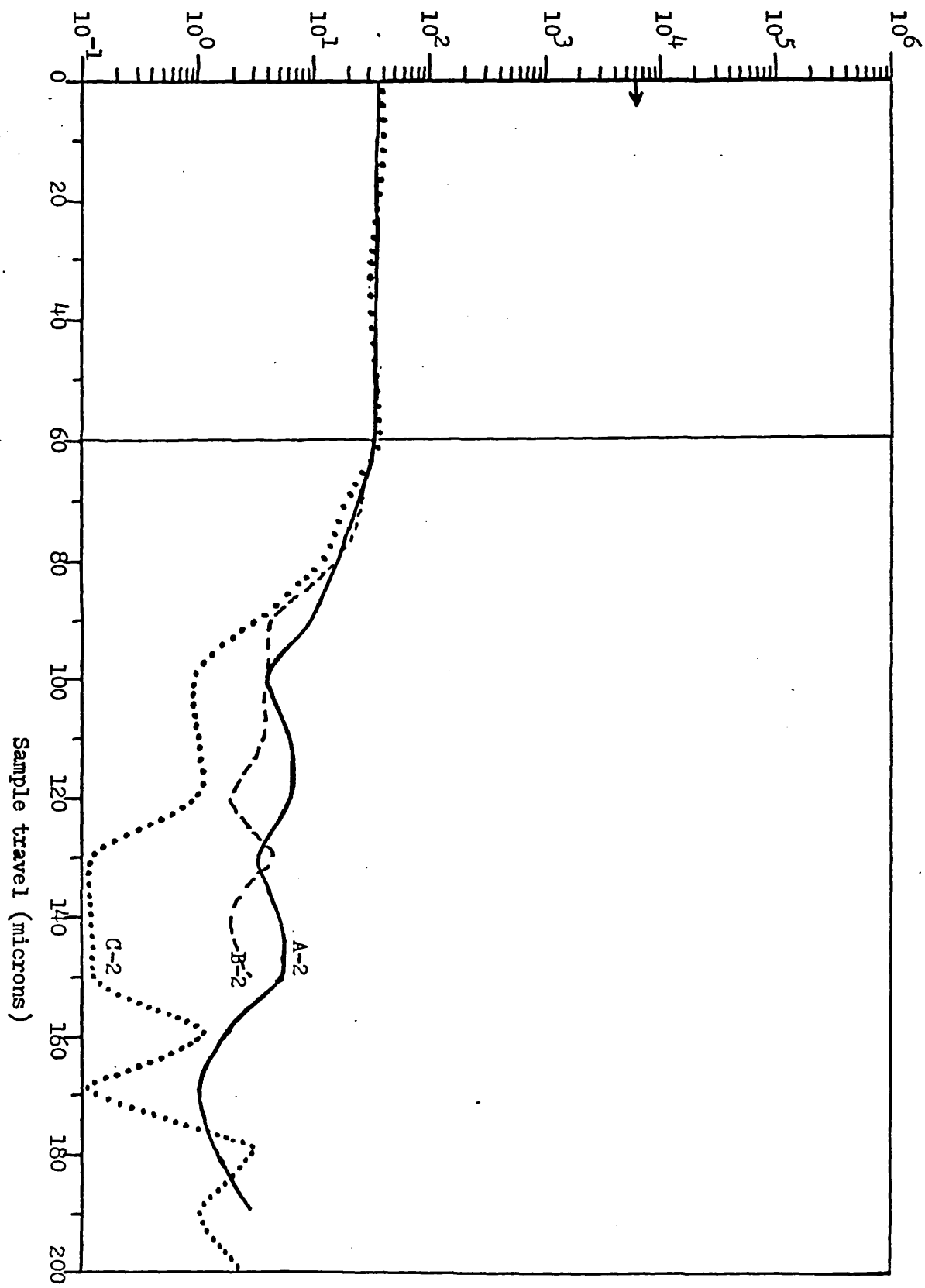
Two of the observed effects of the results of the SIMS analyses are not as expected, namely the decrease in signal intensity in the nitrided region of the $(Cr+14)^+$ and $(Cr+15)^+$ species and the presence of the $(M+14)^+$ and $(M+15)^+$ species, (where M=Cr,Fe) in the core of the sample. These

effects were also observed in the previous experiments on IB and IC. In order to account for the decrease in the chromium species signals one tentative explanation is that under the experimental conditions used during the analyses the primary ion beam did not have sufficient energy to ionise these species. It is well accepted that chromium nitride species are highly stable. The presence of $(M+14)^+$ and $(M+15)^+$ ionic species in the core is indicative of groups other than nitrogen-14 and nitrogen-15 combining with the metal atoms either in the steel sample or more probably in the secondary ion beam. As mentioned previously hydrocarbon contamination is one possible explanation. On comparing the $(Cr+15)^+$ and $(Cr+14)^+$ line scans it is found that for samples A-2 and B-2 the results are virtually superimposable. This is strong evidence in support of these signals arising from contaminant interaction with the sputtered chromium atoms and not chromium nitride species. The decrease in the signal intensity in the nitrided zone is attributed to there being less free chromium atoms available for reaction as a result of nitride formation.

The only minor difference observed in the analyses of these three samples involves the $(Cr+15)^+$ signal. In all cases there is a decrease in intensity between the core and the nitrided region but this decrease is more significant for sample C-2 than for A-2 and B-2 as illustrated in figure 7.21. Also for C-2, the signal begins to increase in

intensity, though not to that of the core level, close to the edge of the sample. This is the region where the nitrogen-15 isotope is expected to be located, however this result is not conclusive evidence that this is in fact the case.

FIGURE 7.21 : Comparison of the $(Cr+15)^+$ Species.



7.3 Summary.

In an attempt to control the final location of the stable isotope nitrogen-15 in the nitrided layer of a steel surface, experiments were conducted whereby the isotope was introduced into the plasma at pre-determined times. SIMS was investigated as a means of determining the nitrogen distribution of both nitrogen-14 and nitrogen-15 throughout the diffusion zone.

Throughout the interpretation of the results it was assumed that any deviation in signal intensity from that measured in the core, be it an increase or decrease in intensity, was attributed to the effects of the plasma nitriding treatments experienced by the sample.

As a result of the initial work carried out at AWRE Aldermaston, several observations were attributed to the effects of the nitriding treatment namely :

- a reduction in the Cr^+ and Fe^- intensities
- an increase in the CN^- signal
- the $(Fe+14)^+$ signal was noticeably stronger than for $(Cr+14)^+$
- the +15 species reacted predominantly with Cr in preference to Fe.

A more thorough and detailed analysis carried out by Surface Analysis Technology plc confirmed many of the above observations. The results of this work revealed that the intensities of the core measurements of the different species were of the same order for all the samples. This is indicative of the reproducibility of the technique. The $(Cr+14)^+$ and $(Cr+15)^+$ signals decreased in intensity in the nitrided zone compared to the core base line readings, wheras $(Fe+14)^+$ increased and no change was observed for $(Fe+15)^+$. It is suggested that this is due to the high stability of the chromium nitride species. However, the $(Cr+15)^+$ signal was higher in intensity close to the edge of sample C-2 compared to further into the nitrided layer which is as predicted from the mechanism of nitriding.

Therefore, at this stage it is not possible to say with authority that control of the distribution of the isotope at different levels within the nitrided layer can be achieved. Further analyses is necessary to determine whether other signals can be measured as a consequence of the nitriding process. It is not unusual for metal nitride compounds to be non - stoichiometric. Also the possibility of measuring the 26 amu and 27 amu signals attributed to CN^- and $C^{15}N^-$ is worthy of further investigation.

CHAPTER 8 : DEVELOPMENT OF A MONITORING TECHNIQUE USING CARBON-13.

The experimental work described in this thesis has involved nitrided steels and nitrogen-15. This chapter outlines how a similar technique may be used with carburised steel and carbon-13. A method is proposed to monitor the wear of key components in an engineering system based on the concept of introducing carbon-13 into the surface of the components and then detecting the isotope as it appears in the wear debris.

8.1. Incorporation of Carbon-13 into the Steel Surface.

Carburisation is one process which incorporates carbon into a steel component as a means of improving its wear resistance. An outline of the different carburising techniques available has been given in section 3.1.1.1. As is the case for nitriding processes, plasma carburising offers several advantages over the more conventional carburising processes including a reduction in energy and gas consumption and process time, thereby resulting in a considerable reduction in the operating costs. Also it is the most controllable method. This technique is favoured to the ion implantation process, which has also been described earlier, because it has been developed as an industrial alternative to the other carburising methods though there is no evidence of its use as such.

Therefore, it is proposed to use the plasma carburising process to incorporate the stable isotope, carbon-13, into the surface of steel components. By adopting a similar experimental approach to the nitrogen studies, namely the addition of the isotope at different times during carburisation and its distribution studied by SIMS, it should be possible to determine the conditions necessary to concentrate carbon-13 within the case-hardened layer. Preliminary exploratory analyses will be necessary to determine which of the ionic species detected in the mass

spectrometer correlate to the carburising process.

Control of the distribution of carbon-13 in the carburised layer is anticipated to be more difficult than for the nitriding work. The mechanism of plasma nitriding lends itself to the build up of a uniform diffusion layer as is observed in the microstructures of the nitrided samples shown in plates 4.1 and 7.1. However, the plasma carburising mechanism is thought to occur by a combination of inter grain boundary diffusion and intra grain diffusion of the nascent carbon followed by formation of iron carbide and consequently, the carbon is deposited at a range of depths below the surface. However, by introducing the isotope into the steel surface at the end of the carburising cycle it may be possible to concentrate it in a zone below the surface.

8.2. Generation of Wear Debris.

As in the case for the development of the monitoring method using nitrogen-15, it is possible to use the cone - on - roller wear machine described in chapter 4 as the means of generating wear debris from carburised test specimens. The rollers will be subjected to a plasma carburising treatment followed by surface hardening and the cones will be nitrided. Removal of the debris from the lubricant will be carried out as described in chapter 4.

8.3. Detection of Carbon-13.

The detection of carbon in metals and alloys involves measuring the carbon dioxide produced by the combustion of the sample as described in section 3.3.2. Various analytical methods are used but for the purpose of this study the infrared method is considered the most suitable as this allows differentiation between the two different stable isotopes : C-12 and C-13. Those difficulties encountered during the nitrogen-15 studies, when attempts to detect nitrogen by infrared spectroscopy proved unsuccessful, are not considered to be a problem in this case. The use of spectroscopic techniques for the detection of carbon in steel is well established.

Commercial analysers have been developed for the rapid determination of CO_2 using infrared absorption equipment as reported by White and Scholes (101) and Koch and Lemm (102). Modifications of the infrared equipment would be necessary to take into account the frequency shift due to the C-13 but this should be possible. Koch and Lemm describe a method for the rapid and simultaneous determination of the carbon and sulphur contents of steel.

The observed wavenumbers of some of the fundamental absorption bands for CO_2 and $^{13}CO_2$ are given in table 8.1 (75).

TABLE 8.1. Some Observed Fundamental Wavenumbers (cm^{-1}) of $^{12}CO_2$ and $^{13}CO_2$.

Fundamental	$^{12}CO_2$ (cm^{-1})	$^{13}CO_2$ (cm^{-1})	Description
ν_3	2349	2284.5	Antisymmetric stretching
ν_1	1354.9	1354.9	Symmetric stretching
ν_2	673	653.8	Bending
ν_4	2396.5	2328.2	Antisymmetric stretching

8.4 Summary.

It is suggested that the replacement of the treatment gas by a carbon-13 containing gas sample towards the end of the plasma carburising cycle could result in a carbon-13 enriched zone below the surface of a steel tribological component. The subsequent detection of the carbon-13 from debris particles generated as a result of wear mechanisms occurring during its operating life would provide a means of measuring the extent of that wear. Equipment is commercially available for the rapid determination of the carbon content of steel which relies upon infrared absorption analysis. Modification of this apparatus to allow for the detection of both carbon-12 and carbon-13 would be necessary, but this could then be used to monitor the condition of the doped component on-site.

CHAPTER 9. CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORK.

Ultimately, the aim of this project was to develop an on-site technique to monitor the progression of wear of an engineering system and to differentiate between tribological components.

One proposed method was investigated based upon incorporating a 'doped' layer of the stable isotope nitrogen-15 into the nitrided layer of a steel component and its subsequent detection by analysis of debris particles generated as a result of the wear mechanisms which take place during its operation.

It was originally believed that a nitrided layer with no compound layer would assist in the detection of the isotope. The nitrogen concentration of the compound layer is considerably greater than that of the diffusion zone and it was feared that this would mask the nitrogen content within the diffusion zone. Therefore, plasma nitriding experiments were conducted to ascertain those treatment parameters necessary to achieve this, prior to the isotopic work whereby nitrogen-15 was added to the process at the start of one experiment and at the end of another.

Two alternative analytical methods were evaluated to detect the isotope, namely infrared spectroscopy and secondary ion mass spectrometry. A test procedure was developed to convert the nitrogen present in the steel to a form in which it could be detected by infrared spectroscopy. Calibration of the nitrogen-14 / nitrogen 14 ratio to the ratio of the observed absorbance bands in the ir spectra was possible, though it was found to be sensitive only when the mol % $(^{15}NH_4)_2 SO_4$ was greater than 30%. However, nitrogen analysis of the wear debris proved to be unsuccessful. The low concentration of nitrogen in a nitrided surface in conjunction with the experimental losses incurred during the analysis is considered to be below the detection limit of the spectrometer. Two possibilities are suggested to overcome this problem, either the use of fourier transform infrared spectroscopy and / or a gas cell of path length in the order of 1 - 10 m.

SIMS was investigated as a possible means of measuring the nitrogen distribution of both N-14 and N-15 through the surface. Differences in signal intensities were observed which were attributed to the effects of the nitriding process, though it is not possible to say with authority that control of the location of the isotope within the layer can be achieved. Further SIMS analyses are required to determine whether other signals can be measured as a consequence of the nitriding process. The 26 amu and 27 amu

signals attributed to CN^- and $C^{15}N^-$ are particularly worthy of investigation.

As the nitrogen-15 work developed the procedures to detect the isotope became relatively time consuming and complicated, requiring expensive and highly sophisticated equipment. This was moving away from the original intentions set out to develop an on-site monitoring method. Therefore, the nitrogen-15 method described in this thesis is not recommended for monitoring the state of an engineering system during operation. However, it has potential as an aid in research and design applications.

A second monitoring method based upon carbon-13 has been proposed though no experimental work has of yet been carried out. This method is considered to be potentially suitable for monitoring systems on-site. Detection equipment is commercially available for the rapid determination of the carbon content in steel. Modifications to this equipment would be necessary to allow for the analysis of both carbon-12 and carbon-13, but this is considered possible as the apparatus can simulataneously determine both the carbon and sulphur contents in steel.

APPENDIX 1.

Calculation of the mol % $(^{15}NH_4)_2SO_4$.

For example :

Consider the mixture containing 0.125 g $(NH_4)_2SO_4$ and 0.02 g $(^{15}NH_4)_2SO_4$.

$(NH_4)_2SO_4$: molecular weight is 132.125
sample contains 99.5 atom % N-14

$(^{15}NH_4)_2SO_4$: molecular weight is 134.119
sample contains 99 atom % N-15

The amount on N-14 present in the N-15 salt, and vice versa, was assumed negligible.

Therefore,

$$\text{number of moles } (NH_4)_2SO_4 = \frac{0.995 \times 0.125}{132.125} \quad (x)$$

$$\text{number of moles } (^{15}NH_4)_2SO_4 = \frac{0.99 \times 0.02}{134.119} \quad (y)$$

$$\text{Mol \% } (^{15}NH_4)_2SO_4 = 13.56\ \% \quad \frac{y}{(x+y)} \times 100$$

APPENDIX 2.

The Beer - Lambert law states that :

$$\text{Abs.} = \frac{I}{I} = \exp(-\varepsilon c l)$$

where Abs. = Absorbance

I = Intensity of transmitted radiation

I = Intensity of incident radiation

ε = Molecular extinction coefficient

c = Molecular concentration

l = Cell path length (cm)

Consider the absorbance band of NH_3 at 966.6 cm^{-1}.

For a given concentration of NH_3,

$$\text{Abs.}(NH_3) = \exp(-x_1)$$

Therefore, an exponential graph will be obtained on plotting the absorbance versus concentration.

Likewise for $^{15}NH_3$ absorbance band at 961 cm^{-1} :

$$\text{Abs.}(^{15}NH_3) = \exp(-x_2)$$

Now consider a sample containing a mixture of NH_3 and $^{15}NH_3$.

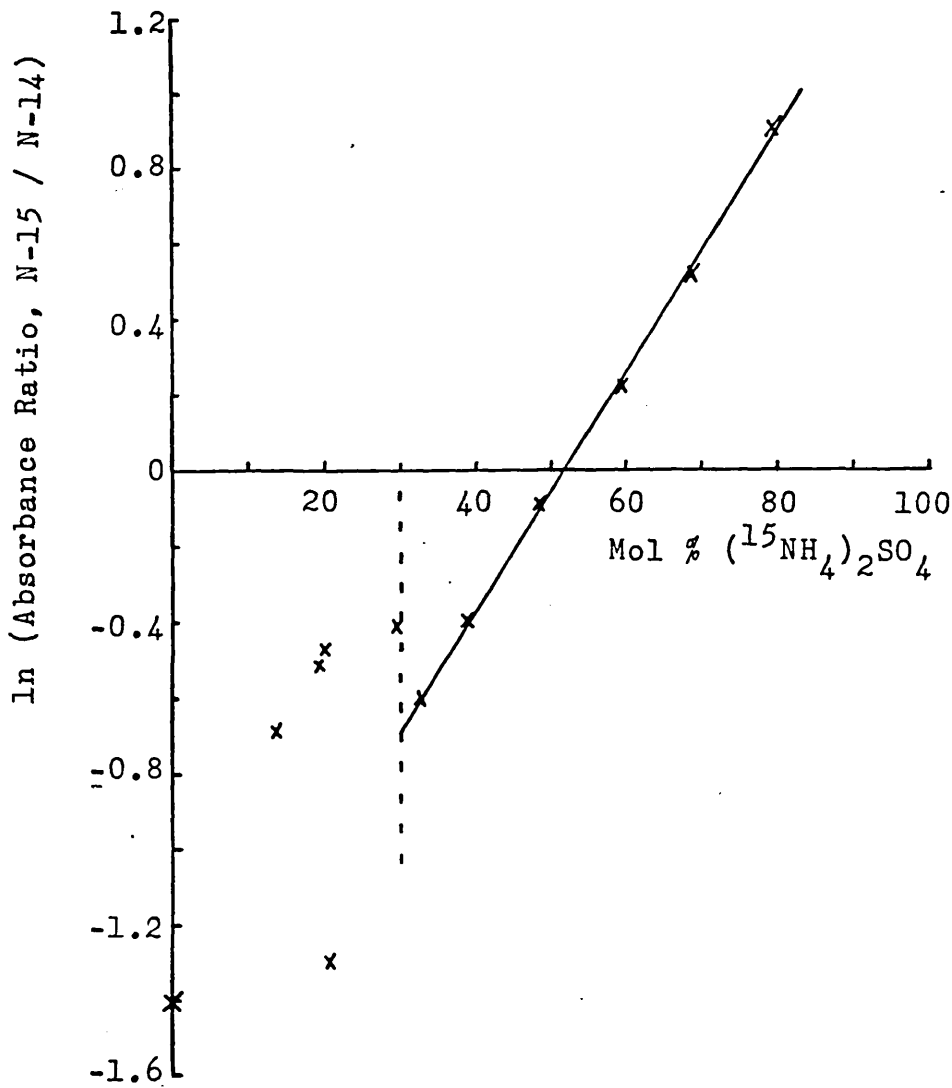
Ratio of the absorbance bands for $^{15}NH_3$ / NH_3 :

$$\frac{\text{Abs.}(^{15}NH_3)}{\text{Abs.}(NH_3)} = \frac{\exp(-x_2)}{\exp(-x_1)}$$

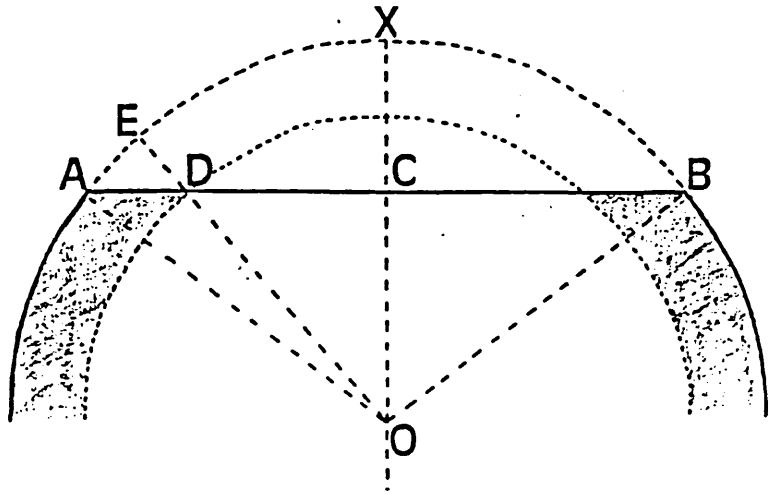
$$= \exp(-x_2 + x_1)$$

Therefore, an exponential graph should also be obtained of the absorbance ratio versus the molecular concentration for a mixture of the two gases.

FIGURE A2.1 : Logarithm Graph of Absorbance Ratio (N-15 / N-14) to the Mol % $(^{15}NH_4)_2SO_4$.



APPENDIX 3.



AB = 2AC = Width of tapered section

DE = Case depth of treated roller

AD = Length of nitrided zone along the line scan

OA = Radius of roller (= OB = OE = OX = 3.175 mm)

To calculate AD :

$$(OC) = (OB) - (BC)$$

$$OD = OE - DE$$

$$(CD) = (OD) - (OC)$$

$$AD = AC - CD$$

$$AD = AC - (OE-DE) - (OB) + (BC)$$

For example, for Sample IA :

OE = OB = 3.175 mm

DE = 0.21 mm

AC = BC = 1.5 mm

therefore, AD = 0.58 mm

For IB, AD = 0.76 mm

IC, AD = 0.64 mm

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