MEASUREMENTS OF ION-INDUCED CHARACTERISTIC X-RAY YIELDS AND SELECTED ANALYTICAL APPLICATIONS

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A thesis presented to the University of Surrey in partial fulfilment for the award of the degree of Doctor of Philosophy.

March 1980
Comparisons between the thin and thick target methods of measuring proton-induced K X-ray production cross-sections have been made. It was concluded that the thin target technique is superior. Cross-sections for the production of K X-rays from thin targets of selected elements in the range Z = 22-34 have been measured with absolute uncertainties of $\pm 5\%$ for the case of irradiation with light ions ($Z \leq 2$) of energy 1-3 MeV. K shell ionization cross-sections have been deduced from these measurements and a modification of the Semi-Classical Approximation fitted to the resulting data. Fitted values for the ionization cross-sections for protons have been generated for all targets with $Z = 18-50$; uncertainties being as low as $\pm 5\%$ in the region $Z = 22-34$. The value of these results for use in particle-induced X-ray emission (PIXE) analysis and in comparisons between the various theories of inner shell ionization is discussed.

A detailed description is given of the apparatus and experimental techniques; especially the methods of measuring ion beam fluence, X-ray detection efficiency and target mass thickness. For each of these cases, significant advances over the more commonly used methods are reported.

The principles, history and present status of PIXE analysis are outlined and comparison made with other methods of producing characteristic X-rays. The technique has been applied to the study of time-resolved deposits of air particulate pollution. Details are given of the air sampling technique and the application of PIXE and electron microprobe X-ray analysis to the characterization of these samples. Analyses of a widely varying selection of other types of sample were performed and conclusions drawn on the suitability of the technique for these cases.

Finally, conclusions are drawn on the achievements of the work and suggestions for future studies are given.
ACKNOWLEDGEMENTS

This thesis has been the result of the first collaboration between the University of Surrey, England and the Central Bureau for Nuclear Measurements (CBNM), Belgium and was financed by the Commission of the European Communities. I would like to express my great appreciation to the members of both institutes who offered me invaluable assistance. In particular, I would like to thank my academic supervisor Walter B. Gilboy for his guidance, objectivity and enthusiasm; and my collaborators at the CBNM, Irving V. Mitchell and Hans L. Eschbach for their instruction and continued support throughout this work. I have received much help from other members of the Analytical Science Group especially Willem D. Dobma, Frans Verheyen, Edgard Louwerix, Pieter Rietveld and Rudolph Werz. Walter Bambynek and his co-workers in the Radionuclides Group have been invaluable, both in the provision of calibrated radioactive sources and for many useful discussions. The Van de Graaff Group have always been most helpful, especially in driving the machine to its limits for me. Cesare Cervini, Guido Ehrenfreund and Richard Shelley have frequently helped me sort out computing tangles. I am very grateful to the members of the Workshop for precision engineering and for understanding what I meant to draw. The work of the Drawing Office, and in particular that of Mrs. Paula Daems, has been of the highest quality. Mrs. Nicole Verboomen has typed this thesis with outstanding accuracy and always in good spirit.

I would like to thank Erik Laegsgaard of the University of Aarhus, Denmark, for helpful discussions on theoretical and experimental aspects of the cross-section work.

My interest in physics has largely derived from the lucid lessons given by my first physics teacher, Fr. Bernard V. Lagrue.

Last, but not least, I would like to express my deepest gratitude to my parents for their many years of encouragement, foresight and faith in me; and also to my brother Paul for his patient support.
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The University of Surrey has now been interested in the study of air particulate pollution for almost a decade. The early work was centred around the taking of daily samples on filter papers which were subsequently analysed using instrumental neutron activation analysis (Hasan et al. 1972). It was found that there was an almost random variation in the elemental levels from day to day, with the changes often being of an order of magnitude. No clear systematic trends were observed over the few weeks which were sampled intensively or over the five years for which spot results were taken. It was therefore concluded that, in order to study these changes in pollution levels, it was necessary to have a method for analysing the particulate content of the atmosphere over periods short compared to the causes of the changes. The two major factors affecting the environment are undoubtedly the weather and human activities such as industrial production, traffic, domestic heating, etc. These parameters often change in a matter of hours. Therefore, in 1976, it was decided to construct a system which produces time-resolved particulate deposits so that the pollution levels could be measured with a temporal resolution of two hours. For such small sampling times, only a small amount of deposit (typically less than 10 μg) is produced and the amounts of the elements of interest are often as low as 1 ng. The most suitable means of analysing such deposits was found by Mason (1978) to be that of proton-induced X-ray emission (PIXE). With this experimental arrangement, a number of elements with atomic number greater than 24 were successfully analysed.

PIXE analysis is based on the irradiation of samples with protons from a Van de Graaff accelerator. The protons, by the Coulomb interaction, occasionally cause inner shell electron vacancies in the atoms present in the sample. The energies of the X-rays, emitted when the vacancies are filled by electrons from higher atomic levels, are characteristic of the elements from which they originate and the number of X-rays of a certain energy is proportional to the number of atoms of the corresponding element in the sample. The availability of high resolution lithium-drifted silicon (Si(Li)) detectors, fitted with very thin entrance windows, enables most elements with Z greater than 9 to be sensitively determined simultaneously and quantitatively in amounts as low as 1 ng. Ideally, samples should be no thicker than 1 mg cm$^{-2}$ because
of projectile energy and X-ray intensity loss effects in thicker samples.

In 1977, the present author was given the opportunity to use the facilities of the Central Bureau for Nuclear Measurements (CBNM) which is the nuclear standards laboratory of the Joint Research Centre of the European Communities (EURATOM). The laboratory was interested in developing ion-induced X-ray analysis as a complement to other existing ion beam analytical techniques. It was decided to use the special equipment and expertise available to investigate some of the fundamental properties of light-ion-induced X-ray emission; especially production cross-sections for this process. The purchase of a high resolution Si(Li) photon detector enabled analysis of elements with atomic numbers as low as 11. Thus many of the lower Z elements of interest in air particulate deposits that could not be analysed with the poorer resolution Ge(Li) detector system used by Mason (1978) were able to be analysed. This led to the setting-up of an air sampling system at the CBNM.

The organisation and contents of the present work will now be outlined. Firstly, a note on terminology. Light-ion-induced X-ray emission is more frequently referred to in the literature as particle-induced X-ray emission. For this reason, the abbreviation PIXE is usually used. Although it is felt that 'light-ions' is a better description of these projectiles than 'particles', the term PIXE will generally be used. Similarly, elastic nuclear backscattering is often referred to as Rutherford backscattering which yields the abbreviation RBS. Strictly speaking this technique should no longer be called Rutherford backscattering as deviations from the Rutherford scattering law are now known to exist. However, for historical and practical reasons, it is convenient to continue to refer to it as the RBS technique. Where references are made, the author's name followed by the year of publication (in brackets) is given. If there is more than one author, then the first author is followed by et al. regardless of the number of co-authors. Figures and tables are numbered successively for a particular sub-section. Thus Fig. 4.4.5.3.b is the second figure of section 4.4.5.3. This should permit easier location of figures than if a continuous numbering system had been used.

In Chapter 2, the early history and present status of PIXE analysis are discussed. In particular, the wide variety of applications published are outlined and comparisons made with other modes of excitation. The theoretical basis for analysis by PIXE is presented in Chapter 3. The reasons for concentrating on one particular PIXE theory are given in
the context of a search for the optimum method of fitting experimentally derived cross-sections. The role of the various background radiations, produced at different projectile energies, in limiting the usefulness of PIXE analysis is quantitatively assessed and illustrated with an example. In Chapter 4, the apparatus and experimental techniques utilised in the PIXE and RBS measurements are described in detail and special attention paid to sources of uncertainty. Of particular importance are the methods of measuring ion beam fluence, X-ray detection efficiency and target mass thickness. In each of these cases, significant advances over the more commonly used methods are reported. The thin and thick target methods of measuring proton-induced K shell ionization cross-sections are compared in Chapter 5. As a result of this comparison, the cross-sections for a variety of elements in the atomic number range \( Z = 22-34 \) for protons, deuterons and alpha-particles were accurately measured using the thin target technique. By fitting these results with a modification of the corrected SCA theory given in Chapter 3, reliable cross-sections over a wide range of \( Z \) were obtained. In addition, some evidence for simultaneous K and L shell ionization is mentioned. In Chapter 6, selected applications of the present PIXE analysis system are discussed. Most effort was concentrated on the analysis of time-resolved air particulate deposits and the problems of quantitative air sampling. A scanning electron microscope, fitted with a Si(Li) detector, was also utilised in order to obtain a fuller understanding of the nature of these deposits. Some practical difficulties in analysing other types of sample are highlighted. Finally, conclusions and suggestions for further work are given in Chapter 7.
CHAPTER 2

THE EARLY HISTORY AND PRESENT STATUS OF PIXE ANALYSIS

2.1 Early history

PIXE analysis is the latest in a long line of techniques based on the detection of X-rays. X-rays were discovered in 1895 by Röntgen who, within a year, applied them in medical and industrial radiography. In fact, the history of X-rays has tended to be one of practical applications rapidly following new discoveries or innovations. Valković (1978), in his review of elemental analysis by X-ray tube, radioactive source and charged-particle excited X-rays, has outlined the early development of X-ray spectrometry. It may be summarised as follows:

1895 W.C. Röntgen Discovery of X-rays
1896 A.W. Wright First photographic paper 'rontgenogram'
1896 J. Perrin X-ray intensity measurement with an air ionization chamber
1909-1911 C.G. Barkla Discovery of absorption edges and emission line series
1912 M. von Laue et al. Diffraction of X-rays by crystals
1912 J. Chadwick Detection of characteristic X-rays induced by alpha-particles from a radioactive source
1913 W.L. Bragg and W.H. Bragg Bragg X-ray spectrometer
1913 H.G.J. Moseley Relationship between the wavelength of X-ray lines and atomic number established
1913 N. Bohr Model of the atom
1913 W.D. Coolidge Hot-filament high vacuum X-ray tube
1913-1923 W.D. Coolidge Measurement of X-ray spectra of the chemical elements
1922 A. Hadding Application of X-ray spectra to chemical analysis of minerals
1923 G. von Hevesy Quantitative analysis by secondary excitation of X-ray spectra
1928 R.G. Cocker and H. Schreiber Applications of X-ray fluorescence spectrometry
1948 H. Friedman and L.S. Birks X-ray emission spectrometer

In 1958 Merzbacher and Lewis presented a comprehensive theoretical treatment of inner shell ionization by protons and alpha-particles in their review of the field. Further details of this and the subsequent
theoretical and experimental developments in the study of ionization cross-sections are given in section 3.1. Khan et al. (1966) appear to be the first group to apply ion-induced X-ray emission to the analysis of the thickness of surface layers. In this pioneering experiment they used 100 keV protons to excite characteristic X-rays from thin aluminium layers. By detecting the X-rays with a gas proportional counter they were able to relate the mass-thickness of the layers to the measured yields. Unfortunately this technique was not readily applicable to multi-elemental analysis because of the poor resolution of gas proportional counters.

Development of the high resolution Si(Li) detectors in the late 1960's revived the interest in the detection of characteristic X-rays and the possible analytical applications. McKenzie (1978) has traced the historical development of semiconductor radiation detectors. The first high resolution \( \gamma \)-ray spectrum obtained with a Ge(Li) detector was reported in 1962. The further development of these and Si(Li) detectors then took some time due to problems of materials purity and also of surface contamination of the crystals. Although the basic limitation on the energy resolution is the statistical fluctuation in the number of ion pairs created for a given photon energy, the effects of the preamplifier noise dominated the width of the photon peaks. The first major step in improving energy resolution came with the development of low noise field-effect transistors (FET's) for the first stage of the preamplifier. Another significant improvement was the introduction of the light-emitting diode (LED) to provide low-frequency feedback with the preamplifier. Low temperature operation of the detector is required in order to reduce the thermal leakage noise. In order to maintain the detector at low temperature and also to protect its surface from contamination by condensation, the detectors are operated inside a vacuum cryostat and a thin beryllium窗 is provided to allow X-rays to reach the detector with the minimum of absorption. The superior resolution obtainable with Si(Li) detectors is compared with other common photon detectors in section 4.4.

High resolution Si(Li) detectors were made commercially available at the end of the 1960's. It was rapidly realised by Johansson et al. (1970) that a combination of X-ray excitation by protons and detection with a Si(Li) detector constitutes a powerful multi-elemental analytical technique of high sensitivity. They showed that it was capable of detecting up to fifteen elements simultaneously at the \( \times 10^{-12} \) g level and that only very small amounts of sample were necessary. There then
followed a rapid expansion in the use of ion-induced X-ray emission analysis with Johansson et al. (1976) being able to quote almost two hundred publications in the field up to January 1976. Similar advances in X-ray tube and electron-beam (in the electron microscope) excited X-ray analysis followed from the innovations in the Si(Li) detector. Recent progress in the field of PIXE analysis will now be discussed.

2.2 Present status

Analytical applications of PIXE have been reviewed up to the year 1976 in an extensive article by Johansson et al. (1976). This provides a good introduction to the field and will be cited frequently throughout this thesis. In order to place the present work in context, the literature for the period 1976-1979 inclusive was also scanned for both theoretical and applications aspects of ion-induced X-ray emission. Some fields not covered by the review of Johansson et al. in older articles were also investigated. Many of these papers are discussed in a comprehensive review of PIXE written in collaboration with I.V. Mitchell and E. De Poli (Mitchell et al. 1979). As well as providing about two hundred references on the subject, many useful tabulations are given. These include ionization cross-sections for the K and L shells for protons of 1, 2 and 3 MeV over the complete periodic table together with the fluorescence yields and the resulting X-ray production cross-sections. Also included are the X-ray yields and Si(Li) detector count-rates to be expected for 'standard' conditions. This allows easy scaling to counting arrangements in other laboratories and is thus very useful for designing PIXE analysis experiments although these calculated cross-sections are not of sufficient accuracy to be of use in absolute quantitative PIXE analysis. Rather than reproducing these data and references, the principle trends in PIXE analysis will be outlined and further details may be found in the review or elsewhere in the present work.

The principles behind the production of characteristic X-rays by light ion bombardment, together with the methods of relating the observed X-ray yields to the amounts of the elements in the samples, are discussed in Chapter 3. The experimental system presently used is described in detail in Chapter 4. Only experimental systems that differ significantly from that of the present work will now be discussed.
2.2.1 Irradiation facilities

Details of the present vacuum irradiation facility are given in Chapter 4. Both the target and the detection system are in vacuo. This minimises projectile energy and photon intensity loss effects and allows accurate ion beam fluence measurements. The possibility that the specimen to be analysed by PIXE may lose volatile elements before and during analysis should be borne in mind. These losses may arise through a number of causes. Normally, the sample must be maintained under vacuum conditions during projectile bombardment unless a special non-vacuum facility, as described below, is used. This means that volatile components and gases contained in the specimen will be removed to a large extent during initial vacuum pump-down. This is especially true for some organic materials and for compounds having high vapour pressures where evaporation and decomposition may take place in a vacuum environment. Hence, the ability to detect certain elements may depend very much on the chemical form they have in the original material.

Non-vacuum irradiation. The main incentive for non-vacuum irradiation studies is to examine liquid and biological materials and samples too large to fit into a vacuum chamber. These normally contain large amounts of water and volatile substances and often prove to be electrically insulating. In a non-vacuum facility, the projectile beam produced by the accelerator usually exits the vacuum system via a thin foil vacuum-window (which can, for example, be of mylar, nickel or beryllium) and the sample together with the X-ray detection system, is situated in an air or helium environment. The use of the gaseous atmosphere reduces material losses and the charging up of the targets. Target manipulation is also made much easier. There are two main advantages in the use of helium as the target environment. Firstly, there is no strong argon K X-ray line in pure helium which is always present in the case of air and secondly the stopping cross-section for the projectile beam in helium is about four times lower than in air. Using an external beam there are normally no special problems in placing the detector near the sample although care must be taken against contamination of the detector window by wet or dirty samples. The main problem in this method is in being able to monitor ion beam fluence accurately. Deconninck (1972), Seaman et al. (1975), Katsanos et al. (1976) and Modjtahed-Zadeh et al. (1975) have all investigated this problem but it appears that much scope remains for experimental work in this area.
Microprobes. The properties of many materials are often as dependent on the spatial distribution as on the concentrations of the component elements present in the matrix. For such measurements there has been considerable interest in recent years in producing spatially well defined particle microbeams. There are a number of similarities between the particle or nuclear microprobe and the electron microprobe, an instrument which has existed for some years as standard equipment in research laboratories. Among the various options, the latter can be used for elemental analysis by detection of the X-rays induced by the electron beam. Electron probe diameters from 0.1 - 0.5 μm are easily attainable. However, because of the strong projectile bremsstrahlung background caused by electrons, the minimum detection limit is about 100 - 1000 ppm in practice. In contrast, a proton beam used as a nuclear microprobe should be capable of routinely achieving 1000 times better results due to its much lower primary bremsstrahlung. The major difficulty is in producing small particle beam diameters. This may be achieved by collimating the particle beam to small dimensions as has been reported by Pierce et al. (1966), Mak et al. (1966) and Horowitz et al. (1975) but always at the expense of a strong reduction in the beam intensity. Alternatively, the beam may be focused either magnetically, which seems to be the most widespread technique at present, or electrostatically. Magnetically focussed proton beam diameters as small as 2 μm have been reported by Cookson et al. (1972). Two novel methods of electrostatic focussing have been reported recently by Augustyniak et al. (1978) and Krejcik et al. (1980) giving beam diameters of about 15 μm and 40 μm respectively. Further details of the present state of the art in microbeam studies can be found in a recent review by Cookson (1979).

2.2.2 Practical target considerations

Elemental losses. When the projectile beam irradiates the target material, energy is deposited in the sample as the projectile slows down in the material and this may cause losses of elements. Legge et al. (1980) have recently reported rapid losses of some elements, such as chlorine, in biological matrices during irradiation in a proton microprobe system. This effect has also been observed for chlorine in dust filters in the present work (Chapter 6). Legge et al. suggest that much of this loss is caused through heating of the specimen by the beam rather than effects directly due to ionization. For example, if
all the energy of a 10 nA beam of 2 MeV protons was converted to heat, this would lead to a deposition of $10^{-2}$ Js m$^{-2}$ in the target. This is equivalent to about 2 Js m$^{-1}$ cm$^{-2}$ when the diameter (1 mm) of the beam is taken into consideration. Consequently, a rise in the temperature of the target can be expected which could be considerable if the target is composed of a material of poor heat conductance, as is often the case in biological specimens, and the loss of volatiles will be enhanced. Valković et al. (1975), Ishii et al. (1975a) and Alexander et al. (1974) all describe experiments where losses of volatiles have occurred, notably bromine. However, generally speaking, apart from biological and organic type materials the effect does not appear to be a large one. Campbell et al. (1974,1975b) and Johansson et al. (1975) found no evidence of volatile elemental losses from their samples.

**Sample preparation.** For the optimum operating conditions, samples of about 20 $\mu$g cm$^{-2}$ should be used when trace elements are to be measured at the 0.1 to 1 ppm level. If thicker specimens are used, in which the projectiles lose a significant fraction of their energy, it should still be possible to determine concentrations in the 1 ppm range although perhaps not for the lightest elements due to the increased bremsstrahlung background below 5 keV. As an illustration, 3 MeV protons impinging on a sample consisting mainly of carbon, will lose about 15% of their initial energy in 4 mg cm$^{-2}$ of the target and will be stopped completely in about 16 mg cm$^{-2}$.

For many types of sample, a backing substrate is often necessary. For these, high mechanical strength, good electrical and thermal conductivity, high chemical purity, resistance to high beam intensities and non-reactivity with the target material itself are amongst the requirements. The background continuum produced by the substrate should be as low as possible and this favours thin backings composed of low Z elements which will produce less proton and secondary-electron bremsstrahlung. If substrates of carbon, beryllium, boron or plastic-like materials can be used, an important advantage will be that very few characteristic X-rays due to the substrate will be detected as most of these will be absorbed by the beryllium detector window and intervening absorbers. In general this will considerably reduce count-rate and pile-up problems. A good choice of substrate thickness is less than 100 $\mu$g cm$^{-2}$. Carbon foils offer high beam tolerance and mechanical strength although their purity and the beam-induced shrinkage effects (see section 4.3.3) must be controlled. Johansson et al. (1972) and Herman et al. (1973) have
both reported using 20 - 40 μg cm$^{-2}$ carbon foils as substrates in their PIXE studies. Plastic foils such as Formvar, Kapton, Mylar, VYNS, polystyrene and Hostaphane have all been successfully used as thin backing materials as has been discussed by Alexander et al. (1974). The electrical and thermal insulation problems in using plastics are often circumvented by metallising the substrate on the beam side. For example, Alexander et al. evaporated a 100 μg cm$^{-2}$ aluminium coating onto 100 - 150 μg cm$^{-2}$ Formvar to overcome the heat dissipation problem. Details of ion beam tolerance for a variety of plastic substrates has been given by Herman et al. (1973). Bearse et al. (1974) have also investigated a number of possible candidates for substrate materials and found that, for their purposes, 8 μm pore size Nuclepore filter material was the most suitable.

For biological tissues and organic material the problems of sample preparation are often severe and usually require complicated procedures. For example, Jolly et al. (1971) used a nebulizer and sonicated biological material with good results. Campbell et al. (1977) reported on the use of a freezing microtome to prepare slices of organic material of about 10 μm in thickness. Preconcentration may be used as a technique to gain orders of magnitude improvements in detection limits. In situations where extreme low detection limits are not required, it may be advantageous to tolerate the increased bremsstrahlung produced by thicker backings. Descriptions of other techniques may be found in the recent review (Mitchell et al. 1979).

In principle, it is always best if the specimen is already in a suitable form for analysis and where no further treatment need be made on it. This has an added advantage in so far as cross-contamination possibilities are much reduced. A practical example of this occurs in air particulate studies where the aerosol filter on which the dust is collected is in a directly suitable form for irradiation as is described in section 2.2.4.1. For non-biological samples such as metals, compounds, etc., physical deposition techniques such as resistive and electron beam evaporation, sputtering, CVD (chemical vapour deposition), anodic oxidation and electro-deposition have all been applied to provide thin uniform layers on both thin and thick substrates (Mitchell et al. 1979).

**Accuracy and precision.** Campbell et al. (1974) have determined the accuracy of PIXE relative to atomic absorption analysis and various laboratories have recently contributed to two inter-laboratory comparison exercises (Camp et al. 1975, Lear et al. 1976) using common distributed
samples. The results of all these measurements seem to indicate that an accuracy of about $\pm 10\%$ is achievable. Akselsson et al. (1978) have recently confirmed this. The accuracy of PIXE analysis determined by an absolute approach with X-ray production cross-section data and other fundamental parameters is not in such a happy state and typically accuracies of only about $\pm 20\%$ can at present be expected in the analysis of the targets with $Z = 22-34$ and for elements where the data are less well known correspondingly poorer accuracies result. However, the cross-section results given in Chapter 5 will considerably improve the situation.

In the case of 'precision' which is a measure of the reproducibility of the analysis, Valković et al. (1975) analysed 150 blood serum samples doped with internal standards. They found for Fe, Cu, and Zn a precision at the 1 ppm level of about $\pm (5 - 10)\%$. Values of precision are generally found to be worse than expected from counting statistics alone. This may be ascribed to several causes such as target preparation procedures giving non-uniform targets, contamination of the samples, non-homogeneous ion beams, small changes in target backing characteristics, beam-induced effects, instrument drift (such as stability of ion beam energy) and miscellaneous operator errors. It is clear from the literature that much work remains to be done in the field of PIXE analysis to improve the precision and accuracy of the measurements and that sample preparation is one of the largest influences on these factors. The parameters that enter into improving precision once the target is prepared are discussed in section 3.1.5. In general, increasing the ion beam current is the most effective but there are often target damage limitations to this.

2.2.3 Comparisons with other modes of excitation

**Alpha-particles.** The detection limits obtained with alpha-particles of $4 - 8$ MeV energy do not differ considerably from those obtained using proton beams of $1 - 2$ MeV. The higher nuclear charge of the helium ion generally gives rise to larger X-ray production cross-sections but this improvement is approximately balanced by larger backgrounds. However, at the higher alpha-particle energies (18 MeV), which have been used by Cahill et al. (1974), the detection limits are poorer due to additional high $\gamma$-ray backgrounds. One of the biggest disadvantages of alpha-particles is that of target heating and deterioration. This arises from the fact that to produce approximately the same X-ray yield for a particular element as is derived from a 2 MeV proton beam, an 8 MeV
alpha beam must be used (i.e. approximately equal velocity particles) but the stopping cross-section for this energy alpha-particle beam is about four times greater than for a 2 MeV proton beam. This means that more energy is deposited within a given depth in the target by the alpha-particles than by protons and thus beam damage due to heating effects is that much greater. Unfortunately, at the present time, a systematic comparison has not been made between these two modes of excitation and consequently it is difficult to draw firm conclusions as to the relative merits of either beam type. Both these particles and deuterons were compared during the present study at an energy of 2.5 MeV for the case of thick carbon backings. As will be discussed in section 5.5, the protons were found to be the most suitable.

Heavy ions. Heavy-ion-induced X-ray spectra are in general more complex than the equivalent light-ion spectra. Although the heavy-ion-induced X-ray production cross-sections are much higher for a given velocity, the spectral complexity and larger bremsstrahlung backgrounds act against the use of heavy-ion PIXE analysis and outweigh many of the advantages of larger cross-sections. In addition, these cross-sections strongly depend on the specific atoms involved in the collision process so that the relatively simple multi-elemental nature of PIXE, experienced with light-ion irradiation, is lost. On the other hand, since the mean range of these ions is small compared with light-ions, this technique may prove to be useful in the field of single-element surface layer analysis. Cairns et al. (1973) and Chemin et al. (1974) have shown that fractions of a monolayer may be detected in this way. Scharager et al. (1980) have recently used heavy-ion-induced X-ray emission to observe trace impurities in CdTe crystals where proton excitation would have given no useful information because of the high background signals due to the matrix elements.

Electrons. The cross-section for X-ray production using electrons in the 10 - 100 keV range is about the same as for MeV protons. Unfortunately, because of the small mass of the electron compared with the proton, the bremsstrahlung due to the primary electron beam is high, having values typically 3 - 4 orders of magnitude higher than that for protons. Hence, the limit of detection is relatively poor (about 1 part per thousand) thereby making the detection of trace elements impossible. However, using a Si(Li) X-ray detector in conjunction with an electron microscope presents excellent possibilities of detecting very small absolute quanti-
ties of the main constituents of a sample; $10^{-16}$ g detection is easily achievable because of the fine focussing of the electron beam and the thinness of the samples. Development of such a finely focussed high energy proton microprobe would provide strong competition to the electron microscope in the field of trace element analysis. At the present time this has not been successfully developed to the same level as electron focussing. Electron excitation using $\beta$-rays from radioactive sources has also been suggested (Johansson et al. 1976) as a powerful analytical tool and may find application in portable analysers. It is interesting to note that relativistic electrons of up to 60 MeV in energy have also been used for X-ray analysis (Hoffmann 1978).

Photons. Excitation with X-rays, the X-ray fluorescence technique, is the main competitor to PIXE for energy dispersive X-ray analysis. It is difficult to obtain an objective view of the relative merits of the two methods since the published comparisons from different groups, and the conclusions they derive from their data, are often in conflict with each other. Thus, Cooper (1973) using X-ray fluorescence believes this is the favoured technique whilst Johansson et al. (1976) using PIXE state that 2 MeV protons provide a better detection limit than X-ray fluorescence; concluding that the minimum detection limit using X-ray fluorescence is about 1-10 ppm whereas 2 MeV protons are capable of giving limits an order of magnitude lower. Moreover, since the proton beam can be focused to smaller dimensions than an X-ray beam, smaller absolute quantities of materials can be analysed. Thus $10^{-12}$ g of element is detectable by PIXE whereas X-ray fluorescence should be able to detect about $10^{-8}$ g. With microbeams of protons, $10^{-14}$ g should be attainable. Where analyses at the ppm level are not required, X-ray fluorescence is a very attractive alternative to PIXE, combining rapid analysis with economic and reliable equipment and the more truly non-destructive nature of X-ray beams. In conclusion, in any comparison of the relative advantages of PIXE and X-ray fluorescence, detailed account must be taken of how the experimental data was obtained, how the experimental conditions were optimised and the type of sample that was analysed.

### 2.2.4 Applications

The PIXE analytical method has been applied to a wide variety of specimens in such areas as pollution monitoring, metals analysis, biological, forensic, geological and archeological analyses, surface ana-
analysis of materials, etc. Whilst the ultimate aim in most of these studies is to obtain trace element information, the specimens themselves and hence the specific application to which PIXE is applied may be divided broadly into two types. Namely thin samples and thick samples where the terms thick and thin are defined in terms of the range of the probing projectile beam. Thin samples are generally less than about $1 \text{ mg cm}^{-2}$ and thick samples greater than $8 \text{ mg cm}^{-2}$ for a 2 MeV proton beam incident on carbonaceous targets.

2.2.4.1 Thin samples

**Aerosol studies.** In recent years, many governments and a number of international agencies have been increasingly concerned by the gradual erosion of the quality of the environment by all manner of industrial and domestic pollutants. Environmental quality investigations have indicated that due to the smallness of the samples generally available, there is a need for highly sensitive multi-elemental procedures capable of ready application to air, water, soil and biological samples. In particular, concern about the harmful effects of air pollution has stimulated an interest in the origin, conversion and eventual dispersal of particulate matter in the environment. The PIXE technique has shown itself well suited to precisely this type of broad range analysis, covering almost the entire spectrum of elements whilst requiring only micrograms of total sample. Studies of air-borne contamination using PIXE and related techniques have been undertaken by several laboratories around the world and they clearly demonstrate its value in environmental science. In at least two laboratories in the U.S.A.; one at Davis, California and the other based at Tallahasee, Florida (e.g. Nelson 1978), the accelerators providing the ion beams are almost totally dedicated to PIXE studies of this kind. Cahill et al. (1975, 1976, 1978), at Davis, have developed a fully automated PIXE system which is fed with about 700 samples a day from an extensive network of aerosol monitoring stations throughout California. The cost per sample analysis is given as 5 dollars.

The air particulate samples are usually collected on thin filter materials which are specially chosen to withstand the ion beam effects and to have low trace element contents. Thus, apart from the actual air sampling, no sample preparation is necessary. The sampling is so designed that the deposits satisfy the $1 \text{ mg cm}^{-2}$ thin target criterion, i.e. there is negligible projectile energy loss and X-ray attenuation
within the deposit. Hence PIXE analysis is well suited to this type of aerosol study. Results from the present investigations are given in section 6.1 where the wider context of air particulate studies is also discussed.

**Biological studies.** Trace elements have an important function in biological systems and the various concentrations found often play an important part in many diseases. For example, many disorders arise in animals as a consequence of trace element deficiencies or excesses. Lear et al. (1976) investigated the cadmium concentration in kidneys and found a correlation with age and the state of disease. Sample preparation is important in these cases as the trace elements are often present in concentrations of around 1 ppm. The biological material, whether in the form of tissue or liquid, must be sampled and converted into a form suitable for PIXE irradiations without any loss of the trace elements or introduction of contaminations by the preparative techniques. Campbell et al. (1975b), Mangelson et al. (1977), and Colaulti et al. (1976) amongst many others have all used different preparative techniques to provide thin targets. The results of a great number of analyses of many different biological and medical samples are given in these papers. Kubo (1974) has investigated the reproducibility of trace element concentration analyses in biological tissue sections and reports precisions of about ±20%. Bâdică et al. (1978) have made a study of the analysis of small concentrations of scandium and chromium found in lyophilised mouse marrow. Biological body fluid samples such as blood and saliva may be prepared by allowing a drop to dry on a thin carbon or plastic support. Valković (1977) and Boro et al. (1975) have investigated such samples. Dyson et al. (1978) have analysed human blood and liver tissue samples for their copper, zinc and iron contents and have found, for example, a diminution of iron in the liver in the case of alcoholic cirrhosis associated with clinical anaemia. Lecomte et al. (1978) report a totally automatic PIXE system for on-line analysis of trace element concentrations in freeze dried blood serum samples. Boulle et al. (1979) have used PIXE in a trace element investigation of human blood samples from children in South West Africa where a higher than normal incidence of methemoglobinemia and anaemia occurs. Using sophisticated pattern recognition procedures they have established a correlation between geographical area of domicile and trace element composition of blood.
Due to the practical difficulties often associated with maintaining the integrity of organic matter under vacuum conditions, many PIXE experiments have been performed in non-vacuum systems as described in section 2.2.1. An interesting application of non-vacuum PIXE was launched by Meyer et al. (1978). Using millimetre beam spot sizes and helium and air environments, they have been able to identify different concentrations of trace elements in healthy and diseased regions of apples. Another example which illustrates the exciting possibilities of non-vacuum PIXE is due to Deconninck (1977). He describes PIXE studies of liquid drops held on the end of a pipette by surface tension effects and irradiated by an external proton beam. This technique removes the problems of solid target preparation but the experimental difficulties are not small.

The non-vacuum technique coupled with a focused microbeam has been used by numerous groups to extend the analytical capabilities of PIXE to the study of localised concentration variations over distances as small as 2-10 μm. This technique has been described by Cookson et al. (1976, 1979) mainly with respect to the proton microbeam facility developed at Harwell (U.K.) which has been used to analyse a variety of samples. Horowitz et al. (1976), using a pinhole aperture and a differentially pumped beam line, describe studies in which the arsenic and mercury distributions along the length of single strands of human hair from victims of poisoning were measured. Pinpointing the time of poisoning could be made by these means. The distributions of several abundant elements in frozen hydrated eye and kidney elements from rats were also investigated by these authors. It has been reported that PIXE surface analysis along the length of, for example, a strand of hair may not necessarily be representative of the concentrations in the bulk of the material. For this reason, Cookson et al. (1975) have made careful measurements of the variation of trace elements over the cross-sectional area of a single hair (~130 μm diameter) using a rectangular microbeam spot of 7 by 17 μm. Montenegro et al. (1979, 1980) have recently developed a correction factor which should be applied to the PIXE analysis of hair samples which are generally relatively thick.

Other applications. Raith et al. (1980) have investigated the detection limits for trace elements in thin targets in an external PIXE arrangement, and their dependence on the exit window material, for proton energies from 1.5 to 4 MeV. Hudson et al. (1980) report using PIXE with simultaneous PESA (proton elastic scattering analysis) to obtain additional trace element information, such as for beryllium, which is unobtain-
able by using PIXE alone. Lichens were used as a way of monitoring local air contamination by Hryniewicz et al. (1980). Analysis was effected by PIXE and NRA (nuclear reactions analysis). Vis et al. (1978) have recently used PIXE in combination with inelastic proton scattering to determine the elemental composition of thin glass fragment samples for forensic applications. Pape et al. (1972) have reported analyses of various mineral waters, beers and vintage wines for their trace element contents. As only small amounts of sample are required, the remainder of the liquid is available for other investigations.

2.2.4.2 Thick samples

It is often difficult to prepare PIXE samples in the form of a thin layer. In these cases thick samples of the specimens of interest may sometimes be used directly. This makes the sample preparation more simple as, for instance, a thick section of tissue, rock or bone may be mounted and irradiated directly, either in vacuum or in a non-vacuum facility. There are nevertheless several disadvantages inherent in using thick samples. Firstly, the trace element composition may not be uniformly distributed throughout the sample and since PIXE analysis probes the near-surface of the material, the results may not be representative of the bulk material composition. Secondly, enhanced deterioration of thick targets such as biological specimens may result because the probing beam is stopped in the target and therefore heat generation in the sample can have a serious effect. This can be avoided by using low beam currents but at the expense of loss of sensitivity and economy. Thirdly, quantitative analysis is more difficult to realise than in the case of thin targets because the energy of the incident projectiles decreases with increasing penetration of the target. In consequence, the X-ray yield also changes with depth and needs to be integrated over the entire projectile path. To achieve this integration a fore-knowledge of the major composition of the matrix in question is pre-supposed which may not always be the case in practice. Finally, absorption of X-rays on their outward path is more severe and must be accurately taken into account. Nevertheless, some of these problems can be overcome when internal standards (i.e. spiked specimens) or comparative standards are used.
Ahlberg et al. (1975) have analysed thick steel samples with the aid of selective X-ray absorption filters and report that concentrations as low as 40 ppm can be measured, which compares favourably with the thin sample case. Ahlberg et al. (1976) have studied the trace elements present in teeth samples at the 1-10 ppm level. PIXE has been used for the trace element analysis of thick solid state and semi-conductor samples by many workers amongst whom may be cited Gray et al. (1973), Demortier (1975) and Chemin et al. (1974). Cairns et al. (1975,1980) describe using PIXE for monitoring the near-surface composition of catalysts and in the design of new catalysts. Very recently, Cohen et al. (1980) reported on the application of PIXE to the measurement of thorium and uranium at the ppm level in thick ore samples, which has important practical implications in the mining industry. Trace element analyses by PIXE have been reported by Chen Jian-Xin et al. (1980) of precious archaeological sword specimens more than 2500 years old and by Tove et al. (1980) on equally priceless and unique antique violins. It is clear that for these applications the reliable and essentially non-destructive nature of the PIXE technique is of paramount importance. All manner of ore, coal and rock samples have been studied for their trace element contents and meteoritic and lunar samples have also been successfully treated in this way (Kugel et al. 1977).

Finally, a number of investigations have been made in an attempt to obtain depth information on trace element concentrations by PIXE analysis. Reuter et al. (1972) varied the beam energy and Pabst (1974) the beam to target orientation, Bahir et al. (1980) combined forward particle scattering with X-ray analysis in coincidence experiments to achieve simultaneous high depth and atomic number resolution. Ahlberg (1975) has obtained simple depth profile information by measuring the $K_p/K_a$ ratios of the characteristic X-rays. However, as is pointed out in section 5.4, the $K_p$ X-rays may be preferentially absorbed in some cases due to multiple ionization effects. This would yield misleading results. It may be concluded that, in general, the X-ray yield from PIXE experiments is not well suited to depth profiling and more work needs to be done in this field to achieve consistent results.

2.2.5 Conclusions

Since its inception about ten years ago, PIXE has been shown to be a powerful analytical method with most applications to surfaces and in particular to trace element concentrations. In this short space of time
it has demonstrated its versatility and usefulness by the diversity of applications to which it has been applied. The results obtained indicate that it is certainly competitive with other more classical analytical methods and that it may be, in addition, a very useful complementary technique when combined with other ion beam methods such as RBS and NRA. It is capable of multi-elemental analysis and more than 20 elements can often be determined simultaneously. The method is a very sensitive one having minimum detectable concentrations of about 0.1-1 ppm for thin targets. Moreover, because only very small samples of the order of a few millimetres diameter are necessary for an analysis, this corresponds to minimum detectable amounts of material of as low as $10^{-13}$ g. Using microbeam techniques, even smaller samples, of the order of tens of micrometres diameter, can be analysed without loss of sensitivity. For elements with atomic number above about 12 and using the appropriate K, L or M characteristic X-ray lines, the minimum detection limits do not vary by more than about a factor of 10; so that practically the whole periodic table can be covered in a single experimental run provided that peak overlap effects are absent.

In principle PIXE is a non-destructive technique as are the other complementary techniques of Rutherford backscattering and nuclear reaction analysis although, for biological and volatile organic materials, this is not entirely true in every case. It is a relatively fast analytical method needing short experimental times, typically of between 5-20 minutes per sample. With the aid of suitable computer programmes, X-ray spectra from routine specimens can be analysed and trace element contents obtained in an equally short time. Background effects in PIXE are in almost all cases lower than those for comparable X-ray techniques using electrons and photons as the exciting source.

One inherent disadvantage of X-ray methods including PIXE is that, for complicated spectra, interferences between K X-rays from light elements and L and M X-rays from heavier elements can occur. This is also true for overlaps between the $K_a$ and $K_p$ X-ray lines from neighbouring elements. Future improvements in the resolution obtainable from energy dispersive Si(Li) X-ray detectors would go some way to reducing these problems. Detecting the X-rays with a wavelength dispersive crystal spectrometer could be used to avoid interferences but at the expense of losing the rapid multi-elemental advantages of the Si(Li) detector. The best results are obtained by PIXE when thin samples less than about 1 mg cm$^{-2}$ are used. However, thick specimens can be investigated but the spectra produced are often more complicated and the resulting detection
limits are somewhat poorer than for thin targets. In general PIXE is not well suited to the depth-profiling of trace elements in a bulk matrix. If this information is desired it is fruitful to combine PIXE with RBS analysis. In addition, because of the small samples generally used in PIXE analysis, care must be taken to ensure that the sampled area is representative of the specimen under investigation.

Whilst it would appear that the need for a large and costly accelerator is an added disadvantage to the general application of the PIXE technique for trace element analysis, this is not necessarily the case. In fact, many more Van de Graaff accelerators of up to 3 MeV energy are steadily becoming available throughout the world as nuclear physicists go to higher energy machines. The smaller Van de Graaff accelerators are ideally suited to PIXE analysis work. It has been shown fairly conclusively (Johansson et al. 1976) that PIXE analysis, even with the use of an accelerator, is an economical proposition and certainly competitive with other more classical techniques such as atomic absorption, emission spectroscopy and X-ray fluorescence spectrometry. For certain applications to low Z analysis, alpha particles from radioactive sources may be used with economic advantage. In comparison with neutron activation analysis (NAA), PIXE costs only a fraction of NAA per sample analysed.

The most likely future advances in PIXE analysis are in improved sample preparation and the development of reliable non-vacuum and microbeam systems.
3.1 Ion-induced X-ray emission

When an energetic positive ion is incident on a target there is a relatively high probability (typically with a cross-section of hundreds of barns) of ejecting an electron from one of the bound inner levels of the target atom. When the resulting vacancy is filled, either an X-ray or an Auger electron, which is characteristic of that atom, is emitted. Detection of such X-rays is the basis of PIXE analysis. As with most analytical techniques, there is a background present which restricts the minimum detection limit of the method. Three aspects of the PIXE process will be considered here. They are the production of the electron vacancy, the subsequent emission of the characteristic X-ray and the photon background production process. The rôle that these parameters play in the choice of operating conditions will also be discussed.

3.1.1 Theories of the ion-induced ionization cross-section

Four basic models are widely used to predict the ionization of the target atom by light ions ($Z < 2$). They all make the assumption that the production of an inner shell vacancy occurs as a result of an interaction of the nucleus of the charged particle with the bound electron. The types of transition which occur to fill this vacancy are illustrated in Fig. 3.1.1.a. In general, transitions to the K shell were of prime interest here although L and M X-rays were utilised for the detection of heavy elements.

In the Plane Wave Born Approximation (PWBA), the incident and the inelastically scattered particles are described by plane waves with the interaction responsible for electron vacancy production being the Coulomb interaction between the bound electron and the incident particle. The initial and final states of the atom are thus described in terms of a transition from the electron's initial bound state to an unbound state described by a continuum wave function with the other electrons remaining in their initial states. Vacancy production due to excitation of the electron to unoccupied orbitals, rather than to the continuum, is negligible (Merzbacher et al. 1958). The PWBA is a high energy
Fig. 3.1.1a  a) Complete energy-level diagram and possible transitions up to the element \( Z = 92 \).

b) Energies of the characteristic K, L and M lines as a function of atomic number \( Z \).

(from Välcovic 1975)
approximation which is strictly only valid for the condition:

\[ \frac{Z_1 Z_2 e^2}{\hbar v} \ll 1 \]  \hspace{2cm} (3.1.1.1)

where \( Z_1 \) is the projectile nuclear charge, \( Z_2 \) the target nuclear charge and \( v \) the relative velocity (Mott et al. 1965). Provided that the target atom is not too small, the condition reduces to \( (E_p/U_K) > 24 \) for proton \( K \) shell ionization where \( U_K \) is the \( K \) shell binding energy and \( E_p \) the proton energy (Garcia et al. 1973). Thus for sulphur \( (Z = 16) \) target atoms, the proton energy must be greater than 60 keV whilst for silver atoms \( (Z = 47) \) it must be greater than 610 keV for the PWBA to be valid. This condition was always satisfied in the present work.

Tables obtained by numerical integration have been published for calculating the PWBA cross-section (Khandelwal et al. 1969, Choi et al. 1973, Rice et al. 1977). These are based on approximations for the minimum and maximum momentum transfer of the projectile. However, recently calculations have been performed for proton impact (Benka et al. 1978) with the exact analytical expressions for the minimum and maximum momentum transfer.

The PWBA cross-section in the centre-of-mass system is given by the formula (Benka et al. 1978):

\[ \sigma_s = \sigma_{os} \theta_s^{-1} F_s \]  \hspace{2cm} (3.1.1.2)

where \( F_s = F_s (\eta_s, \theta_s) \).

Here \( \sigma_s \) is the cross-section for a transition from an initially filled atomic shell (or subshell) to a final state in which one of the \( s \) electrons has been removed from the atom \( (s = K, L_{II}, L_{III} \) or \( L_{IV} \) ). \( \sigma_{os} \) contains the major target atom features and is defined by:

\[ \sigma_{os} = 8\pi a_0^2 Z_e^{-4} \]  \hspace{2cm} (3.1.1.3)

Here \( a_0 \) is the Bohr radius of the hydrogen atom \( (a_0 = 0.5242 \times 10^{-8} \text{ cm}) \) and \( Z_e \) is the effective nuclear charge of the target atoms seen by an electron in an inner subshell \( s \) \( (Z_e = Z - 0.3) \). \( \theta_s \) and \( \eta_s \) are dimensionless quantities given by:

\[ \theta_s = n^2 \frac{U_s}{Z_s^2 R_\infty} \]  \hspace{2cm} (3.1.1.4)

where \( \theta_s \) measures the non-hydrogenic aspect of the \( s \) subshell ionization...
energy $U_s$, $R_\infty$ is the K-shell ionization energy of hydrogen (13.6 eV)
and $n = 1$ for the K shell and $n = 2$ for the L subshells. Also

$$\eta_s = \frac{m}{N} \frac{E}{Z_s^2 R_\infty}$$

(3.1.1.5)

where $E$ is the proton energy $E$, and $m$ and $M$ are the electron and proton
masses.

$F_s(\eta_s/\theta_s^2, \theta_s)$ is called the reduced universal cross-section and is
tabulated by Benka et al. for various values of $\eta_s/\theta_s^2$ and $\theta_s$. Using the
above relationships, PWBA values for the proton-induced K-shell ioniza-
tion cross-sections were calculated and compared to other theories and
to experimental data in Chapter 5.

In the impulse approximation of Garcia (Garcia 1970 a,b), known
as the Binary Encounter Approximation (BEA), the dominant interaction
producing the transition is considered to be a direct energy exchange
between the incident charged particle and the bound electron. The rôle
of the nucleus of the target atom is then simply that of establishing
the momentum distribution of the electron i.e. the electron is treated
as being free. This model has been modified to approximate the effects
of nuclear repulsion on the incident particle (Garcia 1970a). Garcia
et al. (1973) provide tabulations which allow the construction of ioni-
zation cross-section curves. For convenience in machine calculations,
Reuter et al. (1975) have made a log-log power series fit to the data
of Garcia et al. which deviates from the tabular data by less than 1 %.

Hansen (1973) has re-formulated the BEA and obtains significantly
different values especially for L shell ionization. One interesting
result is that the probability of simultaneous K and L shell ionization
by the same projectile in the same atom is calculated to be non-negligible.
It is found that even for simple projectiles such as protons incident on,
for example, titanium atoms this probability is about 10 %. The subse-
quent de-excitation produces some K X-rays with slightly enhanced
energy. The consequences of this for measuring ionization cross-sections,
together with experimental evidence for the phenomenon, are given in
Chapter 5. Also, in that chapter, the predictions of the BEA of Garcia
et al. (1973) are compared with experimental cross-sections. The pre-
dictions of this simple theory are found to be surprisingly accurate.

One advantage of the BEA is that all ionization cross-sections ($\sigma^V_s$)
may be plotted on a universal curve on a graph of $U_s^2 \sigma^V_s/Ze^2$ vs $Em/MU_s$
(see Fig. 3.1.1.b for proton results) where all parameters are as pre-
viously defined. Johansson et al. (1976) have used this scaling to fit
Fig. 3.1.1.b Comparison of the experimental data and BEA theory of GARCIA (1970b) [ionization cross-section $\sigma_K^V$ in cm² with incident proton energy $E$ and K shell binding energy $U_K$ in keV].
a universal curve for proton-induced K and L shell ionization cross-sections to a wide body of experimental data.

Both the simple PWBA and the BEA theories assume straight line trajectories for the projectile. However, at low ion velocities, the nuclear repulsion will deflect the projectile leading to a hyperbolic trajectory which will result in a larger distance of closest approach for a given impact parameter. In the Semi-Classical Approximation (SCA), Bang et al. (1959) treat the ion path classically and the electron-ion energy exchange is treated by first order perturbation theory. The resultant theoretical cross-sections are decreased, which gives a better fit to experimental data. Although computations are difficult with this theory, it does provide a good physical picture of the collision process and, in particular, directly predicts the impact parameter dependences of the cross-sections. Hansteen et al. (1975) have provided tabulations to facilitate SCA calculations of ionization cross-section curves. These results have been reduced to a simple expression by Lund et al. (1978).

As has already been mentioned, the BEA theory is open to universal scaling. The PWBA and SCA also provide for a limited scaling. However, second order corrections will now be considered and the possibilities of universal scaling are consequently more limited.

The Perturbed Stationary State (PSS) theories are essentially second order corrections to the first order theories. The theory of Basbas et al. (1973a) corrects the PWBA for the nuclear repulsion deflection effect on the ion. In addition, there is a correction due to the fact that, again at low velocities, the positive projectile spends a relatively long time within the orbital radius of the bound electron. This leads to an increase in the effective target nuclear charge with a corresponding increase in the electron binding energy and hence a decrease in ionization cross-section.

Recently, there have been experimental studies (Laegsgaard et al. 1978, Chemin et al. 1977) of the dependence of the ionization cross-section on the impact parameter of the projectile. In the data analysis it is assumed that the projectile may be localised as a classical particle and that the projectile is deflected by Rutherford elastic scattering at the target nucleus. These studies represent a finer probe of the ionization mechanism than do measurements of total cross-sections as they yield detailed information about the ionization probability as a function of the impact parameter. McGuire (1974) has derived the impact parameter dependence of K-shell ionization cross-sections in a BEA theory and provides tabulations of results. However, it should be pointed
out that, as also mentioned by McGuire in his conclusion, the theory appears to contradict the uncertainty principle as he uses a precise relationship between the position and velocity of the orbiting atomic electron. It would seem that the best approach from the point of view of the physical assumptions of the models is to use the SCA for both the impact parameter dependence and the second-order corrections. This theory will now be discussed in more detail with a view to utilising it for detailed analysis of the experimental ionization cross-section results.

Whilst the PWBA is normally considered to be a high energy approximation, the SCA is restricted to low 'adiabatic' velocities. It will be convenient to define an adiabatic parameter $\xi$ from the following relationships. At low velocities, projectile-target nucleus distances scale with the adiabatic distance ($r_{ad}$):

$$r_{ad} = \frac{h}{vU_s}$$  \hspace{1cm} (3.1.1.6)

where $h$ is Planck's constant divided by $2\pi$, $v$ is the projectile velocity and $U_s$ is the binding energy of the electron considered. Thus for K-shell ionization the adiabatic parameter is given by:

$$\xi = \frac{r_{ad}}{r_K}$$  \hspace{1cm} (3.1.1.7)

where $r_K$ is the K electron shell radius. The SCA holds for $\xi < 1$. For example, for Ti, the condition is satisfied for protons of less than 2.0 MeV. In contrast, the Ti limit for the PWBA is satisfied for protons of energy greater than 0.12 MeV.

Laegsgaard et al. (1978) have noted that in the low velocity (adiabatic) region, both the PWBA and SCA models lead to a simple expression for the cross-section:

$$\sigma_{ad} = \frac{2^{12\pi}}{45} R_\infty Z_i^2 \frac{r_K}{r_K^2} U_K^{-1} \xi^8$$  \hspace{1cm} (3.1.1.8)

At higher velocities, the PWBA cross-section may be approximated by (Brandt et al. 1973):

$$\sigma_{PWBA} = \sigma_{ad} (1 + 1.72 \xi^2)^{-4}$$  \hspace{1cm} (3.1.1.9)

For $\xi \leq 1$, this expression reproduces to within 1% the results obtained in the PWBA for $\theta = 0.80$ ($\theta$ was defined previously for the PWBA in equation 3.1.1.4). A similar representation of the SCA results (Hansteen et al. 1975) is found to be (Lund 1978):

$$\sigma_{SCA} = \sigma_{ad} (1 + 0.0563 \xi + 1.380 \xi^2 + 0.2191 \xi^3)^{-4}$$  \hspace{1cm} (3.1.1.10)
Laegsgaard et al. also derive a simple formula for the BEA cross-section in the limit $\xi \to 0$:

$$
\sigma_{\text{BEA}}^{\text{ad}} = \frac{2^{11}}{27} R_\infty Z_1^2 \xi^7
$$

(3.1.1.11)

It should be noted that the power of the adiabatic parameter is lower by one for this cross-section.

The total SCA K-shell ionization cross-section will be corrected for three effects which are termed the 'binding correction', 'Coulomb repulsion' and 'relativistic effects'.

At low projectile velocities, the state of the bound electron will be modified during the collision due to the lengthy proximity of the projectile nuclear charge to the target nucleus. This modification was first introduced by Brandt et al. (1966) who suggested that the main effect would be a change (increase) in the electron binding energy which, for a projectile at distance $R$ from a target nucleus, may be evaluated to first order from:

$$
\Delta U_K = \frac{Z_1 e^2}{R} \left[ 1 - (1 + R/R_K) \exp(-2R/R_K) \right]
$$

(3.1.1.12)

This is often known as the distortion approximation. It has been improved by Laegsgaard et al. by also taking into account the perturbation of the electron wavefunctions. An effective value $r'_K$ of the K-shell radius is obtained by variation of $r'_K$ to maximise the binding energy, $U'_K$:

$$
U'_K = -\frac{e^2}{2r'_K} + (Z_2 - 0.3) \frac{e^2}{r'_K} + \Delta U_K (R, R'_K) - \Delta U_{\text{screen}}
$$

(3.1.1.13)

The first term represents the kinetic energy and the second term the potential energy due to the attraction to the target nucleus (corrected for inner screening; the $Z_2 - 0.3$ term). The third term is given by the above equation of Brandt et al. (1966) with $R_K$ replaced by $r'_K$ and the last term represents outer screening by target atom electrons. For the projectile energies and target atomic numbers investigated in Chapter 5, this correction term results in a reduction of the cross-section.

At low projectile velocities, the Coulomb repulsion from the target nucleus may significantly modify the projectile motion and thereby the time dependence of the perturbation experienced by a K-shell electron. This effect was first treated by Bang et al. (1959) in the SCA. The main effect is the slowing down of the projectile in the vicinity of the
nucleus. The deflection of the projectile also reduces the ionization probability but the effect is much smaller and is ignored by Laegsgaard et al. Thus the change in energy of the projectile is given by

\[ E'_{\text{cm}} = E_{\text{cm}} - \frac{Z_1 Z_2 e^2}{R} \]  

(3.1.1.14)

where the distance \( R \) is given by

\[ R = \left[ R_{\text{min}}(p)^2 + r_{\text{ad}}^2 \right]^{1/2} \]  

(3.1.1.15)

This is the form for calculating the correction as a function of impact parameter \( p \). For the total cross-section, the impact parameter \( p = r_{\text{ad}} \) is chosen as representative for the ionizing collision and so the corrected velocity is obtained:

\[ v' = v (1 - b/R)^{1/2} \]  

(3.1.1.16)

where \( b = Z_1 Z_2 e^2/E_{\text{cm}} \)

and \( R \) is given as defined in equation 3.1.1.15 with

\[ R_{\text{min}}(p = r_{\text{ad}}) = b/2 + (b^2/4 + r_{\text{ad}}^2)^{1/2} \]  

(3.1.1.17)

Here \( r_{\text{ad}} \) is calculated from the united atom value of \( U_K \) (i.e. target atom plus projectile as described in the binding correction) and the unmodified velocity \( v \). Variations of the ionization cross-section with impact parameter show that good agreement is achieved with these predictions.

It is also important to correct for electron relativistic effects in the K-shell ionization of atoms by light ions of energies of the order of 10 MeV and less. Amundsen et al. (1976) have formulated a correction procedure for this effect. It becomes increasingly important for lower projectile velocities and higher target atomic numbers. For example, by inspection of Fig. 1 of the paper of Amundsen et al., it is found that the ratio of the relativistic cross-section to the non-relativistic cross-section at 1 MeV is 18, 1.8 and 1.1 for Au \((Z = 79)\), Ag \((Z = 47)\) and Cu \((Z = 29)\) targets respectively, whilst this ratio is only 5.7, 1.3 and 1.0 for 3 MeV projectiles. Laegsgaard et al. (1978) have introduced a modification to this correction in order to compensate for the correlation with impact parameter of the Coulomb repulsion and relativistic effects. The net effect of this modification is to reduce the correction slightly.
Subroutines for the above corrections have been written (Laegsgaard 1979). A programme using these subroutines has been constructed and SCA predictions at the various stages of the correction procedure obtained. Fig. 3.1.1.c shows the results for 0.5 to 3.0 MeV protons incident on a titanium target. All cross-sections have been divided by the uncorrected SCA cross-section in order to bring out the contributions of the various correction procedures. It will be observed that it is the binding energy correction which dominates in this case. Also shown are the experimental values for the cross-sections given by Laegsgaard et al. (1979) and the present work. It is expected (Laegsgaard et al. 1978) that the binding energy correction will break down for $\xi > 1$ and will be a good approximation below $\xi = 0.25$. Although it can be clearly seen that experiment deviates significantly from theory for $\xi > 0.7$ as may be expected, it also appears to do so below $\xi = 0.7$. It has been suggested by Laegsgaard et al. (1979) that the latter effect is due to an inadequate description of the Coulomb correction. It may be concluded from the excellent agreement found between the two sets of experimental data that these experiments are more accurate than the theoretical predictions. Further experimental data, together with their uncertainties, are given in Chapter 5 and are compared with the various theories that have been discussed. In particular, examination of Fig. 5.3.3.1.a shows that the PWBA, SCA and BEA theories all predict the general trend of the cross-section curves, for MeV protons incident on transition metals, to within about $\pm 40\%$.

All of the above theories are continually being improved and, in addition, the work of Pauli et al. (1978) and Langenberg et al. (1977) appears to show promise especially with regard to the 'second order' effects.

3.1.2 The inner shell fluorescence yield and branching ratio

Inner shell vacancies in atoms are filled by electron transitions from higher levels. This results in the emission of mono-energetic X-rays or Auger electrons which are characteristic of the electron transition that filled the vacancy. For instance, if a K shell vacancy is filled by an electron transition from the L shell, then either a $K_a$ X-ray (see Fig. 3.1.1.a) of energy $U_K - U_L$ or an Auger electron may be ejected from the L shell or from an outer shell. In Coster-Kronig transitions, one of the two vacancies produced in the radiationless (electron) decay is in a different subshell of the same principal shell that
Fig. 3.1.1.c Effect of various correction procedures on the SCA theory for protons incident on titanium. The cross-sections have been normalised by dividing them by the unmodified cross-section $SCA(1)$. Thus curve (2) = $SCA(2) \div SCA(1)$ and similarly for the other curves. $SCA(2)$ is the SCA with binding energy corrections, $SCA(3)$ is $SCA(2)$ plus the coulomb repulsion effect and $SCA(4)$ is $SCA(3)$ plus electron relativistic effects. Also shown are experimental results.
contained the initial vacancy. This clearly cannot happen in the K shell.

Bambynek et al. (1972) have reviewed both theory and experiment for X-ray fluorescence yields and also for Auger and Coster-Kronig transition probabilities. The K-shell fluorescence yield, $\omega_K$, is defined as the fraction of K shell vacancies that are filled through a radiative (X-ray) transition. Correspondingly, the Auger yield, $a_K$, is defined as the fraction of such vacancies filled through a radiationless transition. Thus we have:

$$\omega_K + a_K = 1 \quad (3.1.2.1)$$

L shell and higher fluorescence yields will not be considered here as K shell ionization has mainly been studied. However $\bar{\omega}_L$, which may be treated as an averaged L shell fluorescence yield, was required for the calculation of the L X-ray yield from the $^{109}$Cd source utilised in calibrating the efficiency of the Si(Li) X-ray detector. This is discussed in section 4.4.5.3 where various sources of $\omega_L$ values are given.

Bambynek et al. list what they consider to be the 'most reliable' experimental values for $\omega_K$. These are of varying accuracy and have not been measured for all the elements in the range of interest. It is therefore desirable to fit these data with some sort of physically justifiable function in the hope that the curve obtained is an accurate representation of $\omega_K$ as a function of $Z$. To a first approximation, the radiative transition probability $P_R$ calculated from unscreened hydrogenic wave functions is proportional to the fourth power of the atomic number $Z$ and the radiationless transition probability $P_A$ is constant. Thus

$$P_R = a Z^4 \quad \text{and} \quad P_A = b$$

Hence

$$\omega_K = (1 + a Z^{-4})^{-1} \quad (3.1.2.2)$$

where the constant $a = b/a$ is of the order of $10^6$. A modification to allow for screening and relativistic effects is

$$[\omega_K/(1 - \omega_K)]^{1/4} = A + BZ + CZ^3 \quad (3.1.2.3)$$

By fitting various functions to the 'most reliable' data and performing a detailed polynomial regression analysis, Bambynek et al. did indeed find that the latter equation yielded the statistically best approximation to the experimental data. This equation was therefore chosen to obtain fitted values of $\omega_K$. The claimed uncertainties of these fitted values, which take into account both fitting and experimental systematic
uncertainties, are consistent with the $3\sigma$ level (Bambynek 1979). Therefore to remain consistent within the present work, these uncertainties have been divided by 3 in order to state them at the $1\sigma$ level of confidence.

Recently, Krause (1979) has calculated K and L fluorescence yields. These values, divided by those of Bambynek et al. (1972) are plotted for the range $Z = 20$ to 35 in Fig. 3.1.2. It can be seen that for some elements the two sets of data are at variance by up to 3 % which, for a few cases, is greater than the $1\sigma$ uncertainty on the fitted data of Bambynek et al. Because these latter values are based on experiment and have become very widely accepted, they have been adopted throughout.

The relationship between the X-ray production $[\sigma^X(E)]$ and ionization $[\sigma^I(E)]$ cross-sections for K shell ionization is given by

$$\sigma^X_K(E) = \sigma^I_K(E) \omega_K k_K$$

where $k_K$, the branching ratio, is the ratio of the various photon lines that result from the filling of the vacancy. Thus $\sigma^I_K(E)$ is the cross-section for K shell ionization, $\omega_K$ is the fraction of such vacancies that are filled via K X-ray emission and $k_K$ the relative probability that it is a $K\alpha$ X-ray (as opposed to a $K\beta$ X-ray) that is produced. $\sigma^X_{K\alpha}(E)$ is the cross-section for producing $K\alpha$ X-rays. The $K\beta/K\alpha$ ratios determined by Venugopala Rao et al. (1972), from a least squares fit to the available experimental data, are used. Similar expressions are obtained for higher shell ionization where such factors as Coster-Kronig transition probabilities have to be included.

It is important to realise that, in fact, in most particle-induced ionization cross-section 'measurements', it is the emitted X-ray or Auger electron that is detected. To obtain the ionization cross-sections from, for example, X-ray yields, the fluorescence yield must be known. Thus, although the use of the data of Bambynek et al. allows for 'consistent' comparisons between experimental values of ionization cross-section, it should be remembered that these data may have a systematic uncertainty associated with them and that this should be noted in the final statement of the accuracy of ionization cross-section data.

Both $\omega$ and $k$ will depend on the electron vacancy distribution. Thus these parameters will not necessarily be the same when the vacancy has been produced by, for example, nuclear electron capture or proton-induced ionization. Nuclear capture from various subshells will vary according to the different degrees of overlap between the electron wavefunctions and the nucleus whilst for proton-induced ionization a different vacancy distribution will be obtained which is related to the range of impact.
Fig. 3.1.2 Comparison of K shell fluorescence yields values of Bambynek et al. (1972) and Krause (1979).
parameters. For L shells, Brandt et al. (1979a) discuss increases in the fluorescence yield due to multiple ionization. This appears to be more likely the higher the shell and the larger the projectile atomic number. For point charged-particle excitation Johansson et al. (1976) have stated that the emission rates are the same as those for X-ray and electron excited characteristic X-rays. Thus care should be exercised when converting X-ray production cross-sections into ionization cross-sections.

3.1.3 Relationships between detector X-ray counts, ionization cross-section and number of target atoms

3.1.3.1 The determination of ionization cross-sections

Targets of pure elements

For thin targets, i.e. those for which proton energy loss and photon self-absorption corrections are small, the proton-induced ionization cross-section \( \sigma^X(E) \) may be determined by making use of the following relationship

\[
y_K(E) = Q \sigma^X_K(E) N \frac{\Delta \Omega}{4\pi} \varepsilon C_{\text{att}}
\]

(3.1.3.1.1)

Here \( y_K(E) \) is the total number of K X-ray counts, in a full energy peak due to a particular element, in a detector subtending a solid angle of \( \Delta \Omega \) steradian at the X-ray source. \( N \) is the number of atoms of that element per unit area, \( \varepsilon \) the intrinsic full energy peak efficiency of the detector at the energy of the observed transition and \( C_{\text{att}} \) the attenuation factor due to any X-ray absorption in the target. \( Q \) is the number of incident ions of energy \( E \) and \( \sigma^X_K(E) \) is the X-ray production cross-section as defined by equation 3.1.2.4. The factors \( Q, N, \Delta \Omega \) and \( \varepsilon \) must be determined experimentally. The attenuation factor, \( C_{\text{att}} \), is given by

\[
C_{\text{att}} = \exp(-\mu d/\cos \phi)
\]

(3.1.3.1.2)

where \( \mu \) is the linear photon attenuation coefficient for the X-ray of interest emitted at a depth \( d \) in the target material. \( \phi \) is the angle that the detected X-ray makes to the normal to the target surface.

The effective projectile energy is the mean energy in the thin target. For the targets actually used, these corrections were very small.
Thus, once \( y_i(E) \) is measured at a particular energy, a value for \( aY(E) \) at that energy may then be obtained directly from equation 3.1.3.1.1. Hence, in principle, only one irradiation is necessary to determine \( aY_i(E) \) for a particular projectile energy when thin targets are used. This is not the case for thick targets.

The use of thick targets is often necessitated by thin target preparation difficulties or the use of low projectile energies when it may not be possible to make targets thin enough for the projectile energy loss to be small. A thick target is defined here as one which has a thickness greater than the range of the incident projectiles \( [R_p(E)] \). The determination of \( aY_i(E) \) from thick target yields is somewhat complicated and the required equations will now be derived. It seems worthwhile to go through this derivation as a detailed proof has not been found in the literature.

Let the average number of characteristic X-rays, \( Y(E) \), emitted by the target per incident ion of energy \( E \) be given by

\[
Y(E) = \frac{4\pi y_i(E)}{Q \Delta \Omega \epsilon}
\]  

(3.1.3.1.3)

where the other symbols are as previously defined. Now if the projectile energy is increased to \( E + dE \), then, after a distance \( dx \) from the target surface, the projectile will have lost \( dE \) of energy and will again have energy \( E \). Thus for the remainder of its path it will produce \( Y(E) \) X-rays as before. It has been assumed that the layer \( dx \) removes a negligible number of projectiles from the beam. However the \( Y(E) \) X-rays will be further attenuated in passing through the extra layer \( dx \) by

\[
\exp(-\mu \frac{\cos \theta}{\cos \phi} dx)
\]  

(3.1.3.1.4)

where \( \theta \) and \( \phi \) are the angles that the incident beam and detected X-rays make with respect to the normal to the target surface. The production of X-rays in the layer \( dx \) may be treated in the thin target approximation and negligible attenuation assumed. Therefore, if there are \( n \) target atoms per unit volume, then the number of target atoms per unit area is \( n \, dx \). Hence the yield of X-rays from this thin layer is given by (eq. 3.1.3.1.1).

\[
\therefore y = Q aY_i(E) n \, dx \frac{\Delta \Omega}{4\pi \epsilon}
\]  

(3.1.3.1.5)

Thus the number of X-rays per projectile from the layer \( dx \) (corrected for detector efficiency) is

\[
aY_i^x(E) n \, dx
\]  

(3.1.3.1.6)
Hence we obtain the change in X-ray yield, due to the increase in projectile energy \( dE \), is given by

\[
Y(E + dE) - Y(E) = \sigma_i^X(E)n \, dx + Y(E) \exp(-\mu \frac{\cos \theta}{\cos \phi} \, dx) - Y(E)
\]

\[
= \sigma_i^X(E)n \, dx - Y(E) \left[ 1 - \exp\left(-\mu \frac{\cos \theta}{\cos \phi} \, dx\right) \right]
\]  (3.1.3.1.7)

Using a Taylor expansion for the exponential term in eq. 3.1.3.1.7:

\[
\exp(-\mu \frac{\cos \theta}{\cos \phi} \, dx) = 1 + \left( -\mu \frac{\cos \theta}{\cos \phi} \, dx \right) + \frac{(-\mu \frac{\cos \theta}{\cos \phi} \, dx)^2}{2 !} + \ldots
\]  (3.1.3.1.8)

and neglecting second order terms as \( dx \) is defined to be small, the result is obtained that:

\[
Y(E + dE) - Y(E) = \sigma_i^X(E)n \, dx - Y(E) \mu \frac{\cos \theta}{\cos \phi} \, dx
\]  (3.1.3.1.9)

\[
\therefore \frac{dY(E)}{dx} = \sigma_i^X(E)n - Y(E) \mu \frac{\cos \theta}{\cos \phi}
\]  (3.1.3.1.10)

Thus

\[
\sigma_i^X(E) = \frac{1}{n} \left[ \frac{dY(E)}{dx} + Y(E) \mu \frac{\cos \theta}{\cos \phi} \right]
\]  (3.1.3.1.11)

but \( \frac{dY(E)}{dx} = \frac{dY(E)}{dE} \frac{dE}{dx} \) where \( \frac{dE}{dx} = S(E) \) is the stopping power.

Hence

\[
\sigma_i^X(E) = \frac{1}{n} \left[ \frac{dY(E)}{dE} \frac{dE}{dx} + Y(E) \mu \frac{\cos \theta}{\cos \phi} \right]
\]  (3.1.3.1.12)

Similar expressions have been derived by Merzbacher et al. (1958) and Dyson (1973b).

The best curve through the values of \( Y(E) \) vs \( E \) forms the experimental X-ray excitation function with the slope \( \frac{dY(E)}{dE} \) and \( S(E) \) evaluated at the projectile energy of interest. Thus to obtain \( \sigma_i^X(E) \) from eq. 3.1.3.1.12 a large number of measurements is required to accurately determine \( Y(E) \) and \( \frac{dY(E)}{dE} \).

**Targets of chemical compounds**

For thin targets, where the self-absorption corrections are negligible, the only additional major problem in using a compound is the determination of the number of atoms per unit area of the element of interest. As compounds often evaporate in a non-stoichiometric manner, the mass of the deposit formed by evaporation will often not yield the desired information. However, the amount of the element can usually be determined by Rutherford backscattering (RBS) analysis.
In the present work, thick targets of chemical compounds have been prepared by pressing the pure chemical in powder form into a tablet die. The stoichiometry of the freshly prepared thick targets of the compounds was assumed to be that of the pure chemical as the only operation that was performed on the powder was that of pressing. However, in order to obtain $\sigma_i^X(E)$ from measurements on these targets, it is necessary to re-express equation 3.1.3.1.12 in terms of cross-sections because the densities of these targets are difficult to measure. Thus the factors $n, \mu$ and $S(E)$ are replaced by $n', \mu'_\text{mean}$ and $S'_\text{mean}(E)$ which are defined by the following expressions.

The mean number density of target atoms (per atom), $n'$, for a compound of general formula $A_B C_{\ldots}$ is given by

$$n' = s \frac{s}{s + t + u + \ldots}$$

(3.1.3.1.13)

where $A$ represents the target atoms of interest. The photon attenuation cross-section, $\mu'$, is assumed to be a simple algebraic mean with $\mu'_\text{mean}$ given by

$$\mu'_\text{mean} = \frac{s \mu'_A + t \mu'_B + u \mu'_C + \ldots}{s + t + u + \ldots}$$

(3.1.3.1.14)

and similarly the stopping cross-sections, $S'(E)$, for the protons is given by

$$S'_\text{mean}(E) = \frac{s S'_A(E) + t S'_B(E) + u S'_C(E) + \ldots}{s + t + u + \ldots}$$

(3.1.3.1.15)

The validity of the latter relationship, which is commonly known as Bragg's Rule, is a subject of increasing interest. Langley et al. (1976) found a projectile velocity dependent deviation from Bragg's Rule for erbium oxide ($\text{Er}_2\text{O}_3$). The experimental values of stopping cross-section were 9% and 4% below the Bragg's Rule predictions for 0.5 and 1.0 MeV protons respectively. Beyond 2 MeV, no deviations were observed for protons. In the present work, no corrections have been made for this deviation. The validities of the above assumptions, together with experimental results, are discussed in Chapter 5.

3.1.3.2 Quantitative elemental analysis

Absolute PIXE analysis is achieved by again using equation 3.1.3.1.1. This time $\sigma_i^X(E)$ must be known and $N$ is the unknown to be determined. The trace element of interest will be embedded in some sort of bulk matrix. It is this matrix which determines the projectile
energy loss and the photon attenuation in the sample. However, when the element of interest is within a thin layer on the surface of a thick sample (e.g. paint on a vase), the thick backing may be ignored except from the point of view of background radiation.

Very often, one of the parameters such as $\sigma^X(E)$ or $\epsilon$ is not known for the X-rays of a particular element. In such a case, an external 'standard' is often used. This contains a known amount of the element under investigation. By irradiating the known and unknown sample under identical conditions with the same, or scaled, ion beam fluences, the amount of the unknown may be obtained by simple proportion. This assumes that the two targets have identical form i.e. the same bulk elemental composition and thickness. Variations in the composition of the samples may cause significant differences in the X-ray yields due to target self-absorption effects. The standard must be used each time any of the experimental conditions, such as ion beam energy, are changed and it must be stable to these repeated irradiations. Some of the difficulties in preparing such standards have been discussed by Mitchell et al. (1980b) and this work is outlined in Chapter 6. Sometimes a compromise between the two approaches is adopted as was the case for the analysis of air pollution samples.

Thick samples introduce even more difficulties as it is necessary to integrate the X-ray production over the entire projectile path. This requires a knowledge of the composition of the matrix as well as the distribution of the trace elements. For a uniform sample, this calculation may be performed or a standard may be used. It is clearly even more important with thick targets that the sample and standard should have a similar and known composition. The effects of the degree of non-uniformity of the particle beam, matrix composition and matrix thickness on quantitative PIXE analysis have been quantitatively discussed by Montenegro et al. (1979).

### 3.1.4 Background radiation

In any real analysis situation the trace elements to be determined are always within some form of matrix, for example the filter material in aerosol sampling and the organic tissue in medical samples. Due to this, the X-ray signal from the trace elements of interest may be partially or totally masked by an unwanted background in the spectrum due to the backing or host material. The background may be in the form of a continuum or it may contain discrete peaks arising from interfering
characteristic X-rays or γ-rays from the matrix material. Fig. 3.1.4 shows the X-ray spectrum obtained when 1.5 MeV protons are incident on a thin 'pure' carbon foil. It may be seen that several discrete peaks due to trace elements are sitting on a continuous distribution which has a maximum at low energies. The decrease in the continuum at the lowest energies is due to the absorption of the photons in the beryllium window in front of the Si(Li) detector. The background yield at low energies clearly causes difficulties for the easy detection and precise analysis of the light elements in the spectrum.

There are several processes which contribute to the continuum background:

**Incident projectile bremsstrahlung.** The cross section for this process is given by (Folkmann et al. 1974a)

\[
\frac{d\sigma}{dE_{bx}} = C \frac{A_p Z_p^2 Z_T^2}{E_p E_{bx}} \left(\frac{Z_p}{A_p} - \frac{Z_T}{A_T}\right)^2
\]

(3.1.4.1)

where \(E_{bx}\) is the energy of the background radiation, \(Z_p, A_p, E_p\) are the atomic number, mass and energy of the incident particle and \(Z_T, A_T\) that for the matrix.

\(C\) is a slowly varying factor dependent on \(Z_p, Z_T\) and \(E_p\) having a value of about 2-3 eV barn.

This background is illustrated in Fig. 3.1.4 by the line marked (A) and would appear to be the major cause of background at the higher X-ray energies. From equation 3.1.4.1 it can be seen that the cross-section and hence the yield should decrease with increasing energy. Moreover, if \(Z/A\) is the same for the projectile and the matrix, this form of bremsstrahlung will disappear. For most matrices encountered, \(Z_T/A_T\) has the value of approximately 0.5. Consequently there should be little or no incident projectile bremsstrahlung from alpha particles and heavier ions (where \(Z_p/A_T\) is also approximately 0.5). This conclusion has been experimentally verified by Watson (1975).

**Secondary electron bremsstrahlung.** The low energy background is believed to be largely due to the bremsstrahlung caused by the secondary electrons ejected from the target during the collision process. This will have a maximum energy (for free electrons) given by

\[
E_{e(\text{max})} = 4 \left(\frac{M}{M_p}\right)E_p
\]

(3.1.4.2)
Fig. 3.1.4 Spectrum of a thin carbon foil bombarded with 1.5 MeV protons. The line A shows the contribution from the proton-induced bremsstrahlung. The arrow B indicates the maximum energy of the bremsstrahlung produced by secondary electrons from unbound states. The point C is the observed maximum energy of the secondary electron bremsstrahlung.

(from Johansson et al. 1976).
Thus, for example, \( E_{e_{\text{max}}} \) is 4 keV for 2 MeV protons. In Fig. 3.1.4 the arrow marked \( \text{arrow} \) indicates the value \( E_{e_{\text{max}}} \) for the 1.5 MeV protons used in that case. It can be seen that this bremsstrahlung continues up to about 11 keV (point \( \text{point} \) ) indicating that larger energy transfers are occurring and that bound electrons play a significant rôle in the production of this background.

Ward et al. (1978) have derived relationships for the calculation of thick target secondary-electron bremsstrahlung yields due to \( 1s \) electrons and all \( s \) electrons. Their experimental results for 450 keV protons on aluminium indicate that the non \( K \)-shell electrons make a significant contribution to the \( s \) electron induced background below about 5 keV. The thin target calculations of Folkmann et al. (1974a) were also found to be in satisfactory agreement with experiment. However, they do not predict any anisotropy in this type of bremsstrahlung such as been observed by Tawara et al. (1976b) and Ishii et al. (1977) who explained it by incorporating a relativistic retardation effect in the bremsstrahlung production. The main consequence of this observation, from an experimental point of view, is that the background at 135° to the beam direction is about 40 % lower than that at 90° (which is the most commonly used detector angle). Therefore, to minimise this type of bremsstrahlung effect, it is best to position the X-ray Si(Li) detector at as large an angle as possible with respect to the incident beam direction.

The primary process in both the production of characteristic X-rays and secondary electron bremsstrahlung is the ionization event. Therefore the ratio of the height of the X-ray peaks to the background will be more or less the same in a given target for all heavy projectile species having the same velocity. In summary then, as secondary electron bremsstrahlung is usually the dominant form of background, all ions (including protons) will have about the same signal to noise ratio. In other words, using heavier projectiles will not improve the peak to background ratio. In principle, the background could be reduced by making the sample matrix as thin as possible but a practical limit is soon reached (Johannson et al. 1976).

\( \gamma \)-rays. When a projectile is involved in a nuclear reaction with a target atom, \( \gamma \)-radiation may be emitted which will produce a high energy continuum in the spectrum due to Compton scattering in the detector. Moreover, if the \( \gamma \)-rays are of low energy, they may be fully absorbed in the detector and give rise to discrete peaks which may be mistaken for characteristic X-ray peaks. The \( \gamma \)-radiation produced depends on the
projectile species and energy and to a high degree on the elemental composition of the target matrix. This can be seen, for example, for $^{19}$F and $^{23}$Na which may often be found in materials and which have high nuclear reaction cross-sections in the MeV region. The structural composition and physical design of the target vacuum chamber and its contents will also to some extent affect this background by causing $\gamma$-ray backscattering. Folkmann et al. (1974a) have found that this background is dominant for K X-rays from elements with $Z > 30$ and at proton energies between 3-5 MeV. Hence, to keep $\gamma$-ray backgrounds to a minimum, the beam energy should be kept as low as is practicable whilst at the same time being kept high enough to provide sufficiently intense characteristic X-ray yields from the elements of interest. Bombarding energies above the threshold for inelastic scattering to take place with the most abundant nuclides of the matrix, for example $^{12}$C and $^{16}$O, should be especially avoided. In conclusion, it can be stated that protons are preferable because heavier ions such as $^4$He and $^{16}$O having the same velocity as the protons will have much higher incident energies and consequently much larger cross-sections for nuclear reactions to occur. This is one of the main reasons why protons of 1-2 MeV energy are often cited as the best choice for PIXE analysis.

Other possible sources of background. It is often the case that the specimen under investigation is an insulator, or at least a poor conductor of electricity, and consequently it can become highly charged during ion irradiation. This may eventually lead to an electrical discharge from the target to its conducting support or to the vacuum chamber wall. This effect will inevitably result in high continuum backgrounds in the spectrum. This has been well illustrated by Mason (1978) who shows spectra from an insulating air particulate sample before and after the surface of the target holder was made conducting with the aid of aluminium tape. These spectra indicate that this background can be as high as 16 keV and show that trace analysis is almost impossible unless it is removed. Other sources of backgrounds such as Auger electrons and knock-on electrons are believed to make a negligible contribution to the total bremsstrahlung in comparison with the causes mentioned above.

3.1.5 The choice of beam parameters

The usual starting point in optimising an analytical experiment is to calculate the minimum detection limit as a function of the various adjustable parameters. Then, assuming that these parameters, such as
cross-sections, are known with equal accuracy at all values considered, the experiment is operated at the point with the lowest minimum detection limit (MDL) which is defined as the minimum amount that can be reliably detected. However, the MDL is a somewhat 'theoretical' limit and the related but sometimes more practical parameter, the minimum quantitation limit (MQL), gives the values of the adjustable parameters that will yield a detected peak with a stated precision. The definitions of these two limits will be discussed in detail and a practical example is given in Appendix B which illustrates the kind of false conclusions that can be reached when statistically inadequate definitions are utilised.

3.1.5.1 Minimum detection limit

There exist numerous, inconsistent and limited definitions of the minimum detection limit. Eight definitions have been discussed by Currie (1968) who provided the National Bureau of Standards (NBS) method of calculating the MDL for experiments in which the signal follows Poisson statistics. More recently Currie (1978) has applied the method to X-ray fluorescence spectrometry which is analogous, statistically, to PIXE spectrometry. The NBS formalism is adopted throughout this work.

The MDL of a measurement system is determined by the statistical fluctuations in the background which 'conceal' weak signals. The minimum detectable signal count ($N_s$) is defined as:

$$N_s = 3.29 \sigma_o$$  \hspace{1cm} (3.1.5.1.1)

For this limit, the probability of 'false' detection is 5% (not 1% as might appear from casual inspection - see Currie (1968))

and $\sigma_o = \sigma_B \eta^{1/2}$  \hspace{1cm} (3.1.5.1.2)

where $\sigma_B$ is the standard deviation of the blank and $\eta = 1$ if the background (or blank) is well characterised (i.e. the result of many measurements) or $\eta = 2$ if paired observations (at equal counting times) of the sample and blank are made. Assuming that Poisson counting statistics hold, then

$$\sigma_B = \frac{N_B^{1/2}}{\sqrt{N_B}}$$  \hspace{1cm} (3.1.5.1.3)

where $N_B$ is the number of background counts.
If $S$ is the sensitivity function (e.g. counts per proton per $\mu g \ cm^{-2}$) and $Q = \text{ion beam fluence}$, then the MDL is given by

$$MDL = 3.29 \frac{(\eta N_B)^{1/2}}{SQ}$$

(3.1.5.1.4)

Thus the MDL is that amount of the element that will give rise to the defined detectable signal. It should be stressed that the above equation only holds for reproducible blanks. The MDL will be higher if there are fluctuations in the blanks levels. Systematic uncertainties have been neglected in the present determination of MDL's as these uncertainties tend to cancel out when comparing the adequacy of different methods. Also, it should be pointed out that the MDL definitions do not give any value for the precision of the detected peak. Only the MQL provides this.

Unfortunately, a wide variety of definitions of MDL are still in use. In order to stress the importance of choosing a statistically meaningful definition, several popular definitions will be considered in order to illustrate the type of confusion that can arise. Perhaps the most popular definition is that of the International Union of Pure and Applied Chemistry (1976)

$$N_S = 3 \ N_B^{1/2}$$

(3.1.5.1.5)

Thus for a well characterised blank, this definition yields an MDL only 9% less than that of Currie; which is a trivial difference when comparing various analytical systems. Cahill (1975) has discussed this definition and deduces that, according to the Student-t test, the correct definition is given by:

$$N_S = 2 + 2 \ (2N_B + 1)^{1/2}$$

(3.1.5.1.6)

With increasing $N_B$ this definition rapidly approaches values 14% less than those given by the definition of Currie. Once again, except for very low values of $N_B$, the definitions only differ by a constant multiplicative factor. This is not the case for the popular, but misleading definition that

$$N_S = N_B$$

(3.1.5.1.7)

This is used without any apparent theoretical justification. It is immediately seen that the MDL will never improve with increased beam fluence (although the precision does) because the peak to background ratio remains constant. This is clearly implausible. Some of the false conclusions that can be drawn from the use of this definition are discussed in Appendix B.
The principle uses of these MDL calculations in PIXE analysis are for the optimisation of such parameters as ion beam energy, flux etc. in a particular experimental set-up and for inter-comparisons of the precision and MDL's of different techniques. Clearly, if it is known that the element to be analysed is well below the MDL of a particular system, then it is not worthwhile starting the experiment.

It has already been noted in section 3.1.1 that the ionization cross-section goes up with proton energy for the targets and energies of interest in PIXE analysis. It might be deduced that this would improve the MDL. Unfortunately the maximum energy of the secondary electron bremsstrahlung also increases linearly with projectile energy. At higher energies, the background due to $\gamma$-radiation from nuclear reactions also increases. Fig. 3.1.5.1.a shows the X-ray production cross-sections for the K and L shells with 2 MeV proton and alpha particle excitation. These have been calculated using the semi-empirical BEA ionization cross-section formulae of Johansson et al. (1976), the $\omega_K$ fitted values of Bambynek et al. (1972) and the $\omega_L$ formula of Hoffmann (1978) which is discussed in section 4.4.5.3. For most of the range of interest, protons are seen to give a much greater yield. At equal projectile velocities, the alpha particles would give the greater yield ($\sigma \propto Z^2$) but 8 MeV projectiles were not available from the CBNM Van de Graaff accelerator. In practice, it was found that, where the characteristic X-ray was greater than 4 keV in energy (the maximum energy of the 2 MeV proton-induced secondary-electron bremsstrahlung), protons were by far the better choice. Below this energy the choice was more often dictated by target damage considerations (alpha particles were found to be far more damaging than protons when filter samples were analysed as is discussed in Chapter 6). Thus the determination of the MDL for a particular experimental arrangement is a complex affair and should really be determined experimentally. This has been done for the main application of this work viz. the air pollution studies. It is, however, possible to point out some general trends in minimum detection limits.

As the background depends so strongly on the particular matrix in which the trace elements are incorporated, there can be no general expression for the MDL for a particular trace element. However, in many practical situations the matrix is very often composed of carbonaceous or organic type material. For this reason, the emphasis in the following calculations is for carbon backings. Fig. 3.1.5.1.b and Fig. 3.1.5.1.c due to Johansson et al. (1976) and Folkmann et al. (1974b) respectively, illustrate the effect of beam energy and projectile
Fig. 3.1.5.1a Comparison of K and L X-ray production cross-sections for excitation by 2 MeV protons and alpha particles (see text for sources of data).
Fig. 3.1.51b, c  

b) Minimum detectable concentration as a function of atomic number for proton energies 1 and 3 MeV. The following experimental parameters were used: detector resolution 165 eV, solid angle 0.003 x 4π, collected charge 10 μC and target thickness 0.1 mg/cm². (from Johannson et al. 1976)

c) Concentration of trace element corresponding to a peak-to-background ratio of 1, when the background is taken within a width ΔE, corresponding to the resolution of 150 eV at 5.9 keV for a Ge detector, at the energy of the Kα or the Lβ X-rays from the trace element. (from Folkmann 1974b).
species on the variation of MDL with atomic number of the target elements. In both sets of curves, clear minima can be seen indicating that the lowest MDL occurs for protons of 1 MeV energy at about \( Z = 20 \) for K X-rays and \( Z \approx 60 \) for L X-rays. In a similar fashion for protons of 3 MeV, minima occur at about \( Z = 35 \) and \( Z \approx 85 \) for the K and L X-rays respectively. Fig. 3.1.5.1.c indicates that protons provide better detection limits over the whole periodic table than heavier projectiles of equivalent energy per nucleon. However, Fig. 3.1.5.1.c is based on a peak to background ratio of 1 (see eq. 3.1.5.1.7) which has already been said to be a bad choice. If equation 3.1.5.1.1 was applied instead of the criterium of Folkmann et al., this conclusion would not necessarily be valid. The worsening of the MDL for both K and L X-rays at decreasing target atomic number is related to the reduction in the fluorescence yield and the increase in secondary electron bremsstrahlung. To the right of the minima, with increasing Z values, the MDL again increases (worsens) but this time due to a reduction in the X-ray production cross-section. From curves of this type it can be seen that, to some extent, the projectile energy can be chosen to provide an optimum MDL for a certain range of elements. Again this is one of the principal reasons for using 1-3 MeV protons for PIXE analysis when the elemental region of interest is in the 20-30 and 60-80 atomic number range.

Further useful deductions can be made from these figures; for example, it can be seen that beyond an atomic number of about 40 (but depending strongly on projectile energy) better MDL's can be achieved by using L X-rays for analysis rather than K X-rays. This is principally due to the much higher L X-ray production cross-sections (see Fig. 3.1.5.1.a). Moreover, it should be noted from Fig. 3.1.5.1.b that the minimum detectable concentration obtainable over the whole periodic table of elements only varies by about an order of magnitude and has an absolute value of about \( 10^{-6} \). This smooth and slow variation in the MDL's over a wide range of elements is a very useful property in an analytical technique and is an added advantage of PIXE as a multi-elemental method. Nevertheless, these curves should be interpreted cautiously since the calculations used to derive them do not take into account the possibilities of spectral interference and overlaps between low Z K X-rays and high Z L and M X-rays which may occur due to the limited resolution of the Si(Li) detector. For example, the \( K_a \) X-ray line from sulphur at 2.31 keV would not be resolvable from the \( M_a \) X-ray line of lead at 2.34 keV. Both of these elements are commonly found in air pollution samples. Also the 'tails' from intense X-ray peaks may obscure adjacent small peaks.
Finally, it should be added that the calculated MDL's are for the irradiated specimen in its final state. In other words, pre-concentration and other sample preparation treatments prior to analysis may well improve the MDL for particular trace elements with respect to the original state of the sample; but this will always be at the expense of using more base material (which may not always be practicable) and with an increased probability of contaminating the sample with unwanted elements. It is easy to show from the present definition of MDL that the values will scale according to

\[ \text{MDL} \propto \Delta E^1/2_x (\Delta \Omega Q t)^{-1/2} \]

where \( \Delta E_x \) is the FWHM resolution of the X-ray detector and \( t \) is the target thickness. The typical MDL value of \( \sim 1 \text{ppm} \) could thus be improved upon by counting for longer times and by focussing the projectile beam to provide a more intense flux over a chosen region of the target. Optimising the experimental parameters by such techniques can lead to sensitivities of better than \( 10^{-7} \). This corresponds to about \( 2 \times 10^{-14} \text{g} \) of an element in a typical air sampling filter (Johansson et al. 1976). With such low MDL's, the importance of pure target backings and inert and clean handling of the samples becomes paramount. As an example of the limits that have been achieved experimentally, Johansson et al. (1970) have reported the detection of trace elements at the \( 10^{-12} \text{g} \) level on their carbon substrates. MDL values found in the present work are reported in Chapters 5 and 6.

3.1.5.2 Minimum quantitation limit

In addition to a signal being detectable according to the desired signal to background criterion, there must be sufficient counts to provide some degree of precision in quantitative analysis. For intercomparison purposes, let it be assumed that there must be sufficient counts to produce a statistical uncertainty of \( \pm 10\% \). Thus the minimum quantitation signal \( (N_Q) \) is given by (Currie 1978):

\[ N_Q = 10 \cdot f \cdot \sigma_0 \quad (3.1.5.2.1) \]

where \( f = \left[ 1 + 25/(\eta N_B) \right]^{1/2} + \left[ 25/(\eta N_B) \right]^{1/2} \quad (3.1.5.2.2) \]

The factor \( f \) corrects for the effects of small \( N_B \) (Currie 1968). Thus the minimum quantitation limit (MQL) is given by:

\[ \text{MQL} = 10 \cdot f \cdot \frac{(\eta N_B)^{1/2}}{\text{St}} \quad (3.1.5.2.3) \]
In section 5.5 and Appendix B, the results of MDL and MQL calculations for practical examples are compared and it is shown that the MDL consideration alone is not sufficient to determine the optimum experimental conditions.

3.2 Backscattering spectrometry

This form of spectrometry is based on the detection of ions elastically backscattered from target nuclei. From such measurements, it is possible to determine the mass and depth distribution of the target atoms in the matrix. The scattering cross-sections normally used are based on Rutherford's scattering theory. However, recent experiments and refinements of the theory indicate that small corrections have to be made to the Rutherford cross-sections. When these corrections have been made, the experimentally derived cross-sections generally agree with the theory to within a few percent. Because of the general reliability of Rutherford cross-sections, they are often used to normalize ion-induced X-ray emission cross-sections. The principles of backscattering theory are outlined in Appendix C. Also included, in so far they apply to the present work, are brief descriptions of the phenomena of energy loss, energy straggling and angular straggling which take place as ions move through matter.
CHAPTER 4

APPARATUS AND EXPERIMENTAL TECHNIQUES

The apparatus and techniques utilised in the PIXE and RBS measurements will be described in detail. An understanding of the experimental sources of uncertainty is critical in the appraisal of the accuracy of the absolute measurements such as the PIXE cross-section determinations. Of particular importance are the methods of measuring ion beam fluence, X-ray detection efficiency and target mass thickness described in this chapter. In each of these cases, significant advances over the more commonly used methods are reported. Details of techniques specific to the applications work, such as the air particulate sampling, are given in the appropriate chapters.

4.1 The CBNM 3.7 MV Van de Graaff accelerator

This vertically mounted accelerator is capable of delivering protons, deuterons and helium ions (\(^4\)He\(^+\) in our case) with energies in the range 0.8 MeV to 3.7 MeV. The accelerated ion beam is focused with a quadrupole lens and the ions of the desired energy are deflected into the horizontal beam tube with the aid of an analysing magnet. The beam then passes through a set of energy control slits which feed back to the corona load thus maintaining the energy stability. Finally, the ions pass through a circular aperture thereby defining a 6 mm diameter beam at the irradiation facility.

The energy of the projectile beam was calibrated by using the well known reactions: \(^7\)Li(p,n), \(^9\)Be(p,n) and \(^{11}\)B(p,n) which have thresholds at 1.880, 2.059 and 3.015 MeV respectively and the Al(p,\(\gamma\)) resonance reaction which is at 0.992 MeV. This gave an uncertainty of ±2 keV for a proton beam energy of 2 MeV.

4.2 The target chamber

The purpose of the present vacuum chamber is to allow PIXE, RBS and nuclear reactions analysis (NRA). PIXE and either RBS or NRA may be studied simultaneously. This is especially important for resolving ambiguities in RBS spectra (see Appendix C).
4.2.1 Chamber characteristics

The chamber is shown schematically in Fig. 4.2.1.a and a photograph of the general irradiation facility is given in Fig. 4.2.1.b. The defocused ion beam from the Van de Graaff is defined by a beam collimation system. This device permits a choice of four apertures or a quartz viewer to be rotated into the centre of the beam. The viewer provides an approximate means of checking the position, intensity and homogeneity of the beam. The apertures allow the initial 6 mm diameter beam to be collimated down to beams of 0.5, 1 and 2 mm diameter or a rectangular beam of 1 x 2 mm. Apertures of slightly larger dimensions (known as skimmers) are placed 5 mm beyond the collimators to reduce the intensity of slit-scattered particles. The beam collimation apparatus is maintained under vacuum so that the apertures may be changed during an experiment in about one second. This is important when samples of differing sizes are being examined. The ion beam then passes through the foil ion beam monitor and impinges on the targets which are held on a modified 3-axis goniometer (described in section 4.2.3).

The possibility of characteristic X-rays from chamber materials reaching the high resolution Si(Li) photon detector is reduced to negligible proportions by covering all parts of the chamber 'seen' by the detector with graphite sheets. Liquid nitrogen cooling is provided to the areas surrounding the target assembly and the foil monitor in order to prevent the build-up of carbon deposits during irradiation. This 'cryoshielding' reduces the vapour pressure of hydrocarbons around the targets and the foil; thus significantly reducing the probability of thin films of oil etc. being formed which may then be cracked by the ion beam to produce carbonaceous layers.

As the Si(Li) detector has a small sensitive area (10 mm²), it is important to place the detector as close to the target as possible in order to achieve a reasonable collection solid angle. Also, it was necessary to have the detector inside the vacuum system, rather than outside behind an X-ray/vacuum-window, in order to allow the efficient detection of the low energy X-rays from the light elements under investigation in much of this work. A rather elaborate system was designed which would maintain the beryllium window of the detector under vacuum at all times in order to lengthen the life of the window. The fragility of such windows had previously been observed (Barfoot 1976). When not in use, the end of the detector probe is kept between two viton gaskets, which provide the vacuum seal, and a gate valve (see Fig. 4.2.1.a).
Fig. 4.2.1.d  Schematic diagram of the vacuum chamber for PIXE, RBS and NRA.
1. Si(Li) DETECTOR
2. BEAM COLLIMATORS
3. Si(Li) VACUUM VALVE
4. IRRADIATION CHAMBER
5. TURBOMOLECULAR PUMP
6. CONNECTION TO ROTARY PUMP
7. LIQUID NITROGEN COOLING SYSTEM
8. TO VAN DE GRAAFF ACCELERATOR

Fig. 4.2.1.b General view of the irradiation facility.
When the detector is to be used, and the target chamber has been evacuated, the gate valve is opened and probe slid through the gaskets and into the chamber. However, for the accurate PIXE cross-section work, it was found that the reproducibility of the detector re-positioning was not sufficient. Therefore, the detector was kept in a fixed position during these experiments. When not in use, the detector window is covered with a perspex cap to prevent it from being contaminated (principally from the vaporisation of targets). The detector is at 157.5° to the beam direction since it has been shown (Ishii et al. 1977) that the bremsstrahlung background at such angles is half of that at the more commonly used position of 90° (which is the optimum angle for photon-induced X-ray emission as the background from the Compton peak due to the exciting radiation is at a minimum (Dyson 1973a)).

The surface-barrier detector, which is used to detect protons and heavier particles, is placed at 165° to the beam direction. This is as large an angle as is feasible in the present system. It will be shown in Appendix C that the larger the scattering angle, the greater is the mass resolution in RBS. A wheel, which can be rotated from outside the chamber, allows a $^{148}\text{Gd}/^{241}\text{Am}$ alpha-particle energy calibration source, or a set of absorbers, to be positioned in front of the detector.

4.2.2 Vacuum system

The system was designed to be as oil-free as possible. This is to prevent a large build-up of carbon on the targets which, although not affecting PIXE spectra very much, would cause 'shifts' in energy in the particle spectra. Also, carbon has a low threshold for many nuclear reactions, the reaction products of which could produce interferences in the particle spectra.

The vacuum chamber was initially pumped down to 1 Pa with a rotary pump. A liquid nitrogen trap and a flexible electrically insulating tube between the pump and the chamber prevented oil and mechanical vibrations reaching the main system which was electrically isolated. High vacuum ($10^{-4}$ Pa) was achieved with a turbomolecular pump attached to the bottom of the chamber through a gate valve. The Van de Graaff beam line was also evacuated with this type of pump. Satisfactory vacuum for PIXE analysis was typically achieved in 10 minutes. Once high vacuum was achieved, the cryoshielding could then be made operational by filling the liquid nitrogen dewar (see Fig. 4.2.1.b).
4.2.3 Target holders

Target holders were designed so that the sample to be analysed could be positioned accurately with respect to the beam and could also be changed (or moved) without opening up the target chamber. The most stringent requirement was for the analysis of the air particulate 'streak' samples described in Chapter 6. The beam had to remain within the width of the streak and be moved in steps of 2 mm from a known starting position with high accuracy. In the earlier work (Barfoot et al. 1978, Barfoot et al. 1979), this was achieved with a modified mechanical vacuum feed-through with attached Vernier system. Apart from the fact that the positioning was not as accurate as would have been wished, its operation was extremely tedious.

A new target holder system, which was based on a modification of an existing goniometer, was devised. The drive responsible for the circular motion of the goniometer, shown in the bottom left-hand corner of Fig. 4.2.3.a, was extended to the top of the goniometer where the motion is converted by 90° and the drive connected to the target holder. The gearing from the drive of the stepping motor is such that each step produces a vertical motion of the target holder equal to 0.2 mm. The total distance that can be moved is about 100 mm; the physical limitation being due to the table supporting the goniometer. The stepping motor is controlled from the Van de Graaff control room. This permits fast and accurate repositioning of the targets and allows the possibility of the entire data acquisition and sample changing being controlled by a computer system. This is envisaged at the CBNM in the near future.

As can be seen from Fig. 4.2.3.b, the central region of the target holder is made of perspex. This is to insulate the targets from the chamber so that ion beam currents to the targets may be measured. Perspex was chosen because it produces low X-ray backgrounds due to the very low atomic number of the elements of which it is composed. These perspex pieces are easily removed and were designed according to the nature of the samples to be analysed. The one shown is for the 11 mm diameter targets used for the PIXE cross-section measurements.

4.3 Ion beam fluence measurements

Measurements of ion beam fluence, together with the determination of the efficiency of the Si(Li) detector (see section 4.4.5), were the largest sources of experimental uncertainty in the absolute PIXE studies.
Fig. 4.2.3a  Contents of the vacuum chamber viewed from behind the goniometer.

1. Si(Li) DETECTOR
2. POLYETHYLENE ABSORBER
3. LIQUID NITROGEN COOLING
4. FOIL MONITOR
5. SYSTEM FOR CHANGING CALIBRATED FOILS
6. SURFACE-BARRIER DETECTOR
7. WHEEL WITH Am/Gd SOURCE AND ABSORBERS
8. GONIOMETER
9. MODIFICATION FOR TARGET HOLDER MOVEMENT
10. CONDUCTING STRIP

Fig. 4.2.3b  Contents of the vacuum chamber viewed from the beam direction.

1. ELECTRON SUPPRESSOR (NOTE COVERING OF GRAPHITE PAPER)
2. 11mm DIAMETER TARGET POSITIONS
3. PERSPEX INSULATING SUPPORT FOR TARGETS
4. TO CURRENT INTEGRATOR
As can be seen from Chapter 3, an accurate knowledge of the total number of particles incident on the target is required. This may be for widely differing targets.

In principle, one of the most straightforward methods of determining this particle fluence is to integrate the primary ion beam current assuming that the charge state of the particles is known. However, when fast ions impinge upon a solid target, complications arise, due to the production of secondary and tertiary currents, which make accurate current integration a non-trivial task. The magnitude and characteristics of these currents have recently been closely examined by Matteson et al. (1979). Fig. 4.3.1, taken from their paper, illustrates a simple current integration arrangement and the currents that can exist. The incident primary ion beam \( I_1 \) may be accompanied by incident electrons \( I_e \) which originate at the collimator slits or other electron sources. As the incident ions impinge on the target, various secondary currents are generated: secondary electrons are ejected from the target surface \( I_{ie} \), a flux of photons of energies ranging from eV to keV is observed \( \eta_{i\phi} \), backscattered and sputtered ions produce a current \( I_{ii} \) while a flow of neutral metastable atoms \( \eta_{in} \) is also found. When each species of secondary particle encounters the surrounding wall, 'tertiary electrons' are produced. Thus the current actually measured \( I \) by the current integrator is the sum of all these currents i.e.

\[
I = I_1 - I_e + I_{ie} - I_{ii} - (I_{ie}^e + I_{ii}^e + I_{in}^e + I_{i\phi}^e)
\]

where first subscripts indicate the primary species, second subscripts the secondary species and superscripts the tertiary electrons (Matteson et al. 1979).

\( I_e \) can be reduced to negligible proportions (e.g. from 4% to 0.4%) by the use of a shield biased to about -100 volts (Matteson et al. 1977) but \( I_{ie} \) is very difficult to remove. Not only is this current a function of target species (Dearnaley et al. 1973) but it also varies as the secant of the angle that the normal to the target surface makes with the beam (Sternglass 1957). \( I_{ie}/I_1 \) is typically 0.5 for 2 MeV protons and 2 for He\(^+\) beams when no secondary electron suppression is used. This is clearly a complex experimental problem to overcome.

It is often the case that details of these secondary currents are ignored and a Faraday cup arrangement is used. The normal Faraday cup is based on two assumptions: that all secondary currents form loops inside the cup (i.e. it is a 'black box') and that only the ion beam enters the cup from outside. The first requirement can only be approx-
Fig. 4.3.1 Schematic of typical charge integration arrangement and possible ion and electron currents flowing. (From Matteson et al. 1979).
imated. Even when the target is inside the Faraday cup, entrances and exits must be made for the ion beam and detected radiations, thus allowing charged particles to escape. It is often customary for the cup to be placed behind 'semi-thin' targets such as air pollution samples. In this case the beam that enters the Faraday cup is not necessarily the same as that impinging on the target. For instance, a 2 MeV He⁺ beam will become mostly He⁰⁺ after passing through the target. This charge exchange effect, and multiple scattering, can make the measured fluence in error by a factor of two or more (see later in this section and Chapter 6). Whilst secondary electron suppression can effectively remove most of I_e, it can do nothing to correct for the change in the nature of the beam as it passes through the target. The second assumption requires that the electron current, I_e, be removed. Although as stated previously, this can be reduced to negligible proportions (although most workers seem to ignore this problem - see the review by Johansson et al. (1976)), there are still the electrons that may be produced in and around the target. Even with a very careful experimental system, the most accurate current integration so far achieved is claimed (see concluding remarks to section 4.3.3) to have an uncertainty of ±1% (Matteson et al. 1979). A more typical current integration system is likely to produce uncertainties an order of magnitude higher in the measurements of ion beam fluence.

In view of these difficulties with current integration, two other methods of ion beam fluence measurements have been utilised. Both of these rely on ion elastic backscattering for which cross-sections are accurately known. When the particle detector solid angle, scattering angle and the target thickness are also known, the fluence may be calculated. The two methods are target elastic backscattering and the foil ion beam monitor. For most of the ion beam experiments performed in the present work, a combination of these three techniques has been used with the expectation that more accurate results are thereby obtained. The particular combination used in each experiment will be discussed in the relevant section. The three methods of ion beam fluence measurement will now be described in detail and comparison made between them in section 4.3.3

4.3.1 Ion beam current integration

This was achieved by integration of the current measured on the target (when an electrical conductor) or by the use of a Faraday cup
The targets were surrounded by a secondary electron suppressor shield held at -400 volts (see Fig. 4.2.1.a). The Faraday cup, also shown in Fig. 4.2.1.a, had an annular electron suppressor, held at a similar negative potential, surrounding the entrance to the cup. The Faraday cup was only used for PIXE studies of thin samples such as the air pollution streaks. These currents were integrated using a Brookhaven Instruments Corporation current integrator. This device has a very low input impedance (20 Ω) which is important in preventing the target or Faraday cup from becoming positively charged. This would attract electrons and hence produce a low reading. The manufacturers claim an uncertainty of ± 0.02 % in the absolute accuracy of calibration. This uncertainty is negligible when compared to that incurred when converting measured charge to ion beam fluence (see especially equation 4.3.1).

When the monitor foil is between the beam line and the target, or when a Faraday cup measurement is made behind a thin target, corrections for electron exchange must be made. Armstrong et al. (1976) have measured the equilibrium charge-state fractions for helium and hydrogen beams of 0.2 to 6.5 MeV in gold foils. Least squares fitting to their results gives, for the case of helium, the ratio of singly ionised \( F_1^\infty \) to doubly ionized \( F_2^\infty \) charge states:

\[
\frac{F_1^\infty}{F_2^\infty} = (0.284 \pm 0.005) e^{-(2.13 \pm 0.01)}
\]

where \( E \) is the energy of the beam in MeV. Thus for 2 MeV \(^4\text{He}^+\) ions, the measured charge has to be divided by 1.94 and the resultant additional uncertainty in the ion beam fluence is ± 3 %. The number of neutrals is negligible. For the present energy range of interest, the protons retain their single positive charge.

Intercomparisons of the various methods of measuring beam fluences for individual experiments may be found in Chapters 5 and 6. When analysing the streak air particulate samples, the Faraday cup results were found to be too low by about a factor of two. This is thought to be due to multiple angular scattering in the 'semi-thin' air filters and is further discussed in Chapter 6.

4.3.2 Elastic backscattering from the target

When a target with a surface layer of known areal density is used in, for example, PIXE cross-section measurements, the ion beam fluence
may be calculated from the number of backscattered particles when the particle detector solid angle, scattering angle and scattering cross-section are known or can be measured. This is the same method, in principle, as that used in the foil ion beam monitor with the same RBS equations applying (see section 4.3.3). However, with the larger target-to-detector distance, the determination of the angle of scatter and the solid angle is more accurate. The major sources of uncertainty are target mass thickness (typically ± 0.5 % to ± 1 %), solid angle determination (± 0.5 %) and counting statistics during the measurement of the backscattered particles (typically ± 1 % to ± 3 %). Thus, with a typical overall uncertainty of ± 2 % to ± 4 %, this method of ion beam fluence measurement is the most accurate available to us. This method only works for targets of known areal density. However, if it is used in conjunction with the foil ion beam monitor, then the monitor can be calibrated and used during analyses of unknown targets. It was found during the analyses of the streak samples that the backscattering signal from the filter material was a reliable relative method of normalising the spectra from sequential irradiations. This is discussed in more detail in Chapter 6.

4.3.3 The foil ion beam monitor

4.3.3.1 The principle

The main aim of constructing the foil ion beam monitor was to achieve ion beam fluence measurements which are totally independent of the nature of the target and the charge state of the ion beam. This is especially important for insulating or semi-thin targets where the current integration methods fail. The present monitor allows very precise comparisons of yields between sequential irradiations on a wide variety of different targets. The major application so far has been to the PIXE analysis of the streak air particulate samples. The first prototype was built in 1978 (Mitchell et al. 1978b) and the second, more sophisticated version, a year later (Mitchell et al. 1980a).

The principle of the method is quite straightforward and is illustrated in Fig. 4.3.3.a. A thin calibrated self-supporting foil is placed between the beam line and the target. The foil is made thin enough to permit all the beam to pass through without appreciable energy loss. Energy losses can be corrected for; but, the larger the energy loss, the greater is the uncertainty in the beam energy due to energy straggling effects. Similarly, angular straggling must be kept small.
Fig. 4.3.1a  Ion beam monitor arrangement.
so as to ensure that all the transmitted beam reaches the target within a reasonable spot size (e.g. for the streaks the spot size must be less than 2 mm). For ion beam monitoring, the ions backscattered from the foil are counted with an annular surface-barrier detector placed 4 cm 'upstream' of the foil.

The ion beam fluence, i.e. the number of projectiles (Q), passing through the calibrated foil is calculated from the following backscattering equation (see Appendix C):

\[
Q = \frac{A}{\Delta\Omega \left( \frac{d\sigma}{d\Omega} \right)_{E,\theta} N}
\]

(4.3.3)

where \( A \) is the number of backscatter counts from the foil as measured in the annular detector,

\( \Delta\Omega \) is the solid angle in steradian that the annular detector subtends at the foil,

\( \left( \frac{d\sigma}{d\Omega} \right)_{E,\theta} \) is the backscattering differential cross-section, in cm\(^2\) per steradian, calculated at the mean energy of the ion beam as it passes through the foil, and

\( N \) is the foil thickness in atoms per cm\(^2\).

For use as a relative comparator, only \( A \) need be measured and all experimental runs on different target normalised to this. When an absolute value of \( Q \) is required, then \( Q \) may be determined when \( \Delta\Omega \), \( \left( \frac{d\sigma}{d\Omega} \right)_{E,\theta} \) and \( N \) are accurately known. The Rutherford backscattering cross-sections must be corrected for deviations due to electron screening effects as has been noted by l'Ecuyer et al. (1979). It must also be remembered, when using this monitor for ion beam studies, that the energy of the beam at the target under investigation must be corrected for the energy loss in the monitor foil.

Gold was chosen for the foil material as it has a high backscattering cross-section, is well resolved from the low Z contaminants such as carbon and can easily be prepared in uniform thin layers by evaporation techniques. Target preparation details are given in section 4.6. The foils were self-supporting over a diameter of 4 mm and were produced in the range 40 to 400 \( \mu \)g cm\(^{-2}\) in order to determine the optimum thickness.

Carefully made and aligned apertures prevent any backscattered ions from the target from reaching the annular detector. However, the ions which have been backscattered from the interposing calibrated gold
foil enter the sensitive region of the annular detector by means of which they are energy analysed. The signal is amplified in the normal way and an energy window is accurately set over the spectral peak due to the gold foil with the aid of a precision pulser and a ratemeter. The number of pulses in this window is counted in a scaler. A compromise between good counting statistics and low pile-up effects is necessary if good precision is to be achieved in a relatively short analysing time. A count-rate of about 500 s\(^{-1}\) has been found to be optimum.

4.3.3.2 Sources of uncertainty

i) Backscatter angle determination. This could be measured with an uncertainty of \(\pm 2\%\). However, as the backscattering cross-section varies so slowly with angle at 165°, the contribution to the uncertainty in the cross-section was negligible.

ii) Solid angle determination. The solid angle subtended at the centre of the foil by the annular detector was measured by replacing the foil with a thin open calibrated \(^{241}\)Am spot source evaporated onto a platinum backing. Counting statistics of this measurement gave an uncertainty of typically \(\pm 0.25\%\) in the solid angle. However, it should be noted that a 0.1 mm displacement in the distance between the source and detector would result in a 0.5 % change in the solid angle and so great care had to be taken in positioning both the source and the foil. A systematic uncertainty of \(\pm 0.25\%\) was introduced into the solid angle determination due to the wrinkling of the foil under irradiation. Thus, the total uncertainty in the solid angle determination is estimated to be \(\pm 0.5\%\).

iii) Statistical uncertainties. The number of counts accumulated in the energy window should be sufficiently large to reduce this uncertainty to the required accuracy. This was one of the reasons for choosing the high Z element gold where the backscattering cross-section, which is proportional to \(Z^2\), is large. For the streak runs this uncertainty was less than \(\pm 1\%\) but for some of the cross-section measurements on thick targets, where very low currents were used (e.g. 50 pA), it was as high as \(\pm 3\%\).

iv) Beam energy. The uncertainty in the energy of the projectile beam produced an uncertainty of \(\pm 0.2\%\) in the backscattering cross-section.

v) Beam energy loss and straggle in the foil. In order to minimise energy loss and straggling effects, the thinnest self-supporting foils
were chosen. However, a compromise must always be made between this criterion and the stability and life-time of the foils. Foils of 80 \( \mu g \text{ cm}^{-2} \) (about 42 nm) were found to fit these requirements best. The thinner foils were found to be too unstable to mechanical shocks. The energy loss in an 80 \( \mu g \text{ cm}^{-2} \) gold foil is 14 keV for a 2 MeV \(^4\text{He}\) beam (Ziegler 1977) and 2 keV for a 2 MeV \(^1\text{H}\) beam (Andersen et al. 1977). The energy straggle is calculated to be 2.7 keV and 1.4 keV for 2 MeV \(^4\text{He}\) and \(^1\text{H}\) ions (Mayer et al. 1977), although recent experimental results (Hoffman et al. 1976, Werz et al. 1979) indicate that these values may possibly be about 20\% too low. As the shape of the energy distribution is essentially Gaussian, the effective energy of the beam from the point of view of backscattering and PIXE cross-sections will be that of the peak value. As the energy resolution of the surface-barrier detector is about 15 keV FWHM, the increase in beam energy width will not significantly affect backscattering analysis.

vi) Foil-induced angular straggle of the beam. There is an angular stragglng of the beam, as well as an energy stragglng, when it passes through matter (see Appendix C). This multiple angular scattering has been treated in several papers (e.g. Spahn et al. 1975, Cline et al. 1969 and Sakisaka et al. 1970). Calculations based on the results of these papers predict that the FWHM angular spreading of a 2 MeV \(^4\text{He}\) beam passing through a 80 \( \mu g \text{ cm}^{-2} \) Au foil is less than \( \pm 0.25^\circ \). In the present geometrical arrangement, the distance from the foil to the target position is approximately 100 mm and so a beam spot of 1.0 mm at the foil should be spread to about 1.8 mm FWHM at the target. The angular divergence has been observed by scanning a vanadium strip in 0.2 mm steps across the beam. The strip was 0.2 mm wide and 9 mm long (i.e. longer that the total width of the spread beam) and was produced by evaporating vanadium onto a polished vitreous carbon disc. The counts from a single channel analyser (SCA), with energy windows set over the vanadium backscattering peak, were used to measure the intensity variations across the scan. Fig. 4.3.3.b shows the results of this scan for a variety of beams with and without the foil present. Dearnaley et al. (1973) have produced tabulations relating areas under sections of Gaussian curves to the normalised heights of the distribution at the points of interest. Making the approximation that the beam spreading is Gaussian, it is found that 94\% of the 2 MeV proton beam is within a width of 2 mm (the streak width) whereas only 84\% of the \(^4\text{He}\) beam is within this width. If the beam is not exactly in the centre of the streak then more intensity will be lost. For example, if the beam
Fig. 4.3.3.b  Determination of straggled beam diameter.
is off-centre by 0.5 mm then only 74% of the $^4\text{He}$ beam and 87% of the proton beam will be within the streak deposit. Thus the $^4\text{He}$ beam would yield PIXE results, for the streak sample, that are too low by 26%. It is clearly advantageous to use a proton beam. With samples of significantly larger surface area, the loss of intensity will be negligible. However, this widening of the beam will cause the beam spot on the target to become large enough to change the solid angle that the radiation detectors subtend. Therefore this effect would have to be carefully calculated if the detector(s) subtended a large solid angle to the target (not the case in the present work).

vii) Beam current fluctuations. These should have no effect, in contrast to an oscillating or beam chopping method, as all the beam passes at all times through the foil.

viii) Foil thickening and rupture. This is a complex problem which, until recently, has received little attention. Most of the work has been performed with thin ($10 \mu\text{g cm}^{-2}$) carbon foils because of their use as ion beam strippers. Although evidence for changes in metal foil thickness under irradiation has been found (Donnelly et al. 1979, Scanlon 1979, Mertens 1979), no quantitative data from other laboratories is presently available. For this reason, the carbon foil data will be discussed in some detail in order to suggest an explanation for the behaviour of the gold foils.

Studies of the behaviour of carbon stripper foils have been made under widely varying experimental conditions (Dumont et al. 1976, Livingstone et al. 1978, Sander et al. 1979, Tait et al. 1979). Perhaps the most comprehensive study is that of Tait et al. They bombarded carbon foils of areal density 5-20 $\mu\text{g cm}^{-2}$ with 4.8 MeV Ar ions. The visual appearance of the foils after irradiation was very similar to that observed for the gold foils irradiated with 1-3 MeV protons, deuterons and helium ions in the present work. Fig. 4.3.3.c shows a photograph of one of the present gold foils after it has been irradiated for less than one hour with a 1 mm diameter $^4\text{He}$ beam of 20 nA. Previous to beam irradiation, the foil was quite flat. After irradiation a radial wrinkled stress pattern is clearly seen over the foil except where the beam has struck.

The following phenomena are thought by Tait et al. to take place during irradiation of the thin carbon foils. Radiation enhanced diffusion processes cause a shrinkage (thickening) within the irradiated area. This is at first accommodated by the removal of undulations and
Fig. 4.3.3.c  Photograph of gold foil after irradiation with a 1mm diameter helium ion beam.
then by elastic strain (the radial wrinkling). The foil eventually ruptures (usually at the boundary of the irradiated area) due to the limit of the ultimate tensile strength being surpassed. As similar stress patterns are observed in the gold foils, it is assumed that a similar mechanism is responsible for the 'thickening' and rupture of the gold foils. The actual results for their life-times may be orders of magnitude different from carbon foil life-times due to differences in tensile strength and morphology. Livingstone et al. (1978) found that carbon foil life-time was independent of foil thickness over the areal density range 2-22 \( \mu g \text{ cm}^{-2} \) and that it is primarily related to the nuclear stopping power and energy of the projectile beam. Simple scaling from their results indicates that the mean life-time of the gold foils would be about 600 hours for the present beam conditions. Up to the present time, only one foil has been broken in the beam. This was after 60 hours of use. Several other foils have run 120 hours without breakage. However, great care must be taken in handling these foils as mechanically they are very fragile. In particular, the initial pump-down and opening up to atmospheric pressure of the vacuum system must be made slowly if rupture of the foils is to be avoided. It is estimated that about 10 foils have been broken in this manner over a period of 18 months.

A more worrying aspect of this problem would be the possibility of partial foil fracture. If, for example, only a small slit was produced in part of the foil being irradiated, this may not be detected. For this reason it is worthwhile to run standard targets every so often as a check.

Besides being the cause of the foil rupture, the foil 'thickening' causes another problem. In equation 4.3.3, which is used for converting monitor counts to ion beam fluence, it was assumed that the areal density was the original one at the time of weighing. Thus a large change in a foil's thickness would be a serious source of error in the results of the foil ion beam monitor. In future, it is planned to measure this 'thickening' by using the method of Werz et al. (1979) which determines the thickness of thin foils by determining the energy loss of \(^{148}\text{Gd}\) alpha-particles traversing them.

ix) Carbon build-up. In most ion beam experiments, carbon build-up on the targets during irradiation can be troublesome. This is particularly so in RBS experiments where a shift in peak position of the element of interest occurs as carbon accumulates on the surface of the target during analysis. In the present case, where the yield from ions back-
scattered from the gold calibrated foil is used as a monitor, the carbon build-up effect can produce significant errors. Firstly, it alters the position of the gold peak with respect to the SCA window set at the beginning of the experimental run and secondly the backscattering cross-section for the gold foil moves towards higher values as the beam loses energy in the growing carbon layer. For \(^4\)He ions of 2.0 MeV energy and a scattering angle of 165°, the backscattering cross-section for gold changes by about 1% for each 10 keV energy loss in the growing carbon layer (that is for about every 12 \(\mu g\) cm\(^{-2}\) of carbon). The energy loss will be less for lighter ions. The carbon build-up effect has been investigated recently by Dumont et al. (1976) and the rate of accumulation was found to depend on the energy and current density of the bombarding ions as well as upon the conditions of vacuum during the experiment. The amount of carbon was directly measured in the present work by occasionally putting the amplified output signal from the annular detector directly into the multichannel analyser (MCA) instead of the SCA (see spectrum of Fig. 5.3.1.d).

4.3.3.3 Results

For the present purposes, the most practical parameters for the routine use of the calibrated foil ion beam monitor were found to be those given in Table 4.3.3. If different ions and energies were to be used, a different choice of conditions would probably have to be made in order that a reasonable count-rate be achieved without too large an angular straggle in the beam. Typical expected uncertainties (excluding the foil thickening effect) are about ± 2%.

Table 4.3.3.: Parameters found most practical in calibrated foil beam monitor method

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Foil type</td>
<td>Gold</td>
</tr>
<tr>
<td>Foil thickness</td>
<td>80 (\mu g) cm(^{-2})</td>
</tr>
<tr>
<td>Beam species</td>
<td>(^4)He and (^1)H</td>
</tr>
<tr>
<td>Beam energy</td>
<td>1.0 to 3.0 MeV</td>
</tr>
<tr>
<td>Beam current</td>
<td>0.5 - 2.0 nA</td>
</tr>
<tr>
<td>Beam diameter</td>
<td>1.0 mm</td>
</tr>
<tr>
<td>Solid angle of foil to annular detector</td>
<td>10 - 20 msr</td>
</tr>
<tr>
<td>Counts per second in annular detector</td>
<td>400 - 600 cps</td>
</tr>
</tbody>
</table>
An intercomparison of the three methods of measuring beam fluences was carried out to test for any systematic differences. The values for ion beam fluence, as determined from elastic backscattering analysis of a standard target, have an accuracy of \( \pm 3\% \) whilst the current integration measurements (corrected for electron exchange as described in section 4.3.1) are thought to have an uncertainty of about \( \pm 5\% \) for protons and \( \pm 8\% \) for \(^4\text{He}^+\) ions. In all, about 70 measurements of ion beam fluence using the three techniques were made for protons, deuterons and \(^4\text{He}^+\) ions in the energy range 1-3 MeV. Values representing a broad range of energy and fluence are given in Fig. 4.3.3.d. The curves represent least squares fittings of the data to straight lines. It can be seen that all lines pass through the origin as would be expected. The foil monitor and target backscattering values are plotted as the abscissa as these were expected to be the more accurate.

Line A is a plot of measured integrated charge vs target backscattering values from a bismuth implanted silicon standard (Mitchell et al. 1978a) for proton and \(^4\text{He}^+\) beams. The measured charge is 1\% higher than that predicted from the target backscattering. This is very good agreement for two totally independent methods and indicates that, perhaps, the uncertainty of the charge measurements has been over-estimated although such agreement could be fortuitous. The 1\% excess may be due to incomplete suppression of secondary electron emission.

Line B is a plot of measured integrated charge vs foil monitor values for proton and deuteron beams. The measured charge is 5\% lower than the foil value, indicating that the proton and deuteron foil monitor values are about 6\% higher than the target backscattering values.

Line C is the same as line B except that \(^4\text{He}^+\) has been used. The foil monitor values are 8\% higher than the target backscattering values. The difference between the \(Z = 1\) and \(Z = 2\) particles could be due to the correction for electron stripping effects for \(^4\text{He}^+\) which has an uncertainty of \(\pm 3\%\).

Line D is the same as line A except that a previously irradiated gold monitor foil has been used at the target position with a \(^4\text{He}^+\) beam. Lines C and D almost (to within 0.5\%) overlap. This strongly indicates that the major source of discrepancy between the monitor and the other results is the 'thickening' of the gold foil. It is tentatively suggested that, for the present conditions, the foil thickens by \((7 \pm 2)\%\). Tait et al. (1979) found that their standard (i.e. not slackened) carbon foils thickened by 10 to 20\%. Thus the presently
Fig. 4.3.3.d Charge calculated from calibrated foil monitor and reference targets compared with charge measured in current integrator (corrected for $^4\text{He}^{++}$ to $^4\text{He}^+$ ratio).
observed 'thickening' is consistent with these carbon data. If the 'thickening' of foils can be accurately measured and is reproducible, then this source of uncertainty could largely be removed. However, at present, it remains the largest source of uncertainty in the method.

All three ion fluence measurement techniques have been shown to agree to within 8%. This is very promising. The lowest uncertainty so far claimed for such a technique is ±1% for the current integration set-up of Matteson et al. (1979). However, this claim is based upon measurements of a gold standard layer (Lindstrom et al. 1978). Recently l'Ecuyer et al. (1979) have measured a thickness value for this film which is different by 4%. This standard and the results of Matteson et al. therefore need further verification. With more typical current integration methods producing uncertainties of about ±7% (Dyson 1973b), it can be seen that the foil ion beam monitor is already in competition with the more standard techniques.

Whilst the absolute results presented are of a preliminary nature, the method of using a calibrated foil to monitor the ion beam fluence seems to be good. In particular, for insulating targets and for situations where electron suppression at the targets cannot be made, this method should prove extremely useful. If the absolute values from the monitor are not thought to be reliable due to systematic uncertainties, then the values can be normalised by placing a standard target at the target position and counting the elastically backscattered particles in a known geometrical arrangement. The advantages of using such a monitor during the analysis of streak air particulate samples are discussed in detail in Chapter 6.

4.4 The Si(Li) low energy photon detector

As has been mentioned in Chapter 2, it was the development of the high resolution lithium-drifted silicon, Si(Li), detector which triggered off the field of materials analysis by PIXE spectroscopy. With resolutions typically as low as 150 eV full-width at half maximum (FWHM) at 6 keV it is now, in principle, possible to resolve the K X-rays of all elements with atomic number greater than six. This high energy resolution capability, coupled with good total detection efficiency, has enabled very good detection limits to be achieved by energy-dispersive means. The features of the particular detection system presently used will be outlined and the method and results for the full-energy peak detection efficiency determinations discussed in detail.
4.4.1 Principle of operation

In essence, a Si(Li) detector consists of a disk of silicon with a potential applied between its parallel faces. When a photon enters this essentially non-conducting material, the silicon is ionized by energetic recoil electrons resulting in the creation of electron-hole pairs. The number of pairs created is proportional to the energy of the photons. This charge is swept-out by the applied potential forming a charge pulse characteristic of the detected photon. The lithium atoms are drifted into the silicon crystals in order to neutralise the effect of impurities and thereby effectively create intrinsic material of high resistivity. Detectors with resolutions less than 200 eV FWHM were first developed in 1969 (Aitken et al. 1971). The major advances in recent years have been in the preamplifiers attached to these detectors. The charge sensitive pulsed optical feed-back preamplifier provided with the present detector allowed a resolution of 144 eV at 5.95 keV to be achieved.

Ge(Li) detectors have a higher efficiency but generally poorer resolution for X-rays. Another disadvantage with these detectors is the presence of a strong discontinuity in the efficiency at 11.1 keV due to the K absorption edge of the germanium in the dead layer on the surface of the crystal. One problem with both Si(Li) and Ge(Li) detectors is that they have to be operated at liquid nitrogen temperatures to reduce the 'noise' current due to thermally generated charge carriers. Recent work indicates that CdTe and HgI₂ detectors, which can be operated at room temperature, show much promise for the future (see the review by Whited et al. (1979)).

Details of Si(Li) detector construction and operation will not be given as they are covered in many good reviews (e.g. Ewan (1979), Goulding (1977), Aitken et al. (1971), Woldseth (1973) and Bertoloni et al. (1968).

4.4.2 Characteristics of the present system

Manufacturer's specification for the detector:

<table>
<thead>
<tr>
<th>Make</th>
<th>Kevex Corporation, California</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si(Li) crystal area</td>
<td>10 mm²</td>
</tr>
<tr>
<td>Si(Li) crystal depth</td>
<td>3 mm</td>
</tr>
<tr>
<td>Be window thickness</td>
<td>7.6 μm</td>
</tr>
</tbody>
</table>
Distance of front face of crystal from Be window : 6.5 mm
Distance of Be window from end of probe : 2 mm

FWHM resolution at 5.9 keV with 2 μs time constant = 160 eV

8 μs = 144 eV

(the above resolution measured at 1000 c.p.s.)

Electronics:

Amplifier : Canberra X-ray Spectroscopy Amplifier Model 1713
ADC and MCA : Laben 4096 multi-channel analyser system
Data storage system : Spectra transferred to disk storage from which spectra may be directly analysed with the IBM 370 computer

In addition to the above, commonly used nuclear electronics such as SCA's, scalers, a pulse generator etc. were utilised. The actual uses of the electronics will be discussed in the relevant sections.

Due to rise time protection limitations on the input to the ADC, a time constant of 2 μs had to be employed in the amplifier as a pulse-stretcher was not available. For this reason, the Si(Li) detector was not utilised at its optimum resolution. The linearity of the amplifier and ADC was checked with the aid of an Ortec Research Pulse Generator (Model 448). The only indication of non-linearity over the 4096 channels was in the last 300 channels which were never used. In addition, the total Si(Li) and ADC system linearity was checked during PIXE analyses and it was found that the X-rays were always at their expected energies (to within experimental uncertainties). The maximum energy (voltage) drift in the system was found to be 3 channels at channel number 1000. However, in any 8 hour period, the drift was only found to be about 1 channel and the drift followed slowly varying trends. It was thus a simple matter to calibrate the energy gain of the system on a daily basis. With the usual gain settings resulting in 10 eV per channel, this drift was found to be insignificant.

4.4.3 Spectrum analysis

X-ray spectral analysis was achieved with the programme RETEOH which is a modification (Reher 1978) of the programme CUTIPIE developed by Teoh (1973). This programme accurately determines the positions, widths and areas of photopeaks recorded with semiconductor detectors.
It uses the numerical second difference method for automatic peak searching and the method of least squares for the peak fitting. Up to a maximum of six peaks can be unfolded from an overlapping group of lines. Uncertainties, at the 1σ level, are given on the three peak parameters. Because of the symmetry of the peaks found in the present detector, it was found to be advantageous to use the simple version of the programme which consists of a Gaussian peak shape on a straight line background. The programme was found to give its most accurate fits with spectra of about 10 channels FWHM resolution. The only input required was an estimate (to ± 20 %) of the detector resolution. Therefore spectral analysis was simple and fast (< 1 minute computer time per spectrum).

The programme ANGELA (Bastian 1980) was used for the general manipulation of spectra in such operations as addition, subtraction, normalisation and contracting (e.g. changing spectra with FWHM of 40 channels to 10 channels for analysis by RETEOH). The importance of good computer handling of PIXE spectra should be stressed. Even with the above system, the analysis of the large number of spectra (approaching 1000) recorded during the present work required a great deal of time and management.

4.4.4 Detector resolution

As has been mentioned, it is the high resolution and good total efficiency of Si(Li) detectors which makes them ideal for X-ray micro-analysis. Fig. 4.4.4.a, taken from Aitken et al. (1971), compares this resolution with that obtainable with typical proportional counters and NaI detectors. The latter two detectors are clearly unsuitable for multi-element X-ray analysis as, for example, there is only an energy
Fig. 4.4.4a Comparison of the response of various energy dispersive X-ray detectors to the manganese X-ray spectrum resulting from the decay of $^{55}$Fe.
(from Aitken et al. 1971)

Fig. 4.4.4b Measured FWHM resolution for the present Si(Li) detector.
separation of about 500 eV between the Kα X-rays of manganese and those of its neighbours in the periodic table.

The resolution has been measured to within ±5% with the present system using radioactive sources and PIXE and is shown in Fig. 4.4.4.b. No systematic difference was observed for the two cases. The total resolution is the sum, in quadrature, of the intrinsic and electronic noise effects (Woldseth 1973):

\[ \text{FWHM} = \left[ (2.35 \left[ \frac{\text{F}}{\text{E}} \right]^{1/2})^2 + (\text{FWHM}_{\text{noise}})^2 \right]^{1/2} \]

where \( \text{F} \) is the Fano factor (0.1)
\( \text{E} \) is the photon energy in eV
\( \epsilon \) is the average energy required to create an electron-hole pair in silicon at liquid nitrogen temperatures and equals 3.9 eV.

All FWHM's are expressed in eV. The curve in Fig. 4.4.4.b represents the theoretical resolution corresponding to 180 eV FWHM at 5.9 keV (i.e. an electronic noise of 140 eV). This appears to be a slight under-estimation of the true FWHM although it should be remembered that most of these lines are in fact doublets (Kα1,α2 etc) which will cause some extra broadening. When the detector was bought two years ago, the resolution was found to be in agreement with the manufacturer's specifications. Thus the resolution has worsened by about 12% in two years. This may be due to radiation damage or a drifting out of the lithium from the silicon. Worsening of detector resolution over this order of time has been reported by other workers (e.g. Hansen et al. 1973).

The only energy dispersive detector that has superior resolution appears to be the gas proportional scintillation counter (Alice et al. 1975). Although its resolution is superior for very low energy X-rays, it soon becomes inferior at higher energies. For example for C, Al and Mn K X-rays its resolution is 100, 230 and 472 eV compared to 145, 160 and 185 eV for the present Si(Li) detector. Wavelength dispersive detectors have a much better resolution (tens of eV) but much poorer efficiency than Si(Li) detectors. Techniques of wavelength dispersion have been discussed by Liebhafsky et al. (1972) and Berthelot (1976).
4.4.5 The full-energy peak detection efficiency

As was discussed in Chapter 3, the absolute determination of photon intensities requires an accurate knowledge of the detection efficiency. This efficiency, which varies with photon energy and is different for all detectors, is difficult to determine accurately. Only the full-energy peak is of interest as the low energy tail is not readily measurable when more than one photon line is present. This efficiency can be broken up into two parts, that is, into the geometrical efficiency ($\Delta \Omega /4\pi$) and the intrinsic efficiency ($\epsilon$). $\Delta \Omega$ is simply the solid angle that the sensitive region of the detector crystal subtends at the source of photons. $\epsilon$ is the probability that a photon entering the detector produces sufficient ionization for the output pulse to fall within the corresponding full-energy peak.

Above about 15 keV, $\epsilon$ is determined mainly by the photo-electric process. Small additional contributions to the full-energy peak can arise from various types of multiple scattering within the sensitive region. Thus the efficiency in this region may be higher than that predicted simply from the photo-electric cross-section.

Below 15 keV the crystal is expected to absorb all photons and be 100% efficient. However, the photons are attenuated before they reach the sensitive region by the beryllium vacuum window, the gold-layer electrical contact on the front surface of the crystal and a silicon 'dead layer'. The beryllium thickness is usually given by the manufacturer, but the gold and silicon dead layers are not. The thickness of the gold layer is controlled in the manufacturing process and is known to be in the region of 40 $\mu$g cm$^{-2}$ (Jaklevic et al. 1971). Unfortunately the evaporations are typically non-uniform thereby producing attenuation that is at variance with that calculated on a uniform deposit basis. The silicon dead layer is usually thought of as being due to the manufacturing process. However Goulding (1977) has suggested that this dead layer represents a fundamental limit. The explanation appears to be that some of the ionization electrons produced near the photon interaction point diffuse into the surface region where they are lost, before their motion in the collecting electric field removes them from the region of the surface. This escape of thermal electrons should not be confused with that of higher-energy photo-electrons which can escape from much deeper within the detector. Goulding determines that the dead-layer should be about 0.3 $\mu$m thick although much thicker dead-layers have been reported (e.g. 1.89 $\mu$m by Wood et al. (1971)).
The effect of these layers on the intrinsic efficiency is large at low photon energies. For example, 2 keV X-rays are attenuated 10% by 7.56 μm of beryllium, 4% by 40 μg cm⁻² of gold and 28% by a 0.5 μm silicon dead layer. Thus the unknown dead layer can dominate the low energy attenuation. As this layer appears to vary widely between different detectors, it is necessary to empirically determine the detector efficiency. The various approaches to this problem pursued by different authors will be reviewed and the reasons for the combination of techniques used for the present measurements discussed.

4.4.5.1 Approaches to the determination of detection efficiency

Hansen et al. (1973) have made an extensive experimental investigation of Si(Li) and Ge(Li) detector efficiencies. They utilised the common technique of counting photons from standardised radioactive sources for which the intensities of individual photon lines are relatively well known from the literature. For example, ²⁴¹Am is a commonly used standard. Its photon activity is found by measuring the alpha-particle emission rate and using literature values for the number of Np X-rays and γ-rays produced per decay. A variety of nuclides are employed in order to span the photon energy range of interest. The problem then arises as to the method of fitting a curve to these results. By measuring the relevant detector parameters, Hansen et al. found that the theoretical efficiency (based on these parameters) had an uncertainty comparable to that of the experimental efficiency measurements (≈ ± 3%) in the region 5 to 60 keV. Below 5 keV, the experimental efficiency relied on one point, the 3.3 keV M X-ray line of Np, which is only known with an uncertainty of ± 9% (Karttunen et al. 1971). The problem of detector efficiency calibration below about 5 keV has still not been solved adequately.

In order to build up the theoretical efficiency curve, Hansen et al. determined the source to detector distance, the beryllium window thickness, the silicon dead layer thickness and the sensitive depth and sensitive area of the Si(Li) crystal. The measurement of the above parameters requires a large investment of time and experimental equipment and is especially difficult for small Si(Li) detectors. For the typical laboratory, where the Si(Li) detector is used regularly for X-ray microanalysis, it is often not feasible to remove the detector from the irradiation chamber for a sufficient time to follow the method of Hansen et al. (1973).
In the photon energy range 50 to 1500 keV, several authors (Mowatt 1969, Paradellis et al. 1969 and Abreu et al. 1975) have shown that the efficiency of semiconductor detectors may be fitted with a simple parametric equation without recourse to detailed measurements of the detector properties. This is much more difficult to achieve at low energies (<10 keV) because of the influence of the various absorbing layers which produce rapid variations of efficiency. Also, there are discontinuities in the efficiency which are produced by the absorption edges of the gold and silicon dead layers. In addition, an extra absorber may be deliberately introduced in order to suppress the low energy part of the spectrum. This was the case for the majority of the present PIXE cross-section measurements where the use of a 44 mg cm\(^{-2}\) polyethylene absorber reduced the efficiency at 3 keV by a factor of 27. As a consequence, simple fits to the experimental data for the low energy region result in what appear to be physically unrealistic curves (see, for example, the Si(Li) efficiency curve of Campbell et al. (1972)).

Gallagher et al. (1974) and Cipolla et al. (1979) have developed a model-based efficiency calibration procedure for the photon energy range 3 to 140 keV. The essence of this model is that it utilises the fact that, for low Z elements, the photon attenuation coefficient is approximately proportional to \(E^{-2.9}\) where \(E\) is the photon energy. This does not hold near absorption edges and, for this reason, the absorption due to the gold contact is not included in the model even though the absorption due to this layer is expected to be about 8% at 3 keV. Gallagher et al. (1974) found that the low energy efficiency response was significantly lower than that predicted from theory. The most likely explanation for this would appear to be source self-absorption due to the non-negligible thickness of their drop-evaporated sources. Campbell et al. (1977) and Cipolla et al. (1976) have compared the efficiencies measured with thick (drop-evaporated) and thin (vacuum evaporated and ion-implanted) sources. Cipolla et al. found differences of up to 20%. Peterman (1972) has performed Monte Carlo calculations of photon self-absorption and found that for a disk shaped source of radius 0.5 mm and thickness 0.01 mm the 14.4 keV line of \(^{57}\)Co is attenuated by 44.2%. For lower photon energies and for practical sources which have non-uniform deposits, the self-absorption will be much higher. It is therefore necessary that very thin uniform sources be used for X-ray detection efficiency measurements.

The lack of sources emitting well-resolved lines of known intensity with energies less than 5 keV has led to several alternative approaches
being attempted. One method adopted (Rosner et al. 1975, Maor et al. 1978) involves the irradiation of thick compound targets with photons from radioactive sources such as $^{55}$Fe and $^{241}$Am. For example, $K_2SO_4$ is irradiated and the ratio of potassium to sulphur X-rays measured. The number of emitted potassium and sulphur X-rays is calculated from known photo-electric coefficients ($\mu$) and fluorescence yields ($\omega$). The difference between the measured and calculated ratio yields the slope of the efficiency curve for this region. With a knowledge of the thickness (and absorption) of the beryllium and gold layers, the silicon dead layer is determined. Rosner et al. and Maor et al. obtain self-consistent results but do not state the likely uncertainty. The uncertainties in $\mu$ and $\omega$ alone will contribute about $\pm$ 14% and inaccuracies in the knowledge of the beryllium and gold thicknesses and experimental errors are likely to make the total uncertainty in the efficiency about $\pm$ 20%. The self-consistency of the results may be fortuitous due to the fact that the difference of $\mu$ and $\omega$ from the true values is likely to vary in a smooth manner. In particular, $\mu$ near the absorption edges is less accurately known than in the continuum and chemical bonding may introduce fine structure in $\mu$ (Creagh 1979). Hubricht et al. (1977) have adopted a similar approach but utilise a variety of pure element targets in order to avoid problems caused by instability of the chemical compounds in vacuum. Their method is likely to be slightly more accurate, but it is still of insufficient accuracy to perform useful ion-induced X-ray cross-section measurements where the detection efficiency must be known to within $\pm$ 5%.

Gonzalez et al. (1979) have attempted the calibration of a Ge(Li) detector in the range 3 to 14 keV. They used X-ray fluorescence of thin targets and measured the $K_\beta/K_\alpha$ ratios. By comparing with literature values for these ratios, they obtained an efficiency curve for their detector. However, it would appear (from Fig. 1 of their paper) that their method is less accurate than the use of radionuclides. Its major use would be for energy regions where radionuclide lines with known intensities do not exist. Unfortunately, below about 3 keV, Si(Li) detectors presently have insufficient resolution to permit a determination of $K_\beta/K_\alpha$ ratios and so the method was not found useful for the present work.

The above methods may be considered as a representative sample of the available techniques. Further details of techniques utilised before 1975 may be found in the review of Campbell et al. (1975a). As a result of considerations of all these methods, it was decided that
the best approach for the present work was to rely, in the main, on calibrations with thin open calibrated radioactive sources and to fit the results with a physically meaningful curve. This method will now be discussed in detail.

4.4.5.2 Determination of geometrical efficiency

The distance from the end of the detector probe to the source/target position was measured to be \((62.5 \pm 0.3)\) mm. In order to calculate the geometrical efficiency, it is additionally required that the sensitive area and the position of the Si(Li) crystal within the probe be known. The manufacturer's value for the former is \(10 \text{ mm}^2\) and they state that the crystal to end of detector probe distance is \(8.5 \text{ mm}\). The latter distance was also experimentally determined in the present work. A special system was constructed which fitted directly onto the end of the detector probe. This allowed a 100 μCi \(^{55}\text{Fe}\) source to be mounted perpendicular to the central axis of the detector so that the source to probe distance could be varied (in vacuo) in an accurately determined manner. Spectra were recorded at each of the positions for a fixed live-time. As this particular source was essentially a point source, the count-rate followed the inverse square law i.e. \((\text{count-rate})^{-1/2}\) was a linear function of probe to source distance. The intercept with the distance axis thus yields the position of the front face of the Si(Li) as 90% of the photons are stopped within the first 0.07 mm of the silicon. This position was measured to be \(-(10.1 \pm 0.5)\) mm as may be seen from Fig. 4.4.5.2.a. The counting uncertainties were negligible compared to the distance measurement uncertainties. This result indicates that the manufacturer's specifications cannot be entirely relied upon.

Thus with a crystal to source/target distance of \((72.6 \pm 0.6)\) mm and an assumed sensitive area of \(10 \text{ mm}^2\) (based on the manufacturer's specifications), one obtains the result that for point sources the geometrical efficiency is \((1.5 \pm 0.02) \times 10^{-4}\). In order to prevent significant source self-absorption effects, all the calibrated radioactive sources were prepared as thin sources with diameters up to 9 mm. The effect of this upon the geometrical efficiency was calculated with a computer programme (Bortels et al. 1977). The results for the present geometry are shown in Fig. 4.4.5.2.b. The largest diameter used (9 mm) which required a correction of \(+ 0.34\%\). With such small correction factors, it is clearly an advantage to use sources with large surface
Fig. 4.4.5.2.a Measurement of the position of the Si(Li) crystal (the uncertainties are less than the size of the points).

Fig. 4.4.5.2.b The source diameter correction factor.
areas. However, it should be pointed out that the programme only corrects the number of photons entering the front face of the crystal. For very large source diameters, many of the photons will enter at angles greater than $0^\circ$ to the normal to the detector surface. In this case, some of the photons entering around the edge may be lost from the sides of the detector thereby significantly reducing the high energy efficiency. Also, the effective thickness of the dead layers will be greater because of the increased angle of incidence of the photons.

4.4.5.3 Determinations of the total detection efficiency

The use of calibrated radioactive sources allows the determination of the total detection efficiency ($\varepsilon\Delta\Omega/4\pi$) as a function of energy. As has been mentioned, the source deposits were made very thin in order to prevent significant source self-absorption effects. This was verified experimentally for the $^{57}$Co source by placing it normal to and at $45^\circ$ to the detector axis. The $K_{\alpha}$ X-ray intensity was found to be the same to within 0.3% with an experimental uncertainty yielding the result that for this source the self-absorption was less than 1%. As the other sources were of similar dimensions, their self-absorption is expected to be similar.

The sources were prepared by repeatedly spraying the radioactive solutions over an area defined by a circular aperture and then allowing the layers to dry. The source backing material was microscope slide glass. The exception to the above was the $^{241}$Am source which was prepared by vacuum evaporation. A full list of the radionuclides used is given in Table 4.4.5.3.a. The $^{241}$Am source was calibrated by counting the alpha-particles with a plastic scintillator detector in a well-defined low angle geometry (these detectors have 100% intrinsic efficiency). The other sources were calibrated via their main high energy photon line using a Si(Li) detector which has been calibrated with many absolutely measured standards over a number of years within the CBNM Radionuclides Group. The standards themselves has been calibrated using such absolute techniques as $4\pi\beta\gamma$ coincidence counting. In addition, the K X-rays of $^{109}$Cd were also measured as this yield per disintegration is poorly known in the literature.

The two lowest energy calibration points, the 3.3 keV M X-ray from the decay of $^{241}$Am and the 4.6 keV L X-ray from the decay of $^{137}$Cs, both suffer from the fact that their relative yields have a high uncertainty.
Table 4.4.5.3.a.: Data used for deducing the intensity of low energy photon sources

<table>
<thead>
<tr>
<th>Nuclide</th>
<th>Half-life</th>
<th>Energy of photons(keV)</th>
<th>Intensity ratio (photons per high energy photon or alpha-particle)</th>
<th>High energy photon or alpha-particle</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>$^{54}$Mn</td>
<td>(312.16 ± 0.04)d</td>
<td>5.47</td>
<td>0.2514 (+ 0.5 %)</td>
<td>834.8 keV γ</td>
</tr>
<tr>
<td>$^{57}$Co</td>
<td>(271.4 ± 0.5 )d</td>
<td>6.40</td>
<td>0.5727 (+ 2.0 %)</td>
<td>122.1 keV γ</td>
</tr>
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</tr>
<tr>
<td></td>
<td></td>
<td>14.40</td>
<td>0.112 (+ 1.8 %)</td>
<td>122.1 keV γ</td>
</tr>
<tr>
<td>$^{65}$Zn</td>
<td>(244.0 ± 0.2 )d</td>
<td>8.04</td>
<td>0.6596 (+ 0.8 %)</td>
<td>1155.5 keV γ</td>
</tr>
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<tr>
<td></td>
<td></td>
<td>8.90</td>
<td>0.0911 (+ 2.0 %)</td>
<td>1155.5 keV γ</td>
</tr>
<tr>
<td>$^{109}$Cd</td>
<td>(450 ± 5)d</td>
<td>3.1</td>
<td>0.101 (+ 9 %)</td>
<td>Ag Kαβ</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>22.10</td>
<td>22.02 (+ 4.9 %)*</td>
<td>88.0 keV γ</td>
</tr>
<tr>
<td></td>
<td></td>
<td>25.00</td>
<td>4.68 (+ 5.0 %)*</td>
<td>88.0 keV γ</td>
</tr>
<tr>
<td>$^{137}$Cs</td>
<td>(30.5 ± 0.3)y</td>
<td>4.6</td>
<td>0.110 (+ 5 %)</td>
<td>Ba Kαβ</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>32.1</td>
<td>0.0666 (+ 3.0 %)</td>
<td>661.6 keV γ</td>
</tr>
<tr>
<td></td>
<td></td>
<td>36.6</td>
<td>0.0159 (+ 3.1 %)</td>
<td>661.6 keV γ</td>
</tr>
<tr>
<td>$^{241}$Am</td>
<td>(432.9 ± 0.8)y</td>
<td>3.3</td>
<td>0.064 (+ 9 %)</td>
<td>α-particle</td>
</tr>
<tr>
<td></td>
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<tr>
<td></td>
<td></td>
<td>11.9</td>
<td>0.86 (+ 3 %)</td>
<td>α-particle</td>
</tr>
<tr>
<td></td>
<td></td>
<td>13.9</td>
<td>13.2 (+ 4 %)</td>
<td>α-particle</td>
</tr>
<tr>
<td></td>
<td></td>
<td>17.8</td>
<td>19.3 (+ 3 %)</td>
<td>α-particle</td>
</tr>
<tr>
<td></td>
<td></td>
<td>20.8</td>
<td>4.85 (+ 4 %)</td>
<td>α-particle</td>
</tr>
<tr>
<td></td>
<td></td>
<td>26.35</td>
<td>2.4 (+ 4 %)</td>
<td>α-particle</td>
</tr>
<tr>
<td></td>
<td></td>
<td>59.5</td>
<td>35.9 (+ 2 %)</td>
<td>α-particle</td>
</tr>
</tbody>
</table>

- a Calculated in the present work
- b Experimental result of Nix et al. (1973)
- c Experimental result of Karttunen et al. (1971)
- * Because of the high uncertainty of these data, these yields were measured directly to ± 1 %

All other data from review of Campbell et al. (1975a)
(+ 9% and 5% respectively) and are the result of only one measurement reported in the literature. As in other fields, it is quite common that a single measurement is in error by more than the stated uncertainty. It was therefore decided to utilise an additional source of photons. The decay of $^{109}\text{Cd}$ yields 3.1 keV Ag L X-rays. No measurements of the intensity per decay of these X-rays have been reported. However it is possible to calculate the yield by making use of accurately determined electron capture ratios and internal conversion coefficients.

The ratio of the total number of daughter L X-rays to K X-rays emitted by the decay of a electron-capture nuclide may be written as (Bambynek 1978):

\[
\frac{I_L}{I_K} = \left[ \frac{P_L + \frac{a_L}{1 + a_T}}{P_K + \frac{a_K}{1 + a_T}} + \eta_{KL} \right] \frac{\omega_L}{\omega_K}
\]

where $P_K$ and $P_L$ are the probabilities of electron capture from the K and L shells; $a_K$, $a_L$ and $a_T$ are the K shell, L shell and total internal conversion coefficients; $\eta_{KL}$ is the total number of primary L vacancies produced by all Auger and radiative transitions to the K shell; $\omega_K$ is the K-shell fluorescence yield and $\omega_L$ the mean L-shell fluorescence yield (this is not a simple average over the three subshells - see for example Bambynek et al. (1972)). Bambynek et al. (1977) discuss orbital electron capture by the nucleus and review experimental data. For $^{109}\text{Cd}$, Leutz et al. (1965) and Goedbloed et al. (1970) appear to have made the most accurate experiments and their results agree to within their stated uncertainties. In the present calculation of $I_L/I_K$ for the Ag X-rays from the decay of $^{109}\text{Cd}$, the $P_{K,L}$ and $a_{K,L,T}$ values were taken from Leutz et al. and $\eta_{KL}$ and $\omega_K$ from Bambynek et al. (1972). The only systematic compilations of $\omega_L$ known are by Hoffmann (1978) and Krause et al. (1978). Hoffmann has obtained the following fit to experimental data:

\[
\left[ \frac{\omega_L}{(1-\omega_L)} \right]^{1/4} = B_0 + B_1 Z + B_3 Z^3
\]

where $B_0 = 0.556 \times 10^{-2}$

$B_1 = 0.105 \times 10^{-1}$

$B_3 = 0.556 \times 10^{-7}$

and $Z$ is the atomic number of the element.
The data of Krause et al. are theoretical calculations. For Ag, Hoffmann's formula gives $\overline{v} = 0.0610$ and a simple fit to the values of Krause et al. yields $\overline{v} = 0.0545$. Therefore a value of $0.0578 \pm 0.0033$ has been adopted for the calculation of $I_L/I_K$. The result obtained is that

$$I_L/I_K = 0.101 \pm 0.009$$

where the total uncertainty is derived assuming that all the sources of uncertainty are independent and can therefore be added in quadrature.

In an attempt to measure the silicon dead layer, and hence determine the low energy (< 3 keV) efficiency of the Si(Li) detector, electron energy losses in the detector dead layers were measured. The internal conversion electrons from the decay of $^{109}$Cd are monoenergetic and of known energy. A very thin source (~ 0.1 pCi) was prepared so that electron self-absorption would be small. A spectrum recorded with such a source is shown in Fig. 4.4.5.3.a where the electron peaks from K, L and M internal conversion from the 87.7 keV excited state of $^{109}$Ag are clearly observed. By determining the energy losses suffered by these electrons, and by making use of electron energy loss tabulations (Pages et al. 1972), the silicon dead layer was determined to be 3.41 $\mu$m and 2.65 $\mu$m for the K and L electron cases respectively. The energy losses in the beryllium and gold layers were calculated using the thicknesses previously quoted. An average value for the dead layer of $\sim 3 \mu$m is thus obtained.

There are several significant sources of possible error in this preliminary study of the electron energy loss technique. Negligible energy loss within the source was assumed; this should be verified by measuring spectra recorded with the source at different angles to the detector. The energy losses have been measured from the most probable electron energies (i.e. the peaks of the distributions) whereas the electron energy loss tabulations refer to the mean energy loss. The electron energy distributions are clearly non-symmetrical and the mean energy will be less than the most probable energy. Determining this mean energy is not a simple matter as some of the tailing will be due to detector charge collection effects. A better solution would probably be to measure the most probable electron energy losses by adding beryllium absorbers successively. An accurate knowledge of the beryllium window thickness is critical as the electrons will lose ten times more energy in this window than in a 0.5 $\mu$m silicon dead layer. For example, an uncertainty of $\pm 5\%$ in the window thickness would yield a $\pm 50\%$ uncertainty in the silicon dead layer thickness. However, in
Fig. 4.4.5.3.a Si(Li) detector spectrum of the very thin $^{109}$Cd source. The electrons are due to internal conversion of the 88 keV excited state of $^{109}$Ag.
spite of these initial difficulties, further research in this direction is thought to be worthwhile. In the meantime, as the measured value for the dead layer is very high, the commonly used value of 0.5 μm was employed for the present efficiency fit.

Great care was exercised in designing and constructing the source holder and the PIXE target holders so that the sources occupied the identical position to the targets. This ensured that the Si(Li) detection efficiency was the same for PIXE studies as for the radio-isotope counting to within ± 0.5%. The sources were counted under vacuum and with the same settings of the electronics, especially the amplifier, as were used during the PIXE experiments. With the sources only producing count-rates of the order of 1 s⁻¹, counting times were long with three days being typical. Even with only six sources this aspect of the detector calibration occupied over a month. Thus a compromise was necessary between the allocation of time for the efficiency calibration and the other demands on the irradiation system. The resultant efficiency curves represent what is thought to be the optimum compromises with the accuracies tailored to the needs of the applications.

Three different arrangements of the Si(Li) detector were used in the different applications. The efficiency determinations will now be discussed in order of decreasing accuracy.

4.4.5.3.1 Efficiency for thin target ion-induced X-ray cross-section measurements

The targets were in the form of thin metallic layers evaporated onto thick vitreous carbon disks (see Chapter 5). In order to prevent the intense low energy carbon bremsstrahlung from being detected and causing large dead-time problems, a 44 mg cm⁻² layer of polyethylene was placed in front of the detector. This effectively removed all of the unwanted background whilst only reducing the intensity of the lowest energy characteristic X-rays studied (Ti Kα) by a factor of two.

The measured efficiency is shown in Fig. 4.4.5.3.b. The points in the range 5 to 9 keV were determined with the highest accuracy as the X-rays corresponding to the cross-sections to be measured were in the range 4.51 to 9.88 keV. The other points were determined in order to facilitate the fitting of a curve through the region of interest. As has been previously discussed, a simple fit to the data points is not really justified as the various absorbers produce a
Fig. 4.4.5.3.b The full energy peak efficiency of the Si(Li) detector (including polyethylene absorber) measured with calibrated radioactive sources.
curve that is not a simple function of energy. Therefore, the intrinsic efficiency was calculated using the photon attenuation coefficients of Veigele (1973) and the manufacturer's values for the thickness of the detector crystal and the beryllium window, and literature values for the gold contact (40 μg cm^{-2} - Jaklevic et al. 1971) and the silicon dead layer (0.5 μm - Gallagher et al. 1974). The photon attenuation in the polyethylene was measured directly and extrapolated to the lowest energies by using the calculated values of Hubbell (1977). The theoretical efficiency curve obtained was then normalised to the experimental points in the range 4.60 to 8.91 keV with the more accurate K_{\alpha} points having double the weighting of the others in this region. This fit yielded the result that the geometrical efficiency (see Fig. 4.4.5.3.b) was \( (1.028 \pm 0.023) \times 10^{-4} \) with the uncertainty being based on the standard deviation of the points from the normalised curve. It will be remembered that the geometrical efficiency was calculated in section 4.4.5.2 to be \( (1.51 \pm 0.02) \times 10^{-4} \). The most plausible explanation of this 32% discrepancy is that the sensitive diameter of the Si(Li) crystals is 2.95 mm instead of the manufacturer's value of 3.57 mm. The reason for this may be either an error in the specifications (it will be remembered that the position of the crystal was incorrectly stated) or, more likely, that there is a very thick silicon dead-layer at the circumference of the crystal. Both the present author (Barfoot 1976) and Mason (1978) have found that the low energy (< 10 keV) intrinsic efficiency falls to a half at r/5 from the crystal edge of the larger germanium detectors (r = crystal radius). This would account for the discrepancy if the same effect was present in the smaller Si(Li) detectors. Also, as has been discussed by Goulding (1977), the electric field strength is weaker at the edges and incomplete charge collection may become significant. This is more likely to occur for the low energy X-rays because of their poorer penetrating power.

The high energy efficiency falls off much more quickly than would be expected from theory. The dotted line in Fig. 4.4.5.3.b shows the curve for a 3 mm thick crystal whilst the full curve, which represents a 2 mm thickness, is seen to be a much better fit to the data. Once again it was wondered whether the manufacturer's specifications were incorrect. However, a paper by Singh et al. (1979) indicates that the efficiency for higher energy photons is also higher in the centre of the crystal. By collimating their crystals down from a diameter of 10 mm to 2 mm, they observed a 27% increase in intrinsic efficiency for the collimated case. This could well be an explanation for the
present high energy fall-off in efficiency and illustrates the dangers of using theoretical efficiencies without using radioactive sources for confirmation. Such collimation is, however, impractical for use in PIXE studies as the total efficiency would be reduced by about a factor of 25. It should be noted that these problems with the high energy fit do not affect the X-ray production cross-section measurements which were performed for lower energy X-rays.

As the titanium X-ray energy is more than 1 keV outside the most accurately measured region, it was decided to perform a further check. The measured $K_{\beta}/K_{\alpha}$ ratios for protons on thin targets, corrected for efficiency, were compared to literature values as is shown in Table 4.4.5.3.b.

Table 4.4.5.3.b.: Comparison of measured and literature value of $K_{\beta}/K_{\alpha}$ ratios.

<table>
<thead>
<tr>
<th>Element</th>
<th>$K_{\beta}/K_{\alpha}$ ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
<td>0.120 ± 0.002</td>
</tr>
<tr>
<td>V</td>
<td>0.129 ± 0.003</td>
</tr>
<tr>
<td>Co</td>
<td>0.133 ± 0.003</td>
</tr>
<tr>
<td>Cu</td>
<td>0.139 ± 0.004</td>
</tr>
<tr>
<td>Ge</td>
<td>0.151 ± 0.003</td>
</tr>
</tbody>
</table>

The uncertainties are due to the counting statistics only. Since good agreement with the values from the review of Bambynek et al. (1972) is found for all the elements, except titanium, the lowest energy part of the efficiency curve was adjusted so that the titanium $K_{\beta}/K_{\alpha}$ ratio agreed with the literature. It is estimated that this correction adds a further ± 2 % uncertainty to the efficiency for titanium K X-rays.

The resultant full-energy peak efficiency for the characteristic X-rays of interest are given in Table 4.4.5.3.c. The uncertainties are derived from the uncertainty in fitting the theoretical curve to the data in the energy region 4.6 to 8.9 keV.

4.4.5.3.2 Efficiency for comparison of thin and thick target cross-section measurements

The purpose of this experiment was to compare proton-induced X-ray production cross-sections as measured with thin and thick targets of
titanium and copper and to compare the results from different calcium compounds. As low energy X-rays were to be measured, the polyethylene absorber was not used in this case and it was therefore necessary to re-calibrate the detector efficiency. In order to simplify the cross-section calculations, the Si(Li) detector and the beam made equal angles \((11.25°)\) to the normal to target surface. With the sources also in this position, it was to be expected that the geometrical efficiency would be very slightly higher. In fact, the titanium targets were measured in the previously mentioned (section 4.45.3.1) set-up and so only the efficiency for calcium and copper K X-rays was of interest. The comparison of the cross-sections determined by the thin and thick target techniques was of prime importance. For this comparison, the detector efficiency cancels out and so was of secondary interest (for further details see Chapter 5). Thus fewer sources were used and a slightly higher uncertainty tolerated for this efficiency curve.

The same method as described in section 4.4.5.3.1 was again employed and the normalised curve is shown in Fig. 4.4.5.3.c. The efficiencies obtained are given in Table 4.4.5.3.d. The fitted value for the geometrical efficiency was \((1.039 \pm 0.013) \times 10^{-4}\) which is in very good agreement with the previously measured efficiency curve which gave \(\Delta\Omega/4\pi = (1.028 \pm 0.023) \times 10^{-4}\).
The full energy peak efficiency of the Si(Li) detector measured with calibrated radio-active sources.
Table 4.4.5.3.d.: Fitted efficiencies for characteristic X-rays of interest (without polyethylene absorber present)

<table>
<thead>
<tr>
<th>X-ray</th>
<th>Energy (keV)</th>
<th>$\epsilon \Delta\Omega/4\pi \times 10^{-4}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca $K_{\alpha}$</td>
<td>3.69</td>
<td>0.903 ± 0.072</td>
</tr>
<tr>
<td>Ca $K_{\beta}$</td>
<td>4.01</td>
<td>0.930 ± 0.070</td>
</tr>
<tr>
<td>Cu $K_{\alpha}$</td>
<td>8.04</td>
<td>0.983 ± 0.029</td>
</tr>
<tr>
<td>Cu $K_{\beta}$</td>
<td>8.90</td>
<td>1.025 ± 0.031</td>
</tr>
</tbody>
</table>

4.4.5.3.3 Efficiency for PIXE analysis of environmental samples

For environmental samples, especially those of air particulate pollution, it is often of great interest to examine elements as light as sodium ($Z = 11$, K X-ray energy = 1.04 keV). No radionuclide lines with known intensity exist in this energy region. For these applications it was necessary to turn to other methods of efficiency calibration. Proton irradiation of well calibrated layers of light elements and the detection of the induced X-rays with the Si(Li) detector (for known ion beam fluences) permitted the efficiency to be determined to about ± 20 % using the published proton-induced ionization cross-sections and fluorescence yields for these elements. The K X-rays were measured for targets of NaCl, Al, V, Cr, Fe, Cu; the L X-rays for Ag and the M X-rays for Au. The cross-sections were taken from Johansson et al. (1976) for all cases other than the Au M X-ray production cross-section which was due to Ishii et al. (1975). RBS analysis (see Chapter 3) was used to determine the stoichiometry of the NaCl target which was found to be Na : Cl in the ratio of 3 : 2 and therefore a larger uncertainty was assigned to the efficiencies for these elements.

The efficiency at higher energies was also measured using radioactive sources of $^{57}$Co, $^{65}$Zn and $^{241}$Am. The resulting non-normalised values for the efficiency are shown in Fig. 4.4.5.3.d. It appears from the results obtained that any systematic differences between radioactive source and PIXE calibrations are small. The rapid fall-off in efficiency below 2 keV is largely due to the effect of the beryllium window.

The uncertainties and the normalised curve are not shown in Fig. 4.4.5.3.d because, for PIXE analysis, the efficiency curve is not used in an absolute manner and quantification is realised by directly making use of many of the yields from the standard layers. For example, in the case of sodium PIXE analysis the number of sodium K X-rays
Fig. 4.4.5.3.d  The full energy peak efficiency of the Si(Li) detector measured with calibrated radioactive sources and PIXE analyses of calibrated thin targets.
produced per proton per sodium atom was known from the yield measured with the NaCl target. The efficiency curve is only used to extrapolate between the various elements measured e.g. for magnesium between the measured sodium and aluminium yields. Thus in the analysis of aluminium, the only sources of uncertainty are the calibrated target thickness (+1%), the random uncertainty in the proton fluence measurement (+3%) and the statistics of the X-ray peak integration procedure (+1%). The uncertainties for the elements for which no standards were available is typically of the order of ±6%. For any particular analysis, the total uncertainty in the proton fluence and the uncertainty in the X-ray peak area (obtained in the measurement of the 'unknown' sample) have to be combined with the above calibration uncertainties. The overall accuracy is still quite adequate for air pollution studies where elemental levels vary by orders of magnitude and sampling errors can be as high as ±50% (see Chapter 6). It may be noted that the total efficiency is somewhat lower than for the previous case (which was also without a polyethylene absorber) because an earlier type of mechanical target holder was used with slightly different geometry.

4.4.5.4 Some conclusions on Si(Li) detector efficiencies

It is clear that it can be very dangerous to use theoretical detector efficiencies without normalisation to experimental values unless the detector configuration is very accurately known and only the central region of the crystal is used. An error of more than 30% would have been made if this had been done in the present work. Accurate calibration (+2%) is possible in the region 5.4 to 8.0 keV where reliable radionuclide standards are available. Similar accuracy could probably be achieved in the region above 14 keV where there are fewer known radionuclide lines per keV but where the efficiency curve is varying more slowly. This region was not of great interest in the present work and so the optimum achievable accuracy was not realised. A radionuclide yielding a calibration point in the energy region 9 to 13 keV would be of great use in defining the curve in this region. 

$^{71}$Ge, yielding 9.24 and 10.26 keV Ga K X-rays, and $^{75}$Se, yielding 10.53 and 11.72 keV As K X-rays, would appear to be two suitable candidates for standardisation.

The situation below 5.4 keV is clearly not a happy one. Besides the problems of self-absorption of the low energy X-rays, these photons
are often situated on high backgrounds due to scattering of higher energy photons and to electrons from internal conversion processes. For these reasons, a programme has been initiated with the purpose of preparing and calibrating artificial sources. Although this work is still in its early stages, a source of $^{55}$Fe sandwiched between an optimum thickness of aluminium has been fabricated which yields, by fluorescence excitation, an aluminium K X-ray (1.49 keV) with a good peak to background ratio (20 : 1). The source has been calibrated in a $4\pi$ proportional counter (Kacperek 1979). Unfortunately, the source does not have the required degree of isotropy to allow accurate calibration of the Si(Li) detector (which occupies a very small solid angle). Work is continuing and the status of the project is reported in Appendix A.

Two different approaches to the problem have been reported recently. Laegsgaard et al. (1979) have built their own Si(Li) detector and measured directly all the absorbing layers and calculated the detector efficiency. The agreement with results from radioactive sources allows them to claim an uncertainty of $\leq 1\%$ for the peak of their efficiency curve. Although this appears to be a useful advance for the measurement of cross-sections, their detector cannot be readily used for PIXE multi-elemental analysis as the resolution approaches 300 eV. On the other hand, Shima (1979) has calibrated a commercial Si(Li) detector by comparing its X-ray counts to those of a proportional counter of known efficiency, and identical solid angle, when both are simultaneously irradiated with proton-induced X-rays. The results appear to be good but, apart from the cost of a proportional counter and its associated electronics, large modifications would have had to have been made to accommodate the extra detector in the present vacuum system. Finally, it has been suggested (Rose 1979) that Compton backscattering from the source backing may cause additional X-rays to be emitted in the direction of the detector. If this were so, then the calculated photon yields from the radioactive sources would consequently be in error. However simple experiments and calculations indicate that the error introduced is less than 1\% and therefore no corrections were made for this effect. Further theoretical and experimental details of the photon backscattering correction may be found in a recent report (Barfoot 1980b).

4.5 The silicon surface-barrier detector

The detection of elastically backscattered particles was achieved with an Ortec Premium Grade partially depleted silicon surface-barrier
detector. The depletion depth is greater than 100 μm which is the range of 3.4 MeV protons and 13 MeV alpha particles. Ions of higher energy would not deposit all of their energy within the depleted region and therefore no particle spectroscopy was performed at energies greater than 3.0 MeV. The thickness of the gold electrode on the detector surface is about 40 μg cm\(^{-2}\) (20 nm) which causes a 2 MeV \(^4\)He ion to lose about 14 keV. By the nature of the ion stopping process (Appendix C) there will be no loss of intensity and so the detector is 100 % efficient for ions entering its sensitive area. The sensitive area of the detector is 50 mm\(^2\). A collimator of 4 mm diameter defined a central area of 12.6 mm\(^2\) thereby preventing the ions from being absorbed in the edges of the sensitive region. Edge effects can worsen the resolution which was 16 keV for 5.5 MeV \(^4\)He ions incident on the central region. The geometrical efficiency of the detector was determined with a calibrated open \(^{241}\)Am source placed at the usual target position.

Energy calibration was achieved with radioactive sources of \(^{241}\)Am and \(^{148}\)Gd which emit alpha-particles with energies of 5.486 and 3.183 MeV. The thin \(^{241}\)Am source was prepared at the CBNM and there was no evidence of alpha-particle energy loss due to source self-absorption. However, the commercially obtained \(^{148}\)Gd source produced an alpha-particle peak which was considerably broader than the detector resolution indicating source self-absorption. A linear extrapolation was made from these two calibration points and it was assumed that the calibration was also good for protons and deuterons. For work where the energy calibration is of great importance (e.g. for calibrating Van de Graaff beam energies), two small correction terms have to be subtracted from the alpha-particle energy. These are approximately 20 keV to correct for energy loss in the gold surface-barrier layer of the detector and another 10 keV for the nuclear stopping contribution in silicon (l'Ecuyer et al. 1979). Whilst this represents a total correction of only 0.6 % in the \(^{241}\)Am alpha-particle energy, it can involve a much more serious correction at lower energies. Also, evidence is emerging which indicates that He ions produce 1 % larger pulses than H ions of equal energy (Mitchell et al. 1976, Martini et al. 1975, Langley 1973). Thus the measured proton energies could be in error by several per cent due to these two effects. However, in the present studies, the primary use of the surface-barrier detector has been to measure the intensity of the back-scattered particles with only a secondary interest in their energy for the identification of the mass number of the target element.
Standard Ortec equipment was used to amplify the signals which were then fed into the data acquisition system described in section 4.4.2. Due to the fact that backscattering spectral peaks are generally non-Gaussian in nature, computerised spectral fitting was not easily possible and so all spectra were analysed manually.

4.6 The preparation of thin targets of accurately known mass thickness - the CBNM ultra-high vacuum microbalance

An accurate knowledge of the mass thickness, i.e. the mass per unit area, of the evaporated layers used as standard targets is critical in the absolute approach adopted in the present work. The most important application has been in the absolute determination of the ion-induced X-ray production cross-sections where the accurate knowledge of the target thickness, the surface-barrier detector efficiency, the scattering angle and the appropriate backscattering cross-section also allowed the accurate determination of the ion beam fluence to the targets. It is believed that the preparation technique used is the most accurate presently attainable. The principles will now be outlined.

The element or compound to be evaporated is either placed on evaporation filament which is resistively heated or in a carbon boat which is bombarded with electrons from an electron gun. The electron beam technique is preferable for the higher boiling point materials. These methods, which are now quite standard, are well described in the literature (e.g. Maxman 1967). The evaporation proceeds behind a shutter (see Fig. 4.6) until a steady evaporation rate has been achieved. The shutter is then opened until the required amount has been deposited on the substrate. This amount is approximately determined with a quartz oscillator film monitor. For high accuracy, vacuum weighing is imperative as the mass may change under atmospheric conditions. This change may be due to oxidation and other reactions of the layer and substrate or simply due to handling of the substrate. In the CBNM UHV microbalance, the substrate is positioned in an aluminium disk, of accurately known surface area, which forms the 'balance pan'. The mass of the evaporated film is determined by weighing the pan before and after the evaporation in situ.

The weighing procedure of this balance is worth considering in a little detail. The balance is brought into equilibrium with the aid of the coil of a torque motor and this position is observed with an optical system. The substitution principle is applied to the mass determination.
Fig. 4.6  Schematic of the evaporation and microbalance system.
Two calibration weights \( (t_1, t_2) \), which are secondary standards, and the unknown mass \( (m) \) are successively suspended from the balance and the voltages \( T_1, T_2, M \) across the coil necessary to achieve equilibrium are recorded. These readings may be either positive or negative, depending on whether the corresponding masses are heavier or lighter than the mass \( m_0 \) which would bring the balance into purely mechanical equilibrium. The magnitudes of the readings are proportional to the mass differences \( t_1 - m_0, t_2 - m_0 \) and \( m - m_0 \). However, the point of the substitutional method is that \( m_0 \) need not be known. The unknown mass is determined from, for instance, the relationship

\[
m - t_1 = (M - T_1) \frac{t_2 - t_1}{T_2 - T_1}
\]

The total mass on the disk can be determined with an uncertainty of \( \pm 2 \mu g \). Thus, if the area evaporated is \( S \text{ cm}^2 \), the uncertainty per \( \text{cm}^2 \) is equal to \( \pm 2/S \mu g \text{ cm}^{-2} \). The evaporation source to disk distance is sufficiently large (54 cm) to ensure that the deposit is uniform. The whole UHV system is bakeable to 400°C which produces very stable weighing conditions. The construction, operation and accuracy of the microbalance have been discussed more fully elsewhere (Moret et al. 1966, Eschbach 1972).

One of the reasons for describing the microbalance in detail is to illustrate that the method is a true weighing technique. This is not the case for the more commonly used quartz oscillator monitor (QOM). This type of monitor relies on the principle that the frequency of an oscillating quartz will change when its mass changes. Thus the difference in frequency after evaporation is proportional to the mass of the substance deposited on the quartz. Although the QOM measurements are more sensitive than those of the microbalance, it is felt that they are less reliable. Small drifts and random jumps in the quartz’s oscillating frequency are not uncommon in this type of monitor. These instabilities are probably caused by small temperature gradients and stresses set-up on the crystal by the deposited layers (Eschbach et al. 1966).

The relative reproducibility of the two weighing techniques was determined by comparison with two independent methods viz. X-ray fluorescence (XRF) and Rutherford backscattering (RBS). The XRF, RBS and UHV microbalance were found to agree to within \( \pm 2.8 \% \) but the QOM measurements were at variance by up to about \( \pm 25 \% \) (Mitchell et al. 1978a). It is thus felt that measurements which rely on QOM mass thickness determinations are of questionable accuracy.
CHAPTER 5

ABSOLUTE MEASUREMENTS OF ION-INDUCED X-RAY PRODUCTION CROSS-SECTIONS

The need for accurate ion-induced X-ray production cross-sections is two-fold. Firstly, to perform absolute PIXE elemental analysis, accurate cross-sections are required. It will be remembered from section 3.1.3.1 that the equation for absolute quantitative analysis is

\[ y_i(E) = Q \sigma_i^X(E) N \frac{\Delta \Omega}{4\pi} \epsilon \cdot \text{att} \]

All of the above factors, except \( \sigma_i^X(E) \), are known or can be measured to within a few percent. Unfortunately, the uncertainty in the values of \( \sigma_i^X(E) \) commonly used can often be much greater than \( \pm 10\% \). Thus a large improvement in the accuracy of \( \sigma_i^X(E) \) values would lead to significantly more accurate absolute PIXE analysis. Even in relative PIXE analysis, where standards are used, corrections are often required in order to take into account the fact that the mean projectile energy may not be the same in the standard and the unknown. Hence the variation of the cross-sections as a function of energy is also required. Absolute PIXE analysis of thick specimens also requires an accurate knowledge of the variation in cross-section with energy as the projectile slows down through the target. These cross-sections are additionally of use in estimating the minimum detection limits (see section 3.1.5) that are likely to be achieved in various experimental configurations.

The second requirement is to allow the proponents of various ion-induced inner shell ionization theories to compare their results with experiment. The theories are at variance with each other by differing amounts which are often of the order of 40% (see for example Rashiduzzaman Khan et al. 1977). Thus, to differentiate between the theories, the experimental data must have uncertainties of much less than, say, \( \pm 20\% \).

The most common method of determining the ionization cross-section \( \sigma_i^Y(E) \) is to measure the X-ray production cross-section \( \sigma_i^X(E) \) and then, for K shell ionizations, to use the relationship

\[ \sigma_i^X(E) = \sigma_i^Y(E) \omega_i K \]

as discussed in section 3.1.2. Most of the presently available experimental data do not appear to satisfy the above accuracy requirements.
It should be stressed that, for PIXE analysis, X-ray production cross-sections are the prime objective. The measured X-ray production cross-sections are converted to ionization cross-sections in order to allow accurate interpolation to targets and projectile energies not covered in the experiments. This is especially important for elements where it is difficult to construct standards. Thus the measurement of these cross-sections is of great importance to the two fields. This has recently led to the setting-up of an international committee to stimulate and control such cross-section measurements (Brandt et al. 1979b, Paul 1979). The reasons for the choice of projectile species and energy and the target elements used in the cross-section measurements will now be outlined.

5.1 The requirements for and present status of experimental X-ray production cross-sections

It will be remembered from the discussion of section 3.1.5 that, in general, protons are the most suitable projectiles for PIXE analysis. This was also experimentally verified for the present air pollution analyses described in Chapter 6. An examination of Fig. 3.1.5.1.b reveals that for typical operating conditions, the optimum minimum detection limits (<1 ppm by weight) are achieved for K X-rays from elements with \( Z = 14-30 \) when 1 MeV protons, which are widely available from many small accelerators, are used. Fig. 5.1.a shows the essential trace elements for warmblooded animals and the elements which form the bulk of living matter. It can be seen that about 75% of the trace elements and 50% of the bulk elements fall within this optimum Z range. As Na and Mg are bulk elements, the MDL considerations are not so important and they may also be easily detected with a thin windowed Si(Li) detector. In fact, even the K X-rays of fluorine (energy = 0.68 keV) have been detected with the present system. However, it was not thought worthwhile to study this element as photon self-absorption corrections for such low energy X-rays would be high and of large uncertainty. The only bulk elements not detectable with such a system are H, C, N and O which are not usually of as much interest as the heavier bulk elements. The element selenium (\( Z = 34 \)) may be detected with quite a good MDL but the remaining, higher Z, trace elements (Mo, Sn and I) are difficult to detect at concentrations of less than 10 ppm by weight. Air particulate deposits and other environmental samples contain many of these elements but in differing proportions.
Fig. 5.1.a Essential trace and bulk elements (Valkovic 1978).
It thus appears that the most interesting Z region for the PIXE analysis of biological and environmental samples is from Z = 11 (Na) to Z = 34 (Se). A survey of the available literature reveals that the most common range of proton energies used for PIXE work is 1-3 MeV. This is dictated by the energies available with the usual small accelerators and by the MDL considerations just discussed. It was therefore decided that the first priority was to obtain accurate values for $\sigma^p(E)$ for protons of 1-3 MeV with targets of Z = 11-34. The Z region can conveniently be divided into Z = 11-21 and Z = 22-34. In the latter range it is easy to prepare stable thin layers of most of the elements whereas, in the former, aluminium is the only element that is easy to handle. Consequently, there are far more cross-section data for the latter elements.

Experimental results for $\sigma^p(E)$ have been summarised by Rutledge et al. (1973), Johansson et al. (1976) and Gardner et al. (1978). It should be pointed out that these compilations were not exhaustive and that many other results may be found in the literature especially in 'Physical Review A'. Great care should be exercised in using the tabulations of Gardner et al. as very many tabulation errors have been included. It is recommended that the values not be used directly but that the original source of the data be critically examined. As was discussed in section 3.1.1, Johansson et al. (1976) made a fit to the then available experimental data using the universal scaling properties of the BEA theory. This fit was made for widely varying values of Z and proton energy. Fig. 5.1.b shows the percentage deviations, of all the known experimental data from 1970 to 1979 inclusive, from the fitted values of Johansson et al. for 1, 2 and 3 MeV proton excitation. The dashed lines represent linear least-squares fits to these deviations and will be discussed later. A great shortage of low Z data is apparent. Even so, it may be observed that the fit deviates from the experimental values by as much as $-30\%$. The situation in the range Z = 22-34 is somewhat different. Here there are far more results but the spread in values is much greater than can be explained by the stated experimental uncertainties. Rashiduzzaman Khan et al. (1977) discuss some of these data. For instance, the cross-sections for iron vary by up to 130 $\%$ from the smallest value in the 1-3 MeV range. Thus the nine authors quoted by Rashiduzzaman Khan et al. are in very poor agreement; especially as most of them quote uncertainties in the $+10\%$ to $+15\%$ range. The sources of such large errors are not obvious. It is therefore necessary to accurately measure cross-sections in the entire Z range of interest.
Fig. 5.1.b Percentage deviations of experimental data from the BEA fit of Johansson et al. (1976) for elements of Z = 11 to 22. The dashed lines represent linear least-squares fits to the deviations (see section 5.2.4).
Cross-sections may be measured by using either thin or thick targets. Thick targets have some advantages from the point of view of target preparation for difficult elements but complications are thereby introduced in the data analysis. The thin and thick target techniques will now be compared.

5.2 A comparison of thin and thick target methods of determining proton-induced K X-ray production cross-sections

To achieve cross-section measurements for the chemically stable elements, thin or thick targets of the pure element are normally used. However, for the many volatile or reactive elements that exist, especially in the lower region of the periodic table, it is not readily possible to prepare stable targets of the pure element in either thin or thick layer form. Therefore, the feasibility of measuring cross-sections using thick targets of compounds of these elements has been investigated.

In order to elucidate whether the thick target method itself introduces significant uncertainties, ionization cross-sections were derived from X-ray yields measured with thin and thick layers of pure Ti and Cu. Also, cross-sections were obtained using a thick target of the chemically stable compound CuCl so that a comparison could be made between results from targets of the pure element and a compound of known chemical composition. The thick target technique was applied to the highly reactive element calcium and results from thick targets of various calcium compounds exhibiting differing chemical stabilities were compared with each other and with a thin target of CaF₂.

5.2.1 Experimental technique and results

The thick targets of pure Ti and Cu were prepared from spectroscopically pure sheets of the metal. The thin layers of Ti, \((30.1 \pm 0.3) \mu g \text{ cm}^{-2}\), and Cu, \((31.1 \pm 0.3) \mu g \text{ cm}^{-2}\), were vacuum evaporated onto thick polished vitreous carbon backings and weighed in situ on the U.H.V. microbalance as described in section 4.6. The thick targets of the compounds were produced by pressing fine powders of CuCl, CaO, CaCO₃, CaF₂ and CaCl₂ at pressures of \(4 \times 10^4 \text{ N cm}^{-2}\) (typically) in a hydraulic press. No beam-induced degradation of the targets was visible after the irradiations although surface roughening of the CaCl₂ target was apparent (CaCl₂ is deliquescent). Also, the CaO target had expanded in volume by about 30% (CaO is hygroscopic). In addition,
as a check on the Ca cross-section values, a thin target of \(20.1 \, \mu g \, cm^{-2}\) of \(\text{CaF}_2\) was prepared (this was evaporated onto a thick vitreous carbon backing as with the other thin targets). The atomic ratio of \(\text{Ca} : \text{F}\) was determined by 2 MeV \(\text{He}^+\) RBS analysis to be \(1 : (1.89 \pm 0.04)\). Thus the amount of Ca in the layer was determined to be \((11.3 \pm 0.2) \, \mu g \, cm^{-2}\).

The formalism for the data analysis of the X-ray yields was given in section 3.1.3.1. The determination of the Si(Li) detector efficiency for the thick target work with \(\theta = \phi = 11.25^\circ\) was described in section 4.4.5.3.2. At the time this experiment was performed, the foil ion beam monitor was not available. Cross-sections were measured for the thick targets of Cu, CuCl, CaO, CaCO\(_3\), CaF\(_2\) and CaCl\(_2\) and thin targets of Cu and CaF\(_2\). It was later decided to add measurements of thin and thick Ti yields. As this was performed with the detector set up for thin target cross-sections (\(\theta = 0, \phi = 22.5^\circ\) plus a polyethylene absorber — see section 4.4.5.3.1), the thin and thick Cu target yields were remeasured, at the time of the Ti measurements, to examine the internal consistency of the experiments. For the latter measurements, the foil ion beam monitor was available.

Table 5.2.1.a gives the measured thick target yields, \(Y(E)\), of K\(_\alpha\) X-rays per proton as defined by equation 3.1.3.1.3, which are given by

\[
Y(E) = \frac{4\pi \, y_{\text{i}}(E)}{Q \, \Delta\Omega \, \varepsilon}
\]

with the values (plus uncertainties) of \(\Delta\Omega \, \varepsilon\) as given for the appropriate cases in section 4.4.5.3. The values for \(Q\) were determined by current integration on the targets which were surrounded by an electron suppressor held at \(-400\, V\). With a very stable ion beam, there was no detectable change in the current measured on the various targets. This indicates that 'charging-up' of the targets was not a problem and that the errors due to such factors as secondary-electron emission (see section 4.3.1) were constant. Comparisons of the target RBS yields and currents measured for 1.0, 1.5, and 2.0 MeV protons incident on the Cu and CaF\(_2\) thin layers showed that the measured integrated currents needed to be reduced by \((5 \pm 3)\%\) in all cases. The principle uncertainties in this correction came from the determination of the solid angle of the surface barrier detector and the mass per unit area of the thin layers. The most probable cause of this excess charge was incomplete suppression of the secondary electrons emitted from the targets during the proton impact. This result is in excellent agreement with the correction factors determined during the thin target cross-section measurements (see section 5.3).
Table 5.2.1.a.: Thick target yields of Kα X-rays/protons as defined by equation 3.1.3.1.3

<table>
<thead>
<tr>
<th>Incident proton energy (MeV)</th>
<th>Y(E) x 10^3</th>
<th>( \theta = 0, \phi = 22.5^\circ )</th>
<th>( \theta = 11.25^\circ, \phi = 11.25^\circ )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ti</td>
<td>Cu</td>
<td>CuCl</td>
</tr>
<tr>
<td></td>
<td>0.716</td>
<td>0.097</td>
<td>0.095</td>
</tr>
<tr>
<td></td>
<td>1.59</td>
<td>0.259</td>
<td>0.281</td>
</tr>
<tr>
<td></td>
<td>3.81</td>
<td>0.633</td>
<td>0.604</td>
</tr>
<tr>
<td></td>
<td>5.96</td>
<td>1.10</td>
<td>1.10</td>
</tr>
<tr>
<td></td>
<td>8.96</td>
<td>1.81</td>
<td>1.85</td>
</tr>
<tr>
<td></td>
<td>11.6</td>
<td>2.52</td>
<td>2.54</td>
</tr>
<tr>
<td></td>
<td>16.3</td>
<td>3.97</td>
<td>3.85</td>
</tr>
<tr>
<td></td>
<td>20.2</td>
<td>5.40</td>
<td>5.23</td>
</tr>
<tr>
<td></td>
<td>24.0</td>
<td>7.15</td>
<td>6.73</td>
</tr>
</tbody>
</table>

It will be remembered that the thick target X-ray production cross-sections are derived from equation 3.1.3.1.12 viz.

\[
\sigma_{\text{X}}^n(E) = \frac{1}{n} \left[ \frac{dY(E)}{dE} \frac{dE}{dx} + Y(E) \mu \frac{\cos \theta}{\cos \phi} \right]
\]

with the various factors defined in section 3.1.3.1. The values of \( dY(E)/dE \) were determined by least squares fitting of 3rd to 6th order polynomials to \( Y(E) \) and differentiating the resulting fit w.r.t. \( E \). This procedure is common to the thick target technique (e.g. Basbas et al. 1973b, McKnight et al. 1975, Rashiduzzaman Khan et al. 1976, 1977).

In the central regions of the fit there was only a small change in \( Y(E) \) as the order of the polynomial was changed, but at the extremities \( Y(E)_{\text{fit}} \) varied strongly. The order of the fitted polynomial was increased until the first and last point values of \( Y(E)_{\text{fit}} \) only changed by a few percent. Thus although the uncertainties in the central regions (1.5 - 2.5 MeV) were small (1-2 %), the uncertainties at the outer regions were greater (3 - 4 %) and at the last points (1.0 and 3.0 MeV) rather unreliable.

Thus the differentiation of this fitted curve was thought to produce unreliable values for \( dY(E)/dE \) at 1.0 and 3.0 MeV. In any case, the differentiation of the end-points of a high order polynomial fit is likely to produce very dubious results. It is subjectively estimated that the relative uncertainties in \( dY(E)/dE \) are about ± 3 % for pure
element targets and $\pm 5\%$ for the targets of compounds. This does not take into account the absolute uncertainty in $Y(E)$ but this has been included in the final statement of uncertainties (Table 5.2.1.c). The raw values of $Y(E)$, rather than the fitted values, were used to calculate the second term in equation 3.1.3.1.12.

As was discussed in section 3.1.3.1, the values of $dE/dx$ for the various elements were taken from Andersen et al. (1977) and combined for the compounds by using Bragg's Rule. Although Langley et al. (1976) found evidence for a 4\% departure from Bragg's Rule at 1 MeV due to solid state effects, the recent results of Blondiaux et al. (1980) indicate that, for the present region of interest, there is no departure due to the different valency states in which the atoms may exist in different compounds. It has been assumed that Bragg's Rule holds. The values for total photon attenuation coefficients ($\mu$) were also combined in the same way assuming that there were no chemical effects. There are two widely used tabulations of photon attenuation coefficients, those by Veigele (1973) and Storm and Israel (1970). Veigele claims uncertainties of 3-5\% for the values presently used. Fig. 5.2.1.a shows the deviation of Veigele's values of $\mu$ from those of Storm and Israel. It can be seen that the tabulations differ by varying amounts with Veigele's values often being $\sim 6\%$ higher at the K absorption edges. In this work the mean of the two tabulations was taken. Recently, Montenegro et al. (1978) fitted the tabulations of Storm and Israel with a third order polynomial which allows the interpolation of $\mu$ to the precise photon energy of interest. This was found to be more accurate than the simple visual interpolations performed for an earlier presentation of these results (Barfoot et al. 1980a). Thus values of $\mu$ for the various characteristic X-rays were taken from Montenegro et al. and then modified to give a mean of the tabulations of Veigele and Storm and Israel by using Fig. 5.2.1.a. Table 5.2.1.b shows the resulting values of $\mu$ actually used and also the percent correction factor applied to the Montenegro et al. values to obtain the mean. Uncertainties of $\pm 5\%$ have been adopted for all values of $\mu$. This is somewhat conservatively in line with Veigele's statement of uncertainties.

All the peaks of interest in this study were well resolved and lay on small smoothly varying backgrounds. Fig. 5.2.1.b shows one of the poorest spectra from the point of view of resolution of $K_a$ and $K_b$ lines and peak to background ratio. Even for this case the ratio is about one hundred. In most instances the peak areas could be determined to $\pm 1\%$. 
Fig. 5.2.1.a Deviations from each other of two tabulations of total photon attenuation coefficients.
Fig. 5.2.1.b  PIXE spectrum of the thick CaCl$_2$ target obtained with 2 MeV protons.
Table 5.2.1.b.: Photon attenuation data used.

<table>
<thead>
<tr>
<th>X-ray and matrix</th>
<th>Total photon attenuation coefficient $\mu$ (barns/atom)</th>
<th>Correction to values of Montenegro et al.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu $K_a$ X-ray in Cu</td>
<td>$5.593 \times 10^3$</td>
<td>+ 3.2 %</td>
</tr>
<tr>
<td>Cu $K_a$ X-ray in CuCl</td>
<td>$5.884 \times 10^3$</td>
<td>+ 1.6 %</td>
</tr>
<tr>
<td>Ti $K_a$ X-ray in Ti</td>
<td>$8.814 \times 10^3$</td>
<td>+ 2.3 %</td>
</tr>
<tr>
<td>Ca $K_a$ X-ray in CaCl$_2$</td>
<td>$3.855 \times 10^4$</td>
<td>+ 2.3 %</td>
</tr>
<tr>
<td>Ca $K_a$ X-ray in CaF$_2$</td>
<td>$6.796 \times 10^3$</td>
<td>+ 0.6 %</td>
</tr>
<tr>
<td>Ca $K_a$ X-ray in CaO</td>
<td>$6.793 \times 10^3$</td>
<td>+ 1.2 %</td>
</tr>
<tr>
<td>Ca $K_a$ X-ray in CaCO$_3$</td>
<td>$4.139 \times 10^3$</td>
<td>+ 0.3 %</td>
</tr>
</tbody>
</table>

Table 5.2.1.c gives the estimated total uncertainties in the ionization cross-sections. Each source of error is given as an individual contribution to the total uncertainty. Thus, for example, although the uncertainty in $\mu$ is $\pm 5\%$, this only introduces $\pm 3\%$ to the uncertainty in the cross-section as, for most of the targets, the factor $Y(E) \mu \cos \vartheta \cos \phi$ is on average of the order of $\frac{dY(E)}{dE} \frac{dE}{dx}$ (see equation 3.1.3.1.12) and hence contributes only about a half of the cross-section. All of the major sources of uncertainty are discussed in this chapter or in Chapter 4. Slightly different uncertainties for Ti will be observed as these measurements were performed in the more accurate thin target cross-section determination set-up (Si(Li) efficiency more accurate and foil ion beam monitor used - see section 5.3). Some sources of uncertainty were determined to be negligible and these are discussed below. The random and systematic uncertainties have been kept apart and combined in quadrature to form the total random and systematic contributions. The total random and systematic contributions have also been added in quadrature in order to remain consistent with the $1\sigma$ level. This follows from the suggestions of Müller (1979). There is at present a controversy over how, if at all, random and systematic uncertainties should be combined. By tabulating the individual contributions to the total uncertainty, it is possible for other workers with different uncertainty propagation philosophies to make their own estimates of the uncertainties in the present results.

The proton-induced K shell ionization cross-sections derived from the measured X-ray yields are given for Ti and Cu in Table 5.2.1.d and for Ca in Table 5.2.1.e. The results for Cu (averaged over the two measurements), Ti and Ca are plotted in Fig. 5.2.1.c, Fig. 5.2.1.d and
Table 5.2.1.c.: Uncertainties in the determinations of proton-induced K-shell ionization cross-sections

<table>
<thead>
<tr>
<th>Uncertainty in ionization cross-section (%)</th>
<th>Thin Ti</th>
<th>Thick Ti</th>
<th>Thin Cu</th>
<th>Thick Cu</th>
<th>Thick CuCl</th>
<th>Thick Ca compounds</th>
<th>Thin CaF₂</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Random contributions</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Peak area</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
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<tr>
<td>Current integration</td>
<td>3.0</td>
<td>3.0</td>
<td>3.0</td>
<td>3.0</td>
<td>3.0</td>
<td>3.0</td>
<td>3.0</td>
</tr>
<tr>
<td>Proton energy</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>dY(E)/dE</td>
<td></td>
<td></td>
<td>-</td>
<td>-</td>
<td>3.0</td>
<td>5.0</td>
<td>-</td>
</tr>
<tr>
<td>Total random contribution</td>
<td>3.0</td>
<td>4.0</td>
<td>3.0</td>
<td>4.0</td>
<td>6.0</td>
<td>6.0</td>
<td>3.0</td>
</tr>
<tr>
<td><strong>Systematic contributions</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ion beam fluence</td>
<td>2.0</td>
<td>2.0</td>
<td>3.0</td>
<td>3.0</td>
<td>3.0</td>
<td>3.0</td>
<td>3.0</td>
</tr>
<tr>
<td>Target thickness</td>
<td>1.0</td>
<td></td>
<td>1.0</td>
<td></td>
<td>-</td>
<td></td>
<td>2.0</td>
</tr>
<tr>
<td>Detector efficiency</td>
<td>4.0</td>
<td>4.0</td>
<td>2.5</td>
<td>2.5</td>
<td>3.0</td>
<td>8.0</td>
<td>8.0</td>
</tr>
<tr>
<td>Photon attenuation</td>
<td>-</td>
<td>3.0</td>
<td></td>
<td>-</td>
<td>3.0</td>
<td>3.0</td>
<td>5.0</td>
</tr>
<tr>
<td>Stopping power</td>
<td>-</td>
<td>0.5</td>
<td></td>
<td>-</td>
<td>0.5</td>
<td>0.5</td>
<td>-</td>
</tr>
<tr>
<td>Fluorescence yield</td>
<td>3.0</td>
<td>3.0</td>
<td>0.7</td>
<td>0.7</td>
<td>0.7</td>
<td>3.0</td>
<td>3.0</td>
</tr>
<tr>
<td>Total systematic contribution</td>
<td>5.0</td>
<td>6.0</td>
<td>4.0</td>
<td>5.0</td>
<td>5.0</td>
<td>10.0</td>
<td>9.0</td>
</tr>
<tr>
<td><strong>Total uncertainty</strong></td>
<td>6.0</td>
<td>8.0</td>
<td>5.0</td>
<td>7.0</td>
<td>8.0</td>
<td>12.0</td>
<td>10.0</td>
</tr>
</tbody>
</table>
Table 5.2.1.d.: Proton-induced K-shell ionization cross-sections for titanium and copper targets *

<table>
<thead>
<tr>
<th>Proton energy (MeV)</th>
<th>( \theta = 0, \phi = 22.5^\circ )</th>
<th>( \theta = 11.25^\circ, \phi = 11.25^\circ )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Thin Ti</td>
<td>Thick Ti</td>
</tr>
<tr>
<td>1.00</td>
<td>240</td>
<td>(316)</td>
</tr>
<tr>
<td>1.25</td>
<td>389</td>
<td>375</td>
</tr>
<tr>
<td>1.50</td>
<td>590</td>
<td>544</td>
</tr>
<tr>
<td>1.75</td>
<td>764</td>
<td>690</td>
</tr>
<tr>
<td>2.00</td>
<td>956</td>
<td>935</td>
</tr>
<tr>
<td>2.25</td>
<td>1125</td>
<td>1106</td>
</tr>
<tr>
<td>2.50</td>
<td>1306</td>
<td>1339</td>
</tr>
<tr>
<td>2.75</td>
<td>1516</td>
<td>1493</td>
</tr>
<tr>
<td>3.00</td>
<td>1688</td>
<td>(1592)</td>
</tr>
</tbody>
</table>

Table 5.2.1.e.: Proton-induced K-shell ionization cross-sections for targets of calcium compounds *

<table>
<thead>
<tr>
<th>Proton energy (MeV)</th>
<th>Thin ( \text{CaF}_2 )</th>
<th>Thick ( \text{CaO} )</th>
<th>Thick ( \text{CaCO}_3 )</th>
<th>Thick ( \text{CaF}_2 )</th>
<th>Thick ( \text{CaCl}_2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.00</td>
<td>591</td>
<td>(355)</td>
<td>(468)</td>
<td>(630)</td>
<td>(997)</td>
</tr>
<tr>
<td>1.25</td>
<td>1049</td>
<td>694</td>
<td>1216</td>
<td>959</td>
<td>1146</td>
</tr>
<tr>
<td>1.50</td>
<td>1512</td>
<td>969</td>
<td>1636</td>
<td>1249</td>
<td>1250</td>
</tr>
<tr>
<td>1.75</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>2.00</td>
<td>2582</td>
<td>1535</td>
<td>2138</td>
<td>1923</td>
<td>1952</td>
</tr>
<tr>
<td>2.25</td>
<td>3116</td>
<td>1853</td>
<td>2430</td>
<td>2242</td>
<td>1977</td>
</tr>
<tr>
<td>2.50</td>
<td>3830</td>
<td>1900</td>
<td>2426</td>
<td>2533</td>
<td>2567</td>
</tr>
<tr>
<td>2.75</td>
<td>4478</td>
<td>2073</td>
<td>2605</td>
<td>2813</td>
<td>2899</td>
</tr>
<tr>
<td>3.00</td>
<td>5081</td>
<td>(2023)</td>
<td>(2785)</td>
<td>(3018)</td>
<td>(2882)</td>
</tr>
</tbody>
</table>

* Bracketed values are likely to be unreliable - see text.
Fig. 5.2.1.e respectively. Those from the thin target of CaF$_2$ are not shown because the values are so much higher than the rest of the results. Experimental values found in the literature, together with the fitted values of Johansson et al. (1976), are shown for comparison. Not all the known Cu values are given as there are very many and to do so would result in a confusing graph.

The main body of data for both Ti and Cu appear to be in quite good agreement with the present results. The exception is with the data of Bearse et al. (1973) which are consistently about 25% lower. It is rather difficult, with such graphs, to accurately examine the nature of the agreement between the thin and thick target methods. Therefore all of the present cross-section results have been normalised by dividing them by Johansson et al.'s. fitted values and are shown, together with the mean values (for each target) of the present deviations from the fit, in Figs. 5.2.1.f, 5.2.1.g, 5.2.1.h. In the case of Cu, for \( \theta = 0^\circ \) and \( \phi = 22.5^\circ \), the means of the deviations of the thin and thick target results agree to within 1% whilst for \( \theta = \phi = 11.25^\circ \) they agree to within 4%. The uncertainties given in the means are simply the standard deviations of the mean. It may be observed that there are no statistically significant differences between the results from the two set-ups \( (\theta = \phi = 11.25^\circ \text{ and } \theta = 0^\circ, \phi = 22.5^\circ) \) illustrating the internal consistency of the two sets of measurements. It may be concluded that the thick Cu results are about \((3 \pm 4)\%\) below those derived from the thin targets. The same conclusion is reached for Ti although, at energies greater than 2.0 MeV, the agreement is better than 2%. The values derived from the thick CuCl target are \((8 \pm 4)\%\) below those of the thick Cu targets and \((11 \pm 3)\%\) below those of the thin targets. Thus the deviations for CuCl are well beyond the random uncertainties.

5.2.2. Discussion

The thin and thick pure element target data are consistent with their estimated uncertainties. However, although the uncertainty in the fit to \( Y(E) \) may possibly be reduced by using a more physically meaningful fit, the uncertainties in \( \mu \) and \( S(E) \) will tend to produce a systematic bias common to all workers using the thick target technique. The systematic uncertainty in the target thickness in the thin target technique is likely to become a 'random' uncertainty when comparing results from different laboratories. Also, characteristic X-rays created by secondary production processes in the thick targets will again
Fig. 5.2.1.c Proton-induced K-shell ionization cross-sections for Cu.
Fig. 5.2.1.d Proton-induced K-shell ionization cross-sections for Ti.
Fig. 5.2.1.e  Proton-induced K-shell ionization cross-sections for Ca.
Fig. 5.2.1.f Deviations of measured Cu K ionization cross-sections from the BEA fit of Johansson et al. (1976).
Fig. 5.2.1.g Deviations of measured Ti K ionization cross-sections from the BEA fit of Johansson et al. (1976).

- THIN Ti; MEAN = 1.04 ± 0.02
- THICK Ti; MEAN = 1.01 ± 0.03
Fig. 5.2.1.h Deviations of measured Ca K ionization cross-sections from the BEA fit of Johansson et al. (1976) [thick targets only].

- CaO: MEAN = 0.79 ± 0.03
- CaCO$_3$: MEAN = 1.14 ± 0.17
- CaF$_2$: MEAN = 1.02 ± 0.03
- CaCl$_2$: MEAN = 1.05 ± 0.12

MEAN OF ALL PRESENT MEASUREMENTS = 1.00 ± 0.12
produce 'universal' systematic uncertainties; although in the present work the effect due to secondary electrons is less than 1 % of \( \sigma^v_K(E) \) (from the calculations of Akselsson et al. (1974) based on the work of Jarvis et al. 1970). There will be negligible secondary X-ray production by photons as, for the present targets, there are no characteristic X-rays and little bremsstrahlung with energy higher than the K absorption edge of the characteristic X-ray of interest. However, all these systematic uncertainties are certainly small when compared with the large differences in values quoted for \( \sigma^v_K(E) \) by different authors. The present author is thus in fair agreement with the conclusions of Rashiduzzaman Khan et al. (1978) who claim that the thin and thick target techniques are comparable in accuracy for their range of interest. It will be noted from Fig. 5.2.1.c and Fig. 5.2.1.d that the results of Rashiduzzaman Khan et al. (1976) are in good general agreement with the present results for Cu although there is a little levelling off in their high energy cross-sections. Their results for Ti appear to be about 10 % higher. McKnight et al. (1975) have compared the results from the thin and thick target methods. Although they do not quote uncertainties in their comparisons, they conclude that reliable thick target cross-sections can be obtained for the case of Cu K X-ray production by alpha particle bombardment.

If Figs. 5.2.1.e and 5.2.1.h are examined, it can be seen that there are large inconsistencies between the results obtained from the thick targets of calcium compounds. The mean deviation of all the present results from those of Johansson et al.'s fit is \((0 \pm 12)\) %. Cao\( \_2 \), Cao\( \_2 \) and Cao\( \_3 \) are higher than this by \((2 \pm 3)\) %, \((5 \pm 12)\) % and \((14 \pm 17)\) % respectively whilst Cao is lower by \((21 \pm 3)\) %. The literature values for these cross-sections are seen to be 10-20 % below the fit which may not be especially significant as this only represents the results from three laboratories. It should be remembered that there is a large systematic uncertainty in the present Ca cross-sections; largely due to the \(+ 8\) % uncertainty in the detector efficiency for Ca K\( _\alpha \) X-rays.

The 30 % expansion of the CaO target, mentioned earlier, was probably due to the reaction with water vapour to form a hydroxide. This would reduce the effective number density of the Ca atoms and hence give a systematically low result. This is the most likely explanation for the 21 % discrepancy in the cross-sections measured with the CaO target. In the case of Cao\( \_2 \), the target surface had become rougher by the end of the experiment and it was assumed that, due to the deliquescent nature of the compound, water had been absorbed onto the surface.
However it would appear that this cross-section is not too low and is in good agreement with the result from the very chemically stable target of CaF$_2$.

The CaCO$_3$ result is a little difficult to understand. The action of heat on the carbonate could produce the oxide thereby increasing the effective number of Ca atoms at the surface. This might be more significant the nearer the surface and hence the effect would be more noticeable the lower the energy (and therefore range) of the proton. Also, the photon attenuation and/or stopping cross-section data may be inaccurate. The possibility of deviations from Bragg's Law of additivity of stopping cross-sections has already been discussed. It would seem that, if the effect exists at all, then it will be small in the present range of interest. No published experiments are known which investigate similar deviations for photon attenuation coefficients ($\mu$) in compounds. As was seen in Fig. 5.2.1.a, the agreement between the compilations of $\mu$ was poorest near the absorption edges. This may be significant as the value of $\mu$ for Ca K X-rays is very near the Ca K absorption edge. Also, fine structure in $\mu$ around absorption edges, which varies according to the compound, has been observed (Creagh 1979) although no tabulations of this effect are available.

A random uncertainty of $\pm 3\%$ (see Chapter 4) was assigned to the current integration results. Lin et al. (1974) have found the same random effect for their set-up. The systematic correction of $-5\%$ to the integrated current values, which was derived from the thin Cu and CaF$_2$ target RBS measurements, may not be valid for the other targets. However, this is only thought to increase the systematic uncertainty by at most 3%. This was verified, as was described earlier, by measuring the current on all the targets while the Van de Graaff beam was very stable. Finally, it is possible that there are molecular effects in the K-shell ionization cross-section itself. Work by Chaturvedi et al. (1977) has shown that there can be a 10% difference in fluorine cross-sections measured with gas targets of different fluorine compounds. Recently, Bissinger et al. (1980) have found variations of more than 25% in carbon cross-sections measured with various carbonaceous gases. Further work is required to determine whether these effects occur at higher Z.

The strong high proton energy deviation of the CaF$_2$ thin target results remains unexplained. The target gave the same number of X-rays at 2 MeV at the beginning and at the end of the experiment. Besides which, no target deterioration effects could account for an increase. As this
was a thin layer on a thick carbon backing, the peak to bremsstrahlung ratio was lower than for any of the other targets. It was therefore decided to investigate whether the bremsstrahlung with energy greater than the Ca K absorption edge could have excited a significant number of additional Ca K X-rays. By measuring the number and energy distribution of the background registered by the Si(Li) detector and with a knowledge of the photo-electric cross-sections (derived approximately from the tabulations of Storm and Israel 1970), it was quite easy to perform a first order calculation of the number of Ca K X-rays produced in this manner. This effect is greatest at the highest proton energies because of the increased background. For 3.0 MeV protons incident on the thin CaF$_2$ target, it was calculated that for the prevailing experimental conditions, 22 counts would be recorded in the Si(Li) detector. This is to be compared with the total K$_a$ peak area of 69213 counts. Hence the effect is determined to be less than 0.03 %.

5.2.3 Conclusions

The present thin target results for proton-induced K-shell ionization cross-sections for Ti and Cu are in good agreement with values given in the literature. The thick pure element targets of Ti and Cu give slightly lower and less accurate values than the thin targets. Where possible, thin targets are to be preferred because of the reduced possibility of different laboratories being biased by the same systematic uncertainties. In addition, the number of irradiations and the complexity of data analysis is much reduced with thin targets.

The measurements using thick targets of chemical compounds are inconclusive although the spread in results can partly be explained qualitatively in terms of the chemical stabilities of the compounds. It is thus recommended that these data not be used for quantitative PIXE analysis of calcium and that values derived from a modification of the fitted values of Johansson et al. (1976), to be described in the next section, are presently the best choice. It is clear that the stability of the compounds is critical, that more must be ascertained about deviations from Bragg's Rule and that low energy photon attenuation coefficients, especially near the K-absorption edges, need to be more accurately known. The latter requirement has been reviewed by Nylandsted Larsen (1978). It is worth pointing out that these effects may also occur in the PIXE analysis of 'unknown' thick samples. For instance, if a chalk sample was analysed then the transition from carbonate to
oxide would result in too high results. Thin target results would remain largely unaffected because the proton and photon beams are not significantly attenuated.

5.2.4 A modification of the BEA fit of Johansson et al. for 1, 2 and 3 MeV protons incident on Z = 11-22 targets

The results for Ca ionization cross-sections were not accurate enough for the present analytical requirements. Rather than going on to measure other lower Z elements at similar levels of accuracy, it was decided to make use of the published experimental data. The only other element that could have been measured by the pure element thin layer technique is aluminium. Unfortunately, as was pointed out in section 4.4.5.3, the efficiency of Si(Li) detectors cannot be accurately calibrated for this low energy region (1-5 keV). Many of the lower Z results published have been obtained with gas proportional counters which may be calibrated at this energy because the thickness of the detector window may be measured. Such a detector was not available in the present experimental set-up.

Most of the available data is for integer values of MeV projectile energy. Also, a large number of PIXE analyses are performed at 1, 2 and 3 MeV. A fit has therefore been made to the available data, for these energies, based on the fit of Johansson et al. (1976). It was thought to be safer to make a simple modification of an existing fit that has some theoretical justification than to make a completely new one as there are so few data. All the known data were shown in Fig. 5.1.b. The values of Bearse et al. (1973) have not been used because they have been found to be consistently low by about 25% for all the elements studied in the present work.

The percentage deviations of the experimental data from the predictions of Johansson et al. have been fitted with linear least-squares functions in Z for the three energies. The results are shown as dashed lines in Fig. 5.1.b. It is concluded that the predictions of Johansson et al. should be multiplied by \((0.0299 Z + 0.341)\) at 1 MeV, by \((0.0355 Z + 0.272)\) at 2 MeV and by \((0.0290 Z + 0.422)\) at 3 MeV where Z is the atomic number of the target atom for which the cross-section is desired. This results in the values for proton-induced K shell ionization cross-sections given in Table 5.2.4. For these energies the low Z elements are near the peak of the universal cross-section curve and so the cross-section varies slowly with projectile energy whilst for the higher Z elements, such as Ti, the cross-section increases by a factor of 7.
Table 5.2.4.: Modified BEA fitted K shell ionization cross-sections.

<table>
<thead>
<tr>
<th>Atomic Number</th>
<th>Element</th>
<th>1 MeV</th>
<th>2 MeV</th>
<th>3 MeV</th>
</tr>
</thead>
<tbody>
<tr>
<td>11</td>
<td>Na</td>
<td>$3.57 \times 10^4$</td>
<td>$4.46 \times 10^4$</td>
<td>$4.62 \times 10^4$</td>
</tr>
<tr>
<td>12</td>
<td>Mg</td>
<td>$2.14 \times 10^4$</td>
<td>$3.12 \times 10^4$</td>
<td>$3.42 \times 10^4$</td>
</tr>
<tr>
<td>13</td>
<td>Al</td>
<td>$1.29 \times 10^4$</td>
<td>$2.19 \times 10^4$</td>
<td>$2.54 \times 10^4$</td>
</tr>
<tr>
<td>14</td>
<td>Si</td>
<td>$7.91 \times 10^3$</td>
<td>$1.53 \times 10^4$</td>
<td>$1.89 \times 10^4$</td>
</tr>
<tr>
<td>15</td>
<td>P</td>
<td>$4.84 \times 10^3$</td>
<td>$1.06 \times 10^4$</td>
<td>$1.39 \times 10^4$</td>
</tr>
<tr>
<td>16</td>
<td>S</td>
<td>$3.05 \times 10^3$</td>
<td>$7.50 \times 10^3$</td>
<td>$1.03 \times 10^4$</td>
</tr>
<tr>
<td>17</td>
<td>Cl</td>
<td>$1.93 \times 10^3$</td>
<td>$5.28 \times 10^3$</td>
<td>$7.66 \times 10^3$</td>
</tr>
<tr>
<td>18</td>
<td>Ar</td>
<td>$1.24 \times 10^3$</td>
<td>$3.71 \times 10^3$</td>
<td>$5.66 \times 10^3$</td>
</tr>
<tr>
<td>19</td>
<td>K</td>
<td>$7.99 \times 10^2$</td>
<td>$2.62 \times 10^3$</td>
<td>$4.18 \times 10^3$</td>
</tr>
<tr>
<td>20</td>
<td>Ca</td>
<td>$5.24 \times 10^2$</td>
<td>$1.86 \times 10^3$</td>
<td>$3.10 \times 10^3$</td>
</tr>
<tr>
<td>21</td>
<td>Sc</td>
<td>$3.47 \times 10^2$</td>
<td>$1.33 \times 10^3$</td>
<td>$2.31 \times 10^3$</td>
</tr>
<tr>
<td>22</td>
<td>Ti</td>
<td>$2.34 \times 10^2$</td>
<td>$9.63 \times 10^2$</td>
<td>$1.73 \times 10^3$</td>
</tr>
</tbody>
</table>

A linear fit was chosen because, in the absence of any theoretical justification, a higher order function does not appear to be warranted: especially with such a large spread in the few data. The standard deviations of the experimental data from the present fit are about $\pm 6\%$ for $Z = 21-22$ and $\pm 10\%$ for $Z = 13-20$. It is rather difficult to determine the level of expected uncertainty in these predictions. It is interesting to note that the present thin target measurements for Ti are $+2.6\%$, $-0.7\%$ and $-2.3\%$ at variance with the present fit at 1, 2 and 3 MeV respectively. Also, the mean of the thick CaF$_2$ and CaCl$_2$ target results only differs by $+4.2\%$. Therefore, if the fourteen different laboratories that produced the experimental results are making different systematic errors (in both directions), then the standard deviations of the data from the fits may be a fair representation of the uncertainty. The danger in this assumption is that the major systematic errors may be, to varying degrees, common to most laboratories. For example, inefficient secondary-electron suppression in ion beam current measurements results in low cross-section values. Extrapolation to low photon energies, without allowing for the silicon dead layer effect, will generate values for the efficiency which are too high. This again will result in values for the cross-sections which are too low. For the region $Z < 18$ there are only results from two laboratories. There is a clear need for more data. It should not
be too difficult to obtain accurate aluminium results with thin layers of aluminium and the use of a gas proportional counter. This would be of considerable help in interpolating down to this end of the periodic table.

5.3 The accurate determination of proton-, deuteron- and alpha particle-induced K shell ionization cross-sections for selected elements in the range Z = 22-34.

The work described in section 5.2 leads to the conclusion that the thin target method is the more accurate way of measuring ion-induced X-ray production cross-sections. The targets have been chosen to be a representative selection of the elements in the range Z = 22-34 which is typically the most important range for PIXE analysis as was discussed in section 5.1. Also the Si(Li) detector can be calibrated accurately in this region which is not yet possible for lower photon energies.

The aim of the following measurements was to obtain the most accurate proton cross-sections presently achievable in order to make a fit which would reliably predict K shell ionization cross-sections for 1-3 MeV protons on all the elements in the range Z = 22-34. Slightly less accurate results for deuteron and helium excitation are also obtained both as an aid to PIXE analysis and as a test of theory.

5.3.1 Experimental technique

Targets of Ti, V, Co, Cu and Ge were irradiated with 1-3 MeV protons, 1-3 MeV deuterons and 2.5 MeV helium ions. The target elements were chosen as being the most suitable from the point of view of the evaporation procedure, target uniformity and chemical stability. The layers were all of about 30 μg cm⁻² thickness with an uncertainty in the weighing of ± 1 % (see section 4.6). This direct method is believed to be the most accurate way of measuring target thickness as back-scattering spectrometry has larger uncertainties since even the cross-sections for this process are not as well known as is often thought (see section 3.2).

The layers were supported on thick (2 mm) vitreous carbon backings. The vitreous carbon and the polishing and cleaning processes were specially chosen so that there was a negligible contribution to the characteristic X-ray spectra from trace elements within the carbon. This was verified experimentally by PIXE analyses of the vitreous carbon disks after they had been subjected to the various cleaning procedures.
Further details of this may be found section 6.2.1. A thick backing was chosen in preference to the more common thin backing to ensure the stability and integrity of the layers. As was discussed in connection with the foil ion beam monitor (section 4.3.3), changes in the structure of self-supporting foils under irradiation have been observed which may be due to foil thickening. This would result in obtaining cross-sections which are too high and may be one of the causes for the large dispersion in results from laboratories using thin self-supporting foils.

A small drawback in using thick backings is the large bremsstrahlung continuum below about 4 keV. However it has already been shown in section 5.2.3 that this will not induce extra characteristic X-rays in the energy region of interest. Also the amount of background even under the lowest energy peak, that of the Ti $K_{\alpha}$ X-ray, was very small and varied smoothly (see Fig. 5.3.1.a). In order to prevent the bremsstrahlung from creating unnecessary dead-time, a 44 mg cm$^{-2}$ polyethylene absorber was placed in front of the detector. This effectively removed the background whilst only attenuating the characteristic X-rays by a small amount. Typically, ion beam currents of 1-10 nA and irradiation times of 15 minutes were employed.

A spectrum obtained with 2 MeV protons incident on the Ti target is shown in Fig. 5.3.1.a. For the other targets, the resolution of the $K_{\alpha}$ and $K_{\beta}$ X-rays was considerably better. Sufficient counts were obtained such that the uncertainties in the peak areas (with background subtracted) were typically given by the computer programme to be $\pm 1\%$ for protons and $\pm 2\%$ for deuterons and helium ions. Only the results for the $K_{\alpha}$ X-rays were used as the $K_{\beta}$ yields usually had uncertainties of $\pm 5\%$. The $K_{\beta}/K_{\alpha}$ ratio given by Bambynek et al. (see section 4.4.5.3) was then used to obtain the total K X-ray yield. As the $K_{\beta}$ yields are only about 10% of the total K X-ray yield, the small uncertainty in $K_{\beta}/K_{\alpha}$ will yield a negligible uncertainty in $K_{\alpha+\beta}$. The Si(Li) detector efficiency was determined to as high an accuracy as seems feasible with the present techniques, with uncertainties being from $\pm 2\%$ to $\pm 4\%$ in the region of interest (see section 4.4.5.3.1). The recovery time of the Si(Li) detector is considerably faster than that of the ADC and so the controlling dead-times were measured via the ADC. The corrections were typically 0.5%. Consequently a 20% error in this correction would only result in a 0.1% contribution to the uncertainty in the cross-section.

During this series of cross-section measurements, the foil ion beam monitor was available. For each PIXE spectrum the ion beam
Fig. 5.3.1.a  X-ray spectrum obtained with 2MeV proton irradiation of the thin titanium layer.
fluence was simultaneously measured by this monitor and also by conventional current integration. The electron suppressor was held at a potential of \(-400\) V and the appropriate corrections were made for the charge state of the projectiles after passing through the gold foil of the monitor (see section 4.3.1 for correction procedure). In addition, at each projectile energy, a RBS spectrum was taken of a target layer (Ge) at the same time as the current integration and foil ion beam monitor values were recorded. Thus three independent methods were used to determine the absolute amount of the ion beam fluence. The Ge target was chosen as it had the highest RBS cross-section and was the least likely to be affected by non-Rutherford scattering.

Although some problems remain with the absolute accuracy of the foil monitor, it is a precise method of normalising ion beam fluence measurements for a particular projectile energy and species. A consistent pattern in the current integration results was observed. Fig.5.3.1.b shows the percentage difference of current integration values from those of the foil monitor for \(2.5\) MeV protons. On average the current integration values are \(6.6\%\) lower but this varies with element. By making similar plots for all the other energies and projectiles, it was found that, on average, Ti and V gave \(0.5\) and \(1\%\) lower current integration results than Co, Cu and Ge. This is probably due to the different secondary-electron emission properties of the elements and indicates that the electron suppressor is not totally effective. The \(2.5\) MeV proton plot has been chosen as, at this energy, the beam was moved to areas adjacent to the usual beam spot position on the targets in order to check the uniformity of the layers. Thus it is possible to compare the current integration results on the 'well used' and on the clean parts of the elemental layers. It can be seen that there is no significant difference between the two sets of data.

Fig. 5.3.1.c shows the mean percentage difference of the current integration results from those of the foil monitor for all the energies and projectiles used. The data are shown in the order in which the experiments were performed with the same gold foil used throughout. Each point represents the mean difference for that energy with the error bar being equal to the standard deviation of that mean. It can be seen that from experiment 5 onwards the difference is constant to within about \(+1\%\). The most probable cause of this small variation is in the setting of the single channel analyser window over the gold RBS peak. As the carbon is deposited on the gold foil, due to cracking of carbonaceous vapours in the vacuum system, the gold RBS peak acquires a small low energy tail.
Fig. 5.3.1.b Percentage deviation of measured integrated current from foil monitor values for a 2.50 MeV proton beam.
Mean percentage deviations of the current integration values from those of the foil monitor. Also shown for comparison are the ratios of gold foil counts to the carbon layer counts.
A typical foil monitor spectrum is shown in Fig. 5.3.1.d. This spectrum was recorded towards the end of the experiments and the carbon layer had built up to about 100 µg cm$^{-2}$. If all the carbon was on the beam side of the foil, this would result in about a 7% increase in the Rutherford cross-section thereby giving fluence measurements that are too high by 7%. The ratio of gold to carbon RBS counts for the gold foil has also been plotted in Fig. 5.3.1.c for the case of proton irradiation. The value at 1.75 MeV has not been given because a carbon nuclear reaction dominates the RBS peak at this energy. These ratios are fairly constant after experiment 4 which indicates that a constant correction of the order of -7% should be made to the foil ion beam monitor values. The strong variations before this are probably due to a combination of carbon build-up and foil shrinkage. The total fluence of protons passing through the foil in experiments 1 to 4 was about 75 µC, 55 µC, 40 µC and 43 µC respectively. Examination of Fig. 5.3.1.c suggests that the foil shrinkage effect reached completion during experiment 2 after a cumulative dose of around 100 µC and that the carbon build-up reaches a maximum after about 200 µC. When the correction for carbon build-up has been made to the foil monitor results, the two methods agree (after experiment 4) to within 1%.

As a result of 1 MeV proton RBS analyses (during experiment 10) of all the targets, taken simultaneously with foil ion beam monitoring and current integration, and taking into account the corrections to the current integration values caused by the differing secondary-electron emission properties, the result is obtained that the measured current integration values on the Ti target should be reduced by 4%, on V by 3.5% and on Co, Cu and Ge by 4.5%. Thus for all the ionization cross-section measurements the current integration values, with the above corrections, were used in the calculation of the cross-sections.

It is perhaps worthwhile to summarise the conclusions drawn from the ion beam fluence results of the three different methods after all the corrections have been made. The foil ion beam monitor results are 1% below those of current integration and RBS results are 2.5 - 3.5% below those of the monitor. Thus the total systematic spread in fluence results is only 4.5%. It has been decided that the RBS results are likely to be the most accurate as analyses were performed at all energies for Ge and at 1 MeV for all the targets. Any slight deviations from the Rutherford scattering law would appear to be small considering the comparison with the foil monitor. It should be noted that the
Fig. 5.3.1.d Typical foil ion beam monitor particle spectrum showing effect of carbon build-up. (recorded with 2.5 MeV protons).
correction to the current integration results deduced from RBS analyses of known Cu and CaF$_2$ layers was found to be $-(5 \pm 3)$ % during the previous experiment (section 5.2.1). This is in excellent agreement with the present correction factor of $-4.5$ % for the Cu target. It seems reasonable, both from the above discussions and from the mass of data presented at the end of section 4.3.3, to assign a systematic uncertainty of $\pm 2$ % and a random uncertainty of $\pm 3$ % to the ion beam fluence results finally used in the present K-shell ionization cross-section calculations.

All the uncertainties encountered in the K-shell ionization cross-section measurements for protons are listed in Table 5.3.1.a. Uncertainties $<0.1$ are indicated by a zero. Numbers preceded by a $<$ sign indicate the upper limit of small corrections which have not been made. The signs of these vary and they are likely to cancel out. All other uncertainties have been accurately calculated and correspond to the 1σ level. All such sources of uncertainty should always be carefully checked as they may be much greater in different experimental configurations and for different projectile energies, species and targets.

All the sources of uncertainty given in Table 5.3.1.a have either been discussed already, or are trivial to measure, or will be described elsewhere. Into this latter category come the effects of multiple ionization (section 5.4) and photon backscattering (Barfoot 1980b).

5.3.2 Results

The proton-induced K-shell ionization cross-sections deduced from the measured X-ray production cross-sections are given in Table 5.3.2.a. The two sets of 1 MeV results are for two separate runs at this energy. It can be seen that good agreement is obtained between these runs except for the case of Ti. The three sets of results at 2.5 MeV were obtained with the beam spot in its usual position and 2 mm below and above this position. As the beam spot was 1 mm in diameter, the positions at a distance of 2 mm will not have had any carbon build-up due to beam-induced effects. It may be noted that there are no significant differences between the three sets of results. This also confirms the uniformity of the layers. The thin Cu target results obtained in section 5.2.1 are again given here.

The values for deuteron- and helium-induced ionization are given in Tables 5.3.2.b and 5.3.2.c. The absence of ion beam channelling effects was verified with the helium ion beam by additionally measuring
Table 5.3.1.a.: Uncertainties in the determination of K shell ionization cross-sections for protons (in percent)

<table>
<thead>
<tr>
<th>Systematic contributions:</th>
<th>Ti</th>
<th>V</th>
<th>Co</th>
<th>Cu</th>
<th>Ge</th>
</tr>
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<tr>
<td>Detector efficiency</td>
<td>4</td>
<td>3</td>
<td>2</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>Ion beam fluence</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Target thickness</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Fluorescence yield</td>
<td>3</td>
<td>1</td>
<td>2</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>Photon backscattering</td>
<td>&lt; 0.3</td>
<td>&lt; 0.3</td>
<td>&lt; 0.4</td>
<td>&lt; 0.4</td>
<td>&lt; 0.9</td>
</tr>
<tr>
<td>Target layer impurities</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Fluorescence of chamber materials</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>&lt; 1</td>
<td>0</td>
</tr>
<tr>
<td>Method of peak area integration</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Deviation of ion beam position from source position</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Projectile energy loss in target layer</td>
<td>&lt; 0.3</td>
<td>&lt; 0.3</td>
<td>&lt; 0.3</td>
<td>&lt; 0.3</td>
<td>&lt; 0.3</td>
</tr>
<tr>
<td>Photon attenuation in target layer</td>
<td>&lt; 0.1</td>
<td>&lt; 0.1</td>
<td>&lt; 0.4</td>
<td>&lt; 0.3</td>
<td>&lt; 0.2</td>
</tr>
<tr>
<td>Anisotropy of X-ray emission</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Radiation-induced thickening of target layer</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Fluorescence from bremsstrahlung</td>
<td>&lt; 0.03</td>
<td>&lt; 0.03</td>
<td>&lt; 0.03</td>
<td>&lt; 0.03</td>
<td>&lt; 0.03</td>
</tr>
<tr>
<td>Fluorescence from characteristic X-rays</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Secondary electron-induced characteristic X-rays</td>
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<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
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<tr>
<td>Multiple ionization</td>
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<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
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<tr>
<td>Channelling effects</td>
<td>&lt; 0.5</td>
<td>&lt; 0.5</td>
<td>&lt; 0.5</td>
<td>&lt; 0.5</td>
<td>&lt; 0.5</td>
</tr>
<tr>
<td><strong>Total systematic contribution</strong></td>
<td>5</td>
<td>4</td>
<td>4</td>
<td>3</td>
<td>4</td>
</tr>
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</table>

<table>
<thead>
<tr>
<th>Random contributions:</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
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<tr>
<td>Ion beam fluence</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>Peak area</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Projectile energy</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>Dead-time correction</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td><strong>Total random contribution</strong></td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>3</td>
</tr>
</tbody>
</table>

| Total of systematic and random contributions |   | 6  | 5  | 5  | 5  | 5  |
Table 5.3.2.a.: Measured proton-induced K shell ionization cross-sections (barns)

<table>
<thead>
<tr>
<th>Element (Z)</th>
<th>Ti(22)</th>
<th>V(23)</th>
<th>Co(27)</th>
<th>Cu(29)</th>
<th>Cu(29) ( ^a ) Mean Cu(29)</th>
<th>Ge(32)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy (MeV)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.00</td>
<td>264.7</td>
<td>154.6</td>
<td>32.35</td>
<td>16.17</td>
<td>17.01</td>
<td>16.59</td>
</tr>
<tr>
<td>1.25</td>
<td>225.8</td>
<td>156.5</td>
<td>31.77</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1.50</td>
<td>388.7</td>
<td>282.1</td>
<td>60.76</td>
<td>30.73</td>
<td>33.74</td>
<td>32.23</td>
</tr>
<tr>
<td>1.75</td>
<td>589.6</td>
<td>425.1</td>
<td>100.6</td>
<td>53.41</td>
<td>51.81</td>
<td>52.61</td>
</tr>
<tr>
<td>2.00</td>
<td>764.2</td>
<td>555.3</td>
<td>138.8</td>
<td>75.88</td>
<td>-</td>
<td>75.88</td>
</tr>
<tr>
<td>2.25</td>
<td>956.3</td>
<td>689.3</td>
<td>182.5</td>
<td>99.62</td>
<td>102.5</td>
<td>101.1</td>
</tr>
<tr>
<td>2.50</td>
<td>1125</td>
<td>837.0</td>
<td>233.3</td>
<td>130.3</td>
<td>129.4</td>
<td>129.9</td>
</tr>
<tr>
<td>2.75</td>
<td>1282</td>
<td>963.5</td>
<td>266.3</td>
<td>155.5</td>
<td>167.3</td>
<td>69.65</td>
</tr>
<tr>
<td>3.00</td>
<td>1323</td>
<td>975.8</td>
<td>268.6</td>
<td>-</td>
<td>-</td>
<td>160.0</td>
</tr>
<tr>
<td>3.25</td>
<td>1311</td>
<td>968.4</td>
<td>269.4</td>
<td>157.3</td>
<td>-</td>
<td>69.14</td>
</tr>
<tr>
<td>3.50</td>
<td>1516</td>
<td>1133</td>
<td>333.3</td>
<td>193.5</td>
<td>198.0</td>
<td>195.8</td>
</tr>
<tr>
<td>3.75</td>
<td>1688</td>
<td>1263</td>
<td>387.5</td>
<td>229.5</td>
<td>232.6</td>
<td>231.1</td>
</tr>
</tbody>
</table>

* Measurement performed at \( \theta = \phi = 12.5^\circ \) - see section 5.2.1

The cross-sections at + 4°, and - 4° from the usual (vertical incidence) beam direction. Unfortunately the helium results for Co were lost due to a malfunction of the data transfer system. The helium beam lost 13 keV in energy in traversing the Au foil and in reaching the centre of the target layer. This was corrected for by scaling up to 2.500 MeV with the aid of the corrected SCA theory. This correction was less than 2 %.

5.3.3 Discussion

5.3.3.1 Proton irradiation

The results for Ti and Cu have already been shown in Figs. 5.2.1.c and 5.2.1.d where they were compared to other available experimental data and to the BEA fit of Johansson et al. (1979). It can be seen that the present results fall within the main body of data and are somewhat higher than the fit. Similar agreement was obtained with the
Table 5.3.2.b.: Measured deuteron-induced K shell ionization cross-sections (barns)

<table>
<thead>
<tr>
<th>Element(Z)</th>
<th>Ti(22)</th>
<th>V(23)</th>
<th>Co(27)</th>
<th>Cu(29)</th>
<th>Ge(32)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy (MeV)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.00</td>
<td>35.19</td>
<td>21.70</td>
<td>3.986</td>
<td>1.732</td>
<td>0.5881</td>
</tr>
<tr>
<td>2.00</td>
<td>237.4</td>
<td>162.8</td>
<td>35.00</td>
<td>17.21</td>
<td>6.424</td>
</tr>
<tr>
<td>2.50</td>
<td>405.3</td>
<td>276.2</td>
<td>61.44</td>
<td>32.24</td>
<td>12.62</td>
</tr>
<tr>
<td>3.00</td>
<td>573.2</td>
<td>404.6</td>
<td>96.93</td>
<td>52.17</td>
<td>20.19</td>
</tr>
</tbody>
</table>

Table 5.3.2.c.: Measured helium-induced K shell ionization cross-sections (barns)

<table>
<thead>
<tr>
<th>Element(Z)</th>
<th>Ti(22)</th>
<th>V(23)</th>
<th>Cu(29)</th>
<th>Ge(32)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy (MeV)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.50 (+ 4°)</td>
<td>175.7</td>
<td>73.06</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2.50 (0°)</td>
<td>177.0</td>
<td>73.35</td>
<td>8.167</td>
<td>2.820</td>
</tr>
<tr>
<td>2.50 (- 4°)</td>
<td>178.9</td>
<td>76.31</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Other elements. In Fig. 5.3.3.1.a the present results for Ti and Cu are compared to the results of the various theoretical predictions. These are the BEA as described by Garcia (1973), the PWBA as calculated by Benka et al. (1978) and the SCA with binding energy, Coulomb deflection and electron relativistic corrections included as proposed by Laegsgaard et al. (1978). Rather than again plotting a mass of other laboratories' experimental data, it has been decided to compare the results only with those of Laegsgaard et al. (1979), at the University of Aarhus, as these are the only other results with comparable accuracy (+3% to ±10%) to the present ones. Most other workers claim uncertainties in the range ±10% to ±15% and an examination of their methods of data reduction and statements of uncertainties indicates that the uncertainties may often be even higher than claimed. In fact this must be the case as the dispersion in published results is far greater than could be accounted for by considering the stated uncertainties (see section 5.1).
Fig. 5.3.3.1.a Experimental values of proton-induced K-shell ionization cross-sections for titanium and copper compared with the SCA, PWBA and BEA theoretical predictions.
It can be seen that the best fit is given by the BEA theory and that the SCA theory is better than the PBWA at lower projectile energies and higher target atomic numbers. The latter is to be expected from the discussion of section 3.1.1 as the SCA is a low energy approximation and the PWBA a high energy one. The agreement with the BEA may be fortuitous as the correction procedures have not yet been as fully developed. It should be pointed out that the broad agreement between the experimental results and the theories themselves is quite good indicating that the different theories may soon converge. This indicates that, to be of use in comparing theories, experimental values for cross-sections must have systematic uncertainties of less than about ±10%.

In an attempt to cancel out some of the systematic errors in the experimental results, the ratio of Ti to Cu cross-sections are plotted in Fig. 5.3.3.1b along with the theoretical predictions. Here it appears that the PWBA fits the data best. There appears to be little to choose between these theories in the range \(Z = 22-29\) for protons of 0.5 - 3.0 MeV. However, for higher \(Z\) values, the corrected SCA is found to be a very good fit to experimental data as it is the only theory that presently includes a relativistic correction (Laegsgaard et al. 1978) and, by its very nature, the SCA is most suited in predicting impact parameter dependencies of ionization cross-sections. It would therefore appear that this is the most physically interesting of the theories. For these reasons it was decided to concentrate on the SCA with the hope that this was the most likely theory that, with minor modifications, would most accurately predict cross-sections for the present range of interest.

In Fig. 5.3.3.1c all the present thin target cross-sections values, divided by the predictions of the corrected SCA, are plotted as a function of the corrected adiabatic parameter \(\xi\) (which was discussed in section 3.1.1). The theory varies from being too high by 14% to being too low by 34%. Nevertheless, it can be seen that the data lie on a very good straight line. When a similar plot (Fig. 5.3.3.1d) is made using the uncorrected SCA, a much greater dispersion is observed with the higher \(Z\) results being progressively more to the left. Thus, for the present range of \(Z\) and projectile energy, the correction procedures appear to be quite effective.

The straight line shown in Fig. 5.3.3.1c was derived from a linear least squares fit to the data (known hereafter as the present SCA fit). Fig. 5.3.3.1e shows the deviations of these data points and those of Laegsgaard et al. from that straight line. It is apparent that there
Fig. 5.3.3.1.b Experimental values for the ratio \( \sigma_K^y (Ti) / \sigma_K^y (Cu) \) compared to the theoretical predictions.
Fig. 5.3.3.1c  All of the present experimental results for protons compared to the corrected SCA theory of Laegsgaard et al. (1978).

Fig. 5.3.3.1d  All of the present experimental results for protons compared to the uncorrected SCA theory.
Fig. 5.3.3.1.e Ratios of experimental results to those of the predictions of the present fit to the corrected SCA.
is almost double the dispersion in the data of Laegsgaard et al. In Table 5.3.3.1.a, the mean ratios of the data to present SCA fit are given for each element. The uncertainties are the standard deviations of the ratios. The mean ratio of all the data of the Aarhus group is $0.947 \pm 0.027$. However, one element (nickel) is especially low and if this is left out of the average, the result is $0.956 \pm 0.019$. Thus the agreement between the two laboratories is excellent especially as very different experimental approaches have been adopted. Laegsgaard et al. claim uncertainties varying from $\pm 3\%$ to $\pm 10\%$ for their values but they have not included the $1 - 3\%$ uncertainties ($\Delta \omega$) in the fluorescence yield. The present systematic uncertainties (including $\Delta \omega$) go from $\pm 3\%$ to $\pm 5\%$ with random uncertainties of $\pm 3\%$. The claimed levels of uncertainty are thus very similar. Unfortunately, as Laegsgaard et al. have not listed the individual contributions to the total uncertainty, it is not possible to make a more accurate comparison of the uncertainties.

Table 5.3.3.1.a: Mean ratios of experimental data to the present SCA fit

<table>
<thead>
<tr>
<th>Element (Z)</th>
<th>Ti(22)</th>
<th>V(23)</th>
<th>Mn(24)</th>
<th>Fe(26)</th>
<th>Co(27)</th>
<th>Ni(28)</th>
<th>Cu(29)</th>
<th>Ge(32)</th>
<th>Se(34)</th>
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</thead>
<tbody>
<tr>
<td>Present</td>
<td>0.996</td>
<td>1.017</td>
<td>-</td>
<td>-</td>
<td>0.969</td>
<td>-</td>
<td>1.003</td>
<td>1.016</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>$\pm 0.014$</td>
<td>$\pm 0.023$</td>
<td>$\pm 0.024$</td>
<td>$\pm 0.015$</td>
<td>$\pm 0.019$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Laegsgaard et al.</td>
<td>0.999</td>
<td>0.951</td>
<td>0.960</td>
<td>0.940</td>
<td>-</td>
<td>0.893</td>
<td>0.936</td>
<td>-</td>
<td>0.950</td>
</tr>
<tr>
<td></td>
<td>$\pm 0.019$</td>
<td>$\pm 0.029$</td>
<td>$\pm 0.034$</td>
<td>$\pm 0.032$</td>
<td>$\pm 0.014$</td>
<td>$\pm 0.015$</td>
<td>$\pm 0.038$</td>
<td>$\pm 0.019$</td>
<td>$\pm 0.019$</td>
</tr>
</tbody>
</table>

Again examining Fig. 5.3.3.1.e it can be seen that most of the present data fall within $\pm 2\%$ of the fit. The slight structure as a function of energy, apparent in the present results, is most likely due to errors in the calibration of the energy of the proton beam. It is most improbable that structure in the cross-section would appear at the same energy for all the targets. Also there is no evidence of such structure with the data of Laegsgaard et al.

Using the present SCA fit, cross-sections in the range $Z = 18-50$ have been computed and are given in Table 5.3.3.1.b. The standard deviation of the present experimental data from the fit is $\pm 2.7\%$. This standard deviation will include the effect of all the random errors and also the uncertainty in the target thicknesses as these become
random in a series of weighings of different targets (no significant systematic error has been found in the CBNM ultra-high vacuum micro-balance). Except for the uncertainties in the detector efficiency and in the ion beam fluence, all the other systematic errors are small, vary from target to target and have different signs.

Table 5.3.3.1.b.:  Fitted proton-induced K shell ionization cross-sections (in barns) based on modified SCA theory

<table>
<thead>
<tr>
<th>Z</th>
<th>Element</th>
<th>PROTON ENERGY</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>1.0 MeV</td>
</tr>
<tr>
<td>18</td>
<td>Ar</td>
<td>1374</td>
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<tr>
<td>19</td>
<td>K</td>
<td>874.5</td>
</tr>
<tr>
<td>20</td>
<td>Ca</td>
<td>560.6</td>
</tr>
<tr>
<td>21</td>
<td>Sc</td>
<td>368.6</td>
</tr>
<tr>
<td>22</td>
<td>Ti</td>
<td>242.7</td>
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<tr>
<td>23</td>
<td>V</td>
<td>161.2</td>
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<tr>
<td>24</td>
<td>Cr</td>
<td>108.1</td>
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<tr>
<td>25</td>
<td>Mn</td>
<td>73.11</td>
</tr>
<tr>
<td>26</td>
<td>Fe</td>
<td>49.93</td>
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<tr>
<td>27</td>
<td>Co</td>
<td>34.38</td>
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<tr>
<td>28</td>
<td>Ni</td>
<td>23.85</td>
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<tr>
<td>29</td>
<td>Cu</td>
<td>16.61</td>
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<tr>
<td>30</td>
<td>Zn</td>
<td>11.65</td>
</tr>
<tr>
<td>31</td>
<td>Ga</td>
<td>8.224</td>
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<td>32</td>
<td>Ge</td>
<td>5.855</td>
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<td>33</td>
<td>As</td>
<td>4.195</td>
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<tr>
<td>34</td>
<td>Se</td>
<td>3.014</td>
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<tr>
<td>35</td>
<td>Br</td>
<td>2.184</td>
</tr>
<tr>
<td>36</td>
<td>Kr</td>
<td>1.590</td>
</tr>
<tr>
<td>37</td>
<td>Rb</td>
<td>1.167</td>
</tr>
<tr>
<td>38</td>
<td>Sr</td>
<td>0.8615</td>
</tr>
<tr>
<td>39</td>
<td>Y</td>
<td>0.6400</td>
</tr>
<tr>
<td>40</td>
<td>Zr</td>
<td>0.4779</td>
</tr>
<tr>
<td>41</td>
<td>Nb</td>
<td>0.3596</td>
</tr>
<tr>
<td>42</td>
<td>Mo</td>
<td>0.2709</td>
</tr>
<tr>
<td>43</td>
<td>Tc</td>
<td>0.2064</td>
</tr>
<tr>
<td>44</td>
<td>Ru</td>
<td>0.1574</td>
</tr>
<tr>
<td>45</td>
<td>Rh</td>
<td>0.1211</td>
</tr>
<tr>
<td>46</td>
<td>Pd</td>
<td>0.09303</td>
</tr>
<tr>
<td>47</td>
<td>Ag</td>
<td>0.07188</td>
</tr>
<tr>
<td>48</td>
<td>Cd</td>
<td>0.05594</td>
</tr>
<tr>
<td>49</td>
<td>In</td>
<td>0.04350</td>
</tr>
<tr>
<td>50</td>
<td>Sn</td>
<td>0.03393</td>
</tr>
</tbody>
</table>

Therefore it is expected that these will effectively cancel out in the fit. The ion beam fluence measurements have an absolute uncertainty
of $\pm 2\%$ and those of the detector efficiency $\pm 2\%$ to $\pm 3\%$ except for Ti which has one of $\pm 4\%$. Thus the total uncertainty in the present fitted SCA cross-sections is about $\pm 5\%$ for the range $Z = 22-34$. In a more detailed treatment of the uncertainties of the fit, account should be taken of the fact that the fit will be more accurate in the central region of the curve. Making similar calculations with the claimed uncertainties of Laegsgaard et al. gives an uncertainty of about $\pm 4\%$ in the fit using their data as they claim that the detector efficiency uncertainty of $\pm 3\%$ is the only one of significance. However, if one regards Table 5.3.3.1.a and Fig. 5.3.3.1.e then the mean difference in their cross-sections from element to element varies by $10.6\%$ compared to $4.8\%$ for the present experimental results. This would indicate that, in fact, their uncertainties are significantly greater than the present ones. This may originate from the fact that their method relies strongly on the Rutherford scattering law. They measure the Rutherford scattered protons simultaneously with the X-rays using well calibrated detectors. With such a technique, the mass of the target and the ion beam fluence cancel out in the calculation of the X-ray production cross-section. Unfortunately this method requires that the proton scattering accurately follows the Rutherford cross-section for all the energies and targets used. As has been mentioned in section 3.2, Jarjis (1979a) has found evidence for $\pm 5\%$ deviations from this law for 1-4 MeV alpha particles backscattered from Cr and Ni. This corresponds to energies per nucleon of 0.25-1.00 MeV which is well below the Coulomb barrier ($\sim 8$ MeV). Judging from the paper of Jarjis, the evidence for this deviation at these energies appears somewhat tenuous but it should be borne in mind as another possible source of error. Such deviations would only slightly affect the present results as the absolute values of the ion beam fluence measurements are based on effective averages of the Rutherford scattering values for a variety of targets and projectile energies and the target thicknesses were determined in an independent manner.

Until further work is performed on these possible deviations from the Rutherford scattering law, it seems reasonable to give equal uncertainties of $\pm 5\%$ to the fits from the present data and those of Laegsgaard et al. Averaging the two fits gives the result that the present fitted SCA cross-sections should be reduced by $2.2\%$ and the uncertainty in this average is $\pm 4\%$. It is thus recommended that, until evidence emerges to suggest that one set of results is in the ascendency or until another laboratory performs measurements of equal or higher accuracy, the present fitted SCA ionization cross-sections,
reduced by 2.2 %, are accurate to \( \pm 4 \% \) and are by far the best data available. Uncertainties due to the fluorescence yield values have not been included in these discussions. However, if other workers utilise the same values as are presently used (Bambynek et al. 1972) to calculate the X-ray production cross-sections, this uncertainty will largely cancel out. It should be stressed that the above discussion of accuracies only holds for 1-3 MeV protons incident on targets of \( Z = 22-34 \). The accuracies at higher \( Z \) are discussed later.

In Fig. 5.3.3.1.f, the present SCA fit is compared to the other available fitted cross-sections. The BEA fit of Johansson et al. (1976) has already been discussed. Lopes et al. (1979) have suggested that, for any particular energy, the ionization cross-section varies as \( \exp(-Z) \). They also discuss some theoretical evidence for this. It is worthwhile to examine Fig. 5.3.3.1.g. If there was a truly exponential fall-off in cross-section between \( Z = 22-32 \), the experimental data would follow the dotted line. However, the experimental data fall consistently below this line which indicates that the ionization cross-sections follow a function of \( Z \) which is somewhat greater in second derivative than an exponential function. For example, at 1 MeV the present fitted SCA cross-section is 9.7 % below that predicted by the exponential law for the middle of the range \( Z = 22-32 \). Similar conclusions were reached when the experimental data of Laegsgaard et al. were used. Lopes et al. have fitted the available experimental data for proton energies of 0.60, 0.80, 1.00, 1.20, 1.40, 1.60, 1.80 and 2.00 MeV to exponential functions of \( Z \) for the ranges \( Z = 20-26, 27-34, 35-41 \) and 42-50. For example, the results for 2 MeV protons incident on \( Z = 20-26 \) targets are obtained by fitting the experimental data with an exponential function of \( Z \) only for these seven elements. Data for other \( Z \)'s and proton energies do not play any part in the fit. Thus in going from one energy and one \( Z \) range to the next, data from completely different laboratories may be included. This has the effect of producing large discontinuities in the cross-sections predicted by Lopes et al., as can be seen by examining Fig. 5.3.3.1.f. For 1 MeV protons, there is a 15 % jump in the normalised cross-section in going from \( Z = 34 \) to \( Z = 35 \). Such discontinuities seem unphysical and suggest a poor fitting technique has been utilised. However, the greatest deviation of these data from the present SCA fit is 15 %. Part of this deviation is probably also due to the fact that their \( \exp(-Z) \) assumption does not hold.
Fig. 5.3.3.1.f Comparisons of the various available fits for 1, 2 and 3 MeV protons incident on targets with $Z = 18 - 50$. 
Fig. 5.3.3.1.g Test of whether experimental data follows $\exp(-Z)$ law. The points represent the deviations of $\exp(-Z)$ (fitted at $Z=22, 32$) from the present fit whilst the crosses are the experimental results divided by the present fit.
The BEA fit of Johansson et al. is in good agreement with the present SCA fit at \( Z = 22 \) and then becomes progressively lower until at \( Z = 50 \) it is 31% lower for 1 MeV protons. This curve is smooth as it based on a 5th degree polynomial 'universal' BEA scaling law fit for a large region of the periodic table and for widely differing projectile energies. The failure of the fit at higher \( Z \) is probably due to the lack of an electron relativistic correction. For example, this correction for 1 MeV protons on Sn (\( Z = 50 \)) is +52% of the uncorrected cross-section of the SCA theory. If they had fitted over a smaller range of \( Z \) and projectile energy, better results would probably have been achieved.

The accuracy of the cross-sections in the region \( Z = 22-34 \) has already been discussed. As \( Z \) cross-sections for higher \( Z \) elements have not been measured in the present work, no statement of accuracy will be made for cross-sections for \( Z = 35-50 \). However, in Fig. 5.3.3.1.h, the cross-section data taken from the compilation of Gardner et al. (1978) are divided by the present fitted SCA predictions and plotted as a function of \( Z \). The mean deviations (shown as dashed lines) from the predictions are + (5.7 ± 12.3)%, - (8.3 ± 9.3)% and - (10.8 ± 9.3)% for 1, 2 and 3 MeV protons where the uncertainties are the standard deviations of the means. Giving an equal weighting to these three results, it is concluded that on average the experimental data are (4.5 ± 6.0)% below the present fit. Thus if an uncertainty of about ± 10% was assigned for targets with \( Z = 35-50 \), this would probably be consistent with a 1σ confidence level. It has already been stated the two most likely errors (detector efficiency and ion beam fluence) found in most laboratories would make the measured cross-sections too low. Therefore it is to be expected that the 'true' values will be somewhat higher than the mean of the available data. The error in the fits of Lopes et al. do not appear to be any worse in the high \( Z \) region. However the fit of Johansson et al. lies below nearly all the experimental data. It is concluded that this fit is unsuitable for \( Z > 34 \) and the present projectile energy range. It would seem that even in this higher \( Z \) region the present fit to the SCA theory is the most accurate available.

5.3.3.2  Deuteron and alpha particle irradiation

The same fitting procedures were applied to the deuteron and alpha particle results. Figs. 5.3.3.2.a and 5.3.3.2.b show the measured cross-sections divided by the predictions of the corrected SCA theory of Laegsgaard et al. (1978).
Fig. 5.3.31.h Ratio of experimental data, from compilation of Gardner and Gray (1978), to present SCA fit. The dashed lines are the mean deviations from the fit.
Fig. 5.3.3.2.a All of the present experimental results for deuterons compared to the corrected SCA theory of Laegsgaard et al. (1978).

Fig. 5.3.3.2.b All of the present and literature experimental results for 2.5 MeV alpha particles compared to the corrected SCA theory of Laegsgaard et al. (1978). The dashed line is a linear least-squares fit to the results of Soares et al. (1976) and McKnight et al. (1974).
As there are less data for deuterons than for the protons the standard deviation of the fit is $1\%$ higher (i.e. $±3\%$). This yields cross-sections with a total uncertainty of $±6\%$. The predictions are presented in Table 5.3.3.2.a.

Table 5.3.3.2.a.: Fitted deuteron-induced K shell ionization cross-sections (in barns) based on modified SCA theory

<table>
<thead>
<tr>
<th>Z</th>
<th>Element</th>
<th>DEUTERON ENERGY</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>1.0 MeV</td>
</tr>
<tr>
<td>22</td>
<td>Ti</td>
<td>37.05</td>
</tr>
<tr>
<td>23</td>
<td>V</td>
<td>23.10</td>
</tr>
<tr>
<td>24</td>
<td>Cr</td>
<td>14.63</td>
</tr>
<tr>
<td>25</td>
<td>Mn</td>
<td>9.388</td>
</tr>
<tr>
<td>26</td>
<td>Fe</td>
<td>6.106</td>
</tr>
<tr>
<td>27</td>
<td>Co</td>
<td>4.023</td>
</tr>
<tr>
<td>28</td>
<td>Ni</td>
<td>2.678</td>
</tr>
<tr>
<td>29</td>
<td>Cu</td>
<td>1.796</td>
</tr>
<tr>
<td>30</td>
<td>Zn</td>
<td>1.214</td>
</tr>
<tr>
<td>31</td>
<td>Ga</td>
<td>0.8308</td>
</tr>
<tr>
<td>32</td>
<td>Ge</td>
<td>0.5737</td>
</tr>
</tbody>
</table>

To remain consistent with the case of protons, these values may be reduced by $2.2\%$ as the absolute uncertainties are the same as for the proton case (section 5.3.3.1). The cross-sections are very similar to those found with protons of equal velocity. The biggest deviation in the present range is for 2 MeV deuterons on Ge(32) where the deuteron cross-section is $3.9\%$ higher than the 1 MeV proton case. As $Z$ increases the deviation will increase (Laegsgaard et al. 1978). This is probably due to the fact that the neutron reduces the charge to mass ratio and hence reduces the Coulomb deflection effect (see section 3.1.1) consequently increasing the cross-section. The only other thin target deuteron data known for the present energies are the data of Basbas et al. (1978b) for Ni. Their values are $17\%$ and $14\%$ below the present fit for 2 and 3 MeV deuterons. The claimed uncertainties are $±10\%$ in the X-ray production cross-section. Thus the values are consistent with the uncertainties. The present fitted deuteron-induced K-shell ionization cross-sections are essentially the only ones available for deuterons.
and are of sufficient accuracy for PIXE analysis. It is hoped that these may be of use in materials research where, for instance, light surface elements are often analysed by deuteron-induced nuclear reactions. Heavier elements in the range \( Z = 22-32 \) may now be analysed simultaneously by using deuteron PIXE.

The fitted alpha-particle-induced cross-sections are of lower accuracy. Besides the fact that the fit is only derived for one projectile energy and for just four target elements, the foil of the ion beam monitor ruptured following the Ti and V measurements. This required that the Cu and Ge measurements be performed without the monitor. Also, because of the lower cross-sections, the counting statistics were poorer. However, it is not thought that the total uncertainty in the fitted values will be greater than \( \pm 15\% \). These values are given in Table 5.3.3.2.b. A fit to the other experimental data available at this energy yields results 9% to 11% higher than the present fit.

Table 5.3.3.2.b.: Fitted 2.50 MeV \(^4\)He-induced K Shell ionization cross-sections (in barns) based on modified SCA theory

<table>
<thead>
<tr>
<th>Z</th>
<th>22</th>
<th>23</th>
<th>24</th>
<th>25</th>
<th>26</th>
<th>27</th>
<th>28</th>
<th>29</th>
<th>30</th>
<th>31</th>
<th>32</th>
</tr>
</thead>
<tbody>
<tr>
<td>Element</td>
<td>Ti</td>
<td>V</td>
<td>Cr</td>
<td>Mn</td>
<td>Fe</td>
<td>Co</td>
<td>Ni</td>
<td>Cu</td>
<td>Zn</td>
<td>Ga</td>
<td>Ge</td>
</tr>
<tr>
<td>Cross-section</td>
<td>178</td>
<td>111</td>
<td>70.1</td>
<td>44.8</td>
<td>30.0</td>
<td>19.0</td>
<td>12.5</td>
<td>8.27</td>
<td>5.54</td>
<td>3.75</td>
<td>2.57</td>
</tr>
</tbody>
</table>

It may be noted that the deviations of the fit to the present experimental data from the corrected SCA theory of Laegsgaard et al. (1978) are zero at \( \xi = 0.69, 0.71 \) and 0.61 for protons, deuterons and alpha particles respectively. This seems to indicate that the deviation of experimental results from theory is independent of projectile mass but dependent on atomic number. It is suggested that this is either due to an inadequacy in the binding energy correction or inaccuracies in the original uncorrected SCA theory. It is hoped to investigate this trend further by using higher atomic number projectiles. In the meantime, it appears that the binding energy correction is the most open to question. It is perhaps of importance to point out that the idea to fit the experimental data in terms of the corrected adiabatic parameter (\( \xi \)) and the corrected SCA cross-sections resulted from the present author's desire to obtain accurate cross-sections for PIXE analysis but that, at present, the straight line fit has no theoretical justification.
5.4 Evidence for simultaneous K and L shell ionization

During the cross-section measurements with the thin and thick targets of Ti, it was observed that the $K_p/K_a$ ratio for the thick target case did not vary in the manner expected. This ratio is plotted as a function of projectile energy per nucleon mass in Fig. 5.4.a. As the $K_p$ X-rays are of higher energy than those of the $K_a$ transition, it was presumed that the $K_p/K_a$ ratio would be similar to the thin target case at low energies and increase at higher energies since, at higher energies, some photons would be emitted at greater depths and the photon attenuation coefficient is lower for $K_p$ X-rays than $K_a$ X-rays. In fact, at low projectile velocities, it can be seen that the $K_p/K_a$ ratio is actually less than the thin target case. The most likely explanation for this phenomenon follows from the results of a study by Moore et al. (1972). By using a LiF crystal spectrometer, they observed the X-ray spectra created by the irradiation of Ti with protons, alpha-particles and oxygen ions. Satellite peaks with energies 26 eV and 52 eV above the normal $K_a$ and $K_p$ lines respectively were found. These energy differences are in agreement with those expected for transitions when a 2p electron is already absent. This additional vacancy causes an increase in the electron binding energy and hence gives rise to an increased transition energy. For the $K_p$ case, this increase is just sufficient to make the photon energy greater than the K absorption edge for Ti. Thus the photon attenuation coefficient for the $K_p$ satellite X-rays is increased by almost an order of magnitude which results in preferential absorption for these X-rays hence reducing the $K_p/K_a$ ratio. The intensity of these peaks was found to be about one order of magnitude less than the normal characteristic X-ray.

The change in $K_p/K_a$ ratio should provide a measure of the degree of simultaneous K and L shell ionization. However, in order to obtain quantitative information on the number of such vacancies, the $K_p$ yield curve would have to be differentiated as a function of projectile energy in a manner similar to that used for the $K_a$ case during the thick target K shell ionization cross-section measurements. The cross-sections for $K_a$ and $K_p$ production would then have to be compared to those obtained in the thin target case. This would have required much extra work and it is doubtful whether the $K_p$ peaks were of sufficient precision to enable such calculations to be performed accurately. It was therefore decided to take advantage of the fact that the presence of the satellite line would shift the centroid position of the $K_p$ peak. The shift in the
Fig. 5.4.a Measured $K_{\beta}/K_{\alpha}$ ratios for thick targets of titanium (not corrected for detector efficiency).

Fig. 5.4.b The probability ($g_{KL}$) of simultaneous K and L-shell ionization for titanium.
centroid was used to determine the intensity of the \( K_p \) satellite by making the assumption that both peaks were Gaussian in nature.

It was assumed that, to a fair approximation, all the satellite \( K_p \) X-rays would be absorbed in the thick target. Thus the position of the \( K_p \) peak for the thick target was assumed to be the normal position and that for the thin target to be modified by the satellite as just described. Hence the fraction \( \varepsilon_{KL} \) of K X-rays emitted in the presence of an L shell vacancy was determined from measurements of the peak centroid shifts. These results are illustrated in Fig. 5.4.b where they are compared to the theoretical predictions based on the BEA formulations of Gryzinski (1965), as calculated by Li et al. (1973), and of Hansen (1973). Also included are the experimental results of Li et al. which were derived in a different manner and which have uncertainties of typically \( \pm 15\% \). The present statistical uncertainties in \( \varepsilon_{KL} \) are about \( \pm 50\% \). This is principally due to the fact that the peak centroid shift is typically only 0.3 channels (5 eV) and the uncertainty in the measurement of the centroid position is \( \pm 0.1 \) channels. It can be seen that, at energies above 1.25 MeV per nucleon, there is quite good agreement between the experimental results which are about 25\% below the predictions of the theories. The discrepancies at the lower energies may be due to a large error in the approximation that all the satellite lines are absorbed in the thick target as, at the lower projectile energies, the X-rays will be produced nearer the surface.

For protons incident on the thin Ti layers used in the present work, only 0.04\% of the total \( K_p \) X-rays would be absorbed due to the satellite affect. However, if thicker targets (2 mg cm\(^{-2}\)) were used, as was the case in the work of Akselsson et al. (1974), a correction of about 5\% would have to be employed. If the X-ray detector had insufficient resolution to separate the \( K_a \) and \( K_p \) peaks, then the measured total K X-ray peak would have to be increased by approximately 0.5\%. For thick targets this latter correction would be 1\%, 1\% and 4\% for protons, deuterons and alpha-particles respectively. Thus the effects of multiple ionization will become increasingly important with higher Z projectiles and this should be borne in mind when measuring cross-sections with detectors of poor resolution. Also, some work on simple depth profile determination by measuring \( K_p/K_a \) ratios has been performed (Ahlberg 1975). If the element of interest is a major component of the bulk matrix, then significant errors may be encountered due to the enhanced absorption of the \( K_p \) X-ray.
5.5 Minimum detection and quantitation limits for thick carbon backings

The spectra recorded during the thin target cross-section measurements afforded the possibility of comparing the background levels obtained with the different projectiles. For this purpose the targets were considered to be totally carbon as only a negligibly small fraction of the projectile energy loss takes place in the evaporated layer. The spectra from the Ge target were chosen as the Ge K X-ray peaks interfered the least with the background spectra since Ge has the lowest cross-section of the elements measured. Its peaks were also in the higher energy slowly varying part of the background which allowed easy extrapolation of the background through this region. It was decided to compare the spectra at about the energy that had been found the optimum for proton irradiation. Thus the projectile energy of 2.5 MeV was chosen. Some authors prefer to compare at a fixed energy per nucleon in order to compare each projectile species at its optimum energy. This would have meant using an alpha-particle energy of 10 MeV which was not available with the present machine. The primary interest here has been to obtain the optimum combination of conditions for use with 1-3 MeV accelerators which are most widely available throughout the world.

The photon background levels recorded for fluences of 4 µC are shown in Fig. 5.5.a. They have been corrected for the intrinsic efficiency of the detector but not the geometrical efficiency and so the levels should be divided by \((1.028 \pm 0.023) \times 10^{-4}\) to obtain the result in \(4 \pi\) steradians. However, as it is a thick target, the radiation will only be emitted into the forward hemisphere. It should also be remembered that the measurement was performed at a detector-beam direction angle of 157.5°. The results will probably be somewhat different at other angles but, as the backgrounds from the three projectiles differ from each other by typically an order of magnitude, the following conclusions will not be greatly affected. The levels are presented per 200 eV of photon energy as this typically represents the amount of background under 1 FWHM of the peak being analysed (see Fig. 4.4.4.b). In all cases the background levels increase rapidly below 3 keV, but no results below this energy are presented as the reduced efficiency of the detector with the polyethylene absorber distorts the background continuum. It will be remembered that this absorber was added deliberately to reduce dead-time effects during the much more important cross-section measurements.

For all the particles, there is a large rise in the background at low energies. This is due to the secondary-electron bremsstrahlung
Fig. 5.5.a  Photon background levels recorded during irradiation of vitreous carbon by protons, deuterons and alpha-particles of 2.5 MeV energy [see text for experimental parameters].
which has a maximum energy of 5 keV, 2.5 keV and 1.25 keV for 2.5 MeV protons, deuterons and alpha-particles respectively. Hence it can be seen that at the lowest photon energies the lighter projectile has the greater background associated with it. At higher photon energies the background is mainly due to projectile bremsstrahlung and Compton scattered γ-rays from nuclear reactions (see section 3.1.4). The latter effect is probably responsible for the high background level found when deuterons are used.

It might appear from simple background considerations that alpha-particles would be superior for PIXE analysis. Fig. 5.5.b shows the MDL for elements with \( Z = 22-32 \) calculated as described in section 3.1.5.1 and with the assumption that the background is that found for the interval of 200 eV under the peak. The results may be scaled for different experimental arrangements. The X-ray production cross-sections were calculated from the present SCA fit. Except at the lowest \( Z \), the protons are always superior, due to their much larger X-ray production cross-sections, but alpha-particles are comparable up to \( Z = 26 \). Deuterons are 4–20 times worse than protons. The proton MDL only varies by a factor of two in the whole range. This is a most useful property in multi-element analysis. For Fe, the MDL for thick carbon backings corresponds to \( 7.6 \text{ ng cm}^{-2} \). If this result is compared with that found for the \( 4.5 \text{ mg cm}^{-2} \) Sartorius filters discussed in Chapter 6, one may see that the MDL's are very similar. The explanation for this is that, although the proton is creating background along most of its path, after about \( 4.5 \text{ mg cm}^{-2} \) most of this is absorbed in the target before reaching the detector. Thus a thick backing may not be significantly worse than a semi-thick backing.

However, as has been already pointed out, MDL results can be misleading as they give no indication of precision. For instance, in the case of Fe, the MDL requirement is satisfied for 24.4, 56.2 and 4.1 counts for protons, deuterons and alpha-particles. The statistical uncertainty in the alpha-particle result would be \( \pm 65\% \). In fact it is highly unlikely that any computer programme would find such a small peak. For these reasons the minimum quantitation limits (MQL) have also been calculated for the case of a precision of \( \pm 10\% \) and are shown in Fig. 5.5.c. The great superiority of proton PIXE can clearly be seen here. After \( Z = 25 \), deuteron PIXE also yields more precise results than that of alpha-particles. The MQL results are not amenable to simple scaling and different conclusions would be reached with different ion beam fluences. For fluences much higher than 4 μC, the alpha-particles
Fig. 5.5.b  MDL's for 4μC of 2.5 MeV protons, deuterons and alpha-particles incident on a thick carbon backing.

Fig. 5.5.c  MQL's for above conditions.
will become superior to deuterons. It is thus necessary to calculate the MQL for the actual ion-beam fluence used. This may be achieved with the cross-section and background data provided in this chapter. This should prove useful as many samples are composed of carbonaceous materials. However it should be remembered that the present MDL and MQL results are for the trace element of interest being on the surface. The calculation becomes more complicated when the trace elements are distributed throughout the bulk of the matrix.
SELECTED APPLICATIONS OF PIXE ANALYSIS

6.1 Studies of temporal variations of the air particulate content of the atmosphere and work-shop environments

6.1.1 Introduction to the problems of air particulate pollution

The air of the earth's biosphere, which is essential to all life, is not a homogeneous medium but is a mixture of gaseous, liquid and solid components. The solid airborne particles vary widely in chemical composition, size, shape and homogeneity. These particulates are usually referred to as 'aerosols' regardless of their origin. The physical, chemical, medical, biochemical and technological effects of air particulates cannot be gauged exclusively from one analytical method. However, it will be shown that PIXE analysis is well suited to the elemental analysis of these particulates and shows much promise in the study of the transport mechanisms and variations in concentration of this form of pollution. This work has to be put in the context of the fact only one aspect of dust analysis is being considered (the elemental content) and that these particulates are only one component of the air we breathe. Also, the air is only one pathway for pollutants entering man; food and water often contain harmful substances and the inter-relationships between these different sources are extremely complex. However, PIXE analysis can also make a contribution to the latter fields of study.

Recently, Fennelly (1976) has shown that about 90 % of the total air particulate matter is natural rather than anthropogenic (the causes are such diverse factors as volcanic emissions, the wind-erosion of soils etc) although, on a local scale, this may not be so. Thus there will always be an atmospheric dust problem. However, two points should be noted. Firstly, even though these particulates are 'natural' it does not necessarily mean that they are harmless. Moreover, the populations living in today's overcrowded cities may suffer from combinations of these dusts with anthropogenic effects such as smog. Secondly, the types of dusts presently created by mankind are often very different both in form and chemical composition. The heavy metals in the atmosphere are largely due to the effects of industrialization. An understanding of the sources, distributions and effects of such aerosols is a long term target which requires the collaboration of workers from many fields such as meteorology, physics, chemistry and medicine.
Mason (1978) has discussed the early history of air pollution. Prior to the Industrial Revolution, the prime source of thermal energy in England was wood. However, coal had been used in Europe as early as 1200 AD. The unrestricted use of coal for domestic heating gave rise to the first known recorded complaint about the quality of London air, being made by Eleanor, the wife of King Henry III, in 1257. During the reign of Edward I (1272-1307), protests from the nobility on the use of Sea Coal resulted in two special commissions being set up to investigate air pollution. During the reign of Edward II (1307-1327) a man was put to torture for polluting the air with 'a pestilential odour' from the burning of coal. By 1450, Parliament had taken steps to reduce the domestic use of coal both by establishing a coal tax and by limiting the import of coal into London. Despite such early measures, the onset of the industrial era led to increased particulate pollution and peak levels occurred in London during the height of the Industrial Revolution (around 1880). Levels of up to 860 μg m\(^{-3}\) of particulate matter were recorded. The present recommended maximum loading is 80 μg m\(^{-3}\) which is the approximate level at which the World Health Organisation suggest that the condition of those with pulmonary diseases is worsened.

Perhaps the culmination of public awareness of the 'smoke problem' in England occurred during the severe fog of 5-9 December 1952 in London in which it is estimated that about 4000 people died prematurely. The diseases for which mortality figures are quoted are bronchitis, coronary diseases, myocardial degeneration, pneumonia, vascular lesions of the central nervous system, respiratory tuberculosis and cancer of the lung. The people who died were probably already ill but the pollution incident precipitated their deaths. Other tragic air pollution episodes took place in the Meuse river valley in Belgium in December 1930, in Donova, Pennsylvania in the U.S.A. in 1948 and again in London in 1962 (Fennelly 1976). Partly as a result of such incidents, the governments of most of the industrialised countries began to take action against air pollution. For example, in London, only 'smokeless' fuel is now allowed to be burnt. All over Britain local authorities collect daily air particulate samples on filters and measure the level of blackening by reflectrometry. These results are correlated by a central government laboratory at Warren Springs. Although such measurements are rather crude and occasionally unreliable, they have played quite an important rôle in achieving a significant reduction in the level of the total particulate matter in Britain. The probability of the occurrence of such deadly smogs
has now been largely removed and the widespread use of North Sea gas for domestic and industrial purposes has further reduced air particulate levels.

However, it seems that many of the more insidious components of air pollution still remain and may even have increased. Although the levels of the relatively harmless bulk elements, such as carbon, have been significantly reduced, the levels of the more dangerous trace metals do not appear to have followed the same trend. In fact pollution from motor vehicles, especially lead, seems to be on the increase. It is rather difficult to draw firm conclusions on this as wide-scale multi-elemental analyses were not performed until the last decade. A partially successful attempt was made to investigate atmospheric trace element levels over the past decades by neutron activation analysis of tree-rings (Gilboy et al. 1979) although this technique is confused by the active biochemistry of botanical systems.

Acidic sulphur compounds combined with air particulates have been shown by epidemiological studies to be related to impaired ventilatory function in children (Fennelly 1976) and it is well known that lead can cause permanent brain damage. It is not only a question of chemical composition of these particulates but also of their physical nature. Particles with diameters less than a few μm have a good chance (~ 30 %) of bypassing the body's respiratory filters and penetrating deep into the lungs. The probability of retention is dependent on the particle's shape. Even materials such as silicones, which for the most part are chemically inert, can cause acute physical irritation of sensitive lung tissue and lead to diseases such as silicosis (Fennelly 1976). Besides the direct health effects of air particulate pollution, evidence is emerging that the weather, even in a localised way, is being modified. Changnon (1979) has shown that during the summer there is more rainfall downwind of St. Louis (U.S.A.) than in other directions, where the pollution is expected to be less. Cases of the acidic destruction of the surfaces of ancient monuments have been frequently reported and the accelerated deterioration of outdoor metallic structures represents a severe economic penalty in industrial communities. The quality of life can also be affected in less measurable ways. For example, the present author has observed that, whilst living in the town of Dartford, the houses, washing etc. were often covered by a thin layer of white dust when the wind blew from the direction of nearby cement works. Although it is believed that no physical health hazard has yet been proved, the emotional upset and economic consequences resulting from such pollution should be taken into account.
The above cases are only a small selection of the wide-ranging effects of air particulate pollution. Even so, it can be seen that there is now an urgent need to measure the elemental content of air particulates and that this should be done with a temporal resolution comparable with the rates of change of the incidents being studied. As fog episodes are often of only a few hours duration, a temporal resolution of two hours seems a reasonable starting point. Shorter time resolutions would result in less particulate deposit being found and more analyses being necessary. Besides being able to investigate the role of meteorological factors on particulate levels, the effect of patterns of human activity (rush-hour traffic etc.) can also be examined. Until recently, most air sampling work has been performed only with daily samples and so much useful information has been lost. Realising the need, Nelson et al. (1976) at Florida State University (FSU) introduced the 'streak' sampler. The essence of this is a sliding, sucking orifice which produces a long streak of dust deposit on the air filter. Each 2 mm section corresponds to 2 hours of sampled air. To avoid disturbing the air being sampled, a low pumping rate must be used. These practical considerations result in 2 mm sections which contain only nanogrammes of the elements of interest. Thus an analytical technique with low minimum detection limits which can analyse discrete sections of the sample is required. It will be shown that PIXE is well suited to this problem.

In 1976 work was begun on a modification of the FSU system at the University of Surrey. The details of this system were given in a recent thesis (Mason 1978) and will not be repeated here. In 1977 the CBNM PIXE system was developed by the present author. Its primary purpose was the accurate measurement of ion-induced characteristic X-ray yields. However, it was also designed in such a manner that the lighter elements in air particulates, not measurable with the Surrey system, could be detected. In the next section, the present method of analysing the Surrey samples is described. In the section following that, the development of an improved sampler at the CBNM is examined together with some different applications and further work on quantifying the volume of air sampled.

6.1.2 Early work with Guildford samples

6.1.2.1 Introduction

Air particulate pollution, in the town of Guildford, is being studied jointly by the CBNM and the University of Surrey. Elemental
analysis was originally achieved by the use of instrumental neutron activation (INAA) at Surrey. For twenty-four hour samples, the elemental concentrations given by INAA were found to vary from one day to the next by as much as an order of magnitude (Hasan et al. 1972). In order to relate these changes to the time of day and to meteorological factors, a system for 'streak' sampling and subsequent PIXE analysis was developed (Mason 1978, Mason et al. 1978). Elements with Z > 24 were initially determined using 2 MeV protons, and a Ge(Li) photon detector, at the University of Surrey. This system has been outlined previously (Gilboy et al. 1979).

It was found that there is a need to examine the variations in the concentrations of the lighter elements in order to study in more detail the effect of meteorological parameters. This is especially important for Na and Cl levels due to sea winds while sulphur is also of interest as this is a very common industrial air pollutant. Therefore, a programme to analyse the light elements was initiated using the CBNM PIXE system. This section describes the methodology of analysing the air particulate samples and reports some preliminary conclusions on Guildford air particulate pollution.

Quantitative PIXE analysis of the lighter elements (Z < 23) is difficult for a variety of reasons. One of the biggest experimental problems is the low energy (< 5 keV) efficiency calibration of the Si(Li) photon detector as has been discussed in section 4.4.5. In addition, the presence of the large secondary-electron bremsstrahlung background in this region increases the minimum detection limit of the method. There is a scarcity of proton-induced K-shell ionization cross-section data for use in absolute analysis and an almost total lack of such data for alpha-particles (as was discussed in Chapter 5). For elements in the range Z = 11-21, Johansson et al.'s (1976) values have been used but these cross-sections are much less accurate than for the higher Z range (Z = 22-34) where many more accurate experimental values are now available. Also, fluorescence yields are low and typically only known to an accuracy of about ± 4 % for the lighter elements.

Air particulates consist primarily of very light elements such as carbon and oxygen, in compound form, among which the heavier trace elements, often in the form of organic complexes, can be found. It is of great environmental interest to compare the temporal variation of these heavier elements with the variation in the total mass of the deposited air particulates. For this reason, RBS spectra were recorded simultaneously with the PIXE spectra in order to obtain some information on the total mass of the deposits.
6.1.2.2 Apparatus

A uniform 1 mm diameter ion beam was obtained by collimation, with tantalum apertures, of a de-focused beam. The ion beam fluence was measured by the foil ion beam monitor placed between the collimators and the target and, for comparison, also by Faraday cup current integration. To prevent bremsstrahlung and characteristic X-rays from the Faraday cup material reaching the Si(Li) detector, the cup was placed about 12 cm behind the target.

The workings and location of the air sampling system has been described elsewhere (Gilboy et al. 1979). In essence, the sampler consists of a square PTFE orifice of 4 mm² area, connected to an air pump, which moves along behind the filter at 1 mm per hour. Thus any point along the length of the trace represents a two hour moving average. The filters used are Sartorius membrane filters which are made of cellulose acetate and have a 0.45 μm average pore diameter. Each two hour moving average has been measured to correspond to 72 litres of sampled air which is similar to the volume of air breathed by human beings. For the ion beam analyses at the CBNM, the filters were removed from their perspex cassettes and placed in an aluminium target holder. The use of this conducting target holder effectively removed the continuum radiation due to electric discharge effects which occur when non-conducting targets are irradiated in holders of insulating materials (see section 3.1.4).

The streak sampler was situated at a height of 15 m above ground level on the University of Surrey campus in Guildford. There are not any strong local sources of pollution at this site, which makes it suitable for studying pollution transport from distant sources (Mason 1978).

6.1.2.3 Experimental technique

In principle, either an absolute or comparative method can be used for quantitative PIXE analysis. However, for the case of air particulate deposits, good comparator standards do not yet exist, are difficult to fabricate and it is not a simple matter to produce a multi-element internally spiked standard. Therefore, an absolute approach to the quantitative analysis was chosen.

To achieve absolute quantitative analysis, the full energy peak efficiency of the Si(Li) detector needs to be known. If thin calibrated layers of every element of interest were available, it would be un-
necessary to determine the efficiency explicitly since the number of X-ray counts obtained from the known target, for a fixed ion beam fluence, is all that need be measured. However, calibrating the detector response for each element of interest and each ion energy and species used is a laborious task. Moreover, it is not possible to prepare stable calibrated evaporated single element layers of many of the lighter elements (e.g. chlorine). The method of calibrating the Si(Li) detector was described in great detail in section 4.4.3.3. The combination of radioactive source counting and PIXE spectroscopy of standard evaporated layers enabled quantitative PIXE analysis to be carried out with uncertainties (excluding the peak statistics) of typically ±12%.

For quantitative analysis it is necessary that all the beam falls within the target region of interest. The beam was scanned by measuring the number of copper K X-rays produced when a copper wire of 0.2 mm diameter was moved perpendicularly through the beam in steps of 0.2 mm. The beam profile corresponded well to that of a circle over the beam aperture dimensions although there was a little tailing at the edges. Whilst this tail was a negligible fraction of the total beam from the point of view of quantitative analysis, it did necessitate the use of very low atomic number materials for target supports in order to prevent unwanted characteristic X-rays being produced. This beam spreading is discussed in more detail in section 4.3.3.

Routine experimental conditions for the 2 MeV proton PIXE/RBS analysis of the Guildford streak samples are summarised in Table 6.1.2.3.

Table 6.1.2.3.: Routine experimental conditions

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Proton beam fluence</td>
<td>4 μC</td>
</tr>
<tr>
<td>Proton beam diameter</td>
<td>1 mm</td>
</tr>
<tr>
<td>Average beam current</td>
<td>2 to 3 nA</td>
</tr>
<tr>
<td>Time per irradiation</td>
<td>20 to 30 min</td>
</tr>
<tr>
<td>Chamber pressure</td>
<td>10⁻³ Pa</td>
</tr>
<tr>
<td>Si(Li) FWHM resolution at 5.9 keV</td>
<td>165 eV</td>
</tr>
<tr>
<td>Si(Li) solid angle subtended at target</td>
<td>1.2 x 10⁻³ sr</td>
</tr>
<tr>
<td>Si(Li) beryllium window thickness</td>
<td>8 μm</td>
</tr>
<tr>
<td>Surface barrier FWHM resolution at 5.5 MeV</td>
<td>20 keV</td>
</tr>
<tr>
<td>Surface barrier solid angle subtended at target</td>
<td>1.5 x 10⁻³ sr</td>
</tr>
<tr>
<td>Typical count-rate for Si(Li)</td>
<td>150 s⁻¹</td>
</tr>
<tr>
<td>Typical count-rate for surface barrier</td>
<td>300 s⁻¹</td>
</tr>
</tbody>
</table>
Sartorius cellulose acetate filters were used for the Surrey streak sampling. It was immediately found that too high an ion beam current created a hole in the filter target. As the edges of the hole were brown, it was assumed that heat deposition by the beam was the principal mechanism for creating this damage. The stability of the filters as a function of ion species, current density, fluence and beam diameter was investigated. This was done in a qualitative manner by visual inspection of the filters after irradiation. For protons it was found that the higher the beam energy and the lower the current density, the less the damage. For a given current density, it was found that the larger the beam diameter, the greater the damage. This could be due to poor heat conductance causing a 'hot spot' in the centre of the beam spot. With the 1 mm diameter beam used in this work, it was found that the visible browning was very small for currents of less than 2 nA. Above this value the damage was strongly dose dependent with a hole eventually being formed. Little PIXE has so far been performed (by the present author) with helium ions but results show that they produce more damage than protons. This is probably due to the fact that they are totally stopped in the filter thereby depositing most of their energy within the material. As this necessitated using lower currents and as the helium PIXE cross-sections are lower than for protons of equal energy, this confirmed the use of protons for the bulk of the present work.

During analyses of the 4.5 mg cm$^{-2}$ Sartorius filter samples it was noted that, when the filters were first placed in the target position, the current measured in the Faraday cup went down by about a factor of three. As the irradiation proceeded, the current measured in the Faraday cup steadily increased in comparison with the values derived from the beam foil monitor which is totally independent of the target. The effect for one continuous run is shown in Fig. 6.1.2.4.a. The most likely explanation of this effect is that the protons are being multiply scattered such that only about a third of them leave the filter at a solid angle sufficiently small to enter the Faraday cup. Calculations using the theoretical multiple scattering angular distribution curves of Marion et al. (1967) were performed. By making the approximations that the filter is entirely composed of carbon and that the fibrous structure of the filter does not affect the scattering, the result was obtained that, at 2.9° to the original beam direction, the distribution has fallen off to 1/e of its maximum value. This yields the prediction that, with the present Faraday cup, only 76% of the beam will enter
Fig. 6.1.2.4.a The effect of proton-induced filter damage on Faraday cup charge collection.

CHARGE COLLECTION EFFICIENCY FOR CASE OF THEORETICAL ANGULAR STRAGGLING (SEE TEXT)

NUMBER OF 2 MeV PROTONS THAT HAVE BEEN INCIDENT ON FILTER (IN µC)

FRACTION OF BEAM THAT ENTERS FARADAY CUP
the cup when a Sartorius filter is in the target position. This assumes that the axis of the Faraday cup corresponds exactly with the ion beam direction. If the cup is at all off-centre, then less beam will enter it.

Fig. 6.1.2.4.b shows electron micrographs of a sample before and after a long irradiation. As expected, the beam spot corresponds well to the beam dimensions. The damage to the filter is not uniform and in the centre there is more damage with a melting of the filter material clearly having taken place. This is probably due to the formation of a hot spot as described previously.

The effects of the filter on proton beams were further investigated by measuring the material's stopping power for 2-3.5 MeV protons. In order to prevent damage to the filters and excess counts in the surface-barrier detector, the proton beams were first backscattered from a thin gold target (which reduced the beam intensity by about $10^5$) and were then allowed to pass through the filters which were placed directly in front of the surface-barrier detector. It was found that the stopping power corresponded well with that predicted from the tabulations of Andersen et al. (1977) for the case of carbon but that the energy straggling was much greater than that predicted by Bohr (see Appendix C). For example, for 1957 keV protons, the measured result is 106 keV compared to the 18 keV predicted from Bohr's theory. The latter prediction holds for a thin, structureless, homogeneous material. It is believed that the non-uniformity and porous nature of the filters produces this increased energy straggling. Kalz et al. (1978) have investigated the effect of target surface non-uniformity on energy straggling whilst Brady et al. (1977) have made similar measurements for porous materials. The increase in energy straggling is caused by the protons passing through different thicknesses of material. The large energy straggling measured with the filters may be explained in terms of these effects.

No similar work has been done for angular straggling due to multiple scattering. An increase by a factor of 2.7 in the theoretical angular straggling would account for the observed fraction of charge entering the Faraday cup. It will be remembered that the measured energy straggling was 5.8 times higher than that predicted from theory. It is not easy to measure the angular straggling as a collimated beam is required and it is not possible to progressively measure the transmitted flux at various angles as the properties of the filter change with fluence. Such measurements would probably be best achieved simultaneously using a position-sensitive surface-barrier detector. If the porosity and surface roughness explanation holds, it would be expected that, as the
Fig. 6.1.2.4.b Scanning electron micrographs of ion beam damage to cellulose acetate filters.
filter melts, the measured charge should approach that predicted from the multiple angular scattering theory of Marion et al. (1967). Examination of Fig. 6.1.2.4.a indicates that there is such a trend. Also the fraction of projectiles scattered out of the solid angle subtended by the entrance of the Faraday cup should be approximately proportional to the inverse of the square of the projectile energy. Thus at 2.0 MeV the loss should be 3.1 times greater than that at 3.5 MeV. In fact it was measured to be 3.9 which is an indication that multiple angular scattering is the major cause of the 'lost' charge.

Charge exchange effects will not be a problem for current integration with MeV protons. However, singly charged helium ions will become on average almost doubly charged on passing through the filter, thereby giving almost double the Faraday cup current reading, provided that they have a range greater than the target thickness. Armstrong et al. (1965) have discussed the magnitude of such charge exchange effects.

During the runs with protons it was found that, to within statistical uncertainties, there was no loss of material from the deposits with the exception of chlorine. The signal from this element was found to decrease at a rate of about 10 % per μC.

The Faraday cup results could have been improved by bringing the cup nearer to the filter or by widening its entrance. The former would increase the background recorded in the Si(Li) detector and the latter would have resulted in more charge escaping from the cup. However, as the cup was 140 mm from the filter and as it had a 12 mm diameter entrance, the angle it subtended to the filter was only 2.5°. There was thus considerable room for improvement in the arrangement although it is unlikely that such a system would ever be as precise as the foil ion beam monitor.

As has been mentioned, RBS spectra from the filter sample were taken simultaneously with the PIXE spectra during these streak analyses. Fig. 6.1.2.4.c shows a typical RBS spectrum recorded for 4 μC of 2 MeV protons. A strong step due to oxygen can clearly be seen. It was decided to examine whether this peak could also be used to normalise the spectra. These streak samples are thought to consist of about 0.2 mg cm⁻² of air particulates on the 4.5 mg cm⁻² of cellulose acetate filter. A 2 MeV proton beam will only lose on average about 30 keV in traversing the deposit and so variations in the thickness of the deposit will not significantly affect the oxygen peak. It can be seen that oxygen counts come from the filter material and not the deposit on the
Fig. 6.1.2.4.c Typical RBS spectrum obtained with a Guildford "streak" sample.
surface because of the step-like shape of the peak (a surface distribution would give rise to a Gaussian-like peak).

The normalisation method relies on recording the number of oxygen RBS counts in the plateau region away from the nitrogen and oxygen leading edges. This will remove any particulate deposit effects unless the dust has penetrated beneath the filter surface, which is unlikely. Oxygen RBS counts, averaged over ten channels, and the Faraday cup integrated charge were measured for a variety of 2 MeV proton beam fluences as determined by the foil monitor. In the present set-up, RBS and PIXE spectra were recorded simultaneously using two ADC's. This is not necessary if only PIXE analysis is to be performed as the interesting portion of the oxygen RBS peak may be recorded with a single channel analyser and a scaler. The oxygen RBS results are shown in Fig. 6.1.2.4.d. Most of the results were obtained using 4 µ of protons during routine analyses and the error bar shown is the standard deviation of seventeen such results. This standard deviation, which is ± 4.4 %, is much smaller than that obtained for the same number of Faraday cup results (± 10.2 %) which is a further indication that the present Faraday cup measurements are quite unsuitable for the normalisation of the PIXE analyses. From the number of counts in the oxygen RBS peak it would be expected that the standard deviation would be ± 1.3 %. The higher measured dispersion is probably due to ion beam damage effects. It appears that the filter RBS method starts to become unreliable above about 6 µC for a 1 mm diameter beam. If the beam is spread over a greater area, then the method may work for higher fluences. The filter damage limitation on this method may appear to be a large disadvantage but it is likely that the damage criteria will also be a limit on the PIXE analyses.

Thus for a particular filter material and ion beam energy and species, the RBS technique provides a simple routine method for relative normalisation of results for laboratories without devices such as the foil ion beam monitor. To achieve absolute results, a calibrated thin layer of a heavy element could be evaporated onto a filter and an RBS spectrum recorded under the usual operating conditions. The ion beam fluence could then be calculated, using the well known RBS cross-sections, once the solid angle of the surface-barrier detector is known. After the relationship between ion beam dose and oxygen RBS counts has been established for a particular set of parameters, the thin layer calibration would not have to be repeated except perhaps as a periodic check. The method could be applied to other types of target matrices when they are of constant, non-crystalline, bulk composition and
Fig. 6.1.2.4.d Number of RBS counts from oxygen in filter for various 2MeV proton fluences (see text).
produce an RBS peak that has no interferences.

In the present work, all the streak analyses were normalized via the foil ion beam monitor results because of the above difficulties in the other methods.

6.1.2.5 Results

A typical 2 MeV proton PIXE spectrum obtained from a Guildford streak sample is shown in Fig. 6.1.2.5.a. For quantitative analysis of X-rays of energy greater than the K X-ray of argon (3 keV), the background subtraction provided by RETEOH was found to be adequate. In the case of the less energetic X-rays, it was necessary to subtract a normalized clean filter spectrum from the sample spectrum in order to accurately remove the large continuum present.

Total uncertainties in the absolute values of concentrations for the elements with K X-ray energies less than about 5 keV are typically $\pm (12 - 25) \%$. Self-absorption of the X-rays within the target is generally likely to be small for such thin air particulate deposits (see self-absorption calculation of Johansson et al. 1975) although this assumption may not be entirely valid for the lightest elements, such as sodium and aluminium, where the photon attenuation coefficients are large and not so well known. Since the main aim of the streak analyses is to relate the variations in the elemental concentrations to temporal and meteorological factors, it is the relative uncertainty from analysis to analysis that is of prime importance rather than the absolute uncertainty. The relative uncertainty is largely due to the counting statistics in the peak and to variations in the small self-absorption effect. Typical relative uncertainties range from about $\pm 5 \%$ for sulphur (the largest peak) to $\pm 20 \%$ for iron (the smallest peak quantified).

To determine the applicability of the present PIXE technique to the analysis of the streak deposits, the minimum detection limits for the routine experimental conditions have been calculated according to the methods of section 3.1.5.1 with $N_B$, the number of background counts under the signal peak, taken over the FWHM interval of the peak. The backgrounds used in this calculation were measured for different proton energies using the Sartorius filters and are shown in Fig. 6.1.2.5.b for the routine conditions. These yields have not been corrected for detector efficiency.
Fig.6.1.2.5.a Typical PIXE spectrum obtained with a Guildford "streak" sample.
Fig. 6.125b Photon continuum backgrounds measured by the Si(Li) detector for routine conditions.

Fig. 6.125c Minimum detection limits (MDL) for the P1XE analysis of the "streak" air particulate deposits.
The MDL's calculated for 1.0, 2.0 and 3.5 MeV proton beams are illustrated in Fig. 6.1.2.5.c. The uneveness of the plot is due to the conflicting effects of the variations in the X-ray production cross-sections, the continuum background and the Si(Li) intrinsic efficiency (a factor often neglected in such calculations). It can be seen that the increase in X-ray production cross-section for low atomic number elements almost compensates for the rapid low energy increase in background. For the present range of interest, 2 MeV protons provide the lowest MDL for the largest number of elements. In addition, the MDL only varies by a factor of two for these elements. This highly desirable feature is one of the great advantages of using protons of about 2 MeV to analyse light elements. For heavier elements, it is clearly an advantage to go to higher energy protons. Finally, it should again be pointed out that these calculations are of the 'ideal case' MDL. Such factors as peak overlap, pulse pile-up etc. can make the practical MDL significantly worse.

RBS spectra, using protons from 1.5 to 3.2 MeV and helium ions of 2 MeV, were obtained with the air particulate deposits. For the thickness of deposits under consideration, calculated to be about 200 μg cm⁻² assuming an average urban environment (see Cahill 1975), 2.0 to 2.5 MeV protons were the best choice. For incident proton energies greater than 2.5 MeV, spectral interferences occurred due to nuclear reactions and below 2 MeV there was insufficient peak separation to perform analyses. This fact, together with the 2 MeV proton PIXE MDL results and the target damage considerations, made 2 MeV proton PIXE/RBS the best compromise. The only RBS peak that could be separated on a routine basis was that due to lead. Although it was not possible to resolve this peak from those due to other heavy elements, it is highly unlikely that any other similarly heavy elements will be present in comparable concentrations (Valković 1975). In general, even for this peak, uncertainties were large due to poor counting statistics. A typical routine spectrum was shown in Fig. 6.1.2.4.c. Although it was possible to obtain a rough measure of the temporal variation of lead, it was impossible with such statistics to accurately determine the width of the peaks and hence obtain information on the mass thickness of the total deposit for most of the samples. However, for the samples that were more heavily polluted with lead, it was possible to obtain a rough estimate of the deposit thickness from the width of the lead peaks. For the case shown in Fig. 6.1.2.4.c, the deposit thickness was determined to be
(200 ± 70) µg cm⁻² which is in good agreement with the value of Cahill (1975). As the 2 MeV proton PIXE spectra of the streak samples did not show lead L X-rays (see e.g. Fig. 6.1.2.5.a), the RBS method exhibited a better detection limit for this element.

The RBS technique has been shown to be more successful in this field at higher energies. Cahill (1975) uses 18 MeV alpha particles to analyse the lightest elements in air particulates and Jolly et al. (1971) have analysed heavy metals in fish samples using 22 MeV alpha particles. Nelson et al. (1975) successfully analysed the lightest elements in air particulates with 16 MeV protons.

The results of analysing a section of streak sample with simultaneous 2 MeV proton PIXE/RBS will now be discussed. This streak was the result of 60 hours continuous air sampling, during March 1977, at Guildford. Quantitative PIXE values for the temporal variations of S, K, Ca and Fe are shown in Fig. 6.1.2.5.d whilst Na, Al, Si and Cl values are shown in Fig. 6.1.2.5.e. The RBS values for the Pb temporal variation are given in Fig. 6.1.2.5.f. The most striking feature is that the elemental levels can vary by more than an order of magnitude in a few hours. For Fe, variations from less than 12 ng m⁻³ (the MDL) to 300 ng m⁻³ of air were recorded. These effects can only be seen when high temporal resolution air particulate sampling is carried out.

All the elements analysed, with the exception of Na and Cl, exhibit a very strong peak at a position corresponding to approximately 8 o'clock Friday morning. The fact that there is some time lag between peaks (sulphur is noticeably 'earlier') has been reported in other investigations (Pilotte et al. 1976) and may be due to different pollutant transport processes. The chlorine may be partly associated with sodium chloride from sea winds but it is difficult to quantify this relationship, especially with the loss of chlorine discussed in section 6.1.2.4.

Fig. 6.1.2.5.g shows the temporal variation of the inverse of wind speed as measured by the Meteorological Office at Gatwick which is about 30 km S.E. of Guildford. There appears to be a correlation between the largest concentrations of the elements and the inverse of wind speed. Also, it was noted that in the 24 hours previous to 4 a.m. Friday, the wind had been blowing continuously from the North. Therefore the pollution event may be due to emissions from the London region (45 km N.E. of Guildford) and/or the Farnborough region (12 km N.W. of Guilford). From 4 a.m. Friday, and for the remainder of that day, the wind blew from the South West which is the direction of the coast. This could
Fig. 6.1.2.5.d Temporal variations in elemental concentrations for Guildford aerosol from 16.3.77 to 18.3.77 by PIXE analysis.
(Note the different ordinate scales)
Fig. 6.1.2.5.e See caption to Fig. 6.1.2.5.d
Fig. 6.1.2.5.f Temporal variation in lead concentration for Guildford aerosol from 16.3.77 to 18.3.77 by RBS analysis.
Fig.6.1.2.5.g Variation of inverse of wind speed with time 16.3.77 to 18.3.77.
be an explanation for the high chlorine levels present that day and for the reduction in the concentrations of the other elements, noticeably sulphur. The lead levels appear to show strong diurnal variations which may be due to traffic on the nearby A3 trunk road. Further details may be found in a recent publication (Barfoot et al. 1979).

6.1.2.6 Conclusions

Optimum conditions for quantitative proton PIXE analysis of light elements in time-resolved air particulate samples on cellulose acetate filters have been determined. Typical minimum detection limits have been found to be 10 ng m\(^{-3}\) of air sampled. This corresponds to about 1 part in 10\(^{11}\) (by weight) of air or 150 pg of the element detected. To further improve the detection limits of the technique, without going to longer irradiation times, it is necessary to use a filter material which has a lower trace element content, is thinner (to reduce bremsstrahlung background) and can withstand a higher beam current than the cellulose acetate filters used.

The mass resolution obtainable by 1 to 3 MeV RBS analysis of 200 \(\mu g\) cm\(^{-2}\) air particulate deposits was generally insufficient to resolve the elemental peaks and therefore it was not possible to accurately measure the thickness of the deposits in most cases. However, RBS analysis was useful in the determination of the non-stochiometric amounts of sodium and chlorine in the sodium chloride target used in calibrating the Si(Li) detector. When using 2 MeV protons, RBS analysis was found to have a better minimum detection limit for lead than PIXE. In this connection it should be pointed out that the PIXE system of Mason (1978) achieved better MDL's for the higher energy X-rays, such as the 11 keV \(L_a\) X-rays of lead, because of the order of magnitude greater geometrical detection efficiency.

The PIXE analysis of time-resolved air particulate deposits shows much promise for the understanding of the rapid variations in concentrations of the many elements present in the atmospheric aerosol. It is evident that the interpretation of these data require good supporting information on the total particulate matter, weather conditions, geography and a knowledge of the pollution sources over a wide area. These inter-relationships will be discussed in more detail in section 6.1.4.
6.1.3 The development of a sampling system for the CBNM with applications to the monitoring of atmospheric and welding-shop environments

6.1.3.1 Introduction

As a result of the work described in section 6.1.2, several aspects of the streak samples produced in Guildford were thought to require improvement. The most important of these was the choice of filter material. Because of the high secondary-electron bremsstrahlung background and the limit on the ion beam tolerance associated with Sartorius cellulose acetate filters, currents of 3nA together with PIXE analysis times of about 20 minutes, per section of streak, had to be used. This is clearly too long a time for routine analysis as a one week streak sample requires 84 analyses. In the PIXE set-up of Mason (1978) only about 4 minutes were required for analysis as a large diameter Ge(Li) detector was used for the detection of the X-rays. This detector had an order of magnitude higher geometrical efficiency than the present Si(Li) thereby requiring an order of magnitude less fluence. The low resolution (310 eV) of this detector was acceptable to Mason as he was primarily interested in higher energy X-rays, principally the L X-rays of lead, than those studied here. However, it had insufficient resolution to enable the analysis of the lighter elements studied in the present work and so the Si(Li) detector with a resolution of 150 eV was used. It was not possible, with the present vacuum system, to bring the Si(Li) detector much nearer to the targets. The need, therefore, was for a thinner filter material with a higher beam tolerance in order to reduce the irradiation time. It was also felt that more work was needed on the measurement of the air sampling rate, particle retention efficiency and clogging effects of the air sampling system in the field. The opportunity was also taken to modify some of the mechanical design characteristics of the Surrey sampler.

6.1.3.2 The sampling system

A variety of filter materials were tested for their tolerance to 2 MeV proton beams. It was found that Nuclepore filters were by far the best. These polycarbonate filters were found to withstand more than three times greater currents than the Sartorius cellulose acetate filters previously used. In addition, after irradiation, Nuclepore filters retained their structure. Sartorius filters, as discussed in section 6.1.2.4, showed significant radiation-induced changes in
structure and disintegrated after a few days post-irradiation contact with air. This latter effect is very inconvenient as it prevents subsequent re-examination of the filters either by PIXE or other means such as electron microscopy. The enhanced tolerance of Nuclepore is probably due to two factors. The first is that the material is only 1 mg cm$^{-2}$ thick compared to 4.5 mg cm$^{-2}$ for Sartorius filters. Thus the beam will deposit about 80% less energy in Nuclepore. Secondly, the cellulose acetate filters are of a 'honeycomb' membrane structure whereas the Nuclepore is uniform except for the holes normal to the filter surface (see Fig. 6.1.3.3.a). This probably results in better heat conductance in the latter case.

Nuclepore with pore diameters of 0.4 μm was chosen as Spurný et al. (1969) have shown that this is the best pore size for trapping particulates of dimensions that are likely to be retained in the lungs. However, it should be pointed out that the particulate retention on the filter surface is still far from 100% with the efficiency for 0.1 μm particles being as low as 40%. The air velocity in the CBNM sampling head has been measured to be 76 cm s$^{-1}$. Examination of Fig. 5 of the paper of Spurný et al. (1969) indicates that for this velocity, the retention efficiency is greater than 50% for particles greater than 0.05 μm diameter but that below this diameter, the efficiency falls off very rapidly. It should thus be borne in mind that the measured particulates are always less than the amount truly present in the sampled air. In this respect the membrane filters have an advantage in that they have an almost 100% trapping efficiency for particulates (Spurný et al. 1969).

Fig. 6.1.3.2.a shows PIXE spectra recorded with clean Sartorius and Nuclepore filters. It can be seen that the background levels associated with Nuclepore are lower and therefore better suited for PIXE analysis than Sartorius. Mason (1978) has already shown that Sartorius is the purest, from the point of view of PIXE analysis, of the cellulose acetate filters commonly available.

Fig. 6.1.3.2.b shows the present streak air sampling system. In this case the filter, rather than the sampling nozzle, moves at 1 mm hr$^{-1}$. The filters are held in perspex cassettes which contain a conducting layer of graphite paper to prevent beam charging up effects. They are then transferred directly to the vacuum chamber goniometer. This reduces the possibility of contamination during handling of the filters. It also ensures that the streak is kept symmetrically in the centre of the cassettes which allows easy alignment of the ion beam and streak. A microswitch has been installed at the end of the cassette path so
Fig. 6.1.3.2.a 2MeV proton PIXE spectra obtained for equal fluences on Sartorius and Nuclepore filters.
Fig. 6.1.3.2.b The 'streak' air sampling system. [Flow-meter and pump-buffer not shown].
that the pump and motor are turned off at the end of the sampling period. During operation, a perspex cover is placed on top of the sampler to prevent vertical deposition on top of the filters by heavy particulates and to avoid spurious effects caused by the weather. The streak deposit is produced underneath the filter and large particles, which are unlikely to reach the lungs, are not generally collected. The square sampling head is of 4 mm² area and has sharp edges. This has been shown (Mason 1978) to be necessary to ensure uniformity of deposit and a good cut-off at the edge of the aperture. If the edges of the sampling head are flat then an excess of particulates is attracted to that region.

The pumps chosen were the Dymax Mark II and IIa which operate on mains voltage and which have been found by Mason and the present author to be totally reliable so far. These pumps have a throughput in free air of 3000 and 1500 cm³ min⁻¹ respectively. The Mark II was the same as used by Mason. A Crouzet synchronous motor was chose for the drive as this is sensitive to the current frequency rather than the voltage of the mains supply which is less stable. It is most important that the filter moves at a known fixed rate. A deviation of only 1% would produce an error in the sampling position of 1 hour after a period of 4 days.

The flow-rates through the Sartorius and Nuclepore filters were measured for the two pumps. This was achieved with a commercially available gas-flow meter and with a special device constructed during the present experiments. The latter system consisted of a long vertical column and a system for making soap films. The air being measured was allowed to push the film up the column of known volume. The two methods were found to agree to within 3%. It was found that these flow-rates varied considerably from experiment to experiment. It was discovered that this was due to filter vibration against the sampling head caused by the oscillating nature of diaphragm pump. The inclusion of a 2 litre chamber as a buffer in the pumping line was found to remove the effect of pump vibration. The flow-rate was also found to be strongly dependent on the pressure of the sampling head on the filter. Too little pressure and the sampling orifice is not totally covered, too great a pressure and damage is produced on the filter surface. The result in both cases is that air which has not been through the filter goes passes into the pump. Thus if a flow-meter is included in the air circuit, too high an air sampling rate will be recorded. The sampling head pressure on the filters was varied until the flow-rate was a minimum as it is believed
that this represents the pressure at which the largest fraction of the air pumped has passed through the filter. This pressure was then maintained for all subsequent sampling.

With the Dymax Mark II pump, the flow-rate through 0.45 μm pore size Sartorius was found to vary between 200 and 220 cm$^3$ min$^{-1}$. Using the same pump and filter material, Mason (1978) and Gilboy et al. (1979) reported a flow-rate of 600 cm$^3$ min$^{-1}$. When the present system was operated without a buffer and with the sampling head pressure poorly adjusted, it was found that the measured flow-rates could also be as high as 600 cm$^3$ min$^{-1}$. A large part of the discrepancy is probably due to the presence, in the CBNM system, of the 2 litre buffer. The partial vacuum of this chamber may reduce the efficiency of the pump. It is concluded that the Surrey results may possibly be in error due to the lack of a buffer to prevent filter vibration. Using the present optimum settings, the flow-rates were found to vary by ±1.5% on different parts of the same Sartorius filter and by ±5% on different filters of the same batch. This is consistent with the differences found in the measured weights of the filters. The variations of flow-rate are of concern as they will even appear in the relative uncertainties from streak to streak although this effect is still small compared to the order of magnitude changes in the air particulate levels.

Although the above precautions were not found to be so important for Nuclepore, they were still taken. The flow-rate differences from filter to filter proved to be negligible. It should be mentioned that all these flow-rates were measured in an ordinary laboratory environment, which of course contains some air particulates, but only for a period of a few minutes so that the filters were still clean at the end of the experiment. If one continues to measure with the sampling head on the same place, then the flow-rate goes down due to clogging of the filter pores. The effects of this are shown in Fig. 6.1.3.2.c for Nuclepore using the two pumps in the laboratory environment. Although the faster pump produces almost double the initial flow-rate, it rapidly falls off until after 75 min it is lower than that of the slower pump. It appears that over an extended period of time, the two pumps sample approximately the same total volume of air. This is probably due to a limit caused by complete clogging of the filter pores. It was found that saturation was reached much more slowly with Sartorius filters. For example, in the laboratory, the flow-rate only fell by 13% after 16 hours. In order that the sampling rate be as constant as possible over the sampling period, the flow-rate should be as
Fig.6.13.2.c  Variation of flow-rate through stationary Nuclepore filter in room air for the two sampling pumps.
uniform as possible. For this reason, the slower Dymax Mark IIa pump was chosen. Details of the Nuclepore filter pore clogging mechanisms have been investigated by Spurný et al. (1974) using artificial aerosols. The resulting clogging theory is complex and, for the varied nature of particulates actually found in practice, predictions would be even more difficult. It is therefore believed to be necessary to continuously record the flow-rates during the air sampling.

Examination by electron microscopy of sections of streak resulting from pollution episodes revealed that the Nuclepore filters often appeared to be almost totally clogged up. If account is not taken of this fact, then the measured pollution levels will be too low. An investigation of flow-meters, commercially available in Belgium, which provide a voltage output suitable for recording showed that prices of £700 were typical. As pen recorders costing about £500 are also necessary, it was thought that this was far too expensive for an air sampling programme that would eventually require many samplers. For this reason it was decided to construct a flow meter at the CBNM. This simple device is still being developed (Verheyen 1979) but its present status will now be described. In essence, it consists of two equal thermocouples in opposition with a 100 Ω resistor placed equi-distant between them. A voltage of 8.5 V is placed across the resistor which thus becomes warm. When no air is flowing through the system, the two thermocouples rise to the same temperature and hence only a very small current flows in the thermocouple circuit. However, when air is pumped over the thermocouples, the resistor heats up the passing air and so the second thermocouple achieves a higher temperature. This produces a voltage drop of typically 1 mV for the present flow rates. This voltage signal is then fed into a pen recorder in order to obtain a permanent record of the flow-rates. The system is calibrated using the previously described flow-meters which do not provide a continuous permanent record of the flow-rate but only yield the total volume of air that has passed through them during a measurement. Careful calibration is necessary as the flow-rate voltage curve is non-linear. As this is a temperature difference method, it is not thought that variations in air temperature will significantly affect the calibration although strong variations in humidity may do so. The thermocouples and resistor are enclosed in a polystyrene tube which fits into the air pumping circuit. The use of the polystyrene also effectively prevents large losses of heat to the mass of air about to be sampled. The costs are about £5 for the materials and £15 for the stabilised voltage supply. The overall cost
compares most favourably with the £700 required for a commercial meter. It is thought that the accuracy of this simple flow meter is quite adequate for air pollution sampling programmes. Also, it should be possible to link a central pen recorder to a battery of air samplers and to record flow rates in rotation.

In order to avoid significant fractions of the analysing ion beam falling outside the streak region of interest, a nominally 1 mm diameter beam was used to analyse the 2 mm x 2 mm regions of interest. It will be remembered from section 4.3.3 that the beam diameter after passing through the foil monitor was somewhat greater than its nominal value. As all of the sample is not analysed by the beam, it is necessary to check that the streak deposits are uniform across their width at any point. This was verified using a scanning electron microscope fitted with a Si(Li) detector (Verachtert 1980). The fall-off in deposit thickness at the edge of the streaks was found to be sharp. Variations, over intervals of significantly less than 2 mm, were found along the streaks as is to be expected if the air pollution levels are varying over periods of less than 2 hours. It is also of interest to know whether the particulates sampled are deposited uniformly over the 4 mm² area or whether they tend to congregate at the leading edge of the sampling head where the moving filter does not yet have any particulate matter on its surface and is therefore free of any clogging. If this happened, then the conversion from the amount of the element per unit area into the concentration in the air would be incorrect and very short pollution episodes (< 2 hours) may be missed by analysis with the 1 mm beam in steps of 2 mm (≈ 2 hours). In addition, the measured time of the incident would be in error by about one hour. By sampling thick black smoke, produced by burning a candle, over a few minutes, it was found that for normal particulate loadings the deposition was uniform over the 4 mm² area.

6.1.3.3 Atmospheric results

Only a small number of PIXE analyses have so far been performed on streak samples obtained in the regions around the CBNM. In general for the samples taken outside town centres, the levels were similar to those found for Guildford except that the zinc levels were sometimes as much as a factor of 5 higher around Geel. This is most probably due to the presence of a smelting plant about 20 km east of Geel as has been pointed out by Kretzschmar et al. (1978) who have performed a five-year survey of atmospheric metal levels across Belgium. Levels in the centre of
the small market town of Geel were generally found to be higher especially for lead. Visual inspection of the streak samples produced in Geel during the summer showed darkening at fixed times (9.00, 12.00 and 18.00 hours) during week-days, less darkening on Saturdays and only slight darkening on Sundays. As little domestic heating is used at this time of the year, the principle source of pollution was assumed to be motor-vehicle. In fact, the timing of the pollution incidents roughly coincides with the observed peaks in traffic flow past the sampler which was positioned at a height of 3 m above the busy main street of Geel. It was noted that, on week-days, a large fraction of the traffic was composed of heavy diesel lorries whilst on Saturday there was still a great deal of traffic but this mostly consisted of petrol-driven cars. Sunday was relatively quiet as is to be expected.

The samples were also analysed with a scanning electron microscope. For X-ray analyses, about $10^{-10}$ A of 20 keV electrons were typically used. A 100nm thick layer of carbon was evaporated onto the filter to prevent target charging effects. For electron microscopy, an additional 10nm thick conducting layer of gold was found to be necessary and $10^{-11}$ A of 30 keV electrons were used. Beam diameters during X-ray analysis were around 10nm and during microscopy the resolution was about 100nm which is over an order of magnitude better than presently achievable with a proton microprobe. Nuclepore was again found to be superior to cellulose acetate filters as nearly all the particles lay on the smooth Nuclepore surface whereas the particles often go deep into the honeycomb structure of cellulose acetate filters. This penetration will depend on particle size. For example, Nielson et al. (1977) found that calcium-rich particles penetrated 0.5 mg cm$^{-2}$ into Millipore HA cellulose acetate paper whereas the smaller sulphur-rich particles penetrated about 1.2 mg cm$^{-2}$. Besides making electron microscopy difficult, such penetration requires the use of particle-depth and element dependent absorption corrections in X-ray analysis.

Electron microscopy of the samples taken in and around Geel revealed that, in general, large-scale clogging did not occur except during the pollution incidents in the centre of Geel. In these cases it was found that most of the pores were covered by particulates. It is impossible to know at what stage during the pollution incident this occurs and so the actual pollution levels may be much higher than estimated from the amount of deposited material assuming normal flow-rates. It was the discovery of this effect which lead to the decision to stop PIXE analyses of these urban aerosols in order to develop the on-stream
continuously recording flow-meter just described in section 6.1.3.2. It is now thought that without a continuous record of the flow-rate during sampling, the nature and magnitude of pollution incidents cannot be properly understood. At the time of writing, the flow-meter was about to be field tested and it was hoped that the magnitude of the effect on the flow-rate will soon be known. As Nuclepore is used by many other groups studying air particulate pollution, this clogging problem will not be peculiar to the present set-up. However, although a large amount of literature on PIXE analysis of such samples has been examined, no mention of this problem seems to have been made. That the problem exists for other workers can be seen, for example, by examining the photograph of the streak deposit in the paper of Nelson (1978). If significant pore clogging was not taking place, then the amount of deposit should be changing continuously or, during pollution incidents, there should be deposits of at least 2 mm width. Examination of the middle row of Fig. 2.3 of Nelson's paper reveals many dark strips of less than 1 mm width. Thus some sort of clogging or preferential deposition must be taking place as his sampling head is also 2 mm wide. His measured flow velocity is about double that of the present and so, in the same environments, it is to be expected that his filter will clog even faster (see Fig. 6.1.3.2.c). Because of the different nature of Sartorius membrane filters and because of the semi-rural (i.e. cleaner) location of the sampling at Guildford, it is not thought that filter clogging will have been such a problem in that case.

Electron microprobe X-ray analysis of the streak deposits revealed differences in the nature of the particulates found in the town centre and semi-rural locations. Those taken in the centre of Geel will be considered first. Examination of the dark sections of the streak corresponding to week-day pollution episodes revealed large irregular grains (~ 5 μm) containing predominantly S, K and Ca and smaller grains (~ 1 μm) containing Si, S, K, Ca, Fe and a little Ti and Mn. In addition the S, K and Ca were found in rectangular grains of approximate dimension 1 × 5 μm. Small particulates of diameters less than 1 μm largely contained Fe and S plus a little Si. There was a small number of 1 μm particles containing Pb, Br, Cl and a little Sr and Cd. On Saturdays the filters looked much cleaner and there was less sulphur. However, it was found that there were more of the 1 μm Pb, Br, Cl, Sr, Cd particles and a few 0.5 - 1 μm grains containing a large fraction of lead. One such micrograph is shown in Fig. 6.1.3.3.a. As these samples were taken during the summer when little domestic heating is used, it was
Fig. 6.1.3.3.a Scanning electron micrographs of 'streak' samples.

CLEAN NUCLEPORE (x10000)
NOTE WELL-DEFINED PORE SIZE

GEEL CENTRE AEROSOL ON NUCLEPORE (x10000)
NOTE LEAD PARTICULATE IN MIDDLE

WELDING-SHOP AEROSOL ON NUCLEPORE (x3000)
NOTE FILTER SATURATED WITH AGGLOMERATES
thought that the major source of pollutants was likely to be due to motor vehicle exhausts. To further investigate this possibility, the sampler was set up about 1.5 m from the exhaust of a petrol driven saloon car. A large number of 0.5 – 1 μm particles with Pb, Br and Cl in a similar ratio to that found for Saturdays in Geel, along with small amounts of Sr and Cd, were detected. There were also larger (> 1 μm) particles in a variety of shapes, some almost perfect spheres, containing Al, Si, K, Ca, Fe and large amounts of S. Some particles with Ti and Ni were also found. Scanning over regions where no individual particulates could be resolved, which implies that the diameters of the particles are less than the electron microscope resolution of 0.1 μm, revealed S, Cl, Br, Pb and a little K and Ca. It appears that there are two possible conclusions that may be drawn from these results with regard to the harmful lead pollution. Either that although petrol-driven car exhaust looks much cleaner than diesel vehicle exhaust it emits much more lead or that the large amounts of sulphur etc. emitted by diesels physically cover up the lead in the deposits and hence reduce the lead signal. Whilst there may be a combination of these two circumstances, it is believed that, in fact, the lead levels are highest on Saturdays. This is most probably due to the fact that petrol contains much more lead than diesel fuel. This is another indication that judging pollution levels from the visual blackening of filters can be misleading as the blackening is mostly due to carbonaceous components.

For the streak samples taken in residential areas outside Geel, the filters had a much cleaner appearance and the electron microprobe analysis revealed negligible levels of lead. On every filter examined spheres of 1 – 5 μm diameter, containing Al, Si, S, K, Ca, Fe and often Ti, were found. Somewhat less common were elongated particles, about 3 – 4 μm long and 1 μm wide, containing Na, Cl, S, P and sometimes K. In the regions where particle sizes were less than 0.1 μm, sulphur predominated. Valković (1975) has listed the elementary composition of the earth's soil. The highest concentrations are found for C, N, O, Na, Mg, Al, Si, P, K, Ca, Ti, Mn and Fe. The first three elements are not detectable with the present system. It is thus quite possible that a large fraction of the elements found are natural and due to wind erosion of soils. It thus appears that the bulk of the particulate pollution produced in the town remains there; probably due to deposition and washout. Since it is generally accepted that a large fraction of particles approximately 0.5 μm or smaller in diameter can be deposited in the lungs (Valković 1975), the electron microscopy results for Geel
centre indicate that the most likely elements to be retained in the lungs are Pb, Br, Cl, S and the small amounts of Sr and Cd. It is unfortunate that lead, one of the most toxic elements generally found in the air, is found in large quantities in particles of optimum size for retention in the lungs. Paciga et al. (1975) have measured particle-size distributions of lead, bromine and chlorine in urban-industrial aerosols using an Andersen sampler, which separates particulates according to their size, and found the median diameter for lead particulates from automotive exhausts to be 0.7 μm. This is in good agreement with the present measured range of 0.5 - 1 μm.

The use of the electron microscope has well illustrated the point, made in the introduction to this chapter, that a variety of complementary techniques are necessary in order to gain a good understanding of air particulate pollution. The additional information gained, which could not have been obtained from PIXE analysis alone, may be summarised as being on pore clogging, particle-size distributions (which gives more information on the possible harmful effects of the pollutants), identification of pollution sources, the unreliability of filter blackening as a useful measure of pollution levels and general information on the uniformity and depth of the deposits.

6.1.3.4 **Welding-shop results**

Recent concern about air quality in working environments has initiated much effort to decrease the exposure of workers to polluted air. In the welding-shop investigated, the whole room was ventilated rather than the immediate surroundings of the welding operation. Whilst such a system may be expected to maintain the average particulate concentrations at acceptable levels, it is questionable how efficient such a system is during welding operations. Thus the information required is on the level of air particulates over short periods of time comparable with the length of the welding work. The PIXE streak system is well suited to such a problem and its application, together with that of scanning electron microscopy, will now be described. It should be pointed out that there was only one welder at work and so, in busier welding-shops, the pollution levels will be higher (assuming the same degree of ventilation).

The sampling system used was that described in the previous section. The experimental conditions for PIXE analysis were similar to those described for the Guildford samples in section 6.1.2.3. However, the use
of the Nuclepore filter allowed three times higher beam currents to be used and the thinner material produced considerably less background. This resulted in irradiation times of about 5 minutes being chosen which is a factor of 5 improvement on the time necessary for the analysis of Sartorius filters. Thus a full day's streak deposit could be analysed in one hour when the system resolution was two hours. The average flow-rate in the welding-shop was measured to be $148 \text{ cm}^3 \text{ min}^{-1}$ which, as can be seen from the results for the slower pump shown in Fig. 6.1.3.2.c, corresponds well to the average flow-rate over 2 hours. The integrated volume of air sampled every 9 and 15 hours, corresponding to working hours and non-working hours, was noted with the aid of the commercial gas-meter previously described (the electrical flow-meter had not been developed at that time). The average flow rate during working hours was only 4% less than the shut-down hours indicating that, for most of the time, clogging was not taking place. However, total saturation of the filter over a period of, say, 5 minutes at the height of a pollution episode would only result in a 1% lowering of the average flow-rate for the working day whilst the majority of the particulates from the pollution episode may have been missed. Also, for practical reasons, the sampler was a few metres from the welding operations. Therefore the level of particulates that the welder breathes are likely to be higher.

A streak sample with a time resolution of 2 hours was taken over a continuous period of 87 hours. A spectrum obtained for a pollution incident is compared to a night-time spectrum in Fig. 6.1.3.4.a. Large differences in elemental concentrations for the two periods may be observed. The eleven elements that were frequently quantitatively detected are given, together with their temporal variations, in Table 6.1.3.4. A dash signifies that the element was below the quantitative detection limit for the computer programme RETEOH. As may be expected, there are very large and rapid variations in the elemental levels. For example, the highest level of iron is 474 times greater than the lowest. In general the highest levels are found for Fe and Si and the other elements, with the exception of Mg and S, show enhanced concentrations during these pollution incidents. Fig. 6.1.3.4.b shows the variations of the Fe, Si, Ca and S levels. The good correlation between Fe, Si and Ca can clearly be seen whilst there appears to be no correlation with the S levels. Attention is drawn to the fact that concentration scale is logarithmic. Similar trends may be observed with other elements (see Table 6.1.3.4) but to have plotted these would have produced a confusing graph. It is assumed that the principal source of sulphur
Fig. 6.1.3.a 2MeV proton PIXE spectra obtained with Nuclepore streak sample of welding-shop aerosol during night-time and during welding.
Table 6.1.3.4.: Levels of various elements found in welding-shop air particulates for period Monday to Thursday 8-11th October 1979.

<table>
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<tr>
<th>Time</th>
<th>Concentration in air (ng m$^{-3}$)</th>
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<td>280</td>
</tr>
</tbody>
</table>

* Repeat analyses

Welding-shop work schedule

Working hours : 8.00 - 17.00 hours
Tea-break : 10.00 - 10.30 hours
Lunch-break : 12.30 - 13.30 hours
Fig. 6.1.3.A Trace element levels in welding-shop particulates for period 8-11\textsuperscript{th} October 1979. A photograph of the 'streak' sample is also shown for comparison.
is the outside atmosphere. As the levels of magnesium are so low and the peak is on the highest point of the bremsstrahlung background it is difficult to draw any firm conclusions for this element.

The conclusions that may be drawn from this work are that, whilst the space ventilation eventually reduces the concentration of air particulates from welding, on average the elemental levels are an order of magnitude higher during working hours than during the evening and night. Thus over a working lifetime a welder will be exposed to significantly higher particulate pollution levels than ordinary members of the public living in this region. The question arises as to whether these levels are harmful. In an attempt to answer this question, the scanning electron microscope was again used.

The streak sample analysed with PIXE was subsequently subjected to electron microscopy and X-ray analysis. The region around 22.00 on Tuesday (see Fig. 6.1.3.4.b) corresponding to background levels was found to contain particulates of a variety of shapes and sizes containing Ca, Cl, Al, Si, S, Fe and Ti. Most of the particles were less than 3 µm in diameter. The next region analysed was for 16.00 on Wednesday. This section did not show any significant darkening although it corresponds to working hours. However many particulates were found, especially irregular ones, containing Al, Si, S, K, Ca, Ti and a great deal of Fe, also some with predominantly Ca and S which may be atmospheric in origin. Spheres of diameter 1 - 1.5 µm were predominantly Fe with a little Ca and S. Mn was sometimes found with the Fe. The blackest part of the streak (08.30 Wednesday) revealed that the most common particles contained Fe in large amounts, usually with some sulphur. Other particulates contained many elements especially P, Si, Al, S, K, Ca, Cr, Mn, Fe and Ni. The area which visually appeared to have the heaviest deposit, and which PIXE showed to be the most polluted, was a light brown region corresponding to 08.30 on Thursday. Similar particles to the previous pollution incident, together with particulates containing a large amount of Si together with the Fe, were found. A large fraction were less than 0.5 µm in diameter. Scanning over areas of both types of pollution incident revealed that, even where no distinct particulates were resolved, there were large elemental signals. This indicates that a large number of small particulates are present. The main conclusion to be drawn from this electron microprobe work is that a large fraction of the welding generated particulates are of a size (< 1 µm) that makes them likely to be retained in the lungs. The fact that many of the particles are also rough in shape will increase the probability of retention.
Electron microscopy of the filters also revealed that the pores were totally covered during the pollution episodes (see Fig. 6.1.3.3.a). In an attempt to overcome this, the sampler was modified so that it moved at 6 mm per hour and the experiments repeated. Even though the filter sampling system now had a resolution of 20 minutes, the pores still became covered. This indicates that the levels during pollution incidents may be at least six times higher than shown in Fig. 6.1.3.4.b. Hence it may be concluded that the welder is subjected to increases of more than three orders of magnitude in the respirable amounts of air particulate pollution especially iron and silicon. The silicon probably comes from the welding rods which contain large amounts of silicon.

The flow-rates are now being continuously recorded during sampling by using the electrical flow meter previously described. It is also hoped to study the effect of different welding rods on the physical, elemental and quantitative nature of the pollutants. These results will be reported in the near future (Barfoot et al. 1980c). Once again it should be pointed out that only solid matter has been studied. Gaseous emissions, especially of fluorine, are also likely to pose a threat. It is not known whether the levels presented are harmful in the long term but they were certainly observed to have an irritant effect on the lungs. Future progress in this field really requires the collaboration of the medical profession both for planning the goals of the research and for interpreting the significance of the results. Industrial hygienists would also have a strong part to play, especially in the design of more efficient fumigation systems.

6.1.4 Conclusions on the analysis of air particulates

The development of a sampler based on Nuclepore filters has shown a large number of advantages over the use of Sartorius membrane filters. The most important of these is the fact that, being more suited to PIXE studies, shorter irradiation times are more practicable. Also, the Nuclepore samples are not destroyed by the irradiation and they may be used for further studies. The main disadvantages with such filters are the less than 100% particle retention efficiency and the tendency for the pores to become clogged which give results for the particulate levels which are too low. The installation of the simple electrical flow meter should allow corrections for this effect. It appears that other laboratories that use Nuclepore for this type of work have not taken the clogging effect into consideration. From the point of view
of PIXE analysis of the particulate deposits, the technique is now certainly of sufficient accuracy to meet the needs of air pollution studies where changes of orders of magnitude in elemental concentrations are being observed.

Further progress now requires the involvement of a wider range of expertise. For the atmospheric studies, a person with meteorological training is required in order to construct a model of particulate transfer processes so that effects of pollution sources on the environment may be predicted. Even in the short sampling period discussed in section 6.1.2.5 for Guildford, a correlation of a pollution incident with wind direction (from London) was observed. Heidorn (1978) has studied air pollution incidents and wind variability on a daily basis in southern Ontario (Canada). He found that each city examined showed a unique behaviour for the winds during these incidents which was dependent upon the topography and location of the major pollution sources in relation to the monitoring site. If such studies were combined with high resolution temporal sampling and subsequent PIXE analysis, then a deeper understanding of the cause and impact of pollution incidents may be gained. For both atmospheric and industrial environment studies, personnel with medical training are necessary in assessing the possible effects to health. As was mentioned in the introduction (section 6.1.1), most of the atmospheric particulate matter is natural. Therefore the present technique may also have application to the study of the long range transfer of particulate matter within the biosphere. This may have relevance in determining the 'background' levels of particulate concentrations.

6.2 Other applications

Other studies to which PIXE analysis has been applied by the present author will now be discussed briefly. Rather than cataloging each application, a representative selection will be made which highlights some of the advantages and difficulties found in PIXE analysis.

6.2.1 The vitreous carbon implanted standards project

Attempts have been made in the past few years to use the RBS technique as a means of determining thin film thicknesses in an absolute manner. However, the lack of accurate stopping cross-section information and the inability to accurately determine solid angles and the ion beam fluence have prevented absolute determination of thicknesses to much
better than \( +10\% \). The use of a standard, to which the unknown quantity may be compared, is a way of improving the accuracy of the determination. It remains, however, difficult to produce a standard such as a thin evaporated layer that can be transported, used and handled as often as is necessary in RBS analysis. Ion implanted samples are much more robust and inert to the normally prevailing environment (from the point of view of oxidation, abrasion etc.). The problem remains, however, of calibrating the ion implanted standard itself since the normal methods of determining the ion implanted dose involve the same problems of ion beam fluence measurements etc. as do the RBS measurements. In the early work, Mitchell et al. (1978a) showed that it was possible to calibrate such a standard to within \( +2\% \). This was achieved by evaporating accurately known layers (using the CBNM UHV microbalance) of Cu and V onto the surface of a Bi implanted silicon wafer and comparing the RBS yields from the Cu, V and Bi.

Unfortunately, this type of standard showed some disadvantages due to the single crystal nature of the silicon substrate (channelling effects) and also difficulties in measuring oxygen and carbon growth at the surfaces as, being of lower atomic number, the RBS peaks from these elements sit behind the main silicon RBS step. It is important to observe these layers as, for instance, carbon usually builds up on targets after long irradiation and this affects both the energy and yield of the RBS peak from the implanted layer. Also it would be most useful to have a light and a heavy element joint-implanted standard both as a particle energy calibrator, as the lowest energy alpha-particles from radioactive sources are more than 3 MeV in energy, and as an RBS yield normaliser. The latter requirement has been particularly brought to light because of the recent discoveries of deviations from the RBS law (see Appendix C).

Vitreous carbon was chosen as the substrate as it is of low Z, high purity, amorphous and capable of being polished. After polishing, it was necessary to clean the material's surface. Various cleaning methods were tried and the resulting samples analysed by PIXE. The trace element content of the vitreous carbon itself was examined by cleaving a section of the material. PIXE analysis revealed inherent levels of Al, Si, S, Cl and Ca. The polishing process was found to add large amounts of Ti, Cu and Au. Cleaning with Teepol and trichloroethylene was found to be effective in removing these elements but at the expense of adding chlorine. Finally, sonication in ethanol was found to be the best means of cleaning the samples. RBS analysis
(e.g. see Fig. 6.2.1) indicated that the Ca was a bulk impurity whilst
the other elements tended to be found in the near surface regions. Au
and Al were chosen as the two elements for the double implant for
reasons discussed in a recent publication (Mitchell et al. 1980b).

In addition, to being used to check the purity of the carbon
substrates, PIXE analysis was used as a rapid means of comparing the
variations of the relative doses of Al and Au from sample to sample.
The M X-ray of Au and the K X-ray of Al were compared as they produced
similar yields. Although the L X-rays of Au would have been better
from the point of view of resolution and distance from the bremsstrahlung
background, the L X-ray yield was approximately three orders of magnitude
less than the M X-ray yield, thus effectively preventing precise compari­
sons of the Al/Au ratio. Helium ions were chosen as they produce
much less background radiation over the photon energy range used (see
section 5.5). Using currents of 30 nA, it was possible to obtain
4 x 10^5 and 7 x 10^4 counts in the Al and Au peaks in about ten minutes.
A typical spectrum is shown on Fig. 6.2.1. The major source of uncer­
tainty in the result for the Al/Au ratio for any particular sample was
background subtraction. This was especially the case for the Au M
X-ray, of energy 2.16 MeV, which was very close to the S Kα X-ray peak,
of energy 2.31 keV, due to the impurities in the vitreous carbon. As
the S peak was of much lower intensity than the Au peak, it was impos­
stable to resolve them. Therefore it was necessary to subtract a blank
spectrum from the implant spectrum. This correction varied from 1 %
to 4 % and introduced an uncertainty of ± 0.5 % to ± 2 % into the
intensity of the peaks. Normalisation from target to target was
achieved with current integration. The results obtained are summarised
in Table 6.2.1.

Table 6.2.1.: PIXE counts due to Al and Au implantations

<table>
<thead>
<tr>
<th>Sample number</th>
<th>Implantation sequence</th>
<th>Al X-ray counts</th>
<th>Au X-ray counts</th>
<th>Al/Au ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Al + Au</td>
<td>347824</td>
<td>65002</td>
<td>5.35 ± 0.25</td>
</tr>
<tr>
<td>7</td>
<td>Al + Au</td>
<td>374051</td>
<td>67802</td>
<td>5.52 ± 0.25</td>
</tr>
<tr>
<td>3</td>
<td>Au + Al</td>
<td>395272</td>
<td>67768</td>
<td>5.83 ± 0.25</td>
</tr>
<tr>
<td>9</td>
<td>Au + Al</td>
<td>356454</td>
<td>66480</td>
<td>5.36 ± 0.25</td>
</tr>
<tr>
<td>5</td>
<td>Au</td>
<td>--</td>
<td>64409</td>
<td>5.20 ± 0.25</td>
</tr>
<tr>
<td>6</td>
<td>Al</td>
<td>334655</td>
<td>--</td>
<td></td>
</tr>
</tbody>
</table>
Fig 6.2.1.a Typical 2MeV $^4$He$^+$ PIXE spectrum obtained with the double implanted vitreous carbon substrate.

Fig 6.2.1.b Typical RBS spectrum from a double implanted vitreous carbon substrate with evaporated layers.
The mean of the counts ratios is $5.45 \pm 0.020$ where the uncertainty is the standard deviation of the mean. This deviation is approximately twice that expected from summing the expected uncertainties in quadrature. Therefore it may be concluded that there is, in fact, a dispersion in the true Al/Au ratio. Similar results were found in the absolute RBS analyses where it was found that the Al/Au ratio was 4% higher when the Al was the second implant. The PIXE results gives this ratio as 3% higher. However, in both techniques, these differences are less than the uncertainties in the results.

The problems of the production and calibration of this dual-implanted standard were discussed in detail at a recent conference (Mitchell et al. 1980b). More recent results are tending to justify the conclusion that it is implantation effects, rather than the analytical techniques, which cause the dispersion in the results. It appears that PIXE analysis is well suited to the rapid control of many samples but that the RBS technique is the best for giving the absolute quantities of these layers. It is hoped that, from the experience gained in this work, it will be possible to produce multi-element standards of high accuracy for PIXE analysis. The careful handling of such targets is of great importance. For example, the PIXE spectrum shown in Fig. 6.2.1 shows the Fe and, to a much less extent, Ti and V have contaminated the sample. The sources of the contamination are not presently known.

### 6.2.2 The trace element content of coal

Although coal is the most commonly used source of thermal energy in the world, not too much is known about its chemical constituents (Ayanoglu et al. 1978a). It was therefore thought to be of environmental interest to examine the elemental content of coal using PIXE analysis. A powdered sample of European Community Bureau of Reference (BCR) coal was pressed into tablets in the same manner as described in section 5.2.1 for the targets of chemical compounds. They were subsequently irradiated with 2.5 MeV protons. A typical PIXE spectrum, recorded in 32 minutes using 12 µC of integrated charge, is shown in Fig. 6.2.2. X-rays from 23 different elements were detected with a high degree of confidence for more than half of them. The polyethylene absorber was placed in front of the Si(Li) detector and so the low energy peaks were drastically reduced in intensity. A large fraction of the elements detected are metals, several of which (e.g. V) are known to be toxic. It therefore seems worthwhile to analyse all coal types burnt in order to find their impurity contents. In addition to analyses of the coal,
Fig. 6.2.2  2.5 MeV proton PIXE and RBS spectra obtained with the coal sample.
ashes should also be investigated in order to investigate the effects of burning conditions and coal types on percent transference of elements into the environment. This can vary widely, for example Ayanoglu et al. (1978b) found that the amounts in the ashes varied from 45.6 % for Na to 94.7 % for Sr in one type of coal.

The thick target technique was chosen for two reasons. Firstly, it would be difficult to quantify the amount of coal present in a thin ($< 1 \text{ mg cm}^{-2}$) target. Secondly, it is desirable that as much as possible of the coal is irradiated in order to obtain a more representative sample of the material. Electron microscopy of the targets revealed that most of the coal particles were less than 20 $\mu$m in diameter but that some were as large as 100 $\mu$m. These may have been of a hard mineral inclusions. Thus to average out the effects of these inclusions, the beam diameter should be significantly greater than 1 mm. The presently used beam diameter was 1 mm and significant differences, especially for Ca, Cl and S, were found on examination of different parts of the targets. The coal could also be more finely ground to obtain more homogeneous samples but this may introduce extra impurities. With the many volatile elements found in coal, care would also have to be taken to check for element loss effects. Probably the easiest way of obtaining quantitative results would be to construct an artificial thick target standard composed of carbon and the other bulk elements typically found in coal, together with known trace amounts of the elements to be investigated in the unknown sample. Similar arguments would apply to the analysis of coal-ash samples. Finally, for comparison, a RBS spectrum recorded with about 3 $\mu$C of 2.5 MeV protons is also shown in Fig. 6.2.2. The poor elemental resolution of this technique makes it of very little use in analysing the many elements found in such samples. It will however give information on the amount of oxygen (5 atomic % in this case) found in the coal which may be of some interest to fuel technologists.

6.2.3 The pollution of waterways

In an aquatic medium the exchange of elements between sediments, water and the biological chain is a continuous process. This is influenced by various parameters such as pH, total ion concentration, oxygen concentration, salinity and the role of micro-organisms that may absorb, or even concentrate by many orders of magnitude, certain metals in the form of organometallic compounds. Thus, whilst the interpretation of the environmental impact of results may be difficult,
the analysis of sediments may be a more useful indicator of the steady-
state pollution of a waterway than the sampling of the water which may
fluctuate widely in purity in a short time.

A sample taken from a heavily polluted canal in the U.S.A. was
freeze-dried, sieved through 80 mesh, homogenised and dissolved in
perchloric acid using a teflon bomb as described by Verdingh et al.
(1979). The solutions were then spotted onto Nuclepore filters, allowed
to dry and irradiated with 2 MeV protons. The resultant spectrum is
shown in Fig. 6.2.3 where it may be observed that the sediment is rich
in transition metals. The high chlorine levels are probably due to the
perchloric acid. The sediment has been used as part of an intercomparison
of six analytical techniques. Some of the results disagreed by almost
two orders of magnitude (Verdingh et al. 1979), with the best agreement
being found for zinc which yielded \( (2200 \pm 587) \) ppm where the uncertainty
is the standard deviation of the five results used to form the mean.
The present PIXE results were normalised on this zinc result and are
listed in Table 6.2.3. The uncertainties may be as high as \( \pm 50\% \).

Table 6.2.3.: Concentration (in ppm) of trace metals in canal sediment

<table>
<thead>
<tr>
<th>Element</th>
<th>Present result</th>
<th>'Standard' soil composition</th>
<th>Enrichment factor</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mean Range</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ti</td>
<td>( 3 \times 10^3 )</td>
<td>( 5 \times 10^3 ) - 10^4</td>
<td>1</td>
</tr>
<tr>
<td>V</td>
<td>( 1 \times 10^3 )</td>
<td>( 1 \times 10^2 ) 2 x 10 - 5 x 10^2</td>
<td>1 x 10</td>
</tr>
<tr>
<td>Cr</td>
<td>( 1 \times 10^4 )</td>
<td>( 1 \times 10^2 ) 5 - 3 x 10^3</td>
<td>1 x 10^2</td>
</tr>
<tr>
<td>Mn</td>
<td>( 4 \times 10^3 )</td>
<td>( 8.5 \times 10^2 ) 10^2 - 4 x 10^3</td>
<td>5</td>
</tr>
<tr>
<td>Fe</td>
<td>( 5 \times 10^4 )</td>
<td>( 3.8 \times 10^4 ) 7 x 10^3 - 5.5 x 10^5</td>
<td>1</td>
</tr>
<tr>
<td>Ni</td>
<td>( 1 \times 10^3 )</td>
<td>( 4 \times 10 ) 10 - 10^3</td>
<td>3 x 10</td>
</tr>
<tr>
<td>Cu</td>
<td>( 3 \times 10^3 )</td>
<td>( 2 \times 10 ) 2 - 10^2</td>
<td>2 x 10^2</td>
</tr>
<tr>
<td>Zn</td>
<td>( 2 \times 10^3 )</td>
<td>( 5 \times 10 ) 10 - 3 x 10^2</td>
<td>4 x 10</td>
</tr>
</tbody>
</table>

a) Bowen (1966)
b) Present result/Mean value for 'standard' soil composition

Also shown, for comparison, are the values of Bowen (1966) for the
elemental content of 'standard' soil. Except for titanium and iron,
all elements show an enrichment but, in view of the range given by
Bowen, only vanadium, chromium, copper and zinc enhancements appear
significant. To study the enrichment effectively, it is necessary to
know the elemental content of the natural sediments. This may be
Fig. 6.2.3 2 MeV proton PIXE spectrum obtained with the river sediment solution.
achieved by sampling up-stream of the sources of pollution. Much work remains to be done on quantitative target preparation techniques for these samples and such studies require the equal development of an understanding of the factors responsible for the enrichment (pollution) of sediments in aquatic environments.

6.2.4 Impurity contents of GaAs semiconductor wafers

The University of Surrey is interested in the solid-state effects of epitaxially grown GaAs semiconducting wafers containing traces of Cr. A sample, provided by Dr. A. Adams, suspected of containing Cr in the ppm range was investigated with PIXE analysis. Initial analyses revealed that the spectra were dominated by the L X-rays of Ga and As which, because of dead-time and pile-up effects, prevented obtaining a useful count-rate in the K X-ray region. The use of the polyethylene absorber effectively removed the L X-rays and allowed the recording of the spectrum shown in Fig. 6.2.4. 0.6 µC of 2.5 MeV protons irradiated the target over a period of 47 minutes. Even though the total X-ray count rate was only 300 s⁻¹, pulse pile-up effects were beginning to appear and this resulted in a limitation on the data acquisition rate (even though the dead-time was only 1.6 %). No evidence for Cr was observed although Ni and Cu were found at about the 300 and 200 ppm levels assuming that these metals were distributed homogeneously throughout the bulk (if they were on the surface, the 'true' levels would be much lower).

The minimum detection limit for Cr under these conditions was calculated to be about 20 ppm. As described in section 3.1.5.1, the MDL is an inverse function of the square root of the ion beam fluence. Thus to reduce the MDL to 2 ppm would require a hundred times longer irradiation time (78 hours) which would be impractical. A better solution would be to selectively absorb the Ga and As K X-rays. The photon attenuation coefficient for an element is about an order of magnitude higher for photons with energy just above the element's K absorption edge than for those just below. Thus, for example, the use of a suitable thickness of copper foil as an absorber in front of the Si(Li) detector would improve the ratio of Cr to Ga counts and also reduce the background under the Cr peak due to poor charge collection and photon scatter effects of the large Ga peak. However it would still be a difficult task to detect Cr at the ppm level in these samples. RBS, X-ray fluorescence analysis and electron microscopy of the sample revealed no further useful information. It is suggested
Fig. 6.2.4 25 MeV proton PIXE spectrum obtained with the Ga As sample.
that some other analytical techniques, such as nuclear activation analysis, be investigated for these samples. If these prove unsuccessful, then the above mentioned improvements may be worth investigating.

6.2.5 The determination of lanthanides in boron carbide

The determination of rare earth elements in boron carbide by chemical methods is very difficult, suggesting the use of physical techniques, whilst neutron activation analysis also meets with difficulties due to the large capture cross-section of $^{10}\text{B}$ for thermal neutrons. Photon activation analysis has recently been used with success at the CBNM by Berthelot et al. (1979). The analyses were performed at the CBNM linear accelerator using the bremsstrahlung produced by the impact of a 32 MeV electron beam on a water-cooled platinum target. For irradiation times of 7.5 hrs, and the subsequent detection of the induced $\gamma$-ray emitting isotopes with a Ge(Li) detector, Berthelot et al. found minimum detection limits of 0.37, 1.0, 1.3 and 16 ppm (by weight) for Sm, Eu, Gd and Dy in boron carbide. Artificial standards, produced at the CBNM, were used for calibration.

A PIXE spectrum obtained in less than 10 min with such a standard is shown in Fig. 6.2.5, where 9.00 $\mu$C of 2 MeV protons were used and the standard contained 1000 ppm (by weight) of the four rare earths. L X-rays are the most suitable for analysis as the M X-rays would not be resolved and the K X-rays have too low a cross-section at this energy ($\sigma_L^X \approx 10^4 \sigma_K^X$). There is still a problem due to peak overlap. This may be obviated somewhat by improving the resolution which was 175 eV. By using a pulse-stretcher and a shaping time constant of 8 $\mu$s, a 30 eV improvement would be possible with the present system. This, coupled with the use of the computer peak fitting code RETEoh and a library of lathanide X-ray spectra, would enable accurate determinations of these elements provided that no other elements producing X-rays in this energy range were present. The use of the polyethylene absorber would remove the bremsstrahlung background and allow an order of magnitude higher L X-ray count rate. The MDL for the present conditions is about 10 ppm. With the bremsstrahlung X-rays removed, a MDL of 3 ppm would be achieved in the same time. For irradiation times of 100 min, the PIXE technique would have a lower MDL than the photon activation technique (except for Sm) which requires 7.5 hrs of Linac irradiation. However, the present MDL is calculated only on the background criteria and not on the peak overlap effects which will increase both the MDL and the uncertainty of
Fig. 6.25 2.5 MeV proton PIXE spectrum obtained with the boron carbide sample.
the analyses. Also, the photon activation analyses 220 mg of sample whereas the present PIXE only does this for about 1 mg, with a 5 mm diameter proton beam, and is therefore likely that the former will be far more accurate than the PIXE but, where high accuracy is not required, 10 min irradiations with a Van de Graaff are certainly more economical than 450 min Linac irradiations.

6.2.6 The analysis of uranium layers

Being a nuclear standards laboratory, the CBNM is often interested in the preparation and characterisation of targets for nuclear physics experiments. In one such case, targets were prepared by electrospraying (Verdingh et al. 1967) uranium layers onto thick vanadium backings. It was of interest to measure the amount of uranium deposited and the diffusion of uranium into the vanadium as a function of backing temperature. PIXE and RBS spectra were recorded simultaneously using 2 MeV protons. The 3.2 keV M X-rays of uranium were studied as they have a much larger production cross-section than for the L X-rays. The spectra obtained are illustrated in Fig. 6.2.6 where it may be observed that PIXE is superior for quantifying the uranium layer whilst RBS provides the required depth distribution information. PIXE is more suitable for quantitative analysis because it is statistically more accurate (more than five times the number of RBS counts) and does not suffer peak interference effects to such an extent as the RBS analysis. The background under the uranium M X-ray peak may be further reduced, and the permissible uranium count-rate increased, by selectively absorbing the vanadium K X-rays in a manner similar to that described in section 6.2.4.

6.2.7 Conclusions from the selected applications

The applications of PIXE analysis described in this section have been for a wide variety of sample types and have met with varying degrees of success. The major problem with the analyses of the present thin samples was the effect of peak overlap such as was the case for the gold M X-rays and the sulphur K X-rays (from the matrix) of the gold and aluminium implanted standard. In such cases it is necessary to carefully measure the matrix signal in non-implanted regions of the sample. Where such overlaps occur in an unknown sample, and there are no additional lines from the overlapping elements that may be observed, it is impossible to correct for this effect. The analysis of thick targets does not
Fig. 6.2.6 2.5 MeV proton PIXE and RBS spectra obtained with the uranium sample.
result in significantly poorer detection limits but the method of quantification is more difficult. This is probably best achieved with the use of standards which are similar in nature to the unknown or by 'spiking' the unknown with a known amount of a suitable element. 'Spiking' can often produce additional errors when a homogeneous mixing cannot be achieved. Sample preparation techniques for PIXE analysis have not been investigated in much depth in the present work. However, it may be concluded that they can introduce many difficulties to the method, especially for such insoluble materials as sediments. In this connection, thin air particulate deposits are an almost ideal type of sample for analysis. The PIXE technique is not well suited to the analysis of elements which have their X-ray signal lower in energy than those of the matrix material. For example, in the case of the chromium doped gallium arsenide samples, the gallium and arsenic K X-rays produced high count-rate problems and the low energy tails from these elements masked the chromium K X-rays.
CHAPTER 7

CONCLUSIONS

The major achievement of this work has been the accurate measurement of light-ion-induced K X-ray production cross-sections. In particular, the choice of the corrected SCA theory of Laegsgaard et al. (1978) as a means of producing a physically meaningful fit to the data allowed proton ionization cross-sections to be predicted in the range $Z = 22-34$ with an uncertainty of $\pm 4\%$. Comparisons with other fitting techniques were favourable up to $Z = 50$. The BEA fit of Johansson et al. (1976) was found to break down for the higher atomic numbers; probably due to the lack of an electron relativistic correction. The fit of Lopes et al. (1979) to $\exp(-Z)$ for selected energies and ranges of $Z$ appears to be inadequate for two major reasons. Firstly, as only the data for one energy and seven elements are used for each fit, the number of data used can vary considerably and for some cases only a few results are available. Thus the large systematic differences between the results of the various laboratories are not averaged out and the effect is that a discontinuous fit is obtained as may be seen in Fig. 5.3.3.1.f. The second inadequacy is in the assumption that the cross-section varies as $\exp(-Z)$. Fig.5.3.3.1.g indicates that this is at significant variance with the present results.

The agreement between the present results and the only others of similar accuracy (Laegsgaard et al. 1979) is consistent with the stated uncertainties which is most encouraging. There is presently disagreement in the scientific community about how uncertainties should be combined. Nevertheless, the uncertainties of these two sets of data are about three times lower than those of most published results when consistent error philosophies are utilised. To obtain significantly more accurate results would require a very large increase in experimental effort. This is not thought to be worthwhile and a more reliable vindication of these results would come from a third laboratory, with its own different (small) systematic errors, measuring the cross-sections to similar accuracy. Comparison of the present results for protons, deuterons, and helium ions indicates that the deviation of the results from the corrected SCA theory is principally dependent on the projectile atomic number and therefore the failure of the theory is probably due to an inadequacy in the binding energy correction. It is felt that significant improvements in the accuracy of the cross-section data
requires parallel improvements in the measurement techniques and the theory. In the meantime, these fitted cross-sections are of sufficient accuracy for most applications.

The thick target method of determining cross-sections shows no experimental advantages over the thin target technique when the thin target thickness is accurately known and the interpretation of the thick target results is more prone to errors. When it is not possible to make thin elemental targets, as is the case for volatile elements, the use of thick targets of the compounds may be necessary. However, even more sources of error are introduced in this technique and the resultant uncertainties in the values for the cross-sections are greater than those obtained with thin targets of the pure element. The major sources of additional error are the chemical instabilities of the compounds and uncertainties in the photon attenuation coefficients near the absorption edges of the elements in the compounds. Both these factors require further investigation if this technique is to become reliable.

The three principal experimental devices used in the cross-section measurements were made as accurate as is presently feasible. The CBNM method of preparing and weighing evaporated elemental layers is believed to be more accurate than has been achieved anywhere else. The development of the foil ion beam monitor, together with the careful RBS and ion beam current integration measurements, ensured that the large systematic errors often encountered in ion beam fluence measurements were avoided and the systematic and random uncertainties were ± 2% and ± 3% in the present combination of techniques. Although Matteson et al. (1979) have claimed uncertainties of ± 1% in their fluence monitor, other authors have obtained results which are at variance with those of Matteson et al. by 4%. Judging from these papers, it appears that about an order of magnitude increase in experimental effort would be required to halve the present uncertainty. Whether such effort is worthwhile would depend on the required accuracy of the cross-section measurements or PIXE analyses. A large improvement in the accuracy of the foil ion beam monitor would occur if the effects of ion-induced foil thickening could be predicted or controlled. Cleaner UHV vacuum conditions would reduce the effect of the carbon layer on the gold RBS yield. The use of an X-ray detector instead of the surface-barrier detector would remove the problem of peak shift due to the growing carbon layer as a fixed SCA window may be set for all projectile species and energies (the X-ray peak is essentially constant in energy).
The use of the thin sources prepared and calibrated by the Radio-
uclides Group of the CBNM allowed the efficiency of the Si(Li) detector
to be calibrated with an uncertainty of \( \pm 2-4\% \) over the K X-ray energy
range appropriate to the present thin target cross-section measurements.
Similar uncertainties were achieved by Laegsgaard et al. (1979) and, due
to uncertainties in the published radionuclide photon yield data, it is
unlikely that significantly better results will be achieved in the near
future for this range. At lower energies, the calibration of solid-state
detectors is still extremely difficult but it is hoped that the use of
the artificial sources, which produce low Z X-rays, will be an important
contribution to the solution of this problem. Other methods, such as
those discussed in section 4.4.5, should also be investigated further
with the long term goal of finding a quicker method, requiring less
expertise etc., for calibrating such detectors. Manufacturers of Si(Li)
detectors could make a contribution by more accurately measuring the
position, size etc. of the crystals within probe. The Compton backscatter
effect for X-rays emitted from sources and targets on thick backings
should be investigated further as it has relevance to many fields.

This work has concentrated on K X-ray yields for elements in the
lower half of the periodic table as these are usually of most interest.
However, for a wide range of applications, information is also required
on the presence of the higher Z elements (especially the heavy metals).
For the projectile energies presently available, the K X-ray production
cross-sections are far too low for routine analyses and the L X-rays,
with cross-sections typically five orders of magnitude higher, may be
used with advantage. The measurement of the L X-ray production cross-
sections could be achieved with the present system without any modifica-
tions in technique being required but the extraction of L shell ioniza-
tion cross-sections would be more complicated due to the effects of
Coster-Kronig transitions and K-shell cascades. It is difficult to
accurately measure K, L and M shell cross-sections with the corresponding
X-rays less than about 4.5 keV in energy because of the problems of
Si(Li) detector efficiency calibration. A gas proportional counter may
be more useful in such applications as all the relevant detector para-
eters may be more easily measured. The determination of K shell ioniza-
tion cross-sections for heavier projectiles, for the present range
of target Z, would not introduce many extra difficulties. However,
because of the multiple charge states that higher Z projectiles may
have, conventional current integration is not feasible as a means of
measuring the ion beam fluence. In addition, a variety of target
thicknesses would have to be used in order to extrapolate to zero target thickness because, when the heavy ion enters the target, it suffers charge exchange and the ionization cross-section is affected by the charge state of the ion.

Methods of measuring multiple ionization, as discussed in section 5.4, are worth investigating further. One reason for this is that the fluorescence yield used in converting from the X-ray production cross-section to the ionization cross-section is that for an atom with a single vacancy. The effect of multiple vacancies may be to change the fluorescence yield.

With the present experimental system, absolute PIXE measurements of thin unknown layers could be made with systematic experimental uncertainties as low as $\pm 4\%$. Thus with an uncertainty of $\pm 5\%$ in the present fitted cross-section values for the target range $Z = 22-34$, a total uncertainty of $\pm 7\%$ may be obtained in absolute PIXE analyses. However, if comparison is directly made with a standard layer which has an uncertainty of $\pm 1\%$, and the very precise foil ion beam monitor is used, the accuracy obtained will be at least a factor of three better. Thus the use of accurately known standards, where available, together with a target-independent means of fluence monitoring, is the most accurate manner of performing PIXE analyses of 'unknown' samples. However, great care must be exercised in the choice of the standard so that it is very similar to the unknown in elemental content, thickness etc.

The foregoing comments on the attainable analytical accuracy of the PIXE method ignore the possibility of substantial effects due to chemical binding. However, there is some evidence in the present work for $\sim 20\%$ variation in yield between different compounds of calcium, and other recent work has suggested effects of a similar magnitude for carbon and fluorine. It is very important to ensure that this behaviour is not simply due to target degradation effects.

If the phenomenon is found to be a real variation in X-ray production cross-section, it is important to assess its magnitude as a function of target atomic number and projectile species and energy. Further work would then be required to find to what extent ionization cross-sections and/or the fluorescence yields are modified by the chemical state of the target. Also, outer shell transitions are likely to show even bigger chemical effects and L and M X-ray production cross-sections should be accurately measured to test this hypothesis. If such effects are found to be important, they represent a new challenge to the theoretical understanding of PIXE phenomena and may be a serious limitation on the analytical capabilities of the method.
The concept of the minimum detection limit (MDL) should be used with care. Its major application is in the determination of the feasibility of experiments as the MDL is open to simple scaling from a variety of experimental arrangements. However, the results may be misleading as they give no indication of the likely precision of the experiments. The use of the more complicated minimum quantitation limit provides the likely precision and has been shown in the present work to suggest optimum conditions which are at variance to those predicted by MDL considerations. Neither limit takes into account the effects of peak overlaps, count-rate problems, matrix characteristic X-rays, the shape of the background etc. and a combination of experience and 'trial and error' are required in determining the most suitable conditions for PIXE analysis.

The analysis of the air particulate streak samples using the PIXE technique is now well developed and the most significant advance that could now be made is in the automation of the irradiation, sample changing and data acquisition system. Work is already in progress in this direction. The accuracy of the PIXE analyses is presently far higher than that of the air sampling method. The continuous monitoring of the sampled air flow-rates has shown that significant flow-rate variations occur during pollution incidents and it is hoped that such monitoring will allow corrections for this effect (Barfoot et al. 1980c). Useful information may be gained by additionally analysing the streaks for particle size distributions using an electron microscope. Multi-disciplinary teams are required if the causes and effects of air pollution incidents are to be fully understood.

The other applications discussed in Chapter 6 highlighted many of the important advantages and disadvantages of the PIXE analytical technique, some of which were additionally discussed in the conclusion to Chapter 2. In many cases, such as was the case for the gallium arsenide sample, the technique was not found to be adequate and another method had to be sought. It is perhaps sometimes forgotten that, in general, the analytical technique must suite the application and not vice versa. The major areas for future work with these samples are: in quantitative target preparation techniques; the observation and control of losses of material from the target; the optimisation of the experimental parameters, such as the choice of ion beam and selective X-ray absorbers, for the particular application; the production of standards; and improvements in the programmes used for analysing the PIXE spectra.
APPENDIX A

THE DEVELOPMENT OF ARTIFICIAL LOW-ENERGY
(< 5 keV) PHOTON SOURCES FOR THE EFFICIENCY CALIBRATION
OF SOLID-STATE DETECTORS

There are few X-rays with energies less than 5 keV, emitted by radionuclides, for which the intensities per disintegration are known. In addition, source X-ray self-absorption effects and large backgrounds from higher energy scattered photons make accurate efficiency calibrations difficult below about 3 keV, as was discussed in section 4.4.5. A series of experiments were performed to investigate the possibility of making and calibrating artificial low-energy X-ray sources. These consisted of an excitation photon source, in this case $^{55}$Fe, and an absorbing foil from which fluorescence X-rays of the desired energy are produced. $^{55}$Fe was chosen because it has no $\gamma$-rays associated with its decay. This creates spectra with lower backgrounds and also simplifies the calibration of the sources in the $4\pi$ proportional pressure counter.

In order to obtain the maximum amount of fluorescent X-rays, it is necessary to calculate the optimum thickness of the absorbing material. The fluorescence intensity may be found from (Kacperek 1979):

$$I_F = \frac{I_o \sigma_p N_o}{4A} \int_0^d \frac{dE(\mu_F x) E_2(\mu_F (d-x))}{x} dx$$

where

- $I_F$ = fluorescence X-ray intensity
- $I_o$ = primary X-ray intensity
- $\mu_F$ = total attenuation coefficient for the fluorescence X-rays
- $d$ = absorber thickness
- $\sigma_p$ = X-ray fluorescence cross-section
- $\mu_T$ = total attenuation coefficient for primary X-rays
- $N_o$ = Avogadro's Number
- $A$ = atomic weight

This formula was programmed on a PDP II minicomputer and the results for different elements excited by an $^{55}$Fe source are given in Table A.1. Copper, aluminium and silver were in the form of metal foils whilst sulphur, phosphorus and calcium were powders bound by a weak solution (2.5 %) of VYNS. In future, FORMVAR will be used as a binding agent because of the X-ray interference caused by the large proportion (46 %) of chlorine in VYNS. The chlorine absorber was produced by using a
10% dilution of VYNS which was subsequently dried. Electrical conduction was ensured by gold evaporated onto 30 μg cm⁻² VYNS covers.

Table A.1: Optimum thicknesses of absorber foils

<table>
<thead>
<tr>
<th>Absorber material</th>
<th>Mean energy(keV)</th>
<th>X-ray</th>
<th>Calculated thickness(mg cm⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper</td>
<td>0.94</td>
<td>L</td>
<td>0.18</td>
</tr>
<tr>
<td>Aluminium</td>
<td>1.51</td>
<td>K</td>
<td>2.7</td>
</tr>
<tr>
<td>Phosphorus</td>
<td>2.02</td>
<td>K</td>
<td>5.5</td>
</tr>
<tr>
<td>Sulphur</td>
<td>2.32</td>
<td>K</td>
<td>6.0</td>
</tr>
<tr>
<td>Chlorine</td>
<td>2.64</td>
<td>K</td>
<td>6.5</td>
</tr>
<tr>
<td>Silver</td>
<td>3.07</td>
<td>L</td>
<td>1.0</td>
</tr>
<tr>
<td>Calcium</td>
<td>3.77</td>
<td>K</td>
<td>5.5</td>
</tr>
</tbody>
</table>

Kacperek has also noted that a much simpler mathematical treatment yields the equation:

\[ d_1 = \frac{\ell_n \mu_T - \ell_n \mu_F}{\mu_T - \mu_F} \]

where \( d_1 \) is the optimum thickness and the other symbols are as before. This yields optimum thicknesses approximately twice those obtained with the more accurate but difficult equation. As doubling the optimum thickness only decreases the fluorescence intensity by about 15%, the results of the above equation, divided by two, are of sufficient accuracy for the present purposes.

Methane was used as the counting gas in all source calibrations, in preference to argon-methane, because it has a high efficiency for the fluoresced X-rays (< 3 keV) but a low efficiency for the X-rays from the excitation source which are far more intense and are not of interest. The absence of the interfering argon escape peak is an important advantage. Sources producing X-rays via the K transition were found to be far more intense than those via the L transition principally because of the lower L fluorescence cross-section. Further details of the source preparation and calibration techniques have been given by Kacperek (1979).

Fig. A.1 shows the Si(Li) detector spectrum obtained with the excited aluminium source. The source satisfies requirements of low background and lack of interferences; making it possible to determine
Fig. A.1  Si(Li) detector spectrum obtained with $^{55}$Fe/Al source.
the peak area with high accuracy. This spectrum was recorded for 23 hours with the plane of the source at 22.5° to the Si(Li) detector surface. This was the usual geometry for targets during PIXE analysis. The source was also counted at angles of 0° and 60° to the Si(Li) detector surface. The results for the aluminium and manganese X-rays (due to the decay of $^{55}$Fe) are given in Table A.2.

Table A.2.: Variation of artificial source count-rates with angle

<table>
<thead>
<tr>
<th>Angle w.r.t. source plane</th>
<th>X-ray count-rate (s$^{-1}$)</th>
<th>Aluminium K$_{\alpha,\beta}$</th>
<th>Manganese K$_{\alpha}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0°</td>
<td></td>
<td>0.0182 ± 0.0035</td>
<td>2.59 ± 0.08</td>
</tr>
<tr>
<td>22.5°</td>
<td></td>
<td>0.0184 ± 0.0015</td>
<td>2.59 ± 0.02</td>
</tr>
<tr>
<td>60.0°</td>
<td></td>
<td>0.0091 ± 0.0014</td>
<td>1.87 ± 0.05</td>
</tr>
</tbody>
</table>

It can be observed that neither the X-ray count-rates nor the ratio of these count-rates is constant with angle. Thus it is not possible to calibrate the Si(Li) detector, which subtends a solid angle of $1.3 \times 10^{-3}$ sr at the sources, with a non-isotopic source calibrated in $4\pi$. However, preliminary results indicate that, at low angles (< 22.5°) where the differences in X-ray path lengths are small (< 4 %), the emission is quite isotropic. Thus if these sources could be calibrated only over a small well-defined angle to the normal to the source plane, then they would permit the accurate calibration of the Si(Li) detector down to low energies.

The preparation and calibration of such sources is clearly a difficult task which most laboratories would not care to undertake. However, once a Si(Li) detector system has been calibrated in such a manner, aluminium K X-ray production cross-sections may be accurately measured for proton irradiation. This would allow PIXE laboratories to accurately calibrate their own Si(Li) detectors down to 1.5 keV. The work is continuing.
In Chapter 6 it was found that the optimum proton energy, in the range 1.0 to 3.5 MeV, for PIXE analysis of the lighter elements (Z = 11 to 22) in air particulate deposits was about 2 MeV. It is therefore of interest to examine the paper of Moriya et al. (1978) in which they inter-compare MDL's, which they refer to as sensitivities, in light element analysis by 2 MeV and 150 keV PIXE and photon-induced X-ray emission. In particular, they conclude that the MDL for trace element analysis of elements with Z ≤ 18 is lower for 150 keV than for 2 MeV proton excitation. In addition, Shiokawa et al. (1977) state that 200 keV protons are favourable for the determination of light elements.

It is shown that, for this region of the periodic table, the MDL is strongly dependent on the definition of this limit. Using the calculated cross-section data of Moriya et al., it is found that, for aluminium, 2 MeV protons provide a slightly lower MDL and a much lower MQL than 150 keV protons when the more correct definition of statistical significance provided by Currie (1978) is applied. Finally, other criteria relevant to the choice of proton energy are discussed and it is concluded that 2 MeV proton excitation is the best compromise for microanalysis while 150 keV is optimum for surface studies.

The MDL and MQL for aluminium. The MDL and MQL for aluminium have been estimated because Moriya et al. state that the MDL's in this region of the periodic table are far superior when using 150 keV protons. The signals and backgrounds for both energies have been calculated from Fig. 1 and Fig. 2 of their paper. The experimental conditions have been chosen to be those utilised in the present analysis of air particulate deposits (see Chapter 6).

The MDL for the two proton energies are compared in Fig. B.1. 2 MeV protons are slightly superior when a statistically meaningful definition of MDL is used. It is only when the $N_s = N_b$ definition of Moriya et al. is used that 150 keV excitation appears ascendant. It can be seen that this latter definition yields that the MDL will never improve with increased beam fluence (although the precision will of course improve). As has also been pointed out by Folkmann (1975), who at one stage used this definition, peaks with many and few counts may give the same ratio although the intense peak is easier to distinguish from the background.
Variation of minimum quantitation limit (MQL) for aluminium.

Fig. B.2

Variation of minimum detection limit (MDL), as given by two different definitions, for aluminium.

Fig. B.1
When, in Fig. B.2, the MQLs are compared, 2 MeV excitation is seen to be far superior. At 4 µC fluence, as used in the air particulate analyses, the 2 MeV MQL is a factor of eight lower (better). Even at the high fluence of 1000 µC that Moriya et al. illustrate, the 150 keV MQL is still 50 % higher than that for 2 MeV protons. The high values of MQL at low 150 keV proton fluence are due to the low number of counts produced. For instance the MDL condition is satisfied with a signal of 418 counts for 2 MeV protons whereas only 5 counts are needed for the 150 keV case.

Thus it is found that there is no statistically meaningful evidence to suggest that 150 keV excitation is superior. Examination of Fig. 6.1.2.5.c, which illustrates experimentally determined MDLs for the air particulate deposits, shows that the MDL varies very little in the region Z = 11 to 22. Thus a similar result will be obtained for elements other than aluminium. There is good agreement between the experimentally determined MDL and that calculated based on the cross-sections provided by Moriya. Therefore it is believed that their cross-section data are accurate, although it is not understood why their calculated values for the higher energy photon backgrounds are less for protons of 2 MeV than 150 keV. Both Follmann (1975) and the present author (Chapter 6) find that the background increases with proton energy.

Non-statistical considerations. In practice the choice of proton beam energy is strongly dependent on the physical nature of the target to be analysed. In the thin target method, one requires that only a small amount of beam energy is lost in the sample so that a simple average proton energy may be used to calculate the ionization cross-section. For instance, a 2 MeV proton loses 10 % of its energy (14 % of its PIXE cross-section) in 1400 µg cm$^{-2}$ of carbon whilst a 150 keV proton loses 10 % (34 % of its PIXE cross-section) in only 20 µg cm$^{-2}$. Therefore for low proton energies thick target approximation techniques, with their attendant increases in uncertainties, must be utilised. Low energy protons clearly only analyse a thin surface layer. Musket et al. (1973) have calculated that for 150 keV protons incident on steel samples, 90 % of Cr K$_a$ and Fe K$_a$ X-rays come from a depth of about 0.25 µm (about 200 µg cm$^{-2}$).

Ahlberg (1977) has similarly calculated that 75 % of Ti K X-rays come from a depth twenty times greater when 2.5 MeV protons are used. The situation is similar for light elements in a carbon matrix (Ahlberg 1977). Thus any surface chemical or physical non-uniformities in the target will have a strong influence on the X-ray yield for 150 keV protons which makes them a very useful tool for surface analysis as has been described by Musket et al. The difficulties in producing targets which are homogeneous over
such a small thickness are likely to make the precision lower for 150 keV 'bulk' analysis than 2 MeV 'bulk' analysis.

Often, in environmental and bio-medical analysis, the target takes the form of a thin sample deposit on a filter material. These filters will only withstand a limited current density because of the heating effects of the beam (see Section 6.1.2.4). Thus the high 150 keV MQL cannot be compensated by increasing the current. Another disadvantage is that the foil ion beam monitor will not work at 150 keV. It may be noted that Bales et al. (1975) have found that 100 keV protons have significant limitations. Also, at the intermediate energy of 700 keV, Rickards et al. (1975) conclude that their MDL is an order of magnitude higher than the best high energy ion-induced X-results using thick targets.

Conclusions. In contradiction to the findings of Moriya et al. (1978), it is considered that 2 MeV proton excitation is superior to 150 keV excitation. Perhaps 150 keV excitation has some economic advantages, since a smaller accelerator assembly is required, but this aspect has not been discussed by Moriya et al. A possible flaw in the statistical arguments lies in the fact that no account is taken of the shape of the background. A background that varies rapidly with energy, as is the case underneath the aluminium peak in 2 MeV proton excitation, will make it more difficult for any peak fitting routines to accurately determine the peak area. No method of taking this rapid variation into account is known. The final vindication of these conclusions would lie in a carefully controlled experiment performed at the two energies on the same target, preferably with the same apparatus. In connection with this, it should be pointed out that the 2 MeV spectrum shown in the paper of Moriya et al. is from a private communication where a filter has been used to deliberately cut out low energy photons. Therefore the spectrum in no way represents a 2 MeV PIXE system optimised for light element analysis.
Four basic physical concepts determine the capabilities of backscattering spectrometry. They are:

a) Energy transfer from a projectile to a target nucleus in an elastic two-body collision. This process leads to the concept of the **kinematic factor** which allows the determination of the mass of the target nucleus.

b) Probability of occurrence of such a two-body collision. This leads to the concept of **scattering cross-section** and to the capability of **quantitative analysis** of atomic composition.

c) Average energy loss of a projectile moving through matter. This process leads to the concept of **stopping cross-section** and to the capability of determining the **depth** of the target atom in the matrix.

d) Statistical fluctuations in the energy loss of a projectile moving through matter. This leads to the concepts of **energy straggling** and **angular straggling** and to a **limitation in the ultimate mass and depth resolution** of backscattering spectrometry.

These processes will now be outlined in so far as they apply to the backscattering spectrometry performed in the present work. A fuller treatment of both the principles and the applications of this technique may be found, for example, in a recently published textbook (Chu et al. 1978).

a) **The kinematic factor.** The simple elastic collision of two masses \( M_1 \) and \( M_2 \) can be solved fully by applying the principles of conservation of energy and momentum parallel and perpendicular to the direction of incidence. From the three simultaneous equations one obtains, the following relationship may be derived:

\[
\frac{v_1}{v_0} = \left[ + \left( M_2^2 - M_1^2 \sin^2 \theta \right)^{1/2} + M_1 \cos \theta \right] / (M_2 + M_1) \tag{C.1}
\]

where \( v_0 \) and \( v_1 \), are the velocities of the projectile of mass \( M_1 \) before and after the collision with the target \( M_2 \) which is initially at rest. \( \theta \) is the angle of scatter. Unless stated otherwise, all equations refer to a laboratory system of co-ordinates.
For $M_1 \leq M_2$ the plus signs holds. Defining the kinematic factor $K$ by:

$$K = \frac{E_1}{E_0}$$

(C.2)

and substituting into equation (C.1) one obtains:

$$K = \left\{ \frac{1 - (M_1/M_2)^2 \sin^2 \theta} {1 + (M_1/M_2)^2 \cos \theta} \right\}^{1/2}$$

(C.3)

When a target contains two types of atoms that differ in their masses by a small amount $\Delta M_2$, it is important that this difference produces as large a change $\Delta E_1$ as possible in the measured energy $E_1$ of the projectile after the collision i.e. to resolve a difference in masses $\Delta M_2$, $\Delta E_1$ must be greater than the resolution of the particle detector. For all but the smallest values of $M_2$, the largest change of $K$ occurs when $\theta = 180^\circ$. Thus the detector is usually placed at a steep backward angles ($165^\circ$ in the present work). It is for this reason that this form of elastic nuclear scattering spectrometry is known as back-scattering spectrometry. Other methods of increasing mass resolution are to increase $E_0$ (provided that nuclear reactions are not induced) and to use projectiles of larger $M_1$ (as long as $M_1 \leq M_2$). Mass resolution is inherently better for light target atoms than for heavy ones with the effect being proportional to $M_2^{-2}$ (Chu et al. 1978).

b) The scattering cross-section. The differential cross-section for scattering into a small solid angle $d\Omega$ is given by Rutherford formula

$$\frac{d\sigma(E,\theta)}{d\Omega} = \left( \frac{Z_1 Z_2 e^2}{16\pi \epsilon_0 \epsilon_o E} \right)^2 \frac{4}{\sin^4 \theta} \left\{ \frac{[1 - ((M_1/M_2) \sin \theta)^2]^{1/2} + \cos \theta} {[1 - ((M_1/M_2) \sin \theta)^2]^{1/2}} \right\}^2$$

(C.4)

which holds for $M_1 < M_2$. Here $Z_1$, $M_1$ and $Z_2$, $M_2$ are the atomic number and mass of the projectile and target atoms respectively, $\epsilon$ is the electronic charge ($1.60206 \times 10^{-19}$ C) and $\epsilon_o$ the dielectric constant in vacuo ($8.8543 \times 10^{-12}$ As/Vm). $E$ is the energy of the projectile immediately before scattering. This formula, which has given the name Rutherford scattering to elastic nuclear scattering, assumes that the force that acts during the collision of the two particles is well described by the Coulomb repulsion of the two nuclei. This holds as long as the distance of closest approach is large compared with nuclear dimensions but small compared with the Bohr radius (0.53 Å). Tabulations of these cross-sections can be found in the literature (e.g. Mayer...
et al. 1977). The total number of detected particles \( A \) is given by:

\[
A = \sigma(E, \theta) \Omega Q N \tag{C.5}
\]

where

\[
\sigma \equiv \left( \Omega \right)^{-1} \int \left[ \frac{d\sigma(E, \theta)}{d\Omega} \right] d\Omega \tag{C.6}
\]

For very small detector solid angles \( \Omega \) and large scattering angles \( \theta \), which is usually the case, \( \sigma(E, \theta) \) tends to \( d\sigma(E, \theta)/d\Omega \). \( \sigma(E, \theta) \) is known as the average differential scattering cross-section, \( Q \) is the total number of incident particles and \( N \) the number of target atoms per unit area.

Recently, deviations from the Rutherford cross-section at low projectile velocities have been observed (L'Ecuyer et al. 1979, Andersen et al. 1979). For instance, L'Ecuyer et al. found the cross section to be 4% below the Rutherford values for 1 MeV helium ions on bismuth. These deviations can be quantitatively explained by taking into account the screening of the electrostatic potential of the target nucleus by its atomic electrons. For the ion beams used in the present work, this correction only becomes greater than 1% for target atoms with atomic number greater than 40. Where necessary, the correction has been made using the following equations of L'Ecuyer et al.:

\[
\sigma(E, \theta) = \sigma^R(E, \theta) \left[ 1 - \frac{p\alpha}{(aE)} \right] \tag{C.7}
\]

and

\[
p\alpha/a = 0.049 Z_1 Z_2^{4/3} \text{ keV} \tag{C.8}
\]

\( \sigma^R(E, \theta) \) is the Rutherford cross-section for a particular angle \( \theta \) and \( \sigma(E, \theta) \) the corrected cross-section.

For sufficiently high energies \( E \), the distance of closest approach between the projectile and the target nuclei reduces to the dimensions of nuclear sizes \( \left( 10^{-15} \text{ m} \right) \). The short-range nuclear forces then begin to influence the scattering process, and deviations from the Rutherford scattering cross-sections appear. When the scattering process is inelastic, the energy of the scattered particle differs from \( KE \) as well. In other cases, the scattering process is still elastic but the differential scattering cross-section departs from that predicted by Rutherford theory (sometimes by a large amount). In both cases the value of the differential scattering cross-section is strongly dependent on energy, scattering angle and on the particular combination of projectile and target nuclei. Jarjis (1979a) has found evidence for deviations of up to 5% from Rutherford scattering for 1-4 MeV alpha particles on chromium and nickel. It now appears that the Rutherford cross-section has to
be used with care. Jarjis (1979b) is in the process of completing a comprehensive compilation of experimental differential cross-section data for elastic scattering and nuclear reactions on target nuclei in the Z = 1-29 region.

c) Energy loss and the stopping cross-section. When an ion penetrates matter, it will lose energy by collisions with the electrons and nuclei of the target. In electronic collisions, the energy is transferred to individual electrons in the atoms resulting in atomic excitation and ionization processes. In nuclear collisions, the momentum is taken up by the target atom as a whole and, because of the much larger mass involved, such collisions do not make a significant contribution to the energy loss in the energy range (1 to 3 MeV) of interest in the present work. The nuclear collisions do, however, give rise to the phenomenon of multiple scattering by which the incident ions are caused to undergo small changes in direction (see section d).

To first order, this electronic stopping is given by the Bethe-Bloch formula:

\[ -\frac{dE}{dx} = N \sum Z_j \left[ 4\pi (Z_j e^2)^2 / \left( m_e v_j^2 \right) \right] L \]  \hspace{1cm} (C.9)

where \(-\frac{dE}{dx}\) is the stopping power (the energy loss per unit path length) and L is the 'stopping number'. According to quantum-mechanical calculations of Bethe (1930), for MeV particles, L is given by:

\[ L = \rho_n \left( 2 m_e v_j^2 / I \right) \]  \hspace{1cm} (C.10)

I is the mean excitation energy and is usually determined empirically. The other symbols in the above equation have their usual meanings.

In fact, the stopping cross-section, \(\epsilon\), is the more fundamental parameter as it is independent of the target density. It is given by:

\[ \epsilon = (n^{-1}) (dE/dx) \]  \hspace{1cm} (C.11)

where \(n\) is the number of atoms per unit volume of the target.

With increasing accuracy in experimental measurements of \(dE/dx\), it has been found that the energy loss oscillates as a function of the target atomic number \((Z_2)\). This oscillation can be as high as \(\pm 25\%\) as may be observed from the values of Ziegler et al. (1974). Systematics for \(Z_1\) oscillations in stopping powers of five solid materials for \(6 \leq Z_1 \leq 20\) have also recently been investigated by Ward et al. (1979).
The stopping mechanism becomes much more complicated at energies below 1 MeV, due to such phenomena as projectile electron capture, and will not be considered here.

The most accurate tabulations of stopping powers are given by Andersen et al. (1977) and Ziegler (1977) for protons and helium ions respectively. These are semi-empirical fits, based on recent theories, to experimental data judged to be 'good'. Claimed uncertainties in the fitted values are as low as ± 1 % for MeV protons. Earlier tabulations, such as those of Northcliffe et al. (1970), are often in error by as much as 50 % due to neglect of the $Z^2$ oscillations.

With a knowledge of the target matrix and the mass number of a trace element of interest, the position and spread in depth of the trace element can be determined using the relationship:

$$ E_F = \left[ E_0 - \int_{L_1}^0 S(E)\,dl \right] K - \int_{L_2}^0 S(E)\,dl $$

(C.12)

where $L_1 = x \sec \theta_1$ and $L_2 = x \sec \theta_2$. $S(E)$ is the stopping power of the target matrix and the first and second integrals are the energy losses along the incoming and outgoing paths $L_1$ and $L_2$. $x$ is the depth in the material and $\theta_{1,2}$ the angles made by the projectile paths to the normal at the surface. $E_0$ is the incident particle energy and $E_F$ the energy of the emergent particle. $K$ is the kinematic factor for the target atom.

The above equation forms the basis for elastic backscattering depth analysis. The practical use of this equation and the derivation of 'working' approximate solutions of it are discussed in detail in many textbooks on the subject (e.g. Chu et al. 1978, Mayer et al. 1977, Ziegler 1975).

It should be noted that the measured stopping powers strictly only refer to amorphous materials. If the target is monocrystalline and the projectile enters it in a lattice direction, then it will 'see' less atoms. This phenomenon is known as 'channelling' and results in a considerably reduced stopping power.

d) **Energy straggling.** When a beam of charged particles penetrates matter, the slowing down is accompanied by a spreading of the beam energy due to statistical fluctuations in the number of collisions suffered. In many cases of practical interest, the distribution in energy loss is sufficiently close to Gaussian that the spreading around the average value is completely characterised by the mean square
fluctuation, $\Omega^2$, in energy loss. $\Omega^2$, or $\Omega$, is known as the energy straggling. Bohr (1915) has derived a simple expression, in the limit of high projectile velocities, for the straggling due to electronic stopping:

$$\Omega_B^2 = 4\pi \left( Z_1 e^2 \right)^2 n Z_2 t$$

(C.13)

where $t$ is the thickness of the target of $n$ atoms per unit volume. Lindhard and Scharff (1953) extended Bohr's theory and derived a correction factor for low and medium energy projectiles. The state of the theories, together with accurate experimental results, has recently been given in a review by Besenbacher et al. (1980). No measurements of energy straggling in solid compounds are known. In fact, in general, accurate straggling measurements are rare and target texture can have strong effects (see e.g. Besenbacher et al. 1980, Werz et al. 1979). Al-Beri et al. (1976) have found evidence to suggest $Z_1$ oscillations similar to those found for stopping powers.

e) Angular straggling. When a collimated beam of charged particles passes through matter a fraction of the particles will change direction slightly due to multiple nuclear scattering. The angular distribution about the original beam direction is essentially Gaussian but with a slightly higher 'tail' than a Gaussian function. The Gaussian assumption allows the angular straggling to be characterized by a width $\sigma$. Marion et al. (1967) have performed numerical calculations of this process and provide tabulations and a formalism which permit the estimation of the effect for any case of interest. These calculations have been used to determine the angular straggling of the ion beams on passing through the foil ion beam monitor (Section 4.3.3) and the air pollution filters (Section 6.1.2.4). Spahn et al. (1975) have measured the angular straggling of H, He, N and Ne projectiles in solid targets of C, Al, Ni, Sb, Ag and Au for projectiles with energy ranging from 1-11 MeV. The agreement between the theoretical and experimental values was not better than 25%.
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