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SHORT-LIVED ISOTOPES IN NEUTRON ACTIVATION
ANALYSIS APPLIED TO ARCHAEOLOGICAL
AND ENVIRONMENTAL STUDIES

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ABSTRACT

The application of instrumental neutron activation analysis, principally employing short-lived isotopes, to archaeological and environmental studies is described. Techniques for the production and measurement of short-lived isotopes using a reactor facility are discussed and evaluated for a variety of sample matrices by the estimation of elemental detection limits.

Cyclic activation analysis, ideally suited for the measurement of isotopes with $\tau_f < 60$ s, is considered and optimised with respect to the 'signal-to-noise' ratio of a radionuclide of interest. The potential of the technique, in the low energy photon region ($< 250$ keV), is demonstrated by determination of elemental sensitivities in a variety of biological materials.

In an environmental study of Oxford City-Centre, the analysis of air particulates provides results for 8 time-varying elemental concentrations. Correlations are drawn between these elements, traffic flow, filter obscuration and meteorological data, also the concentrations of 5 hydrocarbons measured by gas chromatography.

The suitability of thermal, epithermal and reactor neutrons is investigated for the measurement of bulk, minor and trace elements in soils. The most appropriate method is then applied to the study of variations in elemental concentration with soil depth, for the purpose of locating buried soils of archaeological significance. These results are compared with additional physical measurements performed on the
soils, such as loss on ignition and particle size determination. The technique of cluster analysis is described and employed to aid interpretation of the multi-elemental results obtained.

A method is devised, employing cyclic activation, for the estimation of fluorine, through the $^{20}\text{F}$ isotope ($\frac{1}{2} \approx 11\text{s}$), in a bone matrix. Corrections are applied to eliminate the interference from a fast neutron reaction of sodium. The technique is proven to be multi-elemental, more than 10 elements per biological matrix being detected. Finally, the method is discussed in relation to its potential application for the dating of ancient bone, where the multi-elemental capability is an advantage.
DEDICATED TO MY PARENTS
ACKNOWLEDGEMENTS

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CHAPTER 1

INTRODUCTION TO NEUTRON ACTIVATION ANALYSIS

1.1 Introduction

Neutron activation analysis (NAA) was first proposed by von Hevesy and Levi in 1936 and, although treated as somewhat of a curiosity until the development of reactors with substantial neutron fluxes ($\sim 10^{12} \text{n cm}^{-2} \text{s}^{-1}$) in the mid-1940's, the field has subsequently undergone dramatic growth. This growth, as measured by the number of scientific publications in the field, is exponential and may be conveniently expressed in terms of a 'doubling time' defined as 'the length of time for the literature to double in size, when growing at constant rate'. The doubling time for activation analysis publications has remained constant over the last 4 decades at 3.0 years (Braun, 1977).

There are numerous reasons for this rapid expansion, some of which are outlined below:

a) the most obvious advantage is the very high sensitivity attainable with the techniques. Using a modest (by present standards) reactor neutron flux of $\sim 10^{12} \text{n cm}^{-2} \text{s}^{-1}$ it is possible to detect the majority of elements in the periodic table at the part-per-million (ppm) level or below in a large variety of matrices; notable exceptions being the elements with $Z \leq 7$.

b) under most irradiation conditions it is possible to measure a number of different isotopes simultaneously, making the technique multielemental.
c) nuclear reactions are independent of the chemical state of the elements being measured.

d) the whole mass of a sample is analysed, by virtue of the neutron having no electrical charge which would cause severe attenuation in matter.

e) instrumental neutron activation analysis (INAA) in which no chemical separations are performed before or after irradiation, is essentially non-destructive, although radiation damage may become apparent depending on the material and the neutron fluence to which it is exposed.

f) techniques specifically employing short-lived isotopes are rapid, and therefore economical.

The last decade has seen neutron activation analysis develop into a mature analytical technique, with current research concentrating on novel applications, principally for use on a routine basis. One of the few remaining areas not to have been fully exploited, primarily for technical reasons, is analysis based on the detection and measurement of short-lived isotopes (0.5s < \( T_\frac{1}{2} \) < \( \sim \) hours). Therefore, this work describes the techniques which have been developed for the measurement of short-lived isotopes suitable for routine analysis. A variety of these techniques, applied to archaeology and environmental science, have been examined and, whenever possible, emphasis has been placed on the use of short-lived isotopes enabling a critical assessment of the techniques to be made.
1.2 Neutron Induced Reactions

When an incident neutron interacts with a target nucleus, its energy is rapidly distributed throughout the nucleus resulting in the production of a nuclear excited state. The lifetime of this excited state, typically $10^{-15}$ s, is very long compared with the time required by the neutron to traverse the nucleus ($\sim 10^{-18}$ s for a neutron of energy 0.025 eV), thus it may be concluded that the neutron has been captured to form a compound nucleus. The compound nucleus is highly excited due to the large binding energy of the incident neutron and its kinetic energy. The mode of de-excitation depends only on the excitation level, irrespective of the way in which the compound nucleus was formed. Thus, for any particular nucleus, the most probable or preferred mode of de-excitation depends on the energy of the incident neutron.

The nuclear processes of interest in neutron activation analysis may be divided into the following categories:

1) Radiative capture
2) Transmutation
3) Inelastic scattering

each of which will be considered briefly. The product isotope of any of these reactions may be radioactive and measurement of the delayed emissions of this radioisotope forms the basis of neutron activation analysis.

In general, therefore, when stable nuclei are irradiated with neutrons, the activity, $\mathcal{A}$, of the radioactive product is given by:

$$\mathcal{A} = NR(1 - e^{-\lambda t_i})$$

where $\lambda = \text{decay constant for product isotope}$
\( t_i \) = length of irradiation

and \( NR = 'saturation activity' \)

The number of target nuclei, \( N \), is given by:

\[
N = \frac{N_0 f m}{A} \tag{1.2}
\]

where \( N_0 = \) Avogadro's Number

\( f = \) fractional abundance of target isotope

\( m = \) mass of target element

\( A = \) atomic weight of target element

and the reaction rate per target nucleus, \( R \), in its most general form is expressed as:

\[
R = o \phi \tag{1.3}
\]

where \( o = \) reaction cross-section

and \( \phi = \) irradiating neutron flux,

both of which are functions of the energy of the irradiating neutrons (cf. §1.3.1)

Eq. (1.1) is only correct if the number of target nuclei remains constant. This is never strictly true, but under most circumstances \( N >> R t_i \), and this assumption can be made.

For the purposes of the following discussion, it is useful to classify neutrons according to their energy, although the regions between the various divisions are ill-defined. A common classification (Lapp and Andrews, 1972) is:

High Energy \( > 10 \text{ MeV} \)
A further category of 'cold' neutrons, with energies ≤ 0.002 eV, is sometimes included (Burcham, 1973).

The term thermal neutron refers to a neutron in equilibrium at room temperature; the energy 0.025 eV corresponding to the most probable velocity (2200 m/s) of a Maxwellian distribution at 20°C.

1.2.1 Radiative capture

These reactions occur when the only de-excitation channel of the compound nucleus is through gamma emission, usually described as an '\( n,\gamma \)' reaction. Neutrons of any energy may participate in this type of reaction but thermal neutrons predominate since the absorption cross-section in this energy region is inversely proportional to the neutron velocity for most nuclei (so-called \( \frac{1}{V} \) law). Also, as neutrons are uncharged particles, they do not experience a Coulomb repulsion on approaching close to the target nucleus. Capture of a neutron contributes approximately 8 MeV of binding energy to the nucleus and, to complete the capture process, 'prompt' de-excitation of the compound nucleus occurs by the emission of a single gamma photon, or a sequence of quanta in cascade. Again, this is a highly favoured channel because the gamma photons have no potential barrier to penetrate. Thermal neutrons contribute negligible kinetic energy to the compound nucleus and in radiative capture, therefore, the gamma rays emitted have a total energy of about 8 MeV.
For many isotopes, the absorption cross-section for neutrons in the energy range 0.1 eV - 10 keV (loosely termed epithermal neutrons) consists of a $\frac{1}{v}$ slope with sharp resonances superimposed. Neutrons with energies corresponding to these resonances will be strongly absorbed (resonant capture) and in some instances this mechanism may predominate over thermal neutron capture.

1.2.2 Transmutation

Reactions of this type occur when the compound nucleus de-excites by the emission of a charged particle transmuting the nucleus to that of another element. The \((n,p)\) and \((n,\alpha)\) reactions fall into this class, and, in most cases, require fast neutrons to be initiated. There are two reasons for this. Firstly, many \((n,p)\) and \((n,\alpha)\) reactions are threshold reactions where the mass balance between the reactants and products, the Q-value, is such that extra energy is required before the reaction may proceed. The minimum energy at which the reaction is possible, the threshold energy, is obtained from

$$E_T = -Q \cdot \frac{(m_n + M)}{M}$$

(1.4)

for an endoergic reaction, where \(m_n\) and \(M\) are the masses of the neutron and target nucleus respectively and are required to account for the recoil energy of the compound nucleus. In general, \((n,p)\) and \((n,\alpha)\) threshold energies are a few MeV.

Secondly, any charged particle must have, according to classical theory, sufficient energy to overcome the Coulombic potential barrier before emission can proceed. The barrier for a given reaction is expressed by

$$E_b \propto \frac{Z_a Z_z e^2}{(R + R_a)}$$

(1.5)
which represents the magnitude of the potential when the product nucleus and emitted particle are just tangent (i.e. the maximum value)

where \[ e = \text{electronic charge} \]

\[ Z, R = \text{atomic number and radius respectively of the product nucleus (A) and emitted particle (a)} \]

and the constant of proportionality depends upon the system of units used.

Thus, fast neutrons are required to supply sufficient energy to the compound nucleus to permit \((n,p)\) and \((n,a)\) reactions. Notable exceptions to this rule are to be found for light nuclei (where the potential barrier is low, as shown by Eq. (1.5)) e.g. \(^{10}\text{B}(n,a)^{7}\text{Li}\) which has a thermal neutron cross section of 3900 b (Lapp and Andrews, 1972).

1.2.3 Inelastic scattering

Inelastic scattering differs from the preceding absorption processes in that de-excitation of the compound nucleus is by neutron emission. The scattered neutron comes away from the nucleus with less energy than the incident neutron, the difference in energy going into an excited state of the residual nucleus. Two processes of inelastic scattering are important in the production of radioisotopes, namely the \((n,n')\) and \((n,2n)\) reactions.

The \((n,n')\) reaction is only of interest in activation analysis when the scattered neutron imparts sufficient energy to leave the residual nucleus in a metastable state, that is an excited state with a lifetime, \(\tau = \frac{1}{\lambda}\), long enough to be measurable by simple direct timing techniques (\(\tau > \approx 10^{-5}\text{s}\)) - as compared with the typical lifetime of \(\approx 10^{-15}\text{s}\) for an excited nucleus. Such metastable states occur when de-excitation of the residual nucleus is only possible by a nuclear transition involving large spin changes between levels of small energy difference, which is a relatively
slow process (Burcham, 1973). Nuclei excited to these states will differ from unexcited nuclei only in their radioactive properties (not in charge or mass number) and are said to be isomeric with respect to their ground state. Only fast neutrons are able to undergo inelastic scattering since generally for heavy elements the first excited state is about 100 keV (higher for low Z elements). It should also be noted that isomeric states may be produced as a result of radiative neutron capture reactions, since the compound nucleus is left in a highly excited state which may be long lived if the de-excitation mode satisfies the conditions described above.

In order for the (n,2n) reaction to proceed, the incident neutron must provide adequate energy to the target nucleus to exceed the binding energy of the least bound neutron. In practice this means that the incident neutron must have a kinetic energy of greater than about 8 MeV and this reaction is therefore only feasible for high energy neutrons.

1.3 Neutron Sources

There are a wide variety of techniques available for the production of neutrons in fluxes suitable for activation analysis. These include nuclear reactors, isotopic and photoneutron sources, high energy charged particle accelerators and low energy deuteron accelerators (neutron generators). However, all except the nuclear reactor are outside the scope of this work and will not be discussed further. Similarly, the principles of operation of a reactor are extensively described in the bibliography at the end of this chapter.

Of fundamental importance in activation analysis is an understanding of the reactor neutron spectra and their effect on the nuclear reaction rate
described in §1.1. Unmoderated fission neutrons range in energy from 0-25 MeV with the mean at about 2 MeV and several semi-empirical formulae have been suggested to describe the fission flux, the most widely quoted being the Watt (1952) spectrum. These neutrons are slowed down by collisions with the moderator and in the intermediate energy range show an energy distribution which varies as \( \frac{1}{E} \) for a medium showing negligible neutron absorption or leakage.

Eventually the neutrons reach thermal equilibrium with the moderator in which case the thermal flux as a function of energy is described by a Maxwell-Boltzmann distribution with the most probable neutron velocity corresponding to the moderator temperature \( (T_m) \) through the relation \( E_n = kT_m \) where \( k \) is Boltzmann's constant. Here, again, it is assumed that no absorption or leakage occurs. However, neutron absorption is not negligible in a reactor, and, since the absorption cross section of nearly all materials decreases with energy, the neutrons at lower energies will be preferentially absorbed. This leads to a distortion of the distribution so that it peaks at a higher energy, known as 'hardening' of the spectrum. Neutron leakage also occurs, and is preferential for higher energy neutrons, tending to 'soften' the spectrum, but in general the former effect predominates.

The neutron flux at any position within the reactor is a continuous distribution consisting of some combination of these three energy spectra. It is possible, by the suitable choice of an absorber, to modify the irradiating neutron flux. Cadmium is one such material which has a neutron absorption cross section such that it is effectively opaque to thermal neutrons but transparent to epithermal neutrons above the cadmium cut-off energy, \( E_{Cd} \). The value of \( E_{Cd} \) depends on the thickness of the cadmium filter and irradiation geometry but is approximately 0.5 eV.
1.3.1 Reaction rates for reactor irradiations

When a nuclide is irradiated in a reactor, neutrons with energies spanning some nine decades are available for interaction and, as the cross section for any process is energy dependent, the reaction rate defined in Eq. (1.3) becomes:

\[ R = \int_0^\infty \phi(E)\sigma(E)\,dE \quad (1.6) \]

In the case of radiative capture reactions, the contribution to the reaction rate from raw fission neutrons is so small as to be neglected and \( R \) is usually expressed in the form:

\[ R = \phi_{\text{th}}\sigma_0 + \phi_e I \quad (1.7) \]

where \( \phi_{\text{th}} = \) conventional thermal neutron flux up to \( E_{\text{Cd}} \),

\( \sigma_0 = 2200 \text{ ms}^{-1} \) cross section for a nuclide obeying the \( \frac{1}{v} \) law

\( \phi_e = \) epithermal neutron flux per unit logarithmic energy interval

\( I = \) infinitely dilute resonance integral defined by:

\[ I = \int_{E_{\text{Cd}}}^\infty \sigma(E) \frac{dE}{E} \quad (1.8) \]

The reaction rate for the same material irradiated under cadmium is:

\[ R_{\text{Cd}} = \phi_e I \quad (1.9) \]

and the ratio of the two reaction rates is termed the cadmium ratio (CR):

\[ CR = \frac{\phi_{\text{th}}\sigma_0 + \phi_e I}{\phi_e I} \quad (1.10) \]
The cadmium ratio is a very convenient means of expressing the epithermal activation properties of a nuclide. Irradiation facilities are usually characterised by the cadmium ratio of $^{197}\text{Au}$ (or $^{60}\text{Co}$), as a standard measure of the relative magnitude of the epithermal flux component. Once the $CR_{\text{Au}}$ is known, the cadmium ratio of any nuclide in that specific reactor position, can be calculated according to the following expression:

$$CR_{x} = 1 + \frac{\sigma_{0,x}I_{\text{Au}}}{\sigma_{0,\text{Au}}I_{x}} (CR_{\text{Au}} - 1)$$ (1.11)

provided that the constants $\sigma_{0}$ and $I$ are known for the nuclide in question (denoted by subscript $x$) and assuming a $\frac{1}{E}$ neutron energy distribution in the intermediate region. These values have been tabulated for a large number of commonly encountered nuclides (De Soete et al., 1972; IAEA, 1974) but large gaps do appear in the data, especially for some short-lived isotopes. The cadmium ratio will in most cases be little dependent on the cadmium thickness, unless the absorption cross-section has resonances at or near $E_{\text{Cd}}$.

The reaction rate for threshold (transmutation or inelastic scattering) reactions, which must be initiated by fast neutrons from the fission spectrum, is given by:

$$R = \int_{0}^{\infty} \sigma(E)f(E)dE$$

$$= \int_{E_{T}}^{\infty} \sigma(E)f(E)dE \quad \text{as } \sigma(E) = 0 \text{ for } E < E_{T}$$ (1.12)

where $f(E)$ represents the fraction of the fission neutron flux between $E$ and $E + dE$. A 'fission spectrum averaged cross section', $\bar{\sigma}$, and an 'equivalent fission flux', $\phi_{f}$, are defined as:
\[ \bar{\sigma} = \frac{\int_{0}^{\infty} \sigma(E) f(E) \, dE}{\int_{0}^{\infty} f(E) \, dE} \] 

(1.13)

\[ \phi_f = \int_{0}^{\infty} f(E) \, dE \] 

(1.14)

in which case (1.12) reduces to:

\[ R = \bar{\sigma} \phi_f \] 

(1.15)

Tabulated values of \( \bar{\sigma} \) (IAEA, 1974) are usually calculated with respect to a well-defined, unperturbed fission neutron spectrum, usually that of \( ^{235}\text{U} \). In practice, it is convenient to assume that the reactor fast flux follows this spectrum although this is never strictly true.

1.3.2 The University of London Reactor

All irradiations described in this work were carried out in the University of London Reactor Centre's CONSORT II Reactor. The reactor is of the swimming pool type, being moderated, reflected, cooled and partially shielded by light water. The 24 fuel elements which compose the core are of uranium (80% \( ^{235}\text{U} \)) - aluminium alloy clad in high purity aluminium and situated in a tank of demineralised water approximately 7 m deep and 1 m in diameter. At the maximum operating power of 100 kW, water flow through the core is adjusted to give a temperature rise of 10°C between inlet and outlet, and a steady temperature is maintained by circulating the water through an external air-cooled radiator.

Control of the reactor is achieved by four control rods which move vertically in aluminium ducts located between the fuel elements. The one 'safety' and two 'coarse' rods are of cadmium clad in stainless steel and
the fourth, 'fine', rod is of stainless steel. The rods are raised and lowered electromagnetically and fall under gravity in the event of a shut-down. The biological shield is of concrete having a minimum radial thickness of about 2.5 m except on two opposite faces where removable concrete blocks allow access to irradiation facilities. In the vertical direction, 4 m of water and two concrete filled trolleys comprise the shielding.

1.3.3 Irradiation facilities

The reactor contains a variety of facilities (Burholt, 1976) for the irradiation of samples and for the provision of external beams of neutrons. Three of these are of significance to this work, namely, the in-core irradiation system (ICIS), a core tube (270°/3CT) and a thermal facility (0°STF). Fig. (1.1) indicates the relative positions of each of these installations.

The in-core irradiation system, which has a fast pneumatic transfer system associated with it (§3.2), enables samples to be irradiated in the water moderator at the centre of the core for periods from a few seconds to several hours. Being located so centrally, as shown in Fig. (1.2), this site possesses the highest thermal flux of all the experimental facilities. Fig. (1.2) also shows the aluminium tubes, installed on the 0° and 270° faces of the reactor core, provided for long irradiations (≥ 8 hours). Sample containers are mounted in carriers (maximum of 6/carrier) which are lowered manually into the tubes whilst the reactor is shut-down.

The third position, a thermal facility, is located in a graphite block outside the water tank. Samples are loaded along a horizontal channel by means of a flexible push-rod and removed by a suction tube connected to a vacuum pump. Irradiation time of no longer than about 30 s are possible with this system.
Fig. (1.1): CONSORT II reactor experimental facilities (elevation).
Fig. (1.2) : CONSORT II reactor core (plan) showing irradiation tubes.
a vacuum pump. Irradiation times of longer than about 30 s are possible with this system.

1.3.4 Flux measurements

Although flux monitors or comparator standards were routinely used for individual experiments, measurements were made of the neutron fluxes in these three positions in order to predict the induced activity of irradiated nuclides. Activation detectors, in the form of high purity elemental foils and wires were used for this purpose. This technique has many advantages, principally its discrimination against non-neutron radiation and sensitivity over a wide range of energies by judicious choice of materials, although measurements are limited by the accuracy with which nuclear data of the target nuclides are known and the accuracy with which reaction activities can be determined.

The selection of detectors for activation measurement depends on the energy region of interest and the flux density involved; these criteria are discussed at length by Boot (1977). Gold, cobalt and nickel foils were used for flux measurements in ICIS, gold foils only for the 0°STF whilst iron wire was used in 270°/3CT. The physical and nuclear parameters of these activation detectors are summarised in Table (1.1). Materials were chosen to be as thin as possible such that flux depression and self-shielding errors were minimised. Gold and cobalt both have substantial thermal neutron capture cross sections and dominant resonances in the epithermal region at 4.9 and 132 eV respectively. By irradiating these two foils individually, with and without cadmium shielding, it is possible to obtain not only a value for the thermal neutron flux, but also an estimate of how closely the \( \frac{1}{E} \) law is adhered to in the intermediate energy region.
Table (1.1): Activation detector data for flux calculations

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<th>Co</th>
<th>Ni</th>
<th>Fe</th>
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<td>foil</td>
<td>foil</td>
<td>wire</td>
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<td>99.999</td>
<td>99.99</td>
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<tr>
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<td>$\phi$ 7</td>
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<td>56.2</td>
<td>90.3</td>
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<td>(n,γ)</td>
<td>(n,p)</td>
<td>(n,γ)</td>
</tr>
<tr>
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<td>$^{60}$Co</td>
<td>$^{58}$Co</td>
<td>$^{59}$Fe</td>
</tr>
<tr>
<td>Half-life^a(days)</td>
<td>2.7</td>
<td>1920</td>
<td>71.3</td>
<td>45</td>
</tr>
<tr>
<td>Gamma energy^a(keV)</td>
<td>412</td>
<td>1173</td>
<td>810</td>
<td>1099</td>
</tr>
<tr>
<td>Intensity^a(%)</td>
<td>95</td>
<td>100</td>
<td>99</td>
<td>56</td>
</tr>
<tr>
<td>Detector efficiency (%)</td>
<td>1.9</td>
<td>0.51</td>
<td>0.80</td>
<td>0.55</td>
</tr>
<tr>
<td>Target isotope abundance^a(%)</td>
<td>100</td>
<td>100</td>
<td>67.76</td>
<td>0.31</td>
</tr>
<tr>
<td>Atomic weight^c</td>
<td>196.97</td>
<td>58.93</td>
<td>58.71</td>
<td>55.85</td>
</tr>
<tr>
<td>$\sigma_d^d$(barns)</td>
<td>98.8</td>
<td>38.0</td>
<td>-</td>
<td>1.15^e</td>
</tr>
<tr>
<td>$I^d$(barns)</td>
<td>1550</td>
<td>75.0</td>
<td>-</td>
<td>1.19^e</td>
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<td>Resonance energy^e(eV)</td>
<td>4.9</td>
<td>132</td>
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<td>230</td>
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<tr>
<td>$\sigma_b^b$(barns)</td>
<td>-</td>
<td>-</td>
<td>0.113</td>
<td>-</td>
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</tbody>
</table>

References for Tables (1.1) and (1.2):
- a: Lederer et al., (1968)
- b: Boot, (1977)
- c: De Soete et al., (1972)
- e: Bereznaia and Mac Mahon, (1977)
- f: Burholt, (1977)

Table (1.2): Summary of flux measurements for three facilities (Nov. 1977)

<table>
<thead>
<tr>
<th>Facility</th>
<th>$\phi_{th}^{n}$ cm$^{-2}$s$^{-1}$</th>
<th>CR$_{Au}$</th>
<th>CR$_{Co}$</th>
<th>$\beta^e$</th>
<th>$\phi_{th}^{n}$ cm$^{-2}$s$^{-1}$</th>
<th>(detector)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ICIS</td>
<td>$1.9 \times 10^{12}$</td>
<td>2.08</td>
<td>10.25</td>
<td>+0.010</td>
<td>$9.9 \times 10^{11}$</td>
<td>Ni</td>
</tr>
<tr>
<td>0°STF</td>
<td>$1.1 \times 10^{11}$</td>
<td>$3.59^e$</td>
<td>$15.1^e$</td>
<td>-1.62</td>
<td>$8.2 \times 10^{9^f}$</td>
<td>Ni</td>
</tr>
<tr>
<td>270°/3CT</td>
<td>$1.0 \times 10^{12}$(max)</td>
<td>-</td>
<td>15.7^f</td>
<td>-</td>
<td>$2.9 \times 10^{11}$(max)</td>
<td>Fe</td>
</tr>
</tbody>
</table>
Bereznai and Mac Mahon (1977) have expressed deviations in this region by assuming the epithermal flux energy dependence to be of the form

\[ \phi_e(E) = \frac{\phi_e}{E^{1+\beta}} \]  

(1.16)

and, by also assuming that the reaction cross section follows the \( \frac{1}{v} \) law except at the resonance, have calculated the value of \( \beta \) for a number of detector combinations. Nickel was chosen as a suitable threshold detector for fast flux measurements through the use of the \((n,p)\) reaction, although cadmium shielding of the foil was found necessary to suppress unwanted activity from thermal neutron capture. The reaction rate as a function of energy is such that 90% of induced activity is produced by neutrons with energies between 2.5 and 6.6 MeV (IAEA, 1970).

Foils were irradiated in ICIS and O\textsuperscript{STF} with a fixed geometry for periods chosen to produce activities suitable for counting on a gamma spectrometer. In the case of cobalt and nickel, metastable isotopes are also produced through the reactions \( ^{59}\text{Co}(n,\gamma)^{60}\text{Co}^m \) and \( ^{58}\text{Ni}(n,p)^{58}\text{Co}^m \) with half-lives of 10.5 min and 9.2 h respectively. These isotopes decay by isomeric transition to the ground state and thus their presence interferes with the activity measurements of \( ^{60}\text{Co} \) and \( ^{58}\text{Co} \). Consequently, adequate waiting times were allowed for the metastable isotopes to completely decay before counting commenced thus simplifying the flux calculations. The gold foils used were so thin as to make weighing extremely inaccurate. Cadmium ratios were therefore obtained by irradiating the same foils twice, once with and once without cadmium shielding, and allowing sufficient time between for all activity to decay.
Iron wires were chosen for use in 270°/3CT. Whilst in the other two facilities short irradiations necessitate samples being activated individually, it is practice during long irradiations for as many samples as possible (usually 12) to be activated simultaneously in one container. The standard containers are 75 mm in length and therefore it is reasonable to expect that there will be appreciable flux gradients along the container, resulting in different samples receiving unequal fluences over the irradiation period. This problem is overcome in small research reactions (e.g. TRIGA) by placing the samples in a rotating carousel. This facility is not available in the CONSORT II reactor and so fine iron wires were placed along the whole length of the containers in the two irradiation positions closest to the centre of the core within 270°/3CT. Upon removal from the core, each wire was divided into 6 equal lengths, weighed and their activity measured. Iron has the advantage that the $^{58}\text{Fe}(n,\gamma)^{59}\text{Fe}$ reaction can be used for thermal flux determination whilst at the same time the $^{54}\text{Fe}(n,p)^{54}\text{Mn}$ reaction is a suitable threshold detector. This reaction is an example of a threshold reaction with a positive $Q$-value.

The threshold energy $E_T = -0.09$ MeV ($= -Q$, for an exoergic reaction), but for emission of a proton sufficient extra energy must be available to overcome the Coulomb barrier, and the Effective Threshold Energy, $E_{\text{eff}}$, as defined by Hughes (1953) has a value of 4.4 MeV. Fig. (1.3) shows the thermal and fast flux distribution through the 270°/3 Core Tube, with respect to the horizontal centre-line of the core, as determined by the iron wire monitors. There is a 10.7% difference between the highest and lowest thermal flux values and 13.3% for the fast flux, the steepest gradient being 5% cm$^{-1}$, which would introduce considerable discrepancies in activation measurements between samples, without correction. The errors in the $\phi_{\text{th}}/\phi_{\text{th}}(\text{max})$ and $\phi_{\text{f}}/\phi_{\text{f}}(\text{max})$ values, due principally to weighing and counting are estimated at $\pm 1\%$ and $\pm 3\%$ respectively.
Fig. (1.3) : Vertical distribution of thermal and fast fluxes through the 270°/3 Core Tube.
The iron wires were also used to estimate absolute values for \( \phi_{th} \) and \( \phi_f \), and these are summarised together with the results from the other facilities in Table (1.2). For completeness, missing data has been supplied from other sources as indicated. It is estimated that the flux measurements are accurate to within \( \pm 7\% \) whilst the cadmium ratios have an associated error of \( < \pm 1\% \). These results are generally in close agreement with other more comprehensive flux measurements made by Burholt (1977) and Bereznai and Mac Mahon (1977) and for this reason \( \beta \) values have been included from the latter reference. As mentioned in §1.3.3, ICIS possesses the highest thermal flux due to its central location in the core and, being so close to the fuel, has a very considerable fast flux. Also, at intermediate energies, the data is consistent with a \( \frac{1}{E} \) epithermal neutron spectrum (\( \beta_{ICIS} \rightarrow 0 \)). The 270°/3 Core Tube being located at the side of the core, has thermal and fast fluxes reduced by factors of 1.9 and 3.4 when compared with ICIS, whilst the 0°STF exhibits a vastly different neutron spectrum. The thermal flux is lower by a factor of 17 on ICIS but the fast flux component is reduced by more than two orders of magnitude making this a 'moderately thermal' facility. The \( \beta \) value indicates that here the epithermal spectrum is appreciably 'harder' than on \( \frac{1}{E} \) spectrum (Bereznai and Mac Mahon, 1977).

1.4 Decay Modes of Radioisotopes

Neutron activation analysis, as stated earlier, relies on the detection of radiations emitted by radioisotopes produced through neutron bombardment, the measured activity leading to an estimate of the quantity of a particular element present in the sample. The total number of counts (\( D_{obs} \)), recorded by a radiation detector from the decay of a neutron produced radionuclide is related to the mass of the irradiated element by:
\[ D_{\text{obs}} = \frac{\int_{0}^{\infty} \frac{N_{f} m}{A} \text{Rc}(E)I(E)(1 - e^{-\frac{\lambda t_i}{\lambda}})e^{-\frac{\lambda t_w}{\lambda}(1-e^{-\frac{\lambda t_c}{\lambda}})}}{\lambda} \]  

(1.17)

which is obtained by a combination of Eqs. (1.1), (1.2) and the exponential decay law; the symbols not previously defined referring to:

- \( t_w \) = time between end of irradiation and start of count
- \( t_c \) = counting time
- \( c(E) \) = detector efficiency for emitted radiation of energy \( E \)
- \( I(E) \) = absolute intensity of emitted radiation of energy \( E \)

Decay of a neutron produced radioisotope involves the emission of \( \beta \)-particles (electrons or positrons), electromagnetic radiation (\( \gamma \) or X rays), or, for a very limited number of nuclides, neutrons (e.g. \( ^{17}\text{N} \)) or \( \alpha \)-particles (e.g. \( ^{16}\text{N} \)). Corresponding detection systems of varying degrees of complexity have been designed to measure these radiations, some being specific whilst others cannot discriminate between different types of radiation. However, by far the most versatile, and popular, technique in activation analysis is that of gamma and X-ray spectrometry in which the energy and intensity of the electromagnetic radiation emitted during radioisotope decay is measured. The principal advantage is the fact that the gamma rays are monoenergetic, the energy being entirely determined by the nuclear transitions involved and, therefore, when combined with high energy-resolution detectors, facilitates identification of the parent radionuclides (similarly for X-rays, which result from electronic transitions). Also, depending on the decay schemes involved, the gamma photons may be emitted in cascade making possible the use of coincidence systems in situations where interfering activities are present. Since gamma spectrometry was used throughout the work reported here, the following paragraphs discuss briefly the decay modes resulting in gamma or X-ray emission, whilst subsequent sections describe the detectors used for their quantitative measurement (§1.5) and the data analysis methods (§1.6).
Just as the product nucleus of a neutron induced reaction may be left in an excited state which is relieved by the emission of 'prompt' gamma rays, so the daughter nucleus obtained by $\alpha$, $\beta^-$, $\beta^+$ or electron capture processes may emit gamma rays by transition from an excited state to the ground state. Alpha decaying isotopes are only rarely encountered in activation analysis, but the converse is true for isotopes decaying by $\beta^-$ emission. This is the mode of decay for isotopes showing a neutron excess such as most produced by neutron capture reactions, since nuclear stability is related to the proton-neutron ratio. Emission of a $\beta^-$ particle is the result of

$$n^0 \rightarrow p^+ + \beta^- + \bar{\nu}$$

in which the excess neutron is converted to a proton and a $\beta^-$ particle together with an anti-neutrino.

When a nuclear reaction yields an isotope with a proton excess, $\beta^+$ emission and electron capture (E.C.) are the two competing modes of decay. The proton may be transformed into a neutron with the emission of a positron and a neutrino according to:

$$p^+ \rightarrow n^0 + \beta^+ + \nu$$

The proton mass is less than the neutron mass and therefore conditions for this reaction to occur are only favourable when the daughter isotope is at least two electron masses lighter than the parent. Alternatively, electron capture may occur, in which the nucleus captures an orbital electron to satisfy the reaction

$$p^+ + e^- \rightarrow n^0 + \nu$$
As can be seen, this reaction is energetically more favourable (by 2 electron masses) than positron emission and so predominates when the energy difference between parent and daughter is small. The vacancy, usually in the K-shell is filled by rearrangement of the remaining orbital electrons yielding X-rays characteristic of the daughter nucleus.

Gamma rays will also be emitted when a metastable state (§1.2.3) decays to the ground state, called isomeric transition (I.T.) the gamma rays again representing the energy difference between the two states.

Gamma ray emission abundances are modified by the competing process of internal conversion (IC). A gamma ray, emitted by the nucleus, interacts with an orbital electron resulting in the ejection of that electron with kinetic energy equal to that of the gamma ray minus the electron binding energy. The vacancy is filled in the same manner as for electron capture giving rise to characteristic X-rays. The conversion coefficient defines the degree of competition between internal conversion and gamma emission by the ratio of the number of electrons to the number of γ-rays emitted per excited nucleus.

It is interesting to note that "in β-stable nuclei an isomeric transition is usually accompanied by internal conversion electrons, since the conditions for isomerism are just those for high internal conversion coefficients" (Burcham, 1973), namely low energy nuclear transitions involving large changes in spin. Thus, to generalise, the decay of a metastable state is often associated with the emission of low energy gamma rays and X-rays characteristic of the parent isotope, use of which will be made in Chapter 3.
1.5 Semiconductor Gamma Ray Spectrometers

A block diagram of a semiconductor spectrometer system is shown in Fig. (1.4). Since several combinations of detector/main amplifier/multichannel analyser (M.C.A.) were used during the course of this work, the following sections are restricted to general considerations whilst specific details such as efficiency and resolution are included in the relevant chapters.

1.5.1 Semiconductor detectors

Semiconductor detectors were developed in the early sixties and are now extensively used both for gamma and X-ray spectrometry where the principal requirement is high resolution. These devices consist of a semiconductor diode, generally of germanium or silicon. Electromagnetic radiation impinging on the detector interacts by the photoelectric, Compton scattering or pair production processes, the most probable process depending on the incident photon energy. In the depleted region this transfer in energy excites electrons to the conduction band leaving 'holes' in the valence band.
When a strong electric field is applied across the diode, these charge carriers are collected at their respective electrodes giving rise to an output signal proportional to the amount of energy absorbed. Since there is no electron multiplication, as in an ionisation chamber, low noise, transistorised pre-amplifiers, in intimate contact with the diode, are required to produce signals suitable for further processing.

The energy required to generate an electron-hole pair is only 2.9 eV in germanium and so most detectors are maintained at liquid nitrogen temperature to reduce thermal noise, thus improving resolution. Because of its higher Z number (32 against 14) germanium based detectors have been developed in preference to silicon for gamma ray spectrometry, since the probability of a photoelectric interaction is \( a \sim Z^{4.5} \) of the absorbing material. Two main types of device are in current usage and some of their properties are outlined below:

a) Pure germanium detectors - Ge

These devices make use of the intrinsic conductivity of pure germanium which is usually in thin wafer (planar) form, designed specifically for use in the low gamma and X-ray energy region. Detector efficiency (§3.3.1) exhibits a maximum at about 40-50 keV which decreases rapidly with increasing energy giving a useful operating range from \( \sim 2-400 \) keV. The Compton continuum due to interactions from high energy gamma rays is kept to a minimum by the wafer geometry. A thin window of beryllium foil is generally provided to reduce attenuation of the lowest energy photons.

b) Lithium-drifted germanium detectors - Ge(Li)

Lithium, an electron donor material, is drifted into the p-type germanium to neutralise the effects of acceptor impurities and create an
intrinsic or compensated region, which forms the sensitive volume of the detector.

In planar form, this type of detector may also be used in the low energy photon region, with performance comparable to a pure Ge detector. The Li ions are mobile at room temperature and thus, to avoid damage, the crystal must be maintained at liquid nitrogen temperature.

The efficient absorption of high energy γ-rays requires large volume detectors, since the probability of photoelectric absorption is \( \alpha \epsilon^{-3.5} \). Large volume Ge crystals of sufficiently high purity are difficult to obtain, hence the need for Li drifting. Such detectors (in which the p-type, intrinsic and n-type regions are coaxial) are designed for use with gamma ray energies above \( \sim 50 \) keV, and, although they are more efficient in the low energy region, resolution is inferior to that of a Ge detector due to incomplete charge collection from some photon absorption events in the larger volume detector.

Since semiconductor detectors give output signals proportional to the energy deposited in them, pulse height analysis of these outputs enables the energy spectrum of the incident particles to be established.

### 1.5.2 Spectrometer system

a) H.T. - this unit supplies the required voltage, typically 1-2 kV, and polarity for the detector.

b) Pulser (optional) - injects pulses at a set frequency into the preamplifier resulting in a peak in the γ-ray spectrum, the area of which enables correction for pulse pile-up losses (cf. §6.2.3).
c) Main amplifier - performs further amplification (often × 100) of the analogue voltage pulses output by the preamplifier. Pulse shaping, essential for achieving best resolution, is carried out at this stage. Ideally, long shaping time constants (~6-8 µs) are required to ensure that all the charge liberated in the detector and collected by the preamplifier is processed. However, this represents a rather long processing time per event; in practice, shaping time constants of 1-2 µs are used sacrificing some resolution for the ability to handle high count rates. Provision is also made for base-line restoration when high count rates are encountered, since fluctuation of the base-line due to pulses arriving in close succession has a deleterious effect on resolution.

d) M.C.A. - when operating in the pulse height analysis mode, all signals arriving at the M.C.A. are digitised. This task is performed by an 'anlogue-to-digital convertor' (A.D.C.), the digitised signal being used to increment the contents of the appropriate channel of an addressable memory. The A.D.C. requires an appreciable time to perform these duties, during which time any further pulses arriving at the M.C.A. are ignored. The dead-time per event may be expressed by:

\[ \tau = a + bN + c \]  

(1.18)

where  
\[ a = \text{input pulse rise time ('} \text{rise time protect'} \text{ if preset)} \]
\[ bN = \text{addressing time for the Nth channel} \]
\[ c = \text{time required to update memory.} \]

In some M.C.A.'s, the first two channels are dedicated to storage of the clock time and live time of the system, enabling corrections to be made for the total system dead-time. Since pulses which arrive at the M.C.A. but are outside the region of interest still contribute to the dead-time, a single
channel analyser is usually incorporated as the first stage before the A.D.C. so that these pulses may be discriminated against, thus lowering the dead-time. M.C.A.'s designed for use in conjunction with Ge(Li) detectors require at least 2000 channels, and preferably 4000, to obtain full benefit of the high resolution over a wide range of gamma energies.

e) Output - apart from visual display in the form of a CRT or TV screen, M.C.A.'s are provided with one or more modes of data output. This may be paper-tape (very time consuming for recording more than a few hundred channels) and/or magnetic tape to which large quantities of data may be rapidly written and stored in a manner compatible with computer processing.

1.6 Analysis of Semiconductor Gamma Ray Spectra

In the preceding section, mention was made of the three processes by which electromagnetic radiation interacts with matter, namely the photoelectric effect, Compton scattering and pair production. Each of these processes is responsible for producing certain characteristics of the energy intensity spectrum obtained by a gamma ray spectrometer. All three processes involve the transfer of energy from the incident photon to electrons in the detector, and, if these energy changes are unique peaks will result in the spectrum. Peaks are produced by the photoelectric effect, in which incident photons lose all their energy in a single interaction (full energy peak or photopeak), and pair production. This process yields two peaks from incident monochromatic photons of energy greater than 1.022 MeV, depending on whether only one (single escape peak) or both (double escape peak) annihilation quanta escape from the detector. Energy transfer in a Compton scattering event is variable up to a maximum energy corresponding to a photon scattering angle of 180°. Hence this process contributes to the background continuum under the peaks and is generally considered of nuisance value by interfering with
Identification of isotopes present in an irradiated sample is therefore reasonably straightforward, only requiring knowledge of the energies associated with peaks in the spectrum. However, quantitative determinations involve the estimation of peak areas (usually the photo-peak) above the background continuum. The computation technique employed for peak area determinations is one of the most important facets of gamma spectrometry upon which depends the ultimate precision of the analysis.

When only a few peak areas are required some simple hand calculation may be sufficient but it rapidly becomes evident that multielemental analysis of large numbers of complex spectra typically obtained by high resolution detectors demands some kind of computer based technique, especially if peaks of interest cannot be fully resolved.

These techniques may be divided into two classes, the first of which is the digital calculation method which involves adding together the raw data contained in the photopeak and subtracting the underlying background continuum; no assumption is made about the shape of the peak or the continuum on either side, only the position of the (usually linear) baseline. A number of methods have been proposed to implement this calculation each defining a somewhat different photopeak area. Among the most popular are the Covell method (Covell, 1959; Heydorn and Lada, 1972) and the Total Peak Area (TPA) method (Yule, 1968), both of which are simple enough for hand calculation and ideal for implementation on a mini-computer. The former method defines a calibrated fraction of the peak which is assumed to bear a constant relationship to the total area contained in the peak. The TPA method, as its name implies, relies on linearly extrapolating the continuum under the peak, thus defining the integrated region to be enclosed within the limits of ~ FWTM (corresponding to ~ 97% of a Gaussian peak area). The
precision attainable with these and other digital integration methods has been studied by Baedecker (1971), who found that truncation of the peak boundaries in combination with a base-line approximation similar to that used by the TPA method, lead to improved precision in peak area determination over both the TPA and Covell's methods. A similar result was obtained by Robertson et al. (1975) in a comparison of NaI(Tl) and Ge(Li) detectors for low level γ-ray spectrometry.

The second general class of net peak area computation is the fitting method in which an analytic function, usually of Gaussian form reflecting the statistical nature of system noise and of the charge collection process, is fitted to the observed data. Fitting, by iterative minimisation of the squared-residuals between data and function, requires the power of a computer in all but the most trivial context. Several authors have reviewed the choice of analytic function (Mc Nelles and Campbell, 1975; Takeda et al., 1976) and also the relative merits of digital and fitting methods (Kokta, 1973; Baedecker, 1976; Yule and Rook, 1976). Most are agreed that better precision is obtained with the fitting method at the expense of longer computing times and that the most simple, and yet effective, analytic function consists of a Gaussian distorted by the addition of exponential tails. Tailing is particularly severe on the low energy side of a peak, attributable to incomplete charge collection in the detector, whilst high energy tailing due to pulse pile-up may become appreciable at high count rates. This function forms the basis of the SAMPO gamma ray spectrum analysis code written by Routti and Prussin (1969) which is now one of the most widely used programs of its kind and the one used throughout the work reported here. SAMPO is available as a ULRC library package on the CDC 6600 machine at the University of London Computing Centre (ULCC). The detailed
principles of operation of this program are described fully elsewhere (Routti, 1969; Carder, 1977) and only a brief outline of the more relevant features will be attempted here.

In the Gaussian plus exponential representation, the shape of a peak is defined by three parameters: the width of the Gaussian and the distances from the centroid to the junction points with the exponential tails. These parameters vary smoothly with energy and therefore their values for any peak in a spectrum may be found by interpolation between parameters of neighbouring peaks. The first step in analysis of a spectrum is to use a set of intense and well-isolated peaks as internal calibrations and obtain a corresponding set of shape parameters. This task is performed by the routine SHAPEDO in which the peak function and a quadratic background continuum are fitted to the data by a $\chi^2$ minimisation procedure. Eight parameters are involved in the fitting, the three described above, two for the height and centroid of the Gaussian and a further three for the background continuum. Once the shape-calibration fit has been performed, the best values of the shape parameters from each peak are stored for future recall. They need only be calculated once for each experimental set-up, although caution must be exercised when analysing spectra obtained at different count rates, since peak shape is count rate dependent.

The analysis of peaks on a routine basis is then performed by fitting, again in the least squares sense, the original data points with the peak shapes obtained by linear extrapolation from the calibration data. This technique has two principal advantages: firstly the computing time required to fit each individual peak is reduced since minimisation involves five rather than eight parameters, and secondly the analysis procedure is stabilised by use of the correct shapes for small and overlapping peaks.
from which accurate shape parameters could never be obtained. The routine FITDO is generally used for this purpose; Fig. (1.5) shows an example of the print-out obtained for a particular peak.

Automatic peak search is performed by PEAKFIND. The raw data is first smoothed, the statistical significance of each channel is then calculated and this value is compared with a threshold value (see §1.7) to determine if a peak is present. Peaks so detected must further pass a shape test before acceptance, although all detected peaks are listed in the printout permitting scrutiny by eye.

Many other combinations of options are available in the SAMPO program designed to cope with specific problems, among the most useful being energy and efficiency calibration of the spectra, automatic selection of peak fitting intervals and separation of multiple or overlapping peaks.

Several modifications have been made to the local version of SAMPO, as a result of experience gained through four years' operation. The most important developments concern the presentation of results. A new subroutine, IDENT, has been implemented (Carder et al., 1978) which carries out radioisotope identifications and elemental mass determinations after 'simple' or 'cyclic' thermal NAA. A nuclear data library (Mac Mahon, 1976) which forms part of the subroutine, contains relevant physical and nuclear data for each of about 750 gamma rays and their emitting isotopes that are likely to be encountered. The library contains sufficient information which, when combined with the specific experimental conditions, leads to absolute calculation of the masses of elements present in a sample, through Eq. (1.17).

Absolute activation analysis or a hybrid version known as the 'single comparator method' (Girardi et al., 1965) has until recently been little
Fig. (1.5): Example of SAMPO peak fitting, as performed by FITDO routine.
favoured because of the strict calibration and control necessary to avoid systematic errors, and because of lack of accurate data on cross sections and decay schemes (Ricci, 1975). However, by accurate reactor flux mapping and detector efficiency calibration (3.3.1) Ricci estimates that accuracies of 10-15% can be achieved in the determination of most elements, making this technique competitive with most multicomparator techniques.

The multicomparator method involves irradiating standards containing known quantities of the elements of interest together with samples to be analysed under identical conditions and obtaining elemental mass values by a simple ratio comparison of the peak areas obtained. For this purpose the routine ANALYSIS, a much simplified and less time consuming version of IDENT, has been included in the SAMPO code. ANALYSIS performs peak identification by reference to a library of up to 100 gamma energies supplied by the user. Corrections for dead-time, sample mass and different waiting times between irradiation and counting are all accommodated as are calibration values for energy and multielemental standards, thus enabling calculation, if required, of elemental concentrations in µg/g in an unknown sample. A more comprehensive description of this routine is given by Tout (1977) and Fig. (1.6) shows a typical results table obtained from ANALYSIS.

SAMPO, like all large programs which attempt to be comprehensive, is open to certain criticisms, two of which are worth noting here. The first is its inability to satisfactorily fit strong isolated photopeaks such as those obtained by counting single radioisotope sources. This is due to the inadequacy of the quadratic background to describe the step-like behaviour of the continuum under the peak, and may possibly be improved by the use of a higher order polynomial function. Other authors have encountered similar
### Table of Results

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<th>CHANNEL</th>
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<th>ACTUAL ENGREVE</th>
<th>MICRO G/G</th>
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<td>1.30E+04</td>
<td>CN140</td>
<td>3.02E+03</td>
</tr>
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<td>0.2118</td>
<td>1.5012</td>
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<td>0.3208</td>
<td>1.5013</td>
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<td>3.02E+03</td>
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<td>1.5150</td>
<td>0.744E+02</td>
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<td>0.520E+03</td>
<td>2.37E+03</td>
<td>CN140</td>
<td>3.02E+03</td>
</tr>
</tbody>
</table>

**Typical results table provided by ANALYSIS routine.**

**Notes:**
- **Fig. (1.6):** Typical results table provided by ANALYSIS routine.
problems and have proposed analytic shape functions which include an error function (Dojo, 1974) or a subsidiary Gaussian plus error function riding on a linear background (Jorch and Campbell, 1977) but large numbers of parameters are necessary to describe these functions making their use expensive on computer time. Secondly, IDENT has no provision to compensate for epithermal contributions to the activity of a sample, such as those encountered in irradiations in a mixed reactor neutron flux. However, it is intended to update the nuclear library to include resonance integrals thereby removing the restriction to thermal NAA.

Data may be supplied to SAMPO either by paper tape, magnetic tape or punched card input. The program requires approximately 1s. central processor (CP) time on the CDC6600 to fit one peak; so that analysis of a typical spectrum with approximately 30 peaks, including peak search and results tables uses \( \sim 50-60 \)s CP time. Typical job turnaround times are \( \sim 1 \) hour, but if IDENT is included in the analysis, extra core allocation is necessary to handle the large isotope library resulting in the job running in a lower priority stream with much slower turnaround.

Extensive paper printout from the program is eliminated by diverting all except the peak search and results tables onto microfiche. In this way the quality of each peak fit may be examined (usually a once only task) whilst paper printout of the results is still achieved.

The computer analysis of gamma spectra is now an established feature of most centres involved in NAA. Consequently a wide variety of data reduction programs have been written styled to the needs of individual laboratories and the computing facilities to which they have access. These programs range from the very elementary (yet effective) digital methods
incorporated in mini-computer based MCA's to the highly sophisticated programs, such as SAMPO, requiring considerable (some might argue, Herculean) computing power. Since the ultimate precision depends to a large extent on the spectral analysis technique employed the IAEA (1976) initiated an intercomparison of methods of processing Ge(Li) gamma ray spectra, the purposes of which were two fold:

1) to permit each participant to test the validity of his or her own evaluation method,

2) to permit a comparison of different evaluation methods with a view to helping any worker in the field to select the algorithm most appropriate to his or her own needs and possibilities.

A description of the results of the intercomparison are included in Appendix I, together with a discussion of certain limitations of SAMPO brought to light by this study. At the time of writing, preliminary unpublished results of the inter-laboratory assessment have been made available by Dr. R.M. Parr (IAEA) and a summary of these is also included in Appendix I.

1.7 The Concept of Detection Limits

Whenever new techniques are developed, or existing ones modified, for the measurement of elements occurring at trace levels, the concept of a 'detection limit' is extremely important from the point of evaluation and comparison with alternative methods. The detection limit or 'minimum detectable quantity' of an element is defined in the analytical and radio-chemical literature by a "plethora of mathematic expressions and widely-ranging terminology" which when closely examined (Currie, 1968) span nearly three orders of magnitude! However, despite the vagaries of this term, it is generally agreed that the fundamental limit on the detection of a peak is due to the statistical fluctuations in the background continuum. If it is
assumed that counts in the background (B) underlying a peak are Poisson
distributed, as is generally the case, the standard deviation is \( \pm \sqrt{B} \).
Thus the smallest signal, \( L \), detectable above that background may be
exposed as some multiple of the standard deviation:

\[
L = f \sqrt{B}
\]  

(1.19)

The background is defined here as the continuum counts underlying
the peak 'full width at tenth maximum' (FWTM), these limits enclosing
\( \sim 97\% \) of a Gaussian total peak area.

It is the case in INAA that the limiting factor in activity measurements
is the count rate due to naturally occurring radionuclides and cosmic ray
events, and often the blank sample activity also, if this cannot be avoided.
In which case, for the purpose of this work, the sensitivity of a technique
for a particular element is defined as the value of \( L \), obtained from the natural
plus blank background, converted to \( \mu g \), usually by comparison with a standard.
Clearly, the detection limit of a particular element is also dependent upon
the sample matrix in which it occurs and upon any interfering reactions
involved, and is defined as the corresponding value of \( L \) converted to \( \mu g/g \) of
sample. Consequently it is essential to state not only the type of matrix
but also the sample mass when quoting a detection limit (Spyrou et al., 1973).

Such controversy that exists centres around the choice of the value of
\( f \) which determines the detection limit. Several papers have appeared in the
literature (Sterlinski, 1966; Currie, 1968; Donn and Wolke, 1977) which
discuss at length the relevant criteria. Two kinds of error may occur in
deciding whether or not a peak has been detected, and the associated risks
are quantified by:

\( \alpha \) - the desired maximum probability of falsely concluding that a
peak is present when it actually is not (Type I error)
Based on these two considerations, Currie defines an 'a priori detection limit', \( L_D \), as the minimum true signal level which may be expected to lead to detection:

\[
L_D = 2k\sigma
\]

where the risks of making both kinds of mistake are set equal (\( \alpha = \beta \)) and \( k \) is the abscissa of the standardised normal distribution corresponding to the probability level (1 - \( \alpha \)). The assumption is also made that \( \sigma \), the standard deviation of the net signal is approximately constant. When applied to radiation measurement, \( \sigma = \sqrt{B} \) if the net signal \( L \leq L_D \) and \( B \gg 0 \). \( B \) must be 'well known' through duplicate measurements, as is usually the case. Thus this definition of a detection limit is identical to Eq. (1.19) and has a 'built-in' protection level against both types of risk which may be quantified.

It can be shown that if the criterion for detectability is \( f \sqrt{B} \), the statistical precision of the net signal counts is \( \approx \left( \frac{100\sqrt{2}}{f} \right)\% \). Table (1.3) shows a selection of typically encountered values of \( f \), together with the corresponding risk of a Type I or II error and the statistical precision of the net signal.

It is customary in the M.E.P. group at the University of Surrey to express detection limits with \( f = 2 \). This value corresponds to what must be considered the highest acceptable risk of making a Type I or II error (\( \sim 16\% \)) but peak area determination at this level is only possible with an associated error of \( \pm 71\% \) - certainly not acceptable. For this reason a 'quantitative determination limit' is often set with \( f = 7 \) reducing the statistical error to \( \pm 20\% \).
Table (1.3): Statistical errors associated with the limit of detection

<table>
<thead>
<tr>
<th>( \alpha = \beta ) (%)</th>
<th>0.02</th>
<th>1.0</th>
<th>3.6</th>
<th>5.0</th>
<th>10</th>
<th>16</th>
<th>20</th>
</tr>
</thead>
<tbody>
<tr>
<td>( f )</td>
<td>7.0</td>
<td>4.6</td>
<td>3.6</td>
<td>3.3</td>
<td>2.6</td>
<td>2.0</td>
<td>1.7</td>
</tr>
<tr>
<td>( \pm \frac{100\sqrt{2}}{f} ) (%)</td>
<td>20</td>
<td>30</td>
<td>39</td>
<td>43</td>
<td>55</td>
<td>71</td>
<td>84</td>
</tr>
</tbody>
</table>

Finally, it is interesting to compare the above values with the minimum detectable amplitude, \( a_{\text{min}} \), used by the peak search routine, PEAKFIND, is the SAMPO program:

\[
a_{\text{min}} = 1.33 t \left( \frac{B}{\bar{\sigma}} \right)^{1/2}
\]

(1.21)

where \( t \) = threshold significance for peak fitting

\( \bar{\sigma} \) = average Gaussian peak width parameter

Commonly \( t = 3.0 \) is used and, with \( \bar{\sigma} = 1.2 \) for a typical Ge(Li) detector, gives \( a_{\text{min}} = 3.6\sqrt{B} \). This suggests that the confidence limit involved in using the SAMPO parameters is higher than that based on the \( 2\sqrt{B} \) criterion i.e. > 96.4% by inspection of Table (1.3).
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CHAPTER 2

CYCLIC ACTIVATION ANALYSIS

2.1 Introduction

The employment of short-lived isotopes for NAA has several advantages, some of which were briefly mentioned in Chapter 1; specifically that such techniques are rapid, and, as a consequence economical both on equipment (including the reactor) and personnel time. The somewhat chequered career of short-lived isotopes in NAA and the apparent reluctance of analysts to employ them stems from the inherent technical difficulties in their measurement. Nevertheless, short-lived isotopes provide the possibility for sensitive analyses of certain elements otherwise measurable only through a long-lived activation product (e.g. $^{77}$Se$^m$, $\tau_1 = 17.5s$, as an alternative to $^{75}$Se, $\tau_1 = 120d$) or, in some cases, enable analysis as the only possible $(n,\gamma)$ reaction product (e.g. $^{20}$F, $\tau_1 = 11s$). Techniques employing such very short-lived isotopes must be instrumental simply because timing constraints preclude the option of all but the most simple radiochemical separations. This limitation (or advantage, some might argue) eliminates the use of isotopes which are pure $\beta$-emitters and reliance is therefore placed on gamma spectrometry. It is the intention of this chapter to outline not only the isotopes suitable for analysis, but more especially the approach adopted for their optimum detection and measurement, based principally on Cyclic Neutron Activation Analysis (CNA). This technique is capable, as already stated, of providing extremely rapid, sensitive analyses of particular elements for use on a routine basis. Later chapters will describe applications to specific analytical requirements.
2.2 Short-lived Isotopes

A compilation of neutron induced reactions yielding short-lived isotopes has been written (Spyrou and Kerr, 1976). It summarises, as far as possible, all isotopes with half-lives in the range $300 \text{ ms} \leq \tau \leq 600\text{s}$ which may be produced through $(n,\gamma)$, $(n,p)$ $(n,\alpha)$, $(n,2n)$ or $(n,n')$ reactions together with the relevant nuclear data necessary to estimate neutron activation yields. Even a brief glance at this tabulation is sufficient to realise that nuclear data for many of these reactions are sparse, and it was for this reason that one further essential parameter, namely the resonance integral, was omitted.

It is perhaps interesting to extract some statistics from this compilation, bearing in mind its restrictions as outlined above. Simply considering $(n,\gamma)$ reactions alone, there are 59 isotopes (of which 35 are nuclear isomers) corresponding to some 41 different elements, capable of being produced by neutron irradiation. In certain cases, though, the isotopes may be pure $\beta^-$-emitters or their production cross-section may be very small, and thus they are of little analytical use. Similarly, analysis using pure $\beta^+$-emitters, although detectable by $\gamma$-ray spectrometry through their annihilation quanta, requires special procedures (chemical separation, half-life analysis) to avoid the possibility of interferences in a multielemental sample. Nevertheless, by judicious inspection of the tabulated data, it is found that neutron capture reactions may produce isotopes for the potential analysis of approximately 28 different elements. If this number is viewed in relation to a total of $\sim 70$ elements measurable by NAA, then in perspective, and depending on the analytical sensitivity required, these isotopes may represent as much as 40% of that total. The inclusion of those isotopes produced only by fast neutrons will further expand the catalogue of
measurable elements. Having established the importance of this (relatively) small group of isotopes, it should be emphasised that their 'rôle' in INAA is occasionally competitive, but generally complementary, to their longer-lived counterparts.

There are 2 distinct techniques for the measurement of short-lived activities employed in INAA.

i) The 'conventional' one-shot experiment consisting of a single irradiate-transfer-count sequence, which when performed at a reactor facility usually requires a fast sample transfer system as the waiting time after irradiation must be short compared to the half-life of the isotope of interest, in order to obtain good statistics in the short counting time available. A preferential improvement in sensitivity is obtained for short-lived isotopes if the sample is irradiated in a pulsed reactor, such as the TRIGA type. Miller (1976) reports that, for a 1000 MW pulse of FWHM 12 ms as compared to a steady state saturation irradiation at 250 kW, an enhancement factor of $\sim 35/\tau_{1/2}$ is obtained, where $\tau_{1/2}$ is the half-life (in s) of the induced radionuclide. This represents a considerable improvement since the peak fluxes attainable are $\sim 10^{16} - 10^{17} \text{n cm}^{-2}\text{s}^{-1}$.

ii) Cyclic activation analysis, as discussed in the following sections.

2.3 Cyclic Activation Analysis

The CNAA technique involves the repeated cycling of a sample between the irradiating source and the radiation detector in order to enhance the signal-to-background ratio for the isotope of interest. One of the first experiments of this kind applied to activation analysis was reported in the
literature by Anders (1960 and 1961). Although not termed 'cyclic' samples were repeatedly irradiated by neutrons from the Be target of a 2 MeV Van der Graaff accelerator and counted on a NaI(Tl) detector using a shuttle-rabbit system. Following each irradiation, samples were counted for two consecutive periods of equal length, the spectra obtained being subtracted from each other such that the resulting 'difference' spectra represented only the contributions from the very short-lived isotopes. Preliminary experimental investigations indicated the usefulness of this technique for the determination of 18 elements.

The 'cyclic' epithet was first coined by Caldwell et al. (1966) whilst describing a combination neutron experiment for the remote analysis of lunar and planetary surfaces. This experiment employed a neutron source which could be pulsed in a manner producing short bursts of fast neutrons and a detector system gated to count the activation products between each burst, as one of three complementary analysis modes. A more comprehensive mathematical treatment was provided by Givens et al. (1969) and (1970) who defined 3 main differences between this form of cyclic activation, and the technique of mechanical sample transfer as described above, namely:

a) the sample in most applications of the method is fixed with respect to both the irradiating source and the detector,

b) 'cycling' is electronic rather than mechanical and hence very efficient, and,

c) activities with half-lives down to a few milliseconds may be utilised for analytical purposes.

Givens et al. were able to satisfactorily measure such isotopes as $^{16}$N($\tau _{1/2} = 7.14s$) and $^{24}$Na$^{m}$($\tau _{1/2} = 20 ms$) whilst Tani et al. (1969) who employed
a similar experimental arrangement, were also able to observe γ-ray spectra from $^{205}\text{Pb}^m(\tau_1 = 4 \text{ ms})$ and $^{207}\text{Pb}^m(\tau_1 = 800 \text{ ms})$.

More recent applications of cyclic activation have been demonstrated by Gage et al. (1973) who described a system consisting of a $^{252}\text{Cf}$ neutron source, a gamma spectrometer and a pneumatic transfer facility for the assay of enriched uranium by counting the delayed γ-rays from the short-lived fission products. Mac Murdo and Bowman (1977) modified a similar system by substituting a ring of $12\text{ BF}_3$ counters for the gamma spectrometer, enabling them to count the delayed neutrons after fission, with the same ultimate objective.

However, in order to achieve the necessary sensitivity for CNAA to be a worthwhile trace element analysis technique applicable to small samples, higher fluxes than those used by the authors above are required, and at present are only attainable in a nuclear reactor, thus imposing the restriction of mechanically transporting the sample between irradiation and counting positions.

Such a system, suitable for CNAA, is available on the Consort II reactor and has been successfully used since 1972 (Özek, 1973) for this purpose, published results employing $^{207}\text{Pb}^m$ first appearing in 1974 (Spyrou et al., 1975).

The basic quantity of cyclic activation analysis is the cumulative detector response to radiations from induced activities for $n$ consecutive irradiate-transfer-count-return cycles. For a limited experimental time, the cyclic scheme is more efficient than a conventional one since the short-lived isotopes rapidly reach saturation activity, whereupon further irradiation only serves to increase unwanted activity of the longer-lived species. Likewise after $\sim 2.5 \times \tau_1$, 90% of the activity has undergone decay and there
is no value in continuing the count (indeed, this may be detrimental if longer-lived activities are present which could contribute to the background, thus worsening detection limits). This possibility is discussed in detail by Sterlinski (1966) who derived a relationship between the length of counting time and the background count rate to give the best detection limit for a short-lived radioisotope.

2.3.1 Theory

Each cycle period, $T$, is divided into 4 components:

$$T = t_i + t_w + t_c + t'_w,$$

(2.1)

where $t_i$ = time of irradiation

$t_w$ = time between end of irradiation and start of count

$t_c$ = time of counting

$t'_w$ = time between end of count and start of irradiation and the detector response for the first counting period, $D_1$, is obtained from Eq. (1.17):

$$D_1 = \frac{N R e I}{\lambda} (1 - e^{-\lambda t_i}) e^{-\lambda t'_w} (1 - e^{-\lambda t_c}),$$

(2.2)

all symbols being previously defined. During the second counting period, the detector response, $D_2$, will be made up of the induced activity produced during the second irradiation plus any residual activity from the first cycle. Fig. (2.1) shows schematically the isotope activity varying with cycle period and time. It also illustrates the typical decay of an irradiated sample (isotope of interest plus background matrix) during the counting period, from cycle to cycle as expressed by the analyser dead-time (discussed in §6.2.3). Thus:
\[ D_2 = D_1 + D_1 e^{-\lambda T} = D_1 (1 + e^{-\lambda T}) \]  
\[ \text{and for the } n\text{th counting period:} \]
\[ D_n = D_1 (1 + e^{-\lambda T} + e^{-2\lambda T} + \ldots + e^{-(n-1)\lambda T}) \]
\[ \text{Summing the terms of the series, gives:} \]
\[ D_n = \frac{N ho I}{\lambda} (1 - e^{-\lambda t_i}) e^{-\lambda t_w} (1 - e^{-\lambda t_c}) \cdot \frac{(1 - e^{-n\lambda T})}{(1 - e^{-\lambda T})} \]

Finally, the detector responses to each individual cycle must be combined for all n cycles to give the cumulative detector response, \( D_c \):
\[ D_c = \sum_{i=1}^{n} D_i \]

and thus
\[ D_c = \frac{N ho I}{\lambda} (1 - e^{-\lambda t_i}) e^{-\lambda t_w} (1 - e^{-\lambda t_c}) \left[ \frac{n}{(1 - e^{-\lambda T})} - \frac{e^{-\lambda T}(1 - e^{-n\lambda T})}{(1 - e^{-\lambda T})^2} \right] \]

Eq. (2.7) is the basic relationship for cyclic activation analysis.

2.4 Optimisation of Parameters

The cumulative detector response can be maximised by proper selection of parameters, e.g. for a given total experiment time, \( nT \), the maximum value of \( D_c \) occurs when transfer times are zero and irradiation and counting times are equal, i.e. \( t_w = t_w, = 0 \); \( t_i = t_c = \frac{T}{2} \). In all subsequent discussion, unless otherwise stated, \( t_w = t_w, \).

The following sections deal with the influence of the various parameters on the observed detector response with the express purpose of providing guidelines for their optimum choice. To this end, a suite of Fortran IV
Fig. (2.1) : Isotope activity and analyser dead-time as a function of time into the experiment.

computer programs, under the general name of CYCLOPS were written. Fig. (2.2) gives an example of the output obtained from one of this suite (CYCLOPS/3), namely a summary of the input data together with the variation in detector response as a function of signal half-life presented as a line printer plot. In cases where maximisation of a function were required, this was performed by a simple iterative technique.

In order to preserve the generality of the following discussion, the detection of specific elements will not be considered, except by way of illustration. Moreover, certain of the timing parameters are expressed, not in absolute terms, but rather as multiples of the half-life of the isotope of interest (\( \tau \)), thus:

the total experiment time, \( t_e = nT = m\tau \)

and the cycle period, \( T = \ell\tau \)
Fig. (2.2): Example of output obtained from the CYCLOPS program; normalised cyclic and conventional response versus half-life for the irradiation conditions specified.
such that the number of cycles, \( n = \frac{m}{L} \), with the constraint that \( n \) must be an integer. The suffix '0' is used throughout to indicate the optimum value of a parameter for a set of conditions, thus \( T_0 \) is the optimum cycle period for an isotope, for a given \( t_t \).

2.4.1 The effect of background

In all physical measurements detection of a quantity is dependent on the signal to noise ratio and therefore in choosing the most suitable cyclic timing parameters for an isotope, knowledge of other elements expected in the sample matrix is important, especially those which produce isotopes likely to contribute significantly to the background underlying the signal of interest. This suggests that it is the quantity \( \frac{s_{D_c}}{\sqrt{b_{D_c}}} \) which should be maximised, and not \( s_{D_c} \) as stated above; where

- \( s_{D_c} \) is the cumulative detector response of the signal from the isotope of interest,
- \( b_{D_c} \) is the cumulative detector response of the background underlying the signal, from other isotopes in the matrix,

and the quantity \( \frac{s_{D_c}}{\sqrt{b_{D_c}}} \) is a measure of the detectability of a signal in terms of the standard deviation of the underlying background \( \sqrt{b_{D_c}} \).

It would be an unnecessarily complicated procedure to calculate the absolute contribution to the signal background from an interfering isotope, dependent on the energies and intensities of the gamma rays emitted by the isotopes, the type of detector used and its efficiency as a function of energy. Consequently CYCLOPS, although capable of including up to 9 'background' isotopes, is designed to calculate \( b_{D_c} \) from Eq. (2.7) for the half-life \( b_{\tau} \) of a single isotope predominating in the background underlying the signal. In experimental situations this is often the case, e.g.
$^{28}$Al in soils and rocks. The assumption is then made that $bD_c$ is proportional to the required background and thus the following graphical results are presented in arbitrary units. For generalisation, the ratio $p = \frac{b\tau}{\tau}$ is also used.

2.4.2 The effect of transfer/waiting period

In any cycling system the transfer/waiting time between end-of-irradiation and start-of-counting is finite and, although this value is made very small when the irradiation source can be pulsed (an advantage specified by Givens et al. §2.3), in the present case, where the sample itself is shuttled between irradiation and counting positions, the finite transfer time may be appreciable with respect to the half-life of the isotope of interest and must be taken into account when optimising cyclic conditions. The minimum $t_w$ value of any transfer system is the fundamental limitation on the shortest signal half-life measurable. In exceptional circumstances, when $b\tau << \tau$, it may be advantageous to introduce an additional delay before counting a sample, to allow gross, very short-lived activities, producing rapidly changing system dead-times, to decay.

2.4.3 Results

Fig. (2.3) shows the variation of detector response for the half-life of interest in the cyclic and conventional cases as a function of total experiment time. It is clear that below a certain value of $m (m < 5$ for $t_w = 0$), conventional activation is to be preferred to cyclic, and that in the conventional case no further benefit is to be gained after saturation is achieved ($m \geq 12$) whilst the cyclic response continues to increase. The effect of
Fig. (2.3) : Variation of cyclic and conventional signal with total experiment time, for various waiting times.
waiting period, $t_w$, is to decrease the response in both cases, as expected, and make the crossover point from conventional to cyclic occur at larger $m$ values. However this does not take into account background.

In Fig. (2.4) the ratio of the signal-to-$\sqrt{\text{background}}$ ($s_D^C/\sqrt{b_D^C}$) is plotted versus the total experiment time for different waiting periods expressed in terms of the half-life of the isotope of interest, as a comparison of cyclic and conventional analyses. The half-life of the major contributing isotope to the underlying background of the signal is taken as $100\tau_1$. This is not an unrealistic situation in biological/environmental samples when e.g. $^{77}\text{Se}^m$ (17.5s) and $^{20}\text{F}(11s)$ are measured.

It can now be seen that the background plays a significant rôle in emphasising the difference between conventional and cyclic cases and indicates that the cross-over point from one to the other has moved to lower values of $m$ ($m \leq \sim 2$ for $t_w = 0$) i.e. at even shorter total experiment times. Whilst no improvement was obtained in conventional activation by going to large values of $m$ for $p = 0$ (no background), the situation actually deteriorates when $p = 100$ as clearly shown by the maxima in Fig. (2.4). It is also true to say that prolonging the total experiment time for cyclic activation will always result in an improved 'signal-to-noise' ratio.

Therefore, assuming that a decision has been reached as to the choice of the total experiment time $t_e (= m \tau_1)$ for an isotope of interest - this is usually a compromise between time available per sample analysis and the sensitivity to be achieved by cyclic activation in lieu of the conventional, one shot, analysis. The question still remains: what is the cycle period, $T$, to be used? Fig. (2.5) shows the variation of $s_D^C/\sqrt{b_D^C}$ (as well as $s_D^C$) with cycle period (note: $\xi = \frac{T}{\tau_1^1}$). An isotope half-life of 10s and a 'background'
Fig. (2.4): Variation of cyclic and conventional 'signal-to-noise' ratio with total experiment time, for various waiting times.

Fig. (2.5): Signal and 'signal-to-noise' ratio as a function of cycle period and waiting time, for a fixed length of experiment.
half-life of 1000s have been chosen for a total experiment time, \( m \tau_\frac{1}{2} \), of 100s. The curves go through maxima thus showing that an optimum value of \( t \) exists (\( t_0 \)). Under all conditions, \( t_0 \) is always longer for \( sDc \) than for \( sDc/\sqrt{bDc} \) and an increasing \( t_w \) again substantially reduces the response.

The optimum cycle period has been plotted as a function of total experiment time in Fig. (2.6) for \( t_w = 0 \) and different values of \( p \), to illustrate the effect of 'background' half-life on the timing parameters. It can be seen that \( t_0 \) does not vary appreciably for \( m > 20 \), when background response is taken into consideration; in fact there is little difference in the value of \( t_0 \) after that point for background half-lives \( \geq 100 \tau_\frac{1}{2} \). The converse is also true: that \( t_0 \) is very sensitive to changes in \( m \) when \( m \) is small. Perhaps the obvious should be stated: the optimum cycle time decreases as the background half-life increases, for the same value of the total experiment time, but becomes less pronounced for the conditions mentioned above (i.e. \( p \geq 100 \) and \( m > 20 \)).

Fig. (2.6) considered only the case where \( t_w = 0 \); when optimum cycle period (\( T_0 = t_0 \tau_\frac{1}{2} \)) for the 'signal-to-noise' ratio is plotted against waiting time (Fig. (2.7)), somewhat surprisingly the curve obtained does not vary significantly with background half-life (\( b \tau_\frac{1}{2} = p \tau_\frac{1}{2} \)). Although the relationship shown in Fig. (2.7) is for the case when \( p = 100 \), it holds for all values of \( p \) for which the curve has been computed (\( 10^1 \leq p \leq 10^5 \)) and small deviations occur only at \( t_w/\tau_\frac{1}{2} < 0.05 \).

Moreover this curve was also found to be independent of the total experiment time for the range \( 5 \leq m \leq 1000 \) investigated. Small fluctuations do occur, depending on the \( m \) value, more especially when \( m \) is small, but these may be attributed to the constraint of \( n \) being an integer in the calculations. The fact that this curve is not influenced by \( p \) or \( m \), in
Fig. (2.6): Dependence of optimum cycle period on the total experiment time for a signal in the presence of backgrounds with different half-lives.

Fig. (2.7): Dependence of optimum cycle period on waiting time for a signal in the presence of a background.
complete contrast to the case where \( t_w = 0 \) (Fig. (2.6)), is of great value, since it has applications in a much wider variety of experimental situations i.e. different sample matrices and irradiation modes.

Following the discussion of Fig. (2.4), the question should be posed: How much is gained in detectability by increasing the total experiment time? Fig. (2.8) shows that the gain is considerable if only the signal from the isotope of interest is considered, with no contributing background matrix, as demonstrated by the variation of the optimum response \( (s_{D_c})_0 \) with \( m \). [Note : \( (s_{D_c})_0 \) and \( (s_{D_c}/\sqrt{b^D_{C'}})_0 \) are the optimised signal and 'signal-to-noise' responses respectively, i.e. those responses obtained for an optimum cycling period \( (l_0t_2) \) in a specific total experiment time \( (mt_1) \) as given in Fig. (2.6)]. However, in the more realistic case where the signal sits on a background produced by the sample matrix, the variation of \( (s_{D_c}/\sqrt{b^D_{C'}})_0 \) with \( m \) is not so large and tends to flatten out with increasing total experiment time after some value of \( m \). The longer the half-life of the contributing background (i.e. as \( p \) increases) the flatter becomes the response but it is important to note that the signal to noise ratio is always higher when the background half-life is longer, a feature enhanced by cyclic activation.

In quantitative terms, Egan (1977) has shown that the optimum 'signal-to-noise' ratio can only be improved by a factor of \( \sqrt{2} \) by increasing \( t_t \) if \( b^{t_2} >> t_1 \). For \( n \geq 5 \), to a good approximation:

\[
        s^D_{C'} = n \cdot s^D_1 \quad \text{when } T \text{ is optimised.}
\]

For the long-lived matrix activity:

\[
        b^D_{C'} = b^D_1 + 2b^D_1 + \ldots \ldots n \cdot b^D_1
\]

which, after summing gives:
Fig. (2.8) : Variation of optimum signal and 'signal-to-noise' ratio with total experiment time, for various half-lives of the background.
and therefore

\[ \frac{s_{D_{C}}}{\sqrt{b_{D_{C}}}^{2}} = \frac{n_{s}D_{1}}{\left(\frac{n(n+1)}{2} \cdot b_{D_{1}}\right)^{1/2}} \]

i.e.

\[ \frac{s_{D_{C}}}{\sqrt{b_{D_{C}}}^{2}} + \sqrt{2} \cdot \frac{s_{D_{1}}}{\sqrt{b_{D_{1}}}^{2}} \]

\text{for large } n.

The practical implication of this result is that increasing the experiment time will enhance the photopeak area for the activity of interest, but will not greatly improve the chance of detecting this activity if it has not become apparent in earlier, shorter experiments.

2.4.4 Conclusions

To summarise, it is possible to outline a series of steps, which, if followed, should lead to the best possible detection and measurement of a short-lived isotope by CNAA.

1) Define the half-life of the isotope of interest \( (T_{1/2}) \)

2) Establish the transfer time of the system \( (t_{w}) \)

3) Decide on a total experiment time \( (t_{t}) \), and hence \( m \), based on a compromise between the time available per sample analysis (an economical consideration) and the required sensitivity, as demonstrated in Figs. (2.3) and (2.4).

4) Establish whether a strongly interfering background due to matrix activity
is present, and, if so, this will define $b\tau_1$ and hence $p$.

5) Obtain the optimum cycle period, $T_0$, by use of Figs. (2.5), (2.6) or (2.7), hence $n$ and also $t_i = t_c = \frac{T_0 - 2t_w}{2}$. 
CHAPTER 3

CYCLIC ACTIVATION WITH A LOW ENERGY PHOTON DETECTOR

3.1 Introduction

It was pointed out at the beginning of chapter 2 that a considerable proportion (~60%) of radionuclides produced by \((n,\gamma)\) reactions and with half-lives in the range \(300 \text{ ms} < \tau_j < 600 \text{ s}\) are metastable isomers. When this fact is combined with the knowledge that the decay of a metastable state is frequently associated with the emission of low energy gamma rays and X-rays as a result of the isomeric transition and internal conversion processes (§1.4), the analytical possibilities of cyclic activation in combination with a low energy photon detector (LEPD) must be considered. In fact, out of a total of ~160 metastable isomers produced by neutron induced reactions, approximately 52 have half-lives between 0.1s and 100s. Fig. (3.1) is a histogram of the distribution of these isomers as a function of half-life, also showing those resulting only from \((n,\gamma)\) reactions, in order to emphasise the relative importance of the short-lived fraction.

The work presented in this chapter is a feasibility study of the use of a LEPD for the detection and measurement of short-lived isotopes by low energy \(\gamma\) or X-ray photons in the context of activation analysis. The experimental arrangement used is described and a modified cyclic activation technique is discussed and evaluated with respect to laboratory prepared elemental standards. Results are presented for the sensitivities (in \(\mu g\)) of some 23 different elements investigated, together with the means of calculating their detection limits in a variety of biological/environmental matrices as represented by standard reference materials.
3.2 The In-Core Irradiation System (ICIS)

The University of London Reactor possesses a facility (Spyrou, 1972) specifically designed for work with short-lived isotopes, capable of operating in either the cyclic or conventional modes. ICIS enables samples to be irradiated in the geometric centre of the core and to be rapidly transported backwards and forwards, pneumatically, to a counting position, for a selected number of cycles. The system is shown schematically in vertical section through the reactor (Fig. (3.2a)).

The transfer tube is of aluminium alloy of 19 mm internal diameter and 1.7 mm wall thickness. Inside the reactor this tube is encased in another aluminium tube, the clearance being 2.6 mm. The pneumatic fluid used is
oxygen-free nitrogen working at a pressure of \( \approx 2 \) atmospheres. Movement of the nitrogen is controlled by two solenoid operated valves, the solenoids being triggered by electromechanical clocks. The duration of opening of both valves may be independently controlled. The electromechanical clocks regulate the time for which the sample is irradiated and, in the case of cyclic activation, the time for which the sample is counted. Selection from a number of interchangeable clocks allowstiming settings which are continuously variable in the range 2s to 3 hr.

Samples, placed in low density polyethylene vials, are further contained in an outer capsule (a 'rabbit') of the same material. Polythene spacers are also used to ensure reproducible positioning of the sample within the rabbit. Since the mechanical shocks which the rabbit undergoes may be considerable, especially if repeatedly cycled, the lids of the containers are welded on to prevent accidental opening.

The counting station for cyclic activation, as indicated in Fig. (3.2a) and also shown in Fig. (3.3a), is 7.75m from the irradiation position, and located on the biological shielding above the reactor core. The sample is halted at this point by a steel pin inserted into the transfer tube during the first irradiation period. This arrangement is shown in Fig. (3.2b) and Fig. (3.3b) with the planar Ge detector in position. Depending on the requirement, this detector may be exchanged for a Ge(Li) type, in which case lead shielding is placed around the pipe/detector to reduce the background signal from the reactor environment. However, when the LEPD is employed, fluorescent lead X-rays, induced by the activated sample, make the use of this shielding undesirable. For conventional irradiation requirements the sample is returned directly to the load/unload breech (shown at bottom right hand corner of Fig. (3.3a) together with the two electromechanical clocks) from whence it may be sent to the radiochemical laboratories for unpackaging and subsequent counting.
Fig. (3.2a): Schematic diagram of vertical section through the reactor showing ICIS and cyclic activation counting station.

Fig. (3.2b): Schematic diagram of counting position for cyclic activation analysis.
Fig. (3.3a) : View of CONSORT II reactor showing cyclic activation counting station (centre) and ICIS controls (bottom right).

Fig. (3.3b) : Pure Ge detector located at counting position for cyclic activation analysis.
The characteristics of ICIS have been studied by Egan (1977) who found the transfer time between irradiation and cyclic counting position to be $552 \pm 2$ ms indicating an average velocity of $\sim 14$ m.s$^{-1}$. The capsule was found to bounce once on arrival at the pin but for counting purposes could be considered stationary and in place in $< 1$ s. The consistency of the electromechanical clocks was tested by setting nominal 12s irradiation and counting times repeated over several cycles. The standard deviation of the counting period was found to be $\pm 0.15$ s. Clock accuracy, based on 4 sets of 25 cycles (with cycle period of 24s) checked against two conventional stopwatches (accuracy $\sim 0.5$ s in 300s) showed that a 5 minute irradiation and count programme can be set to better than $\pm 0.3\%$.

### 3.3 The Low Energy Photon Detector System

The LEPD used in this study was an Elscint pure germanium planar detector of 200 mm$^2$ active area and 5 mm thickness (1 cm$^3$ active volume), provided with a 50 μm thick beryllium window, and used in conjunction with a pulsed optical feedback (POF) charge sensitive preamplifier. In addition, a Seforad SR300 spectroscopy amplifier, specifically designed for use with POF systems, was available. The spectrometer system was completed by a Laben Modular 8000 series 4096 channel MCA, 100 MHz ADC and magnetic tape output.

During initial testing of the system using standard radioactive sources giving low counting rates ($< 1000$ c.s$^{-1}$), performance met the manufacturers specifications with energy resolution (FWHM) of 530 eV for the 122 keV photo-peak of $^{57}$Co. However, when the counting rate was increased to $> 10^4$ c.s$^{-1}$, as may be encountered in cyclic activation situations where high count rates are necessary to acquire statistically significant signals in the short times available, performance deteriorated to the point where the system was...
effectively paralysed. This behaviour could be attributed to the design of the main amplifier (Seforad SR300), which has an in-built inhibitor and pile-up rejector, features specifically included to improve resolution. The output signal from the pre-amplifier consists of a series of positive going steps (corresponding to the signals) with a large negative going reset. The reset has various deleterious effects in the main amplifier; resolution suffers since it is undesirable for the baseline recovery circuit to restore on any large negative pulses, saturation of the amplifier (≈ 15v output signal) occurs requiring a long recovery time, and it is possible under certain circumstances, that spurious output pulses may be generated resulting in a false peak in the spectrum obtained. Each time the pre-amplifier resets, a logic pulse is emitted simultaneously. The purpose of the inhibitor, on receiving each logic pulse, is to switch off the baseline recovery circuit and close a gate on the output stage of the amplifier lasting ≈ 6 × peaking time (peaking time = 3.5 × shaping time constant). Similarly, the pile-up rejector closes the same gate for ≈ 7 × shaping time constant each time a signal pulse is detected at the input stage in order to reduce pile-up errors. The situation then arises in this particular amplifier, which has a long, preset, non-adjustable shaping time constant of ≈ 8 μs, that with high counting rates and correspondingly large numbers of resets, the output gate of the amplifier remains permanently closed i.e. the system is paralysed. It was therefore concluded that this amplifier is ideally suited to high resolution, low counting rate applications, unlike the requirements for this study. Consequently a Canberra 1412 research amplifier of more versatile design was substituted.

Experiments, again using standard γ and X-ray sources, were carried out to determine the best amplifier and ADC settings for the spectrometry system. By far the most important variables are the shaping time constants
of the main amplifier. Under ideal circumstances, these should be long (~8 μs) to ensure complete charge collection by the pre-amplifier (§1.5.2) but to allow for high counting rates and also compatibility with a particular ADC, shorter values are commonly used. Fig. (3.4) shows the variation in resolution as a function of the amplifier shaping time constants (the integrate and differentiate constants were always set to the same value, since best resolution was obtained for symmetrically shaped pulses) for the 14.4 and 122.1 keV photopeaks of $^{57}$Co as measured by their FWHM. The source was maintained at a constant geometry giving a count rate in the ADC of $1020 \pm 50$ cs$^{-1}$. The count rate was measured from the SCA output of the ADC using a second MCA in multiscaling mode. Spectra were recorded on magnetic tape for the various amplifier and ADC settings and the FWHM of each peak obtained using the SAMPO SHAPEDO routine. Two curves were obtained for both incident photon energies corresponding to 'High' and 'Low' baseline restorer rate settings of the amplifier. The behaviour of the curves appears energy dependent and is probably a function of the operational design of the Laben ADC used, since this result was not obtained when a Tracor Northern 'Econ II' ADC was substituted, as can be seen from the broken line also shown on Fig. (3.4).

The two ADC's, although both operating on the Wilkinson-ramp principle, differ in the rise time allowed each pulse, which in Eq. (1.18) was referred to as 'a'. The Laben ADC allows this value to be selected and preset by the user, in this case called the Rise Time Protect (RTP), the longest setting being 8 μs. Since the pulse rise time is $\sim 3.5 \times$ shaping time constant, pulses with > 2 μs shaping cannot be handled by this ADC since digitisation would commence too soon on an incoming analogue pulse. This explains the energy dependence of these curves; the analogue signals corresponding to the 14 keV
photons, being smaller, reach maximum amplitude before those of the
122 keV photons and are thus not affected by the 3 µs shaping constants.

The Tracor ADC, on the other hand, has a continuously variable
input pulse rise time from baseline to peak amplitude enabling it to
handle signals with much longer shaping constants. Best resolution of
510 ± 15 eV at 122 keV was obtained for 8 µs shaping using this ADC.
However, since the Laben MCA was used for this study, 2 µs shaping
constants were chosen.

With a count rate \( \sim 10^3 \text{cs}^{-1} \), the 'Low' baseline restorer rate is to
be preferred, but is this true for higher count rates? Fig. (3.5) shows
the variation in spectrometer resolution as a function of count rate
(measured in the manner above) for the 'High' and 'Low' settings. The
count rate was increased by stacking additional \( ^{57}\text{Co} \) sources above the
detector. It can be seen that, for count rates \(< \sim 15,000 \text{cs}^{-1} \), the 'Low'
BLR rate is always preferred. With those settings, an increase in count
rate from \( 10^3 \) to \( 10^4 \text{cs}^{-1} \) worsens the resolution by \( \sim 11\% \).

Gating the pre-amplifier reset pulses by an externally triggered
pulser of variable width (40-100 µs) connected to the anticoincidence input
of the ADC, thus simulating the built-in inhibitor of the Seforad amplifier,
made no improvement on the resolution obtained.

Finally, having determined the best compromise of amplifier/ADC
settings (2 µs shaping time constants; 'Low' rate baseline restorer; 8 µs
rise time protect), the resolution as a function of energy was measured
for a count rate of \( \sim 10^3 \text{cs}^{-1} \). Standard sources were again used for this
purpose, covering the energy range from 26.4 keV \( ^{241}\text{Am} \) to 356 keV \( ^{133}\text{Ba} \)
and the FWHM obtained from the peak width parameter supplied by the SHAPEDO
Fig. (3.4): Resolution (FWHM) of $^{57}$Co photopeaks as a function of amplifier shaping time constants.

Fig. (3.5): Resolution as a function of count rate for 'high' and 'low' BLR settings.
routine. Fig. (3.6) shows the results of the resolution measurements plotted versus photopeak energy, which are satisfactorily described by a linear function fitted, in the least squares sense, to the data.

3.3.1 Efficiency measurement

One of the most important characteristics of a γ or X-ray detector system is the efficiency as a function of incident photon energy. Knowledge of this relationship is essential for absolute calculations (§1.6) in INAA where a single comparator is used as a standard. Furthermore this characteristic effectively defines the range of photon energies over which the detector will usefully operate and thus its suitability for specific applications. It was therefore decided to measure the efficiency of the LEPD as part of this study, and to test the suitability, in the low energy region, of the empirical function provided in the SAMPO code, designed principally for use with Ge(Li) detector data at higher energies, typically above \( \sim 50 \) keV.

A variety of techniques exist for the absolute or relative efficiency calibration of a low-energy photon detector and have been critically reviewed by Campbell and Mc Nelles (1975). By far the most frequently reported technique, and the one employed here, is the use of primary gamma-ray standards supplied by organisations such as the IAEA, NBS or Radiochemical Centre. The metrology laboratory usually supplies information on the absolute disintegration rates of these standards (ascertained e.g. by coincidence counting) and recommends a set of gamma-ray intensities obtained from available nuclear data. These are generally used to calibrate gamma-ray detectors over the energy range \( \sim 100-1800 \) keV. A serious drawback to using γ-ray standards is that they provide insufficient points at
low energies to permit accurate interpolation of an efficiency curve through the experimental data points. This may be overcome in a variety of ways. Firstly, most of the primary γ-ray sources also emit X-rays, of which the intensities may be derived by employing published X/γ ratios (Campbell and McNelles, 1975), or obtained directly from the literature (Hansen et al., 1973), although often these will have larger associated uncertainties than the primary γ-ray standards. Further data points may be obtained by the use of a few radioisotopes that provide a series of lines of known relative intensity and then 'pinning' the resulting relative efficiency curve by interpolation with absolute values obtained from the primary standards. Such isotopes as $^{75}$Se, $^{82}$Br (Gehrke et al., 1977), $^{152}$Eu (Notea and Elias, 1970) and $^{226}$Ra (Zobel et al., 1977) are suitable for use in this manner and may in some cases be produced by the user.

Hnatowicz and Fiser (1978) have suggested a new method for the efficiency calibration of Ge detectors which utilizes the continuous external bremsstrahlung.
trahlung radiation produced by electrons from radioactive β-decay, enabling the efficiency to be determined at any energy in the range 80-500 keV.

Efficiency calibration measurements were made, initially using Radiochemical Centre (Amersham) sealed standard γ-ray sources, in the energy region ~ 5-~ 400 keV for the low energy photon spectrometer described above. Sources of $^{54}$Mn, $^{57}$Co, $^{88}$Y, $^{133}$Ba, $^{137}$Cs, $^{203}$Hg and $^{241}$Am with nominally calibrated activities of 1-20 μCi were placed in a fixed, reproducible geometry by means of a perspex support which slotted over the top of the detector. The source-detector distance was ~ 45 mm. The source strength in each case was chosen to produce a low count rate in the spectrometer giving analyser dead-times of only a few percent. Counting times (live time mode) were then adjusted to obtain $>10^4$ counts in the peaks of interest (and thus a statistical precision of better than 1%), whenever possible. Spectra (4000 channels; 0.1 keV/ch) for each of the standard sources, duplicated in certain cases, were recorded on magnetic tape and subsequently analysed using SAMPO. Absolute efficiencies ($\varepsilon$), in this case defined as the ratio of the number of counts recorded in a particular photopeak to the total number of photons of corresponding energy emitted by the source in all directions during the counting period, for the particular geometry concerned, were calculated by:

$$
\varepsilon = \frac{D}{\lambda \times e^{-\lambda t_w} \times 3.7 \times 10^4 \times t_c}
$$

(3.1)

where 

- $D$ = photopeak area counts
- $\lambda$ = certified activity (μCi) of source
- $t_w$ = time between certification and counting of source
\[ I = \text{absolute photon intensity, i.e. number of photons emitted per disintegration} \]
\[ t_c = \text{analyser live counting time.} \]

which is only applicable in situations where \( t_c \ll \tau \).

Results from these sources, together with the relevant nuclear data, are shown in Table (3.1). By including K and L X-ray peaks where appropriate, 26 efficiency points between 5.47 and 383.87 keV were obtained.

To supplement this data, additional sources of \(^{75}\text{Se}\) and \(^{152}\text{Eu}\), emitting photons of 9 and 8 different energies respectively below \( \sim 400 \text{ keV} \) and thus suitable for relative efficiency measurements, were used. The \(^{152}\text{Eu}\) was a sealed source supplied by PTB (W. Germany) whilst the \(^{75}\text{Se}\) source was produced by irradiation in the University of London Reactor, specifically for the purpose. Approximately 40 µg of Se, in solution form as selenous acid, was transferred by micropipette to a filter paper disc \( \sim 5 \text{ mm} \) in diameter and evaporated to dryness. The disc was subsequently irradiated in a core tube (270°/3CT) for 5 operating days and afterwards mounted on an adhesive tape backing prior to counting. Source activity due to \(^{75}\text{Se}\) (\( \tau = 120 \text{ d} \)) was estimated as \( \sim 1 \mu \text{Ci} \) at the time of counting. Table (3.2) lists the energies corresponding to the peaks detected in the \(^{75}\text{Se}\) and \(^{152}\text{Eu}\) spectra, together with the relative intensities of the peaks. In the case of \(^{152}\text{Eu}\) only 4 peaks were suitable for use, the others being too small or unresolved. To obtain absolute efficiency values, also given in Table (3.2), the relative values were 'pinned' by taking the results from a primary \( \gamma \)-ray standard at an energy as close as possible to one of the peaks in the 'unknown' spectra. In both cases this was a straightforward matter; the 136.33 keV \(^{57}\text{Co}\) value being used for the 136.0 keV \(^{75}\text{Se}\) peak and the 121.97 keV \(^{57}\text{Co}\) value coinciding...
Table (3.1): Efficiency data; values obtained using standard gamma-ray sources

<table>
<thead>
<tr>
<th>Source</th>
<th>Isotopes</th>
<th>E (keV)</th>
<th>Z</th>
<th>σ_int%</th>
<th>τ</th>
<th>σ_t%</th>
<th>σ_{act}%</th>
<th>σ_{fit}%</th>
<th>Absolute efficiency</th>
<th>σ_{fit}% (10^-6)</th>
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Table (3.2): Efficiency data; values obtained using $^{75}\text{Se}$ and $^{152}\text{Eu}$

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<th>Source Isotope</th>
<th>$E$ (keV)</th>
<th>Relative intensity</th>
<th>$\sigma_{\text{int}}$</th>
<th>$\sigma_{\text{stat}}$</th>
<th>$\sigma_{\text{fit}}$</th>
<th>Absolute efficiency ($\times 10^{-8}$)</th>
<th>$\sigma_{\text{tot}}$</th>
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References for Tables (3.1) and (3.2):

a Campbell and McNelles (1975)

b Gehrke et al. (1977)

c Hansen et al. (1973)

d Thein (1977)

e Zobel et al. (1977)
with the 121.8 keV $^{152}$Eu peak. The photopeak energies of the standards and 'unknowns' corresponded so closely that interpolation between two standards was considered unnecessary. Each source was counted in the same reproducible geometry. This was ensured by the use of a specially designed perspex cylindrical arrangement which fitted over the detector, into which standard sources could be slotted. All standards approximated point sources, each being $\sim 1$ mm in diameter; $^{75}$Se was the only exception, although errors due to this fact were not noticeable in the results.

The overall errors ($\sigma_{\text{tot}}$) assigned to each efficiency measurement were estimated in the following manner:

$$\sigma_{\text{tot}} = \left[ \sigma_{\text{int}}^2 + \sigma_{\text{act}}^2 + \sigma_{\text{stat}}^2 + \sigma_{\text{fit}}^2 + \sigma_{\text{pos}}^2 \right]^{\frac{1}{2}}$$

where

- $\sigma_{\text{int}}$ = error associated with photon intensity value
- $\sigma_{\text{act}}$ = error associated with half-life of source
- $\sigma_{\text{stat}}$ = error assigned to activity calibration of source
- $\sigma_{\text{fit}}$ = peak fitting error supplied by the SAMPO code
- $\sigma_{\text{pos}}$ = statistical error in peak area (Poisson)

$$\sigma_{\text{pos}} = \frac{\sqrt{S-2B}}{S} \times 100 \text{ %}$$

where $S$ = peak area and $B$ = background underlying peak

These components which contribute to the total uncertainty in the efficiency calibration are also included in Tables (3.1) and (3.2).

The positioning error was estimated on a $^{203}$Hg source, which was removed and replaced between each of 6 replicate measurements. The error was calculated, for any pair of replicate measurements, on the basis:

$$\frac{S_1 - S_2}{(S_1 + S_2)/2} \times 100 \text{ %} = \left[ \sigma_{\text{fit}}^2 + \sigma_{\text{stat}}^2 + \sigma_{\text{pos}}^2 \right]^{\frac{1}{2}}$$
where the subscripts 1 and 2 refer to values before and after reposi-
tioning of the source. The result of this calculation yielded
\[ \sigma_{\text{pos}} = 0.6\%. \]

Those errors associated with the \(^{75}\text{Se}\) and \(^{152}\text{Eu}\) efficiency values are larger due to the uncertainty introduced by 'pinning' the relative values. Thus in each case \(\sigma_{\text{tot}}\) of the relevant \(^{57}\text{Co}\) efficiency point has been added in quadrature to the error estimate.

It is essential, in efficiency calibrations performed using standard \(\gamma\)-ray sources, to reduce the effects of coincidence summing to an acceptably low level, either by choosing a sufficiently large source-detector distance or by mathematical correction (Gehrke et al., 1977), a procedure which is complex for all but the simplest decay schemes. Possible errors due to coincidence summing were checked for using the efficiency results obtained from \(^{133}\text{Ba}\). The decay scheme of this isotope is such that the gamma rays are emitted in cascade and thus summing in the detector is particularly likely to occur. Upon inspection of the efficiency data obtained using \(^{133}\text{Ba}\), no anomalous results are apparent, indicating that any sum-coincidence effects are masked by other uncertainties in the calibration of the detector. This detector, having only a small sensitive volume (1 cm\(^3\)) compared with a typical Ge(Li) detector (\(\sim 50\) cm\(^3\)) permits a much shorter source-detector distance (\(\sim 45\) mm as compared with 100-150 mm typically) without appreciable errors due to coincidence summing.

Since it was intended to use the LEPD in conjunction with cyclic activation, the complete efficiency calibration was repeated, with the exception of the \(^{75}\text{Se}\) and \(^{152}\text{Eu}\) measurements, with a simulated ICIS cyclic arrangement forming the basis of the geometry. A section of the ICIS aluminium transfer pipe was placed on top of the detector and the standard
γ-ray sources, doubly contained in polyethylene capsules as if to be irradiated, were counted sequentially inside the pipe. The source-detector distance for these measurements was ~52 mm and, in the same manner as previously, $\sigma_{pos}$ was found this time to be 6.9%. The efficiency calibration obtained in this way, and also included in Table (3.1), simulated the experimental conditions encountered when counting a sample during CNAA, exactly reproducing the absorbing effects of the polythene and aluminium surrounding the sample, although positioning errors would be expected to differ depending on the sample under consideration.

The two efficiency curves are plotted in Fig. (3.7) where it can be seen that absorbing effects of the irradiation system become appreciable below ~50 keV, at which energy the detector is also most efficient. There is a discontinuity in the curve obtained without the ICIS pipe at 11.1 keV due to Ge K X-ray escape (Deme, 1971). The latter curve does not extend down to this energy since the X-rays emitted with energies $< \sim 14$ keV were almost totally absorbed in the materials between source and detector. The curves connecting the measured points represent the best visual fits and pass through all the points (i.e. within the error bars which are only plotted in a few essential cases, to avoid confusion) with the exception of one at 20.8 keV due to $^{241}$Am. This energy corresponds to the Np-Ly X-ray which may be subject to unresolved interferences since this line lies in a complex part of the spectrum, as can be seen from the 17.8 and 26.4 keV results which are also subject to large errors.

Although the efficiency curves drawn in Fig.(3.7) represent a visual fit, it is often necessary, for example in absolute activation analysis (§1.6), to fit the measured data points with an analytic function of some form, thus enabling the efficiency at any required energy to be simply calculated. This technique has the advantage over logarithmic interpolation (the standard simpler alternative) that efficiency values can be
Fig. (3.7) : Absolute efficiency of Ge detector as a function of incident photon energy, for two source-detector geometries.

reliably calculated without being strongly influenced by individual measurements with large uncertainties, and further that anomalous data points may be highlighted for special attention.

Several analytic and semi-empirical functions have been proposed (Gallagher and Cipolla, 1974; Singh, 1976; Campbell et al., 1977) specifically for the parametric representation of LEPD efficiency curves and in some cases have proved highly satisfactory for this purpose. However, with absolute activation analysis in mind, it was decided to test the suitability of the function available in the SAMPO program for representing
the efficiency curves shown in Fig. (3.7). This function has been demonstrated (Egan, 1977) to be ideal for Ge(Li) detector efficiency data in the energy region 53-4071 keV and has the advantage over many other functions of being specified by only 4 parameters. The function is of the form:

\[ \varepsilon = aE^{\beta} + e^{\gamma E} \]  

(3.4)

where the parameters \( a, \beta, \gamma \) and \( \delta \) are determined by an iterative \( \chi^2 \) minimisation in the EFFITDO routine. Table (3.3) shows the results of fitting this function to the measured data, initially over the complete energy range and also over truncated energy intervals. The 'goodness of fit' is indicated by the \( \chi^2 \) value supplied by the EFFITDO routine, where the SAMPO definition of \( \chi^2 \) is the summation over all fitted points of the terms \( [(\text{data-fit})/\text{data}]^2 \). It can be seen that the function fails to perform a satisfactory fit on the lowest energy data of both curves, but when the truncated energy interval above 53.14 keV is employed, an excellent fit is
obtained. Thus, in conclusion, the SAMPO analytic efficiency function is suitable for use in conjunction with a LEPD in the energy region above \( \sim 50 \text{ keV} \) and, together with the IDENT routine enables absolute activation analysis calculations to be performed on detected \( \gamma \)-ray peaks (X-ray data have not yet been included in the IDENT library).

3.4 Selection and Preparation of Standards

Since the work on the LEPD in conjunction with cyclic activation took the form of a feasibility study, a number of standards were prepared of those elements considered of potential use analytically. Analysis of these standards was intended to establish elemental sensitivities and thus enable a critical evaluation of the technique. Elements were chosen according to the criteria:

1) The existence of a suitably short-lived neutron activation product.

2) That X-rays or low energy \( \gamma \)-rays (\( E_\gamma \leq 250 \text{ keV} \)) of sufficient intensity are emitted during decay of the isotope produced.

3) That the nuclear parameters (\( \sigma, f \)) are such that the isotope is produced in sufficient quantities to give a reasonable chance of detection.

4) Subject to availability of the element and in a suitable chemical form i.e. not in a form likely to dissociate during irradiation or produce interfering activation products.

A final list of 23 elements fulfilling most of these criteria was compiled: Sc, Co, Ge, Se, Mo, Rh, Ag, In, Sn, Sb, Cs, Ba, Sm, Eu, Gd, Dy, Hf, W, Ir, Pt, Au, Hg and Pb. The majority of these elements were available as
standard 'Specpure' solutions prepared by Johnson and Matthey in concentrations of 1 g/100 ml which were simply diluted to the required concentrations by micropipetting the stock solutions into volumetric flasks and making up to the correct volume with doubly de-ionised distilled water. Standard solutions for Ge, Rh, Sn and Pb were not available in this form and had to be specially prepared. Rh and Pb solutions were obtained by dissolving accurately weighed quantities of chloropentammine rhodium sulphate ([Cl Rh(NH₃)₅]SO₄) and lead acetate ((CH₃COO)₂Pb·3H₂O) respectively in demineralised water. The Ge standard solution was prepared from the oxide (Ge O₂) which, being insoluble in water, required boiling for ~ 1 hr. in a saturated solution of sodium hydroxide to dissolve whereupon it was further diluted using demineralised water. The Sn standards required sufficiently large weights of the element that the powdered metal was used.

Since, in general, the quantity of each element required for irradiation lay in the range 0.1 µg-1 mg, the standard stock solutions were diluted to typical concentrations of 2 µg/0.1 ml from which the desired quantities were micropipetted onto Whatman 1 (1.3 cm diam.) filter discs placed inside clean polythene irradiation capsules. These were placed in an oven at ~ 50°C and evaporated to dryness generally within ~ 5 hrs. Finally, prior to irradiation, these standards were sealed in clean polythene outer containers together with polythene spacers to prevent movement during cycling and maintain a constant counting geometry.

In addition to the elemental standards, a variety of certified, multi-elemental standard materials representing a number of different classes of biological and environmental matrices were prepared for irradiation, doubly contained in polythene, as above. These included IAEA Calcined Bone (80 mg), IAEA Animal Blood (200 mg), IAEA Animal Muscle (200 mg), NBS Bovine
Liver (300 mg), NBS Orchard Leaves (300 mg) and Bowen's Kale (300 mg), the weights following each material indicating the size of sample to be irradiated. Furthermore, a series of clean Millipore 47 mm diameter filter membranes were also included with the standards, in preparation for the air pollution study described in Chapter 4. Blanks, i.e. clean, empty polythene irradiation capsules, completed the list of materials to be irradiated.

3.5 Cyclic Activation Timing Parameters

In deciding upon the timing parameters to be used for the cyclic activation analysis of the prepared standards, two alternatives were available: either to utilise the procedure outlined in §2.4.4 and optimise the parameters for each individual isotope expected to be present, or, to choose a set of parameters which would be suitable (although not optimum) for the majority of cases. As will be shown, the detector response for a given half-life of interest is not strongly influenced by small changes in the timing parameters (e.g. Fig. (2.5)), or rather, for the purposes of this discussion, the detector response for a particular cyclic timing sequence is insensitive to changes in the half-life to be measured. For this reason, and for the sake of simplicity, the second alternative was chosen and a single set of irradiation conditions were used throughout the study; these are shown in Fig. (3.8) and consist of a standard cyclic activation sequence of 312s duration modified by an additional 300s 'conventional' count with the sample stationary at the counting position, 10s after the end of the last cycle period, resulting in a total experiment time per sample of 622s.

The cyclic timing parameters were chosen as being optimum for an isotope such as \(^{77}\text{Se}^m (\tau_1 = 17.5 \text{s})\), which isotope is of particular interest. The additional count in the 'conventional' mode was included in order to
Fig. (3.8): Timing parameters for the cyclic sequence and the conventional counting mode.

obtain better detection limits for the longer lived isotopes (i.e. \( t_i > 1 \text{ min} \)) which may also be produced during the cyclic irradiations.

The procedure adopted during the experiments was to record on magnetic tape the 1000 channel spectrum accumulated by the Laben 4000 channel MCA at the end of each cyclic counting period and erase the memory ready for the next. The 10s pause before the conventional count was sufficient to permit changing of the preset counting time of the analyser. Spectra were recorded on a cycle by cycle basis to enable accurate dead-time corrections (discussed in §6.2.3) to be made, with the result that 13 spectra (12 cyclic + 1 conventional) were obtained for each 10 min. experiment. The cumulative detector response (\( D_{\text{cyc}} \)) for the cyclic experiment is given by Eq. (2.7), and, using the same notation, the number of nuclei, \( N \), activated during a cyclic irradiation of \( n \) cycles and remaining at the end of the last cycle sequence (obtained from Eq. (2.5)) is:

\[
N = \frac{NR}{\lambda} \left( 1 - e^{-\lambda t_i} \right) \left[ \frac{1-e^{-n\lambda T}}{1-e^{-\lambda T}} \right] \tag{3.5}
\]

If then there follows a waiting period \( t_{w_3} \) and a counting period \( t_{\text{con}} \),
the detector response is:

\[ D_{\text{con}} = \frac{N \times e^{-\lambda t_i} \left[ \frac{1-e^{-\lambda t_i}}{1-e^{-\lambda T}} \right]}{\lambda} \quad (3.6) \]

It is also possible to define the detector response ratio between the cyclic and conventional counting as:

\[ R = \frac{D_{\text{cyc}}}{D_{\text{con}}} \quad (3.7) \]

By incorporating Eq. (3.6) into the CYCLOPS program, it was possible to calculate the detector response (for the case \( N \times \text{eI} = 1 \)) as a function of isotopic half-life for the irradiation conditions specified in Fig. (3.8). The three curves obtained, corresponding to \( D_{\text{cyc}} \), \( D_{\text{con}} \) and the ratio \( R \), are shown in Fig. (3.9). It can be seen from the behaviour of \( D_{\text{cyc}} \) that the cyclic timing parameters are ideal for the measurement of isotopes with half-lives in the range \( \sim 6-60\) s, the detector response varying by only a few percent in this region, as mentioned at the beginning of this section.

It must also be evident from Fig. (3.9) that under the conditions chosen the detector response will be higher for isotopes with half-lives of less than 80 s in the cycling phase, whilst those with longer half-lives will be better detected in the second conventional counting phase of the experiment.

If the cycle number is doubled from 12 to 24 as well as the conventional counting period, the detector response will also approximately double for a number of isotopes (see Fig. (3.10), irradiation conditions A and B), however this is achieved at the expense of time and of a broader maximum for the \( D_{\text{cyc}} \) curve. In other words, whereas it is desirable for the cyclic conditions to be suitable for \( \tau_1 \leq \sim 1 \) min, a wider range of half-lives are now
Fig. (3.9) : The variation of responses with half-life for cyclic activation ($D_{cyc}$), conventional counting ($D_{con}$) and their ratio ($r$).

Fig. (3.10) : Comparison of response with half-life for cyclic activation and conventional counting when the number of cycles is doubled (total experiment time doubled).
encompassed, the technique thus losing specificity as well as increasing the background matrix which is all important in the precise determination of the concentration of an isotope. Thus, choice of the cyclic timing parameters enables the experimenter to 'tune-in' to a range of half-lives, the width of that range being determined by the total experiment time.

In Fig. (3.11), the cumulative spectra from the first 4, 8 and 12 cycles in the analysis of 300 mg of NBS Orchard Leaves are shown, indicating the growth of the photopeaks. It must be noted that the rate of growth of each peak varies and depends on the half-life of the isotope. This suggests another facet of cyclic activation - the best detection limit for a particular isotope, which has not been individually considered for optimum cycling conditions may occur at one of the intermediate cumulative stages and not necessarily at the final total cumulative spectrum. Recording of the single spectrum after each cycle is therefore important, not only for dead-time correction, but also in allowing inspection of the spectra, when these are added together, to pick-out such cases.

3.6 Results

The cumulative cyclic and the conventional spectra obtained for each elemental standard, standard biological material and blank were analysed using the SAMPO program, adding together of the individual cyclic spectra together with dead-time correction being a local modification of the DATAIN routine. Unexpectedly high impurity levels were found in the blank polythene containers, attributable mainly to Br and to a lesser extent, Sb (detected through the isotopes $^{79}\text{Br}^m$, $^{80}\text{Br}^m$, $^{82}\text{Br}^m$ and $^{122}\text{Sb}^m$) together with much lower levels of Co and Se. Table (3.4) summarises the principal reactions observed in the standards together with the detector response, expressed in units of counts$\cdot\mu\text{g}^{-1}$, for both the cyclic and conventional analysis modes,
Table (3.4): LEPD response to 'cyclic' and 'conventional' analysis of elemental standards.

<table>
<thead>
<tr>
<th>Element</th>
<th>Principal Reaction Observed</th>
<th>Selected photon energy</th>
<th>Isotope half-life</th>
<th>Detector response 'Cyclic' (counts ug⁻¹)</th>
<th>Detector response 'Conventional' (counts ug⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sc</td>
<td>⁴⁵Sc(n,γ)⁴⁶Sc⁹⁺</td>
<td>142.5</td>
<td>20.</td>
<td>54000.</td>
<td>6100.</td>
</tr>
<tr>
<td>Co</td>
<td>⁵⁹Co(n,γ)⁶⁰Co⁹⁺</td>
<td>58.5</td>
<td>630.</td>
<td>2000.</td>
<td>5400.</td>
</tr>
<tr>
<td>Ge</td>
<td>⁷⁴Ge(n,γ)⁷⁵Ge⁹⁺</td>
<td>139.8</td>
<td>48.</td>
<td>150.</td>
<td>72.</td>
</tr>
<tr>
<td>Se</td>
<td>⁷⁶Se(n,γ)⁷⁷Se⁹⁺</td>
<td>161.6</td>
<td>17.5</td>
<td>4600.</td>
<td>450.</td>
</tr>
<tr>
<td>Mo</td>
<td>¹⁰⁰Mo(n,γ)¹⁰¹Mo⁹⁺</td>
<td>192.0</td>
<td>876.</td>
<td>18.</td>
<td>66.</td>
</tr>
<tr>
<td>Rh</td>
<td>¹⁰³Rh(n,γ)¹⁰⁴Rh⁹⁺</td>
<td>51.4</td>
<td>265.</td>
<td>33000.</td>
<td>60000.</td>
</tr>
<tr>
<td>Ag</td>
<td>¹⁰⁷Ag(n,γ)¹⁰⁸Ag⁹⁺</td>
<td>Pd-Kα</td>
<td>145.</td>
<td>570.</td>
<td>880.</td>
</tr>
<tr>
<td>In</td>
<td>¹¹⁵In(n,γ)¹¹⁶In⁹⁺</td>
<td>In-Kα</td>
<td>2.16</td>
<td>75000.</td>
<td>-</td>
</tr>
<tr>
<td>Sn</td>
<td>¹²²Sn(n,γ)¹²³Sn⁹⁺</td>
<td>160.2</td>
<td>1.5</td>
<td>1.5</td>
<td>5.0</td>
</tr>
<tr>
<td>Sb</td>
<td>¹²¹Sb(n,γ)¹²²Sb⁹⁺</td>
<td>60.7</td>
<td>2520.</td>
<td>420.</td>
<td>860.</td>
</tr>
<tr>
<td>Cs</td>
<td>¹³³Cs(n,γ)¹³⁴Cs⁹⁺</td>
<td>Cs-Kα₁</td>
<td>10440.</td>
<td>97.</td>
<td>420.</td>
</tr>
<tr>
<td>Ba</td>
<td>¹³⁸Ba(n,γ)¹³⁹Ba⁹⁺</td>
<td>165.8</td>
<td>4974.</td>
<td>5.2</td>
<td>18.</td>
</tr>
<tr>
<td>Sm</td>
<td>¹⁵⁴Sm(n,γ)¹⁵⁵Sm⁹⁺</td>
<td>Eu-Kα₁</td>
<td>1380.</td>
<td>-</td>
<td>8900.</td>
</tr>
<tr>
<td>Eu</td>
<td>¹⁵¹Eu(n,γ)¹⁵²Eu⁹⁺</td>
<td>121.8</td>
<td>33480.</td>
<td>-</td>
<td>8300.</td>
</tr>
<tr>
<td>Gd</td>
<td>¹⁶⁰Gd(n,γ)¹⁶¹Gd⁹⁺</td>
<td>Tb-Kα₁</td>
<td>222.</td>
<td>570.</td>
<td>1200.</td>
</tr>
<tr>
<td>Dy</td>
<td>¹⁶⁴Dy(n,γ)¹⁶⁵Dy⁹⁺</td>
<td>Dy-Kα₁</td>
<td>75.6</td>
<td>160000.</td>
<td>130000.</td>
</tr>
<tr>
<td>Hf</td>
<td>¹⁷⁸Hf(n,γ)¹⁷⁹Hf⁹⁺</td>
<td>Hf-Kα₁</td>
<td>18.6</td>
<td>84000.</td>
<td>110000.</td>
</tr>
<tr>
<td>W</td>
<td>¹⁸²W(n,γ)¹⁸³W⁹⁺</td>
<td>W-Kα₁</td>
<td>5.3</td>
<td>1000.</td>
<td>-</td>
</tr>
<tr>
<td>Ir</td>
<td>¹⁹¹Ir(n,γ)¹⁹²Ir⁹⁺</td>
<td>56.8</td>
<td>85.2</td>
<td>600.</td>
<td>590.</td>
</tr>
<tr>
<td>Pt</td>
<td>¹⁹⁸Pt(n,γ)¹⁹⁹Pt⁹⁺</td>
<td>Au-Kα₁</td>
<td>1860.</td>
<td>7.0</td>
<td>19.</td>
</tr>
<tr>
<td>Au</td>
<td>¹⁹⁷Au(n,n')¹⁹⁷Au⁹⁺</td>
<td>Au-Kα₁</td>
<td>7.2</td>
<td>240.</td>
<td>-</td>
</tr>
<tr>
<td>Hg</td>
<td>¹⁹⁶Hg(n,γ)¹⁹⁷Hg⁹⁺</td>
<td>Au-Kα₁</td>
<td>234000.</td>
<td>-</td>
<td>41.</td>
</tr>
<tr>
<td>Pb</td>
<td>²⁰⁶Pb(n,γ)²⁰⁷Pb⁹⁺</td>
<td>Pb-Kα₁</td>
<td>0.8</td>
<td>0.38</td>
<td>-</td>
</tr>
</tbody>
</table>

Reference: a Wakat, (1971)
Isotope identification was facilitated by a number of compilations of gamma-ray energies (Wakat, 1971, Lis et al., 1975) and X-ray energies (Valkovic, 1975) especially in the low energy region (de Bruin and Korthoven, 1972) and for short-lived isotopes (Bode et al., 1975).

Occasionally, the isotope detected may have been produced by a number of competing reactions, e.g. $^{207}\text{Pb}^m$ from $^{206}\text{Pb}(n,\gamma)$ or $^{207}\text{Pb}(n,n')$ or $^{208}\text{Pb}(n,2n)$, in which case only the $(n,\gamma)$ reaction has been included in the table. Furthermore, a number of elements were detectable through more than one isotope, e.g. Se through $^{77}\text{Se}^m$ and $^{79}\text{Se}^m$ as well as the Se K X-rays from the IT decay of both isotopes; those isotopes listed in Table (3.4) represent the most sensitive means of detecting each particular element considered. For this reason, In and W are detectable by two different isotopes depending on whether the cyclic or conventional mode of analysis is employed.

The element Sn, Pt and Hg were more easily determined by their longer-lived products, even under the irradiation conditions described, than by their short-lived counterparts, namely $^{125}\text{Sn}^m(9.5\text{min})$, $^{199}\text{Pt}^m(14.1\text{s})$ and $^{205}\text{Hg}(5.5\text{min})$. $^{207}\text{Pb}^m$ is a prime example of an isotope for which the cyclic irradiation conditions have not been optimised; by shortening the cycle period to 5s, for the same total experiment time the detector response is increased by a factor of 4.6. Br, although easily detectable through $^{79}\text{Br}^m(4.8\text{s})$ and $^{80}\text{Br}^m(4.4\text{h})$ has not been included in Table (3.4) due to the large, non-uniform levels of this element present in the blank preventing the use of a standard with any reliability.

The blank polythene containers and the standard reference materials were irradiated under identical conditions to the elemental standards. Fig. (3.12) shows the spectra obtained from 300 mg of NBS Orchard Leaves, the
Fig. (3.11): Cumulative spectra for the first 4, 8, and 12, cycles in the analysis of NBS Orchard Leaves in a polyethylene container.

Fig. (3.12): Comparison of cumulative cyclic and conventional counting spectra for NBS Orchard Leaves in a polyethylene container.
lower spectrum corresponding to the cumulative cyclic response and the upper spectrum to the conventional count. The way in which the two spectra complement each other in terms of isotopes detected may clearly be seen from this figure. NBS Orchard Leaves was found to be particularly rich in low energy peaks (cf. Fig. (6.4) which shows the 0-4 MeV spectrum obtained by CNAA with slightly different timing parameters), not the case with the other standard materials as summarised in Table (3.5), which list the elements detected in the 6 different standard reference materials and the counting mode by which they are best detected. In nearly all cases, isotopes of O, Br and Sb were detected, but these have been omitted from the table since they are almost entirely attributable to the 'blank' matrix. In those instances where an element has been detected, Table (3.5) provides an estimate of the statistical precision in determining the respective peak area, S, as expressed by $100\sqrt{S + 2B/S^2}$, where B is the background underlying the peak. Elements were detected through the isotopes listed in Table (3.4) with the addition of Mg through $^{26}\text{Mg}(n,\gamma)^{27}\text{Mg}$ ($\tau_\frac{1}{2} = 570s$; $E_Y = 170.8$ keV), I through $^{127}\text{I}(n,\gamma)^{128}\text{I}$ ($\tau_\frac{1}{2} = 25$ min, Te-$K_\alpha$ X-rays) and U through $^{238}\text{U}(n,\gamma)^{239}\text{U}$ ($\tau_\frac{1}{2} = 23.5$ min, $E_Y = 74.7$ keV).

The detection of I in the IAEA Animal Blood was entirely unexpected and the presence of $^{128}\text{I}$ was therefore confirmed by an accurate photopeak energy calibration and a half-life determination. The energy calibration, performed using standard sources, yielded a value of $27.4 \pm 0.1$ keV, whilst the half-life of the isotope, determined by counting each of 4 activated samples 5 times sequentially, was found to be $28.0 \pm 3.5$ min. These values compare well with the published values of $27.47$ keV (Valkovic, 1975) and 25.01 min (de Soete et al., 1972) for $^{128}\text{I}$. The I concentration in IAEA Animal Blood appears much higher than would be expected in mammalian blood which contains typically 0.06 $\mu$g/g (Bowen, 1974)), certainly greater than 0.2 $\mu$g/g (I was not detected in NBS Orchard Leaves).
Table (3.5) : Statistical precision of elements determinable in standard biological reference materials.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Sample size (mg)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mg</td>
<td>Con</td>
<td>80</td>
<td>200</td>
<td>300</td>
<td>200</td>
<td>300</td>
<td>300</td>
</tr>
<tr>
<td>Sc</td>
<td>Cyc</td>
<td>200</td>
<td>300</td>
<td>300</td>
<td>300</td>
<td>300</td>
<td>300</td>
</tr>
<tr>
<td>Co†</td>
<td>Con</td>
<td>39%</td>
<td>21%</td>
<td>21%</td>
<td>ND</td>
<td>66%</td>
<td>ND</td>
</tr>
<tr>
<td>Se†</td>
<td>Cyc</td>
<td>53%</td>
<td>11%</td>
<td>4%</td>
<td>13%</td>
<td>49%</td>
<td>42%</td>
</tr>
<tr>
<td>I*</td>
<td>Con</td>
<td>ND</td>
<td>4%</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>Dy</td>
<td>Cyc</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>4%</td>
<td>ND</td>
</tr>
<tr>
<td>Hf</td>
<td>Cyc</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>7%</td>
<td>ND</td>
</tr>
<tr>
<td>U*</td>
<td>Con</td>
<td>ND</td>
<td>15%</td>
<td>ND</td>
<td>ND</td>
<td>30%</td>
<td>ND</td>
</tr>
</tbody>
</table>

Notes: *
* Elements for which standards were not prepared
† Elements for which blank contribution has been subtracted
ND - Not detected.

3.6.1 Detection limits in standard materials

Having established detector responses in terms of observed counts per unit mass for some 23 different elements, the hand calculation of detection limits in the 8 different matrices investigated would prove a long and tedious task. However, inspection of Fig. (3.12) shows the background continuum of each spectrum to be a smoothly changing curve, a feature common
to spectra from all the materials investigated. This fact enables the background counts as a function of energy, \( b(E) \), to be described by a polynomial expression. Detection limit estimations rely on the background, \( B \), underlying the photopeak of interest; this may be obtained from \( b(E) \) if the detector resolution, usually expressed as a linear function \( (\text{FWHM}(E)) \), is known, since \( B \) is defined here as the background counts underlying a peak within the limits of FWTM \( (= 1.82 \times \text{FWHM}, \text{if a Gaussian peak shape is assumed}) \).

In §1.7 the detection limit was nominally defined as \( 2\sqrt{B} \), which in this instance becomes:

\[
2\sqrt{B(E)} = 2 \sqrt{1.82 \times \text{FWHM}(E) \times b(E)}
\]  

(3.8)

for any particular photopeak energy, \( E \).

Fig. (3.13) shows the background continuum, detector resolution and \( 2\sqrt{B} \) counts within the energy region 0-200 keV for a sample of NBS Orchard Leaves. For computational purposes, a cubic expression was found to be the lowest order polynomial which would satisfactorily describe \( b(E) \). Fitting of the cubic background function and the linear resolution function to the experimental data was performed using 'FATAL' (Salmon and Booker, 1972), a general purpose computer program supplied by AERE Harwell and converted to run on the ULCC CDC 6600. This program provides weighted least-square fitting of data to any desired function which is supplied in the form of a user-written subroutine called MYFUN. Data and instructions are entered into the program by a series of statements which are recognised by a free-format input subroutine, making the program simple to use and also versatile.

Having obtained the parameters of the functions describing \( b(E) \) and \( \text{FWHM}(E) \) by the use of 'FATAL', another short program was written to perform the calculation of Eq. (3.8) and yield values of \( 2\sqrt{B} \) as a function of energy.
as shown in Fig. (3.13). Combination of this data with that of Table (3.4), namely the elemental detector responses in units of counts.µg⁻¹, enables the calculation of detection limits for any of the elements listed in µg/g of Orchard Leaves.

As previously stated, elemental sensitivities for this work are defined as the detection limit of a particular element in the blank matrix, which in this case consists of the polythene 'rabbit', an inner polythene container together with spacers, and a Whatman 1 filter disc. Fig. (3.14) shows the variation in 2/√B for the blank as compared with NBS Orchard Leaves for both cyclic and conventional counting modes. It was found for all materials that the background of the cyclic spectrum was lower than that of the conventional one. From this data elemental sensitivities were calculated for both counting modes and these are presented in Table (3.6) and represent an estimate of the minimum quantity of each element detectable using the irradiation system and timing conditions described.

Figs. (3.15) and (3.16) summarise the 2/√B as a function of energy data for the 8 matrices investigated by the cyclic and conventional counting modes respectively. The cubic functions, from which these curves were plotted, were obtained again using 'FATAL' and in each case 30 data points over the energy range 0-200 keV were used for fitting. The data contained in these two figures enables detection limits to be calculated in the same manner as the values in Table (3.6). It should be noted that for each of the standard reference materials, the sample mass has been standardised to 200 mg.
Fig. (3.13) : Variation of spectrum background count, b, detector resolution (FWHM), and $2\sqrt{B}$ with energy.

Fig. (3.14) : Comparison of $2\sqrt{B}$ counts for NBS Orchard Leaves and blank in cyclic activation and conventional counting modes.
Table (3.6) : Elemental sensitivities obtained for cyclic activation and conventional count modes using a low energy photon detector.

<table>
<thead>
<tr>
<th>Element</th>
<th>Sensitivity (µg)</th>
<th>Cyclic</th>
<th>Conventional</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sc</td>
<td>0.0004</td>
<td>0.005</td>
<td></td>
</tr>
<tr>
<td>Co</td>
<td>0.02</td>
<td>0.008</td>
<td></td>
</tr>
<tr>
<td>Ge</td>
<td>0.1</td>
<td>0.4</td>
<td></td>
</tr>
<tr>
<td>Se</td>
<td>0.004</td>
<td>0.06</td>
<td></td>
</tr>
<tr>
<td>Mo</td>
<td>1.</td>
<td>0.4</td>
<td></td>
</tr>
<tr>
<td>Rh</td>
<td>0.0009</td>
<td>0.0007</td>
<td></td>
</tr>
<tr>
<td>Ag</td>
<td>0.06</td>
<td>0.06</td>
<td></td>
</tr>
<tr>
<td>In</td>
<td>0.0003</td>
<td>0.004</td>
<td></td>
</tr>
<tr>
<td>Sn</td>
<td>13.</td>
<td>6.</td>
<td></td>
</tr>
<tr>
<td>Sb</td>
<td>0.07</td>
<td>0.05</td>
<td></td>
</tr>
<tr>
<td>Cs</td>
<td>0.4</td>
<td>1.</td>
<td></td>
</tr>
<tr>
<td>Ba</td>
<td>4.</td>
<td>2.</td>
<td></td>
</tr>
<tr>
<td>Sm</td>
<td>0.06</td>
<td>0.05</td>
<td></td>
</tr>
<tr>
<td>Eu</td>
<td>0.06</td>
<td>0.04</td>
<td></td>
</tr>
<tr>
<td>Gd</td>
<td>0.0002</td>
<td>0.0003</td>
<td></td>
</tr>
<tr>
<td>Dy</td>
<td>0.0004</td>
<td>0.004</td>
<td></td>
</tr>
<tr>
<td>Hf</td>
<td>0.03</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>W</td>
<td>0.05</td>
<td>0.07</td>
<td></td>
</tr>
<tr>
<td>Ir</td>
<td>4.</td>
<td>2.</td>
<td></td>
</tr>
<tr>
<td>Pt</td>
<td>0.1</td>
<td>0.9</td>
<td></td>
</tr>
<tr>
<td>Au</td>
<td>70.</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

3.7 Discussion and Conclusion

The study has shown that a LEPD may be used to advantage in conjunction with cyclic activation, although careful setting-up of the spectroscopy system is necessary in order to take full advantage of the performance of the equipment, since the ability to cope with high counting rates with minimal sacrifice in energy resolution is a prime requirement.

The restriction of counting the sample within the irradiated 'rabbit' and the aluminium transfer pipe limit the sensitivity which may be achieved
with the technique. Due to absorption effects, detection efficiency is reduced in the photon energy region below \( \gamma 50 \) keV as demonstrated by Fig. (3.7). However, above this energy efficiency calibration of the detector system is sufficiently well known and accurately described by the SAMPO analytic function as to enable absolute activation analysis calculations to be performed using the IDENT routine. The addition of X-ray intensity data to the nuclear library of this routine would further extend its versatility. The high impurity levels, especially of the elements Br and Sb, in the polyethylene irradiation capsules, together with considerable 'rub-off' contamination of elements such as Al from the walls of the ICIS transfer pipe cause an additional reduction in sensitivity by increasing the background continuum of the 'blank' spectrum as discussed more fully in \$4.3.1. The use of much smaller polyethylene capsules in a new cyclic activation system may improve this situation.

The combined cyclic and conventional analysis scheme has been shown in Table (3.6) to yield high sensitivities for a number of elements, e.g. Sc. Rh, In, Dy and Hf may be detected in a blank matrix at sub-nanogram levels with a total experiment time per sample of only \( \gamma 10 \) mins. An additional benefit of the combined scheme resulting in 2 spectra, is the aid to isotope identification which may be obtained by calculating \( r \) (defined by Eq. (3.7)) from the experimental results and then referring to Fig. (3.9) for an approximate estimate of the isotopic half-life.

The method of fitting a polynomial function to the background continuum of a low energy photon spectrum provides a convenient means of estimating elemental detection limits in a number of different matrices. Inspection of Figs. (3.15) and (3.16) show that IAEA Calcined Bone has by far the highest background levels, and therefore worst detection limits, of the materials
Fig. (3.15) : Variation of $2\sqrt{B}$ for standard reference materials and blank with energy, for cyclic activation.

Fig. (3.16) : Variation of $2\sqrt{B}$ for standard reference materials and blank with energy, for conventional counting mode.
investigated. This is probably due to the production of large quantities of \( \beta \)-emitting isotopes from elements such as Na, K, Cl and P, the bremsstrahlung from which makes a significant contribution to the background. Mantel et al., (1978) have reported greatly improved accuracy in the measurement of X-rays in the presence of strong \( \beta \)-emitters by the use of permanent magnets which deflect the \( \beta \)-particles away from the detector region, and may be a possibility deserving further investigation for the ICIS system.

In conclusion, the use of the LEPD provides a complementary technique when combined with cyclic activation, capable of the sensitive detection of a number of elements, such as Sc, Co, Se, Rh, In, Sm, Eu, Dy and Hf at levels below 10 ng, of interest to the biological, environmental and geological sciences. If simultaneous spectral measurements were made using both Ge(Li) and pure Ge detectors, the capabilities of the technique could be extended considerably.
4.1 Introduction

An air particulate may be regarded as any substance that exists as a liquid or solid in the atmosphere under normal conditions and is of microscopic or submicroscopic size ($\sim 10^{-3} - 10^{2}\mu m$); a cloud of such particles being termed an aerosol. Apart from chemical composition, particulates are classified according to source and size. Sources are broadly divided into two categories, natural and man-made, whilst size is based on a diameter, measured in microns ($\mu m$), several definitions of which are discussed by Mason (1978). Ledbetter (1973) defines a pollutant as "the presence in the air of any abnormal material or property that reduces the usefulness of the air resource". The term 'abnormal' refers to material existing in the atmosphere in concentrations above the normal ambient levels; thus either source type, i.e. natural or anthropogenic, may be judged a pollutant. The respiratory system is Man's normal mode of intake of air particulates into the body. The size of inhaled particles is therefore of extreme importance, since it is this parameter which determines the region of deposition within the respiratory system.

Natural sources of air particulates are principally wind-risen dust, sea spray, volcanoes and forest or bush fires. Industrial activities, including agriculture, and the combustion of fossil fuels conveniently summarise Man's contribution to the atmospheric aerosol load. Furthermore secondary anthropogenic sources, such as the conversion of gases to particles by photochemical reactions in the atmosphere, may also be appreciable.
Depending on weather conditions and again on particle size, the trans-
portation of an aerosol may be global, regional or only local, but eventually
the particles will reach the earth's surface, either by rain-out (condensation
on water vapour within clouds), wash-out (below-cloud scavenging by rain
drops passing through the air) or dry deposition.

The sampling and subsequent trace element analysis of air particulates
therefore plays an essential part in establishing 'normal ambient levels' and
monitoring polluted air, by characterising the emissions of various sources,
ultimately for the benefit of human health. By also recording relevant weather
data at or close to the chosen sampling site, the trace element measurements
become potentially more important since significant correlations between both
these data sets may provide an insight into the behaviour of atmospheric
aerosols.

A survey has been carried out over a short summer period in Oxford
city-centre, chiefly aimed at studying the airborne particulates of vehicular
origin, and was initiated by an Environmental Health Officer of the City
Council. This chapter outlines the objectives of the survey together with
a brief description of the sampling, but in particular describes the INAA
techniques employed and the special problems encountered in the elemental
analysis of the aerosol samples obtained. Results are presented for the
elements which were detectable, as are interpretations made in conjunction with
data concerning weather, traffic flow and associated parameters recorded at
the time of sampling. The samples were obtained by M.R. Bartram whose M.Sc.
Thesis (1976) provides a comprehensive description of the sampling procedure,
meteorological data and preliminary measurements made.
4.2 The Sampling of Oxford Air Particulates

The original objectives of this study were:

i) To establish, if possible, correlations between degree of filter staining due to unburnt hydrocarbons and other pollutants of vehicular origin and the prevailing weather conditions.

ii) To acquire samples for the subsequent INAA of airborne trace elements due to vehicular pollution in a busy urban street.

To this end a location (indicated in Fig. (4.1)) was chosen in St. Aldates, a busy main street in the very centre of Oxford carrying heavy two-way traffic through the city. The street in this vicinity is bounded on both sides by six storey-buildings which produce a 'canyon effect', preventing the rapid dispersal of particulates from other sources, such as internal combustion engines. The actual sampling site was situated in a sealed doorway of the Town Hall close to a footpath and the apparatus arranged in such a position as to collect particulates similar to those inhaled by a passing pedestrian. Adjacent to the site, a set of traffic lights significantly slowed the movement of vehicles along the street. Traffic-metering equipment of the conventional type used by local authorities was situated at this point. The meters were set to measure motor vehicles only, the aggregate being recorded on a paper roll at 15 min. intervals. Due to a malfunction, data was only available for North-bound traffic flow, but this was considered sufficient to reflect the overall daily traffic pattern.

The sampling apparatus consisted of an inlet funnel connected directly to a plastic holder containing a 47 mm diameter Millipore membrane filter through which air was drawn at a rate of \( ^\circ 1.2 \text{ m}^3\text{hr}^{-1} \) by an electric pump via a length of PVC tubing. The volume of exhaust air from the pump was recorded.
Fig. (4.1) : Plan of Oxford City-Centre (Kelly's Directories Ltd.)
by a gas meter of the type used by the National Survey of Air Pollution (NSAP). Pump and meter together with a cooling fan were enclosed in a stout portable wooden box, the whole equipment being specifically designed to minimise possible contamination of the filters whilst maintaining high collection efficiency. Further considerations such as proof against theft, vandalism and the elements whilst maintaining easy access to change the filters also influenced design. Millipore filters, currently favoured by a large number of Local Health Authorities, of 0.8 μm pore size were used throughout; packaged as they are in plastic holders enabled filters to be changed 'in the field' simply by exchanging holders without handling of the actual membrane.

Sampling was conducted over 12 complete days, from 07.00 on Monday, 18th August, 1975 to 01.00 on Saturday, 30th August, 1975, inclusive. Each day was divided into four 6-hourly periods as follows: 07.00-13.00; 13.00-19.00; 19.00-01.00; 01.00-07.00; the filter being changed manually between each period. The polluted filters, numbered sequentially, were stored in individual sealed polythene bags. The sampling intervals were chosen to reflect the periods of high and low traffic flow throughout the day.

The meteorological data for the duration of the experiment was provided by the Radcliffe Observatory, Oxford, shown on Fig. (4.1) approximately 1 km. North of the sampling site. Additional information was obtained by Bartram, namely filter obscuration (%) measured by a reflectometer for each of the samples, and daily SO₂ and Standard Urban Smoke values from an NSAP sampling site in the Environmental Health Department some 270 m (as the crow flies) from the St. Aldates site. Daily values for SO₂ and Smoke are available for 9 out of the 12 sampling days.
4.3 Air Particulate Analysis

The elemental analysis of air particulates by INAA presents specific difficulties principally related to a very small sample deposited on a (relatively) large filter. Where possible, in most instrumental analytical techniques, blanks are either avoided completely or their contribution to the gross signal is proportionately reduced by increasing the sample size. Neither option is feasible in this instance without resorting to destructive chemical separation techniques. Taking the values of Stern (1976), particulate matter occurs in polluted air in the concentration range 70-700μg m⁻³. Thus a 7.2 m³ sample, such as the ones obtained in this study, would yield 0.5-5 mg of particulate matter deposited on a Millipore filter weighing typically ~50 mg. Ideally, therefore, high neutron fluxes are necessary to give the required sensitivity and the clean filters (blanks) should have the lowest possible concentrations of elements of interest.

The Millipore filter membranes on which air particulates were collected in this study are unsuitable on both these counts. Heydorn (1976) reports that the filters have a tendency to explode when irradiated in high flux ($\phi_{th} = 10^{14}$n cm⁻²s⁻¹) facilities thus imposing a fundamental limitation on the analytical sensitivity. Moreover, impurity levels in the 'blank' Millipore membranes (Dams et al., 1972) are unacceptably high for such elements as Na, Al, Cl and Br; elements which, upon irradiation, are very 'easily' activated and so impair detection limits of gamma spectrometry by significantly contributing to the background under signals of interest. Dams et al. list a total of 14 impurity elements, all detectable through NAA in the Millipore filters. Spyrou et al., (1976), in a comparison of different types of air filters, also report that 12 impurity elements were detected in the Millipore filters.
Therefore, INAA was performed on the series of filter samples with the intention of 'rescuing' as much information as possible from such a unique and worthwhile experiment. Nine schemes of analysis were employed with varying degrees of success and these are summarised in Table (4.1).

4.3.1 Cyclic activation

Cyclic activation, using ICIS, was the first technique investigated and accounts for 4 of the schemes outlined in Table (4.1). This technique is always attractive in situations where a large number of samples have to be analysed, if the measurable short-lived isotopes are of interest.

Dams et al. (1975) describe a technique (conventional rather than cyclic mode) for the measurement of the short-lived isotopes $^{209}$F(11.1s), $^{46}$Sc$^m$(18.7s), $^{77}$Se$^m$(17.7s), $^{110}$Ag(24.6s) and $^{179}$Hf$^m$(18.7s) all of which have been shown of potential interest in aerosols. Studies in Belgium indicate that Sc, Se, Ag and Hf can be considered as indicators for the main aerosol components, namely the soil derived elements, the volatile pollution elements, a number of non-ferrous metals and the large group of anthropogenically produced pollution components with distributed sources. The importance of F is discussed in Chapter 6. Thus analyses of these elements, requiring only a few minutes per sample, could give an overview of the polluted aerosol.

The samples intended for cyclic activation were all doubly contained in washed polythene capsules prior to irradiation; details of experimental arrangements are described in §3.5 and §6.2.2. The first scheme was specifically selected for the determination of lead, of extreme importance in air pollution studies, through the 0.8s isomer $^{207}$Pb$^m$. Irradiation conditions were similar to those described by Egan and Spyrou (1976) for
Table (4.1): Analysis Schemes

<table>
<thead>
<tr>
<th>Scheme</th>
<th>Mode</th>
<th>Irradiation</th>
<th>Detector System</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Mode</td>
<td>I</td>
</tr>
<tr>
<td>[1]</td>
<td>Cyclic</td>
<td>2s</td>
<td>1s</td>
</tr>
<tr>
<td>[2]</td>
<td></td>
<td>12s</td>
<td>1s</td>
</tr>
<tr>
<td>[3]</td>
<td></td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>[4]</td>
<td>Additional Conventional count</td>
<td>-</td>
<td>10s</td>
</tr>
<tr>
<td>[5]</td>
<td>Conventional</td>
<td>600s</td>
<td>90s</td>
</tr>
<tr>
<td>[6]</td>
<td></td>
<td>6.9h</td>
<td>25h</td>
</tr>
<tr>
<td>[7]</td>
<td></td>
<td>4 operating days</td>
<td>26h</td>
</tr>
<tr>
<td>[8]</td>
<td></td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>[9]</td>
<td></td>
<td>5 operating days</td>
<td>6d</td>
</tr>
</tbody>
</table>
optimum detection. Unfortunately neither the 570 keV nor the 1064 keV gamma rays were detected in the two trial samples by the 20 cm$^3$ Ge(Li) detector system. Based on a $2\sqrt{B}$ calculation, the sensitivity for lead in the blank matrix was estimated to be 12 µg.

The timing parameters selected for schemes [2] and [3] were chosen as being generally ideal for the measurement of all isotopes with half-lives in the range 5-50s, such as those mentioned above, if not in the presence of strongly interfering background signals. This was clearly demonstrated by the broad maximum of the $D_{cyc}$ curve in Fig. (3.9). Trial irradiations in conjunction with the Ge(Li) detector, principally measuring higher energy gamma rays, and the Ge low energy photon detector resulted in the detection of 15 isotopes listed in Table (4.2). Scheme [4], the additional conventional count was included as part of the study described in §3.5. Schemes [1] and [2], not surprisingly, yielded the same list. Of those isotopes detected via [1]-[4], only $^{52}$V does not occur in the blank matrix whilst very few of the others were present at levels in the sample distinguishable above those of the blanks. Those isotopes detectable in the samples, such as $^{52}$V, were the longer lived for which cyclic activation was not the most suitable technique.

The principal reason for the failure of cyclic activation to yield results is the violation of the 'golden rule' to avoid situations where 'small' samples are associated with 'large' blanks. The interferences of the Millipore filter (Na, Al, Cl, Cu, Br) were compounded by those of the polythene containers (Na, Al, Se, Co, Br, Sb) and the air trapped inside (0, A) unavoidable with the present ICIS facility. The new Cyclic Activation System (CAS), at present under development at ULRC, will reduce the blank polythene container from $> 7$ g, as with ICIS, to $\sim 0.7$ g, a vast improvement for CNAA of air filter samples.
Table (4.2) Isotopes detected by respective irradiation schemes.

<table>
<thead>
<tr>
<th>Scheme</th>
<th>Isotopes</th>
</tr>
</thead>
<tbody>
<tr>
<td>[1]* + [2]*</td>
<td>$^{190}$, $^{24}$Na, $^{27}$Mg, $^{28}$Al, $^{38}$Cl, $^{38}$Cl$^\text{m}$, $^{41}$Ar, $^{52}$V, $^{66}$Cu, $^{77}$Se$^\text{m}$, $^{79}$Br$^\text{m}$, $^{80}$Br$^\text{m}$</td>
</tr>
<tr>
<td>[3]*</td>
<td>$^{190}$, $^{77}$Se$^\text{m}$, $^{79}$Br$^\text{m}$, $^{80}$Br$^\text{m}$, $^{82}$Br$^\text{m}$, $^{122}$Sb$^\text{m}$</td>
</tr>
<tr>
<td>[4]*</td>
<td>$^{60}$Co$^\text{m}$, $^{80}$Br$^\text{m}$, $^{82}$Br$^\text{m}$, $^{122}$Sb$^\text{m}$</td>
</tr>
<tr>
<td>[5]</td>
<td>$^{24}$Na, ($^{27}$Mg$^\text{m}$), $^{28}$Al, $^{38}$Cl, ($^{42}$K$^\text{m}$), $^{49}$Ca, ($^{51}$Ti$^\text{m}$), $^{52}$V, $^{55}$Mn, $^{66}$Cu, $^{80}$Br, $^{82}$Br, ($^{116}$In$^\text{m}$), $^{125}$Sn$^\text{m}$, $^{128}$I$^\text{m}$</td>
</tr>
<tr>
<td>[6]</td>
<td>$^{24}$Na, $^{42}$K, $^{82}$Br</td>
</tr>
<tr>
<td>[7]</td>
<td>$^{24}$Na, $^{42}$K, ($^{60}$Co$^\text{m}$), $^{82}$Br, ($^{122}$Sb$^\text{m}$), ($^{140}$La$^\text{m}$), ($^{153}$Sm$^\text{m}$)</td>
</tr>
<tr>
<td>[8]</td>
<td>$^{24}$Na, $^{51}$Cr, $^{60}$Co, ($^{65}$Zn$^\text{m}$), $^{82}$Br, $^{122}$Sb, ($^{153}$Sm$^\text{m}$)</td>
</tr>
<tr>
<td>[9]</td>
<td>$^{24}$Na, $^{51}$Cr, $^{60}$Co, $^{65}$Zn, $^{82}$Br, $^{122}$Sb, ($^{124}$Sb$^\text{m}$), ($^{140}$La$^\text{m}$), ($^{153}$Sm$^\text{m}$)</td>
</tr>
</tbody>
</table>

Notes: * 'Blank' includes polythene irradiation capsule.
- Does not occur in blank
( ) Occurs in < 50% of samples.

During the course of preparing the trial samples it was discovered that Millipore membranes were extremely fragile. This was further borne out by post-irradiation examination of the samples; due to mechanical shocks during cycling the filters were reduced to a mass of fragments, which through static attraction to the polythene containers, could never be fully recovered for further analysis. It was therefore decided to pellet all remaining
samples before irradiation, ensuring a reproducible counting geometry for conventional analysis whilst preserving them for future use. The Millipore filters, when pelleted in a 10 mm diameter die with a pressure of 1000 kg cm$^{-2}$, had a tendency to adhere to the faces of the die. This could only be overcome by wrapping each filter inside a Nuclepore polycarbonate membrane of the same diameter, this material being chosen for its low impurity levels (Ricci, 1975; Spyrou et al., 1976). Contamination from the die, which was of optically polished steel washed with acetone between samples, was negligible.

4.3.2 Conventional activation

Cyclic activation having been abandoned, the short conventional irradiate-wait-count sequence, scheme [5], was investigated for rapid routine analysis. After irradiation with ICIS, another pneumatic shuttle transports the samples to the radiochemical laboratories where they are unpackaged and placed in clean, non-active containers for subsequent counting. Accurate, reproducible waiting times were achieved by the use of a delay timer triggered automatically by an 'out' signal from the ICIS system. The required delay having elapsed, the unit, based on a Harwell 2000 series scaler/timer, switched the Laben MCA to the counting mode. A total of 15 isotopes were detected in some or all of the samples, as shown in Table (4.2), although $^{27}$Mg, $^{42}$K, $^{51}$Ti and $^{116}$In occurred in < 50% of cases. Elimination of the irradiated polythene containers proved of considerable advantage for these samples, enabling at least 8 elements to be determined in the presence of the Millipore/Nuclepore blanks.

In an attempt to obtain further data from the samples, several schemes involving irradiations in the 270°/3 Core Tube for multiples of the 'reactor operating day' (~ 7h) were employed. Scheme [6], a 'one day' irradiation clearly demonstrates the disastrous effects of high impurity levels in the
blanks; ~ 21 peaks in the Ge(Li) spectra being attributable to $^{24}\text{Na}$, $^{42}\text{K}$ and $^{82}\text{Br}$ only.

Finally, of the remaining 3 schemes involving irradiations over 4 or 5 operating days, Table (4.2) shows that scheme [9] proved the most successful, the 6 day waiting time allowing considerable $^{24}\text{Na}$ and $^{82}\text{Br}$ activity to decay away. Irradiation damage to the membranes by an integrated thermal neutron flux $\sim 10^{17}\text{n cm}^{-2}$ rendered them extremely brittle, thus precluding the possibility of longer irradiation periods.

Results are presented in the following sections for elements determined by schemes [5], [8] and [9]. The standard materials NBS Orchard Leaves and Bowen's Kale, also in pellet form for replicate counting geometry, were used to obtain elemental concentrations. Interspersed between the samples, they also served as flux monitors both in ICIS where samples were irradiated serially and in the 270°/3CT where up to 12 samples packaged in one large polythene container were irradiated simultaneously. Flux gradients along these containers were monitored by the use of iron wires as described in §1.3.4. The gamma spectra recorded on magnetic tape were analysed by SAMPO, with corrections for different fluxes and waiting times between samples being included.

4.4 Blank Impurities and Analytical Sensitivity

The consequences of high impurity levels in the blank membranes have already been discussed. Table (4.3) provides the values of 8 elements measured in this work for the combined Millipore/Nuclepore membrane pellets, together with published values (Dams et al., 1972; Ricci, 1975) for the individual materials. The ±% ranges quoted refer to the standard error obtained from measurements on 4 blanks, added in quadrature to the mass calibration error estimate. The results are generally in good agreement with the published data.
Table (4.3) Trace Element Content of 'Clean' Filters (0.8 μm pore size; \( \phi 47 \text{ mm} \)).

<table>
<thead>
<tr>
<th>Element</th>
<th>Millipore + Nuclepore (^c) (μg)</th>
<th>±%</th>
<th>Millipore(^a) (μg)</th>
<th>Nuclepore(^b) (μg)</th>
<th>Millipore(^a) + Nuclepore(^b) (μg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>7.3</td>
<td>9.5</td>
<td>6.9</td>
<td>0.75</td>
<td>7.65</td>
</tr>
<tr>
<td>Al</td>
<td>0.74</td>
<td>12.</td>
<td>0.17</td>
<td>0.73</td>
<td>0.90</td>
</tr>
<tr>
<td>Cl</td>
<td>17.7</td>
<td>11.3</td>
<td>17.3</td>
<td>0.68</td>
<td>18.</td>
</tr>
<tr>
<td>Ca</td>
<td>4.6</td>
<td>18.</td>
<td>6.4</td>
<td>-</td>
<td>(\geq 6.4)</td>
</tr>
<tr>
<td>Cr</td>
<td>0.45</td>
<td>15.</td>
<td>0.26</td>
<td>0.05</td>
<td>0.31</td>
</tr>
<tr>
<td>Cu</td>
<td>0.90</td>
<td>17.</td>
<td>1.0</td>
<td>-</td>
<td>(\geq 1.0)</td>
</tr>
<tr>
<td>Br</td>
<td>0.058</td>
<td>13.</td>
<td>0.03</td>
<td>0.02</td>
<td>0.05</td>
</tr>
<tr>
<td>Sn</td>
<td>0.36</td>
<td>18.</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

References:  
\(a\) Dams et al, (1972)  
\(b\) Ricci (1975)  
\(c\) This work.

Elemental sensitivities, based on the 3.6\(^{\text{th}}\) criterion (since all spectra were routinely analysed using SAMPO) for the blank matrix, were calculated for analysis schemes [5] and [9] and these are listed in Table (4.4) by the isotope detected together with each selected γ photopeak energy. Detection limits, based on a 7.2 m\(^3\) air sample were also calculated for Table (4.5). The isotopes of Ti, In, Sn and I were not detected in the standard materials and therefore absolute calculations were necessary employing Eq. (1.17) and a knowledge of the neutron energy distribution in this irradiation position (§1.3.4).
Table (4.4) Elemental Sensitivities

| Isotope detected | Scheme [5] | | | | Scheme [9] | | | |
|------------------|------------|------------------|------------------|------------|------------------|------------------|------------|
|                  | Isotope detected | Selected γ ray (keV) | Sensitivity (ng) | Isotope detected | Selected γ ray (keV) | Sensitivity (ng) |
| 24Na             | 1368       | 290              | 24Na             | 1368       | 870              |
| 27Mg             | 1014       | 2,800            | 42K              | 1525       | 180 µg           |
| 28Al             | 1779       | 39               | 47Ca             | 1297       | 200 µg           |
| 38Cl             | 1642       | 340              | 46Sc             | 889        | 0.38             |
| 42K              | 1525       | 14 µg            | 51Cr             | 320        | 360              |
| 49Ca             | 3083       | 5000             | 59Fe             | 1099       | 8100             |
| 51Ti             | 320        | 180              | 60Co             | 1173       | 8                |
| 52V              | 1434       | 1.8              | 65Zn             | 1115       | 440              |
| 56Mn             | 1811       | 17               | 76As             | 559        | 31               |
| 66Cu             | 1039       | 120              | 82Br             | 554        | 27               |
| 80Br             | 617        | 27               | 86Rb             | 1077       | 240              |
| 116In\textsuperscript{m} | 1293    | 0.16             | 122Sb            | 564        | 3.2              |
| 125Sn\textsuperscript{m} | 332     | 160              | 131Ba            | 124        | 1000             |
| 128I             | 443        | 6.3              | 140La            | 1596       | 38               |
Table (4.5) Elemental Detection Limits
- based on 7.2 m$^3$ air sample

<table>
<thead>
<tr>
<th>Element</th>
<th>Detection Limit (ng.m$^{-3}$)</th>
<th>Element</th>
<th>Detection Limit (ng.m$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>40</td>
<td>Na</td>
<td>120</td>
</tr>
<tr>
<td>Mg</td>
<td>390</td>
<td>K</td>
<td>25 µg</td>
</tr>
<tr>
<td>Al</td>
<td>5.4</td>
<td>Ca</td>
<td>28 µg</td>
</tr>
<tr>
<td>Cl</td>
<td>50</td>
<td>Sc</td>
<td>0.05</td>
</tr>
<tr>
<td>K</td>
<td>1.9 µg</td>
<td>Cr</td>
<td>50</td>
</tr>
<tr>
<td>Ca</td>
<td>700</td>
<td>Fe</td>
<td>1.1 µg</td>
</tr>
<tr>
<td>Ti</td>
<td>25</td>
<td>Co</td>
<td>1.1</td>
</tr>
<tr>
<td>V</td>
<td>0.25</td>
<td>Zn</td>
<td>60.</td>
</tr>
<tr>
<td>Mn</td>
<td>2.4</td>
<td>As</td>
<td>4.3</td>
</tr>
<tr>
<td>Cu</td>
<td>17</td>
<td>Br</td>
<td>3.8</td>
</tr>
<tr>
<td>Br</td>
<td>3.8</td>
<td>Rb</td>
<td>33.</td>
</tr>
<tr>
<td>In</td>
<td>0.02</td>
<td>Sb</td>
<td>0.44</td>
</tr>
<tr>
<td>Sn</td>
<td>22</td>
<td>Ba</td>
<td>140.</td>
</tr>
<tr>
<td>I</td>
<td>0.9</td>
<td>La</td>
<td>5.3</td>
</tr>
</tbody>
</table>

Detection Limit = $3.6 \times \sqrt{\text{Signal Background}}$

4.5 Interference Reactions

Interfering reactions which compete to produce the same product by a combination of thermal and fast reactions are generally only a problem in a core tube irradiation when several elements are present in large quantities in a matrix (e.g. soil). Such was not the case in this study, since the majority of elements measured were present only in trace quantities. Nevertheless, the one potentially serious interference, namely:

- $^{27}\text{Al}(n,\gamma)^{28}\text{Al}$
- $^{28}\text{Si}(n,p)^{28}\text{Al}$
- $^{31}\text{P} (n,\alpha)^{28}\text{Al}$
was investigated. This was carried out by re-irradiating one of the samples (after all previous activity had decayed) under identical conditions to scheme [5] except that this time the sample was contained in a cadmium box. If the presence in the sample of Al, Si and P is assumed, then for the unshielded case let \( X \) be the photopeak counts contributed by the \((n,\gamma)\) reaction and \( Y \) the combined contribution from the \((n,p)\) and \((n,\alpha)\) reactions. Similarly, when the cadmium cover is present, the \((n,\gamma)\) contribution will be modified to \( X/\text{CR}_{28\text{Al}} \) (§1.3.1) whilst \( Y \) is unchanged since these two reactions are both threshold reactions initiated only by fast neutrons. Thus the two simultaneous equations:

\[
X + Y = Z \\
\frac{X}{\text{CR}_{28\text{Al}}} + Y = Z'
\]

may be solved for \( X \) and \( Y \) by the two irradiations described, \( \text{CR}_{28\text{Al}} \) being simply calculated. \( Z \) and \( Z' \) are the observed counts in the \( {28}\text{Al} \) photopeak following each experiment. After corrections for flux differences, the ratio \( X:Y \) was obtained as 98.5:1.5\%; well within the experimental error of the measurement. It was therefore concluded that the \( {28}\text{Al} \) isotope was entirely attributable to the presence of Al in the sample. This assumption could not be made for the standard materials such as Bowen's Kale in which Al, Si and P are present at concentrations of 37.5, 237 and 4510 \( \mu \text{g/g} \) (Bowen, 1974 and 1975). A calibration factor for Al was obtained by using these values combined with measurements made in the ICIS facility using standards which indicated that these three elements contribute 170, 3.9 and 1.4 counts/mg respectively to the \( {28}\text{Al} \) photopeak area (Minski, 1977).
Due to the destruction of several of the filters, elemental results were only obtained for 9 out of the 12 days; all data are therefore presented for the 9 days only. Figs. (4.2a) and (4.2b) show the measured time variations on a 6-hourly basis in filter obscuration, traffic flow, air temperature, wind speed, sunshine, rainfall, atmospheric pressure and humidity (Bartram, 1976), whilst Figs. (4.3a) and (4.3b) present the corresponding variations in concentration of the elements Al, V, Cr, Mn, Zn, Br, Sb and I which were the total number of elements both measurable and distinguishable from the blank interferences in the majority of samples by the combined INAA techniques previously described. Blank values or detection limits have been included in these figures where appropriate. To avoid confusion, errors have not been indicated but are listed separately. The total percentage error ($\sigma_{\text{tot}}\%$) associated with an individual determination was calculated by:

$$
\sigma_{\text{tot}}^2 = \left[ \frac{\sigma_{\text{ps}}^2}{n_s} + \frac{\sigma_{\text{pb}}^2}{n_b} \right] + \frac{\sigma_{\text{pc}}^2}{n_c} + \sigma_c^2
$$

where $\sigma_{\text{ps}}$, $\sigma_{\text{pb}}$ and $\sigma_{\text{pc}}$ refer to the standard deviations in the photopeak areas of the unknown sample (s), blank (b) and certified standard (c), respectively. $n_b$ and $n_c$ are the number of replicate blanks and certified standards analysed and $\sigma_c$ is the published uncertainty in the certification of the standard. These various components are itemised in Table (4.6).

Standard Smoke and SO$_2$ levels were available as daily measurements and these are plotted in Figs. (4.4a) and (4.4b) together with the calculated daily averages of Al, V, Mn, Br, Sb and I clearly demonstrating the overall trends during the sampling period by 'ironing-out' diurnal fluctuations. Cr and Zn were omitted as their detection was limited to fewer samples.
Fig. (4.2a): Six-Hourly Values

- Temperature
  - 26.9 °C

- Wind Speed
  - 8.1 km/hr

- Filter Obstruction
  - 96.5 %

- Traffic Flow
  - 2964 Vehicles
Fig. (4.2b): Six-Hourly Values

Sunshine

Atmos. Pressure

Rainfall

Humidity
Fig. (4.3a): **Six-Hourly Values** (ng.m\(^{-3}\))
Fig. (4.3b): Six-Hourly Values (ng m$^{-3}$)

- Sb
- I
- Zn
- Br
Fig. (4.4a): Daily Averages

- Al
- Blank
- V
- Standard Smoke
- SO₂
Figure 4.1b: Daily Averages (ng.m⁻³)

Sb

I

Mn

Br
Table (4.6) Uncertainties in elemental concentrations

<table>
<thead>
<tr>
<th>Element</th>
<th>Scheme</th>
<th>$\sigma_{ps}$ %</th>
<th>$\sigma_{pb}$ %</th>
<th>$\left[\frac{\sigma_{pc}}{n_c}\right]^2 + \sigma_c^2$ %</th>
<th>$\sigma_{tot}$ %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr</td>
<td>[9]</td>
<td>5.0</td>
<td>6.7</td>
<td>13.2</td>
<td>16.</td>
</tr>
<tr>
<td>Mn</td>
<td>[5]</td>
<td>3.5</td>
<td>-</td>
<td>10.5</td>
<td>11.</td>
</tr>
</tbody>
</table>

Various general observations may be made concerning these results.

i) The weather, although poor at the beginning of the experiment, with rain, minimal sunshine and moderate winds, improved during the second week to conditions typically expected in August, namely clear skies, light winds and fair weather characteristic of an anti-cyclone.

ii) Superimposed on this weather pattern are the expected diurnal variations clearly seen in the temperature, sunshine, humidity and, to a lesser extent, wind speed data.

iii) Traffic flow also exhibits these daily fluctuations, with less traffic movement through the city during the weekend and Monday, which was a Bank Holiday.

iv) Elemental concentrations in the air particulates sampled are all higher towards the latter part of the experiment corresponding with the period of fine weather. This trend is most clearly seen in the daily averaged
results, the concentrations in some cases closely following the variation in atmospheric pressure. Standard Urban Smoke and SO$_{2}$ levels behaved similarly.

4.6.1 Meteorological effects

The coincidence of anti-cyclonic conditions and elevated levels of air pollution is a well-documented phenomenon (Stern, 1976). An anti-cyclone consists of a low-level diverging air flow from a region of high pressure, which spirals outwards in a clockwise direction (Northern hemisphere) due to the Coriolis forces acting on it. The dimensions of commonly occurring anticyclones are from 100 to 1000 km. Migratory anticyclones in the temperate zones, formed by confrontations between arctic and tropical air, have a lifetime of a few weeks and drift with the prevailing westerly winds at about 800 km/day. Air pollution incidents are related to anti-cyclones through their associated inversion layers. These are layers of air, usually close to the ground, where temperature increases with height. Under these conditions a rising air parcel is cooler than its surroundings, becomes less buoyant and returns, thus the air parcel exists in an extremely stable situation in which vertical mixing is minimal. Furthermore, the light winds, synonymous with anti-cyclonic weather, prevent horizontal mixing. Air pollutants are effectively trapped in the inversion layer, close to their source, being unable to disperse whilst the inversion persists. If the anti-cyclone stagnates, remaining stationary for a considerable period of time, the accumulation of pollutants may have disastrous consequences, as was the case, for example, in London from 5th to 9th December, 1952, where SO$_{2}$ and atmospheric particulates were responsible for approximately 4000 excess deaths (Stern, 1976).
Inversions related to anti-cyclones are usually either 'subsidence inversions' or 'radiation inversions'. The former are produced when cold subsiding air at the centre of the anti-cyclone (which results in the high pressure observed at sea level) is warmed by compression as it descends. The upper layers descend the furthest, experience the greatest pressure change and thus the largest temperature increase. If this temperature increase is sufficient, an inversion will result. Radiation inversions occur mostly at night. The ground, heated throughout the day by the sun, rapidly cools at night when clear skies enhance radiant losses. As a consequence, air closest to the ground loses the most heat by conduction and convection processes, again creating an inversion. Very often the pool of cold air below an inversion may be confined by the local topography.

During the second week of sampling, such meteorological conditions existed and the resulting build-up of elements in the air at street level was easily detected. A detailed discussion of the importance of the meteorological data and its influence on the obscuration measurements is to be found elsewhere (Bartram, 1976), being outside the scope of this work.

4.6.2 Pollutant sources and enrichment factors

The next question to be considered is whether the elemental concentrations measured in Oxford City-Centre are the result of local pollutant sources. Cawse (1976), in a survey of the atmospheric trace elements in the U.K., published average 1975 values for the rural aerosol sampled at Chilton, only some 20 km South of Oxford. These are presented in Table (4.7) together with the means and ranges measured in this study. With the exception of chromium and bromine, the Chilton levels are in close agreement with those of Oxford City-Centre. The mean values for chromium and bromine are, however, > 7 and > 11 times higher, respectively, than those at Chilton indicating local origin.
Table (4.7) Trace element concentrations of air particulates

<table>
<thead>
<tr>
<th>Element</th>
<th>Average Concentration (ng.m(^{-3}))</th>
<th>Range (ng.m(^{-3}))</th>
<th>Average Concentration (ng.m(^{-3}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>260</td>
<td>&lt; 97.6-1057</td>
<td>257</td>
</tr>
<tr>
<td>V</td>
<td>11</td>
<td>0.8-41.5</td>
<td>13</td>
</tr>
<tr>
<td>Cr</td>
<td>18</td>
<td>&lt; 12.5-120.5</td>
<td>2.5</td>
</tr>
<tr>
<td>Mn</td>
<td>17</td>
<td>&lt; 2.4-50.7</td>
<td>11.4</td>
</tr>
<tr>
<td>Zn</td>
<td>120</td>
<td>&lt; 60-325</td>
<td>91</td>
</tr>
<tr>
<td>Br</td>
<td>370</td>
<td>40-972</td>
<td>32</td>
</tr>
<tr>
<td>Sb</td>
<td>2.7</td>
<td>0.28-8.94</td>
<td>2.2</td>
</tr>
<tr>
<td>I</td>
<td>1.5</td>
<td>&lt; 0.9-3.03</td>
<td>3.9</td>
</tr>
</tbody>
</table>

In an air pollution study of Guildford, Hasan and Spyrou (1972) recorded mean concentrations during August, 1971, for Al, V and Mn of 4.0, 0.55 and 0.029 μg m\(^{-3}\) respectively at a sampling site in the City Centre. These levels are considerably higher than those of Oxford; vanadium especially is present in concentrations \(\sim\) 50 times higher. However, during the period 29/12/71-29/1/72 the mean vanadium concentration in Guildford increased to \(\sim\) 4 μg m\(^{-3}\), a factor of \(\sim\) 360 times higher than the August level measured in this study and twice the general population quality standard set by the Soviet Union at 2 μg m\(^{-3}\) (Hasan and Spyrou, 1972).

Several authors (Gordon et al., 1974; Cawse, 1974; Jervis et al., 1976) have found the calculation of an 'enrichment factor' (EF) useful in determining the origin of elements found in air particulates. Measured concentrations vary considerably with meteorological conditions and thus provide only limited information, but the EF indicates the enrichment of an element in the atmosphere with respect to its natural abundance in the earth's crust.

Generally, EF is the ratio of normalised atmospheric and crustal concentrations of an element defined as
where \( x \) and \( c \) are concentrations of the element of interest and an appropriately chosen normalising element respectively. Authors differ on two counts with regard to the calculation of EF's. Firstly, on the use of crustal concentrations Cawse(1974) preferring to use local soil analyses rather than documented crustal concentrations (Jervis et al., 1976; Obrusnik et al., 1976). There are obvious merits to both methods; air particulates may be expected to consist in part of local wind blown dust which would be reflected in EF's based on analyses of local soils. Neverthless, it is certainly the case, especially with the smaller diameter particulates and gaseous pollutants, which pass through the troposphere (up to 15 km altitude) to reach the stratosphere (up to 50 km altitude), that they may be transported on a world wide scale (Cawse, 1977). EF's calculated using crustal abundances would be more appropriate in this situation, also permitting intercomparison of results from widely separated geographical locations.

The second difference between authors is in the choice of a normalising element, which should be predominantly of natural origin, so that a large EF value for a particular element indicates an anthropogenic source whilst one around unity suggests a natural pollutant. Aluminium (Jervis et al., 1976; Obrusnik et al., 1976; Maenhaut and Zoller, 1976), scandium (Cawse, 1974) and iron (Olmez and Aras, 1976) have all been used, choice often being limited by the analytical technique available. Three enrichment factors, all normalised to aluminium, have been calculated for the Oxford measurements, each with respect to a different standard, namely the Earth's Crust (Ahrens, 1965), Chilton soil (Cawse, 1974) (although Chilton and Oxford lie on different geological formations, namely chalk and Oxford clay) and an average soil (Bowen, 1966). These are listed in Table (4.8) from which it would appear
only manganese (apart from aluminium) could be attributed for the most part to natural origins, the other elements and especially bromine having large EF values irrespective of the method of calculation.

Table (4.8) Enrichment Factors for Oxford Air Particulates
(normalised to Al)

<table>
<thead>
<tr>
<th>Element</th>
<th>E.F. w.r.t. Earth's Crust (Ahrens, 1965)</th>
<th>E.F. w.r.t. Chilton Soil (Cawse, 1974)</th>
<th>E.F. w.r.t. Average Soil (Bowen, 1966)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>V</td>
<td>25.7</td>
<td>25.4</td>
<td>30.0</td>
</tr>
<tr>
<td>Cr</td>
<td>56.7</td>
<td>30.2</td>
<td>49.1</td>
</tr>
<tr>
<td>Mn</td>
<td>5.65</td>
<td>1.71</td>
<td>5.46</td>
</tr>
<tr>
<td>Zn</td>
<td>541.</td>
<td>85.2</td>
<td>655.</td>
</tr>
<tr>
<td>Br</td>
<td>46700.</td>
<td>621.</td>
<td>20200.</td>
</tr>
<tr>
<td>Sb</td>
<td>4260.</td>
<td>&gt; 71.2</td>
<td>123.</td>
</tr>
<tr>
<td>I</td>
<td>946.</td>
<td>-</td>
<td>81.9</td>
</tr>
</tbody>
</table>

4.6.3 Correlation coefficients

The inter-relationships between the elemental and meteorological data are summarised by their correlation coefficients, \( r \), defined as:

\[
 r_{x,y} = \frac{\text{covariance}_{x,y}}{\text{standard deviation}_x \times \text{standard deviation}_y} \tag{4.3}
\]

where \( x \) and \( y \) are any 2 data sets each with \( n \) values and means \( \bar{x} \) and \( \bar{y} \). Thus:

\[
 r_{x,y} = \frac{\sum_{i=1}^{n} (x_i - \bar{x})(y_i - \bar{y})}{\sqrt{\sum_{i=1}^{n} (x_i - \bar{x})^2 \cdot \sum_{i=1}^{n} (y_i - \bar{y})^2}} \tag{4.4}
\]

The matrix of correlations is presented in Table (4.9). In cases where
elemental concentrations were below the minimum detection level, this value has been assumed in the calculation of the correlation coefficients. The significance of these coefficients may be assessed by the approximate test (Davis, 1973):

\[ t = r \sqrt{\frac{n-2}{1-r^2}} \]  

(4.5)

which has \((n - 2)\) degrees of freedom. This test is derived from a test for the significance of the correlation between two samples drawn from normal populations. The null hypothesis is that the correlation is zero. Tabulated critical values of \(t\) for \(v\) degrees of freedom and selected levels of significance * are found in most elementary statistics textbooks. Thus by rearranging Eq. (4.5) and choosing \(v = 34\) (each data set contains 36 values) the table of significance levels and corresponding \(r\)-values was obtained (also included in Table (4.9)). All those correlations with significance level \(< 0.1\%\) \((|r| \geq 0.499)\) are shown enclosed in boxes to emphasise their importance.

Certain obvious relationships are apparent, such as those between sunshine, humidity and temperature, and, as such, serve to inspire confidence in this type of analysis. Rainfall and air pressure feature no strong relationships with the other data according to the calculated \(r\)-values, which results are somewhat deceptive. Air pressure, for example, does not exhibit the diurnal variations characteristic of the majority of the data but as mentioned previously, correlates quite well with the daily averages

* Significance level refers to the probability of making a Type I statistical error, namely of rejecting the null hypothesis when it is in fact correct.
of some elements seen in Figs. (4.4a) and (4.4b). The r-values were not calculated for the daily averaged measurements due to the limited number of data available. Rainfall, on the other hand, occurred on only two days for which results were obtained, this information being insufficient to demonstrate possible 'washout'. It is, however, noticeable that the r-values resulting from pairing with all the elements are negative.

More interesting are the correlations between filter obscuration and 6 out of the 8 trace elements showing that simple reflectance measurements may be a good indication of elemental concentrations in the atmosphere. The negative correlation between wind speed and obscuration displays the ability of the wind to disperse pollutants (also reflected in the negative correlations with V, Br and I), again, a well known phenomenon.

Table (4.9) also shows that several strong correlations exist between the various elements measured; antimony particularly, being significantly associated with all other elements, especially bromine. In order to demonstrate the 'strength' of correlation for a specific r-value, a scatter diagram, Fig. (4.5), has been plotted of bromine versus antimony showing the actual spread of the data. This element pair was chosen for its large r-value and the fact that there were no missing data due to the influence of the blank or the minimum detection level. Obviously a certain proportion of the spread in data may be attributed to the uncertainties in photopeak area determination, which from Table (4.6) were 1% and 8% for bromine and antimony respectively.

4.6.4 Cluster analysis

In order to summarise, in a convenient and readily understandable form, the information contained in the correlation matrix, the technique
of cluster analysis has been employed. This is a non-statistical method of classifying data into more or less homogeneous groups, in a manner so that the relation between groups is revealed (Davis, 1973). Originally developed by taxonomists in an attempt to deduce the lineage of living creatures from their characteristics and similarities, this technique is rapidly finding applications in many diverse fields of study.

The clustering method is fully described in Appendix III and only the final results are discussed here. Fig. (4.6) shows the 'dendrogram' ultimately obtained from cluster analysis performed on the 'attributes' (measured data) of each 'object' (6-hourly measurement). The analysis is based on the similarity between the attributes, i.e. the correlation coefficient, which is indicated by the horizontal scale. The attributes, listed vertically, are linked together at similarity levels defined by the junction points of the dendrogram. As can be seen, the clusters so formed outline the structure of the correlation matrix. The 8 trace elements, together with filter obscuration, form a distinct cluster as do traffic flow, temperature and sunshine. Air pressure, as already mentioned, finds itself almost unrelated to any of the other attributes, whilst wind speed, humidity and rainfall form a very separate cluster of their own.

The cluster analysis method, as employed here, suffers from the disadvantage that strong negative correlations between attributes are not immediately apparent from inspection of the dendrogram although they may nevertheless be highly significant. A classic example is the case of humidity and temperature.
Fig. (4.5) : Scatter diagram of bromine versus antimony.

Fig. (4.6) : Dendrogram resulting from WPGMA cluster analysis.
4.7 Conclusions

One of the most important lessons to be learned from this study is the correct choice of filter membrane for air particulate sampling. Spyrou et al. (1976) confirms the findings that Millipore filters are particularly unsuitable for trace element analysis, the high impurity levels significantly worsening detection limits for the elements of interest.

The best results from INAA were obtained using the short conventional irradiation scheme with additional information being provided by a further irradiation lasting one week followed by 'cooling' of a similar period prior to counting. Cyclic activation, in its present state, was found to be of no benefit due to the high impurity levels of the combined filter and polythene capsule 'blanks'.

Although results were only obtained for a limited number of elements present in the Oxford city atmosphere, they are representative of at least two, but probably three, pollution sources. Aluminium, and to a certain extent manganese, may be attributed to natural sources such as wind-blown soil. The concentrations of vanadium in the Oxford aerosol are between 1 and 2 orders of magnitude higher than those reported in remote non-urban regions resulting principally from the combustion of fuel oils and petroleum (Zoller et al., 1973). The measurements by Hasan and Spyrou (1972) also indicate that vanadium may originate from the burning of oil (for heating purposes), since Guildford levels in 1971 were a factor of ~7 times higher in winter than in summer. Zoller et al, suggest that, because of the extreme sensitivity with which vanadium can be analysed by NAA and its behaviour in the atmosphere, it is an additional metal that can be used as a tracer for
hemispheric movement of particulates generated by certain of man's activities. Moreover, vanadium in the atmosphere in the pentoxide form acts as a catalyst to the photochemical production of sulphuric acid from sulphur dioxide making its presence extremely undesirable.

Zinc and antimony form part of a chalcophilic group of elements (i.e. those which form sulphides rather than oxides) which tend to produce volatile compounds and as a consequence have high enrichment factors (Salmon et al., 1977). Their presence in the atmosphere is regarded as the result of high temperature processes although Salmon et al. suggest that as antimony trends match local black smoke changes in the Chilton area, this element is derived from fuel burning rather than industrial processes. The results presented in Figs. (4.4a) and (4.4b) substantiate this, but the high correlation with bromine may indicate automotive sources as well.

Sources of the element iodine are difficult to define. The concentration in Oxford city-centre is identical to that measured in Karlsruhe, W. Germany (Vogg and Hartel, 1976) and 3 times higher than that at the geographical South Pole (Maenhaut and Zoller, 1976). The large enrichment factors suggest anthropogenic sources such as coal burning since it occurs at concentrations of 0.5-5 μg/g in coal (Rowe and Steinnes, 1976) and ∼2 μg/g in fly ash (Maenhaut and Zoller, 1976).

The 6 elements Al, V, Mn, Zn, Sb and I are present at levels similar to those measured in the local rural area of Chilton, and, following the discussion above, are commensurate with natural or anthropogenic sources not specifically related to Oxford City-Centre. Chromium and bromine however occur in concentrations appreciably higher than expected, which, together with high enrichment factors, indicate local origins. Bromine is widely recognised as correlating with vehicular pollution (Valkovic, 1975). It is an additive to petrol in the form of ethylene dibromide, which
is used to interact with lead in the engine combustion chamber arising from the addition of tetraethyl and tetramethyl lead, to improve the fuel octane rating (Oakes et al., 1976). The resulting bromide compounds are emitted through the engine exhaust system. Studies have shown (Habibi, 1973) that the most abundant lead compound in exhaust particulates is lead bromochloride. Jervis et al. (1976) and Desaedeleer et al. (1976) quote Br/Pb ratios of 0.32 ± .04 and 0.235 ± .069 respectively for Toronto and Florida air particulates sampled near urban roadways. The results of Cawse (1976) also yield a Br/Pb ratio of 0.24 for Chilton air. So reproducible are these ratios that a tentative lead level in Oxford city centre may be estimated as ∼ 1-1.5 μg m⁻³, below the CNAA detection limit of ∼ 1.7 μg m⁻³. This estimated lead level is very close to the maximum permitted by the U.S. Environmental Protection Agency of 1.5 μg m⁻³ under new legislation (Federal Register, 1977).

Chromium behaves inexplicably; Salmon et al. (1977) mention that this siderophilic (iron-like) element is probably of anthropogenic origin which certainly seems the case from this study, although the source, not obviously vehicular, is difficult to define since it correlates more strongly with the soil derived elements such as aluminium and manganese.

Finally, the analysis of aerosols collected over short sampling periods makes it possible to comment on the health aspects of elements in the atmosphere. Variations in concentrations with time and diurnal patterns are evidence of local emissions; the sharpness of the variations is indicative of a local residence time in the atmosphere. Since source emissions are at a minimum at night time, the rate of disappearance of pollutants is a measure of the persistence of polluted air masses (Desaedeleer et al., 1976). Meteorological conditions as well as human activities have been shown to
greatly influence the detected levels of air pollutants. The observed
diurnal fluctuations of certain trace element levels have maxima which
occur during the day time when human exposure is at its greatest, e.g. for
pedestrians in a busy thoroughfare; thus daily values, averaged over a
24 hour period, underestimate the risk to such a population.

It is, however, a matter for concern that in Britain there exist
no maximum recommended atmospheric levels for individual trace elements
with regard to public health, although certain regulations are enforced
in the industrial sector. The fate of pollutants inhaled by man is
determined to a large extent by particle size. Most particles exceeding
5 μm are effectively removed in the upper respiratory system while those
in the size range 0.1 to 1 μm are able to penetrate deep into the lung (Stern,
1976). Bahreyni (1976) studied the distribution of elements as a function of
particle size in Guildford air particulates by the technique of Electron
Microprobe Analysis. The elements Al, V and Cr were found to occur more
frequently in < 5 μm diameter particles whilst the converse was true for
Mn, Zn and Pb. Tabulated collection efficiencies of filter membranes for
various particle sizes as a function of pump speed, pore size and pore
density have been published (Spurney and Lodge, 1972). Certainly for
0.8 μm pore size membranes as used in the study, particles as small as
0.1 μm are trapped with appreciable efficiency.

The following few comments come from the review article by Schroeder
(1970). In light of current knowledge, of the 27 metals considered, (which
include Al, V, Cr, Mn, Zn and Sb) only 7 are more or less toxic of them-
selves; of these 7 only 3 represent real or potential hazards to human
health: Ni, Cd and Pb. Two others need careful control: Be and Sb. Cadmium
in air can be minimised or abolished by abatement of zinc, with which it
occurs as an invariable contaminant. Vanadium represents a special problem
as the increasing use of low-sulphur oils, with which it is inversely related, suggests that vanadium emissions will probably increase, although at present concentrations it is doubtful that this element is harmful.

As an extension to this study and to complement the trace element results obtained by INAA, analysis of the air particulate samples by gas chromatography has been performed (Douglas, 1978). This technique enabled the determination of 5 hydrocarbons in the Oxford samples, namely: toluene, ethyl benzene, n-heptane, n-octane and n-nonane, despite the presence of high organic impurity levels in the Millipore membranes.

A description of the gas chromatography technique and the results obtained are included in Appendix II. Cluster analysis (§4.6.4) has been performed on this data, combined with the elemental concentrations and meteorological data; the resulting dendrogram (Fig. (II.3)) is also shown in Appendix II. In conclusion, this work indicates that the organic compounds measured in the Oxford particulate samples are unburnt hydrocarbons probably resulting from incomplete combustion or evaporative losses of vehicle fuel.
5.1 General Introduction

A multiplicity of soil definitions exist which are as diverse as the soil itself, but perhaps the most universally applicable one has been supplied by Barshad (1964) as "the material occupying the outermost part of the earth's crust and possessing distinct morphological, mineralogical, chemical and physical properties resulting from certain inheritance factors, from its unique position on the surface of the earth, and from the environmental factors existing at that position". Thus the chemical composition of soil reflects not only the parent material (i.e. the original rocks and minerals that constituted the materials from which soil is derived) but also "the changes that have occurred and that are still taking place as a consequence of the action of meteorological, geological and biological agencies on these rocks" (Bear, 1964).

Historically, soil chemistry has developed as a result of agricultural demands, as reflected in the lectures on soils in relation to plant nutrition given by Sir Humphrey Davy (1778-1829), credited as the first soil chemist. As a consequence, most current knowledge of the behaviour of elemental soil constituents is confined principally to those elements which may be termed 'essential' for the production of healthy crops and/or animals (including man) which feed on those crops. It is only in recent years that the elemental analysis of soils has found applications in archaeology, although ironically, it is interesting to note that Davy was also responsible for performing some of the first reported chemical analyses of archaeological
artifacts (Davy, 1815). As recently as 1960, Cornwall, in an article on soil investigations in the service of archaeology, wrote: "For the purpose of most soil investigations no great expertise as a chemical analyst is required. There are two main reasons for this. First, the number of significant substances to be sought or estimated is comparatively small. Trace elements, for example, of the highest importance to the agricultural analyst, are generally irrelevant for archaeological purposes. Fluorine and radiocarbon are special exceptions...... Second, great accuracy in quantitative analysis is unnecessary - and may even mislead". It is true that, at the time of writing that article, soil analyses were mainly confined to the metals Na, Mg, Al, K, Ca, Mn and Fe together with the acid radicals carbonate, chloride, sulphate and phosphate and also Si and C (Cornwall, 1960).

Nevertheless, the last decade has seen many more wide-ranging applications of elemental analyses to soils of archaeological interest. To a large extent these centre around the analysis of clays suitable for the manufacture of pottery, in connection with provenance studies (e.g. Perlman and Asaro, 1969; Attas et al., 1977). A large number of elements, and especially those occurring at trace levels, have been found to be of prime importance for this type of application. Moreover, in certain instances, especially with ceramics, the natural spread in elemental concentrations has been shown (Harbottle, 1976) to be much less than the analytical precision, although this is rarely true for soils. Thus the multielemental capabilities of NAA are ideally suited to the situation where the significant elements for interpretation of archaeological data cannot be anticipated.

The work described in this chapter falls naturally into 2 sections: Section A deals with the analytical techniques, based on short-lived isotopes, which have been investigated for the elemental analysis of soils whilst
Section B describes their application to a novel problem in archaeometry, namely that of locating buried soil surfaces. A specific site near Hadrian's Wall possessing fine examples of buried soils was studied as a 'test case' for both the analytical technique and the method of location of the buried soil. The method relies on detecting soil features by the corresponding fluctuations in elemental concentrations with depth through a profile (a vertical section through the soil). These results are presented together with those from physical measurements (particle size analysis, loss on ignition) made on identical samples. Finally, cluster analysis is performed on the multi-elemental data to facilitate interpretation of the results.

A - Analytical Methods for Soils

5.2 Analytical Requirements

The development of INAA techniques for application to soils is governed by a number of constraints due to the varied character and composition of the material.

i) Due to the heterogeneous nature of soil, the analyst is generally faced with a daunting number of samples, many of which are replicates, simply to ensure that the analysis is representative of the 'parent' material. As a consequence, techniques which are both rapid and capable of implementation on a routine basis represent a distinct advantage. The NAA schemes described in the following section, principally employing short-lived isotopes, are fully instrumental and fulfil both these criteria.

ii) Soils, in general, contain significant concentrations of such elements as Na, Al and Mn, which, upon neutron irradiation,
lead to gross activity of the sample. When this fact is combined with the need for samples which are as large as possible (again to ensure representativeness) and which must be counted with only a short delay after removal from the reactor, then sample handling must be kept to a minimum to avoid the analyst receiving a high radiation dose. In addition, the sample-detector distance must be large in order to reduce the spectrometer counting rate to an acceptable level.

iii) Due to the complex elemental composition of the soil matrix, careful checks must be made for the very strong possibility of interferences, either from γ-ray lines of similar energy, or, more particularly, from competing reactions yielding the same product isotope upon irradiation in a mixed neutron energy spectrum.

One of the earliest studies on gamma spectrometry of neutron activated soils was published by Nishita et al. (1966) whilst Brunelle et al. (1969) successfully measured a variety of short-lived isotopes by means of a NaI(Tl) detector following a 10 min irradiation. Subsequent publications have concentrated primarily on the use of longer-lived radionuclides (Kline and Brar, 1969; Tobia and Sayre, 1974; Hopke et al., 1976) whilst Van der Klugt et al. (1977) describe a computerised multi-elemental analysis system which combines both long and short irradiation schemes for the measurement of some 32 elements.

Ellinger et al. (1976) describe a technique for studying elemental profile distributions (the object of this study) which involves irradiating a complete section of the soil profile and subsequently scanning the section
with a well-collimated Ge(Li) detector for the long-lived isotopes present. This technique, although reducing sample preparation to a minimum, suffers from the disadvantage of having much poorer spatial resolution than the usual method of dividing the samples prior to irradiation. Moreover, there is the additional difficulty (especially in a small reactor) of irradiating large samples.

Analyses employing short-lived isotopes are much less frequently reported. Benes et al. (1974) were able to measure an additional 11 elements in an analysis scheme designed to determine $^{128}$I ($\tau = 25$ min) in a variety of different soils whilst Dantas and Ruf (1975) found additional advantage in the measurement of short-lived isotopes in samples irradiated with thermal and epithermal neutrons.

5.2.1 Epithermal neutron activation analysis (ENAA)

The ENAA technique consists of selectively irradiating samples (usually in the reactor core) with neutrons from which the thermal component has been excluded (epithermal neutrons). In this way the activities of those nuclides having an approximately $\frac{1}{\nu}$ cross-section are effectively suppressed with respect to the activities of all nuclides whose cross-sections show high resonances in the epithermal region i.e. those nuclides with large $\frac{1}{\sigma_0}$ values (Eq. (1.7)). Most of the nuclides in soil leading to major activities upon neutron activation have a cross-section as a function of energy not deviating much from the $\frac{1}{\nu}$ law in the low energy epithermal region. This is the case for nuclides such as $^{23}$Na, $^{27}$Al and $^{55}$Mn (Brunfelt and Steinnes, 1969) whilst many trace elements have isotopes with high resonance activation cross-sections. This fact should enable those elements comprising the gross activity of the soil matrix (Na, Al, Mn) to be suppressed with respect to other trace elements of interest, and thus improve their detection limits, upon irradiation by epithermal neutrons.
This technique has been found of advantage for the analysis of both geological (Brunfelt and Steinnes, 1969; Steinnes, 1971; Randa, 1976) and biological materials (Gambarian, 1972; Bagdavadze and Mosulishvili, 1975; Tomberlin and Eckhoff, 1975) as well as for certain minor constituent elements of soils (Dantas and Ruf, 1975).

5.3 Experimental Methods

The experimental methods reported in the following pages represent, where appropriate, a combination of 'cyclic' and 'conventional' analysis modes performed with 3 different neutron energy spectra in conjunction with both pure Ge and Ge(Li) semiconductor detectors, with the intention of evaluating their relative merits for soil analyses. The various analysis schemes are summarised in Table (5.1). A similar study, although employing much longer-lived nuclides has been performed by Baedecker et al. (1977).

Table (5.1) : Analysis Schemes

<table>
<thead>
<tr>
<th>Mode</th>
<th>Facility</th>
<th>Cyclic</th>
<th>Conventional</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal</td>
<td>-</td>
<td>Ge(Li)</td>
<td>Ge(Li); pure Ge</td>
</tr>
<tr>
<td>Core</td>
<td>Ge(Li)</td>
<td></td>
<td>Ge(Li)</td>
</tr>
<tr>
<td>Core (Cd cover)</td>
<td>-</td>
<td></td>
<td>Ge(Li)</td>
</tr>
</tbody>
</table>

Irradiations for this work were performed in two facilities of the CONSORT II reactor, namely 0°STF (thermal facility) and ICIS (core irradiations) shown in Fig. (3.2a). The neutron fluxes at these positions are summarised in Table (1.2). The first of these, a so-called thermal facility, is located in a graphite block at the side of the core. The neutron flux, although not
a purely thermal spectrum, is characterised by \( \phi_f/\phi_{th} \approx 1/13 \). A simple mechanical system (§1.3.3) inserts the samples, contained in polythene, along a horizontal pipe at the side of the reactor and is only suitable for conventional irradiations, since the minimum transfer time to the detector is \( \approx 2 \) min.

The other facility, ICIS (described in detail in §3.2), at the centre of the core, possesses the highest thermal flux in the reactor, approximately 17 times that of the thermal facility, and, being close to the fuel elements, there is a very considerable fast neutron component (\( \phi_f/\phi_{th} \approx 1/13 \)). ICIS is suitable for both cyclic and conventional irradiation schemes. For conventional irradiations, the sample, on removal from the core, is transferred to another pneumatic shuttle which travels to the radiochemical laboratories in a neighbouring building and ejects the encapsulated sample into a fume cupboard. Counting may commence within \( \approx 30 \) seconds.

To enable ENAA, conventional irradiations performed in the core facility have the option of cadmium shielding i.e. samples thus irradiated are wrapped in polythene sheets to avoid 'rub-off' contamination and placed in small boxes constructed of 0.5 mm thick cadmium, sufficient to completely absorb thermal neutrons (Rossitto et al., 1972) with energies below \( \approx 0.5 \) eV. Cadmium boxes are restricted in size to a maximum external surface area of 4 cm\(^2\) which, when placed in the core would lower the reactivity by 0.05%. This corresponds to the normal limit to prevent a reactor trip (accidental shut-down) due to the strong thermal neutron absorption of cadmium. Powder samples thus irradiated require pelleting in order to contain sufficient material within the cadmium box.

Three different semiconductor detectors were available during this study. For cyclic activation, a 20 cm\(^3\) Quartz and Silice coaxial Ge(Li),
of resolution 2.55 keV at 1332.4 keV; for conventional analyses, a 38 cm$^3$
Canberra coaxial Ge(Li) with resolution of 2.4 keV and a 1 cm$^3$ Elscint planar
pure Ge detector, with resolution of 580 eV at 122 keV (§3.3). As required,
the two Ge(Li) detectors were connected via a Canberra (model 1412) spectro-
scopy amplifier to a Laben 8000 series 4000 channel MCA operating in the
range 0-4 MeV. The pure Ge LEPD was used in conjunction with the same
amplifier and a 'Tracor' Northern Scientific 1000 channel MCA calibrated
from 0 to 200 keV. Spectra were recorded either on magnetic tape (4000
channels) or punched paper tape (1000 channels) suitable for subsequent
computer analysis by the modified SAMPO code.

5.3.1 Samples and standards

The soil samples used in this investigation were taken from a single
bulk sample prepared as described in §5.8. Comparatively large samples
(≈ 200-300 mg) were employed where possible in order to reduce sampling
erors due to the heterogeneous nature of the parent material. Since a
certified standard soil is not yet available (one is in preparation by
IAEA) and since the NBS Plastic Clay, Flint Clay or Argillaceous Limestone
standard reference materials are only certified for a number of the bulk
elements, NBS Orchard Leaves and Bowen's Kale were used as comparator
standards.

5.4 Results

Fig. (5.1) shows three spectra obtained by conventional analysis of
identical soil samples which were counted on the 38 cm$^3$ Ge(Li) detector
at a distance of ≈ 24 cms. The irradiate, wait and count times were 10 min.
each; isotopes of Na, Mg, Al, Cl, K, Ca, Ti, V, Mn, Br, Sr, Ba, Sm, Eu and
Dy being detected. The uppermost spectrum represents an irradiation in the
Fig. (5.1): Ge(Li) spectra obtained by conventional analysis of identical soil samples irradiated in different neutron fluxes.
core, the centre one also in the core but with the sample enclosed in a cadmium box and the lower spectrum corresponds to a sample irradiated in the thermal facility (note: scale should be multiplied by 10). The three spectra may be considered to represent activation with predominantly mixed, epithermal and thermal neutron fluxes respectively.

In all cases, the 2.3 min. isotope $^{28}\text{Al}$ renders a sample too active to count immediately after being withdrawn from the reactor, hence the need for a relatively long waiting time. Even so, it is the most abundant isotope in each spectrum and as such contributes to the high Compton background and adversely affects the detection of other isotopes in the lower half of the spectrum. Consequently, a comparison of the spectra may be made by calculating 'advantage factors', (Steinnes, 1971) for all other isotopes detected with respect to $^{28}\text{Al}$.

5.4.1 Advantage factors

The advantage factors are defined here as the ratio of the amount by which the $^{28}\text{Al}$ is suppressed to that of another isotope when comparing two different irradiating fluxes:

$$
F_{Cd} = \frac{(\text{Cadmium Ratio})^{28}\text{Al}}{(\text{Cadmium Ratio})_X}
$$

(5.1)

and

$$
F_{th} = \frac{(\text{Core/Thermal Ratio})^{28}\text{Al}}{(\text{Core/Thermal Ratio})_X}
$$

(5.2)

where $(\text{Cadmium Ratio})_X = \frac{\text{Activity of } X \text{ due to irradiation in core}}{\text{Activity of } X \text{ due to identical irradiation in core under Cd cover}}$

and $(\text{Core/Thermal Ratio})_X = \frac{\text{Activity of } X \text{ due to irradiation in core}}{\text{Activity of } X \text{ due to identical irradiation in thermal facility}}$. 

In practice this means that values of $F_{Cd}$ or $F_{th}$ greater than 1.0 favour irradiations in the core with cadmium shielding and in the thermal facility respectively, as compared with unshielded irradiations. Table (5.2) lists, where possible, advantage factors calculated from the spectra shown in Fig. (5.1).

Table (5.2): Advantage Factors for Soils Irradiated in the Core (± Cd cover) and Thermal Facilities.

<table>
<thead>
<tr>
<th>Isotope</th>
<th>$E_\gamma$ (keV)</th>
<th>$F_{Cd}$</th>
<th>$F_{th}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{169}$Dy</td>
<td>94.6</td>
<td>0.36</td>
<td>1.6</td>
</tr>
<tr>
<td>$^{139}$Ba</td>
<td>165.8</td>
<td>0.57</td>
<td>1.1</td>
</tr>
<tr>
<td>$^{51}$Ti</td>
<td>320.0</td>
<td>0.30</td>
<td>1.2</td>
</tr>
<tr>
<td>$^{80}$Br</td>
<td>617.0</td>
<td>-</td>
<td>0.50</td>
</tr>
<tr>
<td>$^{27}$Mg</td>
<td>1014.1</td>
<td>7.6</td>
<td>0.37</td>
</tr>
<tr>
<td>$^{29}$Al</td>
<td>1273.3</td>
<td>8.8</td>
<td>0.20</td>
</tr>
<tr>
<td>$^{24}$Na</td>
<td>1368.4</td>
<td>0.30</td>
<td>1.1</td>
</tr>
<tr>
<td>$^{52}$V</td>
<td>1434.4</td>
<td>0.24</td>
<td>1.1</td>
</tr>
<tr>
<td>$^{42}$K</td>
<td>1524.5</td>
<td>-</td>
<td>1.3</td>
</tr>
<tr>
<td>$^{28}$Al</td>
<td>1778.9</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>$^{56}$Mn</td>
<td>1810.7</td>
<td>0.56</td>
<td>0.99</td>
</tr>
<tr>
<td>$^{49}$Ca</td>
<td>3083.0</td>
<td>-</td>
<td>0.99</td>
</tr>
</tbody>
</table>

For the majority of isotopes the thermal facility is marginally preferred, except for $^{27}$Mg, $^{29}$Al, and $^{38}$Cl which was only detected in the cadmium shielded sample. $^{29}$Al is produced by a fast neutron reaction from Si, $^{29}$Si(n,p)$^{29}$Al, and so should be enhanced by an epithermal flux.

5.4.2 Interferences

The advantage factors obtained for $^{27}$Mg and $^{38}$Cl were entirely unexpected from simple cross section considerations, but on closer examination
this could be explained by interfering fast neutron reactions from other bulk elements, contributing to the production of these isotopes. Table (5.3) summarises the three isotopes which were found to suffer from interferences due to irradiations in both the core and thermal facilities.

Table (5.3) : Principal Interfering Reactions in a Soil Matrix.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Core irradiation</th>
<th>Thermal irradiation</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^{26}\text{Mg}(n,\gamma))</td>
<td>11.7%</td>
<td>48.0%</td>
</tr>
<tr>
<td>(^{27}\text{Al}(n,p))</td>
<td>87.8%</td>
<td>51.7%</td>
</tr>
<tr>
<td>(^{30}\text{Si}(n,\alpha))</td>
<td>0.5%</td>
<td>0.3%</td>
</tr>
<tr>
<td>(^{27}\text{Al}(n,\gamma))</td>
<td>96.5%</td>
<td>99.5%</td>
</tr>
<tr>
<td>(^{28}\text{Si}(n,p))</td>
<td>3.5%</td>
<td>0.5%</td>
</tr>
<tr>
<td>(^{31}\text{P}\ (n,\alpha))</td>
<td>&lt; 0.01%</td>
<td>&lt; 0.001%</td>
</tr>
<tr>
<td>(^{37}\text{Cl}(n,\gamma))</td>
<td>96.9%</td>
<td>99.5%</td>
</tr>
<tr>
<td>(^{41}\text{K}\ (n,\alpha))</td>
<td>3.1%</td>
<td>0.5%</td>
</tr>
</tbody>
</table>

The relative contributions are calculated on the basis of an average soil composition (Bowen, 1966), and published cross sections (de Soete et al., 1972). Most surprising is that ~ 88% of the \(^{27}\text{Mg}\) photopeak is due to the presence of Al in the soil sample.

Further complementary information may be gained from conventional activation by counting the low energy photons emitted by the sample as shown in Fig. (5.2). This spectrum is the result of an irradiation in the thermal facility with similar timing parameters to those described previously, the sample being counted on the pure Ge detector. Isotopes of 4 extra elements, Co, Nb, Th and U, are present, and although the isotopes
Fig. (5.2) : Low energy photon spectrum of a soil irradiated for 10 mins. in the thermal facility.

of Sm, Eu and Dy were detected previously, the background under each peak is reduced and thus their detection limits improved. Source-detector distance in this case was $\sim 5$ cm.

Cyclic activation, consisting of 30 cycles, each with 5s irradiate and 5s count, combined with the 20 cm$^3$ Ge(Li) detector contributes a further three new elements to the list of those detectable, namely Sc, Se and Hf, as can be seen from Fig. (5.3). Nevertheless, this technique is severely limited, again by the prodigious activity of $^{28}$Al.

5.4.3 Detection limits and statistical precision estimates

To summarise the results obtained from the various irradiation schemes, two quantities have been calculated, namely the minimum detectable quantity of each element and the statistical precision of each isotope signal. The
elemental detection limits are calculated in $\mu g/g$ on a $2/B$ basis for a 200 mg soil sample for the analysis schemes described above, and presented in Table (5.4). Through the use of standards, the interferences have been eliminated where necessary, such that for Mg, Al and Cl, the values quoted are elemental detection limits. Due to the presence of interferences, and also in particular cases e.g. Nb, the lack of a suitable standard, Table (5.5) has been included. This provides an estimate of the statistical precision with which each isotope signal, i.e. photopeak area, may be determined, calculated from $100\sqrt{S + 2B/S\%}$. In this instance the effect of interferences has not been considered, simply the observed photopeak areas; thus Mg is most easily detected in a thermal irradiation, whereas $^{27}$Mg is most precisely determined following an irradiation under cadmium in the core. For both tables, those values enclosed in boxes are the lowest, that is, best results for each element or isotope. These
**Table (5.4): Detection Limits (µg/g)**

<table>
<thead>
<tr>
<th>ELEMENT</th>
<th>THERMAL</th>
<th>CORE</th>
<th>CORE (Cd cover)</th>
<th>THERMAL</th>
<th>CO</th>
<th>THERMAL</th>
<th>CORE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>49.</td>
<td>61.</td>
<td>150.</td>
<td>Co</td>
<td>0.2</td>
<td>Se</td>
<td>0.6</td>
</tr>
<tr>
<td>Mg</td>
<td>540.</td>
<td>780.</td>
<td>1900.</td>
<td>Sm</td>
<td>0.1</td>
<td>Se</td>
<td>0.1</td>
</tr>
<tr>
<td>Al</td>
<td>80.</td>
<td>-</td>
<td>-</td>
<td>Eu</td>
<td>0.06</td>
<td>Hf</td>
<td>0.2</td>
</tr>
<tr>
<td>Si</td>
<td>10.1%</td>
<td>2.3%</td>
<td>0.2%</td>
<td>Dy</td>
<td>0.06</td>
<td>Th</td>
<td>3.4</td>
</tr>
<tr>
<td>Cl</td>
<td>61.</td>
<td>78.</td>
<td>144.</td>
<td>Th</td>
<td>5.4</td>
<td>U</td>
<td>0.1</td>
</tr>
<tr>
<td>K</td>
<td>0.2%</td>
<td>0.3%</td>
<td>0.6%</td>
<td>U</td>
<td>0.1</td>
<td>Th</td>
<td>5.4</td>
</tr>
<tr>
<td>Ca</td>
<td>140.</td>
<td>160.</td>
<td>610.</td>
<td>U</td>
<td>0.1</td>
<td>Th</td>
<td>5.4</td>
</tr>
<tr>
<td>Ti</td>
<td>60.</td>
<td>100.</td>
<td>330.</td>
<td>Th</td>
<td>5.4</td>
<td>U</td>
<td>0.1</td>
</tr>
<tr>
<td>V</td>
<td>1.1</td>
<td>1.6</td>
<td>5.6</td>
<td>Th</td>
<td>5.4</td>
<td>U</td>
<td>0.1</td>
</tr>
<tr>
<td>Mn</td>
<td>1.5</td>
<td>2.3</td>
<td>2.4</td>
<td>Th</td>
<td>5.4</td>
<td>U</td>
<td>0.1</td>
</tr>
<tr>
<td>Br</td>
<td>2.4</td>
<td>4.9</td>
<td>5.2</td>
<td>Th</td>
<td>5.4</td>
<td>U</td>
<td>0.1</td>
</tr>
<tr>
<td>Sr</td>
<td>60.</td>
<td>90.</td>
<td>35.</td>
<td>Th</td>
<td>5.4</td>
<td>U</td>
<td>0.1</td>
</tr>
<tr>
<td>Ba</td>
<td>17.</td>
<td>22.</td>
<td>53.</td>
<td>Th</td>
<td>5.4</td>
<td>U</td>
<td>0.1</td>
</tr>
<tr>
<td>Sm</td>
<td>0.2</td>
<td>0.5</td>
<td>0.1</td>
<td>Th</td>
<td>5.4</td>
<td>U</td>
<td>0.1</td>
</tr>
<tr>
<td>Eu</td>
<td>0.1</td>
<td>0.3</td>
<td>0.5</td>
<td>Th</td>
<td>5.4</td>
<td>U</td>
<td>0.1</td>
</tr>
<tr>
<td>Dy</td>
<td>0.1</td>
<td>0.2</td>
<td>0.4</td>
<td>Th</td>
<td>5.4</td>
<td>U</td>
<td>0.1</td>
</tr>
</tbody>
</table>

**Detection Limit = 2 x \sqrt{Signal Background}**

---

**Table (5.5): Statistical Accuracy of Isotope Signals (%)**

<table>
<thead>
<tr>
<th>ISOTOPE</th>
<th>THERMAL</th>
<th>CORE</th>
<th>CORE (Cd cover)</th>
<th>THERMAL</th>
<th>ISOTOPE</th>
<th>THERMAL</th>
<th>CORE</th>
</tr>
</thead>
<tbody>
<tr>
<td>24Na</td>
<td>1.0</td>
<td>1.2</td>
<td>2.6</td>
<td>27Mg</td>
<td>10.</td>
<td>27Mg</td>
<td>10.</td>
</tr>
<tr>
<td>27Mg</td>
<td>7.8</td>
<td>3.9</td>
<td>0.8</td>
<td>60Co</td>
<td>11.</td>
<td>60Co</td>
<td>11.</td>
</tr>
<tr>
<td>28Al</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>80Br</td>
<td>11.</td>
<td>80Br</td>
<td>11.</td>
</tr>
<tr>
<td>29Al</td>
<td>24.</td>
<td>6.2</td>
<td>1.0</td>
<td>94Nb</td>
<td>15.</td>
<td>94Nb</td>
<td>15.</td>
</tr>
<tr>
<td>38Cl</td>
<td>ND</td>
<td>ND</td>
<td>20.</td>
<td>155Sm</td>
<td>10.</td>
<td>155Sm</td>
<td>10.</td>
</tr>
<tr>
<td>42K</td>
<td>12.</td>
<td>16.</td>
<td>ND</td>
<td>152Eu</td>
<td>12.</td>
<td>152Eu</td>
<td>12.</td>
</tr>
<tr>
<td>49Ca</td>
<td>16.</td>
<td>17.</td>
<td>ND</td>
<td>165Dy</td>
<td>2.3</td>
<td>165Dy</td>
<td>2.3</td>
</tr>
<tr>
<td>51Cr</td>
<td>2.4</td>
<td>3.5</td>
<td>10.</td>
<td>233Th</td>
<td>26.</td>
<td>239U</td>
<td>5.1</td>
</tr>
<tr>
<td>52V</td>
<td>3.7</td>
<td>4.5</td>
<td>15.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>54Mn</td>
<td>2.8</td>
<td>4.3</td>
<td>5.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>80Sr</td>
<td>26.</td>
<td>17.</td>
<td>ND</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>87Sr</td>
<td>ND</td>
<td>ND</td>
<td>38.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>139Ba</td>
<td>7.5</td>
<td>11.</td>
<td>18.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>155Sm</td>
<td>17.</td>
<td>ND</td>
<td>10.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>152Eu</td>
<td>14.</td>
<td>ND</td>
<td>41.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>165Dy</td>
<td>4.9</td>
<td>10.</td>
<td>23.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
results agree well with those of Schock (1977), who, in a comparison of Ge(Li) and Ge detectors in INAA of geological materials, found that in nearly all cases, analyses using the planar Ge detector yielded smaller counting errors for nuclides measurable by both detectors.

5.5 Discussion and Conclusions

Table (5.4) shows that conventional activation in the thermal facility yields best results for 11 elements when combined with the Ge(Li) detector and a further 6 when the Ge low energy photon detector is included. Cadmium shielding for core irradiations is only of advantage for 3 elements, whilst, in general, the detection limits obtained by irradiation in the core without shielding approach those from the thermal facility. This is not entirely surprising since, as mentioned previously, the 0°STF does not possess a well-thermalised neutron energy spectrum although interference effects are beneficially reduced by the use of this facility. With the addition of 3 elements detected through cyclic activation, the total number measurable by these techniques, all of which require no more than 30 minutes experiment time per sample, is brought to 23.

Cyclic activation in conjunction with the pure Ge detector has been investigated principally for the analysis of biological materials (Chapter 3). However, it was found unsuitable for soils principally because the Bremsstrahlung resulting from the production of intense $\beta^-$-emitters contributed to an excessively high background which masked detection of most of the signals.

In conclusion, INAA of soils based on the use of short-lived isotopes is able to detect some 23 different elements by a judicious combination of analytical schemes. The limiting factor for all the schemes employing Ge(Li) detectors would appear to be the sample activity due to the production of $^{28}\text{Al}$,
which, emitting $\gamma$-photons of energy 1778.9 keV, masks a considerable part of the spectrum by its contribution to the Compton continuum. The production of this isotope seems unavoidable, irrespective of the choice of irradiation facility, as it is produced by both neutron capture and threshold reactions (Table (5.3)). Cyclic activation is the technique worst afflicted, and has proven to be only of marginal benefit in the analysis of soils.

The calculation of experimental advantage factors has been shown to provide a good indication of the occurrence of interfering reactions, although their comparison with theoretical predictions is not always possible due to incomplete cross-section data on short-lived isotopes, although some compilations are available (Steinnes, 1971; Van der Linden et al., 1974).

B - Tarraby : an Archaeological Test Case

5.6 Background Introduction

The techniques described above are applicable to the majority of soil types likely to be encountered in an archaeological context. By way of illustration, they have been applied to a particular problem, namely the location of a buried soil.

The problem originated (Keeley, 1975) as a result of construction work on the M5 motorway in Somerset, the progress of which was monitored by a small excavation team in the interest of rescue archaeology. Evidence of archaeological sites was sought by geophysical surveying and also by examination of the continuous ditch sections which were cut parallel to the motorway. During the course of this work, several hedgebanks and the soils which were buried at the time of building (probably Medieval, from documentary evidence), were sectioned. Excavators were interested in
i) establishing if the hedgebanks were built on a full profile or if the soil was truncated (i.e. deturfed) and ii) whether there was any evidence of a second phase of hedge-building, which would be indicated by two buried soils, one below the other.

Unfortunately, it was impossible to tell where the buried surfaces lay. The soils, developed on Keuper Marl whose characteristic dark red colour obscured any visual differences, also provided no environmental evidence, either in the form of snails, or pollen which were not preserved due to the high soil pH. However, the possibility of locating the buried surfaces by variations in concentration of particular elements with depth through the profile was considered, the buried turf-line perhaps being indicated by elements expected to accumulate in topsoil due to recycling by plants (e.g. Mn, Co).

Initial results at this site proved inconclusive and it was therefore decided to repeat the measurements on a profile with a clearly defined buried soil, ideally in an area with similar parent material, with the hope that results from the 'test-case' would aid interpretation of data obtained from other sites. This was not possible as suitable sites are rare. Nevertheless, the DoE Central Excavation Unit revealed very fine examples of buried soils at a section of Hadrians Wall, near Carlisle.

5.7 Site description

The profiles possessing buried soils were located in an area surrounding a ruined section of Hadrians Wall at Tarraby (G.R. 405 576), a plan of which is shown in Fig. (5.4)*. 'The site is within an area of low, rounded hills

* courtesy of the Ancient Monuments Laboratory, Department of the Environment.
situated along the north bank of the lower river Eden. These occupy a central position within the broad vale of the Cumberland lowland which is developed on sedimentary rocks of Permo-Triassic age' (Wilkinson, 1977).

Two specific profiles were sampled and these are indicated on Fig. (5.4) as Sites I and II. Fig. (5.5a) is a schematic diagram of both profiles, indicating the various horizons (component layers of a profile) which are also to be seen in Fig. (5.5b). The profiles were cut through banks which had been built as part of the Roman defence system and thus had buried soils beneath. To mark the Southerly limit of the Hadrians' Wall fortifications, a bank (or vallum) was constructed. Due to erosion and agricultural activities (ploughing, etc.) this now appears only as an undulation in the field but is clearly seen, due to its lighter colour, in the Site I profile with the present topsoil above and the buried soil (very dark horizon) and subsoil below.

A similar fate has befallen the fighting bank which marked the Northern-most military rampart and thus the first line of defence. The Site II profile exposed to a depth of ~120 cm shows this bank in a similar fashion to that of Site I except for the presence of an additional clearly-defined narrow horizon between the buried soil surface and the subsoil which is loosely termed a 'leach' layer due to its very pale colour.

5.8 Sample Preparation

Prior to sampling, each profile was cleaned back with a teflon coated trowel to expose a fresh face which was undisturbed. Sampling of each horizon always commenced with the lowest, to avoid contamination with soil falling from the higher levels. Approximately 1 kg (wet weight) of soil was taken for each sample from the points indicated by the black circles in Fig. (5.5b). At Site I, the profile was exposed to a sufficient width
Fig. (5.5a): Schematic diagram of Sites I and II

Fig. (5.5b): Photographs of Sites I and II
to permit 2 series of samples, spaced ~35 cm apart, to be taken.

Results from these samples should show whether elemental concentrations exhibit large variations horizontally across the feature.

The soils contained significant quantities of water and therefore the first step preparatory to irradiation was drying. Four procedures were investigated, on soils from one sample, with varying degrees of 'hostility' to the sample, as summarised in Table (5.6).

Table (5.6) : Drying procedures

<table>
<thead>
<tr>
<th>Soil wt.</th>
<th>Drying method</th>
<th>Drying temp.</th>
<th>Drying time</th>
<th>Percentage wt. loss</th>
</tr>
</thead>
<tbody>
<tr>
<td>20 g</td>
<td>Freeze-drying</td>
<td>~-60°C</td>
<td>17 h</td>
<td>13.5%</td>
</tr>
<tr>
<td>20 g</td>
<td>Oven</td>
<td>60°C</td>
<td>112 h</td>
<td>12.8%</td>
</tr>
<tr>
<td>10 g</td>
<td>Oven</td>
<td>140°C</td>
<td>2 h</td>
<td>13.1%</td>
</tr>
<tr>
<td>20 g</td>
<td>Oven</td>
<td>500°C</td>
<td>2 h</td>
<td>15.3%</td>
</tr>
</tbody>
</table>

The greater weight loss as a result of oven drying at 500°C is due to ashing of the sample (Allen, 1974). Analyses by INAA ($5.9$), consisting of 10 replicate freeze-dried samples and 2 each from the other procedures, showed no measurable elemental losses through volatilisation from any of the samples, since all measured concentrations lay within ±2 standard deviations of the data obtained from the freeze-drying.

Freeze-drying is the technique usually recommended for biological material (Pillay, 1976; Othman et al., 1978) and was therefore employed in this case. Approximately 20 g of soil was removed from each sample by quartering (Allen, 1974), deep frozen for ~4 hours and freeze-dried for ~17 hours (until constant pressure obtained), all samples being dried simultaneously under the same conditions. The dried samples were then placed in a grinder/homogeniser for ~30s. This operates on the principle
of vibrating the sample container at high frequency whereupon aggregates within the sample break up under their own weight reducing the majority of the soil to a fine thoroughly mixed powder. This powder was passed through a \(\sim 1 \text{ mm}^2\) nylon mesh (Salmon, 1975) to remove coarse debris. Approximately 200 mg quantities were then weighed into polythene capsules ready for irradiation.

5.9 Neutron Activation Analysis

Since the elements which would be of diagnostic value were not known, the choice of analysis scheme was governed to a great extent by the criterion of obtaining the maximum information concerning elemental concentrations with the minimum of analysis time per sample — hence the use of short-lived isotopes. The 'conventional' scheme employed (cyclic analysis having been shown of little benefit) was that described in §5.4, namely \(t_i = t_w = t_c = 600\text{s}\). ICIS was preferred to the thermal facility purely on practical considerations with only marginal sacrifice in detection limits obtainable (Table (5.4)). A reproducible sample — detector distance of \(\sim 24\text{ cm}\) was necessary for both soils and standards, with the advantage that the signal from an irradiated 'blank' container was so small as to be neglected, thus eliminating the need for either blank subtraction or transfer of irradiated samples to new containers. Samples were irradiated in random order, interspersed with standards, to prevent biasing of the analysis.

The 4000 channel spectra, recorded on magnetic tape, were analysed using the SAMPO routine. Since only the relative variations in elemental concentration are of interest, the standards were used simply to monitor the flux between soil irradiations, and results are presented in units of counts/mg for the isotopes detected.
5.10 Results and Discussion of Elemental Analyses

In order to estimate the reproducibility of the measurements within each sample, 10 replicates from the bank (vallum) and buried soil (organic horizon) of Site II were analysed, and these results expressed as percentage deviations ($\Delta$) from the mean ($\bar{x}$) are plotted in histogram form in Fig. (5.6a,b,c) for 13 of the 15 isotopes detected. $\Delta$ is defined by:

$$\Delta = \frac{(x_i - \bar{x})}{\bar{x}} \times 100 \% \quad (5.1)$$

where $x_i$ = concentration of isotope in $i$th replicate sample where $1 \leq i \leq 10$. Concentrations falling below the detection limits have also been indicated, except for $^{38}\text{Cl}$ and $^{49}\text{Ca}$ which were detected in < 50% of the samples and therefore excluded.

The majority of isotopes measured are more narrowly distributed in the buried soil horizon than the bank (perhaps suggesting the bank comprises a disturbed soil?). This is demonstrated particularly clearly by $^{24}\text{Na}$ and $^{28}\text{Al}$; whilst it is noticeable that two of the most abundant elements in the soil, silicon detected through $^{29}\text{Al}$ and potassium show similar distributions in both horizons as might be expected. It should be noted however that the larger spread for some isotopes such as the rare earths is due in part to the statistical error involved in their measurement (Table (5.5)). This is certainly not the case for Mn, suggesting a non-uniform distribution within the soil samples.

Due to the large quantity of data involved, graphical results are only presented for the variations in concentration of 10 elements with depth through the Site II profile, as shown in Fig. (5.7 a,b,c). The isotopes
Fig. (5.6a): Percentage deviations from the mean of $^{24}\text{Na}$, $^{27}\text{Mg}$, $^{28}\text{Al}$ and $^{52}\text{V}$ measured in Site II soils.

Fig. (5.6b): Percentage deviations from the mean of $^{29}\text{Al}$, $^{42}\text{K}$, $^{51}\text{Ti}$, $^{139}\text{Ba}$, $^{152}\text{Eu}$, $^{155}\text{Sm}$ and $^{165}\text{Dy}$ measured in Site II soils.
Fig (5.6c) : Percentage deviations from the mean for $^{80}\text{Br}$ and $^{56}\text{Mn}$ measured in Site II soils

$^{38}\text{Cl}$, $^{40}\text{Ca}$, $^{80}\text{Br}$, $^{152}\text{Eu}^{\text{m}}$ and $^{155}\text{Sm}$ have been specifically excluded since they are present in concentrations very close to the limit of detection and results for them are incomplete. The vertical errors plotted on these results correspond to ± 2 standard deviations (s), as estimated from the replicate samples from the bank and buried soil. These are supplied separately in Table (5.7), expressed as $s/\bar{x}\%$ for both horizons. These values for each isotope embrace not only the elemental variations in concentration within the soil but also the experimental errors associated with the technique ($\sim 1-2\%$) and those incurred in the computer analysis of the spectra ($< 1\% - \sim 15\%$ depending on the peak size).

Although standard deviations were only measured for 2 of the 6 samples from this profile, namely the upper part of the bank and the buried soil, further replicate analyses (2 at each depth) showed that, with the exception
of the bank, the spread in all results could be included within ± 2s of the buried soil data.

Table (5.7): Percentage standard deviations of isotopes measured in soils from Site II.

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Standard deviation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Bank</td>
</tr>
<tr>
<td>24Na</td>
<td>3.8</td>
</tr>
<tr>
<td>27Mg</td>
<td>3.0</td>
</tr>
<tr>
<td>28Al</td>
<td>4.3</td>
</tr>
<tr>
<td>29Al</td>
<td>6.0</td>
</tr>
<tr>
<td>42K</td>
<td>9.1</td>
</tr>
<tr>
<td>51Ti</td>
<td>6.3</td>
</tr>
<tr>
<td>52V</td>
<td>6.6</td>
</tr>
<tr>
<td>56Mn</td>
<td>19.8</td>
</tr>
<tr>
<td>139Ba</td>
<td>13.1</td>
</tr>
<tr>
<td>165Dy</td>
<td>11.6</td>
</tr>
</tbody>
</table>
The behaviour with depth of the 10 elements detected in all the samples falls into two categories.

i) Si, Ti, Ba and Dy concentrations appear approximately constant with depth in the profile.

ii) Na, Al, K, V, Mn and $^{27}$Mg, which comprises to a large extent the Al interference, exhibit a gradual increase in concentration from the topsoil to the bank followed by a sharp fall at the bank/buried soil boundary. Lowest concentrations of these elements are found in the buried soil horizon whilst the subsoil generally has a higher value similar to that of the topsoil. The highest concentrations for all these elements occur in the bank.

Results obtained for the Site I profile are very similar to those of Site II, the same elements behaving in the manner described by the 2 categories above; for this reason, numerical data for Site I have not been included here. Agreement between the two vertical series is generally close, suggesting that these trends extend over a large part of the buried feature. The largest discrepancies occur in the bank (vallum), most especially for Mn (c.f. Fig. (5.7b)).

At both sites, the 3 rare earths measured, Eu, Sm and Dy, are present in the lowest levels in the subsoil. Cl and Ca, although detectable in < 50% of the samples exhibited their own trends, Ca generally being detected only at shallow depths within the profile (topsoil region) whilst Cl only occurred in the subsoil region in detectable quantities.

In addition, a series of measurements specifically designed for the determination of Co was carried out on the soils from the Site II profile.
Co was considered of particular importance (together with Mn) as these elements are micronutrients of great agricultural importance (Hodgson, 1963) and may therefore accumulate in horizons with significant plant activity. Samples were irradiated in the 0°STF (thermal facility) and subsequently counted on the pure Ge detector (§5.4). The results obtained showed Co to behave in an identical manner with the other elements included in category ii) above.

Mitchell (1964), in a very comprehensive discussion of trace elements in soils, states that one of the most important factors governing their distribution in profiles is the effect of drainage, and reports accumulation of elements, especially in soluble form, in the sub-surface layers of poorly-drained soils; a fact also mentioned by Hodgson (1963). Similar results, namely the increased elemental concentrations in the vallum horizon of both profiles have been observed in the Tarraby soils, which are poorly-drained with waterlogging being a common feature (Wilkinson (1977)).

The results obtained for K are in agreement with those of Mattingly and Williams (1962) who have shown that the total K content of a soil buried since Roman times is the same as the surrounding surface soil, thus supporting the archaeological evidence that the buried soil was once exposed at the surface.

The manner in which elements are distributed within a profile is the result of a complex combination of processes. "As rocks weather into soils, the micronutrient elements, like all elemental constituents, are subjected to the leaching waters passing through the soil. Plant roots, absorbing surfaces, and coprecipitating ions compete with the leaching soil solution, with the result that each element, responding to these forces in different ways, becomes distributed in the soil in a characteristic manner". (Hodgson,
1963). Thus any attempt to explain the results presented in this section should comprise to a considerable extent of soil chemistry, which is beyond the scope of this work.

Nevertheless, these results suggest that, for this site in particular, it is possible to locate soil features within a profile by studying the variations in concentration of certain elements, Na, Al, K, V and possibly Mn. Due to the elevated concentrations of these elements, the bank appears easier to identify than the old ground surface which it buries, although the concentration gradient at the interface between these two horizons is very sharp.

5.11 Supplementary Physical and Chemical Analyses

In addition to the elemental analysis, various standard physical and chemical measurements were made on the soils from the Site II profile, the various horizons perhaps being segregated by more characteristics than just their colour (elemental considerations apart).

The simplest of these, loss on ignition measurements, were made by heating ~ 5 g of each (previously freeze-dried) soil in a furnace at 450°C (Allen, 1974) for 22 hours. The samples were then rapidly transferred to the freeze-dryer and allowed to cool under vacuum, to prevent the absorption of moisture. Percentage weight losses as a result of this treatment are given in Table (5.8). Loss on ignition measurements are used as an approximate guide to carbon and organic matter content of soils.

A more accurate estimate of the organic carbon content was obtained (Jones, 1978) by a technique which relies on measuring the quantity of CO₂ released as a result of chemical oxidation of the soil. These values, together with organic matter contents, are also given in Table (5.8).
Table (5.8) : Organic matter and particle size analyses of Site II soils.

<table>
<thead>
<tr>
<th>Horizon</th>
<th>Topsoil</th>
<th>Bank</th>
<th>Buried soil</th>
<th>Subsoil</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample depth (cm)</td>
<td>20-30</td>
<td>50-60</td>
<td>75-84</td>
<td>90-94</td>
</tr>
<tr>
<td>Loss on ignition (%)</td>
<td>5.0</td>
<td>2.8</td>
<td>2.7</td>
<td>3.0</td>
</tr>
<tr>
<td>Organic carbon (%)</td>
<td>2.16</td>
<td>0.45</td>
<td>0.02</td>
<td>0.71</td>
</tr>
<tr>
<td>Organic matter (%)</td>
<td>3.72</td>
<td>0.77</td>
<td>0.03</td>
<td>1.22</td>
</tr>
<tr>
<td>Particle size analyses</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>600 μm - 2 mm (%)</td>
<td>6</td>
<td>9</td>
<td>7</td>
<td>2</td>
</tr>
<tr>
<td>200 μm - 600 μm (%)</td>
<td>17</td>
<td>18</td>
<td>16</td>
<td>11</td>
</tr>
<tr>
<td>60 μm - 200 μm (%)</td>
<td>34</td>
<td>25</td>
<td>25</td>
<td>38</td>
</tr>
<tr>
<td>2 μm - 60 μm (%)</td>
<td>30</td>
<td>31</td>
<td>32</td>
<td>36</td>
</tr>
<tr>
<td>&lt; 2 μm (%)</td>
<td>13</td>
<td>17</td>
<td>20</td>
<td>13</td>
</tr>
</tbody>
</table>

Various factors are used for the conversion of organic carbon to organic matter. The ratio between the two has long been accepted as 1.72 and is based on the assumption that soil organic matter contains 58% carbon (Allen, 1974). The results obtained by loss on ignition are higher than the organic matter estimates because, at the temperature of ashing, some bound water is also lost from the clay minerals in the soil.

These results clearly show the location of the old ground surface, since the organic matter content is much higher than in the neighbouring horizon, although not so high as the present topsoil. This is probably due to several hundreds of years leaching and alternate seasonal wetting and drying having reduced the original organic matter content of the buried soil. The horizon termed the 'leach' layer, 94-99 cm deep, has a very low organic matter content, thus explaining its characteristic pale, sandy colour, whilst the topsoil and buried soil are noticeably the darkest horizons.
Particle size analyses were also performed (Jones, 1978) on the soils from Site II. The methods employed for this purpose are fully described by Shackley (1975) and are based on a combination of dry and wet sieving for particles larger than 60 μm and sedimentation for the smaller size fractions. The particle size distributions are also included in Table (5.8). Fig. (5.8) shows the particle size classes defined by the Soil Survey of England and Wales (Hodgson et al., 1976) with groupings based on the proportions of sand, silt and clay size grades. The 6 samples are marked on this diagram, lying closely together on the sandy loam/clay loam boundary, from which it may be seen that the various Site II horizons cannot be distinguished. However, inspection of Table (5.8) shows that the bank horizon has a proportionately higher clay content than the other horizons.

This is not entirely a surprising result since the concentrations of such elements as Co (Kubota, 1972), and a number of other trace elements including V (Le Riche and Weir, 1963) appear to be associated with the clay content of the soil, their concentrations being higher than in the sand or silt fractions, a fact also noted by other reviewing authors (Hodgson, 1963; Mitchell, 1964). This is reflected in the results obtained for Co and V from Site II. In contradiction, Le Riche and Weir found that the elements Ti, Sr and Ba showed little variation in concentration between the sand/silt/clay fractions; again in complete agreement with the Ti and Ba results from Site II. It is also perhaps interesting to note that the mineral components in soils may be divided into 2 classes, primary and secondary. Primary minerals are derived from rock and are usually almost all to be found in the coarser particle size grades, whereas secondary minerals, formed by interaction of primary minerals and the soil solution, are almost entirely confined to the clay grade (Limbrey, 1975). Thus it would appear to be the secondary minerals which are richer in the elements measured in this study.
Fig. (5.8): Particle size classification (Hodgson et al., 1976) of Site II soils; topsoil (1), bank (2,3), buried soil (4), leached soil (5) and subsoil (6).

5.12 Cluster Analysis of Tarraby Data

Typical of any multielemental analysis of a large number of samples is an $m \times n$ results table, where $m$ is the number of elements determined in $n$ samples. Various approaches may be adopted to its interpretation. Graphs may be plotted, as in Figs. (5.7a,b,c), of individual elemental variations between samples, which are ideal when $m$ and $n$ are small. However, if, as is generally the case with INAA, the number of elements determined is large ($m \geq 10$, say), and the same is true for the number of samples analysed ($n \geq 10$), then interpretation of the results by inspection or simple graph plotting becomes a tedious, even bewildering, task. Multivariate data analysis methods are therefore required, which will reduce this $m \times n$ matrix to an easily assimilable
form, by revealing its structure without any unacceptable distortion or loss of information. One such non-statistical technique, which finds its origins in biological science, is that of cluster analysis. A comprehensive review of the applications of this classification method to activation analysis data in archaeology is given by Harbottle (1976). There exist a large number of permutations of the technique discussed in detail in that review and even more fully by Sneath and Sokal (1973). The particular technique described in Appendix III is after Davis (1973), whose computer program CLUSTR was implemented and modified to perform cluster analysis on the Tarraby data.

Although classification of the Tarraby soil samples, according to site and horizon of origin, is known, cluster analysis has been performed on the samples (objects), characterised by their elemental compositions (attributes), for two reasons. Firstly, since the Tarraby site has been used as a test-case for the location of buried soils, the well-documented data is ideally suited to assess the performance of the cluster analysis technique together with choice of similarity coefficient and form of input data to obtain the best classification of soils e.g. from a profile with indistinguishable horizons. Secondly, the results of the clustering may enable further interpretation of the data.

Therefore, the results from both Sites I and II including replicate analyses, a total of 47 samples, each characterised by 10 elemental concentrations, were combined in a random fashion and subjected to WPGMA clustering (Appendix III). Dendrograms were obtained for clustering performed using the Mean Euclidean Distance applied to the raw, standardised and logarithmic data, and also using the Correlation Coefficient applied to the raw and standardised data. The characteristics of the dendrogram are summarised below, according to similarity coefficient and form of input data.
a) Mean Euclidean Distance

i) **Raw data.** Two principal clusters are evident, one consisting of the buried bank samples from both sites, whilst the other encloses the remainder of the samples with no strong classification according to horizon or site. Thus this clustering procedure tends to emphasise those samples which are very different to the majority, a feature also noted by Davis (1973).

ii) **Standardised data.** The dendrogram obtained is shown in Fig. (5.9). This method provides the best classification of the Tarraby data. Again, two principal clusters are evident, one of which comprises the buried bank samples from both sites (except for 2 topsoil samples located directly above the Site I bank). The other main cluster is subdivided into buried soil, topsoil and 2 separate subsoil groups. The 10 replicate samples from 2 Site II horizons form tight clusters within the main divisions, whilst there is even some indication of differentiation between the 2 sites. Thus standardisation appears to emphasise the more subtle variations within the data in this instance.

iii) **Logarithmic data.** No distinct classification is apparent, except possibly the topsoil. Many samples, even from the replicate analyses are misclassified.

b) Correlation Coefficient

i) **Raw data.** Since the data matrix is unstandardised, all the $r_{ab}$ values are $\geq 0.988$ resulting in a 'compressed' dendro-
Fig(5.9) : Dendrogram resulting from WPGMA cluster analysis performed on standardised data, using Mean Euclidean Distance ($d_{a,b}$) as similarity coefficient.
gram. However, with the exception of 4 samples, this method provides complete segregation between Sites I and II as can be seen from Fig. (5.10). Within the Site II cluster, the buried soils are particularly well classified, although, in general, this method does not resolve the individual horizons with any degree of success.

ii) **Standardised data.** This method results in very straggled, loosely bound clusters with several examples of mis-classification.

Thus, it can be seen from these results that the quality and type of classification is extremely dependent on the similarity coefficient, the form in which the data is supplied, and, although not demonstrated here, the clustering method used. For the location of particular soil horizons, the subject of this test-case, the Mean Euclidean Distance calculated on standardised data provides the best results. It is worth noting that when this method was applied to the data for only 8 elements (with the omission of Mn and Dy), the bank could still be identified but several other samples were mis-classified. This is a demonstration of Sneath and Sokal's (1973) first principle of Numerical Taxonomy: "The greater the content of information in the taxa of a classification and the more characters on which it is based, the better a given classification will be". Thus an NAA scheme designed to yield results suitable for cluster analysis should aim for as many elements as possible.

5.13 **Conclusions**

Measurement of the distribution of elements throughout a soil profile has been used to locate a buried soil horizon in two separate profiles at Tarraby, Carlisle. The results for 10 elements have been compared with the
Fig (5.10) : Dendrogram resulting from WPGMA cluster analysis performed on raw data, using Correlation Coefficient ($r_{a,b}$) for similarities.
organic matter contents and particle size distributions throughout one profile to provide an indication of some of the processes affecting the elemental distributions. The buried soil is lower in organic matter content than the present soil, probably as a result of leaching during the hundreds of years of burial, but possibly as a result of de-turfing practiced by the Romans who used the turves to reinforce their banks (Webster, 1965). Also, those elements expected to be accumulated by plants are conspicuously absent.

The mechanical translocation of clay, cited by Mitchell (1964) as one of the chief factors involved in the profile differentiation of trace elements, appears to influence the results of this study. The bank horizon is richer in clay particles than any other horizon, and also in the elements Na, Al, K, V and Mn, although other factors, such as waterlogging must certainly be considered to have played a part.

During the process of construction of a defensive ditch, the spoil from the ditch was usually used to build the associated bank, or rampart, (Webster, 1965). Thus the composition (elemental, organic, particle size) of the buried bank at Tarraby might be expected to be similar to the subsoil - a result definitely not obtained. Cluster analysis shows the buried bank to be the most easily distinguishable of all the horizons due to its differences in elemental composition, whilst all corresponding horizons appear very similar between profiles at locations several hundred metres apart.

In conclusion, therefore, these results suggest that, for this site in particular, it is possible to locate soil features within a profile by studying elemental distributions. NAA, as performed here, although more elaborate than the organic matter or particle size analyses, provides a
much more conclusive segregation of the various horizons, especially when used in conjunction with cluster analysis methods. As a refinement for future use, the elemental contents of separate particle size fractions (particularly < 2 μm fraction) may provide an even clearer picture of the horizons within a soil profile.
6.1 Introduction: The Dating of Fossil Bone

The relics of early life and of evolutionary progress are inherited in several forms, one of the most important being bone which may have survived thousands and even millions of years of burial. It is the discovery of fragments of human skeletons that has enabled palaeontologists and anthropologists to trace the development of man from his primitive origins. Needless to say, the accurate dating of bone is essential in the understanding of its significance, and is a problem to which scientists and archaeologists have addressed themselves for hundreds of years.

Apart from radiocarbon dating, there exists no recognised, reliable method for the absolute dating of ancient bones per se. (Note: absolute dating implies assigning an age to an object, e.g. in years Before Present, BP, whilst relative dating may locate an object within a chronological sequence of other objects, of which the absolute ages are unknown). This technique is well-suited to the dating of bones for the period 50,000 BP to the present day (Tite, 1972), but suffers from the disadvantage that, the older the bone, the less associated organic material remaining and therefore the larger the bone sample required to yield the amount of carbon necessary for analysis. Thus, for a unique and particularly ancient find, the situation might arise in which the whole bone is destroyed in the process of dating it! Clearly, there exists a need for additional methods of dating to supplement that of radiocarbon.
Several alternative dating techniques have been postulated which are related to the complex chemical and physical alteration processes which a bone undergoes after burial. These techniques rely on the progressive accumulation or depletion of substances, which are either present in normal bone, or foreign to it, as a function of time. Cook (1960) has extensively reviewed the dating of prehistoric bone by chemical analysis, and the following paragraphs summarise the various methods.

The composition of bones can be divided into two components, organic and inorganic. The disappearance of a variety of organic substances, such as fat, citric acid (necessary for the mineralisation of bone in vivo), organic carbon (related to the total organic content, i.e. fat, protein and carbohydrate), nitrogen (due to bone protein) and amino acids (components of the protein) have been investigated for the purposes of dating.

Fat and citric acid disappear rapidly (≈ few hundred years) after burial whilst the bone protein (collagen) persists for much longer periods of time. Indeed, Cook reports that collagen fibres have been demonstrated with the electron microscope in bone from Neanderthal man (≈ 35-85,000 years old), although chemical assay of much more recent bones (14,000 years old) suggests that the proteinaceous material has almost completely disappeared and that only the collagen structure is retained as part of the process of fossilisation (Race et al., 1968). Ezra and Cook (1957) draw the conclusion that decomposition of protein proceeds extremely slowly over many thousands of years but tends to release in the process certain amino acids while retaining others with great tenacity.

Thus the measurement principally of nitrogen, of which there is 4-5% in fresh bone, provides a useful guide to the relative antiquity of a bone.
(Oakley, 1963); relative because the rate of decline depends on the physical, chemical and bacteriological conditions of interment. Due to the minute quantities of protein remaining, Cook considers the determination of organic matter by total nitrogen can be of real use no further back than the upper Pleistocene period (≈ 25,000 years BP).

The inorganic component of bone, including dental enamel and dentine, consists of a calcium carbonate-phosphate containing much smaller, but measurable quantities of water and a variety of minor and trace elements. This bone mineral exists in a single crystalline phase of carbonate-hydroxyapatite (McConnell, 1962). Fossilisation involves the chemical alteration of bone mineral by a variety of complex processes which may result in changes in the content of carbon dioxide, chemically combined water, or the major or minor constituent elements, including the possibility of absorption of elements foreign to bone. Thus the complexity of the interactions that a bone undergoes during burial cannot be expressed as a simple, unitary, recognisable process, which prompts Cook to state, "A universal dating system based upon the normally occurring inorganic constituents of bone is a priori impossible. It is only when we encounter a completely foreign element which may quantitatively unite with hydroxyapatite that we have the potentiality for a valid dating system. Such an element is fluorine, and to it considerable attention must be devoted".

One of the earliest analyses of fluorine in fossil bones for the purposes of dating was reported by Middleton (1844) to the Geological Society of London. The element fluorine occurs in most percolating ground water, from which it is absorbed by bone as the anion F⁻ by exchange with the hydroxyl (OH⁻) ion in the apatite lattice, thus gradually converting hydroxyapatite to fluorapatite. The amount of fluorine increases with geological age, from ≈ 1500 µg/g in fresh mammalian bone (Bowen, 1966) up to a theoretical maximum of 3.77% F by weight for fluorapatite. For example, the fluorine
content of certain American Miocene (~7-26 million years old) bones has been reported as ~3% (Parker et al., 1974). The rate of accumulation of fluorine in bone varies from site to site, but depends on the fluoride concentration in the ground water, the surrounding soil type including the presence of any inhibiting or facilitating agents, climate and hydrological conditions, and finally the penetrability of the bone. Due to these factors, fluorine analysis can only be regarded as a relative dating technique. Cook also mentions that chlorine, as well as fluorine may be absorbed in the crystal lattice by a similar substitution for the hydroxyl ion, fluorine absorption predominating in acidic rocks, whereas that of chlorine predominating in basic rocks.

In addition, uranium, also from the ground water, may be accumulated by bone through a substitution reaction with calcium, its absorption rate being governed by similar factors to those of fluorine, enabling its potential use as a dating method (Baud, 1960; Seitz and Taylor, 1974; Hamaguchi et al., 1975). Thus the conditions of burial are of extreme importance (Groff, 1971), and even the depth within the soil, since elemental concentrations can vary markedly, as demonstrated in Chapter 5.

For a particular bone-bearing deposit, the rate of accumulation of fluorine will depend on the type of bone, i.e. whether it is compact or spongy (cancellous), the absorption rate being slightly higher in the latter type, due to its greater porosity. Compact bone and dentine have similar absorption rates whilst that of enamel is much slower. Parker et al. (1974) found fluorine levels in enamel to be as much as 4-5 times lower than in bone/dentine, and explained this in terms of their differing microstructures. Crystal size in enamel is ~200 time larger than bone/dentine and therefore the smaller surface area per unit crystal volume together with longer diffusion distances from the crystal boundaries results in slower absorption
rates for fluorine into enamel. Consequently, the fluorine method should only be applied for the relative dating of bones, selected, where possible, for their similar structure.

The question: 'What time interval is adequate to allow differentiation by fluorine analysis?' has been answered by Oakley (1963). In Britain the method would be suitable for clearly differentiating between modern (~100 years BP), Bronze Age (~4200-2700 years BP) and Pleistocene (2.5 million-10,000 years BP) material, but the fluorine content is a series of Bronze age and Saxon (~4th-9th Century AD) bones may well overlap. In general terms, the usefulness of the method is limited to distinguishing modern from prehistoric, pre- or protohistoric from Pleistocene, and Late Pleistocene from Early Pleistocene or Tertiary (>7 million years BP) bones (Oakley, 1963).

Perhaps the most widely publicised application of this technique was in exposing the supposedly Pleistocene fossil fragments of 'Piltdown Man' as being fakes, and of modern origin. The jawbone was found to contain <0.03% F (Hoskins and Fryd, 1955) compared with 2.7% F in an elephant molar also fraudulently 'found' at the same site but certainly dating from Pleistocene times (Tite, 1972).

Cook (1960) in the summary of his review makes two generalisations:

1) "There exist in fossil bone a number of substances, the removal or accumulation of which follow a well-established secular trend. Ideally these would furnish a battery of dating indices. However, in practice, each such index must be treated on a statistical basis, leaving partially unsolved the problem of the date of the individual bone".
2) "The errors introduced by apparently random variation can be reduced and the indices systematised only if the quantities of substance found in the bone be adjusted to conform with the environmental soil conditions which regulate rates of decomposition. We are at present at an impasse. A real breakthrough can occur only as a result of renewed study of the chemistry and physics of soil and fossilisation."

More recent literature on the chemical composition of fossil bones has considered in detail the effects of climate (Rottlander, 1976; Buczko and Vas, 1977) the penetrability of elements in bone (Farquhar et al., 1978), and the contaminating influence of the soil (Blotcky et al., 1978) on a multi-elemental basis. Eisenbarth and Hille (1977) have described a dating technique for fossil bones, capable of both relative and absolute results, based on measured elemental ratios. The ratios N/F, P/Ca and N/Ca, measured on bones recovered from a variety of locations in Lower Austria with ages lying in the approximate ranges of $10^3$-$10^6$ years old, were found to be strongly correlated, in a linear sense, with age. The ratio P/Ca was found to be almost constant, independent of age as might be expected, since these two elements are major components of the bone mineral. These results demonstrate that for the restricted area of Lower Austria, it may now be possible to estimate the absolute ages of fossil bones with reasonable accuracy by a modified version of the fluorine method.

The use of elemental ratios, rather than concentrations (e.g. in μg/g or % by weight) has been advocated by other authors (Cook, 1960; Oakley, 1963) since the degradation processes result in a change (usually a reduction) in bone density. This may be overcome by expressing the fluorine content of a bone with respect to some quantity (usually $P_2O_5$) which is directly related to the apatite. In theory, this value should be independent of the
bone density and also the relative apatite content of the specimen, since even partial destruction of the apatite should not affect the fluorine/phosphate ratio of the remainder although the occurrences of carbonate-phosphate substitution reactions during burial may invalidate this (McConnell, 1962). Alternatively, X-ray diffraction measurements have shown a gradual change in the unit cell dimensions as crystalline hydroxyapatite changes to fluorapatite (Niggli et al., 1953), thus relating fluorine to the bone mineral and also eliminating the need for chemical analysis.

McConnell (1962), however, expresses grave doubts about the validity of this method, since variations in the unit cell dimensions may also be the result of variations in the carbonate or chlorine content of the bone mineral, "which are of such a nature as to make any correlations between the ages of the fossils and the X-ray diffraction measurements quite fortuitous"!

Clearly, therefore, any analytical technique of potential use for the dating of fossil bone by the fluorine method should ideally fulfil a number of requirements, namely:

1) Capable of detecting fluorine with high precision (<\~5%, say) at concentrations > ~ 1500 µg/g of bone

2) Capable of multi-elemental determinations, enabling the estimation of elemental ratios (e.g. F/Ca, N/P etc.)

3) Applicable to very small samples (< 100 mg, say), since large quantities of fossil bone are generally not available for analysis

4) Rapid, permitting the economical analysis of statistically significant numbers of samples
5) Non-destructive, such that fragments of unique specimens may be replaced after analysis.

The suitability of INAA to fulfill these criteria is investigated in the following sections, specifically for the analysis of fluorine in bone.

6.1.1 Fluorine in the environment

The behaviour of fluorine, the most electronegative and reactive of all elements (Valkovic, 1975), in relation to the environment has been extensively reviewed by Hodge and Smith (1972), Bowen (1977) and Marier (1977). The 13th most abundant element in the earth's crust, it has only fairly recently been proven essential for animal life (Schwarz and Milne, 1972). It is an avid bone seeker, 99% of the human body burden comprising skeletal fluoride (Hodge and Smith, 1972). Fluoride intake is rapidly and efficiently transported by blood from whence it is removed by bone ($\tau_{\text{biol}} \sim 30 \text{ min}$) or excreted via the kidneys ($\tau_{\text{biol}} \sim 2-3 \text{ hrs.}$).

Exposure to low levels of fluorine has a beneficial effect on the reduction of dental caries (WHO, 1970) and a lowering of the incidence of osteoporosis in the elderly (Bernstein et al., 1966) whilst no significant increase in the occurrence of cancer has been reported (Kinlen, 1975). However, heavily fluoridated drinking water (2-8 ppm F) produces mottled dental enamel and large repeated doses of a fluorine (20-80 mg daily) can lead to crippling fluorosis over a period of years (Hodge and Smith, 1972).

The principal industrial sources of atmospheric fluorine are associated with the production of bricks, ceramics, aluminium, the processing of rock phosphate fertilisers and the burning of coal. Concentration ranges of fluorine in polluted air have been reported (Bowen, 1966; Dams et al., 1975) as 0.01-1.8 $\mu$g F.m$^{-3}$. 
The literature contains many references to the measurement of fluorine using a variety of nuclear techniques most of which are fast and non-destructive. Nuclear reactions are preferable to X-ray excitations for a low-Z element such as fluorine, since the characteristic X-rays (~680 eV) are strongly absorbed. Charged particle analyses of fluorine have been performed using a variety of reactions (Englemann, 1971; Lee et al., 1971; Ahlberg et al., 1975; Deconninck et al., 1976; Giles and Peisach, 1976; Boulton and Ewan, 1977). The cross-section of these reactions often exhibit sharp resonances, enabling accurate depth distribution measurements, but for the same reason they are not suitable for the bulk analysis of a sample.

Photon activation analysis has also been applied (Hislop and Williams, 1970; Englemann and Scherle, 1970) via the $^{19}\text{F}(\gamma,n)^{18}\text{F}$ and $^{19}\text{F}(\gamma,2p)^{17}\text{N}$ reactions, respectively. However, radiochemical separation is necessary in the first instance to eliminate other interfering $\beta^+$-emitters; whilst in the second case, the counting of delayed neutrons emitted by $^{17}\text{N}$ suffers from interference due to the competing reaction $^{18}\text{O}(\gamma,p)^{17}\text{N}$, a serious problem in a biological matrix.

Neutron activation analysis provides the possibility of a rapid, non-destructive, multi-elemental, bulk analysis technique with sensitivity for fluorine approaching that of the techniques described above. The possible reactions which fluorine may undergo, upon irradiation by neutrons, are summarised in Table (6.1), together with the principal interfering reactions. Also included are the relevant physical and nuclear data, namely target isotopic abundance, activation cross-section ($\sigma_0$ or $\bar{\sigma}$ depending on whether a thermal or fast neutron reaction, cf §1.3.1), product half-life, threshold energy, $E_T$ (Eq. (1.4), §1.2.2) and most intense $\gamma$-ray emitted by
the product isotope. The \((n,p)\), \((n,\alpha)\) and \((n,2n)\) reactions have been used with accelerator neutron sources (Weber and Guillaume, 1970; Bibby and Guinn, 1976; England et al., 1968; Eisenbarth and Hille, 1977) and epi-cadmium reactor neutrons (Dams et al., 1975; Henkelmann et al., 1969) for the determination of fluorine, but for a reactor neutron spectrum, the \(^{19}\text{F}(n,\gamma)^{20}\text{F}\) reaction offers the best sensitivity, although interfering fast reactions must be taken into account.

Table (6.1): Possible neutron induced reactions for the determination of fluorine together with principal interfering reactions.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Target isotopic abundance(^a), %</th>
<th>Activation cross-section(^c), mb</th>
<th>Product half-life(^b), (\text{sec})</th>
<th>E(^c) T, MeV</th>
<th>Most intense (\gamma)-ray(^a), MeV (intensity)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^{19}\text{F}(n,\gamma)^{20}\text{F})</td>
<td>100.</td>
<td>9.8</td>
<td>10.6s</td>
<td>1.63</td>
<td>1.63 (100%)</td>
</tr>
<tr>
<td>(^{20}\text{Ne}(n,p)^{20}\text{F})</td>
<td>90.92</td>
<td>0.08</td>
<td></td>
<td>6.56</td>
<td></td>
</tr>
<tr>
<td>(^{23}\text{Na}(n,\alpha)^{20}\text{F})</td>
<td>100.</td>
<td>0.8</td>
<td></td>
<td>4.03</td>
<td></td>
</tr>
<tr>
<td>(^{19}\text{F}(n,p)^{19}\text{O})</td>
<td>100.</td>
<td>1.4</td>
<td>27.2s</td>
<td>4.25</td>
<td>0.197 (97%)</td>
</tr>
<tr>
<td>(^{18}\text{O}(n,\gamma)^{19}\text{O})</td>
<td>0.204</td>
<td>0.2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(^{19}\text{F}(n,\alpha)^{16}\text{N})</td>
<td>100.</td>
<td>7.9</td>
<td>7.1s</td>
<td>1.60</td>
<td>6.13 (69%)</td>
</tr>
<tr>
<td>(^{15}\text{N}(n,\gamma)^{16}\text{N})</td>
<td>0.365</td>
<td>24.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(^{16}\text{O}(n,p)^{16}\text{N})</td>
<td>99.759</td>
<td>0.02</td>
<td></td>
<td>10.24</td>
<td></td>
</tr>
<tr>
<td>(^{19}\text{F}(n,2n)^{18}\text{F})</td>
<td>100.</td>
<td>0.007</td>
<td>109.8(^a) min</td>
<td>10.98</td>
<td>(\gamma^+) 0.511 (194%)</td>
</tr>
</tbody>
</table>

References:  
\(^a\) Lederer et al., (1968)  
\(^b\) Bode et al., (1975)  
\(^c\) IAEA (1974)
In a typical biological matrix, the sodium interference is the only one of importance. Several measurements have been made using the \((n, \gamma)\) reaction (Dams et al., 1975; Henkelmann et al., 1969; Miller and Guinn, 1976) and some with specific application to bone and teeth (De Aisenberg et al., 1973; Behne et al. 1976; Tomura and Ohta, 1976; Brätter et al., 1977; Mernagh et al., 1977). In each case, measurements were based on a single irradiate-wait-count sequence (no radiochemical separation being possible due to the short half-life of \(^{20}\text{F}\)). The following sections investigate the improvement in sensitivity and detection limits for fluorine in bone, and other biological matrices, by employing CNAA.

6.2.1 Standards and samples

The problems involved in the choice of a suitable fluorine standard for activation analysis have been discussed by Mitchell et al. (1975) who found that the most suitable fluorides were those of lithium, sodium, magnesium and calcium. Upon irradiation, the unwanted background activities of \(^{24}\text{Na}, ^{27}\text{Mg}\) and \(^{49}\text{Ca}\) are easily produced making their use undesirable. Lithium fluoride was thus employed, the possibility of neutron self-shielding due to the high resonant cross-section for the reaction \(6^\text{Li}(n,\alpha)^3\text{H}\) being considered negligible under the experimental conditions employed. Sixteen standards were prepared (2 \(\mu\)g \(\leq \) F \(\leq\) 240 \(\mu\)g) by dissolving the lithium fluoride (99.5% pure) in demineralised water, micropipetting aliquots of this solution onto filter discs in polythene irradiation capsules, which were then oven dried at \(\sim\) 50°C.

Sodium standards were also prepared (3.7 mg \(\leq\) Na \(\leq\) 7.3 mg) from weighed quantities of Analar, anhydrous sodium sulphate to determine the extent of the interference from the \((n,\alpha)\) reaction. In order to evaluate the techniques, not only for bone, but also a variety of other biological materials, samples
were prepared from a number of Standard Reference Materials (SRM's): IAEA Calcined Bone (~ 100 mg), IAEA Animal Muscle (~ 200 mg), NBS Bovine Liver (~ 200 mg), NBS Orchard Leaves (~ 150 mg) and Boven's Kale (~ 150 mg). It is interesting to note that the fluorine content is not certified for any of these materials. Blanks, i.e. capsules with and without filter paper (Whatman 1) were also prepared. The use of SRM's, which are in powder form, overcame the problem of obtaining a homogeneous sample, representative of the parent material; a problem which is particularly acute for bone (Iyengar, 1976).

6.2.2 Irradiation and counting

The cyclic activation timing parameters were optimised for fluorine ($\tau_\frac{1}{2} = 11s$) in the presence of an interfering background activity due to $^{28}\text{Al}$ ($\tau_\frac{1}{2} = 2.3 \text{ min}$), produced principally by the $(n,\alpha)$ reaction from $^{31}\text{P}$. For a waiting time, $t_w$, of 1s, Fig. (2.7) shows the optimum cycle period, $\xi_0 \tau_\frac{1}{2}$, to be $2 \tau_\frac{1}{2} = 22s$. A total experiment time, $t_e$, of ~300s was chosen as a suitable compromise between sensitivity achievable and analysis time per sample. Thus the cyclic period was subdivided in the manner shown by Fig. (6.1).

![Figure 6.1: Subdivision of the cycling period](image-url)
The samples, contained in polyethylene rabbits, were irradiated in the ICIS facility (§3.2) and counted by a 20 cm$^3$ Quartz and Silice Ge(Li) detector of 2.55 keV resolution at 1332.4 keV, located directly above the reactor, as shown in Figs. (3.2a) and (3.3a). The efficiency of this detector as a function of energy has been accurately measured by Egan (1977). The spectroscopy system was completed by a Canberra 1412 Research Amplifier and the Laben 8000 series MCA. Timing synchronisation between the sample arriving at the detector and the MCA commencing to count was achieved by the use of an electronic 'start' pulse. This pulse, which also opens the 'transfer-out' valve of the ICIS pneumatic system, triggered a Harwell 2000 series scaler/timer (acting as a timing delay-variable in multiples of 1s) which, having completed its preset counting time (in this instance, set as 1s to eliminate the chance of sample bounce at the stop-pin) in turn started the MCA to count. This system was also used to achieve the timing conditions described in §3.5.

6.2.3 Dead-time and pulse pile-up correction

Cyclic activation is usually employed for the determination of short-lived isotopes in a matrix of longer-lived products, therefore the activity of a sample may change considerably during a counting period as short-lived isotopes decay (Miller and Guinn, 1976) but will also increase from cycle to cycle as the matrix activity due to the longer-lived products increases. This is shown schematically in Fig. (2.1), the sample activity being reflected by the analyser dead-time. The problems of correction for rapidly changing detection system dead-times as well as the high dead-times encountered with biological samples of a representative mass and the associated losses due to pulse pile-up have been reviewed by Egan (1977) with reference to CNAA. A satisfactory technique which overcomes these problems
accumulating and processing the $\gamma$-ray spectra in a number of steps, as follows:

a) A pulser of constant frequency ($\sim 75$ Hz) was introduced into the spectrometer system as indicated in Fig. (1.4). The pulse amplitude was adjusted to avoid interference with photopeaks in the spectrum obtained.

b) Individual spectra were accumulated for each of the 14 cycles. At the end of each counting period, the spectrum was written onto magnetic tape and the analyser memory erased prior to the next counting period.

c) As the first stage in processing the data, each spectrum was individually corrected for dead-time by multiplying the contents of each channel by the clock time/live time ratio obtained from the MCA clocks (and recorded in channels 0 and 1 of the spectrum). The approximation of a constant fractional dead-time during each counting period ($d_1$, $d_2$, etc. in Fig. (2.1)) was found to be satisfactory for all the materials analysed in this study. In exceptional circumstances where large quantities of a very short-lived isotope are produced (e.g. $^{38}$Cl (\(t_\frac{1}{2} = 0.7\text{s}\)) in blood) an extended waiting period, $t_w$, may be necessary to allow this isotope to partially decay before commencing counting.

d) The 14 spectra for each sample were added together.

e) The photopeak areas, together with the pulser peak area, were determined on the cumulative spectrum by the SAMPO program.

f) Pulse pile-up losses were corrected for, by reference to a pulser peak acquired with $\sim 0\%$ dead-time. The correction factor, $F_p$, applied to
The use of a constant frequency pulser was considered to be adequate under the dead-time conditions described above.

6.3 Results

Fig. (6.2) shows the calibration curve obtained from the lithium fluoride standards, the area counts referring to the area under the 1633.1 keV $^{20}\text{F}$ photopeak. The broken line shows the same curve without pulse pile-up correction, indicating the need for this correction factor at higher counting rates. Fluorine and sodium were not detectable in any of the blanks, therefore eliminating the need for blank subtractions. Errors plotted on the figure range from 1% - 16% for the photopeak area counts, and from 1% - 13% for the mass of fluorine present; the larger errors in the latter case being due principally to measurement uncertainties whilst using the 10 ul micro-pipette.

A linear least-squares fit was performed on this data to obtain the gradient: $33.4 \pm 0.2$ counts/µg F.

Analysis of the sodium standard spectra provided values for the ratios

$$r_{\text{Na}} = \frac{n_F}{n_{\text{Na}}} \quad (6.2a) \quad \text{and} \quad r_{\text{Ne}} = \frac{n_F}{n_{\text{Ne}}} \quad (6.2b)$$

where $n_F$ - photopeak area of 1633.1 keV $^{20}\text{F}$ $^{23}\text{Na}(n,\alpha)^{20}\text{F}$;

$n_{\text{Na}}$ - photopeak area of 1368.4 keV $^{24}\text{Na}[^{23}\text{Na}(n,\gamma)^{24}\text{Na}]$;

$n_{\text{Ne}}$ - photopeak area of 440.0 keV $^{23}\text{Ne}[^{23}\text{Na}(n,p)^{23}\text{Ne}]$.

These ratios are a measure of the sodium interference in the absence of fluorine, 1 µg of sodium appearing as equivalent to $\sim 27$ µg of fluorine.
Fig. (6.2) : Fluorine calibration graph

Fig. (6.3) shows a typical spectrum from a sample of the IAEA Calcined Bone. This spectrum covers the energy range 0-2 MeV, and was obtained using only half of the 4096 channel memory of the Laben MCA, to reduce the dead-time. It was subsequently found that little advantage was to be gained by this procedure, and later spectra were recorded for the energy range 0-4 MeV.

Results obtained from the IAEA Calcined Bone samples were corrected for the sodium interference using the ratios defined above in the following manner:

\[ C_{Na} = \left( n_F^I - r_{NaNa} n_{Na} \right) \]  \hspace{1cm} (6.3a)

and

\[ C_{Ne} = \left( n_F^I - r_{NeNe} n_{Ne} \right) \]  \hspace{1cm} (6.3b)

where

- \( C_{Na} \) - photopeak area of 1633.1 keV \(^{20}F\), interference corrected using \( r_{Na} \);
- \( C_{Ne} \) - photopeak area of 1633.1 keV \(^{20}F\), interference corrected using \( r_{Ne} \);
- \( n_F^I, n_{Na}, n_{Ne} \) - refer to photopeak areas in the sample spectrum.
Fig. (6.3) : Typical cumulative spectrum (0-2 MeV) of an IAEA Calcined Bone sample.

Within statistical and experimental errors, $C_{Na}$ and $C_{Ne}$ are identical and, since $n_{Na}^1$ and $n_{Ne}^1$ were measurable with similar precision, the best value for the $^{20}$F photopeak area, $C$, was taken as:

$$C = \frac{C_{Na} + C_{Ne}}{2}$$

Results for $C$, from 5 replicate samples, combined with the calibration gradient previously determined, produced an estimate for the fluorine concentration in IAEA Calcined Bone of 566 µg/g with a standard error of ± 20 µg/g. It was also possible to estimate the sodium concentration in this standard material as 11.5 mg/g with a standard error of ± 0.3 mg/g. A $^{20}$F photopeak was detected in all other materials, with the exception of NBS Orchard Leaves, but in each case it was attributable to the sodium interference.
6.3.1 Sources of error

Various sources of error have been considered which influence the accuracy and precision of the fluorine content of the IAEA Calcined Bone.

i) Accuracy of the cyclic irradiation and counting scheme as controlled by the ICIS clocks is better than ± 0.3% (§3.2).

ii) Maximum possible error associated with the assumption of constant fractional dead-time per cycle is < 1% (Egan et al., 1977).

iii) Two sources of error are associated with the pulser correction. Firstly the pulser peak area determination, estimated as ~ 1%. Secondly the use of a constant rate pulser, rather than a pulser whose rate decays with the activity of the sample being counted. Under the counting conditions described above, this is expected to be << 1% (Azuelos et al., 1977).

iv) Errors in the estimation of $r_{Na}^-$ and $r_{Ne}^-$ originate from determination of the relevant photopeak areas after dead-time and pulse pile-up correction. Both ratios were estimated from 3 separate measurements resulting in a standard error of ± 3%.

v) Errors related to $C_{Na}^-$ and $C_{Ne}^-$ are similar to iv). Statistical error of 1633 keV $^{20}F$ peak, 1368 keV $^{24}Na$ peak and 440 keV $^{23}Ne$ peak in the IAEA standard were 3.3%, 3% and 3% respectively, resulting in a standard deviation of $C_{Na}^-$ and $C_{Ne}^-$ of ± 6.3%.

vi) Weight of bone samples were precise to ± 0.2%.
vii) Least squares fitting of standard calibration curve yielded an error of ± 0.5% for the gradient.

viii) Sample to sample variation in irradiating neutron flux were taken as < 1%. The standard error on C, estimated from 5 replicate samples, is a combination of the components itemised above and was found to be v ± 3.5%.

6.4 Detection Limits

The detection limit of an isotope is defined in §1.7 as the smallest photopeak which can be distinguished with a certain confidence above the background activity of the sample. This is expressed by

\[ L = f \sqrt{B} \quad (1.19) \]

In the case of a sample matrix where the sodium interference is negligible, a detection limit for fluorine may be estimated by direct application of Eq. (1.19). On the other hand, the same treatment applied to the spectrum of a sample with high levels of sodium, will yield a detection limit for \(^{20}\text{F}\) not necessarily attributable to the element fluorine. In such a case it is possible to estimate two detection limits; the first, as described above, being the detection limit for \(^{20}\text{F}\) (expressed either in area counts or in equivalent μg of fluorine, per unit mass of material). Secondly a detection limit may be derived for fluorine in the presence of sodium in the sample matrix using Eq. (6.3a).

If \( B_F \) and \( B_{Na} \) are the background areas under the 1633 and 1368 keV peaks respectively, then the standard deviations of the peak areas are given by

\[ \sigma_{Na} = \left[ n_{Na}^2 + 2B_{Na} \right]^{\frac{1}{2}} \quad (6.4a) \]
and

\[ \sigma_F = [n_F^2 + 2B_F]^\frac{1}{2} \quad (6.4b) \]

Now, if, as a first approximation, the standard deviation of \( r \) is neglected, the standard deviation of \( c_{Na} \) is given by

\[ \sigma_c = \left[ \sigma_F^2 + (r_{Na}\sigma_{Na})^2 \right]^\frac{1}{2} \]

\[ = \left[ n_F^2 + 2B_F + (r_{Na}n_{Na}^2 + 2B_{Na}) \right]^\frac{1}{2} \quad (6.5) \]

by substitution of Eq. (6.4a,b).

This may be considered as the 'best' estimate of \( \sigma_c \) as it is assumed that \( r \) is accurately known from an infinite number of measurements. Returning to Eq. (1.19), the detection limit for fluorine in the presence of sodium is

\[ \ell = f \sigma_c \quad (6.6) \]

Detection limits for \( ^{20}\text{F} \) and the element fluorine in the 5 standard biological materials, a sodium standard and a blank filter paper, have been estimated where appropriate; the results are summarised in Table (6.2). These

Table (6.2) : Detection limits for \( ^{20}\text{F} \) and fluorine

<table>
<thead>
<tr>
<th>Material</th>
<th>( \text{Wt} ) (mg)</th>
<th>Detection limit for ( ^{20}\text{F} ) (L)</th>
<th>Detection limit for fluorine (( \mu ))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>area counts</td>
<td>( \mu g\text{F} )</td>
<td>( \mu g\text{F} / g )</td>
</tr>
<tr>
<td>IAEA Calcined bone</td>
<td>100.</td>
<td>90</td>
<td>2.7</td>
</tr>
<tr>
<td>IAEA Animal Muscle</td>
<td>200.</td>
<td>44</td>
<td>1.3</td>
</tr>
<tr>
<td>NBS Bovine Liver</td>
<td>200.</td>
<td>43</td>
<td>1.3</td>
</tr>
<tr>
<td>NBS Orchard Leaves</td>
<td>150.</td>
<td>57</td>
<td>1.7</td>
</tr>
<tr>
<td>Bowen's Kale</td>
<td>150</td>
<td>52</td>
<td>1.6</td>
</tr>
<tr>
<td>Sodium std.</td>
<td>3.7</td>
<td>53</td>
<td>1.6</td>
</tr>
<tr>
<td>Blank filter paper</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
limits have been calculated on the basis of $f = 2$; the corresponding probabilities of a Type I or II error and the statistical precision of the net signal are given by Table (1.3).

One of the great advantages of activation analysis is the potential to determine a number of isotopes from only a single experiment. For this reason, Table (6.3) has been included listing all the isotopes detected in one sample of each of the SRM's investigated, in the region 0-4 MeV, using Table (6.3): Isotopes detected in the standard reference materials.

<table>
<thead>
<tr>
<th>Isotope</th>
<th>$E_x$ (keV)</th>
<th>IAEA Calcined Bone</th>
<th>IAEA Animal Muscle</th>
<th>NBS Bovine Liver</th>
<th>NBS Orchard Leaves</th>
<th>Bowen's Kale</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{165}$Dy$^m(?)$</td>
<td>108.2</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>✓</td>
<td>ND</td>
</tr>
<tr>
<td>$^{46}$Sc$^m$</td>
<td>142.5</td>
<td>✓</td>
<td>ND</td>
<td>ND</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>$^{77}$Se$^m$</td>
<td>161.9</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>$^{19}$O</td>
<td>197.4</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>$^{79}$Br$^m$</td>
<td>208.0</td>
<td>ND</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>$^{179}$Hf$^m$</td>
<td>214.3</td>
<td>✓</td>
<td>ND</td>
<td>ND</td>
<td>✓</td>
<td>ND</td>
</tr>
<tr>
<td>$^{23}$Ne</td>
<td>440.0</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>$^{86}$Rb$^m(,82Br)$</td>
<td>555.8</td>
<td>ND</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>$^{80}$Br</td>
<td>617.0</td>
<td>ND</td>
<td>ND</td>
<td>✓</td>
<td>ND</td>
<td>✓</td>
</tr>
<tr>
<td>$^{38}$Cl$^m$</td>
<td>670.0</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>$^{27}$Mg/$^{56}$Mn</td>
<td>844 - 7</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>$^{27}$Mg</td>
<td>1014.1</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>$^{66}$Cu</td>
<td>1039.0</td>
<td>ND</td>
<td>ND</td>
<td>✓</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>$^{24}$Na</td>
<td>1368.4</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>ND</td>
<td>✓</td>
</tr>
<tr>
<td>$^{52}$V</td>
<td>1434.4</td>
<td>✓</td>
<td>✓</td>
<td>ND</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>$^{42}$K</td>
<td>1524.7</td>
<td>ND</td>
<td>✓</td>
<td>✓</td>
<td>ND</td>
<td>✓</td>
</tr>
<tr>
<td>$^{20}$F</td>
<td>1633.1</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>$^{38}$Cl</td>
<td>1642.0</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>$^{28}$Al</td>
<td>1778.9</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>$^{56}$Mn</td>
<td>1810.7</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>✓</td>
<td>ND</td>
</tr>
<tr>
<td>$^{56}$Mn</td>
<td>2112.8</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>✓</td>
<td>ND</td>
</tr>
<tr>
<td>$^{38}$Cl</td>
<td>2166.8</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>$^{24}$Na</td>
<td>2753.6</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>ND</td>
<td>✓</td>
</tr>
<tr>
<td>$^{49}$Ca</td>
<td>3083.0</td>
<td>✓</td>
<td>ND</td>
<td>ND</td>
<td>✓</td>
<td>✓</td>
</tr>
</tbody>
</table>

Notes: ND = Not detected; † = Due to Na
the irradiation conditions previously described. The cumulative spectrum obtained from a sample of NBS Orchard Leaves (Fig. (6.4)) has also been included, demonstrating the lack of fluorine (\(4 \mu g\) F/g) or sodium (82 \(\pm\) 6 \(\mu g\) Na/g) signals, but more especially for comparison purposes with the results obtained using the Low Energy Photon Detector, described in Chapter 3 (c.f. Fig. (3.11)). This spectrum clearly shows the richness of peaks in the low energy region and therefore the benefit for determination of certain elements (e.g. Dy) by the complementary use of a LEPD.

6.5 Discussion

The linearity of the standard calibration graph, even at high fluorine levels, demonstrates the validity of the dead-time and pulse pile-up corrections and confirms that self-shielding due to lithium (in LiF used as standard) was negligible. Repeated analysis of standards suggests a precision of \(\sim 3\%\).

Sodium interference, through the \((n,\alpha)\) reaction, was found to be considerable. In the bone matrix, for example, sodium contributed \(\sim 35\%\) of the total \(^{20}\text{F}\) peak area. Use of both the \(^{20}\text{F}/^{24}\text{Na}\) and \(^{20}\text{F}/^{23}\text{Ne}\) ratios reduced the error on the sodium subtraction by \(\sim 30\%\). The detection limit for fluorine in the sodium standard indicates that it is unreasonable to measure the element with any confidence if, in a sample, the ratio \(\text{Na}/\text{F} \geq 10^3\).

The detection limit in a blank filter paper of 0.6 \(\mu g\) F is effectively an estimate of the sensitivity of the technique and reflects a marked improvement over the conventional irradiate-wait-count sequence. The detection limit in a bone matrix, (IAEA Calcined Bone) even with a Na/F ratio \(\approx 20\), is approximately an order of magnitude lower than fluorine.
levels found in human bone, whilst the converse is generally true for the other standard materials investigated.

Results summarised in Table (6.3) show that 10-12 elements may be measured simultaneously using CNAA. In some cases, for example selenium, the alternative method of analysis (using $^{75}$Se) requires an analysis time extending over at least a week. In other cases, one isotope is enhanced with respect to another whose gamma rays are of similar energy (e.g. $^{86}$Rb and $^{82}$Br at $E_{\gamma} = 555$ keV).

6.6 Conclusions

CNAA has been shown to achieve significant improvements in both sensitivity and detection limits for the measurement of fluorine when compared to conventional neutron activation techniques. As regards its applicability to the dating of ancient bone, this technique fulfills most
of the criteria outlined at the end of §6.1. The precision and accuracy of the fluorine determination are both below the 5% level, as demonstrated on the IAEA Calcined Bone. The technique permits the simultaneous measurement of 10 other elements in bone and a similar number in the other SRM's, enabling the estimation of elemental ratios (e.g. F/Ca), although, unfortunately, it is not possible to determine nitrogen by this technique. Moreover the technique is rapid (300s experiment time/sample), applicable to small samples and essentially non-destructive. On a purely trial basis, two samples each of Roman sheep tibia and Pleistocene elephant tusk from unknown sources were analysed and found to contain 240 µg/g and 1.4% by weight of fluorine respectively, thus demonstrating the suitability of the method.
7.1 Conclusions

The versatility of neutron activation analysis has been demonstrated, with particular emphasis on the employment of short-lived isotopes. The 'cyclic' technique (CNAA) has been discussed in detail, with respect to both the theoretical aspects of optimising the 'signal-to-noise' ratio of a radionuclide of interest by suitable choice of the timing parameters, and the experimental applications of the technique in a number of different contexts. The merits of each particular analysis scheme, devised for a specific requirement, have been evaluated by the calculation of elemental detection limits and also, in the majority of cases, the statistical precision with which an element may be quantitatively determined in the sample matrix, (e.g. Standard Biological Reference Materials, soil, air filter).

The advantages of the techniques have been enumerated (§1.1, §2.1, §3.7, §6.6) as have the limitations, such as high 'blank' impurity levels (§3.6, §4.4) and the occurrence of interfering reactions which either reduce detection limits by contributing to the spectrum background (§5.4) or yield, in competition, the isotope of interest (§4.4, §5.4.2, §6.2); although limitations of the types mentioned are common to all activation analysis techniques for multielemental samples. Thus the applications have served, not only as individual studies in their own right, but also as a broad testing ground for the neutron activation techniques by providing samples representative of vastly differing matrices. At the end of each chapter,
conclusions have been drawn relevant to the results of that particular study; consequently the discussion here is restricted to more general comments principally concerning the techniques of analysis.

CNAA must be regarded, not as a panacea for all analytical requirements, but as complementary to other INAA techniques, a point occasionally overlooked in its enthusiastic advocacy. An interesting facet of the cyclic mode of irradiation, which incidentally, could be applied to the measurement of any radionuclide, (although for $\tau_\frac{1}{2} > \tau$ mins, the technique becomes impracticable), is the ability through judicious manipulation of the timing parameters to enhance one signal with respect to another, and effectively 'tune-in' to a band of half-lives of interest, the width of the band being a function of the total experiment time (§3.5). It is also true to say, however, that 'optimisation' of the timing parameters will result in 'percentage' rather than 'order of magnitude' improvements in the signal obtained, as shown, for example, by Figs. (2.5) and (3.9). A more important consideration is the transfer or waiting time, $t_w$, in circumstances where $t_w \geq \tau_\frac{1}{2}$, and may be regarded as the limiting factor on the measurement of very short-lived isotopes (e.g. $^{38}$Cl$^m$, $\tau_\frac{1}{2} = 0.7s$; $^{207}$Pb$^m$, $\tau_\frac{1}{2} = 0.8s$).

Consequently the measurement by CNAA of such radionuclides as $^{24}$Na$^m$ ($\tau_\frac{1}{2} = 19.3$ ms), $^{75}$As$^m$ ($\tau_\frac{1}{2} = 16.2$ ms), $^{114}$In$^m$ ($\tau_\frac{1}{2} = 40.4$ ms) and $^{205}$Pb$^m$ ($\tau_\frac{1}{2} = 5.31$ ms) are only possible using electronically pulsed neutron sources, such as a 14 MeV neutron generator (Golánski, 1969), or a TRIGA-type reactor for reasons outlined in §2.3.

The Low Energy Photon Detector described in Chapter 3 has been shown to extend the 'repertoire' of elements measurable by CNAA, best results, i.e. highest sensitivities, being obtained for those elements of interest not
only to the biological (e.g. Co, Se) but also the environmental (e.g. Sc, In) and geological (e.g. Sc, Rh, rare earths, Hf) sciences.

Chapters 4 and 5 demonstrated how a selection of different analysis modes may complement each other in obtaining the final set of results. Moreover, the influence of the neutron energy spectrum on the elemental detection limits was found to be considerable. For application to air particulate and soil analyses, use was made of the powerful multi-elemental capability of the INAA technique, an essential feature in both these studies. As a consequence, however, multivariate data reduction, in the form of cluster analysis, was necessary to facilitate interpretation of the results.

CNAA proved indispensable for the determination, with sufficient sensitivity, of bone fluorine, described in Chapter 6. Pulse pile-up losses, the result of high counting rates in the spectrometer system, were found to affect the accuracy of the analysis, but could be satisfactorily corrected by the introduction of a pulser signal at the preamplifier stage.

Finally, therefore, INAA has been successfully applied to the study of elemental distributions within soil profiles and the estimation of bone fluorine concentrations; the archaeological significance of these results having been discussed. Similarly, the analysis of air particulate samples obtained from Oxford City-Centre by both INAA and Gas Chromatography, has enabled correlations to be drawn between airborne trace elements and hydrocarbons, the meteorological/traffic flow data and filter obscuration measurements. Studies of the type described in the three applications above, all require large numbers of samples to be analysed in order to obtain statistically meaningful results; the analytical procedures which have been devised are ideal for this requirement. The NAA techniques have been
demonstrated as rapid, instrumental and suitable for routine applications, the gamma ray spectrum analysis program (SAMPO) has been shown to yield consistently accurate and reliable data on peak areas and positions, and cluster analysis has been found a powerful multivariate technique to facilitate interpretation of the multi-elemental results.

7.2 Recommendations for Further Work

The potential of cyclic activation analysis employing epithermal neutrons (ECNAA) in conjunction with $\gamma$ or X-ray spectrometry remains, as yet, unexplored. Epithermal neutron activation analysis (ENAA) has been described in §5.2.1 for the analysis of soils and advantage factors (§5.4.1) have been calculated. The technique relies on suppressing major activities, due to isotopes having approximately '1/$v$' epithermal cross-sections, with respect to those isotopes (of interest) with large $I/\sigma_0$ values. Depending on the isotope of interest and the sample matrix in which it is present, ECNAA may result in a considerable improvement in the detection limit.

In §2.2 comment was made on the sparsity of nuclear data for some of the short-lived isotopes, especially the values of resonance integrals. Nevertheless, by way of example, the cross-section compilations of Steinnes (1971) and Van der Linden (1974) have been used to calculate theoretical advantage factors for some radionuclides with $T_1 < 1$ min. The advantage factor, $F_a$, in this instance is defined as:

$$F_a = \frac{CR_{1/v}}{CR_x}$$

(7.1)

where $CR_{1/v} = \text{the cadmium ratio (§1.3.1; §5.4.1) of a (hypothetical) nuclide following the } \frac{1}{v} \text{ law in the thermal and epithermal regions}$

and $CR_x = \text{the cadmium ratio for the isotope of interest}$,
The advantage factors have been calculated for ICIS, using the $CR_{Au}$ given in Table (1,2). The $CR_{1/v}$ was obtained from Eq. (1.11) by making the assumption that the resonance integral of a $^{11}$ absorber, $I_{1/v}$, is given by $I_{1/v} = 0.44 \sigma_0$ (Steinnes, 1971). Thus, for ICIS, $CR_{Au} = 2.08$ which results in $CR_{1/v} = 39.5$. Several nuclides, such as $^{23}$Na and $^{27}$Al, which lead to major activities upon neutron irradiation with consequent deterioration in detection limits, follow the $^{11}$ law in both the thermal and epithermal regions—hence the choice of $CR_{1/v}$ in the calculation of $F_a$. The advantage factors and relevant nuclear data are given in Table (7.1); the isotopes of Na and Al being included as representative of undesirable background interferences. Of the isotopes considered, ECNAA may prove advantageous in the measurement of the elements F, Ge, Rh, Pd, Ag, Ce, Hf and Pt, but not for O, Na, Al, Sc and Se.

A pilot experiment was conducted to investigate the possibilities of ECNAA. Since the CONSORT II reactor is not, at present, equipped with a thermal neutron shielded core tube, and as ICIS is the only facility suitable for cyclic irradiation, the sample must be shielded inside the irradiation capsule. Cadmium is unsuitable as a shielding material in this situation due to the gross gamma activity produced during irradiation which would prevent detection of the signals of interest. Boron, however, is often used as an alternative thermal neutron absorber (Rossitto et al., 1972) since the thermal neutron cross section for the $^{10}$B(n,$\alpha$)$^{7}$Li reaction is $\approx$ 3900 barns ($\S1.2.2$). $^{7}$Li is a stable isotope and thus $^{10}$B shielding of samples would be acceptable for ECNAA. Two pellets, each consisting of 50 mg of isotopically enriched $^{10}$B (94%) were used, in sandwich form, to shield a filter paper on which standards had been evaporated. This 'sandwich' was packaged in the usual manner and ECNAA performed for 10 cycles with a period of 10s.

Reactor power, as shown on the trace in Fig. (7.1), fell by $\approx$ 12% during each
Table (7.1): Advantage factors in ICIS, for some short-lived isotopes, compared with a hypothetical \( \frac{1}{\nu} \) absorber.

<table>
<thead>
<tr>
<th>Isotope produced</th>
<th>Half-life (s)</th>
<th>( \sigma_0 ) (b)</th>
<th>I (b)</th>
<th>Ref</th>
<th>CR (calculated)</th>
<th>Fa (calculated)</th>
</tr>
</thead>
<tbody>
<tr>
<td>'( \frac{1}{\nu} ) absorber'</td>
<td>-</td>
<td>( \sigma_0 )</td>
<td>0.44 ( \sigma_0 )</td>
<td>a</td>
<td>39.5</td>
<td>1.0</td>
</tr>
<tr>
<td>( ^{19}O )</td>
<td>26.9</td>
<td>( 0.16 \times 10^{-3} )</td>
<td>( 0.94 \times 10^{-3} )</td>
<td>b</td>
<td>3.88</td>
<td>1.0</td>
</tr>
<tr>
<td>( ^{20}F )</td>
<td>11.2</td>
<td>0.098</td>
<td>2.3</td>
<td>a</td>
<td>1.72</td>
<td>23.</td>
</tr>
<tr>
<td>( ^{24}Na )</td>
<td>15 h</td>
<td>0.534</td>
<td>0.29</td>
<td>a</td>
<td>32.2</td>
<td>1.2</td>
</tr>
<tr>
<td>( ^{28}Al )</td>
<td>138</td>
<td>0.232</td>
<td>0.18</td>
<td>a</td>
<td>22.8</td>
<td>1.7</td>
</tr>
<tr>
<td>( ^{46}Sc^m )</td>
<td>18.7</td>
<td>9.</td>
<td>4.9</td>
<td>b</td>
<td>32.1</td>
<td>1.2</td>
</tr>
<tr>
<td>( ^{75}Ge^m )</td>
<td>48.9</td>
<td>0.16</td>
<td>0.39</td>
<td>b</td>
<td>7.95</td>
<td>5.0</td>
</tr>
<tr>
<td>( ^{77}Ge^m )</td>
<td>54.3</td>
<td>0.10</td>
<td>0.84</td>
<td>b</td>
<td>3.02</td>
<td>13.</td>
</tr>
<tr>
<td>( ^{77}Se^m )</td>
<td>17.5</td>
<td>21.</td>
<td>16.</td>
<td>b</td>
<td>23.2</td>
<td>1.7</td>
</tr>
<tr>
<td>( ^{104}Rh )</td>
<td>42</td>
<td>139.</td>
<td>1060.</td>
<td>a</td>
<td>3.22</td>
<td>12.</td>
</tr>
<tr>
<td>( ^{107}Pd^m )</td>
<td>21</td>
<td>0.013</td>
<td>5.96</td>
<td>a</td>
<td>1.04</td>
<td>38.</td>
</tr>
<tr>
<td>( ^{110}Ag )</td>
<td>24</td>
<td>89.</td>
<td>1600.</td>
<td>a</td>
<td>1.94</td>
<td>20.</td>
</tr>
<tr>
<td>( ^{139}Ce^m )</td>
<td>56</td>
<td>0.015</td>
<td>1.21</td>
<td>b</td>
<td>1.21</td>
<td>33.</td>
</tr>
<tr>
<td>( ^{179}Hf^m )</td>
<td>18.7</td>
<td>50.</td>
<td>980.</td>
<td>b</td>
<td>1.86</td>
<td>21.</td>
</tr>
<tr>
<td>( ^{199}Pd^m )</td>
<td>14.1</td>
<td>0.027</td>
<td>0.45</td>
<td>b</td>
<td>2.02</td>
<td>20.</td>
</tr>
</tbody>
</table>

References:

a Steinnes, (1971)
b Van der Linden et al., (1974).

Irradiation period, even after compensation using the coarse control rod. It was apparent that such a system would be impractical for ECNAA due to the huge power (and therefore flux) variations which would not be reproducible from one sample to another.
Fig. (7.1) : Variation in reactor power as a function of time including period of Epithermal Cyclic Neutron Activation Analysis.

A new cyclic activation system (CAS) is under construction at ULRC; one of the features of the irradiation pipe is a Cd sleeve which may be lowered, if required, into the core to enable ECNAA, thus eliminating the inherent difficulties of cycling the shielding material as well as the sample.

Almost inevitably, as a result of the work described in Chapter 3, it is evident that combining both a Ge(Li) and a pure Ge detector for the simultaneous counting of a sample, must increase the versatility of a cyclic, or indeed, conventional analysis scheme. The judicious use of a routing
box, which behaves as a digital biased amplifier, should enable spectra from both detectors to be accumulated by a single 4000 channel MCA (0-1000 channels for Ge; 1000-4000 channels for Ge(Li), say), thus avoiding the extravagant requirement of a second MCA. In addition, the introduction of permanent magnets to deflect β-particles, as suggested by Mantel et al. (1978), may improve the measurement accuracy of X-rays in the presence of strong β-emitters (e.g. in soils, rocks, biological materials) when using the LEPD.

The pure Ge LEPD has proven itself indispensable for the measurement of γ and X-rays with energies below ~ 80 keV. However a photon energy interval exists between ~ 50 keV and ~ 200 keV, over which the useful operating ranges of a small volume (~ 1 cm³) planar Ge and a large volume (~ 50 cm³) coaxial Ge(Li) detector overlap. A critical evaluation of the relative merits of each type of detector over this energy region would be of considerable benefit to the activation analyst. Such an evaluation would be based on characteristic parameters such as resolution, efficiency, peak-to-Compton and/or peak-to-valley ratio, all of which are functions of the incident photon energy. Additionally, sample matrix, counting geometry, detector system counting rate and also cost should be included.

Modifications to improve performance of the SAMPO program are continually being implemented, some having been described by Egan (1977) and Tout (1977). Mention has been made in §1.6 of the inability of SAMPO to satisfactorily fit strong, isolated photopeaks due to the inadequacy of the quadratic background to describe the steplike behaviour of the continuum under the peak. Under such circumstances, a background consisting of a step function, with the constraint that the discontinuity should occur at the peak centroid channel, would improve the fitting procedure considerably.
With emphasis being placed increasingly on the use of single comparator standards, the inclusion of resonance integral cross-sections in the IDENT nuclear data library would remove the restriction of absolute mass calculations being applied to thermal neutron irradiated samples only. The Cadmium Ratio of a flux monitor such as cobalt or gold would be the only additional information required for each sample spectrum analysed.

Further air particulate studies of the type described in Chapter 4 should take considerable care over the choice of filter membrane on which the particulates are collected. Spyrou et al. (1976) recommend the use of 'Nuclepore' membranes, having low elemental impurity concentrations, as suitable for trace element analysis. It is also interesting to note that these membranes have a low 'blank' contribution to the gas chromatographic analysis (Douglas, 1978) described in Appendix II.

The techniques described in Chapter 5 were shown to be suitable for the measurement of elemental distributions through soil profiles. It is, however, essential that these measurements be repeated on buried soils at other archaeological sites to ascertain whether the elemental distribution patterns exhibit similar trends. A study of the elemental distributions within individual particle sizes of each sample may indicate that, for example, analysis of the clay fraction alone, is the best approach to the delineation of horizons within any profile.

A brief analysis programme of a number of Roman, Saxon and Medieval animal bones *, performed principally for fluorine analysis, yielded results

* (Supplied by T. O'Connor and D. Brothwell, Institute of Archaeology, London).
for a number of other elements, as outlined in Table (6.3). Negative results, i.e. no correlation of elemental concentration with age, were found for all elements with the exception of vanadium. On the basis of 4 samples (all taken from the shaft of sheep tibiae) from each of the periods, washed for 2 hrs. in an ultrasonic bath of demineralised water prior to analysis, the results for vanadium (±σ) were Medieval, 9.0 ± 2.4 counts/mg, Saxon 19.6 ± 3.2 counts/mg and Roman, 50.4 ± 3.7 counts/mg. Vanadium was present at the limit of detection (~1 count/mg) in IAEA Calcined Bone which is representative of fresh mammal bone. These results suggest that for the Winchester site from which these bones were obtained, the vanadium concentration may serve as an indicator of the relative ages of bones, in a similar manner to the fluorine method, but applicable over a much shorter time scale. It is evident that these results, based on only 12 samples, can hardly be regarded as a rigorous study. Further vanadium analyses of bones from the same site and also from sites with different soil types are necessary to thoroughly test the potential of these preliminary results. Vanadium is measured through the neutron activation product $^{52}\text{V}$ ($\tau_\frac{1}{2} = 3.75 \text{ min}$). Thus a conventional irradiation and counting scheme of $t_1 = t_\text{c} = 600s$, with the minimum of waiting time in between, would permit the simultaneous determination of $^{52}\text{V}$ and $^{49}\text{Ca}$ ($\tau_\frac{1}{2} = 8.8 \text{ min}$) as well as ~10 other elements, thus enabling the calculation of elemental ratios such as V/Ca which would relate the vanadium to the bone mineral content of the samples.
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APPENDIX I

THE IAEA INTERCOMPARISON OF METHODS FOR PROCESSING Ge(Li) GAMMA-RAY SPECTRA

An intercomparison of methods of processing Ge(Li) gamma-ray spectra has been organised by the IAEA, the purposes of which are described in §1.6. This Appendix describes briefly the form of the intercomparison (IAEA, 1976) and summarises the principal results of the evaluation (Parr et al., 1978; Parr, 1978). Nine spectra were provided, each covering an energy range of $\sim 1$ MeV and, with one exception, contained isolated single peaks. The other spectrum consisted of a series of doublets (double peaks with varying relative intensities and degrees of overlap. The spectra were (artificially) generated to typify three specific classes of problem, namely:

i) the detection of small single peaks near the limit of detection,

ii) the determination of position and area of more easily detectable single peaks,

iii) the determination of position and area of doublets.

The nine spectra were routinely analysed by SAMPO in an identical procedure to that used for all gamma-ray spectra (§1.6). For each peak found, the centroid and area, with corresponding errors, were reported. These results were evaluated by the IAEA and returned together with ranking scores indicating their relative quality in the intercomparison (Parr et al., 1978).

Reference Spectrum 100

This spectrum consisted of 20 strong, isolated peaks which were used in conjunction with the SHAPEDO routine to obtain the characteristic peak
shape parameters (Gaussian width, lower and higher tailing) as a function of channel number. It is interesting to note that the results obtained were independent of the peak fitting interval chosen, due to the excellent counting statistics and uniform background continuum. Intervals of 1, 2, 4 and 6 channels either side of the peak and a constant 50 channels window were examined.

Test Spectrum 200

This spectrum consisted of 22 peaks close to the limit of detection. The PEAKFIND routine, described in §1.7, located 16 true peaks and no spurious peaks, when a threshold significance corresponding to $3.6\sqrt{B}$ (Eq. (1.21)) was used. It is true that this detection limit is more conservative than the usual $2\sqrt{B}$ values reported in the preceding chapters; nevertheless, it is debatable whether peak areas obtained from the fitting of less significant peaks are at all precise (i.e. the limit of determination in this instance is $3.6\sqrt{B}$). The ranking position for this test was 25 out of 192 sets of submitted results. Although all true peaks were detected by at least 2 different peak-search methods, no method was able to detect more than 19 of the 22 true peaks. According to the IAEA evaluation, no one particular peak-search method is overwhelmingly superior in detecting a large number of true peaks, but visual methods and the use of the second derivative (e.g. PEAKFIND) are capable of marginally superior performance.

Test Spectra 300-305

Six identical spectra, except for differences due to counting statistics, consisting of 22 peaks, were analysed by the FITDO routine to evaluate the effects of counting statistics. Difficulty was only encountered in the case of one peak located on a Compton Edge for which the FITS routine
was required, enabling closer control over the fitting parameters. The evaluated ranking positions for peak area and position were 8 and 4 respectively out of a total of 205 sets of submitted results.

A significant defect of the SAMPO program was evident from the results of this test, namely underestimation of the calculated standard deviations of the results. This is most apparent for the standard deviations of peak position as evidenced by the results for these spectra, which are too low by a factor of 10, or more, in many cases. The error determinations on peak areas were satisfactory in most cases, with the exception of the peak in the neighbourhood of a Compton Edge, for which the standard deviation was underestimated by a factor of 2.

Test Spectrum 400

Analysis of this spectrum, consisting of 9 doublets with various relative intensities and degrees of overlap, by the automatic FITDO routine, fitted all but 2 as singlets! The FITS routine was thus employed, although great difficulty was experienced in resolving one doublet with peak separation of 1 channel and relative intensity of 10:1. In a routine analysis situation, at least 2 of these doublets would have been mistaken as single peaks. Two ranking positions, one for the estimates of relative intensity and the other for separation of the doublets, were both 5 out of 144 submitted sets of results.

In conclusion SAMPO has been shown to fare well in this intercomparison, yielding consistently accurate and reliable peak area and position estimates. Peak position errors have been shown as considerably underestimated, although peak area errors, of more importance to the studies reported here, were generally found to be satisfactory. Automatic peak search and fitting,
employing PEAKFIND and FITDO routines, is liable to treat doublets as a single peak, unless they are separated by a minimum of \( \approx 3 \) channels; hence the need for visual examination of each fitted peak, provided on microfiche by the FITDO routine.

Parr et al. in summarising the evaluation, found that the general principles underlying the methods of analysis did not correlate with the wide range of reported performances, although some methods appeared capable of producing better results than others, namely:

- for peak detection - visual methods and the use of the 2nd derivative;
- for determination of peak position - the fitting of a parabola or modified Gaussian function;
- for determination of peak area of singlets or doublets and peak position of doublets - the fitting of a modified Gaussian function.

Parr et al. conclude that "success in evaluating the test spectra is not so much dependent on the principle of the method used but more on the details of how this method is applied. This can perhaps best be described as the 'fine-tuning' of the method".
APPENDIX II

ANALYSIS BY GAS CHROMATOGRAPHY OF OXFORD AIR PARTICULATES

Gas chromatography (GC), as described here, is a technique for the quantitative analysis of organic components separated from a mixture on the basis of their molecular weight and chemical structure. The principle of GC separation is the distribution of a sample between two phases. One of these phases is a stationary bed of large surface area, and the other (the mobile phase) is a gas which percolates through the stationary bed. Separation occurs when one component is held more strongly on the stationary phase than the other components, which tend to move on faster in the mobile phase.

The stationary phase consists of an inert support material (in this case, Celite 100-120 mesh) coated in a non-volatile liquid (5% OV-17) Nitrogen, the carrier gas into which the sample is injected, comprises the mobile phase and passes through the column at a flow rate of 20 ml.min⁻¹. A schematic diagram of the GC system is shown in Fig. (II.1). The column containing the stationary phase is enclosed in an oven, the temperature of which follows a programmable cycle for each sample. The temperature programme maintains a constant 60°C for 5 min followed by an increase of 8°C.min⁻¹ up to a maximum of 125°C. A cycle of this kind enables the sample to pass through the column as quickly as possible whilst at the same time achieving separation of the components. The temperature 'ramp' is necessary to speed-up the passage of the slower moving sample components.

Quantitative analysis of the components was performed by a Flame Ionisation Detector (FID), at the end of the column. In this detector, the carrier gas is mixed with hydrogen and air and burnt in a jet. A collector
Fig. (II.1): Schematic diagram of a gas chromatography system.

electrode, with a DC potential applied, is placed above the jet and measures the conductivity of the flame. With pure hydrogen the conductivity is quite low; however as organic compounds are combusted the conductivity increases, proportionately with the quantity present, and the resulting FID signal is amplified and displayed as a trace on a chart recorder. As each organic component passes through the column, a peak appears on the trace, the area under which corresponds to the quantity of that particular component.

The advantages of the GC technique are:

a) Speed - complex analyses may be accomplished in a matter of minutes

b) Resolution - separation of complex mixtures which are either extremely difficult or impossible by other techniques are routinely performed by GC.

c) Qualitative analysis - the retention time, i.e. the time taken from sample introduction to peak maximum, is a characteristic of the sample stationary phase and column temperature. Several compounds can have similar or identical retention times, but each compound has only one
retention time, unaltered by the presence of other components in
the sample mixture.

d) Sensitivity - the FID has a large linear range (1-10^7) and easily
detects organic compounds present in ppm concentrations in small samples
(typically 10 μl sample solution).

Analysis of the Oxford Air Particulate Samples

The pelleted filter membranes, following INAA, were stored for
sufficient time to allow measurable radioactivity to decay to a safe level
(< 0.1 μCi/sample). The filters were then subjected to GC analysis by
S.G. Douglas at Brunel University (Douglas, 1978). The hydrocarbons were
extracted in warm (46°C) carbon disulphide. The volume of carbon disulphide
was reduced to 100 μl and a 10 μl sample introduced to the chromatograph.
Spiked samples of similar concentration were processed in the same manner
and no loss of sample found. Prior to extraction the filters were physically
disturbed to allow more efficient mixing of the sample and solvent.

Analysis of the air filter samples proved to be difficult due to the
high organic impurity levels of the clean 'Millipore' filter membranes
(blanks); 'Nuclepore' membranes were found to contain much lower impurity
levels. However, judicious selection of the operating conditions permitted
the analysis of the following hydrocarbons: Toluene, Ethyl benzene, n-heptane,
n-octane and n-nonane. These results are presented in Fig. (II.2). The
measured concentration (in ppb) are generally lower than expected in an
urban atmosphere as shown by the comparison in Table (II.1) of mean
concentrations of the organic pollutants in the Oxford City-Centre, Brunel
University and Zurich atmospheres.
Fig (II.2): Six-Hourly Values (ppb)

- Toluene
- Ethyl Benzene
- n-heptane
- n-octane
- n-nonane
Table (II.1): Mean concentrations of organic pollutants in the atmosphere of Oxford, Uxbridge and Zurich.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Oxford City-Centre (this work)</th>
<th>Brunel University, Uxbridge (Douglas, 1977)</th>
<th>Zurich (Grob and Grob, 1971)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ppb</td>
<td>ppb</td>
<td>ppb</td>
</tr>
<tr>
<td>toluene</td>
<td>19.5</td>
<td>49.9</td>
<td>39</td>
</tr>
<tr>
<td>ethyl benzene</td>
<td>3.8</td>
<td>16.1</td>
<td>8.7</td>
</tr>
<tr>
<td>n-heptane</td>
<td>5.8</td>
<td>-</td>
<td>34</td>
</tr>
<tr>
<td>n-octane</td>
<td>4.6</td>
<td>13.5</td>
<td>3.4</td>
</tr>
<tr>
<td>n-nonane</td>
<td>5.3</td>
<td>10.1</td>
<td>1.7</td>
</tr>
</tbody>
</table>

This may be due to the long storage time prior to sample analysis, during which partial volatilisation of the organic components may have occurred. Furthermore, ~5 days irradiation in the reactor may have enhanced these losses (core coolant temperature ~40°C). The possibility of radiation damage to the organic compounds should also not be excluded. However, although the more heavily polluted filters will have suffered greater losses than the 'cleaner' ones, it is reasonable to assume that these losses will not influence the relative variations significantly, since the organic compounds are present in similar (order of magnitude) concentrations in all the samples.

Cluster analysis has been performed on these results, in combination with the trace element analyses and environmental data, in an identical manner to that described in §4.6. The line printer version of the dendrogram is shown in Fig. (II.3) where it can be seen that the hydrocarbons form a cluster of their own with ethyl benzene as an outlier. Significantly, the organic compounds are not clustered either with obscuration and the trace elements, or with traffic flow. However, close examination of the similarity matrix (not reproduced here) shows that the hydrocarbons are more
Fig. (11.3): Dendrogram resulting from WPGMA clustering of combined data.

highly correlated with bromine than any other parameter. The correlation coefficients with bromine are: toluene (0.46), ethyl benzene (0.30), n-heptane (0.37), n-octane (0.69) and n-nonane (0.60). It is the 'non-overlapping' property of the clustering procedure (Appendix III) i.e. that an object or attribute, once clustered, cannot be moved to a new cluster, that separates the bromine from the hydrocarbons and distorts the results as presented in the dendrogram. Despite this fact, it is significant that of all the parameters, the hydrocarbons should correlate with bromine since it was concluded
in §4.7 that bromine in the atmosphere is principally of vehicular origin. This indicates that the organic compounds measured in the Oxford particulate samples are unburnt hydrocarbons resulting from incomplete combustion or evaporative losses of vehicle fuel.

The results of this study show how two complementary techniques such as INAA and GC may be successfully used in combination to provide greater insight into a specific problem. The 'non-destructive' nature of the INAA technique is ideally suited for collaboration of this nature.
APPENDIX III

CLUSTER ANALYSIS

The cluster analysis procedure starts from a matrix of similarities which records the relationships between n objects (the samples), each characterised by m attributes (e.g. measured elemental concentrations). Although a large number of measures of the similarity between objects have been postulated (Sneath and Sokal, 1973), the principal one employed for this study is the Mean Euclidean Distance, \( d_{a,b} \). Each sample, characterised by m attributes, may be represented by a single point in m-dimensional space. The distance, \( d_{a,b} \), between any 2 points, a and b, in m-space is defined as:

\[
d_{a,b} = \left[ \frac{1}{m} \sum_{i=1}^{m} (a_i - b_i)^2 \right]^{\frac{1}{2}} \tag{III.1}
\]

where \( a_i \) and \( b_i \) are the concentrations of element i in samples a and b respectively (\( 1 \leq i \leq m \)). The smaller the value of \( d_{a,b} \), the more similar are the objects a and b, and the task of clustering samples with similar elemental composition becomes a matter of searching for clusters of points in m-space. Inspection of Eq. (III.1) shows that \( d_{a,b} \) will be influenced most strongly by the variable which has the greatest magnitude. Two options are available to overcome this. Either the m x n raw data matrix is standardised (to give each elemental distribution a mean of 0 and standard deviation of 1) prior to computing the distance measurements, thus ensuring that each variable is weighted equally; or the data is converted to log concentrations in order to give equal weight to the same fractional change in any element, regardless of its concentration range. The latter method is preferred by Harbottle (1976) since the data does not form a closed set, being an
absolute scale, and so may be added to at any time when additional data become available. Computation of the similarities between all possible pairs of objects results in an $n \times n$ symmetrical matrix upon which the clustering is performed.

The program CLUSTR performs clustering according to the weighted pair-group method using arithmetic averages (WPGMA). The first step in this procedure is to locate pairs of objects with the mutually highest similarities to form the centres of clusters i.e. pairs of objects for which the similarity coefficients $d_{a,b}$ and $d_{b,a}$ are the highest coefficients in their respective columns. The similarity matrix is then recomputed, treating clustered pairs as single objects. Recalculation of the similarity matrix involves finding the arithmetic average of the similarities between any object and the two comprising the clustered pair. The clustering cycle is now repeated such that each new cluster that is formed, or each existing one that is added to, is again treated as a single object for the purposes of recalculating the similarity matrix. As the analysis proceeds, the dimensions of the matrix reduce until finally a $2 \times 2$ matrix of similarities between the last remaining two clusters is obtained at which point all the objects have been clustered.

The results of the clustering procedure are most clearly displayed by a 'dendrogram', in which the objects are linked together at similarity levels (indicated by a scale at the side of the diagram) defined by the junction points of the dendrogram (c.f. Fig. (5.9)).

The WPGMA method is one of a range of clustering techniques employing the SAHN approach (Harbottle, 1976), which stands for 'Sequential', 'Agglomerative', 'Hierarchic' and 'Non-overlapping'. According to Harbottle,
'Sequential' implies a recurring mathematical operation which gradually attacks the universe of sample points in hyperspace (m-space), by linking together ('agglomerative') the points into clusters'. 'Hierarchic' means that, during the course of clustering, small clusters may be combined to form larger ones, with the result that, on completion of the analysis, all objects are included in one large cluster. 'Non-overlapping' means that, at any point during the analysis, an object, once it has been assigned to a cluster, may not belong to more than one cluster and also may not be moved.

The principal criticism levelled at the WPGMA method (Sokal and Sneath, 1973; Davis, 1973) is that objects most recently assigned to a cluster are weighted equally with all existing members, due to the method of recalculating the similarity matrix, with the result that objects which are admitted in the latter stages of analysis, distort the cluster disproportionately with their importance. This effect is more appreciable, the larger the number of objects to be clustered.

Cluster analysis may also be performed on attributes simply by transposing the raw data matrix supplied to the CLUSTR program. This facility suits the requirement of identifying relationships between various parameters measured on a large number of objects e.g. elemental and meteorological data in relation to air particulate samples (§4.6.4). Another obvious modification to the clustering method is the choice of an alternative similarity coefficient. In addition to the Mean Euclidean Distance, \( d_{a,b} \) (Eq. (III.1)), the CLUSTR program also makes available the Correlation Coefficient, \( r_{a,b} \), (Eq. (4.4)) used to produce the dendrogram in Fig. (4.6).