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14 MeV Neutron Activation Analysis
in Non-Aqueous Flowing Systems

by

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Summary

The fundamental techniques, feasibility and advantages of fast neutron activation analysis in a non-aqueous flowing system using economical irradiation techniques have been investigated. The methods developed have been applied to the determination in solution of elements producing short half-life isotopes in the range 5.88 - 29.8 s.

Optimum flow rates for the determination of each element have been obtained at which analytical sensitivity is maximised while interferences are minimised. The limits of detection of each element have been investigated on the flowing system and a method for any given system has been found whereby the optimum flow rate for the analysis of any element producing an isotope of known half-life may be predicted.

A high linear flow rate flowing system in which irradiation and detection efficiencies have been improved, has been developed for the analysis of ultra short half-life products down to half-lives of 0.80 s. The problems encountered due to the proximity of a sensitive radiation detector to a $10^{11}$ n s$^{-2}$ fast neutron generator as well as those involved in the critical design of efficient irradiation and detection flow cells for ultra short half-lives have been solved or minimised.

The determination of a further range of elements
producing half-lives between 0.8 and 60 s has been shown to be both feasible and reproducible. Optimum flow rates and detection limits were again investigated and the general validity of the expression for the prediction of optimum flow rates was further demonstrated. The use of digital computer techniques in the optimisation of the experimental techniques used as well as in the resolution of complex gamma-ray spectra has also been investigated.
Acknowledgments

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1. INTRODUCTION
1.1. Description and History

Activation analysis is an analytical technique involving the production of radionuclides by the bombardment, with sub-atomic particles or photons, of atomic nuclei in a matrix. Qualitative and quantitative analysis may then be carried out by a careful study of the radioactive nuclear reaction products present in the irradiated sample. These reaction products undergo radioactive decay with the emission of characteristic radiations. Measurement of the rate of decay and of the energy and type of radiation emitted, can lead to the identification of the reaction products and hence to the original target element. Quantitative measurements of the activity of the irradiated material can be related to the concentration of the target element in the sample. As the technique involves nuclear and not chemical reactions, only elemental analysis is possible, the method being independent of the state of chemical combination of the constituent elements present.

The phenomenon of naturally occurring radioactivity was discovered by Becquerel in 1896, when he found that uranium salts emitted penetrating radiation both continuously and of their own volition. The radiation was detectable by its darkening effect on photographic emulsions. It was not discovered until the 1930's however that the radiations from naturally occurring
radioisotopes could themselves induce nuclear transformations in previously stable nuclei. In 1939 Bothe and Becker discovered that bombardment of the light elements: lithium, beryllium and boron with alpha particles from polonium produced a penetrating radiation, which was shown by Curie and Joliot (1931) to eject high energy protons from paraffin. Chadwick in 1932 explained the penetrating radiation encountered in the above and in his own experiments, as being due to the neutron, a subatomic particle first postulated by Lord Rutherford in 1920. Many important discoveries were made during 1934. Curie and Joliot observed that positron emission continued from boron, aluminium and magnesium targets even when the exciting source of radiation (polonium alpha-particles) was removed. This was the first example of the production of artificial radioactivity. In the same year Fermi witnessed the fission of the uranium nucleus but the correct explanation of his results was only furnished in 1939 by Hahn and Strassman.

The first example of neutron activation analysis occurred in 1936 when Hevesy and Levi (1) determined dysprosium impurities in yttrium using thermal neutron irradiation. They went on in 1938 to detect europium traces present in gadolinium, by a similar technique (2).

The volume of nuclear data increased tremendously during the second world war with the wide variety of
research carried out during the "Manhattan" project, which resulted in the production of an atomic bomb. The program eventually led to the construction of nuclear reactors and particle accelerators of various types. Nuclear reactors produce, by the fission of uranium, thorium, or plutonium, neutrons with a wide range of energies and they are the most powerful neutron sources in existence today. A pulsed research reactor of the current TRIGA type can produce a total neutron output of as high as $10^{15}$ neutrons per pulse. Relatively low output isotopic neutron sources employing either alpha-particles or photons to eject neutrons from a light element e.g. beryllium, are available. Neutrons may also be produced by fusion reactions induced in particle accelerators. Commercial fast neutron generators using this principle have been available since about 1960.

High counting efficiency scintillation counters were introduced in the 1950's. The output signal from such a detector consists of voltage pulses proportional in size to the energy absorbed in the crystal scintillator, and hence pulse height spectrometry and qualitative and quantitative analysis can be performed. The advent of the multichannel analyser, a device which can continuously scan and arrange voltage pulses according to size, subsequently recording their number in a memory,
made pulse height spectrometry much easier. Relatively recently, semiconductor detectors have been produced whose energy resolution far exceeds that of the best scintillation detectors available. These new detectors currently suffer from the disadvantages of high cost, low detection efficiency (due to their small volume) and the fact that they need to be maintained constantly at liquid nitrogen temperatures to preserve their properties.

Currently much research is in progress to extend the sensitivity and applications of neutron activation analysis. Continuing efforts are being made to improve semiconductor detectors and to produce higher output neutron sources. Novel means of neutron production are being investigated as is also the production of compact, reliable, high output sealed tube neutron generators. Digital computer techniques are being applied increasingly to the data treatment of results, resulting in the unravelling of complex spectra, the rapid calculation of results, and the use of computerised on-line neutron activation analysis process control systems.
1.2. **Advantages**

Activation analysis possesses a number of advantages over other analytical techniques which may be summarised as follows:

1. Extremely low detection limits are possible with many elements, due to the fact that under favourable circumstances as little as $10^4 - 10^6$ radioactive atoms can currently be detected, (Eg. 1 g mol. of an element contains $6 	imes 10^{23}$ atoms). A number of elements have been detected in concentrations as low as one part per billion, a sensitivity which may only be surpassed by the mass spectrograph and the field ion microscope. Further the detection limits currently attainable will improve as more efficient detectors and higher output neutron sources become available.

2. The method can be made non-destructive by arranging for the analysis to depend on the measurement of the physical properties of the radionuclides produced, namely their rate of decay, and the energy and type of characteristic radiation emitted. Usually this is possible without any radiochemical processing of the irradiated material.

3. The analysis of specific nuclides is possible as the physical properties of the parent nuclide and radio nuclides, produced (reaction cross section, type and energy of radiation emitted, and rate of decay) depend
on nuclear energy states and these are unique to the nuclide. Similarly analysis of isotopes of the same elements, and trace analysis of minor constituents in chemically interfering matrices is possible.

4. The technique is usually more rapid than other means of analysis and can provide the ready analysis of elements such as nitrogen, oxygen, fluorine, and silicon which are difficult or tedious to analyse by other means.

5. Errors arising from reagent blanks or by contamination of the sample are excluded or minimised as any chemical processing required, usually takes place after irradiation.

6. Neutrons penetrate through the bulk of the sample and hence the technique is free from errors introduced by surface effects.

7. The penetration of neutrons through the sample facilitates the analysis of large samples and thus reduces or eliminates sampling errors.

1.3. Disadvantages

As with any method of analysis, activation analysis suffers from a number of disadvantages and limitations.

1. The irradiation stage of the method requires the provision of equipment with high capital costs: i.e. a nuclear reactor, a neutron generator, or a large isotopic neutron source. Unless a large number of
samples are to be continually analysed the technique will be expensive. However access to irradiation facilities and an activation analysis service are available nationally.

2. Radiation hazards occur with all sources of neutrons but they may be minimised with suitable shielding material. The radioactivity of the irradiated sample may pose a problem depending on the half lives of the radionuclides produced in the irradiation.

3. The technique is prone to a number of interferences and errors which will be described in detail later.

4. Applications

Owing to its unique advantages activation analysis has been applied to a wide range of problems, many of them of topical interest.

The non-destructive nature of the method is a considerable advantage, particularly where the sample may be irreplaceable e.g. in the fields of forensic science, and in the dating and identification of antiquities. Arsenical poisoning may be detected and proven by careful analysis of the victim’s hair and of certain parts of the body, whilst glass fragments may now be largely characterised from their trace element composition. Analysis of the metallic composition of coins and other objects is being carried out to give total percentage composition. Misleading results have been obtained in
the past from non-destructive analytical techniques which examine only the surface layer of a sample.

Activation analysis has a number of biomedical applications. In vivo analysis for nitrogen, sodium, phosphorus, chlorine, calcium, and iodine, has been carried out in the whole body using both fast and thermal neutrons. The ability to determine trace elements in a complex matrix has been used in pathological studies of trace element distribution and concentration in the healthy body, and also to characterise disease by the abnormal levels of certain trace elements encountered.

The method has found wide use in geochemical analysis and dating of rock samples both of terrestrial and extra-terrestrial origin, replacing previous tedious wet chemical methods. Activation analysis was chosen as the method of examination of the first samples of lunar material brought back to earth.

Industrially, the petroleum industry is using neutron activation as a method of crude oil analysis, and small portable neutron generators are being used on site in the operation of well logging. Neutron activation provides a rapid means for the determination of light elements; nitrogen (as a measure of the protein content) in foodstuffs, fluorine in organic compounds, and the oxygen content of steels. Activation analysis has also
been applied to the study of wear in many fields, e.g. car engine bearing wear from the measurement of the indium and lead contents in the engine lubricating oil. The application of the technique to continuous analysis and automated process control has been investigated by the neutron generator manufacturers and by others. A number of commercial analysers using isotopic neutron sources are also in production.

The latest application of neutron activation is in the analysis of environmental samples (3). Investigations are under way to characterise oil slicks (4) enabling the prosecution of offending tanker captains, and also to measure airborne pollutants (5).

1.5. Literature Review

The majority of the literature to date deals with activation involving reactions using thermal neutrons from nuclear reactor sources. However the volume of literature on fast neutron activation analysis has steadily risen since 1960 when the first 14 Mev neutron generators were produced commercially, and will continue to increase as their use becomes more widespread.

A number of books in English have been published (6,7,8,9,10) on the subject of neutron activation analysis. Bowen and Gibbons (6) (1963) have covered
the general principles involved and have elaborated with numerous specific applications, including radiochemical separations of the elements, in the fields of chemistry, biology and geochemistry. The book by Lyon (7) (1964) concentrates more on the basic principles, techniques and the equipment used in the method. The last chapter however includes a number of detailed examples of typical applications and problems of the technique for the student to carry out himself.

Taylor (8) (1964) deals with some potential applications to automated process control including on stream analysis. Lenihan and Thomson (9), in 1963, have compiled a thorough treatise of the principles and applications of both fast and thermal neutron activation analysis. The work is based on a series of advanced lectures given by international authorities in the field. Their latest book (10) is published as the first of a series of comprehensive reviews providing up to date information on the latest activation and detection techniques, as well as new applications of neutron activation analysis. Guinn (11) and Strain (12) have published other reviews in "Progress in Nuclear Energy".

A number of reports have been published by some neutron generator manufacturers such as Kaman Nuclear and Texas Nuclear, listing nuclear data (13) for fast neutron activation analysis as well as information on
applications and techniques (14). A complete bibliography on all aspects of activation analysis (edited by Lutz et al (15), is published and periodically updated by the U.S. National Bureau of Standards. Earlier bibliographies were published by Koch (16), Gibbons (17) and Raleigh (20). Activation analysis bibliographies are published periodically by the Western Regional Hospital Board summarising their own work which is largely in the biochemical and forensic fields (16), (17). Activation analysis reviews are included in the supplements to the Journal of Radioanalytical Chemistry and in the biannual reviews in nuclear chemistry carried out by the journal "Analytical Chemistry". Techniques covering all aspects of the field may be found in the published proceedings of the three international conferences devoted to modern trends in activation analysis (24, 25, 26). A book by Marion and Fowler (27) deals comprehensively with the physics of fast neutrons.

Mathur (28) has published a wide compilation of nuclear reactions initiated by 1 MeV neutrons together with their cross-sections and Q values. The reaction products are also well characterized and data is provided on their half-lives, and on the type and energy of radiation emitted. Calkai (29) has published a concise but fairly extensive survey of nuclear data related to activation analysis. Of particular use and interest are his graphs
illustrating the variation of reaction cross sections for various types of nuclear reaction, with the atomic number of the target element. Possible nuclear reactions occurring in materials under neutron bombardment may be predicted using the compilation of neutron reaction threshold energies produced by Howerton et al (30). Decay schemes of radioactive nuclides giving radii of decay, particle and photon energies, and branching ratios are listed in a book by Izhevlev and Poxer (31). More up to date information can be found in Nuclear Tables (32) and Nuclear Data Sheets (33). Heath (34) has catalogued the gamma ray spectra and proton energies for many radioisotopes, as has Crouthamel (35). Adams and Rams (36) have currently revised and enlarged Crouthamel's previous volume. Cuypers and Cuypers (37) have made a most useful collation of the spectra obtained after the irradiation by the 14 MeV neutrons of numerous elements. The detection limits for many elements using alternative nuclear reactions are also given. This volume supersedes the earlier computation of Bibbs (38). The quantitative treatment of spectra data in a simple gamma-ray spectrum has been discussed by Covell (39) and recently by Baedeker (40). Other workers have described the resolution of complex gamma-ray spectra by the application of digital computer techniques, involving least squares analysis (41 - 44) and more recently by the application
of Fourier transforms (45).

Digital computers have also been applied to the calculation of the best timing sequences for irradiation, decay and measurement of the required induced activity, in determinations on discreet samples (46). Neutron flux monitors have been compared by Iddings (47), who discussed the properties of boron trifluoride proportional counters, specially loaded plastic scintillators for neutron detection, and even the use of target coolant activity, as flux monitoring devices. Little differences in accuracy were found between boron trifluoride and plastic scintillator neutron monitors. An accepted system of neutron calibration against fast neutron flux has been devised by Heath (25), involving the activation and counting of copper foils under standard conditions. The accuracy and reproducibility of activation analysis has been discussed by Mott (25, 48) who suggests that local flux variations in the sample under irradiation, caused by variations in tritium density in the target and in deuterium ion density in the beam, may be overcome by sample rotation and the use of standards. The design principles and factors affecting the necessary biological shielding of neutron sources are dealt with exhaustively by Blizard and Abbott (49). These are covered in less detail by Lyon (7) and Prud'homme (13). Dibbs (38) and Darrall and Oldham (50) describe actual shielding designs.
and the provision and installation of neutron generator facilities.

Activation analysis as a means of continuous analysis with process control applications was first suggested by Anders (51). Reviews of this application of neutron activation have been made by Gray (52) and by Rhodes (53). A study of some of the fundamental principles involved in on-stream analysis in aqueous solution using an isotopic source was made by Gluck et al., (54). They investigated the effects on solution activity of variations in irradiation and detection cell volumes, solution flow rates and residence and cooling times, with solutions of vanadium, manganese, indium and silver. Calculated sensitivities for many elements were also given. Isotopic neutron sources have subsequently been the basis of a number of analysis investigations (55 - 64) including commercial analysis systems (55, 57, 60). Systems involving the recirculation activation analysis of slurries and liquids have been described by Stånes (56), Asher et al., (58), and by Fall (60). The on-line analysis system at the Warren Spring laboratory (available on a contract basis to industry) has been described by Carr-Brion and Stuart (57).

Fast neutron activation analysis using 14 MeV neutron generators has been applied to the continuous analysis (for process control) of solids and slurries, usually
employing moving conveyor belt techniques (63-68).
Gorin and Yavorsky (63) and Martin et al. (65) have attempted the direct analysis of coal, the carbon analysis by fast neutron inelastic scattering, and aluminium and silicon (ash content) by neutron activation methods. Martin et al. (67) have determined the concentrations of aluminium and silicon in cements, of solids in tars, of aluminium in bauxites and of iron and silicon in taconite iron ores (68).

Nargolwalla and Jervis (69, 70) have carried out 14 MeV neutron activation analysis of flowing aqueous solutions containing fluorine, vanadium and uranium, using a twin stream (standard and sample) system. Feasibility studies have been described (65, 66, 70, 71) involving analyses in liquid loop activation analysis systems. Hood (70), performed preliminary experiments on a number of potential process applications using a large scale liquid loop system. He investigated the feasibility of the determination of sea water salinity and trace element composition, the nitrogen content of foodstuffs (ammonium sulphate in water) and the sodium to phosphorus ratio in detergents. Analyses of trace elements in hydraulic fluid in the investigation of wear products and of the sulphur content of oils were attempted by the analysis of discrete samples using a pneumatic sample transfer system, but the sensitivities
he obtained were poor. Later, simulated solutions of trace elements in oils (aqueous solutions of aluminium, chromium and copper) were irradiated on the liquid loop facility with slightly better results. Bieby and Oldham (71), investigated the fundamental principles of 14 MeV neutron activation analysis in flowing aqueous systems, with a number of short half-life reaction products. Al-Charistami and Jarvis (72) have discussed the basic concepts and have given a mathematical treatment of methods to optimise the performance of continuous flow systems.

Little work has been published describing fast neutron activation analysis in non-aqueous flowing systems. Gorski et al. (73), have performed feasibility studies using fast neutron activation to determine the water, salt and sulphur contents of crude oils. The work was done in an effort to monitor drying and desalination procedures used to minimise pipeline and distillation column corrosion.

As the volume of published work in the field of on-stream analysis by fast neutron activation, especially in non-aqueous systems is small, it was decided that work should proceed to investigate the fundamental principles and problems associated with analysis in this medium. Further, determinations in an oxygen free
(hydrocarbon) solvent should be uncomplicated by the interferences encountered in the analysis of aqueous systems, arising from solvent activation. Relatively few interferences (74) would be expected, and a number of workers in the petroleum industry (75), have indicated that there is a need for activation analytical techniques for the determination at trace levels, of a large number of elements of interest.
2. PRINCIPLES
2.1. Nuclear Reactions

A nuclear reaction may be described as the interaction of an atomic nucleus with any sub-atomic or atomic particle, or photon, to produce a new or excited nucleus and particles or photons, as the reaction products. The product nucleus may be unstable and undergo radioactive decay to a stable nuclear state, and this is usually the case, although stable products may be formed directly. Nuclear reactions such as:

\[
\begin{align*}
^{140}_{58}\text{Ca} + ^1_n & \rightarrow ^{139}_{58}\text{Ca} + ^{2}_0\text{n} \\
^{139}_{58}\text{Ca} + 2^{0}_0\text{n} & \rightarrow ^{140}_{58}\text{Ca}
\end{align*}
\]

may be expressed in the shortened form:

\[
^{140}_{58}\text{Ca} (n, 2n) ^{139}_{58}\text{Ca}
\]

The initial and product nuclides are written outside the brackets, whilst the symbols inside the brackets denote the incident and emitted particles, (or photons) as shown. The in-going particle and initial nuclide are often referred to as the "probe" and "target" respectively.

Unlike chemical reactions these factors must also be equalised to balance the nuclear reaction equations: atomic number, total number of nucleons, momentum and angular momentum, and mass (energy). A consideration of the latter, the mass (energy) balance leads to the concept of the nuclear reaction energy denoted by the latter "\(Q\)" and defined as the energy absorbed or liberated in the
course of a nuclear reaction. The value of Q may be calculated from the differences in mass between products and reactants using Einstein's mass-energy inter conversion relationship, $E = mc^2$. Exothermic reactions in which energy is liberated are deemed to have a positive Q value whilst endothermic reactions have a negative Q value (by convention written on the right hand side of the equation). A reaction may be initiated by probes of zero energy if it has a positive Q value, but more usually reactions have in fact a negative Q value. In this case an incoming particle (or photon) must have a minimum energy theoretically equal in magnitude to the negative Q value of the reaction, for the reaction to take place. The reaction $^{19}_{9}$Fe($n$, $p$)$^{19}_{8}$O has a Q value of $-4.24$ MeV, and thus the incident neutron must possess at least this energy for the reaction to occur at all. In practice since we are dealing with collision processes, the law of the conservation of momentum requires that in the collision at least $\frac{1}{19}$ of the kinetic energy of the neutron be retained by the products, leaving only $\frac{18}{19}$ of the kinetic energy of the neutron available to initiate the reaction. Thus the actual minimum neutron energy which could cause the reaction to occur would be $4.24 \times \frac{18}{19}$, about $4.16$ MeV, which is called the threshold energy of the reaction.

In the case of a charged particle reaction, the coulombic repulsion forces between the nuclei which have to be
overcome, will further increase the threshold energy of the reaction above the $Q$ value, although there is a finite possibility that low energy probes may tunnel through the coulombic barrier. Therefore, as a neutron carries no charge, neutron induced reactions occur at lower probe energies than do charged particle reactions. Finally, a direct collision between probe and target is not necessary. Particles may interact when they pass close to the nucleus, "close" being defined as a quantised distance. In the case of such an interaction, the minimum probe energy required will be higher as an additional energy barrier (a centrifugal barrier) will have to be overcome.

Nuclear reactions can be conveniently described using the "liquid drop" theory first put forward by Niels Bohr in 1936 (76). His theory is based upon two assumptions:

a) The distance between nucleons is of the same order as the range of nuclear forces - i.e. reactions occur between neighbouring nucleons.

b) The interaction energy between nucleons is of the same order as the kinetic energy of the incident particle.

Bohr postulated that a nuclear reaction involved a two stage process. Firstly, the probe interacts with the target to form a highly excited compound nucleus existing with a finite life time of the order of $10^{-14}$ - $10^{-12}$ seconds. The kinetic and binding energies of the probe are distributed amongst all the nucleons in the compound nucleus.
Secondly the compound nucleus disintegrates thus forming the reaction products. The disintegration of the compound nucleus is believed to involve a reorientation of energy amongst the nucleons, until at a given instant of time a nucleon or group of nucleons possess sufficient energy to overcome the nuclear binding forces, and are emitted. Emission of a photon of electromagnetic radiation may also occur. As this reorientation of energy is a random process, similar compound nuclei can and do disintegrate in different ways giving rise to a range of reaction products. This process may be illustrated by the following example:

\[
\begin{align*}
\text{Al}^{27} + n &\rightarrow \text{Al}^{28} \rightarrow \text{Al}^{27} + n \\
13 + 0 &\rightarrow 13 + 1 \\
&\rightarrow 13 + 2n \\
&\rightarrow \text{Mg}^{27} + \text{H}^{1} \\
&\rightarrow \text{Na}^{24} + \text{He}^{2}
\end{align*}
\]

All of these reactions occur to a greater or lesser extent when aluminium is bombarded by neutrons. The disintegration of the compound nucleus is thus independent of the mode of production (77). The energy of the excited compound nucleus will vary with the energy of the probe and this will alter the yield of the individual reaction products.

The yield of a particular product will depend on the reaction cross section which is defined as the probability
that a particular nuclear reaction will occur, and is usually quoted for a particular probe energy. The variation in cross section with probe energy of a reaction is called an excitation function. A consideration of the excitation functions for the various possible nuclear reactions in the last example would allow a prediction to be made of the yield of each reaction at a given probe energy. Consider a beam of $P$ particles per square metre per second incident on a thin target $x$ metres thick and containing a target nuclei per square metre, then the number of interactions of a particular type $P$ per cubic metre per second may be expressed by:

$$ P = nx\sigma $$

where $\sigma$ is the probability of the reaction (cross-section)

or, rewriting the expression

$$ \sigma = \frac{P}{nx} $$

Sigma has the dimensions of an area (square metres per nucleus) and may be said to represent, for a given nuclear reaction, the effective area that a nucleus presents to a probe of given energy. The unit of cross-section is the $\text{barn (b)}$ which is defined as an area of $10^{-28} \text{ m}^2$ per nucleus. The barn is rather a large unit where fast neutron reactions are concerned, when cross sections are more usually expressed in millibarns ($\text{mb}$). A total cross-section for an element may be given and this is taken to be the sum total
of the cross sections for all the possible nuclear reactions occurring with a given probe.

2.2. Nuclear Reactions used in Activation Analysis

Nuclear reactions may occur through the bombardment of a target with charged particles (protons, deuterons, tritons, helium ions or heavy ions) or with neutrons or photons. Charged particle and photon reactions are really outside the scope of this thesis and will only be mentioned in passing.

2.2.1. Charged Particle and Photon Reactions

The linear accelerator, the cyclotron and the linac, may all be used as sources of charged particles. A major disadvantage of charged particle activation analysis is that the particles have a limited range in solid matter and hence extremely thin targets are required to achieve a uniform irradiation. This itself creates problems of adequate target cooling, loss of volatile material, and thermal decomposition of the target. The method is particularly suited however to the analysis of small areas of a surface e.g. for surface impurities.

Electron accelerators (Bremsstrahlung sources) producing photons from the deceleration of electrons in the field of the nucleus of a heavy element, or isotopic
sources, are the major photon sources used in activation. Photon activation is not used in many applications to date and is restricted to a few well characterised specific cases as an analytical technique. Biological shielding for high energy photon sources must be massive and hence expensive, whilst the production of photons with high enough energies to promote a wide range of nuclear reactions (15 - 25 MeV) requires very expensive, powerful, electron accelerators. These "cost" factors explain the limited application of photon activation analysis.

2.2.2. Neutron Activation

There are two distinct types of neutron activation analysis (fast and thermal) depending upon the energy of the neutron probes used. Thermal neutrons are classed as neutrons with energies up to a maximum of 0.025 eV, and fast neutrons are defined as neutrons with 1 MeV or more in energy. Neutrons with energies between these limits are referred to as epithermal neutrons. Fast neutrons from generator sources (employing the fusion of deuterium with tritium) produce neutrons with a maximum energy of about 14 MeV.

2.2.2.1. Thermal Neutron Sources

The most commonly encountered source of thermal neutrons in activation analysis is the thermal reactor, although
the low neutron outputs from isotopic sources and from "machine" produced moderated fast neutrons have also been used. Thermal reactors are the most common type of nuclear reactor where the fast fission spectrum of neutrons released by the fission of suitable fuels (U, Th, Pu), lose energy during collisions with a neutron moderator (light elements H, Be, C, O) and attain thermal energies where the fission reaction cross-sections are large. Maximum continuous neutron fluxes of the order of $10^{13} - 10^{14} \text{ n cm}^{-2} \text{ s}^{-1}$ are available for irradiation but the neutron flux and neutron energies depend on the actual location of the irradiation position within the reactor core. Pulsed reactors (TRIGA) have attained neutron fluxes of $2 \times 10^{15} \text{ cm}^{-2} \text{ s}^{-1}$ during pulses having durations of the order of micro seconds. Fast neutrons from other sources such as accelerators and cyclotrons may be moderated to thermal levels. The thermal fluxes available however are low, of the order of $10^{10}$th or less than that of the initial fast flux. This is due to the increased separation of sample and source brought about by the interposition of the neutron moderator (paraffin wax, polythene, water). In any case the fast neutron output of such devices is vastly inferior to that of the nuclear reactor.

Isotopic neutron sources employing the photonuclear reaction on beryllium are available with neutron fluxes of
the order of $10^{-6}$ of that obtained from a reactor. This particular photo nuclear reaction has a threshold energy of $1.57 \text{ MeV}$ and the isotope antimony $\text{Sb}$, with a half-life of 60.3 days, photon energy $1.63 \text{ MeV}$ is often used as the photon source. A major disadvantage of the isotopic source apart from its low output is the continuous decay of the photon emitter, whether the source is being used productively or not, necessitating source replacement.

2.2.2.5. Thermal Neutron Reactions

The most common nuclear reaction occurring with thermal neutrons is that of neutron radiative capture, the $(n,\gamma)$ reaction:

\[
\text{Al}^{27} (n,\gamma) \rightarrow \text{Al}^{28}
\]

Most elements ($Z = 10 - 80$) will interact with thermal neutrons by this reaction to produce radioactive products which may be used in analysis. Light elements do not activate indeed some are used as neutron moderators, whilst some heavy elements undergo fission, into lighter fragments, on neutron capture. The sensitivity of analysis can be very high (1 ppb) due to the high flux of neutrons available from a reactor and also due to the large nuclear reaction cross-sections for neutrons of this energy (of the order of barns or greater). The major disadvantage of the
technique is the cost involved in the provision and maintenance of a nuclear reactor. Also as previously stated the actual location of the sample in the core affects the irradiation conditions, whilst the heat from the core also imposes limitations on the materials which may be irradiated.

2.2.2.3. Fast Neutron Sources

The fast fission component of the neutron fluxes in a reactor may be used for fast neutron activation. As the neutron flux is not homogeneous in energy throughout the core, irradiation locations within the core may be specially selected for fast neutron activation analysis. Samples are usually enclosed in a good thermal neutron absorber to remove the thermal component of the neutron flux, and minimise interferences from thermal activation of the sample. The other most common sources of fast neutrons are machine sources of various kinds and isotopic sources.

The commercial fast neutron generator (up to \(10^{11} \text{ ns}^{-1}\)) is the most frequently encountered machine source of fast neutrons in activation analysis and consists of a low powered particle accelerator (100 - 200keV) producing neutrons by the D - T reaction. This reaction involves the fusion of deuterium with tritium by the reaction

\[ ^2_1 \text{H} ( \text{H, n}) ^4_2 \text{He}, \Delta E = +17.6 \text{ keV}, \text{ producing fast neutrons with} \]

\[ ^2_1 \text{H} \]
a maximum energy of 14.7 keV, and having a marked resonance (a large increase in cross section) at energies of 100 keV. The fusion reaction is accomplished by bombarding a target containing titanium tritide (though other hydrides have been used), with deuterium ions produced in an ion source and accelerated through a potential gradient of up to 200 kV. Neutrons are also produced from the bombardment of many elements with protons, deuterons or alpha particles of suitable energies. Some examples which have been used include: $^{7}\text{Li}(p, n)^{7}\text{Be}$, whilst the highest neutron outputs (per unit ion current) have been obtained from the high energy deuteron reaction $^{1}H(\alpha, n)^{4}\text{Be}$. Isotopic fast neutron sources employ the ($\alpha$, n) reaction, producing fast neutrons from the alpha-particle bombardment of light elements. Radium, and now plutonium to some extent, are commonly used as the alpha-emitter, whilst beryllium and boron are used as targets. Neutrons are produced by the reaction $^{9}\text{Be}(\alpha, n)^{12}\text{C}$ or by the reaction $^{5}\text{B}(\alpha, n)^{7}\text{N}$. These sources have been used for activation analysis but suffer the limitation of high cost for adequate neutron output due to the Pu or Ra contents.
2.2.2.4. Fast Neutron Reactions

Reactions commonly occurring are the \((n, 2n)\), \((n, p)\), \((n, \alpha)\), \((n, n)\), and the \(n, f\) fission reaction which applies to a few heavy elements. Fast neutrons possess enough energy to induce a number of possible reactions in a target element and irradiation with fast neutrons often produces a mixture of products. Such a mixture of products may complicate the analysis of mixtures, but in practice the irradiation and detection conditions can often be specially selected to favour the production and detection of a certain reaction product. The number of possible reactions however allows a wider scope in the selection of a product isotope, half life and type of emission, for analysis than in the case of thermal neutrons. Also product half lives tend to be short, minimising post irradiation storage problems and allowing rapid analysis even when selective decay procedures are used.

Fast neutron activation analysis suffers from a number of disadvantages partly due to inherent limitations of the technique, and partly due to limitations imposed by the use of neutron generator neutron sources, these will be discussed separately below.

Inherent Disadvantages

(i) The same product isotope may be formed from different
fast neutron reactions on different elements occurring close together in the periodic table. Clearly this constitutes a most serious interference. Problems associated with interferences will be discussed fully later.

(1) 14 MeV nuclear reaction cross sections are usually of the order of one thousandth of those for thermal neutron reactions, i.e. in the millibarn region. Similarly the neutron fluxes available from neutron generators and other sources are lower than the thermal flux available from a reactor. Thus sensitivities and detection limits of analysis are correspondingly worse and are usually of the order of micrograms per gram.

Disadvantages of Neutron Generators

(1) The neutron flux available from a neutron generator falls rapidly with time as the tritium becomes depleted in the surface layers of the target. Tritium is lost mainly by outgassing from the target due to the heating effect of ion bombardment and not as might be expected by reaction with deuterium to produce neutrons. Thus the technique usually involves short irradiations with the production of short lived radionuclides. Frequent target changes are necessary if the highest neutron fluxes are to be maintained.

(11) The available neutron flux at the irradiation station
near the generator target decreases sharply with distance and axial location. Consequently irradiation geometry, and sample thickness must be maintained to high standards if reproducible results are to be obtained.

(111) Neutron fluxes are irreproducible between irradiations and the methods of flux measurement and the subsequent calibration of flux monitors are not sufficiently precise. The neutron flux depends on a number of parameters which are governed by the operating conditions used on the generator. Neutron output depends on ion current, surface layer tritium content of the target, accelerating voltage, and on the ion beam focussing conditions. The deuteron beam tends to vary unless close control is kept over operating conditions whilst targets may be inhomogeneous in their tritium content or may be made so by incorrect operating conditions. Thus no two irradiations are made under identical conditions.

The last two disadvantages may be minimised by the use of internal standards, and sample rotation during irradiation. An absolute method of measuring neutron flux is now under development at the National Physical laboratory. The availability of reliable high output sealed-tube neutron generators, using mixed beams of tritium and deuterium, and having an allegedly "constant" neutron output for periods exceeding 1000 hours, may minimise the disadvantages outlined in (1). In spite of these disadvantages,
the commercial fast neutron generator is still the cheapest and most versatile fast neutron source available to the activation analyst.

2.3. Theoretical Calculations

2.3.1. Theoretical Calculation of the Induced Activity

The amount or activity of a radionuclide produced in the irradiation of a given target element can be calculated theoretically and should thus provide a means for absolute determinations to be made. Unfortunately, this is not possible in practice as the resultant error in the so-called "activation equation" derived below, produced by the constituent errors in the experimentally obtained parameters of the equation, invalidates absolute determinations. Calculations of the activity induced in a sample, however, are important in feasibility studies and in the selection of the best nuclear reaction and technique to minimize interferences, and maximize sensitivities in a particular case.

Consider the case of a radionuclide being produced at a constant rate \( P \) atoms \( s^{-1} \), by a constant neutron flux \( f = n s^{-1} \). The nuclide is also undergoing radioactive decay at a rate governed by its disintegration constant \( \lambda (s^{-1}) \). At a given instant \( t \) the rate of growth of the nuclide will be given by:

\[
\frac{dN}{dt} = P - \lambda N
\]  \hspace{1cm} (1)
where \( N \) represents the number of atoms of the nuclide present.

For an irradiation time of \( t \) seconds integrating (1) gives:

\[
N = \frac{P}{\lambda} (1 - e^{-\lambda t}) + N_0 e^{-\lambda t}
\]

(2)

where \( N \) is the number of atoms of the nuclide present at the beginning of the irradiation. Usually \( N \) will be zero, and hence:

\[
N = \frac{P}{\lambda} (1 - e^{-\lambda t})
\]

(3)

At the end of the irradiation the activity \( \Lambda_{(t)} \) of the nuclide, which is the rate of decay of the radionuclide, will be given by

\[
\Lambda_{(t)} = \lambda N = P(1 - e^{-\lambda t})
\]

(4)

The rate of production of the radionuclide \( P \) during the irradiation will depend on the neutron flux \( \Phi \) \((= m^{-2} s^{-1})\), the reaction cross-section of the target nucleus \( \sigma \) (mmb per nucleus) and on the number of target atoms \( N \) of the target element present. Thus \( P \) may be obtained from the equation:

\[
P = N \sigma \Phi
\]

(5)

Now \( N \) may be calculated from

\[
N = \frac{Lm}{k}\frac{A}{\text{at}}
\]

(6)

where \( L \) = Avogadro's number \((6.023 \times 10^{23} \text{ atoms per mole})\),
\( k \) = the fractional isotopic abundance of the target element,
\( m \) = mass of the element irradiated,
\( \text{at} \) = atomic weight of the element.
Substitution of \( P \) from equations (5) and (6) into equation (4) gives:

\[
A(t_1) = \frac{\ln k}{\ln \text{Nat}} \sigma \cdot f (1 - e^{-\lambda t_1})
\]  
(7)

This equation is usually referred to as the "activation equation". As may be seen the activity induced, and hence the sensitivity, depends on the reaction cross section \( \sigma \), the neutron flux \( f \), the isotopic abundance \( k \) and on the atomic weight of the element \( \text{Nat} \). This general equation also applies to all types of activation analysis.

In practice a counting rate instead of an absolute activity is obtained and so allowance must be made for the counting efficiency \( \beta \), and the branching ratio \( b \) (the percentage of the radionuclide decaying by the nuclear transition we wish to utilise in counting). In a counting interval \((t_2 - t_1)\), measured from the end of the irradiation, the counts \( C \) recorded by the detecting equipment will be given by:

\[
C = b \beta \int_{t_1}^{t_2} A \cdot e^{-\lambda t} \, dt
\]

which on integration gives:

\[
C = b \beta A \left( e^{-\lambda t_1} - e^{-\lambda t_2} \right)
\]  
(8)

Substitution of the value of \( A(t_1) \) from (7) into equation (8) gives:

\[
C = \frac{\ln k}{\ln \text{Nat}} \sigma \cdot f (1 - e^{-\lambda t_1}) (e^{-\lambda t_1} - e^{-\lambda t_2})
\]
Rearranging the last equation gives the relationship

\[ m = \frac{C}{E \delta \mathbf{f}} \left( \frac{\lambda}{Lk} \right) \left( 1 - e^{-\lambda t_1} \right) \left( e^{-\lambda t_1} - e^{-\lambda t_2} \right) \]  

Equation (9) would allow the calculation of the mass \( m \) of an element present as all the other terms are known or may be obtained experimentally. Such an absolute determination cannot be made in practice due to uncertainties in the following terms:

1. The neutron flux \( \mathbf{f} \) passing through the sample cannot be determined with sufficient accuracy.
2. The nuclear reaction cross-section \( \sigma \) is also not known with a sufficiently high degree of accuracy (±3 -10%). In any case the value of \( \sigma \) which is experimentally measured varies with neutron energy (an excitation function).
3. The detector efficiency \( \mathbf{K} \) and the branching ratio \( \mathbf{b} \) of the radio-nuclide are also the result of experimental measurement and thus contain their own sources of error.

It is thus normal practice to utilise techniques involving some kind of comparative method in activation analysis determinations.

Comparison with a standard sample of known composition and similar physical proportions, irradiated under similar conditions may be made. Simultaneous irradiation of sample and standard with rotation is required for the very best results although irradiation at different times under identical conditions is usually adequate. The unknown
weight of the element \( \text{Wx} \) is determined by comparison of its count \( C_x \) with that of a standard \( C_0 \), of known weight \( \text{Ws} \).

\[
\text{Wx} = \frac{C_0 \times C_x}{C_0}
\]

An extension of this basic technique may be used if many samples covering a range of element concentrations are to be analysed. A number of standards covering the concentration range likely to be encountered are prepared, irradiated and then used to obtain a calibration graph of activity against sample weight, from which unknowns may be determined by comparison.

Another method often employed is the standard addition method, whereby the unknown sample is divided into two samples, and a measured amount of the element to be analysed is added to one of them. Both samples are subsequently irradiated and counted, when, if \( C_e \) is the count obtained from the sample with the added standard, and \( C_x \) is the weight of standard added, then

\[
\text{Wx} = \frac{C_e \times C_x}{(C_e - C_x)}
\]

These methods minimise errors, and overcome those inherent in the activation equation as described previously.

Unless simultaneous irradiation of both sample and standard is possible, a reliable flux monitor must be used in order that the results obtained may be normalised by the comparison of the fluxes used in each irradiation. This in itself
may introduce further errors.

2.3.2. Calculated Limits of Detection

Hypothetical detection limits may be calculated from the activation equation (1), once the various parameters have been measured or obtained from tables. Many of the published detection limits tables tend to be optimistic, especially the older ones. Comparisons between different facilities are not readily made unless "conversion factors" are obtained between facilities.

2.3.3. Selection of Conditions for Irradiation Decay and Counting Times

In an irradiation at a constant neutron flux, the measured activity of the sample is found to rise quite steeply initially and then to level off progressively with time. This may be readily explained as follows.

Equation (4), obtained in 2.3.1, gives the activity of a nuclide produced during an irradiation time \( t_1 \):

\[
A(t_1) = P(1 - e^{-\lambda t_1}) \tag{4}
\]

now \( \lambda = \frac{0.693}{t_\frac{1}{2}} \) where \( t_\frac{1}{2} \) is the half-life of the nuclide

\[
A(t_1) = P(1 - e^{-0.693 t_1/t_\frac{1}{2}})
\]

A simple calculation will show that when

\[
\begin{align*}
t_1 &= t_\frac{1}{2} & A(t_1) &= \frac{1}{2}P \\
t_1 &= 2t_\frac{1}{2} & A(t_1) &= \frac{1}{4}P \\
t_1 &= 3t_\frac{1}{2} & A(t_1) &= \frac{1}{8}P
\end{align*}
\]

and so on.
Normally, for the determination of a single element, irradiation for one half-life is adequate, whilst irradiations lasting longer than three half-lives are of dubious value even in maximum sensitivity determinations. Irradiation for three half-lives is often possible for short half-life product nuclides but for long lived products irradiation for fractions of a half-life only will be possible. When using neutron generator sources (excluding sealed tube generators), irradiations longer than ten minutes or so are impractical due to the fall off of neutron output with time. Mixtures may often be analysed using a short irradiation to determine the short half-life reaction products followed by a longer irradiation for the analysis of longer lived products. This procedure minimises interference and maximises sensitivity.

The counting of single elements should be undertaken as soon as possible after irradiation and continued for a period of three or four half-lives, the counting period depending on the detector background. The criterion used in selecting a counting period is that the greatest number of source counts should be collected in as short a time as possible to maximise the source to background ratio. As counting continues the accuracy of the determination will steadily decrease due to the increased "background" content of the counts recorded. This gives rise to an increase in statistical error even though the total number of counts
recorded is increasing. In the analysis of mixtures, decay times may be selected to allow unwanted interferences to die away before counting the required products. Decay time control, the successive counting of a sample with time, may also be useful in resolving a sample into short and long lived components. For long half-lives the counting time is selected to give a good statistical counting accuracy.

The selection of the optimum timing sequence of irradiation, decay and counting in activation analysis using computer techniques has been discussed by Isenhour (78). Federoff (79) more recently has also discussed the selection of these criteria.

2.4. Nuclear Radiation Detectors

The detection of the radiation emitted by radionuclides may be accomplished using physical properties based upon their interaction with matter. Currently, two principal categories of detection device are employed, the one based on the ionization properties of nuclear radiation in gases and solids (gas-filled and semiconductor detectors), the other based upon the production of light (scintillation detectors) when radiation interacts with certain materials.
2.4.1. Ionisation Detectors

2.4.1.1. Gas-Filled Devices

Gas-filled detector assemblies usually consist of two electrodes maintained at a steady potential difference by the associated electronics and housed in a gas-filled enclosure. The electrodes attract the ions and electrons produced when ionisation of the gas occurs due to interaction with nuclear radiation, and this causes a small current to flow temporarily across an external high resistance. Once all the ions and electrons have been collected, the current ceases and the detector is ready for another ionising event to take place. The voltage pulse developed across the external resistance is monitored and recorded as a "count" by the associated electronics. There are three types of gas-filled detector: the ionisation chamber, the proportional counter and the Geiger-Müller or Geiger counter.

If the potential difference between the two electrodes is low, the ions and electrons produced in an ionising event (primary ions) will not acquire sufficient kinetic energy in moving towards the electrodes to cause further ionisation by collision (secondary ionisation) in the gas. These conditions are utilised in the ionisation chamber where the minute current from the collection of primary ions is measured directly by means of an electrometer. Ionisation chambers are used to calibrate radioactive...
sources but in practice these devices suffer from poor sensitivity. Fairly active sources (of the order of 0.1 μCi for β-emitters, 1 μCi for γ-emitters) are needed in order to produce measurable and significant ion currents. These detectors would not normally be used in activation analysis.

As the voltage between the electrodes is increased, secondary ionisation will occur and a voltage region is encountered where the number of secondary ions produced and collected is directly proportional to the initial number of primary ions formed. A counter working in this voltage region is called a proportional counter and the gas multiplication in such a device (number of secondary ions produced per primary ion) is of the order of $10^6$. The output pulse size for each count recorded from the detector depends upon the energy of the radiation and on the specific ionisation of the radiation interacting in the detector. The proportional counter is an efficient detector of alpha- and beta-particles, but shows poor counting efficiency for gamma-radiation due to its low specific ionisation.

If the potential difference between the electrodes is increased further the Geiger-Müller region is reached. In this voltage region gas multiplication is of the order of $10^9$. Thus a single primary ion-pair can produce an "avalanche" of secondary ions in the detector resulting
in almost complete ionisation and hence a virtual discharge occurs between the electrodes. A halogen gas or alcoholic vapour is incorporated as a component in the gas filling of a Geiger detector in order to "quench" the discharge within the tube. The quenching agent operates by removing energy by collision from the system, leading to dissociation of the quenching agent without producing further ionisation. Since an "avalanche" of secondary ions is produced from the production of a single ion-pair, the output pulse size from the Geiger detector is independent of the energy and type of radiation producing the primary ions and hence this detector cannot be used for spectrometry.

Applications of Gas-Filled Detectors as Neutron Counters

Neutrons are commonly detected and counted by means of the boron trifluoride (BF₃) proportional counter, or by fission chambers. The BF₃ counter monitors thermal neutrons by the nuclear reaction $^{10}\text{B}(n,\alpha)^7\text{Li}$ and contains boron trifluoride gas often enriched in the boron-10 isotope. The alpha-particle and lithium-7 nucleus produced in the nuclear reaction cause large-scale ionisation within the detector and hence a large output pulse is obtained which may easily be detected and recorded by the associated electronics. The counter is readily adapted
for fast neutron detection by encasing the BF$_3$ tube in a neutron moderator such as polythene to slow down fast neutrons to thermal levels. This type of detector is well suited to neutron monitoring in neutron generator installations due to the large size of output pulse produced. Neutron generators are also intense sources of X-radiation and gamma radiation.Prompt gammas are produced by neutron inelastic scattering, and also from neutron activation of the shielding. The weaker pulses produced in the proportional counter by the interaction of X- and $\gamma$-radiations can readily be removed by pulse size discrimination, so that only the required pulses are recorded by the scaling equipment. The large pulse size of the proportional counter is an added advantage in that long cable lengths between detector and scaler through the generator biological shielding may be accommodated without the need for elaborate preamplification. The fission chamber is another type of "proportional" neutron detector. The counter is coated inside with a fissionable isotope, uranium $^{235}$ or uranium $^{238}$ respectively for thermal and fast neutron detection. The fission fragments produced from the capture of a neutron by the uranium nucleus produce massive ionisation and hence large pulses in this proportional type detector (cf BF$_3$ counter).
2.4.1.2. Semiconductor Detectors

Semiconductor detectors of various types have only been in existence for a few years, but due to their high energy resolution compared with that of scintillation detectors they have become increasingly important as radiation detectors. Although silicon semiconductor devices have previously been used as detectors in activation analysis, they have been replaced almost completely by the lithium drifted germanium detector for high resolution gamma-ray spectrometry. The function of this detector will be described in outline below but a detailed theoretical description may be found elsewhere [80].

N-type germanium is created when a material which can act as an electron donor is introduced into the germanium lattice as an impurity, the pentavalent elements (P, As, Sb) being frequently employed for this purpose. Extra electrons are thus introduced into the lattice when such a pentavalent impurity occupies a site normally holding a tetravalent covalently bonded germanium atom. Electrical conduction will take place if an electric field is applied to the crystal, due to the movement of the free electrons from the impurity donor atoms. These electrons are free to move due to the weak nature of the bond and the high dielectric constant of the medium. Analogously p-type germanium is formed by the introduction of trivalent atoms (B, Ga, In), which can act as electron
acceptors, into the tetravalent germanium lattice. This will conduct electricity by movement of electrons from the valence band (lowest energy band) into the positive holes created in the tetravalent lattice by the presence of trivalent atoms.

A p - n junction can be formed if a readily ionizable metal such as lithium is diffused into p -type germanium. The germanium where lithium is present will exhibit n -type properties as the number of free holes from the trivalent impurity will be outnumbered by the number of free electrons from the lithium. Thus the p - n junction occurs at the interface of the p and n - type germanium where no imbalance of either holes or electrons exists. Clearly in this depletion layer only intrinsic conduction, due to thermal excitation of electrons, is possible, and even this way not occur if the crystal is cooled to liquid nitrogen temperatures. If the p-side of a crystal is subjected to a negative voltage at 40-60°C lithium ions will slowly drift towards the p-side forming neutral dipoles with, and compensating the migration of, the negative lattice ions of the impurity acceptors. Thus the depleted region is extended by the drift of lithium from the n-type germanium until they cease to drift due to the competing process of the intrinsic conduction of the compensated layer in the applied voltage field. Electrons collected at the n-region lower the mobility of the lithium
ions in the field as they counteract the excess charge of the lithium. Similarly positive charges collected in the p-region tend to replace lithium ions in the compensation of the negative fixed charges. The competition of charge carrier collection will increase as the extent of the compensated layer and hence intrinsic conduction increases, until no further lithium drift occurs. Intrinsic conduction may now be prevented by cooling the crystal, still with a reverse bias applied, in liquid nitrogen. The lithium-drifted germanium crystal may now be used as a radiation detector, the so-called p-i-n diode.

The function of the device as a radiation detector is analogous to the operation of the gas-filled ionisation chamber. Electron-hole pairs are produced (Cf ion-pairs) when a $\gamma$-ray passes through the region of intrinsic conduction and is absorbed, causing ionisation in the medium. The electron-hole pairs are collected at the electrodes and a voltage pulse is obtained from the crystal detector and recorded by the associated electronics. The size of the voltage pulse is dependent on the number of electron-hole pairs produced in the absorption of the photon and hence is proportional to the energy of the gamma-ray. Hence pulse-height spectrometry can be carried out.

The main advantage of the p-i-n diode over the scintillation counter is that of higher spectral resolution. The higher resolution may be explained by the fact that
only about 3eV of energy is required to initiate one event (an electron-hole pair) in the detector compared with about 300eV in a NaI(Tl) crystal to initiate a productive scintillation event. Statistical fluctuations in the pulse production train are much smaller for the semiconductor detector. The observed resolution of these detectors is in practice worse than that predicted theoretically due to a combination of background noise from detector leakage and from associated electronics.

The detector suffers from two main disadvantages at the present time: low detection efficiencies (of the order of 10% of that of a 75 x 75 mm NaI(Tl) crystal for a 100 cc detector) and the need for constant cooling to liquid nitrogen temperatures if the properties of the semiconductor are to be maintained. Detection efficiency will improve as larger and larger intrinsic volume detectors become available. The detectors must be maintained at least below -80°C as damage to the detector will occur above this temperature. Precipitation of lithium (present in high concentration) may occur in the n-region due to lithium ion mobility and lattice defects, and/or lithium may migrate at higher temperatures from the acceptor centre due to the weakness of the pairing bond. Heath (81) has reviewed the current advances in detectors.
2.4.2. Scintillation Detectors

A scintillation detector assembly comprises a scintillator material linked optically to a photomultiplier tube with accompanying associated electronics. An input of energy to the scintillator material from the absorption of energy by interaction with nuclear radiations are produced and light scintillations which are viewed by the photomultiplier tube. The flash of light from the scintillator is turned into an electronic pulse by the photomultiplier and this is recorded as a "count" by the associated electronics. Since the size of this electronic pulse is dependent on the energy given up to the scintillator, pulse-height spectrometry may be carried out. The component parts of a scintillation detector are described below.

2.4.2.1. Scintillator Materials

Virtually all gamma-ray scintillation spectrometry in activation analysis is performed using inorganic crystal scintillators. The most widely used inorganic scintillator is thallium activated sodium iodide, NaI(Tl), which has a high detection efficiency for γ-radiation due to its high density. This material has further advantages in that NaI(Tl) possesses a high conversion efficiency of radiation energy into light, a short luminescence decay time, good light transmission properties, and may,
owing to its crystal structure, readily be grown into large single crystals. A qualitative description of the scintillation process in ionic crystals (which even currently is not fully resolved) is given in terms of the bond theory of ionic crystals by Birks (82). As sodium iodide is hygroscopic the crystal must be hermetically sealed in a suitable container incorporating an optically transparent window.

Other scintillator materials include organic materials such as anthracene and paraterphenyl. Plastic scintillators (dispersions of an organic scintillator in a plastic) and liquid scintillators (solutions of an organic scintillator in a suitable solvent) are usually used for $\beta$-particle counting or for certain special limited applications.

Cerium activated silicate glasses containing lithium have been used for neutron detection and possess high sensitivity. These detectors give large amount of light from interaction of the reaction products of the nuclear reaction $^6$Li($n$, $\alpha$)${}^3$H with the glass. Various organic scintillators (e.g. specially loaded plastic scintillators) have also been used in neutron detection.

2.4.2.2. Photomultipliers

The scintillator is optically coupled, using a silicone oil or grease, to a light sensing device, the photomultiplier tube, and this combination (called a detector assembly)
is housed in a light-tight enclosure.

The photomultiplier is a vacuum-tube containing a light-sensitive photocathode located beneath or on an optically transparent window, a series of secondary electrodes called dynodes, and a final collecting electrode or anode. The anode is maintained at a high potential with respect to the cathode by the associated electronics, whilst the series of dynodes are maintained at successively lower potentials along the tube towards the photocathode. Light photons originating from the tiny flash of light in the scintillator interact with the photocathode giving up their energy and causing electrons to be emitted by the photoelectric effect. These primary electrons are accelerated towards the first dynode which is positive with respect to the cathode, thus giving kinetic energy in transit. On striking the electrode they impart their energy to it and as a result more secondary electrons are emitted from the dynode. Since more secondary electrons are emitted than the primary electrons giving rise to them, electron multiplication has taken place. These secondary electrons are accelerated down the tube towards the second dynode when a similar sequence of events occurs. Further electron multiplication occurs at each successive dynode until finally a large burst of electrons is collected at the anode. Typical overall amplifications in photomultipliers can be as high as $10^7$ and the burst of
electrons is amplified and recorded by the associated
electronics. The photomultiplier or P.M. tube is itself
a source of background counts over and above those recor-
ded owing to scintillations occurring due to natural
background. Thermionic emission of electrons in the P.M.
tube produces electronic noise pulses (dark current)
which are usually smaller in amplitude than those arising
from "genuine" events. An electron originating from
thermionic emission will not receive the full amplifica-
tion of the tube as few such electrons will be emitted
from the first dynode but on average will originate from
the centre of the tube. In recent years P.M. tubes have
improved considerably with the advent of the multielement
composition photocathode and new design dynodes. These
improvements have led to increased efficiencies and gain
signals and lower noise levels. Noise signals may be
minimised (but not eliminated) if the P.M. tube is refri-
gerated thus reducing thermionic emission. The design
and construction of photomultipliers is dealt with
exhaustively by Adams and Dams (36) and by Birks (82).
Finally photomultipliers are usually enclosed in an
earthed mu-metal screen in order to minimise the effects
on their operation of external electrostatic and magnetic
fields.
2.4.2.3. Photon Interactions

A gamma-ray photon is subject to three principal modes of interaction within matter, and may be either completely absorbed, or simply degraded in energy. All or any combination of these modes of interaction may occur in the passage of the photon through matter, and these modes are:

(1) The Photoelectric Effect
(2) Compton Scattering
(3) Pair Production

The photoelectric effect is the principal mode of interaction of low energy gamma-rays up to 0.5 MeV in energy. In this type of interaction a gamma-ray photon collides with, and transfers all its energy to, a firmly bound electron in an inner shell of an atom and thus disappears. The electron is ejected from its shell with kinetic energy of motion equal to the energy of the absorbed quantum minus the binding energy of the electron in its shell. Usually electrons are ejected from the K-shell of an atom and these are known as conversion electrons. When the vacancy in the K-shell is filled by an electron from an outer shell this will be accompanied by X-radiation equivalent to the energy difference between the shells. This X-radiation may be transferred to another outer electron and eject it. The latter electron is known as an Auger electron. Provided all these interactions are absorbed in the scintillator
within its resolution time they will be seen as one event. Hence, to the counter (scintillator and photomultiplier) the total absorption of the gamma-rays is also observed as a single event. A single narrow peak is therefore observed in the pulse-height spectrum for a monoenergetic gamma-ray and this is called the photopeak. The photopeak is the most important feature of the spectrum since its location in the spectrum depends on the characteristic energy of the gamma-ray. This factor is used in qualitative analysis and the peak area for quantitative analysis.

Compton scattering is the predominating mode of interaction for medium energy gamma-rays in the energy range 0.5 - 2.0MeV. This interaction involves a partial transfer of energy by elastic collision from the incident gamma-ray to an unbound electron. A scattered electron possessing kinetic energy ($E_e$), and a scattered gamma-ray ($E_\gamma^1$) degraded in energy are the products of the interaction. The proportion of the original photon energy ($E_\gamma$) transferred to the electron depends on the angle ($\theta$) through which the gamma-ray is scattered and the energy of the products is given by:

$$E_\gamma^1 = \frac{E_\gamma}{1 + E_\gamma (1 - \cos \theta)/mc^2}$$

and $E_e = E_\gamma - E_\gamma^1$

where $m$ = mass of an electron

$c$ = velocity of light
The scattered electron subsequently imparts its energy to the scintillator resulting in the production of light. The gamma-ray pulse height spectrum due to this effect contains a sharp edge (the Compton edge) located just below the photopeak, and leading to a continuum (the Compton continuum) right down to zero pulse height.

This may be explained as follows. The scintillation in the detector arises from the transfer of energy from the scattered electron to the scintillator. The energy of the electron can lie between zero and a maximum energy $E_e (\text{max})$ described by the function:

$$E_e (\text{max}) = \frac{E_0}{1 + (mc^2/E_0)}$$

The Compton edge occurs when $E_e = E_e (\text{max})$ and contributions to the continuum will occur at electron energies between zero and $E_e (\text{max})$.

The degraded gamma-ray may undergo further Compton interactions, the photoelectric effect, or may even escape from the crystal. If further Compton scattering or the photoelectric effect occurs, the gamma-ray appears to be absorbed within the resolution time of the detector. This sequence of events cannot be distinguished from a photoelectric interaction and hence a pulse is produced which contributes to the photopeak. Large NaI(Tl) crystals are therefore best to minimise partial interactions leading to the escape of a degraded gamma-ray and thus
minimise the Compton continuum, but unfortunately they suffer from a decrease in spectral resolution with an increase in size. 75 x 75 mm crystal detectors are a popular size for activation analysis and represent a good compromise between spectral resolution and photo-peak efficiency. The Compton continua from higher energy gamma-rays contribute to the photopeak in the spectrum of a lower energy gamma-ray. This is a source of interference in activation analysis which must be corrected for.

A positron-electron pair may be created by interaction of the incident photon with the coulombic field of an atomic nucleus. This process requires at least 1.02 MeV of energy (the energy of formation of the pair) the remaining photon energy being carried away and shared equally as kinetic energy of the pair. As before the electron will dissipate its energy in the scintillator and produce a scintillation. The positron on deceleration rapidly annihilates with an electron and two quanta of 0.51 MeV radiation are emitted in opposite directions (at an angle of 180°) to each other. Once again a photo-electric equivalent event may occur. If both quanta of 0.51 MeV radiation are absorbed in the crystal, the energy of the original photon will appear to have been completely absorbed within the resolution time of the detector, and a "count" in the spectrum will be recorded
in the photopeak. If one 0.51 MeV quantum escapes from the crystal, a peak will appear in the spectrum (called the first or single escape peak) at a pulse height equal to 0.51 MeV in energy lower than the photopeak. If both 0.51 MeV quanta escape a double escape peak (1.02 MeV below the photopeak) occurs.

2.4.2.4. The Resolution of Scintillation Detectors

The spectral resolution of a scintillation detector may be described as its ability to resolve or distinguish between the absorption of two photons having similar but slightly different energies. Since the photopeak is the most important feature of the pulse height (energy) spectrum, resolutions are usually quoted as a photopeak line width. Detector resolution as a percentage is expressed as the width of the $^{137}$Cs 0.662 MeV photopeak (keV) at half the peak height, divided by the photopeak position in keV (the number of channels from zero energy on the pulse height or channel number scale). Occasionally resolution is expressed as the ratio of the height of the $^{60}$Co 1.17 MeV gamma-ray to the height of the valley between the 1.17 and 1.33 MeV gamma-rays of this isotope.

Photopeak line width is due to statistical variations occurring in each step following the initial interaction in the crystal to the final production of a pulse from the photomultiplier.
Amongst the most important are:

(i) The various events (see the previous section) leading to the production of light scintillations within the resolution time of the detector.

(ii) Variations in the efficiency of light collection and transfer to the photocathode of the P.M. tube caused by local variations in light transmission in the crystal, and in the reflection of light from the reflector round the crystal.

(iii) Local variations over the photocathode surface in the efficiency of the process whereby the energy absorbed from light photons is converted to the emission of photo-electrons.

(iv) Variations in electron amplification down the length of the P.M. tube due to local variations in the electron emission of the dynode surfaces and also in the efficiency of electron collection between the electrodes in the tube.

NaI(Tl) crystals may be specially selected from a process batch for their high resolution. Similarly photomultipliers possessing exceptionally low noise, high gain and linearity of response may also be specially selected. Carefully selected and constructed detector assemblies can produce resolutions (for $^{137}$Cs) below 7% (cf 0.2% or less for a solid state detector). The resolution of a good quality $75 \times 75$ mm NaI(Tl) crystal detector commonly used in activation analysis (because
of their sensitivity) are now of the order of 2% or less.

2.4.3. Gamma-ray Spectrometry

The major features present in the gamma-ray spectrum obtained from scintillation detectors (NaI(Tl)) have been described in the previous Section 2.4.2 under Photon Interaction. In addition a number of other features are often present in a gamma-ray spectrum due to minor interactions and these will be described below:

(1) A broad peak is observed in the energy region of 0.2 MeV due to absorption in the crystal of gamma-rays which have lost energy by elastic collision by interactions with the material (e.g. shielding) surrounding the detector. This peak is termed the backscatter peak. The energy of the scattered photon $E'_{\gamma}$ being given by:

$$E'_{\gamma} = \frac{E_{\gamma}}{1 + E_{\gamma}(1 - \cos\theta)/mc^2}$$

which is virtually independent of the incident gamma-ray ($E_{\gamma}$) energy if the scattering is larger than 120°.

(1½) If the photoelectric effect occurs in material surrounding the detector X-radiation characteristic of the element may be produced (e.g. Pb x-ray from Pb shielding) and absorbed in the crystal resulting in an X-ray peak occurring in the spectrum.

(11) If the photoelectric effect occurs near the surface of the crystal so that iodine K X-radiation (28keV) can
escape, a second peak, the X-ray escape peak may be observed. This peak will be observed at an energy of 28 keV less than the photopeak, but in any case this effect decreases rapidly with increasing gamma-ray energy and will not occur for energies less than 33.2 keV, the energy of the K-edge of iodine.

(iv) A peak at 0.51 MeV in energy will be observed in cases where positron electron pair formation (2.4.2) occurs, due to absorption of the 0.51 MeV positron annihilation radiation (a positron annihilates to produce two 0.51 MeV photons emitted at 180° to each other).

Further another peak, the annihilation plus backscatter peak may be observed from the summation of the absorption of the 0.51 MeV gamma-ray with its 180° backscattered complementary 0.51 MeV, photon. If pair formation occurs in the material surrounding the detector a 1.02 MeV peak may be observed if both 0.51 MeV photons are absorbed in the detector.

(v) Other peaks due to the summation of events occurring in the detection system are possible and are of two types, coincident summation and random summation. Consider the case of a non-monoenergetic gamma-ray emitter. If two different photons are emitted sequentially and are absorbed within the resolution time of the detector, a pulse from the photomultiplier will be produced, corresponding in energy to the sum of the photon energies.
giving rise to a "sum" peak (indistinguishable from a weak photopeak) in the pulse-height energy spectrum. In practice such sum peaks will be very weak compared to the photopeaks of the gamma-energies giving rise to them, as the frequency of coincident summing is small. Random summing events are possible due to the random summation of any event or pulse but result in broadened peaks which do not resemble photopeaks in appearance.

2.5. Sources of Errors in Activation Analysis

Errors occurring in activation analysis are broadly of two types:— those commonly relating to most analytical techniques as a result of unavoidable operations such as sampling, weighing or the contamination of the sample, and those relating to the production and detection of nuclear radiation. Post-irradiation processing of the sample (e.g. radiochemical separations) is to be preferred since only the contamination of the sample with radioactive material will introduce errors. The former sources of errors are well known and will not be covered in this description.

Usually the experimental error in a determination is expressed as the standard deviation of a number of determinations and should be expressed together with the estimated error inherent in the procedure and due to the technique used. These in principle should agree
and this is the technique adopted in the experimental section of this thesis for the presentation of errors. It is often invalid to compare the results obtained by activation analysis with those obtained by other analytical techniques in order to estimate errors, as any analytical procedure will be subject to error or even bias. If this method of the comparison of results is to be used the average value of a number of determinations carried out by as many different analytical techniques as possible should be used to estimate fairly any error or bias in an activation analysis technique.

2.5.1. Irradiation Errors

The majority of these errors may be eliminated or minimised if a technique involving the simultaneous irradiation and rapid rotation of a sample and a standard (§5. 43) is carried out. The sample and standard should be of similar chemical composition, bulk and packing density to minimise any errors occurring due to self-shielding effects (the attenuation of neutrons or of the radiation emitted by successive layers of the sample or standard due to the presence of elements of high cross-section). The sample and standard should also be of similar isotopic composition and abundance; these are sometimes different owing to natural or artificial separation having occurred or they may simply
vary with the geographical origin of the materials.

If simultaneous irradiation of a sample and standard is not possible successive irradiations under "similar" conditions may be carried out to retain some of the advantages of a comparative technique, but this may introduce additional sources of error. Absolute determinations are not made due to uncertainties in the various parameters in the activation equation (see section 2.3.1.). Neutron flux monitors must be used to normalise the results obtained in successive determinations but as yet no absolute method of determination of fast neutron flux has been developed for their calibration. The standardised procedure of Heath (25) involving the activation of copper foils is now widely accepted in lieu of an absolute technique. This technique may be used to give satisfactory comparative results but great care must be taken to ensure that the irradiation geometry is accurately reproducible. The fall off of neutron flux with increasing distance from the generator target is extremely marked (48, 83), and to avoid errors of this kind samples must be irradiated in containers of uniform and reproducible dimensions. These must be located against the target each time in a positive and reproducible manner. As previously stated the sample and standard must be of a similar bulk and packing density.
irradiation conditions may occur due to deuteron beam inhomogeneity or instability (wandering of the beam over the target), and due to non-uniform tritium distribution in the target. Such variations are unlikely to be monitored by flux monitors and may only be overcome by techniques involving simultaneous sample and standard irradiation and rotation. Finally the neutron flux monitor calibration may be altered during generator servicing operations, if removable biological shielding is disturbed, as in many installations, only neutrons scattered from the generator surroundings are monitored by such devices.

2.5.2. Counting Errors

The radioactive decay of any nuclide is a statistical process and hence the true "activity" of a nuclide may only be expressed as a mean disintegration rate. This value may be defined as the average value which would be obtained if the disintegration (or practically, the counting rate) were measured an infinite number of times, or for an infinite length of time. In practice any measurement of the disintegration or count rate will yield a value differing from the mean, but lying between certain limits on either side of the mean. The radioactive decay of atoms is thought to follow a Poisson distribution, and hence:-
68% of the measured values will differ from the
mean by \( \pm \sigma \)
96% of the measured values will differ from the
mean by \( \pm 2\sigma \)
99% of the measured values will differ from the
mean by \( \pm 3\sigma \)

where \( \sigma = \sqrt{\frac{N}{N}} \) and \( N \) is the number of counts recorded.

Thus if only one measurement is made there is a one per
cent chance of obtaining a value which may differ from
the mean by more than three standard deviations. A
major error in counting measurements may therefore be
introduced due to counting statistics. This error may
be minimised by obtaining a very high total count such
that \( \sqrt{N/N} \) tends to zero. \( 10^6 \) counts yields a sigma
value of 0.1%. Such low levels of statistical error
may not in practice often be attained since the required
activity produced in an irradiated sample may yield a
relatively low counting rate. Therefore all the results
quoted in a determination should include an estimate
of their statistical error for a given confidence level.
In any estimate of total error, cumulative and consequen-
tial errors due to the mathematical treatment of results
must be considered and calculated, using the accepted
conventions for the propagation of errors.

Any kind of radiation-detector will have a "dead-
time" and this may be described as a time interval
directly following a detection event, during which the
detector will be insensitive to further events (i.e. the
time for the detector to return to steady state conditions).
This "dead-time" is small with scintillation and semi-
conductor detectors but may be relatively large with
gas-filled detectors. The dead-time or resolution time
from the associated electronics is however usually the
predominant limiting factor on the counting rate, that
may be detected. The resolution time may be described
as the time taken to "resolve" or process and record
an output pulse from a radiation detector. Whilst a
simple scintillation counter may have a low dead-time,
multichannel analysers tend to have relatively high
dead-times (as more processing of input pulses is carried
out), the larger the number of channels available in
the instrument, the higher the dead-time. At a relatively
high counting rate, $N_t$ cps, the observed count rate
$N_{obs}$ cps will require dead-time correction and this may
be calculated from:

$$N_t = \frac{N_{obs}}{1 - N_{obst}}$$

where $t$ is the dead-time of the detector (electronics)
clearly the highest dead-time present in the combination
(either the electronics or the detector) should be used
in this expression as this will be the count-rate limiting
factor.

Errors may be introduced from the electronic equip-
ment present in an activation analysis system. The
performance and response of the best electronics is finite and errors may occur due to the equipment used ranging from the generation and recording of spurious signals to errors in the measurement of time. Further the response of the electronics may drift from the settings chosen with the effects of both time and temperature. Similarly the gain and hence the spectral resolution of scintillation detector assemblies varies with both temperature and count-rate (current through the P.M. tube) and this will also affect the energy calibration of the detection system. These errors may be minimised with the adoption of the best quality electronics (preferably left permanently in operation) coupled with frequent recalibration of the equipment with standards and electronic performance testing. In very extreme cases where the utmost stability is required for long periods of time, a constant temperature room may be necessary for the detection equipment and electronics.

The counting-rate of a sample will depend markedly on the sample to detector distance and also on the relative position of the sample to the detector. Hence a reproducible counting geometry is extremely important. Variations in geometry will be more important still when small volume (e.g. solid-state detectors) are used.

Finally errors may be introduced due to interfering and competing nuclear reactions in the sample and these will be discussed in the next section.
2.6. Sources of Interference in Activation Analysis

Interferences may be conveniently classified into two types:- purely spectral interferences, and interferences occurring due to the unwanted production of the isotope of interest by activation of other sample constituents by other nuclear reactions.

Spectral interferences can occur from the production of radionuclides emitting photons of different but similar energies to the gamma-ray photon of interest in a determination. Clearly the extent of this type of interference will depend on the detector resolution and will be less significant with high resolution solid state detectors than with sodium iodide crystals. A further spectral interference may occur from the Compton continuum of nuclides emitting higher energy photons than the energy of interest if these nuclides are present in large quantities compared to the nuclide of interest. Corrections for spectral interferences may be possible and often these interferences may be minimised by selective decay before counting, if there is a significant difference in the half lives of the required and interfering activities.

A major interference can occur if the radionuclide of interest in a determination can be produced by nuclear reactions on more than one element present in the sample if these are close together in the periodic table. This
may be illustrated by the hypothetical example of the
determination of indium in the presence of cadmium and
tin using the nuclide $^{115}\text{Cd}$ when the following reactions
can occur:

$$
\begin{align*}
^{115}\text{In} & (n, p)^{115}\text{Cd} \\
^{115}\text{Cd} & (n, \gamma)^{115}\text{Cd} \\
^{116}\text{Cd} & (n, n)^{115}\text{Cd} \quad \text{(interfering reactions)} \\
^{118}\text{Sn} & (n, \alpha)^{115}\text{Cd}
\end{align*}
$$

Such an analysis may still be possible if the interfering
target elements can be determined using different reaction
products to the interference and hence their interference contribution calculated. Alternatively pre-
irradiation chemical separation may be carried out in
extreme cases.

Further interferences may be produced by the presence
of particles other than those required in the flux of
bombarding particles. In hydrogen containing materials
recoil protons will be produced with energies up to the
energy of the incident fast neutron. These may give
rise to interfering reactions, but this effect is only
of significance in a limited number of cases (74).

Similarly interferences may also be induced by the thermal
neutron component of the fast neutron flux inducing thermal
neutron reactions with certain elements. Finally second
order reactions, defined as the further interaction of
a product nuclide with a bombarding particle are a
theoretical source of interference. In practice second order reactions are of little significance in neutron generator fast neutron activation analysis due to the relatively low neutron fluxes involved and the short irradiation times used. Interferences encountered in 14 MeV activation analysis when using sodium iodide detectors have been reviewed by Nathur and Oldham (64).
3. EXPERIMENTAL
3. Experimental

3.1. Equipment and Apparatus

The major part of the experimental work described in this thesis involves fast neutron activation analysis in non-aqueous flowing systems. Analysis was performed using a 14 MeV neutron generator to irradiate the solutions or material under test. The sample was examined by gamma-ray scintillation spectrometry using a sodium iodide detector. Examination of the gamma spectra obtained from nuclear reaction products present in the irradiated material enabled qualitative and quantitative analysis to be carried out. The major constituents of the experimental system are listed below. Minor constituents or items of equipment used infrequently will be described as and when they occur in the experimental work.

1. Fast neutron generator
2. Detection equipment for gamma-ray scintillation spectrometry
3. Pneumatic transfer system
4. Neutron flux monitoring system
5. Liquid loop systems

The equipment was housed in a suite of two rooms which were identical in size (3.3 × 3.3 × 3.3 metres). The first, or inner room, housed the fast neutron generator with its associated fixed and movable biological shielding, and the BF₃ flux monitor. The outer room
contained the power, control and the associated systems of the neutron generator as well as the pneumatic transfer system and counting equipment. The installation, commissioning and layout of the above equipment has been described in detail by Darrall and Oldham (50). In addition the second room also contained the elements of the flowing system currently in use, in the investigations described later, with the exception of the detection station in the first flowing system constructed. This was housed elsewhere, at an increased distance from the neutron generator in order to minimize interference.

3.1.1. Fast Neutron Generator

A Kaman Nuclear fast neutron generator, type A-1003, capable of generating up to $10^{11}$ ns$^{-1}$ was used in these investigations. The manufacturer's technical specification of the Kaman generator is given in table 1.

The generator is a positive ion linear accelerator producing fast neutrons by the "D-T" reaction, the fusion of deuterium with tritium. Deuterium ions are accelerated through a high potential gradient and strike a tritium containing target. When the exoergic reaction

$$\text{^2H} + \text{^3H} = \text{^4He} + \text{^1H} + Q = \pm 17.6 \text{MeV}$$

occurs. The excitation function of this reaction is reported (27) to reach a maximum, due to a resonance, of 5 barns at an incident deuteron energy of 110 KeV. Neutrons are produced isotropically at the target and their energy is dependent on their angle of emission. The energy of neutrons
<table>
<thead>
<tr>
<th><strong>Table 1</strong></th>
<th><strong>Model 5-100 Neutron Generator Specifications</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>Measured Neutron Output</td>
<td>$10^{11}, 14.3$ MeV ns$^{-1}$</td>
</tr>
<tr>
<td>Neutron Flux (at irradiation position)</td>
<td>$\sim 2 \times 10^{13}$ cm$^{-2}$ s$^{-1}$</td>
</tr>
<tr>
<td>Type of Output</td>
<td>Continuous</td>
</tr>
</tbody>
</table>

**Accelerator Assembly**

<table>
<thead>
<tr>
<th>Dimension</th>
<th>0.305 m at the dome, 50.8 - 60.4 mm diameter at the target, overall length 1.55 m</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type</td>
<td>Positive Ion</td>
</tr>
<tr>
<td>Ion Source</td>
<td>P. I. C. Type</td>
</tr>
<tr>
<td>Potential</td>
<td>0.205 kV</td>
</tr>
<tr>
<td>Beam Current</td>
<td>0.2 mA</td>
</tr>
<tr>
<td>Focus</td>
<td>Adjustable 6.2 - 25.4 mm</td>
</tr>
</tbody>
</table>

**Vacuum System**

<table>
<thead>
<tr>
<th>Type</th>
<th>Sputter Ion Pump</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pumping Rate</td>
<td>1.8 l/s$^{-1}$</td>
</tr>
<tr>
<td>Static Pressure</td>
<td>less than $10^{-8}$ cm Hg</td>
</tr>
<tr>
<td>Operating Pressure</td>
<td>approx. $1 \times 10^{-5}$ cm Hg</td>
</tr>
<tr>
<td>Roughing Pump required</td>
<td>Down to $10^{-3}$ cm Hg</td>
</tr>
<tr>
<td>Table 1 continued</td>
<td></td>
</tr>
<tr>
<td>-------------------</td>
<td></td>
</tr>
<tr>
<td>Power Supply</td>
<td></td>
</tr>
<tr>
<td><strong>Type</strong></td>
<td>Cockcroft-Walton, selenium rectifiers</td>
</tr>
<tr>
<td><strong>Input</strong></td>
<td>110V Ac, 60 cpr single phase 30A</td>
</tr>
<tr>
<td><strong>Output</strong></td>
<td>0 - 205kV Ac, 5.5 mA</td>
</tr>
<tr>
<td><strong>Ripple</strong></td>
<td>1.2% RMS max.</td>
</tr>
<tr>
<td>Target Assembly</td>
<td></td>
</tr>
<tr>
<td><strong>Type</strong></td>
<td>Drift tube mounted, isolated and at ground potential</td>
</tr>
<tr>
<td><strong>Target</strong></td>
<td>Tritiated Tritonium, 25.4 - 38.1 mm diameter</td>
</tr>
<tr>
<td><strong>Cooling</strong></td>
<td>Closed Freon system</td>
</tr>
</tbody>
</table>
emitted in the opposite direction to the deuteran beam are lower than those of neutrons emitted in the same direction but the difference is dependent on deuteran energy. The neutron energy in the forward direction is stated to be 14.74 MeV (27) for a deuteran energy of 150 kV. The energy at 180° to the beam is 1.57 MeV less than this, but at a deuteran energy of 100 kV the energy difference is said to fall to 1.15 MeV.

The neutron generator installation may be conveniently divided into a number of major components:

(1) Particle Accelerator and Target
(11) Biological Shielding and Interlock System
(111) Power Supply, Control Console and Operation

These will be described in outline. For a detailed description and specific operating instructions reference should be made to the maker's operating manual (25).

3.1.1.1. The Particle Accelerator and Target

A schematic diagram of the accelerator column and target and its internal construction is given in Fig. 1. As may be seen the accelerator consists of an ion-source and palladium leaks mounted at the top of the accelerator, followed by acceleration, extraction and intermediate electrodes. A vacuum ion-pump, beam deflector plates and finally the target and cooling jacket complete the accelerator assembly. The high voltage electrodes, negative in polarity, the ion-source and leaks are enclosed in an earthed, stainless steel dome filled with an insulating freon gas (difuoro-dichloromethane at
Fig. 1. Schematic Diagram of Kaman Neutron Generator
300 psig \( (2 \times 10^5 \text{Nm}^{-2}) \) and since the target is at earth potential no external parts of the generator are at a high voltage.

Under static conditions the vacuum in the accelerator is maintained by a sputter ion-pump to better than \( 10^{-8} \text{mm of Hg} \) \( (13) \), the high vacuum being necessary to minimise the scatter of accelerated ion beams in the system. In operation deuterium gas is "leaked" slowly into the ion-source by diffusion through an electrically heated palladium leak which is porous to hydrogen when hot and the vacuum, in the ion-source only, falls to about \( 10^{-6} \text{mm of Hg} \). The only link between the ion-source or ion-bottle and the rest of the accelerator is a small exit hole in the lower cathode which is too small to permit a large gas flow but through which ions are extracted by the extractor electrode. Thus the vacuum in the accelerator proper is maintained at \( 10^{-8} \text{mm of Hg} \) by the ion-pump. The palladium leak is cylindrical in construction and normally passes of the order of 20ml of deuterium per hour during generator operation, at deuterium pressure applied to the leak of \( 2 \times 10^5 \text{Nm}^{-2} \) \( (30 \text{psig}) \). The ion-source is enclosed in a glass envelope to form an ion-bottle and is of the Penning Ionisation Gauge (P.I.G.) type. The P.I.G. source consists of a cylindrical anode separated by ceramic insulators from disc-shaped cathodes at either
end, and is itself surrounded by a cylindrical permanent magnet with a field strength of 1000 gauss (Fig.1).

Initially free electrons in the deuterium gas, or electrons emitted thermonically from the cathodes are accelerated towards the anode, but they are forced to travel in a spiral path through the ion-source due to their interaction with the external magnetic field. Here, they cause intense ionisation by collision with gas molecules. Due to the ion focussing effect of the applied voltage on the anode, the majority of the ions produced strike the central region of the cathode. Ions striking the lower cathode can be extracted through the central hole in the cathode and into the accelerator column by passing through the small hole in the conical extractor electrode. The extractor electrode is maintained at a fixed fraction of the accelerator electrode voltage, the exact proportion being adjustable on the control console. The difference between the accelerator and extractor electrode voltages governs the ion-beam focussing conditions and hence the size of the ion-beam on the target. An intermediate electrode mounted below the extractor electrode, but above the ion pump, together with the earth electrode at the target at the end of the drift tube complete the main features of the accelerator. These electrodes are mounted on an insulated column and the size of the electrodes and their spacing within the
accelerator fundamentally governs the ion-beam conditions. The ion-beam may be deflected off the target by the application of a potential of 2.5 kV across two deflection plates mounted in the drift tube and the switching of this provides a neutrons on/off facility. The production of neutrons in pulses is also available by pulsing the voltage on the deflection plates.

The generator target consists of a layer of titanium tritide (0.02 mg mm$^{-2}$) deposited on a copper foil, 38 mm in diameter and 0.25 mm thick, which is located in a demountable cooling jacket assembly (Fig. 1). Neutron generator targets are manufactured by heating the target foil to about 400$^\circ$C in tritium gas and then allowing the foil to cool slowly, thus forming the interstitial titanium hydride. In practice the tritium content of a target prepared in this way can vary widely and will also depend on the actual thickness of the titanium deposited on the copper backing. Therefore targets of only a nominal tritium loading (between specified limits and usually of the order of 0.75 Ci mg$^{-1}$ of Ti) can be purchased. Targets may be checked for the homogeneity of tritium distribution by autoradiography using the tritium bremsstrahlung ($\gamma$-rays). The targets should be stored in sealed containers, preferably in a vented enclosure, to minimise loss of tritium by the attack of atmospheric moisture on the titanium tritide. Further
they should be handled carefully to avoid flaking of this layer. During operation the tritium content and hence the neutron output of the target falls due mainly to outgassing of the target produced by the heating effect of the ion-beam. Losses also occur due to sputtering with loss of tritium to the vacuum system. Very little tritium (0.01% (86)) is believed to be actually consumed by the D-T reaction. Thus a considerable amount of tritium will be accumulated in the ion-pump over a period of time which could be released if the generator vacuum collapsed for any reason. This also makes the dismantling of the accelerator column a hazardous procedure unless special equipment is available. The operational characteristics of targets in this generator have been described by Bibby, Oldham and Ware (86, 87). The fall in neutron output with time is said to follow an exponential decay consisting of two components. Initially there is a rapid fall in neutron output with a half-life of 117 minutes due to the rapid depletion of the surface layers of tritium by sputtering, ion bombardment and outgassing. This is followed by a slower fall in neutron outputs with a half-life of the order of 1100 - 1200 minutes which is believed to depend on the diffusion of tritium to the surface layers from the lower layers in the target. Further it has been shown (87) that the tritium in a depleted target may be thermally
redistributed, thus providing strong evidence of the diffusion process. The performance of the "reconditioned" targets was found to be partially but significantly restored.

The target is cooled by a pumped flow of a liquid freon (trifluoro-trichloroethane) which is itself cooled by water in a heat exchanger. The freon used possesses excellent heat transfer and electrical insulation properties. Coolant enters the cooling-jacket and impinges directly onto the back of the copper foil via a flow guide and then passes on to cool the ion-source. Up to 100 watts may be dissipated at the target and the ion-source could be up to 200 kV in potential with respect to the target. Provision is made for target changing by sealing off the drift tube from the remainder of the accelerator with a high vacuum isolation valve. Another valve is then opened to admit nitrogen to the drift tube for target changing operations and is subsequently used to evacuate the drift tube or even the whole generator in an emergency by means of an external pump. This must reduce the pressure to $10^{-2} - 10^{-3}$ mm of Hg at which the ion-pump can take over. After admission of nitrogen the lower part of the cooling jacket, containing the target, may be removed and a new target inserted.

Vacuum sealing is obtained by means of the copper edge of the target and an "O" ring sealing against the drift
tube when the lower part of the cooling jacket is bolted into position. Target changing must be carried out carefully to ensure that a good vacuum seal is obtained. Suitable precautions should be taken during the target changing operation due to the high tritium content of the target which poses a health hazard from ingestion. The target should be handled with disposable gloves, and the exhaust of the external vacuum pump should be discharged into the open air outside the building. Since tritium will be outgassed on pumping down the drift tube, urine monitoring of the operator for tritium is also a sensible precaution.

3.1.1.2. Biological Shielding and Interlock System

A generator of the type described in 3.1.1.1 is both a direct and an indirect intense source of a broad spectrum of nuclear radiation. Apart from its high output \((10^{11} \text{ns}^{-1})\) of fast neutrons, intense X-radiation is produced whenever high voltage is applied to the accelerator whether fast neutrons are being generated or not, and further, during neutron production their interaction with surrounding material gives rise to a high flux of gamma-radiation. Consequently although the generator is housed in a room \(3.3 \times 3.3 \times 3.3\) metres the majority of the room, except for a space 0.5 metres square where the generator is housed vertically, consists of biological
shielding (50). Access is provided to the generator via two removable steel water tanks (1.07m long, 0.9m wide and 2.12m high), which are mounted on rails. The remainder of the room, except for a gap of 1.18 metres below the roof, is filled with concrete blocks, and the generator cavity is closed by a cover of concrete 0.25m thick. A small gap remaining between the concrete blocks and the walls of the room is filled with boric acid to absorb thermal neutrons. This shielding provides more than adequate biological protection from electromagnetic radiation whilst the fast neutron dose is reduced below the maximum permissible level of 0.1 n.m⁻².s⁻¹. In the event, in the second part of the research work described in this thesis, this level of radiation, although biologically safe, was found to be inadequate when a sensitive radiation detector was used near the wall of the inner room. The shielding was then reinforced, and additional detector shielding built.

The generator and operator are protected by interlock switches connected in series which ensure that the generator cannot be operated unless all the interlock connections are made. Radiation protection for the operator is ensured since an interlock switch is operated by each of the water tanks, which must be properly located before contact is made. The generator is protected by interlock switches operating on both the flow and temperature of
the freon coolant and on the insulating gas pressure in the dome. Electrical overload protection is provided by quick acting trips on the various high voltage power supplies to the generator electrodes, and on the overall power line. Micro switches are closed when the variacs controlling the accelerator extractor and ion-source voltages are set at zero volts. These micro-switches must be closed before the generator can be started up and they thus provide protection against power surges. The closing of the interlocks is indicated by neon lights which all come on when the power key switch is turned on. Energising the start relay via the start button applies power to the power supplies providing the interlocks are completing the circuit, and also switches out of circuit the trips on the zero point of power variacs. The stop button breaks the interlock line and thus switches off power to the power supplies.

3.1.1.3. Power Supply and Control Console

The main components of the Cockcroft-Walton power supply are housed in two oil-filled high voltage tanks located in the outer room. Heavy duty high voltage cables pass through a hole in the wall just below ceiling level and then over the concrete shielding to the generator. A transformer, fed with 110 V AC from the 240 : 110 V AC matching transformer transforms the main voltage to
75 kV, which is then doubled to the various required voltages by the two Cockcroft-Walton voltage doubling circuits. Spark gaps are provided to accommodate high voltage surges and gravity operated shorting switches connect the high voltage outputs to earth if power is interrupted for any reason. Such a situation could occur if the interlock line were broken either through normal switching off procedure or through a fault condition or even through a general power failure. One of the power supply tanks supplies the high voltage to the accelerator, extractor and intermediate electrodes, whilst the other provides the leak and ion-source voltages. All the voltages are fully adjustable and are controlled by variable voltage transformers which alter the input voltages to the various primaries of the power supply transformer windings.

The voltages applied to the accelerator are as follows.

a) The main accelerator voltage, (0 - 150 kV + 0 -50 kV d.c. in series which is equivalent to a voltage range of 0 -200 kV). The voltage is applied between the ion-source and the target (earth).

b) The extractor electrode voltage, 0 - 150 kV d.c.

c) The intermediate electrode voltage which is always maintained at half the extractor electrode voltage.

d) The ion-source voltage (0 - 10 kV) which is applied
across the ion-source cathode and anode and is superimposed on the accelerator voltage.
e) The leak voltage. (0 - 6.3 VAC), which controls the heating current passing through the palladium leak and hence the rate of flow of deuterium into the ion-source.
f) The ion-pump power supply (0-5 kV).

The control console permits remote operation of the generator and power supplies and hence the direct exposure of the operator to radiation or high voltages may be avoided. The console contains meters on which are displayed the leak voltage. the "ion-beam" or target current. the accelerator or extractor voltages. and the ion-pump current. The "ion-beam" current is, in reality. the total current drain on the 0-look V power line, but the target current is actually the current flow through the target, monitored as the current flow through a resistor connected between the target and earth. The ion-pump current is directly proportional to the vacuum in the accelerator (85) and is used as a guide for leak voltage control. The varieas controlling the ion-source. ion-pump accelerator and extractor voltage. as well as the leak voltage control are mounted on the control panel together with the interlock lights. The console contains an overall key switch which prevents unauthorised use. the start and stop buttons and the resettable overload trips for the various power lines. A leak selector
switch, a manual control for the beam deflection facility (a "neutrons on/off switch") coolant and ion-pump switches complete the major controls. Either of two irradiation timers (0 - 60 seconds and 0 - 12 minutes) may be selected for fixed time irradiations. These may be operated manually or automatically in conjunction with the pneumatic solid sample transfer system. They operate by switching off the beam deflection voltage for the preset length of the irradiation thus allowing the deuteron beam to impinge on the target and produce neutrons. Provision is made for pulsing of neutrons by pulsing the voltage on the beam deflection plates. This facility did not work well in practice since a sharp neutron cut off could not be obtained. This usually requires that the ion-source is also pulsed.

3.1.1.4. Operation and Operating Problems

The generator is put into operation by first switching on the console power via the key switch. The ion-pump operates continuously and is independent of this switch and therefore only requires switching on or off in an emergency. The freon coolant pump and the cooling water to the heat exchanger are then turned on, and the deuterium gas pressure to the leak is adjusted to $2 \times 10^5 \text{ Nm}^{-2} \text{ (30 ± 3 psi).}$ If all the interlock neon are glowing, and the accelerator, extractor and source variacs are at zero
the start button may be pressed thus supplying mains power to the high voltage supplies. The deuterium leak voltage may then be raised via the "Leak Vernier" to the required level so as to increase the ion-pump current from a quiescent value of about 10\(\mu\)A to the order of 0.5 - 5ma depending on the ion-beam current required.

The high voltages on the ion-source and the extractor electrode (and hence the intermediate electrode) must be optimised together for a given acceleration voltage. Since all these voltages are interdependent, adjusting any one can affect the others, consequently a correct sequence for voltage adjustment must be followed for optimisation of the controls. The acceleration voltage is slowly adjusted to the required level with the extractor variac turned to maximum. The ion-source voltage may then be adjusted. As the ion-source voltage is adjusted, two peaks in ion-beam current (reflecting the efficiency of ionisation) will be observed, the second much larger than the first. The optimum value is taken as five divisions of the variac below the peak beam current observed. The extractor variac is then adjusted (with the beam deflection off) to five divisions of the variac below or above the peak target current recorded, thus defocussing the beam to cover the target. A focussed ion-beam could burn through the target or cause severe local overheating resulting in target inhomogeneity.
The generator is now ready to produce fast neutrons whenever the beam deflection voltage is removed, either manually or automatically using the irradiation timer.

A number of problems have arisen in the operation of this generator, most of them attributable to the age of the machine which has been in frequent use for six years. The long running time of the accelerator is reflected in the reduced accelerator voltages (120 kV maximum) that may now be applied, presumably due to a breakdown in the accelerator column insulation. This is believed to be caused by deposits of condensed metal vapour, produced by sputtering, in the accelerator.

Strong evidence for this theory is provided by the fact that the glass drift tube has a slight but visible metallic sheen. Further the "beam" current (the total current drain on the 0 - 200 kV line) rises rapidly to overload conditions above 130 kV even when no deuterium is being leaked in or ionised and this would be caused by a partial short-circuit in the accelerator. More serious however, and probably for the same reason, is that ion-source short-circuits, with operation of overload protection, occur every few hundred minutes of irradiation time. It is believed that metal whiskers grow until they bridge the ceramic insulators between the ion-source anode and the cathodes, thus producing a short-circuit. This condition was investigated and has been cured successfully by a
relatively simple procedure. The ion-source is not readily replaceable since it is an integral part of the accelerator and contains a glass to metal seal. First of all access was obtained to the ion-source terminals by partial dismantling (removal of the outer and inner domes) of the top of the accelerator column. The ion-source high voltage supply cable was disconnected from the source terminals, when a low resistance of the order of 1 -2 ohms was found to be present in the ion-source itself. It was decided to attempt to destroy the metal whisker and thus the short circuit by the application of a high current at a low voltage. This procedure with some modifications was found to be successful in practice. On reconnection and application of the ion-source voltage the whisker often seems to reform producing another short-circuit which is then destroyed in the usual way. A number of these operations may be necessary and then the ion-source voltage is slowly raised to the maximum thus destroying any other potential short-circuits. All these operations were carried out with the interlock system shorted out by means of a key switch which will allow the partial operation of the generator in a partly disassembled state. It is now the accepted practice to raise the ion-source voltage slowly up to the maximum to burn off partly formed whiskers before leaking deuterium gas into the ion-source and applying the other high voltages. Presumably a final irreparable ion-source short-
circuit will eventually occur requiring the return of the generator to the makers for the fitting of a new ion-source and the cleaning of the accelerator column. This should fully restore the performance of the generator.

The pores of the palladium leak periodically become partially blocked with gaseous impurities even when high purity deuterium gas is used. In order to avoid the use of excessive leak voltages this condition may be reversed by periodically pumping out the deuterium line to the leak. Finally another fault that has occurred periodically is a high voltage short circuit in the accelerator due to the deposit of rust in the coolant lines in regions of high electrostatic and magnetic fields. This involves the fitting of new nylon coolant lines including a rust trap consisting of a few metres of nylon pipe coiled round the ion-pump magnet, together with the necessary cleaning of the glass coolant pipes.

3.1.2. Detection Equipment for Gamma-ray Scintillation Spectrometry

A block diagram of the full system is given in Fig. 2. Two nominally identical 75×75 cm NaI (Tl) crystal detector assemblies (Nuclear Enterprises (N.E.) type 12/TEL 2/12) were used in these investigations. One was used for counting solid samples, located i., the pneumatic transfer
Fig. 2: Overall Counting System
system, whilst the other was employed in the liquid loop systems. The differences encountered in practice between these "similar" detectors forms the basis of work described later in this thesis. These N.E. detection assemblies contained the NaI (Tl) crystal, which was optically coupled to a selected E.M.I. 9531 K photomultiplier tube. A preamplifier N.E. type 5282 was mounted at the bottom of the photomultiplier tube base to boost the pulses before they travelled along the cables coupling them to the multichannel analyser. Originally a Laben 100A (100 channels) analyser was used, but later on in the investigations a Laben 400A (400 channels) became available and this was used since it provided a number of features in addition to those of the 100A model.

A schematic diagram of the component parts showing the mode of operation of a multichannel analyser is given in Fig. 3. The high voltage supply for the detector is incorporated as shown in the analysers. Pulses from the detector preamplifier are amplified with a low dead-time by a linear amplifier and then passed on to the single channel analyser. This will only accept pulses falling within a certain pulse height range (or window) which is adjustable in width by means of the back bias and upper threshold controls (lower and upper discriminators). Again this is accomplished with a low dead-time.
Fig. 3. Schematic Diagram of Laben Multichannel Analyser
From here the variable height pulses (an analog signal) are converted according to their pulse size into a number of smaller pulses (a digital signal) by the analog to digital converter or A.D.C., and are passed to the address register. This device sorts out each chain of digital pulses from the A.D.C. and allocates them to the appropriate channel in the ferrite core memory. The process in the A.D.C. involves a relatively high dead time and is the major source of dead time in the instrument. This is particularly important since dead time will be introduced by incoming signals handled by the A.D.C. but subsequently allocated by the address register to channels lying outside the scope (or energy/channel calibration) of the memory. This dead time rises with channel number. Consequently the single channel analyser window should really be set to the narrowest limits consistent with obtaining the spectral data required to minimise dead time.

A form of dead time correction when counting is incorporated into the automatic timing section of the analyser. Each time the A.D.C. handles a pulse, the timing pulses driving the "live" timer are prevented from reaching it during the dead time or the time that the A.D.C. is taking to deal with the pulse. Once the A.D.C. is free to accept another pulse, the live timer is driven once more by the timing pulses. Thus the "real" clock
time which has elapsed under "live time" counting conditions is the preset live time set on the instrument plus the total dead time. The differences between real and live times may be marked for high counting rates and clearly a valid automatic dead time corrections cannot be made by the instrument for short half-life, rapidly decaying, isotopes. Thus an external real timer, continuously driven by the analyser timing pulses, has been incorporated in the system and enables accurate dead-time corrections to be calculated. Further the dead time of the analyser may, when counting in the live mode be either a fixed value for each pulse (greater than the maximum dead time for any pulse), or may be variable i.e. depending on the channel number of the pulses handled.

The approximate percentage dead time is also displayed on a meter, as a rough guide when counting. The analyser may also be used to count in the real time mode when no dead time correction is applied. Another timer, the waiting timer, is incorporated and thus the analyser can be set to count and wait automatically in turn.

The analyser may be operated to count in the multi-scaler mode, when the single channel output is fed in each turn to a channel of the memory for a fixed counting time. This is then followed by a preset waiting time. A record is thus obtained of the variation of total sample activity, with time in the energy range set by the single
channel window, enabling isotope decay curves to be obtained.

Finally the 400 channel analyser incorporates additional features. The 400 channel memory may be split into 4 x 100 or 2 x 200 channels for activation analysis. Thus a number of consecutive spectra may be recorded without the need for a data read out and this facility is provided automatically when counting in the multichannel analyser mode. Spectrum subtraction or stripping is also possible between the first and second 200 channel sub groups of this analyser.

The single channel output of the analyser (Fig. 2) can be connected to a logarithmic/linear range ratemeter (N.E. type 5457). This was used to indicate the total counting rate of the sample and the ratemeter deflection was simultaneously displayed on a Philips fast pen recorder having a maximum speed of 1.33 mm s⁻¹ with a balancing time for 95% deflection of one second. The spectra recorded by the multichannel analyser were recorded digitally by an IBM electric typewriter having a typing speed of about five characters per second.

Towards the end of the investigations a Bryan 21001, x - y recorder was purchased, enabling the direct plotting of the recorded spectra to be achieved using the analog output of the analyser. A major disadvantage of the system is that no equipment for the digital output
of spectral data in a computer compatible form (punched paper tape or magnetic tape) was available. This tended to restrict the application of computer treatment (appendix iii) of spectral data to cases where this was felt to be essential, since each spectrum recorded had to be punched manually onto cards, channel by channel.

3.1.3. Pneumatic-transfer System

The pneumatic transfer system provides a means for the automatic transfer, irradiation and counting of discrete samples and has been described in detail elsewhere (50). The system consists essentially of a length of reinforced nylon piping, equipped with a loading post, which links the neutron generator to a sample counting system. The counting system consisted of a 75 75 mm NaI (Tl) detection assembly coupled to a multi-channel analyzer (3.1.2.). The detection assembly, except for a sample access hole to the end face of the crystal, was encased in a lead shield 50 mm thick. This gave a background of 22 counts s⁻¹ over the range 0.1 - 1.95 MeV, but the presence of the lead shielding in close proximity to the detector tended to produce large backscatter peaks. There is no direct path for radiation leakage from the generator via the nylon transfer piping, since two gradual bends, in different planes to each other, are incorporated into the passage of the pipework through the biological.
shielding. The pipework terminates at the irradiation position of the neutron generator in a machined nylon end-piece. This ensures the accurate location and re-location of the polythene sample bottles used in the transfer system. Samples are blown from the loading port to the neutron generator by compressed air from an air-blower, and then sucked back (by reversing the air flow) to the detection station. The returning sample bottles pass through the loading port, over the passage to the detector and strike an obstruction in the assembly. The bottles bounce back from this obstruction thus reversing direction and fall down a machined passage to land on the end-face of the NaI (Tl) detector. This procedure not only provides reproducible counting geometry but also inverts the bottles so that the end nearest the neutron generator during irradiation, is also nearest the detector during counting. Samples may be removed from the counting station through a moveable perspex slide. Transfer times from the neutron generator to the detector of 1 - 2 seconds are typically obtained. The blower motor is controlled by a relay logic system linked in with sensing devices in the pipework, and to the associated equipment of the activation analysis system. Operation is as follows:-

(1) The sample bottle is loaded into the transfer system, via the loading port, with the neutron generator controls set to their operating level.
(11) On pressing the transfer system "start" button, the blower operates, blowing the sample bottle to the neutron generator and simultaneously resetting the BF3 neutron monitor scaler units (3.1.4.)

(iii) The sample bottle, on arrival at the irradiation position of the generator, breaks a light beam falling onto a photo-transistor. The resultant signal is used indirectly to start the irradiation by switching off the beam deflection voltage on the accelerator. The signal simultaneously starts the pre-set irradiation timer on the generator console, and also the neutron monitor timer-scaler.

(iv) At the end of the pre-set irradiation time, a signal from the timer is used to initiate the transfer of the sample bottle to the detector and start an external timer. The same signal stops the neutron monitoring scaler, and also stops neutron production by restoring the beam deflection voltage to the accelerator.

(v) The returning sample bottle breaks another light beam and drops onto the detector. The photo transistor light sensor is located between the obstruction in the port assembly and the loading port, and the signal from this device is used to switch off the blower motor.

(vi) The external timer operates for a fixed time and then starts the multichannel analyser in its automatic cycle of counting and data output. This delayed start
thus allows the sample to undergo radioactive decay for
a preset time before counting begins. The accurate
irradiation time and the total BF$_3$ count recorded during
the irradiation may be obtained from the neutron flux
monitor timer-scaler unit. During the irradiation, audible
and visible signals are given out thus providing a gene-
ral warning that the neutron generator is in operation.
A number of operation warning lights are incorporated
into the transfer system and provide a rapid means of fault diagnosis.

3.1.4. Neutron Flux Monitor

A boron trifluoride proportional counter is used
to monitor the neutron flux during irradiations. The
detector contains BF$_3$ gas enriched in the boron-10 iso-
tope contained in a tube 100 mm long and 12 mm in diameter.
This mounted on the wall of the recess in the shielding
which houses the accelerator at a distance of 1m from
the target and is sensitive to thermal neutrons. A fast
neutron generator produces indirectly a thermal neutron
component associated with its fast neutron flux. This
component arises partly from thermalisation of fast neut-
rons in the target and cooling jacket, but mainly from
thermalisation of neutrons due to scattering processes
occurring in the generator surroundings. The BF$_3$ detector
is encased in a polythene tube 60 mm in diameter and this
increases the thermal neutron flux by a factor of two. A preamplifier is mounted above the biological shielding and is connected to the BF$_3$ tube by a short length of cable. The output pulses from the preamplifier are fed via a linear amplifier to a timer scaler and ratemeter unit which can be controlled by the pneumatic transfer system. The output of the ratemeter is automatically redirected into a fast pen-recorder (3.1.2.) during irradiations thus providing a visual display of flux variations. At the end of the irradiation, the pen recorder is automatically switched back to monitoring the output of the ratemeter (3.1.2.). The total BF$_3$ count recorded by the flux monitor during an irradiation is taken as a measure of the total neutron flux passing through a sample located at the irradiation position of the generator (3.2.2.)

3.1.5. Non-Aqueous Flowing Systems

The systems and the techniques developed and used for fast neutron activation analysis in non-aqueous flowing systems form the major portion of the work described in this thesis and will be described in detail later. Basically these systems consisted of a solution reservoir, an irradiation cell counted under the neutron generator, a detection cell wound around the NaI (Tl) crystal detector, and a waste solution reservoir. Nylon piping was used to interconnect these basic units and solutions were formed round
the system by the application of nitrogen gas pressure to the solution reservoir. Stainless steel needle valves and a range of interchangeable flowmeters enabled a wide range of steady flow rates to be maintained.

3.2. Initial Calibration Procedures

3.2.1. Detector Resolution and Efficiency

The energy resolution of the two $75 \times 75 \text{ mm}^{2} \text{NaI (Tl)}$ detection assemblies was measured when they were coupled to the 100 channel analyser (3.1.2.). Two methods were used in the measurement of their energy resolution. The first method was based on the full photopeak width at half the peak height (FWHM) of the 0.662 MeV gamma-ray of the isotope caesium-137. The second method utilised the peak to valley ratio in the gamma-ray spectrum of cobalt-60, measured between the 1.17 MeV photopeak and the valley between the 1.17 and 1.33 MeV photopeaks of this isotope. A source to detector distance of 25 mm was used for these measurements of resolution, with the caesium photopeak or the cobalt-60 valley located centrally (i.e. on channel 50) in the analyser. Energy resolutions of 8.0% and 8.3% respectively were obtained for the liquid loop detector and the pneumatic transfer system detector. Peak to valley ratios of 5.2:1 and 3.7:1 were similarly obtained for these detectors.
The efficiency, at the counting position, of the NaI crystal detector located in the pneumatic transfer system was measured for 0.511 MeV gamma-ray photons. This efficiency of detection was required in the calculation involved in neutron flux calibration experiments (3.2.2.). The positron annihilation radiation from a standardised disc source of the isotope Na - 22 (supplied by the Radiochemical Centre) was used in the measurement of detector efficiency. The gamma-ray spectrum of this source, with the 0.511 MeV annihilation photopeak placed on channel 50 was recorded with the 100 channel analyser. The peak area between 0.42 - 0.61 MeV was determined by the method of Covell (39), giving a measured efficiency of 10.9% for this energy range. Since the copper foils which are counted using this detector in flux calibration experiments are of a different diameter (22 mm) to that of the Na - 22 source (5 mm), the measured efficiency must be corrected for this change in source size. A correction factor, of approximately a two per cent reduction of the measured efficiency, is given by Heath (34) for changes in source size of this order. Accordingly a detection efficiency of 10.7%, at 0.511 MeV, was used for this detector in neutron flux calibration calculations.

The efficiency of the liquid loop detector, when used in conjunction with the detection cells of the non-aqueous flowing systems, was also investigated. The
main purpose of this investigation was to show that the detection cells could be reproducibly located and reloca-
ted on the crystal. This was found to be the case and hence the detection system could be dismantled and reas-
sembled as required without affecting the reproducibility of results. In addition the effectiveness of the design of a detection cell is reflected by the detection efficiency per unit volume of the cell, and hence detection cells which are different in design may be compared. The efficiency of the detection cells was measured by filling the cells with an aqueous solution of potassium chloride (1M) and counting the naturally occurring radioisotope potassium-40. This isotope is 0.0112% abundant and has a half-life of $1.27 \times 10^9$ years and it was felt that these physical properties minimised the risk of permanent serious contamination of the cell. The multichannel analyser was adjusted so as to bring the 1.45 MeV photo-peak in the spectrum of K-40 on to channel 50 in the memory, due to the low specific activity of this isotope. Samples were counted for 40,000 seconds to ensure good counting statistics in the K-40 peak ($1.32 - 1.58$ MeV). The cells were thoroughly washed out after the efficiency determination, and no residual potassium-40 activity above background was found. It was considered unwise to measure the detection efficiencies using solutions of the more common standards (e.g. Cs - 137) which have
higher specific activities than K-40. Any contamination of the cell would render it useless for further work.

3.2.2. Calibration of the Neutron Flux Monitor

3.2.2.1. Neutron Flux through the Solid Sample Position

The neutron flux monitor (3.1.4.) may be calibrated against neutron flux by the method of Heath (25). This method is based on the fast neutron activation of copper which for short irradiations produces mainly the isotope copper-62, a positron emitter. The nuclear reaction used is:

\[ ^{63}\text{Cu} \ (n, \ 2n) \ ^{62}\text{Cu} \ \ \ \ \ \text{t}_\beta \ 588 \text{ seconds} \]

The neutron flux can be calculated by determining the activity of the irradiated copper and substituting this value into the activation equation as defined in section 2 as the values of the other parameters in the equation are known. The efficiency of detection has already been measured as 10.7% (3.2.1.). the branching ratio for positron emission for copper-62 is given by DzhelepoV and Peker (31) as 0.98 and the reaction cross-section was taken as 600 ± 30 millibarns for 14.7 MeV neutrons (33).

Copper foils (2\(\frac{3}{4}\) mm in diameter) were irradiated for 60 seconds, cooled for 60 seconds, and the positron annihilation radiation from the sample was counted under conditions of known counting efficiency (3.2.1.). The
samples were counted for a live time of 60 seconds and the real counting time, the BF$_3$ count, and the accurate irradiation time were also noted. The procedure described was carried out using the fully automated solid-sample activation analysis system (3.1.3).

The absolute activity of the copper-62 isotope present at the end of an irradiation may be calculated by finding the instant in time at which the mean copper-62 activity occurred. This activity does not in fact occur halfway through the counting period since the copper-62 activity is decaying noticeably during the count. This average value of the copper-62 activity may then be corrected to zero decay time i.e. to the end of the irradiation. The value of the neutron flux required to produce this copper-62 activity may then be calculated from the activation equation. A calibration graph of the measured neutron flux, from the irradiation and counting of a number of copper foils, against the observed BF$_3$ flux monitor readings may then be prepared. In practice the calculations involved in the flux calibration procedure were carried out using a FORTRAN computer program. This program, NCO2B, and its use is fully described in appendix (1). The program calculated the experimental neutron fluxes, and then applied a least squares fit to the experimental points to obtain the straight-line graph of neutron flux against the BF$_3$ counter reading.
The production of copper-64, also a positron emitter by the reaction:

\[ ^{63}\text{Cu}(n, 2n) ^{64}\text{Cu} \quad t_\frac{1}{2} = 12.8 \text{ hours} \]

could constitute a source of interference, and hence a major source of error. The interference of this isotope is negligible, however when short irradiation and counting periods (60 seconds) are used. These short periods are extremely unfavourable for the production and detection of relatively long lived radioisotopes. The copper-64 activity has been calculated to be of the order of \(10^{-6}\)
of the copper-62 activity, produced and detected using the flux calibration procedure described.

3.2.2.2. Neutron Flux through the Irradiation Cell

The total neutron flux passing through the volume of the irradiation cells used in the non-aqueous flowing systems was determined by irradiating the cell filled with an aqueous solution of copper sulphate. A modification of the method of Bibby and Oldham (83) for the determination of the fast neutron flux in irradiated solutions was used. The neutron flux was calculated from the copper-62 positron activity present in the irradiated solution, and this was related to the neutron count recorded by the BF3 flux monitor. As before, the cross-section of the \(^{63}\text{Cu}(n, 2n)^{62}\text{Cu}\) reaction was taken as \(600 \pm 30\) millibarns (83) and a branching ratio of 0.98 (31) for the copper-62 isotope was used.
Liquid samples were counted using a Panax 45 x 45 mm NaI(Tl) well type crystal detector which was coupled to the 100 channel analyser. The efficiency of this detector was measured for a counting volume of 5 ml of solution by counting the 0.662 MeV and the 0.364 MeV gamma-radiation emitted from solutions containing respectively the isotopes Cs-137 and I-131. It was assumed that the variation in counting efficiency with gamma-ray energy would be linear over such a narrow energy range.

A standard solution of Cs-137 supplied by the Radiochemical Centre and a solution of I-131 which was standardised before use were used in the efficiency determinations. A stock solution of I-131, $t_\frac{1}{2}$ 8.09 days, in its "Amersham bottle" was standardised by measuring the ionisation current obtained when the bottle was placed in an N.P.L. design ionisation chamber. A portion of this solution was immediately diluted and 30% dilution on the well-crystal. The interpolated value of the counting efficiency of this detector for a 5 ml sample volume emitting 0.511 MeV radiation was taken as 9.0%. The resolution of the well-crystal was measured at 0.511 MeV and was found to be 11.8%.

An almost saturated aqueous solution of analytical reagent grade copper sulphate (15% wt/vol) was used in the flux measurement experiment. The solution was continuously passed through the cell until no more bubbles
issued from the exit pipe of the cell. This procedure ensured that the cell was completely filled with solution and that no air bubbles remained trapped in the cell. Any air bubbles left in the cell would naturally be located under the top surface of the cell and hence would occupy the regions of highest neutron flux. This could introduce gross errors into the measurement.

Access to the neutron generator was made via the removable shielding water tanks (3.1.1.) and the cell was clamped into position against the generator target cooling jacket. The irradiation cell was then irradiated for an accurately measured length of time so as to obtain \( EF_3 \) counts a statistical giving accuracy for a 68% confidence level of the order of 0.1% (2.5.2.). The neutron generator high voltages, and the deuterium leak voltage were then reduced to zero, as quickly as possible, and the irradiation cell was removed.

It was deemed desirable to monitor the radiation level coming from the cell and its contents before any handling operations were carried out. A total neutron dose of the order of \( 10^{42} \text{ ncm}^{-2} \) was delivered in flux calibration determinations. A Philips type PH 4012/01 portable radiation monitor was used to measure the radiation level coming from the cell. This was found to be of the order of 20 mR/hour after 5 - 10 minutes cooling and the radiation level had fallen to 4 mR/hour after
a decay of half an hour. The major source of the radiation levels measured is due to the activation of the large mass of copper and brass in the cell materials. Activation of copper will give rise to the following reactions and products in addition to $^{62}\text{Cu}$ and $^{65}\text{Cu}$:

- $^{63}\text{Cu}(n, \alpha) ^{60}\text{Co}$
  - $t_\frac{1}{2} = 10.5$ minutes
- $^{63}\text{Cu}(n, \alpha) ^{60}\text{Co}$
  - $t_\frac{1}{2} = 5.27$ years
- $^{65}\text{Cu}(n, p) ^{65}\text{Ni}$
  - $t_\frac{1}{2} = 2.55$ hours

Further products will arise from the activation of the zinc contained in the brass of the cell:

- $^{64}\text{Zn}(n, 2n) ^{63}\text{Zn}$
  - $t_\frac{1}{2} = 38$ minutes
- $^{66}\text{Zn}(n, 2n) ^{65}\text{Zn}$
  - $t_\frac{1}{2} = 245$ days
- $^{66}\text{Zn}(n, p) ^{66}\text{Cu}$
  - $t_\frac{1}{2} = 5.1$ minutes

The flux calibration measurements were usually carried out when the neutron generator target was considerably depleted in tritium. This resulted in irradiation times of ten minutes or more which were required in order to achieve the desired $\text{BF}_3$ count. Thus the production of significant quantities of isotopes with half-lives of the order of minutes or hours was quite likely. The relatively long-lived isotopes, $\text{Co-60}$ and $\text{Zn-65}$ were detected in the gamma-ray spectra of the cells only when they had been in service for a number of months and had received $20 - 30$ hours of fast neutron irradiation. Cobalt-60 will arise directly and indirectly from the...
After the irradiation cell and its contents had been removed from the neutron generator, the cell was emptied, together with its washings, into a graduated flask and the volume was made up to the mark with distilled water. The final volume of the copper sulphate solution naturally depended on the size of the irradiation cell under test. In order to minimise the reduction in the specific activity of the irradiated solution due to dilution, the minimum amount of cell washing was performed. The cell was blown through with nitrogen gas repeatedly, before and after the addition of washing water, in order to clear the cell as efficiently as possible of its liquid contents. After the graduated flask had been shaken well, to ensure good mixing, a 5 ml aliquot was pipetted into a counting-bottle and counted on the well crystal. With practice the copper-62 isotope could be counted within ten minutes or so of the end of the irradiation. The peak area of the 0.511 MeV annihilation radiation photopeak was determined by the method of Covell (39). The production of the positron emitter nitrogen-13 (t½ 10 minutes) from the recoil proton activation of the oxygen present in the aqueous solution of copper sulphate will constitute a source of interference in the measurement of copper-62. The contribution of this source of interference to the copper-62
annihilation photopeak was determined by filling the irradiation cell with water and then carrying out the same experimental flux calibration procedure. It was found that 1.5% of the measured positron activity present in a copper-62 determination could be attributed to the isotope N-13. A smaller source of interference in the copper-62 determination arises from the production of copper-64. The interference due to this isotope was determined by counting a 5 ml sample of the irradiated copper sulphate solution after the copper-62 and nitrogen-13 activities had decayed to a negligible level of activity. The level of the copper-64 interference was found to be of the order of 0.2% using the experimental procedure described. The extent of the interference will of course depend on the decay time of the shorter lived copper-62 isotope. The neutron flux through the cell was calculated in a similar way to that described in the previous section, on solid-sample flux calibration. The flux through the irradiation cells used on the non-aqueous flowing systems could thus be related to the counts recorded by the BF$_3$ counter. Flux calibration could of course be carried out using the lower specific activity interference free copper-64 isotope. This yielded similar results to the copper-62 determinations but increased the time taken for each determination, considerably.
The variations in neutron flux around the target of this neutron generator have been investigated by Bibby and Oldham (83). The relative values of the neutron fluxes through cells of different sizes were found to reflect the effect of increased sample to target distance (83) when larger volume irradiation cells were used.
3.3. Activation Analysis in a Non-Aqueous Flowing System of Elements producing Short Half-Life Radioisotopes

3.3.1. Selection of Solvent

The criteria adopted for the selection of a suitable solvent for the investigations were that the solvent should possess the following properties:

(i) Minimal interfering activities.

(ii) Good solution properties.

(iii) Low volatility and toxicity.

(iv) Low flammability.

(v) Availability.

A number of solvents including various boiling range petroleum ethers, benzene, colourless kerosene and commercial paraffin were considered. Samples of these solvents were placed in sample bottles and irradiated using the automated pneumatic transfer system (3.1.3). Irradiation, cooling and counting times were varied so as to favour in turn the production and detection of both relatively short and longer lived product nuclides.

The multichannel analyser was normally set to cover the energy range 0.1 - 1.95 MeV. Each sample was also examined for the presence of oxygen. This element may be detected from the production of the isotope N-16 from the reaction $^{16}\text{O}(n,p)^{16}\text{N}$, and the high energy
gamma-rays from $^7$N (7.12 MeV downwards) may be readily detected. Short irradiations and minimum cooling times (2s) were used, and the analyser was set to cover the energy range 2.0 - 7.5 MeV. Little activity was found to be induced in any of the solvents tested, presumably due both to the small volume of solvent which could be irradiated, and also to the relatively low neutron fluxes (\( \sim 10^{12} \text{n m}^{-2} \text{s}^{-1} \)). No discernible oxygen activity was observed at these neutron fluxes, but a small rise in the count rate of the channels in the energy region of 0.5 MeV was observed. This feature was slightly more noticeable in the case of irradiated commercial paraffin which contained a dyestuff. Experiments on this flowing system, described later, showed this peak to be due to positron emission from the isotope nitrogen-13 produced by the proton recoil reaction $^13$C(p, n)$^{13}$N (7\(^{14}\)). Activation of the nitrogen in the dyestuff present in the commercial paraffin would also yield N-13 by the fast neutron reaction $^{14}$N(n, 2n)$^{12}$N and this is believed to account for the slight increase in positron emission which was observed. Paraffin was accordingly rejected as a suitable solvent. The petroleum ethers were rejected due to their flammability and benzene was rejected because of its toxicity.

Reagent grade colourless kerosene supplied by Hopkins and Williams (C.G. 0.79 \( g/1 \)) was finally chosen as the most suitable solvent for these investigations.
3.3.2. Description and Construction of Non-Aqueous Flowing System

A flowing system was constructed whereby solutions are passed from a reservoir through irradiation and detection cells to a waste reservoir. Nitrogen gas was used to pressurise the reservoir and hence force solutions round the system. A flow meter and flow control valve, were located downstream of the detection cell to provide a means of accurate flow control. Preliminary experiments were made to determine the compatibility of kerosene with various polymeric materials. Polythene, P.V.C. various rubbers and silicone rubbers were found to undergo more or less rapid swelling on contact with kerosene. Only nylon and P.T.P.E. appeared to be kerosene resistant, and care was taken that only kerosene resistant materials were used in the construction of the flowing system.

Nylon pipework, 6 mm internal diameter, was used throughout to interconnect the various components of the system except that narrower nylon piping, 11.9 m long and 4 mm internal diameter, was used between the irradiation and detection cells. The narrower piping between these cells reduced the transit time between them. Glass solution and waste reservoirs with a nominal capacity of 4.5 l were used and the solution reservoir was found to withstand $1.65\times10^5 \text{Pa m}^{-2}$ (25 p sig) when pressurised with nitrogen. It was felt that this pressure was more
than adequate to achieve the desired range of flow rates, but as a safety precaution the solution reservoir was covered with a wooden shield then pressurised. Two interchangeable flow meters, "rectrates" type P and G, complete with glass, stainless-steel and high density steel floats provided a means of flow-rate measurement in the range 0.2 - 30 ml.s
A precision stainless-steel needle-valve. Hone Instruments type 4300/5 was used to control the flow-rate of solutions passing through the system. Pipework connections were usually made by forcing the nylon tubing when hot, over the pipework of the component to be connected, and then firmly clamping the joint with a "Jubilee" clip.

An irradiation cell was made in the form of a shallow, cylindrical, brass box 100 mm in diameter and 6 mm deep. Previous work by Bibby and Oldham (73) on the variations in neutron flux around the target of this generator precluded any design of irradiation cell other than one which could be located directly beneath the target. A cell made of nylon tubing wound around the drift tube, for example, would suffer from the disadvantage of being in a region of low neutron flux. The cell was constructed from a thin section of brass tubing 100 mm in diameter and the cell top, bottom and the internal double spiral were made from brass sheet 0.85 mm thick. The irradiation cell top and the inlet and outlet pipes.
were silver soldered to the brass cylinder and since slight distortion had occurred, the cell top was cautiously ground flat. The inside of the cell top and the brass double spiral were tinned with soft solder and the double spiral was assembled and located in position in the irradiation cell by means of asbestos spacers. The cell and spiral were then cautiously heated until the soft solder melted and the spiral sank slowly into place. The soldered joint joining the spiral to the cell top was then examined for gaps, and then the unwanted voids in the irradiation cell were filled with an epoxy resin which had been shown to be kerosene resistant. The cell was then ground flat in order to provide a good mating surface for the demountable cell bottom. A PTFE gasket 0.85 mm thick was used to seal the cell bottom to the brass spirals and to the cell sides. The irradiation cell was rigidly clamped together between dural plates secured by a ring of eight bolts. A hole in the centre of the upper clamping plate was machined to fit the neutron generator target cooling jacket and its attendant coolant pipes. The adjustable end-piece of the pneumatic transfer system was used to hold the irradiation cell assembly against the target cooling jacket (Fig. 4). The machined hole providing a means for the positive location of the irradiation cell in this position. The volume of the cell was found to be 24 ml and was measured by weighing
Fig. 4. A Irradiation Cell in Position
B Plan View of Irradiation Cell
the cell both empty and full of water at a known temperature. Correction was made for the volume of water held in the inlet and outlet pipes. The cell was immersed in water and was pressure tested with nitrogen gas to a pressure of $2 \times 10^5$ Pa $^{-2}$ (30 psig).

This form of irradiation cell design, incorporating a brass double spiral was thought to represent a good compromise between reproducibility of results and irradiation efficiency. The horizontal flow of liquid through the cell will tend to sweep away bubbles if and when they are formed. These would otherwise occupy space below the cell top, i.e. in the region of highest neutron flux (Fig. 5) and could thus be a source of error. The double spiral design ensures a definite, and thus reproducible flow path through the cell for flowing liquids, and also prevents mixing of the active and inactive streams. It was calculated that at the highest flow rates likely to be used on the system the Reynolds' number of the flowing liquid would be less than 2100 and thus only reproducible streamline or laminar flow conditions would prevail. The PTFE sealing gasket was naturally used to seal the cell bottom and not the cell top, and thus the liquid in the irradiation cell is located as close as possible to the neutron generator target. Further, the effects of any changes, with time, in the shape of the gasket on the reproducibility of results would be minimized since the
Fig. 5. Irradiation Cell and Relative Flux Contours
gasket is located in a region of relatively low neutron flux (Fig. 5). A pre-requisite of any irradiation cell assembly was that the pneumatic transfer system (3.1.3.) should remain operational with the availability of moderate neutron fluxes at the irradiation position for undergraduate teaching experiments. Neutron flux calibrations were carried out by irradiating copper foils at this irradiation position. Fast neutron fluxes of the order of 10% of those available at the normal irradiation position under the target, were measured, and these were thought to be adequate for the teaching experiments. The neutron flux passing through the irradiation cell was measured by irradiating the cell filled with copper sulphate solution (3.2.2.). The average neutron flux passing through the cell was found to be \(1.7 \times 10^6\) ns\(^{-1}\) ml\(^{-1}\). Giving an integrated flux of \(3.5 \times 10^7\) ns\(^{-1}\), compared with a flux of \(1.8 \times 10^8\) ns\(^{-1}\) as measured by a copper foil located at the irradiation position of the generator. The flux through the cell is thus about 20% of the flux available at the irradiation position under the target cooling jacket. The relative neutron flux contours surrounding the target of this generator have been investigated by Bibby and Oldham (63) and the irradiation cell is shown superimposed on these contours in Fig. 5. It may be seen that for a cell of this size, 50 mm in radius, the inner 25 mm radius of the cell will
lie approximately within the 10% flux contour line, whilst the outer 25 mm radius lies between the 10% and 2.5% flux contours. The ratio of the relative volumes of the cell inside these high and low flux regions is of the order of 1:3. Thus the experimentally measured fluxes through the irradiation cell are of the right order of magnitude compared to those measured by the copper foil.

The detection station was located in a nearby room at a distance of 7.6 m from the neutron generator, and consisted of a detector cell and a sodium iodide crystal. The 75 x 75 mm NaI(Tl) detector (3.1.2.) was housed in a low background lead cave, 350 x 350 x 330 mm high which was constructed from standard interlocking lead bricks. The wall thickness of the cave was 100 mm and access to the detector and cell, which were located centrally within the cave, was provided by dismantling the bricks forming the cave top. It was decided to adopt a consistent spectral energy range (0.1 - 1.95 MeV) for these activation analysis investigations. The background as measured by the detector in the cave over this energy range was found to be 6.8 counts s⁻¹. The main features of the background spectrum as might be expected were the various peaks from radium present in the lead and from naturally occurring potassium-40 present in the earth crust and in the building structure. Two detection cells were used in these investigations and they were both designed to provide
a definite flow path for liquids passing through them.

The first cell was of a similar construction to the irradiation cell and was 100 mm in diameter and 15 mm high. However the cell contained a brass single spiral, and the cell bottom was glued in position with epoxy resin. Liquids entered the cell at the centre of the spiral and finally left the cell via a pipe in the cell side. This cell held a volume of 115 ml and was pressure tested to $10^{5}$ Pa$^{-2}$ (15 psig.) without leakages. This cell was designed so as to fit against the end face of the crystal detector since the sides of the detector were in use for another purpose. The efficiency of the cell was measured by filling it with potassium chloride solution and counting the naturally occurring K-40 isotope (3.2.1.). An overall efficiency in the range, 0.1 - 1.95 MeV. of 8.2%, 1.65% in the K-40 peak (1.38 - 1.52 MeV) was recorded, giving a count rate per unit volume in the peak of 0.003 counts s$^{-1}$ ml$^{-1}$. This latter value enables cells of different design and dimensions to be compared. Unfortunately the epoxy resin holding the cell top failed during preliminary investigations and it was decided to discard the cell and build another.

A new detector cell (Fig. 6) was constructed so as to fit over the detector, by winding thin walled nylon tubing 4.3 mm internal diameter, around a polythene former which had been machined to the dimensions of the crystal detector.
Fig. 6. A Detection Station
B Nylon Detector Cell
The cell design incorporated three layers of tubing. The cell volume was 237 ml, and the tubing layers were wound so as to utilize both the end-face of the detector as well as the sides. This cell also provided a definite flow path for flowing liquids. Liquids entered the first layer of tubing which was located against the centre of the end-face of the crystal, and after flowing around it passed into the coils surrounding the detector sides and hence into the second layer. The flow path through the third layer of tubing was similar to that through the first layer, whilst that through the second layer was in the opposite direction. The efficiency of the cell was measured as before, by counting the K-40 isotope present in a solution of potassium chloride (3.2.1.). In the energy range 0.1 - 1.95 MeV, an overall efficiency of 13.2% was measured. An efficiency of 3.3% in the K-40 peak, 1.32 - 1.58 MeV, and a count rate per unit volume in the peak of 0.0170 counts s⁻¹ ml⁻¹ were measured. The efficiency in the peak and the latter value are virtually double those measured for the brass detector cell, reflecting the improvement due to design and to the use of the whole of the detector. It is reported by Heath (34) that the absolute efficiency of a point source of 1.46 MeV gamma-radiation at distances of 5 mm and 10 mm from a 75 x 75 mm NaI(Tl) detector are 17% and 13% respectively. Although these values are not strictly comparable with those obtained for the detector cell, which is a diffuse
source, the overall measured efficiency of 13.3\% would appear to be of the correct order for an efficient design.

3.3.3. Fast Neutron Activation of Kerosene Solvent

An investigation of the interference produced on fast neutron activation of the solvent, colourless kerosene was considered essential to these investigations. It would be expected that the amount of any activity or interference produced on fast neutron activation of the solvent would be governed by the flow rate of the flowing stream as well as by the neutron flux incident on the irradiation cell. The flow rate of the stream will determine the residence times in the irradiation and detection cells, as well as the decay time due to the transit through the pipe work between the cells. Therefore the extent of any interference produced by activation of the solvent could be fully investigated by irradiating and counting the flowing kerosene stream over the range of flow rates attainable on the system.

3.3.3.1. Irradiation and Counting Techniques at High Flow-Rates

This technique was used generally for the investigation of shorter half-life product isotopes in the flowing system. These isotopes require relatively high flow rates up to 11 ml s\(^{-1}\) through the system in order to reduce the
radioactive decay due to transit to levels which will allow their activity to be detected. The multichannel analyser was set to cover the energy range of interest, usually 0.1 - 1.05 MeV by calibration with standard isotopes of known gamma-ray energy. The output of the single channel analyser of the multichannel analyser was coupled to a logarithmic ratemeter which was coupled to a fast pen-recorder (3.1.2.) The single channel analyser of the multichannel analyser provides a continuous output whether the analyser is switched in a counting mode or not. Thus the pen-recorder trace provided a continuous monitoring of the level of the activity present in the detector cell as measured by the liquid loop detector. The flowing kerosene was then maintained at a steady flow rate by manual adjustments of the needle-valve controlling the flow, coupled with observations of the flow-meter. In practice flow-rates were extremely steady and adjustment was required infrequently. The flowing stream was irradiated at as nearly as possible a constant flux. Any wide variations in flux other than those due to counting statistics would be instantly observable on the neutron flux monitoring system (3.1.3.). The pen-recorder trace of the activity present in the detection cell under these irradiation conditions was observed to rise slowly and finally level out at a constant value. This indicated that equilibrium conditions had been attained in the
flowing stream, and counting then began for a preset period of time. The BF$_3$ counter was started a fixed period of time in advance of the start of the counting of the activity in the liquid in order to allow for the transit of the activity through the pipework. The fixed time used was equal to the detection time measured on the pen-recorder trace Fig. 7, and the counting time of the BF$_3$ counter was the same as the preset counting time selected for the counting of the flowing stream. This procedure was carried out in order that the neutron fluxes giving rise to the actual activity counted were monitored by the BF$_3$ counter. The total BF$_3$ count recorded was taken as a measure of the total neutron dose to the irradiation cell. Results were expressed as the total activity measured in the liquid above background in a stated energy range, divided by the total BF$_3$ count recorded. Expressing results in this form enables the comparison of results obtained at different neutron fluxes and irradiation times. The activity/BF$_3$CT is the measured activity of the liquid normalised to that neutron dose which on passing through the irradiation cell will give rise to an equivalent BF$_3$ count of unity ($\sim 10^5 n$).

A representation of a typical pen-recorder trace obtained using the above irradiation and counting procedure is shown in Fig. 7. Only a very slight increase
Fig. 7. Equilibrium Level of Activity, Irradiation and Counting Technique
in background due to extraneous generator induced activity is visible since the detector is housed at a considerable distance from the generator (3.3.2.). A time, the detection time, Fig.7, elapses from the start of the irradiation before any significant increase in the activity of the flowing stream is monitored. The detection time is composed principally of the minimum transit time taken by the flowing stream to traverse the pipework to the detector cell, and is also partly due to the response times of the logarithmic ratemeter and the pen-recorder (3.1.2.). The rise in activity with time could ideally be a perpendicular rise, once the "slug" of irradiated liquid had reached the detector. Due to the effects of pipe-wall drag, the leading edge of the "slug" of active liquid is degraded to a parabolic activity profile and a gradual rise in activity is observed. For stream-line flow in a pipe, the velocity of a flow element \( x \), \( (V_x) \), at a distance \( r \) from the centre of the pipe is given by (9)

\[
V_x = \frac{\Delta P}{l} \left( \frac{d_1^2}{16/\mu} \left( 1 - \frac{2r}{d_1} \right)^2 \right)
\]

where \( \Delta P \) = pressure drop across the pipe

\( l \) = length of the pipe

\( d_1 \) = internal diameter of the pipe

\( \mu \) = viscosity of the liquid

Thus the velocity profile of the liquid flowing in a pipe, and hence the activity profile of such a liquid, are
parabolic in form. Clearly the maximum velocity \( (V_{\text{max}}) \) will occur when \( r = 0 \) at the centre of the pipe:

\[
V_{\text{max}} = \frac{\Delta P}{1} \frac{d^2}{16\mu}
\]

It may be shown (91) that the mean linear velocity, defined as the liquid flow rate divided by the cross-sectional area of the pipe, is half the maximum velocity. Thus the main component of the detection time, Fig. 7, is mainly due to the transit time of the component of the activity profile which is travelling at the maximum linear velocity. Theoretically the pen-recorder trace of activity with time should only reach an equilibrium value after an infinite length of time had elapsed. The equilibrium activity is approached asymptotically but an "equilibrium" value can be readily observed in practice.

This irradiation and counting technique worked well at high flow rates, up to 11 ml s\(^{-1}\) and suffered only from the disadvantage of a slight increase in background due to extraneous neutron generator induced activity. As the flow rates were progressively reduced the technique became less satisfactory, and at the lower flow-rates could be extremely wasteful of neutron generator time, and also yield increasing irreproducible results. Counting the equilibrium level of activity in the flowing stream depends on irradiation at a constant neutron flux. The longer the irradiation time, the more difficult it
becomes to maintain a constant neutron flux, particularly when the high neutron fluxes attainable with a new target are used. The effect of flux variations on the reproducibility of results is minimised at high flow rates when the detection and equilibrium times are short. The flowing stream thus rapidly attains a new equilibrium value following the change in neutron flux. At lower flow rates there can be a considerable lag in the response of the level of the activity of the flowing stream to flux variations. Thus the technique can yield progressively more irreproducible results as the flow rate is lowered. Clearly the target running time during which equilibrium conditions are attained is wasted. Economically unless this time is short, compared to the more useful irradiation time during which counting proceeds, the cost of each irradiation can be considerably increased especially for high fluxes.

The time to reach equilibrium is dependent on the flow rate of the liquid, and at the higher flow rates equilibrium was attained within periods of 30 - 180 s and this was deemed to be satisfactory. At the lowest flow rates attainable on the system (less than 1 ml s\(^{-1}\)), equilibrium conditions could take, depending on the flow rate, 900 - 1800 s. Clearly the procedure is economically unacceptable at the lower flow rates and will tend to yield irreproducible results. These factors led to the
development of the single pulse irradiation and counting technique described below.

3.3.3.2. Irradiation and Counting Technique at Low Flow Rates

This technique was developed to overcome the limitations of the irradiation and counting technique at low flow rates described above. The flow rate of the flowing liquid was set to the steady value required using the needle-value in conjunction with observations of the flowmeter. The flowing stream was then irradiated for a fixed period of time by switching the neutron generator on for the duration of the irradiation. This was carried out by raising the accelerator voltage to the operating level for the length of the irradiation, and then lowering it to ca. 60 kV a voltage at which no detectable neutron flux is produced. The manually operated beam deflection control was not used since the deuteron beam deflection system (3.1.1.1.) only provides a neutrons ON/OFF ratio of about 10:1. During the irradiation time the BF$_3$ counter was switched on and a total BF$_3$ count for the irradiation was recorded. After a predetermined delay, the multichannel analyser was switched to count for a preset counting period. The counting period was chosen such that all the activity produced during the irradiation in the flowing stream was counted. As before
3.3.3.1. results were expressed in the form of Activity

A diagrammatic representation of the irradiation and counting technique is shown in Fig. 8. The technique involves the production and detection of a single pulse of activity in the flowing stream and will be referred to as the single pulse technique. The active plug of liquid is drawn out as shown due to pipe wall friction as described in 3.3.3.1. The duration of the irradiation, delay and counting times were determined from preliminary experiments carried out over a range of flow rates for each activity of interest. In these preliminary experiments, the pen-recorder trace of the variation in the total activity passing through the irradiation cell with time was replaced by a more accurate technique. The multichannel analyser was set, by means of the upper threshold and back-bias controls, to record pulses only corresponding to a narrow energy range. Thus the analyser could be set to cover, for example, only counts corresponding to a single photopeak of interest. The flowing stream was then irradiated for a short period at a high neutron flux with the multichannel analyser counting in the multiscaler mode (3.1.2.). Counting continued until the level of activity in the flowing stream had fallen to the order of natural background. The resultant multiscaler trace was similar in appearance to that shown in Fig. 8. The preliminary procedure enabled the various
Fig. 8. Single Pulse Irradiation and Counting Technique
time intervals involved in the single pulse technique to be more accurately determined for the product isotope of interest. The delay time and the duration of the counting period were chosen so as to encompass all the activity present in the active pulse of liquid. It may be seen, Fig. 8, that the maximum irradiation time allowable is governed by the detection time or the minimum transit time (3.3.3.1.) of the activity between irradiation and detection. A delay time of 5 s must also be allowed in order to terminate the irradiation by decreasing the accelerating voltage on the accelerator to less than 60 kV, and to start the multichannel analyser counting.

In order to obtain the best counting statistics, only the activity present in the pulse of active liquid that is significantly above background, should be counted. Such a counting procedure would maximise the accuracy of results by minimising the effects of statistical fluctuation. An attempt was made to optimise the starting point and the length of the counting period using the criterion developed by Outeridge (92). This criterion of figure of merit was developed originally to enable scintillation counters to be adjusted for optimum counting performance in the presence of interfering background noise.

The criterion is based on the relationship that the value of \( \frac{\sigma^2}{B} \) must be maximised for optimum performance.
\[ S = \text{Source counts above background,} \]
\[ B = \text{Background (or noise) count.} \]

For any starting point of the counting period, the sum of the source counts above background \( (S) \) will rise continually as the pulse of activity passed the detector and will finally level out at the end of the pulse. The sum of the background throughout the counting period will rise continually. Thus the optimum counting time for any fixed starting point will be when
\[ \frac{S^2}{B} \text{ or } \left( \frac{\text{Integrated Source Count in the pulse}}{\text{Integrated background}} \right)^2 \]

is a maximum. A computer program, OTCRIT, (appendix (ii)) was therefore written, in FORTRAN IV. This was used to apply Cutteridge's criterion to the multiscaler traces obtained, in digital form, from the preliminary experiments carried out at each flow rate. The program (appendix (ii)) calculates values of \( \frac{S^2}{B} \) from a fixed starting point. When this value of \( \frac{S^2}{B} \) is maximised, the program begins at a new starting point and recalculates a maximum value of \( \frac{S^2}{B} \). This procedure continues until the optimum starting point and length of the counting period, yielding an overall maximum \( \frac{S^2}{B} \) value, are attained. The statistical variations usually encountered in the data obtained from the multiscaler traces were often large, due to the low counting rates of the flowing stream. These statistical fluctuations made the use of
the procedure increasingly uncertain especially when dilute solutions were used. Eventually selection by inspection of the multiscaler traces was readopted.

Usage of the single pulse technique can result in an economical experimental procedure since all the irradiation time is usefully employed. Economical use of the neutron generator target was considered to be a particular advantage when a new target and high flux irradiations were in use. Further the irradiation time can be selected and minimised according to the concentration of the target element thus resulting in an even more economical procedure. The single pulse technique yields results which are virtually independent of variations in neutron flux since the total activity present in the active pulse, for a total BF$_3$ count, is measured. A further, though slight advantage, on this system, is that counting takes place in the absence of extraneous neutron generator induced background activity.

This technique was found to be extremely satisfactory at the lower flow rates investigated. As the flow rate increases, the maximum permissible irradiation time progressively shortens, and thus the analytical sensitivity of the technique becomes worse. At high flow rates the single pulse technique becomes virtually unusable when the technique described in the previous section (3.3.3.1) must be used. For intermediate flow rates the appropriate
technique must be selected.

Dead time corrections using either irradiation and counting technique were not usually made, since in general the low solution counting rates gave dead times of less than 1%. Any error due to dead time, in such cases, would be small in magnitude compared to the possible variations arising from statistical fluctuations in the sample counting rate.

3.3.3.3. Investigation of Nitrogen-16 as an Interference

Previous experiments involving the irradiation and counting of discrete samples of solvent (3.3.1.) using the pneumatic transfer system had not shown the presence of the isotope nitrogen-16. This isotope is produced by the fast neutron activation of oxygen-16 by the reaction $^{16}\text{O}(n, p)^{16}\text{N}$, half-life 7.35s, cross section $30\text{mb}$ (30) and threshold energy $10.2\text{ MeV}$ (30). Reagent grade colourless ketone might well contain small amounts of oxygen present as traces of water or as organic impurities. It was decided therefore to reinvestigate the extent of interferences, produced by activation of oxygen, on the flowing system. The sensitivity of such investigations would be expected to be higher than those previously carried out (3.3.1.) since larger volumes of solvent would be irradiated and counted, and also since the higher neutron fluxes available from a new target could be utilised.
Flowing kerosene was irradiated at constant neutron flux and the equilibrium level of activity in the solutions was counted. The highest flow rate attainable on the system, 11 ml s\(^{-1}\), was used in these investigations. This flow rate required a nitrogen gas pressure of \(1.65 \times 10^5\) N m\(^{-2}\) (25 psig), applied to the solution reservoir, and its use was necessary due to the short half-life (7.35 s) of N-16. Since the volume of the transit pipe between the irradiation and detection cells was 150 ml, a flow rate of 11 ml s\(^{-1}\) will give a mean transit time of 13.6 s, i.e. approximately two half-lives decay for N-16. The multichannel analyser was set to cover the energy range 2.0 - 7.5 MeV as before. No nitrogen-16 activity detectable above background in the energy range 2.0 - 7.5 MeV was observed in these investigations, even when counting times of up to 1200 s were employed. Thus the extent of nitrogen-16 interference was judged to be negligible on this system. This observation may be explained by either the presence of very low levels of oxygen in the kerosene, or the combination of the presence of low levels of oxygen together with decay of the activity at the flow-rate investigated. Clearly at lower flow-rates than 11 ml s\(^{-1}\), the presence of N-16 is even more unlikely due to the effect of even longer decay times on the activity of an isotope of such a short half-life.
3.3.3.4. Investigation of Nitrogen-13 Interference

Kerosene was irradiated over a wide range of flow-rates using where applicable, either the single pulse (3.3.3.2.) or the equilibrium activity (3.3.3.1.) irradiation and counting techniques. The multichannel analyser was normally set to cover the spectral energy range 0.1 - 1.95 MeV. The only activity that was observed in the gamma-ray spectra obtained after fast neutron irradiation of the kerosene solvent was a small peak corresponding to an energy of 0.51 MeV. This peak was relatively more prominent at lower flow rates.

A peak occurring in the gamma-ray spectrum at an energy of 0.51 MeV would normally be assigned as 0.511 MeV positron annihilation radiation (2.4.2.3.). Annihilation radiation could arise either from the annihilation of positrons from a positron emitter, or from positrons produced in pair formation events (2.4.2.3.). Positron electron pair formation is only significant as a mode of interaction with matter of relatively high energy photons. A photon must have a greater energy than 1.02 MeV for the interaction to be theoretically possible (2.4.2.3.). Peaks corresponding to high energy photons were not observed in the gamma-ray spectra (2.0 - 7.5 MeV) of irradiated kerosene recorded in previous experiments on the flowing system (3.3.3.2.). The most likely source of such photons, the isotope N-16, half-life 7.35 s.
had therefore already been eliminated. Further, the short half-life of this isotope would only favour its detection at relatively high flow rates.

An attempt was made to measure the half-life of the positron emitter to enable an accurate assignment of the 0.51 MeV activity. The multichannel analyser was set to record pulses corresponding only to the positron peak, over an energy range of 0.42 - 0.61 MeV. Thus, by using the analyser and counting in a multiscaler mode, the decay of the positron emitter present in the irradiated kerosene could be followed. An assessment of the half-life of the positron emitter would be made from the decay curve obtained. Kerosene was irradiated at a constant neutron flux at the constant flow rate which appeared to yield the largest amounts of the positron emitter. The output of the single channel analyser, which indicated the total positron activity present in the detection cell, was monitored as before with a logarithmic rate meter coupled to a fast pen-recorder. When the pen-recorder trace had levelled off, indicating that an equilibrium level of activity had been attained, the flowing stream was halted by closing the needle-valve. The irradiation was terminated by reducing the acceleration voltage to below 60kV and the multichannel analyser was set to count in the multiscaler mode. A logarithmic plot of the variation of the activity of the positron
peak, above background, with time, yielded a straight line graph. This indicated that only one component isotope was present. A half-life, within the limits of experimental error, of 600 s was obtained from the slope of the graph. The only positron emitter with a half-life of 600 s is the isotope nitrogen-13 which is known to be produced by fast neutron irradiation of hydrocarbons \((7\text{h})\). The positron activity produced in kerosene by fast neutron irradiation was therefore assigned to the isotope nitrogen-13.

The isotope nitrogen-13 could be produced by fast neutron irradiation of kerosene by a number of possible nuclear reactions:

\[
\begin{align*}
14_7N \ (n, \ 2n) & \ 13\ N \\
16_0\ (p, \ \alpha) & \ 13\ N \\
12\ C \ (p, \ \alpha) & \ 13\ N \\
13\ C \ (p, \ n) & \ 13\ N
\end{align*}
\]

Equation (1), a fast neutron reaction is a possible mode of production, since nitrogen gas is used to force the kerosene round the liquid loop system and gas could be dissolving under pressure in the solvent. However, the nitrogen-13 level of activity was found to be enhanced at the lower flow rates investigated, and these are attainable at the lowest applied nitrogen gas pressures. Experiments were carried out at high applied nitrogen gas pressures but at low flow rates and no increase in
the level of positron activity was observed, and this possibility of \( ^{13}\text{N} \) production was rejected. The presence of oxygen in the sample was not confirmed by fast neutron activation. The level of the associated proton flux present in fast neutron irradiated hydrocarbons would be expected to be much lower \(^\text{(74)}\) than the neutron flux giving rise to it. Thus it would appear unlikely that oxygen would be detected by a proton reaction (equation \( \text{(11)} \)). Recoil or "knock-on" protons are produced when hydrogen containing matrices are subjected to fast neutron irradiation. Gilmore and Hall \(^\text{(76)}\) showed that the level of \( ^{13}\text{N} \) activity measured in a range of hydrocarbons was proportional to the number and ratio of hydrogen and carbon atoms present in the matrix, and hence to the recoil proton flux. Marion and Fowler \(^\text{(27)}\) state that the energy spectrum of recoil protons due to single scattering events will be distorted due to multiple scattering of neutrons. An angular energy spectrum for recoil protons assumes \(^\text{(27)}\) that the neutron-proton scattering cross-section is isotropic. In a hydrogen containing matrix, the single scattered recoil proton flux may be calculated from the equation

\[
P = N_H \sigma_{n-p} f
\]

where \( P \) = protons flux

\( N_H \) = number of hydrogen atoms in the matrix

\( \sigma_{n-p} \) = neutron proton scattering cross-section \(^\text{(93)}\)

\( f \) = fast neutron flux
A recoil proton flux of \(7.5 \times 10^6 \text{ns}^{-1} \text{ml}^{-1}\) would be obtained for 1 ml of kerosene (assumed to be \(C_9H_{18}O\)) in a neutron flux of \(1.7 \times 10^6 \text{ns}^{-1} \text{ml}^{-1}\) in the irradiation cell (3.3.2.).

Thus N-13 may be produced by the proton reactions (iii) and (iv). Gilmore and Hall (74) calculated that the recoil proton reaction (iv) \(^{13}C(p,n)^{13}N\) was the predominant mode of N-13 formation, and that the reaction \(^{12}C(p,\gamma)^{13}N\) could only account for a small proportion of the observed level of N-13 activity. Clearly the N-13 activity produced by activation of the solvent will constitute a source of interference in the activation analysis in non-aqueous solutions of elements which activate to produce positron emitters.

**Variation of N-13 Activity with Flow-Rate**

Kerosene was irradiated and counted over a range of flow rates, as previously stated, using the single pulse irradiation technique. Irradiation times of 120 s were used, and the counting periods in which the total activity of the active pulse of liquid was counted, varied between 2400 s at a flow rate of 0.22 ml s\(^{-1}\) to 1000 s at 1.20 ml s\(^{-1}\). The multichannel analyser was set to cover the range 0.1 - 1.95 MeV and the N-13 activity was determined as 0.51 MeV positron annihilation radiation, measured between 0.42 - 0.61 MeV. The activity
of the positron peak above background was evaluated and the results were normalised to a BF$_3$ count of unity (3.3.3.1.) and are expressed as activity or cts/BF$_3$ Ct. The results obtained are shown in Fig. 9 and table 2.

The variation in activity with flow rate for H-13, the half-life 600 s is a smooth curve rising to a maximum at a flow rate of 0.35 ml s$^{-1}$. Fig. 9. The maximum of the curve, $0.35 \pm 0.03$ ml s$^{-1}$ is the optimum flow rate for the determination of nitrogen-13 or of a 600 s half-life product isotope, on this flowing system.

Below the optimum flow rate, the curve falls away due to the loss of activity by increased radioactive decay during transit. The loss of activity by radioactive decay is not compensated by any increase in the measured activity due to increased residence times in the irradiation and detection cells. Above the optimum flow rate, the curve falls more slowly. Here, any decrease in measured activity due to a reduced residence time in the irradiation and detection cells, is partly compensated by the decrease in the transit time through the pipework.

The reproducibility and the standard deviation of the results obtained, table 2, are within the limits of statistical error (2.5.2.) of the counts obtained, and of the method used to obtain the values of Cts/BF$_3$ Ct.

The H-13 positron activity will interfere in the determination of positron emitters in solution in kerosene.
<table>
<thead>
<tr>
<th>Flow Rate</th>
<th>Activity</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0 ± 0.01</td>
<td>0.0113</td>
</tr>
<tr>
<td></td>
<td>0.0105</td>
</tr>
<tr>
<td></td>
<td>0.0110</td>
</tr>
<tr>
<td>average</td>
<td>0.0110</td>
</tr>
<tr>
<td></td>
<td>± 0.0009</td>
</tr>
<tr>
<td>0.50 ± 0.01</td>
<td>0.0123</td>
</tr>
<tr>
<td></td>
<td>0.0115</td>
</tr>
<tr>
<td></td>
<td>0.0124</td>
</tr>
<tr>
<td>average</td>
<td>0.0124</td>
</tr>
<tr>
<td></td>
<td>± 0.0007</td>
</tr>
<tr>
<td>0.49 ± 0.01</td>
<td>0.0116</td>
</tr>
<tr>
<td></td>
<td>0.0127</td>
</tr>
<tr>
<td></td>
<td>0.0125</td>
</tr>
<tr>
<td>average</td>
<td>0.0123</td>
</tr>
<tr>
<td></td>
<td>± 0.0006</td>
</tr>
<tr>
<td>0.76 ± 0.01</td>
<td>0.0106</td>
</tr>
<tr>
<td></td>
<td>0.0115</td>
</tr>
<tr>
<td></td>
<td>0.0116</td>
</tr>
<tr>
<td>average</td>
<td>0.0115</td>
</tr>
<tr>
<td></td>
<td>± 0.0009</td>
</tr>
<tr>
<td>1.20 ± 0.01</td>
<td>0.0030</td>
</tr>
<tr>
<td></td>
<td>0.0033</td>
</tr>
<tr>
<td></td>
<td>0.0032</td>
</tr>
<tr>
<td>average</td>
<td>0.0030</td>
</tr>
<tr>
<td></td>
<td>± 0.0003</td>
</tr>
</tbody>
</table>
Fig. 9. Variation of Nitrogen-13 Activity with Flow Rate
Clearly the level of the interference will be a maximum for determinations carried out at a flow rate of 0.25 ml s⁻¹, the optimum flow rate for the production and detection of N-13. The N-13 activity and hence the interference level falls continuously once the optimum flow rate is exceeded, and below this flow rate the N-13 activity falls even more sharply. Thus the level of the N-13 interference will be the greatest in the determination of either positron emitters or of nuclides emitting photons in the 0.42 - 0.61 MeV region of the energy spectrum, which have similar half-lives to the N-13. Interference will also occur from the Compton continuum of N-13 in the determination of product isotopes emitting gamma-rays of less than 0.42 MeV. The extent of this interference will also be dependent on the difference in half-life between the isotope and N-13.

3.3.4. Fast-Neutron Activation Analysis of Elements with Product Isotopes with Half-Lives varying between 6.8 a and 51.6 a

The interference levels measured in kerosene due to activation (3.3.2.4.) were found to be very much lower than those encountered in the activation analysis of aqueous systems (18). In the latter system interference at low flow rates from the reaction \(^{14}O(p, \gamma)^{15}N\) predominates while at high flow rates the reaction...
16O(n, p)16N occurs. Interference is therefore encountered in both the determination of short and long-lived product nuclides. The interference due to 16N is marked since the isotope is produced by a fast neutron reaction on a target element of relatively high isotopic abundance. Further the gamma-radiation and Compton continuum of N-16 stretches from 7.12 MeV downwards.

Owing to the low levels of interference measured in the activation of the solvent kerosene, the analysis of a range of elements in non-aqueous solution on the system was considered feasible. Fast neutron activation analysis of a range of elements producing product nuclides with half-lives between 0.88 seconds and 29.4 seconds was therefore attempted in order to investigate the fundamental principles of analysis in non-aqueous media. In each case the variation in activity with flow rate, the variation in activity with target element concentration, and the limits of detection for each element were investigated. Analysis of a range of elements will also enable the variation in optimum flow rate with product nuclide half-life, to be investigated. The elements determined in non-aqueous solution together with their relevant nuclear data are given in Table 3.
### Table 2

<table>
<thead>
<tr>
<th>Half-Life</th>
<th>Target Element and Nuclear Reaction</th>
<th>Cross Section</th>
<th>Principal Energy MeV</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.38s</td>
<td>$^{63}$Cu(n, m) $^{62}$Cu</td>
<td>$600 \pm 30$</td>
<td>0.51</td>
</tr>
<tr>
<td>1.38s</td>
<td>$^{79}$Br(n, m) $^{78}$Br</td>
<td>$1050 \pm 35$</td>
<td>0.51</td>
</tr>
<tr>
<td>2.21s</td>
<td>$^{52}$Cr(n, p) $^{52}$V</td>
<td>$115 \pm 15$</td>
<td>1.45</td>
</tr>
<tr>
<td>1.43s</td>
<td>$^{28}$Si(n, p) $^{28}$Si</td>
<td>$237 \pm 14$</td>
<td>1.78</td>
</tr>
<tr>
<td>1.60</td>
<td>$^{140}$Ce(n, m)$^{139}$Ce</td>
<td>$1593 \pm 130$</td>
<td>0.75</td>
</tr>
<tr>
<td>19.3</td>
<td>$^{19}$F(n, p) $^{19}$O</td>
<td>$51 \pm 10$</td>
<td>0.20</td>
</tr>
</tbody>
</table>
3.3.4.1. Copper

Fast neutron activation of copper using short period irradiation techniques yields almost exclusively the isotope copper-62, half-life 580 s. Analysis of copper using this nuclide was chosen so as to provide a relatively long half-life isotope for these investigations on the flowing system. Copper-62 is produced by a fast neutron reaction on the 63.3% abundant stable isotope of copper, copper-63. The reaction occurring is $^{63}$Cu(n, 2n) $^{62}$Cu, cross-section $60 \pm 40$mb, (28) threshold energy 11.01 MeV (30). Copper-62 decays with a 93% branching ratio by positron emission (31). A number of other nuclear reactions on the target element copper-63 could occur, but these were not observed. Presumably this is due to the long half-lives of the reaction products ($^{63}$Ni, half-life 120 years, $^{60}$Co, half-life 5.27 years) which will thus yield very low specific activities after a short period irradiation. The only significant interference could arise from fast neutron activation of the 30.2% abundant stable isotope of copper, copper-65, giving $^{64}$Cu, half-life 12.8 hours (31). The reaction occurring is $^{65}$Cu(n, 2n)$^{64}$Cu, cross-section $380 \pm 70$ mb (38) with a threshold energy of 10.05 MeV (39). Copper-64 is a positron emitter and will interfere in the determination of copper using the copper-62 isotope. The long half-life of Cu-64 coupled with the lower isotopic
abundance of the target isotope Cu-62 ensured that only a very small amount of Cu-64 would be produced in these experiments. It was calculated that in each irradiation the ratio of Cu-62 to Cu-64 positron activity would be 600:1 on average. Cu-64 activity due to its long half-life would build up during irradiation and re-irradiation of solutions containing copper. In practice, with the single pulse technique, only a small proportion of the order of 1%, of the total volume of the solution is irradiated and hence a further dilution of the Cu-64 activity by a factor of 100 occurs. With the provision of overnight periods of decay between experiments, it was considered that the build up of Cu-64 would be negligible.

A solution of cupric naphthenate in kerosene was prepared so as to contain 200 ppm of copper. The reagent grade cupric naphthenate used was stated by the manufacturers to contain 5.0% copper by weight. The copper concentration was determined, by a wet ashing procedure followed by a volumetric analysis technique according to the method of Vogel (33), and was found to be 50% within the limits of experimental error. The variation of activity with flow rate for 100 ppm copper-62 was investigated on the flowing system using the single pulse irradiation and counting technique. The timing periods for this procedure were determined in the usual way (3.3.3.4.). An
Irradiation time of 120 s was used and counting times varied between 1000 s at 1.20 ml s\(^{-1}\) to 2400 s at 0.22 ml s\(^{-1}\). The spectrum of copper-62 was recorded over the range 0.1 - 1.25 MeV and the positron annihilation photopeak was counted between 0.62 MeV and 0.61 MeV. The results obtained for the variation of copper-62 activity with flow-rate are shown in Fig. 10 and Table 4, and are expressed as photopeak counts above background normalised to a \(\text{BF}_3\) count of unity. The reproducibility of these results was determined by the limit of statistical error of the experimentally obtained counts and was within ± 0.3% at the optimum flow rate. The low level of \(N\)-13 interference may be seen from the curves, shown on the same axes, (Fig. 10), of the total positron activity, \(N\)-13 corrected copper activity and of the nitrogen-13 activity. Clearly even this low level of interference will raise the detection limit of copper. The optimum flow rate for the production of a 589 s half-life, copper-62 \(\%\) was taken as 0.37 ± 0.03 ml s\(^{-1}\) from the variation of the copper-62 activity with flow rate.

The variation of the copper-62 activity, at the optimum flow rate, with copper concentration was investigated using the same experimental conditions with solutions of 400, 200, 100 and 50 ppm of copper respectively. The results obtained are shown in table 5, and combined with the previous results obtained for 800 ppm copper, at the
Fig. 10. Variation in Copper-62 Activity with Flow Rate
Table 4

Variation of Copper-62 (Half-Life 588 s) Activity with Flow Rate

<table>
<thead>
<tr>
<th>Flow Rate (mL/s)</th>
<th>Activity* (Cts/30s)</th>
</tr>
</thead>
</table>
| 0.02 ± 0.01      | 0.112  
|                  | 0.117  
|                  | 0.115  
| average          | 0.115  
| Copper only      | 0.104  σ = ± 0.001 |
| 0.08 ± 0.01      | 0.122  
|                  | 0.123  
|                  | 0.122  
|                  | 0.122  
|                  | 0.122  
| average          | 0.122  
| Copper only      | 0.111  σ = ± 0.001 |
| 0.40 ± 0.01      | 0.121  
|                  | 0.119  
|                  | 0.118  
| average          | 0.119  
| Copper only      | 0.107  σ = ± 0.001 |
| 0.75 ± 0.01      | 0.035  
|                  | 0.031  
|                  | 0.032  
| average          | 0.032  
| Copper only      | 0.082  σ = ± 0.002 |
| 1.20 ± 0.01      | 0.070  
|                  | 0.070  
|                  | 0.070  
| average          | 0.070  
| Copper only      | 0.061  σ = ± 0.000 |

* Copper + kerosene H-18 (Table 2)
### Table 2

<table>
<thead>
<tr>
<th>Copper Concentration (PPM)</th>
<th>Activity (Cts/DP^2 Ct)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>
| 400                        | 0.063, 0.063, 0.065, 0.063, 0.063, 0.067, 0.067
|                            |                         |
|                            | average: 0.067          |
| Copper only                | 0.055 ± 0.001           |
| 200                        | 0.041, 0.043, 0.043, 0.040, 0.043, 0.043, 0.041
|                            |                         |
|                            | average: 0.043           |
| Copper only                | 0.027 ± 0.001           |
| 100                        | 0.024, 0.028, 0.026, 0.025, 0.027, 0.027, 0.028
|                            |                         |
|                            | average: 0.027           |
| Copper only                | 0.014 ± 0.001           |
| 50                         | 0.018, 0.019, 0.017, 0.019, 0.019, 0.019, 0.018
|                            |                         |
|                            | average: 0.019           |
| Copper only                | 0.007 ± 0.005           |
optimum flow rate, are shown in Fig. 11. A straight line calibration graph, passing through the origin was obtained for the variation of copper-65 activity with the concentration of copper. Thus it may be assumed that the system and method have a linear response to concentration changes, and the calibration graph could be used for the determination of unknown copper concentrations. As would be expected, the reproducibility of the results falls continuously as the copper concentration is reduced. The reproducibility of results was within counting statistics and varied from \( \pm 2\% \) for 400 ppm Cu to \( \pm 3.5\% \) for 50 ppm Cu. Reproducibility worsens as the copper concentration is reduced due to the decrease in the total count obtained during each determination with a corresponding increase in statistical fluctuations.

The detection limits for copper and the other elements investigated are discussed together in section 3.3.4.9.

3.3.4.6. Bromine

Bromine was determined in solution in aerodene by a fast neutron reaction on the 79.52\% abundant isotope of bromine, bromine-80. The nuclear reaction used was \( ^7\text{Br}(n, \text{\gamma})^8\text{Br} \), half-life 5.11 s, cross-section 1060 \( \pm 35 \text{ mb} \) (25), and threshold energy 8.43 MeV (30). Bromine-80 decays principally by positon emission but also decays
Fig. 11. Variation in Copper-62 Activity with Copper Concentration
to a small extent with the emission of a 0.62 MeV gamma-ray. This gamma-ray was just visible in the gamma-ray spectra of the most concentrated solutions irradiated. Apart from kerosene N-15 activity, no other interferences were expected or encountered. Fast neutron activation of bromine-79 or Br-80 to yield significant quantities of interferences is unlikely with short duration irradiations, due to the relatively long half-lives of the production isotopes (of the order of hours) combined with their low reaction cross-sections.

Redistilled ethylene dibromide was used to prepare a solution, containing 200 ppm of bromine in kerosene. No chemical analysis of the ethylene dibromide was carried out since it was considered that this material was chemically pure after purification by distillation. The variation of bromine-79 activity with flow rate was investigated using the 200 ppm solution of bromine. The single pulse technique was used with irradiation times of 110 s and counting times which varied between 2100 s at 0.36 ml s\(^{-1}\) to 300 s at 1.66 ml s\(^{-1}\). The positron peak was counted in the energy range 0.48 - 0.65 MeV and the results obtained, expressed as C(\(^{79}\))B(C\(^{80}\))/C(\(^{79}\))B, are shown in Fig. 12 and Table 6. The reproducibility of the results obtained at the optimum flow rate was within ± 3% and all the results obtained were within the limits of statistical error of the counts obtained. Since bromine-79 is a positron emitter,
Fig. 12. Variation in Bromine-78 Activity with Flow Rate
### Table 6

**Variation in Bromine-78 Activity (Half-Life 37± s) with Flow Rate**

<table>
<thead>
<tr>
<th>Flow Rate (mL/min)</th>
<th>Activity (Ct/min/μg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.56 ± 0.01</td>
<td>0.033</td>
</tr>
<tr>
<td></td>
<td>0.038</td>
</tr>
<tr>
<td></td>
<td>0.022</td>
</tr>
<tr>
<td>average</td>
<td>0.029</td>
</tr>
<tr>
<td>Bromine only</td>
<td>0.022</td>
</tr>
<tr>
<td></td>
<td>σ = ± 0.001</td>
</tr>
<tr>
<td>0.59 ± 0.01</td>
<td>0.109</td>
</tr>
<tr>
<td></td>
<td>0.103</td>
</tr>
<tr>
<td></td>
<td>0.102</td>
</tr>
<tr>
<td>average</td>
<td>0.109</td>
</tr>
<tr>
<td>Bromine only</td>
<td>0.097</td>
</tr>
<tr>
<td></td>
<td>σ = ± 0.001</td>
</tr>
<tr>
<td>0.57 ± 0.01</td>
<td>0.109</td>
</tr>
<tr>
<td></td>
<td>0.117</td>
</tr>
<tr>
<td></td>
<td>0.109</td>
</tr>
<tr>
<td>average</td>
<td>0.117</td>
</tr>
<tr>
<td>Bromine only</td>
<td>0.117</td>
</tr>
<tr>
<td></td>
<td>σ = ± 0.002</td>
</tr>
<tr>
<td>0.50 ± 0.05</td>
<td>0.101</td>
</tr>
<tr>
<td></td>
<td>0.107</td>
</tr>
<tr>
<td>average</td>
<td>0.107</td>
</tr>
<tr>
<td>Bromine only</td>
<td>0.095</td>
</tr>
<tr>
<td></td>
<td>σ = ± 0.004</td>
</tr>
</tbody>
</table>

* Bromine + kerosene N-13 (table 2)
<table>
<thead>
<tr>
<th>Flow Rate ml s⁻¹</th>
<th>Activity* Cts/EP₃ Ct</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.05 ± 0.02</td>
<td>0.036</td>
</tr>
<tr>
<td></td>
<td>0.100</td>
</tr>
<tr>
<td></td>
<td>0.101</td>
</tr>
<tr>
<td>average</td>
<td>0.099</td>
</tr>
<tr>
<td>Bromine only</td>
<td>0.088 ± 0.003</td>
</tr>
<tr>
<td>1.27 ± 0.02</td>
<td>0.031</td>
</tr>
<tr>
<td></td>
<td>0.085</td>
</tr>
<tr>
<td></td>
<td>0.087</td>
</tr>
<tr>
<td>average</td>
<td>0.083</td>
</tr>
<tr>
<td>Bromine only</td>
<td>0.072 ± 0.003</td>
</tr>
<tr>
<td>1.46 ± 0.02</td>
<td>0.076</td>
</tr>
<tr>
<td></td>
<td>0.081</td>
</tr>
<tr>
<td></td>
<td>0.081</td>
</tr>
<tr>
<td>average</td>
<td>0.073</td>
</tr>
<tr>
<td>Bromine only</td>
<td>0.071 ± 0.003</td>
</tr>
</tbody>
</table>

* Bromine + kerosene N₁₃ (table 2)
activation of the solvent to give N-13 will interfere in the determination of bromine. The level of this interference will be less in this case than for copper-62 (1.2-5 hr.) since the half-life of bromine-79 (3310 s) is significantly different from that of N-13 (600 s). Thus the optimum flow rates for the production and detection of these isotopes are also significantly different. The optimum flow rate for a 3310 s half-life isotope, bromine-79, was taken as 0.58 ± 0.03 ml s⁻¹ from the graph of the variation of activity with flow rate (Fig. 12).

The variation in bromine-79 activity with bromine concentration was measured at the optimum flow rate (0.58 ml s⁻¹). Solutions containing 500, 100, 50 and 50 ppm of bromine were irradiated and counted in turn on the flowing system. An irradiation time of 120 s and a counting time of 1800 s were used in the single pulse technique. The results obtained are shown in table 7 and Fig. 13, and include the results obtained at the optimum flow rate for 800 ppm bromine. A straight line analytical calibration graph of bromine-79 activity to bromine concentration, which passed through the origin, was obtained. The reproducibility of the results varied from ±1.5% for 500 ppm Br, to ±7% for 50 ppm of bromine. The reproducibility of the results was within that predicted from counting statistics (2.5, 3.) and progressively worsened with concentration as the total count decreased.
Fig. 13. Variation in Bromine-78 Activity with Bromine Concentration
### Table 7

**Variation in Bromine-78 Activity with Bromine Concentration**

<table>
<thead>
<tr>
<th>Bromine Concentration (ppm)</th>
<th>Activity* ( \text{Cp} / \text{mg} )</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>100</strong></td>
<td>0.000, 0.000, 0.000, 0.000, 0.000, 0.000</td>
</tr>
<tr>
<td>average</td>
<td>0.001</td>
</tr>
<tr>
<td>Bromine only</td>
<td>0.008 ( \sigma = 0.0008 )</td>
</tr>
<tr>
<td><strong>200</strong></td>
<td>0.025, 0.026, 0.028, 0.026, 0.026</td>
</tr>
<tr>
<td>average</td>
<td>0.026</td>
</tr>
<tr>
<td>Bromine only</td>
<td>0.022 ( \sigma = 0.0018 )</td>
</tr>
<tr>
<td><strong>100</strong></td>
<td>0.022, 0.023, 0.022, 0.022, 0.022</td>
</tr>
<tr>
<td>average</td>
<td>0.022</td>
</tr>
<tr>
<td>Bromine only</td>
<td>0.012 ( \sigma = 0.0004 )</td>
</tr>
<tr>
<td><strong>50</strong></td>
<td>0.021, 0.018, 0.021, 0.019, 0.019</td>
</tr>
<tr>
<td>average</td>
<td>0.020</td>
</tr>
<tr>
<td>Bromine only</td>
<td>0.007 ( \sigma = 0.0005 )</td>
</tr>
</tbody>
</table>

* Bromine + kerosene H-13 (table 2)
The detection limits of bromine are discussed in section 3.3.4.6.

3.3.4.6. Chromium

Chromium was irradiated and determined in non-aqueous solution using the nuclear reaction $^{52}$Cr(n, p)$^{52}$V having a product half-life of 286 s. The target isotope, chromium-52, is 99.7% abundant, and the fast neutron reaction used to produce vanadium-52 has a cross-section of $115 \pm 15$ nb (26), with a threshold energy of 3.67 MeV (20). The isotope vanadium-52 undergoes radioactive decay by beta-particle emission to Cr-52, (100%) (31) and in the process a 1.42 MeV gamma-ray is also emitted. Clearly N-13 activity from irradiated kerosene will not interfere in the determination of chromium using the product isotope V-52. No other peaks were observed in the gamma-ray spectra obtained from irradiated solutions of chromium in kerosene other than the 0.71 MeV peak of N-13, and the 1.43 MeV peak of V-52. Interferences or other products from activation of Cr-52 by other nuclear reactions, or from activation of the other isotopes of chromium would not be expected with short period irradiations. The majority of the reaction products are produced from the relatively low abundance isotopes of chromium and produce long half-life products or stable isotopes. The photopeak from the naturally occurring isotope potassium-40, a gamma-energy 1.46 MeV, will interfere to a slight extent.
in the measurement of the 1.43 MeV gamma-radiation from V-52. The level of K-40 activity is very low indeed due to the lead shielding used in the cage housing the detector, (3.3.2.). The contribution of activity from K-40 to the 1.43 MeV photopeak can be corrected for in the background correction which is applied to all results.

Chromium naphthenate, of stated chemical composition containing 9.5% Cr, was used to prepare a solution of 8000 ppm of chromium in benzene. This concentrated solution was used due to the lower cross-section of the $^{52}$Cr(n, p) $^{52}$V nuclear reaction. This solution was used to investigate the variation in V-52 activity with flow rate. The 1.43 MeV photopeak of V-52 was counted between 1.23 and 1.28 MeV, with the multichannel analyser set to cover an energy range of 0.1 - 1.55 MeV. The single pulse irradiation and counting technique was again used, and the timing periods in the technique were determined by irradiating the flowing solution over a range of flow rates followed by counting in the multiscalar mode. Irradiation times of 100 s were used for low flow rates in the range 0.33 - 1.14 ml s$^{-1}$ and the counting times used varied between 1000 s and 600 s. The limitations of the single pulse technique (3.3.3.2.) began to be experienced at the higher flow rates investigated. At 1.52 and 1.85 ml s$^{-1}$, the irradiation times had to be cut to 60 s and 60 s respectively and counting times of 400 s and
300 s were used. The variation in vanadium-52 activity with flow rate is shown in Fig. 14 and Table 3. The results are expressed as the V-52 photopeak count above background divided by the total BF₃ count recorded during the irradiation leading to the measurement. The background correction included a correction for the 1.86 MeV peak of X-192. The reproducibility of the results was within the statistical limits of error determined by the total counts obtained in each measurement, and at the optimum flow rate was within ±1.5%. The graph of the variation in V-52 activity with flow rate is a smooth curve, (Fig. 14), with a maximum at 0.30 ± 0.03 ml s⁻¹. This value was taken as the optimum flow rate for the production and detection of this system of an isotope with a half-life of 266 s.

The variation of V-52 activity with chromium concentration was investigated at the optimum flow rate with solutions containing 6000, 4000, 2000, 1000 and 500 ppm of chromium. The same experimental conditions were used with an irradiation time of 100 s and a counting time of 700 s. The results obtained are shown in Table 3 and the full results for the variation in V-52 activity with chromium concentration are shown in Fig. 15. A linear relationship between V-52 activity and chromium concentration, passing through the origin was obtained (Fig. 15). The reproducibility of the results varied between ± 2%
Fig. 14: Variation in Vanadium-52 Activity with Flow Rate
<table>
<thead>
<tr>
<th>Flow Rate ( \text{ml s}^{-1} )</th>
<th>Activity ( \text{Cts/20\text{sec}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.20 ± 0.01</td>
<td>0.030</td>
</tr>
<tr>
<td></td>
<td>0.035</td>
</tr>
<tr>
<td></td>
<td>0.033</td>
</tr>
<tr>
<td>average</td>
<td>0.035 ( \sigma = +0.00 )</td>
</tr>
<tr>
<td>0.30 ± 0.01</td>
<td>0.037</td>
</tr>
<tr>
<td></td>
<td>0.033</td>
</tr>
<tr>
<td></td>
<td>0.033</td>
</tr>
<tr>
<td>average</td>
<td>0.033 ( \sigma = +0.00 )</td>
</tr>
<tr>
<td>0.60 ± 0.01</td>
<td>0.071</td>
</tr>
<tr>
<td></td>
<td>0.070</td>
</tr>
<tr>
<td></td>
<td>0.070</td>
</tr>
<tr>
<td>average</td>
<td>0.070 ( \sigma = +0.00 )</td>
</tr>
<tr>
<td>0.87 ± 0.02</td>
<td>0.075</td>
</tr>
<tr>
<td></td>
<td>0.077</td>
</tr>
<tr>
<td></td>
<td>0.075</td>
</tr>
<tr>
<td></td>
<td>0.075</td>
</tr>
<tr>
<td>average</td>
<td>0.075 ( \sigma = +0.00 )</td>
</tr>
<tr>
<td>Flow Rate ml s^{-1}</td>
<td>Activity Cts/47.5 \mu C</td>
</tr>
<tr>
<td>---------------------</td>
<td>-------------------------</td>
</tr>
<tr>
<td>1.14 \pm 0.02</td>
<td>0.072</td>
</tr>
<tr>
<td></td>
<td>0.073</td>
</tr>
<tr>
<td></td>
<td>0.073</td>
</tr>
<tr>
<td>average</td>
<td>0.073 \pm 0.001</td>
</tr>
<tr>
<td>1.52 \pm 0.03</td>
<td>0.066</td>
</tr>
<tr>
<td></td>
<td>0.067</td>
</tr>
<tr>
<td></td>
<td>0.067</td>
</tr>
<tr>
<td>average</td>
<td>0.066 \pm 0.001</td>
</tr>
<tr>
<td>1.85 \pm 0.03</td>
<td>0.057</td>
</tr>
<tr>
<td></td>
<td>0.056</td>
</tr>
<tr>
<td></td>
<td>0.056</td>
</tr>
<tr>
<td>average</td>
<td>0.056 \pm 0.003</td>
</tr>
<tr>
<td>Chromium Concentration</td>
<td>Activity (counts/EP&lt;sub&gt;2&lt;/sub&gt;Cr)</td>
</tr>
<tr>
<td>------------------------</td>
<td>-----------------------------------</td>
</tr>
<tr>
<td>40000 ppb</td>
<td>0.037, 0.036, 0.035, 0.034</td>
</tr>
<tr>
<td></td>
<td>0.037, 0.036</td>
</tr>
<tr>
<td>average</td>
<td>0.032 ± 0.0017</td>
</tr>
<tr>
<td>4000 ppb</td>
<td>0.037, 0.036, 0.037, 0.037</td>
</tr>
<tr>
<td></td>
<td>0.027, 0.037</td>
</tr>
<tr>
<td>average</td>
<td>0.032 ± 0.0004</td>
</tr>
<tr>
<td>1000 ppb</td>
<td>0.030, 0.021, 0.020, 0.021</td>
</tr>
<tr>
<td></td>
<td>0.021, 0.020</td>
</tr>
<tr>
<td>average</td>
<td>0.021 ± 0.001</td>
</tr>
<tr>
<td>1000 ppb</td>
<td>0.011, 0.011, 0.011, 0.011, 0.011,</td>
</tr>
<tr>
<td></td>
<td>0.012, 0.011</td>
</tr>
<tr>
<td>average</td>
<td>0.011 ± 0.0005</td>
</tr>
<tr>
<td>500 ppb</td>
<td>0.058, 0.056, 0.059, 0.055, 0.055,</td>
</tr>
<tr>
<td></td>
<td>0.056, 0.056</td>
</tr>
<tr>
<td>average</td>
<td>0.058 ± 0.003</td>
</tr>
</tbody>
</table>
Fig. 15. Variation in Vanadium-52 Activity with Chromium Concentration
for 1000 ppm of chromium to +3% for the solution containing 500 ppm of chromium. The reproducibility of results decreased as usual with decreasing target element concentration, but all the results obtained were within the limits of statistical error dictated by the counting statistics.

The detection limits of chromium are discussed in section 3.3.4.8.

3.3.6. Silicon

The nuclear reaction used to determine silicon in these investigations was $^{29}\text{Si}(n, p)^{29}\text{Al}$, half-life 143 s. The cross-section of this fast neutron reaction is given as $237 \pm 14 \text{ mb}$ (37) and the threshold energy as 3.9 MeV (39). Silicon-28, the target isotope, has an isotopic abundance of 28.21%. The product isotope, aluminium-28, decays by beta-particle emission only to silicon-28 (21). A gamma-ray of 1.78 MeV is also emitted. Other reaction products from fast neutron activation of silicon-28 or from activation of the other stable isotopes of silicon would not be expected. Such reaction products, in this case, either have half-lives too short to be detected on this flowing system or are the products of reactions involving low abundance target isotopes coupled with low reaction cross-sections. The relatively high gamma-ray energy of Al-28, 1.78 MeV, is well above the K-\(^{13}\)O peak in the
background, and is even farther removed from 13-N activity in the solvent. Determinations in the presence of low levels of background and matrix interference would be expected, and this should enhance the limits of detection of this element.

Spectroscopic grade tetramethyl silane (TMS) containing 31.83% of silicon was used as the source of silicon. A solution containing 20,000 p.p.m. of silicon was prepared in order to investigate the variation in Al-28 activity with flow rate. The multichannel analyzer was set to go on an energy range of 0.1 - 1.25 MeV as usual, and the 1.79 MeV peak of Al-28 was measured over the range 1.72 - 1.77 MeV. The single pulse irradiation and counting technique was again used and the irradiation times varied between 60 s at the lowest flow rate, 0.25 ml s\(^{-1}\), to 30 s at the highest flow rate, 2.45 ml s\(^{-1}\). It was decided that at this point the limit for the application of the single pulse technique had been reached.

The analysis of any element producing a shorter lived product isotope than Al-28 would require the use of the irradiation and counting technique described in 3.3.3.1. The variation in Al-28 activity expressed as Cts/Be\(_3\)Ct, above natural background, with flow rate is shown in table 10 and Fig. 16. The optimum flow rate for the determination of a 14\(\gamma\) a half-life product isotope, Al-28, was taken as 1.48 ± 0.03 ml s\(^{-1}\). The reproducibility of
<table>
<thead>
<tr>
<th>Flow Rate ( \text{m}^{-1} )</th>
<th>Activity Cts/hr ( 1^2 \text{Cl} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.3 ( \pm ) 0.01</td>
<td>0.072( \pm ) 0.003</td>
</tr>
<tr>
<td></td>
<td>0.046</td>
</tr>
<tr>
<td></td>
<td>0.038</td>
</tr>
<tr>
<td>0.3 ( \pm ) 0.01</td>
<td>0.149</td>
</tr>
<tr>
<td></td>
<td>0.148</td>
</tr>
<tr>
<td></td>
<td>0.142</td>
</tr>
<tr>
<td>Average</td>
<td>0.130 ( \pm ) 0.002</td>
</tr>
<tr>
<td>1.0 ( \pm ) 0.02</td>
<td>0.188</td>
</tr>
<tr>
<td></td>
<td>0.187</td>
</tr>
<tr>
<td></td>
<td>0.186</td>
</tr>
<tr>
<td>Average</td>
<td>0.188 ( \pm ) 0.002</td>
</tr>
<tr>
<td>1.0 ( \pm ) 0.02</td>
<td>0.213</td>
</tr>
<tr>
<td></td>
<td>0.213</td>
</tr>
<tr>
<td></td>
<td>0.212</td>
</tr>
<tr>
<td>Average</td>
<td>0.213 ( \pm ) 0.001</td>
</tr>
<tr>
<td>1.0 ( \pm ) 0.03</td>
<td>0.233</td>
</tr>
<tr>
<td></td>
<td>0.233</td>
</tr>
<tr>
<td></td>
<td>0.233</td>
</tr>
<tr>
<td>Average</td>
<td>0.233 ( \pm ) 0.001</td>
</tr>
<tr>
<td>Flow Rate (ml s⁻¹)</td>
<td>Activity (cts/mg·Ct)</td>
</tr>
<tr>
<td>-------------------</td>
<td>----------------------</td>
</tr>
<tr>
<td>1.60 ± 0.03</td>
<td>0.213</td>
</tr>
<tr>
<td></td>
<td>0.219</td>
</tr>
<tr>
<td></td>
<td>0.220</td>
</tr>
<tr>
<td></td>
<td>0.225</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>1.78 ± 0.03</td>
<td>0.235</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>2.02 ± 0.04</td>
<td>0.240</td>
</tr>
<tr>
<td></td>
<td>0.245</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>2.45 ± 0.04</td>
<td>0.260</td>
</tr>
<tr>
<td></td>
<td>0.265</td>
</tr>
<tr>
<td></td>
<td>0.265</td>
</tr>
<tr>
<td></td>
<td>0.265</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Fig. 16. Variation in Aluminium-28 Activity with Flow Rate
all the results was within the limits of the statistical error of the counts obtained and at the optimum flow rate was within + 1.3%.

The variation of Al-26 activity with silicon concentration was investigated with solutions containing silicon concentrations of 1000, 2000, 500, 250 and 20 ppm of Si respectively. These were irradiated and counted using the single pulse technique with irradiation times of 60 s and counting times of 500 s. The results obtained at the optimum flow rate for the solutions are shown in Table 11 and combined with the results for a solution containing 10000 ppm of silicon are shown in Fig. 17. A straight line calibration graph, passing through the origin was obtained from the investigation of Al-26 activity with silicon concentration, Fig. 17. The reproducibility fell as would be expected, with decreasing silicon concentration, and varied from +2.1% for 1000 ppm Si to -0.8% for 250 ppm Si.

The detection limits of silicon are discussed in 3.3.4.3.

3.3.4.3. Cerium

Cerium was obtained in non-aqueous solution by a fast neutron reaction on the 60.76% abundant isotope of cerium, cerium-142. The nuclear reaction used was

\[^{140}\text{Ce}(n, \gamma)^{142}\text{Ce}, \text{cross-section } 15\mu\text{b to } 128\text{ mb (36)}\text{ and threshold energy } 7.5\text{ keV (30). The isotope Ce-142m has}\]

<table>
<thead>
<tr>
<th>Silicon Concentration (ppm)</th>
<th>Activity (Cts/TP_2Ct)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4000</td>
<td>0.028, 0.027, 0.032, 0.034, 0.032</td>
</tr>
<tr>
<td>average</td>
<td>0.032 ( \pm 0.002 )</td>
</tr>
<tr>
<td>2000</td>
<td>0.015, 0.015, 0.018, 0.015, 0.015</td>
</tr>
<tr>
<td>average</td>
<td>0.016 ( \pm 0.001 )</td>
</tr>
<tr>
<td>1000</td>
<td>0.006, 0.006, 0.006, 0.005, 0.005</td>
</tr>
<tr>
<td>average</td>
<td>0.006 ( \pm 0.0005 )</td>
</tr>
<tr>
<td>500</td>
<td>0.0038, 0.0037, 0.0038, 0.0038, 0.0038</td>
</tr>
<tr>
<td>average</td>
<td>0.0038 ( \pm 0.0001 )</td>
</tr>
<tr>
<td>250</td>
<td>0.0030, 0.0027, 0.0030, 0.0030, 0.0030</td>
</tr>
<tr>
<td>average</td>
<td>0.0030 ( \pm 0.0002 )</td>
</tr>
<tr>
<td>50</td>
<td>0.0011, 0.0009, 0.0009, 0.0009, 0.0009</td>
</tr>
<tr>
<td>average</td>
<td>0.0009 ( \pm 0.0003 )</td>
</tr>
</tbody>
</table>
Fig. 17. Variation in Aluminium-28 Activity with Silicon Concentration
a half-life of 60 s and decays to Cs-139 with the emission of a 0.75 MeV gamma-ray. A number of reaction products are possible from fast neutron activation of Cs-138 and from the activation of the other low abundance isotopes of cerium. With one exception, the product isotope from the reaction $^{140}$Cs($n$, $\alpha$) $^{137m}$Ba, having a half-life of 156 s, all the products have relatively long half-lives and for this reason would not be produced in significant amounts with short period irradiations. Even Ba-157 m was not observed in the gamma-ray spectra obtained from irradiated cerium solutions, since the reaction cross-section for its production is given as only 3 mb (20). Nitrogen-13 activity produced by activation of the solvent will not interfere in the measurement of Cs-139 m. The gamma-ray energy of the cerium isotope is higher than, and is sufficiently removed from, this interference. In any case the levels of N-13 activity at the flow rates used to determine a 60 s product isotope will be very low.

Cerium naphthenate of stated chemical composition (0.6% Ce), was used to prepare a solution containing 800 ppm of cerium in hexane. This concentration of cerium was chosen because of the relatively high cross-section of the nuclear reaction producing Cs-139 m, and the solution was used to investigate the variation in activity with flow rate of this isotope. The 0.75 MeV
peak of Ca-133 m was measured between 0.67 and 0.84 MeV, with the multichannel analyser set to cover the range 0.1 - 1.33 MeV. The single pulse irradiation and counting technique was only used for the two lowest flow rates investigated, 0.62 and 1.33 ml s⁻¹. Irradiation times of 120 s, and counting times of 300 s were used at these flow rates. At higher flow rates, 1.69 - 6.63 ml s⁻¹, the flowing solutions were irradiated at as nearly as possible a constant neutron flux and the equilibrium level of activity in the solution was then counted (2.3.3.1.). Counting times of 60 s were used. Detection times varied between 100 s and 22 s, and equilibrium was attained at time intervals which varied between 105 s and 32 s. The detection times and the time to reach an equilibrium level of activity, the saturation time, were determined in the usual way by counting in the multiscaler mode (2.3.3.1.). The results obtained for the variation in Ca-133 m activity with flow rate are shown in table 12 and Fig. 18. The results are expressed as the Cts/F3 of the 0.75 MeV photopeak corrected for natural background, and also for the low level of neutron generator induced background. Using the two different experimental techniques gave a smooth curve, Fig. 18, for the variation in activity with flow rate of the isotope Ca-133 m. The optimum flow rate for the determination of this isotope, half-life 60 s, was taken as 3.4 ± 0.2 ml s⁻¹.
<table>
<thead>
<tr>
<th>Flow Rate</th>
<th>Activity</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.62 ± 0.01</td>
<td>0.0032</td>
</tr>
<tr>
<td></td>
<td>0.0032</td>
</tr>
<tr>
<td></td>
<td>0.0032</td>
</tr>
<tr>
<td>average</td>
<td>0.0032</td>
</tr>
<tr>
<td></td>
<td>σ = + 0.0004</td>
</tr>
<tr>
<td>1.63 ± 0.03</td>
<td>0.034</td>
</tr>
<tr>
<td></td>
<td>0.034</td>
</tr>
<tr>
<td></td>
<td>0.034</td>
</tr>
<tr>
<td>average</td>
<td>0.034</td>
</tr>
<tr>
<td></td>
<td>σ = + 0.0007</td>
</tr>
<tr>
<td>2.03 ± 0.03</td>
<td>0.047</td>
</tr>
<tr>
<td></td>
<td>0.047</td>
</tr>
<tr>
<td></td>
<td>0.047</td>
</tr>
<tr>
<td>average</td>
<td>0.047</td>
</tr>
<tr>
<td></td>
<td>σ = + 0.000</td>
</tr>
<tr>
<td>2.49 ± 0.06</td>
<td>0.055</td>
</tr>
<tr>
<td></td>
<td>0.055</td>
</tr>
<tr>
<td></td>
<td>0.055</td>
</tr>
<tr>
<td>average</td>
<td>0.055</td>
</tr>
<tr>
<td></td>
<td>σ = + 0.000</td>
</tr>
<tr>
<td>3.18 ± 0.03</td>
<td>0.069</td>
</tr>
<tr>
<td></td>
<td>0.069</td>
</tr>
<tr>
<td></td>
<td>0.069</td>
</tr>
<tr>
<td>average</td>
<td>0.069</td>
</tr>
<tr>
<td></td>
<td>σ = + 0.0003</td>
</tr>
<tr>
<td>4.17 ± 0.07</td>
<td>0.058</td>
</tr>
<tr>
<td></td>
<td>0.058</td>
</tr>
<tr>
<td></td>
<td>0.058</td>
</tr>
<tr>
<td>average</td>
<td>0.058</td>
</tr>
<tr>
<td></td>
<td>σ = + 0.0007</td>
</tr>
<tr>
<td>Flow Rate (mL s⁻¹)</td>
<td>Activity (cts/2π Ct)</td>
</tr>
<tr>
<td>-------------------</td>
<td>----------------------</td>
</tr>
</tbody>
</table>
| 5.20 ± 0.03       | 0.806  
|                   | 0.822  
|                   | 0.817  
| average           | 0.818  
|                   | σ = ± 0.001 |
| 5.77 ± 0.02       | 0.026  
|                   | 0.025  
|                   | 0.025  
| average           | 0.025  
|                   | σ = ± 0.0007 |
| 6.60 ± 0.10       | 0.031  
|                   | 0.032  
|                   | 0.032  
| average           | 0.032  
|                   | σ = ± 0.0007 |
Fig. 18. Variation in Cerium-139m Activity with Flow Rate
The reproducibility of the results at the optimum flow rate was within $\pm 1.3\%$, and the reproducibility of all the results was within counting statistics.

Solutions containing 600, 400, 200, 100 and 50 ppm of cerium were irradiated and counted in turn at the optimum flow rate in order to investigate the variation in Ce-135 activity with cerium concentration. The equilibrium level of activity was counted for 60 s and the results obtained are shown in Table 1. The combined results determined at the optimum flow rate are shown in Fig. 13. The variation of Ce-135 activity with cerium concentration gave a straight line calibration graph which passed through the origin at a cerium concentration of zero ppm, (Fig. 13). The reproducibilities of the results were within those determined by the counting statistics of the counts obtained and varied from $\pm 1.0\%$ to $\pm 1.5\%$ for cerium concentrations of 400 ppm and 50 ppm respectively.

The detection limits for cerium are discussed in section 5.3.4.2.

3.3.4.6. Fluorine

The nuclear reaction used to determine fluorine in non-aqueous solution was $^{13}I(n, p)^{13}O$, cross-section $31 \pm 10$ mb (22) and threshold energy 0.8 MeV (20). The product fragment 0-10 has a half-life of 29.7 s and was
<table>
<thead>
<tr>
<th>Carbon Concentration (ppm)</th>
<th>Activity (cpm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>600</td>
<td>0.015, 0.017, 0.016, 0.015, 0.016, 0.016</td>
</tr>
<tr>
<td><strong>average</strong></td>
<td>0.016 ± 0.0003</td>
</tr>
<tr>
<td>400</td>
<td>0.020, 0.022, 0.022, 0.030, 0.021, 0.020</td>
</tr>
<tr>
<td><strong>average</strong></td>
<td>0.020 ± 0.0003</td>
</tr>
<tr>
<td>200</td>
<td>0.0155, 0.0152, 0.0152, 0.0152, 0.0155, 0.0153</td>
</tr>
<tr>
<td><strong>average</strong></td>
<td>0.0155 ± 0.0001</td>
</tr>
<tr>
<td>100</td>
<td>0.070, 0.081, 0.087, 0.089, 0.073, 0.071</td>
</tr>
<tr>
<td><strong>average</strong></td>
<td>0.0808 ± 0.00015</td>
</tr>
<tr>
<td>50</td>
<td>0.0053, 0.0051, 0.0053, 0.0054, 0.0032, 0.0046</td>
</tr>
</tbody>
</table>
| **average**               | 0.0053 ± 0.0001
Fig. 19. Variation in Cerium-139m Activity with Cerium Concentration
the shortest half-life product investigated on this 
system. The target isotopes, fluorine-19 has an isotopic 
 abundance of 100%. The (n,\alpha) reaction, intra-particle 
 reaction to fluorine-19 and this is accompanied by param- 
 etrication of 0.20 MeV (21). Photons of 0.42 and 1.26 
 MeV are also emitted but in much less intensity compared 
 to the 0.20 MeV photon (21). The other possible reaction 
 product from fast neutron activation of P-19, are P-18 
 and N-16. The former will not be produced in significant 
 quantities by short period irradiation techniques due 
 to its relatively long half-life. The latter isotope, 
 formed by the reaction $^{14}N(n,\alpha)$ could constitute 
 an interference in the determination of fluorine using 
 the product isotope 0-19. At the h' highest flow rates 
 available on this fluorine system, 0-19 half-life 
 1.68 h. will under a decay of 0-19 half-11 as due 
 to transit through the flow work. In practice N-16 was 
 not observed in significant quantity in irradiated 
 solutions of fluorine. The Compton continuum from N-16 
 will contribute energy to the 0.20 MeV peak of 0-19 and 
 corrections for N-16 activity will be required. The 
 flow rates used in the determination of fluorine are 
 far removed from the optimum flow rate for the production 
 and detection of N-16, half-life 590 s and low levels of 
 N-16 interference would therefore be expected.

Trifluoro-trichloroacethane (Tracer 113) was used
to prepare a solution containing 10,000 ppm of fluorine in acetone. This compound contains as many chlorine atoms as fluorine atoms but was in fact readily available in a pure state. Americium-241 is the fission product used as a primary coolant in the neutron generator cooling system (2.1.1.1). The presence of chlorine in the compound would yield a number of short half-life product isotopes by fast neutron activation:

\[
\begin{align*}
\text{Cl}(p, \alpha)^{35}\text{Cl} & \quad \text{Half-life: 14.4 s} \\
\text{Cl}(p, \gamma)^{37}\text{Cl} & \quad \text{Half-life: 706 s} \\
\text{Cl}(\gamma, \alpha)^{37}\text{P} & \quad \text{Half-life: 17.8 s}
\end{align*}
\]

Chlorine-37 would not be observed due to its very short half-life. Sulfur-37 is produced from the 36.2% abundant isotope of chlorine. The reaction cross-section is given as 55 mb (100) and S-37 decays with the emission of a 3.1 keV photon (31). The optimum flow rate for an isotope with a 306 s half-life, would be far lower than from the optimum flow rate for P-10, half-life 53.8 s, and this coupled with the low cross-section should reduce the level of interference expected. Phosphorus-33 is also produced by activation of Cl-37 and the reaction cross-section is given as 98 mb (31). This isotope decays with the emission of low intensity photons (photon energy of 2.10 and 4.0 keV energy (31, 27). At the flow rates used for the determination of fluorine, this isotope would undergo between 1 - 2 half-lives radioactive decay.
due to transit through the pipework and this should reduce the level of interference expected. The Compton continuums from the various gamma-rays emitted by S-37 and P-32 will interfere to some extent in the determination of fluorine. The level of interference was assessed by irradiating and counting a solution containing chlorine as carbon tetrachloride under identical conditions and concentrations to those in the fluorine determinations. These results were used to apply a correction for the contribution to the 0.20 MeV peak of oxygen-19 arising from the activation of chlorine. The variation of oxygen-19 with flow-rate was investigated using the solution containing 10,000 ppm of fluorine. The 0.20 MeV peak was measured over the energy range 0.14 - 0.25 MeV with the multichannel analyzer set to cover the range 0.1 - 1.00 MeV. The flowing solutions were irradiated at a constant neutron flux and the saturation level of activity was counted for 50 s. The detection and saturation times were determined in the normal way (2.3.2.1.) by irradiations of the flowing solution at a constant flux. The O-19 activity was then counted using the multichannel analyzer in the multiscalar mode. Saturation times varied between 110 s and 60 s over a flow rate range of 2.1 - 10.8 cm$^{-1}$. The results obtained are shown in table 14 and Fig. 10 and results are expressed as O-19, 0.20 MeV photon-beh corrected counts normalized to a BF$_3$ count of
<table>
<thead>
<tr>
<th>Table 14</th>
</tr>
</thead>
<tbody>
<tr>
<td>Variation in Oxygen-15 (Half-Life 20.4 s) activity with Flow Rate</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>Flow Rate</td>
</tr>
<tr>
<td>2.10 ± 0.05</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>4.45 ± 0.07</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>5.00 ± 0.09</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>5.25 ± 0.10</td>
</tr>
<tr>
<td></td>
</tr>
</tbody>
</table>
Table 14 continued

<table>
<thead>
<tr>
<th>Flow Rate</th>
<th>Activity</th>
<th>Activity/µg Cr</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.25 + .16</td>
<td>0.711</td>
<td>0.233</td>
</tr>
<tr>
<td></td>
<td>0.313</td>
<td>0.233</td>
</tr>
<tr>
<td></td>
<td>0.313</td>
<td>0.233</td>
</tr>
<tr>
<td></td>
<td>0.313</td>
<td>0.233</td>
</tr>
<tr>
<td></td>
<td>0.313</td>
<td>0.233</td>
</tr>
<tr>
<td>average</td>
<td>0.313</td>
<td>0.233</td>
</tr>
<tr>
<td>0-19 only</td>
<td>0.297</td>
<td>± 0.003</td>
</tr>
<tr>
<td>7.33 + .15</td>
<td>0.101</td>
<td>0.066</td>
</tr>
<tr>
<td></td>
<td>0.111</td>
<td>0.066</td>
</tr>
<tr>
<td></td>
<td>0.106</td>
<td>0.066</td>
</tr>
<tr>
<td></td>
<td>0.106</td>
<td>0.066</td>
</tr>
<tr>
<td></td>
<td>0.106</td>
<td>0.066</td>
</tr>
<tr>
<td>average</td>
<td>0.106</td>
<td>0.066</td>
</tr>
<tr>
<td>0-19 only</td>
<td>0.283</td>
<td>± 0.003</td>
</tr>
<tr>
<td>10.80 + .18</td>
<td>0.302</td>
<td>0.209</td>
</tr>
<tr>
<td></td>
<td>0.302</td>
<td>0.209</td>
</tr>
<tr>
<td></td>
<td>0.302</td>
<td>0.209</td>
</tr>
<tr>
<td></td>
<td>0.302</td>
<td>0.209</td>
</tr>
<tr>
<td></td>
<td>0.302</td>
<td>0.209</td>
</tr>
<tr>
<td>average</td>
<td>0.302</td>
<td>0.209</td>
</tr>
<tr>
<td>0-19 only</td>
<td>0.278</td>
<td>± 0.010</td>
</tr>
</tbody>
</table>
Fig. 20. Variation in Oxygen-19 Activity with Flow Rate
unity. Corrections were made for natural background, the low level of neutron generator induced background, the Compton continuum of N-16 and for the activation products of chlorine. The two curves, (Fig. 10), show the variation in activity with flow rate of the trifluoro, trichloroethane in benzene, and of the oxygen-18 alone. The interference from P-32, S-27 and P-37 would appear to be reduced at lower flow rates indicating that the main source of interference is due to a short half-life isotope. Although the interference was attributed to P-32, half-life 12.9 s, it is possible that a small contribution could arise from the Compton continuum of N-16. The level of the interference at the optimum flow rate for fluorine determination was of the order of 5% of the oxygen-18 activity. This level of interference was considered to be tolerable. The level of interference will decrease linearly with fluorine and hence chlorine concentration and so the interfering activity will tend to be a constant proportion of the oxygen-18 activity. The optimum flow rate for the determination of a 29.4 s half-life product was taken as 0.7 ± 0.3 ml min⁻¹. The reproducibility of the results at the optimum flow rate was within ±1.3% and all the results were within the limits of error determined by the statistics of counting of the results.

The variation in oxygen-18 activity with fluorine
concentration was investigated by preparing solutions containing 8,000, 6,000, 4,000, 2,000 and 1,000 ppm of fluorine. These solutions were irradiated and counted in turn at the optimum flow rate, and the equilibrium level of activity was counted for 60 s. The results obtained are shown in Table 15, and combined with the results for 10,000 ppm of fluorine are shown in Fig. 21. The results are expressed as Ce/Ce/F of oxygen-18 activity corrected for natural background as well as for interference arising from the activation products of chlorine. A straight line calibration graph of oxygen-18 activity to fluorine concentration was obtained. The reproducibility of the results obtained was within counting statistics and varied from ± 2.4% to ± 5.8% for fluorine concentrations of 8,000 and 1,000 ppm respectively.

The detection limits of fluorine are discussed in 3.4.4.8.

3.3.4.7. The Variation in Optimum Flow Rate with Product Isotope Ratio (SF6 - SF4, H2)

The activity to flow rate curves of the six elements with product isotopes in the range SF6 - SF4, H2 (3.3.4.1. - 6) are shown together in Fig. 22. In order to aid presentation and place all the curves on the same scale, the activities of the curves for fluorine and chlorine were reduced by a factor of two and three respectively. These
<table>
<thead>
<tr>
<th>Fluorine Concentration (ppm)</th>
<th>Activity (Cts/EF₃Ct)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8000</td>
<td>0.257, 0.257, 0.262, 0.264, 0.246, 0.246</td>
</tr>
<tr>
<td></td>
<td>average: 0.256</td>
</tr>
<tr>
<td></td>
<td>0-19 only: 0.231 (+/− 0.008)</td>
</tr>
<tr>
<td>6000</td>
<td>0.192, 0.193, 0.196, 0.189, 0.181, 0.181</td>
</tr>
<tr>
<td></td>
<td>average: 0.190</td>
</tr>
<tr>
<td></td>
<td>0-19 only: 0.165 (+/− 0.007)</td>
</tr>
<tr>
<td>4000</td>
<td>0.136, 0.143, 0.143, 0.142, 0.134, 0.139</td>
</tr>
<tr>
<td></td>
<td>average: 0.140</td>
</tr>
<tr>
<td></td>
<td>0-19 only: 0.115 (+/− 0.003)</td>
</tr>
<tr>
<td>2000</td>
<td>0.078, 0.075, 0.078, 0.076, 0.075, 0.079</td>
</tr>
<tr>
<td></td>
<td>average: 0.077</td>
</tr>
<tr>
<td></td>
<td>0-19 only: 0.052 (+/− 0.001)</td>
</tr>
<tr>
<td>1000</td>
<td>0.055, 0.058, 0.058, 0.055, 0.056, 0.058</td>
</tr>
<tr>
<td></td>
<td>average: 0.057</td>
</tr>
<tr>
<td></td>
<td>0-19 only: 0.022 (+/− 0.001)</td>
</tr>
</tbody>
</table>
Fig. 21. Variation in Oxygen-19 Activity with Fluorine Concentration
Fig. 22. Combined Activity to Flow Rate Curves

1 - Cu
2 - Br
3 - Cr
4 - Si
5 - Ce
6 - F
curves would therefore correspond to element concentrations of 100 and 5000 ppm respectively. The maximum of each curve occurs at the optimum flow rate for the determination of each element of product isotope of given half-life. The optimum flow rate for each element, together with the half-life of the product isotope, is given in table 18. The variation in optimum flow rate with product isotope half-life is shown in Fig. 23 and could be either hyperbolic or exponential in nature. A straight line graph was obtained, (Fig. 24), when the logarithm of the optimum flow rate for each element was plotted against the logarithm of the product isotope half-life. The relationship between the optimum flow rate and the product isotope half-life is therefore of the form

\[ FT^c = k \]

In this expression, \( F \) is the optimum flow rate, \( T \) is the product isotope half-life, and \( k \) is a constant peculiar to the flowing system. The value of \( c \) was found to be 1 (0.97) to within the limits of experimental error and the intercept \( k \) was found to be 18.3 for this system. The units of \( c \) and \( k \) will depend on the units of flow and time used in the expression. The optimum flow rate for the determination of any element on any flowing system containing irradiation and detection cells, interconnected by pipework in which radioactive
Table 16

Variation in Optimum Flow Rate with Product Isotopes

Half-Life

<table>
<thead>
<tr>
<th>Optimum Flow Rate (ml s⁻¹)</th>
<th>Product Isotopes</th>
<th>Half-Life (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.37 ± 0.03</td>
<td></td>
<td>583</td>
</tr>
<tr>
<td>0.58 ± 0.03</td>
<td></td>
<td>384</td>
</tr>
<tr>
<td>0.90 ± 0.03</td>
<td></td>
<td>226</td>
</tr>
<tr>
<td>1.48 ± 0.03</td>
<td></td>
<td>143</td>
</tr>
<tr>
<td>3.4 ± 0.2</td>
<td></td>
<td>60</td>
</tr>
<tr>
<td>6.9 ± 0.5</td>
<td></td>
<td>23.6</td>
</tr>
</tbody>
</table>
Fig. 23. Variation in Optimum Flow Rate with Product Isotope Half-Life.
Fig. 24. Log Plot of Optimum Flow Rate against Product Isotope Half-Life
decay occurs, could be predicted once the experimental values of c and k have been determined.

3.3.4.8. Detection Limits

It would be unrealistic to quote detection limits utilising the maximum neutron output of the neutron generator \(2 \times 10^{13} \text{ nm}^{-2} \text{s}^{-1}\) since the highest neutron fluxes are only attainable for a few minutes of irradiation time with each new target. The detection limits quoted in this section therefore refer to a neutron generator output of the order of one third of the maximum available, \(6 \times 10^{12} \text{ nm}^{-2} \text{s}^{-1}\). These neutron fluxes would be attainable for a period of 450 - 500 minutes of irradiation time, for each target, on the Kaman 1003 A neutron generator (86). At this neutron flux the total neutron dose to the irradiation cell would be of the order of \(4 \times 10^8 \text{ ns}^{-1}\).

A number of criteria have been proposed in order to determine the minimum quantity of radioactive material which is detectable in the presence of a natural background or of a matrix interference. Amongst the most often used is the criterion that the activity of interest is equal to twice the level of the background over the energy range being measured. This criterion however would suggest that in the presence of significant levels of matrix interference or of high backgrounds, only very
high concentrations of elements could be determined. In these cases, the background or matrix interference, because of its relatively high level, can be determined within smaller limits of statistical error. Thus small fluctuations in activity superimposed on the matrix or background level of activity may be readily detectable, and thus low levels of elements could be determined. A criterion that the activity of interest is greater than three standard deviations (3σ) of the background or matrix interference level of activity, was put forward by Cuypers and Cuypers (37). This criterion would appear to give more sensible limits of detection in cases where significant matrix interference or high backgrounds, are encountered. The statistics of counting (2.5.2.) follow a Poisson distribution. Hence the criterion that a detection limit should be greater than 3σ- of the background or interference level of activity would give detection limits based on a 99.7% statistical confidence level.

The detection limits of the six elements investigated on the flowing system are given in table 17, for a neutron flux of $6 \times 10^{12}$ $\text{n cm}^{-2} \text{s}^{-1}$ at the irradiation position of the generator. For the elements copper, bromine, and fluorine the 3σ-criterion for the limit of detection was used since these determinations were made in the presence of matrix interference. Copper and bromine are both positron emitters with half-lives somewhat similar to that of the interference produced by activation of the
### Table 17

**Limits of Detection**

<table>
<thead>
<tr>
<th>Target Element</th>
<th>Detection Limit</th>
<th>ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>25</td>
<td></td>
</tr>
<tr>
<td>Br</td>
<td>25</td>
<td></td>
</tr>
<tr>
<td>Cr</td>
<td>200</td>
<td></td>
</tr>
<tr>
<td>Si</td>
<td>60</td>
<td></td>
</tr>
<tr>
<td>Ce</td>
<td>30</td>
<td></td>
</tr>
<tr>
<td>F</td>
<td>200</td>
<td></td>
</tr>
</tbody>
</table>

* For a neutron flux of $6 \times 10^{12}$ nm$^{-2}$ s$^{-1}$ at the irradiation position of the generator, giving $4 \times 10^8$ ns$^{-1}$ through the irradiation cell.
solvent. Nitrogen-13 produced by activation of the solvent is also a positron emitter and because of the similarity in half-lives nitrogen-13 interference cannot be reduced to a very low level by flow rate control. The detection limit for copper and bromine was therefore governed by the criterion that the positron activity of these elements at the optimum flow rate was greater than three standard deviations above the N-13 activity at the same flow rate. In the case of fluorine, although there is some interference from the Compton continuum of N-13, the major source of matrix interference lies elsewhere. The main matrix interference was from the Compton continua of the various activation products of the chlorine which was present in the compound used as a source of fluorine. In this case the detection limit taken was that the oxygen-19 activity was greater than 30 of the combined matrix interference. Clearly the use of increased neutron fluxes would not result in a linear increase in the limits of detection of Cu, Br and F, where matrix interference occurs. The experimental criterion for the limits of detection of the elements chromium, silicon and cerium was that the count rate of the activity of interest was equal to twice the background. No matrix interference is present in the cases of chromium and silicon and clearly the detection limits are neutron flux dependent. Usage of the maximum output
of the neutron generator would further improve the detection limits given. Due to the fact that in the determination of cerium counting was carried out during irradiation, any increase in neutron flux increased the detector background. The use of higher neutron fluxes would improve the detection limit of cerium, but the resulting increase in detector background would finally limit the detection limit for this element.
3.4. Activation Analysis in a Non-Aqueous Solution of Elements Producing Ultra-Short Half-life Radioisotopes

It was decided in view of the results obtained in the previous work (3.3.4.1. - 3.3.4.8.), to extend the present investigations to the analysis in hydrocarbon solution of elements producing ultra-short half-life products. Such products would require short irradiations and relatively short counting periods and thus on-line analysis could be made extremely rapidly and economically. Further, the general validity of the expression derived for the variation in optimum flow rate with product isotope half-life, could be tested over another range of half-lives and on a new flowing system. The shortest half-life considered practicable for these investigations was the product isotope lead-207 m ($t_x = 0.80$ s), which is obtained by the fast neutron activation of lead. The half-life range which it was originally planned to investigate was from 0.80 s to 20 s, but during the course of the investigations the range was extended to include product isotopes of 29.4 s and 60 s. Thus a comparison could be made for these isotopes between the new flowing system and the old.

A new flowing system was designed and constructed geared to the analysis of lead using the 0.80 s half-life product isotope Pb-207 m. It was realised that the analysis of such a short half-life product, the design of the
irradiation cell, and more particularly of the detector cell would be critical. An efficient detector cell design could allow a significant proportion of the short-lived activity to decay before it was efficiently counted. A preliminary investigation was therefore made with a view to optimising the design of the detector cell. In this investigation the variation in spatial efficiency around the NaI(Tl) detectors was investigated. Further it was clear that extremely rapid transit would be required between the irradiation and detection cells in order to minimise radioactive decay. This could be achieved by using high linear solution velocities through the pipework, and this could be attained by producing a high volumetric flow through narrow pipework. Another method of minimising transit time would be to minimise the separation of the irradiation and detection cells, by locating the liquid loop detector in its cave, as near as possible to the biological shielding of the neutron generator. A further preliminary investigation was therefore made to examine the levels of background and interference that would be encountered at such a location, and to develop a means of reducing them to tolerable levels.

3.4.1. Preliminary Investigations

3.4.1.1. Spatial Variations in Detector Efficiencies

The variation in sensitivity around the detector was
investigated for the two 75 \times 75 \text{mm} \text{NaI(Tl)} crystal detector assemblies which are in use in the pneumatic transfer and liquid loop analysis systems. The variation in spatial sensitivity was found by counting a standard source of Cs-137 in different positions all around each detector. The two crystal detector assemblies were nominally identical (N.E. type 12 EX-2/12) (3.1.2.) and indeed were identical in external appearance. The investigation was carried out in order to obtain guidance for the design of an efficient detection cell. Also, should any differences be found, the appropriate detector for liquid loop work could be selected.

A source of 0.662 MeV gamma-radiation was prepared by evaporating a measured volume of a solution of caesium-137 in a recess in a perspex strip. The Cs-137 solution was a standard solution supplied by the Radiochemical Centre, Amersham, and the perspex strip measured 70 \times 10 \times 4.5 \text{mm}. The recess was 1 \text{mm} deep and 3 \text{mm} in diameter and contained 1 \mu\text{Ci} of Ba-137 m. The multichannel analyser was set to cover only the 0.662 MeV photopeak in the energy range 0.58 - 0.76 MeV. Starting from the centre of the end face of one of the detectors, a series of counts were taken, with the source placed in turn every 3 \text{mm} along a diameter of the end face. The measurements at each fixed position were repeated at varying source to detector distances by the inter-position
of perspex spacers between the source and the end face of the detector. The source was then placed on a perspex rider, machined to fit the side of the crystal can, and another series of counts were taken at fixed points along an axis of the detector side. This series of counts was repeated at varying source to detector distances which were varied by means of the perspex spacers used previously. The experimental procedure was repeated using the second 75 × 75 mm NaI(Tl) detector assembly. X-ray radiographs were made of the two detectors following the practice of Heath (24) to reveal their internal construction. Graphs of the variation in detection efficiency with source to detector distances were plotted for each fixed position on the two detectors. A series of efficiency contours around each detector were obtained from these graphs and these are shown in Fig. 25. The location of the sodium iodide crystals within their canning material was determined from the X-ray radiographs taken of the two detectors (Fig. 26).

The contour maps show that detector A is considerably more sensitive in the end face position than detector, B, the distance from the canning material to the 9% contour being 3 mm and 1 mm respectively at the centre. Along the detector side, however, A is slightly less sensitive than B, the maximum distances of the 9% contour from the canning material being 2 mm and 1 mm in this case. A
Fig. 25. Efficiency Contours
Fig. 26. X-ray Radiograph (positive print) of Detectors
study of the X-ray radiographs of the sodium iodide crystals in their cans (Fig. 26) shows good agreement between the actual positions and the observed results. Crystal A is longer than B and the crystal material ends much closer to the cannning material at the end face, accounting for the increased sensitivity at this position. As would be expected the distance from the 9% contour to the crystal itself, measured from the radiograph, was found to be the same in each case (7.55 mm at the centre). Little difference can be seen in the radiograph between the detectors along the crystal sides to account for the observed differences in sensitivity, crystal B appearing to be only marginally nearer the cannning material than A. The distance at the point of maximum sensitivity from the 9% contour to the crystal was again found to be the same (4 mm) for the two crystals. From a consideration of the solid angle of crystal material subtended by a radiation source at various points the positions of greatest sensitivity occur at the centre of the end face and at the midpoint of the actual crystal side as observed.

As a result of these studies, the increased sensitivity of A in the end face position was utilised in the counting of the irradiated solid samples delivered by the pneumatic transfer system from the neutron generator. Detector B was selected for liquid loop work. Clearly the winding of detection cell coils should be governed
by the shape of the efficiency contours. The marked reduction in counting efficiency shown by the contour map as the end face is approached, indicates there is little advantage in winding coils nearer than 20 mm from the end face in the initial layers.

3.4.1.2. Investigation of the Detector Background

An investigation was made into the levels of neutron generator induced background as measured by the liquid loop detector when placed near to the biological shielding of the generator. A detection station at such a location was considered desirable in order to minimise radioactive decay during transit between irradiation and detection cells. The liquid loop detector was located in the generator control room at a position opposite the generator, and at a distance of 340 mm from the biological shield. The detector was housed, as before, 3.3.2, in a lead cavity of wall thickness 100 mm, and which measured 350×350×330 mm. The cave occupied a position at a distance of 170 mm from the biological shielding. The level of natural background in the cave was found to be 6.80 cts s⁻¹ over the spectral energy range that was used for activation analysis (0.1 - 1.90 MeV). A 1000 s count over this energy range was made with the neutron generator producing a neutron flux of 2×10¹² mm⁻²s⁻¹ at the irradiation position of the generator. An
unacceptable increase in background amounting to a
twelve fold increase over natural background levels.
was obtained. The main feature of the spectra recorded
was a broad peak in the energy range 0.1 - 0.5 MeV. A
similar count was made with the analyser set to cover
the energy range 0.1 - 0.7 MeV in order to resolve the
broad peak into its constituents but a broad peak was
again obtained. Further counts were made with the analyser
set to cover the range 1.9 - 7.5 MeV but apart from
a general increase in background no further peaks were
observed. A linear accelerator fast neutron generator
in both a direct and indirect source of a broad spectrum
of different radiations, some of which, due to their
nature, will penetrate an adequate biological shield
to produce increases in the measured levels of background.
Neutron activation of the materials of the biological
shield will produce high energy gamma-radiation both
from the emission of prompt capture gamma-rays and from
photons emitted in the decay of short lived radionuclides.
Another source of high energy gamma-radiation will arise
from fast neutron scattering processes which occur through-
out the shielding. Although the shielding is designed to
provide adequate biological protection, leakage of neut-
rons will still occur. These will be principally thermal
neutrons but a proportion of epithermal and fast neutrons
will also escape from the shielding.
The overall increase in background over the three spectral energy ranges investigated, 0.1 - 0.7, 0.1 - 1.3, and 1.3 - 7.5 keV, may be assigned to the production of high energy gamma-rays and their energy degraded products within the shielding. The broad peak in the 0.4 - 0.5 keV energy region could be produced by neutron activation of the crystal detector by a number of nuclear reactions which yield products emitting photons in this energy region. The following thermal neutron reactions are possible:

\[ ^{23}_{\text{Na}} (n, \gamma) ^{24}_{\text{Na}} \text{ half-life } 20 \text{ s} \]  
\[ ^{127}_{\text{I}} (n, \gamma) ^{128}_{\text{I}} \text{ half-life 32 minutes} \]

These reactions are quite likely to occur since thermal neutrons will be produced due to the thermalization of fast neutrons in the concrete shielding. The following fast neutron reactions may also occur:

\[ ^{22}_{\text{Na}} (n, p) ^{22}_{\text{Ne}} \text{ half-life 29 s} \]  
\[ ^{22}_{\text{Na}} (n, \alpha) ^{19}_{\text{Ne}} \text{ half-life 7.59 years} \]

and activation of the thallium present in the crystal is possible by the reaction:

\[ ^{203}_{\text{Tl}} (n, \alpha) ^{199}_{\text{W}} \text{ half-life } 7.7 \mu\text{s} \]

Reactions (iv) is most unlikely since the reaction has a high threshold energy, 16.28 keV \( (30) \), and the flux of neutrons of such a high energy in the central room would be expected to be very low. Further since the product nuclide has a very long half-life compared to the
irradiation periods of these investigations, the specific activity of this isotope would also be very low. Activation of thallium-203 (v), is again unlikely to be a major contributor to the observed peak, since this reaction has a threshold energy of 7.92 MeV (30). The multi-channel analyser was adjusted to cover the energy range 0.3 - 0.5 MeV and counts of 500 μs duration were made with the analyser in the multiscaler mode. The neutron generator was switched on and off by means of the beam deflection control whilst counting proceeded, but the spectral decay of Tl-203 m was not observed and thus the possibility of reaction (vi) occurring was discounted. A similar procedure, with a counting time of 40 s was used to discount the possibility of reaction (111) occurring. Fast neutron reactions would be less likely to account for the observed peak in the 0.3 - 0.5 MeV energy region since the fast neutron flux would be expected to be low compared to the thermal neutron flux. Also fast neutron reactions in general have cross-sections which are much lower than thermal neutron reactions. After several consecutive 1000 s irradiation and counting periods had been carried out in these investigations, a small amount of residual activity in the 0.3 - 0.5 MeV region was observed to be present. The radioactive decay of this activity was monitored and was assigned to the isotope iodine-128 (11), produced by thermal neutron
activation of the iodine in the crystal. The activity of this isotope was very low and could be assumed to be negligible with short period irradiations. Thus the major source of the activity in the 0.4 - 0.5 MeV region was assigned to the isotope Na-24 m produced by thermal neutron activation of the crystal. The decay of this isotope which emits 0.47 MeV photons was observed by irradiation followed by counting in the multiscaler mode with a counting time of 20 ms. Attempts were made to reduce the level of neutron generator induced background by the addition of suitable shielding (27). The effects of various simple shielding configurations are shown in table 18. Since different neutron fluxes were used, the results are expressed as Cts/Me²·Gr, in a specified energy range. The Na-24 m peak was measured between 0.34 and 0.61 MeV.

The addition of neutron moderator at the front of the cave in the form of a wall of paraffin wax, 350 x 30 \( \delta \) cm led to a slight increase in the level of neutron generator induced background (b). This was believed to be due to an enhancement of the thermal neutron flux from epithermal neutrons thermalized in the paraffin wax. A progressive decrease in the observed background levels was obtained with the various simple shielding configurations outlined, table 18. The shielding above the neutron generator at the front of the inner room was
<table>
<thead>
<tr>
<th>Shield</th>
<th>Activity (Ci/kr-Cl)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.1 - 1.00 keV</td>
</tr>
<tr>
<td></td>
<td>0.25 - 0.61 keV</td>
</tr>
<tr>
<td>(a) Cave only</td>
<td>0.140</td>
</tr>
<tr>
<td>(b) + paraffin wax at cave front</td>
<td>0.111</td>
</tr>
<tr>
<td>(c) boric acid instead of wax</td>
<td>0.114</td>
</tr>
<tr>
<td>(d) boric acid inside cave wax outside at front</td>
<td>0.033</td>
</tr>
<tr>
<td>(e) as above + addition to generator shield</td>
<td>0.031</td>
</tr>
<tr>
<td>(f) as above + 100 cm water on cave top</td>
<td>0.012</td>
</tr>
</tbody>
</table>
reinforced (a) up to roof level with a number of interlocking concrete blocks. This provided an additional 150 mm thickness of concrete at this location. This was carried out in order to reduce the neutron flux falling onto the top of the cave. As may be seen (c), the best results were obtained with a combination of neutron moderator and neutron absorber. The cave was infilled with boron acid; the cave top was shielded by 100 mm of water, and the front of the cave was shielded by paraffin wax slabs. This combined shield reduced the level of neutron generator induced background by a factor of about two.

A more elaborate shield was then constructed by first surrounding the cave with a wooden frame 750 mm long, 550 mm wide and 300 mm high, and infilling the cave surround with polythene chippings. This cave was the largest that could be accommodated with the space available between the high voltage tanks and the rails for the removable water tanks in the neutron generator biological shield. Thus the cave sides were protected by 100 mm, and the cave rear by 200 mm of polythene chippings. The cave front was shielded by 89 mm of paraffin wax and 81 mm of polythene chippings. The results obtained with the various improvements in shielding on this basic design are shown in table 19. These results show clearly the effects of shielding the sides
<table>
<thead>
<tr>
<th>Shield</th>
<th>Activity (Cts/MeV Cts.)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.1 - 1.85 MeV</td>
</tr>
<tr>
<td></td>
<td>0.34 - 0.61 MeV</td>
</tr>
<tr>
<td>(s) Cave + polythene chippings 100 mm</td>
<td>0.0290</td>
</tr>
<tr>
<td>polynene on the top</td>
<td>0.0083</td>
</tr>
<tr>
<td>(h) as above but 100 mm of water on the top</td>
<td>0.0270</td>
</tr>
<tr>
<td>(i) as above + 100 mm of polynene chippings</td>
<td>0.0819</td>
</tr>
<tr>
<td>on top</td>
<td>0.0055</td>
</tr>
<tr>
<td>(j) + additional water shielding to neutron</td>
<td>0.0138</td>
</tr>
<tr>
<td>generator</td>
<td>0.0051</td>
</tr>
<tr>
<td>(k) as above + Cd screen</td>
<td>0.0137</td>
</tr>
<tr>
<td>on the detector</td>
<td>0.0040</td>
</tr>
</tbody>
</table>
and rear as well as the front and top of the cave. This shows that thermal neutrons impinge on the cave from all directions as would be expected. A further reduction in neutron generator background was obtained by increasing the shielding on the cave top to 100 cm of water followed by 100 cm of polythene chippings (1). There was relatively little biological shielding above the level of the top of the [removable] water tanks.

Additional shielding in the forwards direction at this location was provided by two rows of water cans which were placed on top of the inner water tank. This provided a water shield 290 cm thick and 290 cm high across the top of the tank. This gave a further reduction in background showing again the importance of the neutron flux falling on the cave from above. This, combined with the fitting of a cadmium sleeve, 0.5 cm thick, to the crystal detector, led to the final shielding configuration (k). The addition of a neutron absorber in the form of the cadmium sleeve resulted in a further reduction in background of the order of 20%. The final layered shield therefore consisted of a neutron moderator/absorber in the form of water or polythene chippings and thermal neutron absorbers in the form of boric acid and cadmium. The backgrounds recorded over various energy ranges by the liquid loop detector in the 100 cm lead cave with and without the final neutron shielding are
shown in Table 20. Thus it may be seen that the neutron generator induced background has been reduced by a factor of ten. This level of generator background was found to be approximately twice natural background over the energy range 0.1 - 1.90 MeV for neutron fluxes of $2 \times 10^4$ cm$^{-2}$sec$^{-1}$. This low level of background was considered acceptable for liquid loop work. It was felt that any further reductions in background would require extremely elaborate shielding and the effects of further shielding would be governed by the law of diminishing returns.

The addition of the extra shielding to the 100 mm lead cave and to the neutron generator shielding produced a number of additional beneficial changes. The level of natural background was found to have been reduced from 6.25 cps to 5.32 cps in the energy range 0.1 - 1.90 MeV by the additional shielding, (table 20). Further, the liquid loop detector was found to be extremely stable to gain shift over periods of time of the order of days, This was believed to be partly due to the use of the newer 400 channel analyser, but mainly due to the thermal stability of the detector environment. The volume of boric acid and polythene chippings surrounding the detector assembly insulates the detector from any short term fluctuations in room temperature, and thus increases stability. The provision of additional shielding in the
Table 30

Comparison of the Levels of Background Recorded in the 100 cm Lead Cane with and without Neutron Shielding

<table>
<thead>
<tr>
<th>Energy Range</th>
<th>Cave Only</th>
<th>With Neutron Shielding</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1 - 1.30</td>
<td>0.20 cpm</td>
<td>5.52 cpm</td>
</tr>
<tr>
<td>Natural</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Background</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.1 - 0.7</td>
<td>0.110</td>
<td>0.011</td>
</tr>
<tr>
<td>Generator</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Background</td>
<td>0.25 - 0.62</td>
<td>0.090</td>
</tr>
<tr>
<td>(Cts/HPy/ct)</td>
<td></td>
<td>(Washout peak)</td>
</tr>
<tr>
<td>0.1 - 1.30</td>
<td>0.140</td>
<td>0.0127</td>
</tr>
<tr>
<td>1.3 - 7.5</td>
<td>0.056</td>
<td>0.0051</td>
</tr>
</tbody>
</table>
form of water cans and concrete blocks to the neutron
generator biological shielding resulted in a marked
effect on the life of the thermionic valves in the DF₃
counter preamplifier (2.1.4.). The preamplifier is
mounted on top of the normal biological shielding at
a distance of 700 mm from the aperture in which the
generator is housed. The performance of the valves
in the preamplifier was found to deteriorate presumably
due to neutron bombardment. This resulted in unaccept-
able noise levels and necessitated the replacement of
the valves every three months. The valves currently
in use however have been in the preamplifier for ten
months and were in fact changed when the additional
shielding was installed. The DF₃ preamplifier appears
to be still performing efficiently.

Access to the detector in the lead case, e.g. for
energy calibration was achieved by removing the polythene
chippings and the water cans from the top of the case.
A hole in the inner layer of 50 mm lead bricks located
above the crystal may be exposed by sliding three bricks
cut out of the top layer of bricks. The lead bricks and
water cans were covered by polythene sheeting to prevent
polythene chips from falling between the cans or between
the joints of the bricks.
3.4.2. Description and Construction of the New Flowing System

A new high linear flow rate flowing system of a basically similar design to the previous flowing system (section 3.3.4.) and containing the elements described in the preliminary investigations was therefore constructed. A number of changes were made in order to achieve high linear solution velocities in the new system. Nylon pipework of a larger diameter, (6.5 mm i.d.) than that used in the previous system, was used throughout to interconnect the units of the system except for the pipework joining the irradiation cell to the detection cell. Here, pipework of 3.2 mm internal diameter, was used, and the location of the detection station near to the biological shield of the neutron generator (3.4.1.2.) allowed the length of this pipework to be reduced to 2.5 m. The size of the narrow bore pipework is governed by the maximum pressure that may be applied to the system and it was found that narrower pipework required the application of prohibitively high pressures in order to achieve high linear flow rates through the length of the pipework. A stainless steel tank, 650 mm high, 32 mm in diameter, and 12 mm thick, with stainless steel inlet and outlet pipes 4 mm internal diameter, was used as a solution reservoir. This was pressure tested to $6.89 \times 10^2$ Nm$^{-2}$ (100 psig.) A steel
can having a capacity of 33 l was normally used as the waste solution reservoir. A high capacity rotameter was used as an additional flowmeter for high flow rates covering the range 10 - 60 ml s⁻¹. A larger brass control needle valve provided a means of flow over this flow rate range. All pipework connections were made using pressure couplings in conjunction with the appropriate "olives" depending on whether the joint was to nylon or metal pipework. As before, nitrogen gas was used to pressurise the solution reservoir in order to force liquids round the flowing system. An additional high pressure gas regulator provided a range of gas pressure up to $1.03 \times 10^6$ Pa m⁻² (150 psig). 

A new irradiation cell was made in the form of a cylindrical brass box 100 cm in diameter, and 20 cm deep, with a cell volume of 100 ml. This cell was constructed of brass (1 cm thick) in a similar way to the previous irradiation cell and was similar in design to the first detector cell which was constructed (2.2.2.). The irradiation cell contained a single brass spiral and was designed so that liquids entered the cell at the side, spiralled into the centre, and left the cell through the bottom. A large diameter copper pipe, 10 cm internal diameter and a narrower copper pipe, 5 cm internal diameter, were used as inlet and outlet pipes. The cell bottom was made of brass plate 5 cm thick and contained
Fig. 27. Irradiation Cell
a machined tapered recess in the centre. The tapered recess provided a smooth decrease in cross-sectional area between the centre of the spiral, (10 mm internal diameter), and the outlet pipe, (5 mm internal diameter). The detachable cell bottom and the rest of the cell were ground flat and sealed together with a nylon gasket 3 mm thick which was equipped with a central hole. The cell was clamped together between steel plates with a ring of eight bolts. As before the upper plate was machined to fit the neutron generator target cooling jacket thus providing a means of positive location and relocation under the generator target. The irradiation cell was held in position using the adjustable end-piece of the pneumatic transfer system. Hot water, (60 - 80°C), was continuously passed through the cell to soften the nylon gasket while the clamping bolts were being tightened. This procedure provided a good seal between the internal spiral and the gasket. When the cell, assembled in this way, was pressure tested, it was found that the cell would withstand pressures of $5.9 \times 10^5$ Pa $\text{m}^{-2}$ (85 psig.) without leakage. The design of the irradiation cell ensures a definite flow path for irradiated liquids passing through the cell, and liquids leave the cell in the region of the highest neutron flux. Clearly the latter design factor will be important in the analysis of short-lived
isotopes. The neutron flux through the irradiation cell was measured using the procedure described in 3.2.2. The average neutron flux per unit volume through the cell was found to be \(6.7 \times 10^5\) ns\(^{-1}\)\(\cdot\)m\(^{-2}\) giving an integrated flux of \(7.3 \times 10^7\) ns\(^{-1}\) compared with \(1.0 \times 10^3\) ns\(^{-1}\) as measured by a copper foil at the irradiation position of the generator. The flux through the cell is thus about 4.5% of the flux available at the irradiation position under the target cooling jacket. The relative neutron flux contours surrounding the neutron generator target have been investigated (83) and were shown together with the previous irradiation cell in Fig. 5. The new irradiation cell also has a radius of 30 cm, but has a depth of 20 cm instead of 6 cm. Thus the neutron flux through the cell would be expected to be much lower than that through the previous cell, since a considerable portion of the cell is relatively far removed from the target. The first 24 cm of the radius of the cell lies on average within the 10% flux contour, and the next 16 cm and 10 cm radii lie within the 25% and 2.5% flux contours respectively. The ratio of the relative volumes of the cell within the 10%, 25% and 2.5% contours is thus approximately 1:2:2 giving an overall estimated efficiency of the order of 5%. The measured value of 4.5% is therefore of the correct order of magnitude.
The detection cell was made from annealed copper tubing wound around a former machine to crystal detector dimensions. The coils of each layer of the cell were soldered into position and the design incorporated three layers giving a volume of 117 ml. The investigation of the variation in spatial detection efficiency around the volume of the liquid loop detector has been described in section 3.4.1.1. The investigation reported therein had shown that there was little advantage to be gained by winding coils nearer than 20 cm from the end face of the crystal. This factor, and the efficiency contour map of the liquid loop detector (3.4.1.1) was used as a guide to efficient construction. The end result was a cell similar in shape and size to the 1% efficiency contour of the detector. The mode of winding of the cell coils superimposed on the efficiency contour map of the liquid loop detector is shown in Fig. 28. This design of flow cell again provides a definite flow path for liquids flowing through it. The detection station was located up against the biological shielding of the neutron generator. The combined neutron and gamma-ray shielding, and the levels of both natural and neutron generator induced background are described in the previous section 3.4.1.2. The cell and detection station are shown in Fig. 28.

The efficiency of the cell was measured by filling
Fig. 28.  
A Detection Station and Cell  
B Mode of Cell Coil Winding
it with potassium chloride solution and counting the naturally occurring K-40 isotope as described in 3.2.1.

An overall efficiency in the energy range 0.1 - 1.30 MeV of 14.6% 3.1% in the K-40 peak between 1.28 - 1.52 MeV was recorded, and the count rate per unit volume was found to be 0.0150 counts s\(^{-1}\) ml\(^{-1}\). These last two values represent an improvement of about 10% on those obtained with the previous nylon detector cell, but even this difference could be important with ultra short half-life isotopes. The overall efficiency obtained is of the correct order of magnitude compared with the values of Heath (3b) of 17.3 - 13% for sources of 1.46 MeV gamma-radiation at distances of 10 cm and 5 cm from a 75 X 75 cm NaI(Tl) detector.

The flowing system was specifically designed to enable the analysis of lead in solution using the 0.20 s half-life product Pb-207 m to be carried out. The irradiation and detection cells were purposely made of a similar volume, (100 ml, 117 ml), and at the highest flow rates attainable on the system the average residence time in each cell was of the order of 2.5 - 2.9 half lives for Pb-207 m. The volume of the transit pipe, including connections, between the irradiation and detection cells was calculated to be 75 ml. At the maximum flow rate attainable on the system (38.3 ml s\(^{-1}\)) this gave an average transit time of 0.15 s for laminar flow
with a minimum transit time of the order of 0.2 s. The flow rate of 58.3 ml s\(^{-1}\) was obtained by the application of a nitrogen gas pressure of \(5.9 \times 10^{3}\) Pa m\(^{-2}\) (85 psig) to the solution reservoir. The application of higher pressures was considered unsafe due to the risk of an irradiation cell burst with serious consequential damage to the neutron generator.

3.4.3. Fast Neutron Activation Analysis of Elements with Product Isotopes with Half-Lives of 0.80 - 60 s

The flowing system constructed was considered to be satisfactory for an attempt to be made to analyse lead as well as other elements in non-aqueous solution, producing ultra-short half-life products on fast neutron activation. A preliminary investigation was made into the levels of interference which would be experienced due to the activation of the solvent, colourless kerosene. The kerosene was irradiated at a constant neutron flux over a range of flow rates up to 50 ml s\(^{-1}\). The equilibrium level of activity present in the flowing stream was then counted for 300 s. These investigations indicated that the \(\text{R}-13\) levels would be very low and, except at the slowest flow rates, would be of the same order, or less, than the neutron generator induced background in the energy region 0.42 - 0.61 MeV. These interference levels are discussed in section 3.4.3.2.
describing the analysis of chlorine using the positron emitter chlorine-36. At the higher flow rates, low levels of N-16 activity, presumably due to the activation of oxygen in the kerosene, were detected. These levels were only really significant at the detection limit of oxygen in solution and are described together with the analysis of this element in section 3.4.3.5.

Analysis was attempted of a range of elements producing half-lives between 0.80 and 60 s in order to investigate the fundamental principles of analysis using ultra short half-life products in non-aqueous media. The elements and their relevant nuclear data are listed in table 21. The variation in activity with flow rate was investigated for all the elements and the results were used to investigate the variation in optimum flow rate with product isotope half-life (3.4.3.8.). The variation in activity with target element concentration and the limits of detection were also determined for some of the elements namely Pb, O and Ce.

3.4.3.1. Lead (using the isotope Pb-207 n)

The nuclear reaction used to determine lead in a non-aqueous solution was \(^{208}\text{Pb}(n, 2n){^{207}}\text{Pb}\), cross-section \(930 + 120\) mb (101) and threshold energy 6.76 MeV (30). The product isotope Pb-207 n has a half-life of 0.80 s and was the shortest half-life product isotope
<table>
<thead>
<tr>
<th>Half-Life Studied (Seconds)</th>
<th>Target Element and Nuclear Reaction</th>
<th>Cross Section FB</th>
<th>Principal Energy MeV</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.80</td>
<td>$^{208}\text{Pb}(n, 2n)^{207}\text{Pb}$</td>
<td>930 ± 120</td>
<td>0.57, 1.06</td>
</tr>
<tr>
<td>1.53</td>
<td>$^{35}\text{Cl}(n, 2n)^{37}\text{Cl}$</td>
<td>~2</td>
<td>0.51</td>
</tr>
<tr>
<td>2.66</td>
<td>$^{32}\text{S}(n, 2n)^{31}\text{S}$</td>
<td>~10</td>
<td>0.51</td>
</tr>
<tr>
<td>6.0</td>
<td>$^{204}\text{Pb}(n, 2n)^{203}\text{Pb}$</td>
<td>~1000</td>
<td>0.83</td>
</tr>
<tr>
<td>7.35</td>
<td>$^{16}\text{O}(n, p)^{16}\text{N}$</td>
<td>29 ± 2</td>
<td>7.12</td>
</tr>
<tr>
<td>29.4</td>
<td>$^{19}\text{F}(n, p)^{19}\text{O}$</td>
<td>51 ± 10</td>
<td>0.20</td>
</tr>
<tr>
<td>60</td>
<td>$^{140}\text{Ce}(n, 2n)^{139}\text{Ce}$</td>
<td>1593 ± 10</td>
<td>0.75</td>
</tr>
</tbody>
</table>

* Cross-section estimated from the curves of the variation in cross-section with atomic and mass number published by Csikai et al (29).
investigated. The target isotope Pb-203 has an isotopic abundance of 52.3% and the product Pb-207 m decays with the emission of photons of 0.57 and 1.06 MeV to the stable isotope Pb-207. The isotope Pb-207 m may also be produced by a fast neutron reaction on Pb-207, $^{207}$Pb(n, n)$^{207m}$Pb. Other gamma-ray emitters may be produced from fast neutron activation of the Pb-203 and of the other stable isotopes of lead:

- $^{208}$Pb(n, p)$^{208}$Tl
- $^{208}$Pb(n, $\alpha$)$^{205}$Hg
- $^{204}$Pb(n, 2n)$^{203}$Pb

The products of reactions (i) and (ii) were not observed. These reactions have cross-sections of the order of 1 mb (102), and this coupled with their relatively long half-lives compared to Pb-207 m would ensure that only extremely low levels of these isotopes would be produced and detected during the analysis of lead. Lead-203 m was observed and corrected for at the lower flow rates used in these investigations, and was itself used as a product isotope in the analysis of lead in later experiments 3.4.3.4. This isotope is produced by reaction (iii) and the reaction has an estimated cross-section of 1000 mb (29) and a threshold energy of 8.42 MeV (30). Interference from the isotope Na-24 m, produced by thermal neutron activation of the crystal detector 3.4.1.2., and from low levels of N-13, were encountered and corrected for by the
procedures described later in this section. Pure tetraethyl lead, without stabilizers, was used to prepare a solution containing 4000 ppm of lead in kerosene. The tetraethyl lead, because of its volatile and poisonous nature was normally kept in a refrigerated metal container sealed with a metal screwplug and was only handled with gloves in a fume cupboard. The variation in Po-207 activity with flow rate was investigated over a range of high flow rates from 8.3 - 53.2 ml s\(^{-1}\). The flowing stream was irradiated at a constant neutron flux and the equilibrium levels of activity were counted for 30 s with the multichannel analyser set to cover the energy range 0.1 - 1.90 MeV. The timing intervals for this irradiation and counting technique were determined in the usual way (3.3.3.1.). At the high flow rates used in the analysis of lead, equilibrium was attained within 40 s.

The results were processed both manually, and by using the computer program H139. This program is a modified version of Schonfeld’s program "Alpha" (42), for the resolution of complex gamma-ray spectra. Program "Alpha" resolves a complex gamma-ray spectrum into its constituent parts by fitting in turn spectra from a library of standards, using the method of least squares. The program applies background subtraction, gain and threshold shift compensation, as well as correction for radioactive decay and spectrometer dead time if required. Parameters are
output showing the quality of the "fit" and a provision is also made for applying the fit parameters obtained from one sample to another. The program was converted as for use on the university's ICL 1904A computer, in its original form it was not designed for activation analysis and was tedious to apply for this purpose. The program was therefore rewritten and modified to deal with the results from liquid loop work and activation analysis generally and is described in detail in appendix (iii).

The spectra obtained from the analysis of lead in solution using the isotope Pb-207 m would consist of a complex mixture of components. These would include natural background, generator induced activity including Na-24 m, N-13 activity from the activation of kerosene, and the isotopes Pb-207 m, and Pb 203 m produced by the activation of lead. Program II 132 was used to resolve these complex spectra and a number of library spectra over the range 0.1 - 1.90 MeV were prepared for this purpose. Standard spectra of Pb-207 m and Pb-203 m were obtained by the irradiation and counting of samples of A.R. grade lead powder, using the pneumatic transfer system. A cyclic irradiation and counting procedure was used in order to favour the production and detection of either Pb-207 m or Pb-203 m. Pb-207 m standard spectra were obtained with irradiation and counting times of 1 s coupled with the minimum delay time due to transit before
counting. Several different samples of lead were irradiated and counted in turn in this way to prevent the build up of lead 203 m. The irradiation and counting cycle continued until a statistically satisfactory standard spectrum of Pb207 m, with a peak height of the order of 20,000 counts for the 0.57 MeV peak had been obtained. The procedure was repeated for Pb203 m using irradiation and counting times of 6 s coupled with a decay time of 8 s, in order to allow the attendant Pb-207 m activity to decay to a negligible level. A 40,000 s count of the natural background of the liquid loop detector, and 1000 s counts of the generator and kerosene backgrounds, completed the library spectra. The library and sample spectra were punched on to cards and used in the least squares computer program H 139.

The results calculated by hand were based on the 1.06 MeV photopeak of Pb207 m over an energy range of 0.95 - 1.20 MeV and are expressed as counts/EF3 Ct. Corrections were made for the very low levels of kerosene background, generator induced background, and natural background, in this energy region. Measurements were made on this photopeak, since it is virtually interference free, the 0.57 MeV peak of Pb-207 m contains contributions from N-13 (0.51 MeV), Na-24 m (0.47 MeV) and from the Compton continuum of Pb203 m (0.83 MeV). A small sum peak corresponding to an energy of 1.33 MeV (0.57 + 1.06 MeV) was also
visible in the spectrum. The results obtained for the variation in lead-207 m activity with flow rate and calculated by hand are shown in table 22 and Fig. 29. A smooth curve would be expected with a maximum at the optimum flow rate for the determination of the element as previously obtained (3.3.11 - 5), representing the best compromise between irradiation and detection efficiency against decay time in transit. The curve shown in Fig. 29 is in fact levelling off, but it is apparent that the highest flow rates attainable on the system are incapable of exceeding the optimum flow rate for a 0.80 s half-life, lead-207 m. The optimum flow rate was taken as 58.3 ml s⁻¹ but a true optimum flow rate probably lies slightly above this value. The reproducibility of all the results was within counting statistics and was within ± 4% at the optimum flow rate of 58.3 ml s⁻¹.

The spectra recorded from the variation of lead-207 m activity with flow rate were processed a number of times by the least squares computer program I 39. Computations were carried out over different spectral energy ranges in order to obtain the best spectral "fit" and to minimize the observed standard deviation of the results. The program option in which the sample spectrum is compared with the library spectra and is corrected automatically for any gain or threshold shifts was used. Sets of spectra obtained at the same flow rate, were processed individually
<table>
<thead>
<tr>
<th>Flow (ml s⁻¹)</th>
<th>Activity (cts/EP₂·ct)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.3 ± 0.1</td>
<td>0.0134, 0.0136, 0.0126, 0.0135, 0.0122, 0.0147, 0.0136, 0.0143</td>
</tr>
<tr>
<td></td>
<td>average 0.0125 ± 0.0003</td>
</tr>
<tr>
<td>16.6 ± 0.1</td>
<td>0.044, 0.040, 0.039, 0.042, 0.040, 0.040, 0.046</td>
</tr>
<tr>
<td></td>
<td>average 0.041 ± 0.0025</td>
</tr>
<tr>
<td>25.0 ± 0.2</td>
<td>0.068, 0.075, 0.070, 0.069, 0.070, 0.067, 0.066, 0.069</td>
</tr>
<tr>
<td></td>
<td>average 0.069 ± 0.003</td>
</tr>
<tr>
<td>33.3 ± 0.3</td>
<td>0.105, 0.093, 0.098, 0.092, 0.093, 0.094, 0.095, 0.090</td>
</tr>
<tr>
<td></td>
<td>average 0.095 ± 0.005</td>
</tr>
<tr>
<td>41.6 ± 0.4</td>
<td>0.117, 0.120, 0.119, 0.122, 0.115, 0.119, 0.120, 0.122</td>
</tr>
<tr>
<td></td>
<td>average 0.119 ± 0.002</td>
</tr>
<tr>
<td>Flow (ml s⁻¹)</td>
<td>Activity (Cts/EP₃Cl)</td>
</tr>
<tr>
<td>--------------</td>
<td>----------------------</td>
</tr>
<tr>
<td>50.0 ± 0.5</td>
<td>0.128, 0.127, 0.130, 0.129, 0.130, 0.122, 0.127, 0.120</td>
</tr>
<tr>
<td></td>
<td>average 0.127, σ = ± 0.004</td>
</tr>
<tr>
<td>50.3 ± 0.6</td>
<td>0.122, 0.127, 0.125, 0.125, 0.126, 0.133, 0.135, 0.125</td>
</tr>
<tr>
<td></td>
<td>average 0.130, σ = ± 0.004</td>
</tr>
</tbody>
</table>
Fig. 29. Variation of Lead-207 m Activity with Flow Rate (by hand)
by the program and then the answers were combined. The individual values, an average and a standard deviation were then computed and printed. One of the modifications made to the program allowed all the computed activity values to be output as Cts/MT3 Cts. Computations were performed between 0.25 - 1.79 MeV, 0.25 - 1.27 MeV and 0.42 - 1.17 MeV. The first energy range stretched from the backscatter peak to the end of the main peak of Pb-207 m, and the second from the backscatter peak to just beyond the 1.05 MeV photopeak. The energy range 0.42 - 1.17 MeV covered only the two main peaks of Pb-207 m, and provided a sharper "cut off" of the 1.05 MeV photopeak. This energy range included the Na-24 m peak produced by neutron activation of the crystal but not the backscatter peak. The best results and spectral fit were obtained when the program fitted the library spectra to the sample spectrum over the energy range 0.42 - 1.17 MeV and these results are shown in Table 23 and Fig. 30. Fitting the spectra over a wider energy range introduced additional error and this was thought to be due to the increased statistical uncertainty of fitting channels containing small numbers of counts. Further, differences between the library standard spectra for lead, and the sample spectra which were recorded on different but similar detectors in different environments, will be accentuated when the backscatter peak is included. These differences will tend to
<table>
<thead>
<tr>
<th>Flow (ml s⁻¹)</th>
<th>Computed Activity (Cts/yr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2 ± 0.1</td>
<td>0.0462, 0.0545, 0.0437, 0.0527, 0.0430, 0.0227, 0.0180, 0.0048</td>
</tr>
<tr>
<td></td>
<td>average: 0.0311, α = ± 0.0033</td>
</tr>
<tr>
<td>16.6 ± 0.1</td>
<td>0.176, 0.174, 0.154, 0.172, 0.166, 0.159, 0.166, 0.170</td>
</tr>
<tr>
<td></td>
<td>average: 0.167, α = ± 0.008</td>
</tr>
<tr>
<td>25.0 ± 0.2</td>
<td>0.276, 0.288, 0.288, 0.298, 0.289, 0.303, 0.269, 0.286, 0.275</td>
</tr>
<tr>
<td></td>
<td>average: 0.285, α = ± 0.012</td>
</tr>
<tr>
<td>33.3 ± 0.3</td>
<td>0.397, 0.356, 0.369, 0.391, 0.374, 0.395, 0.377, 0.371</td>
</tr>
<tr>
<td></td>
<td>average: 0.372, α = ± 0.014</td>
</tr>
<tr>
<td>41.6 ± 0.4</td>
<td>0.506, 0.500, 0.496, 0.471, 0.447, 0.436, 0.457, 0.464</td>
</tr>
<tr>
<td></td>
<td>average: 0.472, α = ± 0.026</td>
</tr>
<tr>
<td>Flow</td>
<td>Computed Activity</td>
</tr>
<tr>
<td>--------------</td>
<td>-------------------</td>
</tr>
<tr>
<td>ml s(^{-1})</td>
<td>Cts/EP (_2) Ct</td>
</tr>
<tr>
<td>50.0 ± 0.5</td>
<td>0.523, 0.513, 0.528, 0.525, 0.539, 0.538, 0.514, 0.500</td>
</tr>
<tr>
<td></td>
<td>average 0.524 ± 0.014</td>
</tr>
<tr>
<td>58.3 ± 0.6</td>
<td>0.573, 0.560, 0.570, 0.536, 0.500, 0.511, 0.525, 0.538</td>
</tr>
<tr>
<td></td>
<td>average 0.540 ± 0.025</td>
</tr>
</tbody>
</table>
Fig. 30. Variation of Lead-207 m Activity with Flow Rate (by computer)
produce a poorer "fit" and to introduce additional error into the computed results. A smooth curve, Fig. 30, virtually indistinguishable from the results calculated by hand, Fig. 29, was obtained. The optimum flow rate was clearly not exceeded, and an optimum flow rate of 58.3 ml s⁻¹ was taken, as before. The reproducibility of the results was slightly worse than those calculated by hand and at the optimum flow rate reproducibility was within ± 0.7%.

The variation of Pb-207 m activity with lead concentration was investigated with solutions with a lead content of 2000, 1000, 500, 250, 125 and 60 ppm. The equilibrium level of activity was again counted for 30 s and all the determinations were carried out at a flow rate of 58.3 ml s⁻¹. The results were again calculated by hand first of all and are shown expressed as Cts/ BF₃Ct in table 24 and Fig. 31. A straight line, analytical calibration graph, passing through the origin, (Fig. 31) was obtained for the variation in lead-207 m activity with lead content. The reproducibility of the results fell with decreasing lead content but was still within ± 0.6% at 60 ppm of lead.

The results obtained by spectral analysis by the least squares computer program [129] are shown in table 25 and Fig. 32. These results were expressed as Cts/ BF₃Ct, and were computed over the same spectral energy
<table>
<thead>
<tr>
<th>Lead Concentration (ppm)</th>
<th>Activity (Cts/Mg\textsubscript{2}O\textsubscript{2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>2000</td>
<td>0.039, 0.041, 0.053, 0.063, 0.073, 0.083, 0.093, 0.103</td>
</tr>
<tr>
<td></td>
<td>average 0.069 ( \pm 0.004 )</td>
</tr>
<tr>
<td>1000</td>
<td>0.033, 0.036, 0.039, 0.043, 0.046, 0.049, 0.053, 0.056</td>
</tr>
<tr>
<td></td>
<td>average 0.042 ( \pm 0.001 )</td>
</tr>
<tr>
<td>500</td>
<td>0.0153, 0.0173, 0.0183, 0.0193, 0.0213, 0.0233, 0.0253, 0.0273</td>
</tr>
<tr>
<td></td>
<td>average 0.0217 ( \pm 0.001 )</td>
</tr>
<tr>
<td>250</td>
<td>0.0035, 0.0031, 0.0037, 0.0043, 0.0047, 0.0053, 0.0057, 0.0063</td>
</tr>
<tr>
<td></td>
<td>average 0.0043 ( \pm 0.0005 )</td>
</tr>
<tr>
<td>125</td>
<td>0.0027, 0.0027, 0.0033, 0.0037, 0.0047, 0.0053, 0.0057, 0.0063</td>
</tr>
<tr>
<td></td>
<td>average 0.0032 ( \pm 0.0003 )</td>
</tr>
<tr>
<td>60</td>
<td>0.0023, 0.0023, 0.0023, 0.0023, 0.0023, 0.0023, 0.0023, 0.0023</td>
</tr>
<tr>
<td></td>
<td>average 0.0023 ( \pm 0.0002 )</td>
</tr>
</tbody>
</table>
Fig. 31. Variation of Lead-207 m Activity with Lead Concentration (by hand)
Table 26
Variation in Lead-207 Activity with Lead Concentration
Using Least Squares Resolution of Spectra

<table>
<thead>
<tr>
<th>Lead Concentration</th>
<th>Enriched Activity C15/C17, O.0701.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000</td>
<td>0.050, 0.288, 0.294, 0.252, 0.238, 0.239, 0.249, 0.228</td>
</tr>
<tr>
<td>average</td>
<td>0.270, $\alpha = \pm 0.023$</td>
</tr>
<tr>
<td>1000</td>
<td>0.127, 0.177, 0.187, 0.131, 0.135, 0.135, 0.145, 0.128</td>
</tr>
<tr>
<td>average</td>
<td>0.152, $\alpha = - 0.009$</td>
</tr>
<tr>
<td>500</td>
<td>0.0701, 0.0636, 0.0557, 0.0565, 0.0713, 0.0707, 0.0640, 0.0691</td>
</tr>
<tr>
<td>average</td>
<td>0.0686, $\alpha = \pm 0.0020$</td>
</tr>
<tr>
<td>250</td>
<td>0.0348, 0.0372, 0.0336, 0.0363, 0.0364</td>
</tr>
<tr>
<td>average</td>
<td>0.0322, $\alpha = - 0.0024$</td>
</tr>
<tr>
<td>125</td>
<td>0.0170, 0.0160, 0.0136, 0.0192, 0.0151, 0.0135, 0.0209, 0.0177</td>
</tr>
<tr>
<td>average</td>
<td>0.0168, $\alpha = - 0.0021$</td>
</tr>
<tr>
<td>60</td>
<td>0.0095, 0.101, 0.0035, 0.0100, 0.0088, 0.0078, 0.0080, 0.0084</td>
</tr>
<tr>
<td>average</td>
<td>0.0092, $\alpha = - 0.0003$</td>
</tr>
</tbody>
</table>
Fig. 32. Variation of Lead-207 m Activity with Lead Concentration (by computer)
range (0.96 - 1.17 nCi) as before. A straight line graph passing through the origin was obtained for the variation of lead-207 activity with lead concentration. The reproducibility of the results also fell with decreasing lead concentration and at 10 ppm was within +10%. The reproducibility of the results tended to follow those calculated by hand, but once again the least squares results were slightly worse. The detection limits for lead and the other elements analysed on this system are discussed in section 2.1.3.

As a practical test of the system and the method, an attempt was made to determine the lead content of a commercial motor fuel, with a 98 octane rating. Tetraethyl lead is added to petrols to improve their octane rating and "antiknock" properties. Using suitable fire precautions, petrol was irradiated at a flow rate of 28.3 ml s⁻¹ and the equilibrium level of activity in the flowing stream was counted for 10 s. The results obtained manually and using the computer program 2.150 are shown in Table 26. The results calculated by hand gave the lead content of the petrol as 370 ± 30 ppm, and the reproducibility of the results was better than ±5%. Least squares analysis of the spectra indicated a lead content of 350 ± 30 ppm, and the reproducibility of the results was within ±3.1%. The two lead contents agree well with each other and the measured lead concentration is within the
### Table 26

**Determination of Lead in 63 Octane Petrol**

#### Activity (by Hand)

\[ \text{ctn/TPCt} \]

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>0.030</td>
<td>0.034</td>
<td>0.039</td>
</tr>
<tr>
<td>0.035</td>
<td>0.030</td>
<td>0.029</td>
</tr>
</tbody>
</table>

Average: 0.030 ± 0.009

Load content = 370 ± 50 ppm \hspace{1cm} (Fig. 31)

#### Activity (by Computer)

\[ \text{ctn/TPCt} \]

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>0.127</td>
<td>0.136</td>
<td>0.136</td>
</tr>
<tr>
<td>0.136</td>
<td>0.129</td>
<td>0.129</td>
</tr>
</tbody>
</table>

Average: 0.130 ± 0.004

Load content = 250 + 50ppm \hspace{1cm} (Fig. 32)
permitted levels. The maximum permissible level of lead in U.K. petrol (102) is given as 0.3%, i.e., 1100 -
1200 ppm. A typical spectrum of the 95 octane petrol,
obtained at a neutron flux of $3.1 \times 10^{13}$ nm$^{-2}$s$^{-1}$ at the
irradiation position of the converter is shown in Fig.23.
Little or no interference was visible in the spectrum
other than that from $^{63}$Cu. The relatively large back-
scatter peak is presumably due to the copper and cadmium
in close proximity to the detector. Co-line analysis of
the relatively high content of lead in petrol should be
possible at relatively low neutron fluxes without signifi-
cant interference.

No marked differences were found between the results
obtained by hand and by computer. Computer processing of
the spectra recorded in the analysis of the other elements
in this section was therefore only performed when consider-
able interference occurred.

3.4.3.6. Chlorine

Chlorine was activated in non-aqueous solution by a
fast neutron reaction on the 35.45% standard isotope of
chlorine, chlorine-35. The nuclear reaction used was
$^{35}$Cl($n$, $\gamma$)$^{36}$Cl, estimated cross-section $\sigma$ = 10$^{-3}$, and
threshold energy 12.5 MeV (29). The cross-section was
estimated from the curve of the variation in cross-section
with atomic and mass number published by Gjikai (29). The
Fig. 33. Gamma-Ray Spectrum of 98 Octane Petrol
isotope Cl-37 has a half-life of 1.53 s and decays by positron emission (21). Other reaction products could theoretically arise from fast neutron activation of the 24.47% abundant isotope of chlorine, Cl-37.

\[
\text{^{37}Cl(n, p)^{37}Ar \text{ half-life 306 s}}
\]

\[
\text{^{37}Cl(n, d)^{37}P \text{ half-life 12.4 s}}
\]

The cross-section of the reaction producing S-37 is given as 25 mb (100), and this isotope decays with the emission of a 2.1 MeV gamma-ray (31). The Compton continuum from this isotope could interfere in the measurement of the positron annihilation radiation from Cl-37. The optimum flow rate for the production and detection of a 306 s half-life will be very far removed on this system from the flow rates used in the analysis of a 1.53 s half-life, and since these half-lives also differ by a factor of 24 the expected levels of interference would be of a negligible order. Phosphorus-38 is produced by activation of Cl-37 and the reaction cross-section is given as 28 mb (23). P-34 decays by pure beta-emission (75%) and the remainder of the isotope decays by beta-emission accompanied by a 2.1 MeV photon (24.2%) and a 4.0 MeV (0.2%) photon (31, 36). The Compton continuum from these weak peaks will also interfere in the measurement of Cl-37 to some extent. The level of interference from this isotope will again be markedly reduced in practice by flow rate control since the half-lives of P-34 and Cl-37 differ by a factor of
eight. Peaks from either of these interferences were not observed as would be expected and therefore no corrections were made for these activities.

Interference will occur from activation of the solvent to give low levels of the positron emitter K-43. This interference was covered by irradiating kerosene over a range of flow rates at a constant neutron flux and counting the equilibrium level of activity for 300 s. The spectra were recorded over an energy range of 0.1 - 1.20 MeV. The K-43 activity, including the generator background, expressed as Cts/125 Cl, in the energy range 0.7 - 0.61 MeV, is shown in Fig. 2b. The combined kerosene and generator background activities were used to correct the activities of the two positron emitters 34 Cl and 37 Ar, which were measured in solution. The results are scattered about a smooth curve due to statistical fluctuations in the data since only low levels of activity were obtained even with 300 s counting time. Clearly the K-43 and generator background activity is slowly levelling off at the higher flow rates.

Redistilled carbon tetrachloride was used as a source of chlorine and a 50,000 ppm solution of chlorine in kerosene was prepared for the investigation of the variation in Cl-37 activity with flow rate. The multichannel analyzer was set to cover the energy range 0.1 - 1.05 MeV. The flowing stream was irradiated at a constant neutron
Fig. 34. Kerosene (N-13) Correction for Positron Emitters
flux and the equilibrium level of activity was counted for 60 s. The results obtained for the variation in Cl-36 activity with flow rate, expressed as Cts/EPg Cl and corrected for kerocene and generator background (Fig. 34), are shown in Table 27 and Fig. 25.

A smooth curve was obtained, (Fig. 35) for the variation in Cl-36 activity with flow rate, and the optimum flow rate for a 1.3Fr half-life was taken as 32.3 ± 1.0 ml s⁻¹. The reproducibility of the results was within counting statistics and at the optimum flow rate was within ±10.5%. Only relatively low levels of activity were counted in these investigations. Even with a solution containing 20,000 ppm of chlorine, recorded was only of the order of seven times the combined generator and X-13 backgrounds. The variation of Cl-36 activity with chlorine concentration was therefore not investigated.

Clearly fast neutron activation analysis of chlorine using the product isotope Cl-36 would yield poor detection limits.

3.4.3. Sulphur

A 2.66 s half-life product isotope was obtained in non-aqueous solution by the fast neutron activation of the 33.7 abundant isotope of sulphur, S-33. The nuclear reaction used was S³³(n, 2n)³²S, threshold energy 13.31 MeV (30) with an estimated cross-section (30) of less
<table>
<thead>
<tr>
<th>Flow (ml s⁻¹)</th>
<th>Activity (c.c./hr. ft)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.0 ± 0.1</td>
<td>0.0180, 0.0178, 0.0183, 0.0182, 0.0180, 0.0172, 0.0183</td>
</tr>
<tr>
<td></td>
<td>average: 0.0182 ± 0.0013</td>
</tr>
<tr>
<td>3.2 ± 0.1</td>
<td>0.0181, 0.0180, 0.0183, 0.0183, 0.0203, 0.0190, 0.0151, 0.0203</td>
</tr>
<tr>
<td></td>
<td>average: 0.0182 ± 0.0028</td>
</tr>
<tr>
<td>14.6 ± 0.1</td>
<td>0.0220, 0.0220, 0.0210, 0.0223, 0.0213, 0.0222, 0.0210, 0.0223</td>
</tr>
<tr>
<td></td>
<td>average: 0.0221 ± 0.0027</td>
</tr>
<tr>
<td>25.0 ± 0.1</td>
<td>0.0263, 0.0266, 0.0266, 0.0268, 0.0260, 0.0266, 0.0257, 0.0259</td>
</tr>
<tr>
<td></td>
<td>average: 0.0260 ± 0.0025</td>
</tr>
<tr>
<td>30.0 ± 0.1</td>
<td>0.0260, 0.0260, 0.0257, 0.0266, 0.0264, 0.0268, 0.0264, 0.0268</td>
</tr>
<tr>
<td></td>
<td>average: 0.0264 ± 0.0024</td>
</tr>
<tr>
<td>32.3 ± 0.3</td>
<td>0.0255, 0.0245, 0.0255, 0.0250, 0.0256, 0.0235, 0.0255, 0.0255</td>
</tr>
<tr>
<td></td>
<td>average: 0.0255 ± 0.0029</td>
</tr>
</tbody>
</table>
Table 27 continued

<table>
<thead>
<tr>
<th>Flow ( \mu \text{m}^{-1} )</th>
<th>Activity ( \text{cts/}2 \mu \text{g Ce} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 37.9 \pm 3 )</td>
<td>0.0250, 0.0261, 0.0283, 0.0262, 0.0272, 0.0275</td>
</tr>
<tr>
<td></td>
<td>\text{average} 0.0272 ( \pm 0.0011 )</td>
</tr>
<tr>
<td>( 41.0 \pm 5 )</td>
<td>0.0270, 0.0263, 0.0236, 0.0289, 0.0270</td>
</tr>
<tr>
<td></td>
<td>\text{average} 0.0278 ( \pm 0.0013 )</td>
</tr>
<tr>
<td>( 50.0 \pm 5 )</td>
<td>0.0270, 0.0263, 0.0229, 0.0293, 0.0270</td>
</tr>
<tr>
<td></td>
<td>\text{average} 0.0265 ( \pm 0.0019 )</td>
</tr>
<tr>
<td>( 60.0 \pm 6 )</td>
<td>0.0270, 0.0263, 0.0249, 0.0224, 0.0270</td>
</tr>
<tr>
<td></td>
<td>\text{average} 0.0266 ( \pm 0.0012 )</td>
</tr>
</tbody>
</table>
Fig. 35. Variation of Chlorine-34 Activity with Flow Rate
than 10 mb. The product isotope $^{31}\text{P}$ decays by positron emission (100%) to silicon-31 (21). Fast neutron activation of sulphur-32 and of the other isotopes of sulphur, by other nuclear reactions, yield stable isotopes or pure beta-emitters with the exception of the reaction $^{32}\text{S}(n, p)^{32}\text{P}$. The target isotope $^{32}\text{S}$ has an isotopic abundance of 4.26%, the cross-section of the reaction is given as $22 \pm 8$ mb (37), and the product isotope $^{32}\text{P}$ has a half-life of 12.5 s. Phosphorus-32 decays with a 311 branching ratio by pure beta-emission, the remaining portion of this isotope decays by beta-emission with the accompanying emission of 2.1 MeV (64.8%) and 1.0 MeV (0.2%) photons (21, 36). The Compton continuum from these relatively low intensity photons could interfere in the measurement of the positron annihilation radiation of $^{32}\text{S}$. From a consideration of the reactive cross-sections of the reactions and of the isotopic abundances of the target isotopes producing $^{32}\text{S}$ and $^{32}\text{P}$, the amount of $^{32}\text{S}$ produced will be some six times greater than the amount of $^{32}\text{P}$. Further, since only 22% of the $^{32}\text{P}$ decays with the accompanying emission of gamma-radiation, the relative activity of $^{32}\text{S}$ will be some 24 times that of $^{32}\text{P}$. Since there is a factor of 5 between the half-lives of the two isotopes, flow rate control will tend to further reduce the level of the $^{32}\text{P}$ interference to a negligible level. Interference will, of course, occur from the isotope $^{31}\text{P}$, as in the
determination of all positron emitters in this flowing system. Corrections were made for the activity of this isotope, using the results obtained for the variation of $^{3}$He activity with flow rate obtained in the previous section, 3.4.3.2. (Fig. 34).

Carbon disulphide was used as a source of sulphur and a solution containing 20,000 ppm of sulphur was prepared in order to investigate the variation in $^{3}$He activity with flow rate. The equilibrium level of activity in the flowing stream was counted for 60 s and the multi-channel analyzer was set to cover the spectral energy range 0.1 - 1.0 MeV. The 0.31 MeV peak of $^{3}$He was measured between 0.42 and 0.61 MeV, and the results obtained were corrected for the combined kerosene and neutron generator backgrounds, table 23.

Very low levels of $^{3}$He activity were produced, even with a sulphur content of 20,000 ppm. A smooth but distinct activity to flow rate curve was obtained (Fig. 26), and the optimum flow rate for the production and detection of a 2.66 s half-life isotope, $^{3}$He, was taken as $20.7 \pm 0.2\mu l s^{-1}$. At the optimum flow rate, the corrected $^{3}$He activity was only equal in magnitude to the combined kerosene and neutron generator induced background, (Fig. 24). The reproducibility of the results obtained at the optimum flow rate was $\pm 15\%$, which is within counting statistics. At flow rates widely removed from the optimum flow rate, statistical fluctuations in the kerosene and neutron
<table>
<thead>
<tr>
<th>Flow Rate</th>
<th>Activity (C/C_0)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.3 ± 0.1</td>
<td>0.0021, 0.0024, 0.0030, 0.0030, 0.0027, 0.0024, 0.0027, 0.0030</td>
</tr>
<tr>
<td></td>
<td>average 0.0027 ± 0.0004</td>
</tr>
<tr>
<td>5.6 ± 0.1</td>
<td>0.0024, 0.0028, 0.0031, 0.0036, 0.0027, 0.0028, 0.0036</td>
</tr>
<tr>
<td></td>
<td>average 0.0028 ± 0.0003</td>
</tr>
<tr>
<td>12.5 ± 0.1</td>
<td>0.0027, 0.0033, 0.0027, 0.0026, 0.0032, 0.0035, 0.0036, 0.0033</td>
</tr>
<tr>
<td></td>
<td>average 0.0031 ± 0.0004</td>
</tr>
<tr>
<td>13.8 ± 0.1</td>
<td>0.0039, 0.0040, 0.0040, 0.0027, 0.0038, 0.0041, 0.0039, 0.0036</td>
</tr>
<tr>
<td></td>
<td>average 0.0037 ± 0.0005</td>
</tr>
<tr>
<td>20.8 ± 0.1</td>
<td>0.0014, 0.0028, 0.0048, 0.0045, 0.0042, 0.0036, 0.0033, 0.0033</td>
</tr>
<tr>
<td></td>
<td>average 0.0030 ± 0.0005</td>
</tr>
<tr>
<td>35.0 ± 0.1</td>
<td>0.0029, 0.0037, 0.0033, 0.0025, 0.0029, 0.0036, 0.0032, 0.0032</td>
</tr>
<tr>
<td></td>
<td>average 0.0032 ± 0.0005</td>
</tr>
</tbody>
</table>
Table 28 continued

<table>
<thead>
<tr>
<th>Elevation</th>
<th>Activity (Ci/m^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>22.1 ± 1.5</td>
<td>0.0027, 0.0019, 0.0027, 0.0031, 0.0017, 0.0019, 0.0027, 0.0021</td>
</tr>
<tr>
<td>33.3 ± 1.3</td>
<td>0.0024, 0.0013, 0.0016, 0.0028, 0.0013, 0.0018, 0.0020, 0.0032</td>
</tr>
<tr>
<td>41.6 ± 1.4</td>
<td>0.0022, 0.0015, 0.0022, 0.0027, 0.0021, 0.0016, 0.0023, 0.0022</td>
</tr>
<tr>
<td>50.5 ± 1.5</td>
<td>0.0024, 0.0014, 0.0017, 0.0016, 0.0024, 0.0019, 0.0017, 0.0014</td>
</tr>
</tbody>
</table>
Fig. 36. Variation of Sulphur-31 Activity with Flow Rate
generator induced background will tend to produce even more irreproducible results. The reproducibility at 50 ml min⁻¹ was within ± 22%, possibly for this reason. It was considered unwise to further increase the concentration of sulphur beyond 30,000 ppm in order to produce more activity and obtain more reproducible results. Loss of carbon disulphide by evaporation would become increasingly likely and the health hazard of prolonged exposure to carbon disulphide vapour would be accentuated. The variation in S-31 activity with sulphur concentration was therefore not investigated and again analysis of sulphur using this isotope would yield poor detection limits.

3.3.3.4. Lead (using the isotope Pb-203 m)

The isotope lead 203 m was used to provide a 6 s half-life product on the flowing system. This isotope is produced by the nuclear reaction 208 Pb(n, 2n) 203m Pb and the product isotope Pb-203 m decays with the emission of a 0.83 MeV photon (21). The main interference in the measurement of this isotope will arise from the nuclear reaction 208 Pb(n, 2n) 207n Pb which will occur with the more abundant target isotope Pb-208. This isotope decays with the emission of 0.57 and 1.66 MeV photons (21). A full description of the relevant nuclear data and of possible interfering reactions in the determination of lead
using Pb-207 m are discussed in section 3.4.3.1. Lead-207 m will constitute a serious interference in the measurement of Pb-203 m, since the Compton continuum from the 1.05 keV peak of this isotope will contribute counts to the 0.83 keV photopeak of Pb-203 m. Further, although the cross-sections for the production of both isotopes appear to be similar (3.4.3.1.), the target isotope Pb-208 is nearly 40 times more abundant than the target isotope Pb-207 m. Clearly except at the lower flow rates when the majority of the Pb-207 m activity will decay before being counted, the spectra recorded will consist mainly of Pb-207 m. Na-24 m activity from the generator background, and K-13 from activation of kerosene will not constitute an interference since the gamma-ray energies of these isotopes are below that of Pb-203 m. Attempts were made to correct for the Pb-207 m interference using the method of Coveill (39) and using the computer program H 139 (appendix III) with the library spectra obtained as indicated in section 3.4.3.1.

A solution containing 10,000 ppm of lead as tetraethyl lead was prepared and used for the investigation of Pb-203m activity with flow rate. The flowing stream was irradiated at a constant neutron flux and the equilibrium level of activity present in the solution at each flow rate was counted for 600 s. The long counting time was used in order to obtain a high total count and thus minimise
statistical errors in the counts. This procedure would make hand calculation as well as computer analysis and separation of the components of the spectra more accurate. The multichannel analyzer was set to cover the energy range 0.1 - 1.50 MeV, and the results obtained were calculated by hand using the method of Covell (29). The Pb-203 m peak was measured between 0.74 and 0.96 MeV and the calculated results are shown in table 29. Clearly Covell's method (29) is not correcting adequately for the Compton continuum of Pb-207 m, and the net result is a curve which rises rapidly initially and then continues to rise more slowly.

The spectra recorded were processed using the least squares computer program H 13). The standard library spectra for Pb-203 m and Pb-207 m were fitted to the sample spectra in the energy range 0.51 - 1.22 MeV. The Na-24 m spectrum was not included. This isotope was not fitted since initial fitting had produced Na-24 m activities of a negligible level. The program was once again used with the program option which provided automatic correction for gain of threshold shifts if a comparison of the library and standard spectra indicated that this was necessary. The results obtained are shown in Table 30 and are expressed as computed Cts/EV3Ct. An estimated error in the result based on the counting statistics of the individual spectral component is also printed out as Cts/EV3Ct.
### Table 22

**Variation in Pb-208 (Half-Life 6.8) Activity with Flow Rate**

<table>
<thead>
<tr>
<th>Flow Rate (ml s⁻¹)</th>
<th>Activity (by hand) Cts/SPECT</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.34 ± .03</td>
<td>0.0079</td>
</tr>
<tr>
<td>6.18 ± .05</td>
<td>0.0117</td>
</tr>
<tr>
<td>6.56 ± .06</td>
<td>0.0129</td>
</tr>
<tr>
<td>9.68 ± .03</td>
<td>0.0157</td>
</tr>
<tr>
<td>10.0 ± .1</td>
<td>0.0167</td>
</tr>
<tr>
<td>15.0 ± .1</td>
<td>0.0171</td>
</tr>
<tr>
<td>15.0 ± .1</td>
<td>0.0222</td>
</tr>
<tr>
<td>20.0 ± .1</td>
<td>0.0256</td>
</tr>
<tr>
<td>Flow Rate (1/min)</td>
<td>Initial Activity (cts/273 Cl)</td>
</tr>
<tr>
<td>------------------</td>
<td>-----------------------------</td>
</tr>
<tr>
<td>0.18 ± .03</td>
<td>0.020 ± 0.0014</td>
</tr>
<tr>
<td>5.18 ± .05</td>
<td>0.0208 ± 0.0012</td>
</tr>
<tr>
<td>6.18 ± .08</td>
<td>0.0207 ± 0.0013</td>
</tr>
<tr>
<td>8.43 ± .08</td>
<td>0.0281 ± 0.0013</td>
</tr>
<tr>
<td>10.0 ± .1</td>
<td>0.0321 ± 0.0027</td>
</tr>
<tr>
<td>12.0 ± .1</td>
<td>0.0198 ± 0.0023</td>
</tr>
<tr>
<td>15.0 ± .1</td>
<td>0.0165 ± 0.0023</td>
</tr>
<tr>
<td>20.0 ± .1</td>
<td>0.0151 ± 0.0021</td>
</tr>
</tbody>
</table>
It was found that the computer program was successful in resolving the complex sample spectra into their constituents, Pb-203 m and Pb-207 m. The variation in Pb-203 m activity with flow rate is shown in Fig. 37 and was found to be a smooth curve, similar in shape to the activity to flow rate curves previously obtained for other elements. The optimum flow rate for the production and detection of a 6 s half-life product isotope was taken as lying between 8.50 and 10.0 ml s⁻¹. It may clearly be seen (table 30) that the computer estimated error for the lead 203 m component falls initially as the activity of the lead-203 m rises without a corresponding marked rise in the Pb-207 m interference. As would be expected as the flow rate increases the Pb-207 m activity increases sharply and the estimated error in the Pb-203 m component rises rapidly and continuously as this isotope becomes an increasingly minor component of the total spectrum. The estimated error in the Pb-207 m activity falls continuously as this isotope becomes the major constituent of the mixture, and as its total activity increases. The variation in the estimated error of the Pb-203 m activity is also represented in Fig. 37, and the activity to flow rate curve was obtained by drawing the best curve through the points taking into account the statistical errors as indicated by the error bars.

Clearly analysis of lead using the 6 s product
Fig. 37. Variation of Lead-203 m Activity with Flow Rate (by computer)
isotope lead-203 m would be difficult and prone to error
and would yield a poor limit of detection. The investiga-
tion of the variation in Pb-203 m activity with lead con-
centration was therefore not carried out. The use of
computer analysis of the spectral data was clearly a
considerable advantage. The success of the program in
these cases is thought to be due to the counting statis-
tics of the spectra obtained which allowed a more accurate
fit of the components to be carried out.

2.4.3.5. Oxygen

Oxygen was determined in non-aqueous solution by the
fast neutron reaction $^{16}\text{O}(n, 2n)^{16}\text{N}$, cross-section $29 \pm
2 \text{ mb (39)}$ and threshold energy $10.22 \text{ MeV (30)}$. The target
isotope, oxygen-16 has an isotopic abundance of $99.76\%$, and
the product of the reaction, nitrogen-16, has a half-
life of $7.35 \text{ s}$. Nitrogen-16 decays by pure beta-emission
(branching ratio $24\%$) to oxygen-16. The remainder decays
by beta-emission associated principally with the emission
of photons of energies $6.13 \text{ MeV}$ and $7.12 \text{ MeV}$, but a number
of low intensity photons of energies $8.88, 2.75, 1.90$ and
$1.72 \text{ MeV}$ are also emitted (31). Oxygen is usually deter-
mined by counting the gamma-radiation of $N-16$ above about
$4 \text{ MeV}$. The very high gamma-ray energy of the high intensity
photons of $N-16$ ensures that oxygen determinations are
virtually interference free. Further the presence of
oxygen in the sample frequently constitutes a serious source of interference in the activation analysis of many elements. The levels of natural background and generator-induced background were naturally very low in this energy region and since these levels were known, a correction could be made for their activity. Low levels of N-16 were found to be present in irradiated kerosene streams and these will interfere directly in the analysis of oxygen. The solvent, colourless kerosene, could well contain traces of oxygen present either as water or as organic impurities. The N-16 level in irradiated kerosene gas assessed by irradiating the flowing solvent at a constant neutron flux and counting the equilibrium level of activity for 300 s. The results obtained were used to apply a correction to the measured N-16 levels in irradiated solutions containing oxygen.

A solution containing 10,000 ppm of oxygen was prepared for the investigation of activity with flow rate, redistilled ethyl acetate being used as the source of oxygen. The flowing stream was irradiated at a constant neutron flux and the equilibrium level of activity present in the solution was counted for 30 s. The multichannel analyzer was set to cover the energy range 1.09 - 7.5 MeV, and the peaks of nitrogen-16 were measured in the energy range 3.8 - 7.5 MeV. Corrections were made for natural and generator-induced backgrounds and for the low level
of 3-16 activity present in the irradiated kerosene.
The results reported are shown in Table 31 and are
expressed as \( \text{Ct} / \text{MW}_{\text{Ct}} \). A smooth activity to flow rate
curve, Fig. 33 was obtained and the optimum flow rate
for the production and detection of a 1.33 s half-life
isotope was taken at \( 3.0 \pm 0.3 \text{ ml s}^{-1} \). The reproducibility
of the results near the optimum flow rate was within
\( \pm 15 \%) and all the results obtained were within counting
statistics with the reproducibility varying between 1
and 2%. The main feature of the spectra was the presence
of three photopeaks in the region 3.0 - 7.0 MeV. These
were thought to be caused by the high intensity 6.13 MeV
gamma-ray of 3-16. The three peaks observed actually
being 5.13, 6.13 - 0.51, and 6.13 - 1.02 MeV, due to the
positron-electron pair formation with the subsequent
escape of one or two quanta of 0.51 MeV positron annih-
lation radiation. The first escape peak 5.62 MeV was the
most intense and the 6.13 and double escape peaks were
of approximately equal intensity. Peak peaks corresponding
to 7.13 and 7.13 - 0.51 MeV were also obtained. Again
the intensity of the first escape peak was higher than
that of its corresponding parent gamma-ray. These pheno-
menon may be explained as follows. The total probability(\( \tau \))
for gamma-ray absorption in a sodium iodide crystal is
given by (37)
\[
\tau = \tau_{\text{photoelectric}} + \tau_{\text{Compton}} + \tau_{\text{pair production}}
\]
<table>
<thead>
<tr>
<th>Flow Rate</th>
<th>Activity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cto/FP&lt;sub&gt;2&lt;/sub&gt;Ct</td>
</tr>
<tr>
<td>1.75 ± 0.02</td>
<td>0.211, 0.222, 0.206, 0.203, 0.195, 0.197, 0.206, 0.210</td>
</tr>
<tr>
<td></td>
<td>average 0.206 ± 0.005</td>
</tr>
<tr>
<td>3.23 ± 0.03</td>
<td>0.240, 0.248, 0.249, 0.235, 0.240, 0.238, 0.240, 0.236</td>
</tr>
<tr>
<td></td>
<td>average 0.239 ± 0.005</td>
</tr>
<tr>
<td>5.26 ± 0.06</td>
<td>0.283, 0.285, 0.280, 0.237, 0.206, 0.207, 0.213, 0.207</td>
</tr>
<tr>
<td></td>
<td>average 0.223 ± 0.007</td>
</tr>
<tr>
<td>6.05 ± 0.06</td>
<td>0.463, 0.476, 0.475, 0.465, 0.470, 0.471, 0.474, 0.473</td>
</tr>
<tr>
<td></td>
<td>average 0.471 ± 0.003</td>
</tr>
<tr>
<td>11.1 ± 0.1</td>
<td>0.494, 0.493, 0.496, 0.492, 0.479, 0.482, 0.483, 0.482</td>
</tr>
<tr>
<td></td>
<td>average 0.487 ± 0.007</td>
</tr>
<tr>
<td>15.3 ± 0.1</td>
<td>0.436, 0.436, 0.443, 0.448, 0.443, 0.443, 0.443, 0.447</td>
</tr>
<tr>
<td></td>
<td>average 0.443 ± 0.005</td>
</tr>
<tr>
<td>$\eta \pm 1$</td>
<td>Activity</td>
</tr>
<tr>
<td>----------------</td>
<td>------------------</td>
</tr>
<tr>
<td>$19.0 \pm 0.1$</td>
<td>0.336, 0.338, 0.390, 0.306, 0.373, 0.382, 0.389, 0.380</td>
</tr>
<tr>
<td></td>
<td><strong>average</strong> $0.383 \quad \alpha = \pm 0.007$</td>
</tr>
<tr>
<td>$22.1 \pm 0.2$</td>
<td>0.346, 0.348, 0.355, 0.388, 0.237, 0.346, 0.396, 0.350</td>
</tr>
<tr>
<td></td>
<td><strong>average</strong> $0.359 \quad \alpha = \pm 0.012$</td>
</tr>
<tr>
<td>$23.2 \pm 0.3$</td>
<td>0.241, 0.246, 0.247, 0.241, 0.242, 0.244, 0.242, 0.239</td>
</tr>
<tr>
<td></td>
<td><strong>average</strong> $0.246 \quad \alpha = \pm 0.009$</td>
</tr>
<tr>
<td>$32.2 \pm 0.3$</td>
<td>0.218, 0.210, 0.212, 0.200, 0.209, 0.213, 0.216, 0.215</td>
</tr>
<tr>
<td></td>
<td><strong>average</strong> $0.211 \quad \alpha = \pm 0.006$</td>
</tr>
</tbody>
</table>
Fig. 38. Variation of Nitrogen-16 Activity with Flow Rate
The probability of pair production makes an increasing contribution to $\gamma$ as the gamma-ray energy rises above 1.02 MeV, and is quite high at these energies (6 - 7 MeV).

The variation of nitrogen-16 activity with oxygen concentration was investigated by irradiating and counting in turn solutions containing 4,000, 2,000, 1,000 500, 200 and 100 ppm of oxygen at the optimum flow rate. The results recorded are shown in Table 32 and Fig. 39. A straight line analytical calibration graph, passing through the origin was obtained for the variation of N-16 activity with oxygen concentration. The reproducibility of the results was within counting statistics and worsened continuously as the oxygen concentration decreased. Reproducibilities varied from $\pm 1\%$ for a content of 4,000 ppm of oxygen to $\pm 15\%$ for 100 ppm of oxygen. The results obtained at 100 ppm were virtually twice the combined neutron generator and kerosene backgrounds in the energy range 3.8 - 7.4 MeV. The majority of this background is due to N-16 activity in the kerosene. The neutron generator background, (table 20) amounted to 0.0051 Cts/EF$_2$ Ct between 1.7 and 7.5 MeV. Over the range 3.8 - 7.4 MeV this was found to have dropped to 0.00035. The kerosene background at the optimum flow rate for N-16 was found to be 0.0053 Cts/EF$_2$ Ct indicating an oxygen content of about 100 ppm. This level of oxygen would arise from
<table>
<thead>
<tr>
<th>Concentration (ppm)</th>
<th>Activity $^{39}Ar/^{38}Ar$</th>
<th>$\alpha$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4000</td>
<td>0.123, 0.127, 0.194, 0.195, 0.138, 0.193, 0.193, 0.193</td>
<td>$0.002$</td>
</tr>
<tr>
<td>2000</td>
<td>0.036, 0.032, 0.038, 0.097, 0.031, 0.034, 0.034, 0.034</td>
<td>$0.002$</td>
</tr>
<tr>
<td>1000</td>
<td>0.047, 0.047, 0.048, 0.054, 0.050, 0.053, 0.053, 0.051</td>
<td>$0.002$</td>
</tr>
<tr>
<td>500</td>
<td>0.026, 0.026, 0.027, 0.025, 0.028, 0.028, 0.028, 0.028</td>
<td>$0.002$</td>
</tr>
<tr>
<td>200</td>
<td>0.0130, 0.0120, 0.0120, 0.0110, 0.0120, 0.0110, 0.0110, 0.0110</td>
<td>$0.001$</td>
</tr>
<tr>
<td>100</td>
<td>0.0036, 0.0034, 0.0057, 0.0056, 0.0060, 0.0062, 0.0064, 0.0065</td>
<td>$0.0009$</td>
</tr>
</tbody>
</table>
Fig. 39. Variation of Nitrogen-16 Activity with Oxygen Concentration
the presence of less than 0.1 ml of water per litre of kerosene and either this, and/or the presence of some organic impurity would account for the N-16 levels in kerosene. The detection limits of oxygen are discussed in section 3.4.3.4.

3.4.3.5. Fluorine

Fluorine was activated in non-aqueous solution to produce a 29.8% half-life isotope, oxygen-19, which is formed by the reaction $^{19}$F(n, p)$^{19}$O. Fluorine was determined in solution on the previous flow system, (3.3.1.6.), and the relevant nuclear data and possible interferences, both from the chemical source of fluorine and from other sources are discussed in that section. The levels of these interferences were assessed as before by irradiating and counting both kerosene and an equivalent solution of chlorine in kerosene. On this flow system an additional source of interference will be present. The Compton continuum from Na-24 will contribute counts to the 0.20 MeV peak of oxygen-19 and extraneous neutron generator induced activity will also increase the background in this energy region. However the level of these interferences has been previously determined (3.4.1.2.), and therefore their contribution can be subtracted.

A solution containing 10,000 ppm of fluorine was used
for the investigation of the variation in oxygen-19 activity with flow rate. This was irradiated at a constant neutron flux over a range of flow rates and the equilibrium level of activity in the solution was counted for 60 s. The multichannel analyser was set to cover the energy range 0.1 - 1.30 MeV and the oxygen-19 peak was measured between 0.14 and 0.23 MeV. The results obtained, expressed as Cts/DpGt of oxygen-19 activity corrected for natural and generator backgrounds, and for the activation products of chlorine are shown in table 23.

A typical, smooth, activity to flow rate curve (Fig. 40) was obtained for the 29.4 s half-life product O-19. The optimum flow rate for the production and detection of this isotope was taken as 2.5 ± 0.03 ml s⁻¹. The reproducibility of the results was within ±2.5% near the optimum flow rate and the reproducibility of all the results was within counting statistics. The detection limits of fluorine on the previous system have been discussed in section 3.3.4.8. These were found to be directly dependent on the matrix background. Any improvement in irradiation or detection efficiency on this system will have similar effects on both the sample and matrix levels of activity and hence similar detection limits to those obtained previously would be expected. The variation in O-19 activity with fluorine concentration was therefore not investigated.
### Table 32

**Variation in Oxygen-18 (Half-Life $22.6$ a) Activity with Flow Rate**

<table>
<thead>
<tr>
<th>Flow Rate (ml/s)</th>
<th>Activity (Cts/10 min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.03 ± .01</td>
<td>0.357, 0.356, 0.358, 0.357, 0.357, 0.528, 0.528, 0.357, 0.346</td>
</tr>
<tr>
<td>Average</td>
<td>0.350 ± 0.007</td>
</tr>
<tr>
<td>1.56 ± .01</td>
<td>0.550, 0.573, 0.565, 0.555, 0.551, 0.564, 0.555, 0.568</td>
</tr>
<tr>
<td>Average</td>
<td>0.551 ± 0.012</td>
</tr>
<tr>
<td>2.00 ± .02</td>
<td>0.625, 0.615, 0.622, 0.643, 0.622, 0.618, 0.606, 0.622</td>
</tr>
<tr>
<td>Average</td>
<td>0.621 ± 0.011</td>
</tr>
<tr>
<td>2.43 ± .02</td>
<td>0.615, 0.620, 0.617, 0.635, 0.622, 0.623, 0.620, 0.662</td>
</tr>
<tr>
<td>Average</td>
<td>0.622 ± 0.016</td>
</tr>
<tr>
<td>2.89 ± .02</td>
<td>0.615, 0.622, 0.617, 0.633, 0.632, 0.622, 0.642, 0.653</td>
</tr>
<tr>
<td>Average</td>
<td>0.622 ± 0.015</td>
</tr>
<tr>
<td>3.26 ± .03</td>
<td>0.621, 0.622, 0.623, 0.642, 0.619, 0.607, 0.623, 0.600</td>
</tr>
<tr>
<td>Average</td>
<td>0.622 ± 0.014</td>
</tr>
</tbody>
</table>
Table 33 continued

<table>
<thead>
<tr>
<th>Flow Rate ml s(^{-1})</th>
<th>Activity Cts/15 min</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.73 ± 0.03</td>
<td>0.591, 0.602, 0.611, 0.602, 0.629, 0.607, 0.661, 0.616</td>
</tr>
<tr>
<td>average</td>
<td>0.603 (\alpha = \pm 0.010)</td>
</tr>
<tr>
<td>4.17 ± 0.08</td>
<td>0.533, 0.579, 0.587, 0.583, 0.591, 0.511, 0.611, 0.614</td>
</tr>
<tr>
<td>average</td>
<td>0.552 (\alpha = \pm 0.010)</td>
</tr>
<tr>
<td>5.10 ± 0.25</td>
<td>0.539, 0.557, 0.556, 0.547, 0.539, 0.511, 0.551, 0.548</td>
</tr>
<tr>
<td>average</td>
<td>0.550 (\alpha = \pm 0.007)</td>
</tr>
<tr>
<td>6.10 ± 0.06</td>
<td>0.505, 0.501, 0.52, 0.493, 0.512, 0.512, 0.530, 0.529</td>
</tr>
<tr>
<td>average</td>
<td>0.519 (\alpha = \pm 0.014)</td>
</tr>
</tbody>
</table>
Fig. 40. Variation of Oxygen-19 Activity with Flow Rate
3.4.3.7. Cerium

Cerium was determined in solution in kerosene using the fast neutron reaction $^{140}\text{Ce}(n, 2n)^{139}\text{mCe}$. The analysis of cerium on the original flow tube system has already been described in section 3.3.4.5, and the relevant nuclear data, the chemical source, and possible interferences have already been discussed in that section. In the current investigations, the neutron generator induced activity will raise the background across the 0.73 MeV peak of Ce-133 a but a correction for this can be made.

A solution containing 200 ppm of cerium was prepared and was used to investigate the variation in Ce-139 m activity with flow rate. At the two lowest flow rates, 0.02 and 0.03 ml s$^{-1}$, the single pulse irradiation and counting technique was used, with an irradiation time of 120 s and counting times of 200 s and 500 s respectively. The timing periods for this technique were obtained in the usual way. At the other, higher flow rates, the flowing stream was irradiated at a constant neutron flux and the equilibrium level of activity was counted for 60 s. The multichannel analyser was set to cover a spectral energy range of 0.1 - 1.50 MeV, and the Ce-139 m peak was measured between 0.54 and 0.83 MeV. The results obtained for the variation of Ce-139 m activity with flow rate, expressed as Ct/s/EP$_m$St, corrected for generator and solvent
backgrounds are shown in table 2.

The optimum flow rate, (Fig. 41), for the production and detection of a 60 s half-life product Ce-139 m was taken as $1.25 \pm 0.05$ ml s$^{-1}$. The reproducibility of all the results was within counting statistics and was within $\pm 1.2\%$ at the optimum flow rate.

The variation in Ce-139 m activity with cerium concentration was investigated by irradiating and counting in turn, solutions containing 400, 200, 100, 50, 20 and 5 ppm of cerium. The results obtained expressed as corrected Ce$^{5+}$/Er$^{3+}$ are shown in table 39. A straight line analytical calibration graph (Fig. 42), passing through the origin, was obtained showing the variation in Ce-139 m activity with cerium concentration. The reproducibility of the results was within counting statistics and decreased continuously with decreasing cerium concentration. The reproducibility varied from $\pm 3.2\%$ for 400 ppm of cerium to $\pm 60\%$ for 5 ppm of cerium. The corrected results obtained at 5 ppm are virtually equal to the neutron generator and solvent background. The detection limits of cerium are discussed in section 3.4.3.9.

3.4.3.9. The Variation in Cerium Flow Rate with Product Isotope Half-Life (60 s - 60 s)

The curves showing the variation in product isotope activity with flow rate for the seven elements investigated on the flowing system are shown in Fig. 43. The activity
<table>
<thead>
<tr>
<th>Flow Rate (ml/min)</th>
<th>Activity (mCi/ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.57 ± 0.01</td>
<td>0.050, 0.060, 0.061, 0.061, 0.059, 0.059, 0.059</td>
</tr>
<tr>
<td></td>
<td>average: 0.054 ± 0.006</td>
</tr>
<tr>
<td>0.73 ± 0.01</td>
<td>0.078, 0.078, 0.078, 0.080, 0.080, 0.080, 0.080</td>
</tr>
<tr>
<td></td>
<td>average: 0.079 ± 0.003</td>
</tr>
<tr>
<td>1.00 ± 0.01</td>
<td>0.093, 0.092, 0.092, 0.092, 0.092, 0.092, 0.092</td>
</tr>
<tr>
<td></td>
<td>average: 0.093 ± 0.003</td>
</tr>
<tr>
<td>1.25 ± 0.01</td>
<td>0.089, 0.091, 0.091, 0.091, 0.091, 0.091, 0.091</td>
</tr>
<tr>
<td></td>
<td>average: 0.091 ± 0.003</td>
</tr>
<tr>
<td>1.50 ± 0.01</td>
<td>0.088, 0.089, 0.089, 0.089, 0.089, 0.089, 0.089</td>
</tr>
<tr>
<td></td>
<td>average: 0.089 ± 0.002</td>
</tr>
<tr>
<td>1.93 ± 0.02</td>
<td>0.084, 0.084, 0.086, 0.086, 0.086, 0.086, 0.086</td>
</tr>
<tr>
<td></td>
<td>average: 0.086 ± 0.001</td>
</tr>
<tr>
<td>Flow Rate (mL s⁻¹)</td>
<td>Activity (C/dpm/μL)</td>
</tr>
<tr>
<td>-------------------</td>
<td>---------------------</td>
</tr>
<tr>
<td>0.35 ± 0.01</td>
<td>0.071, 0.074, 0.072, 0.084, 0.073, 0.071, 0.072, 0.085</td>
</tr>
<tr>
<td></td>
<td>average 0.072 ± 0.002</td>
</tr>
<tr>
<td>3.00 ± 0.02</td>
<td>0.078, 0.077, 0.078, 0.075, 0.076, 0.078, 0.076, 0.078</td>
</tr>
<tr>
<td></td>
<td>average 0.077 ± 0.001</td>
</tr>
<tr>
<td>4.50 ± 0.01</td>
<td>0.078, 0.073, 0.077, 0.071, 0.077, 0.078, 0.077, 0.067</td>
</tr>
<tr>
<td></td>
<td>average 0.076 ± 0.001</td>
</tr>
</tbody>
</table>
Fig. 41. Variation of Cerium-139 m Activity with Flow Rate
### Table 16

Variation of Counting Activity with Carbon Concentration

<table>
<thead>
<tr>
<th>Carbon Concentration</th>
<th>Activity Cts/Br₂Ct</th>
</tr>
</thead>
<tbody>
<tr>
<td>800</td>
<td>0.069, 0.035, 0.069, 0.032, 0.068, 0.032, 0.062, 0.030</td>
</tr>
<tr>
<td></td>
<td>average 0.061 ± 0.008</td>
</tr>
<tr>
<td>600</td>
<td>0.030, 0.031, 0.029, 0.032, 0.032, 0.031, 0.033, 0.030</td>
</tr>
<tr>
<td></td>
<td>average 0.031 ± 0.001</td>
</tr>
<tr>
<td>400</td>
<td>0.0170, 0.0170, 0.0170, 0.0151, 0.0153, 0.0150</td>
</tr>
<tr>
<td></td>
<td>average 0.0161 ± 0.0003</td>
</tr>
<tr>
<td>20</td>
<td>0.0088, 0.0087, 0.0082, 0.0092, 0.0077, 0.0087, 0.0036</td>
</tr>
<tr>
<td></td>
<td>average 0.0087 ± 0.0005</td>
</tr>
<tr>
<td>10</td>
<td>0.0023, 0.0027, 0.0025, 0.0029, 0.0027, 0.0025, 0.0025</td>
</tr>
<tr>
<td></td>
<td>average 0.0025 ± 0.0005</td>
</tr>
<tr>
<td>5</td>
<td>0.0011, 0.0009, 0.0006, 0.0010, 0.0013, 0.0010, 0.0013, 0.0011</td>
</tr>
<tr>
<td></td>
<td>average 0.0010 ± 0.0002</td>
</tr>
</tbody>
</table>
Fig. 42. Variation of Cerium-139 m Activity with Cerium Concentration
Fig. 43. Combined Activity to Flow Rate Curves

1 - Ce
2 - F
3 - O
4 - Pb
5 - S
6 - Cl
7 - Pb
curves shown for lead-102, nitrogen-16 and oxygen-17 have been reduced by factors of two, ten and ten respectively in order to aid presentation. The curves would therefore represent concentrations of 5000 ppm of lead and 1000 ppm of oxygen and fluorine respectively. The maximum of each curve denotes the optimum flow rate for the production and detection of each isotope of given half-life. These optimum flow rates and product half-lives are listed in table 35. A straight line graph, (Fig. 16), was again obtained (2.33\%), when the logarithm of the optimum flow rate was plotted against the logarithm of the product isotope half-life. The relationship between them is therefore of the form

$$F \cdot T^C = k$$

where $F$ is the optimum flow rate

$$T = \text{product half-life}$$

and $k$ is a constant for the flowing system. For this system the value of $c$ was found to be 0.30 and the value of $k$ was found to be 0.2. The units of $c$ and $k$ will depend on the units of flow rate and time introduced into the expression. The optimum flow rate for any element on this system, producing a product isotope of known half-life may now be predicted. The optimum flow rate for the determination of any element on a similar flowing system may be determined once the values of $c$ and $k$ have been measured experimentally.
Table 36
The Variation in Optimum Flow Rate with Product Half-Life

<table>
<thead>
<tr>
<th>Optimum Flow Rate $x_{l} \text{ cm}^{-1}$</th>
<th>Product Half-Life $t_{1/2}$ s</th>
</tr>
</thead>
<tbody>
<tr>
<td>58.3</td>
<td>3.80</td>
</tr>
<tr>
<td>57.3 ± 1.0</td>
<td>3.86</td>
</tr>
<tr>
<td>50.7 ± 0.2</td>
<td>3.66</td>
</tr>
<tr>
<td>0.2 ± 0.2</td>
<td>2.0</td>
</tr>
<tr>
<td>0.0 ± 0.0</td>
<td>7.25</td>
</tr>
<tr>
<td>0.25 ± 0.03</td>
<td>20.0</td>
</tr>
<tr>
<td>0.25 ± 0.05</td>
<td>20.0</td>
</tr>
</tbody>
</table>
Fig. 44. Log Plot of Optimum Flow Rate against Product Isotope Half-Life
3.4.3.2. Limits of Detection

The criteria adopted for detection limits both in the presence and absence of matrix interference have been previously discussed in section 3.3.8.8. Once again it was felt unreasonable to quote detection limits requiring the full output of the neutron generator. The detection limits quoted are therefore for a neutron flux of $6 \times 10^{12} \text{ns}^{-1}$ at the irradiation position of the generator, as before. This corresponds to a total neutron count of $7 \times 10^{10} \text{ns}^{-1}$ to the irradiation cell.

The detection limits for the six different elements investigated on the flowing system are shown in Table 37. In practice the levels of background activity both from the neutron generator extraneous activity and from activation of the kerosene were very low. The criterion adopted for the limits of detection of all the elements was that the sample activity should be equal to twice the background level of activity. In the case of the elements, chlorine and sulphur, which produce positron emitters, the variation in product isotope activity with target element concentration was not investigated. A detection limit could however be estimated since the activities of solutions containing 50,000 ppm of these elements were found to be equal to seven times, and double the background levels of activity respectively. A detection limit for chlorine was similarly assessed and
Table 57

<table>
<thead>
<tr>
<th>Target Element</th>
<th>Detection Limit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe (Fe 376 keV)</td>
<td>30</td>
</tr>
<tr>
<td>Cl</td>
<td>3000</td>
</tr>
<tr>
<td>Ni</td>
<td>100</td>
</tr>
<tr>
<td>O</td>
<td>100</td>
</tr>
<tr>
<td>P</td>
<td>100</td>
</tr>
<tr>
<td>Co</td>
<td>10</td>
</tr>
</tbody>
</table>

*For a neutron flux of $5 \times 10^{12} \text{cm}^{-2}\cdot\text{s}^{-1}$ at the irradiation position of the generator giving $3 \times 10^{17} \text{nc}^{-1}$ through the irradiation cell.*
was found to be of the same order as before, 100 ppm (2.3.4.8.). The detection limits of lead and cerium could be improved if higher neutron fluxes were used. Further, quantities of 10 ppm of lead, and 5 ppm of cerium were determined experimentally in solution (2.4.2.1. and 2.3.2.1.) at neutron fluxes of 0.3 and $1.0 \times 10^{12} \text{m}^{-2} \text{s}^{-1}$ at the irradiation position of the generator. The detection limit for oxygen is limited by the K-15 activity found to be present in the kerosene solvent. Clearly any increase in neutron flux would not improve this detection limit.
Conclusion
4. Discussion and Conclusion

Currently, a large number of applications of fast neutron activation analysis of discrete samples have been reported covering a wide range of interests in the fields of commerce and pure science. Relatively little work has been published on fast neutron activation analysis of flowing systems, especially of non-aqueous flowing systems. A flowing system has been designed and constructed to investigate the fundamental principles of analysis in a non-aqueous media. Suitable irradiation and counting techniques were devised and the analysis of a range of elements producing short half-life products was attempted.

The activity in a flowing stream is drawn out to a parabolic activity profile due to the effects of pipe wall friction. In order to obtain reproducible results it is therefore necessary to incorporate a fixed flow path for the flowing stream, particularly in the irradiation and detection flow cells. The cells constructed did provide a fixed flow path for the flowing liquid and further they were designed so as to dislodge any bubbles that might be formed within them. The success of these flow cell designs was reflected in the reproducibility of the activation analysis results, which varied between ±0.5 and ±2.2% with the most concentrated solutions used. An experimental technique was developed whereby a short irradiation of the flowing stream produced
an active pulse of liquid, whose total activity was then counted. This technique provided an economical irradiation procedure and an additional advantage was that counting was carried out in the absence of extraneous neutron generator background. Since the total activity produced by a total neutron dose, as monitored by the total BF$_3$ count, to the irradiation cell was counted, the effect of any variations in neutron flux or of the duration of the irradiation, were minimised. However the counting of all the activity in the pulse can affect the reproducibility of the results by the introduction of increased statistical error then activities are of the same order as the background. An attempt to optimise the counting period of the pulse using a computer program, was unsuccessful.

This irradiation and counting technique results in a lengthy procedure at very slow flow rates, which makes it inapplicable in such circumstances. At high flow rates only very short duration irradiations are possible before the activity reaches the detector, and this factor leads to increasingly poor analytical sensitivity. Another irradiation and counting technique was therefore used thereby the flowing stream is irradiated at a constant neutron flux and the equilibrium level of activity is counted. This technique provides a rapid activation analysis procedure at high flow rates but requires the
use of a constant neutron flux. Further, the equilibrium level of activity will lag behind in its response to variations in neutron flux. Although this lag can be offset flux variations will affect the reproducibility of results more than in the single pulse technique. Counting is carried out during irradiation, and analytical sensitivity may be affected by the presence of extraneous neutron generator backgrounds. At lower flow rates the time to reach equilibrium can be very long, and this will result in a relatively expensive and wasteful irradiation procedure. Thus the single pulse and equilibrium level of activity techniques are best suited to relatively high and low flow rates respectively. Intermediate flow rates can present a problem since these can result in unacceptably short or long duration irradiation procedures depending on the technique used. The actual irradiation procedure and duration of irradiation in these cases must therefore be carefully selected depending on whether the concentration of the target element is high or low.

Activation of the kerosene solvent used in these investigations produced low levels of the 600 s half-life product, nitrogen-13. This isotope, a positron emitter, was produced by a proton recoil reaction and both the photopoint and Compton continuum arising from N-13 could interfere in the analysis of elements in non-aqueous solution. The N-13 activity was found to decrease
steadily with increasing flow rate once the optimum conditions for the production and detection of this isotope were exceeded. Activation analysis of a range of elements in non-aqueous solution, producing products with half-lives between 29.4 and 530 s, proved to be both feasible and reproducible.

An investigation into the variation of product isotope activity with flow rate was made for each product. In each case smooth curves rising up to a maximum and then falling away more slowly were obtained. The flow rate corresponding to the maximum of each curve was deemed to be the optimum flow rate for the production and detection of the particular isotope or product half-life. This flow rate represents a balance between the residence time in the irradiation and detection cells, and hence irradiation and detection efficiency against loss of activity by radioactive decay due to transit through the pipe work. Below the optimum flow rate the curve falls away sharply since any increased activity due to greater irradiation and detection efficiency is more than counter balanced by increased radioactive decay due to the increased transit time. Above the optimum flow rate the curve falls away more slowly since any reduction in activity due to reduced irradiation and detection efficiency, is partly compensated by reduced radioactive decay due to the decreased transit time. A
reference to the activity to flow rate curves for the isotope of interest and of any possible interferences will enable interferences to be minimised and the required activity to be maximised, by careful selection of flow rate. A relationship was obtained for the variation in optimum flow rate with product isotope half-life. Once the constant terms in this expression have been evaluated on a system the optimum flow rate for the production and detection of any product activity of given half-life can be predicted. The variation of the product isotope activity with target element concentration was found to follow a linear relationship for all the elements investigated. The analysis of unknown concentrations of elements could therefore be rapidly and reproducibly carried out. Detection limits for each element were determined at a modest neutron flux and these limits varied in sensitivity according to the nuclear constants of the reactions and target and product isotopes. The detection limit for each element also depended upon the level of matrix interference or background present and could be improved with the use of higher neutron fluxes. Where any matrix interference occurs, any improvement in detection limit will not be linear with increasing neutron flux.

The physical dimensions of the flowing systems limited the range of product half-lives that could be investigated. The analysis of elements producing isotopes
with half-lives greater than 600 s was in any case not considered feasible since these would require extremely lengthy experimental procedures. Shorter half-life products than 29.8 s would require shorter experimental procedures since rapid transit between irradiation and detection cells would be necessary in order to minimise radioactive decay. A new more efficient flowing system for the analysis of elements producing ultra short half-life product isotopes was designed and constructed in order to further investigate the fundamental principles of analysis in a non-aqueous medium. The analysis of a range of elements producing product isotopes with half-lives in the range 60 s - 0.80 s was then attempted.

The irradiation efficiency was improved by the construction of a larger volume irradiation cell of a different design. It was felt that the double spiral design used previously would be inefficient for short half-life products. Activity would be lost due to radioactive decay as the liquid passed from the region of the highest neutron flux in the centre of the cell, round the spiral to the outlet pipe in the side of the cell and thus through regions of decreasing neutron flux. The single spiral design of the new irradiation cell had the outlet pipe located at the centre of the cell, and hence the active liquid left the cell in the region of highest neutron flux. The variation in spatial efficiency around
the volume of the two sodium iodide detectors available was investigated and the detector most suitable for liquid loop work was selected. The differences observed between the two nominally identical detector assemblies show the desirability for X-ray photographs of detectors to determine the crystal location within the counting material before detectors are used for a particular application. The design and construction of an efficient detection flow cell was carried out using the efficiency contours of the liquid loop detector as a guide. The improvements in irradiation and detection efficiencies and dwell time on the new flowing system are reflected in a comparison of the results obtained for the elements fluorine and cerium which were determined on both systems. The activities of solutions of identical concentration on the new system were found to be double those previously obtained. These improvements in efficiency are also due to the relatively low transit time of the flowing stream through the pipework linking the irradiation and detection flow-cells. High linear solution velocities through the pipework, to minimise transit time, were achieved by forcing the solutions through the flowing system by the application of such higher gas pressures than before. This procedure required that the components of the flowing system should withstand relatively high pressures without leakage. The length of the transit pipe between the flow
cells was reduced to a minimum by locating the detection station near to the neutron generator biological shield. The presence of a sensitive radiation detector in such a location presented problems of unacceptable levels of extraneous neutron generator induced activity. These were found to be caused by neutron activation of the crystal detector and also due to interactions and activation of elements in the surroundings and shielding of the neutron generator. An investigation was made into the design of a suitable shield for the detector to reduce the extraneous neutron generator activity to acceptable levels. The final adoption of a shield around the detector consisting of a layer of neutron moderator followed by a layer of thermal neutron absorber, and the addition of extra shielding to the biological shield of the neutron generator, reduced the level of extraneous activity by a factor of ten. This level of activity was about double that of natural background over the energy range 0.1 - 1.30 MeV, but was mainly concentrated in the photopeaks of the isotope Na-24 (0.47 MeV) which is produced by thermal neutron activation of the sodium in the crystal detector. It is felt that this level of background is acceptable and could only be reduced further with the adoption of increasingly bulky and cumbersome shielding.

The irradiation and counting technique involving the counting of the equilibrium level of activity was
used almost exclusively in this short transit time flowing system. The final flowing system had a minimum transit time between irradiation and detection of about 0.1 s. Activation of the boron nitride yielded low levels of the isotopes 7-12 and 9-14, but the extent of their interferences was unknown. The 7-12 activity was of such very low intensity in the rates since the system flow rate for a 7-12's half-life product was

mainly excruciating. Inference from the low levels of 7-12 was found to be of sufficient only in the determination of the element, except for or near the limit of detection. Proactive analysis of a further range of elements in nonaqueous solution produced products with half-lives between 0.2 s and 1.2 s proved feasible to be credible and comparable.

The spectra obtained consisted of a complex mixture of components from the activation of both the target ele-

ment, together with various interferences including those from solvent and target activation. An attempt was

made to resolve these spectra using a computer program.

The program fitted library or standard spectra of each
component in turn to the mixture and then the proportion
of each component present was determined. The results
obtained using the procedure for the analysis of lead using
the isotope Pb 207 were found to agree well with those
theoretical by hand using the limits of detection. The
reproducibility of the computed results was however consistently slightly worse than those obtained by hand. This was explained as follows. The program was originally developed to analyze spectra of Nielson product mixtures which were counted in a low backround counting system and in which the total count remained too high. The program permits 12 under/linear conditions to resolve both relatively minor and major components. As might be expected the quality of the results obtained using the program is directly dependent on the statistical error present in the sample and in its components. In the case of the current activation analysis investigations the statistical error present in the spectra is often and unavoidably of a much higher level. Further the program attempted to accurately resolve three minor constituents, Na-24, S-32 and Po-210 in a mixture which also contained varying proportions of a major constituent, Po-210. Thus cumulative errors could occur from the combination of the errors in fitting the three minor but important components to spectra containing a relatively large statistical error. Small but possibly significant differences will exist between the library and sample spectra if these are not determined under identical conditions. This is not always possible and can lead to the introduction of further errors. These errors were minimized by using the computer to fit spectra over a region of the sample spectrum that did not contain the backscatter peak and in which the activity of the components of the sample
above background was examined.

The program worked well with the spectra obtained from the analysis of the relatively high lead content of a petrol. The reproducibility of the results obtained was only marginally worse than those obtained by hand, presumably due to good counting statistics. The program produced successfully the spectra obtained from the investigation of the variation of Po-212 activity with flow rate, in the presence of considerable interferences, when hand calculation had failed. In this case particular attention was paid to obtaining spectra containing low levels of statistical error, although this resulted in a relatively lengthy procedure. The computer results obtained, further reinforced the belief that the error in any component depends upon the statistical error present in the whole as well as in the component. It is felt that if data output in a computer-compatible form is available, routine processing of data by computer program can be a considerable advantage. This procedure is becoming increasingly commonplace.

The variation of activity with flow rate for all the elements, produced a similar family of curves to those obtained previously. The use of the optimum flow rate for each product half-life will again minimize the required activity and minimize interferences by flow rate control. Since the curves have flattened tops the results obtained...
will be relatively immune from the effects of small
counter in flow rate. The relationship between the opti-
mal flow rate and the product isotope half-life was simi-
lar to that obtained in the first system. The values
of the constant terms of the expression were found to be
different in this system, as might be expected. Thus the
optimal flow rate for the production and detection of
any product isotope of known half-life can be produced
once the constant terms have been evaluated. This rela-
tionship would appear to be valid over a wide range of
half-lives for any flowing system containing irradiation
and detection flow cells linked by a transit pipe in
which radioactive decay occurs.

The variation in product isotope activity with target
element concentration was found to be a linear relationship
in those cases where this was investigated. The activity
of some of the products was so low even with activation
of concentrated solutions that they were only used as
a source of a particular half-life product for the acti-
vity to flow rate investigations. The linear relationship
obtained for the variation of activity with target element
concentration for the elements investigated, would indi-
cate that the analysis of unknown concentrations of ele-
ments could be rapidly and reproducibly carried out.
Detection limits were again determined or estimated for
each target element and the limits quoted again require
only relatively modest neutron fluxes. The detection limits varied in sensitivity according to the nuclear constants for the nuclear reactions and for the target and product isotopes. The limits of detection will also be dependent on the level of matrix interference or background and therefore will not be linearly dependent on neutron flux.

Any analytical technique should cover as wide a range of elements as possible. In radiation analysis of flowing systems this would require the production and detection of a wide range of product half-lives and varying radiations. The present work has shown the feasibility of analysis using gamma-ray emitters with half-lives in the range between 6.0 and 0.8 s. A flowing system could be designed to incorporate interchangeable components so that a continuous range of half-lives could be determined. Little work has been carried out on analysis using products emitting other nuclear radiations than gamma-radiation and in certain cases detection limits or the effect of interferences could be reduced by the use of complementary detection systems.

Currently with the fast neutron fluxes available from reactors, the limits of detection for many elements is above 100 ppm, which is poor compared to some other techniques. Fast neutron activation, however, offers
advantages of speed and ease of operation for process control. The penetrating nature of fast neutrons ensures that the bulk of the process stream is activated and thus sampling errors are eliminated. The nuclear radiation subsequently emitted is also readily detectable in most instances. In many cases of industrial importance, the control of a process is maintained only within certain limits. Under such conditions of operation, activation analysis can provide a rapid and reasonably economical method of bulk process control.
S. Jinnah

(Remainder of Complimentary Introductions)
Appendix I
NO. CH. A Computer Routine for Neutron Flux Calibration

The program NO. CH. evaluates the results obtained
from neutron flux calibration experiments (E.E.E.) in
which copper foils are irradiated and counted under
standard conditions. The neutron flux measured experi-
mentally from the neutron activation of the foil may
then be directly related to the total number of counts
recorded by the BF$_3$ counter which is used for neutron
flux monitoring. The relationship between the BF$_3$
counter recorded (y) during an irradiation and the neutron
flux (f) is assumed to be linear and ideally should be of
the form

$$y = A \cdot f$$

The program assumes the relationship to be of the form

$$y = c + A \cdot f$$

where $c$ is a constant in which an allowance is made for
the occurrence of sporadic counts originating from elec-
tronic noise. In practice $c$ is found to be very low.

For the highest accuracy neutron flux calibration
using the above relationship may be performed by carrying
out a number of individual flux calibrations using a wide
range of neutron fluxes. The program NO. CH. can then be
used to apply a least squares fit to the experimental
neutron fluxes and calculate theoretical neutron fluxes.
from the values of \( A \) and \( c \) obtained from the least squares fit. The differences between the experimental and the calculated values of the neutron flux will draw attention to atypical results as well as providing a measure of the accuracy of individual determinations. A flow chart illustrating the mode of operation of HO2H is given below, and the detailed program steps are described as follows:

1. The activity of the copper foil at the end of the irradiation \( A(I) \), is calculated by applying a correction for radioactive decay to the measured activity of the foil \( C(I) \). Since significant radioactive decay occurs during the counting period \((T_{C})\), the decay time used in correcting \( c(I) \) for radioactive decay is not just the 60 seconds decay which occurred before counting began.

If \( T_{X} \) is the time at which the average count rate occurred during the counting period, then it may be shown that

\[
T_{X} = -1 \log e \frac{1 - e^{-\lambda T_{C}}}{\lambda T_{C}}
\]

The total decay time = \( T_{X} + 60 \) seconds

\[
A(I) = \frac{C(I)}{e^{-\lambda(T_{X} + 60)}}
\]

2. The experimental neutron flux is calculated from the activation equation (2)

\[
\Phi = \frac{A \cdot \text{Nat.}}{e \cdot d \cdot \text{Bk.} \cdot (e^{-\lambda t})}
\]
Flow Chart of H024

START

READ NUMBER

READ Irrad'n No.
FOIL WT.
BF3 CT.
IRRAD'N TIME
POIL CT.
REAL TIME

CORRECT FOR COPPER DECAY
CALCULATE EXPERIMENTAL
FLUX FROM ACTIVATION EQUATION
STORE VALUE

LEAST SQUARES FIT TO
EXPT FLUXES
CALCULATE THEORETICAL FLUXES
STORE VALUES

WRITE EXPT & CALCULATED FLUXES
and % DEVIATION
SLOPE, CONST,
INPUT DATA

FINISH
It should be noted that the units of the neutron flux \( f \), obtained from the activation equation are actually \( \text{ns}^{-1} \) normalised to a copper foil weight of 1 gram. The measured flux will also depend on the dimensions of the copper foil which should be stated. Neutron fluxes are expressed both as \( \text{ns}^{-1} \), and as fluxes per unit area, in the program. The latter are of course based on the standard copper foil used in these investigations, which is 21 cm in diameter. In the program the experimental flux \( E(I) \) for each determination is calculated from

\[
F(I) = \frac{A(I)}{x(I) \cdot D \cdot (1 - e^{-N(I)})}
\]

where \( N(I) \) is the recorded irradiation time.

\( x(I) \) is the weight of the copper foil and \( D \) is a constant incorporating the constant terms contained in the activation equation.

(iii) The \( \text{BF}_3 \) counts recorded per unit time may be related to the experimental flux by the relationship

\[
Y = A_f f + c
\]

or in the program

\[
X(I) = \text{slope} \cdot F(I) + \text{CONST}
\]

where \( X(I) = A_k N(I) \)

\( N(I) \)

A least squares fit is applied to the experimental fluxes to determine the values of SLOPE, and CONST more accurately.
The principal of the least squares is well-known and in this case

\[ \sum_{i=1}^{\text{NUMBER}} (x(i) - \text{SLOPE} \cdot p(i) - \text{CONST})^2 \]

must be a minimum. \( \text{NUMBER} \) is the number of experimental results, and it may be shown that if

\[ \text{SUMX} = \sum_{i=1}^{\text{NUMBER}} x(i) \]

and similarly

\[ \text{SUMP} = \sum_{i=1}^{\text{NUMBER}} p(i) \]

\[ \text{SUMXP} = \sum_{i=1}^{\text{NUMBER}} (p(i) \cdot x(i)) \]

\[ \text{SUMPS} = \sum_{i=1}^{\text{NUMBER}} (p(i))^2 \]

then

\[ \text{SLOPE} = \lambda = \frac{(\text{NUMBER} \cdot \text{SUMXP}) - (\text{SUMX} \cdot \text{SUMP})}{(\text{NUMBER} \cdot \text{SUMPS}) - (\text{SUMP})^2} \]

\[ \text{CONST} = \psi = \frac{(\text{SUMX} \cdot \text{SUMPS}) - (\text{SUMP} \cdot \text{SUMXP})}{(\text{NUMBER} \cdot \text{SUMPS}) - (\text{SUMP})^2} \]

Thus a theoretical value of the neutron flux \( FC(i) \) can be calculated for each irradiation from the BF3 Cts/sec \( x(i) \) and the values of \( \lambda \) and \( \psi \).

The program assumes cooling and live counting times of sixty seconds. The card input for program and data, and line printer output of results were normally used.

The output contains the BF3 cpc, the experimental and calculated neutron fluxes, as ns\(^{-1}\) and as ns\(^{-1}\) cm\(^{-2}\), the percentage deviation between them, the values of SLOPE and CONST, and the original input data.

The instructions for using the program are given below.
Instructions

The program and the data were input on cards in the original program.

Data Cards Input

Card 1 (control Card)  Format (II)
Cols 1 - 2 (NUM)      Number of irradiations or data cards input (Card 2).
Card 2 (Data Card for each irradiation)  Format (F5.0, 1x, F5.4, 1x, F8.0, 1x, F5.1, 1x, F8.0, 1x, F8.1)
Cols 1 - 5 (IR)       Irradiation identification number
Cols 7 - 12 (W)       Copper foil weight (g)
Cols 14 - 21 (AS)     HP5 counter Total Count
Cols 23 - 27 (TS)     Irradiation Time (s)
Cols 29 - 35 (C)      Total counts from the copper foil
Cols 39 - 41 (TC)     Real Counting Time

A listing of the program H024 follows overleaf.
C NEUTRON FLUX CALIBRATION USING COPPER FOILS
C FOIL SIZE OF 21MM DIAMETER, 3.8 CM, SQ, IS ASSUMED FOR FLUX/UNIT AREA
C IRR=AN IDENTIFICATION NO., W=FOIL WT. (G), AN=BF3 CT., \( \tau_{\text{N}}=\text{IRR. TIME(S)} \)
C C=FOIL CT., TC=REAL TIME(S), NUMBER IS THE NO. OF FOILS USED
C DECAY TIME=60(S), LIVE TIME CT. \( \approx 60(S) \), ARE ASSUMED
C REAL IRR(30)
C D IS A CONSTANT INCORPORATING BRANCHING RATIO (.9A) ISOTOPIC ABUND
CANCE (.6909) CROSS SECTION (600MB) DETECTOR EFFICIENCY (.10) AVOGA
C DROS NO AND ATOMIC WEIGHT (63.54)
D=3.930-04
READ(1,1) NUMBER
1 FORMAT(I2)
D03I=1
READ(1,2) IRR(I), W(I), AN(I), TN(I), C(I), TC(I)
2 FORMAT(F5.0,1XF6.4,1XF8.0,1XF5.1,1XF8.0,1XF4.1)
X(I)=AN(I)/TN(I)
X(I)=X(I)/(1-8.0E-06*X(I))
TX=-1.0/0.0011786*ALOG(1.-EXP(-0.0011786*TC(I)))/(0.0011786*TC(I))
A(I)=C(I)/(60.*EXP(-0.0011786*(TX*60.)))
F(I)=A(I)/(W(I)*D*(1.-EXP(-0.0011786*TN(I))))
SUMX=0
SUMF=0
SUMFS=0
D04I=1
SUMX=SUMX+X(I)
SUMF=SUMF+F(I)
SUMFX=SUMFX+(X(I)*F(I))
4 SUMFS=SUMFS+F(I)**2
SLOPE=((NUMBER*SUMFX)-(SUMX*SUMF))/((NUMBER*SUMFS)-(SUMF)**2)
CONST=((SUMX*SUMFS)-(SUMF*SUMFX))/((NUMBER*SUMFS)-(SUMF)**2)
DO5I=1,NUMBER
FC(I)=(X(I)-CONST)/SLOPE
5 P(I)=((F(I)-FC(I))*100.)/F(I)
WRITE(2,6)
6 FORMAT(25X'ACTIVATION ANALYSIS, 19X24HNEUTRON FLUX CALIBRATION/')
WRITE(2,7)
7 FORMAT('5X3HIRR, 13X3HBF3, 14X10HEXPT. FLUX, 14X10HCAI/C. FLUX, 10X9HDEV
1IATION, 12X3HIRR/')
WRITE(2,16)
16 FORMAT('5X3HNO., 12X5H(C/S), 10X17H(N/SEC/GRM OF CU), 7X17H(N/SEC/GRM
10F CU), 10X1H%, 16X3HNO.,/)
DO9I=1,NUMBER
Z=IRR(I)
9 WRITE(2,10)IRR(I), X(I), F(I), FC(I), P(I), Z
10 FORMAT('4XF5.0, 9XF7.0, 12XE12.6, 12XE12.6, 10XF6.2, 12XF5.0/')
WRITE(2,7)
WRITE(2,8)
8 FORMAT('5X3HNO., 12X5H(C/S), 12X13H(N/SQ.CM/SEC), 11X13H(N/SQ.CM/SEC),
112X1H%, 16X3HNO.,/)
DO17I=1,NUMBER
Z=IRR(I)
F(I)=F(I)/3.8
FC(I)=FC(I)/3.8
17 WRITE(2,10)IRR(I), X(I), F(I), FC(I), P(I), Z
WRITE(2,11)
11 FORMAT(28X5HSLOPE,41X8HCONSTANT/)
   WRITE(2,12)SLOPE,CONST
12 FORMAT(25XF13.11,39XF7.1/)
   WRITE(2,13)
13 FORMAT(4X,HITR(I),10X,HW(I),17X,MAN(I),19X,HTN(I),14X,HC(I),13X,HT
   IC(I)/)
   DO 14 I=1,NUMBER
14 WRITE(2,15)IRR(I),HW(I),AN(I),TN(I),HC(I),TC(I)
15 FORMAT(4X,F5.0,10X,F6.4,14X,F8.0,16X,F5.1,12X,F8.0,12X,F4.1)
END
FINISH
Appendix II H 113
A Program for the Optimization of the Counting Period
in the Single Pulse Technique

In the single pulse irradiation and counting technique 3.3.3.2., the total activity present in an active pulse of liquid is counted. The level of activity present in the initial and final stages of the pulse may only be of background order and the counting of these activities will introduce increased statistical error into the determination. In order to minimise statistical error, only the activity of the pulse that is significantly above background should be counted. An attempt was made to optimise the starting point and duration of the counting period using Outteridge's criterion (32). This criterion was used to optimise the counting period of a source activity S in the presence of a background or interference B. The criterion states that counting should continue until $S/B$ is a maximum.

The integrated count of the activity in the pulse above background will slowly rise with counting time and then will level off when all the activity has passed the detector. The integrated background however will continuously rise with counting time. The counting of the activity of the pulse may therefore be optimised by counting from a fixed starting point until the integrated source count $S$ integrated background is a maximum.
However, there will be an optimum starting point which will yield an overall maximum value of $\sigma^2/B$. This starting point and its associated counting period will be the optimum values for the counting of the activity present in the pulse of active liquid.

This optimization procedure is paralleled in the program and computation begins from the first channel of data I (the beginning of the trace) and values of $\sigma^2/B$ (OTCRIT in the program) are calculated in turn for each channel J. The procedure continues along the trace until a maximum value of OCRIT (J) is obtained, which is stored as AMAX (I). A new starting point one channel removed from the previous one is then fixed (I = I+1) and computation continues until a second maximum value of OCRIT is obtained. This AMAX value is tested against the previous AMAX value until an overall maximum value of OCRIT (AMAX) is obtained. The optimum starting point and duration of the counting period are then output on the line printer.

The instructions for using the program are given below.

Instructions

The program and data were input on cards in the original program.

Data Cards Input

Card 1 (control card):

Cola 1 - 2 (INT): Format I 3

Number of multisector traces to be input.

Card 2 (Data card for each trace):

Format 2 I 5, E 5.0
Cols 1 - 5 (NB)  
First channel of data

cols 6 - 10 (NB)  
Last channel of data

cols 11 - 15 (BKg)  
Background count/channel

cols 16 - 20 (T)  
Counting time/channel

Card 3 (Data card)  
Format (10F5.0, 2X)

cols 1 - 5 etc (Y) channel data.

A listing of the program follows overleaf.

Appendix III N.132

A Computer Program for Activation Analysis using Least
Square Resolution of Gamma-Ray Spectra

This program is based on program "Alpha", described
by Schenfield (42), which is designed for the resolution
of complex gamma-ray spectra. The program quantitatively
resolves a complex spectrum by fitting the standard library
spectra of possible components in turn to it, by the
method of least squares. The program provides correction
for gain or threshold shifts and applies background cor-
rections, and decay and dead time corrections if these
are required by the user. "Alpha" was originally written
to analyse the spectra obtained from fission product mix-
tures, and contains a number of facilities, such as
evaporation and dilution factors, geared to the analysis
of these mixtures. The full range of facilities and
operation of "Alpha" are thoroughly described in the
report by Schenfield (42) and will not be reiterated here.
MASTER COUNTING TIME

DIMENSION Y(100),AMAX(100),OTCRIT(100)

READ(1,1) NUM

1 FORMAT(13)

100 NUM=NUM-1

IF(NUM.LT.0) GO TO 200

READ(1,2) N,NE,BKG,T

2 FORMAT(2I5,2F5.0)

READ(1,3) (Y(J),J=1,NE)

3 FORMAT(10(F6.0,2X))

VSUM=0.0

R=0.0

DO 5 I=1,NE

J=0

6 J=J+1

VSUM=VSUM+Y(J)

B=BKG*J

VDIF=VSUM-B

OTCRIT(J)=(VDIF*VDIF)/R

IF(J.EQ.1) GO TO 6

IF(OTCRIT(J).GT.OTCRIT(J-1)) 7,7,6

7 AMAX(I)=OTCRIT(I-1)

IF(I.EQ.1) GO TO 5

IF(AMAX(I).GE.AMAX(I-1)) 8,8,5

5 CONTINUE

3 T=I-1

J=J-1

CTG=T*J

WRITE(2,9) J

WRITE(2,10) CTG
0 FORMAT(29H0OPTIMUM CHANNEL FOR START = 13)
10 FORMAT(29H0OPTIMUM COUNTING TIME = 7.0//)
GO TO 100
200 CONTINUE
STOP
END
FINISH
Schonfield's basic program was converted to run on an ICL 1904A computer, corrections being made for the differences encountered in FORTRAN language. The efficacy of the program was tested by using it to analyse synthetic spectral mixtures of known composition. These were prepared by counting a number of standard radiation sources in turn, for varying lengths of time, to obtain a single but complex spectrum. The basic program was found to work well in fitting the library spectra of the standard sources to the synthetic mixtures.

"Alpha" was found to be tedious to apply to activation analysis results since eight control cards were required for each sample spectrum. The spectra obtained from liquid loop work consisted mainly of sets of similar spectra which were in fact usually repeats of a single measurement. The large number of sample control cards in the basic program was due to the availability of different modes of computation which could be applied to the sample spectrum in turn. The majority of these, and of some other optional facilities were rarely if ever used in liquid loop work.

A simplified form of "Alpha" [sic] was prepared to cater for the activation analysis of sets of similar spectra. Schonfield's method of spectrum resolution and all the basic features and options were retained in this program. A provision was added to input the BF₃ count
associated with each spectrum to allow the normalisation of results and also in order to compute the activity of each component as counts/EP3 count. This reduced the number of control cards from eight for each spectrum to three for each set of spectra. An additional data card was input with each set of spectra and this contained the EP3 counts for the set. The final version of the program H 139 was retained in binary form on the chemistry department's magnetic tape to avoid a waste of computer time through compilation each time the program was used.

The program H 139 was checked using the synthetic spectral mixtures used previously, and the results obtained were compared with those from "Alpha". Identical results were obtained in each case. The mode of operation of H 139 is shown in a flow chart overleaf and the directions for use where these differ from "Alpha" are given below.

Instructions

The program was input on magnetic tape and the data was input on cards.

Data Cards Input

Card 1 (Control card for sample set) X-1 in Alpha
Card 2 (Control card for sample set), X-4 in Alpha
Card 3 (Control Card for sample set), X-6 in Alpha
Card 4 (Data card for sample set) (10 (16, 2x)

Cols 1 - 6 (KEP3) EP3 count for spectrum 1
Cols 8 - 14 EP3 count for spectrum 2
Cols 16 - 22 etcetera, six columns and two spaces for each additional spectrum up to ten

A listing of H 139 follows overleaf.
Simplified Flow Chart of H.139

START

Read Control Cards for Standards
Standard Spectra
Background spectrum

Computations on Standards

Read Control Cards for Sample Spectra
BF3 COUNTS for sample spectra

Resolution of each spectrum with automatic gain and threshold shift compensation if required

WRITE Activities of Components
Activities as Cts/BF3Ct.

Store values

Combine answers and calculate average value for the set.

WRITE Average values

FINISH
PROGRAM (H139)
 INPUT50 = CRO
 OUTPUT51 = LPO
 USE6 = NTO/FORMATED
 TRACE 2
 END

MASTER ALPHA MK1

MARK I MODIFIED BY C.C.HAYWARD

VERSION FOR THE ACTIVATION ANALYSIS OF SIMILAR SAMPLE BATCHES
VERSION GOOD UP TO 96000;0 * LARGER CONVERTED TO ZERO
IF IT FINDS 99999, INTERPOLATES BETWEEN NEIGHBORING CHANNELS

DIMENSION A(22,22), Y(100), Z(22), S(32,100), STD(22), B(22),
 I(100), W(100), PER(100), VT(100), IR(100),
 2BA(100), SS(30), FM(12), AC(30), IS(32), TST(32), HAT(22),
 4HA(30), IT(22), 7TT(30), STDZ(30), SSS(30)
 5,NBF3(10), ZTZZ(30)

COMMON S,BA,R,IR,DER,Y

CHANGE THIS CARD TO MAX NR OF ISOTOPES IN THE LIBRARY
NSTO=30
READ (50,56) (FM(I), I=1,10)
WRITE (51,700)

700 FORMAT (2AH1, CONTROL CARDS FOR STANDARDS,/
WRITE (51,140) (FM(I), I=1,10)
READ (50,28) NS, M, NIT, NBA, NZ, MF, NH, NF, NTS, NTM, NQ, TB, Q
WRITE (51,141)
WRITE (50,56) (TISOT(I), I=1,NS)
WRITE (51,142) (TISOT(I), I=1,NS)
SS (I) = 0.0
DO 39 J=NZ,MF

39 SS (I)=SS (I)+S (I,J)
WRITE (51,164)
WRITE (51,244) (SS (I), I=1,NS )
DO 9933 I=1,NS

9933 SS (I)=SS (I)
DO 64 I=1,NS
64 SS (I)=SS (I)**2
MIN=0

13 WRITE (51,129)
120 FORMAT (23H1CONTROL CARDS FOR DATA/)
READ (50,9922) XIDT,NOPT,NBR,NBS,TB,TSA,VRED,DAY,VM

9922 FORMAT (1X,A6,1X,12,4X,11,4X,11,9X,11,5E10,3)
IF (NOPT) 1211,1210,1210
1210 WRITE (51,1466) XIDT,NOPT,NBR,NBS,TB,TSA,VRED,DAY,VM
1466 FORMAT (12H CARD M=1 ,A6,13,15,15,110,5E11.3)
IF (VH) 160,160,161
160 VH=1.0
161 IF (VRED) 162,162,163
162 VRED=1.0
163 IF (TB) 131,131,132
131 FS=0.0
GO TO 133
132 FS=TSA/TB
133 EX=FS+FS**2
IF (NBR) 37,37,36
76 READ (51,52) (TNAME(I), I=1,10)
WRITE (51,53) (TNAME(I), I=1,10)
READ (NTM, FM) (BA(I), I=1,M)
WRITE (51, 22) (BA(I), I=1,M)
READ (NTM, 57) (TNAME(I), I=1,10)
WRITE (51, 57) (TNAME(I), I=1,10)
READ (50, 50) NP, KT, 1V, NEUST, K23D, O1H, NDET, (IS(I), I=1, NP)
WRITE (51, 143) NP, KT, 1V, NEUST, K23D, O1H, NDET, (IS(I), I=1, NP)
0011 FORMAT ((10(16, 2X)))
WRITE (51, 9900)
9000 FORMAT (21H0BF3 CTS.; FOR SPECTRA)
WRITE (51, 9911) (NBF3(IN), IN=1, NDT)
DO 80 IN=1, NDT
READ (HTM, FM) (Y(I), I=1,M)
WRITE (51, 702)
702 FORMAT (30H1SAMPLE SPECTRUM AND CALCULATED RESULTS;//)
WRITE (51, 22) (Y(I), I=1,M)
N=NP
3800 CONTINUE
DO 43 I=2,M
IF (Y(I)-96000.0) 43, 43, 41
41 IF (Y(I)-99999.0) 42, 43, 42
42 Y(I)=0.0
43 CONTINUE
DO 165 I=3,N
IF (Y(I)-99999.0) 165, 48, 165
43 Y(I)=(Y(I-1)+Y(I+1))/2.0
165 CONTINUE
IF (NBS) 45, 45, 46
66 NO 47 I=1,M
47 Y(I)=Y(I)-BA(I)*FS
45 $3=0.0$
40 40 I=NZ, MF
40 $3=S_1+S_2$ at (1)
41 $s_1=0.0$
42 $s_2=0.0$
43 3 I=NZ, MF
43 $s_1=S_1+V(I)$
44 $s_2=S_1+SN+FX$
45 WRITE (51, 147) S_1, S_1
46 130 I=1, M
130 $V_T(I)=V(I)$
131 $RH=QH$
132 $K=0$
133 $NT=N$
134 91 J=1, N
135 92 I=1, NS
136 IF $(IS(J)-I) 93, 93, 92$
137 CALL COPYA(TISO(J), TISO(T(I)))
138 TO 01
01 CONTINUE
02 CONTINUE
03 CONTINUE
04 96 J=1, NT
05 $V_T(J)=J$
06 71 J=1, H
07 $V(J)=V_T(J)$
08 $P=1.0$
09 $SN=1.0$
10 TF $K_Y$ 84, 44, 44
11 TF $K_Y+2$ 73, 83, 73
12 TF $K_K$ 74, 74, 83
74 READ (50,58) FTT, SHCI
75 WRITE (51,58) FTT, SHCI
83 CALL SHIFT (Y, N, SH, FTT, SHCI)
84   FP=FTT
85   CMSH=SHCI
86   TS(N+1)=NST0+1
87   TS(N+2)=NST0+2
88   NT=NT+1
89   CHT=1.E20
90   DO 101 I=1, NIT
91   M=M
92   DO 101 I=1, NIT
93     TF(LJ) = 29, 13, 12
94   101 U(I)=1.0
95   GO TO 14
96   T=Y(I) + BA(I)*FX
97     IF (T= 1.0) 32, 32, 34
98   32 U(I)=1.0
99   GO TO 14
100  U(I)=1.0/T
101  CONTINUE
102  GO TO 33
103  DO 31 I=1, NIT
104  31 U(I)=1.0/(Y(I)+1.0)
105  IF (KT) 26, 26, 16
106  N=N+1
107  I=M-1
108  N5=1S(N)
109  DO 17 J=2, 1
110     C=J
111  26 CONTINUE
112  DO 101 I=1, NIT
113    TF(LJ) = 29, 13, 12
114  17 CONTINUE
115
IF(Y(J+1)-1.0) 136,136,134
134 IF(Y(J-1)-1.0) 136,136,135
135 DER(J)=(Y(J+1)-Y(J-1))/2.0
GO TO 17
136 DER(J)=0.0
17 S(N5,J)=DER(J)*(C+gH)/100.0
S(IS(H),1)=S(IS(N),2)
S(IS(N),M)=S(IS(N),M-1)
IF(K23N) 26,26,19
19 N=N+1
I=I-1
N5=IS(N)
10 DO 27 J=2,1
27 S(N5,J)=DER(J)
S(IS(H),1)=S(IS(N),2)
S(IS(N),M)=S(IS(N),M-1)
26 DO 1 L=1,N
N5=IS(L)
N2 K=L,N
N6=IS(K)
SA=0.
10 DO 3 I=N5+1
3 SA=SA+S(N6,I)*S(N5,I)*W(I)
A(K,L)=SA
A(L,K)=A(K,L)
2 CONTINUE
1 CONTINUE
10 NO 4 K=1,N
N6=IS(K)
SA=0.
NO 5 1=112,11F
SX=SX*S(NA,I)*Y(I)*U(I)
5 CONTINUE
4 R(K)=SX
   CALL INVERT (A,N)
   NO 7 J=1,N
   SUM=0.
   NO 8 J=1,N
   SUM=SUM+A(J,I)*R(I)
3 CONTINUE
7 Y(J)=SUM
   CH=0.0
   VV=0.0
   HH=0.0
   VU=0.0
   NO 11 J=NZ,1
   SV=0.0;
   NO 9 J=1,N
   NS=IS(I)
9 SV=SV+S(NS,I)*Z(I)
   RR=Y(J)-SV
   THE=2
   VV=VV+1*(J)*T
   VU=VU+T
   TMP=ABS(S,1+SV+BA(J)*FX)
   RT=T/TMP
   CH=CH+RT
   TMP=SORT(TM)
   RR=Y(J)*RR/TMP
   TE=Y(J)*BA(J)*FX
IF (TF=1.0) 65,65,66
65 TT=TT
GO TO 67
66 TT=TT/TE
67 CHS=CHS+TT
11 CONTINUE
   DN=IF-N-NZ+1
   CHDF=CH/DN
   VY=VY/DN
   CHDFS=CHS/DN
   GO 15 I=1,N
   E=A(I,1)*VY
   STD(I)=E
15 CONTINUE
   IF (KY) 500,500,100
500 WRITE (51,155) CHDF
GO TO 90
100 IF (K230) 104,104,103
103 $H=H-1$
   $SH=SH$ T(N)
   $CHC=1.0$ T(N)
   GO TO 105
104 $H=H$
   $SHC=0.0$
105 $F=1.0$ T(N)/100.0
   $FP=FP+F$
   $SHSNC=SHSNC+SHC$
   WRITE (51,155) CHDF,SHSNC,FP
   T=(CHT-CH)/CH
   IF (T+.05) 90,90,97
IF (T- 0.05) 90,90,111
IF (CHDF = 1.2) 90,90,107
CALL SHIFT(Y,M,SH,F,SHC)
CONTINUE
101 CONTINUE
90 DO 49 I=1,NT
A(I,I)=SS(IS(I))*A(I,I)*VY/VU
49 WRITE (51,156)
WRITE (51,24)(AT(J), J=1;NTT)
90 DO 95 I=1,NT
95 STD(I)=SORT(STD(I))
IF (NDFT) 90,90,98
93 CALL DTIME (A,STD,Z,HAT,TSA;NT;KK,NDFT)
90 DO 94 J=1,HT
ZT(J)=Z(J)
94 STD(T)(J)=STD(J)
WRITE (51,157)
WRITE (51,24)(TISO(J),ZT(I),STD(T);I=1;NTT)
90 DO 994 I=1,NTT
ZT(I)=(ZT(I)+SSS(IS(I)))/NBF3(IN)
STDZ(I)=(STD(I)+SSS(IS(I)))/NBF3(IN)
7T(I)=(STDZ(I)/ZTT(I))*100.
994 CONTINUE
7T7=0.0
703 I=1,NTT
7T7=ZT7+(ZT(I)+SSS(IS(I)))
7T7=((ZT7-S1)/S1)*100.
WRITE(51,704)(S1)
WRITE(51,705)(ZT7)
WRITE(51,706)(ZZZ)
704 FORMAT(12H0SAMPLE SUM=,E12.3)
705 FORMAT(12H0FITTED SUM=,E12.3)
706 FORMAT(12H0% DEVIAT.=,E12.3)
WRITE(51,9955)
9955 FORMAT(16H0ACTIVITY/BFP CT,/)  
WRITE(51,9998)(ZTT(I),STDZ(I),I=1,NT)
WRITE(51,8888)(ZTTZ(I),I=1,NT)
8888 FORMAT(14H0,18X,14H % DEVIATION #,3(E11.2,26X))
9998 FORMAT(12X,3(8X,E13.4,E11.274X))
1F(HEUST) 35,79,72
72 KK=KK+1
1F(KK-2) 75,79,79
75 DO 78 I=1,NT
1F(Z(I)/STD(I)=0) 77,77,78
77 IS(I)=0
73 CONTINUE
KK=0
NO 76 J=1,NT
1F(IS(J)) 76,76,81
31 KK=KK+1
1S(KR)=IS(J)
1T(KR)=J
76 CONTINUE
1F(KR) 127,79,127
127 IF(KR-NT) 82,79,82
82 NH=SH
GO TO 8899
35 FTT=FP
SHC1$S~ISHC
79 IF (NDT) 150,150,151
150 IF (ND) 152,152,151
152 CONTINUE
153 WRITE(51,153)
154 WRITE(51,57)(R(J),J=1,MF)
155 K=0
156 N2=MF-2
157 DO 85 J=NZ,N2
158 T=ABS(R(J))
159 IF(T<10.) 89,89,88
160 IF(R(J-1)-2.0) 85,86,86
161 IF(R(J)-2.0) 85,87,87
162 IF(R(J+1)-2.0) 85,88,88
163 K=K+1
164 TR(K)=J
165 CONTINUE
166 WRITE((51,159)
167 WRITE(51,51)(IR(I),I=1,K)
168 WRITE(NF,154)(ZTT(I),STDZ(I),I=1,NTT)
170 CONTINUE
171 ND=NDT
172 END FILE NF
173 REWIND NF
174 CALL DECAY (TISO,NTT,ND,NF,NH,TNAME)
175 NNN=0
176 ND=0
177 REWIND NF
178 GO TO 18
180 FORMAT(5110,3F10.5)
20 FORMAT(10F6.1)
21 FORMAT(12X,3(X,AB,E13.4,F11.2,F4X))
22 FORMAT(1X,10(2X,F10.4))
23 FORMAT(15,2X,4E10.2,E12.2,E12.4,3X,2E10.2,5X,2E10.2)
24 FORMAT(1X,E11.4,F9.14)
25 FORMAT(1X,A6,1X,12,4X,I1,4X,I1,1X,16,2X,11,5E10.3)
26 FORMAT(6I5,3X,2I1,3I5,E10.3,E10.2)
27 FORMAT(110,2F20.0)
28 FORMAT(14,4I2,F6.2,12,3012)
29 FORMAT(1X,30T4)
30 FORMAT(10A7)
31 FORMAT(1X,10A7)
32 FORMAT(3(A8,E10.3,E8.1))
33 FORMAT(12F6.0)
34 FORMAT(10A10)
35 FORMAT(1H0,10(?X,F10.4))
36 FORMAT(3F10.3)
37 FORMAT(3E15.4)
38 FORMAT(12H0CARD S-1) .10A8)
39 FORMAT(12H0CARD S-2) .615,2I1,3I5,2E12.3)
40 FORMAT(12H0CARD S-3) .10A8)
41 FORMAT(12H0CARD S-4) .8E12.4)
42 FORMAT(12H0CARD S-5) .8E12.4)
43 FORMAT(12H0CARD S-6) .8E12.4)
44 FORMAT(25H1BACKGROUND AND STANDARDS;)
45 FORMAT(12H BACKGD SUM=,E12.3,16H SAMPLE SUM=,E12.3)
46 FORMAT(12H CARD H-6) .14,4I2,F6;2,3112;)
47 FORMAT(5H FIT=,E11.3,11H THR SHIFT=,F5.2,12H GAIN SHIFT=,F6.4)
48 FORMAT(4H ALPHA FACTORS)
49 FORMAT(67H RESULTS=CONCENTRATIONS AND EST STANDARD ERRORS;) 1985
150 FORMAT(4HEOHATIO OF RESIDUALS OVER STD DEV PER CHANNEL ) 1990
151 FORMAT(20HEOHIOUSIVE CHANNELS) 1995
153 FORMAT(1OA7,215) 2000
154 FORMAT(4E11.3,4E9.1)) 2005
164 FORMAT(17HOSUM OF STANDARDS/) 2010
1711 CONTINUE 2015
STOP 2020
END 2025
SUBROUTINE SHIFT(Y,M,H,F,SHC) 2030
DIMENSION X(100),Y(100),XC(100),VC(100) 2035
DO 7 I=1,10 2040
7 XC(I)=I 2045
DO 8 J=1,10 2050
8=J 2055
Y(J)=7+F*SH*(F-1.) 2060
3 Y(J)=X(J)*SHC 2065
DO 9 J=1,10 2070
9 Y(J)=X(J)+SHC 2075
IF (XC(I)-X(J))50,45,40 2080
5 VC(I)=Y(J)/F 2085
GO TO 60 2090
45 CONTINUE 2095
GO TO 60 2100
40 CONTINUE 2105
IF(J-1)60,60,51 2110
51 YC(I)=(Y(J)-Y(J-1))/(X(J)-X(J-1)) 2115
VC(I)=Y(J-1)+YC(I)*(XC(I)-X(J-1)) 2120
HC(I)=VC(I)/F 2125
GO TO 40 2130
60 CONTINUE 2135
GO TO 10 I=1,10 2140
30 VC(I)=YC(I)
\[ v(1) = 0.0 \]

RETURN

END

SUBROUTINE DECAY (TISO, NT, NK, NF, NH, TNAME)

INTEGER TISO, TNAME

DIMENSION Z(10, 10), W(10, 10), A(10), S(10), SUMA(10), V(10), TISO(10)

1, TNAME = 12

DO 12 J = 1, NK

12 READ (NF, 5) (Z(I, J), W(I, J), I = 1, NT)

IF (NH) 21, 21, 20

20 WRITE (51, 10)

10 FORMAT (1H15H) PROCEDURE F/

DO 1 I = 1, NT

SUM = 0.0

SUM1 = 0.0

DO 2 J = 1, NK

U(I, J) = 1.0 / W(I, J)**2

V(I, J) = SUM = SUM + U(I, J)

2 SUM = SUM1 = SUM + U(I, J) * Z(I, J)

A(I) = SUM1 / SUM

1 SUMA(I) = SUM

20 IF (NH) 4, 4, 20

DO 3 I = 1, NT

SUM = SUMA(I)**2

DO 4 J = 1, NK

SUM = SUMA(I)**2 * (Z(I, J) - A(I))**2

4 SUM = SUM + W(I, J) * (Z(I, J) - A(I))**2

T = NK - 1

V(I) = SUM / T

3 SIGMA(I) = SIGMA(V(I) / SUMA(I))

GO TO 100

5 PROCEDURE \( H \)
PROCEDURE H/)
T=HK
DO 23 I=1,NT
  SUM=0.0
DO 24 J=1, HK
  IF (Z(I,J)) 25,25,24
25 Z(I,J)=0.0
24 SUM=SUM+Z(I,J)
23 A(I)=SUM/T
DO 27 I=1,NT
  SUM=0.0
  DO 26 J=1, HK
  26 SUM=SUM+(A(I)-Z(I,J))*2
  V(I)=SORT(SUM/(T-1.0))
27 S(I)=V(I)/SQRT(T)
100 WRITE (51,6) (T100(I),A(I),S(I),V(I),I=1,NT)
  DO 30 I=1,NT
  S(I)=(S(I)/A(I))*100;
30 V(I)=(V(I)/A(I))*100;
9 FORMAT(10,3(6X,14H % DEVIATION =,,E9:1,E9:1))
WRITE(51,9) (S(I),V(I),I=1,NT)
RETURN
5 FORMAT(4(E11.3,E9.1))
4 FORMAT(3X,A8,E11.3,E9.1,E9.1))
END
SUBROUTINE DTIME (A,STD,Z,HAT,TS,A,NT,KK,NDET)
DIMENSION A(22,22),STD(22),Z(22),HAT(22),D(30)
IF (NDet) 31,31,30
30 IF (KK) 9,9,10
9 READ (50,20) TC, DT, NP, NSI
10 READ (51,22) TC, DT, NP, NSI
WRITE (50,21) D(I), I=1, NP
WRITE (51,23) D(I), I=1, NP

10 TT=NP-2
   DT=DB=TT*DT
   NEX=NP-NSI
   IT=NP-1
   N0 2, I=1, NT
   T=DT
   NO 1, J=1, NT
   T=T+DT
   A(I,J)=(1.0-D(J))*EXP(-0.693*T/HAT(I))
   CONTINUE
   T=T+DT
   A(I,NSI)=(1.0-D(NP))*EXP(-0.693*T/HAT(I))
2 CONTINUE
   N=(NSI-1)/2 -1
   NO 7 I=1, NT
   SUM=0.0
   NO 3 J=1, N
   SUM=SUM+4.0*A(I,2*J)+2.0*A(I,2*J+1)
   CONTINUE
   AR=A(I,1)+SUM+4.0*A(I,NSI-1)+A(I,NSI)
   AR=AR+DT/3.0
   IF (NP-NSI=1) 4,5,6
   5 AR=AR+(A(I,NSI)+A(I,NSI+1))*DT/2.0
   GO TO 4
   6 AR=AR+(A(I,NSI)+A(I,NSI+1))*DT/2.0+(A(I,NSI+1)+A(I,NSI+2))*DTT/2.0
   4 T=TSA/AR
$7(1) = 2(1) * T_{E} \\
\text{STD}(1) = \text{STD}(1) * T_{E} \\
7 \text{ CONTINUE} \\
\text{GO TO 100} \\
31 \text{ IF (KK) 32, 33} \\
32 \text{ READ } (50, 21) \text{ DET} \\
\text{WRITE } (51, 23) \text{ DET} \\
33 \text{ TC} = \text{TSA} / (1.0 - \text{DET}) \\
\text{DO 34 I = 1, N} \\
\text{TEM} = 0.603 * \text{TC} / \text{HAT}(I) \\
\text{TEM} = \text{TEM} / (1.0 - \exp(-\text{TEM})) \\
7(I) = 2(1) * \text{TEM} \\
\text{STD}(I) = \text{STD}(I) * \text{TEM} \\
34 \text{ CONTINUE} \\
20 \text{ FORMAT}(2E10.3, 2I5) \\
21 \text{ FORMAT}(3E10.3) \\
22 \text{ FORMAT}(12H \text{ CARD M=7 }, 2E11.3, 2I5) \\
23 \text{ FORMAT}(12H \text{ CARD M=8 }, 8E11.3) \\
100 \text{ RETURN} \\
\text{END} \\
\text{SUBROUTINE INVERT (A,N)} \\
C \text{ GAUSS-JORDAN METHOD * VERSION BY} \\
C \text{ H LIFTZKE ET AL (ORNIL-3430)} \\
\text{DIMENSION A(22,22), B(22), C(22), LZ(22)} \\
\text{WRITE } (51, 992) \\
992 \text{ FORMAT}(14H \text{ INVERT CALLED}) \\
\text{DO 10 J = 1, N} \\
10 \text{ L7(J)=J} \\
\text{DO 20 I = 1, N} \\
K = 1
\[ V = A(I, I) \]
\[ L = I - 1 \]
\[ L = I + 1 \]
\[ IF(N = LP) 14, 11, 11 \]
\[ I = 13, J = LP + 1 \]
\[ U = A(I, J) \]
\[ IF(ABS(U) = ABS(V)) 13, 13, 12 \]
\[ V = U \]
\[ \text{CONTINUE} \]
\[ I = 15, J = 1, 16 \]
\[ C(J) = A(J, K) \]
\[ A(J, K) = A(J, I) \]
\[ IF(Y) 995, 996, 995 \]
\[ IF(C(J)) 993, 997, 993 \]
\[ A(J, I) = 0 \]
\[ GOTO 990 \]
\[ A(J, I) = A(J, I) - C(J)/V \]
\[ IF(A(I, J)) 998, 1000, 998 \]
\[ A(I, J) = A(I, J)/V \]
\[ GOTO 1015 \]
\[ A(J, I) = 0 \]
\[ IF(A(I, J)) 1000, A(I, J) = 0 \]
\[ R(J) = A(I, J) \]
\[ IF(Y) 1061, 1002, 1004 \]
\[ A(I, I) = 0 \]
\[ GOTO 1003 \]
\[ A(I, I) = 1.0/V \]
\[ J = LZ(I) \]
\[ I = LZ(K) \]
LZ(K)=I
DO 19 K=1,N
TF(I-K)16,19,16
16 DO 18 J=1,N
TF(I-J)17,13,17
17 A(K,J)=A(K,J)+B(J)*C(K)
18 CONTINUE
19 CONTINUE
20 CONTINUE
DO 200 I=1,N
TF(I-LZ(I))100,200,100
100 K=1+1
TF(I-N)300,200,200
200 DO 200 J=K,N
TF(I-LZ(J))500,500,500
200 M=LZ(I)
IZ(I)=IZ(J)
IZ(J)=M
DO 700 L=1,N
C(L)=A(I,L)
A(I,L)=A(J,L)
700 A(J,L)=C(L)
500 CONTINUE
200 CONTINUE
RETURN
END
FINISH
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The feasibility and advantages of fast neutron activation analysis in a non-aqueous flowing system, using economical irradiation techniques are outlined. The application of the method to the determination in solution of elements producing isotopes with half lives in the range 588 — 29.4 sec, the selection of the optimum flow rate to minimise interferences for each element, and their limits of detection are also given. A method for the prediction of the optimum flow rate, on a given system, for the determination of any element producing an isotope of known half life is also given.

Introduction

The feasibility of neutron activation analysis in flowing systems, for a range of elements, has been demonstrated by a number of authors, using both isotopic and generator neutron sources. Little work has been published describing the activation analysis of non-aqueous flowing systems, yet analysis in a non oxygen containing (hydrocarbon) solvent is relatively uncomplicated by interferences produced by activation of the solvent, and there are many potential applications such as, for example, in the petroleum industry. Aqueous systems suffer the inherent disadvantage of a solvent background consisting of a mixture of $^{16}\text{N}$ (T = 7.35 sec) and $^{35}\text{N}$ (T = 600 sec) from activation of the oxygen present; both isotopes contributing to the large 0.51 MeV peak observed, whilst the Compton continuum and higher energy peaks of $^{16}\text{N}$ stretch from 7.12 MeV downwards.

The object of these investigations was to demonstrate the feasibility of routine neutron activation analysis of non-aqueous flowing systems, using an economical pulse technique where applicable. The solvent background from a variety of hydrocarbons was first of all examined and as little difference was observed between the more inflammable hydrocarbons, reagent grade colourless kerosine was finally chosen as a suitable solvent for the present investigations. A flowing system was then constructed of solvent resistant material, and the analysis of a range of elements, giving product nuclei with varying half lives was attempted. The results obtained demonstrated the feasibility of using economical techniques for the activation analysis of a range of elements in hydrocarbon solvents.
Materials and method

A Kaman 1003A fast neutron generator, capable of generating $10^{11} \text{n} \cdot \text{sec}^{-1}$ and a $75 \times 75 \text{mm NaI(Tl)}$ crystal detector assembly coupled to a Laben 400 multichannel analyser were used in these investigations. A boron trifluoride counter coupled to a scaler and a ratemeter linked to a fairly fast pen recorder (chart speed 1.3 mm · sec$^{-1}$ balancing time at 95% of scale approximately 1 second) were used to monitor the output of the generator.

The flowing system described comprised a liquid reservoir connected to an irradiation cell with nylon tubing (6 mm internal diameter), which was coupled to a detector cell by narrower tubing (4 mm internal diameter). Liquids were forced round the system by nitrogen gas pressure; a needle valve and interchangeable flowmeters enabled a wide range of steady flow rates to be selected.

The irradiation cell (24 ml) was of soldered brass construction, cylindrical in section (100 mm diameter, 6 mm deep), with copper inlet and outlet pipes (5 mm internal diameter), and contained a brass double spiral (1 mm thick) so as to maintain, as far as possible, streamline flow through the cell. The demountable cell bottom was sealed by a PTFE gasket, the cell being clamped together between bolted dural plates. A hole in the upper plate, machined to fit the generator target cooling jacket provided positive location.

A three layer, nylon tubing (4.3 mm internal diameter) detector cell was wound on to a polythene former machined to crystal detector dimensions, so as to utilize the end face of the detector, as well as the sides. Layers were embedded in epoxy resin and the cell volume was 237 ml.

In these investigations a single pulse irradiation technique (resulting in short irradiations and hence in a relatively inexpensive procedure) was adopted except for the shortest half lives examined (< 60 sec). After a steady flow rate had been achieved, the neutron generator was switched on, in our case by rapidly raising the accelerating voltage to the operating level for the duration of the irradiation. After a pre-determined delay, the total activity of the active plug of liquid passing through the detector cell was measured by counting for a pre-set time. The irradiation time was selected to be consistent with the flow rate (and hence transit time between irradiation and detection). The delay and counting times were determined using the multichannel analyser in the multiscaler mode and investigating the variation in the activity of the flowing solution in the detector cell with the time elapsed from the end of the irradiation. For half lives below 60 sec irradiation at constant flux was used with the subsequent counting of the saturation activity in the solution.

The total BF$_3$ count recorded during the irradiation was taken as being proportional to the total number of neutrons passing through the irradiation cell. The dimensions of the system ensured that streamline flow conditions prevailed over the range of flow rates investigated, the decaying active plug of liquid being drawn out to a parabolic activity profile.

Irradiation of the chosen hydrocarbon solvent, colourless kerosine in the

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flowing system, produced a 0.51 MeV peak, decaying with a half life of 600 sec and this was assigned to the isotope $^{15}$N. The presence of $^{13}$N in neutron irradiated hydrocarbons from the proton recoil reaction $^{12}$C(p,n)$^{15}$N, $Q = -3.0$ MeV, has been previously reported, the $^{13}$N activity being dependent on the number of carbon and hydrogen atoms present. As would be expected the recoil proton flux is dependent on the incident neutron flux, the neutron proton elastic scattering cross-section, and the number of hydrogen atoms present, whilst the recoil proton energy varies uniformly up to the maximum energy of the bombarding neutrons.

The spectrum of kerosine which was obtained between 0.1 and 1.95 MeV was assigned mainly to the 0.51 MeV peak from $^{13}$N and this will, of course, interfere in the measurement of positron emitters.

The 0.51 MeV peak observed was considerably smaller than that found in irradiated water, and furthermore decreased continuously in size with flow rate, once the optimum flow for $^{13}$N (0.35 ml sec$^{-1}$) was exceeded.

### Table 1

Elements studied in standard solutions

<table>
<thead>
<tr>
<th>Half life studied, sec</th>
<th>Target element and nuclear reaction</th>
<th>Cross-section, mb</th>
<th>Principal $\gamma$-energy, MeV</th>
</tr>
</thead>
<tbody>
<tr>
<td>588</td>
<td>$^{63}$Cu(n, 2n)$^{65}$Cu</td>
<td>600 ± 40</td>
<td>0.51</td>
</tr>
<tr>
<td>384</td>
<td>$^{79}$Br(n, 2n)$^{79}$Br</td>
<td>1060 ± 35</td>
<td>0.51</td>
</tr>
<tr>
<td>226</td>
<td>$^{52}$Cr(n, p)$^{52}$V</td>
<td>115 ± 15</td>
<td>1.43</td>
</tr>
<tr>
<td>143</td>
<td>$^{28}$Si(n, p)$^{28}$Al</td>
<td>297 ± 14</td>
<td>1.78</td>
</tr>
<tr>
<td>60</td>
<td>$^{140}$Ce(n, 2n)$^{140}$Ce</td>
<td>1593 ± 130</td>
<td>0.75</td>
</tr>
<tr>
<td>29.4</td>
<td>$^{19}$F(n, p)$^{19}$O</td>
<td>51 ± 10</td>
<td>0.20</td>
</tr>
</tbody>
</table>

Standard solutions, in kerosine, of a range of elements (Table 1), with half-lives between 29.4 and 588 sec were prepared and irradiated in turn on the flowing system. The variation of product isotope activity (in the peak) with flow rate, the variation of activity with target element concentration and detection limits were investigated.

### Results and discussion

The results obtained for the investigation of activity with flow rate are shown in Fig. 1, reproducibility at the optimum flow rate of the points being $\pm 0.5\%$ to $\pm 2\%$. The curve maxima show the optimum flow rate for each element (or product half life), representing a balance between irradiation and detection efficiency against cooling time in transit. The curves broaden as the half life decreases, but careful selection of flow rate enables interferences to be minimised.
Straight line calibration graphs for the system, determined at optimum flow rates, were obtained for the variation of solution activity with target element concentration.

It was felt that it was unrealistic to quote detection limits utilising the maximum neutron output of the generator, attainable in any case only for a limited period with each new target, and hence detection limits at \( \approx 1/3 \) of the maximum neutron flux available (Table 2) are quoted.

At these limits of detection the results were found to be reproducible within \( \pm 8\% \). Where a kerosine background occurred (Cu, Br, F), the criterion selected for the limits of detection was that a product isotope count, equal to three standard deviations above the solvent induced background, was obtained. The use of

![Diagram](image)

**Fig. 1. Variation of activity with flow rate**

<table>
<thead>
<tr>
<th>Target element</th>
<th>Concentration used for activity to flow rate curves, ppm</th>
<th>Detection limit, ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>800</td>
<td>25</td>
</tr>
<tr>
<td>Br</td>
<td>800</td>
<td>25</td>
</tr>
<tr>
<td>Cr</td>
<td>8000</td>
<td>200</td>
</tr>
<tr>
<td>Si</td>
<td>5000</td>
<td>80</td>
</tr>
<tr>
<td>Ce</td>
<td>800</td>
<td>30</td>
</tr>
<tr>
<td>F</td>
<td>1000</td>
<td>100</td>
</tr>
</tbody>
</table>

* For a neutron flux of \( 6 \cdot 10^{12} \text{ n} \cdot \text{m}^{-2} \cdot \text{sec}^{-1} \) at the irradiation position of the generator.
increased neutron fluxes in the determination of these elements would not therefore result in a linear increase in the limits of detection. For the elements Cr, Si, and Ce, the experimental criterion adopted for the limits of detection was that the solution count rate was equal to twice background. Clearly for these elements, the limits of detection are neutron flux dependent, but in the case of cerium (counting during irradiation), an increase in neutron flux would also result in increased background due to activation of the detector and of the surroundings.

Plotting the logarithms of the optimum flow rates determined, against the logarithms of the corresponding product isotope half-lives, yielded a straight line graph (Fig. 2). The relationship between the optimum flow rate \( F \), and the isotope half life \( T \) was found to be:

\[
FT^c = k
\]

where \( k \) is a constant peculiar to each flowing system, and also depends on the units of flow and time. \( c \) was found to be 1 within the limits of experimental error. Hence the optimum flow rate for any isotope on a particular system may be found, once \( k \) has been determined.
Conclusion

It has been shown that fast neutron activation analysis in non-aqueous flowing systems is both feasible and economical.
Once the flowing system is calibrated, determinations of unknown concentrations may be carried out rapidly and reproducibly.
The method may well find potential applications in automated process control.

One of the authors (C.C.H.) wishes to thank the Science Research Council for their sponsorship.

References

The effect of spatial variation in detector (NaI) efficiency on flow cell design

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MS received 23 December 1970

Abstract An important factor in the design and construction of detection cells for short half life (<10 s) radio isotopes is the variation in sensitivity around the detector volume. In flowing streams, with sodium iodide detectors, considerable differences were found between nominally identical detectors, and these are related to differences in their internal construction. These observed differences show the desirability of the crystal location inside the detector to be accurately known before a detector is selected and used for a particular application.

1 Introduction
A detector cell consisting of tubing wound in layers around a NaI (Tl) crystal detector has been used by Bibby and Oldham (1970) in the determination of the activity of γ-ray emitters \((t_{1/2} = 40-600 \text{ s})\) in flowing systems. In extending the system to cover short half-life radionuclides \((t_{1/2} < 10 \text{ s})\), knowledge of the variation in spatial sensitivity around the crystal detector assembly was considered to be essential since this governs the location of the cell coils on the detector and their mode of winding in layers.

The present work deals with the determination of the variation in sensitivity around a sodium iodide detector, preparatory to cell construction and the differences in the measured sensitivities of two nominally identical detectors.

Clearly the shorter the half-life of the elements being studied in flowing liquids, the more important is the careful design and construction of the detection cell used.

2 Experimental
A Laben 400 multichannel analyser coupled to a 75 mm × 75 mm NaI (Tl) crystal detector assembly and preamplifier (Nuclear Enterprises type 12/DM-2/12) was used in these investigations. A source of 0.662 MeV γ-radiation (1 µCi Ba-137 m) was prepared by evaporating a measured volume of a standard solution of caesium-137 (obtained from the Radiochemical Centre, Amersham) in a recess (3 mm diam., 1 mm deep) in a perspex strip (70 mm × 10 mm × 4.5 mm). A series of counts at varying distances from the detector were taken with the source at fixed positions around the detector, along a diameter of the end face and along the detector side parallel to the axis. The multichannel analyser was calibrated to cover only the 0.662 MeV photopeak (0.58–0.76 MeV). Perspex spacers were used to vary the source-to-detector distance and a perspex rider, machined to fit the crystal can, was used for measurements along the detector side.

The procedure was repeated using a second 75 mm × 75 mm NaI (Tl) detector assembly nominally of the same type, 12/DM-2/12. This detector differed little in appearance and had the same external dimensions as the first detector tested. X-ray radiographs of both detectors were made following the practice of Henth (1964) to reveal their internal construction.

3 Results and discussion
Graphs of the variation in detection efficiency with distance were drawn for each position on the detectors. From these graphs, the efficiency contours around each detector were obtained and these are shown in figure 1. The position of the sodium iodide crystals within their canning material was determined from x-ray radiographs (figure 2).

The contour maps show that detector A is considerably more sensitive at the end face position than detector B, the distance from the canning material to the 9% contour being...
Notes on experimental technique and apparatus

Figure 2 X-ray radiograph of the detectors A and B respectively

3 mm and 1 mm respectively at the centre. Along the detector side, however, A is slightly less sensitive than B, the maximum distances of the 9% contour from the canning material being 2 mm and 1 mm in this case.

A study of the x-ray radiographs of the sodium iodide crystals in their cans (figure 2) shows good agreement between the actual crystal positions and the observed results.

Crystal A is longer than B and the crystal material ends much closer to the canning material at the end face, accounting for the increased sensitivity at this position. As would be expected, the distance from the 9% contour to the crystal itself (measured from the photograph) was found to be the same in each case (7.5 mm at the centre). Little difference can be seen in the photograph between the detectors along the crystal sides to account for the observed differences in sensitivity, crystal B appearing to be only marginally nearer the canning material than A. The distance at the point of maximum sensitivity from the 9% contour to the crystal was again found to be the same (4 mm) for the two crystals. From a consideration of the solid angle of crystal material subtended by a radiation source at various points, the positions of greatest sensitivity occur at the centre of the end face and at the midpoint of the actual crystal side as observed.

As a result of these studies, the increased sensitivity of A in the end face position is utilized in the counting of irradiated solid samples delivered by the pneumatic sample transfer system from the authors' neutron generator. Detector B is in use in the authors' liquid loop activation system, and clearly, in practice, the winding of detector cell coils should follow the contour shape. For efficient winding, the marked reduction in counting efficiency as the edge is approached, shown by the contour map, indicates there is little advantage in winding coils nearer than 20 mm from the edge in the initial layers.

4 Conclusion

It has been shown that in the winding of a detector cell on to a NaI (Tl) detector assembly, efficient construction and design is considerably aided by reference to the efficiency contours around the detector.

The differences observed between the two nominally identical detector assemblies show the desirability for x-ray photographs of detectors to determine the crystal location within, before detectors are used for a particular application.

Acknowledgments

One of the authors (C.C.H) wishes to thank the Science Research Council for their sponsorship.

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FAST NEUTRON ACTIVATION ANALYSIS OF TRACE LEVELS OF LEAD IN A NON-AQUEOUS FLOWING SYSTEM
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Accepted 22 April 1971

A system has been developed for the fast neutron activation analysis of lead in non-aqueous solution using the product isotope $^{207}\text{Pb}^{(T = 0.80 \text{ sec})}$. The determination of lead down to trace levels has been shown to be both feasible and reproducible. The method has been successfully applied to a practical example, namely the determination of the lead content of petrol.

INTRODUCTION

Neutron activation analysis of flowing systems, particularly as an aid to process control, was first suggested by Anders\(^1\) in 1962. The fundamental techniques involved in the activation analysis of flowing streams have been investigated by a number of authors, who have also demonstrated the feasibility of the analysis of a variety of elements in solution. Although few publications have dealt with activation analysis in non-aqueous flowing systems, the advantages of a non-oxygen containing solvent which gives a marked reduction in interferences from solvent activation have been reported by the authors elsewhere.\(^2\)

The current investigations are concerned with the extension of the techniques developed by the authors, to the determination of trace levels of lead in non-aqueous flowing
solutions, using the product isotope $^{207m}_{\text{pb}}$ with $T = 0.80$ sec. It was clear that this short half-life would create a number of problems. In order to minimise decay during transit between irradiation and detection cells the latter would have to be located as close as possible to the biological shield. This in turn would mean that very special attention would have to be devoted to the shielding around the detector cell in order to minimise background radiation. In the event the solution of these problems enabled the feasibility of the determination of trace levels of lead in non-aqueous solution to be demonstrated.

EXPERIMENTAL

A Kaman 1003A fast neutron generator capable of generating $10^{11}$ n sec$^{-1}$ and a 75 x 75 mm NaI/Tl/ cylindrical crystal detector assembly coupled to a Laben 400-multichannel analyser, were used in these investigations. The neutron output of the generator was monitored with a boron trifluoride counter en­cased in a polythene cylinder, and placed at a distance of 1 m from the target. This was coupled to a scaler and a ratemeter linked to a fast pen recorder.

The flowing system used in these investigations consisted of a stainless steel solution reservoir connected via nylon pipe­work to irradiation and detection flow cells. A high capacity rotameter and needle valve, placed in the pipework after the detection cell, enabled a wide range of steady flow rates to be maintained. Solutions were forced round the system by nitrogen gas pressure and a stainless steel waste reservoir completed the system.
All joints were secured by pressure couplings, and nylon tubing /6.5 mm internal diameter/ was used throughout, except for the pipework connecting the irradiation and detection cells. Here, narrow bore /3.5 mm internal diameter/ pipework was used. Positioning the detector and detection cell near to the concrete shielding of the neutron generator allowed the length of narrow bore tubing to be reduced to 2.5 m, thus minimising solution decay during transit between the cells. The size of narrow bore pipework adopted is governed by the maximum pressure that may be applied to the system. In this case a flow rate of 58.3 ml sec$^{-1}$ was obtained with a gas pressure of $5.9 \times 10^5$, Nm$^{-2}$, giving a minimum transit time of the order of 0.4 sec. The application of higher pressures was considered unsafe due to the risk of an irradiation cell burst with serious consequential damage to the neutron generator.

The irradiation cell /109 ml/ was of soldered brass construction, cylindrical in section /100 mm diameter, 20 mm deep/ and fitted with copper inlet /10 mm i.d./ and outlet /5 mm i.d./ pipes.

The cell contained a single brass spiral /1 mm thick/ designed so that liquids entered the cell at the side, spiralled into the centre, leaving the cell through the bottom. The demountable cell bottom was sealed by a nylon gasket, the cell being bolted together between steel plates. A hole in the top plate, machined to fit the generator target cooling jacket, provided positive location and relocation of the cell. The design of the cell ensures a definite flow path for irradiated liquids, and liquids leave the cell in the region of maximum neutron flux.
A detection flow cell /117 ml/, was made from annealed copper tubing /6 mm internal diameter/, wound around a former, machined to crystal detector dimensions and soldered into position. The detection cell and detector were housed in a lead cave 350 x 350 x 330 mm /wall thickness 100 mm/. As expected owing to the close proximity of the neutron generator /2.5 m/ an unacceptable increase in background radiation was observed during neutron irradiation. The main feature of the $\gamma$-ray spectrum of this background was a broad peak over the energy range 0.4 - 0.5 MeV. This was assigned mainly to the isotope $^{24}$mNa, $/T = 20$ ms/, $\gamma$-energy 0.47 MeV, produced by thermal neutron activation of the sodium in the crystal. The generator induced activity was reduced by a factor of ten, with the adoption of a shield consisting of thermal neutron absorber and neutron moderator. The detector was fitted with a thin cadmium sleeve /0.5 mm/, the lead case was infilled with boric acid, and then surrounded by water shielding /100 mm/. The final shielding consisted of a layer of polythene chippings /100 mm/ surrounding the water shield.

In these investigations, irradiation at a steady neutron flux was practised with the subsequent counting of the "satura-
tion" level of activity in the solution. Except at the limit of detection of lead, 30 sec irradiations were found to be adequate.

The total BF$_3$ count recorded during each irradiation was used as a measure of the total number of neutrons passing through the irradiation cell.

Fast neutron irradiation of hydrocarbons will produce the positron emitter $^{13}$N $/T = 50$ sec/, from the proton recoil re-
action $^{13}\text{C}/p,n/^{13}\text{N}$. In practice, with the high flow rates used in these investigations, only very low levels of $^{13}\text{N}$ activity were observed because the short solution residence times in the irradiation and detection cells are unfavourable for the production and detection of relatively long half-life isotopes.

A standard solution of lead in kerosine /4000 ppm Pb, as tetraethyl lead/ was prepared and irradiated over a range of flow rates on the flowing system, to investigate the variation in product isotope, activity with flow rate. Subsequently the variation in activity with lead concentration, and the limit of detection, were determined.

The nuclear reaction used was:

$$^{208}\text{Pb}/n,\ 2n/^{207}\text{Pb}$$

\[ \sigma = 9.90 \pm 12.0 \text{ mb} \]

\[ T = 0.80 \text{ sec} \]

\[ \gamma\text{-ray energies} = 0.57, 1.06 \text{ MeV}. \]

Finally, as a practical test of the technique and system, an attempt was made to determine the lead content of a sample of 98 octane petrol.

RESULTS AND DISCUSSION

All measurements were made on the 1.06 MeV photopeak of $^{207}\text{Pb} /0.95 - 1.20 \text{ MeV}/$, and are expressed as the photopeak activity divided by the total BF$_3$ count recorded during the irradiation. Corrections were made for background, kerosine activity, and for extraneous neutron generator induced activity.
The results obtained for the investigation of activity with flow rate are shown in Fig. 1. Reproducibility was within counting statistics, and varied between 2 and 4 per cent at the higher flow rates investigated. A smooth curve would be expected with a maximum at the optimum flow rate for the determination of the element, representing the best compromise between irradiation and detection efficiency against decay time in transit. Clearly the curve shows that the highest flow rate attainable on the present system is incapable of exceeding the optimum flow rate for a 0.80 sec half-life.

The investigation of the variation of solution activity with lead concentration gave a straight line calibration graph. A detection limit of 20 ppm Pb /100 s irradiation at $8.5 \times 10^{12} \text{n} \text{cm}^{-2} \text{sec}^{-1}$, and reproducible to within ±10% was obtained, this being within counting statistics. This detection limit was based on the criterion that the $^{207m}\text{Pb}$ activity was equal to twice the combined kerosine and neutron generator induced background. Clearly the detection limit is not linearly dependent on neutron flux.
A typical spectrum obtained from the irradiation of 98 octane petrol on the flowing system is shown in Fig. 2. The reproducibility of the results was ±3%, and indicated a lead content of 970 ± 30 ppm. The maximum permissible level of lead in U.K. petrol, is given as 0.84 g/litre, i.e. 1100-1200 ppm. Little or no interferences are visible in the spectrum, other than that from $^{24m}$Na. The relatively large backscatter peak is presumably due to the cadmium and copper in close proximity to the detector.
CONCLUSION

The determination of lead down to trace levels in non-aqueous flowing systems has been shown to be both feasible and reproducible. The rapid transit time between irradiation and detection makes the technique less susceptible to errors caused by neutron flux variation during each irradiation.

The analysis of the relatively high level of lead in petrol could be accomplished without significant interferences even at low neutron outputs, and this may be of interest in atmospheric pollution control.

One of the authors C.C.H. wishes to thank the Science Research Council for their sponsorship.

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