Determination of 36Cl and other long-lived radionuclides in decommissioning concrete wastes

Determination of ^{36}Cl and Other Long-Lived Radionuclides in Decommissioning Concrete Wastes

by

Linda Ashton

A Doctoral Thesis submitted in the partial fulfilment of the requirements for the award of

Doctor of Philosophy

of the Loughborough University October 2000

Research Supervisor: Professor P. Warwick

ABSTRACT

The decommissioning of nuclear power stations will lead to the production of a number of contaminated components. The materials produced will consist of process and structural wasteforms. Before this waste can be disposed it will be necessary to obtain a full inventory of those radionuclides contained in those wastes. This will be necessary to ensure that the waste is handled in a suitable manner and that full information is available so that reliable risk assessment can be carried out on the proposed disposal site.

A number of radionuclides have been highlighted as significant in terms if their half-life, terrestrial mobility and predicted levels in decommissioning wastes.

A selection of these radionuclides have been investigated, and methods developed for their determination in concrete.

It was a requirement of this work that the methods developed were robust and that the minimum detectable amount was below that of the de minimis of 0.4Bq g^{-1}.

ACKNOWLEDGEMENTS

I would like to thank a long list of people for their time, effort and encouragement. Tony Hall and Peter Warwick for their guidance and support whilst I was involved in the Environmental Research Group at Loughborough University.

I would also like to thank a variety of people whom I worked alongside including, Samantha King, Helen Carter, Karen Verrall and Sarah Stephens. Special thanks go to Linda Sands for her inspiration and belief, Mark Sutton for his specialness, minty breath and Captain Germany Tales, and Vanessa Pashley for bouffant hair and glass sharp wit.

Amongst the other people who helped me through include, Sonia, Jill, Dave, Di, Mike, Sandra, John and Gordon who all provided light-hearted relief and assistance when things did not go to plan.

I would like to express my gratitude to all those at Magnox, who have provided their time and assistance, special thanks to Colin Harvey and David Giddings for advice and support.

I would also like to thank Canberra Packared and Eicrom Industries Ltd for all their help and free samples for 'feasibility studies', Liz, Michaela and Lesley you have no idea how much time, effort and money your generousity has saved.

Special thanks to my family who have supported and inspired me, you are all so incredibly special.

Finally thanks to Lee, you have always been my inspiration, my shoulder to cry on and my friend. Thank you for believing in me, supporting me and making me aspire to be something that I never thought I could be.

ABBREVIATIONS

AGR	Advanced Gas Reactor
AES	Atomic Emission Spectrometry
AMS	Accelerator Mass Spectrometry
HGW	Heat Generating Waste
HLW	High Level Waste
HPLC	High Performance Liquid Chromatography
ICP-AES	Inductively Coupled Plasma Atomic Emission Spectrometry
ICP-OES	Inductively Coupled Plasma Optical Emission Spectrometry
ILW	Intermediate Level Waste
LLW	Low Level Waste
LSC	Liquid Scintillation Counting
MDA	Minimum Detectable Amount
MS	Mass Spectrometry
NAA	Neutron Activation Analysis
OA	Oxidising Agent
ppt	Precipitate
PWR	Pressurised Water Reactor
RA	Reducing Agent
TBP	Tri-butyl phosphate
TnOA	Tri-n-octylamine
TWH	Tera Watt Hours
(v/v)	volume to volume
(w/v)	weight to volume

The question should be, is it worth trying to do, not can it be done.

Allard Lowenstein

CONTENTS

LIST OF TABLES

LIST OF FIGURES

1.0 Introduction

1.1 History

Although nuclear research came about due to the military efforts associated with World War II, it soon became apparent that there was potential to modify and control the release of energy from a nuclear device. If the energy release, which is primarily in the form of heat, could be controlled, then it would be possible to generate steam, run turbines and ultimately generate electricity. Consequently, technologies that had been developed in an offensive manner could now be used to help communities recover after the onslaught of war.

On the 27th of August 1962 the first Magnox nuclear reactor came on line and started providing electricity to the National Grid. The power station located near the small village of Berkeley in Gloucestershire was the first commercial nuclear power station in the country. It had been built in 5 years and had utilised much of the science and technologies developed within the Manhattan project.

Due to the circumstances surrounding the implementation of the nuclear power programme, there was little consideration as to what would happen once the station had ceased electricity production. These ventures were at the forefront of scientific knowledge and consequently issues such as time-scales, costs and environmental concerns were not fully realised nor understood. Since this research was unsubstantiated by previous work a lot of the original time scales were improvised and an arbitrary time chosen. Originally, Magnox power stations were commissioned for 25 years. However, due to the excellent engineering and maintenance programmes many stations had there lives extended for a further 25 year period.

There are a number of considerations that will affect the operational life time of a nuclear power station. As well as scientific considerations such as graphite

embrittlement or reactor integrity, political and social attitudes will also influence the final outcome.

After 27 years of power production totalling 40TWh, Berkeley power station was brought off-line in 1989. The power station is now well on its way through the decommissioning process.

Currently there are 4 nuclear power stations being decommissioned, these being Hinkley A in Somerset, Berkeley in Gloucestershire, Trawsfynnyd in Wales and Hunterston A in Scotland. All four power stations are of the original Magnox type. Other reactor designs have also been implemented, these being Advanced Gas Reactors (AGR) and Pressurised Water Reactors (PWR). However, at the present time, all of the stations based on the AGR and PWR design are still operational and as of yet there has been no decommissioning date set.

1.2 Reactor design

In Britain there are three commercial reactor designs. Originally, power stations were built around the Magnox type reactor, later with the advancement of technologies, design strategies were modified. This led to the commission of the Advanced Gas Reactors (AGR) and Pressurised Water Reactors (PWR).

1.2.1 Magnox reactors

In a Magnox reactor, uranium metal is used as the fuel. The uranium is not enriched, that is, the uranium composition in the fuel is identical to that of the ore it was produced from (typically 0.7% ^{235}U). The uranium metal is then machined into a rod and placed into a canister made from a magnesium aluminium alloy, this is how the reactor got its name Magnox (MAGnesium No OXidation). This canister is often called the fuel cladding. The shape and dimensions of these fuel elements will differ for each power station.

In a Magnox reactor, the heat created from the controlled nuclear reaction is transferred from the reactor core to the heat exchangers (boilers), using pressurised CO_2. These heat exchangers are located outside the concrete shield. Within the boilers, steam is generated which powers the turbines; this in turn then generates the electricity.

1.2.2 Advanced Gas Reactor (AGR)

An AGR runs at higher fuel and gas temperatures than a Magnox reactor [1]. Consequently, Magnox fuel cannot be used since it cannot generate the heat required for an AGR. The uranium fuel that is used in an AGR, must be enriched. Consequently, the percentage of fissile uranium (^{235}U), in the fuel will be increased. AGR's typically require a fissile ^{235}U content of about 3% [1], although this will vary from station to station. After the fuel has been enriched it is converted to UO_2 pellets, these pellets are then loaded into a stainless steel tube to form a fuel pin. The fuel pins are then assembled to create the fuel element.

The basic principles of the Magnox reactor also apply to the AGR. However the AGR runs at higher gas and fuel temperatures, this in turn increases the efficiency within the steam cycle. The coolant used within an AGR is CO_2, however since the boiler is located inside the concrete pressure vessel the CO_2 is at an elevated gas temperature as compared to the Magnox system.

1.2.3 Pressurised Water Reactor (PWR)

The PWR also uses enriched uranium as fuel, generally 3% fissile material is required. In a PWR, UO_2 is also used as the fuel, however the pellets are loaded into a zirconium alloy (Zircaloy) tube to form the fuel pins. The fuel pins are then assembled into a square lattice to create the fuel element.

In a PWR the heat transfer media is pressurised water. Water acts as both a reactor coolant and a neutron moderator. The efficiency of the PWR is greater than both that of the AGR and the Magnox reactor. In a PWR the actual reactor size is

considerably smaller than either a Magnox or an AGR, however the neutron flux is considerably higher [2].

Although the modifications between each reactor type may seem small, these alterations have significant effects on the waste output. Different materials are used to house the fuel; consequently the components within the activated fuel cladding will differ greatly from a Magnox station as compared to an AGR and PWR. The reactor coolants are also different, this in turn will lead to different contamination 'fingerprints' across the station. Consequently, it is not possible to treat the three systems as identical, in fact there is such variation within each design that each power station has to be considered individually. Throughout the lifetime of the station waste will be produced. This waste will differ significantly in radionuclidic content, activity and form. Understanding reactor design, purpose of materials used, and origin of waste makes it possible to categorise this waste. It is realistic to assume that areas that have direct contact with the fuel, such as the fuel loading bay and the cooling ponds will potentially be contaminated with fission products. However this can only be used as a guide, a full detailed inventory will require not just total activity, but also a breakdown of each constituent; *i.e.* a list of all those radionuclides contained in the inventory and the levels of activity associated with each radioisotope. Consequently, the waste will have to be analysed by both chemical and mathematical means, before a true assessment of the nature of the waste can be obtained.

1.3 Types of waste

Waste will generally fall into two categories. Firstly, waste which is produced whilst the power station is producing electricity and, secondly, waste that will be produced once the power station has been closed and the station is following the decommissioning programme. The wastes will be either classified as operational or decommissioning wastes.

1.3.1 Operational waste

Once the power station is on-line contaminated waste will be produced. Operational waste will consist of many different components. Over time the fuel will become contaminated or poisoned by certain products in the reactor, this will lead to a decrease in the rate of heat generation. Consequently the poisoned fuel rods must be replaced with fresh fuel. However, contained within the poisoned fuel is viable nuclear material. Policy within the U.K. has recommended that this spent fuel is reprocessed. In doing so, the detrimental components in the fuel are removed and the fuel can then be used again. This reprocessing procedure reduces the amount of raw material required (uranium ore). However, significant volumes of highly activated waste are produced. Virtually all stocks of High Level Waste (HLW) in the U.K. are generated as a result of the reprocessing programme. Routine maintenance procedures such as pond cleaning will generate a variety of activated wastes including filter resins and paper towels. The way in which this waste is treated and handled depends upon the characteristics of the waste including the matrix type and associated activity.

1.3.2 Decommissioning waste

Once the power station is being decommissioned the nature of the waste will change. Decommissioning waste will primarily consist of building materials and larger plant items. The waste will be contaminated by a variety of different contaminants. The extent of this contamination will depend upon a number of factors including the matrix characteristics, type of exposure, and contact time. During the decommissioning programme the majority of waste produced will be of low activity, consequently a substantial proportion of the decommissioning waste may be disposed of either by landfill routes or in the low level waste repository at Drigg in Cumbria. However, before either of these routes are used it must be shown that the waste meets the requirements to be handled in such a manner.

1.4 Classification of waste

The waste generated during the operation and decommissioning phase of the reactor will need to be classified. This classification will determine how the waste is to be treated and disposed.

1.4.1 Low Level Waste (LLW)

Currently, Britain has a disposal facility at Drigg in Cumbria. At this site, waste that is classified as low level waste (LLW) is disposed. Before waste can be disposed of in this manner, a full inventory associated with that waste is required. If waste is to be disposed as LLW it needs to fulfil certain requirements. The waste activity must be less than 12GBq/t (γ,β) and less than 4GBq/t (α) [1]. Other criteria include limitations on fissile content. It is envisaged that over 90% of LLW will be generated whilst the power station is being decommissioned. The other 10% having been formed over the operational lifetime of the station.

1.4.2 Intermediate Level Waste (ILW)

Waste that has an activity greater than 12GBq/t (γ,β) and no heat generating capacity, is classified as intermediate level waste (ILW). There is at the present time, no designated storage/disposal facility for ILW. The waste is currently stored on the originating site. Many processes will lead to the generation of ILW, these include reprocessing and general maintenance of the power plant. It is estimated that approximately 55% of all ILW will arise during the decommissioning of the power station, the remainder being generated during the operational phase. Establishment of a facility for the purpose of storing/disposing ILW will require an accurate inventory detailing the constituents contained within the waste.

1.4.3 High Level Waste (HLW)

High level waste (HLW) is also termed heat generating waste (HGW). The majority of HLW is generated whilst the power station is operational. The principal components of HLW are nitric acid solutions, which contain a high level of fission products. These solutions are generated during the primary stage of reprocessing. For safety, some of this material has been immobilised in a glass matrix. During

decommissioning it is expected that no HLW will be generated. Currently there are no facilities available within the U.K. to store/dispose of HLW. Presently all HLW is stored at the place of origin (Sellafield). If, however a facility became available to dispose/store HLW, an accurate assessment of the components contained within that waste would be required.

1.5 Decommissioning strategy

The deferred safestore strategy is the approach that is currently under consideration in the U.K. The strategy involves the implementation of a three-stage plan. Initially 99% of the activity shall be removed from the reactor by simply removing the fuel. However, the 1% of activity that remains would still give an unacceptable dose to construction staff. Consequently the approach has been adopted, whereby the site will be left in a secure manner so that the levels of radiation are allowed to decrease to a more acceptable level via radioactive decay.

Initially during stage 1, the fuel from the reactor will be removed, thereby removing over 99% of the activity. This fuel will be removed from site and will be vitrified or reprocessed. A plan of care and maintenance will be implemented to ensure the integrity of the equipment and buildings on site.

Stage 2 of the safestore strategy will involve the dismantling of some of the plant and buildings. A safestore construction will be erected to ensure that all active equipment and materials are secure and safe from the elements. A care and maintenance plan will then be put into effect to ensure that the safestore remains weatherproof and intact.

Stage 3 will involve the complete dismantling of the safestore and the buildings within it. The full dismantling of the station will occur ~125 years after the station shut down.

1.5.1 Characteristics of waste at each stage

During stage 1 of the programme highly active wastes such as fuel from the reactor and activated ion exchange resins and sludges will be removed from the pond areas. These forms of waste will be highly contaminated with fission and activation products.

Decommissioning wastes generated at stage 2 of the programme will primarily consist of structural materials and plant equipment from areas in close proximity to the reactor. It is expected that the waste will be of relatively low activity. The waste will be dominated by activation products.

During the final stage of the decommissioning programme, the waste will consist of building materials and plant equipment from all areas of the power station. The waste will generally consist of LLW and some ILW. Long-lived activation products such as ^{36}Cl and ^{94}Nb may feature significantly in many ILW forms.

1.6 Man-made radionuclides in the environment

Man-made radionuclides are formed by fission of the uranium in the nuclear device, whether by a nuclear detonation or in the nuclear power reactor. These products are referred to as either activation products or fission products. A number of events have resulted in the presence of activation and fission products in the environment. During the 1950's and the early part of the 1960's a significant amount of radioactivity was released into the environment due to the atmospheric testing of nuclear weapons. Nuclear accidents have also released considerable quantities of activity into the atmosphere, the most significant being Chernobyl in 1986 [3]. Small amounts of activity are also discharged routinely from nuclear power stations, hospitals and academic research institutes.

1.6.1 Radionuclides in decommissioning wastes

Many of the radionuclides expected to be found in decommissioning wastes will be formed by either activation of the parental element, or as a consequence of nuclear fission.

The principle isotope of U used to generate heat is ^{235}U. In the reactor, this isotope may capture a neutron to form ^{236}U. This species is unstable and will decay to produce a number of fission products, γ photons, heat, neutrinos and 2 to 3 neutrons. It is as a consequence of this process that radioactive components are formed.

$$^{235}U \xrightarrow{n} {}^{236}U \xrightarrow{\text{spontaneous fission}} FP^1 + FP^2 + FP^3 + \upsilon + \gamma + energy + 2-3 neutrons$$

Where FP^1 = mass 90-101

FP^2 = mass 132-143

$FP^3 = {}^3H$

Fission product radionuclides

In the reactor the fissile material, ^{235}U may absorb a neutron. If this occurs, there are then a number of events which may then take place. The species formed may spontaneously split into a number of components, this process will also lead to neutrons being released into the system. These components, called fission products, will be radioactive, generally the fission products formed will be of the mass region 90-101 and 132-143 [4]. It is in this manner that ^{129}I is formed. In the fissioning of uranium, approximately 100 different radionuclides are produced. Typically radionuclides formed by fission processes will decay by γ or β emission. However, if ^{238}U absorbs a neutron, another category of species will be formed, these are called the transuranic radionuclides.

Transuranic radionuclides

All nuclear reactors will contain ^{238}U, this species will absorb neutrons of specific energy to form ^{239}U. This product is radioactive and will decay by β emission to

^{239}Np. This nuclide is also unstable and further β emission leads to the formation of ^{239}Pu.

$$^{238}U \xrightarrow[t_{\frac{1}{2}}]{n} {}^{239}U \xrightarrow[23.5m]{\beta-} {}^{239}Np \xrightarrow[2.35d]{\beta-} {}^{239}Pu \xrightarrow[2410y]{\alpha} {}^{235}U$$

These products are called either *actinides* or *transuranic elements*, and is the term applied to all elements that have an atomic number greater than 89 [5]. All of the actinides are radioactive and the majority decay by α emission. They therefore must be taken into account when considering safety and disposal because of their mode of decay and relatively long half lives (typically, many thousands of years). Consequently, actinides if released into the environment will be present for significant periods of time.

Neutron activated radionuclides

In a nuclear reactor the atomic nuclei of the uranium compound, formed when ^{235}U captures a neutron, is unstable. Consequently, neutrons will be ejected from the nucleus spontaneously, resulting in a more stable nucleus configuration. Some of the neutrons released from the nucleus will encounter other ^{235}U nuclei and the reaction will be self-propagating. However, some of the neutrons will be absorbed by non-fissile material. All materials that have been exposed to high neutron flux for extensive periods of time will become contaminated with active products in this manner. The concrete reactor shield is a typical area. Here components within the concrete matrix will become activated, this may lead to instabilities within the nucleus. To regain a stable configuration particles/energy may be released from the activated nucleus. Many components inherent in concrete will become activated by this mechanism. These include calcium, chlorine and samarium. These parent species will lead to the formation of ^{41}Ca, ^{45}Ca, ^{36}Cl and ^{151}Sm. Generally the species formed will decay by γ and β emission.

Many factors will need to be assessed to determine the significance of the radionuclidic species, including the half-life, the mode of decay and the contribution

to the inventory. Table 1.1 shows a list of some of the radionuclides that are considered radiologically important.

Table 1.1 Radiologically important radionuclides

	Radionuclide	Half-life	Fission yield %	Major decay mode
Activation products	C-14	5715y	-	β
	P-32	14.3d	-	β
	S-35	87.2d	-	β
	Cl-36	300000y	-	β
	Ca-41	103000y	-	E.C
	Ca-45	162.7d	-	β
	Cr-51	27.7d	-	E.C
	Mn-54	312d	-	E.C
	Fe-55	2.7y	-	E.C
	Co-58	70.8d	-	β
	Fe-59	44.5d	-	β
	Co-60	5.3y	-	β
	Ni-63	100y	-	β
	Mo-93	3500y	-	E.C
	Nb-94	24000y	-	β
	Zn-65	244d	-	β^+
	Ag-110m	250d	-	β
	Sm-151	90y	-	β
	Ho-166m	1200y	-	β
Fission Products	H-3	12.4y		β
	Kr-85	10.8y	0.29	β
	Sr-89	51d	4.79	β
	Sr-90	29.1y	5.77	β
	Zr-93	1500000y	6.45	β
	Nb-94	24000y	6.13	β
	Zr-95	64d	6.20	β
	Tc-99	213000y	6.32	β
	Ru-106	369d	0.38	β
	I-129	17000000y	0.8	β
	I-131	8d	3.1	β
	Xe-133	5.3d	6.62	β
	Cs-137	30y	6.15	β
	Ce-144	284d	6.00	β
	Pm-147	2.6y		β
	Sm-151	90y	0.44	β
	Eu-154	16y	0.08	β
Transuranic Products	Pu-238	88y	-	α
	Pu-239	24100y	-	α
	Pu-240	6600y	-	α
	Pu-241	14y	-	β
	Am-241	433y	-	α
	Cm-244	19y	-	α
	Np-237	2200000y	-	α

Removing those radionuclides that have relatively short half-lives (<5 years) has further refined this list. The revised list is displayed in Table 1.2. Radionuclides that are particularly relevant to decommissioning wastes are shown in bold.

Table 1.2 Radiologically important radionuclides with $t_{1/2}$>5 years

	Radionuclide	Half-life	Fission yield %	Major decay mode
Activation products	C-14	5715y	-	β
	Cl-36	**300000y**	-	β
	Ca-41	**103000y**	-	**x-ray**
	Co-60	**5.3y**	-	β
	Ni-63	100y	-	β
	Mo-93	3500y	-	β
	Nb-94	24000y	-	β^+
	Sm-151	**90y**	-	β
	Ho-166m	**1200y**	-	β
Fission products	**H-3**	**12.4y**		β
	Kr-85	10.8y	0.29	β
	Sr-90	29.1y	5.77	β
	Zr-93	1500000y	6.45	β
	Nb-94	24000y	6.13	β
	Tc-99	**213000y**	6.32	β
	I-129	**17000000y**	**0.8**	β
	Cs-137	**30y**	6.15	β
	Sm-151	**90y**	0.44	β
	Eu-154	**16y**	0.08	β
Transuranic Products	Pu-238	88y	-	α
	Pu-239	24100y	-	α
	Pu-240	6600y	-	α
	Pu-241	14y	-	β
	Am-241	433y	-	α
	Cm-244	19y	-	α
	Np-237	2200000y	-	α

1.7 Safety Assessment

The adverse health affects associated with radiation have been understood for many years. It is known that exposure to high levels of radiation can induce cancers, genetic abnormalities, and, in extreme cases, instantaneous death. However, there is no 'safe' activity limit, therefore, any release can be considered as hazardous. Consequently, the levels of activity released into the environment are monitored closely. Monitoring this activity, relies upon methodologies available to determine

radiologically significant species in a number of different matrices. Accidental releases of activity have led to there being a comprehensive set of analytical methodologies available for those radionuclides associated with environmental materials, *e.g.* ^{137}Cs, ^{90}Sr and $^{239/240}Pu$.

It is a legal requirement that operational power stations must monitor waste that is produced. Consequently, there exists a programme of work where operational waste is analysed to ensure that it is handled, treated and disposed of using adequate procedures. Within the next decade, large amounts of radioactive waste will arise with the dismantling of redundant nuclear power stations. Before this waste can be disposed of in a safe and responsible manner, it will need to be analysed and categorised. Therefore, it will be necessary to develop methods by which the waste can be analysed and an accurate and complete inventory thereby established.

For risk assessment after disposal, the information required includes the chemical nature of the element, the interaction of the chemical species with the immediate environment; (*e.g.* degradation products of packaging materials), interaction of the species with the near and far-fields and a reliable inventory, *i.e.* a detailed list of radionuclides contained within the waste and the activity associated with that waste.

Radionuclides that have short half-lives (<1 year) or those, which are strongly retained by the disposal barrier, will have decayed to insignificant levels by the time they reach the Geosphere. However, those radionuclides that have significant half-lives or those which have enhanced mobility through the terrestrial environment, may pose a significant radiological hazard once they reach the Geosphere. Consequently, it is those radionuclides that have appreciable half-lives and increased mobility in the environment, which dominate safety case disposal strategies. Nuclear Industries Radioactive Waste Executive (Nirex) data has been used to compile a list of radionuclides that are considered to be radiologically significant. This list features a number of radionuclides including ^{36}Cl, ^{99}Tc, ^{129}I, ^{151}Sm and ^{166m}Ho. Currently, mathematical data are relied upon to forecast the extent to which these radionuclides are present in nuclear waste.

However, to gain greater confidence, analytical methodologies are required. It is only then, with accurate and reliable data, that a safety case for the disposal of decommissioning waste can be made with any degree of confidence.

Although there is extensive information available with regards to the chemical nature of many of the elements found in decommissioning wastes, there are areas where information is scarce. Consequently, this lack of information leads to uncertainties within the disposal scenario, this in turn introduces the possibility of inaccuracies being incorporated into risk assessment strategies.

1.8 Radionuclides of special interest

Nirex data has been used to select those radionuclides that warrant detailed investigation with regards to developing analytical methodologies to determine their content in decommissioning wastes. A number of factors have been considered, including the half-life, mode of decay, and extent of production. Using this rationale, ^{36}Cl, ^{99}Tc, ^{129}I and the lanthanides, ^{151}Sm and ^{166m}Ho are considered to be of significant radiological importance. Therefore these radionuclidic species have been investigated.

Although decommissioning wastes will consist of a variety of different matrices, for this study, concrete wastes have been selected for further investigation. Since chloride and samarium are associated with concrete there is a strong possibility of finding their activated components contained within the waste form. Areas within the plant that have contact with the fuel routes may also be contaminated with fission products, such as ^{99}Tc. Although the majority of concrete waste will be of low activity, it would be impractical to store all concrete waste arisings. Consequently that waste that is not in contact with either the reactor or fuel, and has not been contaminated will be analysed, and if below the de-minimis (0.4Bq g^{-1}), will be disposed of as general waste [1]. Waste that has come into contact with the reactor, or activated by-products of the fuel, may be contaminated. However the extent of this contamination will vary. For both environmental and financial considerations it

is necessary to analyse and categorise this waste. Suitable measures will then be taken to dispose of that waste that meets the requirements for disposal at Drigg. Wastes that are not suitable for transfer to the Drigg repository will remain at the originating site.

Those radionuclides that have been selected for more thorough investigations are shown in Table 1.3.

Table 1.3 Radionuclides selected for further investigation

Isotope	Half-life	Principal route of production	Principal mode of decay	Associated emissions
^{36}Cl	300,000y	Activation	β emitter 710keV	-
^{99}Tc	213,000y	Fission	β emitter 293keV	-
^{129}I	17,000,000y	Fission	B emitter 191keV	Xe k X-ray, 0.0396Mev
^{151}Sm	90y	Activation/Fission	β emitter 76keV	0.02154MeV (<1% intensity)
^{166m}Ho	1,200y	Activation	β emitter 70kev	Er k X-ray 0.184MeV

The occurrence, properties and current analytical methodologies are discussed in sections 1.10 through to 1.13.

1.9 Radioanalytical considerations

From Table 1.3, it can be seen that ^{36}Cl and ^{99}Tc have no associated γ emissions, consequently it is impossible to determine the activity of either ^{36}Cl or ^{99}Tc in a sample by non-destructive counting techniques. Therefore, the activity in the sample must be determined using β counting techniques such as liquid scintillation counting, (LSC) or β proportional counting. When assessing methodologies for the determination of β emitters, a number of factors must be considered. Firstly, the sample should be as chemically pure as possible. Secondly, because the activity in the sample may be low, it may be necessary to take large sample sizes so that the total amount of activity is quantifiable. Thirdly, the yield of the method must be

high, and finally the counting method should take into account not only the counting efficiency, but also the background signal, *i.e.* the figure of merit must be considered.

Although the other isotopes listed in the table have associated γ emissions, it is difficult to quantify low γ energies. Consequently, those materials that contain low energy γ emitting radionuclides will also have to undergo chemical separation and purification, since the identifying γ spectra may be 'drowned out' by more predominant γ emitting radionuclides, such as ^{154}Eu. The counting efficiency of a NaI detector is relatively poor (~3%), at low γ energies [Private Communication C.Harvey, Magnox 1996]. Consequently the minimum detectable amount will be compromised, however, use of a well-type detector will increase the counting efficiency to ~60%. Therefore, although it may be possible to determine ^{129}I, ^{151}Sm and ^{166m}Ho by their γ emissions, this is only possible if the sample is chemically pure. Consequently, materials containing these radionuclides will have to be purified and radiochemical interferences removed during the chemical analysis. Only in this way will it be possible to determine accurately the activity of these radionuclides in decommissioning wastes.

1.9.1 Possible radionuclidic interferents in decommissioning concrete wastes

The concrete matrix will consist of complex particulate matter. This waste form will become contaminated with radioactivity through either absorption of neutrons and the production of activation products, or because of direct contact with the fuel, whereby fission product contamination will result. Consequently, the material will contain a variety of radionuclides. Certain radionuclides feature significantly in all waste forms produced from the station. These products are generally high fission yield products such as ^{154}Eu, ^{137}Cs or activation products such as ^{60}Co. The half-life of these species (16y, 30y and 5y respectively) mean that they have an appreciable specific activity. Consequently, it is important that these isotopes are removed from the sample before counting since the activity from these isotopes would dominate the spectra and 'drown out' the activity from the analyte of interest.

1.9.2 Radioanalytical methodologies

If the analyte to be determined is a β emitter, it will be necessary to employ separation techniques. The final sample must be as chemically pure as possible, free from the bulk of the matrix and free from both chemical and radiochemical interference. There are a number of factors that need to be considered. The most important consideration (although, generally overlooked) is the nature of the yield monitor, sometimes termed the yield tracer.

1.9.3 Yield monitor considerations

It is now possible to obtain direct quantitative measurement of many radionuclides in bulk matrices, using computer assisted gamma spectrometry. However, there are a number of radionuclides that decay by processes that do not involve gamma emission, *e.g.* α,β decay or isomeric transitions. For these radionuclides it is generally not possible to measure their activity in the presence of the matrix. This is because the emissions are either severely degraded or absorbed by the matrix before detection occurs. At very low concentrations, even those radionuclides that emit gamma photons may be difficult to detect and quantify, due the interference of other components that may be present in the sample. Consequently, it is only possible to determine many radionuclides that are of low concentration after these elements have been separated from the matrix.

The chemical processes that must be undertaken to isolate the analyte in a chemically pure state so that identification and quantification are possible, can comprise of several stages. These stages are unlikely to be quantitative, and it is therefore necessary to have a means of determining the relationship between the amount of analyte detected in the sample and the amount originally contained in the sample. In practice this is achieved by adding a known concentration of substance, this is known as the yield monitor, and is used to quantify the recovery of the analyte of interest.

The success of the analytical methodology is heavily reliant upon the performance of the yield monitor. The yield monitor is relied upon to act in an identical manner to the analyte, at each stage of the analytical scheme. Although this may seem to be

easily achieved, it can in practice, be very difficult to obtain a reliable yield monitor. There are a number of criteria that a yield monitor must perform if it is to be used to gain information about the analytical process. An ideal yield monitor:

1) must have identical chemical properties to that of the analyte under investigation.
2) should attain equilibrium with the analyte early in the analytical procedure.
3) may be determined in the presence of the analyte.

These factors are discussed in greater detail below.

For many analyses, it is obvious that the most suitable yield monitor will be the stable element of the analyte to be determined, in this way the yield monitor also acts as an elemental carrier. However, there are a number of elements that have no stable isotope. This includes amongst others, all the transuranic elements, technetium and promethium. Obviously in these situations it is impossible to use a stable, chemically identical isotope. For many of these radionuclides it is possible to use a different isotope of the same chemical species. Although these isotopes have different physical properties *e.g.* mass, they have the same atomic number, and therefore, identical chemical properties. These physical differences such as decay process, or mass, may be used as yield monitors for each other, examples of this being ^{242}Pu is used as a yield monitor for ^{238}Pu, and ^{239}Np is used to monitor ^{237}Np. In both cases the chemistry is identical but both Pu isotopes decay by alpha emission. However, the emission energies of the process are distinctly different, and quantification is possible from the same spectra. The situation involving Np is slightly more complicated, here the yield monitor is a beta emitter, whilst the analyte of interest decays by alpha emission. In this instance the sample is initially alpha counted and then alpha/beta counted. The data are then mathematically manipulated to account for alpha contribution due to the ^{239}Np, counting efficiencies and decay (^{239}Np has a 2.3d half-life). In this manner, the yield monitor activity and therefore recovery of the analytical procedure can be determined.

During the analytical procedure, the chemical form of the analyte may change. At each of these stages there is a possibility that the analyte may be lost or only a proportion of the analyte will undergo the chemical alteration. Consequently, the yield monitor must be introduced at the earliest possible stage so that it can accompany the analyte through the majority of the analytical processes. In an ideal situation, the yield monitor should be added as an identical species to that of the analyte in the sample, however this is rarely achieved in practice since the speciation of the analyte in the matrix may be complex or even unknown.

The yield monitor employed in an analysis must be determined in a manner that does not compromise the quantitation of the analyte of interest, *i.e.* the assay of the yield monitor should not interfere with the determination of the analyte. However, in practice it is generally found that the optimum conditions are compromised. This may be due to spectral interference between the analyte and the yield monitor, the elemental relationship, or contaminant introduction to the sample from the tracer. Isotope dilution analysis is the optimum way in which to carry out a radiochemical analysis, however, in practice there are few analytical situations which can employ this analytical technique. In isotope dilution analysis, the yield monitor and analyte are chemically identical and the means of their determination in the sample is also identical. For the assay of many radionuclides true isotopic dilution analysis is not possible due to physical and chemical considerations. Table 1.4 summarises the relationship between the yield monitor and analyte.

Table 1.4 Relationship between analyte and carriers used in analytical chemistry schemes

Type	Determination		Elemental Relationship	Typical Example	
	Yield Monitor	Analyte		Analyte	Yield Monitor
A1	Alpha Spec	Alpha Spec	Same	$^{239+240}Pu$ ^{243}Am	^{238}Pu ^{241}Am
A2	Alpha Spec	Beta Count	Same	^{237}Np	^{239}Np
A3	Alpha Spec	Alpha Spec	Different	^{242}Cm	^{243}Am
B1	Beta Count	Alpha Spec	Same	^{241}Pu	^{236}Pu
B2	Beta Count	Gamma Count	Same	^{99}Tc	^{99m}Tc
B3	Beta Count	Gravimetric	Different	^{147}Pm ^{99}Tc	Stable Nd Stable Re
C1	X-ray count	Gravimetric	Same	^{55}Fe	Stable Fe
D1	Accelerator Mass Spec	Accelerator Mass Spec	Same	^{240}Pu ^{129}I	^{242}Pu ^{127}I
D2	Accelerator Mass Spec	Accelerator Mass Spec	Different	^{237}Np	^{242}Pu

From the table, it can be seen that only those analyses that fall into the A1 and D1 categories can be classified as true isotope dilution analysis. Although accelerator Mass Spectrometry (AMS) techniques have become more widespread in recent years, these techniques have their own drawbacks. There are several AMS's in the world, and limited facilities in the U.K. Consequently, it would not be feasible for this technique to be employed for the day-to-day analysis of samples such as those expected from decommissioning wastes. Although alpha spectrometry techniques can also be used for isotope dilution analysis, in the case of this work, it would be inappropriate since the radionuclides of interest are not alpha emitting species.

The ideal analytical yield monitor will satisfy the three criteria as discussed earlier. However, it can be seen from the table that several of the analytical schemes utilise a different element as a tracer, *e.g.* category B3. In this example, stable neodymium is used as the chemical tracer for promethium-147 (β emitter). These applications result when there is no suitable isotopic yield monitor. Although there are several isotopes of promethium, each has a number of practical drawbacks. Those isotopes that have a suitably long half-life (>1 year) are not readily available. At first glance it would seem that ^{148m}Pm would be an ideal yield monitor, since it also decays by beta emission. Consequently, use of this isotope as a yield monitor for ^{147}Pm would

result in the analysis being true isotope dilution. However, for beta emitting isotopes, isotope dilution analysis is not considered to be the most suitable approach. This is because of the nature of the beta spectra. Whereas an alpha and gamma spectra results in a series of discrete peaks that can be used to identify and quantify the analyte, a spectrum produced by liquid scintillation counting will result in a continuum spectrum that ranges from the E_{max} to the lower energies. Even for a pure beta emitter there will be substantial tailing. Consequently, it is impossible to use isotope dilution analysis techniques for β emitting radio-isotopes. The one special case is that of analysis of strontium. In this analysis ^{90}Sr is determined using ^{89}Sr, however the yield monitor uses a special type of beta counting called Cerenkov counting, whereas the ^{90}Sr is inferred from the counting of ^{90}Y by beta counting techniques. Figure 1.1 illustrates the spectral differences between radiometric spectra.

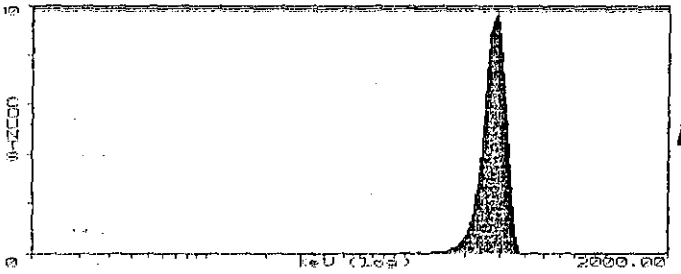


Figure 1.1a α spectra

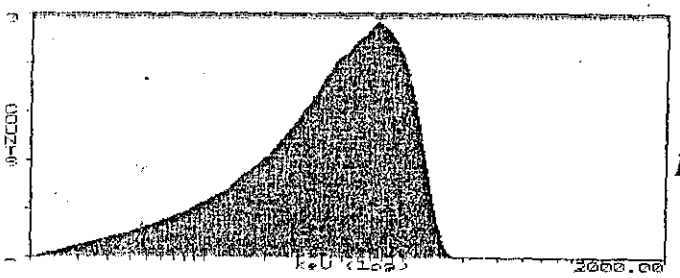


Figure 1.1b β spectra

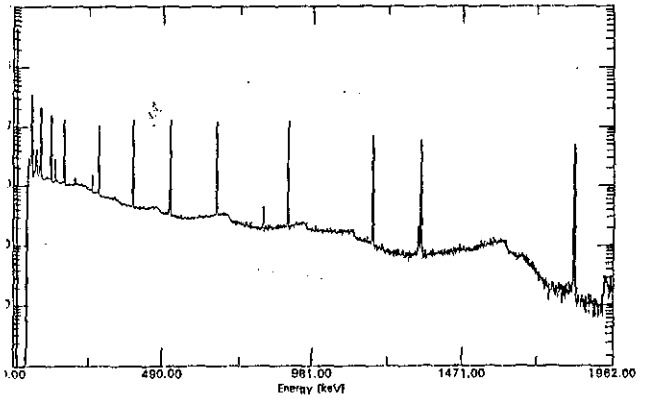


Figure 1.1c γ specra

Figure 1.1 Spectral characteristics of radioanalytical spectra

In those situations where non-isotopic yield monitors are used, there will always be some concern as to whether the yield monitor behaves in the same manner as the analyte. Consequently to ensure that the yield monitor is acting as a reliable tracer, it will be necessary to carry out extensive investigations to determine if the analyte and yield monitor follow each other through each stage of the analytical procedure.

Other factors will also influence which yield monitor is employed in the analysis. For those analyses that use a stable yield monitor the main consideration will be the way in which the analyte and tracer are determined. However, if the yield monitor is radioactive, there will be a variety of other factors that will require consideration. Not only must there be no interference, but the yield monitor should have a convenient half-life and be readily available at a suitable activity, and chemical/radiochemical purity.

1.9.4 General considerations

1.9.4.1 Digestion

Many analytical procedures will require some degree of dissolution (digestion), of the sample. This will enable the analyte of interest to be released from the matrix into the surrounding solution. The characteristics of the analyte of interest need to be considered when developing dissolution schemes, *e.g.* analytes that form volatile compounds will be digested differently to those species that do not form volatile compounds. However, the way the analyte is chemically isolated and purified from the bulk matrix will differ not only for different analytes, but also the same analyte in different matrices. Consequently, methods adopted are not only reliant on the analyte but also the sample matrix and sample size. Determination of an analyte in a simple matrix (*e.g.* groundwaters), will require less chemical work up than for the same analyte in a complex matrix (*e.g.* concrete). The nature of the sample matrix can greatly affect the yield of the chemical process and consequently, it is the matrix that can have the greatest affect on the sensitivity and minimum detectable amount (MDA).

1.9.4.2 Pre-treatment

The sample is pre-treated to remove the matrix bulk, and to therefore concentrate the analyte. The pre-treatment of the sample will depend on the nature of the sample. If the sample is a solid, it will be dried and then ashed. For samples in the liquid form, the sample will be evaporated, and then ashed. However, care must be taken if the analyte forms volatile complexes. Typically the ashing process occurs by slowly ramping the temperature up to 200°C over 1-2 days, and then raising the temperature rapidly to ~550°C and maintaining at this temperature for 2-3 days. The remaining residues are then treated with acid. This process removes organics present in the sample, which may interfere with the chemical procedure. However, this method of ashing is only suitable for non-volatile species. Wet ashing is the preferred technique for ashing samples where the analyte of interest forms volatile species (*e.g.* Po or Ru). Here the sample is ashed using a selection of mineral acids and a suitable oxidising agent. However, the volume of reagents required can be considerable, thus increasing the possibility of contaminant introduction. For simple matrices, this method of concentration may be adequate and no further work up is required.

However, for many materials more elaborate chemical separation schemes will be required. Microwave digestion techniques are also becoming widely used pre-treatments in the laboratory environment. The sample is broken down at an accelerated rate, due to the high temperatures and pressures involved. Since smaller volumes of reagents are used, the likelihood of contamination introduction is greatly reduced. The limitation with this digestion process is the necessity to use a small amount of material (<1g), thus reducing the amount of analyte in the sample. These techniques are limited in that they are only suitable for those samples that contain non-silicaceous materials or samples which contain small amounts of silica. For those samples that have a high silica or mineral content it will be necessary to use total dissolution methods, such as alkali fusion of HF digestion.

In alkali fusion techniques, the sample is mixed with a fluxing agent, typically in a 1:4 sample:flux ratio. The sample is then heated at a high temperature, generally 800-1000°C. At these temperatures the flux turns into a molten liquid. Prolonged

contact of the molten flux with the sample ensures that the sample matrix is broken down [6, 7]. Sodium hydroxide, lithium metaborate and potassium pyrosulphate are fluxing agents that are used extensively. There are a number of drawbacks with the fusion techniques such as a limitation in sample size (<0.5g), introduction of appreciable salt content, and contamination from both the flux material and the flux vessel. Fusion techniques are also only suitable for those analytes that are non-volatile. In many circumstances it will be necessary to use hydrofluoric acid to break down silica based matrix. Although there are many safety hazards that must be considered when using this reagent, the advantage with using HF is that the dissolution will be effective, relatively quick and a relatively large (>2g) sample size can be tolerated.

After the analyte has been solubilised and a suitable yield monitor added, it will be necessary to isolate the analyte of interest from other components contained in the sample. The separation scheme, typically follows one of three general approaches, ion-exchange, selective precipitation or solvent extraction. For complex matrices it is unlikely that a single isolation procedure would result in a contaminant free sample. Therefore, it will be necessary to use a multi-stage approach, where a number of clean-up, isolation and concentration steps are required before the analyte can be determined.

1.9.4.3 Analyte determination

In the last 10 years the number of analytical tools that have been made available to the analyst have increased. In the past if the analyte of interest was radioactive, it followed that radiometric counting techniques such as alpha spectrometry, liquid scintillation counting or gamma spectrometry would be the mode of quantitation and quantification. However, with the advent of techniques that utilise other physical and chemical properties of the analyte, the counting choice is now no longer as clearly defined [8 -14].

Radioanalytical counting techniques rely on the emission of a particle or photon from the radionuclide. The emission of this energy is a purely random process and

therefore the whole quantification process relies on random emissions. For those analytes that have very long-half lives (>10^4 years), the specific activity will be low. The relationship between specific activity and half life is determined using the equation detailed:

$$\frac{\ln 2}{t_{\frac{1}{2}}} \times \frac{1}{RAM} \times Av.No = Bq \quad g^{-1}$$

The specific activity for the analytes of interest are shown in Table 1.5.

Table 1.5 Specific activity of selected analytes

Isotope	Half life	Half life (s)	Specific activity (Bq/g)
^{36}Cl	300,000y	9.47E+12	1.22E+09
^{129}I	17,000,000y	5.36E+14	6.03E+06
^{99}Tc	213,000y	6.72E+12	6.27E+08
^{151}Sm	90y	2.84E+9	9.73E+11
^{166m}Ho	1200y	3.79E+10	6.64E+10

Therefore, the number of emissions in a given time will be very small, and may approach the background signal. Consequently for those species with long half-lives there will always be a compromise between the level of analyte in the sample and the background signal. It therefore follows that for those analytes with long half-lives it may be more useful to rely on a physical attribute that does not rely on a random decay process. It is for this reason that there has been a move towards using mass spectrometry techniques to determine low-level species in many sample matrices. However, these techniques are only useful for those radionuclides with appreciable half-lives (>10^4years), these techniques are also limited in that only small sample sizes are tolerated (<0.2g solids). Therefore, although the MDA may be much lower, there is severe limitation in the sample size (and therefore limited analyte), consequently, the detectable quantity may not differ considerably from that obtained when using radiometric techniques.

The radionuclides that have been targeted in this study may be present in decommissioning concrete wastes at very low levels. It will therefore be necessary to isolate these species from the matrix before the analyte is determined. Since the concrete matrix is complex, it will be necessary for a multi stage analytical procedure. It is only in this way that the analyte of interest will be in a radiochemically pure form. This will enable the analyte to be identified and quantified. Since the analyte concentration will be at a low level, the analytical methodologies adopted must be capable of analysing large amounts (>1g) of sample material. If the analytical methodology is to be used in commercial applications, the procedure should be robust and easily scaled up for multiple sample/batch analysis.

1.10 Chlorine

1.10.1 Occurrence and properties.

Chlorine-36 is a β emitter with an E_{max} of 710keV and a half-life of 300,000 years [15].

This nuclide is formed by two different mechanisms; cosmogenic production *e.g.* neutron interaction with ^{36}Ar in the troposphere [16], and neutron activation of ^{35}Cl. The most significant production route of ^{36}Cl is the n,γ reaction involving stable ^{35}Cl, as shown below:

$$^{35}Cl \xrightarrow{n,\gamma} {}^{36}Cl$$

Many of the decommissioning wastes, such as steel, graphite and concrete, will contain small amounts of chloride [17-19]. Generally this will be of trace concentration, however due to the amount of concrete, the total chloride available for activation is significant. This, together with the thermal neutron cross section (43 barns), suggest that ^{36}Cl will feature significantly in decommissioning wastes [20-21]. Since ^{36}Cl is an activation product, it follows that the extent of contamination will be confined to the surface of the concrete, however contamination may diffuse through the matrix if organic chloro-species are formed. These organic species will

tend to be highly volatile, therefore they will be removed from the originating area by diffusion/evaporation mechanisms.

The speciation of Cl in nuclear waste has yet to be fully established, however studies have indicated that the main chemical form will be that of the anionic chloride, Cl^- [22]. Under environmental redox and pH conditions, Cl will tend to form the Cl^- anion, and, therefore will not be retarded to any significant extent in either the near or far field of a waste repository [23-24]. Consequently, ^{36}Cl is considered a radiologically significant nuclide.

1.10.2 Environmental speciation of Cl

The speciation of chlorine will depend upon a number of environmental factors. By far the most important will be the temperature, pH and Eh of the system. Pourbaix diagrams can be used to deduce the most likely form of the chlorine species in the environment [25]. The Pourbaix diagram for chlorine is shown in Figure 1.2. It can be seen that at neutral pH and under environmental Eh condition the chlorine will be predominantly found in the Cl^- form.

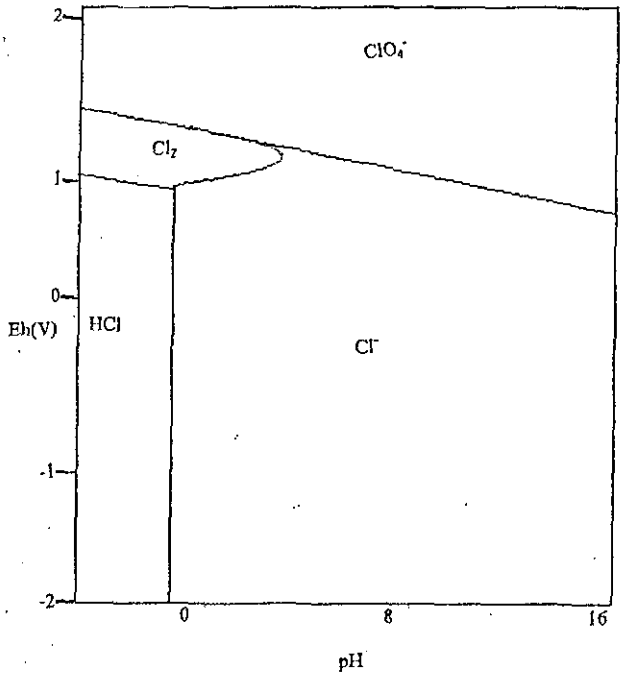


Figure 1.2 Pourbaix diagram of Cl at 25°C

1.10.3 Determination of ^{36}Cl in concrete wastes

As ^{36}Cl is a beta emitter with no associated γ emissions, it follows that the sample cannot be analysed by using non-destructive analytical techniques such as γ counting. It is therefore necessary to remove interfering radionuclides, and concentrate the analyte of interest before determining the activity of ^{36}Cl. The separation, isolation and purification of the analyte from the matrix may require elaborate, time intensive procedures.

Review of the literature indicates that there is a lack of information with regards to the determination of Cl in concrete. The measurement of Cl in concrete is of significant importance in the structural engineering arena. The extent of Cl in concrete will have a dramatic effect on steel corrosion in reinforced concrete systems [26-30], therefore the majority of the literature concerning Cl in concrete is based in the engineering literature rather than chemical publications. Engineering data are concerned with the 'free' (non-chemically bound) chloride since it is this species that is responsible for enhanced corrosion rates of structural materials [26-30]. Measurement of free chloride rely on gentle leaching techniques followed by Cl^- determination by either potentiometric methods [28] or titration [27]. It is therefore not possible to transfer these methodologies to the determination of ^{36}Cl in concrete, since these detection methods are of inadequate sensitivity, and they are unable to differentiate between active and non-active chloro-species. Nuclear Activation Analysis (NAA) has also been used to determine Cl in both concrete [30] and in steel [31].

In NAA the ^{38}Cl gamma photon emission is used (based on the n;γ nuclear reaction on ^{37}Cl). Consequently, it is then relatively simple to determine the total ^{35}Cl. Using this technique it is possible to calculate the ^{36}Cl activity, however, this requires both accurate Cl content and the materials activation history. This technique relies upon data that may not be known *e.g.* original inactive Cl content, therefore there will always be some uncertainty in using this procedure as a means of estimating ^{36}Cl in the matrix. This method, has however been used to estimate the level of ^{36}Cl in steels and metal alloys [31].

1.10.3.1 Matrix breakdown

Aggressive conditions are necessary to breakdown complex matrices such as concrete. This can lead to problems in that the analyte of interest may be altered into a form that is readily lost from the sample, thereby decreasing sample recovery. It has been found that if digestion is carried out in an open vessel under moderately acidic conditions Cl^- will be lost as HCl. If the oxidation potential is increased by using a more concentrated oxidising acid, Cl_2 will be formed [15] and greater analyte losses will occur. It is possible to use this ease of volatilisation so that the analyte (*e.g.* the halide) may be removed from other, less volatile components in the system. The determination of chlorine at low levels is difficult since many of the reagents will have small trace quantities of inactive Cl contaminants. Consequently, it will be necessary to carry out a blank analysis to determine the Cl contribution from the reagents. This is especially true if gravimetric methodologies are to be adopted as a means of determining chemical yield. For low level analytical work (ppm and ppb), many schemes now utilise inductively coupled plasma techniques such as atomic emission spectrometry (AES) or mass spectrometry (MS). However, chloride cannot be determined by this method since the emission wavelength of the Cl (135nm) is too low to be detected by conventional optical emission techniques. There are also drawbacks in using ICP methodologies for solid matrices such as concrete, in that the ICP will not tolerate more than 0.2g of solubilised solid in 100ml of solution. [Private Communication G.D.Woods, Hewlett Packard, 1999]. This drastically limits the sample size and adversely affects the limit of detection of the procedure. Analysis of such a complex matrix leads to problems in that there are many interferents contained within the sample. Since in this case, the sample will contain radioactive species, it is of paramount importance to remove other chemical and radiochemical impurities.

1.10.3.2 Radionuclidic interferents

Since ^{36}Cl must be determined using β counting techniques, *e.g.* liquid scintillation counting (LSC), all radionuclides will contribute to the resulting pulse height spectrum. It therefore becomes imperative that radionuclidic interferents must be removed from the sample. Two of the major interferents will be ^{60}Co and ^{137}Cs [17-

18], the decay energies of these radionuclides will cause interference on the ^{36}Cl spectrum, consequently, resolution of the components would be impossible, the decay energies being 0.71MeV, 2.8Mev and 1.18MeV for ^{36}Cl, ^{60}Co and ^{137}Cs respectively. Both these interferents will feature significantly in decommissioning wastes. Consequently, the sample must be free from these contaminants. Elaborate, time intensive separation schemes may be necessary to achieve the required sample purity.

1.10.3.3 Chemical separation

As has been previously mentioned, it is possible, with careful control of the redox potential to oxidise the halide to the halogen gas. It then becomes simple to remove the gas from the sample by simple purging techniques. Major metallic interferents such as ^{60}Co, ^{152}Eu and ^{137}Cs are therefore separated from the analyte of interest, since they are not volatilised under these reaction conditions. Easily oxidised species such as SO_2, tritiated water, $HTCO_4$ and CO_2 may also pass into the analyte collection vessel, however further isolation and purification schemes can be used to remove these species from the system. These purification schemes generally involve isolation of the analyte on an anionic exchange column [6, 32-33]. Here the resin is carefully selected so that the analyte is either retained or released preferentially to other components. If it is suspected that the sample contains cationic species then it is possible to use a cationic exchange column, here the anionic species will pass through the resin whereas cationic species will be retained. In either case the chloride is purified from other components present within the sample. For those samples that are to be analysed by liquid scintillation counting techniques, it is important to concentrate the sample so that the maximum amount of analyte will be contained in the counting matrix. For halides this is typically achieved by precipitating as the silver halide [6]. The precipitate is generally re-dissolved in a suitable solvent and mixed with a compatible cocktail before the activity is measured by LSC.

1.11 Technetium

1.11.1 Occurrence and properties.

The technetium isotope, ^{99}Tc is a high fission yield product (6%) with a significant half-life of 213,00years [15]. Since it is formed as a consequence of fission, wastes from wet fuel routes are liable to be contaminated. Although there are many technetium isotopes produced during the fissioning of uranium, ^{99}Tc is considered to be the most radiologically significant due to the high fission yield and long half-life [19-20]. Technetium-99 is a β emitter with an E_{max} of 293keV. There are no stable isotopes of Tc, the half-lives, range from seconds to millions of years [15].

Typically, those areas that have direct contact with the fuel will be contaminated, depth-profiling studies have indicated that the contamination will be at the surface of the material rather than throughout the matrix [Private Communication, W. Westall, Magnox, 1996]. The extent of penetration will depend upon the porosity and degree of fractures and crevices found within the sample. Technetium will be formed inside the fuel can, therefore, those cannisters that are corroded or have physical defects may release fission products, including technetium, into the locale. Areas such as the cooling ponds will become contaminated in this manner. Those areas where fuel is stored after it has been used in the reactor are the most prone to fission product contamination. These areas have decontamination units in place, such as the caesium (^{137}Cs) removal unit (CRU). Since this species is also a product of the fission process it follows that those areas contaminated with ^{137}Cs will also be contaminated with other fission products including ^{99}Tc. On a Magnox station, the fuel is stored in a high pH aqueous environment [2], these conditions reduce the corrosion rate of the magnox can [2].

1.11.2 Environmental speciation of Tc

Although the elemental state of Tc is metallic, in the environment the most likely speciation of Tc will be the pertechnetate ion TcO_4^- [22]. The chemistry of Tc is extensive, technetium compounds have been found to exist for all oxidation states from +7 to –1. The +4 and +7 oxidation states are the most stable [22]. The

principal form of technetium in aqueous solution under reducing environmental conditions will be Tc^{IV}, found as $TcO(OH)_2$ [34]. Under oxidising conditions the Tc^{VII}, TcO_4^- ion will predominate and transport through the environment will be rapid [35]. However, the presence of organic ligands may reduce the technetium from the +7 oxidation state to +4 [22]. The reduced species would have a greater affinity for the geological matrix and a decrease in mobility would be observed.

1.11.3 Determination of ^{99}Tc in concrete wastes

Like ^{36}Cl, ^{99}Tc is also a beta emitting radionuclide with no associated gamma photon emission [15]. Therefore it is impossible to determine this radionuclide using non-destructive analytical methodologies. A multi-stage analytical scheme is necessary to remove the majority of other chemical and radiochemical components from the concrete matrix. Since there are no stable isotopes of Tc [15] it follows that there is no satisfactory way of adding elemental carriers to the sample. It is therefore necessary to analyse these samples with extreme care to avoid significant sample loss. There is no outright suitable yield monitor for ^{99}Tc analysis, and this is evident from the literature, where a variety of different yield monitors are used. The most appropriate yield monitor will be dependent upon sample (size and matrix), methods for determining the analyte and other components contained within the sample.

Some workers have used stable rhenium as a technetium analogue [36-37]. Although the chemistry of Tc and Re is similar, it is not identical. Those groups that have used Re/Tc systems have indicated that care must be taken to ensure that the Re carrier follows Tc faithfully through the chemical scheme. It has also been indicated that the chemistry of Re does, under some circumstances, deviate from that of Tc, several authors suggest measures that are required to overcome this [37-38]. Over the last 10 years mass spectrometry techniques have become commonplace for those analyses involving ^{99}Tc [10, 12, 39]. In this instance ^{97}Tc can be used as the analytical yield monitor [10], thereby removing the uncertainty of chemical deviation. However, mass spectrometry techniques have their drawbacks in that iso-baric interference from ^{99}Ru and ^{99}Mo are encountered [32, 40]. In those analyses adopting radiometric methodologies, both ^{99m}Tc and ^{95m}Tc [32, 40-41] have been used as internal yield

monitors. Both isotopes have relatively short half-lives (61d and 6h respectively), therefore both isotopes have a much greater specific activity than ^{99}Tc. Some researchers have got over this obstacle by using ^{99m}Tc and after analysis, immediately counting the yield monitor by gamma photon spectrometry. The sample is then retained for several days to allow the ^{99m}Tc to decay and the ^{99}Tc determined. This is possible since the half-life of the isotope is short, however this leads to problems in that there must be a source of fresh ^{99m}Tc to ensure that there is a constant supply of the yield monitor. In schemes that use ^{95m}Tc as a yield monitor, it is general practice to determine the yield monitor by gamma spectrometry and the analyte using inductively coupled plasma mass spectrometry techniques. To get over the inherent problems associated with yield monitors involved in the analysis of ^{99}Tc, it is common practice to determine the yield by analysing duplicate samples. Each of the samples are identical, however one of the samples will have a known amount ^{99}Tc added. In this scheme, it is assumed that the samples will behave in an identical manner and that the corresponding yield recoveries will be the same. However, the recovery of identical samples can vary, consequently since the analytical result relies so heavily on the yield, many laboratories are now moving away from this technique and focusing on analytical schemes that do not rely on sample duplication. Since addition of a stable Tc carrier is impossible, there are concerns that at trace level, significant losses can occur by processes including adsorption to glassware. For this reason it is common to find Re added as a chemical carrier (but it is not used as a yield monitor) alongside the analyte and the yield monitor *e.g.* ^{97}Tc.

1.11.3.1 Matrix breakdown

Studies have indicated that under certain conditions the pertechnetate ion will be oxidised and lost from the sample due to the formation of the volatile product, technetium anhydride, Tc_2O_7 via the formation of pertechnic acid $HTcO_4$ [42]. Since the concrete matrix will require harsh reagents to ensure that the sample is fully solubilised, there is a great likelihood of losing some of the analyte in this manner. However, this can be avoided, or at least substantially reduced, by carrying out digestion under a slight vacuum and collecting any volatile products in a chemical trap.

1.11.3.2 Radionuclidic interferents

If ^{99}Tc is to be analysed, it will be necessary to remove other radionuclidic interferents from the sample. Consequently, the sample that is prepared for counting must be chemically pure.

1.11.3.3 Chemical separation

Technetium, has predominantly two stable oxidation states, these being Tc^{IV} and Tc^{VII}. Under strongly reducing conditions the Tc will be found as TcO_2, this is insoluble and will form a precipitate in the reaction vessel. A limited number of studies have utilised this process to isolate Tc from the sample. However, for there to be a measurable amount of Tc precipitate it follows that there must be a significant amount of Tc in the sample. For those samples that have a very low level of Tc this form of isolation is not feasible. Rather than isolation of Tc from the sample using reduction mechanisms it is more common to isolate the Tc using oxidative processes. However, care must be taken to ensure that the sample is not lost as the volatile Tc_2O_7 species. Therefore control of the chemical conditions will allow separation and partial isolation from other radionuclides in the sample.

Concentration of technetium in the sample can be achieved using ion-exchange methodologies. In general reaction schemes, the conditions are controlled so that the Tc is present as the pertechnetate ion. This complex is readily absorbed to many anion exchange resins, and it is in this manner that other species in the sample (*e.g.* cationic products) are removed. The efficiency of this scheme will depend largely upon the sample matrix. For those matrices that contain a large anion content (*e.g.* analysis of seawater), it may be necessary to use other separation schemes such as precipitation and or solvent extraction techniques. As has already being discussed, there is no suitable isotope of Tc available for use as a chemical carrier. In precipitation schemes, rhenium (Re) is used as an analogue for Tc. Here the Tc is co-precipitated alongside the rhenium as the ReO_2 [34]. Precipitation mechanisms can lack selectivity, consequently a number of separation and purification schemes are generally employed in the analysis. Solvent extraction techniques are highly selective and relatively quick. However, the efficiency of the extraction is reliant

upon the sample being relatively clean, therefore this procedure is generally used in the final clean-up stages. A variety of complexing agents has been used to extract and purify Tc from a variety of different matrices. Those that are used extensively include tri-n-butyl phosphate (TBP) and tri-n-octylamine (TnOA). The carrier solvent and nature of the matrix (*e.g.* acid concentration) will greatly affect the efficiency of the chosen extraction scheme [43-46]. Other species in the system (*e.g.* Fe^{3+}, Ca^{2+}) will adversely affect the rate at which the Tc passes from the aqueous to the organic phase [43-46]. It is possible to extract the Tc into a small volume of organic extractant. The Tc-organic complex that is formed is not especially volatile. It is then possible to reduce the volume of the organic solvent even further by allowing the sample to evaporate. The residue can then be mixed with a small aliquot of suitable organic and mixed directly with the scintillation cocktail. Care must be taken to ensure that the organic extractant chosen does not greatly reduce the counting efficiency *i.e.* there must be little chemical or colour quenching observed.

1.12 Iodine

1.12.1 Occurrence and properties

There are over 30 different isotopes of iodine, with ^{127}I being the only stable isotope [15]. Of the isotopes, ^{129}I and ^{131}I are the most radiologically significant [2]. Both isotopes are formed by fission of uranium and are high yield fission products (1% and 3.1% respectively) [2]. Iodine-129 is present in the environment from both man-made and natural sources. The production of natural ^{129}I through spontaneous and induced fission of uranium ores was demonstrated in the 1950's [3]. Natural levels of ^{129}I are also found in the environment due to cosmic ray interactions with atmospheric xenon. However, the main process that has led to the levels of ^{129}I currently in the environment are due to nuclear weapons testing programmes of the 1950's and the nuclear fuel reprocessing programmes. Iodine-129 has a long half-life (17 million years) and consequently a low specific activity. Conversely, ^{131}I has a relatively short half-life (8d) and a high specific activity. Both isotopes are β emitters, ^{129}I having an E_{max} of 191keV, and ^{131}I 971keV. During the normal

operation of a nuclear reactor, fission products will be produced within the fuel. Consequently, fission product contamination has been found in those areas that have direct contact with the fuel and with the primary coolant. Limited progress has been made in identifying the mechanisms by which gaseous compounds of iodine are released from irradiated fuel. As early as 1964, experimental schemes were devised to investigate the non-elemental iodine species formed during the fuel irradiation [47]. It was found that there were three distinct types of iodine compounds. Elemental and particulate iodine was easily identified, however the third class of iodine compound was then further classified. The fraction was found to consist of two distinct iodine containing species. Fraction A was found to partition equally between both benzene and 0.02M sulphuric acid, whereas fraction B was readily soluble in benzene. Iodine in fraction B was identified as CH_3I using gas chromatography and molecular weight determination. Fraction A has never been fully characterised [47]. These iodo-organic products will be highly volatile, consequently they will be easily removed from the originating site by evaporation. Gaseous discharge of these species must be monitored closely due to the radiological hazards associated with iodine. The radiological consequences of radio-iodine in the environment are well understood. Incidents where a large amount of radio-iodine has been accidentally released into the environment have increased our understanding of the transport mechanisms involved. Any gaseous product formed in the fuel can will lead to a rise in pressure and the potential to cause the can to burst, releasing the gaseous product into the reactor. However the release of these gaseous species must be carefully monitored and controlled. If the gas was released as it was formed this would lead to an unacceptable activity release into the environment. Consequently, the gases are passed through filters and adsorbed onto charcoal beds. This delays the rate in which the species is released into the environment. Generally, this adsorption process delays the release by ~50 days, and the activity of the ^{131}I ($t_{1/2}$ 8d) will decay significantly. However, the activity of ^{129}I ($t_{1/2}$ 17million years) will not be affected.

1.12.1 Environmental speciation of I

There are many concerns regarding radio-iodine in the environment, the speciation of the iodo species will depend upon the chemical nature of the surroundings. Extensive studies have been carried out to investigate the behaviour of iodine complexes in the bio-sphere [3, 48-51]. Iodine and its complexes move rapidly through the marine and terrestrial environments [22, 24, 51-52, 54]. Iodine is incorporated throughout the tissue in many organisms including plant and mammalian species (seaweed, thyroid *etc*). The hazards associated with radio-iodine in the environment are reasonably well understood; the air-pasture-cow-milk chain being regarded as a critical exposure pathway in the event of an accidental release [55]. Iodine exhibits several oxidation states, the predominant species in the environment being I^- and IO_3^-. Simple anionic iodo species will not be retarded to any considerable extent since the affinity between the anionic fissures in the geological matrix and the iodo-species is insignificant [22, 48, 50-51]. In the aquatic environment, a number of parameters will influence the speciation of iodine, amongst these Eh and pH will be the most significant. Reference to a Pourbaix diagram indicates the likely speciation of the environmental iodo species. This is shown in Figure 1.3.

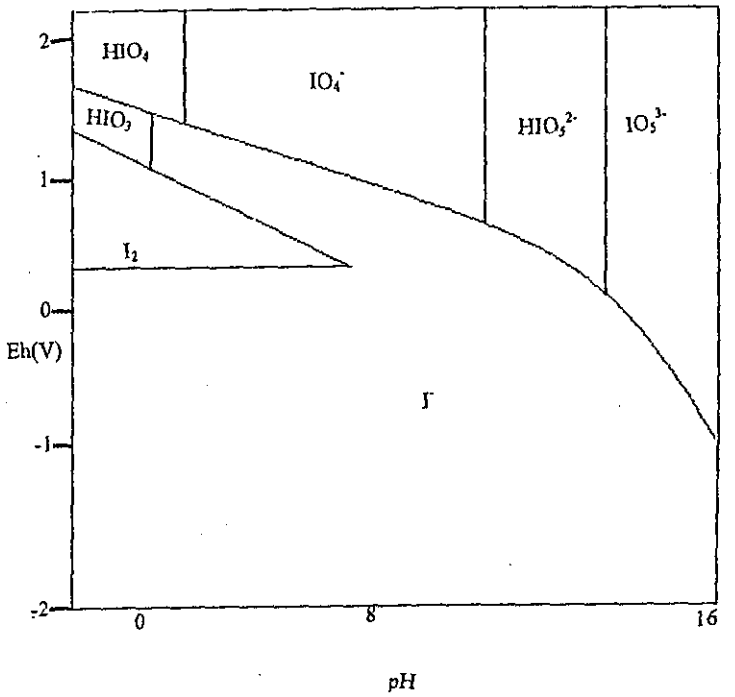


Figure 1.3 Pourbaix diagram of I at 25°C

1.12.2 Determination of ^{129}I in concrete wastes

Since ^{129}I is a weak beta emitter, it is generally determined by detection and quantification of its gamma photon at 0.0396MeV. For many gamma emitting radionuclides it is not necessary to separate the radionuclide from the matrix. With radionuclides such as ^{152}Eu and ^{137}Cs the radionuclide can be determined directly in the sample matrix. In these instances, corrections are made to account for the sample geometry and sample density. However, for ^{129}I it is not possible to count the sample in the matrix because of other interferents that may 'drown out' the ^{129}I signal. Therefore it is necessary to separate the ^{129}I from other radionuclides in the sample before gamma detection. Counting ^{129}I by gamma spectrometry severely limits the MDA of the analytical procedure, since the counting efficiency of the gamma detector is generally less than 5% for a flat NaI crystal, or ~ 60% if a well-type detector is used. However, the major advantage in counting the sample by γ spectrometry is that the sample does not have to be of high radiochemical purity. Thus reducing the analytical work up required. Generally ^{129}I activities are estimated using FISPIN calculations. However, a limited number of samples have been radiochemically analysed. Typically the methodologies adopted are based on the determination of ^{129}I in highly active liquor solutions. However, for environmental and decommissioning samples it is not possible to use these techniques since the activity of ^{129}I is several orders of magnitude lower in these samples than in fuel reprocessing solutions. Consequently, analytical data is reported as a 'less than' rather than as a quantified activity. This can lead to over compensation of the activity reported, which in turn may lead to an over estimation in the inventory. This may then render the sample unsuitable to be disposed of at the Drigg site. In these situations, the sample may be stored on site unnecessarily until a suitable disposal route is made available. If the ^{129}I content could be determined using other counting techniques such as liquid scintillation counting (LSC), then the MDA would be reduced significantly since the counting efficiency is much higher (~90%). However if the sample is to be determined using LSC, the sample must be radiochemically pure. This will call for extensive, and therefore costly, analytical methodologies.

Analytical schemes involving the analyses of ^{129}I in environmental samples have been limited to 'simple' matrices such as groundwaters [52, 56] or vegetation [57]. The measurement of ^{129}I in environmental matrices is becoming of great importance due to the radiological implications. Consequently, in the last several years many analytical techniques have been utilised to determine ^{129}I in several different matrices. Methods that have been used to determine ^{129}I include γ spectrometry [58-60], X-ray spectrometry [61], liquid scintillation counting [62-65], low level beta counting, neutron activation analysis [53, 56, 66-67] and mass spectrometric methodologies [50, 68-70]. For analyses of environmental samples, mass spectrometry techniques are being used extensively to determine the $^{127/129}I$ ratio, an important factor in determining the accumulation of iodine in the bio-sphere.

1.12.3.1 Matrix breakdown

The ease of volatilisation of iodine is well understood. Therefore, it is necessary to carefully control the reaction conditions to ensure that the analyte of interest is not lost from the sample during the digestion stage of the analytical procedure. Analysis of the concrete matrix leads to many analytical problems. The most significant being the harsh conditions necessary to bring about the release of the analyte from the matrix. These conditions are such that they may also lead to the loss of the analyte from the sample due to the formation of I_2.

1.12.3.2 Chemical separation

In some limited cases, it is possible to determine ^{129}I directly without any analytical work-up, however, this generally applies to only active ^{129}I doped liquors or heavily contaminated tissue such as the thyroid gland. For many matrices that may have low levels of analyte or contain other radionuclides, chemical separation and isolation of the analyte is required. As has been previously discussed iodine is easily volatilised, many analytical methodologies used to determine iodine utilise this process to separate iodine from other species within the sample. Although other volatile species may also pass over into the chemical trap, schemes are available so that these species are removed. After the iodine has been removed from the sample, the rest of the analytical process will rely on the way in which the ^{129}I is to be determined.

The low specific activity of ^{129}I means that for low level samples appreciable counting times will be required to gain a statistically viable result. The background signal may approach, or even surpass the signal due to the sample, thus affecting the MDA. For this reason, other techniques, such as Accelerator Mass Spectrometry (AMS) have been utilised for determining ^{129}I in environmental matrices. This technique relies upon the physical properties (*e.g.* atomic weight) of the analyte rather than a random decay emission. However, there are drawbacks associated with this technique, in that iso-baric interferences must be removed prior to analysis.

Neutron Activated Analysis (NAA) has been used to determine ^{129}I in matrices such as milk [65] and vegetation [57]. In this technique, the ^{129}I is exposed to thermal neutrons and the ^{130}I is formed by an n,γ nuclear reaction. The ^{130}I has a much shorter half-life than ^{129}I (12.4hours *c.f.* 17million years), thus the specific activity is much greater and the measurement of the associated activity has less uncertainty. Since there are many species which lead to the formation of ^{130}I, ^{133}Cs (n,α), ^{128}Te (n,γ,β) and ^{129}I (n,γ), the technique relies on elaborate multi-stage work up schemes to remove these contaminants prior to irradiation. The requirement of an 'in-house' neutron reactor also renders this method unsuitable for routine laboratory analysis.

Although counting techniques that rely upon the natural decay of ^{129}I have some limitations, in terms of detection limit and sensitivity, it is these methods that have been used routinely in the analytical laboratory. If the determination is to be carried out using γ spectrometry or mass spectrometry techniques, then it is possible to count a solution containing ^{129}I directly. However, the literature indicates that if the ^{129}I content is to be determined by γ spectrometry it is preferable to absorb the iodine onto a suitable extractant such as activated charcoal. If the ^{129}I is to be determined using low-level beta counting it will be necessary to produce a point source. This is generally achieved by precipitating the iodide as AgI or PdI_2. However, this can lead to problems in that the self-absorption of ^{129}I in the sample will increase uncertainty associated with the measurement. Liquid scintillation techniques are not at the present time used routinely. Samples prepared for LSC need to be of high

radiochemical purity since all other active species will contribute to the spectra, thus introducing uncertainty to the result.

1.13 Lanthanide's – Samarium and Holmium

1.13.1 Occurrence and properties

The *4f* elements are also called the lanthanides or rare earth elements (REE). The lanthanide elements all have similar chemistry, and this has posed many analytical problems. Both ^{151}Sm and ^{166m}Ho are beta emitters that have associated γ photon emissions. The formation of both isotopes is as a consequence of fission of the uranium, and activation of the parental element.

1.13.1.1 ^{151}Sm

The natural, stable ^{150}Sm isotope is 7.4 % abundant [15], and is inherent in concrete waste forms. This isotope has a high thermal neutron cross sectional area (102 barns). Consequently, neutron exposure of samples containing ^{150}Sm will result in the production of ^{151}Sm. Other natural isotopes of Sm will also become activated, and the properties of these isotopes are given in Table 1.6.

Table 1.6 Isotopic properties of naturally occurring Sm nuclides

Parent Isotope	Natural Abundance (%)	Thermal neutral cross section (barns)	Produced Isotope	Half-life
^{144}Sm	3.1	1.6	^{145}Sm	340d
^{147}Sm	15.0	56.4	^{148}Sm	7E+15y
^{148}Sm	11.3	2.4	^{149}Sm	10E+16y
^{149}Sm	13.8	40100	^{150}Sm	Stable
^{150}Sm	7.4	102	^{151}Sm	90y
^{152}Sm	26.7	206	^{153}Sm	1.93d
^{154}Sm	22.7	7.2	^{155}Sm	22.2m

It can be seen that, of those isotopes which have a half-life greater than 1 year, only ^{151}Sm is important. The other isotopes have such long half lives that they can be considered to be of low radiological significance. From the table, it can also be seen that any parental ^{149}Sm will also contribute to the total ^{151}Sm in the inventory, due to

the appreciable neutron cross section for the nuclear reaction. To summarise ^{151}Sm is formed via the following mechanisms:

a)

$$^{235}U \xrightarrow{n} {}^{236}U \xrightarrow{\text{spontaneous fission}} Fission\ Products + n's$$

b)

$$^{150}Sm \xrightarrow{n,\gamma} {}^{151}Sm$$

$$^{149}Sm \xrightarrow{n,\gamma} {}^{150}Sm \xrightarrow{n,\gamma} {}^{151}Sm$$

Figure 1.4 Production routes of ^{151}Sm

Although ^{151}Sm is a relatively low energy (76keV) β emitter with associated γ photon emission [15], it is impossible to determine the ^{151}Sm content in a sample by direct γ spectrometry techniques. The associated γ photon has a low energy of 0.0215MeV and low intensity of less than 1%. Unless full radiochemical separation is carried out, the γ photon signal from ^{151}Sm may be masked by other radionuclidic interferents found in the sample *e.g.* ^{152}Eu. Since ^{151}Sm is formed by the activation of ^{150}Sm and the fissioning of uranium, it follows that those areas that come into contact with the fuel may be contaminated with a variety of fission products, including ^{151}Sm. From the table above, it can be seen that several of the samarium isotopes have a high thermal neutron cross section. For this reason samarium is used in biological shield structures. The biological shield will be exposed to high neutron flux throughout the operational life-time of the reactor, therefore activated samarium will be found within those structures used to shield the reactor.

1.13.1.2 ^{166m}Ho

Holmium-166m is a beta emitter with a half-life of 1200 years [15]. Associated with the β decay of the isotope, are a number of γ photons. As with ^{151}Sm if the content of ^{166m}Ho is to be determined it will be necessary to remove other radionuclidic interferents from the sample prior to counting.

There is only one stable isotope of holmium, ^{165}Ho. This isotope has a relatively small thermal neutron cross section of 3.4 barns [15]. At first glance it is difficult to determine why ^{166m}Ho is considered to be radiologically significant, since it would seem that the direct production route would result in very small quantities of the isotope being formed. However, ^{166m}Ho will also be produced by the β decay of ^{166}Dy. The whole production scheme of ^{166m}Ho is complex and occurs in many stages as seen in Figure 1.5.

$$^{165}Ho \xrightarrow{n} {}^{166m}Ho$$

$$^{164}Dy \xrightarrow{n} {}^{165}Dy \xrightarrow{n} {}^{166}Dy \xrightarrow[3.4d]{\beta^-} {}^{166m}Ho$$

Figure 1.5 Production route of ^{166m}Ho

Consequently, the levels of ^{166m}Ho formed will depend on the original levels of both holmium and dysprosium contained within the matrix. It should also be noted that recent applications of dysprosium include the use of dysprosium cermet (ceramic beads in a metal matrix) in cooling nuclear reactor rods. Thus increasing the likelihood of ^{166m}Ho contamination due to the dysprosium production route.

1.13.2 Environmental speciation of Ho and Sm

The most stable oxidation state of the lanthanides is the +3 form. However, both Sm and Eu also form stable +2 complexes. In the presence of air, Sm^{2+} will rapidly oxidise to Sm^{3+}, consequently, it is reasonable to assume that the environmental speciation of both Sm and Ho will be as the Ln (III). The aqueous chemistry of the lanthanides is both complicated and vast [4]. In aqueous solutions the $[Ln(H_2O)_9]^{3+}$ ion is formed [4]. Transportation through the terrestrial environment will be slow due to the size of the ion and retardation effects will occur due to the sorption of the complex on to the geological matrix. Association with colloidal materials may enhance the rate of transportation through the Geosphere. In the investigation of lanthanide transport in the environment, europium has been used as an analogue for both Sm and Ho, however the information obtained from these studies should be applied with caution to those systems involving other lanthanide elements.

1.13.3 Determination of the lanthanides in concrete wastes

There is very little data available in the literature with regards to analysis of the lanthanides in environmental matrices. Recent analytical developments such as the availability of Rare Earth resins by Eichrom have enabled the determination of the selected lanthanides in a variety of matrices. There are several drawbacks in the use of these resins. The main disadvantage with these resins is the necessary purity of the solution. Chemical contaminants in the sample will greatly affect the efficiency of the isolation/separation scheme. Associated with the concrete will be a number of contaminants whose presence will adversely affect the performance of the resin. These contaminants include bismuth, calcium and barium and, as these elements will be of much greater concentration than the analyte, the resin may be saturated by these elements. Consequently, these resins are used during the final clean-up stages rather than as a general overall analytical procedure. Although the decay of ^{151}Sm and ^{166m}Ho is primarily by β emission with associated γ photon release, it is impossible to determine these isotopes in a quantifiable manner without some form of isolation from the sample matrix. There is also the strong possibility of the sample being contaminated with other lanthanide isotopes including ^{152}Eu and ^{154}Eu, both of which have several γ lines. These spectral peaks may overlap those of the ^{151}Sm and ^{166m}Ho thereby limiting the analytical information that can be obtained from γ spectrometry. Consequently, not only is it necessary to separate the analyte of interest from bulk contaminants in the matrix, but the analyte must also be separated from other lanthanides that may be contained within the sample.

The problem in fully isolating individual lanthanides is that the chemistry of each lanthanide element is very similar [4]. The lanthanides may be separated from other elements in the matrix by using fluoride precipitation techniques [15]. The rare earth fluorides being insoluble and dropping out of solution before other components [4]. The best separation schemes enabled the 'heavy' lanthanides (the cerium group, lanthanum to europium) to be isolated from the 'lighter' rare earth elements (the yttrium group, gadolinium to lutetium) [71]. It was then possible to isolate the rare earths further by carefully controlling the oxidative conditions [71]. In this manner it was possible to separate those lanthanide elements that existed in the +2, +3 and +4

oxidation states [71]. Ion exchange processes have been used with limited success to fully separate the lanthanides [71]. The lanthanide containing solution is passed through a cation exchange column and the lanthanide ions are tightly bound to the resin in a quantitative manner. The lanthanide ions are then removed from the resin by passing through a solution of ethylenediaminetetraacetic acid (EDTA). Anionic species are formed with the lanthanides [71]. The lanthanide which forms the most stable M(EDTA) complex is eluted first [71]. As the stability of the complex is inversely related to the size of the metal cation, the metal complexes are eluted in reverse order of atomic weight [71].

Analysis of the literature shows that there is very little data available for the analysis of samarium and holmium. Although a number of schemes have been suggested for ^{151}Sm analysis, the matrices investigated have been spiked solutions [72], active effluent samples [73-74], soils [75] and silicaecous materials [76]. A review of the literature for analytical schemes involving the isolation, purification and quantification of Ho using chemical techniques indicated that there were no analytical procedures available in the open literature. The lack of reporting of measurements of Ho is in part due to the difficulties associated with separating the lanthanides from each other as well as the lack of suitable yield tracers. The radionuclides ^{151}Sm and ^{166m}Ho have been highlighted as being particularly important in decommissioning waste scenarios. However, these radionuclides are not available in a form that is both chemically and radiochemically pure and, consequently, it is very difficult to develop analytical methods for their analysis.

1.13.3.1 Matrix breakdown

As the lanthanides are metallic in nature, harsh digestion procedures can be employed to break down the matrix without incurring loss due to volatilisation processes. For siliceous materials, hydrofluoric acid can be used to break down the mineral content in the sample. However, if appreciable amounts of rare earths are contained within the sample, use of hydrofluoric acid may lead to the formation of the lanthanide fluorides. Since all of the rare earth fluorides are insoluble, it follows

that the formation of this precipitate will render the analytical scheme limited in that it will be difficult to isolate the lanthanide elements further.

1.13.3.2 Radionuclidic interferents

Although ^{151}Sm and ^{166m}Ho have γ photon emissions associated with their β decay, it is impossible to determine the activity of these radionuclides in a sample by direct γ spectrometry techniques. Spectral information from the nuclides may be concealed by spectral signals from other radionuclides that may be of greater dominance or of higher specific activity. Therefore, it will be necessary to isolate the radionuclides of interest from other components in the sample matrix. The activity of ^{151}Sm and ^{166m}Ho may be determined using either LSC or γ spectrometry, however, regardless of which method it utilised, it will be necessary to have a clean, radiochemically pure source available for counting. If other radioactive components are associated with the source, then these contaminants will contribute to the spectra. The resultant spectrum may be complex, and quantification of the activity due to ^{151}Sm or ^{166m}Ho will be difficult, if not impossible. The lanthanides are readily isolated from many of the components contained in the concrete matrix. Elements such as calcium, iron and silica can be easily removed. However, contained within the sample will be other rare earth elements, *e.g.* ^{154}Eu and ^{147}Pm, which may be formed from either fission of the reactor fuel or by activation processes.

1.13.3.3 Chemical separation

It will be necessary to isolate the lanthanides from other bulk contaminants as well as other rare earth species contained within the matrix. As has been previously discussed, there is limited data available on the isolation of the rare earth elements in complex matrices. Rather than individual separation schemes, in the past the lanthanides have been separated into the heavy and light rare earth fractions. These analytical schemes relied upon the stability of the complex formed between the lanthanide element and a large complexing agents such as EDTA. Since the stability of this complex was found inversely proportional to the size of the lanthanide cation, the heavier rare earth elements will be eluted before their lighter counterparts. Although these schemes did not enable the individual lanthanide elements to be separated, they did offer some degree of separation from the matrix and other

lanthanides contained in the sample. With the advent of more sophisticated analytical instrumentation, it has been possible to isolate individual rare earth elements. Generally, these schemes have employed the use of solvent extraction techniques or HPLC (high performance liquid chromatography) methodologies.

Varieties of organic extractants have been used in solvent extraction methodologies. Although the term solvent extraction is used, this term covers a number of different mechanisms, all of which have been used in the extraction of the rare earth elements. The three main extraction mechanisms are: formation of ion pairs, solvation of salts and formation of chelation complexes with acidic extractants. Each mechanism differs in its ability to separate the lanthanide. This difference is due to a number of factors, however thermodynamic and kinetic characteristics are the main considerations [71].

However even using these techniques there are some situations in which it is still virtually impossible to separate particular lanthanide elements. It has been reported that there are particular pairs of rare earths that are more difficult to separate than others. This is most noticeable in Eu-Gd system [4] and is due to the half-filled shell effect [71]. As would be expected there is a greater degree of stabilisation in the f^0, f^{14} and the f^7 shell configuration, however it has also been found that internal division of f^3-f^4 and f^{10}-f^{11} pairing occurs. This is termed the 'double-double effect'. This degree of stabilisation explains many of the chemical characteristics of the lanthanide series, including the analytical difficulty in obtaining complete isolation of the lanthanide species. Generally, high separation factors can be obtained for La-Ce, Pm-Sm, Gd-Tb and Er-Tm pairs, whilst lower separation factors are observed for Pr-Nd, Eu-Gd, Dy-Ho and Yb-Lu. Consequently, in the development of analytical methodologies for ^{151}Sm and ^{166m}Ho, care should be taken to ensure that the associated paired element (Pm and Dy) is removed from the sample. This is especially true for the Sm-Pm system. Since ^{147}Pm is a high fission yield product (~2%), with a comparatively short half-life (2.6y), it follows that the specific activity will be higher than that of ^{151}Sm (0.44% fission yield, $t_{1/2}$~90y). Consequently, in those wastes where ^{151}Sm is present it is highly probable that appreciable activity

will be due to promethium isotopes in the sample. Since ^{147}Pm decays by β emission, this isotope will contribute to the LSC spectrum. It is impossible to select a suitable window for counting ^{151}Sm in the presence of ^{147}Pm, since the β decay energy of ^{147}Pm is greater than that of ^{151}Sm (224keV *c.f.* 76keV). Therefore, the tail of the spectrum from ^{147}Pm will contribute to the peak of the ^{151}Sm, making quantification of the spectrum impossible.

Generally, β-diketones have been used as the extracting agent, these include thenoyltrifluoroacetone and various neutral oxo-donors [71, 77]. It has also been observed that a combination of two extractants may result in a greater degree of extraction than either of the individual extractant species. This phenomenon is known as the synergistic effect. In synergistic extraction systems, there are various agents used, these include two different neutral or acidic ligands, or a chelating agent and a neutral (or acidic) ligand [78]. Analysis of the literature indicates that the most popular synergistic system uses β-diketones as the chelating agent and acidic organophosphorus compounds as the acidic agent. The metal chelates that result are called adducts. These compounds are then co-ordinately saturated by reacting with neutral ligands such as tri-n-butyl phosphate (TBP). The enhanced extraction capability is assumed to take place due to the formation of this mixed adduct species [71].

In samples that contain macro amounts of rare earth element, it is possible to use infra-red (I.R) techniques or titration schemes [71]. However, when analysing samples that contain trace levels (<1ppm) of analyte other detection schemes with greater sensitivity and lower limits of detection are required. Due to the difficulty in obtaining radiochemical lanthanide standards, much of the research and method development into this area has utilised AAS or ICP-MS techniques. Over the last decade a range of extraction chromatographic materials has been developed that allow isolation of the lanthanide species. Initially these materials, developed at Argonne National Laboratory, were designed for separating radionuclides from highly active waste liquors. However, the high selectivity and capacity of these resins have made them an attractive analytical tool when applied to the development

of analytical procedures involving geological and environmental matrices. This has led to some problems in that the concentration of the analyte is typically many orders of magnitude less than the bulk element concentration. Consequently, loading of the solution onto the column would lead to undesirable breakthrough scenarios. Therefore, it is necessary to remove the majority of bulk contaminants prior to loading on to the chromatographic material to ensure adequate separation.

The advent of these materials has led to a resurgence in interest in this analytical area. These materials have been used successfully in actinide separations involving many different geological and environmental materials.

There has, undoubtedly, been more analytical interest in the actinide area. This is in part due to the perceived waste management hazards associated with the actinide elements and the availability of radioanalytically pure actinide yield tracers.

Tabulated below are those radionuclides that are to be investigated and, alongside the radionuclides of interest, are those elements that will feature as contaminants within the matrix.

Table 1.7 Properties of selected long-lived radionuclides and elements that are expected to feature in concrete decommissioning wastes.

Radionuclides of interest				
Isotope	**Half-life**	**Principal formation route**	**Principal mode of decay (keV)**	**Secondary emissions (keV)**
^{36}Cl	300,000y	Activation	β^-, 710	None
^{99}Tc	213,000y	Fission	β^-, 290	None
^{129}I	17,000,000y	Fission	β^-, 191	Xe k x-ray 39.6
^{151}Sm	90y	Fission	β^-, 76	21.54 (discounted <1% intensity)
^{166m}Ho	1,200y	Activation	β^-, 70	Er k x-ray 184.07,711.69, 810.31
Predominant radionuclides in decommissioning wastes				
^{3}H	12.3y	Fission	β^-, 18.6	None
^{14}C	5730y	Activation	β^-, 157	None
^{60}Co	5.3y	Activation	β^-, 2824	1173
^{90}Sr	29.1y	Fission	β^-, 546	None
^{137}Cs	30.2y	Fission	β^-, 1176	661
^{147}Pm	2.6y	Fission	β^-, 224	None
^{155}Eu	4.7y	Fission		87, 105
Bulk contaminants				
Ca	N/A	Inherent	N/A	N/A
Fe	N/A	Inherent	N/A	N/A

1.14 Objectives of the work reported in this thesis

The primary aim of the work described is to develop analytical methods to determine a number of radionuclides in decommissioning concrete wastes. The methods should be robust and applicable to batch analysis schemes. Another requirement of the proposed methods are that they should be sensitive and the minimum detectable activity achievable should be less than 0.4Bq g^{-1} of sample. To reach these levels of activity each analytical parameter will need to be optimised to ensure that each chemical stage is of sufficient efficiency. Consequently, the chemical separation and counting procedure efficiencies are discussed at length. Since decommissioning samples may be highly contaminated with a variety of radionuclides, it would be beneficial if any analytical method developed could be used in tandem. That is, a single sample may be used to determine a number of different radionuclidic species. In this way only one digestion procedure would need to be carried out which would drastically reduce the overall time and production of hazardous waste products. If only one sample was taken for full radiochemical analysis, this would also reduce the activity dose to the analyst. The developed methodologies should have a limit of detection that is less than 0.4Bq g^{-1}, thus providing accurate and reliable information for waste management/performance assesment scenarios. Although concrete wastes have been analysed, the methods developed during this project may be applicable to other waste matrices. The applicability of the developed methods on graphite, steel and resins are beyond the remit of this work.

2.0 Studies into ^{36}Cl and ^{129}I Analysis

2.1 General Considerations

The analyses of samples containing chlorine and iodine are difficult because of the inherent problems associated with the digestion of the matrix. The sample generally requires digestion of some type which usually involves the use of acidic reagents such as nitric or sulphuric acid. The use of such acids can lead to volatilisation of the analyte and potential loss. Studies have shown that up to 90% of a halide can be lost in this manner [Personnal Communication, C. Harvey, Magnox, 1996]. The ease with which halides are volatilised can be exploited if a purged gas system is used. If the sample is treated with a strong mineral acid, (depending upon acid conditions) either the halide or halogen product will be formed [15, 46]. This species is then driven off the sample and trapped in a suitable trapping agent. An aliquot of the trapping agent can be used to directly measure the amount of halogen in the system by a number of analytical techniques. Since the concentration of the analyte may be low, it may be necessary to pre-concentrate the analyte. This may be achieved by using precipitation techniques. In this manner, all the analyte of interest is available for the determination, thus improving the likelihood of an accurate and reliable result.

Preliminary investigations studied the reaction conditions necessary to volatilise the chloride and iodide in the sample.

2.2 Reagents and instrumentation

2.2.1 Reagents

Pre-prepared concrete powder was purchased from a hardware retailer and was prepared following the instructions supplied. Radionuclides used in this work included ^{36}Cl and ^{125}I, both were supplied from ICN Biomedicals Inc., USA. For the

purpose of this work ^{125}I was substituted for ^{129}I. The primary working solution of ^{36}Cl had a specific activity of 1kBq g^{-1}. Subsequent stocks had a range of activities ranging from 100Bq g^{-1} to 0.1Bq g^{-1}. Stocks of ^{125}I solution were freshly prepared for each experimental set because of the short half-life of the isotope (60d). All solutions of ^{125}I were made from a working stock of specific activity 100kBq g^{-1}. Subsequent dilutions were prepared from the working solution. The specific activity of these radiotracer solutions ranged from 1kBq g^{-1} to 10Bq g^{-1}, inactive carrier was added. When using ^{36}Cl, the final concentration of chloride was 1mM (NaCl). When using ^{125}I, the final iodide concentration was 1mM. Adding additional halide, minimised/prevented analyte loss due to adsorption to the glassware. All tracer solutions were of neutral pH.

A number of analytical reagents were prepared and 18MΩ deionised water was used throughout. Grade A volumetric glassware was used to prepare solutions. All reagents were of Analytical Reagent grade and were supplied by Aldrich, Poole, UK. Solutions of the following reagents were used in the development of the analytical procedure for ^{36}Cl and ^{129}I: sodium hydroxide (0.1M to 6M), nitric acid (0.1M to 15.8M), concentrated hydrofluoric acid (48%), 2% (w/v) potassium permanganate, 6% (v/v) hydrogen peroxide, 0.2M sodium persulphate, 0.1M iron (III) nitrate, 0.1M iron (II) sulphate, saturated sulphurous acid, concentrated hydrazine, 0.1M silver nitrate, concentrated ammonia.

A number of solid reagents were also used, these were of Analytical Reagent grade and supplied by Aldrich: sodium nitrite, sodium hydroxide (pearl), anhydrous sodium carbonate, potassium thiosulphate and manganese dioxide.

Several scintillation cocktails were also investigated these are listed below:
BDH Liquid Scintillation Cocktail, BDH, Merck Limited, Lutterworth UK; Ecoscint, Nuclear Diagnostics, Hull, UK; Optiphase, EG&G Wallac, Milton Keynes, UK; Hionic Fluor, Ultima Gold LLT, Ultima Gold AB and Ultima Gold XR, Canberra Packard, Pangbourne, UK.

2.2.1.1 Preparation of spiked solutions

^{36}Cl spiked chloride solution

To a 25ml volumetric flask 0.25ml of 1M (calibrated) sodium chloride solution were added. To the flask ^{36}Cl tracer was added (0.1Bq to 1kBq). The sample made up to volume using de-ionised water. An aliquot of the tracer was then mixed with scintillant and counted on the LSC.

^{125}I spiked iodide solution

To a 25ml volumetric flask, 0.25ml of 1M (calibrated) sodium iodide solution were added. ^{125}I was added to the flask and the volume made up to the mark using de-ionised water. An aliquot was transferred to a γ vial and counted.

2.2.1.2 Preparation of doped concrete

Certified concrete standards containing ^{36}Cl and ^{125}I are not available. Consequently, samples had to be prepared 'in-house'. The composition of the standard should be identical to that of the sample; however, the chemical composition of concrete is not constant. The characteristics of the mix will be dependent upon a number of factors including the chemical and geological nature of the quarrying site and the cement:sand ratio. Decommissioning samples will be expected to contain a small amount of naturally abundant chlorine, ^{35}Cl and ^{37}Cl. However, this will generally be less than 2% of the total weight and therefore will not contribute significantly. Consequently, decommissioning samples will contain ^{36}Cl but will not contain significant inactive chloride. Consequently, the standards were prepared to mimic this, *i.e.* they contained ^{36}Cl and the chloride inherent in the concrete mix. Active concrete samples containing iodide were also prepared using ^{125}I only, inactive iodide carrier was not added.

To ensure the concrete mix was identical for each batch of standards, the concrete was mixed with water in a 5:1 concrete:water slurry. Portions of the slurry were then placed in small weighing boats and doped using either ^{36}Cl, ^{125}I or both. The samples were then placed in a dry room to dry at ambient temperature. The samples were left to cure for at least 1 month prior to use. After the samples had being cured

for 1 month, they were ground into a fine powder using a mortar and pestle. The powdered samples were then stored in an airtight container. The concentration of ^{36}Cl and ^{125}I can be accurately determined by taking the activity added and the dry weight of the concrete into account.

2.2.2 Instrumentation

^{36}Cl was counted on a Canberra Packard 2750 ultra low-level liquid scintillation counter. ^{125}I was counted in a well crystal (NaI (Tl)) Panax counter.

2.3 Optimisation of counting conditions

Initial investigations concerned the development of analytical methodologies for ^{36}Cl and ^{129}I. However, ^{125}I was used as a substitute for ^{129}I. ^{125}I is a γ photon emitter; therefore, the sample could be counted directly, either in solution or as a precipitate. Preliminary experiments were conducted using ^{36}Cl, which is a β emitter and its activity must be determined by liquid scintillation counting. The sample will need to be mixed with a scintillant prior to counting. Consequently, the characteristics of the scintillant will have a significant effect on the counting efficiency. Since low levels of activity will be determined it is important to optimise the counting conditions. Initial experiments would focus on the transfer of the analyte of interest, therefore samples would be counted directly at each stage of the analysis. Consequently, it was important to investigate the proposed chemical compatibility with counting conditions (scintillant, pH *etc.*) at each stage of the analysis.

Prior to any experimental development work, it was necessary to determine the counting efficiency of the scintillant with ^{36}Cl. It was also important to determine if there would be any compatibility problems, possibly due to the pH or salt concentration of the sample. A number of experimental parameters were investigated, these included the counting efficiency of the scintillant with ^{36}Cl, miscibility of scintillant with alkali, loading capacity of the scintillant with AgCl, degradation of efficiency with time.

2.3.1 Efficiency of scintillant with ^{36}Cl

To a series of scintillation vials 20ml of scintillation cocktail were added. To each vial 0.1g (100Bq) of stock solution were added. The samples were then shaken vigorously to ensure thorough mixing. The samples were left to dark adapt for 1 hour prior to counting. The samples were then counted on the LSC for 15 minutes using a pre-set counting programme. The table below shows the relative counting efficiency of each of the scintillants.

Table 2.1 Counting efficiency of cocktail scintillant

Scintillant	Characteristics	% Relative Efficiency
BDH	2 Phase	25.5
Ecoscint	1 Phase	99.2
Hionic Fluor	1 Phase	99.9
Opti-Phase	Precipitate	100
Safe-Fluor	1 Phase	99.4
Ultima Gold AB	1 Phase	99.9
Ultima Gold LLT	1 Phase	99.8
Ultima Gold XR	1 Phase	99.8

From the table, it can be seen that the majority of cocktail scintillants would be suitable for the counting of ^{36}Cl. BDH liquid scintillation cocktail would be unsuitable because of its low counting efficiency. Although Opti-Phase gave the highest counting efficiency, this cocktail would also be unsuitable since a precipitate resulted. Since the salt concentration was low (0.1g of 1mM NaCl) and the pH was neutral, this incompatibility is possibly due to aqueous intolerance.

2.3.2 Miscibility of scintillant with alkali

To a set of scintillation vials, 0.1g of ^{36}Cl tracer were added to each vial followed by 1.9ml of 1M NaOH.. The resulting mixture was then mixed with 18ml of scintillant. The samples were then treated as detailed in 2.3.1. Table 2.2 shows the effect of alkali on the counting efficiency.

Table 2.2 Effect of alkali on the counting efficiency of scintillant

Scintillant	Characteristics	% Relative Efficiency
BDH	2 Phase	19.9
Ecoscint	Precipitate	63.4
Hionic Fluor	1 Phase	100
Opti-Phase	Precipitate	51.8
Safe-Fluor	2 Phase	96.9
Ultima Gold AB	1 Phase	97.3
Ultima Gold LLT	2 Phase	51.6
Ultima Gold XR	2 Phase	53.4

Investigation into the effect of alkali on counting efficiency indicated that there was a significant decrease in efficiency when alkali was introduced into the system. These experiments showed that several of the scintillants are incompatible with high pH systems. This was supported by both the decrease in counting efficiency and the formation of multi-phase systems.

From the previous set of experiments, it was found that Hionic-Fluor had a relatively high counting efficiency for ^{36}Cl in the presence of 1M sodium hydroxide. It was necessary to determine the alkali tolerance of this scintillant to ensure that alkali doping did not exceed this limit.

2.3.3 Loading capacity of Hionic-Fluor scintillant with 1M sodium hydroxide

To ensure that the effect that was observed was due to alkali burden all vials were made up to a final aqueous volume of 5ml 1M sodium hydroxide solution was added to each vial in 0.5ml increments. To each vial 0.1g of ^{36}Cl tracer were added. The solution was then mixed with Hionic-Fluor. The sample was then treated as previously discussed. Table 2.3 shows how the scintillant is affected by hydroxide loading.

Table 2.3 Effect of alkali on the counting efficiency of scintillant

Volume 1M NaOH (g)	Characteristics	% Relative Efficiency
0.5	Clear 1 phase	99.76
1.0	Clear 1 phase	99.82
1.5	Clear 1 phase	99.64
2.0	Clear 1 phase	100
2.5	Clear 1 phase	99.49
3.0	Opaque 1 phase	97.15
3.5	Opaque 1 phase	94.52
4.0	Opaque 1 phase	92.34
4.5	Precipitate	78.42
5.0	Precipitate	76.38

The results in the table show that even at high alkali burden, the counting efficiency is high (~80%), however, for optimum conditions the experiments indicate that the alkali burden should not exceed a 2.5ml of alkali.

For reliable counting statistics it may be necessary to count the sample for prolonged periods of time, consequently it was necessary to determine whether the scintillant degraded with time.

2.3.4 Degradation of scintillant with time

Samples from 2.3.3 were counted continuously over a 48 hour period. It was found that there was little decrease in efficiency. The efficiency remaining over 99% during the count period.

2.4 Effect of reaction conditions on halide transfer

The electrode potential of each of the halides is significantly different. This difference enables a method to be adopted whereby it is possible to selectively oxidise the halide species. In doing so, the halide is then separated from other components in the bulk matrix as well as other halides contained in the sample.

In this work, nitric acid was used as the digesting agent. This acid was selected because of its oxidising capability and inability to form insoluble products. Observation of the electrode potentials of the half reactions in the analysis, indicate

that whilst nitric acid will oxidise I^- to I_2 it will not oxidise Cl^- to Cl_2. However, the Cl^- ion may become protonated, forming HCl, itself a volatile product.

$Cl_2 + 2e^- \rightarrow 2Cl^-$	1.36V
$I_2 + 2e^- \rightarrow 2I^-$	0.54V
$NO_3^- + 3H^+ + 2e^- \rightarrow HNO_2 + H_2O$	0.934V

Consequently, the digestion was carried out in apparatus as shown in Figure 2.1. The system was checked to ensure that there were no loose connections and that the system was airtight. To the apparatus, a test solution containing ^{36}Cl, ^{125}I and halide carriers were added. To the solution, 50ml of 8M nitric acid were added. The system was heated at 80°C and stirred continuously. The volatile products were trapped in 1M NaOH. Aliquots were taken from the hydroxide trap every 30 minutes to examine the rate of halide transfer. The results obtained from the experiment are shown in Table 2.4. It can be seen that under these conditions the iodide is transferred in an almost quantitative manner over a three-hour digestion period, whereas there is no transfer of the chloride.

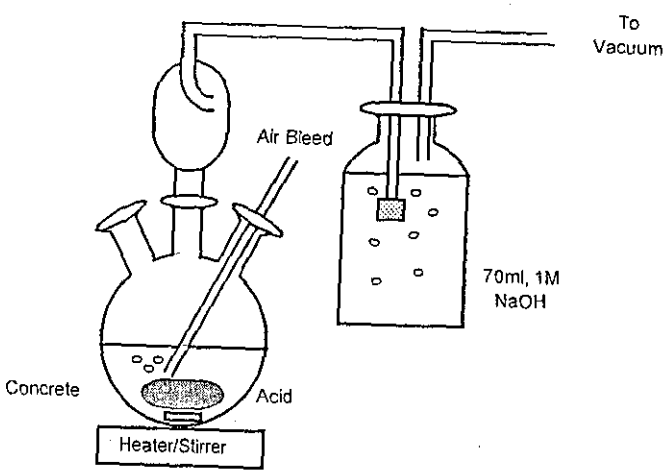


Figure 2.1 Digestion apparatus

Table 2.4 Rate of halide transfer with 8M nitric acid

Time (minutes)	% Iodide		% Chloride	
	Reaction Vessel	Trap	Reaction Vessel	Trap
30	24	76	100	0
60	14	86	100	0
90	18	82	100	0
120	6	94	100	0
150	6	94	100	0
180	6	94	100	0

2.4.1 Effect of oxidising agent on rate of halide transfer

Although nitric acid is an oxidising agent, it was found that this was too weak to oxidise the chloride to chlorine. Consequently, a stronger oxidising agent is required to oxidise the Cl^- to Cl_2. Hydrogen peroxide was thought to be a suitable reagent because of its oxidising potential [15]. An advantage when using H_2O_2 is that the reduced form is water and therefore the potential for detrimental side reactions are reduced. Other oxidising agents were also investigated, these being, manganese dioxide, and potassium permanganate.

Initially the effect of the oxidising agent on the transfer of the halide was investigated on separate Cl^- and I^- solutions.

To the reaction vessel containing inactive halide and radioactive tracer, the oxidising agent was added, (10ml 6% (v/v) H_2O_2 or 0.2g $KMnO_4$ or 0.2g MnO_2). To the reaction, 50ml of 8M nitric acid were added and the solution heated to 80°C. The reaction was carried out using a gas purge, all gases passing through a 1M NaOH trap. From the trap a 2ml aliquot was removed every 30 minutes over an 8 hour period. This aliquot was then mixed with Hionic Fluor scintillant (if Cl^-) or if I^-, the aliquot was counted directly in the well crystal γ detector. The % activity transfer at the end of the experiment is shown in Table 2.5. The rates of transfer of the halide species to the hydroxide trap are shown in Figure 2.2 and 2.3.

Table 2.5 % Halide activity transferred to 1M NaOH trap

^{36}Cl Activity		
Reaction Conditions	% Reaction Vessel	% Hydroxide Trap
8M nitric acid	100	0
Acid + H_2O_2	40.2	59.8
Acid + MnO_2	10.2	89.8
Acid + $KMnO_4$	9.2	90.8
^{125}I Activity		
8M nitric acid	0	100
Acid + H_2O_2	7.6	92.4
Acid + MnO_2	88.9	11.1
Acid + $KMnO_4$	100	0

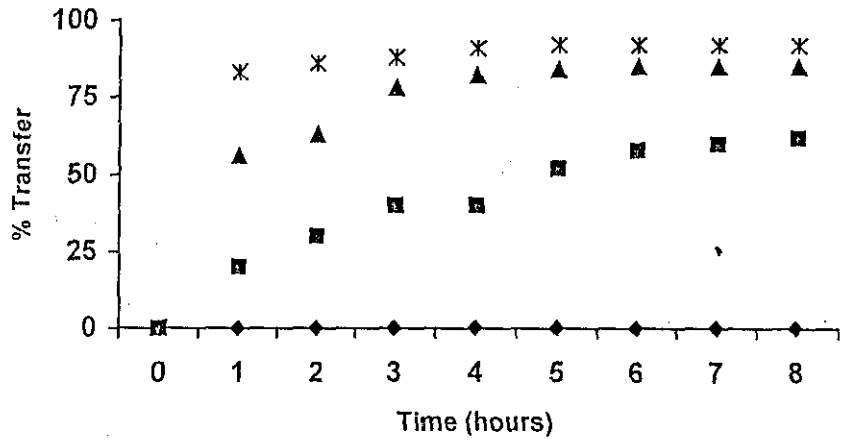


Figure 2.2 Cl_2 transfer from reaction vessel to halide trap

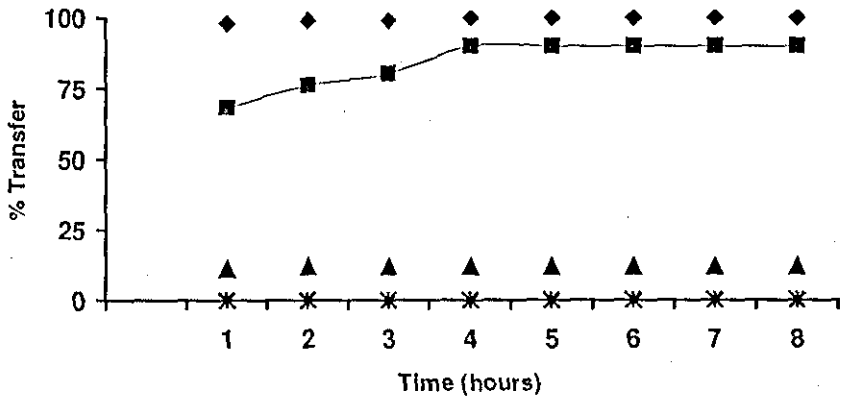


Figure 2.3 I_2 transfer from reaction vessel to halide trap

From both the table and graphs, it is clear that the oxidation of iodide requires a different oxidising agent than that of chloride. In fact, it should be noted that the most effective oxidising agent for the iodide system (HNO_3) is the least effective for the chloride system. It was also observed that the most effective oxidising agent for the chloride system ($KMnO_4$) did not oxidise the iodide to iodine. The stronger oxidising agents will oxidise the iodide species to the iodate, therefore transfer of the volatile I_2 species will not occur since under these oxidising conditions it is not formed. Although hydrogen peroxide was found effective for oxidation of both the chloride and iodide, use of this reagent would lead to the formation of both I_2 and Cl_2. Therefore both halides would be transferred together and halide separation would not occur. Consequently, it was decided to use nitric acid to oxidise the iodide to iodine and after all the iodine had been transferred, potassium permanganate would be added to oxidise all the chloride in the system to chlorine. If any iodide remained in the reaction vessel it would be oxidised to the iodate and remain in the reaction vessel. This procedure would enable both the halides to be transferred separately from the reaction vessel.

These simple experiments indicated that the oxidative conditions within the reaction vessel could be manipulated so that the halides could be separated from the bulk matrix and isolated from each other. Experiments were then carried out to investigate the possibility of separating the halides from the matrix by selective oxidation.

To the reaction vessel, a calibrated mixed halide solution containing NaCl, NaI, ^{36}Cl and ^{125}I was added. The apparatus was set up as shown on Figure 2.1. The system was then purged under a slightly reduced pressure, all gases being passed through a 1M NaOH trap. To the vessel 50ml of 8M HNO_3 were added. The system was then agitated continuously and heated to 80°C. All volatile products were trapped in the 1M NaOH. Every hour an aliquot of the hydroxide was removed for both γ and β analysis. After three hours, the trapping apparatus was dismantled and the hydroxide was replaced with a fresh 1M solution. The system was then re-connected and 10ml of 2% (w/v) $KMnO_4$ solution were added. The experiment was continued for a

further four hours. An aliquot of hydroxide was removed for γ and β analysis every hour. The % activity transfer at each analysis point are shown in Table 2.6. The rates of transfer of the halide species to the hydroxide trap are shown in Figure 2.4.

Table 2.6 Transfer of halide under selective oxidising conditions

Transfer of ^{125}I Activity	
Time (hours)	% Hydroxide Trap
1	92
2	95
2	99
Transfer of ^{36}Cl Activity	
4	53
5	81
6	86
7	88

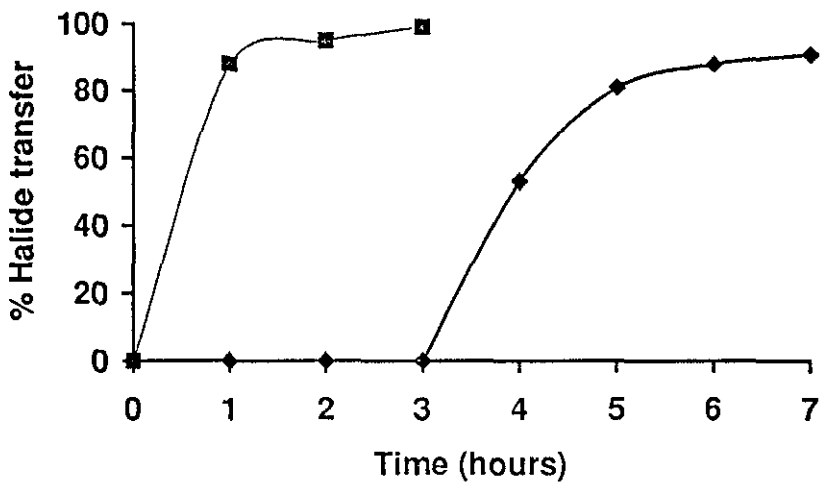


Figure 2.4 Rate of halide transfer using 2 stage oxidation

As can be seen in Figure 2.4 the 2 stage oxidation process was successful in that the oxidation conditions could be controlled. By controlling the oxidation conditions, it was possible to selectively oxidise the analyte of interest. Consequently, the halide could be removed from the bulk matrix and separated from other halides in the sample.

Experiments were also carried out to determine if ICl was formed. If radioactive iodide and chloride were used it would be difficult to determine if the product was being formed. The transfer of iodine from the reaction vessel to the trap was easily observable due to the formation of purple gas. Consequently, initial experiments used inactive iodide with inactive chloride and ^{36}Cl. The 2 stage oxidation reaction was then carried out. Initially nitric acid was added and the formation of I_2 was observed. After three hours an aliquot from the hydroxide trap was taken for γ and β analysis. The reaction was then continued for a further four hours using fresh hydroxide solution, addition of 2% potassium permanganate increased the oxidation potential of the reaction system. At the end of the experiment, an aliquot of hydroxide was analysed by both γ spectrometry and LSC. An identical experiment was also carried out using inactive chloride with inactive iodide with ^{125}I. Results are shown in Table 2.7.

Table 2.7 Investigation into the formation of ICl

Oxidation Conditions	Oxidation Stage 1	Oxidation Stage 2
^{36}Cl		
Experiment 1	Inactive I, no ^{36}Cl activity	Inactive Cl + ^{36}Cl activity
^{125}I		
Experiment 2	Inactive I + ^{125}I	Inactive Cl, no ^{125}I activity

Counting of the hydroxide aliquots indicated that in experiment 1, no β activity was associated with the hydroxide solution from stage 1 of the oxidation reaction. All β activity was associated with stage 2 oxidation. In experiment 2 it was found that all γ activity was associated with the first oxidation stage, no γ activity was found in the hydroxide solution under stage 2 oxidation conditions. These experiments indicated that no ^{36}Cl came over under the initial oxidising conditions. During the second oxidation stage, no ^{125}I came over with the Cl_2. Therefore, these experiments proved that if any ICl was formed during the reaction it was not transferred from the reaction vessel.

ICl hydrolyses easily in the presence of aqueous media. As the reaction vessel contains aqueous solution, it follows that if ICl was formed it would hydrolyse in the

aqueous solution and would therefore not be transferred as ICl to the sodium hydroxide trap.

Consequently, these experiments indicated that selective oxidation was a viable separation process. As these experiments had been carried out using spiked solutions, it was necessary to investigate the effectiveness of this process when Cl and I were associated with the concrete matrix.

2.5 Investigation into the digestion of the concrete matrix

In this study three concrete digestion procedures were investigated: acid digestion, alkali digestion and total dissolution schemes.

All concrete samples used in these investigations were prepared as concrete blanks, *i.e.* no radiotracers had been used to dope the sample.

2.5.1 Acid digestion

The acid used has two roles. The primary function of the acid is to break down the matrix and to ensure that the analyte of interest is in solution. The second function is to oxidise all oxidisable species that are in solution. Heat will increase the rate of matrix breakdown and therefore encourage analyte solubilisation. Since it is matrix breakdown that is being analysed and not analyte loss, digestion studies were carried out in vessels open to the atmosphere.

To glass beakers a 5g aliquot of milled concrete was added. To each beaker, 25ml of nitric acid (0.1M to conc.) were added. The samples were then stirred continuously and heated at 80°C for 1 hour. After the allotted time the samples were removed from the hotplate and then allowed to cool. The samples were then filtered under suction and the solids transferred to a petri dish. The solids were then oven dried at 110°C overnight. The samples were then transferred to the dessicator to cool. When cool the samples were weighed, and the mass loss determined. The results are shown in Table 2.8.

Use of nitric acid solubilised ~ 25% of the concrete. However, since the matrix was not fully solubilised there may be uncertainty as to whether all of the analyte of interest had been leached from the matrix. At high acid concentrations the reaction between the concrete and the acid was vigorous, due to the H^+ reaction with the alkali based matrix. This generated significant heat and some sample was lost due to foaming. Any volatile products formed were likely to be lost at this point.

Table 2.8 Acid digestion: - Effect of acid concentration on concrete matrix breakdown.

Solvent	Milled Wt Before (g)	Milled Wt After (g)	Appearance	% Wt Loss
Deionised Water	5.082	4.97	Grey/brown	2.27
0.1M HNO_3	5.009	4.84	Grey/brown	3.32
2M HNO_3	5.031	4.00	Grey/orange	20.41
4M HNO_3	5.020	3.58	Pale grey/white	28.62
8M HNO_3	5.003	3.22	Pale grey/white	35.71
12M HNO_3	5.056	3.19	Pale grey/white	36.83
conc. HNO_3	5.014	3.10	Pale grey/white	38.17

2.5.2 Alkali digestion

Since the concrete itself is alkali in nature, due to the calcium carbonate and calcium oxide components, it was thought that strong alkali would have little effect on breaking down the concrete. However, if the matrix could be broken down with alkali this would prove advantageous since there would be no possible loss of analyte as volatile products would not be formed under these conditions.

To a glass beaker 5g of milled concrete were added. To each beaker 25ml of sodium hydroxide (0.1M to 6M) were added. A watchglass was placed over each sample and then heated at 80°C for 1 hour. After filtering the solids were transferred to a petri dish and dried overnight at 110°C. The samples were dried in a dessicator and weighed. Weight loss was then determined. The results are shown in Table 2.9.

From the table, it can be seen that the use of hydroxide does not successfully digest the concrete. Even at high alkali concentrations (6M), the amount of the sample digested is less than 5%.

Table 2.9 Alkali digestion: - Effect of alkali concentration on concrete matrix breakdown

Solvent	Milled Wt Before (g)	Wt Insolubles (g)	Appearance	% Wt Loss
Deionised Water	5.006	4.89	Grey/brown	2.38
0.1M NaOH	5.018	4.87	Grey/brown	2.96
1M NaOH	5.073	4.90	Grey/brown	3.42
2M NaOH	5.052	4.87	Grey/brown	3.61
4M NaOH	5.069	4.89	Grey/brown	3.49
6M NaOH	5.022	4.83	Grey/brown	3.86

2.5.3 Total dissolution

2.5.3.1 HF digestion

Total dissolution procedures rely on HF/HNO_3 digestion for silica containing matrices. Since HF will attack and solubilise any silica within the sample, then special reaction equipment is required. For HF digestion, the samples must be digested in Teflon beakers, since this is one of the few materials that can withstand continuous HF attack. Extreme care must be taken when using HF because of the health hazards associated with this chemical. Safety precautions must be applied and adhered to at all times. Introduction of any H^+ species will result in loss of the analyte due to the formation of volatile species.

1g of milled concrete was transferred to a Teflon beaker. To the beaker 5ml of concentrated nitric acid and 15ml of 48% hydrofluoric acid were added. The beaker was then covered using a Teflon watch glass and heated at 80°C for 1 hour. The cover was then removed and the sample dried. The sample was then checked for any insoluble material. If insoluble material was present, further portions of nitric acid/hydrofluoric acid mixtures were added until the entire sample had been solubilised. When the sample had been fully solubilised, the sample was dried several times with concentrated nitric acid to ensure that all the hydrofluoric acid had been driven off. The sample was then filtered and insolubles determined. The results are shown in Table 2.10.

Table 2.10 Mixed acid digestion - Effect of concrete mass

Sample	Milled Wt Before (g)	$HF:HNO_3$ (ml)	Number of attacks required	Milled Wt After (g)	Appearance	% Wt Loss
1	1.021	15:5	3	0	All solubilised	100
2	2.028	30:10	5	0.37	White residues	82
3	1.008	15:5	3	0.02	White residues	98
4	2.061	30:10	4	0.27	All solubilised	87
5	1.019	15:5	2	0	All solubilised	100
6	1.997	30:10	4	0.44	White residues	78
7	1.068	15:5	3	0	All solubilised	100
8	2.034	30:10	4	0.20	White residues	90

Acid digestion of the concrete matrix is unsuitable for many radionuclides if a volatile species is produced. In the presence of H^+, chloride ions will form HCl. Unless the sample is digested in a closed environment, this gas will then be lost to the atmosphere. Due to the particularly harsh nature of hydrofluoric acid, it is not possible to carry out digestion of the concrete in a closed environment, since the digestion apparatus for such a procedure is not available. If HF digestion was to be used on a routine basis, it must be shown that loss of the analyte does not occur.

A set of experiments was performed to investigate the loss of analyte (Cl^-) with different digestion conditions.

To a set of Teflon beakers 1g of milled concrete was added. To each beaker 1ml of calibrated NaCl solution (0.9382M) was also added. To each beaker ~5ml of water were added to produce a slurry. This was left overnight so that isotopic exchange could occur. To the sample a 3:1 mixture of HF/HNO_3 was added and the sample heated. The sample was repeatedly attacked with the HF/HNO_3 mixture until the sample was fully dissolved. The sample was then dried to incipient dryness and the sample diluted with 100ml of deionised water. The pH of the sample was altered to 3 using dilute nitric acid. To the sample excess 0.1M $AgNO_3$ solution was added. The precipitate formed was then filtered and washed using dilute nitric acid (0.01M). The recovery of the chloride was then determined by the gravimetric technique. See Table 2.11.

Table 2.11 Loss of chloride by HF/HNO_3 acid digestion

Sample	1	2	3	4
Wt Milled Concrete (g)	1.0082	1.0265	1.0012	1.0006
Wt 0.9382M NaCl (g)	1.0532	1.0526	1.0529	1.0522
Theoretical Wt AgCl (g)	0.1418	0.1417	0.1418	0.1417
Wt AgCl	0.0340	0.0282	0.0216	0.0264
% Recovery	23.98	19.90	15.23	18.63

Mixed acid digestion led to unacceptable analyte loss. Since hydrofluoric acid is a weak acid, there was the possibility that HF digestion alone would not cause such significant losses of chloride as HCl. Therefore, experiments were set up to investigate Cl^- loss by HF digestion.

The experiment was performed following the protocol as discussed previously. However, the matrix was attacked with 48% HF. Nitric acid was not used. After the samples had been attacked six times, the samples were cooled and de-ionised water added to make up the final volume to 100ml. To the sample 0.1M $AgNO_3$ was added to form the AgCl precipitate. The precipitate was filtered and washed using 0.01M HNO_3 to prevent colloid formation. The precipitate was then dried to constant mass and the Cl^- recovery determined by gravimetric techniques. See Table 2.12.

Although the concrete was attacked continuously, there remained unsolubilised particulates in the beakers. Consequently, HF digestion is not as effective as HF/HNO_3 mixed acid digestion. However, from the table it can be seen that the chloride losses were still unacceptably high.

Table 2.12 Effect of HF digestion on chloride loss

Sample	1	2	3	4
Wt Milled Concrete (g)	1.0192	1.0024	1.0046	1.0137
Wt 0.9382M NaCl (g)	1.0462	1.0512	1.0502	1.0487
Theoretical Wt AgCl (g)	0.1409	0.1415	0.1414	0.1411
Wt AgCl	0.0211	0.0265	0.0239	0.0204
% Recovery	14.98	18.73	16.90	14.46

2.5.3.2 Fusion techniques

There are a variety of alkali salts that can be used to fuse materials such as rock, minerals and concrete. There are many factors that need to be considered when selecting an optimum flux agent and these include:

i) Fluxing Temperature
ii) Sample Mass
iii) Crucible Material

Flux Temperature If the analyte of interest forms volatile products above 800°C, then using a fluxing agent with fusion temperature of 1100°C would lead to significant losses and would prove to be of little use.

Sample Mass Many fluxing agents have an optimum flux:sample ratio. Consequently, the total size of the flux:sample mixture will be limited due to the size of the crucible. Obviously, a fluxing agent:sample mixture that is in the ratio of 7:1 (*e.g.* lithium metaborate) will have less sample than a fluxing agent with optimum flux:sample ratio of 4:1 (*e.g.* sodium hydroxide). Therefore, if the analyte of interest is at a very low concentration, and a large sample size is required, then the lowest flux:sample reagent would be preferable.

Crucible Material The fluxing agent will invariably attack the crucible to a small extent. It is for this reason that the resultant solutions cannot be analysed for elements contained in the crucible. The cost of the crucibles (*e.g.* platinum) can be prohibitive if large scale multi sample analyses are to be performed. For fluxing reagents that flux at very high temperatures *e.g.* 800-1000°C then platinum or graphite crucibles are the only option. For lower temperature fluxing agents (300-500°C) zirconium or nickel crucibles can be used.

Samples are generally placed in a muffle furnace and the temperature ramped up to the flux temperature. Ramping the temperature ensures that the sample is heated throughout and ensures an even melt. The sample can also be heated using a Meker

burner, however this strong method of heating may lead to spluttering of sample and consequent sample loss.

Various fluxing agents were investigated; fluxes that fused at lower temperatures were studied, since at higher temperatures loss of the halide may occur. Porcelain and zirconium crucibles were used, initially unspiked concrete was prepared and this was fused with the fluxing material under investigation.

To a crucible 1g of milled concrete was added. To the sample fluxing agent was added in the ratio of 5:1 as compared to the sample weight. The sample was then transferred to a muffle furnace where the temperature was ramped slowly until the fluxing temperature had been reached. The sample was then heated at this temperature for 2 hours to ensure that the melt had had sufficient time to attack and breakdown the matrix. The resulting melt was then dissolved in dilute nitric acid. The acid concentration was always kept below 2M, which ensured that the acid was not acting as an oxidising agent and therefore did not lead to analyte loss. The sample was then filtered and the insolubles determined. Results are shown in Table 2.13.

One of the main disadvantages in using fusion techniques is that high salt levels are introduced into the sample. There may also be a small level of contaminant of the analyte of interest *e.g.* Cl^-, and although the contaminant will be inactive, this impurity may affect the analysis if gravimetric determination is used as the recovery indicator.

Table 2.13 Fusion conditions investigated to breakdown the concrete.

Sample	1	2	3	4	5	6
Milled Wt Before (g)	1.021	2.028	1.008	2.061	1.019	1.997
Flux Agent	NaOH	NaOH	Na_2CO_3	Na_2CO_3	$K_2S_2O_7$	$K_2S_2O_7$
Ratio Flux:Sample	1:4	1:4	1:5	1:5	1:4	1:4
Flux Melting Pt (°C)	320	320	850	850	300	300
Fuse Temp (°C)	700	700	950	950	700	700
Temp Maintained (min)	30	60	30	60	30	60
100% Solubilisation?	Yes	Yes	No	No	No	No
Ease in Dissolving Alkali Melt	Yes	No	n/a	n/a	n/a	n/a

To reduce problems caused by the high salt concentration, the concrete sample was also digested using a lower flux:sample ratio. Here the flux is mixed in a 2:1 ratio with the sample, when the flux becomes ignited it will attack the concrete matrix and break it down to an extent that renders it soluble when dissolved in acid media. This process is called sintering and is usually carried out at a lower temperature, generally not that different from the flux melting point. This temperature is typically maintained for 1-2 hours. The three flux salts were investigated to determine their possible use as sintering agents.

The concrete sample was added to the crucible along with the alkali salt. The ratio of flux:salt was low, typically less than 1:3. The sample was then placed in a muffle furnace and the temperature ramped up to a maximum. This temperature was maintained for 2 hours. After 2 hours the sample was removed from the furnace and cooled. The resultant melt was then dissolved using dilute nitric acid and insoluble material determined. The results are shown in Table 2.14. From the table it can be seen that the sintering agents were unable to solubilise the concrete. Consequently, this digestion method is unsuitable for the concrete matrix.

Table 2.14 Effect of sintering on concrete solubilisation

Sample	1	2	3	4	5	6
Milled Wt Before (g)	1.006	2.009	1.082	2.038	1.004	2.018
Flux Agent	NaOH	NaOH	Na_2CO_3	Na_2CO_3	$K_2S_2O_7$	$K_2S_2O_7$
Ratio Flux:Sample	1:2	1:3	1:3	1:3	1:2	1:2
Flux Melting Pt (°C)	320	320	850	850	300	300
Fuse Temp (°C)	400	400	900	900	400	400
Temp Maintained (hours)	1	2	1	2	1	2
100% Solubilisation?	No	No	No	No	No	No

2.5.4 Adopted digestion/dissolution procedure

From the digestion studies it was found that mixed acid digestion and NaOH fusion were the best digestion procedures to dissolve the concrete matrix. However, it was also shown that these methods were only suitable for a small sample size, generally less than 2g. There was the possibility that digestion of the matrix using hydrofluoric acid would lead to intolerable losses of chloride due to the formation of HCl,

experiments using inactive concrete with NaCl carrier confirmed that chloride loss occurred. Initially unspiked concrete was digested using a nitric/hydrofluoric acid mixture, although the sample was fully solubilised, over 80% of the chloride was lost.

It was also shown that NaOH was a suitable fluxing agent. Although three fusion agents were investigated only sodium hydroxide proved to be feasible. Sodium carbonate and potassium pyrosulphate did not fully digest the matrix, particulate matter was still evident even after the sample had been fused for several hours. Although sodium hydroxide broke down the concrete matrix it has several limitations with respect to being used as a standard laboratory reagent for the analysis of cementitious materials. These include the high flux:sample ratio required, and the introduction of a high salt content. Since there must be 4 parts fluxing agent to 1 part sample it follows that this severely limits the size of the sample that can be analysed. Many radionuclides within the concrete matrix will be at extremely low levels (mBq g^{-1}) and, consequently, it would be advantageous if a large sample size (>2g) could be taken for analysis. Another problem with fusion techniques becomes evident if the resultant solution is to be analysed using AAS or ICP-AES methods. High salt concentrations can cause erratic performance of nebulizers, high background signals and clogging of the apertures. Sintering techniques can be used to reduce the salt concentration, however experiments performed during this work suggest that this process is not useful for cementitious material.

Selective leaching techniques were also investigated. In these experiments the matrix is slightly broken down and the analytes of interest leached from the matrix. Concentrated acid and alkali leachants were studied. Both lead to some dissolution, however dissolution was greater when acid leaching agents were used. With the alkali it was found that the matrix was not physically affected to any great extent since the concrete matrix itself is a basic material. It was shown that the integrity of the matrix was not visibly affected. Break down of the matrix was insignificant, as was indicated by weight loss. Even at high alkali concentrations weight loss did not exceed 5%. Acid attack digested the matrix to a greater extent. At high acid

concentration the matrix was visibly affected. This was evident from both the weight loss and the physical nature of the matrix after digestion had occurred. The concrete was partially solubilised and a gelatinous sludge resulted. At high acid concentrations the concrete changed from a grey/brown powder to a grey/white sludge. Weight loss of the sample was significant with nearly 40% of the sample becoming solubilised. It was shown that at high acid concentrations a 5g sample could be significantly broken down. Although under these conditions chloride will be lost, if the digestion takes place in a closed environment, chloride loss as HCl cannot occur.

Due to the large sample tolerance and indications that significant solubilisation of the concrete matrix occurs it was decided to selectively leach the halide from the matrix using acid digestion. This dissolution method also circumvented the need for hazardous reagents such as hydrofluoric acid. Methods relying on fluxing techniques were also ruled out due to the problems associated with high salt content, and the limitation with sample size.

2.6 Trapping of halide

When the halogen gas dissolves in the hydroxide, the resulting solution contains a *mixture of products*. The products that will be formed will be the halide and the halate ion. The ratio of these two species is thought to be 5:1 (halide to halate), however, this ratio is not fixed and is dependent upon a number of factors including the temperature and concentration of hydroxide.

$$3X_2 + 6OH^- \rightarrow 5X^- + XO_3^- + 3H_2O$$

During the digestion process it is likely that water vapours will come across and be absorbed by the hydroxide. Consequently the concentration of the hydroxide will change during the experiment this will then affect the ratio of halide to halate species. If an aliquot from the solution was going to be taken for analysis the ratio of the species would not be a consideration. However, since the concentration of the

analyte of interest is at such a low level, then to improve detection, all of the species must be taken for measurement. For the halide species this can be easily achieved using silver precipitation methods followed by gravimetric determination. Consequently, it is of paramount importance that there is only one species in solution or the accurate ratio of species is known. As discussed earlier the ratio of halide to halate is variable, therefore if gravimetric determination is to be used it will be necessary to either oxidise the halide to the halate or reduce the halate to the halide.

2.6.1 Oxidation of Halide to Halate

As it is proposed that the species formed will be used to gravimetrically determine the yield of the procedure it follows that the solid must have a very low solubility in a given solvent. For analysis of β emitters, the sample should be dissolved in a suitable solvent and mixed with a scintillant. This mixture should be stable over a long counting period. For γ emitters the physical nature of the counting source is not as important.

Since the halate species are more soluble than the halide, it would be advantageous to convert the halide species to the halate using a suitable oxidising agent (OA):

$$X^- + OA \rightarrow XO_3^-$$

OA = oxidising agent in the above equation

Several oxidising agents were investigated: hydrogen peroxide, nitric acid, potassium permanganate and iron (III) salts.

To reduce the possibility of losses to the atmosphere, all reactions were carried out under reflux to minimise losses of volatile products.

To a round-bottomed flask 1ml of 1M calibrated halide carrier was added. To the solution the oxidising agent was added (10ml of 6% H_2O_2; 1g of $Na_2S_2O_8$, 10ml of 1M HNO_3, 5ml of 1% $KMnO_4$ or 10ml of 1M Fe (III) nitrate). The sample was then heated gently and reacted for 1 hour under reflux. The reaction was then stopped and reflux continued for a further hour whilst the sample cooled. The reaction vessel was

immersed in cold water to increase the rate of cooling. The samples were then filtered and the filtrate and washings transferred to a beaker. The pH of the sample was adjusted to pH 4 using dilute nitric acid. To the solution an excess of 0.1M $AgNO_3$ solution was added to precipitate the halide. The precipitate was then filtered from the sample. Since AgCl is a white solid and $AgClO_3$ is yellow, AgI is yellow and $AgIO_3$ is a white precipitate, the effect of the oxidising agent is easily observed due to colour of the resulting precipitate. The results are shown in Table 2.15.

From the table, it can be seen that the oxidising agents investigated were unsuitable, *i.e.* all agents investigated were unable to convert the halide to the halate species.

Table 2.15 Effect of oxidising agent on halide oxidation

Sample	Anion	Oxidising Agent	Addition of $AgNO_3$	Inference	Oxidation?
1	I^-	H_2O_2	Yellow ppt	AgI	No
2	I^-	$Na_2S_2O_8$	No ppt	I^- lost	No
3	I^-	HNO_3	No ppt	I^- lost	No
4	I^-	$KMnO_4$	Yellow ppt	AgI	No
1	Cl^-	H_2O_2	White ppt	AgCl	No
2	Cl^-	$Na_2S_2O_8$	No ppt	Cl^- lost	No
3	Cl^-	HNO_3	White ppt	AgCl	No
4	Cl^-	$KMnO_4$	No ppt	Cl^- lost	No
5	Cl^-	Fe (III)	White ppt	AgCl	No

Experiments indicated that conversion of the halide to the halate was difficult, therefore ways in which the halate could be converted to the halide were investigated.

2.6.2 Reduction of Halate to Halide

Investigations were carried out to determine if the halate could be reduced to the halide using readily available reducing agents (RA).

$$XO_3^- + RA \Rightarrow X^-$$

RA = reducing agent in the above equation.

A number of reducing agents were studied, these include: $NaNO_2$, H_2SO_3, N_2H_4 and Fe (II) sulphate.

As in previous experiments, the reduction was carried out under reflux to minimise halide losses due to the formation of volatile gaseous products.

To a round-bottomed flask 1ml of 1M calibrated halide carrier was added. The reducing agent was then added to the reaction vessel, (1g of $NaNO_2$, 2ml of H_2SO_3, 2ml of N_2H_4 or 10ml of 1M Fe (II) sulphate). Heat was then applied to the system for 1 hour. The sample was then cooled. Since there were no solids in the reaction vessel, it was unnecessary to filter the samples. To the samples, dilute nitric acid was added to adjust the pH to 2. Excess 0.1M $AgNO_3$ solution was then added to the sample to precipitate the halo-species. Observation of the precipitate indicated that many of the reducing agents had converted the halate to the halide. Consequently, it was necessary to determine the efficiency of the reduction process. The precipitate was filtered and then dried. The yield of the chloride and halide was determined by gravimetric techniques. The results are shown in Table 2.16.

Table 2.16 Effect of reducing agent on halate reduction

Sample	Anion	Reducing Agent	Addition of $AgNO_3$	Inference	Reduction?	% Conversion
1	IO_3^-	$NaNO_2$	Yellow ppt	AgI	Yes	82.3
2	IO_3^-	H_2SO_3	Brown ppt	n/a	n/a	88.6
3	IO_3^-	N_2H_4	Yellow ppt	AgI	Yes	98
1	ClO_3^-	$NaNO_2$	White ppt	AgCl	Yes	95
2	ClO_3^-	H_2SO_3	White ppt	AgCl	Yes	65
3	ClO_3^-	Fe (II)	White ppt	AgCl	Yes	81

2.6.3 Adopted Method for Mixed Species Conversion

From Table 2.16, it can be seen that the halate species could be reduced with relative ease to the halide (95%). A number of reducing agents were suitable. Sodium nitrite gave the best yield for systems containing the chlorate species and was selected for the reduction procedure. Although sodium nitrite reduced the iodate species to iodide, it was found that the extent of conversion was poor as compared to hydrazine. Hydrazine gave a yield consistently greater than 90% and so was chosen as the reducing agent for the iodate/iodide system.

2.7 Concentration of Halide Species

Halide species have been removed from solution using silver nitrate for many years. Although it has been shown that precipitation methods involving the formation of AgX are consistent, reproducible and accurate, the technique does in fact have a number of limitations. These include the light sensitivity of the compound, lack of chemical selectivity and expense. Various reagents were investigated as a possible alternative to silver nitrate solution. To be considered as a useful alternative, several objectives had to be met. The reagent must form a halide product of low solubility, otherwise gravimetric yield determination would not be possible, the halide product should form a stable compound, *i.e.* should not be air, light and moisture sensitive, and the alternative reagent must also be cost effective when compared to silver nitrate. A literature search indicated that there were a number of suitable alternatives and these are shown in Table 2.17.

Table 2.17 Literature search Alternatives to silver nitrate precipitation

Precipitation Cation	Halide	Chemical Product	Solubility (g/100ml) in H_2O (°C)	Re-solubilise in	Feasibility?
Ag^+	Cl^-	AgCl	8.9E-5 (10)	NH_4OH,$Na_2S_2O_3$,KCN	GOOD
Ir^{3+}	Cl^-	$IrCl_3$	Insoluble	Alkali	POOR
Pb^{2+}	Cl^-	$PbCl_2$	0.99 (20)	NH_4OH	Solubility too High
Mo^{2+}	Cl^-	$MoCl_2$	Insoluble	Alkali, H_2SO_4	POOR
Rh^{3+}	Cl^-	$RhCl_3$	Insoluble	Aqua Regia	POOR
Ag^+	I^-	AgI	2.8E-7 (10)	NH_4OH,$Na_2S_2O_3$,KI, KCN	GOOD
Pb^{2+}	I^-	PbI_2	0.044 (0)	Alkali, NH_4OH	TOXIC
Mo^{2+}	I^-	MoI_2	Insoluble	acid (slightly)	POOR
Pd^{2+}	I^-	PdI_2	Insoluble	KI	POOR
Pt^{2+}	I^-	PtI_2	Insoluble	KI	POOR
Tl^+	I^-	TlI	6.0E-4 (20)	Alcohol	POOR

From the table, it can be seen that there are a variety of cations which can be used to precipitate the chloride and iodide ions. However, salts of palladium (Pd), platinum (Pt), rhodium (Rh), thallium (Tl) and iridium (Ir) are all more expensive than silver nitrate. Although molybdenum is relatively inexpensive, the majority of commercially available salts are in the halide form; consequently, they are unsuitable for halide analysis. Lead nitrate is freely available and inexpensive, however, lead

chloride has too high a solubility for the gravimetric determination. Lead iodide is toxic, consequently, if other precipitation methods are available they will be encouraged. Therefore from the list of suitable alternatives, all but silver have been dismissed, consequently, the silver cation Ag^+ is the most suitable for the gravimetric determination of halides in solution.

2.7.1 Dissolution of Silver Halide Precipitate

From Table 2.17, it can be seen that there are a number of solvents that can be used to dissolve the silver halide precipitate. Due to the hazards associated with potassium cyanide it is not considered suitable. The suitability of the other solvents was investigated.

Silver iodide was determined by counting the γ emitting isotope of ^{125}I. Consequently, there was no need to investigate the dissolution of the AgI precipitate since it was counted as the solid AgI precipitate. However, ^{36}Cl is a β emitter, therefore it is preferable to dissolve the AgCl precipitate before mixing with a cocktail scintillant.

To a glass vial an accurately weighed amount (approx. 0.15g) of inactive silver chloride precipitate were added. To the vial 5ml of each solvent were added. The vial was then shaken and the efficiency of dissolution determined.

Table 2.18 Solubility of AgCl in ammonia and sodium thiosulphate

Wt of AgCl (g)	Solvent	Volume (ml)	Appearance
0.1488	NH_4OH	1	Opaque
0.1492	NH_4OH	2	Clear
0.1504	NH_4OH	3	Clear
0.1497	NH_4OH	4	Clear
0.1509	NH_4OH	5	Clear
0.1496	$Na_2S_2O_3$	1	Opaque - light degrades rapidly
0.1489	$Na_2S_2O_3$	2	Opaque - light degrades rapidly
0.1511	$Na_2S_2O_3$	3	Clear - light degrades rapidly
0.1499	$Na_2S_2O_3$	4	Clear - light degrades rapidly
0.1503	$Na_2S_2O_3$	5	Clear - light degrades rapidly

2.7.2 Adopted Method for AgCl Solubilisation

From the results shown in Table 2.18 it was found that concentrated ammonia was the best solvent for solubilisation of AgCl. The main problem encountered with this dissolution method is the limited solubility of the AgCl precipitate. However, the final mass of the silver chloride precipitate is dependent upon the amount of inactive chloride carrier added. Therefore, as long as the carrier added forms less than 0.15g of silver chloride, these solubility limitations will be prevented. In some instances, it may be necessary to heat the AgCl/ammonia mixture. This will lead to increased pressure in the vial and care must be taken to ensure that sample is not lost as the pressure is equalised.

2.8 Optimisation of Counting Conditions.

Experiments indicated that ammonia was the most suitable solvent for the solubilisation of the silver chloride precipitate. It was then necessary to optimise the solvent:aqueous:scintillant cocktail ratio. A number of scintillation cocktails were investigated. As the solvent used is ammonia, it follows that the scintillant must be compatible with alkali solutions that contain a high salt concentration. Many of the Ultima Gold range of scintillants are suitable for use under these conditions, Ecoscint and Hionic Fluor scintillants were also investigated for their applicability.

To a glass scintillation vial 0.15g of inactive silver chloride were added. To each vial 2ml of conc. ammonia were also added and the sample solubilised. To each vial a different aqueous:scintillant mix was added. The sample was mixed to ensure that the contents were homogeneous. The samples were left in the dark for 30 minutes. The samples were then visually analysed to determine optimum mix conditions. Results are shown in Table 2.19.

From Table 2.19, it can be seen that the high aqueous burden scintillants were suitable. However, when Ultima Gold was used as the scintillant it was found that after 12 hours a multi-phase mixture resulted. It was found that Ultima Gold AB was suitable over long count times and many days later the sample was still clear and

consisted of one phase. It must be noted that all samples degraded with time. If the samples were exposed to light for a significant length of time (days) then darkening of the solution occurred.

Table 2.19 Optimisation of aqueous:scintillant conditions

Wt of AgCl (g)	Volume NH_4OH (ml)	Scintillant	Volume of Scintillant (ml)	Volume H_2O	Appearance
0.1511	2	Ecoscint	10-18	0-8	Opaque, multi-phase
0.1522	2	Hionic Fluor	3-8	10-15	Opaque, multi-phase
0.1508	2	Hionic Fluor	9-13	5-9	Opaque
0.1502	2	Hionic Fluor	14-18	0-4	Opaque
0.1498	2	Ultima Gold LLT	3-8	10-15	Opaque
0.1499	2	Ultima Gold LLT	9-13	5-9	Slightly Opaque
0.1501	2	Ultima Gold LLT	14-18	0-4	Opaque, multi-phase
0.1502	2	Ultima Gold AB	3-8	10-15	Opaque
0.1512	2	Ultima Gold AB	9-13	5-9	Clear
0.1507	2	Ultima Gold AB	14-18	0-4	Opaque
Optimum Conditions					
0.1528	2	Ultima Gold AB	13	5	1 Phase, Clear

All the experimental parameters had been investigated and optimised. The method now had to be tested on concrete standards.

2.9 Analysis of Concrete Standards

The concrete samples were digested using 8M nitric acid and the chloride and iodide oxidised to the respective halogen. Although it had been shown that the chemistry of the proposed method worked when using spiked solutions, it was necessary to show that the chemistry was not affected by the matrix or components within the matrix.

The milled concrete sample was accurately weighed into a round-bottomed flask, and the apparatus connected as shown in Figure 2.1. To the digestion vessel, inactive chloride and iodide solutions were added. To the sample 60ml of 8M nitric acid were added, the sample was heated and stirred continuously for 3 hours. The iodine evolved may precipitate out on the cool inner surfaces of the glassware and for this reason it was necessary to lag the apparatus using pipe cladding. After three hours, the sodium hydroxide solution was transferred quantitatively to a beaker. Fresh

sodium hydroxide was added to the halide trap. The trap was then re-connected to the apparatus and 25ml of a 2% (w/v) potassium permanganate solution were added. The sample was heated and stirred for a further three hour period. After three hours, the sodium hydroxide was transferred to a beaker. The reaction mixture was then cooled and transferred to a plastic bottle for storage.

2.9.1 Iodine in NaOH

The pH of the sample was adjusted to ~3 using dilute nitric acid. To the sample ~2ml of hydrazine were added, the sample was transferred to the hotplate and heated for 1 hour at 70°C. The sample was then removed from the hotplate and cooled, dilute nitric acid was then added until the system was at pH 2. To the sample 10ml 0.1M silver nitrate were added to precipitate all the iodide. The sample was then cooled and filtered under suction. The sample was washed with 0.01M nitric acid and air dried. The precipitate was then placed in a dessicator overnight to dry. The sample was then weighed and transferred to a γ counting vial. From the weight, the iodide recovery was determined. The sample was then counted for at least five minutes in triplicate.

2.9.2 Chlorine in NaOH

The sample was placed on the hotplate and heated for 30 minutes at 70°C. The pH of the sample was adjusted to 2 using dilute nitric acid and then cooled. To the cool sample 1g of sodium nitrite was added and left for 1 hour (preferably overnight). The sample was then heated to drive off all NO_x vapours. The pH of the sample was then determined, and if necessary, adjusted to pH 2 using dilute nitric acid. 0.1M silver nitrate solution was added in slight excess to precipitate the silver chloride. The sample was then heated to aid coagulation. The sample was then cooled and filtered under suction. The sample was washed using 0.01M nitric acid and air dried. The sample was then placed in a dessicator overnight to dry. The sample was then weighed and transferred into a liquid scintillation vial. To the vial 2ml of concentrated ammonia were added and the precipitate solubilised. To the solution 5ml of water and 13ml of Ultima Gold AB scintillant were added, the sample was

shaken to ensure all components were mixed thoroughly. The sample was then allowed to dark adapt for at least 1 hour prior to counting.

Since the experimental yield is based upon the inactive carrier added at the beginning of the analysis, it is possible to apply a yield correction factor to the measured activity of the sample. This corrects for any losses of the sample during the analysis. However, for this relationship to hold, the carrier must be acting in an identical manner to that of the analyte contained in the matrix. Since in this case the level of activity is known it should follow that activity yield and the gravimetric yield should be the same, *i.e.* have a ratio of 1. For each of the samples analysed, the gravimetric yield and the activity yield was calculated. The ratio of weight yield:activity yield was determined. These results are shown in Table 2.20.

Table 2.20 Weight and activity yields - results from concrete standards

	AgI			AgCl		
Sample	**% Weight yield**	**% Activity yield**	**Ratio**	**% Weight yield**	**% Activity yield**	**Ratio**
1	102	51.2	1.99	54.6	54.1	1.01
2	77.3	45.7	1.69	64.1	67.1	0.96
3	90.2	46.2	1.95	68.9	65.4	1.05
4	97.5	38	2.57	85	86	0.99

It can be clearly seen that the iodide carrier was not acting as a tracer. The gravimetric yield for the analysis was always greater than the activity yield, suggesting that the iodide carrier is being oxidised/transferred at a preferential rate. Since the weight difference between the iodide carrier and active iodide is small (125 *c.f.*127), this cannot be the reason for this enhanced transfer rate. Indeed if this were the case, the active iodide would be preferentially transferred since the atomic weight of the active iodide (^{125}I) is less than stable iodide carrier (^{127}I).

In the spiked concrete samples the chemical form of the ^{125}I added is Na^{125}I, the inactive carrier is also in the same chemical form. It was suggested that the iodide may be being lost during the concrete drying process, however investigations proved that this was not the case. The other factor that may affect the transfer rate of the active iodide is the physical nature of the matrix. Since nitric acid had been shown to

be the most suitable oxidising agent it was known that substantial losses of the analyte of interest would occur if the sample was digested in a beaker on the hotplate, due to the formation of HCl and HI. However, there was also the possibility that the introduction of the acid to the digestion apparatus would volatilise the iodide carrier (solution) preferentially to the iodide (active) contained in the concrete. Consequently, the inactive iodide would not be acting as a carrier since it would be more susceptible to volatilisation. This discrepancy may have been due to the matrix and consequently would not have occurred in initial experiments where the active and non-active species were both in solution. Consequently, the acid was unable to fulfil the two analytical roles of a leaching, and that of an oxidising agent. From Table 2.20, it can also be seen that the chloride analysis was unaffected. This supports the theory that the discrepancy was due to matrix considerations since by the time the chloride was oxidised to chlorine, the matrix had been vigorously attacked for several hours by the acid. Consequently, the matrix had been broken down and the ^{36}Cl leached into solution. Therefore the active and non-active chloride were in the same chemical environment, a discrepancy in chloride yields was not apparent and the ratio approached the theoretical ideal of 1.

Experiments were carried out to determine if the inactive iodide was being preferentially transferred from the reaction vessel to the hydroxide trap and, to determine whether this discrepancy was due to the matrix.

The concrete to aqueous ratio was maintained as before. The doping procedure differed in that inactive and active iodide was either absent or present in the sample. The samples were prepared and cured as described earlier (2.2.1.2). Four different combinations of blocks were prepared as shown in Table 2.21:

Table 2.21 Concrete blocks prepared to investigate matrix effects

Sample	1	2	3	4
^{125}I	✗	✓	✗	✓
^{127}I	✗	✗	✓	✓

After drying, each block was milled and then transferred to an airtight container. Aliquots of each were taken for analysis and the iodide yields determined.

To sample 1, inactive ^{127}I and active ^{125}I were added as solutions.

Sample 2 mimicked the samples that had been previously prepared, since ^{125}I was entrapped within the matrix whilst the carrier was added as a solution.

To sample 3, active ^{125}I was added as a solution whilst the inactive carrier was already contained within the concrete itself.

Sample 4 contained both the active ^{125}I and non-active ^{127}I. Since both were added as sodium iodide, it follows that both would be in the same chemical form within the concrete.

The samples were then analysed following the proposed method. Results of the analysis are shown in Table 2.22.

Table 2.22 Determination of cause of analytical discrepancy.

Sample		1	2	3	4
Doping details	^{125}I	Solution	Matrix	Solution	Matrix
	^{127}I	Solution	Solution	Matrix	Matrix
Gravimetric yield %		93	91	59	90
Activity yield %		94	53	89	88
Gravimetric/Activity ratio		0.99	1.72	0.66	1.02
Explained by matrix effects?		YES	YES	YES	YES

From the results shown in Table 2.22, it can be clearly seen that the discrepancy is due to the matrix. It follows that the analyte contained in the matrix did not react as quickly as that which was in solution. Since the acid was being used to breakdown the matrix and also oxidise the iodide to iodine, *any iodide already in solution was distilled over at a faster rate than that which has not yet solubilised.* Consequently, this would explain why the gravimetric yields were always greater than the activity yields. To overcome this matrix effect, the dissolution step required modification. The digestion step must avoid using acids that have the potential to oxidise the iodide to iodine. However the conditions must be harsh enough to breakdown the matrix, or at least impair the integrity of the matrix so that the iodide is leached from the

sample. Iodide is readily oxidised to iodine, even at low acid concentrations. Consequently, the likelihood of matrix discrepancies occurring if acid is used as the digestion reagent are high. From previous experiments, it is known that if the sample is digested using strong alkali solution the concrete is not dissolved to any great extent. However, under these conditions iodide will not be oxidised. Consequently if the sample can be digested for a suitable length of time **before** the acid is added, the iodide from the concrete and the carrier iodide will act in an identical manner, thus overcoming the problem associated with the matrix. Experiments using strong alkali and water were carried out to determine the feasibility of using hydroxide as an initial digestion step. Concrete standards that had been previously prepared were used in the analysis.

To a round bottomed flask 2g of milled concrete were added. To the sample either inactive carrier or active ^{125}I was added. The apparatus was set-up as previously detailed. The sample was then digested using either 25ml of deionised water or 25ml of 6M NaOH for 1 hour at 80°C. After 1 hour 45ml of 8M nitric acid were added to the reaction vessel, thus the acid concentration was 3M, which was effective in oxidising the iodide to iodine. The sample was then treated as before, results using the modified digestion/leaching conditions are shown in Table 2.23.

Table 2.23 Modified dissolution of concrete

Sample		1	2	3	4
Doping details	I-125	Solution	Matrix	Solution	Matrix
	I-127	Solution	Solution	Matrix	Matrix
Water dissolution					
Gravimetric yield %		88	93	64	92
Activity yield %		90	67	87	91
Gravimetric/Activity ratio		0.98	1.39	0.74	0.99
Matrix effect observed?		YES	YES	YES	YES
6M NaOH dissolution					
Gravimetric yield %		92	86	90	83
Activity yield %		89	89	88	84
Gravimetric/Activity ratio		1.03	0.97	1.02	0.99
Matrix effect observed?		NO	NO	NO	NO

The results indicate that alkali digestion is effective in leaching the iodide from the concrete matrix. Under these conditions matrix effects do not occur. Although

previous experiments have shown that hydroxide attack does not visibly impair the integrity of the matrix, the experiment above shows that the conditions are harsh enough to leach the analyte from the matrix, thus bringing it into solution. The carrier iodide and ^{125}I are then in a form where isotopic exchange can take place, therefore eliminating matrix effects.

2.9.3 Analysis of Concrete Standards Using Modified Dissolution Step

The concrete blocks that were prepared containing ^{36}Cl and ^{125}I were analysed in order to test the modified dissolution procedure and measurement of the radionuclides.

A 2g mixed standard concrete sample was taken and placed in a round-bottomed flask. To the sample 25ml of 6M NaOH were added and the sample was heated for 1 hour. After an hour, 25ml of 12M HNO_3 acid were added and the system heated for 3 hours. After 3 hours the hydroxide trap was replaced with fresh alkali. To the reaction vessel 25ml of 2% (w/v) potassium permanganate were added along with 25ml 12M HNO_3. The mixture was heated for a further 3 hours.

The resultant hydroxide solutions were treated in the same manner as previously detailed, (see Cl_2 in NaOH and I_2 in NaOH). Results for the analysis of the concrete using the alkali dissolution process are shown in Table 2.24.

Table 2.24 Weight and activity yields - results from concrete standards using alkali dissolution

	AgI			AgCl		
Sample	% Weight yield	% Activity yield	Ratio	% Weight yield	% Activity yield	Ratio
1	85.1	89.0	0.96	85.1	86.0	0.99
2	83.1	80.9	1.03	59.6	64.0	0.93
3	92.0	86.8	1.06	48.1	50.1	0.96
4	88.1	90.5	0.97	89.0	88.0	1.01
5	89.4	91.1	0.98	90.6	86.9	1.04
6	91.3	86.0	1.06	69.0	67.3	1.03

From the table it can be seen that the alkali dissolution method overcomes the problems associated with the matrix, this alternative dissolution process does not

adversely affect the results obtained for either iodine or chlorine contained within the concrete matrix.

2.10 Limitations of Procedure.

Since this method will be used to analyse samples which contain both intermediate and low levels of activity, it is necessary to determine the maximum sample size that can be analysed. Samples that originate from areas that have been subjected to high neutron flux for many years will have appreciable activity and therefore a small sample size of less than 1g may be sufficient for analysis. However, for samples that originate from areas where the flux may be less, a larger sample may be required to obtain a measurable amount of activity. Consequently, it is necessary to determine the maximum amount of concrete that can be analysed.

Experiments were carried out to determine the effect of sample size on recovery. It was also necessary to ensure that the introduction of a larger sample size did not lead to discrepancies in the yield and activity results.

To a round-bottomed flask between 1-10g of pre-dosed concrete were added. Calibrated NaI and NaCl solutions were then added to the reaction vessel. The sample was then digested in 6M NaOH for 1 hour. To the sample nitric acid was added to bring the H^+ concentration to 3M. The evolved iodine was collected in the 1M NaOH trap. After 3 hours the alkali trap contents were transferred to a beaker and the iodide determined. A trap containing fresh hydroxide solution was re-connected to the apparatus. To the reaction vessel 25ml of 2% (w/v) potassium permanganate were added. The reaction was continued for a further 3 hours. After 3 hours the trap contents were transferred to a beaker and the chloride determined. The halide was then precipitated using 0.1M silver nitrate solution. The dried iodide precipitate was weighed and then counted on the Panax well crystal detector. The dried chloride precipitate was weighed and transferred to a scintillation vial. The contents were then dissolved in 2ml of ammonia. To the sample 5ml of water and

15ml of Ultima Gold AB were added and the sample counted by LSC. The results are shown in Table 2.25.

Table 2.25 Results from analysis of prepared concrete - effect of sample size.

	AgI			AgCl		
Weight (g)	% Weight yield	% Activity yield	Ratio	% Weight yield	% Activity yield	Ratio
1.5964	84.6	81.5	1.04	74.0	70.3	1.05
2.5079	82.4	83.1	0.99	84.1	80.3	1.05
2.5434	89.4	91.1	0.98	90.6	86.0	1.05
2.5679	79.5	76.4	1.04	79.1	78.8	1.00
2.8414	83.4	80.0	1.04	80.1	76.9	1.04
3.0729	88.7	83.2	1.07	94.2	92.0	1.02
4.6425	91.3	94.0	0.97	83.5	80.1	1.04
4.3654	86.0	85.1	1.01	89.8	88.5	1.01
6.8335	82.2	80.8	1.02	90.1	89.3	1.01
7.3291	91.3	88.7	1.03	69.0	67.3	1.03
8.1053	80.4	88.3	0.91	41.7	41.7	1.00
10.4913	82.3	87.4	0.95	84.0	78.3	1.06
Average			1.00			1.03

From the results, it can be seen that the analysis is not affected by sample size. However, it should be noted that as sample size increases, the chemical yield decreases. This is possibly due to the particulates impeding the reaction. Consequently for large sample sizes (>5g), it may be necessary to react the sample for a longer length of time. There were concerns that an increase in sample size may lead to a disagreement in weight and activity yields due to matrix effects. However, these experiments did not support this. A carrier must act in an identical manner if it is to be used as an indicator for sample recovery. Consequently, there should be no difference in the weight yield, determined gravimetrically and, the activity yield, determined by radiometric counting methods. Therefore, the ratio of these two should be 1. In an actual sample, the activity is unknown and the analyst relies on this ratio to determine the activity in the sample. An analytical method is unsuitable if the two yields are dissimilar. From the table it can be seen that the 'average' ratio for AgI is 1.00, for AgCl it was shown to be 1.03, this deviates from what was expected by ~3%. The result, however is within experimental error. From the graphs below (Figures 2.5 & 2.6), it can be seen that a linear response is recorded over a large activity range. The R^2 values show good correlation between the results.

The gradient of each graph is very close to 1 and deviates by < 5%, this is well within experimental error.

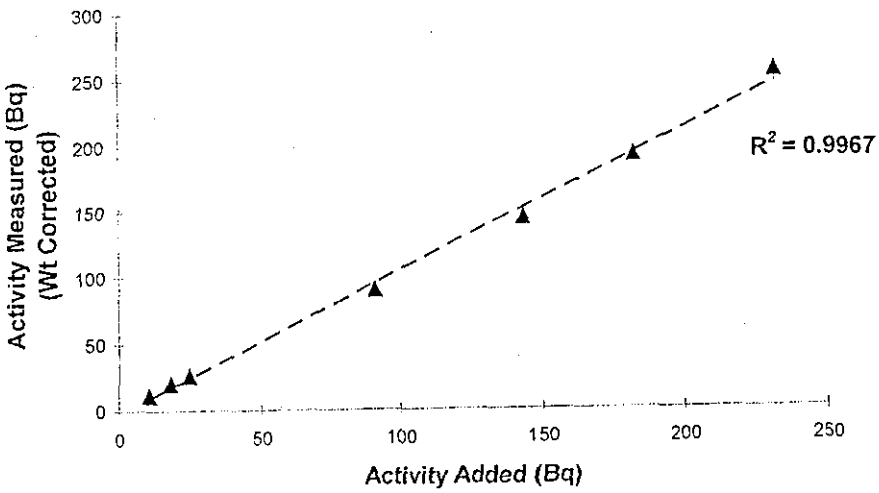


Figure 2.5 Relationship between activity added vs activity measured for ^{36}Cl

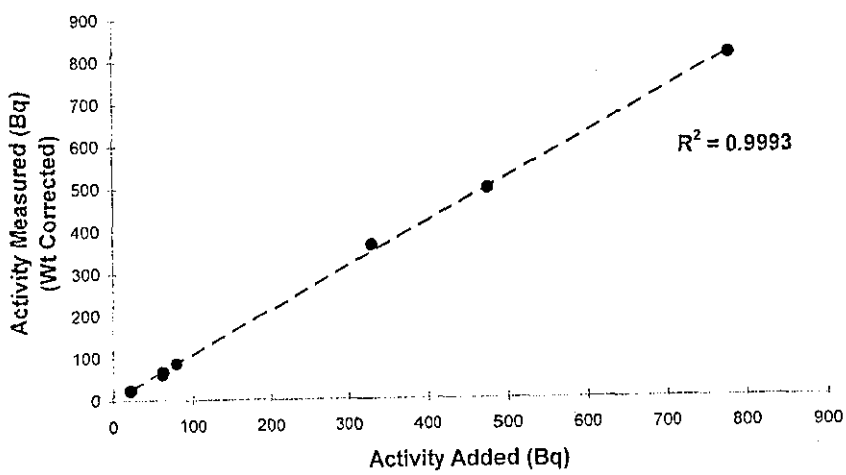


Figure 2.6 Relationship between activity added vs activity measured for ^{125}I

2.11 Proposed analytical scheme for the determination of ^{36}Cl and ^{129}I in concrete wastes

2.11.1 Leaching of Halide from the Matrix

To a round bottomed flask add the concrete sample (typically between 1-5g), the calibrated halide carriers and 25ml of 6M NaOH. To the reaction vessel add a small magnetic flea. To a Dreschel bottle add 70ml of 1M NaOH. Connect the apparatus as shown in Figure 2.1. Lag the glassware between the alkali trap and the reaction vessel with polystyrene pipe cladding. Attach the system to a water pump and draw air through the reaction system, ensure that the air bleed is in the solution. Heat the system on a magnetic hotplate to 80°C and maintain at this temperature throughout the experiment. After 1 hour add 25ml of 12M nitric acid, this is introduced into the reaction vessel using the air bleed, the sample is then digested for a further 3 hours. After 3 hours the alkali trap is disconnected and replaced with another Dreschel bottle containing fresh hydroxide, the lagging can also be removed at this point. To the reaction system 25ml of 2% (w/v) potassium permanganate solution is added along with a further 25ml of 12M nitric acid. The system is reacted for a further 3 hour period. After 3 hours the alkali trap is disconnected. The reaction vessel contents are discarded or retained for further cation analysis.

2.11.2 Reduction of Chlorate to Chloride and AgCl Precipitation

The contents of the Dreschel bottle are transferred quantitatively to a beaker. The solution is then heated gently on the hotplate for 30 minutes to ensure that Cl_2 is not released from solution on addition of H^+. The sample is then cooled and the pH is adjusted to 2 using dilute nitric acid. To the sample 1g of $NaNO_2$ is added and the sample left for 1 hour (preferably overnight). The sample pH is then determined, and if necessary adjusted to 2 using dilute nitric acid, the sample is then heated for 10 minutes. To the hot sample 10ml 0.1M $AgNO_3$ solution is added to precipitate all the chloride. The sample is then heated for a further 15 minutes to aid the coagulation of the precipitate. The sample is then cooled in a darkened place. When cooled the sample is filtered under suction washing with dilute (0.01M) HNO_3. The precipitate is then transferred to a dessicator and dried to constant mass, preferably in

a darkened cupboard to minimise light degradation. The sample is transferred to a scintillation vial and weighed accurately. The precipitate is then dissolved in 2ml of concentrated ammonia. To the solution 5ml of deionised water is added to the sample, 13ml of Ultima Gold AB cocktail scintillant is added, the sample is then shaken to ensure thorough mixing. The sample is then placed in the liquid scintillation counter and dark adapted for 1 hour prior to counting on a pre-determined protocol.

2.11.3 Reduction of Iodate to Iodide and AgI Precipitation

The contents of the Dreschel bottle are transferred quantitatively to a beaker and the pH adjusted to 4 using dilute HNO_3. To the sample ~2ml of hydrazine solution (30%v/v) is added. The sample is then heated gently for 30 minutes. The pH of the sample is determined and if required, adjusted to pH 2 using dilute HNO_3. To the sample 10ml of 0.1M $AgNO_3$ is added to precipitate all the iodide. The sample is then heated for a further 15 minutes. The sample is then cooled in a darkened place. When cooled the sample is filtered under suction. The precipitate is then placed in a dessicator and dried to constant mass. The precipitate is transferred to a γ vial and the mass recorded. The sample is then counted on a well type detector. Each sample is counted for a minimum of 5 minutes in triplicate.

3.0 Investigation into the Analysis of ^{99}Tc

3.1 General Considerations

As with chlorine and iodine, technetium can, under certain conditions, form volatile species and be lost from the sample during analysis. Consequently, it is important to ensure that the digestion process for the sample does not lead to the production of volatile technetium compounds such as pertechnic acid, $HTcO_4$. Under oxidising conditions, the predominant technetium species will be the pertechnetate ion, TcO_4^-. In the presence of H^+, $HTcO_4$ may be formed and may be lost at high reaction temperatures as technetium anhydride Tc_2O_7 [42]. As with the previously detailed Cl_2/I_2 analysis, it is necessary to carefully control the redox conditions of the reaction system if analyte loss is to be avoided. As there are no stable carriers of Tc, nor any clear radiotracer, it is important to choose the yield monitor that is the most appropriate for both the matrix and adopted analytical procedure. Initial experiments investigated the transfer of the Tc species under selective oxidation conditions. It was necessary to determine how the Tc behaved in the Cl_2/I_2 reaction system. Since the Tc will form volatile complexes, it was important to investigate the rate of transfer of this species from the reaction vessel. It was also necessary to determine if the Tc complex came over preferentially with the I_2 or Cl_2 fraction. Since the concrete matrix will be contaminated by a variety of radionuclides it will be necessary to determine the activity of ^{99}Tc in the presence of other radionuclides.

3.2 Reagents and instrumentation

3.2.1 Reagents

Radionuclides used in this work include ^{99}Tc, ^{65}Zn, ^{22}Na, and ^{137}Cs all supplied by Nycomed Amersham, Bucks, UK. ^{152}Eu provided by Gresham Scientific Marlow, UK, and ^{36}Cl and ^{125}I, both of which were purchased from ICN Biomedicals Inc., USA. The working solutions in this work ranged from 0.1Bq g^{-1} to 1kBq g^{-1}. To

ensure the technetium was not lost due to formation of Tc(IV), the Tc standards were prepared using 1M NH_4OH. ^{152}Eu was made up in 1mM Eu $(NO_3)_3$, ^{137}Cs in 1mM $CsNO_3$, ^{22}Na was made up in 1mM NaCl solution, ^{65}Zn was made up in 1mM $ZnCl_2$ solution and the iodide and chloride tracers were prepared as detailed in 2.2.1.

All aqueous solutions were prepared using 18MΩ deionised water. All chemical reagents were of Analytical grade and were supplied by Aldrich, Poole, UK. In the development of methodologies for the determination of ^{99}Tc in concrete wastes the following solutions were required: ammonia, sodium hydroxide (0.1M to 6M), nitric acid (0.1M to 15.8M), 2% (w/v) potassium permanganate, 6% (v/v) hydrogen peroxide, 0.1M $CaCl_2$, 0.1M $FeCl_3$ and 100ppm Ru solution.

5% (v/v) TnOA in xylene was used during the development of this analytical methodology.

A number of analytical ion-exchange resins were investigated, all were of analytical grade: Amberlite IRA-400 (Cl^-), Dowex 1×8 (100-200), (Cl^-), all were supplied by Aldrich, Dorset. All were pre-treated by flushing with de-ionised water and then conditioning with 1M HCl. Cationic ion-exchange resins were also investigated, Dowex 50W×2-100 and Amberlyst 15. Both resins are strongly acidic and were used in the hydrogen form by pre-treating the resin with 1M H^+. The cation exchange resins were of Analytical Grade and were supplied by Aldrich, Dorset.

3.2.1.1 Preparation of spiked solutions

^{99}Tc spiked solution

To a 50ml volumetric flask, 3.55ml of concentrated ammonia were added. To the volumetric flask ^{99}Tc tracer was added so that the final activity was 1kBq g^{-1}. The solution volume was then made up to the mark using de-ionised water, resulting in a 1M NH_4OH solution. Subsequent stocks were then prepared at 0.1-100Bq g^{-1}. The activity was then determined by mixing with a suitable scintillant and counting by LSC.

^{152}Eu spiked solution

To a 50ml volumetric flask 0.5ml of 0.1M europium nitrate solution were added. To the flask ~45ml of de-ionised water were added. To the solution ^{152}Eu tracer was added resulting in a solution with a final activity of 1kBq g^{-1}. The solution volume was then made up to 50ml using de-ionised water. An aliquot of solution was transferred to a counting vial and γ counted.

^{137}Cs spiked solution

To a 50ml volumetric flask 0.5ml of 0.1M caesium nitrate were added. To the solution ~ 45ml of water were added. To the flask ^{137}Cs was added resulting in a final solution of 1kBq g-1. The sample volume was then made up to 50ml using de-ionised water. Aliquots of the solution were removed, an aliquot was counted by γ spectrometry and by LSC.

3.2.1.2 Preparation of doped concrete

Concrete standards containing radioactive species are not available. Therefore, all doped concrete samples had to be prepared. Consequently, the samples are not of a certified activity. All concrete samples prepared contained the concrete powder, water and the radioactive tracer. Inactive carrier was not added to the concrete mix.

The concrete was mixed with water in a 5:1 concrete:water slurry. Portions of the slurry were then placed in small weighing boats and doped following the doping regime detailed below:

Set 1) ^{99}Tc

Set 2) ^{99}Tc + ^{152}Eu

Set 3) ^{99}Tc + ^{36}Cl + ^{125}I + ^{137}Cs + ^{152}Eu + (inactive)Ru.

The samples were then stored at ambient temperature for 1 month. After 1 month, the samples were ground into a fine powder using a mortar and pestle. The powdered samples were then stored in an airtight container. The concentration of

each radionuclide was determined by taking the activity added and dividing by the dry weight of the concrete.

3.2.2 Instrumentation

^{99}Tc, ^{36}Cl and ^{137}Cs were counted on a Canberra Packard 2750 ultra low-level liquid scintillation counter. ^{125}I was counted in a well crystal (NaI (Tl)) Panax counter. ^{152}Eu was counted on a Philips P4800 Gamma Counter and the Ru was determined on the Perkin Elmer Plasma II Inductively Coupled Plasma Optical Emission Spectrometer.

3.3 Optimisation of counting conditions

Preliminary studies investigated the transfer of Tc from the reaction vessel (acidic) to the volatile product traps (alkali). Previous work (section 2.3), had indicated that Ecoscint could be used for the measurement of Tc in the acidic fraction and, Hionic Fluor could be used for measuring the activity of Tc in the alkali trap. As the radioactive tracer was made up in a 1M NH_4OH solution, all counting standards were prepared using Hionic Fluor cocktail scintillant since it is compatible with high pH solutions.

3.4 Effect of oxidising agent on Tc transfer

As it was the aim of this work to obtain multi-chemical data from a single sample, it was necessary to investigate the effect of reaction conditions on the analyte of interest. Previous experiments indicated that oxidising agents were required to oxidise the iodide and chloride to iodine and chlorine. Consequently the effect of these oxidising agents on the Tc complex were investigated. In the reaction vessel, there were three distinct stages. Firstly, a high pH system will be set up during the initial digestion phase. Secondly a low pH system will be established by the use of an acid which will also affect the oxidation potential of the reaction. Finally, the use of a stronger oxidising agent will further increase the oxidation potential of the system. The effect of each of these conditions on the Tc needed to be considered.

Initial reactions were carried out using ^{99}Tc in solution. Although it was the intention of this work to determine Tc transfer during oxidation of iodide and chloride, the active halide species were not used. Since ^{99}Tc is a β emitting radionuclide, a complex spectrum would have been obtained if both technetium and chlorine came over in the same fraction. Indeed if this were to happen, quantification would be impossible without some further degree of separation. Consequently, it was decided that inactive halides would be used to look at the chemical interaction without introducing complexity in the form of interference due to radioactive decay of multiple species. Consequently, if counts were observed in the halide traps this would have been due to the transfer of the Tc species. Further experimentation could then be carried out to determine if the presence of Tc in the apparatus affected the rate of halide transfer.

To the apparatus shown in Figure 2.1 1ml of 1M calibrated NaCl solution, 0.5ml of 1M NaI and 100Bq of ^{99}Tc were added. The apparatus was checked to ensure that the system was airtight. To the apparatus, 25ml of 6M NaOH were added and the sample was heated at 80°C for 1 hour. After an hour, 25ml of 12M HNO_3 acid were added and the system reacted at 80°C for 3 hours. After 3 hours the hydroxide trap was replaced with fresh alkali. To the reaction vessel 25ml of 2% (w/v) potassium permanganate were added along with 25ml 12M HNO_3. The mixture was heated at 80°C for a further 3 hours. After three hours the reaction was stopped. Aliquots from each of the traps were counted on the LSC using Hionic Flour scintillant cocktail. The reaction vessel contents were cooled. When cool, the contents were filtered to separate the solution from the MnO_2 (reduced form of $KMnO_4$). The final weight of the solution was determined and an aliquot removed, mixed with Ecoscint and analysed by LSC. Finally the MnO_2 precipitate was transferred to a small beaker and dissolved in a minimum quantity (~15ml) of concentrated HCl, the sample was not heated since analyte loss may occur due to the formation of $HTcO_4$, leading to the production of the volatile Tc_2O_7 compound [42]. If difficulty was experienced in taking the MnO_2 up in 15ml of concentrated HCl, the sample was sonicated for 10 minutes. An aliquot from the solution was then mixed with Ecoscint and counted by

LSC. Since the Mn solution was dark brown, the counting sample was slightly coloured. Therefore, after counting, the sample was doped with a further aliquot of ^{99}Tc tracer and the counting efficiency of each sample determined. The % ^{99}Tc associated with each fraction is shown in Table 3.1. The remainder of the hydroxide from the alkali trap was used to gravimetrically determine the transfer of the chloride and iodide from the reaction vessel. These results are also shown in Table 3.1.

Table 3.1 Effect of oxidising agent on Tc transfer

% ^{99}Tc Activity			% Cl	% I
Reaction Conditions	Reaction Vessel		Alkali Trap	
	Filtrate	MnO_2		
8M nitric acid	98.8	n/a	0	0	96
Acid + $KMnO_4$	99.1	0.9	0	92	0

From the table it can be seen that the conditions within the reaction vessel do not lead to the transfer of the Tc species from the reaction vessel to the alkali trap. It should also be noted that virtually all of the Tc is associated with the filtrate, *i.e.* there is very little partitioning of the Tc between the liquid and solid phases present in the reaction vessel. Consequently this experiment indicated that it was not possible to adsorb the Tc species on to the MnO_2 precipitate. These experiments also indicated that the rates of the oxidation of the halide were not affected by the presence of technetium in the system. Consequently, it was possible to determine chloride, iodide and technetium from the same sample. The reaction conditions ensured that the technetium remained in the Tc (VII) form. If the technetium had been reduced to the Tc (IV) then it would have been associated with the MnO_2 fraction since TcO_2 is insoluble. Therefore since there was virtually no activity associated with the MnO_2 it can be assumed that all of the Tc remains as Tc (VII).

During the digestion of the solution containing Tc, $HTcO_4$ would be produced. However, $HTcO_4$ will reflux under the reaction conditions detailed. The formed pertechnic acid would dissolve in the condensed water vapours in the system, consequently the volatile compound, technetium anhydride (Tc_2O_7) would not be formed and analyte loss would not occur. Therefore, a number of cationic species and TcO_4^- will remain in the reaction vessel. The next stage of analysis requires the

separation of the Tc from the other species. Since the ionic form of the species in the reaction vessel fall into two distinct categories, anionic and cationic, it may be possible to separate then from each other by either ion exchange or precipitation methods.

3.5 Separation of anionic and cationic species

Both precipitation and ion-exchange methods were investigated to determine the feasibility of each process. Although ion-exchange methods may provide for a better separation, ion-exchange methods can be time consuming and a large amount of hazardous reagents may be produced. Precipitation mechanisms are generally preferred because they are quicker. Previous experiments indicated that Tc was not associated with MnO_2, however it was necessary to determine the distribution of cationic species between the two phases.

3.5.1 Separation using precipitation methods

3.5.1.1 Distribution of cationic species in aqueous/MnO_2 systems

Easily identified γ emitters were used to investigate the distribution of cations between the aqueous and solid MnO_2 phases. To a 3M HNO_3 solution (reaction conditions of the digestate) the radioactive tracers were added (1kBq ^{22}Na, ^{137}Cs, ^{65}Zn or ^{152}Eu). To the system 25ml of 2% (w/v) $KMnO_4$ were added. The system was then exposed to air until the purple coloration of the system changed to a clear solution containing a black/brown precipitate. The solution was then filtered through a 0.45µm membrane and washed using 3×5ml aliquots of de-ionised water. All washings were added to the filtrate. The filtrate was transferred to a 100ml plastic pot and made up to 100ml using de-ionised water. The precipitate was transferred to a beaker and dissolved in conc. HCl. The solution was then transferred to a 100ml plastic pot and made up to 100ml using de-ionised water. All samples were then placed on a NaI detector to count overnight. Counting standards were prepared by adding the same amount of radioactive tracer to 100ml of de-ionised water. Since the samples are being counted by γ spectrometry, colour and chemical effects will not affect the efficiency and, therefore it is not necessary to prepare identical

chemical standards. In γ counting the biggest effect on the detected count rate is the geometry of the sample. Consequently in all of these experiments the counting geometries of the samples and standards were identical. The activity associated with each fraction was determined by ratioing the counts in the sample to the counts in the standard. As the activity added to each was identical and they had been counted in the same geometry this simple division technique was adequate for looking at trends within each sample set. The results are shown in Table 3.2. The details from the previous experiment showing the distribution of ^{99}Tc between the two phases are also shown in the table. All experiments were carried out in triplicate and reagent blanks were prepared and counted.

Table 3.2 Distribution of activity between the filtrate and MnO_2

Radionuclide	% Distribution of activity	
	Filtrate	MnO_2
$^{22}Na^{+}$	100/ 100/ 100	0
$^{137}Cs^{+}$	100/100/100	0
$^{65}Zn^{2+}$	83/75/86	14/28/10
$^{152}Eu^{3+}$	3/5/9	99/89/96
$^{99}TcO_4^{-}$	99/98/92	0/0/4

From the table it can be seen that as the cationic charge on the ion increases so does the rate of MnO_2 adsorption. In a physisorption system this effect would be expected. Since higher charged species will be attracted to a greater extent than lesser charged species. A divalent ion was investigated because in the digested concrete matrix, the predominant cation will be Ca^{2+}. From the results it can be seen that MnO_2 sorption will not be effective for the ions in the solution. Other precipitation schemes needed to be investigated.

3.5.1.2 Distribution of cationic species with aqueous/FeO(OH) systems

As before easily identified γ emitters were used to investigate the distribution of cations between the solid and aqueous phase in the FeO(OH) system. To a 3M HNO_3 solution, the radioactive tracer was added (1kBq of ^{22}Na, ^{137}Cs, ^{65}Zn or ^{152}Eu, ^{99}Tc). To the acid, 5ml of 0.1M $FeCl_3$ solution were added and the pH adjusted to 5 using 6M NH_4OH. The precipitate was then centrifuged and the filtrate transferred to a 100ml plastic pot. The precipitate was then re-dissolved in HCl and 10ml de-

ionised water added. The pH was adjusted to 5 using 6M NH_4OH and FeO(OH) was formed. The sample was centrifuged once more, the supernatant was added to the contents of the 100ml plastic pot. The precipitate was then re-dissolved and transferred to another 100ml plastic pot. The sample volumes were made up to 100ml using de-ionised water. All γ samples were then placed on a NaI detector to count. Counting standards that had been previously prepared were used to determine counting efficiency. An aliquot from both fractions of the ^{99}Tc experiment was mixed with Ecoscint and counted on the LSC. The results are shown in Table 3.3. The experiment was carried out in triplicate to investigate reproducibility. Reagent blanks were prepared, counted and subtracted from the analyte measurements.

Table 3.3 Distribution of activity between the filtrate and FeO (OH)

Radionuclide	% Distribution of activity	
	Filtrate	FeO(OH)
$^{22}Na^{+}$	100/100/100	0
$^{137}Cs^{+}$	100/100/100	0
$^{65}Zn^{2+}$	48/37/44	55/63/59
$^{152}Eu^{3+}$	2/1/5	96/101/93
$^{99}TcO_4^{-}$	96/102/98	3/0/0

The results indicate that the FeO(OH) precipitate can be used to partially separate the anionic species from the cationic species. However, monovalent and divalent species are not adsorbed in a quantifiable manner.

3.5.1.3 Distribution of cationic species using aqueous/$CaHPO_4$ systems

Since the divalent cation Ca^{2+} will feature significantly in concrete digestion mixtures, it may be possible to remove this ion from solution by precipitating it as a calcium salt. Calcium phosphate precipitations have been used extensively in radiochemical analyses as a means of co-precipitating other radionuclides including strontium [79], the lanthanides [79] and actinides [73]. To a system containing readily identifiable γ emitters, or ^{99}Tc, 3M HNO_3 acid was added. To the solution 1ml of 1M $CaCl_2$ was added along with 1ml of conc. H_3PO_4, the pH was adjusted to pH 5 using 6M NH_4OH. The fine precipitate was left for 2 hours to settle prior to filtering. The solution was passed through a 0.45µm membrane under suction and washed using 3×5ml aliquots of de-ionised water. The filtrate was transferred to a

100ml plastic pot, the volume being made up to 100ml using deionised water. The filtration equipment was disconnected from the vacuum and to the precipitate 3X 10ml of 1M HNO_3 were added to dissolve the solids. The filtration apparatus was washed with 3X 10ml of de-ionised water. The solubilised precipitate was transferred quantitatively to a 100ml plastic pot and the sample volume made up to 100ml using de-ionised water. All samples were placed on the γ spectrometer to count overnight. The sample containing ^{99}Tc was filtered and the filtrate transferred to a beaker. The sample was then dried down gently (60°C) until the volume was ~ 10ml, a 2ml aliquot from the sample was taken, mixed with Ecoscint scintillation cocktail and counted by LSC. The precipitate was transferred to a scintillation vial and dissolved in 2ml of 2M HNO_3. To the sample Ecoscint was added and the sample counted by LSC. All experiments were carried out in triplicate and reagent blanks were prepared and used as backgrounds.

Table 3.4 Distribution of activity between the filtrate and $CaHPO_4$

Radionuclide	% Distribution of activity	
	Filtrate	$CaHPO_4$
$^{22}Na^{+}$	100/ 100/ 100	0
$^{137}Cs^{+}$	100/100/100	0
$^{65}Zn^{2+}$	42/37/46	55/65/58
$^{152}Eu^{3+}$	3/5/9	95/98/87
$^{99}TcO_4^{-}$	95/98/100	6/0/0

From the table it can be seen that the monovalent ions are not associated with the precipitate. There was significant association between the precipitate and the di-and trivalent cations.

From all the precipitation experiments performed, it was found that only the multi-valent species are associated with the precipitates to any significant degree. The monovalent species investigated (Cs and Na), were not associated with the precipitates.

Ion exchange methods may be required to separate the anionic species from cations especially the mono-valent species *e.g.* Cs.

3.5.3 Separation using ion-exchange

The technetium in the sample can be separated from the cations using either anion or cation exchange resins. If the solution is passed through a cation exchange column, the cations in the solution will be retained on the resin whilst the anions will pass through undeterred. The counter ion released into the solution will be either sodium or protons and will depend on the conditioning solution. Care should be taken if further analysis of the cations is to be determined since highly charged species may be difficult to remove from the resin quantitatively. If the sample is passed through an anion exchange column the technetium will be retained on the resin and the cations will pass through unhindered. The technetium will then be eluted from the column using a solution with an anion that displaces the Tc complex, *e.g.* NO_3^-. In the latter approach the analyte of interest can be eluted in a small volume. It is therefore possible to separate and concentrate the analyte of interest from the bulk solution.

3.5.3.1 Separation using cation exchange resin

Batch experiments were performed. The effect of acid, acid concentration, resin and radionuclide were investigated. To a centrifuge tube 10ml of acid were added (HNO_3 and HCl) at different acid molarities (0.1M, 1M, 4M, 8M, conc). To the centrifuge tube 0.5g of pre-treated resin were added (Dowex 50W×2-100 and Amberlyst 15). Both resins are strongly acidic and were in the hydrogen form. To each centrifuge tube either ^{99}Tc or ^{152}Eu were added. The samples were then agitated for 15 minutes. After 15 minutes the supernatant was removed and the activity in the solution determined by counting an aliquot by either γ spectrometry or LSC. Results are shown in Table 3.5. From the table it can be seen that there was difficulty in obtaining full recovery of ^{152}Eu. This was due to the affinity of the tri-valent species with the cation exchange resin. The recovery of europium was not quantitative. Even when the sample was stripped using concentrated acids, it is found that ~10% of the Eu was associated with the resin. From the table it can also be seen that in nitric acid, there was virtually no retention of the Tc on the resin. At high nitric acid concentrations it was found that >98% of the Tc remained in solution. In hydrochloric acid it was found that at high acid concentrations (>4M) a greater %

activity was associated with the resin, however rather than adsorption mechanisms, this effect is possible due to the reduction of Tc (VII) to Tc (IV). The solubility of Tc (IV) is less than that of Tc (VII), consequently, the effect observed may be due to partial precipitation rather than adsorption.

Table 3.5 Retention of ^{99}Tc and ^{152}Eu on cation exchange resin

Resin	Acid	Molarity (M)	% in solution
		^{99}Tc	
Dowex	HNO_3	0.1	88
Dowex	HNO_3	1	93
Dowex	HNO_3	4	94
Dowex	HNO_3	8	98
Dowex	HNO_3	Conc	99
Dowex	HCl	0.1	90
Dowex	HCl	1	92
Dowex	HCl	4	88
Dowex	HCl	8	86
Dowex	HCl	Conc	85
Amberlyst	HNO_3	0.1	84
Amberlyst	HNO_3	1	96
Amberlyst	HNO_3	4	99
Amberlyst	HNO_3	8	100
Amberlyst	HNO_3	Conc	100
Amberlyst	HCl	0.1	92
Amberlyst	HCl	1	96
Amberlyst	HCl	4	94
Amberlyst	HCl	8	93
Amberlyst	HCl	Conc	84
		^{152}Eu	
Dowex	HNO_3	0.1	0
Dowex	HNO_3	1	1.1
Dowex	HNO_3	4	43
Dowex	HNO_3	8	73
Dowex	HNO_3	Conc	92
Dowex	HCl	0.1	0
Dowex	HCl	1	0
Dowex	HCl	4	32
Dowex	HCl	8	70
Dowex	HCl	Conc	88
Amberlyst	HNO_3	0.1	0
Amberlyst	HNO_3	1	1
Amberlyst	HNO_3	4	36
Amberlyst	HNO_3	8	68
Amberlyst	HNO_3	Conc	95
Amberlyst	HCl	0.1	0
Amberlyst	HCl	1	0
Amberlyst	HCl	4	36
Amberlyst	HCl	8	76
Amberlyst	HCl	Conc	91

3.5.3.2 Separation using anion exchange resin

As previously described (3.5.3.1) batch experiments were carried out to determine the association between ^{99}Tc and ^{152}Eu with the anion exchange resins investigated. Results are shown in Table 3.6

Table 3.6 Retention of ^{99}Tc and ^{152}Eu on anion exchange resin

Resin	Acid	Molarity (M)	% in solution
		^{99}Tc	
Dowex	HNO_3	0.1	1
Dowex	HNO_3	1	5
Dowex	HNO_3	4	25
Dowex	HNO_3	8	60
Dowex	HNO_3	Conc	94
Dowex	HCl	0.1	0.1
Dowex	HCl	1	0.1
Dowex	HCl	4	0.1
Dowex	HCl	8	0.5
Dowex	HCl	Conc	0.9
Amberlite IRA-400	HNO_3	0.1	2
Amberlite IRA-400	HNO_3	1	8
Amberlite IRA-400	HNO_3	4	26
Amberlite IRA-400	HNO_3	8	75
Amberlite IRA-400	HNO_3	Conc	98
Amberlite IRA-400	HCl	0.1	0.1
Amberlite IRA-400	HCl	1	0.1
Amberlite IRA-400	HCl	4	0.4
Amberlite IRA-400	HCl	8	0.8
Amberlite IRA-400	HCl	Conc	0.7
		^{152}Eu	
Dowex	HNO_3	0.1	98
Dowex	HNO_3	1	100
Dowex	HNO_3	4	100
Dowex	HNO_3	8	100
Dowex	HNO_3	Conc	100
Dowex	HCl	0.1	100
Dowex	HCl	1	99
Dowex	HCl	4	100
Dowex	HCl	8	100
Dowex	HCl	Conc	100
Amberlite IRA-400	HNO_3	0.1	100
Amberlite IRA-400	HNO_3	1	100
Amberlite IRA-400	HNO_3	4	97
Amberlite IRA-400	HNO_3	8	100
Amberlite IRA-400	HNO_3	Conc	100
Amberlite IRA-400	HCl	0.1	100
Amberlite IRA-400	HCl	1	100
Amberlite IRA-400	HCl	4	100
Amberlite IRA-400	HCl	8	100
Amberlite IRA-400	HCl	Conc	100

From the table it can be clearly seen that the separation between the cation and anions is complete. There is very little association between the Tc complex in HNO_3. Whilst in the hydrochloric media the Tc complex is strongly retained on the resin at all acid concentrations. Consequently, these experiments suggest that it may be possible to separate Tc from other species in the sample by loading the solution on the resin in HCl and eluting the Tc complex off the column using HNO_3. Under these column conditions, the cationic species investigated exhibited no affinity to the resin, as indicated by the % of ^{152}Eu activity remaining in solution (>98%).

3.5.4 Isolation of ^{99}Tc using solvent extraction

Chemically, technetium is similar to another group VIIB element, rhenium, Re. Consequently it is for this reason that some analytical methods adopt Re as a chemical carrier, thus minimising losses of Tc. However, ruthenium, Ru, is also found alongside technetium, since it too is a fission product of ^{235}U (0.4%). Ruthenium-106 is a β emitter and difficult to separate from technetium using ion-exchange and precipitation schemes. Consequently, as a final purification step, solvent extraction techniques can be employed to isolate the technetium from other species such as the actinides, molybdenum and ruthenium [32, 80-83]. A variety of organic extraction agents have been employed to isolate Tc from other species in solution. These include, ammonium pyrrolidinedithiocarbamate (APDC) in chloroform [41], Aliquat 336 nitrate (predominantly methyltrioctylammonium nitrate) in 1,3-diisopropyl benzene, tri-n-octylamine (TnOA) in mineral acids [32] and TEVA Spec. an aliphatic quaternary ammonium salt supported on non-ionic acrylic ester polymer beads [84].

This work investigated the isolation of Tc from Ru containing solutions using tri-n-octylamine in mineral acids and the use of TEVA Spec. chromatographic ion-exchange resins.

3.5.4.1 Isolation of ^{99}Tc from Ru using tri-n-octylamine (TnOA) in mineral acids

To a centrifuge tube 10ml of mineral acid were added. To the solution ^{99}Tc tracer and 1ml of 100ppm Ru solution were added. To the sample 5ml of 5% TnOA in xylene were added and the sample shaken for 15 minutes. Once the aqueous and

organic phases had settled out, the organic phase was transferred to a LSC vial, mixed with scintillant and counted. The sample was extracted using the organic solvent mixture three times. The concentration of the Ru in the aqueous phase was determined by ICP-OES. The effect of acid concentration on the isolation of Tc from Ru is shown in Table 3.7.

Table 3.7 Effect of acid and acid concentration on Tc isolation

Acid	Concentration (M)	% Tc – Organic phase			% Ru aqueous
		1st Ext^n	2nd Ext^n	3rd Ext^n	
HNO_3	0.1	99.8	0	0	68
HNO_3	1	96.4	1	0	71
HNO_3	2	81.4	3	0	70
HNO_3	4	31.7	5	0	88
HNO_3	8	6.23	4	0	91
HCl	0.1	99	0	0	74
HCl	1	98.9	0	0	77
HCl	2	98.4	0	0	76
HCl	4	97.7	0	0	79
HCl	8	95.6	1	0	81
H_2SO_4	0.1	95.6	1	0	94
H_2SO_4	1	97.8	0	0	97
H_2SO_4	2	100	0	0	96
H_2SO_4	4	98.1	0	0	95
H_2SO_4	8	95.5	1	0	97
H_3PO_4	0.1	90.73	0	0	84
H_3PO_4	1	80.2	6	0	83
H_3PO_4	2	83.9	4	0	88
H_3PO_4	4	62.8	8	0	81
H_3PO_4	8	51.7	12	0	84

From the table it can be seen that use of sulphuric acid led to an effective separation of Tc and Ru at all acid concentration investigated. Although hydrochloric acid systems had good Tc recovery, it was found that up to 25% of the Ru passed into the organic fraction. Consequently, optimum Tc removal is obtained using 2M H_2SO_4. It was also shown that under these condition ~ 96% of the Ru remained in the aqueous solution. Therefore, under these reaction conditions the sample extracted into the organic phase is virtually free of Ru contamination.

3.5.4.1.1 Optimisation of Tc extraction

In the reaction scheme the Tc is extracted into the TnOA xylene extractant for 15 minutes. It was important to determine if this sample contact time was long enough

for optimum extraction of the Tc. It was also necessary to determine the rate of extraction.

To a set of centrifuge tubes 10ml of 2M H_2SO_4 were added. To the acid ^{99}Tc tracer was added. To the sample a 5ml aliquot of 5% TnOA in xylene were added. The mixture was then shaken for between 1-15 minutes. The phases are then allowed to settle for 1 minute. The organic phase was then removed, mixed with Ecoscint and counted on the LSC. The experimental results are shown in Table 3.8, and shown diagrammatically in Figure 3.1.

Table 3.8 Optimisation of sample:organic contact time

Time (minutes)	% ^{99}Tc extracted
1	83
2	95
3	99
4	100
5	99
6	100
7	100
8	100
9	98
10	100
11	100
12	100
13	99
14	98
15	100

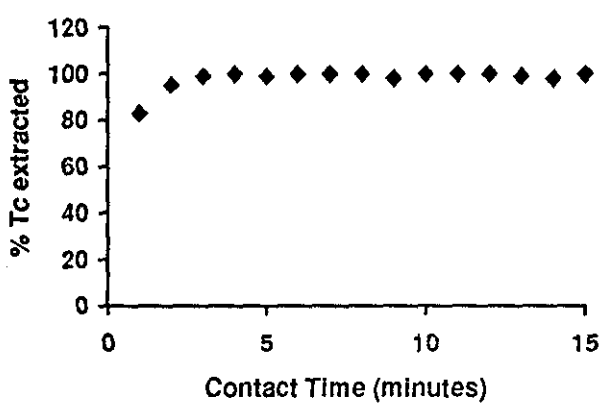


Figure 3.1 Rate of extraction of ^{99}Tc into TnOA

From the table it can be seen that the kinetics of the extraction are fast. The experiments indicated that virtually all of the Tc had been removed from the aqueous phase within 3 minutes. Consequently, the 15 minutes contact time initially proposed was revised and a contact time of 5 minutes was adopted.

3.5.4.2 Isolation of Tc from sample using TEVA Spec. resin

The efficiency of the TEVA Spec. resin was determined using methods obtained from Eichrom Industries [82]. To two centrifuge tubes 10ml of 0.1M HNO_3 were added. To tube A, ^{99}Tc tracer was added. To tube B 1ml of 100ppm Ru solution was added. To both samples, 2ml of 6% H_2O_2 were added. The lids of the tubes were then placed loosely on the tubes and the tubes were placed in a hot water bath and heated at 90°C for 1 hour; or until gas evolution has ceased. Once cool the sample volume was made up to 15ml using deionised water. The sample was then passed through a TEVA Spec. column and the resin washed using ~ 50ml of 1M HNO_3. The analyte was stripped from the resin using 20ml 11M HNO_3. All eluants were collected in 5ml aliquots and the Ru determined by ICP-OES. To the ^{99}Tc fractions 1ml of conc. NH_4OH was added and the samples dried down gently to incipient dryness. The sample was then dissolved in 2ml of 1M HNO_3 and Ecoscint cocktail scintillant was added. The ^{99}Tc was then determined using LSC. The results are shown in Table 3.9.

Table 3.9 Isolation of ^{99}Tc using TEVA Spec. resin

Fraction	% Tc	% Ru
Loading solution		
0-5	0	17
5-10	0	24
10-15	0	23
TOTAL	0	64
1M HNO_3 Wash		
0-5	0	16
5-10	0	10
10-15	0	5
15-20	0	4
20-25	0	0
25-30	0	0
30-35	0.3	0
35-40	0.9	0
40-45	1.1	0
45-50	1.4	0
TOTAL	3.7	35
11M HNO_3 Tc Strip		
0-5	17	0.5
5-10	53	0
10-15	16	0
15-20	2	0
TOTAL	88	0.5

From the table, it can be seen that the TEVA Spec. column retains the Tc, whilst the Ru passes through the column in the loading solution and subsequent wash. It was found that over 64% of the Ru was not retained on the resin. Experiments indicated that less than 1% of the Ru was found in the Tc fraction.

If the analyte is to be determined using ICP measurement it will be necessary to remove iso-baric interference due to Mo. However, if ^{99}Tc is to be measured using radiometric techniques, the β emitting radionuclide ^{106}Ru will need to be removed. This work has focussed upon radiometric methodologies and consequently, methods developed have been concerned with ^{106}Ru decontamination rather than iso-baric Mo purification. Both of the isolation techniques investigated were successful in that high levels of Tc separation were achieved. However, the solvent extraction technique was much quicker (and cost effective) than using the TEVA Spec. resin.

Therefore the solvent extraction technique using TnOA was investigated further with regards to the feasibility of using this isolation technique in concrete waste forms.

3.6 Isolation of Tc from concrete

In a concrete matrix a number of species may impair the chemical procedure of an analytical method. Consequently, it was necessary to determine the effect of the concrete matrix on each of the analytical stages.

3.6.1 Analyte solubilisation from the concrete

It was necessary to determine if the concrete leaching conditions used in the Cl_2/I_2 analysis led to the complete leaching of the Tc from the concrete matrix.

To a round-bottomed flask, 2g of concrete (Set 1) were added. The digestion apparatus was set up as shown in Figure 2.1. To the reaction system, 6M NaOH was added. After an hour of alkali digestion nitric acid was added, resulting in a 3M acid concentration. To the system 25ml of 2% (w/v) $KMnO_4$ were added and the system heated at 80°C for three hours. After the reaction was complete, the system was cooled whilst remaining under reflux. When cool, the contents of the reaction vessel were filtered. The filtrate was weighed and an aliquot taken for analysis by LSC. The precipitate mixture containing non-solubilised concrete and MnO_2 was transferred to a beaker and heated with 6M HCl. The sample was then filtered and the solubilised MnO_2 retained for analysis by LSC. The results are shown in Table 3.10.

Table 3.10 Leachability of ^{99}Tc from concrete

Wt of concrete (g)	% Filtrate	% MnO_2	% ^{99}Tc concrete
1.02	97	1	2
2.18	92	1	7
3.62	95	0	5
4.27	94	0	6
5.04	95	1	4

From the table it can be seen that the digestion procedure developed to leach halides from the concrete matrix can also be used to solubilise the ^{99}Tc. The amount of ^{99}Tc

bound to the concrete has been estimated by difference as opposed to determined using a counting method. For the ^{99}Tc associated with the concrete full sample digestion (as opposed to leaching) would be necessary. This would be achieved using HF digestion methods. However, this would have to be carried out in a system under reflux to prevent loss of the analyte due to the formation of volatile species. The apparatus would need to be made out of HF resistant material such as Teflon but the apparatus must also be air-tight, apparatus of this nature is not widely available. From the table it can also be seen that the digestion procedure can be used to solubilise the analyte from large sample sizes, with virtually no adverse affect on the degree of analyte dissolution. This is of obvious benefit if the analyte is of low concentration.

3.6.2 Separation of Tc from Ru and ^{152}Eu

To the apparatus 2g of concrete (Set 2) were added, to the vessel 1ml of 100ppm Ru solution was added. The sample was then leached from the matrix as described in Section 3.6.1. The sample was filtered and the filtrate retained. To the filtrate, 1ml of conc. H_3PO_4 and 1ml of 1M $CaCl_2$ were added. The pH of the system was adjusted to 5 using 6M NH_4OH. The precipitate was left to settle for 1 hour. The sample was filtered and the precipitate retained for analysis. Concentrated HCl was added to the filtrate until the acid concentration was 1M, the solution was then passed through a Dowex anion exchange column. The column was washed with 20ml of 1M HCl. The Tc was then eluted using 30ml of conc. HNO_3. An aliquot of the eluant was taken for γ and ICP-OES analysis. The remainder of the sample was dried down gently and taken up in 2M H_2SO_4. To the sample 5ml of 5% TnOA in xylene were added and the sample shaken for 5 minutes. The Tc extraction was repeated and the organic phases combined. The organic phase was then mixed with Ecoscint and the ^{99}Tc determined by LSC. The aqueous phase was analysed for ^{152}Eu by γ spectrometry and the Ru was determined using ICP-OES, an aliquot of the aqueous phase was analysed using LSC. The precipitate was dissolved in ~10ml of 2M nitric acid, an aliquot was taken for γ, β and ICP-OES analysis. LSC standards containing γ activity were prepared so that any ^{152}Eu contribution could be subtracted

from the LSC spectrum, resulting in the activity due to ^{99}Tc. The results are summarised in Table 3.11.

Table 3.11 Isolation of ^{99}Tc from Ru and ^{152}Eu doped concrete

Analytical Stage	% ^{99}Tc	% Ru	% ^{152}Eu
MnO_2 precipitation	2	3	36
Phosphate precipitation	4	3	44
Precipitation and anion exchange – loading solution	ND	2	6
Precipitation and anion exchange – Eluant	ND	68	6
Extraction –Organic phase	86	ND	ND
Extraction – Aqueous phase	0	24	0

ND = not determined

The results indicate that there is a small association of the ^{99}Tc with the $CaHPO_4$ precipitate. However, this may be due to occlusion rather than affinity. In this system it was also shown that the Eu was not associated to the MnO_2 quantitatively, this may be due to the competition between the cations (including protons, 3M H^+) and the available binding sites. However, the experiments indicate that the $CaHPO_4$ precipitation can be used to further remove other cations from the solution. Observation of the $CaHPO_4$ precipitate indicated that the Fe inherent in the sample was removed. It was observed that there was some difficulty in dissolving the $CaHPO_4$ precipitate which was probably due to the formation of FeO(OH) due to the presence of Fe^{3+} in the sample. This may be circumvented by dissolving the precipitate in HCl.

3.6.2.1 Optimisation of contact time between concrete solution and TnOA

Initial experiments using solutions containing ^{99}Tc indicated that the Tc complex was extracted into the organic phase within 3 minutes. However, in the presence of other ions present within the concrete matrix, the rate of extraction may be affected. Therefore it was necessary to determine if the presence of these ions inhibited the extraction rate.

To a large round bottomed flask 20g of blank concrete were added. To the vessel, 200ml of 6M NaOH were added and the system heated to 80°C for 1 hour. To the vessel conc. nitric acid is added until the final H^+ concentration is 3M. The sample is then cooled and filtered through a 0.45μm membrane. To a set of centrifuge tubes

10ml of the concrete filtrate were added. The solution was evaporated and the residue re-dissolved in 2M H_2SO_4. To each tube ^{99}Tc tracer was added. To the tubes 5ml of 5% TnOA in xylene were added. The rate of extraction of the Tc into the TnOA extractant was determined by removing the organic phase at 1 minute interval contact times and determining the ^{99}Tc by LSC. The results are shown in Table 3.12.

Table 3.12 Extraction of Tc into TnOA from concrete solutions

Contact Time (minutes)	% ^{99}Tc extracted
1	76
2	83
3	95
4	98
5	100
6	98
7	99
8	100
9	98
10	100
11	97
12	100
13	99
14	99
15	98

From the table it can be seen that the extraction rate of the Tc into the organic complex is marginally slower than from spiked solutions. However, it should be noted that there is still near quantitative extraction of the Tc with a 5 minute aqueous:organic contact time. Consequently these experiments indicate that a 5 minute contact time between the two phases leads to almost quantitative Tc recovery.

3.6.3 Isolation of ^{99}Tc from ^{36}Cl, ^{125}I, ^{137}Cs, ^{152}Eu and Ru doped concrete

To the apparatus 2g of concrete (Set 3) were added. The sample was digested as previously discussed (section 3.6.1). The alkali traps were analysed for ^{36}Cl and ^{125}I, they were also analysed for ^{99}Tc to ensure mixed Tc-species had not been transferred from the reaction vessel. The reaction sample was filtered and the filtrate retained. To the filtrate $CaHPO_4$ was precipitated, after settling for 1 hour, the sample was filtered through a 0.45μm membrane. The precipitate was retained for analysis. The acid concentration was adjusted to 1M using conc HCl, and passed through a pre-treated Dowex anion exchange column. 20ml of 1M HCl was used to wash the

column, all washings were retained for analysis. The Tc was eluted using 30ml of conc. HNO_3. As before (section 3.6.2. an aliquot of the eluant is analysed by γ spectrometry and ICP-OES). The remainder of the sample was dried down gently and the residues taken up in 2M H_2SO_4. The ^{99}Tc was extracted into 5ml of 5% TnOA in xylene. The extraction was repeated and the organic fractions combined for LSC. The aqueous phase was analysed for ^{137}Cs and ^{99}Tc by LSC, ^{152}Eu by γ spectrometry, and the Ru was determined using ICP-OES. The precipitate was dissolved in ~5ml of 2M HCl, the fraction was analysed by γ and β spectrometry, and ICP-OES. The results are shown in Table 3.13.

Table 3.13 Isolation of ^{99}Tc from Ru and ^{152}Eu doped concrete

Analytical Stage	% ^{125}I	% ^{36}Cl	% ^{137}Cs	% Ru	% ^{152}Eu	% ^{99}Tc
1st Stage digestion- alkali trap	91	0	ND	0	ND	No β
2nd Stage digestion – alkali trap	0	87	No γ	0	No γ	ND
MnO_2 precipitation	ND	ND	2	7	41	6
Phosphate precipitation	ND	ND	1	4	53	4
Precipitation and anion exchange – loading solution	ND	ND	88	4	5	ND
Precipitation and anion exchange – Eluant	ND	ND	0	63	3	ND
Extraction –Organic phase	ND	ND	ND	ND	ND	83
Extraction – Aqueous phase	No γ	No β	No β	18	No γ	No β
Total %	91	87	91	96	102	93

ND = not determined

The yield recovery of all analytes were typically >90%. From the analytical scheme it can also be seen that the anion exchange step is required to effectively remove all monovalent ions from the sample prior to solvent extraction. From the table it can be seen that the proposed method can be used to sequentially extract a number of radionuclides from the same sample, thus reducing the number of samples required and minimising the production of hazardous waste products.

3.7 Proposed analytical scheme for the determination of ^{99}Tc in concrete

3.7.1 Leaching of Tc from concrete

3.7.1.1 Single element determination

To a twin necked round bottomed flask, add the concrete sample, to the sample add 25ml of 6M NaOH. To the reaction vessel a small magnetic flea is added. To the reaction vessel attach a reflux condenser. Heat the system on a hotplate-stirrer to 80°C, maintain this temperature throughout the experiment. After 1 hour add 25ml of 12M nitric acid, this is introduced into the reaction vessel using the suba-sealed neck, the sample is then digested for a further 3 hours. After 3 hours the apparatus is cooled under reflux. Once cool, the sample is filtered and the filtrate retained.

3.7.1.2 Multi element determination (Tc, Cl_2, I_2)

The sample is digested as previously described in 2.1.11. The contents of the reaction vessel are filtered through a 0.45µm membrane. The filtrate is retained for analysis; discard the solid fraction. The contents of the hydroxide traps are analysed for ^{36}Cl and ^{129}I using methodologies described in 2.11.2 and 2.11.3.

3.7.2 Separation of Tc from other elements

To the filtrate 1ml of 1M $CaCl_2$ and 1ml of conc. H_3PO_4 is added. To the sample 6M NH_4OH is added until the pH is pH 5. After 1 hour the sample is filtered through a 0.45µm membrane. The precipitate is discarded and the filtrate is evaporated gently at 60°C. To a column Dowex anion exchange resin is added until a 100mm-bed depth is obtained. Pre-treat the resin by washing through with ~ 100ml of 1M HCl. The sample is taken up in 10ml of 1M HCl and loaded on to the column. The column is washed with 5×10ml aliquots of 1M HCl. Elute the Tc using 30ml of conc. HNO_3. Discard the HCl washes, the HNO_3 eluant is transferred to a beaker and dried down gently at 60°C.

3.7.3 Isolation of Tc from Ru

The sample is taken up in 10ml of 2M H_2SO_4. Extract the Tc from the sample using 2×5ml aliquots of 5% TnOA in xylene. Shake the samples for 2 minutes, leave the samples for 5 minutes to allow the phases to completely separate. Combine the two organic phases and mix with Ecoscint scintillation cocktail prior to determination by LSC.

4.0 Determination of selected Lanthanides in concrete

4.1 General Chemistry

The lanthanides are that group of elements whose atomic number ranges from 58 through to 71. The mass numbers associated with this group range from 132 to 171. As has previously being discussed (section 1.6.1), significant quantities of lanthanide isotopes will be formed during the fission process. The fissioning of the uranium atom is an asymmetrical process; *i.e.* the products formed are dissimilar in both atomic number and weight. Generally, two large mass units will be formed alongside several fast neutrons. The larger mass units formed, will typically be in the mass region of 90-101 and 132-143, the heavier mass unit coincides with that of the lighter rare earths. Experimental evidence indicates that in decommissioning and operational waste, radionuclides such as ^{139}Ce, ^{144}Ce, ^{147}Pm, ^{151}Sm, ^{152}Eu and ^{154}Eu are produced. A number of the lanthanide elements are considered to be radiologically significant, this is due to a variety of factors, including half-life and rate of production (*i.e.* quantities expected). There is therefore a need to accurately determine these radionuclides in wastes produced during the operational and decommissioning phase.

The lanthanides are found in a variety of minerals, including monazite and bastnaesite [4]. The minerals will contain a mixture of the lanthanides, *i.e.* the lanthanides are found alongside each other. The chemistry of the lanthanide elements is very similar, this similarity leads to a variety of problems in separating and determining each individual lanthanide component. The lanthanide elements are becoming increasingly important in many new technologies. The rare earth elements are being utilised in many diverse areas of industry including catalysis, ceramics, magnets and nuclear technologies. Consequently, there has been an increased demand for these elements and compounds. Due to the nature of the applications, it is important that the rare earths obtained are of high chemical purity. Due to the

increased demand for these elements; metallurgical separation and purification methodologies have become increasingly important.

However, this interest has been confined to the bulk separation *i.e.* the purification of the lanthanides from the ore. The trace element separation of these species has not yet had the same surge in interest.

The isolation and separation of the lanthanide analyte from both the bulk matrix, and other rare earths contained in the sample will require a variety of separation and purification techniques. Techniques investigated include solvent extraction, precipitation and ion-exchange. It should be noted that in this work radio-isotopes for Sm and Ho were unavailable, consequently the determination of these elements was carried out by ICP-OES.

4.2 Reagents and instrumentation

4.2.1 Reagents

Standards used in this work include 1000ppm Sm solution (w/v). The Sm solution has a low natural specific activity because of the presence of ^{147}Sm, ^{148}Sm and ^{149}Sm. 1000ppm solution of Ho (w/v) was also used

Various radionuclides were used in the development of a method for the determination of Sm and Ho in concrete wastes. Initial work used ^{148}Gd and ^{152}Eu to investigate the separation of the lanthanides from the matrix bulk.

Radionuclides used include, ^{152}Eu provided by Gresham Scientific Instruments LTD, Buckinghamshire,UK; ^{148}Gd was supplied by Magnox Electric PLC, Gloucestershire; ^{99}Tc and ^{137}Cs were supplied by Amersham Pharmacia Biotech Buckinghamsire, UK; and ^{36}Cl and ^{125}I, were both purchased from ICN Biomedicals Inc., USA. The working solutions ranged from 0.1Bq g^{-1} to 1kBq g^{-1}.

All aqueous solutions were prepared using 18MΩ deionised water. All chemical reagents were of Analytical grade and were supplied by Aldrich, Poole, UK. Solutions required in the development programme for the determination of Sm and Ho in concrete wastes include; ammonia, sodium hydroxide (0.1M to 6M), nitric acid (0.1M to 15.8M), 2% (w/v) potassium permanganate, 0.1M $CaCl_2$, 0.1M $FeCl_3$, 1000ppm Sm and Ho solutions (prepared using 99.99% pure nitrate salt).

Solvents used include 5%(v/v) TnOA in xylene, iso-butyl-alcohol, and ethanol.

A number of analytical ion-exchange resins were investigated all of which were of analytical grade: Amberlite IRA-400(Cl^-), Dowex 1×8 (100-200),(Cl^-), all of which were purchased from Aldrich, Dorset, UK. All resins pre-treated by flushing with deionised water and then conditioning with 1M HCl. Cationic ion-exchange resins were also investigated, Dowex 50WX2-100 and Amberlyst 15. Both resins were strongly acidic and were used in the hydrogen form, the cation resins were pre-treated by conditioning with 1M H^+. The cation exchange resins were of Analytical Grade and were supplied by Aldrich, Dorset, UK.

4.2.1.1 Preparation of spiked solutions

The solutions used in Section 3.2.1.1 were also used for this work. The solutions used were as follows:

^{99}Tc spiked solution, ^{152}Eu spiked solution, ^{137}Cs spiked solution were made up from stocks as detailed previously in Section 3.2.1.

^{148}Gd solution, the solution was received from Magnox Electric PLC in 0.1M HCl, no carriers were added.

4.2.1.2 Preparation of spiked concrete

As there are no concrete samples ready mixed with radioactive standards, it was necessary to produce secondary concrete standards. The inactive concrete was doped with suitable radiotracers and left to dry. The sample was then ground into a fine powder and the activity determined by taking into account the total activity added and the total weight of sample. Although these samples were not certified nor standardised, they were used in this work to determine the overall feasibility of the

methods developed. Inactive carriers were not added to the matrix, since appreciable amounts of the element (*e.g.* Ho) would not be expected in a genuine concrete sample.

Water was added to the concrete powder until a water:concrete ratio of 1:5 was reached. The resulting slurry was then placed in a weighing boat and activity was added. The contents of the weighing boat were mixed thoroughly to ensure even dispersion of the activity through the matrix. The concrete was doped as detailed below:

Set 1)	1000ppm Sm
Set 2)	1000ppm Ho
Set 3)	1000ppm Sm and Ho
Set 4)	1000ppm Sm, Ho and ^{137}Cs
Set 4)	1000ppm Sm, Ho, ^{137}Cs and ^{152}Eu
Set 5)	1000ppm Sm, Ho, ^{137}Cs, ^{152}Eu and ^{148}Gd
Set 6)	1000ppm Sm, Ho, ^{137}Cs, ^{152}Eu, ^{148}Gd, ^{36}Cl, ^{125}I and ^{99}Tc

The samples were then dried at room temperature for 1 month prior to grinding. Once the samples were cured, they were transferred to a mortar and ground using a pestle. The samples were ground until all the contents passed through a 250μm sieve. The powdered samples were then stored in a sealed container ready for use.

4.2.1.3 Preparation of synthetic concrete solution

The simulated solution principally contains the significant cations. However, the exact chemical profile of each sample will differ considerably, therefore this concrete solution contains a reasonable estimate of the possible elements expected in a concrete solution as determined by Law *etal* [85], taking into account the amount of aggregates and sand added to the cement mix.

Analysis of concrete for a 1g sample containing 1 part cement, 2 parts sand and 1 parts aggregate would contain the following components:

Constituent	Wt (%)	Species	Wt (%)	Simulated concrete conc.(M)
CaO	18	Ca^{2+}	13	1.0
SiO_2	79	Si^{4+}	37	/
Al_2O_3	1.8	Al^{3+}	0.94	0.03
Fe_2O_3	0.75	Fe^{3+}	0.53	0.01
Bi_2O_3	0.20	Bi^{3+}	0.33	0.002
Others	0.25	/	/	/

The simulated concrete solution was made by dissolving 236g of $CaNO_3.4H_2O$, 12g of $Al(NO_3)_3.9H_2O$, 1.7g of $FeCl_3$ and 0.90g of Bi_2O_3 in 1L of 0.1M HNO_3 acid. Consequently, the solution contained 40g of calcium, equivalent to ~300g of concrete. The simulated solution was used instead of HF digested concrete, therefore Si^{4+} was not added since this would be driven off as SiF_6 during the digestion process. Every 10ml aliquot was equivalent to 3g of concrete. The solution was stored in an airtight container, ready for analysis.

4.2.2 Instrumentation

^{99}Tc, ^{36}Cl, ^{148}Gd and ^{137}Cs were counted on a Canberra Packard 2750 ultra low-level liquid scintillation counter. ^{125}I was counted in a well crystal (NaI(Tl)) Panax counter. ^{152}Eu was counted on a P4800 Philips Gamma Counter. The samarium and holmium were determined using a Perkin Elmer Plasma II Inductively Coupled Plasma Optical Emission Spectrometer. Boussmann tables were used to select the most appropriate wavelengths, taking into account the intensity and expected interferences (*e.g.* Ca^{2+}, Fe^{3+}) contained within the sample.

CEM MSD2100 Microwave digester.

4.2.2 Sample Pre-treatment

As the lanthanide elements are metallic species, the tendency to form volatile compounds is small. Consequently, digestion under a partial vacuum is not required. Samples were totally digested using HF/HNO_3 acid mixtures. Leaching experiments were also carried out using the adopted dissolution procedure for both technetium and the halides.

4.3.1 Total digestion

For Sm and Ho analyses ICP-OES was used to determine the concentration of the analyte of interest. Since the solids tolerance of the ICP-OES is limited (~0.2g), experiments were carried out using Sm and Ho with determination by ICP-OES and also using ^{152}Eu and ^{148}Gd with determination of these isotopes by γ spectrometry and LSC. Since ^{152}Eu and ^{148}Gd are to be determined using radiometric techniques larger sample sizes can generally be tolerated.

To a Teflon beaker the concrete was accurately weighed. The sample was then etched with 15ml of nitric acid. Once the foaming had subsided, 10ml of concentrated hydrofluoric acid were added. The sample was then covered with a Teflon watch glass and heated. After 2 hours the sample was dried and then attacked once more with the nitric/hydrofluoric acid mixture. The sample was repeatedly attacked until the sample was solubilised. The sample was then taken to dryness to ensure the complete removal of HF. The sample residues were dissolved in 1M nitric acid and stored awaiting analysis.

4.3.2 Leaching

The powdered concrete was accurately weighed into a round-bottomed flask and the apparatus set up as shown in Figure 2.1. To the flask 25ml of 6M NaOH were added and the sample was heated for 1 hour. After an hour 25ml of 12M HNO_3 acid were added and the system heated for 3 hours. The sample was then treated with 25ml of 2% (w/v) potassium permanganate and 25ml 12M HNO_3. The mixture was heated for a further 3 hours. The sample was then filtered to separate the filtrate from the MnO_2 particulate. Previous work (Section 3.5.1.1) had indicated that Eu was associated with the precipitate, consequently the filtrate and precipitate was analysed using ICP-OES to determine the distribution of the lanthanide element between the two phases.

4.3.2.1 Filtrate

The filtrate was collected and then dried down to incipient dryness. The sample was then taken up in 2% (v/v) nitric acid.

4.3.2.2 Precipitate

The precipitate was transferred to a beaker and dissolved in ~10ml of 2M hydrochloric acid. The sample was then dried down and taken up into 2% (v/v) nitric.

ICP standards were prepared using standard solution and diluting to the desired concentration using 2% (v/v) nitric acid. The results are shown in Table 4.1 and 4.2.

Table 4.1 Solubilisation of lanthanide by total dissolution and leaching methods

Concrete Mass (g)	Lanthanide	% Concrete solubilised	% Lanthanide leached
Total Dissolution			
0.1	Eu	96	99
0.1	Gd	94	93
0.1	Ho	98	96
0.1	Sm	97	94
1	Eu	92	99
1	Gd	95	96
2	Eu	86	84
2	Gd	89	92
Leaching			
0.1	Eu	27	97
0.1	Gd	22	95
0.1	Ho	24	97
0.1	Sm	18	96
1	Eu	13	94
1	Gd	16	96
2	Eu	12	93
2	Gd	8	96

Table 4.2 Distribution of lanthanide between MnO_2 and filtrate

Concrete Mass (g)	Lanthanide	% Associated with Filtrate	% Associated with MnO_2
0.1	Eu	8	92
0.1	Gd	11	89
0.1	Ho	96	4
0.1	Sm	98	2
1	Eu	13	94
1	Gd	76	96
2	Eu	17	93
2	Gd	68	96

From the tables above it can be seen that the lanthanide is removed from the matrix and bought into solution by both the total digestion and leaching methodologies. Although limited samples were taken it should be noted that as sample size increases it becomes difficult to breakdown the sample fully using HF/HNO_3 acid mixtures. Consequently for large sample sizes it may be useful to leach the analyte from the matrix rather than try to fully breakdown the sample using HF/HNO_3 acid dissolution.

Although previous experiments indicated that MnO_2 could be used to remove highly charged species from solution, these experiments indicated that this was a characteristic associated with Eu rather than the lanthanides in general.

4.3.3 Microwave Digestion

Microwave digestion methods have gained wide acceptance. Digestion in this manner relies on heating the sample under high temperature and pressure. These conditions increase the rate of reaction between the attacking solution and the matrix. To investigate the feasibility of microwave digestion, a limited number of samples were digested using this technique.

Inactive concrete was added to the microwave digestion vessels, which had been fitted with a safety pressurisation disc. To the sample 1ml of HNO_3, 4ml HCl and 4ml of HF (all concentrated) were added and the samples placed in the carousel. Each experimental run contained six samples, and the samples were digested using the following protocol:

Run Conditions	Stage 1	Stage 2
Power (%)	100	100
Pressure (psi)	150	60
Run Time (minutes)	40	20
Time at Pressure (minutes)	20	5

After the samples had cooled the contents were transferred to a Teflon beaker and dried down. The samples were then taken up into nitric acid and the extent of solubilisation determined. The results are shown in Table 4.3.

Table 4.3 Microwave digestion – effect of sample mass

Sample Size	% Solubilised
0.1	93
0.1	88
0.25	91
0.25	89
0.5	87
0.5	83
1.0	78
1.0	71
2.0	58
2.0	64

From the table it can be seen that as the mass of sample increases the percentage solubilisation decreases. Since the analyte of interest will be at trace concentration, it will be necessary to take a large sample for analysis (typically >2g). These experiments indicated that the extent of solubilisation for samples >1g was poor. Consequently microwave digestion was not investigated any further.

4.4 Sample Isolation

Initial experiments were carried out on solutions containing a lanthanide ion in an aqueous matrix. Since the chemistry of the lanthanides is similar, ^{152}Eu and ^{148}Gd were used as anologues of Sm and Ho. The advantage of using these radio-isotopes rather than Sm and Ho is that the analytical result could be determined rapidly using radiometric techniques.

4.4.1 Separation based on atomic size

There are many solid products in nature that have a regular fixed arrangement of atoms or lattice. This arrangement of atoms may lead to channels or pores within the solid framework. These 'holes' are as a consequence of the ordered nature of the atoms contained in the solid framework. There are many applications where these materials (sometimes termed zeolites or molecular sieves) have been used to remove species from either a liquid or gas phase [86-87]. The interaction between the zeolite frame and the interacting species may be due to size or charge, however it is generally a combination of the two. For many years clinoptolinite, a naturally occurring molecular sieve, has been used to selectively extract caesium from nuclear

waste solutions [88]. The interest in this area has grown such that over the last decade many novel, man-made, molecular sieves have been engineered for use in the nuclear industry [86-87]. Consequently, molecular sieves were investigated with regards to their selectivity for lanthanide ions in the presence of other ionic species. The ionic radii of the lanthanides are very similar, and in fact this is the primary reason that the lanthanides exhibit very similar chemical characteristics. Therefore, although individual separation of the lanthanides from each other may not be feasible, it may be possible to separate the lanthanides from other ions in solution, *e.g.* Ca^{2+} (a major interferent in concrete waste forms). Consequently Zeolite A was prepared. Zeolite A is used commercially as a water softener. The aluminosilicate framework interacts and removes the Ca ions in solution and replaces them with Na. At first glance it may seem ludicrous to remove this material since it is hoped to selectively remove the lanthanides from a calcium laden solution, however, the lanthanides have virtually identical atomic radius to that of the Ca^{2+} ion. Consequently any selectivity exhibited will be as a consequence of the increased charge on the lanthanide ion compared to the calcium (Ln^{3+} *c.f.* Ca^{2+}), and thus increased interaction.

The lanthanide elements investigated are shown in Table 4.4 alongside the Ca^{2+} ion.

Table 4.4 Ionic radii of the rare earth elements

Element	Oxidation State	Radius ( )	Ln - Ca
Cerium	Ce^{3+}	1.03	0.044
	Ce^{4+}	0.92	-0.07
Praseodymium	Pr^{3+}	1.01	0.023
Neodymium	Nd^{+3}	0.99	0.00
Promethium	Pm^{3+}	0.98	-0.01
Samarium	Sm^{+2}		-0.99
	Sm^{+3}	0.96	-0.03
Europium	Eu^{2+}	1.09	0.1
	Eu^{3+}	0.96	-0.03
Gadolinium	Gd^{3+}	0.94	-0.05
Terbium	Tb^{+3}	0.92	-0.07
Dysprosium	Dy^{3+}	0.91	-0.09
Holmium	Ho^{3+}	0.89	-0.1
Erbium	Er^{3+}	0.88	-0.11
Thulium	Tm^{3+}	0.87	-0.12
Ytterbium	Yb^{+2}	0.93	-0.06
	Yb^{+3}	0.86	-0.13
Lutetium	Lu^{+3}	0.85	-0.14
Calcium	Ca^{2+}	0.99	N/A

From the information detailed above, it is reasonable to assume that those rare earth elements that have an atomic radius between 0.95 and 1.03Å may be removed from solution due to the interaction between Zeolite A and the lanthanide ion. Experiments were set up to investigate the selectivity of Zeolite A for the lanthanide ions, in the presence and absence of calcium ions. Preliminary experiments looked at the feasibility in using Zeolite A to extract selected lanthanides from an aqueous solution. Further experiments studied the effect of calcium ions using simulated concrete solution. The capacity of the zeolite was also investigated by applying simple batch contact equilibrium experiments.

4.4.1.1 Preparation of Zeolite A

To a large (1L) beaker containing 300ml of deionised water, 25g of NaOH were added. To the solution 13.5g of $NaAlO_2$ was added and the solution boiled. A second solution was prepared containing 14.2g of $Na_2SiO_3.9H_2O$ dissolved in 200ml

of deionised water. The two solutions were mixed and the resultant solution heated at 90°C for 4 hours. The solution was then filtered hot, and the solid washed with deionised water (~600ml). The solid was transferred to a watchglass and dried in an oven at 110°C until constant mass was reached.

4.4.1.2 Capacity of Zeolite A

To ensure that the zeolite material was capable of selectively extracting the lanthanide ion from solution, it was necessary to determine the capacity of the molecular sieve.

To a set of centrifuge tubes varying amounts of Ca^{2+} were added. The system was then doped with 100Bq of ^{45}Ca. After the solution had been left to equilibrate, 0.1g of dried zeolite were added. The solution was left for two hours. An aliquot of the supernatant was removed and the activity determined by LSC. The results are shown in Table 4.5, and further illustrated in Figure 4.1.

Table 4.5 Determination of the capacity of Zeolite A for Ca^{2+}

Moles Ca added	% Ca in Solution	% Associated with Zeolite A	Moles of Ca on Zeolite A	Moles of Ca g^{-1} zeolite
$1x10^{-5}$	1.7	98.3	$9.83x10^{-6}$	$9.83x10^{-5}$
$5x10^{-5}$	2.6	97.4	$4.87x10^{-5}$	$4.87x10^{-4}$
$2x10^{-4}$	4.7	95.3	$1.91x10^{-4}$	$1.91x10^{-3}$
$4x10^{-4}$	42.7	57.3	$2.29x10^{-4}$	$2.29x10^{-3}$
$6x10^{-4}$	59.3	40.7	$2.44x10^{-4}$	$2.44x10^{-3}$
$8x10^{-4}$	67.7	32.3	$2.54x10^{-4}$	$2.54x10^{-3}$
$1x10^{-3}$	70.6	29.4	$2.94x10^{-4}$	$2.94x10^{-3}$

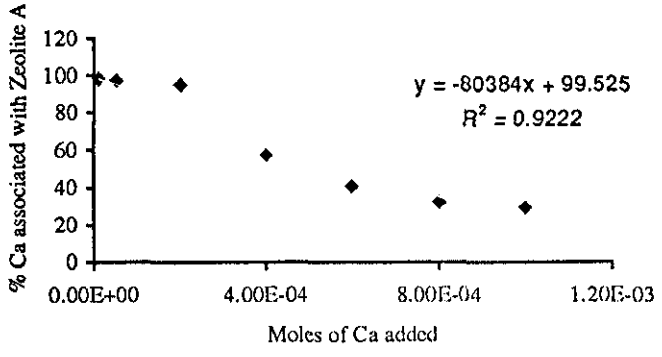


Figure 4.1 Determination of Ca capacity for Zeolite A

From both the table and graph it can be seen that the capacity of the resin for Ca is of the order of $2x10^{-3}$ moles for each gram of Zeolite A.

The selectivity of the molecular sieve for lanthanides was then investigated using ^{152}Eu and non-active Sm. The association of the lanthanide with the zeolite was determined by analysing an aliquot of solution. Europium was determined by γ spectrometry, and samarium by ICP-OES. The results are shown in Table 4.6.

Table 4.6 Extraction of lanthanides using Zeolite A

Moles Ln added	% Eu in Solution	Moles of Eu on Zeolite A	Moles of Eu g^{-1} zeolite	% Sm in Solution	Moles of Sm Zeolite A	Moles of Sm g^{-1} zeolite
$1x10^{-5}$	0.87	$9.9 x10^{-6}$	$9.9 x10^{-5}$	3.8	$9.6 x10^{-6}$	$9.6 x10^{-5}$
$5x10^{-5}$	5.5	$4.7 x10^{-5}$	$4.7 x10^{-4}$	22.1	$3.9 x10^{-5}$	$3.9 x10^{-4}$
$2 x10^{-4}$	44.9	$1.1 x10^{-4}$	$1.1 x10^{-3}$	36.8	$1.3 x10^{-4}$	$1.3 x10^{-3}$
$4 x10^{-4}$	54.1	$1.8 x10^{-4}$	$1.8 x10^{-3}$	47.6	$2.1 x10^{-4}$	$2.1 x10^{-3}$
$6 x10^{-4}$	65.2	$2.1 x10^{-4}$	$2.1 x10^{-3}$	62.9	$2.2 x10^{-4}$	$2.2 x10^{-3}$
$8 x10^{-4}$	74.4	$2.0 x10^{-4}$	$2.0 x10^{-3}$	73.9	$2.1 x10^{-4}$	$2.1 x10^{-3}$
$1 x10^{-3}$	81.6	$1.8 x10^{-4}$	$1.8 x10^{-3}$	80.3	$2.0 x10^{-4}$	$2.0 x10^{-3}$

From the table it can be seen that the zeolitic material was effective in removing the lanthanide from solution. It should also be noted that the capacity of Zeolite A for the lanthanides and calcium are of a similar order of magnitude. However, since the concrete matrix will contain very high levels of calcium, it is necessary to determine the selectivity of the molecular sieve for lanthanides in the presence of calcium ions.

To a set of centrifuge tubes $2x10^{-4}$ moles of Ca solution were added. To the tubes, varying amounts of doped lanthanide solution were added. The contents were made up to 20ml using deionised water. To each tube 0.1g of Zeolite A were added. The samples were then shaken gently for two hours. After this time the tubes were centrifuged, and an aliquot of the supernatant taken for analysis. The Eu samples were counted on the γ spectrometer as taken since they had been doped with the γ emitting radionuclide ^{152}Eu. In this work the Sm samples were made up in 2% nitric acid and the concentration determined by ICP-OES. The results are shown in Table 4.7.

Table 4.7 Extraction of lanthanides using Zeolite A in the presence of Ca

Moles Ln added	Moles of Ca added	% Eu in Solution	% Sm in Solution
$1x10^{-5}$	$2x10^{-4}$	81	68
$5x10^{-5}$	$2x10^{-4}$	86	76
$2x10^{-4}$	$2x10^{-4}$	92	86
$4x10^{-4}$	$2x10^{-4}$	94	97
$6x10^{-4}$	$2x10^{-4}$	96	92
$8x10^{-4}$	$2x10^{-4}$	93	98
$1x10^{-3}$	$2x10^{-4}$	97	95

The results from these experiments indicated that Zeolite A was highly selective towards calcium ions. Virtually all sites on the material were taken up by the calcium ions rather than the lanthanides. Consequently Zeolite A cannot be used to selectively remove lanthanides in the presence of calcium. However this material may be useful for other non-calcium containing matrices including steel and graphite.

4.4.2 Separation using ion-exchange

A variety of radioactive components will be found in contaminated decommissioning concrete wastes. However, the principal radioisotopes will be ^{137}Cs, ^{60}Co and ^{90}Sr. This is due to the very high fission yield (>6%) and relatively long half-life (decades). A limited number of isotopes have a greater fission yield, however they are of little radiological significance since they are either stable products or have very short half lives (hours or minutes). Consequently the most significant radiological contamination will be due to ^{137}Cs or ^{90}Sr. Therefore it is important that the developed analytical method must isolate the rare earth species from these radiological components. In the concrete matrix itself, the bulk will consist of high concentrations of calcium, bismuth, iron and silicaceous materials, many of which may have become activated. Consequently it is necessary to isolate the lanthanide from both matrix contaminants and other radiologically active species.

Caesium and strontium are generally found in the +1 and +2 oxidation state respectively. The electronic configuration is such that chemical complexes are not formed. However, the lanthanides will co-ordinate with a variety of ligands to form

a charged complex. It would then be relatively simple to separate those species that form complexes from those that do not by passing through a column containing ion-exchange resin.

In organic systems the rare earth chlorides will form the $[LnCl_6]^{3-}$ complex, whereas Ca, Bi and Sr will form the MCl_2 species. It is possible to separate these compounds by passing through an anion exchange column. The Ln complex would be retained on the column whilst the non-complexed species would pass through in the loading solution.

Experiments were set up to investigate the efficiency of removing the interfering ions from solution by forming the lanthanide-chloro complex.

The lanthanide chloride was dried down with conc.HCl repeatedly. The sample was then taken up in dry ethanol. The sample was loaded on to a preconditioned anion exchange column. Aliquots were taken for analysis prior to loading on the column, an aliquot of the eluent was also analysed for ^{152}Eu and Sm. Analysis of the washes indicated that the lanthanide formed $LnCl_3$ rather than $[LnCl_6]^{3-}$, as indicated by the results shown in Table 4.8. This may have been due to the organic solvent containing some water, since in the presence of water molecules the hydrated Ln^{3+} ion will be formed resulting in the $LnCl_3$ species, which, since it is not charged, will pass unhindered through the resin.

Table 4.8 Ln removal due to the formation of the lanthanide chloro-complex

Lanthanide	^{152}Eu	Sm
% lost during conversion to chloride	0	0
% dissolved in ethanol	98	96
% in eluent	84	87
% retained by the column	14	9

From the table it can be seen that the lanthanide passed through the column and was not retained to any significant extent. Therefore it was concluded that the ethanol, although dried over sodium, contained a small amount of moisture and the predominant lanthanide species formed was $LnCl_3$.

4.4.3 Separation using solvent extraction

A number of organic solvents have been used in the separation of the lanthanides from bulk matrices. Three main extraction mechanisms have been applied to the rare earth separations, these being; formation of chelate complexes with acidic extractants, ion-pair formation and solvation of salts. However the greatest interest has been in the separation of the lanthanides via the use of acidic extractants. HDEHP (di(2-ethylhexyl)phosphoric acid) is the extractant that has been widely used in lanthanide separation applications [71]. The extraction of the lanthanide in HDEHP can be represented by the following:

$$Ln^{3+}_{aq} + 3(HDEHP)_{2\ org} \leftrightarrow Ln[H(DEHP)_2]_{3\ org} + 3H^{+}_{aq}$$

Extraction mechanisms employing TTA (2-thenoyltrifluoro-acetone), TBP (tri-butylphosphate) and Aliquat 336-SCN (methyltricaprylylammonium thiocyanate) as the extracting agent have been used with moderate success.

Preliminary worked reported here, concentrated upon the investigation of using TTA in xylene. Solutions containing the lanthanide in nitric acid at pH 3.4 were shaken with 0.1M TTA in xylene. The samples were left to settle and the organic phase removed. The extraction was repeated several times, finally an aliquot of the aqueous solution was analysed for lanthanide concentration. It was found that the conditions used to extract the lanthanide ion (pH>3.4) were identical to those reported in the literature for the extraction of Am from solution [71]. Experiments indicated that Eu, Gd and Sm were not quantitatively extracted into solution with over 30% of the lanthanide remaining in the aqueous layer after several extractions. The extraction was difficult since the organic and aqueous layer required several hours for complete separation. The rate of extraction from synthetic concrete solutions were also investigated. However, at the optimum europium extraction pH (3.4), iron was also extracted. Consequently liquid-liquid solvent extraction techniques using TTA were not investigated any further. Results are shown in Table 4.9.

Table 4.9 Feasibility of TTA –Ln^{3+} extraction

	% Ln^{3+}			
Lanthanide	Aqueous	1st and 2nd Extn	3rd and 4th Extn	5th and 6th Extn
Eu	22	58	12	4
Gd	28	56	10	6
Sm	38	37	16	8

Although these experiments were unable to extract the lanthanides quantitatively from solution, it is interesting to note that the extraction characteristics for both Gd and Eu are virtually identical. These experiments suggest that Gd and Eu are analogous species.

4.4.4 Separation using ion-chromatography

Eichrom resins have been used extensively in the nuclear field over the last decade. The resins were originally developed for highly active nuclear waste solutions, however, as the environmental emphasis has increased, these resins are now been utilised for a variety of environmental analyses. Initially these resins were used to extract trace chemicals from relatively chemically pure, nuclear waste solutions. Intolerance to certain ions, *e.g.* Ca and Fe etc. was not a major concern since these species were not present at high concentration in the fuel solution. However, the utilisation of these resins in the analysis of environmental samples indicated that these resins were unable to deal with significant concentrations of certain species. Although the resins were selective for the ion of interest, it was found that the active sites were taken up by other species such as Ca^{2+}, Fe^{3+}, and Bi^{2+}. Consequently the sample must be chemically clean before being placed on the resin. This intolerance to certain ions means that the resins must be used as a final clean-up/isolation step rather than during the initial stages of analysis. Eichrom have developed a number of resins for lanthanide separation, including Eichrom RE, Eichrom Ln1 and Eichrom Ln2. The characteristics of all the rare earth specific resins are detailed:

Resin	Extractant	Support	Particle size	Suggested selectivity
RE	Octyl(phenyl)-N,N-diisobutylcarbamoyl-methylphosphate oxide in tributyl phosphate (CMPO/TBA)	Non acrylic ester polymer	20-50μm 50-100μm 100-150μm	Group Separation
Ln1	Di(2-ethylhexyl)orthophosphoric acid (HDEHP)	Non acrylic ester polymer	20-50μm 50-100μm 100-150μm	Individual Lanthanides
Ln2	Undisclosed – awaiting patent	Undisclosed – awaiting patent	20-50μm 50-100μm 100-150μm	Individual Lanthanides

Since Eichrom RE resin cannot be used to separate the individual lanthanides, this work investigated the use of Ln1 and Ln2 resin. For this work the particle size used has been 100-150mm, the flow rate of the columns being gravity assisted. It is imperative that the solution be chemically clean prior to loading on to the column, since contaminants may cause breakthrough of the analyte from the column. For this reason all preliminary column work was performed using mixed lanthanide stocks in pure aqueous solution. It was necessary to ascertain the optimum loading and elution solution conditions.

The lanthanide was loaded on to the column in either 0.01M HNO_3 or 0.01M HCl. The column was then washed with various concentrations of acid. All eluates were retained and the lanthanide concentration/recovery determined. The results are shown in Table 4.10 and further illustrated in Figure 4.2 and 4.3.

Table 4.10 Elution characteristics of the lanthanides on Ln1 Resin

Hydrochloric Acid			Nitric Acid		
Lanthanide	**[H⁺]**	**% Recovery**	**Lanthanide**	**[H⁺]**	**% Recovery**
Ho	H_2O	2.75	Ho	H_2O	2.0
Ho	0.1	1	Ho	0.1	0.75
Ho	0.25	1	Ho	0.25	0.75
Ho	0.50	1	Ho	0.50	0.75
Ho	0.75	2.75	Ho	0.75	4.75
Ho	1.0	15.5	Ho	1.0	41.25
Ho	2.0	53.75	Ho	2.0	48.75
Ho	4.0	17.25	Ho	4.0	4
Ho	8.0	3.5	Ho	8.0	0.75
Ho	conc.	1.25	Ho	conc.	0.75
Sm	H_2O	21.2	Sm	H_2O	17.4
Sm	0.1	0.8	Sm	0.1	1.3
Sm	0.25	29.6	Sm	0.25	36.4
Sm	0.50	39.5	Sm	0.50	40.8
Sm	0.75	0.4	Sm	0.75	1.9
Sm	1.0	0.6	Sm	1.0	0.8
Sm	2.0	0.4	Sm	2.0	0.6
Sm	4.0	0.6	Sm	4.0	0.7
Sm	8.0	0.2	Sm	8.0	0.4
Sm	conc.	0.4	Sm	conc.	0.4
Eu	H_2O	0.2	Eu	H_2O	0.2
Eu	0.1	0.1	Eu	0.1	0.6
Eu	0.25	0.3	Eu	0.25	0.6
Eu	0.50	61.8	Eu	0.50	73.8
Eu	0.75	29.2	Eu	0.75	26.1
Eu	1.0	0.6	Eu	1.0	0.4
Eu	2.0	0.8	Eu	2.0	0.3
Eu	4.0	0.4	Eu	4.0	0.4
Eu	8.0	0.3	Eu	8.0	0.6
Eu	conc.	1.1	Eu	conc.	1.4
Gd	H_2O	0.2	Gd	H_2O	0.2
Gd	0.1	0.3	Gd	0.1	0.1
Gd	0.25	0.5	Gd	0.25	0.3
Gd	0.50	62.3	Gd	0.50	56.8
Gd	0.75	36.2	Gd	0.75	36.2
Gd	1.0	0.3	Gd	1.0	0.8
Gd	2.0	0.4	Gd	2.0	0.4
Gd	4.0	0.6	Gd	4.0	0.6
Gd	8.0	0.2	Gd	8.0	0.4
Gd	conc.	0.8	Gd	conc.	1.1

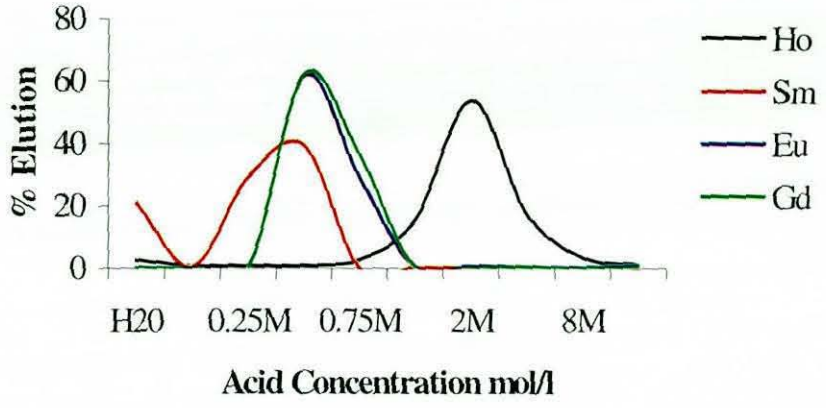


Figure 4.2 Elution profile of the lanthanides on Ln1 resin in hydrochloric media

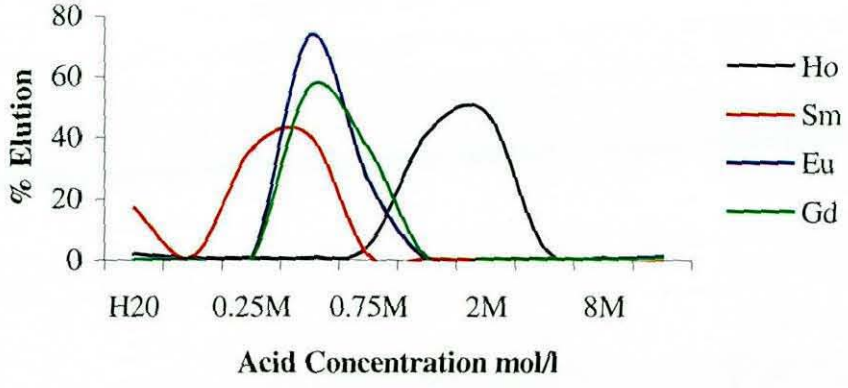


Figure 4.3 Elution profile of the lanthanides on Ln1 in nitric acid media

From the elution profiles it can be seen that Ln1 resin is not able to separate the lanthanide into individual components under the experimental conditions investigated. The profiles indicate that Eu and Gd act in an identical fashion on the resins. Although both resins separate Ho from Sm there is overlap with the Eu and Gd, consequently this resin cannot be used to separate the lanthanides of interest from the matrix. The same experimental methodology was adopted for the

investigation of the lanthanide elution profile from Ln2 Eichrom resin. The results are shown in Table 4.11 and illustrated in Figure 4.4 and 4.5.

Table 4.11 Elution characteristics of the lanthanides on Ln2 Resin

Hydrochloric Acid			Nitric Acid		
Lanthanide	**[H⁺]**	**% Recovery**	Lanthanide	[H⁺]	**% Recovery**
Ho	H_2O	0.50	Ho	H_2O	0.80
Ho	0.1	0.30	Ho	0.1	0.51
Ho	0.25	0.29	Ho	0.25	0.29
Ho	0.50	0.33	Ho	0.50	0.64
Ho	0.75	41.1	Ho	0.75	47.9
Ho	1.0	48.2	Ho	1.0	46.7
Ho	2.0	1.06	Ho	2.0	2.10
Ho	4.0	0.30	Ho	4.0	0.57
Ho	8.0	0.30	Ho	8.0	0.29
Ho	conc.	0.31	Ho	conc.	0.48
Sm	H_2O	79.6	Sm	H_2O	60.3
Sm	0.1	1.8	Sm	0.1	24.3
Sm	0.25	7.1	Sm	0.25	4.6
Sm	0.50	0.9	Sm	0.50	1.7
Sm	0.75	4.2	Sm	0.75	0.01
Sm	1.0	2.0	Sm	1.0	2.8
Sm	2.0	1.2	Sm	2.0	0.01
Sm	4.0	0.39	Sm	4.0	1.3
Sm	8.0	1.0	Sm	8.0	1.7
Sm	conc.	1.8	Sm	conc.	3.2
Eu	H_2O	0.09	Eu	H_2O	0.01
Eu	0.1	0.10	Eu	0.1	0.01
Eu	0.25	99.72	Eu	0.25	99.52
Eu	0.50	0.43	Eu	0.50	0.13
Eu	0.75	0.27	Eu	0.75	0.03
Eu	1.0	0.08	Eu	1.0	0.03
Eu	2.0	0.01	Eu	2.0	0.01
Eu	4.0	0.05	Eu	4.0	0.01
Eu	8.0	0.02	Eu	8.0	0.05
Eu	conc.	0.01	Eu	conc.	0.36
Gd	H_2O	0.02	Gd	H_2O	0.11
Gd	0.1	0.07	Gd	0.1	0.01
Gd	0.25	95.14	Gd	0.25	98.96
Gd	0.50	2.01	Gd	0.50	0.07
Gd	0.75	0.20	Gd	0.75	0.05
Gd	1.0	0.04	Gd	1.0	0.02
Gd	2.0	0.05	Gd	2.0	0.01
Gd	4.0	0.02	Gd	4.0	0.01
Gd	8.0	0.01	Gd	8.0	0.1
Gd	conc.	0.30	Gd	conc.	0.01

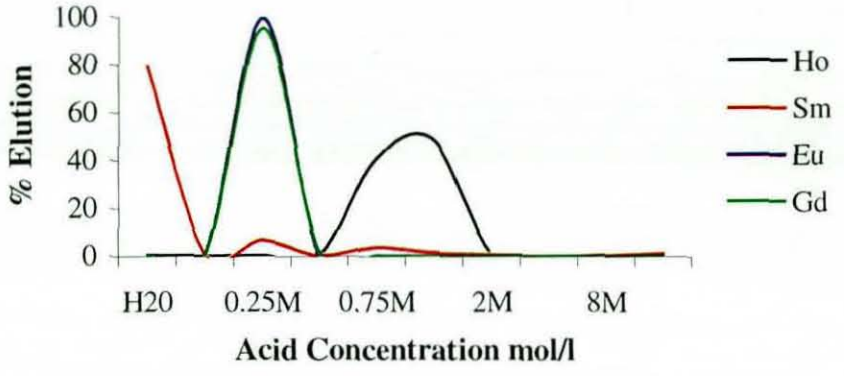


Figure 4.4 Elution profile of the lanthanides on Ln2 resin in hydrochloric media

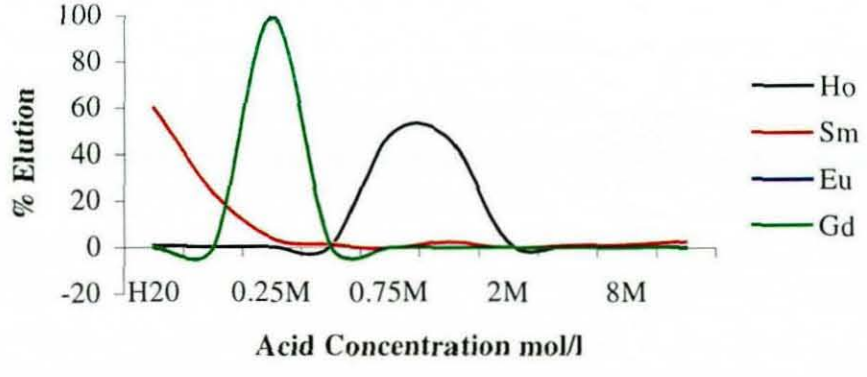


Figure 4.5 Elution profile of lanthanides on Ln2 resin in nitric acid media

From the graphs it can be seen that separation of Sm and Ho is possible using Ln2 resin. Better separation between the Sm and Ho is obtained if hydrochloric acid is used to elute the analytes. Using this resin it is also possible to separate both the Sm and Ho from other lanthanides including Gd and Eu. Attention is once again drawn to the similar behaviour of Gd and Eu on the resin in both acidic media.

The resins were then used to separate a mixed lanthanide solution. This was prepared by spiking de-ionised water with a mixture of lanthanide species. The solution was placed on the Ln2 resin in neutralised nitric acid. The column was then washed with 50ml of deionised water, 50ml of 0.25M HCl and the 50ml of 1M HCl. All eluates were analysed for lanthanide concentration and the recovery determined. Results are shown in Table 4.12.

Table 4.12 Separation of lanthanides using optimised elution data

	% Recovery using Elution Media – solution			
Lanthanide	**Loading solution**	**0.25M HCl**	**1M HCl**	**conc. HCl**
Ho	0.76	0.21	94.6	1.3
Sm	89.9	7.1	0.2	2.6
Eu	0.02	99.68	0.01	0.24
Gd	0.04	99.47	0.01	0.16

Experimental data shows that Eichrom Ln2 resin can be used to separate lanthanides from each other. These experiments were carried out using pure solutions, however, it is known that the efficiency of the resins can be significantly affected by other ions present in the loading solution. Consequently it was necessary to determine the separation characteristics using a sample that was similar in chemical content to that of solubilised concrete. Synthetic concrete solutions containing the lanthanides were used to determine the effect of Ca^{2+}, Bi^{3+} and Fe^{3+} on the efficiency of separation.

10ml of synthetic concrete solution (equivalent to 3g of concrete), were added to 30ml of deionised water. The mixed lanthanide solution was added and the solution neutralised. The sample was loaded on to the resin. The lanthanides were then eluted off using the same elution media as detailed in previous experiments. Results are shown in Table 4.13

Table 4.13 Effect of synthetic concrete solution of Ln2 resin

	% Recovery using Elution Media – synthetic concrete			
Lanthanide	**Loading solution**	**0.25M HCl**	**1M HCl**	**Conc. HCl**
Ho	68.7	28.6	0.01	0.01
Sm	95.8	0	0.01	0.01
Eu	58.9	40.7	0.01	0.01
Gd	56.8	39.2	0.01	0.01

From the table it can be seen that the resin, in the presence of the synthetic concrete solution does not retain the lanthanides. The binding sites on the resin are probably taken by the Ca^{2+}, Bi^{3+} and Fe^{3+} ions, consequently it will be necessary to remove these ions from solution before loading the solution on to the resin. Methods to remove the calcium and iron from the sample were investigated. However, it was necessary to determine if the proposed clean-up strategies would affect the lanthanide recoveries, *i.e.* any decontamination procedure must be selective for the contamination ion and must not strip any of the lanthanide from solution.

4.4.5 Separation utilising selective precipitation

Precipitation schemes have been used extensively to separate analytes from solution. Generally these schemes involve the formation of a precipitate and the analyte is either brought down, or if at low concentration, it is co-precipitated along with the bulk precipitant. Co-precipitation schemes have been used throughout analytical chemistry, it is in this way that the first actinide separation schemes were developed. Generally the bulk precipitant is usually calcium. However, since it is anticipated that further isolation schemes may be intolerant to Ca it is necessary to investigate other precipitation systems.

4.4.5.1 Bismuth phosphate

The level of bismuth found within the concrete is not constant. Consequently the levels within each sample will vary considerably and will depend upon the characteristics of the quarrying site. Bismuth phosphate precipitations are attractive since the bismuth and phosphate are inherently present in the concrete. However, the efficiency of the lanthanide specific resins is impaired for those samples that contain appreciable amounts of Bi^{2+}. As with calcium, it is found that the Bi^{2+} occupies the Ln specific sites on the resin. Consequently either the lanthanide will be eluted off the resin via displacement, or may not become bound due to the competition between the limited Ln^{3+} ions and the significant quantity of Bi^{2+} ions. Bismuth phosphate is insoluble in neutral/alkali solutions, consequently the bismuth is precipitated from solution by adjusting the pH using alkali solution.

$$Bi.^{3+} + PO_4^{3-} \rightarrow BiPO_4\downarrow$$

To a set of beakers, bismuth nitrate was added to 0.1M nitric acid along with 10ml of 1M calcium nitrate. To the samples radiolabelled lanthanide (^{152}Eu,^{148}Gd, Ho or Sm) and orthophosphoric acid were added. The $BiPO_4$ precipitate was formed by adjusting the pH to ~ 5 using ammonia gas and ammonia solution. The samples were filtered under suction through a 0.45μm membrane. An aliquot of the filtrate was analysed. The precipitate was dried, weighed and the yield determined. The yield of the precipitate in all cases was in excess of 95%. The precipitate was then dissolved in 3ml of 6M hydrochloric acid and the lanthanide concentration/activity determined. From Table 4.14 it can be seen that the bismuth phosphate did not quantitatively co-precipitate the lanthanide present in the sample.

Table 4.14 Association of lanthanide with bismuth phosphate precipitate

	% Lanthanide associated with precipitate			
Sample	^{152}Eu	^{148}Gd	Ho	Sm
1	9.86	7.93	3.28	6.33
2	9.16	8.52	4.09	5.98
3	8.63	7.38	4.59	6.29
4	7.65	6.24	4.82	6.14
Synthetic Concrete 1	6.88	5.72	4.94	5.81
Synthetic Concrete 2	7.14	7.64	5.06	6.72

Consequently it was necessary to investigate other co-precipitation schemes.

4.4.5.2 Calcium oxalate precipitate

To a set of beakers 10ml of 1M calcium chloride were added to25ml of 6M HCl. To the solution the lanthanide was added. The calcium oxalate was then precipitated using ammonium oxalate solution.

$$Ca^{2+} + C_2O_4^{2-} + H_2O \rightarrow CaC_2O_4.H_2O\downarrow$$

The system was neutralised using dilute ammonia. The samples were filtered under suction through a 0.45μm membrane. The precipitate was transferred to a petri dish and dried for 3 hours at 110°C and the yield determined. An aliquot of the filtrate was analysed. The precipitate was dissolved in 5ml of 3M nitric acid and the lanthanide concentration determined. Analysis indicated that over 97% of the oxalate had been precipitated. Although the recovery of the lanthanide was typically >70%, it was not quantitative. The results are shown in Table 4.14. Use of synthetic

concrete solutions indicated that Fe^{3+} was associated with the precipitate. This led to a decreased counting efficiency in the ^{148}Gd sample because of the intensive coloration of the counting sample which resulted in considerable colour quenching. The results are shown in Table 4.15. Generally the precipitate formed was ~ 1.1g, due to the addition of $1x10^{-2}$ moles of Ca. The solution corresponds to a concrete weight of ~1.0g, therefore for larger quantities of concrete, the mass of $CaC_2O_4.2H_2O$ formed would increase. Since many of the lanthanides will be associated with this precipitate, it will be necessary to separate the lanthanides further. This may be achieved by using the Eichrom Lanthanide specific resin, however each column can only tolerate ~100mg of calcium. Therefore a limitation of 0.7g of concrete could be analysed. For low level waste it may be necessary to take a larger sample size, consequently further precipitation protocols were investigated.

Table 4.15 Association of lanthanide with calcium oxalate precipitate

	% Lanthanide associated with precipitate			
Sample	^{152}Eu	^{148}Gd	Ho	Sm
1	72.6	76.1	81.3	74.3
2	78.1	83.8	77.9	77.4
3	74.7	77.6	69.5	72.6
4	81.6	82.7	76.1	79.7
Synthetic Concrete 1	77.4	78.6	74.3	74.6
Synthetic Concrete 2	73.2	79.8	78.4	72.7

4.4.5.3 Calcium phosphate precipitate

To a set of beakers 10ml of 1M calcium nitrate solution were added to 25ml of 0.1M nitric acid. To the solution 5ml of orthophosphoric acid and the lanthanide were added. The pH of the samples were adjusted to pH6.5 using ammonia and dilute ammonia solution.

$$Ca^{2+} + H_2PO_4^- + 2H_2O \rightarrow CaHPO_4.2H_2O_{\downarrow} + H^+$$

The samples were filtered through a 0.45μm membrane. The precipitate was transferred to a petri dish, dried to constant weight and the yield determined. The precipitate was dissolved in 3ml of 0.1M nitric acid and the lanthanide association determined. Analysis of the precipitates indicated that over 95% of the lanthanide

was associated with the calcium phosphate precipitate. The yield of the precipitate was > 98% for all samples. The results are shown in Table 4.16.

Table 4.16 Association of lanthanide with calcium phosphate precipitate

	% Lanthanide associated with precipitate			
Sample	^{152}Eu	^{148}Gd	Ho	Sm
1	98.6	95.7	96.1	94.6
2	97.3	98.2	97.5	97.6
3	98.1	98.6	93.4	96.9
4	94.6	97.4	94.8	92.7
Synthetic Concrete 1	92.8	94.8	89.4	95.7
Synthetic Concrete 2	93.7	97.5	92.7	92.6

Although the results indicated that calcium phosphate could be used to precipitate the lanthanide, the amount of calcium contained within the precipitate was still too high for loading on to Eichrom resins. Observation of the synthetic concrete solutions indicated that significant amounts of Fe^{3+} were associated with the precipitate.

It was necessary to investigate methods to reduce the amount of precipitate formed, enabling the sample to be loaded on to the Eichrom Resin. Consequently, further experimental parameters were investigated, including the effect of [Ca] on lanthanide co-precipitation. During these experiments the [Ca] was varied whilst the total volume, [H_3PO_4] and [Ln] were kept constant. All samples were taken to pH 6.5. The precipitate was treated as previously described. The results are shown in Table 4.17.

Table 4.17 Effect of [Ca^{2+}] on lanthanide co-precipitation

[Ca^{2+}]	Volume ml	Moles	Precipitate wt (mg)	Yield (%)	Lanthanide	% Ln co-pptd
1M	0.1	0.0001	None	0	Eu	0
1M	0.5	0.005	66	76.7	Eu	88.7
1M	1	0.001	168	97.7	Eu	94.2
1M	2	0.002	334	97.1	Eu	97.6
1M	4	0.004	679	98.7	Eu	92.7
1M	6	0.006	1027	99.5	Eu	94.3
1M	8	0.008	1374	99.9	Eu	96.8
1M	10	0.01	1699	98.8	Eu	95.7
1M	0.1	0.0001	None	95.9	Gd	0
1M	0.5	0.005	71	82.5	Gd	78.5
1M	1	0.001	165	95.9	Gd	96.8
1M	2	0.002	329	95.6	Gd	94.7
1M	4	0.004	682	99.1	Gd	95.9
1M	6	0.006	1036	100.4	Gd	96.1
1M	8	0.008	1382	100.4	Gd	94.9
1M	10	0.01	1687	98.1	Gd	94.4
1M	0.1	0.0001	4	23	Sm	6
1M	0.5	0.005	69	80.2	Sm	85.6
1M	1	0.001	166	96.5	Sm	96.5
1M	2	0.002	333	96.8	Sm	93.7
1M	4	0.004	675	98.1	Sm	97.4
1M	6	0.006	1029	99.7	Sm	95.5
1M	8	0.008	1380	100.3	Sm	92.8
1M	10	0.01	1710	99.4	Sm	94.5
1M	0.1	0.0001	None	0	Ho	6
1M	0.5	0.005	55	63.9	Ho	78.6
1M	1	0.001	167	97.1	Ho	98.4
1M	2	0.002	338	98.2	Ho	94.5
1M	4	0.004	671	97.5	Ho	98.3
1M	6	0.006	1029	99.7	Ho	97.0
1M	8	0.008	1386	100.7	Ho	99.3
1M	10	0.01	1674	97.3	Ho	97.8

From the table it can be seen that the lanthanide is removed from the solution in a quantitative manner. The rate of removal is independent of precipitate yield. However, at very low [Ca] there is virtually no precipitate formed. This is possibly because the solubility limitation has not been exceeded. At low concentrations the phosphate yield is poor and this may be due to transfer losses during precipitate manipulations. The correlation between phosphate yield and % Ln association is also erratic at low [Ca], which may be because there is not enough carrier precipitate to bring down all of the lanthanide. However, since the amount of Ca in the sample will be determined by the amount of concrete taken for analysis, it is impossible to limit the [Ca] without limiting the sample size. Consequently it is necessary to investigate ways in which the amount of precipitate may be controlled. During the experiments it was observed that a precipitate was formed at relatively low pH (~ pH4). Consequently, the affinity of the lanthanide with the precipitate formed at low pHs were investigated.

4.4.5.4 Partial calcium phosphate precipitation

To a set of beakers 10ml of 1M calcium nitrate solution were added (equivalent to 3g of concrete) to 25ml of 0.1M nitric acid. To the sample orthophosphoric was added. To the sample 100Bq of ^{45}Ca was added. The pH of the sample was adjusted using dilute ammonia solution. At a specified pH the sample was filtered through a 0.45μm membrane and the precipitate yield determined as has been previously detailed. The activity associated with each fraction was determined by counting the sample by LSC. The precipitate yield associated with the pH of the solution is shown in Table 4.18 and illustrated in Figure 4.6.

Table 4.18 Effect of pH on $CaHPO_4.2H_2O$ yield

pH	% Yield
1.987	0
2.498	0.1
3.004	1.8
3.503	12.6
3.995	39.4
4.496	46.0
5.016	64.9
5.504	72.1
5.993	85.8
6.489	96.7
7.004	98.8
7.511	99.5
8.012	99.7

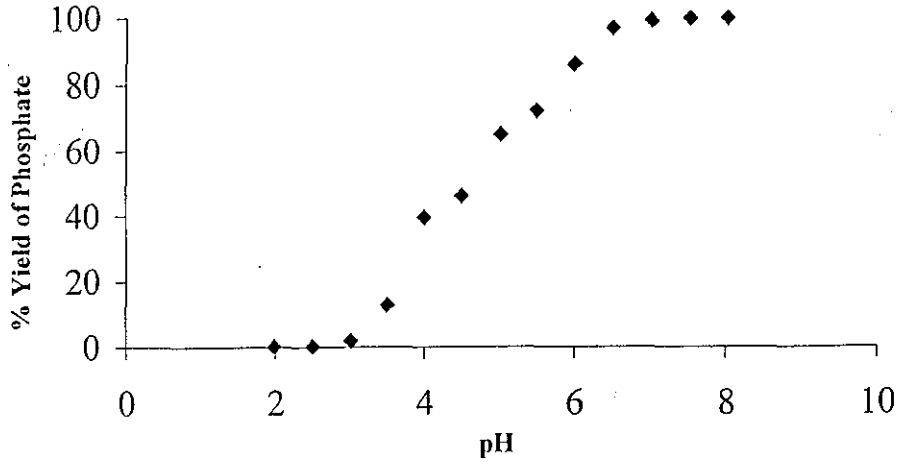


Figure 4.6 Effect of pH on calcium phosphate yield

From the experiments it was found that by carefully controlling the pH, the weight of calcium phosphate precipitate could be restricted. As it was possible to control the rate of precipitation, it would be possible to ensure the formation of the amount of precipitate that could be tolerated by the ion-chromatography resin. It was then necessary to determine if this partial calcium phosphate precipitation step would

affect the degree of lanthanide association with the precipitate. Consequently experiments were set up to investigate the effect of pH control on the affinity of the lanthanide with the precipitate.

10ml of 1M calcium nitrate were added to 40ml of 0.1M nitric acid. To the solution the lanthanide and orthophosphoric acid were added and the solution mixed to ensure thorough dispersion. The pH of the solutions were adjusted to the required value using ammonia and dilute ammonia solution. The samples were filtered and the filtrate and precipitate retained for analysis. The precipitate being transferred to a petri dish and dried to constant weight at 110°C. Once the mass had been noted and the yield determined, the precipitate was dissolved in the minimum 1M HNO_3 (<5ml) and the lanthanide activity/concentration determined. It had been observed that when using synthetic concrete solutions the resulting precipitant was off-white. This discoloration was due to Fe^{3+} contamination. All concrete samples will contain moderate quantities of iron, however the resin has a tolerance limit to this species. Therefore it is necessary to ensure that the sample is reasonably clean prior to column loading. Consequently the association of the Fe^{3+} ion with the calcium phosphate precipitate was also investigated as a possible clean-up stage. The iron was determined spectrometrically using the thio-cyanate method [6]. The results are shown in Table 4.19.

The results indicated that a stage was reached whereby the precipitation of the lanthanide plateaus even when the yield of phosphate precipitate was still increasing. This is illustrated for each lanthanide and iron, in Figures 4.7 through to Figure 4.11. It should be noted that the shape of the graph and relationship between the analyte and the calcium precipitate is similar for the lanthanides, whereas the shape of the graph for the phosphate/Fe system is very different. The shape of the graphs indicate that the solubility of the lanthanide complex is less than the calcium phosphate and hence the observed enhanced rate of Ln^{3+} removal. Conversely, the Fe complex is more soluble than the calcium phosphate and therefore the Fe is more likely to remain in solution under conditions where the Ln^{3+} is co-precipitated.

Table 4.19 Effect of pH on lanthanide association with $CaHPO_4.2H_2O$

$[Ca^{2+}]$	Volume ml	pH	Precipitate wt (mg)	Ppt yield (%)	Lanthanide	% Co-pptd
1M	10	1.003	None	0	Eu	0
1M	10	1.504	None	0	Eu	0
1M	10	2.011	21	1.2	Eu	29.7
1M	10	2.508	59	3.4	Eu	60.8
1M	10	3.002	124	7.2	Eu	79.7
1M	10	3.498	280	16.3	Eu	86.7
1M	10	3.995	650	37.8	Eu	97.1
1M	10	4.512	1120	64.9	Eu	97.6
1M	10	5.016	2280	75.4	Eu	96.4
1M	10	1.014	None	0	Gd	0
1M	10	1.499	None	0	Gd	0
1M	10	2.006	14	0.8	Gd	4.8
1M	10	2.497	50	2.9	Gd	33.7
1M	10	2.989	117	6.8	Gd	65.4
1M	10	3.513	334	19.4	Gd	96.2
1M	10	4.007	719	41.8	Gd	98.1
1M	10	4.501	1096	63.7	Gd	98.9
1M	10	5.000	1391	80.9	Gd	99.4
1M	10	1.004	None	0	Sm	0
1M	10	1.492	None	0	Sm	0
1M	10	2.004	None	0	Sm	0
1M	10	2.500	24	1.4	Sm	0.9
1M	10	3.012	79	4.6	Sm	16.8
1M	10	3.510	246	14.3	Sm	49.8
1M	10	4.005	645	37.5	Sm	79.1
1M	10	4.492	1025	59.6	Sm	98.6
1M	10	5.010	1240	72.1	Sm	99.0
1M	10	0.996	None	0	Ho	0
1M	10	1.505	None	0	Ho	0
1M	10	2.008	9	0.5	Ho	7.1
1M	10	2.497	31	1.8	Ho	18.2
1M	10	3.002	115	6.7	Ho	42.6
1M	10	3.510	310	18.0	Ho	62.7
1M	10	4.004	795	46.2	Ho	93.1
1M	10	4.488	1085	63.1	Ho	95.7
1M	10	4.997	1486	86.4	Ho	99.6
1M	10	1.000	None	0	Fe	0
1M	10	1.496	None	0	Fe	0
1M	10	1.997	None	0	Fe	0
1M	10	2.504	18	1.1	Fe	0
1M	10	3.013	162	9.4	Fe	0.5
1M	10	3.508	390	22.7	Fe	0.6
1M	10	4.002	754	43.8	Fe	0.4
1M	10	4.505	1041	60.5	Fe	42
1M	10	5.009	1266	73.6	Fe	78

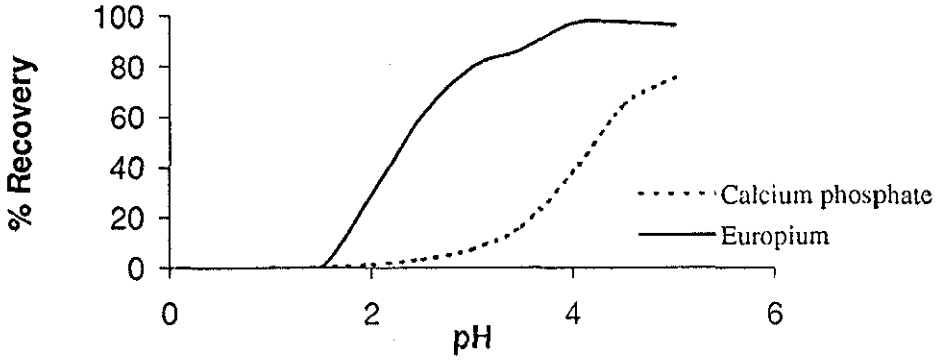


Figure 4.7 % Recovery of Eu with $CaHPO_4.2H_2O$ at different pH's.

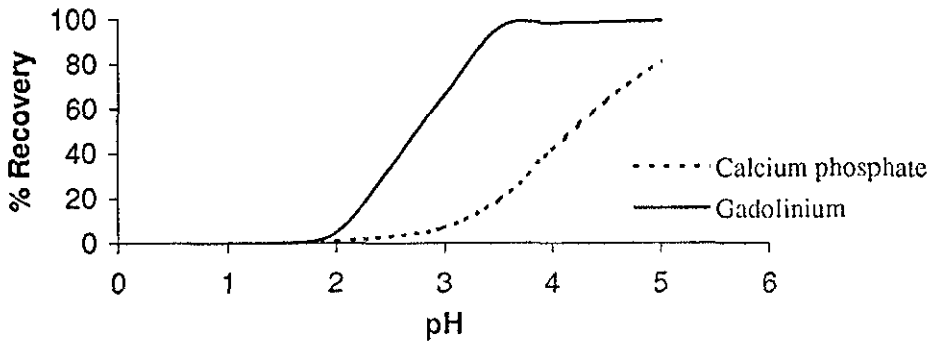


Figure 4.8 % Recovery of Gd with $CaHPO_4.2H_2O$ at different pH's

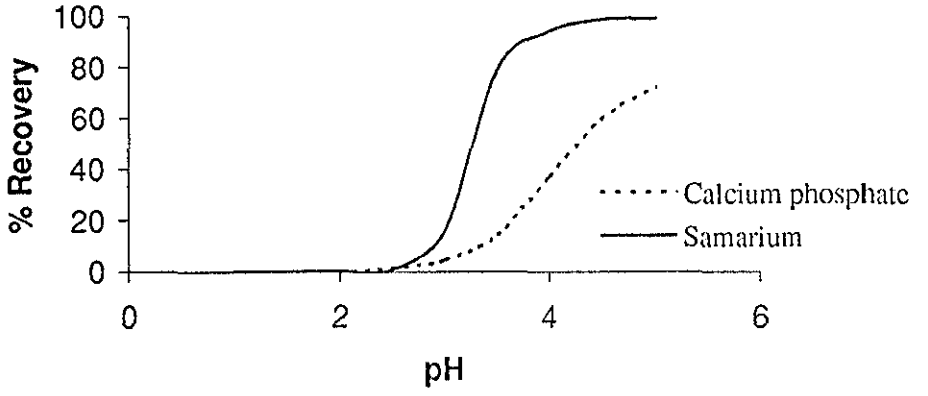


Figure 4.9 % Recovery of Sm with $CaHPO_4.2H_2O$ at different pH's

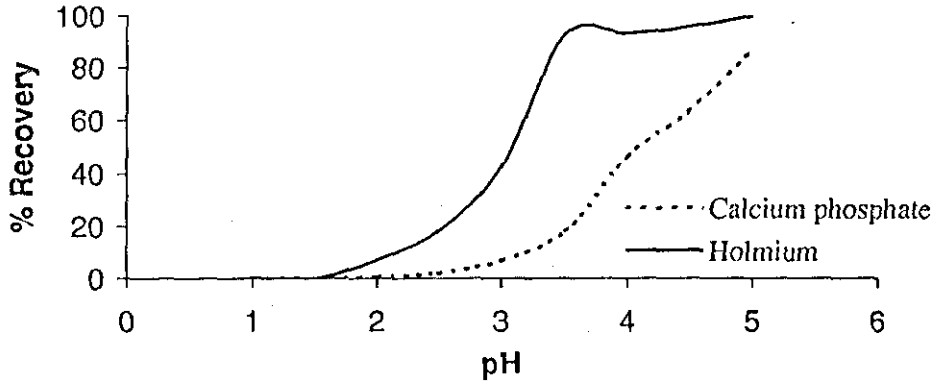


Figure 4.10 % Recovery of Ho with $CaHPO_4.2H_2O$ at different pH's

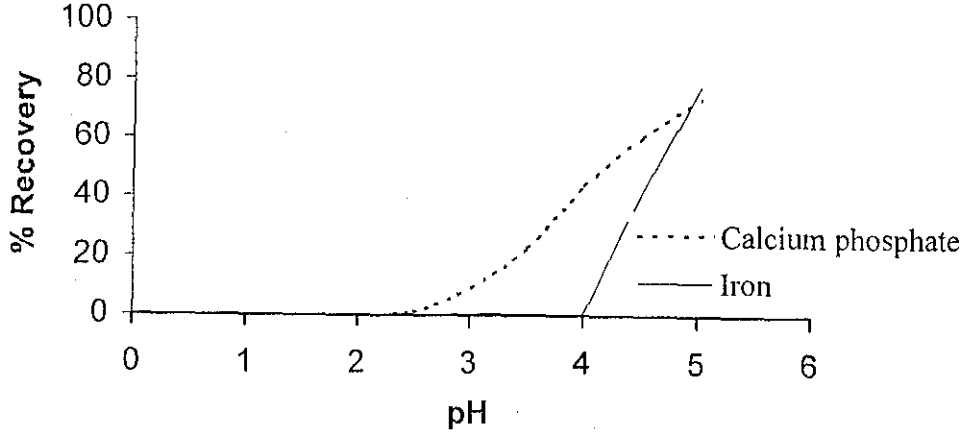


Figure 4.11 % Recovery of Fe with $CaHPO_4.2H_2O$ at different pH's

From the experiments it was found that partial precipitation of the calcium phosphate could be used to remove lanthanides quantitatively from solution. However, there were two factors to consider, firstly the analysis required high lanthanide recoveries, and secondly that the Ca^{2+} concentration must be minimal. From the table it can be seen that it is impossible to adhere to both of these criteria. To obtain a high Ln yield it is necessary to precipitate the maximum solid, whereas to ensure a high Ln separation it is necessary to ensure minimum Ca interference. Consequently a compromise between Ln yield and mass of precipitate must be reached.

Experimental results indicate that the lanthanide should be precipitated from solution at a pH <4. At this point the lanthanide recovery is typically >85%, the calcium phosphate recovery is limited and the Fe recovery is minimal.

During the experiments it was found that on addition of ammonia the pH increased. However there was a point at which the addition of a further drop caused the pH to drop rapidly. This pH drop was significant and required ~30 minutes before the pH stabilised. It was also observed that at this point the rate of precipitation increased, this was evident by the rapid increase in turbidity of the sample. With each sample the point at which this phenomena occurred was different. Consequently this point was not reached by taking the set of samples to a particular pH, but instead was achieved by adding ammonia dropwise, and continuing until a significant pH drop (as opposed to pH fluctuation) was observed. These experiments also indicated that at lower pH values, the precipitate formed, quantitatively removed the lanthanide from solution whilst the majority of Fe^{3+} remained in solution. Consequently this step not only significantly reduces the sample bulk but also selectively removes the analyte of interest from solution and leaves other contaminants such as Fe^{3+} and Cs^{+} in the solution phase. The partial phosphate precipitation scheme was repeated. However the pH was adjusted to the point at which 1 further drop of ammonia caused the pH to drop ~ 0.5pH units.

To a series of beakers 10ml of 1M calcium nitrate and 0.1ml of 1M iron chloride were added to 40ml of 0.1M nitric acid. The lanthanide and phosphoric acid were added and the pH adjusted until the addition of 1 further drop led to a significant decrease in the sample pH. The point at which this pH decrease occurred was noted. The samples were left to stand until the pH had stabilised. The point at which the pH stabilised was also recorded. The samples were then filtered and the precipitate dried to constant mass. Both the aqueous fraction and the dissolved precipitate were then analysed for lanthanide and iron content. The results are shown in Table 4.20.

Table 4.20 Spontaneous pH reduction: effect on lanthanide co-precipitation

$[Ca^{2+}]$	Volume ml	Initial pH	Stabilised pH	Lanthanide	Wt of Ca ppt (mg)	Ppt yield (%)	% Ln co-pptd
1M	10	2.80	2.333	Eu	172	10	89.6
1M	10	2.891	2.528	Eu	241	14	95.1
1M	10	3.220	2.889	Eu	189	11	94.8
1M	10	2.30	1.683	Gd	120	7	92.2
1M	10	2.41	2.104	Gd	155	9	89.6
1M	10	2.54	1.883	Gd	155	9	101
1M	10	3.82	2.971	Sm	241	14	92.7
1M	10	3.24	2.776	Sm	155	9	102
1M	10	3.89	2.844	Sm	224	13	96.1
1M	10	3.218	2.779	Ho	206	12	98.0
1M	10	3.894	3.184	Ho	206	12	95.2
1M	10	2.843	2.492	Ho	172	10	91.8
1M	0.1	3.064	2.483	Fe	224	13	8.6
1M	0.1	2.782	2.138	Fe	172	10	4.7
1M	0.1	3.187	2.761	Fe	241	14	6.9

4.6 Removal of iron contamination

From the experiments it was evident that very little Fe^{3+} was associated with the precipitate. However, if further separation is to be carried out using Eichrom resin it is necessary to ensure that the sample is virtually iron free. Consequently, a further clean-up stage involving the removal of iron was investigated. This stage will be important for those matrices that contain significant amounts of iron, including reinforced concrete and steel samples.

4.6.1 Solvent extraction

Many organic solvents have been used to extract Fe from solution. Extractants include iso-propyl alcohol [6], diethyl ether [6] and iso-butyl acetate [6]. In this work iso-butyl acetate was investigated since it has a low volatility and insignificant temperature rise during extraction. The flash point of iso-butyl acetate is also more convenient than that of diethyl ether (17°C *c.f.* –45°C).

From the synthetic concrete data, it is known that concrete will contain approximately 5-10mg Fe g^{-1}. Therefore experiments using 20-100mg of concrete were investigated. If the sample is analysed in a sequential manner, the Fe should be in the Fe^{3+} state. However, since these extraction schemes rely on speciation of the ion, the use of an oxidising agent was considered.

To 25ml 6M HCl, iron were added (20-100mg of Fe^{2+}, Fe^{3+} or Fe^{2+}+Fe^{3+}). To the sample 5ml of hydrogen peroxide were added and the samples heated. Once the peroxide had fully broken down, the samples were cooled and 10ml of iso-butyl acetate added. The samples were then shaken vigorously for 10 minutes. The organic/aqueous layer separated on standing for 5 minutes. The organic extraction was repeated twice more using 10ml of iso-butyl acetate. The organic fractions were then combined and the Fe back extracted into water. The Fe concentration was then determined by the thiocyanate method [6]. For comparison, the experiments were also carried out without using an oxidising agent. It was found that the Fe^{3+} was

extracted into the organic layer, which was evident by the resulting colour change of the organic phase from clear, to yellow. No colour changes were observed in the Fe^{2+} system. Results are shown in Table 4.21.

Table 4.21 Fe extraction using iso-butyl acetate

Sample	Oxidised	% Fe		
		Aqueous	Organic	Back extractant
Fe^{2+}	No	91	7	0
Fe^{3+}	No	4	6	89
Fe^{2+} + Fe^{3+}	No	48	7	43
Fe^{2+}	Yes	5	4	90
Fe^{3+}	Yes	4	6	88
Fe^{2+} + Fe^{3+}	Yes	4	7	86

From the Table it can be seen that iso-butyl acetate quantitatively removed Fe^{3+} from solution, however Fe^{2+} was not extracted. A suitable oxidising agent is hydrogen peroxide, the major advantage being that the reaction product is water. Although the extraction rate of Fe is dependant upon acid concentration, a few ml of water in 25ml 6M HCl will not affect the concentration significantly, and extraction will remain at a maximum. During the experiments the samples were shaken for 15 minutes, however it was necessary to determine the extraction rate of Fe^{3+} in iso-butyl acetate.

To 25ml of 6M HCl 20mg of Fe^{3+} were added. The samples were then shaken with iso-butyl acetate for varying lengths of time. The organic layer was removed from the samples and back extracted into water. The Fe concentration was then determined in the back extractant media using the thiocyanate method. The results are shown in Figure 4.12.

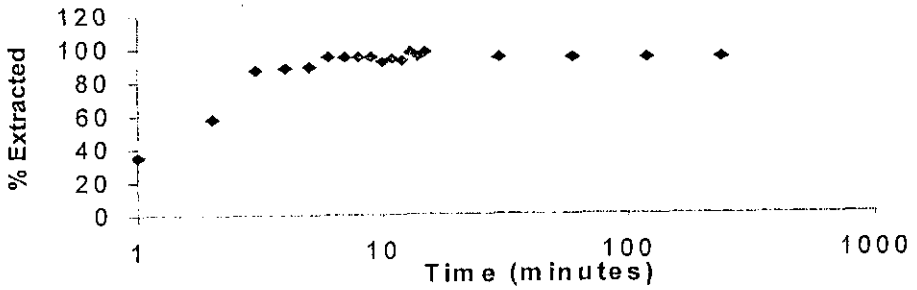


Figure 4.12 Effect of extraction time on Fe recovery

The results suggest that the Fe is extracted at a rapid rate from solution. The extraction agent iso-butyl acetate is not wholly selective for Fe^{3+}. Therefore, it was necessary to determine if this extractant also removed lanthanides from solution.

To 25ml 6M HCl, 20mg of Fe^{3+} and lanthanide were added. The Fe was then extracted into iso-butyl acetate (3× 10ml). The organic fractions were combined and washed using 3× 10ml deionised water. An aliquot of each fraction was then analysed for Fe^{3+} and Ln^{3+} using the thiocyanate method [6], ICP and radiometric methods. The results are shown in Table 4.22.

Table 4.22 Ln^{3+} extraction into iso-butyl acetate

	% Fe^{3+}			% Ln^{3+}		
	Aqueous	Organic	Back Wash	Aqueous	Organic	Back Wash
Eu-Fe	4	7	87	97	0	0
Gd-Fe	6	3	90	94	1	0
Sm-Fe	3	3	92	96	0	0
Ho-Fe	4	5	89	95	0	0

From the table it can be seen that iso-butyl acetate does not extract the lanthanide from solution, consequently this procedure can be used to remove iron contamination from samples during the lanthanide analysis without adversely affecting the separation.

4.7 Determination of ^{151}Sm and ^{166m}Ho in concrete

4.7.1 Single Element determination

The analytical methodology has been created in such a manner that the analyte of interest can be determined solely or sequentially from the sample matrix. This type of adopted procedure reduces hazardous waste, reduces analysis time, reduces the sample size required and consequently reduces the potential dose to the analyst. However, it is necessary to ensure that each of the analytical processes can be used independently. To a beaker, concrete containing a combination of lanthanides was added. The sample was then leached in sodium hydroxide for 1 hour. The sample was neutralised using nitric acid and digested for 3 hours. The sample was then

filtered and the aqueous fraction dried down and solids discarded. After drying the precipitate was taken up in 6M HCl. When cool, the sample was shaken with iso butyl acetate three times. The organic fraction was discarded and the aqueous fraction dried down. The sample was taken up in 0.1M nitric acid and orthophosphoric acid added. To the sample ammonia was added until pH 2, and then dilute ammonia was added carefully until a pH drop was observed. The sample was left to settle and filtered. The precipitate was dissolved in 50ml of 0.01M hydrochloric acid and loaded on to the Eichrom Ln2 column, which had been pre-conditioned using deionised water. After the sample had been loaded on to the resin, the column was washed using 25ml of 0.1M HCl. This wash was combined with the loading eluant. The column was washed with 50ml of 0.25M HCl , 50ml 1M HCl and 25ml of concentrated HCl. All eluants were collected. Each eluant was then dried down and taken up in either minimum acid (Eu and Gd – radiometric determination) or in 2% nitric acid for ICP determination. The concentration of each lanthanide was determined and the recovery calculated. Results are shown in Table 4.23.

Table 4.23 Lanthanide determination in concrete – radiologically pure

	% Lanthanide Recovery			
Concrete (g)	**Ho**	**Sm**	**Eu**	**Gd**
0.5	88.7	92.6	89.7	90.1
1	82.1	92.1	87.6	86.7
2	90.4	89.3	93.2	92.8
3	85.4	81.6	78.4	75.4
4	80.6	75.9	72.6	71.9
5	73.8	77.6	61.4	63.8

From the table it can be seen that good recoveries were achieved for the concrete samples. As the mass of sample increases a slight downward trend in the lanthanide recovery is observed, however, the recovery is still greater than 60%. It should be noted that the Eu and Gd behave very similarly throughout the analysis.

4.7.1.1 Determination of ^{151}Sm and ^{166m}Ho in concrete contaminated with activation and fission products

To a round bottomed flask concrete containing 1000ppm Sm, Ho, ^{137}Cs, ^{152}Eu, ^{148}Gd, ^{36}Cl, ^{125}I and ^{99}Tc was added. To the sample 6M NaOH was added and the sample

digested for 1 hour. To the sample nitric acid was added, to bring the H^+ concentration to 3M. After the sample had been digested for three hours, the sample was filtered. The solid material was discarded and the aqueous sample dried down. The sample was taken up in 6M HCl and the Fe^{3+} extracted into iso-butyl acetate. The aqueous fraction was dried down and taken up in 0.1M nitric acid. To the sample orthophosphoric acid was added and the pH was adjusted to the point at which the pH decreased on the addition of 1 drop of dilute ammonia solution. The precipitate was filtered and dissolved in 50ml 0.01M hydrochloric acid. The sample was loaded on to the Ln2 Resin and washed with 25ml of 0.1M HCl. Both eluants were combined. The column was washed with 0.25M HCl, 1M HCl and conc. HCl. All eluants were collected and placed on the hotplate to dry down. The residues were dissolved in a suitable media and the lanthanide concentration determined. The results are shown in Table 4.24.

Table 4.24 Lanthanide determination in concrete – radiologically contaminated

	% Lanthanide Recovery			
Concrete (g)	Ho	Sm	Eu	Gd
0.5	85.8	89.3	86.7	88.4
1	92.1	87.0	82.9	84.5
2	89.4	92.6	85.7	84.1
3	87.6	88.4	88.7	85.4
4	79.8	81.7	76.5	78.3
5	75.7	86.3	72.7	73.2

From the table it can be seen that the contamination radio-isotopes had very little effect on the recovery of the lanthanides. The recovery of each of the lanthanides is still very high with at least 70% of the analyte being recovered. As before the similar chemistry of Gd and Eu is evident.

4.7.2 Multiple Element determination

To determine if the lanthanides could be analysed in the sequential system, it was necessary to take a contaminated concrete sample and run it through the whole analytical procedure for the determination of ^{36}Cl, ^{125}I, ^{99}Tc and ^{151}Sm and ^{166m}Ho. However, ^{137}Cs is a major fission product and to reflect this, the matrix to be analysed contained ~ 100Bq g^{-1} of ^{137}Cs.

To a round bottomed flask the contaminated concrete was added. To the concrete chloride and iodide carriers were added. The apparatus was arranged for partial vacuum digestion as shown previously in Figure 2.1 using 1M NaOH in the gas traps. The sample was alkali digested using 6M NaOH for 1 hour at 80°C. After the initial digestion, concentrated nitric acid was added until the final acid concentration of the reaction system was 3M, the system temperature was maintained at 80°C throughout the halide analysis. Collection of the evolved iodine continued for 3 hours. The solution from the traps was transferred to a beaker and fresh hydroxide was placed in the gas collection vessel. The apparatus was re-connected and to the reaction vessel and 25ml of 2% $KMnO_4$ were added. The evolved chlorine was trapped in the alkali solution. After 3 hours further digestion the apparatus was disconnected. The hydroxide solution was transferred to a beaker for chloride analysis.

Stage 1

The contents of the reaction vessel were filtered and the solids discarded. The aqueous solution was dried down and then taken up into 0.1M nitric acid. To the sample orthophosphoric acid was added and the calcium phosphate precipitated using dilute ammonia. Initially the pH was taken to ~5. The sample was filtered and both the aqueous and solid fraction retained for analysis. The aqueous phase was dried gently at 60°C. The sample was dissolved in 1M HCl and loaded on to a pre-conditioned (1M HCl) Dowex anion exchange column. The column was washed using 5X10ml aliquots of 1M HCl solution. Tc was eluted using 30ml of concentrated nitric acid. The eluate was dried and washed using 3X2ml aliquots of deionised water. The sample was dissolved in 10ml of 2M sulphuric acid and extracted into 5% TnOA in xylene. The samples were shaken for 5 minutes and left to settle for 5 minutes. The organic extraction being repeated several times. The organic fractions were combined, mixed with scintillation cocktail and the ^{99}Tc content determined by LSC.

Stage 2

The iodate fraction was reduced to iodide using hydrazine and the chlorate by sodium nitrite. To the halide solutions silver nitrate was added. The precipitate filtered, dried and the recovery determined. The AgCl was dissolved in ammonia, mixed with cocktail scintillant and the activity determined by LSC. The AgI activity was determined by γ spectrometry.

Stage 3

The calcium phosphate precipitate was re-dissolved in 6M HCl and the Fe^{3+} extracted into iso-butyl acetate. The organic fraction was discarded and the aqueous fraction placed on the hotplate to dry down. The residues were dissolved in 0.1M nitric acid and the pH adjusted to 2 using ammonia. To the sample, ammonia was added until 1 further drop caused a significant drop in the pH of the solution (>0.5pH units). This was accompanied by an increase in the turbidity of the sample. The sample was filtered and the precipitate retained for analysis. The precipitate was dissolved in 0.01M HCl and loaded on to the Eichrom Ln2 column. The column was washed with 25ml of 0.1M HCl, 50ml 0.25M HCl and 50ml 1M HCl. All eluant fractions were dried down and the lanthanide concentration determined. Results from the analysis are shown in Table 4.25.

From the table it can be seen that the elements selected can be separated from each other with relatively high recoveries. Even though the sample contains large amounts of iron and calcium analytical method removes these contaminants prior to final separation. It should also be noted that ^{137}Cs did not interfere with the separation and quantification of any of the analytes of interest.

Table 4.25 % Recoveries for stated species in contaminated concrete

Analytical Process	Species									
	^{125}I	^{36}Cl	^{137}Cs	^{99}Tc	Ca	Fe	Sm	Eu	Gd	Ho
I_2 Evolution	91.0	0	0	0	0	0	0	0	0	0
Cl_2 Evolution	0	87.6	0	0	0	0	0	0	0	0
Full $CaHPO_4.2H_2O$ precipitation (aq)	0	0	88	98	2	16	1	0	0	0
Anion Exchange	0	0	0	93	0	2	0	0	0	0
Solvent Extraction – TnOA	0	0	0	86	0	1	0	0	0	0
Full $CaHPO_4.2H_2O$ precipitation (ppt)	0	0	10	2	97	80	97	99	98	94
Partial $CaHPO_4.2H_2O$ precipitation	0	0	0	0	12	5	94	97	95	91
Solvent Extraction – IBA	0	0	0	0	0	4	0	0	0	0
Ion chromatography – Loading Solution	0	0	0	0	2	0	81	0	0	0
Ion chromatography – 0.1M HCl	0	0	0	0	0	0	11	0	0	0
Ion chromatography – 0.25M HCl	0	0	0	0	0	0	0	92	94	0
Ion chromatography – 1M HCl	0	0	0	0	0	0	0	0	0	89

4.8 Suggested radiotracers for ^{151}Sm and ^{166m}Ho

Concrete samples will contain a small amount of natural samarium within the matrix, consequently it would be possible to digest the sample and take an aliquot of solution and determine the concentration of samarium in the sample. After analysis another aliquot could be taken, the concentration determined and consequently the yield of the analysis calculated. However, the general technique used in lanthanide determinations is measurement using ICP-OES and all these methodologies are intolerant to large amounts of particulate matter. Therefore this method of determination has limitations with regards to sample size. During the experimental work it was found that repeatable results were obtained for Ho and Sm when using synthetic concrete solutions, however when concrete was analysed the repeatability between identical samples was poor. This was overcome by using a high Sm and Ho (1000ppm) doped concrete.

However, true samples will not contain such high levels of either of these lanthanides, therefore it is important to consider other species that may prove useful radiotracers in the analysis of ^{151}Sm and ^{166m}Ho. If a radioactive species is used it must have a moderate half-life and a means of convenient detection. Analysis of literature data has indicated that ^{145}Sm and ^{163}Ho could be used as theoretical radiotracers.

Samarium-145 decays by electron capture, and has a half life of 340days. The photons released have a variety of energies, although the highest intensity line is the $K_{\alpha 1}$ at 38.8keV (73.8%). The relatively high electron capture energy of this isotope presents a number of possibilities in its detection. X-ray and γ spectrometers could be used, however the combined efficiency and background characteristics may lead to poor limits of detection. In X-ray counting the counting efficiency is very low (<5%), however the background noise is also very small, conversely in γ spectrometry although the counting efficiency is higher, so is the noise. Consequently since the minimum detectable activity (MDA) is proportional to the

efficiency, but inversely proportional to the background count rate it follows that these two modes of detection may have a similar detection limit. It is also possible to measure ^{145}Sm by LSC using the highest energy photon, since the energy of ^{145}Sm is different to that of ^{151}Sm (62keV *c.f.* 76keV). However, since ^{151}Sm is a pure β emitter (99.2%), and therefore has a continuum spectra, it will overlap and obscure the lower energy spectra of ^{145}Sm. Consequently it would be impossible to determine the recovery of ^{145}Sm and measure the quantity of ^{151}Sm by LSC.

Holmium-163 decays by electron capture, and has a half life of 4500years. Although a variety of photons are released, the relative intensities are very low, thus reducing the detection ability. The $K_{\alpha 1}$ at 47.6keV is the highest intensity line at 5.8%.

Consequently to determine ^{145}Sm and ^{163}Ho in the presence of β emitting species the radiotracers activity must be determined by another detection method.

Samarium-145 decays by electron capture, the decay product is ^{145}Pm, itself a product that decays by electron capture to ^{145}Nd. However the half-life of ^{145}Sm is such that further decay species should not be present to any significant extent. Holmium-163 decays by electron capture to ^{163}Dy, this species is a naturally abundant lanthanide and it would be necessary to determine how this species followed the analytical path. If it was found that Dy eluted off the column at the same time as Ho, ^{163}Ho could not be used as a radiotracer since there would be a reserve of ^{163}Dy already present in the sample

4.9 Proposed analytical scheme for the determination of ^{151}Sm and ^{166m}Ho in concrete wastes

4.9.1 Sm and Ho determination

To a beaker add the concrete and suitable tracers. Digest the concrete in alkali for 1 hour at 80°C. To the concrete slurry, add nitric acid so that the H^+ concentration is 3M. Continue to heat the sample at 80°C for a further three hours. Filter the sample

and discard the solid material. Dry down the aqueous fraction and then take up in 0.1M nitric acid. To the sample add orthophosphoric acid, adjust the pH of the sample using ammonia solution. The point at which 1 further drop of ammonia solution causes a significant decrease in the sample pH, is that point at which the sample will begin to precipitate out. Stop the addition of ammonia and leave the sample to stand for 1 hour prior to filtration. Filter the sample and discard the aqueous solution. Dissolve the precipitate in 0.01M hydrochloric acid and load on to a pre-conditioned Ln2 column. Wash the loading solution through with 0.1M HCl. Collect this fraction and combine it with the eluted loading solution. Pass 50ml of 0.25M HCl, through the column, discard this fraction. Elute the Ho from the column using 50ml of 1M HCl. Dry down all the retained eluants, take up in 2% (v/v) HNO_3 and determine the concentration of analyte and recovery of tracer.

4.9.2 Determination of Sm and Ho – Sequential analysis

To a round bottomed flask add the concrete. To the concrete add suitable carriers and radiotracers. Arrange the apparatus as shown in Figure 2.1. Add 1M NaOH to the halide traps. Digest the sample under reflux for 1 hour at 80°C in 6M NaOH. To the sample add nitric acid so that the effective H^+ concentration is 3M. Collect the iodine formed for three hours. After this time disconnect the halide trap and transfer the contents to a beaker. Fill the halide trap with fresh hydroxide and re-connect to the apparatus. Add the oxidising agent (2% $KMnO_4$) continue the reaction for a further three hours. After this time disconnect the apparatus, transfer the hydroxide trap to another beaker and analyse for chloride and iodide as detailed in Section 2.91 and 2.92. Filter the reaction vessel and discard the solids. Dry the filtrate down. Dissolve the residues in 0.1M nitric acid and add orthophosphoric acid. Precipitate all the calcium phosphate by adjusting the pH of the sample to~5 using dilute ammonia solution. Filter the sample and store both the precipitate and filtrate. The filtrate is dried gently at 60°C. Dissolve the sample in 1M HCl and load on to a pre-conditioned (1M HCl) Dowex anion exchange column. Wash the column using 5× 10ml aliquots of 1M HCl solution. Elute the Tc using 30ml of concentrated nitric acid. Transfer the eluate to the hotplate and dry down at 60°C, wash the residues 3× with deionised water to remove the chloride ions. Dissolve the residues in 10ml of

2M sulphuric acid and extract the Tc into 5% TnOA in xylene. Shake the samples for 5 minutes and leave to settle for 5 minutes. Repeat the organic extraction several times. Combine the organic fractions, mix with scintillation cocktail and determine the ^{99}Tc content by LSC.

Take the calcium phosphate precipitate and re-dissolve in 6M HCl. Extract the Fe^{3+} into iso-butyl acetate. Discard the organic fractions and place the aqueous sample on the hotplate to dry down. Dissolve the residues in 0.1M nitric acid and adjust the pH to 2 using ammonia. Continue to add dilute ammonia dropwise until the pH decreases on the addition of 1 further drop of ammonia. Filter the sample and discard the filtrate. Dissolve the precipitate in 0.01M HCl and load on to the Eichrom Ln2 column. Wash the column with 25ml of 0.1M HCl, 50ml 0.25M HCl and 50ml 1M HCl. Dry down all the eluant fractions, take up in a suitable media and determine the lanthanide concentration.

5.0 Summary of Methods and determination of MDA.

5.1 General Considerations

There was a requirement for methods to be developed that would enable the low level determination of long-lived radionuclides in decommissioning concrete wastes. It was necessary that these adopted methodologies were able to measure accurately the content of these radionuclides to below that of the *de minimis* of 0.4Bq g^{-1}. If waste can be shown to have a total inventory of less than 0.4Bq g^{-1}, it can be disposed of using normal waste routes. This will drastically reduce the cost associated with the decommissioning programme. However, it is also necessary to have a complete inventory associated with those wastes that will be stored. This enables a more accurate safety case to be developed for repository sites. Consequently, it was necessary to develop methods with optimised parameters so that low MDA's were achieved. The MDA is determined using the following equation as detailed by Currie [89]:

$$MDA = \frac{k^2}{T} + 2k\left(\frac{2R_b}{T}\right)^{\frac{1}{2}}$$

Where

MDA = minimum detectable amount (Bq g^{-1})

k = 95% confidence factor, 1.65

T = is the counting time (s)

R_b = is the background count rate (counts per second)

The MDA shown above takes into account those parameters introduced by the detection method. However, the overall MDA will also be affected by the chemical characteristics of the analysis, *i.e.* the chemical yield, mass of sample analysed and the counting efficiency of the radionuclide. Therefore, it is more accurate to describe the MDA using the following equation:

$$MDA = \frac{k^2}{T} + 2k\left(\frac{2R_b}{T}\right)^{\frac{1}{2}} \times \frac{100}{M_c + E_c + Y_c}$$

Where

MDA = minimum detectable amount (Bq g^{-1})

k = 95% confidence factor, 1.65

T = is the count time (s)

R_b = is the background count rate (cps)

M_c = mass of concrete (g)

E_c = counting efficiency

Y_c = yield of carrier

Here it can be seen that the MDA for the analysis will be affected by the counting parameters and the analytical parameters of the analysis.

Factors that will influence the MDA are

1) counting efficiency of the detector
2) the background count rate of the detector
3) count time
4) mass of sample analysed
5) yield of the chemical analysis

Factors 1 and 2 cannot be controlled to any great extent, except that it is essential that the detector chosen for the counting of the sample should be the most appropriate with regards to the radionuclide of interest.

Factor 3, can be easily altered, and depending on sample activity, provisions can be made for this in the counting protocol. Obviously, those samples of lower activity will need to be counted for longer periods. This factor will be affected by constraint of available instrument time.

Consequently, factors 4 and 5 are those which can be fully optimised. Alternative methods may differ considerably in sample tolerance and sample yield. Generally those schemes that tolerate small sample sizes have greatest chemical yield, and conversely those where sample constraints are not rigid have impaired sample recovery. Typically, this reduced chemical yield is because of the high concentration of other contaminants in the matrix. These contaminants may reduce the overall efficiency of the analytical process; since further analytical stages will need to be introduced to the scheme, to ensure the chemical purity of the final counting sample.

5.1.2 Theoretical MDA's of the Canberra Packard Ultra Low-Level Liquid Scintillation Counter and EG&G Ortec Hyperpure Detector (GMX-25)

The MDA for the Canberra Packard LSC is based on a count time of 360 minutes and a background count rate of 0.257 counts s^{-1}. A long count time not only offers a lower MDA value but also improves counting statistics associated with the sample.

$$MDA = \frac{(1.65)^2}{(360\times 60)} + (2\times 1.65)\left(\frac{2\times 0.257}{(360\times 60)}\right)^{\frac{1}{2}} = 0.0177 counts \quad s^{-1}$$

The MDA for the EG&G Ortec Hyperpure Detector is based on a count time of 24 hours and a background count rate of 0.032 counts s^{-1}.

$$MDA = \frac{(1.65)^2}{(24\times 60\times 60)} + (2\times 1.65)\left(\frac{2\times 0.032}{(24\times 60\times 60)}\right)^{\frac{1}{2}} = 0.0029 counts \quad s^{-1}$$

Based on counting parameters only, both the LSC and the γ detector can be used to determine activity below that of the *de minimis* of 0.4 counts s^{-1}. However, the counting efficiency and yield recovery of the nuclide may suppress the MDA to a value above that of limit required. Consequently, it is necessary that all methods developed have a high chemical recovery and a high sample tolerance.

The decay energy of ^{36}Cl is sufficiently high (E_{max} 0.71MeV) that the counting efficiency approaches 100%. Using the LSC system described the counting efficiency using Ultima Gold AB scintillation cocktail was found to be 98%.

The E_{max} of ^{99}Tc is 0.293MeV, the counting efficiency of this isotope in Ultima Gold AB scintillant is 98%.

The decay of ^{129}I is primarily by low energy β emission, however, gamma photons are also released. Consequently the isotope can be measured by either LSC or γ detection. However, it is necessary to determine which detection method will result in the lower limit of detection. The β decay of ^{129}I releases low energy electrons (0.189Mev) with an associated LSC counting efficiency is ~ 90%. However, the low specific activity of this nuclide combined with the relatively high background, can compromise the detection limit. Although the counting efficiency of ^{129}I by γ spectrometry is low (10%), the lower background count rate may results in a more favourable detection.

The E_{max} of ^{151}Sm β particles is very low at 0.076MeV. The associated counting efficiency of the LSC is ~ 60%. Unlike ^{129}I, ^{151}Sm decays by β emission only, consequently no other radiometric method is available for detection. Non-radiometric techniques have been applied to the determination of Sm, however unless mass spectrometry techniques are used, it is impossible to determine the ^{151}Sm content from the natural Sm contained in the sample. Associated with ionisation spectrometry techniques is the limitation of sample size, generally the sample size must be less than 0.2g. The detection limit of ^{151}Sm using the Canberra Packard LSC is 0.03Bq.

Although the decay of ^{166m}Ho is primarily by β emission, detection on high level samples is generally by γ spectrometry on the associated photon release, or by neutron activation. However, for low level analysis the analyte needs to be isolated in order to measure its activity. Reliable ^{166m}Ho radiotracers are not widely

available, consequently it was impossible to determine the absolute counting efficiency on the LSC. However, the E_{max} β energy of the isotope (0.07MeV) is similar to that of ^{151}Sm [15], consequently the efficiency was assumed to be the same. The detection limit of ^{166m}Ho based on the counting efficiency of 60% was calculated as 0.03Bq. The counting efficiency of ^{166m}Ho on the γ detector is ~ 7%, resulting in a detection limit of 0.04Bq. Analysing samples that decay by a combination of β and γ processes can lead to problems in that the compton photons may cause an electronic disturbance in the outer shell of the organic molecule, found in the scintillant cocktail. This disturbance will contribute to the spectra and inaccuracies in the activity measurement may occur.

Due to the absence of suitable radiotracers the lanthanide yields were determined using ICP-OES. Since the detection tolerance to particulates is limited, it was necessary to dope the samples analysed with enhanced levels of the element, typically 1000ppm g^{-1} concrete. In this manner it was possible to analyse a large amount of concrete (up to 10g), take a fraction of the sample for analysis, (<0.2g), dilute to a reasonable concentration, and determine on the ICP instrument. The chemical yields were then used to calculate the effective MDA for radiometric techniques involving either LSC or γ spectrometry.

5.2 Method for the determination of ^{36}Cl in concrete.

The concrete is added to a round bottomed flask, associated inactive chloride carrier is added. The sample is digested under slight negative pressure, all gaseous products being trapped in a 1M hydroxide trap. The sample is digested initially with 6M hydroxide, and the acid concentration increased on the addition of concentrated nitric acid. To the system 25ml of 2% potassium permanganate solution are added. The sample is digested for 3 hours at a temperature of 80°C. After digestion and halide transfer, the contents of the hydroxide trap are transferred to a beaker. To the sample the reducing agent sodium nitrite is added to ensure the reduction of the chlorate to chloride. The chloride is quantitatively precipitated using 0.1M silver nitrate

solution. The precipitate is dried and chemical yield determined. The precipitate is dissolved in ammonia, mixed with a suitable scintillant and counted on the LSC.

5.2.1 Demonstration of the validity of the proposed methodology

The concrete samples were prepared 'in-house', since concrete reference materials containing ^{36}Cl were not available. A variety of concrete standards were prepared, the activity ranged from 0.1 to 100Bq g^{-1}. Three standards were used during the investigation, the details are shown in Table 5.1.

Table 5.1 Activity profile of concrete standards used for ^{36}Cl experiments

Concrete Standard	Activity Bq g-1
1	0.1
2	10
3	100

To the concrete, calibrated NaCl solution was added as a chemical carrier. Aliquots of concrete were taken for analysis and the chemical and radiochemical recoveries are shown in Table 5.2

Table 5.2 Recovery of chloride from concrete

Concrete standard	Specific activity of concrete (Bq g^{-1})	Mass (g)	Total activity (Bq)	Carrier recovery (%)	^{36}Cl recovery (%)	Ratio of carrier/^{36}Cl
1	0.1	0.5	0.05	85.8	84.6	1.01
1	0.1	1.0	0.1	81.7	83.0	0.984
1	0.1	2.0	0.2	72.9	73.1	0.997
1	0.1	3.0	0.3	74.9	74.6	1.00
1	0.1	4.0	0.4	73.8	73.8	1.00
1	0.1	5.0	0.5	68.9	69.3	0.994
1	0.1	8.0	0.8	68.7	67.9	1.01
1	0.1	10.0	1	64.2	64.5	0.995
2	10	0.5	5	89.7	88.4	1.01
2	10	1.0	10	92.7	91.8	1.01
2	10	2.0	20	93.1	92.9	1.00
2	10	3.0	30	86.4	86.6	0.998
2	10	4.0	40	87.2	85.4	1.02
2	10	5.5	55	79.6	79.8	0.997
2	10	8.0	80	80.2	81.0	0.99
2	10	10.0	100	76.4	77.6	0.985
3	100	0.1	10	91.2	90.8	1.00
3	100	0.5	50	89.9	89.6	1.00
3	100	1.0	100	79.6	78.7	1.01
3	100	2.0	200	84.3	83.9	1.00
3	100	3.0	300	80.6	81.2	0.993
3	100	4.0	400	84.7	84.6	1.00
3	100	5.0	500	68.8	68.5	1.00
3	100	10.0	1000	71.3	70.9	1.01
					Mean	**1.0015**

From the table it can be seen that there is excellent agreement between the activity added and the recovery of the chemical carrier. The ratio of chemical carrier:^{36}Cl recovery was determined, ideally this should be 1.00, these experiments indicated that the ratio is 1.0015, the slight deviation is well within experimental error.

From the recoveries it was possible to determine the MDA values for the weights analysed. All weights that were analysed in triplicate and the mean recoveries are shown below in Table 5.3.

Table 5.3 Average ^{36}Cl recovery for different weights of concrete

Concrete weight (g)	Average % recovery
1.0	84.5
2.0	83.3
3.0	80.8
4.0	81.3
5.0	68.9
10.0	71

The MDA for each weight investigated was determined by substituting the recovery and mass of concrete taken for analysis, into the equation below. The figure is based on a count time of 360 minutes, a background count rate of 0.257 counts s^{-1}, a counting efficiency of 97% and corrected for the average recovery and sample mass, resulting in a MDA figure with units of Bq g^{-1}. All results are quoted at the 95% confidence limit. Results are shown in Table 5.4.

$$MDA = \frac{(1.65)^2}{(360\times 60)} + (2\times 1.65)\left(\frac{2\times 0.257}{(360\times 60)}\right)^{\frac{1}{2}} \times \frac{100}{M_c + 97 + Y_c} = Bq\ g^{-1}$$

Table 5.4 Effect of sample size on calculated MDA for ^{36}Cl

Sample weight (g)	Average recovery (%)	MDA (Bq g^{-1})
1.0	84.5	0.0216
2.0	83.3	0.0109
3.0	80.8	0.0075
4.0	81.3	0.0056
5.0	68.9	0.0053
10.0	71	0.0026

As the sample mass increases the carrier recovery decreases. However, since the method can be used to analyse large sample sizes, the MDA for the proposed analytical scheme is suitably low so that it can be used for the determination of ^{36}Cl in decommissioning concrete wastes. The MDA for a 10g sample is ~ 2 orders of magnitude below the *de minimis*, for smaller sample sizes the MDA is still an order of magnitude less than the *de minimis* of 0.4Bq g^{-1}.

A sample of concrete taken from the reactor shield was analysed using the proposed analytical method. The sample had been analysed following the established method for ^{36}Cl analysis at BNFL, Magnox Generation. The results obtained from the proposed analytical scheme were compared to the result obtained from Magnox Generation. Due to the limitation in sample size, small masses were taken so that the analysis could be repeated. Results are shown in Table 5.5.

Table 5.5 Analysis of concrete reactor shield for ^{36}Cl

Weight of sample (g)	Carrier recovery (%)	Activity (Bq g^{-1})
1.3060	86.0	2.30
0.9423	90.9	1.63
1.1761	95.2	1.88
2.2243	93.6	1.87
Proposed Method	Mean activity (Bq g^{-1})	1.92
Magnox Generation Method	Activity (Bq g^{-1})	1.91

5.3 Method for the determination of ^{125}I (^{129}I) in concrete.

The concrete is added to a round bottomed flask, inactive iodide in the form of calibrated NaI is added. As in section 5.2 the sample is digested under negative pressure, and gaseous products collected in a 1M hydroxide trap. To the sample 6M hydroxide is added and the sample digested. After 1 hour concentrated nitric acid is added until the resulting H^+ concentration is ~3M. The sample is digested at 80°C for a further 3 hours. Since the gaseous iodine may condense in the delivery tube of the hydroxide trap, it is useful to lag the tube with polystyrene insulating pipe. After three hours the hydroxide trap is disconnected from the apparatus and the alkali contents transferred to a beaker. The reducing agent hydrazine is added to reduce the

iodate species to the iodide. The iodide is precipitated on the addition of 0.1M silver nitrate solution. The precipitate is transferred to a petri dish, dried and the chemical yield determined. The precipitate is then γ counted and the activity determined.

5.3.1 Demonstration of the validity of the methodology for ^{125}I in concrete

A variety of concrete standards were prepared, the activity ranged from 1.0 to 100Bq g^{-1}. The standards used are detailed in Table 5.6. Recoveries from the analyses are shown in Table 5.7

Table 5.6 Activity profile of validation standards used for ^{125}I

Concrete Standard	Activity Bq g^{-1}
1	1.0
2	10.0
3	100.0

Table 5.7 Recovery of iodide from concrete

Concrete standard	Specific activity of concrete (Bq g^{-1})	Mass (g)	Total activity (Bq)	Carrier recovery (%)	^{125}I recovery (%)	Ratio of carrier/^{125}I
1	1.0	0.5	0.5	96.4	95.7	1.01
1	1.0	1.0	1.0	92.6	90.9	1.02
1	1.0	2.0	2.0	89.7	89.6	1.00
1	1.0	3.0	3.0	92.3	90.7	1.02
1	1.0	4.0	4.0	88.4	88.3	1.00
1	1.0	5.0	5.0	86.1	85.9	1.00
1	1.0	10.0	10.0	84.6	83.6	1.01
2	10	0.5	5	95.8	95.7	1.00
2	10	1.0	10	97.6	95.8	1.02
2	10	2.0	20	96.8	94.3	1.03
2	10	3.0	30	79.8	80.3	0.99
2	10	4.0	40	84.6	86.1	0.98
2	10	5.0	50	88.7	89.2	0.99
2	10	10.0	100	79.8	81.2	0.98
3	100	0.1	10	91.3	89.9	1.01
3	100	0.5	50	94.6	92.7	1.02
3	100	1.0	100	88.5	90.1	0.98
3	100	2.0	200	91.0	87.6	1.04
3	100	3.0	300	86.4	89.1	0.97
3	100	4.0	400	82.6	84.6	0.98
3	100	5.0	500	77.9	74.6	1.04
3	100	10.0	1000	74.3	76.8	0.97
					Average	1.0054

From the table it can be seen that there is good agreement between the two recoveries. Unlike the ^{36}Cl results there is a moderate degree of scatter, however this is possibly due to the extrapolation of the activity. Since the samples were analysed up to a year after preparation, the original activity had decayed through 5 half lives and the level of activity in the sample was very small. The samples were counted in triplicate, however, the results did vary considerably between each count. Although the degree of scatter associated with these results was ±3%, this was still an acceptable degree of uncertainty. Averaging of the carrier:activity ratios indicates that there is no experimental bias in the analysis. The MDA of the analysis was determined as before, the average recoveries for each weight were calculated, and are shown in Table 5.8.

Table 5.8 Average recoveries of ^{125}I for different weights of concrete

Concrete weight (g)	Average % Recovery
1.0	88.2
2.0	92.2
3.0	86.7
4.0	86.3
5.0	83.2
10.0	80.5

As ^{129}I can be determined using both γ spectrometry and liquid scintillation counting techniques, the MDA's for each technique was calculated. The γ detection figure is based on a count time of 24 hours, a background count rate of 0.032 counts s^{-1}, a counting efficiency of 10% and corrected for the average recovery at each sample weight. The LSC figure is based on a count time of 360 minutes, a background count rate of 0.257 counts s^{-1}, a counting efficiency of 90% and corrected for the average recovery at each sample weight All results are quoted at the 95% confidence limit. Results are shown in Table 5.9.

Table 5.9 Effect of sample size on calculated MDA for ^{129}I

Sample weight (g)	Average recovery (%)	MDA (Bq g^{-1}) LSC	MDA (Bq g^{-1}) γ
1.0	88.2	0.022	0.033
2.0	92.2	0.011	0.016
3.0	86.7	0.008	0.011
4.0	86.3	0.006	0.008
5.0	83.2	0.005	0.007
10.0	80.5	0.002	0.004

As before, increasing the sample size reduces the overall radiochemical yield. However, since a large sample size can be analysed, the MDA of the analysis is suitably low so that it can be used to determine the activity of ^{129}I in low level concrete wastes. For a 1g sample the MDA is an order of magnitude below the deminimis, at the upper sample weight range the MDA for ^{129}I is 2 orders of magnitude below the *de minimis* value of 0.4Bq g^{-1}. From the results calculated, it can be seen that a lower MDA is achieved if the ^{129}I was determined by measurement of the β particle rather than by measurement of the γ photon. This is the greater counting efficiency counteracts the poorer background figure. The figure of merit for both detection methods can be calculated using the equation detailed:

$$\frac{E^2}{B}$$

Where E = efficiency (%)

B = background count rate (cps)

It was found that the figure of merit for ^{129}I by LSC was >31000 and that by γ detection was an order of magnitude lower at 3100.

The method could not be tested by analysis of a genuine sample. In the nuclear industry the ^{129}I content is calculated using FISPIN codes rather than by analysis, this is in part, due to the lack of a suitable method for the determination of ^{129}I in wastes. Consequently the experiments detailed in this section have been used to assess the feasibility of the proposed analytical method. The results obtained indicate that there is no experimental bias within the method, and that the gravimetric determination of AgI can be used as an accurate yield monitor for iodine isotopes in concrete wastes.

5.4 Method for the determination of ^{99}Tc in concrete

The concrete is digested in 6M NaOH, in a round bottomed flask at 80°C. To the sample nitric acid is added and the sample further digested for 3 hours. Once cool, the sample is filtered and the filtrate retained. To the filtrate calcium chloride and orthophosphoric acid are added. Ammonia is added to the sample until the pH is ~5.

The precipitate is left to settle and the contents are filtered through a 0.45μm membrane under vacuum. The filtrate is transferred to the hotplate and dried down at 60°C. The sample residues are taken up into 10ml of 1M HCl and loaded on to a pre-conditioned Dowex anion exchange column. The technetium is eluted in 30ml of conc.HNO_3. The nitric acid is dried gently on the hotplate at 60°C. The sample residues are dissolved in 2M H_2SO_4 and extracted into 5% TnOA in xylene. The organic phase is mixed directly with the scintillant and counted on the LSC.

5.4.1 Demonstration of feasibility of proposed analytical method

Concrete standards that were prepared were used to determine the feasibility of the proposed method. There are no stable isotopes of technetium, consequently the recovery was determined by comparing the activity recovered with the activity added. Different weights and specific activities of concrete were analysed, these are detailed in Table 5.10.

Table 5.10 Activity profile of concrete standards used for ^{99}Tc

Concrete Standard	Activity Bq g^{-1}
1	0.1
2	1.0
3	100.0

The activity recoveries of ^{99}Tc with differing weights of concrete are shown in Table 5.11.

Table 5.11 Recovery of technetium from concrete

Concrete standard	Specific activity of concrete (Bq g^{-1})	Mass (g)	Total activity (Bq)	^{99}Tc recovery (%)
1	0.1	1.0	0.1	89.6
1	0.1	2.0	0.2	91.3
1	0.1	3.0	0.3	90.8
1	0.1	4.0	0.4	93.7
1	0.1	5.0	0.5	86.7
1	0.1	5.0	0.5	82.1
1	0.1	10	1.0	76.0
2	1.0	1.0	1.0	84.5
2	1.0	2.0	2.0	88.4
2	1.0	3.0	3.0	79.4
2	1.0	3.0	3.0	81.0
2	1.0	4.0	4.0	80.4
2	1.0	5.0	5.0	68.7
2	1.0	10	10.0	72.9
3	100	0.5	50	84.6
3	100	0.5	50	79.2
3	100	1.0	100	80.6
3	100	2.0	200	82.4
3	100	3.0	300	83.5
3	100	4.0	400	79.0
3	100	5.0	500	77.1
3	100	10.0	1000	75.4

The recovery of the Tc is typically greater than 70%. The losses of Tc are greater than those found experimentally for Cl and I. This may be due to there being no carrier in the Tc analysis, consequently transfer losses will be more significant. The average recoveries for selected concrete weights were calculated. These are shown in Table 5.12.

Table 5.12 Average recoveries of ^{99}Tc for different weights of concrete

Concrete weight (g)	Average % Recovery
1.0	86.2
2.0	86.3
3.0	83.6
4.0	84.4
5.0	76.0
10.0	74.8

The MDA for ^{99}Tc was calculated, the figure was based on on a count time of 360 minutes, a background count rate of 0.257 counts s^{-1}, a counting efficiency of 98% and corrected for the average recovery at each sample weight. All results are quoted at the 95% confidence limit. Results are shown in Table 5.13.

Table 5.13 Effect of sample size on calculated MDA for ^{99}Tc

Sample weight (g)	Average recovery (%)	MDA (Bq g^{-1})
1.0	86.2	0.019
2.0	86.3	0.010
3.0	83.6	0.007
4.0	84.4	0.005
5.0	76.0	0.004
10.0	74.8	0.002

From the table it can be seen that the MDA for ^{99}Tc in concrete wastes is below the *de minimis*, consequently this method could be used to determine the activity of this radionuclide in concrete wastes.

5.5 Method for the determination of ^{151}Sm in concrete

To a beaker add the concrete and suitable tracers. Digest the concrete in alkali for 1 hour at 80°C. To the concrete add nitric acid until the effective H+ concentration is 3M. Continue to heat the sample at 80°C for a further three hours. Filter the sample and discard the solid material. Dry down the aqueous fraction and then take up in 0.1M nitric acid. To the sample add orthophosphoric acid, adjust the pH of the sample using ammonia solution. Continue to add ammonia until 1 drop of ammonia solution causes a significant drop in pH. Leave the sample to settle for 1 hour prior to filtration. Dissolve the precipitate in 0.01M hydrochloric acid and load on to a

pre-conditioned Ln2 column. Wash the loading solution through with 0.1M HCl. Collect this fraction and combine it with the eluted loading solution. Dry down the solution and take up in 10ml 2% nitric acid. Take 1ml of solution and dilute to 50ml using 2% nitric acid. Determine Sm concentration on the ICP.

5.5.1 Demonstration of suitability of proposed analytical method

Concrete standards were prepared containing a high concentration of Sm, typically 1000ppm (w/v) Sm g^{-1} concrete. The ICP will not tolerate large quantities of particulate matter. Consequently by preparing such concentrated samples it was possible to take an aliquot of sample for the final analysis. The aliquot was further diluted, thus reducing the concentration of the dissolved particulates to a level tolerated by the instrument. The concrete standards used in the method are shown in Table 5.14, and the recovery of samarium from different weights of concrete are shown in Table 5.15.

Table 5.14 Activity profile of validation standards used for Sm

Concrete Standard	[Sm] ppm (w/v)
1	100
2	1000

Table 5.15 Recovery of samarium from concrete

Concrete standard	Concentration of Sm (ppm g^{-1})	Total Mass (g)	Total Solution Volume (ml)	Aliquot (ml)	Diluted Volume (ml)	Equivalent mass of concrete (g/ml)	Recovery (%)
1	100	1.0	10	1	50	0.002	89.6
1	100	2.0	10	1	50	0.004	87.8
1	100	3.0	10	1	50	0.006	82.9
1	100	4.0	10	1	50	0.008	91.8
1	100	5.0	10	1	50	0.010	83.7
1	100	10	10	1	50	0.020	79.4
2	1000	1.0	10	1	50	0.002	91.2
2	1000	2.0	10	1	50	0.004	90.3
2	1000	3.0	10	1	50	0.006	87.6
2	1000	4.0	10	1	50	0.008	92.5
2	1000	5.0	10	1	50	0.010	81.9
2	1000	10	10	1	50	0.020	78.9

The recovery of the samarium is high, typically greater than 80%. The average recoveries for selected concrete weights were calculated. These are shown in Table 5.16.

Table 5.16 Average recoveries of Sm for different weights of concrete

Concrete weight (g)	Average % Recovery
1.0	90.4
2.0	89.1
3.0	85.3
4.0	92.2
5.0	82.8
10.0	79.2

The MDA for ^{151}Sm was calculated using the average recovery data for Sm obtained by ICP. The MDA figure is based on a count time of 360 minutes, a background count rate of 0.257 counts s^{-1}, a counting efficiency of 60%. The MDA has been corrected for the average sample recovery for each sample weight. All results are quoted at the 95% confidence limit. Results are shown in Table 5.17.

Table 5.17 Effect of sample size on calculated MDA for ^{151}Sm

Sample weight (g)	Average recovery (%)	MDA (Bq g^{-1})
1.0	90.4	0.031
2.0	89.1	0.015
3.0	85.3	0.011
4.0	92.2	0.007
5.0	82.8	0.006
10.0	79.2	0.003

5.6 Method for the determination of ^{166m}Ho in concrete

Add the concrete to a beaker, add suitable tracers. Digest the concrete for 1 hour in alkali at 80°C. Add nitric acid to the sample, continue to heat at 80°C for a further three hours. Filter the sample and discard the solid material. Dry down the aqueous fraction and then take up in 0.1M nitric acid. To the sample add orthophosphoric acid and adjust pH using ammonia solution. Continue to add ammonia until 1 drop of ammonia solution causes a significant drop in pH. Leave the sample to settle for 1

hour and filter through a 0.45µm membrane under vacuum. Dissolve the precipitate in 0.01M hydrochloric acid and load on to a pre-conditioned Ln2 column. Wash the loading solution through with 0.1M HCl. Wash the column with 0.25M HCl, discard all fractions. Elute the Ho using 1M HCl, collect and then dry down on the hotplate. Take up the residues in 10ml 2% nitric acid. Take 1ml of solution and dilute to 50ml using 2% nitric acid. Determine Ho concentration on the ICP.

5.6.1 Demonstration of applicability of proposed analytical method

As with the Sm concrete standards, the holmium standards were doped with a high concentration of Ho. Thus the sample taken can be reduced to such an extent that the particulates contained in the aliquot will be tolerated on the instrumentation. The concrete standards used in the method validation are shown in Table 5.18. The recoveries of the analyte are shown in Table 5.19.

Table 5.18 Activity profile of concrete standards used for Ho

Concrete Standard	[Ho] ppm (w/v)
1	100
2	1000

Table 5.19 Recovery of holmium from concrete

Concrete standard	Concentration of Ho (ppm g^{-1})	Total Mass (g)	Total Solution Volume (ml)	Aliquot (ml)	Diluted Volume (ml)	Equivalent mass of concrete (g/ml)	Recovery (%)
1	100	1.0	10	1	50	0.002	86.9
1	100	2.0	10	1	50	0.004	87.2
1	100	3.0	10	1	50	0.006	83.6
1	100	4.0	10	1	50	0.008	90.4
1	100	5.0	10	1	50	0.010	81.6
1	100	10	10	1	50	0.020	78.5
2	1000	1.0	10	1	50	0.002	91.2
2	1000	2.0	10	1	50	0.004	93.7
2	1000	3.0	10	1	50	0.006	89.4
2	1000	4.0	10	1	50	0.008	92.6
2	1000	5.0	10	1	50	0.010	88.2
2	1000	10	10	1	50	0.020	84.8

The recovery of the holmium in the concrete standards were high. Generally the recovery was greater than 85% and considering the complexity of the matrix and sample size this level of analyte recovery is excellent. The average recoveries for selected concrete weights were calculated so that the theoretical MDA could be determined. The average recoveries are shown in Table 5.20.

Table 5.20 Average recoveries of Ho for different weights of concrete

Concrete weight (g)	Average % Recovery
1.0	89.1
2.0	90.5
3.0	86.5
4.0	91.5
5.0	84.9
10.0	81.7

The MDA for ^{166m}Ho was calculated using the recovery information obtained by ICP. The MDA (LSC) figure is based on a count time of 360 minutes, a background count rate of 0.257 counts s^{-1}, and a counting efficiency of 60%. The figure has been corrected for the average sample recovery for each sample weight. Since ^{166m}Ho can also be detected using a γ detector, the MDA using the EG&G Ortec instrument has also been calculated. The figure is based on a count time of 24 hours, a background count rate of 0.058 counts s^{-1} and a counting efficiency of 8.1%. All results are quoted at the 95% confidence limit. Results are shown in Table 5.21. As before the Figure of Merit is greater for LSC than for γ counting, consequently the lower MDA is obtained by determining the activity of ^{166m}Ho by β counting on the scintillation counter.

Table 5.21 Effect of sample size on calculated MDA for ^{166m}Ho

Sample weight (g)	Average recovery (%)	MDA (LSC)	MDA (γ detector)
1.0	89.1	0.038	0.053
2.0	90.5	0.014	0.026
3.0	86.5	0.010	0.018
4.0	91.5	0.007	0.013
5.0	84.9	0.006	0.011
10.0	81.7	0.003	0.006

5.7 Method for the sequential analysis of selected radionuclides in concrete

To a round bottomed flask add the concrete and suitable carriers. Arrange the apparatus as shown in Figure 2.1. Digest the sample under reflux for 1 hour at 80°C in 6M NaOH, collecting all gaseous products in the halide trap. To the sample add nitric acid so that the effective H^+ concentration is 3M. Collect the iodine formed for three hours. After this time disconnect the halide trap and transfer the contents to a beaker. Replace the exhausted alkali with a fresh solution. Add the oxidising agent (2% $KMnO_4$) to the reaction vessel and continue the reaction for a further three hours. After this time disconnect the apparatus, transfer the hydroxide trap to another beaker and analyse for chloride and iodide as detailed in Section 2.9.1 and 2.9.2. Filter the reaction vessel and discard the solids. Dry the filtrate down. Precipitate calcium hydroxide fully by adding orthophosphoric acid and taking to pH 5 using ammonia solution. Filter the sample and store both the precipitate and filtrate. Take the filtrate and dry down gently at 60°C. Dissolve the sample in 1M HCl and load on to a pre-conditioned (1M HCl) Dowex anion exchange column. Elute the Tc using 30ml of concentrated nitric acid. Transfer the solution to a hotplate and dry down at 60°C, wash the residues 3X with de-ionised water. Dissolve the residues in 10ml of 2M sulphuric acid and extract the Tc into 5% TnOA in xylene. Shake the samples for 5 minutes and leave to settle for 5 minutes. Repeat the organic extraction several times. Combine the organic fractions, mix with scintillation cocktail and determine the ^{99}Tc content by LSC.

Take the calcium phosphate precipitate and re-dissolve in 6M HCl. Extract the Fe^{3+} into iso-butyl acetate. Discard the organic fractions and place the aqueous sample on the hotplate to dry down. Dissolve the residues in 0.1M nitric acid and adjust the pH to 2 using ammonia. Continue to add dilute ammonia dropwise until the pH decreases on the addition of 1 further drop of ammonia. Filter the sample and discard the filtrate. Dissolve the precipitate in 0.01M HCl and load on to the Eichrom Ln2 column. Wash the column with 25ml of 0.1M HCl, 50ml 0.25M HCl

and 50ml 1M HCl. Dry down all the eluant fractions, take up in a suitable media and determine the lanthanide concentration.

5.7.1 Test of the proposed analytical method for sequential analysis

The concrete referred to as Set 6 (Section 4.2.1.2) was used to demonstrate the validity of the sequential analysis methodology. The concrete had been doped with a variety of active and non active components, the full details are given in Table 5.22. The recoveries of each nuclide are shown in Table 5.23.

Table 5.22 Activity profile of validation standards used for sequential analysis

Concrete Standard	^{36}Cl (Bq g^{-1})	^{125}I (Bq g^{-1})	^{99}Tc (Bq g^{-1})	^{137}Cs (Bq g^{-1})	^{148}Gd (Bq g^{-1})	^{152}Eu (Bq g^{-1})	[Sm] (ppm)	[Ho] (ppm)
Set 6	100	100	100	100	100	100	1000	1000

Table 5.23 Recovery of various radionuclides from concrete

Concrete Standard	Mass (g)	Recovery (%)				
		^{36}Cl	^{125}I	^{99}Tc	Sm	Ho
Set 6	1	91.3	88.7	88.3	86.5	89.6
Set 6	2	88.4	92.3	85.6	81.3	84.6
Set 6	3	86.3	82.4	87.2	88.6	91.2
Set 6	4	87.2	86.3	79.8	84.6	78.4
Set 6	5	82.9	77.9	83.8	86.2	88.3
Set 6	10	79.9	72.8	79.8	79.5	80.3
Set 6	1	88.6	82.6	90.3	83.9	86.2
Set 6	2	91.7	84.3	82.6	88.4	80.6
Set 6	3	85.4	83.2	88.7	80.6	73.8
Set 6	4	88.2	80.1	86.1	75.6	81.6
Set 6	5	80.4	76.8	85.6	83.4	87.3
Set 6	10	82.6	78.2	82.1	82.0	80.5

As before the average recoveries for selected concrete weights were calculated so that the theoretical MDA could be determined. The average recoveries are shown in Table 5.24.

Table 5.24 Average recoveries of radionuclides analysed by sequential analysis

Concrete mass(g)	Average Recovery (%)				
	^{36}Cl	^{125}I	^{99}Tc	Sm	Ho
1	90.0	85.7	89.3	85.2	87.9
2	90.1	88.3	84.1	84.9	82.6
3	85.9	82.8	88.0	84.6	82.5
4	87.7	83.2	83.0	80.1	80.0
5	81.7	77.4	84.7	84.8	87.8
10	81.3	75.5	81.0	80.8	80.4

The MDA for each radionuclide was determined to investigate if there was a significant difference in the values obtained by sequential analysis compared to individual element determination.All MDA's quoted are for determination by liquid scintillation counting since the calculated MDA values for ^{129}I and ^{166m}Ho are lower when counted by LSC rather than by γ spectrometry. The values are shown in Table 5.25.

Table 5.25 MDA for individual and sequential radionuclide determination

Concrete mass (g)	MDA (Bq g^{-1})									
	^{36}Cl		^{129}I		^{99}Tc		Sm		Ho	
	Ind	Seq	Ind	Seq	Ind	Seq	Ind	Seq	Ind	Seq
1	0.022	0.022	0.022	0.023	0.019	0.020	0.031	0.035	0.038	0.034
2	0.011	0.010	0.011	0.010	0.010	0.011	0.015	0.018	0.014	0.011
3	0.008	0.007	0.008	0.08	0.007	0.007	0.011	0.012	0.010	0.011
4	0.006	0.005	0.006	0.006	0.005	0.006	0.007	0.009	0.007	0.009
5	0.005	0.004	0.005	0.005	0.004	0.004	0.006	0.007	0.006	0.006
10	0.003	0.002	0.002	0.003	0.002	0.002	0.003	0.004	0.003	0.002

Where Ind = Individually analysed in Sections 5.2, 5.3, 5.4, 5.5 and 5.6.

Seq = Sequentiually analaysed as discussed in Section 5.7

From the table it can be seen that the MDA obtained for each radionuclide was not dependent on the analytical methodology adopted. Those radionuclides that were determined in a sequential fashion had similar MDA's to those obtained by individual element analysis. From the table it can be seen that the proposed analytical methodology can separate selected radionuclides from concrete. The proposed method can be used to separate the nuclides individually or sequentially, with little effect on the MDA. It has been shown that either approach resulted in a

radiochemically pure product of high yield. Consequently the MDA calculated for each analyte was low, typically at least one order of magnitude below that of the *de minimis* of 0.4Bq g^{-1}.

6.0 Conclusions and further work

The main objective of this work has been to develop routine analytical methodologies for selected radionuclides in decommissioning wastes. It was a requirement of the analytical methodology that the MDA be less than the *de minimis* of 0.4Bq g^{-1}. This has been achieved for all the radionuclides investigated.

The proposed analytical scheme has many advantages to those methodologies currently used. The proposed methods have high, reproducible chemical yields, generally in excess of 80%. The methods are able to analyse very large sample masses, up to 10g of sample was analysed routinely with very little effect on analyte recovery. Consequently, the methods can be used to determine very low levels of radioactivity in a sample. One of the main advantages of the analysis is that the determination of the radionuclides can be carried out in a sequential fashion, that is, analytical data for five radionuclides can be obtained from a single concrete sample.

At the present time four nuclear power stations are being decommissioned. Many of the areas that are contaminated by fission and activation products are still radiologically out of bounds for routine sampling regimes, consequently the availability of decommissioning samples are limited. Therefore, if a full chemical inventory is required, current techniques generally require separate aliquots of sample for each radiochemical analysis. This may result in *less than* figures being reported, thus increasing the uncertainties associated with the inventory data.

However, if numerous analytical measurements are to be obtained from a single sample, then it is possible to take a larger quantity of sample, thus increasing the likelihood of a positive result and thus providing reliable and accurate inventory data. For those samples of moderate activity, having a sequential analysis programme means that a single sample can provide significant analytical data, thus the dose that the analyst receives is minimised.

There are many advantages to sequential analyte determination, firstly, since only a single sample needs to be analysed, there is a significant reduction in the production of hazardous waste products. Analysis of a sample of limited size will also reduce the potential dose to the analysts involved, thereby adhering to the *as low as reasonably practicable* principle (ALARP). Analysis of a matrix by sequential analysis is generally less labour intensive as compared to the individual analyses. Consequently, the overall analysis scheme is more time efficient and associated labour costs are significantly reduced.

Generally sequential analysis protocols, result in a poorer chemical yield compared to individual analysis. However, in this work the calculated MDA's for the individual element determination compared to the sequential determination are similar.

As the radionuclides of interest are all β emitting radionuclides it is impossible to use isotope dilution techniques. Consequently, the means of determining the analyte will be different to that of the carrier. Therefore it may be necessary to use chemical tracers that may be less than perfect. Analytical judgement will need to be applied and will depend on sample matrix characteristics and availability of reagents.

The greatest problem in analysing concrete matrices is the inherent levels of calcium and iron contained within the sample. However, these contaminants were effectively removed from solution using a controlled calcium phosphate precipitation step. This analytical step removed, quantitatively, the lanthanides from the bulk matrix. Associated with the lanthanide elements, was a minor amount of iron and reduced levels of calcium, both of which could be tolerated on the Eichrom Ln2 chromatographic resin. Not only was this resin able to separate the lanthanides of interest, but consideration of the elution profile indicated that the predominant europium isotopes could be separated from the solution without adversely affecting the holmium and samarium recovery.

6.1 Future work

The work reported in this thesis investigated selected radionuclides in a concrete matrix. However, other matrices are also important with regards to decommissioning wastes.

Other than concrete, significant amounts of iron and graphite will also result from the decommissioning of nuclear power stations. These matrices will be activated with significant quantities of activation products. The steels will be contaminated by various species including, ^{93}Nb, ^{99}Mo, ^{99}Zr and ^{166m}Ho. Whereas graphite may contain significant levels of ^{14}C and ^{36}Cl.

Although the methods developed in this work pertain to concrete matrices, it would be useful to determine their suitability for the analysis of graphite and steels samples. The suggested methods described in this work would need modifying to remove other bulk contaminant such as carbon and iron.

It would also be useful to determine the analytical fate of the actinides following the proposed method for lanthanide determination in concrete samples. As was suggested in Section 4.8. It is also necessary to determine the behaviour of dysprosium on the Ln2 Resin before making a decision on suitable chemical tracers in the analysis of samarium and holmium.

7.0 References

1. *A Review of the Processing Contributing to Radioactive Waste in the UK. Report No. 699. DOE/RAS/96.005.* 1996, UK Nirex Ltd.

2. *Nuclear Power Generation.* 3rd ed. Modern Power Station Practice, ed. D.J. Littler, Davies, E.J., Johnson, H.E., Kikby, F., Myerscough, P.B. & Wright, W. Vol. J. 1992: Pergamon Press.

3. Chamberlain, A.C., *Fission Product Aerosols*, in *Radioactive Aerosols.* 1991, Cambridge University Press. p. 61-114.

4. Greenwood, N.N., & Earnshaw, A., *The Lanthanide Elements (Z=58-71)*, in *Chemistry of the Elements.* 1994, Pergamon Press. p. 1424-1449.

5. Greenwood, N.N., & Earnshaw, A., *The Actinide Elements (Z=90-103)*, in *Chemistry of the Elements.* 1994, Pergamon Press. p. 1450-1486.

6. Jeffrey, G.H., Bassett, J., Mendham,J. & Denney, R.C., *Vogel's Textbook of Quantitative Chemical Analysis.* 5th ed. 1989: Longman Scientific & Technical.

7. Smith, L.L., Markin, F. & TenKate, T., *Comparison of Acid Leachate and Fusion Methods to Determine Plutonium and Americium in Environmental Samples.* 1992, Argonne National Laboratory.

8. Allen, P.G., Siemerang, G.S., Skuh, D.K., Bucher, J.J., Edelstein, N.M. & Langton, C.A., Technetium Speciation in Cement Waste Forms Determined by X-ray Absorption Fine Structure Spectroscopy. *Radiochimica Acta*, 1997. **76**: p. 77-86.

9. Alvarado, J.S., Neal, T.J., Smith, L.L. & Erickson, M.D., Microwave Dissolution of Plant Tissue and the Subsequent Determination of Trace Lanthanide

and Actinide Elements by Inductively Coupled Plasma-Mass Spectrometry. *Analytica Chimica Acta*, 1996. **322**: p. 11-20.

10. Beals, D.M., Determination of Technetium-99 in Aqueous Samples by Isotope Dilution Inductively Coupled Plasma-Mass Spectrometry. *J. Radioanal. Nucl. Chem., Articles*, 1996. **204**(2): p. 253-263.

11. Gastel, M., Becker, J.S., Kuppers, G. & Dietze, H-J., Determination of Long-Lived Radionuclides in Concrete Matrix by Laser Ablation Inductively Coupled Plasma Mass Spectrometry. *Spectrochimica Acta Part B*, 1997. **52**: p. 2051-2059.

12. Hepiegne, P., Dall'Ava, D., Clement, R. & Degros, J.P., The Separation of ^{99}Tc from Low and Medium-Level Radioactive Wastes and its Determination by Inductively Coupled Plasma Mass Spectrometry. *Talanta*, 1995. **42**(6): p. 803-809.

13. Karandashev, V.K., Turanov, A.N., KuB, H.M., Kumpmann, I., Zadnepruk, L, V. & Baulin, V.E., Extraction Chromatographic Separation of Y, REE, Bi, Th. and U from the Matrix Suitable for their Determination in Pure Iron and Low-Alloyed Steels by ICP-MS and ICP-AES. *Mikrochim. Acta*, 1998. **130**: p. 47-54.

14. Meirav, G., Adam, M., Boaretto. E., Dias, S.A., Johnson, R.R., Paul, M. & Venczel., Measurements of ^{129}I in a Nuclear Power Reactor by Accelerator Mass Spectrometry. *Appl. Radiat. Isot*, 1992. 43(11): p. 1420-1424.

15. *CRC Handbook of Chemistry and Physics*. 72nd ed, ed. D.R. Lide. 1992: CRC Press.

16. Attendorn, H.G. & Bowen, R.N.C., Radioactive and Stable Isotope Geology. Chapman & Hall 1997.

17. Woollam, P.B., *The Radioactive Inventory of a Decommissioned Magnox Power Station Structure. 1. Measurements of Neutron Induced Activity in Samples from the Reactor Island. RD/B/N4231.* 1978, Central Electricity Generating Board.

18. Woollam, P.B., & Pugh, I.G., *The Radioactive Inventory of a Decommissioned Magnox Power Station Structure. 2. A Summary of Neutron Induced Activation, Waste Disposal and Dose Equivalent Rates for the Reactor Island Structure. RD/B/R4350.* 1978, Central Electricity Generating Board.

19. Felstead, L.D., & Woollam, P.B., *An Assessment of all Known Isotopes to Determine Which Might be Important in the Decommissioning of Thermal Nuclear Reactors. TPRD/B/0386/N84.* 1984, Central Electricity Generating Board.

20. *Development and Application of Methods for the Determination of Chlorine-36 and Other Long-Lived Radionuclides in Decommissioning Wastes. Ref No. WD/GNSR/5009.* 1996/1997, IMC.

21. Raymond, A., Muller. W., Gens, R., Gili, M., Morales, A. & Yates, A., Inventory and Characterization of Important Radionuclides for the Safety of Storage and Disposal. Correlation with Key Radionuclides in Typical Waste Streams. *J. Radioanal. Nucl. Chem., Articles*, 1995. **183**(2): p. 377-390.

22. Smith-Briggs, J.L., *Review of Speciation and Solubility of Radionuclides in the Near and Far Field. DOE/HMIP/RR/92/096 Part 1.* 1992, Her Majesty's Inspectorate of Pollution.

23. Ogard, A.E., Thompson, J.L., Rundberg, R.S., Wolfsberg, K., Kubik, P.W., Elmore, D. & Bentley, H.W., Migration of Chlorine-36 and Tritium from an Underground Nuclear Test. *Analytica Chimica Acta*, 1988. **44-45**(1): p. 213-217.

24. Holtta, P., Hautojarvi, A. & Hakanen, M., Transport and Retardation of Non-Sorbing Radionuclides in Crystalline Rock Fractures. *Radiochimica Acta*, 1992: p. 285-290.

25. Pourbaix, M., *Atlas of Electrochemical Equilibria in Aqueous Solutions*. 1966.

26. Dhir, R.K., Jones, M.R. & Ahmed, H.E.H, Determination of Total and Soluble Chlorides in Concrete. *Cement and Concrete Research*, 1990. **20**: p. 579-590.

27. Glass, G.K., Wang, Y. & Buenfield, N.R., An Investigation of Experimental Methods used to Determine Free and Total Chloride Contents. *Cement and Concrete Research*, 1996. **26**(9): p. 1443-1449.

28. Haque, M.N., & Kayyali, O.A., Free and Water Soluble Chloride in Concrete. *Cement and Concrete Research*, 1995. **25**(3): p. 531-542.

29. Hope, B.B., Page, J.A. & Poland, J.S., The Determination of the Chloride Content of Concrete. *Cement and Concrete Research*, 1985. **15**: p. 863-870.

30. Schiekel, M., Scheibe, P., Shneck, U. & Lemmen, T., Determination of Chloride Content in Concrete by Nuclear Methods. *J. Radioanal. Nucl. Chem., Articles*, 1993. **174**(2): p. 199-204.

31. Parry, S.J., Bennett, B.A., Benzing, R., Redpath, D., Harrison, J., Wood, P. & Brown F.J., Radiochemical Neutron Activation Analysis for Trace Chlorine in Steels and Alloys. *Anal. Chem.*, 1997. 69(15): p. 3049-3052.

32. Wigley, F., Warwick, P.E., Croudace, I.W., Caborn, J. & Sanchez, A.L., Optimised Method for the Routine Determination of Technetium-99 in

Environmental Samples by Liquid Scintillation Counting. *Analytica Chimica Acta*, 1999. **380**: p. 73-82.

33. Faix, W.C., Caletka, R. & Krivan, V., Element Distribution Coefficients for Hydrofluoric Acid/Nitric Acid Solutions and the Anion Exchange Resin Dowex 1X8. *Anal. Chem.*, 1981. **53**: p. 1719-1721.

34. Greenwood, N.N., & Earnshaw, A., *Manganese, Technetium, and Rhenium*, in *Chemistry of the Elements*. 1994, Pergamon Press. p. 1211-1241.

35. Kaplan, D.I.S.R.J., Pertechnetate Exclusion from Sediments. *Radiochimica Acta*, 1998. **81**: p. 117-124.

36. Butterworth, J.C., Livens, F.R. & Makinson, P.R., Development of a Method for the Determination of Low Levels of Technetium-99. *The Science of the Total Environment*, 1995. **173-174**: p. 293-300.

37. Harvey, B.R., Williams, K.J., Lovett, M.B. & Ibbett, R.D., Determination of Technetium-99 in Environmental Materials with Rhenium as a Yield Monitor. *J. Radioanal. Nucl. Chem.* 1992. **158**: p 417-436.

38. Long, S.E., & Sparkes, S.T., A Literature Survey of Techniques for the Analytical Determination of Tc-99. *AERE Report R12742*, 1988.

39. Rameback , H., Albinsson, Y., Skalberg & Eklund, U.B., Determination of ^{99}Tc in Bentonite Clay Samples Using Inductively Coupled Plasma Mass Spectrometry. *Fresenius J. Anal. Chem.*, 1998. **362**: p. 391-394.

40. Chaudrey, M.A., Ahmad, S.N. & Iqbal, M.Z., Separation of Mo-99 and Tc-99m by Using TOA-Xylene Based Supported Liquid Membrane. *Radiochimica Acta*, 1996. **73**: p. 101-103.

41. Ishanullah, Lossess of Technetium During Various Steps in the Development of a Procedure for Environmental Samples. *J. Radioanal. Nucl. Chem., Letters*, 1993. **176**(4): p. 303-313.

42. Harvey, B.R., Ibbett, R.B., Williams, K.J., & Lovett, M.B., MAFF Directorate of Fisheries Research; Auqatic Environmental Protection. *Analytical Methods*, 1991. 8; p 1.

43. Chiu, J.-H., Chu, T-C. & Wend, P-S, Extraction of Technetium-99 by complexation with Ammonium Tetramethylenedithiocarbamate into Chloroform and its Application to the Determination of Technetium-99 in Low-Level Radioactive Wastes. *Analytica Chimica Acta*, 1992. **256**: p. 293-299.

44. Luxmi Varma, R., Reddy, L.P., Prasado Rao, T., Iyer, C.S.P. & Damodaran, A.D., Bis(2-ethyhexly)-N,N-diethylcarbamoylmethyl phopsphonate as a Synergist in the Extraction of Tirvalent Lanthanides by 1-Phenly-3-methyl-4- triflouroacetyl-pyrazolone-5. *Radiochimica Acta*, 1995. **72**: p. 133-136.

45. Reddy, L.P., Luxmi Varma, R., Ramamohan, T.R., Prasado Rao, T., Iyer, C.S.P. & Damodaran, A.D., Mathur, J.N., Murali, M.S. & Iyer, R.H., Mixed-Ligand Chelate Extraction of Trivalent Lanthanides and Actinides with 3-Phenly-4-Benzoyl-5-Isoxazolone and Neutral Oxo-Donors. *Radiochimica Acta*, 1995. **69**: p. 55-60.

46. Zhu, Y., The Separation of Americium from Light Lanthanides by Cyanex 310 Extraction. *Radiochimica Acta*, 1995. 68: p. 95-98.

47. Chamberlain, A.C., *Fission Product Aerosols*, in *Radioactive Aerosols*. 1991, Cambridge University Press. p. 115-152.

48. Brauer, F.P., & Tenny, H., ^{129}I Analysis Methodology. BNWL-SA-5287. 1975: p. 1-36.

49. Dermelj, M., Slejkovic, Z., Stegnar, P., Coh, V., Cujes, K. Novic, M., Rapid Radiochemical Separation and Determination of Chlorine, Bromine and Iodine in Water Samples Using Ion Exchange. *J. Radioanal. Nucl. Chem., Letters*, 1992. **164**(1): p. 59-69.

50. Handl, J., Concentrations of ^{129}I in the Biosphere. *Radiochimica Acta*, 1996. **72**: p. 33-38.

51. Jedinakova-Kriziva, V., Migration of Radionuclides in the Environment. *J. Radioanal. Nucl. Chem.*, 1998. **229**(1-2): p. 13-18.

52. Milton, G.M., Cornett, R.J., Kramer. S.J. & Vezina, A., The transfer of Iodine and Technetium from Surface Waters to Sediments. *Radiochimica Acta*, 1992. **58/59**: p. 291-296.

53. Nedveckaite, T., & Filistowicz, W., Detemination of Gaseous and Particulate ^{129}I in Atmospheric Air by Neutron Activation Analysis. *J. Radioanal. Nucl. Chem., Articles*, 1993. **174**(1): p. 43-47.

54. von Gunten, H.R., & Benes, P., Speciation of Radionuclides in the Environment. *Radiochimica Acta*, 1995. **69**: p. 1-29.

55. Bullman, R.A., *Iodine Speciation in the Environment*, in *Speciation of Fission and Activation Products in the Environment*. 1985, Elsevier Applied Scince Publishers.

56. Parry, S.J., Bennett. B.A., Benzing, R. & Lally, A.E., Radiochemical Methods in Nuclear Waste Management. *J. Radioanal. Nucl. Chem.*, 1997. **219**(2): p. 191-196.

57. Parry, S.J., Bennett, B.A., Benzing, R. Lally, A.E., Birch, C.P. & Fulker, M.J., The Determination of ^{129}I in Milk and Vegetation Using Neutron Activation Analysis. *The Science of the Total Environment*, 1995. **173/174**: p. 351-360.

58. Matuszek, J.M., Daly, J.C., Goodyear, S., Paperiello, C.J. & Gabay, J.J., Environmental Levels of ^{129}I. *IAEA/SM-180/39*, 1973.

59. Brauer, F.P., & Kaye, J.H., Detection Systems for the Low Level Radiochemical Analysis of Iodine-131, Iodine-129 and Natural Iodine in Environmental Samples. *IEEE Trans. on Nucl. Sci. NS-21*, 1974.

60. Thomas, C.W., Thin NaI(Tl) Detectors for Measuring ^{129}I at Sub-Picocurrie Levels. *BNWL-1850 Part 4*, 1973.

61. Brauer, F.P., Kaye, J.H. & Connally, R.E., X-ray Coincidence Spectrometry Applied to Radiochemical Analysis of Environmental Samples. *Radionuclides in the Environment*, 1967: p231-353.

62. Yerick, R.E., & Ross, H.H., Liquid Scintillation Counting of Iodine-129 and Iodine-125. *Departement of Chemistry, Lamar State College of Technology, Beaumont, Texas.*

63. Rhodes, B.A., Liquid Scintillation Counting of Radioiodine, *Anal. Chem.*, 1965, **37**.

64. Horrocks, D.L., Measurement of ^{129}I by Liquid Scintillation and NaI(Tl) Scintillation Methods. *Nucl. Instrum. Methods*, 1974. **120**: p 345-350.

65. Jansta, V., Determination of ^{131}I in Milk Using Heterogenous Liquid Scintillation Counting. *J. Radioanal. Nucl. Chem., Letters*, 1989. **135**(5): p. 313-320.

66. Muramatsu, Y.Y., S., Neutron Activation Analysis of Iodine in Soil. *J. Radioanal. Nucl. Chem., Articles*, 1993. **169**(1): p. 73-80.

67. Jansta, V., Determination of ^{131}I in Milk Using Heterogenous Liquid Scintillation Counting. *J. Radioanal. Nucl. Chem., Letters*, 1989. **135**(5): p. 313-320.

68. Ravi, P.M., Neelakandhan, K.N. & Iyer, M.R., Specitation and Estimation of Radiodine in Reactor Coolant Water. *J. Radioanal. Nucl. Chem., Articles*, 1992. **162**(2): p. 399-405.

69. Nakhara, T.M., T., Analyte Volatilization Procedure for the Determination of Low Concentrations of Iodine by Inductively Coupled Plasma Atomic Emission Spectrometry. *J. Anal. Atomic Spectrometry*, 1994. **9**: p. 159-165.

70. McHugh, J.A., & Sheffield, J.C., Mass Analysis of Sub-nanogram Quantities of Iodine. *Anal Chem.* 1965. **37**: p1099-1101.

71. *Journal of Chromatography Library - Volume 2 Extraction Chromatography.* ed. T. Braun & G. Ghersini. 1975. Elsevier Scientific Publishing Company.

72. Burnett, B., & Cable, P.H. Analysis of Promethium-147 in Aqueous Samples. *43rd Annual Conference on Bioassay, Analytical and Environmental Radiochemistry,* South Carolina, November 1997.

73. Martin, J.P. *The Determination of Promethium-147 and Samarium-151 Using Extraction Chromatography.* in *Environmental Radiochemical Analysis.* 1998. The De Vere Hotel,Blackpool, UK.

74. Smith, M.R., Farmer III, O.T., Reeves, J.H. & Koppenaal, D.W., Radioanalytical Methods Applied to the Nuclear Fuel Cycle (continued). *J. Radioanal. Nucl. Chem., Articles*, 1995. **194**(1): p. 7-13.

75. Yoshida, M., Sumiya, S.H., Watanabe, H. & Tobita, K., A Rapid Separation Method for Determination of Promethium-147 and Samarium-151 in Environmental Samples with Hight Performance Liquid Chromatography. *J. Radioanal. Nucl. Chem., Articles*, 1995. **197**(2): p. 219-227.

76. Pin, C., Briot, D., Bassin, C. & Poitrasson, F., Concomitant Separation of Strontium and Samarium-Neodymium for Isotopic Analysis in Silicate Samples, Based on Specific Extraction Chromatography. *Analytica Chimica Acta*, 1994. **298**: p. 209-217.

77. Sujatha, S., Reddy, L.P., Ramamohan, T.R., Damodaran, A.D., Mathur, J.N., Murali, M.S., Nager, M.S. & Iyer, R.H., Synergistic Solvent Extraction of Trivalent Lanthanides and Actinides by mixtures of 1-Phenly-3-methyl-4- triflouroacetyl-pyrazolone-5 and Neutral Oxo-Donors. *Radiochimica Acta*, 1994. **65**: p. 167-172.

78. Thakur, P., Dash, K.C., Reddy, L.P., Luxmi Varma, R., Ramamohan, T.R. & Damodaran, A.D., Crown Ethers as Synergists in the Extraction of Trivalent Lanthanides by 1-Phenly-3-methyl-4- triflouroacetyl-pyrazolone-5. *Radiochimica Acta*, 1996. **75**: p. 11-16.

79. Cobbs, J. Determination of Strontium in Environmental Materials. *PhD Thesis, Loughborough University* 1995.

80. Rohal, K.M., van Seggen, D.M., Clark, J.F., McClure M.K., Chambliss. C.K. & Strauss, S.H., Solvent Extraction of Pertechnetate and Perrhenate ions from Nitrate-Rich Acidic and Alkaline Aqueous Solutions. *Solvent Extraction and Ion Exchange*, 1996. **14**(3): p. 401-416.

81. Banavali, A.D., Raimondi, J.M., Moreno, E.M. & McCurdy, D.E., The Determination of Technetium-99 in Low-Level Radioactive Waste. *Radioactivity & Radiochemistry*, 1995. 6(3): p. 26-35.

82. *Technetium-99 in Water. Procedure TCW01*. 1995, Eichrom Industries, Inc.

83. Jordan, D., Schupfner, R. & Schuttelkopf, H., A New Very Sensitive LSC Procedure for Determination of Tc-99 in Environmental Samples. *J. Radioanal. Nucl. Chem., Articles*, 1995. **193**(1): p. 113-117.

84. Fadeff, S.K., *Technetium-99 Analysis Using Extraction Chromatography. Procedure RP550-1.*, Eichrom Industries, Inc.

85. Law, O.-W., Lam, L. & Luk, S-F., Analysis of Cement an Cement Raw Meal by Atomic Absorption Spectrophotometry Using a New Fusion Agent. *Talanta*, 1995. **42**: p. 1265-1271.

86. Durrani, S.K., Dyer, A. & Blackburn, R., Self-Duffusion of Barium and Caesium Cations in Neutron- and Gamma- Irradiated High-Silica Zeolites and Boron-Zeotypes. *Zeolites*, 1993. **13**: p. 2-13.

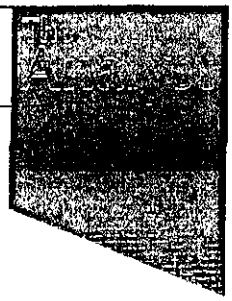
87. Bagosi, S., & Csetenyi, L.J., Immobilization of Caesium-Loaded Ion Exchange Resins in Zeolite-Cement Blends. *Cement and Concrete Research*, 1999. **29**: p. 479-485.

88. Sinha, P.K., Satyasai, P.M., Shanker, R., Muthiah, R., Bera, S., Narasimhan, S.V., Pandey, A.N. & Jaleel, A., Removal of ^{137}Cs from an Intermediate Level Liquid Waste by Using Various Ion-Exchange Media. *J. Radioanal. Nucl. Chem.*, 1999. **242**(2): p. 341-348.

89. Currie, L.A., Limits for Qualitative Detection and Quantitative Determination. *Analytical Chemistry*, 1968. **40**(3): p. 586-593.

8.0 Appendices – Peer Reviewed Publications

The measurement of ^{36}Cl and ^{129}I in concrete wastes



Linda Ashton,[a] Peter Warwick[a] and David Giddings[b]

[a] *Department of Chemistry, Loughborough University, Loughborough, Leicestershire, UK LE11 3TU*
[b] *Magnox Generation, Berkeley, Gloucestershire, UK GL13 9PB*

Received 27th November 1998, Accepted 2nd March 1999

A method has been developed for the measurement of chlorine and iodine radionuclides in concrete wastes generated from the decommissioning of nuclear power stations. Sequential oxidation of ^{129}I and ^{36}Cl from samples of concrete takes less than 7 h and the method is relatively simple and can be used to reliably determine low levels of ^{129}I and ^{36}Cl. Generally, recoveries for the procedure are high (in excess of 70%) and large sample sizes can be tolerated (~ 1–10 g). This paper describes the development of the method and demonstrates a relatively simple, repeatable process for the measurement of ^{129}I and ^{36}Cl in concrete wastes. The equipment and the methods used should be available at most reactor sites or nuclear plants.

1 Introduction

The decommissioning of nuclear power stations will, inevitably, create large volumes of wastes. Of particular concern is concrete, not only because of the large volume of concrete wastes, but also because concrete may contain radionuclides. Accurate measurements of these radionuclides are therefore essential if the radionuclide inventory of the waste is to be reliable. Furthermore, if it can be shown that the activity of the concrete is less than 0.4 Bq g^{-1}, the concrete can be treated as 'ordinary' waste which negates the expense of disposal as radioactive waste.[1] ^{36}Cl and ^{129}I, along with a number of other radionuclides have been cited as being of 'significant radiological importance'.[1]

^{36}Cl is one of the most radiologically significant radionuclides[2] and is produced in concrete by a n,γ neutron activation reaction of ^{35}Cl. ^{36}Cl is a β^- emitter (E_{max} = 0.71 MeV) and is a relatively long-lived radionuclide ($t_{1/2} = 3.0 \times 10^5$ y).[3] ^{35}Cl is found as an impurity in concrete and many other components associated with the reactor.[4–6] Although the levels of ^{35}Cl are low (ppm), the high neutron reaction cross section (43 barns), and the volume of material (tonnes), result in the nuclear reaction being an important contributor to the radionuclide inventory of the concrete. The full speciation of chlorine in nuclear wastes has yet to be determined, but studies have indicated that ^{35}Cl in concrete will be mainly present as chloride.[7] ^{36}Cl is radiologically significant because of its long half-life and its potential mobility through the geosphere.[8] Although the mobility of this radionuclide has been investigated, little work has been reported on measurements of the radionuclide in nuclear waste materials.

^{129}I is a gamma emitting (E_γ = 0.04 MeV)[3] radionuclide of long half-life ($t_{1/2} = 1.7 \times 10^7$ y).[3] ^{129}I is formed as a fission product (< 1% of the total fission yield)[9] and, because of possible physical defects in the fuel canisters, may be present as a contaminant on the surface of waste materials. Again, as with ^{36}Cl, ^{129}I is an important radionuclide because of its potential mobility and its long half-life. In recent years interest in radioiodine has increased significantly.[10] ^{129}I may be measured by accelerator mass spectrometry[11–14] and this technique has been used to determine ^{129}I : ^{127}I ratios in environmental samples and in highly active nuclear fuel solutions.[12–14]

Analysis of ^{36}Cl and ^{129}I in concrete may be carried out by using ashing or fusion with an alkali reagent but these methods are limited to the use of small amounts of sample (< 0.5 g) which limits the accuracy and sensitivity of these methods.

This paper reports the development of a method which is capable of measuring ^{36}Cl and ^{129}I in concrete at sufficient accuracy and sensitivity to satisfy the needs of decision making on waste disposal and radionuclide inventory.

2 Experimental

2.1 Reagents and equipment

18 MΩ deionised water was used throughout. Pre-prepared concrete powder was purchased from a hardware retailer and was prepared following instructions. All other reagents were of AR grade and were purchased from Aldrich. ^{36}Cl and ^{125}I were purchased from ICN Biomedicals Inc., USA. For the purpose of method development and testing ^{125}I (E_γ = 0.035 MeV)[3] was substituted for ^{129}I. Extraction and trapping of radionuclides from samples of concrete were carried out in the apparatus shown in Fig. 1.

^{36}Cl was counted on a Canberra Packard 2750 ultra low-level liquid scintillation counter using Canberra Packard Ultima Gold AB liquid scintillation cocktail.

^{125}I was counted in a well crystal (NaI(Tl)) Panax counter.

Carrier solutions of 0.9382 M NaCl and 0.7548 M NaI were prepared. The molarities of the solutions were determined gravimetrically by precipitation and weighing of the silver halides.

Samples of concrete, thought to contain radionuclides were supplied by Magnox Generation, and were taken from two power stations currently at stage 1 of the decommissioning programme. The concrete samples were taken from the reactor shield.

2.2 Method development

The principle of the method is to leach chlorine and iodine radionuclides from a sample of concrete and then add suitable oxidising agents to selectively convert the halides to halogens. The gaseous halogens are then transferred to traps containing solutions of sodium hydroxide. To increase the efficiency of leaching, the leaching solution and sample is heated and stirred.

To increase the efficiency of transfer of the halogen from the leaching solution to the trap, air is passed through the leaching solution by using an air bleed and partial vacuum (Fig. 1).

Initial studies using only ^{125}I and ^{36}Cl (added to water as $Na^{125}I$ and $Na^{36}Cl$) in solution, showed that the addition of nitric acid oxidised iodide to iodine which was then trapped in a solution of sodium hydroxide (1 M). Gamma counting of an aliquot of the solution in the flask showed that all ^{125}I had been removed from the solution. Liquid scintillation counting showed that the ^{36}Cl specific activity of the solution after removal of iodine was equal to the initial specific activity of the solution before iodine removal and therefore ^{36}Cl was not being removed along with ^{125}I. Investigations on the efficiency of removal of iodine from solution showed that the most effective acid concentration was 3 M and above. After removal of iodine, addition of a solution of potassium permanganate to the solution oxidised chloride to chlorine which was then trapped in fresh sodium hydroxide solution. The transfer and trapping procedure was completed in about six hours. Results (Fig. 2) showed that ~90% of the iodine activity and ~70% of the chlorine activity was transferred from the reaction vessel to the alkali traps. 100% recoveries of iodine and chlorine are not essential as inactive iodide and chloride carrier solutions can be added to the leaching solution. The recoveries of the carriers in the sodium hydroxide solutions can be determined gravimetrically after addition of silver nitrate solution.

2.3 Preparation of spiked concrete samples

Samples of concrete containing known amounts of radionuclides are not available. Therefore, concrete 'standards' were prepared using the following method.

The concrete powder was passed through a 2 mm sieve to remove large particles. The powder (25 g) was then mixed with water (15 g) to form a slurry. The slurry was transferred to suitable moulds and ^{36}Cl and ^{125}I were added in varying activities and intimately mixed with each sample of concrete. The samples were left to dry for at least one month. After drying the samples were milled and transferred to an airtight vessel for storage. The specific activity (Bq g^{-1}) of the concrete was calculated by dividing the added activity by the dry weight. Before use, the concrete was ground to a fine powder in a mortar and pestle.

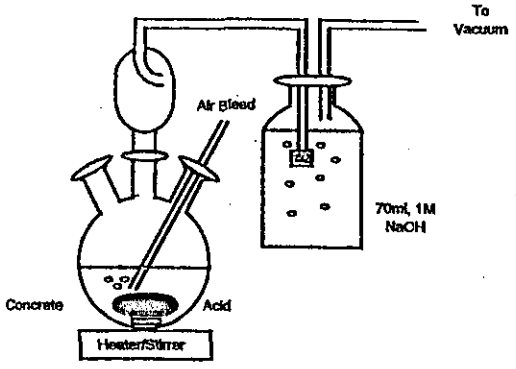


Fig. 1 Digestion and separation apparatus.

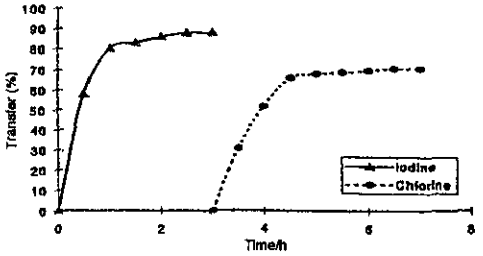


Fig. 2 Transfer of chlorine and iodine from solution.

2.4 Initial analysis of concrete

Approximately 2 g of ground concrete were accurately weighed into the reaction flask (Fig. 1) and 1 g of NaCl and 0.7 g of NaI carrier solutions added. 50 cm^3 of 3 M nitric acid were added to the flask and the sample was then heated (70 °C) and stirred for 3 h. After 3 h the sodium hydroxide in the trap was transferred to a beaker (T1) and replaced by fresh sodium hydroxide. Potassium permanganate solution was added to the flask to oxidise chloride to chlorine. The sample was heated and stirred for a further three hour period. After three hours, the sodium hydroxide was transferred to a beaker (T2). Halogen gas dissolving in sodium hydroxide solution will form halate and halide species. To reduce the halate species to halides, hydrazine was added to T1 to reduce iodate to iodide and sodium nitrite solution was added to T2 to reduce chlorate to chloride. Silver nitrate solution was then added to T1 and T2 to precipitate the silver halides which were then washed, dried and weighed. The recoveries of the carriers were then calculated. ^{125}I activity was determined by direct counting of the precipitate in a well crystal (NaI(Tl)). ^{36}Cl activity was determined by dissolving the AgCl precipitate in the minimum volume of concentrated ammonia and diluting to 5 cm^3 with water. After addition of 13 cm^3 of liquid scintillation cocktail (Ultima Gold AB), the sample was allowed to dark adapt before counting in a Canberra Packard 2750 liquid scintillation counter.

Table 1 shows the results from four different concrete samples. The results show that the gravimetric yield of the inactive iodide carrier is much higher than the recoveries of the ^{125}I. However, the recoveries of the inactive chloride carrier are similar to the chloride activity recoveries. These results suggest that the iodide carrier is oxidised and transferred to the sodium hydroxide trap faster than the leaching rate of ^{125}I from the concrete sample. This effect was not observed in initial studies on transfer efficiency when both inactive and active iodide were present in solution and concrete was absent (Table 2). To investigate this problem further, four recovery experiments were carried out in which active $^{125}I^-$ and inactive $^{127}I^-$ were both in solution (concrete absent), $^{125}I^-$ was mixed into the concrete and $^{127}I^-$ added as a solution, $^{127}I^-$ was mixed with the concrete and $^{125}I^-$ added as a solution and, finally, both $^{125}I^-$ and $^{127}I^-$ were mixed with concrete. The results shown in Table 2 show that when the active and inactive iodide are either both in solution or in the concrete, the gravimetric recovery of the inactive carrier is similar to the yield of the active iodide. However, if one is present in the concrete and the other is added as a solution, the transfer rate from solution is higher than the leaching rate from the concrete and therefore the added iodide only acts as a carrier for that fraction of the ^{125}I that has been

Table 1 Weight and activity recoveries—results from concrete standards

	AgI			AgCl		
Sample	Carrier recovery (%)	Activity recovery (%)	Ratio	Carrier recovery (%)	Activity recovery (%)	Ratio
1	102	51.2	1.99	54.6	54.1	1.01
2	77.3	45.7	1.69	64.1	67.1	0.96
3	90.2	46.2	1.95	68.9	65.4	1.05
4	97.5	38	2.57	85	86	0.99

leached from the concrete. The effect observed is that leaching is incomplete so the ^{125}I in the sample has not attained equilibrium with the carrier. Problems do not arise with the chloride analysis because the concrete was contacted with nitric acid for a sufficient time to allow all the chloride to leach from the concrete before addition of potassium permanganate. Thus, both inactive and active chloride were present in solution and were removed from solution at the same rate.

The experiments and results described above, show that nitric acid can not be used to break down the concrete and leach the halides. The halides must be leached from the concrete before oxidation to halogens. With this in mind, subsequent experiments were conducted using sodium hydroxide solution, containing inactive halide carriers. The hydroxide was used to leach the halides from concrete and bring them into solution. After a suitable contact time, addition of nitric acid oxidises both carrier and active iodine which are then removed from solution at the same rate.

2.5 Revised analysis of concrete

To a sample of concrete containing ^{125}I and ^{36}Cl, iodide and chloride carrier solutions were added. The concrete was partly digested and leached with sodium hydroxide (20 cm^3, 6 M) for 1 h at 70 °C. After 1 hour, 45 cm^3 of 8 M nitric acid were added to the reaction vessel which resulted in a nitric acid concentration of approximately 3 M. Maintaining the temperature at 70 °C, air was passed through the reaction mixture to purge iodine from the flask. The radioactive and inactive iodine were trapped in sodium hydroxide. After approximately three hours, the sodium hydroxide solution was changed and potassium permanganate solution added to the flask. After a further three hours of air purging, purging was stopped and hydrazine was added to the iodine containing sodium hydroxide and sodium nitrite solution to the chlorine containing sodium hydroxide solution. Silver nitrate solution was added to both solutions and silver iodide and silver chloride precipitated. After washing, drying and weighing both precipitates, the recoveries of the carriers were calculated and iodine activity measured in the well crystal. Ammonia was added to the silver chloride solution before adding the liquid scintillation cocktail and counting the chlorine in a liquid scintillation counter.

The experiments shown in Table 2 were repeated using the modified digestion/leaching process and the results are shown in Table 3. The results show that the modified digestion/leaching method produces similar recoveries for both the active and inactive iodine. Data shown in Fig. 3 from a large number of separate determinations of activity and carrier recoveries for iodine and chlorine shows that, within acceptable experimental error, the method reliably gives activity/carrier recoveries close to one. Within Fig. 3, it may be noted that there is a greater degree of scatter associated with the results obtained for iodine measurements. The enhanced scatter is due to the short counting time (5 min), the relatively high background (0.6 cps) and the low levels of activities (~0.8 Bq g^{-1}) of the ^{125}I in the samples.

Figs. 4 and 5 show the results obtained from the analyses of 2 g concrete samples spiked with different activities of ^{125}I and ^{36}Cl. The results show excellent correlation between added activities and recovered activities.

3 Statistical analysis

3.1 Counting efficiency

Counting efficiency, E_c, was calculated for the gamma counter (^{125}I) and the liquid scintillation counter (^{36}Cl) using the following expression:

$$E_c = \frac{C_t - C_s}{A_s M} \quad (1)$$

in which C_t and C_s are the count rates (counts s^{-1}) for the sample plus standard and the sample respectively, A_s is the specific activity of the standard (Bq g^{-1}) and M is the mass of the radioactive standard (g) added. The counting efficiency for ^{36}Cl was 97% and for ^{125}I was 21%. The counting efficiency for ^{129}I was 10% and this was determined on an EG&G Ortec Hyperpure detector (GMX-25) at Magnox Generation.

The specific activity (A) of the concrete is calculated using the following:

$$A\left(\text{Bq g}^{-1}\right) = \frac{\left(C_s - R_b\right)}{M_c E_c R_c} \quad (2)$$

Where C_s is the count rate of the sample, R_b is the background count rate (both in counts s^{-1}), M_c is the mass of concrete analysed (g), R_c is the carrier recovery and E_c is the counting efficiency.

Table 2 Analysis of concrete blocks indicates that discrepancy in AgI results were due to matrix effects

Sample		1	2	3	4
Doping details	I-125	In solution	In matrix	In solution	In matrix
	I-127	In solution	In solution	In matrix	In matrix
Carrier recovery %		93	91	59	90
Activity recovery %		94	53	89	88
Carrier/activity recovery ratio		0.99	1.72	0.66	1.02
Explained by matrix effects?		Yes	Yes	Yes	Yes

Table 3 Dissolution of concrete using concentrated alkali overcomes matrix problems encountered using acid dissolution

Sample		1	2	3	4
Doping details	I-125	In solution	In matrix	In solution	In matrix
	I-127	In solution	In solution	In matrix	In matrix
Sodium hydroxide dissolution					
Carrier recovery (%)		92	86	90	83
Activity recovery (%)		89	89	88	84
Carrier/activity recovery ratio		1.03	0.97	1.02	0.99
Matrix effect?		No	No	No	No

3.2 Counting error

The error is determined at the 95% confidence level (k = 1.65) and is based on a count time of 30 min for spiked concrete. For decommissioning samples the count time was increased to 360 min to reduce uncertainty associated with the result. The error, which is based on counting statistics alone is calculated using:

$$\text{Counting error} = \frac{1.65(\text{total count} + \text{background count})^{\frac{1}{2}}}{T E_c} \quad (3)$$

Where T is the total counting time in seconds.

3.3 Minimum detectable amount (MDA)

The MDA of ^{129}I or ^{36}Cl in a concrete sample can be calculated by using:[15]

$$\text{MDA} = \frac{k^2}{T} + 2k\left(\frac{2R_b}{T}\right)^{\frac{1}{2}} \times \frac{1}{M_c E_c R_c} \quad (4)$$

Where T is the total counting time in seconds, R_b is the background count rate in counts s^{-1}, k is the error multiple (95% confidence limit, k = 1.65). In a typical analysis 2 g of concrete is analysed. For ^{36}Cl, the average carrier recovery is generally between 80 and 90% and the counting efficiency about 97%. For a background count rate of 0.257 counts s^{-1} and a 360 min count, the MDA for ^{36}Cl is 9.7 mBq g^{-1}. For ^{129}I, the average carrier recovery is approximately 90% and the counting efficiency ~10%. For a count time of 360 minutes and a background count rate of 0.032 counts s^{-1}, the MDA for ^{129}I is 31.7 mBq g^{-1}. For ^{125}I (used in the development work) the average carrier recovery was 90%, the counting efficiency was 21% and the background count rate was found to be 0.577 counts s^{-1}, based on these figures the MDA for ^{125}I was found to be 0.33 Bq g^{-1}. The MDA for ^{36}Cl and ^{129}I are much less than the required deminimis limit of 0.4 Bq g^{-1}.

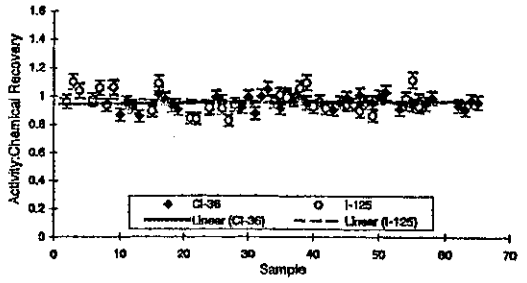


Fig. 3 Reproducibility studies. Analysis of Cl-36 and I-125 in concrete.

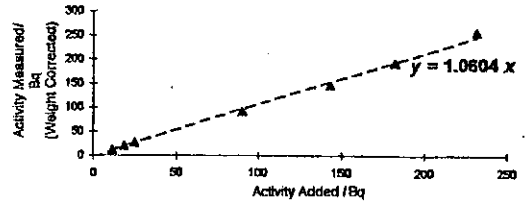


Fig. 4 Graph showing relationship between activity added and activity measured for ^{36}Cl in concrete samples (2 g), R^2 = 0.9964.

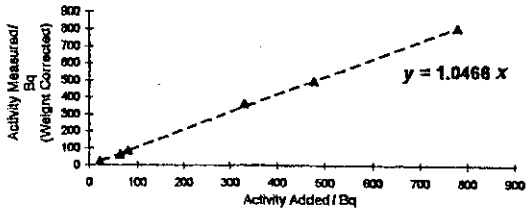


Fig. 5 Graph showing relationship between activity added and activity measured for ^{125}I in sample (2 g), R^2 = 0.9993.

4 Control experiments

4.1 Counting efficiency of ^{125}I/^{129}I and ^{36}Cl

The counting efficiency of ^{125}I or ^{129}I depends largely on the mass of silver iodide precipitate counted. If the mass of precipitate remains constant, the counting efficiency remains constant. The mass of the iodide precipitate is determined by the mass of added carrier since concrete is not likely to contain iodide to any great extent. However, ^{36}Cl is counted by liquid scintillation counting and, as concrete may contain chloride, the mass of chloride recovered may not simply depend upon the mass of the added carrier. The effect of mass of chloride in the counting sample was therefore determined by adding a known activity of ^{36}Cl to varying amounts of chloride as carrier. After addition of silver nitrate solution, the precipitates were dried and weighed. The precipitates were then dissolved in 2 cm^3 of concentrated ammonia and 5 cm^3 of water added along with 13 cm^3 of Ultima Gold AB. The samples were then mixed thoroughly and dark adapted for 1 h before being counted. After each sample had been counted it was spiked with a known amount of ^{36}Cl and re-counted. Results showed that the counting efficiency for ^{36}Cl varied from 96.7% to 98.2% and was therefore almost independent of the amount of chloride present (between 0.09 g and 0.15 g of AgCl).

4.2 Determination of background

When analysing concrete samples which may contain radionuclides close to MDA values, accurate determinations of background count rates are essential. To determine background count rates, three inactive concrete samples (2 g each) were prepared to which calibrated inactive sodium chloride and sodium iodide solutions were added. After following the method described above, the background count rates were determined as 0.257 counts s^{-1} for ^{36}Cl, 0.577 counts s^{-1} for ^{125}I and 0.032 counts s^{-1} for ^{129}I.

4.3 Stability of aqueous–cocktail mixture

When counting aqueous samples in liquid scintillation counting for long count times, it is essential that the mixture remains stable during the counting time. To check this, a counting standard was prepared by adding AgCl and ^{36}Cl to 2 cm^3 of concentrated ammonia. 5 cm^3 of water and 13 cm^3 of Ultima Gold AB were added to the ammonia solution. The sample was counted repeatedly for 30 min over 1 month. The count rate was found to remain constant (within counting statistics) over the counting period.

4.4 Reproducibility

To determine the reproducibility of the method, six aliquots of concrete of different masses were taken from a prepared concrete standard. The standard had been spiked with 11.8 Bq g^{-1} of ^{36}Cl and 15.06 Bq g^{-1} of ^{125}I. The concrete samples were then analysed by the method previously described. Table 4 shows the results of the repeatability tests. The results have been corrected for counting efficiencies, carrier recoveries and

Table 4 Repeatability of proposed method for ^{36}Cl and ^{125}I

^{36}Cl

Sample	Concrete mass/g	Activity recovery (%)	Carrier recovery (%)	Ratio activity : carrier	Concrete activity/Bq g^{-1}	^{36}C Recovery (%)
1	1.3389	65.8	69.2	0.951	11.25	95.3 ± 1.21
2	1.4555	65.6	65.9	0.995	11.72	99.3 ± 1.25
3	2.0446	79.2	81.2	0.975	11.64	98.6 ± 1.62
4	4.8521	75.5	74.4	1.015	12.07	102 ± 2.38
5	2.8414	76.2	77.1	0.988	11.43	96.6 ± 1.83
6	6.8335	89.2	87.1	1.024	11.90	101 ± 3.00
			Average activity/Bq g^{-1}		11.66 ± 0.6	
				Error (%)	5.15	

^{125}I

Sample	Concrete mass/g	Activity recovery (%)	Carrier recovery (%)	Ratio activity : carrier	Concrete activity/Bq g^{-1}	^{125}I Recovery (%)
1	1.3389	82.7	102	0.77	11.63	77.3 ± 9.6
2	1.4555	78.7	83.5	0.94	14.19	94.3 ± 10.5
3	2.0446	78.2	83.1	0.94	14.16	94.0 ± 15.0
4	4.8521	77.2	86.3	0.90	13.49	89.6 ± 18.7
5	2.8414	79.8	83.4	0.96	14.40	95.6 ± 18.4
6	6.8335	74.7	86.4	0.86	13.01	86.4 ± 23.1
			Average activity/Bq g^{-1}		13.48 ± 2.1	
				Error (%)	15.6	

weights of sample. For ^{36}Cl the results show that there is good agreement between carrier and activity recoveries and that the recoveries are high even at high sample masses. For ^{125}I the carrier and activity recoveries are not in as close agreement. This is due to a number of factors including the activity of ^{125}I in the sample and the associated counting errors. Since ^{125}I has a half-life of 60 days, the activity of the sample had decreased significantly by the time the sample was analysed. When counted the activity of the sample had decayed to 0.6 Bq g^{-1} (*cf.* MDA 0.33 Bq g^{-1}), this low activity coupled with the low counting efficiency (21%) led to significant uncertainties within the result and subsequent scatter. The results for the analyses of ^{125}I appear to show that there is a systematic difference between the percentage activity recoveries and the percentage carrier recoveries. However, Fig. 3 shows that this is not the case and there are positive and negative deviations from the ideal ratio of 1.

5 Analysis of real concrete samples

Samples of concrete were supplied by Magnox Generation and came from the reactor shield in a power station currently at stage 1 of the decommissioning programme. The concrete consisted of coarse aggregate material and a small amount of fine powdered particulates.

Samples of concrete were analysed using the proposed method. Only small sample sizes were used in the analyses because of the limited sample size and because the repeatability of the analyses needed to be checked using real samples.

Table 5 shows the results of the analyses which have been corrected for counting efficiencies and for carrier recoveries.

Table 5 Results obtained for analysis of ^{36}Cl in decommissioning sample

Decommissioning concrete sample		
Weight of sample/g	Carrier recovery (%)	Activity/Bq g^{-1}
1.3060	86	2.30 ± 0.02
0.9423	90.9	1.63 ± 0.02
1.1761	95.2	1.88 ± 0.02
2.2243	93.6	1.87 ± 0.03
	Average activity/Bq g^{-1}	1.92 ± 0.05

6 Conclusion

A method has been developed to determine radionuclides of iodine and chlorine in concrete. Sequential oxidation of iodine and chlorine from samples of concrete provide high recoveries and low minimum detectable amounts of radionuclides. The MDAs for ^{129}I and ^{36}Cl are significantly less than the required limit of 0.4 Bq g^{-1}. Major advantages of the method are that large samples of concrete may be analysed and the method is reliable, simple and requires little operator supervision. The method uses apparatus and equipment normally available at most reactor sites or nuclear plants.

Acknowledgements

This work was funded under the UK Nuclear Industry Management Committee programme and is published with the permission of Magnox Electric. The authors would like to thank Magnox Generation for the supply of concrete material.

References

1 Atomic Energy and Radioactive Substances 1986 No. 1002. The radioactive Substances (Substances of Low Activity) Exemption *Order 1986.*

2 IMC Programme on Waste Decommissioning, 1996/1997. IMC Reference No.WD/GNSR/5009.

3 *CRC Handbook of Chemistry and Physics*, ed. D. R. Lide, CRC Press, Boca Raton, FL, 72nd edn., *1991.*

4 H. E. Gabler and K. G. Heumann, *Fresenius' J. Anal. Chem.*, 1993, 346, 426.

5 L. D. Felstead and P. B. Woolham, *A Central Electric Generating Board Report No.TPRD/0386/N84*, 1984.

6 UK Nirex Ltd., The 1994 Radioactive Waste Inventory, 1996, *Report No. DOE/RAS/96.001.*

7 A. E. Ogard, J. L. Thompson, R. S. Rundberg, K. Wolfsberg, P. W. Kubik, D. Elmore and H. W. Bentley, *Anal. Chim. Acta.*, 1988, 44–45, 213.

8 P. Höltä, A. Hautojärvi and M. Hakanen, *Radiochim. Acta*, 1992, 58/59, 285.
9 E. Glueckauf, *Atomic Energy Waste—Its Nature, Use and Disposal*, Intersciences Publishers Incorporation, New York, 1961.
10 J. Handl, *Radiochim. Acta.*, 1996, 72, 33.
11 O. Meirav, M. Adam, E. Boaretto, S. A. Dias, R. R. Johnson, M. Paul and E. Venczel, *Appl. Radiat. Isot.*, 1992, 43, 420.
12 N. Boukis and E. Henrich, *Radiochim. Acta*, 1990, 54, 103.
13 J. D. Lamb, F. R. Nordmeyer, R. G. Smith, A. Van Orden, R. Allison and R. P. Lash, *J. Radioanal. Nucl. Chem.*, 1992, 159, 285.
14 L. K. Swafford, A. M. Meeks and J. M. Keller, Eichrom Technical Note, Eichrom Industries, Inc, 8205 S. Cass Ave., Suite 107 Darien, IL 60561, USA.
15 L. A. Currie, *Anal. Chem.*, 1968, 40(3), 586.

Paper 8/09292C