Method development for the determination of radionuclides in environmental materials

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Method Development

for the Determination of Low-levels of Radionuclides in

Environmental Materials

by

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Doctor of Philosophy
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A philosopher once said "It is necessary for the very existence of science that the same conditions always produce the same results" - Well, they don't.

Richard Feynmann.

CONTENTS

ABSTRACT

^{90}Sr is one of the most biologically hazardous radionuclides produced by nuclear fission. If released into the environment, it can be transferred to humans via the food chain, principally from dairy products. Due to its chemical similarity to calcium, it becomes incorporated into the bones where it emits its moderately energetic β-particles with a half-life of 28.8 years. It is therefore important that the levels of ^{90}Sr in the environment and foodstuffs are closely monitored.

Many of the current methods for ^{90}Sr determinations in environmental materials are time consuming and labour intensive, which gives rise to costly methods of analysis. Here, the development of a semi-automated method for the determination of ^{90}Sr in milk and other liquid matrices using ion-chromatography, which attempts to overcome these problems, is described. The method is based on the isolation and measurement of the ^{90}Y daughter in secular equilibrium with ^{90}Sr to derive the ^{90}Sr activity present.

^{90}Y is initially extracted from the sample solution, buffered to pH 5, onto an iminodiacetic acid chelating resin. At this pH, transition metals, lanthanides and actinides are also extracted. The extracted metals are then transferred to an anion-exchange column for separation as weak acid anionic complexes. ^{90}Y is separated from other extracted metals using an oxalate - diglycolate eluant. The eluted ^{90}Y, which is free from interfering radionuclides, is then fraction collected and β-counted.

The ion-chromatography system permits the analysis of water samples with a minimum of sample pretreatment, however, the analysis of milk is hampered by the inability of the chelating resin to successfully extract ^{90}Y in the presence of large concentrations of calcium. The use of strontium-selective crown ether resins was investigated to provide a simple step to reduce the calcium present to suitable levels for the ion-chromatography system. However, the success of these resins was limited by the large concentrations of potassium present in milk.

The analysis of milk was facilitated by partially precipitating $CaHPO_4.2H_20$ from an acid digested sample. The precipitate quantitatively carries ^{90}Y and the calcium present on the precipitate is sufficiently low for the ion-chromatography system. The analysis of urine is also facilitated by the inclusion of an oxalate precipitation step. Chemical recoveries of 92, 90 and 81 % for natural waters (1 litre), urine (300 ml) and milk (1 litre)respectively are reproducibly achievable using the developed methods. The minimum detectable activities achievable using gas flow proportional counting are 20, 60 and 22 mBq l^{-1} for water, urine and milk respectively. The methods have been validated using reference materials

The developed methods were subsequently applied to the analysis of lanthanide fission products and chemical recoveries similar to those for the ^{90}Sr method are achievable. The use of ion-chromatography in conjunction with precipitation steps therefore provides potential for multi-radionuclide determinations in liquid matrices.

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Chapter 1

INTRODUCTION

1 INTRODUCTION

1.1 Overview and objectives

Radionuclides are present in the environment from several sources. Some are naturally occurring and others are in the environment due to man. The presence of naturally occurring radionuclides has meant that we have always been exposed to radioactivity and its associated hazards. Since the advent of the nuclear era, a large variety of new radionuclides have been added to the environment, thus providing us with new sources of exposure. Public concern over environmental pollution with man-made radionuclides has meant that the levels of these have to be closely monitored. As a result of this, many laboratories have become involved with the environmental monitoring of radionuclides and considerable efforts have been made to develop methods for their determination from various environmental sources. The Environment and Energy section at AEA Technology, Harwell Laboratory, Oxfordshire is one of the laboratories involved in the monitoring of radionuclides in the environment and is constantly looking for improved methods of analysis for use in their monitoring programme.

^{90}Sr is a particularly biologically hazardous radionuclide that has been released into the environment as a result of nuclear fission processes. Unfortunately, many of the methods currently available for monitoring ^{90}Sr are labour intensive, which gives rise to time consuming and costly analyses. The primary objective of the work presented in this thesis was to develop an improved method for the determination of ^{90}Sr in environmental materials to replace the solvent extraction approach currently in use in AEA Technology's monitoring programme. The sample material of principal interest was milk because this provides a major route for transfer of ^{90}Sr to man from the environment. A secondary objective of the work was to determine if it was possible to develop the ^{90}Sr method in such a way that it could be applied to the analysis of

other radionuclides of interest, thus providing a more general method of analysis.

This chapter aims to provide a brief introduction to radionuclides in the environment, the properties of ^{90}Sr and current approaches for its determination in environmental materials.

1.2 Radionuclides in the environment [1-2]

Radionuclides in the environment can be divided into two principal categories according to their origin. There are those that occur naturally in the environment and there are those that are man-made.

1.2.1 Naturally occurring radionuclides

There are three types of naturally occurring radionuclides present in the environment. These are primordial radionuclides, radionuclides produced by the decay of primordial radionuclides and cosmic ray produced radionuclides. Primordial radionuclides have been present since the formation of the earth and generally have half-lives of approximately the age of the earth (4.55×10^9 years). The most common of this type of radionuclide present in the environment is ^{40}K (half-life = 1.28×10^9 years) which has an isotopic abundance of 0.0118 % giving rise to an activity of approximately 30.7 Bq g^{-1} of potassium. Other important primordial radionuclides include ^{238}U (half-life = 4.51×10^9 years); ^{235}U (half-life = 7.1×10^8 years); ^{232}Th (half-life = 1.4×10^{10} years). These are the parents of three natural decay series, which involve a sequence of intermediate radioactive decays which gives rise to the formation of other radionuclides and finally terminates in a stable lead isotope. An important radionuclide produced by the decay of ^{238}U is ^{222}Rn (half-life = 3.82 days), which presents a serious radiological hazard due to its gaseous nature, which means that it is readily inhaled. It is of particular interest

because it may be found in high concentrations in houses built in areas where the natural uranium concentration is high.

Cosmic ray produced radionuclides are produced at a relatively constant rate by nuclear reactions involving the interaction of cosmic rays with the earth's atmosphere. ^{14}C (half-life = 5730 years) is the most familiar radionuclide of this type and is produced by the capture of neutrons by ^{14}N in the atmosphere.

1.2.2 Man-made radionuclides

Man-made radionuclides are produced by the fission of uranium in a nuclear reactor and by the explosion of nuclear weapons or by the interaction of neutrons with reactor fuels or other materials. These are referred to as fission and activation products respectively. The primary source of man-made radionuclides released into the environment was the atmospheric testing of nuclear weapons during the periods 1955 to 1958 and 1961 to 1962. Man-made radionuclides have also been released into the environment in discharges from nuclear power stations and as a result of nuclear power plant accidents, notably the accident at Chernobyl on April 26th 1986.

Table 1.1 shows fission and activation products which may be released into the environment and are of concern in human exposure [3].

1.2.3 Transfer of radionuclides in the environment to humans [1,3]

Once radionuclides are released into the environment, human beings can become exposed to the associated radioactive emissions in several ways. External exposure can occur from radionuclides deposited on surfaces and from airborne radionuclides that may be deposited on the skin. Internal exposure can occur due to inhalation of airborne radionuclides and by the ingestion of water and foodstuffs that have become

contaminated. Figure 1.1 shows the routes to human exposure for radionuclides released into the atmosphere, which may arise due to a nuclear weapons explosion or a nuclear reactor accident. Figure 1.2 shows the routes for radionuclides released into ground and surface waters which may be present due to controlled discharges from nuclear power stations.

	Radionuclide	Half-life	Fission yield %	Major decay
Fission products	Sr-89	50.5 d	4.77	β^-
	Sr-90 , Y-90	28.8 a, 64.1 h	5.76	β^-,β^-
	Zr-95, Nb-95	640.9 d, 35.0 d	6.51	$\beta^-\gamma$, $\beta^-\gamma$
	Mo-99 , Tc-99m	2.747 d, 6.006 h	6.09	$\beta^-\gamma$, $\beta^-\gamma$
	Ru-103 , Rh-103m	39.272 d, 56, 116 min	3.03	$\beta^-\gamma$, $\beta^-\gamma$
	Ru-106, Rh-106	372.6 d, 29.92 s	0.4	β^-, $\beta^-\gamma$
	Te-129m	33.6 d	0.661	$\beta^-\gamma$
	I-131	8.021 d	2.875	$\beta^-\gamma$
	Te-132	76.856 h, 2.3 h	4.282	$\beta^-\gamma$, $\beta^-\gamma$
	Cs-137, Ba-137 m	30.0 a, 2.55 min	6.136	β^-, γ
	Ba-140 , La-140	12.751 d, 1.6779 d	6.134	$\beta^-\gamma$, $\beta^-\gamma$
	Ce-144 , Pr-144	284.45 d, 17.28 d	5.443	$\beta^-\gamma$, $\beta^-\gamma$
Activation products	H-3	12.35 a		β^-
	C-14	5730 a		β^-
	Fe-55	2.75 a		EC
	Fe-59	44.53		$\beta^-\gamma$
	Mn-54	312.5 d		EC, γ
	Co-60	5.27 a		$\beta^-\gamma$
	Zn-65	243.9 d		EC, γ
	Cs-134	754.2 d		$\beta^-\gamma$
	Np-239	2.355 d		$\beta^-\gamma$
	Pu-241, Am-241	14.35 a, 432.0 a		β^-, $\alpha\gamma$
	Cm-242	162.94 d		α
	Pu-238	87.7 a		α
	Pu-239	2.411×10^4 a		α
	Pu-240	6.563×10^3 a		α
	Pu-242	3.735×10^5 a		α

Table 1.1 Fission and activation products which may be of concern in human exposure[3]

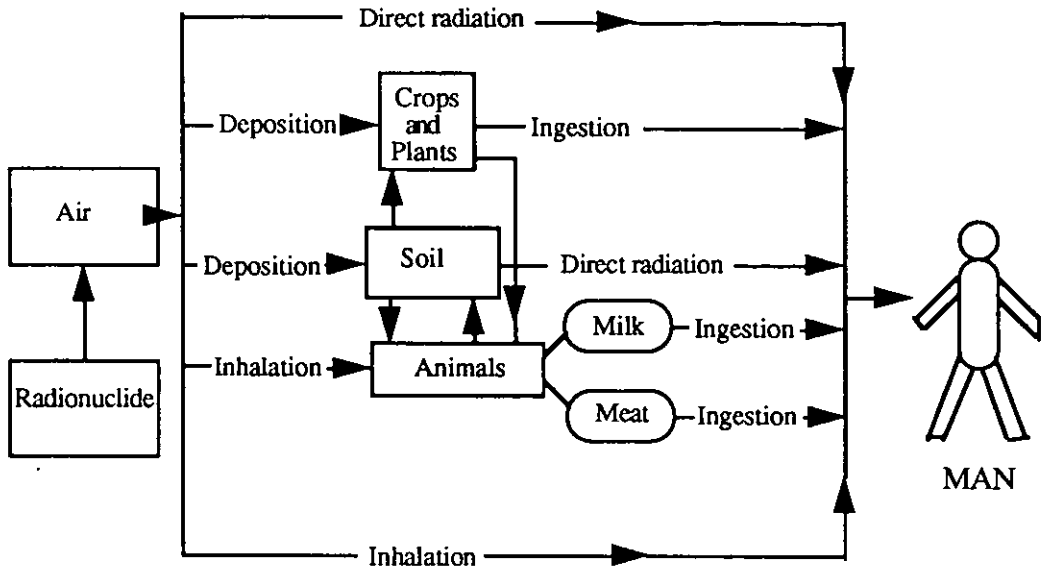


Figure 1.1 Pathways between radionuclides released into the atmosphere and man

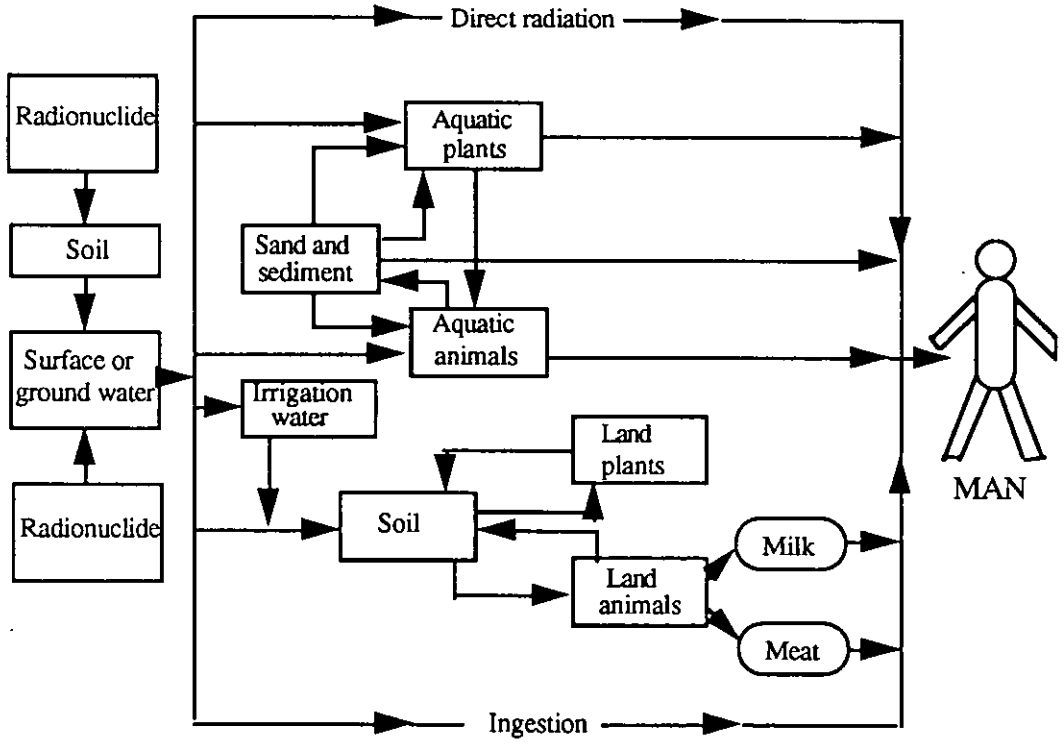


Figure 1.2 Pathways between radionuclides released into ground and surface waters and man

The exposure of humans to radionuclides is of great concern due to the health hazards associated with their radioactive emissions [4]. It is therefore important that the levels of radionuclides released into the environment are closely monitored to ensure that the levels do not pose a serious threat to human health. To enable the successful monitoring of radionuclides in the environment, methods of analysis are required to permit the determination of radionuclides of radiological importance in a variety of environmental materials. Many of the commonly used methods are documented in readily available procedures manuals [5-6]. The radionuclides that are considered of major importance in the contamination of environmental materials and foodstuffs are listed in table 1.2.[3]

Sample	Radionuclide
Air	^{131}I , ^{134}Cs , ^{137}Cs
Water	^{3}H , ^{89}Sr , ^{90}Sr , ^{131}I , ^{134}Cs , ^{137}Cs
Milk	^{89}Sr , ^{90}Sr , ^{131}I , ^{134}Cs , ^{137}Cs
Meat	^{134}Cs , ^{137}Cs
Other foods	^{89}Sr , ^{90}Sr , ^{134}Cs , ^{137}Cs
Vegetation	^{89}Sr , ^{90}Sr , ^{95}Zr , ^{95}Nb , ^{103}Ru , ^{106}Ru , ^{131}I , ^{134}Cs , ^{137}Cs , ^{141}Ce , ^{144}Ce
Soil	^{90}Sr , ^{134}Cs , ^{137}Cs , ^{238}Pu , ^{239}Pu , ^{240}Pu , ^{241}Pu , ^{242}Cm

Table 1.2 Radionuclides of major importance in the contamination of food and environmental samples

It is clear from table 1.2 that ^{90}Sr is of considerable importance in contamination of environmental materials and foodstuffs, hence the need for methods for its analysis in particular.

1.3 Strontium-90

1.3.1 Occurrence and properties of ^{90}Sr [1,7]

^{90}Sr is a fission product of ^{235}U and it was released into the environment mainly as a result of the nuclear weapons testing during the 1950's and 1960's. It is produced with a fission yield of approximately 5.76 % which is equivalent to 3.7×10^{15} Bq of ^{90}Sr per megaton of fission. ^{90}Sr may be formed directly as a result of the fission process or it may be formed shortly after the fission by the decay of the short lived ^{90}Kr as described below:

$$^{90}Kr \xrightarrow[\text{half-life= 32.3 s}]{\beta^-} {}^{90}Rb \xrightarrow[\text{half-life= 2.6 min}]{\beta^-} {}^{90}Sr$$

Essentially all the ^{90}Sr released into the atmosphere as a result of the weapons testing prior to the test ban agreement in 1963 was deposited on the earth's surface by 1970. The worldwide deposition of ^{90}Sr reached a peak of approximately 4.6×10^{17} Bq by 1967 and the amount of ^{90}Sr deposited has diminished at a rate of 2.5 % per year due to radioactive decay although this has been partially offset by tests by France and China since the agreement. More recently, approximately 8.1×10^{15} Bq of ^{90}Sr was released into the atmosphere as a consequence of the Chernobyl nuclear power plant accident.

^{90}Sr is a pure β-emitter which decays to ^{90}Y which is also a pure β-emitter which in turn decays to the stable isotope ^{90}Zr. The decay sequence is summarized below:

$$^{90}Sr \xrightarrow[\text{half-life= 28.8 a}]{\beta^-} {}^{90}Y \xrightarrow[\text{half-life= 64.1h}]{\beta^-} {}^{90}Zr \text{ (stable)}$$

The maximum β-particle energies ($E_{\beta max}$) of ^{90}Sr and ^{90}Y are 543 keV and 2280 keV respectively [8] and the average β-particle energies for ^{90}Sr and ^{90}Y are 200 keV and

930 keV respectively [9]. An effect of the half-life of the ^{90}Sr parent being much greater than that of the ^{90}Y daughter is that a state of radioactive equilibrium is established between the two radionuclides in which the activity of the two radionuclides is equal and the activity of the ^{90}Sr parent does not decrease measurably during many of the ^{90}Y daughter's half-lives. This state of radioactive equilibrium is referred to as secular equilibrium. A more detailed description of radioactive equilibria is described by Frielander et. al. [10]. If pure ^{90}Sr is isolated, the ^{90}Y will ingrow and establish secular equilibrium after approximately fifteen days. At secular equilibrium, it is possible to measure the levels of ^{90}Sr in a material by directly measuring the levels of ^{90}Y present and this is made use of in many of the current methods available for the determination of ^{90}Sr.

Strontium is a divalent element of the alkaline-earth metal group. Its electronic structure is [Kr] $5s^2$ and the ionic radius of Sr^{2+} is 127 pm [11]. Its chemical properties are similar to those of calcium. The chemical similarity of strontium and calcium means that in many of the methods for determining ^{90}Sr in environmental samples, a critical step is the isolation of ^{90}Sr from calcium.

It was previously discussed that ^{90}Sr determinations may be based on the separation and measurement of the ^{90}Y daughter at secular equilibrium. Yttrium is a trivalent element with an electronic structure [Kr] $4d^1\ 5s^2$ and the ionic radius of Y^{3+} is 88 pm [11]. Its chemical properties are similar to those of the trivalent lanthanide elements, particularly Er^{3+} and Ho^{3+} which have ionic radii of 88 and 89 pm [11] respectively.

1.3.2 ^{90}Sr in humans [9,12-14]

Using the data from Reference Man [9], the total strontium content of the body is 0.32 g, essentially all of which is present in the skeleton and 3.3 mg is present in the

soft tissues. The daily intake of strontium in food and fluids is 1.9 mg. The fractional uptake of dietary strontium and soluble salts of the element from the gastrointestinal tract is in the range 0.2 to 0.5, however, $SrTiO_3$ is only poorly absorbed from the gastrointestinal tract. If inhaled, soluble strontium compounds are rapidly cleared from the lungs, however less soluble compounds such as $SrTiO_3$ are much more strongly retained.

Strontium retained by the body is essentially concentrated in the bone, and ^{90}Sr, like all isotopes of alkaline-earth metals with half-lives of greater than fifteen days, is assumed to be distributed throughout the volume of mineral bone following its deposition in the skeleton [13]. It has a biological half-life of approximately seven years and in that time remains in the bone until it decays. The moderately energetic β-particle ejected by the decay can cause ionization damage to the bone and the surrounding tissues, as can the highly energetic β-particle of the ^{90}Y daughter. A detailed account of the effect of ^{90}Sr decay and the subsequent ^{90}Y decay on the bone is presented in ICRP* publication 20, 1973 [13]. The annual limits on intake for ^{90}Sr are 1×10^6 Bq for oral intake and 7×10^5 Bq for inhalation of soluble strontium compounds [14].

1.3.3 Transfer of ^{90}Sr from the environment to humans [1,3]

The transfer of ^{90}Sr from the environment to humans follows the similar pathways as described in figures 1.1 and 1.2. On entering the environment ^{90}Sr becomes incorporated into the calcium pool and the principal pathway followed to man is:

soil → plant → cow's milk → humans

^{90}Sr may be incorporated into the plant by uptake from soil via the roots or more

* International Commission on Radiological Protection

directly by foliar deposition. In the latter case, ^{90}Sr can be absorbed metabolically by the plant and then transferred to the animal which consumes the plant or more likely is directly transferred to the animal by consumption. It is found that although strontium and calcium behave similarly along the pathway from the environment to man, there is some degree of discrimination in the uptake of calcium and strontium at the various stages of the transfer. In discussions concerning the transfer of ^{90}Sr through food chains, the degree of discrimination is quantified using the strontium unit (SU) where 1SU is defined as 1 pCi ^{90}Sr per gram of calcium
(1 pCi = 0.037 Bq).

The overall effect of metabolic differentiation between ^{90}Sr and calcium in passing from soil to human bone can be summarized for a milk diet as follows, starting with soil containing 1 SU:

1SU (in soil) → 1 SU (in plant) → 0.13 SU (in milk) → (0.02 SU in human bone)

Thus, very little discrimination is observed in the uptake of ^{90}Sr and calcium by plants from the soil, whereas the two other stages of the transfer show significant discrimination in the uptake of calcium relative to ^{90}Sr. These two stages can therefore essentially be considered as ^{90}Sr decontamination stages.

1.4 Determination of ^{90}Sr in environmental materials

1.4.1 General considerations [15-16]

Since the decay of ^{90}Sr and ^{90}Y is not accompanied by any γ-emission, it is not possible to measure the activity of ^{90}Sr in a sample by a direct, non-destructive method. The measurement of ^{90}Sr is achieved by the β-counting of either the ^{90}Sr itself or the ^{90}Y daughter. To convert the sample to a form that is suitable for

β-counting necessitates a complex radiochemical separation procedure. Several factors must be considered when such procedures are required. Firstly, the levels of ^{90}Sr in environmental materials may be low (1 mBq kg^{-1} to 50 Bq kg^{-1} in the northern hemisphere for various materials [1]), therefore to have a detectable amount of activity may require a large sample size. Secondly, the separated radionuclide should be obtained in high yield and with a good degree of purity. Thirdly, the radioactive emissions being measured should be detected with as high an efficiency as possible.

In order to obtain ^{90}Sr or ^{90}Y with a good degree of purity requires that the separated radionuclide is free from other radionuclides which may interfere with the β-counting and that negligible quantities of the matrix elements are present. In the methods used for the determination of ^{90}Sr in environmental materials, there are three general approaches to produce a purified fraction suitable for β-counting:

i) ^{90}Sr is separated from the sample and β-counted;

ii) ^{90}Sr is separated from the sample, the ^{90}Sr fraction is stored to permit ^{90}Y to attain secular equilibrium and the ^{90}Y is then separated and β-counted;

iii) The sample is stored prior to analysis to permit ^{90}Y to attain secular equilibrium and is then separated and β-counted.

When using an approach where ^{90}Y is separated and counted, it is important to know when it has been isolated from ^{90}Sr. The reason for this is that ^{90}Y decays rapidly due to its short half-life and in order for a reliable ^{90}Sr activity to be derived, the ^{90}Y count rate has to be accurately corrected for its decay.

The mass of ^{90}Sr and ^{90}Y that may be present in a sample (1 Bq of ^{90}Sr has a mass equivalence of approximately $2x10^{-13}$ grams) is very small compared to the several

grams of matrix elements which may be present in a suitable sample size. The very small mass prevents the use of selective precipitation techniques for the isolation of ^{90}Sr or ^{90}Y and makes their successful isolation difficult because they may be easily lost by adsorption onto glassware or filters etc. that may be used in the separation procedure. In order to increase the mass of strontium and yttrium present in the sample and therefore help to overcome these problems, milligram amounts of inactive strontium and yttrium carriers are usually added to the sample prior to separation. These may also act as chemical yield monitors for the separation procedure. In some procedures, a γ-emitting radionuclide of strontium, ^{85}Sr, may be added to the sample to act as a yield monitor [17].

1.4.2 Interferences in ^{90}Sr determinations in environmental materials [15]

Table 1.1 shows that a large variety of radionuclides may be released into the environment as a result of fission and activation processes. Therefore any method for the successful determination of ^{90}Sr must be capable of removing these potential interferences. Particularly important radionuclide interferences in ^{90}Sr determinations are ^{89}Sr, ^{140}Ba and the naturally occurring radioisotopes of radium. These, like strontium, are members of the alkaline-earth group, are chemically similar and are therefore difficult to separate from each other. The short-lived fission product ^{89}Sr (half-life = 50.5 days) is a β-emitter ($E_{\beta max} \approx 1460$ keV) [8] and since it is another strontium isotope is impossible to chemically separate from ^{90}Sr. The counting technique must therefore discriminate between the two strontium isotopes. The potential presence of ^{89}Sr is one of the reasons why many methods separate and count ^{90}Y in preference to ^{90}Sr because this provides a chemical means of removing the ^{89}Sr interference.

In addition to radionuclide interferences, various inert materials must be separated

from the ^{90}Sr. The most significant of these inert materials is calcium, which may be present in large quantities (e.g. 1 litre of milk typically contains 1 to 1.5 g of calcium [5]). Again, the chemical similarity of the two makes them difficult to separate and their separation is an essential step in many ^{90}Sr determinations in order to produce a source suitable for counting. The difficult separation step can however be avoided if ^{90}Y is isolated directly, since yttrium is trivalent, unlike the divalent strontium and calcium and it is therefore much simpler to separate ^{90}Y from calcium than it is to separate ^{90}Sr from calcium.

In determinations where ^{90}Y is directly isolated from the sample, the most important radionuclide interferences are those of the trivalent lanthanides, e.g. ^{140}La, ^{141}Ce and ^{147}Nd. This is due to the chemical similarity between the lanthanides and yttrium which makes them difficult to separate. The presence of the short -lived fission product, ^{91}Y (half-life = 58.5 days), also presents a potential interference when ^{90}Y is directly isolated. ^{91}Y is also a β-emitter ($E_{\beta max}$ = 1546 keV) [8] and if present, the counting technique would have to discriminate between it and ^{90}Y.

1.5 Methods for the determination of ^{90}Sr in environmental materials [16]

Although numerous methods are available for determining ^{90}Sr in environmental materials, they generally involve three main stages:

i) Sample pretreatment;
ii) Chemical separation of ^{90}Sr or ^{90}Y;
iii) β-counting.

The sample pretreatment and counting stages are similar for many of the methods, whereas the chemical separation step can vary significantly from method to method.

1.5.1 Sample pretreatment

The role of the sample pretreatment stage is to concentrate the analyte prior to its chemical separation by removing a large proportion of the original sample matrix. Sample pretreatment usually consists of the drying and ashing of solid samples, the evaporation and ashing of liquid samples and then acid digestion of the resulting residues. This converts the sample material to a dissolved form which is free from organic materials which may interfere with the subsequent chemical separation. The concentration of ^{90}Sr or ^{90}Y from aqueous samples may be achieved directly from the sample using co-precipitation, ion-exchange or solvent extraction techniques. These may yield radiochemically pure strontium and yttrium fractions at the sample pretreatment stage or soon after without elaborate chemical separation schemes. However, for more complex materials, chemical separation work is required.

1.5.2 Chemical separation

The chemical separation step in ^{90}Sr determinations follow three general approaches which are based on selective precipitations, solvent extraction and ion-exchange.

1.5.2.1 Chemical separation using selective precipitations

The classical approach for the determination of ^{90}Sr involves the near specific precipitation of strontium as strontium nitrate from cold fuming nitric acid solution, which was first reported by Willard and Goodspeed [18] and later studied in detail by Sundermann and Meinke [19]. This precipitation permits the separation of ^{90}Sr from the large amounts of calcium present due to the greater solubility of calcium nitrate under these conditions. Barium and radium are precipitated with the strontium but can be removed by a barium chromate precipitation at pH 5[20]. The purified strontium fraction can then be precipitated as the oxalate and counted [20]. If ^{90}Y rather than ^{90}Sr is counted, then the purified strontium fraction is stored to allow ^{90}Y

to attain secular equilibrium and then separated from the ^{90}Sr by precipitation of yttrium hydroxide [3,5] or ferric hydroxide [17]. The yttrium is then converted to the oxalate and counted [3,5]. Table 1.3 presents a version of the 'nitric acid' procedure described by Wilken and Diehl [17]. This demonstrates one of the disadvantages of the procedure, which is that it contains many steps and is therefore labour intensive. Other disadvantages associated with the method are the hazardous nature of fuming nitric acid and that it is time consuming (typically six samples can be processed in approximately twenty days, including the ^{90}Y ingrowth period). Although the method has these disadvantages, it does permit the reliable determination of ^{90}Sr and has been commonly used since the 1950's.

1. Homogenization, drying and ashing of sample
2. Addition of ^{85}Sr for chemical yield determination of Sr separation
3. Hydrochloric acid extraction, sulphate precipitation
4. Soda disintegration of sulphates
5. Calcium/strontium separation using fuming nitric acid
6. Barium/strontium separation by chromate precipitation
7. Yttrium separation by ferric hydroxide precipitation
8. Measurement of ^{85}Sr using γ-ray detector to determine chemical yield
9. Wait for approximately 15 days for ^{90}Y ingrowth
10. Addition of yttrium nitrate, yttrium separation and ^{90}Y measurement
11. Determination of chemical yield for yttrium separation

Table 1.3 Procedure for ^{90}Sr determination using the 'nitric acid' approach

In order to overcome the problem of using fuming nitric acid, alternative selective precipitation approaches were developed. Weiss and Shipman isolated ^{90}Sr from calcium on strontium rhodizinate at pH 5-7 [21] and this was later applied by Boni to the analysis of a variety of environmental and biological materials [22]. Eakins and Gomm used the precipitation of strontium sulphate in the presence of ethylenediamminetetraacetic acid (EDTA) at pH 4.5 to isolate ^{90}Sr from calcium for urine samples [23]. Both these approaches required the inclusion of the barium chromate precipitation step to remove barium and radium isotopes. Bunzl and Kracke isolated ^{90}Sr from calcium based on the different solubilities of strontium and calcium oxalates at pH 2 when calcium is present in large excess [24]. Under these conditions calcium oxalate is precipitated whereas strontium oxalate remains in solution. After the ^{90}Sr separation, ^{90}Y is ingrown then isolated using both cation-exchange and solvent extraction steps. This approach is particularly suited to the analysis of calcium rich samples such as milk, bones or soils. Although these approaches negate the use of fuming nitric acid they are still time consuming and labour intensive.

1.5.2.2 Chemical separation using solvent extraction

Solvent extraction approaches have been used for ^{90}Sr determinations in a variety of environmental and biological materials. They are usually based on the extraction of ^{90}Y from strong nitric acid solutions using tributylphosphate followed by back extraction into dilute nitric acid [25-28] or by extraction into di-2-ethylhexyl phosphoric acid (HDEHP) from nitric acid solution [29-33] followed by back extraction into hydrochloric acid solution. Typically, n-hexane, n-heptane and toluene are employed as diluents for the extractants. Several extractions using different extractant and acid concentrations are required to ensure that ^{90}Y is separated from ^{90}Sr and short lived rare-earth fission products that may be present such as

^{141}Ce,^{144}Ce,^{140}La and ^{147}Nd [31], although some methods utilize single extraction conditions, thereby assuming the rare-earths to be absent. Since ^{90}Y is directly extracted, ^{90}Sr and ^{90}Y should be in secular equilibrium at the time of analysis or the position of equilibrium known accurately.

An alternative to simple solvent extraction using HDEHP was reported by Toth [34], in which the extractant was supported on an inert material and was used as the stationary phase in a chromatographic separation of ^{90}Sr. In this method ^{90}Sr was extracted onto the stationary phase from neutral solution and was finally eluted using nitric acid. This however, has not been applied to the analysis of environmental materials.

Other extractants that have been used in ^{90}Sr determinations include 2-thenoyltrifluoroacetone (TTA) [15], a cobalt complex of 3,3 - commo-bis(undecahydro-1,2-dicarbo-3-closo-decaborate) (referred to as dicarbolide-H+) [35] and macrocyclic crown ethers [36-42]. The procedure using TTA involves the extraction of ^{90}Y from solutions buffered to pH 5 followed by back extraction into hydrochloric acid. The procedure using dicarbolide-H+ involves the extraction of ^{90}Sr from nitric acid using nitrobenzene as the diluent. The crown ether employed in ^{90}Sr determinations is a dicyclohexyl-18-crown-6 which selectively extracts strontium largely based on its ionic size. The extraction permits the separation of strontium from large amounts of calcium, but further separation is required to remove barium which is also extracted by the crown ether[36]Solvent extraction separations using the crown ethers have been reported for the determination of ^{90}Sr in water and milk samples. The ^{90}Sr is extracted by the crown ether in diluents such as chloroform or dichloroethane and then back-extracted into hydrochloric acid. To ensure successful isolation of ^{90}Sr the extraction has to be carried out in conjunction

with a barium chromate precipitation [36] or ion-exchange separation [41]. Recently, resins impregnated with the crown ether have become commercially available and have been utilized for ^{90}Sr determinations in environmental samples [43-45]. These resins are described in more detail in chapter 3.

Another solvent extraction separation procedure reported by El-Dessouky et. al. [46] in which ^{90}Sr was separated from the calcium present in milk samples using a 1:1 mixture of ethanol and diethyl ether. Extraction of calcium into the organic phase occurs from nitric acid solutions whereas ^{90}Sr remains in the aqueous phase. Although the procedure separates ^{90}Sr from calcium, further steps were required to ensure total isolation of ^{90}Sr.

The procedure currently in use at AEA Technology for the determination of ^{90}Sr in milk is based on solvent extraction and is summarized in table 1.4 [33]. The procedure typically permits the simultaneous determination of six samples in two to two and a half days, excluding the ^{90}Y ingrowth period prior to analysis. The major problems with this type of solvent extraction approach are that they tend to be labour intensive and that the organic extractants and diluents used are hazardous.

1. Evaporation and ashing of milk sample
2. Addition of strontium and yttrium carriers
3. Wet ashing and dissolution of sample in nitric acid
4. Extract yttrium into HDEHP in toluene
5. Back extract yttrium into hydrochloric acid
6. Evaporate to dryness and ash, redissolve in hydrochloric acid
7. Precipitate yttrium oxalate, weigh to determine chemical yield
8. Count ^{90}Y using a proportional counter

Table 1.4 AEA Technology procedure for ^{90}Sr determination in milk by a solvent extraction approach

1.5.2.3 Chemical separation using ion-exchange

Both cation- and anion-exchange approaches have been used or the determination of ^{90}Sr in environmental and biological materials. The approaches are usually based on the elution of either ^{90}Sr or ^{90}Y from ion-exchange resins using complexing agents over a specified pH range and a few examples are presented here.

Stanley and Kruger described a method based on the adsorption of ^{90}Sr and ^{90}Y onto a cation-exchange resin followed by separation of ^{90}Y using ammoniacal citrate solution as eluant [47]. The method was later modified by Bryant et. al. to separate ^{90}Y from rare-earth fission products on a cation-exchange resin using α-hydroxybutyric acid at pH 4-5 as eluant [48].

The separation of ^{90}Sr from calcium and barium on a cation-exchange resin using ammonium lactate at pH 7-8 has been reported by several authors [49-52]. Natsume et. al. isolated ^{90}Sr from other fission products on a cation-exchange resin using ammonium citrate at pH 6.9 as eluant [53]. Amano and Yanase adsorbed ^{90}Sr and ^{90}Y onto a cation-exchange resin and eluted other fission products and calcium with a 1:1 mixture of ammonium acetate and methanol and subsequently eluted ^{90}Sr using ammonium acetate [54].

Other methods have been reported in which ^{90}Sr is adsorbed onto a cation-exchange resin and isolated from calcium and other interferences simply using dilute hydrochloric acid as eluant. One example of this approach reported by Oravec and Navarcik was a batch approach in which ^{90}Sr was concentrated onto the resin by mixing the resin with raw milk samples, then packing the resin into a column for separation of ^{90}Sr [55].

An anion-exchange approach commonly used involves adsorbing ^{90}Y as a citrate complex, buffered to pH 5, onto an anion-exchange resin [56]. The ^{90}Y is subsequently eluted using dilute hydrochloric acid.

An alternative to simple column chromatography was recently reported by Lamb et. al. who described an automated method for isolating ^{90}Sr from nuclear reprocessing solutions using ion-chromatography [57]. ^{90}Sr was adsorbed onto a cation-exchange concentrator column and then eluted onto a second cation-exchange column with other alkali- and alkaline-earth metals using D,L-2,3-diaminopropionic acid as eluant. ^{90}Sr was then isolated from the alkaline-earths using L-histidine monohydrochloride.

Although the ion-exchange procedures appear to offer a less labour intensive approach to the selective precipitation and solvent extraction approaches, they are generally hampered by the large quantities of calcium present in environmental samples and have to be used in combination with the other approaches to reduce the calcium levels and also to ensure complete decontamination of ^{90}Sr or ^{90}Y from other radionuclide interferences. Therefore, the overall procedures involving ion-exchange separations are no less labour intensive or time consuming than the other approaches. The degree of automation provided by the ion-chromatography approach should provide a significant reduction in labour intensity, however, the success of the method in the presence of environmental levels of calcium has not been demonstrated.

1.5.3 β-counting of the separated radionuclide

After chemical isolation of ^{90}Sr or ^{90}Y from the sample, the pure β-emissions from these radionuclides may be detected by proportional counting, liquid scintillation

counting or Cerenkov counting. Detailed descriptions of these counting techniques may be found in the literature and here brief descriptions of each of the counting techniques and their applicability to the counting of ^{90}Sr and ^{90}Y are presented.

1.5.3.1 Proportional counting [10,58]

Proportional counting involves the detection of radioactive emissions based on the ionization of a gas. The detector part of a proportional counter consists of a metal tube which has a thin gas tight window at one end and an insulated support for a thin central wire at the other end. The tube contains a mixture of argon and methane which becomes partially ionized when radiation enters the detector. The central wire is maintained at a high positive potential with respect to the tube wall. The electrons formed on ionization move rapidly towards the wire, while the positive ions drift slowly towards the wall. The arrival of negative charge to the wire causes the wire potential to drop. This causes current to flow from the power supply until the wire potential has been restored which gives rise to a voltage pulse. In a proportional counter, the wire potential is such that the potential difference between the wire and the wall permits the electrons produced by the ionization to cause secondary ionization. Therefore the electrons collected at the wire are greater than, although proportional to, the number created by the passage of radiation through the detector gas. The number of voltage pulses produced is proportional to the activity of the sample.

The presence of the thin window between the radioactive source and the counting gas prevents α- and low-energy β-particles entering the detector with a high efficiency. Poor detection efficiencies are also obtained for γ-radiation above approximately 100 keV because the higher energy γ-photons pass through the detector without causing ionization. The problem of particle absorption by the window can be

overcome using a gas flow proportional counter. This type of detector operates without a window, which permits the radioactive source to be placed virtually inside the counter gas, thus improving the counting efficiencies of α- and β-particles of all energies. The counter operates with a steady flow of counting gas being continually passed through the counting chamber throughout the counting.

Proportional counting is the oldest and most well established counting technique used for ^{90}Sr determinations. For the moderate to high β-particle energies of ^{90}Sr and ^{90}Y, counting efficiencies of approximately 40 % can be achieved and the presence of any pure α- or γ-emitters does not present a major interference problem. Modern, low-level, gas flow proportional counters have low backgrounds of around 1 count per minute and permit the simultaneous measurement of a large number of samples.

The main disadvantage of proportional counters is their inability to discriminate between β-particles of different energies. This is a problem for the direct counting of ^{90}Sr due to the presence of ingrowing ^{90}Y and also the possible presence of ^{89}Sr. This may be overcome by counting the source after ^{90}Y has attained equilibrium and removing the ^{90}Sr and ^{89}Sr contribution by placing a β-absorber between the source and the counting chamber. This however results in a reduced counting efficiency for ^{90}Y. The counting of separated ^{90}Y is preferable to the above approach, since this removes the interference of ^{90}Sr and ^{89}Sr without affecting the counting efficiency of ^{90}Y. However, counting of ^{90}Y directly separated from a sample may be complicated by the presence of ^{91}Y. The contribution due to the lower energy ^{91}Y again could again be removed using a β-particle absorber.

1.5.3.2 Liquid scintillation counting [58,59]

Liquid scintillation counting (LSC) is based on the production of light when the

emissions from a radionuclide interact with a scintillator solution, which comprises an aromatic hydrocarbon solvent, such as toluene or xylene, containing a highly conjugated organic solute, such as 1-phenyl,4-phenyloxazole (PPO). The emitted radioactive particle collides with the solvent molecules and the energy transfer resulting from the collision results in the formation of electronically excited solvent molecules. These then transfer their excitation energy to the solute molecules which become electronically excited and relax to the ground state by non-radiative processes or by the emission of photons. The latter is the important process in LSC. The solute is chosen such that the wavelength of the emitted photons is in a region that can be conveniently detected by a photomultiplier tube (PMT), which converts the photons to an electronic pulse. The presence of a secondary solute in the scintillator solution may be required in order to achieve this. A commonly used secondary solute is 1,4-di-2-(4-methyl-5-phenyloxazoyl) benzene (DMPOPOP). Most liquid scintillation counters operate with two PMTs to detect the light emissions in order to discriminate against electronic noise.

In LSC, the number of photons emitted per radioactive emission, hence the pulse height, is proportional to the energy of the emission. A liquid scintillation counter therefore acts as an energy spectrometer. The number of pulses produced is proportional to the activity present. Using pulse height discrimination, it is possible to select the range of pulse heights (the counting channel) for counting a particular radionuclide with as high a counting efficiency as possible, but keeping the background signal to a minimum.

A problem encountered in LSC is quenching, which reduces the number of photons emitted from the scintillator solution for a given decay energy. The magnitude of the pulse height reported by the PMTs is reduced and as a result, the counting efficiency

in a particular counting channel varies according to the degree of quenching. Quenching falls into two categories, referred to as impurity quenching and colour quenching. Impurity quenching occurs as a result of the de-excitation of the electronically excited solvent or solute molecules by some material in the scintillator solution and colour quenching occurs as a result of the absorption of the emitted photons by materials, usually coloured, in the scintillator solution. The effect of quenching on the counting efficiency can be estimated and corrected for by the application of a quench correction method. Although several methods of quench correction are available, the basic procedure is the same in that sets of standards of constant known activity, containing different amounts of quench material are used in order to obtain a relationship between the amount of quench in a sample and the observed count rate. Examples of quench correction methods include the sample channels ratio and external standard channels ratio methods [58], the H number method [60], the end point [61] and spectral index methods [62].

LSC permits the β-counting of ^{90}Sr and ^{90}Y with counting efficiencies of greater than 90 %. Most low-level liquid scintillation counters can be used to obtain a simultaneous β-spectral distribution for ^{90}Sr, ^{90}Y and ^{89}Sr if present. However, the counters are unable to resolve the three components of the spectrum. Benzi et. al. [63] have shown that the ^{90}Y contribution can be measured independently of the others with a counting efficiency of approximately 3-4 %. This approach requires the ^{90}Sr - ^{90}Y equilibrium status to be accurately known to derive a reliable ^{90}Sr activity. As with proportional counting the measurement of the separated ^{90}Y presents a simpler counting procedure, however again if ^{90}Y is directly isolated, ^{91}Y may interfere. This problem was discussed by Zhu et. al. [28] who eliminated the interference by graphic subtraction of the ^{91}Y decay diagram for the total decay plot of the ^{90}Y - ^{91}Y fraction.

The principal advantage of LSC for the measurement of ^{90}Y over proportional and Cerenkov counting is the high counting efficiency obtainable. A disadvantage of LSC is that the effect of quenching needs to be carefully evaluated in order to derive a reliable ^{90}Sr activity. Another disadvantage of LSC is that if contamination is suspected during the count, elaborate chemical treatment is required to bring the radionuclide back into an aqueous matrix for clean-up. LSC also presents the problem of organic waste disposal.

1.5.3.3 Cerenkov counting [58,64]

Cerenkov counting is a technique that permits the measurement of high energy β-emitters in solution without the addition of scintillator solution. Cerenkov radiation is ultraviolet radiation which is generated when a β-particle travels through a medium with a velocity greater than that of light in the same medium. The minimum particle velocity, hence the threshold energy for the production of Cerenkov radiation depends on the refractive index of the medium involved. For water, the threshold energy is 263 keV. As the energetic β-particles pass through the medium emitting Cerenkov radiation, they quickly lose energy by excitation and ionization processes and fall below the Cerenkov threshold. Cerenkov radiation in solution therefore appears as brief flashes of light which may be detected and counted in a liquid scintillation counter.

The counting efficiency of Cerenkov counting in a liquid scintillation counter is a function of the sample volume, therefore samples should be counted at the same predetermined optimum sample volume. Impurity quenching does not occur in Cerenkov counting, but colour quenching does present a problem. This may be overcome using one of the quench correction methods used in LSC.

^{90}Sr has an average β-particle energy of 200 keV, which is below the Cerenkov threshold for water. Its counting efficiency is very low making it difficult to measure by this technique. ^{90}Y has an average β-particle energy of 930 keV and can be determined by Cerenkov counting with a counting efficiency of up to 65 %. Therefore determinations of ^{90}Sr by Cerenkov counting are based on the measurement of ^{90}Y and can be achieved without separation from ^{90}Sr. However, if ^{89}Sr is present it interferes with the counting, although this can be compensated for [65].

Although the counting efficiency of ^{90}Y measured by Cerenkov counting is lower than that achievable by liquid scintillation counting, it is compensated for by a lower background signal. Another advantage it has over scintillation counting is that the problems associated with the use of scintillator solutions are negated. Other advantages include that the sample preparation is simple and that there is built in discrimination against low energy β-emitters, α-emitters and pure γ-emitters.

1.5.4 Summary of the current methods for the determination of ^{90}Sr in environmental materials

Although many methods are available for ^{90}Sr determinations in environmental materials, no particular chemical separation approach or counting technique is clearly superior to other alternatives and the sample pretreatment is similar in most of the methods. In many cases, the three chemical separation approaches are not used in isolation, but in combination with one or both of the other approaches in order to produce a ^{90}Sr or ^{90}Y source suitable for β-counting. As a consequence of this, many of the chemical separation procedures are labour intensive and time consuming.

For the three counting techniques described, it appears that the isolation and measurement of ^{90}Y is advantageous since this will only produce one signal, or in the

worst case two signals if ^{90}Y is directly isolated and ^{91}Y is present, whereas the counting of ^{90}Sr may give rise to three signals.

1.6 Proposed approach for the determination of ^{90}Sr in milk

The primary aim of the work described here was to develop an improved method for determining ^{90}Sr in milk, to replace the solvent extraction technique described in table 1.4, currently in use at AEA Technology, Harwell. The principal feature of the method which required improvement was to reduce the labour intensity relative to the current method. A possible approach that was considered to reduce the labour intensity was to develop a method which involved some degree of automation. In section 1.5.2.3, an automated method was described for the isolation of ^{90}Sr by ion-chromatography and this was considered to be a reasonable route to follow. However, it was considered that the isolation of ^{90}Sr by an ion-chromatographic approach would be severely hampered by the presence of the high levels of calcium present in milk and it was considered that direct isolation of ^{90}Y would provide a means to overcome this problem. This would mean that the method may be subject to ^{91}Y interference, however, the current solvent extraction method is subject to the same potential interference. Therefore the developed method would have the same potential weakness as the method in current use. Ideally, the developed method apart from reducing the labour intensity should be at least comparable with respect to analysis time, chemical recoveries and reproducibility relative to the current method.

Another feature of using ion-chromatography for the chemical separation step was that it offered the potential for separation of other radionuclides, which was a secondary aim of the work. Therefore the approach investigated for the determination of ^{90}Sr in milk involved the isolation of ^{90}Y using ion-chromatography. The development of the ion-chromatographic separation is described in chapter 2.

Another requirement of the developed method was that the minimum detectable activity achievable should be less than 100 mBq l^{-1} of milk. The achievement of this is dependent on the efficiency of the chemical separation procedure and on the counting procedure. Therefore a comparison of the counting of ^{90}Y by proportional, liquid scintillation and Cerenkov counting using three commercially available counters was made and is described in chapter 5.

Chapter 2

STUDIES USING THE DIONEX ION-CHOMATOGRAPHY SYSTEM

2 STUDIES USING THE DIONEX ION-CHROMATOGRAPHY SYSTEM

2.1 Ion-chromatography [66-68]

Ion-chromatography is a liquid chromatographic technique for the separation of ionized or ionizable species. The technique was first reported in 1975 by Small, Stevens and Baumann when they described a novel ion-exchange chromatographic method for the separation and detection of anionic and cationic species [69]. The term 'ion chromatography' was introduced when the technology was licensed to the Dionex Corporation.

Ion-chromatography can be divided into three types depending on the separation procedure involved. These are high performance ion-chromatography (HPIC), high performance ion-chromatography exclusion (HPICE) and mobile phase ion-chromatography (MPIC). It is the first of these techniques that is the basis of the separation procedure for the ^{90}Sr method and only this technique is discussed here.

The essential principle of HPIC is the same as that for classical ion-exchange chromatography. The separation is based on an ion-exchange process between an ionic species in a mobile phase (or eluant) and the exchange groups of opposite charge that are covalently bound to a stationary phase. Using anion-exchange as an example, the ion-exchange equilibrium for binding an anion, A^{x-}, to a stationary phase which has been conditioned with an eluant containing a competing anion, E^{y-}, is given by

$$y\,A_M^{x-} + x\,E_R^{y-} \rightleftharpoons y\,A_R^{x-} + x\,E_M^{y-} \qquad (2\text{-}1)$$

The equilibrium is characterized by the selectivity coefficient, $K_{A,E}$ which is given by

$$K_{A,E} = \frac{[A_R^{x-}]^y [E_M^{y-}]^x}{[A_M^{x-}]^y [E_R^{y-}]^x} \qquad (2\text{-}2)$$

where R and M refer to the stationary and mobile phases respectively.

The exchange of the ions is controlled by their different affinities for the stationary phase. The affinity differences are essentially controlled by the physical properties of the solvated ions. The stationary phase shows preference for:

i) the ion with the higher charge;

ii) the ion with the smaller solvated radius;

iii) the ion which has the greater polarizability.

The solvated ionic radius limits the electrostatic interaction between ions, and the polarizability determines the van der Waals' interaction. Together these factors control the energy of interaction between oppositely charged species and therefore their tendency to exist as ion pairs on the stationary phase.

The partitioning of A^{x-} between the stationary phase and the mobile phase is described by the concentration distribution ratio, D_A and is given by

$$D_A = \frac{[A_R^{x-}]}{[A_M^{x-}]} \qquad (2\text{-}3)$$

This can be related to the capacity factor, k_A', by

$$k_A' = D_A \frac{w}{V_M} \qquad (2\text{-}4)$$

where w is the weight of the stationary phase and V_M is the volume of the mobile

phase. k_A' can also be related to the ion-exchange capacity of the column, Q, by

$$k_A' = \frac{w}{V_M} (K_{A,E})^{1/y} \left(\frac{Q}{y}\right)^{x/y} [E_M^{y-}]^{-\frac{x}{y}} \qquad (2\text{-}5)$$

For a second anion, B^{z-}, and the same competing anion, an equilibrium analogous to equation (2-1) will exist and $K_{B,E}$, D_B and k_B' may be written similarly to equations (2-2) to (2-4).

An ion-exchange equilibrium between the two anions A^{x-} and B^{z-} will also exist and is given by

$$z\, A_M^{x-} + x\, B_R^{z-} \rightleftharpoons z\, A_R^{x-} + x\, B_M^{z-} \qquad (2\text{-}6)$$

The selectivity coefficient for the two anions is given by

$$K_{A,B} = \frac{[A_R^{x-}]^z [B_M^{z-}]^x}{[A_M^{x-}]^z [B_R^{z-}]^x} \qquad (2\text{-}7)$$

In order to separate two anions from each other, it is necessary that one is taken up by the stationary phase in preference to the other. This is expressed by the separation factor $\alpha_{A,B}$ where

$$\alpha_{A,B} = \frac{k_A'}{k_B'} = \frac{[A_R^{x-}]\,[B_M^{z-}]}{[A_M^{x-}]\,[B_R^{z-}]} \qquad (2\text{-}8)$$

It can be shown that

$$\log \alpha_{A,B} = \frac{1}{z} \log K_{A,B} + \frac{x-z}{z} \log \left(\frac{k_{B'} V_M}{w} \right) \qquad (2\text{-}9)$$

Equation (2-5) shows that the capacity factor for an anion, A^{x-}, being eluted with a competing ion, E^{y-}, is dependent on the selectivity coefficient, the ion-exchange capacity, the ratio of the stationary and mobile phases and the concentration and charge of the competing ion in the eluant. Increased solute charge leads to increased capacity factors and increased eluant charge leads to decreased capacity factors.

For ions of the same charge, equation (2-9) simplifies to

$$\log \alpha_{A,B} = \frac{1}{z} \log K_{A,B} \qquad (2\text{-}10)$$

In this case the separation factor is independent of the charge or type of competing ion in the eluant. However, if the two ions have different charges, the separation factor depends on the capacity factor of one of the solute ions and is therefore dependent on the charge and concentration of competing anion.

In practical terms, classical ion-exchange chromatography involves the use of small particles of ion-exchange material loosely packed in glass columns as the stationary phase. The sample solution and the mobile phase are eluted through the stationary phase under gravity. The column eluate is then fraction collected to be later analysed for the components of interest. The process is very slow due to the low flow-rates, the chromatographic efficiency is poor and the detection procedure is inefficient.

HPIC is an improvement on classical ion-exchange chromatography providing rapid, efficient separations. The improvement is due to the use of high efficiency ion-exchange materials combined with continuous flow through detection. The particles

of ion-exchange material used in HPIC are of uniform size and are very much smaller than those used in classical ion-exchange chromatography and are packed into a rigid column material. The mobile phase is pumped through the stationary phase and the sample is introduced into the mobile phase via an injection port and is carried to the column for separation. The column eluate is then transferred to a flow through detection device. The instrumentation used in HPIC is summarized in figure 2.1.

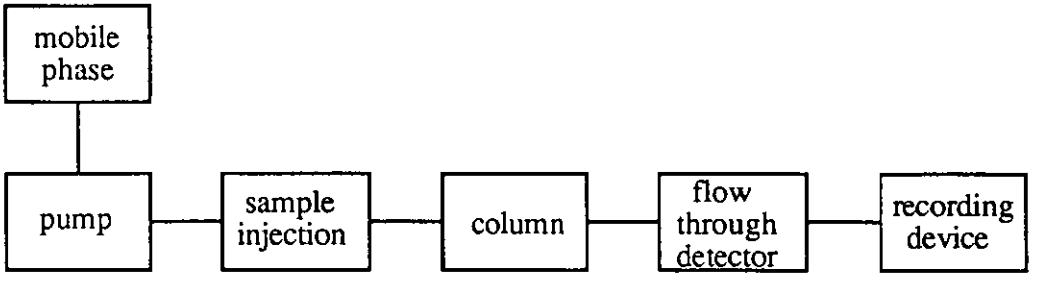


Figure 2.1 Instrumentation used in HPIC

The stationary phase in HPIC is typically a styrene based resin which has been crosslinked with divinylbenzene. For anion-exchange, the exchange group is usually a quaternary amine, $-NR_3^+$, and for cation-exchange, a sulphonate group is usually used, $-SO_3^-$. The functional groups can be introduced onto the resin bead by chemically treating the resin surface or by attaching a monolayer of latex carrying the functional groups onto the resin bead. These are referred to as surface functionalized and agglomerated resins respectively. The particle size of the resin beads used in HPIC are typically 10-30 μm. The resin beads can be produced to be essentially solid, non-porous materials or to contain internal pores. These are referred to as microporous and macroporous respectively. Microporous resins provide a rigid structure and macroporous resins provide a large surface area.

In addition to anion- and cation-exchange resins, resins are available onto which ligands are immobilized which interact with metal ions by chelation rather than by simple ion-exchange. Examples of ligands used include iminodiacetic acid [70,71], β-diketones [72] and dithiocarbamates [73]. Although these resins cannot strictly be classed as HPIC resins, they are mentioned here because one of this type of resins is used in the column system used for the ^{90}Sr method described here.

2.2 The Dionex ion-chromatography columns

In the proposed method for the determination of ^{90}Sr in milk, the separation stage was to involve the isolation of ^{90}Y by ion-chromatography using a three column system. The three columns are commercially available from the Dionex Corporation and are referred to as the MetPac CC-1 column, the TMC-1 column and the IonPac CS5 column. The three columns contain chelating, cation-exchange and anion-exchange resins respectively.

2.2.1 MetPac CC-1 column [74]

The MetPac CC-1 column contains a macroporous resin comprising iminodiacetic acid functional groups in a styrene-divinylbenzene matrix. The resin is shown schematically in figure 2.2.

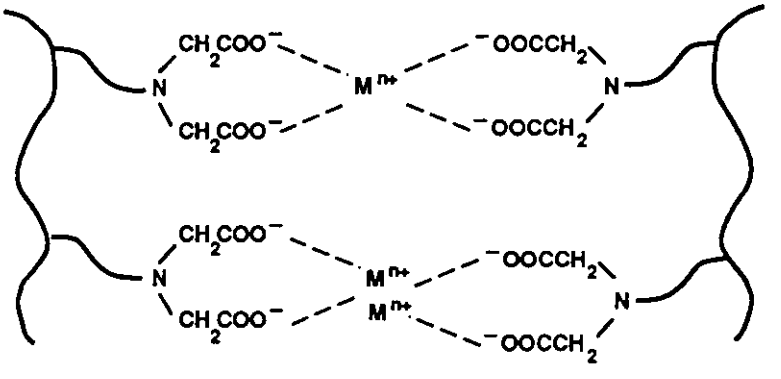


Figure 2.2 Schematic diagram of the CC-1 column resin

The iminodiacetic acid functional groups exist in different forms at different pH values according to the equilibrium described in figure 2.3 [71]. The equilibrium shows that the resin can behave as an anion, cation or chelating exchanger.

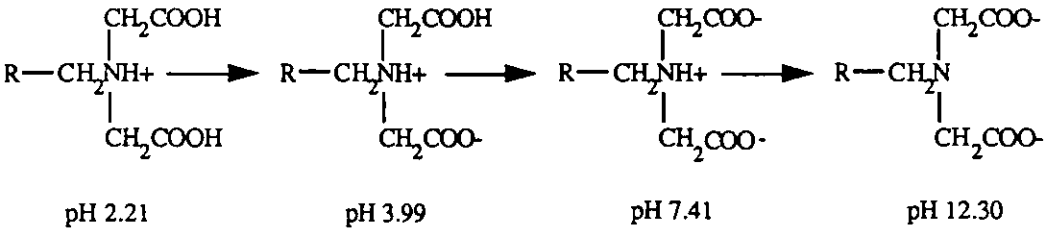


Figure 2.3 The iminodiacetic acid functional group at different pH values

When the resin is being used as a chelating exchanger, the iminodiacetate functional groups have roughly the same affinity for metal ions that EDTA has i.e. singly charged alkali-metal cations are held most weakly, then divalent alkaline-earth cations, then divalent and trivalent transition metal cations and then trivalent lanthanide cations. In the presence of trace quantities of metal ions, complexes of the ratio 1 metal ion: 2 functional groups are formed, although in the presence of an excess of metal ions complexes of the ratio 1:1 are formed [70].

In the pH range 5-6, the resin is selectively optimized for the extraction of lanthanides and transition metals relative to alkali- and alkaline-earth metals [75]. Using ammonium acetate as an eluant in this pH range selectively elutes alkali- and alkaline-earth metals from the column whereas lanthanides and transition metals remain strongly bound to the resin. The lanthanides and transition metals can then be eluted from the resin using dilute mineral acids. The use of this type of resin has been reported as a concentration step in the determination of transition metals in water samples containing high concentrations of alkali and alkaline-earth metals. [75,76]

Using the resin as a chelating exchanger with the above conditions should permit the extraction of yttrium due to its chemical similarity to the lanthanides. Thus in the proposed method, the CC-1 column would be used to concentrate ^{90}Y from the milk sample solution and also to remove the large quantities of alkali- and alkaline-earth metals present.

2.2.2 IonPac CS5 column [77]

The IonPac CS5 column contains a surface sulphonated cation-exchange material on a hydrophobic core of a styrene-divinylbenzyl copolymer, onto which anion-exchange capacity has been introduced by coating with a quaternary amine latex. The column material is schematically shown in figure 2.4.

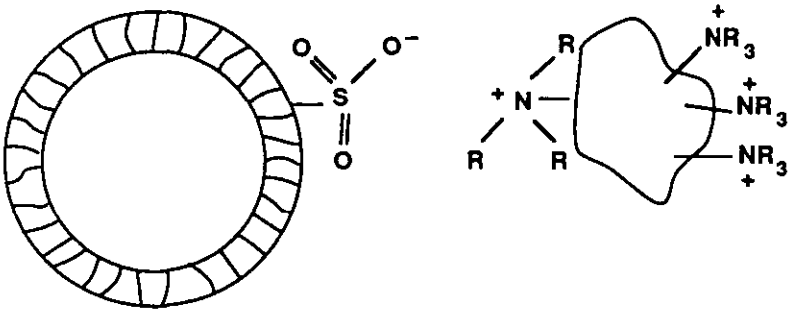


Figure 2.4 Schematic diagram of CS5 column resin

The amine latex does not completely cover the sulphonate functionalities on the core particle. The material therefore exhibits both anion- and cation-exchange properties, however, anion-exchange is the dominant retention mechanism. This column material has been used for the separation of transition metals and lanthanides using weak acid eluants [77,78]. The separation is typically achieved using the ionized form of pyridine-2,6-dicarboxylic acid (PDCA) as the eluant. PDCA forms anionic complexes with metal ions according to equations (2-11) - (2-13) [78].

$$M^{3+} + 2PDCA^{2-} \rightleftharpoons [\,M(PDCA)_2\,]^{-} \quad \text{where} \quad M^{3+} = Fe^{3+}, Ga^{3+}, Cr^{3+} \text{ etc.} \qquad (2\text{-}11)$$

$$M^{2+} + 2PDCA^{2-} \rightleftharpoons [\,M(PDCA)_2\,]^{2-} \quad \text{where} \quad M^{2+} = Cu^{2+}, Ni^{2+}, Zn^{2+} \text{ etc.} \qquad (2\text{-}12)$$

$$M^{3+} + 3PDCA^{2-} \rightleftharpoons [\,M(PDCA)_3\,]^{3-} \quad \text{where} \quad M^{3+} = La^{3+}, Ce^{3+}, Pr^{3+} \text{ etc.} \qquad (2\text{-}13)$$

The difference in charge between the lanthanide and transition metal complexes permits their separation on the CS5 column using PDCA as the eluant. The monovalent and divalent transition metal complexes are readily eluted from the column whereas the trivalent lanthanide complexes remain strongly bound. After elution of the transition metals, the elution and separation of lanthanides is achieved by gradient elution using oxalic and diglycolic acids [77]. These form stronger complexes with the lanthanides than PDCA and therefore a ligand exchange process occurs. The oxalate or diglycolate complexes thus formed are in the ratio 1 metal:2 ligand which means that the charge of the complex is reduced from -3 in the PDCA complex to -1 in the oxalate or diglycolate complex. The lower charged complex is therefore more readily eluted. A radiochemical application of the CS5 column using the PDCA eluant system reported by Bridle et. al. was the separation of γ-emitting transition metal radionuclides from pressurized water reactor coolant [79].

In the proposed method, the CS5 column would be used for the final separation of ^{90}Y from other interfering radionuclides still present after the initial extraction of ^{90}Y by the CC-1 column.

2.2.3 TMC-1 column [74]

The TMC-1 column contains a fully sulphonated cation-exchange resin and in the Dionex column system, it is placed between the CC-1 and CS5 columns. The column is required because the mineral acid used to elute metal ions from the CC-1 column would disturb the pH of the weak acid eluants used for the CS5 column which would

adversely affect the CS5 column separation. To prevent this, the metal ions are eluted from the CC-1 column onto the TMC-1 column where the pH is adjusted to a level suitable for the weak acid eluants by eluting the column with ammonium nitrate at pH 3.5.

2.2.4 Summary of the proposed Dionex column separation procedure

i) The milk sample is pretreated to ensure that the ^{90}Y is in solution and is in a suitable form to load onto the CC-1 column.

ii) The resulting solution is loaded onto the CC-1 column; polyvalent cations including ^{90}Y are extracted by the column.

iii) The column is then eluted with ammonium acetate to remove residual alkali- and alkaline- earth metals.

iv) The extracted metal ions are eluted from the CC-1 column onto the TMC-1 column using dilute nitric acid as eluant. The TMC-1 column is then eluted with ammonium nitrate at pH 3.5.

v) The metal ions are eluted from the TMC-1 column onto the CS5 column as anionic complexes using a PDCA eluant. The transition metals are separated and eluted from the CS5 column using the PDCA whereas the lanthanides and ^{90}Y are retained.

vi) ^{90}Y is then separated from the lanthanides by gradient elution using a mixture of oxalic and diglycolic acids as eluant.

2.3 Preliminary studies using the Dionex columns

The Dionex columns can be incorporated into complete chromatography systems that are commercially available from the Dionex Corporation. The systems comprise

sample delivery pumps, gradient pumps for eluant delivery and detector systems. However, these systems are expensive, so prior to purchasing a complete system, the suitability of the columns for the extraction and separation of ^{90}Y was investigated. This was to be achieved by determining the behaviour of ^{90}Sr, ^{90}Y and ^{141}Ce on each of the columns in turn. The investigation was carried out using the Dionex columns incorporated into a 'home made' system using equipment already available in the laboratory. The preliminary work also involved the setting up of radiometric detectors for the measurement of radionuclides used throughout the method development.

2.3.1 Instrumentation and reagents

The 'home made' system used in the preliminary studies comprised the following components: a Metpac CC-1 concentrator column; a Dionex TMC-1 column ; an Ionpac CS5 separator column; a Pharmacia P1 peristaltic pump, for loading the sample onto the CC-1 column; a Philips PU4100 HPLC pump for eluant delivery; Rheodyne valves for switching the flow of the eluants to the columns. Teflon tubing was used for connections where possible, however some metal tubing was required.

The eluants used as, recommended by Dionex [74,77], were 2 M ammonium acetate buffered at pH 5.5, 1 M nitric acid, 0.1 M ammonium nitrate at pH 3.5, a solution comprising 6 mM pyridine-2,6-dicarboxylic acid (PDCA), 40 mM sodium hydroxide and 90 mM acetic acid and a solution comprising 26 mM oxalic acid, 24 mM diglycolic acid and 95 mM lithium hydroxide. All chemicals were Analytical Reagent grade and all solutions were prepared in HPLC grade water (Rathburn) and filtered through a 0.45 μm filter (Gelman Sciences FP-450) prior to use. Before using the column system and after each sample run, the CC-1, TMC-1 and CS5 columns were equilibrated with 30 ml of the ammonium acetate, 30 ml of the nitric acid and

30 ml of the PDCA eluant respectively. The test solutions used in the preliminary studies were prepared by spiking HPLC water with either ^{90}Sr and ^{90}Y in secular equilibrium or ^{141}Ce.

2.3.2 Measurement of the radionuclides

Due to the uncertainties associated with radioactivity measurements, the results presented in the thesis are quoted with uncertainties that were calculated using the methods described in the Appendix. The quoted uncertainties are based on the radioactivity measurements only. For the method development, the uncertainties quoted are for 1 standard deviation.

During the method development, the measurement of ^{90}Sr and ^{90}Y was achieved by liquid scintillation counting. The measurement of ^{90}Y was also achieved by Cerenkov counting. Both of the counting techniques were carried out using an LKB Wallac Rackbeta 1215 Liquid Scintillation Counter. The counting was carried out in 20 ml polythene vials and the scintillant used was Ecoscint A (National Diagnostics).

^{90}Y was also qualitatively detected using an ISOFLO radiometric flow cell detector (Nuclear Enterprises). The detector cell contained an yttrium silicate crystal. The output from this detector was recorded on a Philips PU 6000 and 6003 data acquisition system.

2.3.2.1 Liquid scintillation counting of ^{90}Sr - ^{90}Y

Initially, the counter was set up to measure ^{90}Sr - ^{90}Y by liquid scintillation counting. A sample was prepared by adding 30 Bq each of ^{90}Sr and ^{90}Y in secular equilibrium to 10 ml of scintillant which was then counted. The counter's L.E.D. display showed the approximate window for counting ^{90}Sr - ^{90}Y and this was programmed into the counter. A background sample of 10 ml of scintillant was also counted in this

window. The window was subsequently adjusted to produce the optimum counting conditions. The counting window on the 1215 counter can be set from channel 0 - 256 and for ^{90}Sr - ^{90}Y the window was set from channel 40 - 256.

Determining the behaviour of ^{90}Sr and ^{90}Y through the Dionex column system required counting different solution types which may have caused impurity quenching effects. This would cause a reduction in the counting efficiency in the counting window. None of the solutions used in the development were coloured, so colour quenching was not considered a major problem. In order to estimate the effect of impurity quenching and to compensate for it, a quench correction curve was produced using the external standard channels ratio method. For the 1215 counter, the external standard is a ^{137}Cs source.

The quench correction curve was produced in the following manner. 110 ml of scintillant was spiked with 300 Bq of ^{90}Sr - ^{90}Y. 10 ml aliquots of the active scintillant were pipetted into scintillation vials which were then counted to check that the count rates were similar. If any of the samples were significantly different, then they were rejected and replaced. Varying aliquots of carbon tetrachloride from 0 to 1 ml were added to the vials, then the total volume in the vials was made up to 12 ml with inactive scintillant. The samples were then recounted and the quench correction curve produced as shown in figure 2.5 was programmed into the counter.

In producing this curve, a 100 % initial counting efficiency was used. Thus any subsequent measurements were quench corrected to a corrected count rate rather than an absolute disintegration rate. This was acceptable in the method development because liquid scintillation counting was only used comparatively and not to determine absolute disintegration rates.

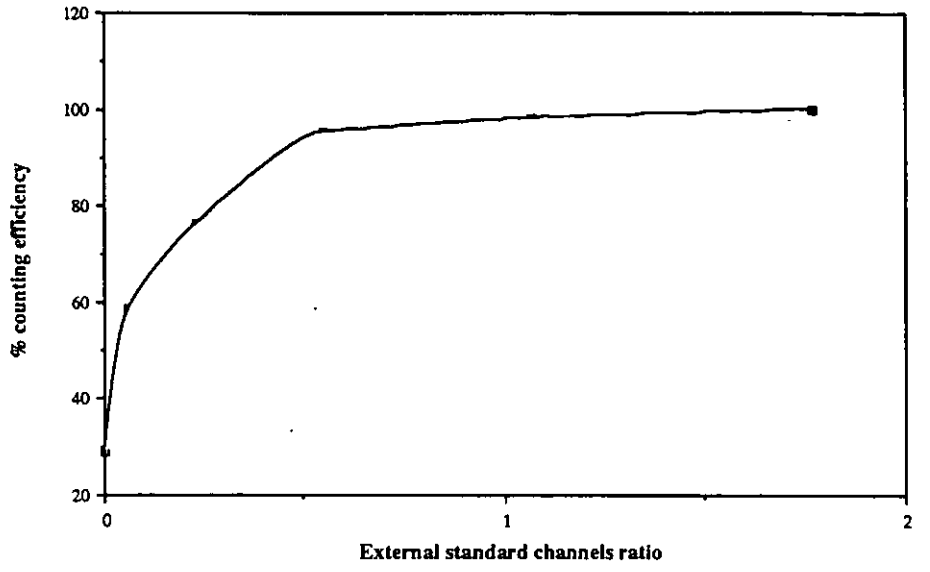


Figure 2.5 Quench correction curve for impurity quenching of ^{90}Sr - ^{90}Y

2.3.2.2 Cerenkov counting of ^{90}Y

The Cerenkov counting of ^{90}Y was carried out in the preset ^{3}H window of the 1215 counter, which is set from channel 8 - 110. Cerenkov counting is dependent on the sample volume, therefore the optimum sample volume was determined. 1 ml of a solution containing ^{90}Sr and ^{90}Y was Cerenkov counted and the count rate noted. The solution was then diluted by the addition of 1 ml of water and recounted and this was repeated such that the solution was counted at increasing solution volumes. Figure 2.6 shows that the optimum volume for Cerenkov counting in the 1215 counter was 13 ml.

The average β-particle energy of ^{90}Sr is below the Cerenkov threshold for water and it was expected that the counting efficiency for ^{90}Sr would be very low compared to that of ^{90}Y. The counting efficiencies of ^{90}Sr and ^{90}Y by Cerenkov counting were therefore determined.

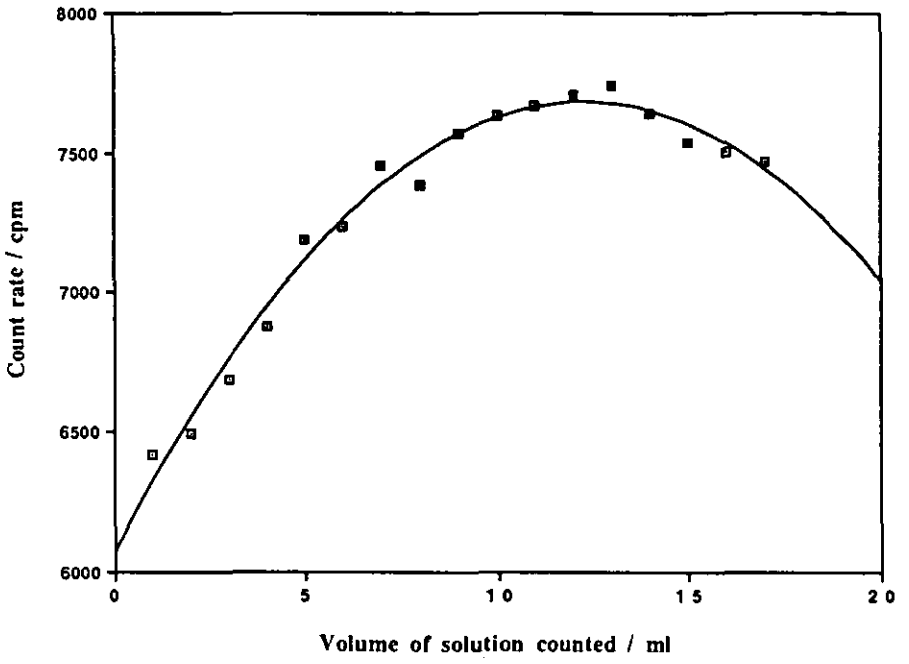


Figure 2.6 Optimum volume for the Cerenkov counting of ^{90}Sr - ^{90}Y

To a solution containing a known activity of ^{90}Sr and ^{90}Y in secular equilibrium, 2 mg each of strontium and yttrium carriers were added. The pH of the solution was adjusted by the addition of 6 M ammonia solution to precipitate yttrium hydroxide, which was then isolated by centrifugation. The precipitation was then repeated on the supernate and the precipitates were combined. The combined precipitates were dissolved in 8 M hydrochloric acid, diluted with water and reprecipitated. The yttrium hydroxide precipitate which contained the ^{90}Y was then dissolved in a minimum volume of 8 M hydrochloric acid and diluted to 25 ml with deionized water. The supernate which contained the ^{90}Sr was also diluted to 25 ml. 13 ml of the resulting solutions were then counted. The results for this, in table 2.1, show that the counting efficiency for ^{90}Sr was negligible compared to the moderately high counting efficiency for ^{90}Y, therefore when counting ^{90}Sr and ^{90}Y together, the count rate was approximated to being due to ^{90}Y alone.

Radionuclide	Activity added /dpm	Source count rate /cpm	Background count rate /cpm	Background corrected count rate /cpm	% counting efficiency
^{90}Sr	224.2	13.1 ± 0.5	11.1 ± 0.4	2.0 ± 0.6	0.9 ± 0.3
^{90}Y	224.2	107.9 ± 1.3	11.1 ± 0.4	96.8 ± 1.4	43.2 ± 0.6

Table 2.1 Cerenkov counting of ^{90}Sr - ^{90}Y using the 1215 liquid scintillation counter

2.3.2.3 Measurement of other radionuclides.

A number of other β-emitting radionuclides, ^{147}Pm, ^{99}Tc, ^{45}Ca, ^{63}Ni, were used in the method development and these were also measured by liquid scintillation counting. The counting windows and quench correction curves were determined as described previously. ^{147}Pm, ^{45}Ca and ^{99}Tc are β-emitters of similar $E_{\beta max}$ which are 225, 257 and 293 keV [8] respectively and a channel was set from 20 -184 which was suitable for counting the three radionuclides. ^{63}Ni is a low energy β-emitter ($E_{\beta max}$ = 65 keV) [8] and the channel set for this was from 10 - 150. The quench correction curve for the three radionuclide window was produced using ^{99}Tc. The quench curve for this window and that for ^{63}Ni are shown in figures 2.7 and 2.8 respectively. α-emitting radionuclides used in the method development were also measured by liquid scintillation counting using the full counting window of the 1215 counter.

The γ-emitting radionuclides used in the method development, ^{141}Ce, ^{57}Co, ^{137}Cs and ^{152}Eu, were measured using a Philips PW4800 Automatic Gamma Counter. The detector employed in the counter was a thallium activated sodium iodide crystal.

Using this counter, the counting windows can be set from channel 0 - 1800 and the windows for the γ-emitters used were set as follows: ^{141}Ce channel 60 - 155; ^{57}Co channel 60 - 155; ^{137}Cs channel 80 - 180; ^{152}Eu 10 - 1800. The radionuclides were counted at a constant 1 ml volume.

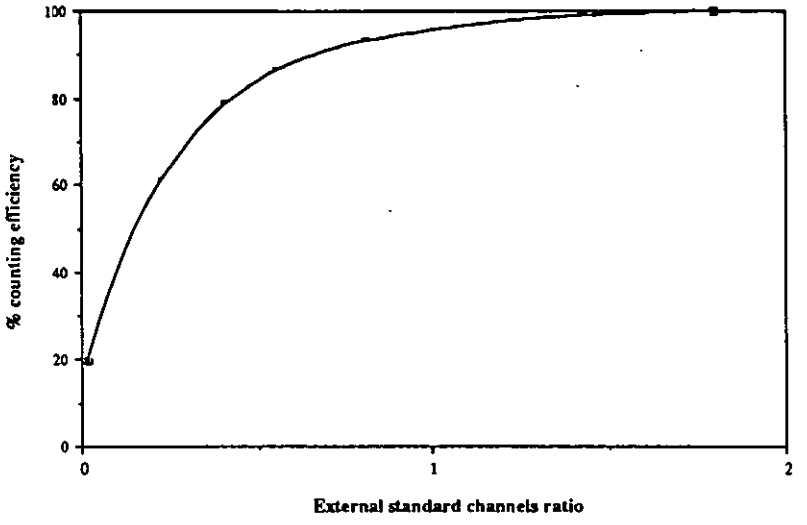


Figure 2.7 Quench correction curve for impurity quenching of ^{147}Pm, ^{45}Ca and ^{99}Tc

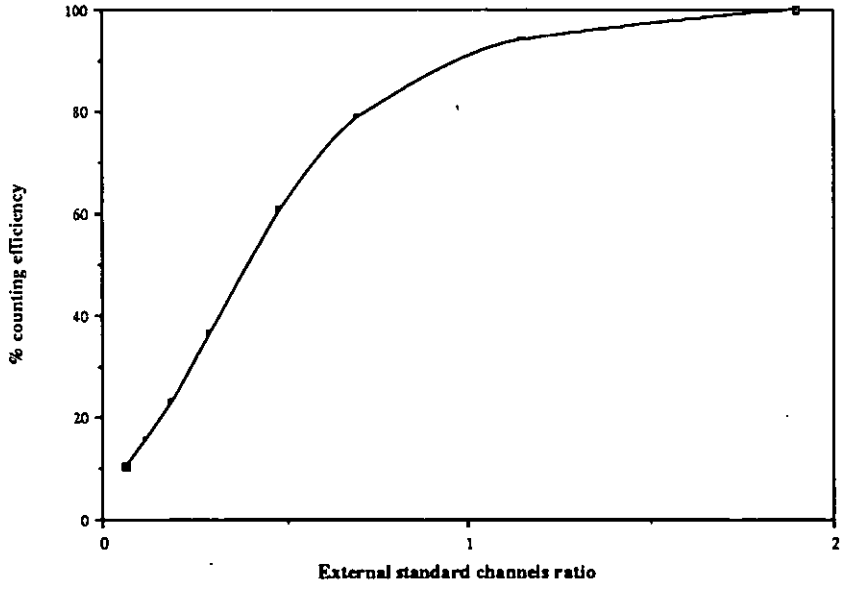


Figure 2.8 Quench correction curve for impurity quenching of ^{63}Ni

2.3.3 Study of the CC-1 chelation column

The CC-1 column is the first column encountered by the sample in the Dionex column system and initially, the interaction of the radionuclides with this column was investigated. 10 ml of deionized water spiked with a known count rate of either ^{90}Sr - ^{90}Y or ^{141}Ce were loaded onto the CC-1 column at a flow-rate of 1 ml min^{-1} and the eluate was collected. The column was then eluted with 2 M ammonium acetate at a flow-rate of 0.5 ml min^{-1}, the eluate was collected in 0.5 ml fractions. 1 M nitric acid was then passed through the column and the eluate was collected in 0.5 ml fractions. Each of the collected eluates were then counted. The percentage recoveries relative to the original sample count rate present in the various column eluates for ^{90}Sr - ^{90}Y and ^{141}Ce are shown in tables 2.2 and 2.3 respectively.

For the ^{90}Sr - ^{90}Y secular equilibrium solution, a count rate was detected in both the sample eluate and the ammonium acetate eluate. 8 ml of ammonium acetate was required to reduce the count rate eluted from the column to background levels. 30 to 40 % of the loaded count rate was recovered in the combined sample and ammonium acetate eluates and 40 to 60 % of the loaded count rate was recovered in the nitric acid eluate. 8 ml of nitric acid was required to reduce the count rate to background levels.

Since the count rate in the nitric acid eluate was approximately equal to the count rate in the combined sample and ammonium acetate eluates, it appeared that the column was separating the ^{90}Sr and ^{90}Y, since the activity of each present in the original sample solution was equal. To confirm this, the nature of the radioactivity in the ammonium acetate and nitric acid eluates was determined. This was achieved by monitoring the variation in the count rate of the eluates over a period of twenty days. Figure 2.9 shows a graph of the change in count rate in the eluates as a function of time.

Sample number	Count rate added /cpm	Recovery of count rate in eluate				
			Sample eluate	Ammonium acetate	Nitric acid	Total
1	58075 ± 773	cpm	4031 ± 204	17984 ± 379	33960 ± 521	56012 ± 676
		%	6.9 ± 0.4	31.0 ± 0.8	58.5 ± 1.2	96.4 ± 1.7
2	41241 ± 630	cpm	2720 ± 162	15093 ± 348	21687 ± 417	39500 ± 567
		%	6.6 ± 0.4	36.6 ± 1.0	52.6 ± 1.3	95.8 ± 2.0
3	35051 ± 572	cpm	2555 ± 155	14227 ± 337	15026 ± 347	31808 ± 508
		%	7.3 ± 0.5	40.6 ± 1.2	42.4 ± 1.2	90.7 ± 2.1
4	49328 ± 806	cpm	2907 ± 170	21063 ± 411	23924 ± 438	47894 ± 624
		%	5.9 ± 0.4	42.7 ± 1.1	48.5 ± 1.2	97.1 ± 2.0
5	40190 ± 636	cpm	2492 ± 158	15915 ± 357	18970 ± 390	37377 ± 552
		%	6.2 ± 0.4	39.6 ± 1.1	47.2 ± 1.2	93.0 ± 2.0

Table 2.2 Recoveries of ^{90}Sr - ^{90}Y from the CC-1 column

Sample number	Count rate added /cpm		Recovery of count rate in nitric acid eluate
1	50035 ± 224	cpm	46436 ± 272
		%	92.8 ± 0.7
2	47618 ± 213	cpm	43188 ± 263
		%	90.7 ± 0.7
3	46218 ± 209	cpm	42952 ± 272
		%	92.9 ± 0.7

Table 2.3 Recoveries of ^{141}Ce from the CC-1 column

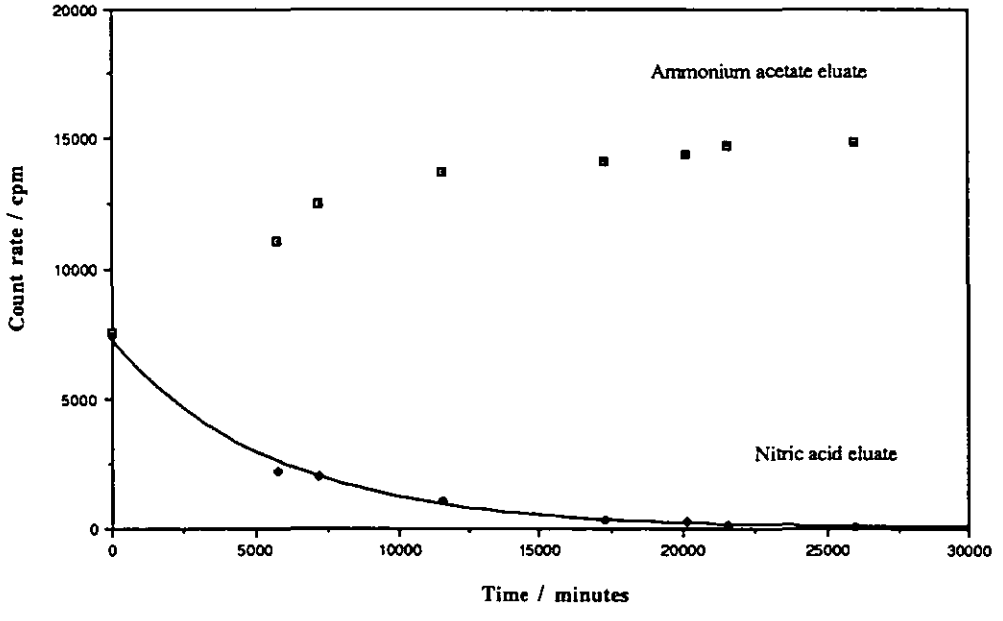


Figure 2.9 Variation in the count rate of the CC-1 column eluates with time

The count rate in the ammonium acetate eluate increased exponentially with time, reaching a constant level after approximately fourteen days. This is indicative of ^{90}Y ingrowing and attaining secular equilibrium with freshly separated ^{90}Sr. Thus, predominantly ^{90}Sr must have been originally present in the ammonium acetate eluate. The count rate in the nitric acid eluate decreased exponentially with time, due to the decay of ^{90}Y. It was possible to confirm that the decay in the nitric acid eluate was due to ^{90}Y by plotting the natural log of the count rate as a function of time which is shown in figure 2.10.

From this graph it was possible to determine the half-life of the decaying radionuclide, providing the graph was linear. The graph is derived from the decay law and is in the form

$$\ln C = \ln C_o - \lambda t \qquad (2\text{-}14)$$

where t is time, C is the count rate at time t, C_o is the initial count rate, λ is the decay constant of the radionuclide where

$$\lambda = \ln 2 / t_{1/2} \qquad (2\text{-}15)$$

and $t_{1/2}$ is the half-life of the radionuclide

From the graph gradient = λ

Therefore $t_{1/2} = \ln 2 /$ gradient

Here $t_{1/2} = 0.693 / 1.7828 \times 10^{-4}$ minutes

Therefore $t_{1/2} = 3888$ minutes = 64.8 hours

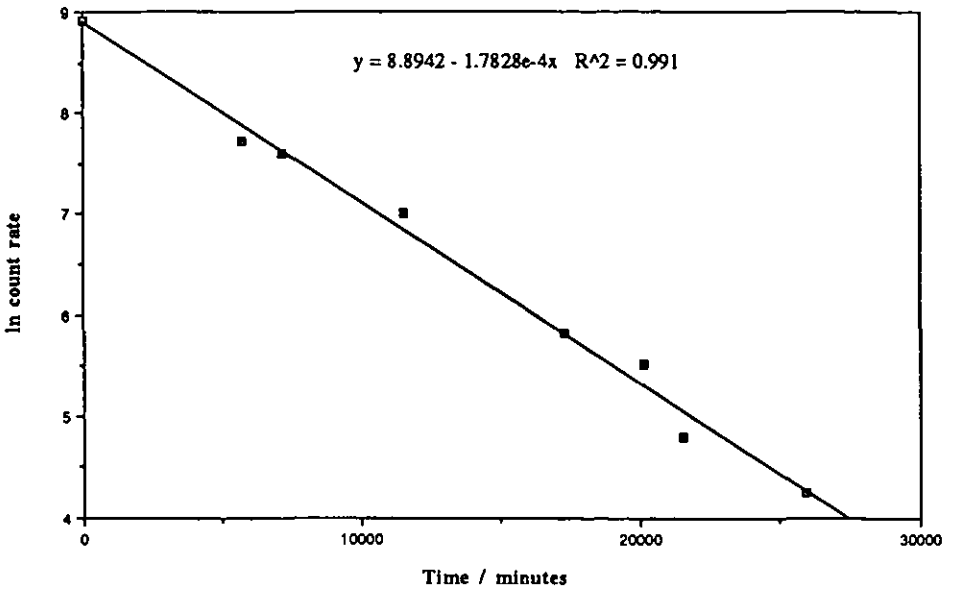


Figure 2.10 Variation in ln count rate with time for the nitric acid eluate

The derived half-life is in good agreement with the literature value for ^{90}Y, which is 64.1 hours [8] therefore confirming that pure ^{90}Y was originally present in the nitric acid eluate. The CC-1 column therefore separated ^{90}Y from ^{90}Sr, with only ^{90}Y being retained by the column. Therefore only ^{90}Y would be passed on for further separation by the column system.

For ^{141}Ce, no significant count rate above background was detected in the sample eluate or in the ammonium acetate fractions up to a volume of 8 ml. Greater than 90 % of the loaded count rate was eluted from the column in the nitric acid eluate. Thus ^{141}Ce was also retained by the CC-1 column in high recovery, which demonstrated that to isolate ^{90}Y would require further separation using the column system.

2.3.4 Study of the TMC-1 column

The elution of ^{90}Y and ^{141}Ce from the TMC-1 column using the PDCA eluant was investigated. 10 ml of sample of known count rate were loaded onto the CC-1 column, which was then eluted with 8 ml of 2 M ammonium acetate. The retained radionuclides were transferred to the TMC-1 column by eluting the CC-1 column with 8 ml of 1 M nitric acid. The TMC-1 column was then converted from the hydroxonium form to the ammonium form by eluting the column with 0.1 M ammonium nitrate at pH 3.5. The PDCA eluant was then eluted through the TMC-1 column at a flow-rate of 0.5 ml min^{-1} and the eluate was collected in 0.5 ml fractions and counted. The results for this study are shown in table 2.4.

Approximately 40 to 50 % of the original ^{90}Sr - ^{90}Y count rate and 90 % of the original ^{141}Ce count rate was recovered in the PDCA eluate. This implied that almost all the ^{90}Y and ^{141}Ce loaded onto the CC-1 column was eluted from the TMC-1 column and would be transferred to the CS5 column for the subsequent final separation.

Sample number	^{90}Sr - ^{90}Y			^{141}Ce		
	Count rate added /cpm		Count rate recovered in PDCA eluate	Count rate added /cpm		Count rate recovered in PDCA eluate
1	58075 ± 337	cpm	21933 ± 419	49163 ± 220	cpm	44640 ± 267
		%	43.4 ± 0.4		%	90.8 ± 0.7
2	37934 ± 268	cpm	16117 ± 0.4	48279 ± 217	cpm	44755 ± 268
		%	42.4 ± 0.4		%	92.7 ± 0.7
3	40327 ± 284	cpm	17704 ± 376	50135 ± 225	cpm	46375 ± 272
		%	43.9 ± 0.4		%	92.5 ± 0.7
4	38043 ± 269	cpm	18527 ± 385			
		%	48.7 ± 0.5			
5	41946 ± 297	cpm	19967 ± 400			
		%	47.6 ± 0.5			
6	37243 ± 263	cpm	16276 ± 361			
		%	43.7 ± 0.4			

Table 2.4 Recoveries of ^{90}Sr - ^{90}Y and ^{141}Ce from the TMC-1 column

2.3.5 Study of the CS5 separator column

10 ml of sample of known count rate were loaded onto the CC-1 column, which was then eluted with 8 ml of 2 M ammonium acetate. The retained radionuclides were transferred to the TMC-1 column by eluting the CC-1 column with 8 ml of 1 M nitric acid. The TMC-1 column was then converted from the hydroxonium form to the ammonium form by eluting the column with 0.1 M ammonium nitrate at pH 3.5. The column was then eluted with 8 ml of the PDCA eluant to transfer the radionuclides to the CS5 column. The CS5 column was then eluted with the oxalic acid - diglycolic acid eluant at a flow-rate of 0.5 ml min^{-1}. This flow-rate was the maximum possible without causing the system to leak. The eluate was monitored for radioactivity using the ISOFLO (Nuclear Enterprises) radiometric flow cell detector, although quantitative data was not determined. The ^{90}Y and ^{141}Ce were eluted from the CS5 column 55 and 44 minutes after transfer from the TMC-1 column respectively. Chromatograms for ^{90}Y and ^{141}Ce are shown in figures 2.11 and 2.12 respectively. The chromatograms show that the ^{90}Y and ^{141}Ce were separated by the CS5 column and eluted in the order expected if both ions were present in the tripositive state. The peaks observed were broad and tailing occurred, which could be a result of the low eluant flow- rate, the relatively long times the ions were retained by the separator column and possibly the effect of the radionuclides becoming adsorbed to metal tubing present in the system.

2.3.6 Summary of the preliminary studies using the Dionex columns

The 'home made' chromatography system used in the preliminary studies was not ideal because the maximum flow-rate possible was limited due to system leakage and the system contained metal surfaces which could have caused adsorption of the radionuclides. The possibility of adsorption onto metal surfaces could have affected the recoveries of radionuclides from the system which may become a significant

Figure 2.11 Chromatogram for the elution of ^{90}Y from the CS5 column

Figure 2.12 Chromatogram for the elution of ^{141}Ce from the CS5 column

problem when determining low-levels of radionuclides. However, the system demonstrated that the three columns permitted the separation of ^{90}Y from ^{90}Sr, since only the ^{90}Y was retained by the column system and was eluted from the CS5 separator column. This confirmed that the columns could be used for the determination of ^{90}Sr by separation and measurement of the ^{90}Y daughter. ^{141}Ce was also retained by the column system and eluted from the CS5 column with a different retention time to ^{90}Y which tentatively demonstrated that the Dionex columns would permit the separation of ^{90}Y from other rare-earth metal ions. As a result of the preliminary studies, a complete Dionex ion-chromatography system was purchased to continue the method development.

2.4 Studies using the Dionex ion-chromatography system

2.4.1 Instrumentation and eluants

The following components were used in the Dionex ion-chromatography system: Metpac CC-1 concentrator column; TMC-1 column; Ionpac CS5 separator column and Ionpac CG5 guard column; Two Dionex series 4000i gradient pumps, one of the pumps was used to deliver eluants to the CC-1 and TMC-1 columns and the other was used to deliver eluants to the CS5 column; DQP sample pump; eluant degas module, to degas the eluants and to pressurize the eluant reservoirs with helium at 7 psi; two Dionex inert high pressure valves operated with air at 80 psi, to control eluant switching between the columns; variable wavelength detector module to detect stable metals eluted from the CS5 column following post column derivitization; reagent delivery module, for delivering post column reagent; membrane reactor coil, for mixing post column reagent with the CS5 column eluate; Yew type 305 chart recorder for recording the output from the variable wavelength detector; Pharmacia LKB Redifrac fraction collector for collecting radionuclides eluted from the CS5 column. Figures 2.13 and 2.14 show a schematic diagram and a photograph of the Dionex ion-chromatography system.

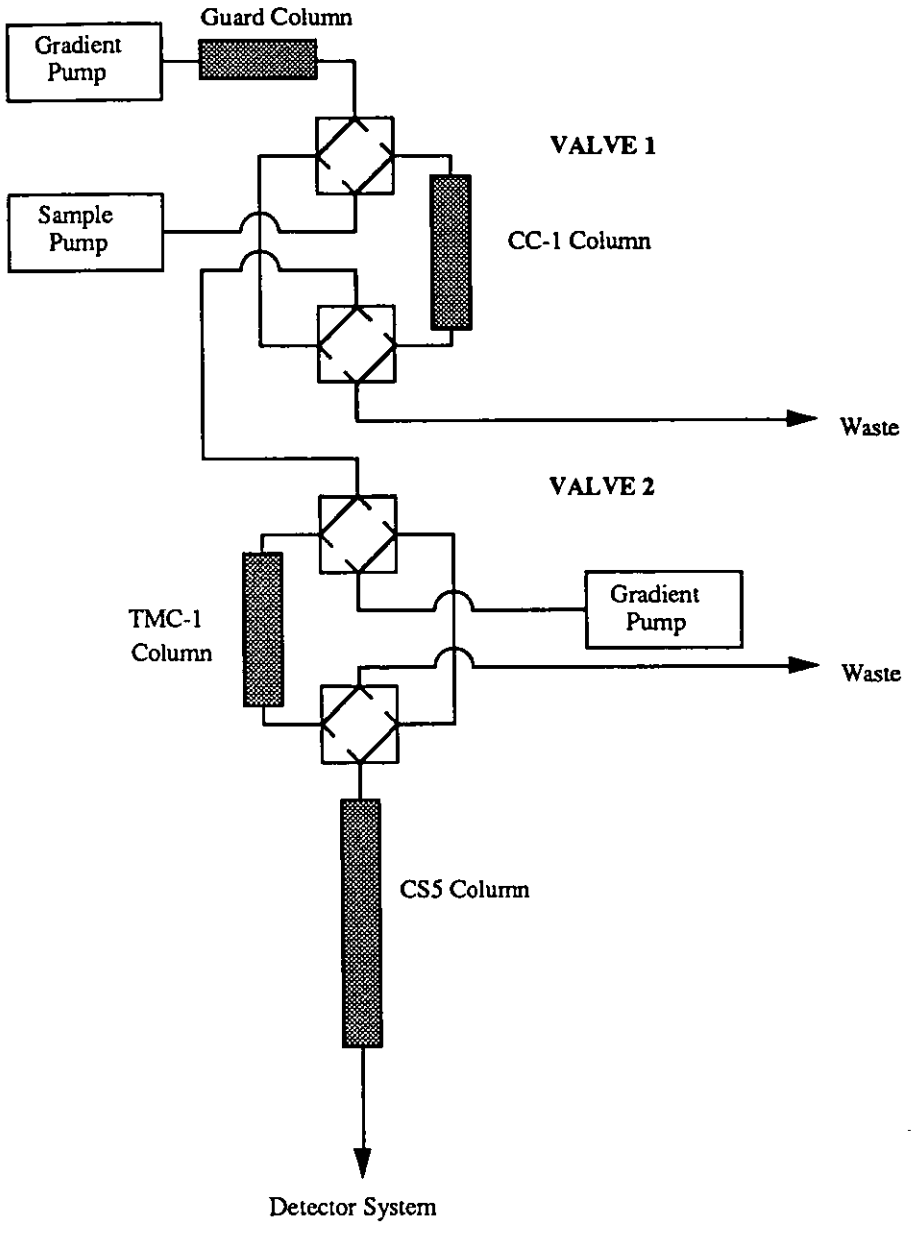


Figure 2.13 Schematic diagram of the Dionex ion-chromatography system

The eluants delivered to the CC-1 and TMC-1 columns were: HPLC grade water; 2 M ammonium acetate (pH 5.5); 2 M nitric acid; 0.1 M ammonium nitrate (pH 3.5). The eluants delivered to the CS5 column were: HPLC grade water; PDCA eluant (pH 4.8), which comprised 6 mM PDCA, 50 mM sodium acetate and 50 mM acetic

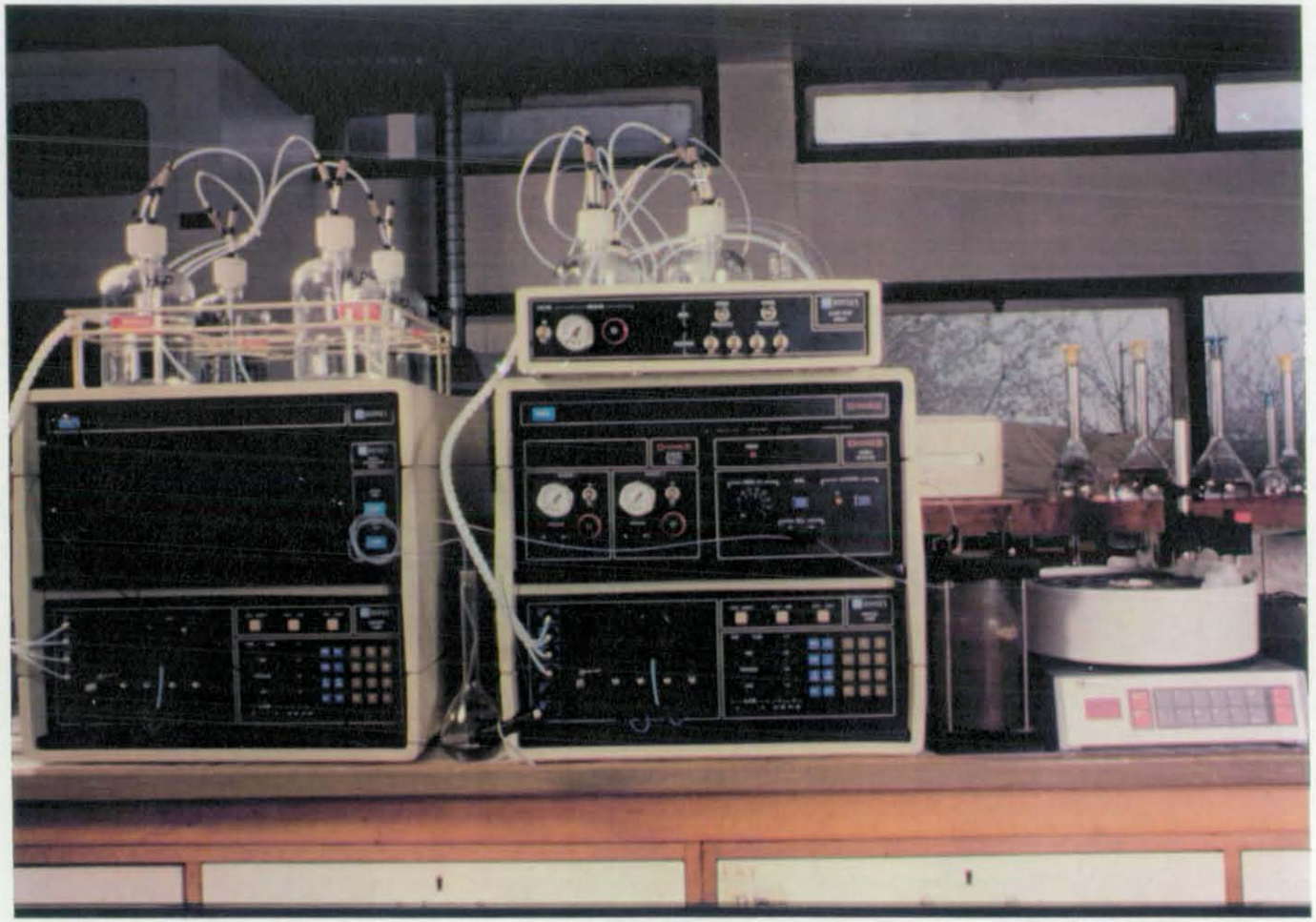


Figure 2.14 Photograph of the Dionex ion-chromatography system

acid; oxalate eluant (pH 4.8), which comprised 100 mM oxalic acid and 190 mM lithium hydroxide; diglycolate eluant (pH 4.8), which comprised 100 mM diglycolic acid and 190 mM lithium hydroxide. Before use, the CS5 column was equilibrated for 30 minutes with the PDCA eluant and between sample runs was equilibrated for a minimum of 10 minutes.

Some of the following experiments involved the use of stable elements. These were detected by UV - visible detection following post column derivitization with a reagent which comprised 0.2 mM 4-(2-pyridylazo) resorcinol (PAR), 3 M ammonium hydroxide and 1 M acetic acid. PAR, which is shown in figure 2.15, is a particularly suitable post column reagent for the determination of transition metals and lanthanides. It is capable of displacing the eluant ligands used on the CS5 column from the eluted metal ion and the colour produced by the metal - PAR complex thus formed can be measured at 520 nm [80].

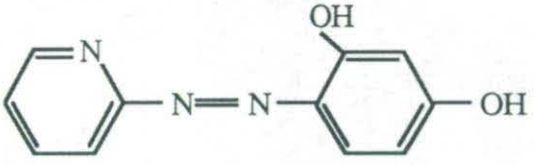


Figure 2.15 The structure of PAR

2.4.2 Studies using stable yttrium

2.4.2.1 Determination of when yttrium is eluted from the CS5 column

The behaviour of yttrium using the full chromatography system was initially examined using stable yttrium. The experiments followed the same general procedure, which was to load an yttrium standard onto the CC-1 column at a flow-rate of 2 ml min^{-1} and then to run the elution program outlined in table 2.5. The

yttrium standards used were prepared by dissolving a known mass of yttrium nitrate hexahydrate in HPLC grade water.

GPM 1

	Time / min	% water	% 2 M ammonium acetate	% 2 M nitric acid	% 0.1 M ammonium nitrate	Flow rate / ml min^{-1}
Step 1	0.0	0	100	0	0	3.0
	0.1	0	100	0	0	3.0
	2.5	0	100	0	0	3.0
Step 2	2.6	72	0	28	0	3.0
	5.0	72	0	28	0	1.0
Step 3	5.1	0	0	0	100	3.0
	6.6	0	0	0	100	1.0
Step 4	6.7	0	0	100	0	3.0
	7.7	0	0	100	0	3.0
Step 5	7.8	0	100	0	0	3.0
	9.3	0	100	0	0	3.0
Step 6	9.4	100	0	0	0	0.0

GPM 2

	Time /mins	% water	% PDCA	% oxalate	% diglycolate	Flow rate /ml min^{-1}
Step 7	6.6	0	100	0	0	1.0
	18.6	0	100	0	0	1.0
Step 8	18.7	100	0	0	0	1.0
	23.6	100	0	0	0	1.0
Step 9	23.7	40	0	60	0	1.0
	27.6	20	0	80	0	1.0
Step 10	27.7	20	0	80	0	1.0
	36.6	51	0	26	23	1.0

Step 1: Elution of alkaline-earth metals from CC-1 column to waste
Step 2: Elution of extracted metals from CC-1 column to TMC-1 column
Step 3: Conversion of TMC-1 column from hydroxonium to ammonium form
Steps 4, 5 and 6: Regeneration of the CC-1 and TMC-1 columns
Step 7: Elution of TMC-1 and CS5 columns with PDCA eluant
Step 8: Elution of CS5 column with water
Step 9: Elution of CS5 column with oxalate eluant
Step 10: Elution of CS5 column with oxalate - diglycolate eluant

Table 2.5 The Dionex ion-chromatography elution program

Figure 2.16 shows a typical chromatogram obtained for an yttrium standard. The chromatogram showed that four peaks were observed with retention times of approximately 5, 9.5, 12 and 36 minutes. The first three peaks occurred during the PDCA elution of the CS5 column, which was characteristic of transition metal ions. Whereas the peak at 36 minutes occurred during the oxalate - diglycolate elution, which was more characteristic of lanthanide ions. The preliminary studies also demonstrated that yttrium was eluted from the CS5 column using the oxalate - diglycolate eluant. Therefore it was more likely that the peak at 36 minutes was due to the yttrium. An HPLC water blank was run through the system which produced the chromatogram shown in figure 2.17. The peaks at 5, 9.5 and 12 minutes were still present, but the peak at 36 minutes was absent. This confirmed that the peak at 36 minutes was due to yttrium and also that no yttrium from the previous yttrium standard elution was retained by the column system and carried over into the blank run. Since the peaks present in the blank were eluted when transition metals were expected to be eluted, these peaks were probably due to transition metal impurities in the HPLC water or the reagents used to prepare the eluants. The yttrium peak was reproducibly eluted from the CS5 column after 36 minutes for more than forty yttrium standard runs.

2.4.2.2 Response of the Dionex system to constant and varying masses of yttrium

The response of the system to a constant mass of yttrium was investigated. Five solutions containing approximately 250 ng of yttrium were loaded onto the Dionex system. The areas of the resulting peaks were determined by multiplying the peak height by the peak width at half the peak height since the peaks approximated to an isosceles triangle. The areas were then normalized to the loading of 250 ng of yttrium. The results are shown in table 2.6. The normalized areas were similar, ranging from 100 to 107 mm^2 which demonstrated that the peak areas for constant loading of yttrium were reproducible.

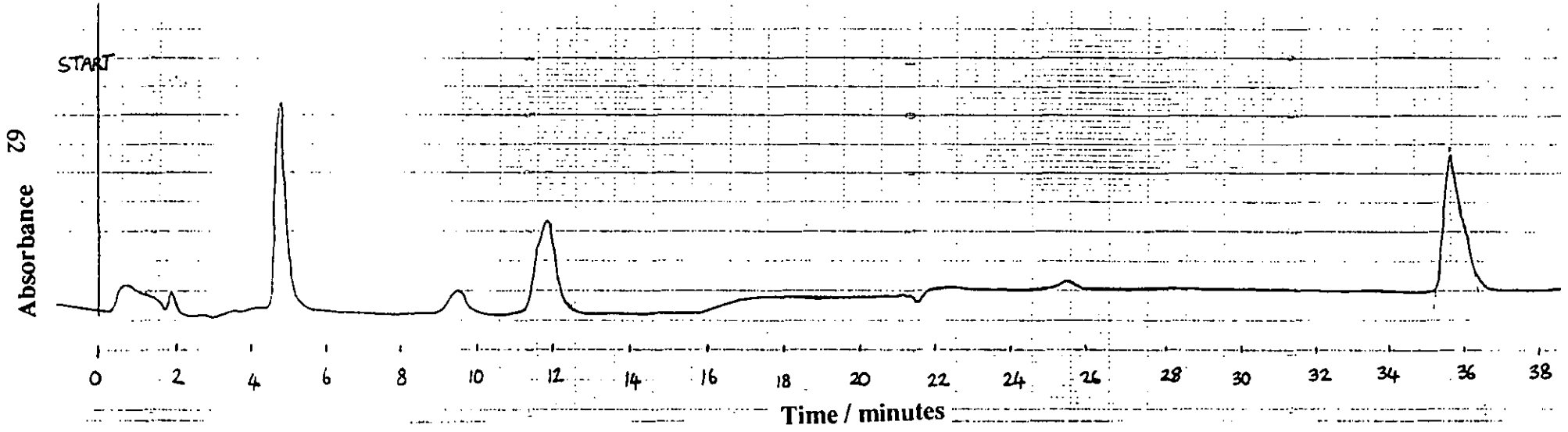


Figure 2.16 Chromatogram for an yttrium standard on the Dionex system

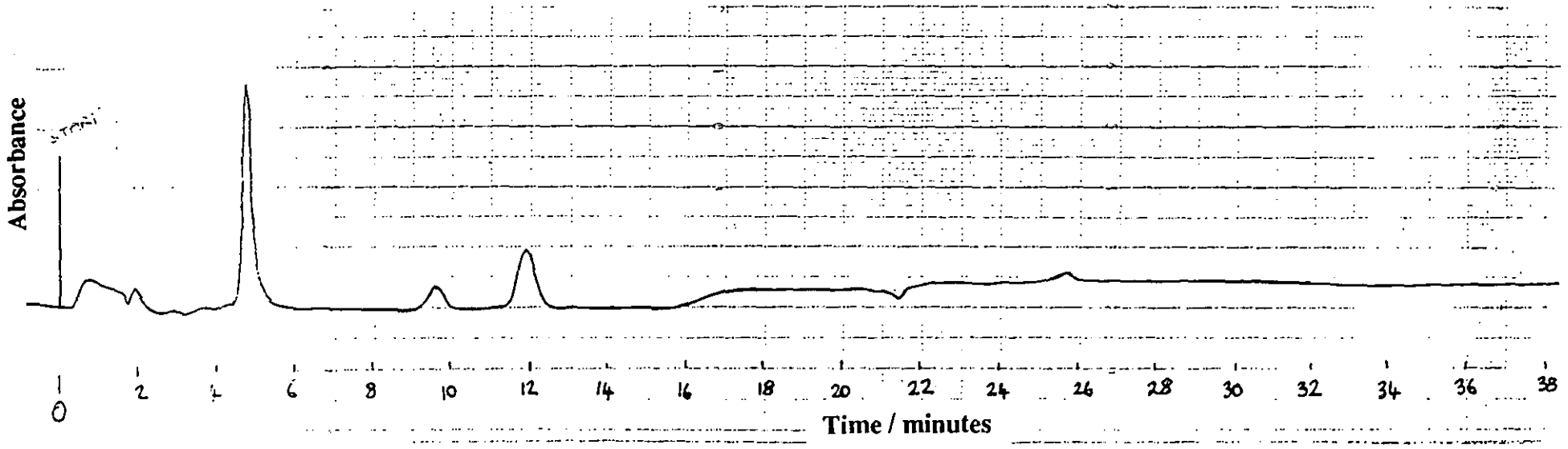


Figure 2.17 Chromatogram for HPLC water on the Dionex system

Mass of yttrium loaded / ng	Peak area /mm²	Peak area equivalent to 250 ng /mm²
247	105	106
237	95	100
254	109	107
219	88	100
244	103	106

Table 2.6 Peak areas for constant loading of yttrium onto the Dionex system

The response of the system to the variation in the mass of yttrium loaded from 40 ng to 250 ng was investigated and the results are shown as a graph in figure 2.18.

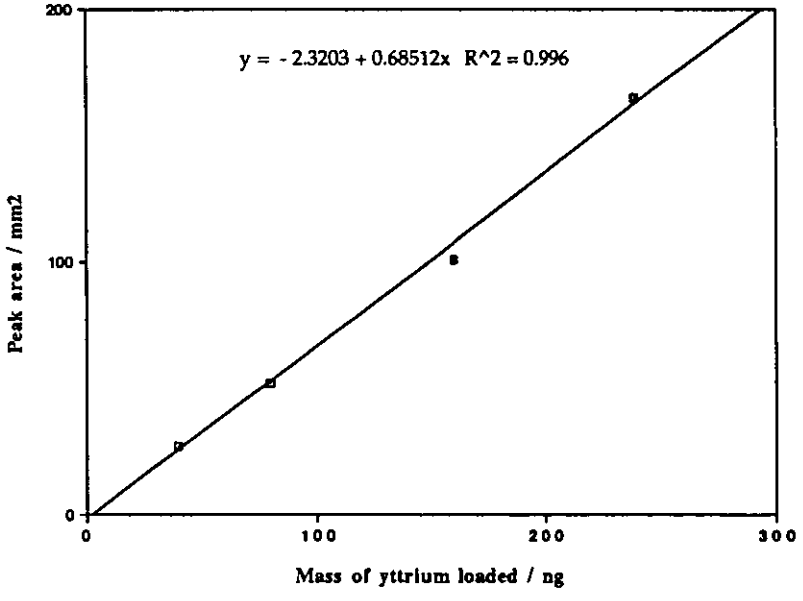


Figure 2.18 Response to changes in mass of yttrium loaded onto the Dionex system

This shows that the response to the variation in mass of yttrium loaded was linear over the range used. It was observed that over the mass range used, the increase in area was not simply due to an increase in the peak height but also an increase in the peak width. The peak width increased from 0.9 minutes to 1.5 minutes over the range used. A consideration in the method development was the addition of stable yttrium carrier to the sample to act as a yield monitor and also to reduce losses of ^{90}Y due to adsorption. The increase in peak width of 0.6 minutes for an increase in mass of yttrium loaded from 40 to 250 ng implied that an increase to milligram levels would produce a very broad peak which would provide poor separation from other rare-earths. This is exemplified by the chromatogram in figure 2.19 which shows that the peak produced for the loading of 100 μg of yttrium has a peak width of approximately 10 minutes. Thus it would not be feasible to load milligram levels of stable yttrium to act as a yield monitor.

2.4.2.3 Summary of the studies using stable yttrium

The studies using stable yttrium demonstrated that yttrium could be eluted from the Dionex system with a reproducible retention time of 36 minutes. The response to a constant loading of yttrium was constant and the response of the system to changes in the mass of yttrium loaded was linear. It would not be possible to add milligram levels of stable yttrium to a sample to act as a yield monitor because such levels of yttrium would be eluted from the CS5 column as a very broad band which would not provide sufficient separation from other rare-earths. It would still be possible to add nanogram to microgram levels of stable yttrium to act as carrier. To determine chemical recoveries of ^{90}Y would require an external standard containing a known ^{90}Y activity to be run with each batch of samples. Using this approach would require that the separation process was reproducible and preferably that the recoveries from the system for yttrium were high.

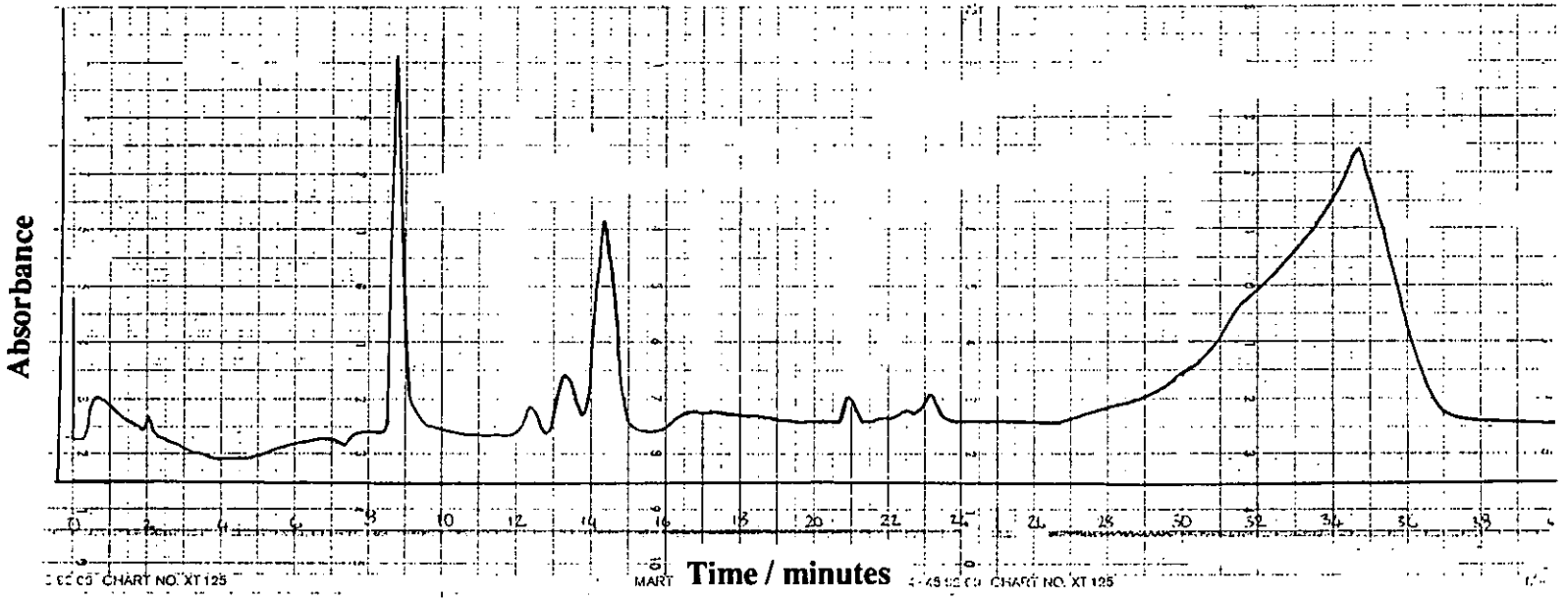


Figure 2.19 Chromatogram for 100 μg of yttrium loaded onto the Dionex system

2.4.3 Quantitative determination of ^{90}Y

15 ml of a test solution which comprised 2 M ammonium acetate at pH 5.5 spiked with a known count rate of ^{90}Sr and ^{90}Y were loaded onto the CC-1 column at a rate of 2 ml min^{-1}. The elution program outlined in table 2.5 was run and the eluate from the CS5 column was collected in 2 ml fractions using a Pharmacia Redifrac fraction collector. The fractions were then counted by liquid scintillation counting. A count rate was observed in the 34 and 36 minute fractions, which was consistent with the retention time determined using stable yttrium. Figures 2.20 and 2.21 show β-spectra of the sample loaded onto the CC-1 column and of the eluate from the CS5 column. The sample spectrum shows two peaks, the lower energy peak is due to ^{90}Sr and the higher energy peak is due to ^{90}Y. The CS5 eluate spectrum shows only the higher energy peak due to ^{90}Y. This further demonstrated that the column system successfully separated ^{90}Y from the ^{90}Sr.

The recoveries of ^{90}Y from the CS5 column for six replicate test solutions are shown in table 2.7. The mean recovery of ^{90}Y was 95.0 ± 1.3 %, therefore ^{90}Y could be extracted by and eluted from the Dionex system with a high, reproducible recovery.

Sample	^{90}Y count rate added /cpm	^{90}Y count rate recovered /cpm	% ^{90}Y recovery
1	3486	3343	95.9
2	3652	3546	97.1
3	3438	3239	94.2
4	1734	1632	94.1
5	1692	1607	95.0
6	1784	1672	93.7
			mean = 95.0 ± 1.3

Table 2.7 Quantitative determination of ^{90}Y from the Dionex system

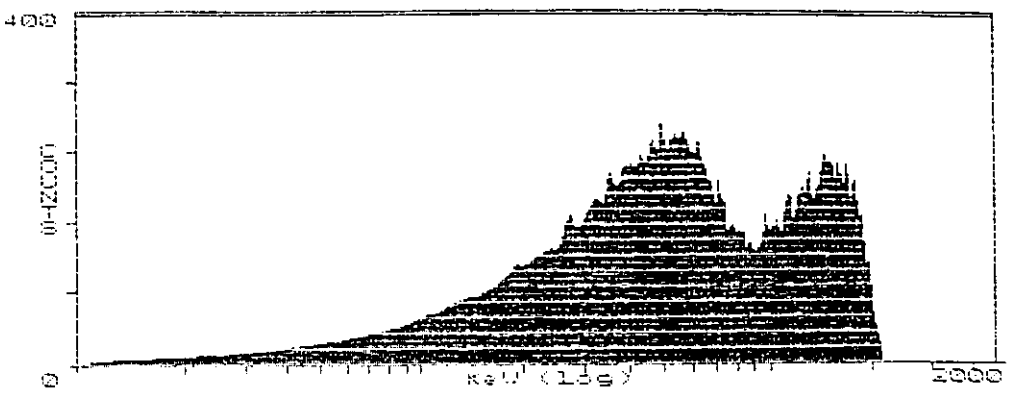


Figure 2.20 β-spectrum of ^{90}Sr - ^{90}Y solution prior to separation on the Dionex system

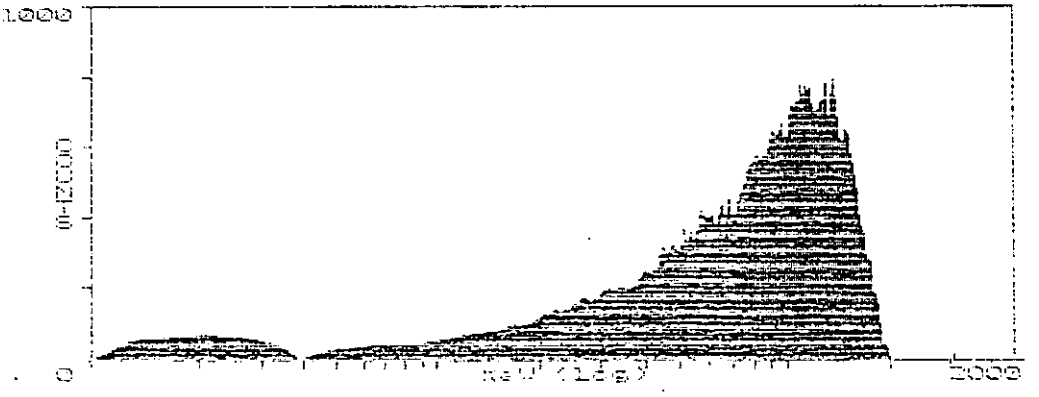


Figure 2.21 β-spectrum of ^{90}Sr - ^{90}Y solution after separation on the Dionex system

2.4.4 Study of the CC-1 column

The CC-1 column is the column onto which the sample solution is loaded and is where the ^{90}Y is extracted and separated from the ^{90}Sr. It was therefore important to investigate what effect a real sample solution might have on the extraction of ^{90}Y by the CC-1 column. The sample matrix of principal interest was milk. Sample preparation for milk would involve evaporation, wet ashing and acid digestion. Therefore the sample presented to the CC-1 column would be in the form of an acid digested solution. Since 0.56 M nitric acid is used to elute yttrium from the CC-1 column onto the TMC-1 column it was unlikely that an acid digested solution would be suitable for loading yttrium onto the CC-1 column. Therefore, the effect of sample pH on the loading of yttrium onto the CC-1 was investigated in order to determine the optimum sample pH for extraction of yttrium by the CC-1 column.

2.4.4.1 Effect of sample pH on the extraction of ^{90}Y by the CC-1 column

The test solutions used in the experiments were prepared by spiking 15 ml of 2 M ammonium acetate solution with 50 Bq each of ^{90}Sr and ^{90}Y. The pH of the samples was adjusted with either 5 M nitric acid or 0.880 ammonia solution. The volume of the solutions were then made up to 25 ml and the pH of the resulting solutions were remeasured. 13 ml of the test solution were Cerenkov counted and then loaded onto the CC-1 column at a flow-rate of 2 ml min^{-1}. The column was then eluted with ammonium acetate and nitric acid according to table 2.5, however in this case, the CC-1 column was disconnected from the TMC-1 column and the nitric acid eluate was collected and then Cerenkov counted. The results of this experiment are shown in figure 2.22.

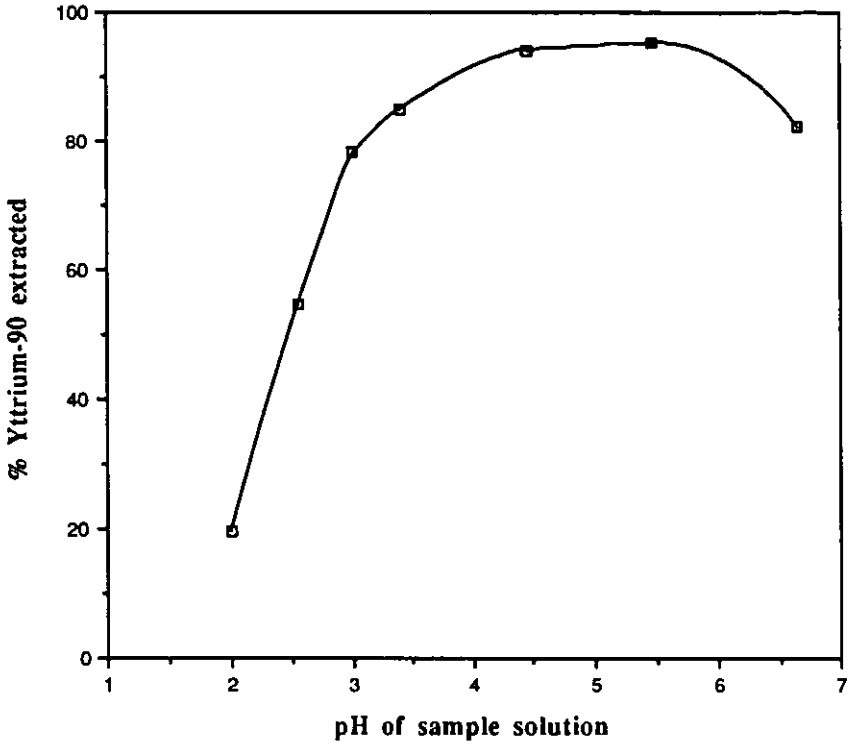


Figure 2.22 Effect of sample pH on the extraction of ^{90}Y by the CC-1 column

The optimum pH range for the extraction of ^{90}Y by the CC-1 column was between pH 4.5 and 6.0, below this pH range the extraction of ^{90}Y was sharply reduced. This was due to the protonation of the chelation sites on the resin, thus reducing the number of sites available for ^{90}Y to interact with. Above pH 6, yttrium starts to hydrolyse forming reduced charge hydroxy-species [81] which will have a weaker interaction with the chelation sites, hence the lower extraction above pH 6. In order to achieve the optimum pH for yttrium interaction it was decided to buffer sample solutions to pH 5 using the 2 M ammonium acetate eluant buffered to pH 5.5.

2.4.4.2 Effect of cations on the extraction of ^{90}Y by the CC-1 column

The major cation present in milk is calcium, which may be present in concentrations of approximately 1 to 1.5 g per litre of milk [5]. Thus if calcium was extracted by the

CC-1 column to any significant degree, then the large quantity of calcium present relative to the ^{90}Y likely to be present may effect the extraction of ^{90}Y by the CC-1 column. Therefore the effect of calcium on the extraction of ^{90}Y by the CC-1 column was investigated.

The test solutions used in this experiment were prepared by adding suitable volumes of a calcium stock solution to 2 M ammonium acetate at pH 5.5 spiked with 50 Bq each of ^{90}Sr and ^{90}Y and diluted to 25 ml. The calcium stock solution was prepared by dissolving 12.4 g of calcium nitrate tetrahydrate in 2 M ammonium acetate and diluting to 50 ml. 13 ml of the test solution were Cerenkov counted and then loaded onto the CC-1 column at a flow-rate of 2 ml min^{-1}. The elution program shown in table 2.5 was run and the nitric acid eluate from the CC-1 column was collected and Cerenkov counted. The results for this experiment in figure 2.23 show that the extraction of ^{90}Y by the column decreased as the amount of calcium in the sample increased. This implied that the interaction of calcium with the chelation sites of the CC-1 column resin was significant enough for it to be extracted and because it was present in large excess, it successfully competed for the sites thereby reducing the extraction of ^{90}Y by the column.

Since the test solutions were prepared in 2 M ammonium acetate sample, it was possible that its concentration may have affected the extraction of ^{90}Y by the column in the presence of calcium. To investigate this, the calcium experiment was repeated with test solutions in which the ammonium acetate concentration was 1 M or 0.5 M. These were prepared by diluting the 2 M ammonium acetate at pH 5.5 with HPLC water. On dilution, the pH of the solutions remained at approximately pH 5.5.

The results of these experiments are shown in figures 2.24 and 2.25. The results show that diluting the ammonium acetate from 2 M to 1 M improved the extraction

of ^{90}Y by the CC-1 column, although dilution from 1 M to 0.5 M did not provide a significant improvement in the extraction. By dilution of the ammonium acetate to 1 M, the maximum amount of calcium that could be loaded onto the CC-1 column was approximately 200 mg.

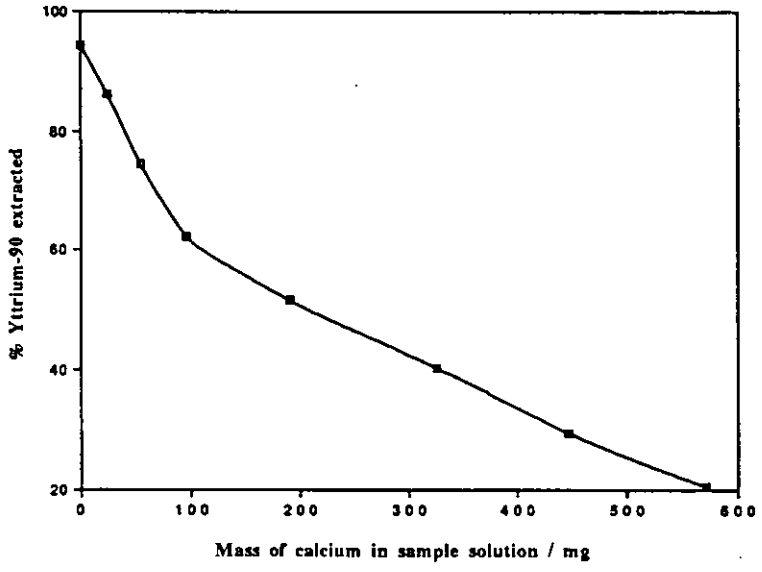


Figure 2.23 Effect of calcium on the extraction of ^{90}Y by the CC-1 column from 2 M ammonium acetate solution

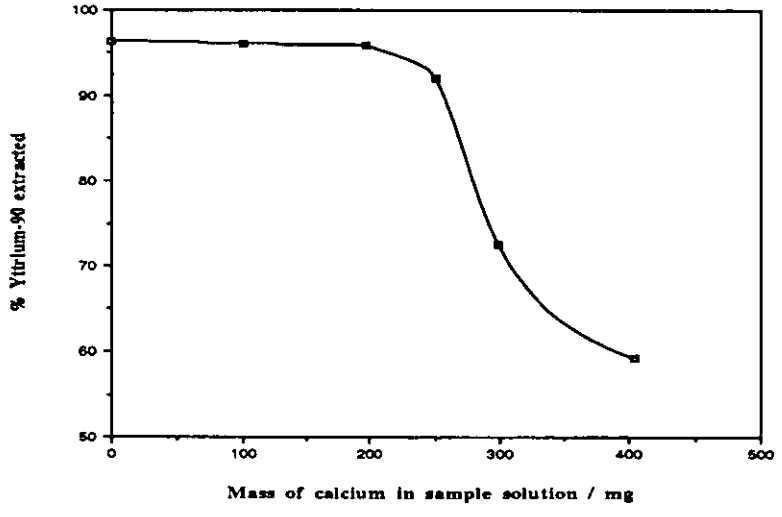


Figure 2.24 Effect of calcium on the extraction of ^{90}Y by the CC-1 column from 1 M ammonium acetate solution

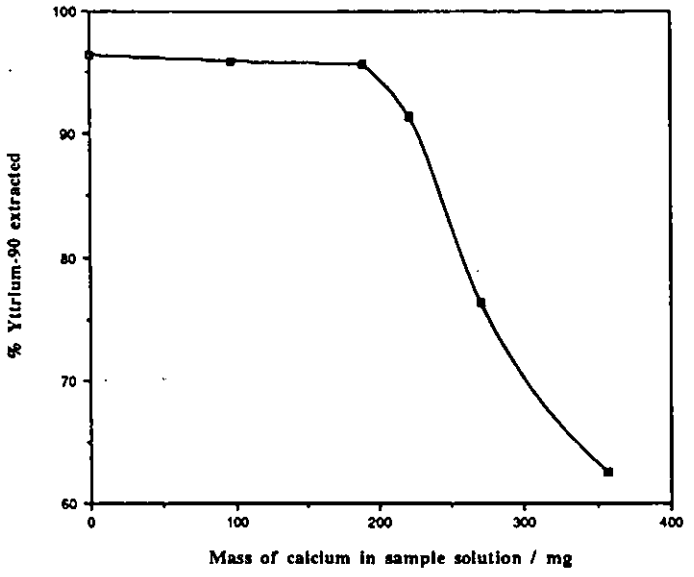


Figure 2.25 Effect of calcium on the extraction of ^{90}Y by the CC-1 column from 0.5 M ammonium acetate solution

Apart from divalent calcium, the effect of monovalent and trivalent cations on the extraction of ^{90}Y by the CC-1 column was investigated. The most abundant monovalent cation present in milk is potassium which is present in a comparable concentration to calcium and the most abundant trivalent cations are aluminium and iron which may be present in concentrations of up to approximately a milligram per litre of milk [5]. For the experiments, sodium and aluminium were chosen in preference to potassium and iron because the Cerenkov counting would be complicated by the presence of ^{40}K in natural potassium and by the colour quenching effect of the iron. The procedure followed was analogous to the calcium procedure described above, with test solutions being prepared using the nitrate of either sodium or aluminium and the final solutions were 1 M with respect to ammonium acetate. Figure 2.26 shows the results for the effect of aluminium, sodium and calcium on the extraction of ^{90}Y loaded from the 1 M ammonium acetate solutions. The presence of up to 1 g of sodium had little effect on the extraction of ^{90}Y, whereas no more than

approximately 2 mg of aluminium could be present before a reduction in the ^{90}Y extraction was observed.

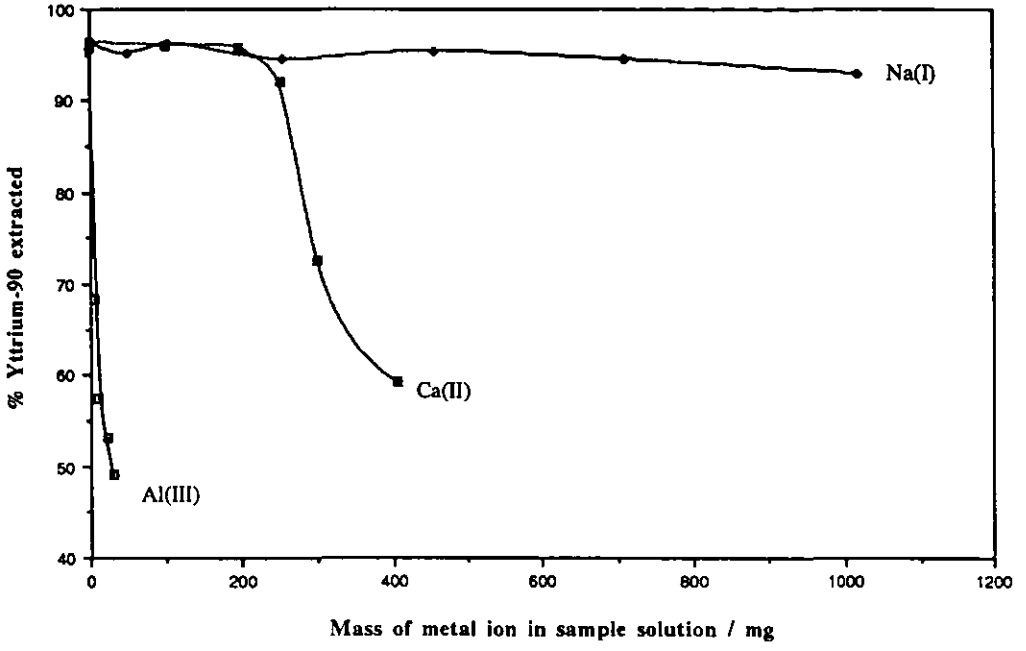


Figure 2.26 Effect of different valency metal ions on the extraction of ^{90}Y by the CC-1 column

The monovalent ion used demonstrated no significant interaction with the CC-1 column since it did not affect the extraction of ^{90}Y by the column. The trivalent cation used demonstrated a significant interaction with the column due its significant effect on the extraction of ^{90}Y. However, since the concentrations of trivalent cations in milk are relatively low, they may not be present in significant quantities to greatly affect the extraction of ^{90}Y from milk samples. The most significant problem of the CC-1 column with respect to milk analysis was its inability to cope with more than approximately 200 mg of calcium. This would limit the Dionex system to the analysis of only 150 to 200 ml of milk.

2.4.4.3 Retention behaviour of a series of radionuclides on the CC-1 column

Having established some of the conditions and limitations of the CC-1 concentrator column for the extraction of ^{90}Y, the behaviour of a series of radionuclides on the column was investigated. ^{90}Sr - ^{90}Y, ^{45}Ca, ^{141}Ce, ^{57}Co, ^{137}Cs, ^{152}Eu, ^{63}Ni, ^{147}Pm, ^{99}Tc, ^{242}Pu, ^{243}Am, ^{232}U and ^{229}Th were separately loaded onto the CC-1 concentrator column from 20 ml of 1 M ammonium acetate solution at a flow-rate of 2 ml min^{-1}. The column was then eluted with 2 M ammonium acetate followed by 0.56 M nitric acid according to the program described in table 2.5. The sample eluates, ammonium acetate eluates and nitric acid eluates from the column were collected and their radioactivity was measured by either liquid scintillation counting or gamma counting. The recoveries of the radionuclides in the various eluates are shown in table 2.8.

Radionuclide	% of the count rate loaded in sample eluate and ammonium acetate eluate	% of the count rate loaded in nitric acid eluate	% of the total count rate loaded recovered
^{90}Sr - ^{90}Y	48 ± 2	49 ± 1	98 ± 2
^{45}Ca	79 ± 3	19 ± 2	98 ± 2
^{141}Ce	–	97 ± 3	97 ± 3
^{57}Co	–	97 ± 2	97 ± 2
^{137}Cs	97 ± 2	–	97 ± 2
^{152}Eu	–	99 ± 4	99 ± 4
^{63}Ni	–	96 ± 2	96 ± 2
^{147}Pm	–	98 ± 1	98 ± 1
^{99}Tc	96 ± 3	–	96 ± 3
^{242}Pu	–	21 ± 1	21 ± 1
^{243}Am	6 ± 2	90 ± 3	96 ± 4
^{232}U	45 ± 3	48 ± 1	93 ± 3
^{229}Th	19 ± 2	77 ± 2	96 ± 3

The values here are the mean of three determinations

Table 2.8 Retention behaviour of radionuclides on the CC-1 column

The recoveries for the ^{90}Sr - ^{90}Y in the nitric acid eluate show that approximately

50 % of the count rate loaded was extracted by the CC-1 column. The count rate in the extracted fraction has previously been shown to be due to the ^{90}Y which implied that under the optimized conditions, ^{90}Y was essentially quantitatively extracted by the CC-1 column. The trivalent lanthanide and divalent transition metal radionuclides were also almost quantitatively extracted by the CC-1 column. Approximately 20 % of the ^{45}Ca loaded was extracted by the CC-1 column which indicates that Ca^{2+} does have a significant interaction with the chelation sites of the resin, but the interaction is much weaker than that of the lanthanides and transition metals. This weak interaction explains why the extraction of ^{90}Y by the column was greatly reduced by the presence of large quantities of calcium. ^{137}Cs and ^{99}Tc were not extracted by the CC-1 column, the latter due to it being present as the anion, TcO_4^- [82] under the column loading conditions. The extraction of these radionuclides by the CC-1 column i.e. lanthanide/ transition metal $>Sr^{2+} > Ca^{2+} > Cs^+$ (TcO_4^-), was consistent with that expected for an iminodiacetic acid resin as described in section 2.2.1.

The extraction of actinides by the CC-1 column varied depending on the particular actinide. 90 % of the ^{241}Am loaded was extracted and was probably present as Am^{3+} [83]. Only 77 % of the ^{229}Th loaded was extracted by the column. At pH 5, thorium is likely to be present as two species, $ThOH^{3+}$ and $Th(OH)_2^{2+}$[84]. The reduced extraction of thorium by the column could be explained by the higher charged species alone having a significant interaction with the chelating sites of the resin. At pH 5, uranium is also likely to be present as two species, UO_2^{2+} and UO_2OH^+[84]. Again, it is probable that only the higher charged of the two species has a significant interaction with the chelating sites of the resin, which explains why only 40 % of the ^{232}U loaded was extracted by the column. In total, only 20 % of the ^{242}Pu loaded was recovered in the column eluates. The remaining plutonium was recovered by eluting the column with further portions of 2 M nitric acid. The plutonium was therefore

very strongly bound to the chelating sites of the resin since more vigorous conditions were required to elute it than were used for the elution of yttrium. At the loading pH, plutonium is likely to be present as PuO_2^{2+} [85]. However, the log of the stability constant for a one to one complex between iminodiacetic acid and PuO_2^{2+} is similar to that for iminodiacetic acid and UO_2^{2+} (8.50 and 8.96 respectively at 25 °C and an ionic strength of 0.1) therefore they should behave similarly on the CC-1 column. The uranium extracted by the resin was readily eluted during the 0.56 M nitric acid elution whereas plutonium remained strongly bound. The plutonium may therefore have been extracted as some other species, for example Pu^{3+}.

The CC-1 column permitted the almost quantitative extraction of ^{90}Y from the test solutions. Lanthanides, transition metals, actinides and calcium were also extracted by the column in varying degrees, so further separation of ^{90}Y was therefore essential. Other radionuclides including ^{90}Sr were not retained by the column. Thus the column not only successfully concentrates ^{90}Y from the sample solution, it also acts as a purification step prior to the analytical separation of ^{90}Y.

2.4.5 Separation of ^{90}Y from other radionuclides retained by the Dionex system

^{90}Sr - ^{90}Y,^{147}Pm,^{152}Eu were loaded onto the Dionex system from 20 ml of 1 M ammonium acetate at a flow-rate of 2 ml min^{-1}. The elution program was run and the eluate from the CS5 column was collected in 0.33 ml fractions and then either liquid scintillation or gamma counted. A chromatogram from the CS5 separator column is shown in figure 2.27. This shows that the ^{147}Pm,^{152}Eu and the ^{90}Y were eluted from the CS5 column with retention times of 30.7, 32.0 and 34.0 minutes respectively using the oxalate - diglycolate mixture as the eluant. The europium and promethium peaks overlap slightly and the yttrium peak is only just separated from the europium peak. The peak widths for all the peaks are approximately 1.5 minutes.

Since the retention times of the two lanthanides and yttrium were within 5 minutes of each other and considering that the peak widths were approximately 1.5 minutes, it was thought that the differences in retention times were not sufficient since other lanthanides would probably co-elute with these. The separation of these radionuclides could be improved by adjustment of the eluant. It was the presence of the diglycolate ion in the eluant that accelerated the elution of the lanthanides from the CS5 column, therefore it was considered that reducing the diglycolate ion concentration of the eluant could improve the separation of the lanthanides. The concentration of diglycolate ion could be reduced in two ways. One was to reduce the pH of the diglycolate eluant which would protonate more of the diglycolate ions thus reducing the free diglycolate ion in the eluant to complex with the lanthanides. The other way to reduce the diglycolate ion in the eluant was simply to adjust the elution program such that the percentage composition of the diglycolate eluant in the eluant mixture was reduced. This second approach was used to try to improve the separation.

The effect of changing the CS5 column eluant from 51 % water - 23 % diglycolate - 26 % oxalate to 51 % water - 19 % diglycolate - 30 % oxalate and 51 % water - 15 % diglycolate - 34 % oxalate is shown in figures 2.28 and 2.29. Decreasing the percentage of diglycolate in the eluant increased the retention times and improved the separation of the three elements. The separation of yttrium from europium was greatly improved using the 15 % diglycolate eluant, although the peak widths increased to over two minutes. It was not considered necessary to further reduce the concentration of diglycolate because the eluant containing 15 % diglycolate eluted the yttrium approximately 4 minutes after the europium was totally eluted.

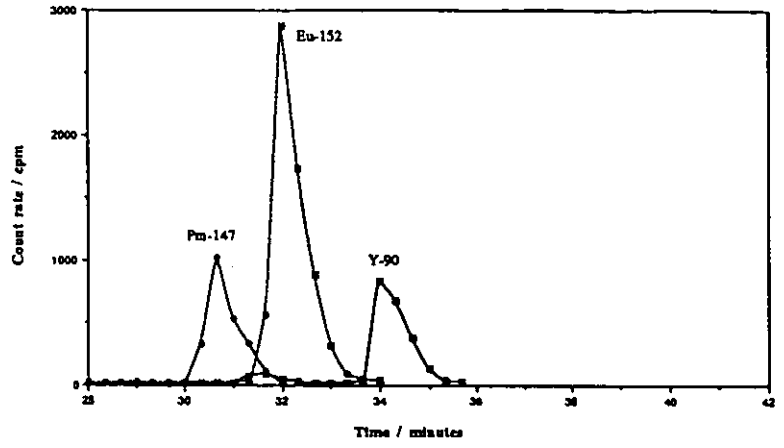


Figure 2.27 Chromatogram from the Dionex CS5 column using 51% water - 26% oxalate - 23% diglycolate

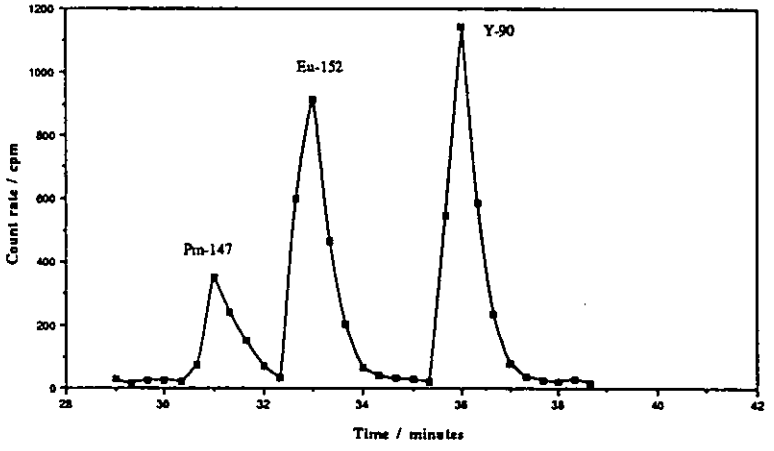


Figure 2.28 Chromatogram from the Dionex CS5 column using 51% water - 30% oxalate - 19% diglycolate

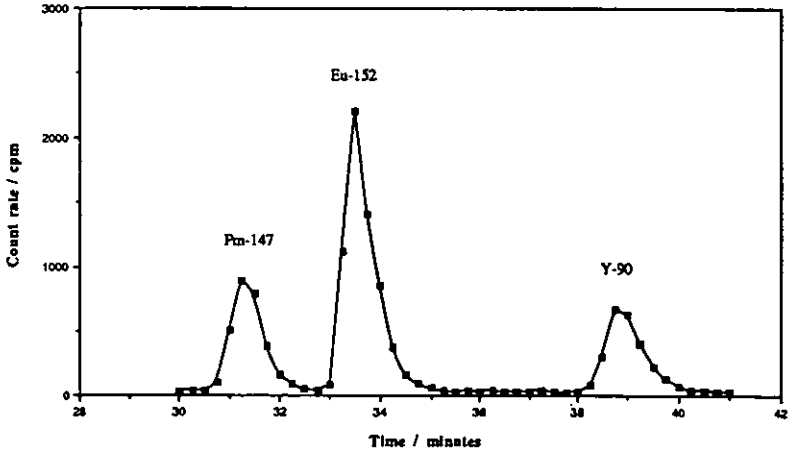
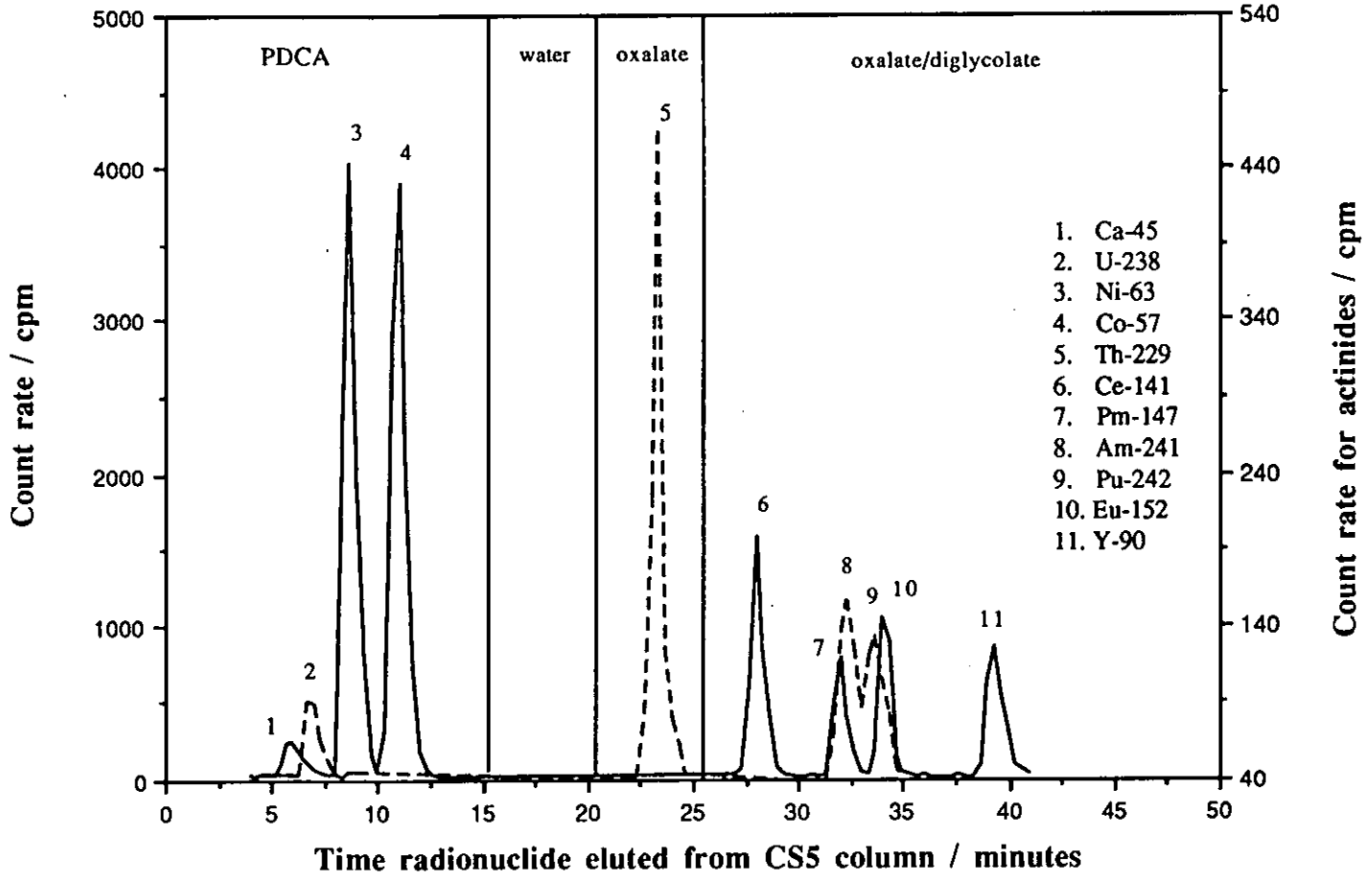


Figure 2.29 Chromatogram from the Dionex CS5 column using 51% water - 34% oxalate - 15% diglycolate

Having established the elution program for the yttrium and the two lanthanide radionuclides, the elution behaviour of the other radionuclides retained by the CC-1 column was determined. Figure 2.30 shows a complete chromatogram for the radionuclide separation. The chromatogram shows that ^{45}Ca, ^{232}U,^{63}Ni and ^{57}Co were eluted with retention times of 6.0, 6.3, 8.7 and 11.0 minutes respectively using the PDCA eluant. The other radionuclides, ^{229}Th, ^{141}Ce, ^{241}Am, and ^{242}Pu were eluted using the oxalate eluant or the oxalate - diglycolate eluant with retention times of 23.0, 28.3, 32.3, and 33.7 minutes respectively. Uranium was eluted with a retention time in between that of Ca^{2+} and Ni^{2+} which implied that it was eluted from the column as UO_2^{2+}. The elution order of the lanthanides and yttrium was consistent with them being present as trivalent cations. Am^{3+} was co-eluted with Pm^{3+} which was not unexpected because both of these have similar ionic radii (97.5 and 97.9 pm respectively) [11] and would be expected to behave similarly. Plutonium was effectively co-eluted with Eu^{3+} which initially implied that it was being eluted as Pu^{3+}. However, if this was the case, then plutonium should have been eluted with a shorter retention time than americium. In fact, the reverse elution order was observed which makes it unlikely that plutonium was present as Pu^{3+}. It is more likely that it was present as PuO_2^{2+} which forms a complex with oxalate containing 2 ligands and a complex with diglycolate that contains one ligand [86]. This constitutes a change in charge from -2 to 0 which would explain why the introduction of diglycolate would accelerate its elution from the CS5 column. Thorium was eluted in the oxalate eluant alone. Th^{4+} forms complexes with the oxalate ion, in the ratio 1 metal : 3 ligand which are divalent anionic complexes [87]. However, under the elution pH conditions, thorium is more likely to be present as $Th(OH)^{3+}$ and it is possible that this may only interact with two oxalate ligands forming a monovalent anionic complex which may explain why it is more readily eluted from the CS5 column than americium and plutonium.

Figure 2.30 Separation of yttrium-90 from other radionuclides using the Dionex system



The most important feature of the chromatogram with respect to the ^{90}Sr method development, is that ^{90}Y was well separated from the other radionuclides retained by the system, so these would not cause an interference problem with the subsequent β-counting of ^{90}Y.

2.4.6 Separation of a stable lanthanide standard using the Dionex system

Having established that ^{90}Y was isolated from the other radionuclides used, it was considered important to determine whether yttrium was successfully separated from other lanthanides using the Dionex system. This was investigated by analysing stable lanthanide standards using the Dionex system. Standards containing approximately 1 ppm of the stable lanthanides were loaded onto the Dionex system from 20 ml of 1 M ammonium acetate solution. The lanthanides in the CS5 column eluate were detected following post column derivitization with PAR by a UV-visible variable wavelength detector at 520 nm. Chromatograms of the stable lanthanides including and excluding yttrium are shown in figures 2.31 and 2.32 respectively and the retention times of the stable lanthanides measured using UV-visible detection and the lanthanide radionuclides measured by radiometric detection following fraction collection are shown in table 2.9.

Directly comparing a radioisotope and its stable isotope shows that the retention times differ, but the difference was consistently 1.4 minutes for the different elements. This difference in retention time must be due to the different pathways to the relevant detectors. Yttrium was eluted with a retention time similar to dysprosium and holmium. However, this should not be a major problem in the analysis of ^{90}Y since the only long lived β-emitting isotope of either of these elements is the metastable ^{166m}Ho. This isotope has an $E_{\beta max}$ of 67 keV [8] compared to that for ^{90}Y which is 2260 keV. Therefore the two isotopes could be easily distinguished when β-counting, whether using proportional, liquid scintillation or Cerenkov counting. It

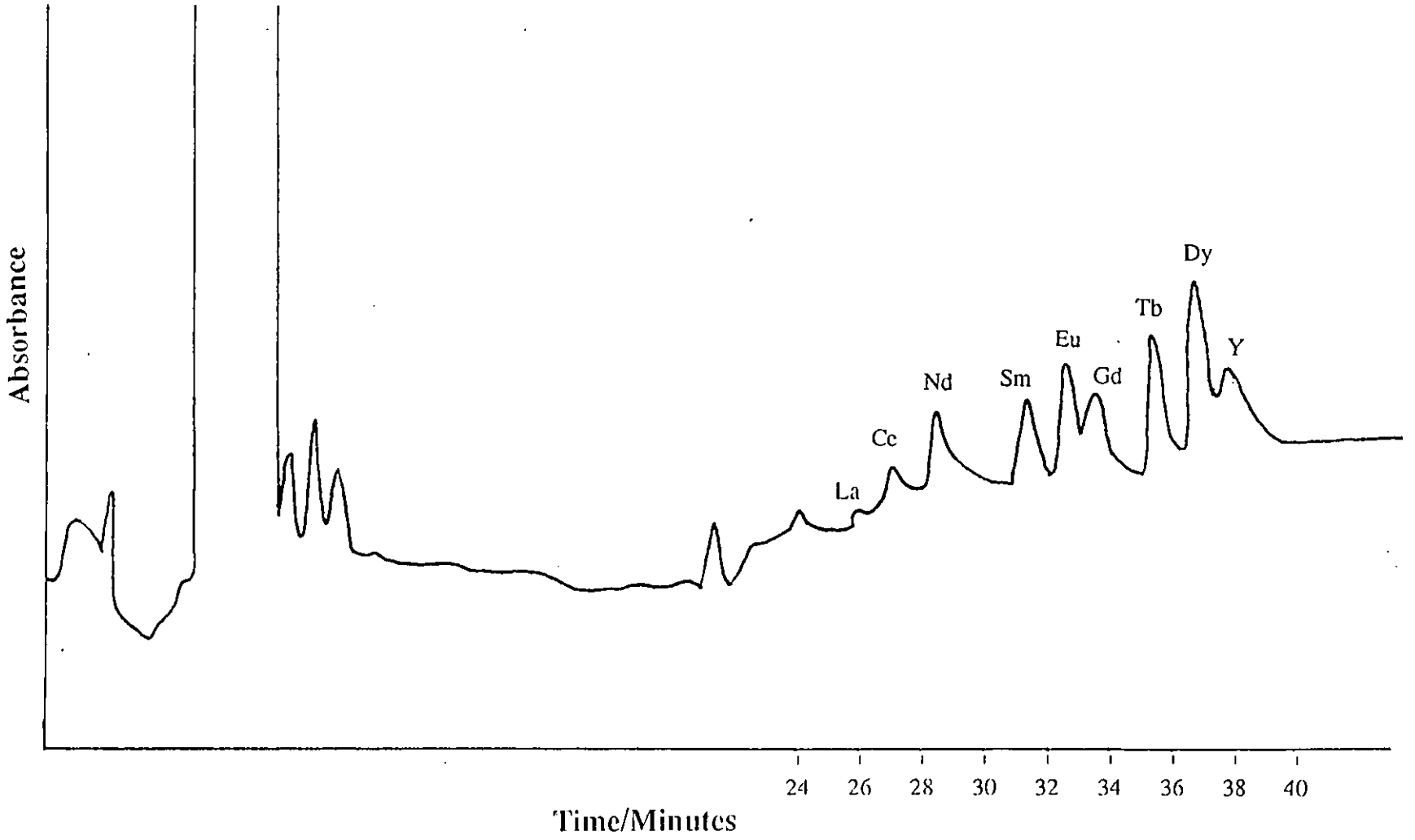


Figure 2.31 Chromatogram of stable lanthanide standard including yttrium

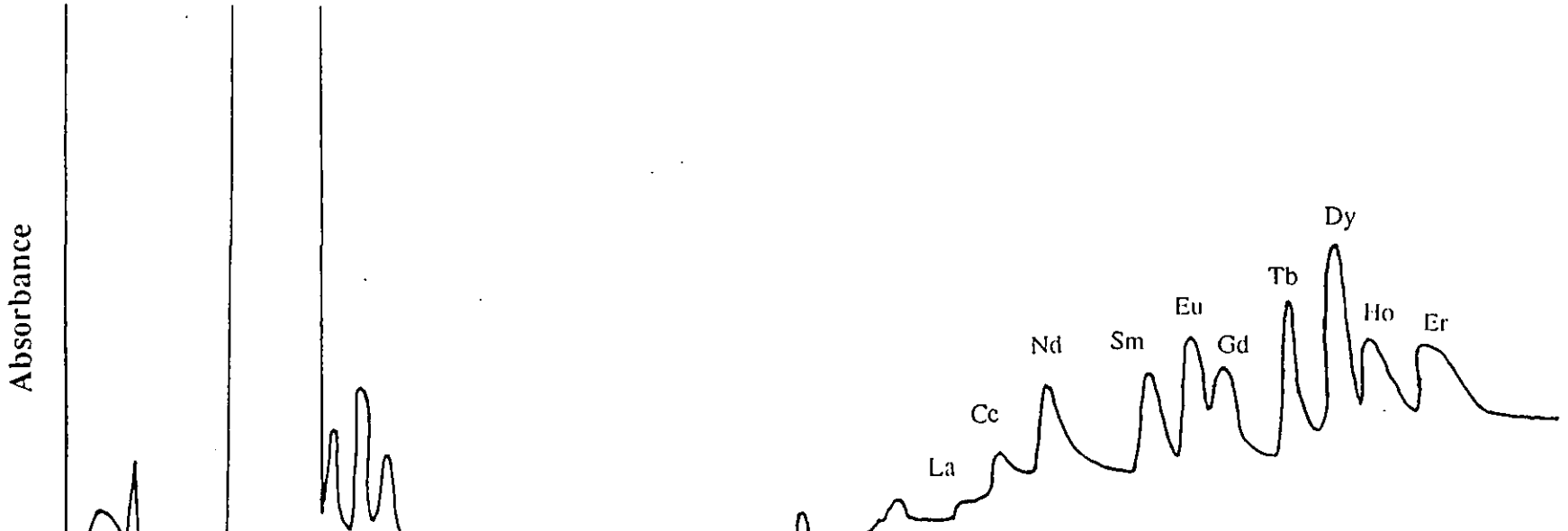


Figure 2.32 Chromatogram of stable lanthanide standard excluding yttrium

was also possible that actinides heavier than americium could co-elute with yttrium but it was not possible to demonstrate this due to the lack of availability of these actinides. However the presence of heavy actinides should not be an interference problem in the counting of ^{90}Y since the half-lives of the heavy α-emitting actinides are very short and the use of thin window proportional counting would exclude any contribution to the count due to α-emission.

Lanthanide	Retention time / minutes	
	uv-visible detection	Fraction collecting
La	26.0	–
Ce	27.0	28.3
Nd	28.6	–
Pm	–	31.3
Sm	31.4	–
Eu	32.6	34.0
Gd	33.6	–
Tb	35.4	–
Dy	36.8	–
Y	37.9	39.3
Ho	37.8	–
Er	40.0	–

Table 2.9 Retention time of lanthanides eluted from the CS5 column

Although the Dionex system permits the isolation of ^{90}Y from other interfering radionuclides, the approach of directly extracting ^{90}Y means that the presence of the short-lived radionuclide ^{91}Y would interfere with the counting of ^{90}Y. This radionuclide decays rapidly and would only be a significant problem soon after an accident scenario. If believed to be present, then the two radionuclides could be distinguished at the counting stage.

2.4.7 Quantitative determination of lanthanide radionuclides using the Dionex system

The recoveries of ^{90}Y, ^{141}Ce, ^{147}Pm and ^{152}Eu were determined using the Dionex system. A known count rate of each of the radionuclides were individually loaded onto the Dionex system from 20 ml of 1M ammonium acetate solution at a flow-rate of 2 ml min^{-1}. The radionuclides were collected in 2 ml fractions from the CS5 column and were measured by either Cerenkov, liquid scintillation or gamma counting. The recoveries of each of these radionuclides is shown in table 2.10.

Radionuclide	Count rate added /cpm	Count rate recovered /cpm	% Recovery
^{90}Y	1431 1614 1579 1440	1391 1588 1514 1394	97.2 98.4 96.8 96.8
			mean = 97.1 ± 1.0
^{147}Pm	1462 1442 1449	1418 1344 1464	97.0 94.8 100.9
			mean = 97.6 ± 3.1
^{141}Ce	1926 1839 1911	1861 1760 1802	96.6 95.7 94.3
			mean = 95.5 ± 1.2
^{152}Eu	2468 2731 2943	2396 2603 2778	97.1 95.3 94.4
			mean = 95.6 ± 1.4

Table 2.10 Quantitative determination of lanthanide radionuclides using the Dionex system

The recoveries for all the radionuclides used were greater than 90 % and were reproducible, which shows that the Dionex system permits the successful separation of yttrium and lanthanides in high yield.

2.4.8 Summary of the studies using the Dionex ion-chromatography system

The Dionex ion-chromatography system permitted the reproducible isolation of ^{90}Y in almost quantitative yield from test solutions. Using the elution program outlined in table 2.5 adjusted such that the final eluant composition was 51% water - 15% diglycolate - 34% oxalate, ^{90}Y was eluted from the CS5 column with a retention time of 39.3 minutes and was separated from other interfering radionuclides. The possibility of interference from ^{166m}Ho, ^{91}Y and heavy actinides could easily be dealt with at the counting stage.

The successful extraction of ^{90}Y by the CC-1 column was significantly affected by the presence of calcium. No more than approximately 200 mg of calcium could be present for successful extraction of ^{90}Y which meant that the system would only permit the analysis of 150 to 200 ml of milk. In order to improve the chances of detecting radionuclides at low-levels it is important to analyse as much sample as possible. Typically, 1 to 5 litres of milk are analysed in ^{90}Sr determinations and 500 ml was considered to be the minimum volume that should be analysed. Therefore, the Dionex system was unable to cope with what was considered the minimum sample volume required for milk analysis. It was therefore decided to investigate the possibility of including a simple clean-up step to permit larger sample sizes of milk to be analysed, by reducing the quantities of calcium present to a suitable level for the Dionex separation. The use of crown ether impregnated resins was investigated for the clean-up step and is discussed in chapter 3.

For the analysis of real samples, the addition of sufficient stable yttrium to act as a yield monitor was not possible using the Dionex system because the separation of yttrium was adversely affected. This meant that recoveries would have to be monitored by running an external ^{90}Y standard with each batch of samples. It was still possible to add nanogram levels of stable yttrium to act as a carrier.

Although it appeared that the Dionex system was not suitable for the direct analysis of milk samples, it should be suitable for the analysis of natural water samples since the calcium clean-up step would not be required. However, a pretreatment step would still be required to ensure the sample is in a suitable form for loading onto the CC-1 column and this is described in section 2.5.

Apart from ^{90}Y, the Dionex system demonstrated that it could be used to analyse other radionuclides of interest such as lanthanide fission products. This presents the possibility of a single analysis for several radionuclides.

2.5 Sample pretreatment for the analysis of water samples using the Dionex system

The Dionex system has permitted the isolation of ^{90}Y in high recovery from small volume solutions. For the low-level determination of ^{90}Sr in natural water samples, much larger sample volumes would be required, which would greatly increase the sample loading time onto the CC-1 column. More significantly, natural water samples may contain colloidal organic materials such as humic acid, which may bind to the ^{90}Y and the chelating resin used in the CC-1 column will not extract metal ions bound in this way [75]. In order to overcome these problems, the use of a simple pretreatment step, described below, involving evaporation, ashing and dissolution was investigated.

To 1 litre of surface water collected from Moscar, Derbyshire, UK, a known count rate of ^{90}Sr and ^{90}Y, 40 ng of yttrium carrier (yttrium nitrate hexahydrate in 2 M nitric acid) and 20 ml of nitric acid (s.g. 1.42) were added. The water was evaporated to dryness and the residue ashed at 550 °C in a muffle furnace to destroy any organic material present. The ash was then dissolved in 25 ml of 1 M nitric acid and the resulting solution was Cerenkov counted. The recoveries of ^{90}Y for three replicate water samples are shown in table 2.11.

^{90}Y count rate added / cpm	^{90}Y count rate recovered/cpm	% Recovery
1854	1773	95.6
1728	1641	95.0
1629	1584	97.2
		mean = 95.9 ± 1.1

Table 2.11 Recoveries of ^{90}Y from the pretreatment step for water samples

The recoveries were reproducible and high and the mean recovery was 95.9 ± 1.1 %. This shows that the pretreatment step would be suitable for the analysis of natural water samples. In the complete method, the nitric acid solution would be buffered to pH 5 with 2 M ammonium acetate and then loaded onto the CC-1 column.
The method for the determination of ^{90}Sr in natural water samples is described in chapter 5.

Chapter 3

STUDIES USING CATION-SELECTIVE EXTRACTION RESINS

3 STUDIES USING CATION SELECTIVE EXTRACTION RESINS

3.1 Crown ether resins

Crown ethers having the ability to form strong complexes with alkali and alkaline-earth metals were first synthesized by Pederson in 1967 [88]. Since then, considerable efforts have been made to apply these compounds to problems in analytical chemistry. The utility of crown ethers in analytical chemistry rests in their ability to complex cations of a specific size. When the cation is bound to the crown ether, it imparts a positive charge which is balanced by the presence of a suitable anion. The selectivity of the crown ether for a particular cation is governed by the cavity size relative to the cation, the substituents present on the crown ring and the nature of the associated anion.

M^{c} Dowell et. al. [89] demonstrated by solvent extraction studies that the cavity size and the flexible structure of the dicyclohexano-18-crown-6 and its derivatives provide a very selective complexing environment for strontium ions. As a result, this crown ether has been used as a selective solvent extraction reagent in methods for the determination of ^{90}Sr [36-42]. However, disadvantages associated with these methods include that high pHs are required for the strontium separation and that losses of the crown ether occur from the organic phase due to partial dissolution into the aqueous phase. In order for these crown ethers to be useful in environmental analysis, the crown ether should be soluble in a solvent which is immiscible with water, be practically insoluble in water and ideally have a high complexing ability in acidic media since samples are usually acid digested prior to separation. The complexation should also be easily reversible, possibly by simply increasing the pH of the aqueous phase.

Recently, Horwitz et. al. [90] negated the use of solvent extraction procedures using the crown ethers by producing chromatographic resins which were prepared by

adsorbing bis-4,4(5) (t-butyl) cyclohexano-18-crown-6 (DCH18C6) onto Amberlite XAD-7 from a 1 M solution of 1-octanol. The resins are commercially available from EIChroM Industries, Inc. under the trade name Sr.Spec. Figure 3.1 shows the crown ether used in the resins. The cavity size of the DCH18C6 is 260-320 pm and is highly selective for strontium which has an ionic diameter of 254 pm.

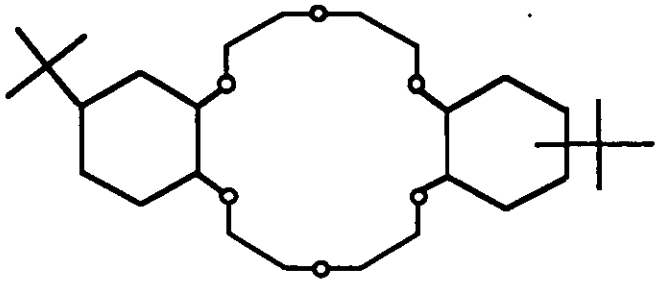


Figure 3.1 Structure of the extractant used in the Sr.Spec resins

Strontium is extracted by the DCH18C6 on the resin as a neutral nitrate complex from nitric acid solutions according to the extraction equilibrium described below:

$$Sr^{2+} + 2NO_3^- + DCH18C6 \rightleftharpoons Sr(NO_3)_2(DCH18C6) \qquad (3\text{-}1)$$

Other cations that may have a weak interaction with the DCH18C6 can be eluted from the Sr.Spec resin using dilute nitric acid. However, under these conditions lead, barium and mercury also have been shown to have a strong interaction with the DCH18C6 and are retained by the resin [44]. The eluant used to remove strontium from the resin is water which complexes with the strontium and competes effectively with the crown ether.

Horwitz reported that the extraction of strontium by the resin was not affected by the presence of macro quantities of calcium [43]. It was therefore considered that the

Sr.Spec resin could be used as the simple clean-up step to reduce the large quantities of calcium present in milk samples to a level suitable for the Dionex system. Using these resins, ^{90}Sr, ^{89}Sr and a few other cations would be isolated from the sample. Therefore, an ^{90}Y ingrowth period would be required prior to the Dionex separation of ^{90}Y. Since strontium is extracted by the resin from nitric acid solution, the extraction of ^{90}Sr could be carried out directly from acid digested samples. The Sr.Spec resin used in the following experiments was present in prepackaged 2 ml columns which have a maximum capacity of 17.8 mg of strontium and a recommended working capacity of 2 - 4 mg [91].

3.2 Preliminary studies using the Sr.Spec columns

Initially, the behaviour of strontium on the Sr.Spec resin was investigated to determine its suitability for extracting strontium in the presence of the levels of calcium equivalent to 1 litre of milk.

3.2.1 Separation of ^{90}Sr from ^{90}Y on the Sr.Spec columns

Test solutions comprising approximately 15 Bq each of ^{90}Sr and ^{90}Y in 25 ml of 3 M nitric acid were loaded onto the Sr.Spec column at the gravity flow rate of approximately 0.7 ml min^{-1}. An aliquot of the sample eluate was then liquid scintillation counted to determine the count rate present. The column was then eluted with 2 ml aliquots of 3 M nitric acid until the count rate in the eluates was reduced to background. Three 2 ml aliquots of nitric acid were required to reduce the count rate in the eluate to background. The column was then eluted with 2 ml aliquots of HPLC grade water until the count rate in the eluates was reduced to background. Three 2 ml aliquots of water were required to reduce the count rate in the eluate to background. The results of this experiment are summarized in row 1 of table 3.1 which shows that approximately 50 % of the count rate loaded was present in the nitric acid and was not extracted by the resin and approximately 50 % of the total count rate was present

in the water and was extracted by the resin. Since the resin is strontium selective, it was assumed that the count rate retained by the resin was due to ^{90}Sr and the count rate not retained was due to ^{90}Y. This was checked by repeating the experiment except that in this case, the sample solution and column eluates were Cerenkov counted. Row 2 of table 3.1 shows that a negligible count rate was observed for the water eluate and approximately 100 % of the original count rate was observed in the nitric acid eluate. These results combined with the liquid scintillation counting results demonstrated that ^{90}Y was not extracted by the column whereas the ^{90}Sr was extracted essentially quantitatively by the resin.

3.2.2 Behaviour of calcium on the Sr.Spec columns

Test solutions were prepared by dissolving 1.2 g of calcium, as calcium nitrate tetrahydrate, in 3 M nitric acid. The solutions were then spiked with approximately 30 Bq of ^{45}Ca and made up to 25 ml with 3 M nitric acid. The test solutions were loaded onto Sr.Spec columns at the gravity flow rate and the columns were then eluted with 2 ml aliquots of 3 M nitric acid until the count rate in the eluate was reduced to background. The column was then eluted with 2 ml aliquots of HPLC water. The count rates in an aliquot of the test solution, the test solution eluate and nitric acid eluates were determined by liquid scintillation counting. The results for this experiment are summarized in row 3 of table 3.1. The count rate due to ^{45}Ca was predominantly recovered in the test solution eluate and the count rate was reduced to background after the column had been eluted with 6 ml of 3 M nitric acid. A negligible count rate was observed in the water eluates. The ^{45}Ca was essentially quantitatively eluted from the column after the nitric acid elution. Assuming that the ^{45}Ca was evenly distributed within the inactive calcium in the sample, the results show that the mass of calcium equivalent to that present in a litre of milk had no significant interaction with and was easily eluted from the resin. Therefore it should have been possible to isolate ^{90}Sr in the presence of this amount of calcium using the resin.

Sample	Count rate added / cpm	Count rate in HNO_3 / cpm	Count rate in water / cpm	Count rate recovered / cpm	% count rate in HNO_3	% count rate in water	% Total recovery
1. ^{90}Sr - ^{90}Y in 25 ml of 3 M nitric acid. Liquid scintillation counted	1859	894	931	1825	48.1	50.1	98.2
	1874	898	886	1784	47.9	47.3	95.2
	1866	886	896	1782	47.5	48.0	95.5
				mean	47.8±0.3	48.5±1.5	96.3±1.7
2. ^{90}Sr - ^{90}Y in 25 ml of 3 M nitric acid. Cerenkov counted	998	974	10	984	97.6	1.0	98.6
	986	966	8	974	97.8	0.8	98.6
	979	961	8	969	98.2	0.8	99.0
				mean	97.9±0.3	0.9±0.1	98.7± 0.2
3. 1.2 g of Ca^{2+} + ^{45}Ca in 25 ml of 3 M nitric acid	32059	30328	<1	30328	94.6	<1	94.6
	35072	33915	<1	33915	96.7	<1	96.7
	34683	33470	<1	33470	96.5	<1	96.5
				mean	95.9±1.1	<1	95.9±1.1
4. 1.2 g of Ca^{2+} + ^{90}Sr - ^{90}Y in 25 ml of 3 M nitric acid. Liquid scintillation counted	1973	983	911	1894	49.8	46.2	96.0
	1862	884	894	1778	47.5	48.0	95.5
	1869	899	914	1813	48.1	48.9	97.0
				mean	48.5±1.2	47.7±1.4	96.2±0.8
5. 1.2 g of Ca^{2+} + ^{90}Sr - ^{90}Y in 25 ml of 3 M nitric acid. Cerenkov counted	918	911	7	918	99.0	0.8	99.8
	867	858	7	865	99.0	0.8	99.8
	871	860	8	868	98.7	0.9	99.6
				mean	98.9±0.2	0.8±0.1	99.7±0.1

Table 3.1 Behaviour of ^{90}Sr - ^{90}Y and calcium on the Sr.Spec columns

3.2.3 Effect of calcium on the extraction of ^{90}Sr by the Sr.Spec columns

Test solutions were prepared as described in section 3.2.2, but in this case, the solutions were spiked with approximately 15 Bq each of ^{90}Sr and ^{90}Y. The solutions were loaded onto the Sr.Spec columns which were then eluted with 10 ml of 3 M nitric acid followed by 10 ml of HPLC water. Aliquots of the test solutions and each of the column eluates were initially Cerenkov counted and then liquid scintillation counted. The results from this experiment are summarized in rows 4 - 5 of table 3.1. The count rates recovered in the water eluates and the combined test solution and nitric acid eluates for liquid scintillation counting were both approximately 50 %. For Cerenkov counting, approximately 100 % of the loaded count rate was present in the combined test solution and nitric acid eluates. This confirmed that even in the presence of a large excess of calcium, equivalent to that may be present in a litre of milk, ^{90}Sr was essentially quantitatively extracted by the resin.

3.3 Studies of environmental samples using the Sr.Spec columns

3.3.1 Separation of strontium from environmental samples

Since the Sr.Spec columns permitted the successful extraction of ^{90}Sr in the presence of greater than 1 g of calcium, it was considered useful to determine whether ^{90}Sr could be successfully extracted from real environmental samples. Four samples each of milk and cabbage were analysed. The cabbage samples were prepared by digesting 5 g of cabbage ash (equivalent to approximately 600 g of raw cabbage) in 3 M nitric acid. The milk samples were prepared by digesting 7 g of milk ash (equivalent to approximately 1 litre of milk) in 3 M nitric acid. The eight samples were then spiked with 40 Bq each of ^{90}Sr and ^{90}Y. The total sample volume in each case was approximately 50 ml, which was the minimum volume required to keep the samples in solution.

The samples were loaded onto the Sr.Spec columns at the gravity flow rate. The columns were then eluted with 10 ml of 3 M nitric acid followed by 10 ml of HPLC water. The water eluates were then liquid scintillation counted. The recoveries of ^{90}Sr are shown in table 3.2.

Sample Type	Total count rate added / cpm	Total count rate recovered / cpm	% Recovery
Cabbage 1	5068 ± 60	182 ± 4	3.6 ± 0.1
Cabbage 2	5103 ± 61	176 ± 4	3.5 ± 0.1
Cabbage 3	4953 ± 60	192 ± 4	3.4 ± 0.1
Cabbage 4	5139 ± 63	204 ± 4	4.0 ± 0.1
Milk 1	5163 ± 97	140 ± 3	2.7 ± 0.1
Milk 2	5098 ± 96	163 ± 3	3.2 ± 0.1
Milk 3	5216 ± 87	185 ± 4	3.6 ± 0.1
Milk 4	5000 ± 87	148 ± 3	3.0 ± 0.1

Table 3.2 Recoveries of ^{90}Sr from spiked environmental samples using the Sr.Spec columns

The count rates recovered in the water eluates for all the samples were less than 5 % of the total count rate added to the sample, which implied that the ^{90}Sr recovered in each case was less than 10 %.The low recoveries of ^{90}Sr from the Sr.Spec columns implied that some part of the sample matrix affected the interaction of ^{90}Sr with the Sr.Spec column. In order to determine whether the low recoveries could be attributed to any particular part of the sample matrix, the behaviour of strontium and other principal cations at various stages of the separation was monitored using inductively coupled plasma atomic emission spectroscopy (ICP-AES).

3.3.2 ICP-AES analysis of the Sr.Spec column separation

Two milk and two cabbage samples were prepared as described in section 3.3.1 and one of each of the samples was spiked with approximately 3 mg of inactive strontium as strontium nitrate. No radioactive spike was added to the samples. The acid digested samples were loaded onto Sr.Spec columns at the gravity flow rate. The columns were then eluted with 4 x 5 ml of 3 M nitric acid followed by 20 ml of HPLC water. All of the eluates and aliquots of the acid digested sample were retained for ICP-AES analysis. The results of these analyses are summarized in tables 3.3 - 3.6.

The recoveries of strontium in the water eluate for the spiked samples were 6.9 % for cabbage and 8.7 % for milk which were consistent with the results from section 3.3.1. Approximately 80 % of the loaded strontium in each case was recovered in the sample eluate and 10 % in the first nitric acid eluate for both the milk and cabbage samples. The levels of the other principal cations were also high in the sample eluates and the first nitric acid eluates. For both the milk and cabbage samples, the most significant cations present in the water eluates apart from strontium were potassium and calcium. Calcium on it own had been previously shown not to have a significant effect on the extraction of strontium by the Sr.Spec resin. It was therefore possible that it was the large quantities of potassium in the sample or a combination of the potassium and calcium that had a significant effect on the extraction of strontium by the resin.

Since approximately 90 % of the strontium was eluted after the first nitric acid elution and was eluted in approximately constant amounts in the subsequent nitric acid elutions, it was considered that strontium could be simply breaking through the column. A breakthrough curve and the effect of potassium on the extraction of strontium were therefore determined.

Table 3.3 ICP-AES analysis of a milk sample passed through a Sr. Spec column

	Mass of principal cations present / μg						
	Sr	Ca	Mg	Na	K	Zn	Fe
Sample prior to column	108	>963510	>80603	>233608	>87800	3623	348
Sample eluate	72	>1077001	>89843	>265162	>974306	3258	318
1st HNO_3 eluate (5ml)	8	>36849	2981	8956	>38940	95	21
2nd HNO_3 eluate (5ml)	3	64	8	14	145	<1	4
3rd HNO_3 eluate (5ml)	3	59	8	12	116	<1	4
4th HNO_3 eluate (5ml)	2	58	8	12	112	<1	4
Water eluate	16	15	<1	5	105	<1	<1

Table 3.4 ICP-AES analysis of milk sample spiked with inactive strontium passed through a Sr. Spec column

	Mass of principal cations present / μg						
	Sr	Ca	Mg	Na	K	Zn	Fe
Sample prior to column	3374	>905291	>75890	>220561	>821773	3096	389
Sample eluate	2546	>864873	>72079	>209868	>774382	2943	351
1st HNO_3 eluate (5ml)	224	>38192	3057	9149	>39072	130	15
2nd HNO_3 eluate (5ml)	68	78	7	16	198	<1	12
3rd HNO_3 eluate (5ml)	68	50	6	11	85	<1	3
4th HNO_3 eluate (5ml)	69	47	6	10	82	<1	3
Water eluate	292	19	<1	3	40	<1	<1

Table 3.5 ICP-AES analysis of a cabbage sample passed through a Sr. Spec column

	Mass of principal cations present / μg						
	Sr	Ca	Mg	Na	K	Zn	Fe
Sample prior to column	203	>267623	>46216	>42611	>789317	1435	4148
Sample eluate	159	>297881	>51627	>47615	>877106	1285	3693
1st HNO_3 eluate (5ml)	11	10835	1891	1759	>38071	42	157
2nd HNO_3 eluate (5ml)	3	148	16	19	769	3	5
3rd HNO_3 eluate (5ml)	3	61	9	13	787	<1	5
4th HNO_3 eluate (5ml)	3	59	8	12	118	<1	4
Water eluate	19	181	6	9	531	7	2

Table 3.6 ICP-AES analysis of a cabbage sample spiked with inactive strontium passed through a Sr. Spec column

	Mass of principal cations present / μg						
	Sr	Ca	Mg	Na	K	Zn	Fe
Sample prior to column	3383	>284370	>46183	>46366	>824728	1376	3413
Sample eluate	2887	>284774	>46400	>46733	>825103	1413	3408
1st HNO_3 eluate (5ml)	210	>12012	1892	1978	>40577	57	145
2nd HNO_3 eluate (5ml)	45	45	6	10	151	<1	3
3rd HNO_3 eluate (5ml)	44	42	6	9	78	<1	3
4th HNO_3 eluate (5ml)	42	41	6	9	75	<1	3
Water eluate	226	146	<1	4	65	6	3

3.3.3 Determination of breakthrough curves for the Sr.Spec columns

Samples comprising 15 Bq each of ^{90}Sr and ^{90}Y in 10 ml of 3 M nitric acid and 30 Bq ^{45}Ca in 10 ml of 3 M nitric acid were loaded onto Sr.Spec columns. The columns were then eluted with 2 ml aliquots of 3 M nitric acid, the eluates were collected and liquid scintillation counted. The resulting breakthrough curves are shown in figure 3.2.

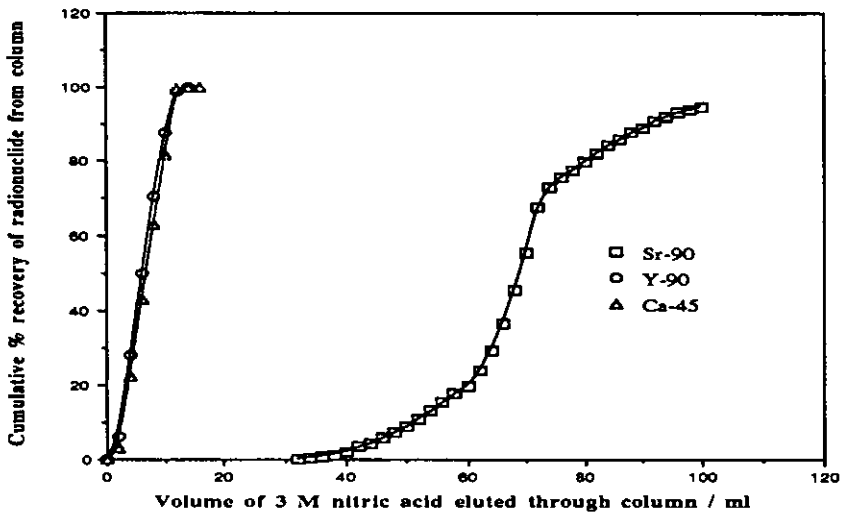


Figure 3.2 Breakthrough curves for ^{90}Sr, ^{90}Y and ^{45}Ca on the Sr.Spec columns

The ^{90}Y and the ^{45}Ca were eluted from the column after washing the column with 6 ml of 3 M nitric acid which further demonstrated the negligible interaction that calcium and yttrium have with the Sr.Spec columns. ^{90}Sr began to elute from the column after 32 ml of 3 M nitric acid had been eluted through the column (including the 10 ml sample volume). Therefore the column was limited to a maximum loading volume of approximately 32 ml before ^{90}Sr breakthrough occurred. This therefore limits the maximum working loading volume to approximately 25 ml since 6 ml nitric acid would be required to elute residual cations from the column. The limitation in the loading volume would therefore limit the actual amount of sample which could be analysed, since the maximum amount that could be analysed would

be that which could be dissolved to a total volume of 25 ml unless some other preconcentration step was included.

The breakthrough of ^{90}Sr from the Sr.Spec column as a function of the volume of nitric acid eluted through partially explains the low recoveries of strontium from the environmental samples, because a 50 ml sample volume was used, which exceeded the breakthrough capacity of the column. However, if the sample volume alone were the only factor affecting the interaction of strontium with the column, then according to the breakthrough curve only approximately 20 % of the strontium loaded would have been present in the sample eluate for the environmental samples whereas 80 % was actually observed. This further implied that other ions present in the sample matrix, probably potassium, must also have contributed to the reduced recoveries of strontium from the column.

3.3.4 Effect of potassium on the extraction of strontium by the Sr.Spec columns

Test solutions were prepared by dissolving varying masses of potassium nitrate in HPLC grade water. 1 mg of strontium was added, as the nitrate, to the solutions which were then diluted to 25 ml with water. The solutions were loaded onto the Sr.Spec columns at the gravity flow rate and the columns were eluted with 6 ml of 3 M nitric acid followed by 6 ml of water. The strontium content in the water eluates was measured by ICP-AES. Figure 3.3 shows that the extraction of strontium by the column is reduced significantly as the mass of potassium present increased. The potassium therefore must have a significant interaction with the DCH18C6 present on the resin and must successfully compete with strontium for the complexing sites. When potassium is present in large excess it must 'swamp' the available sites, preventing significant extraction of strontium. The interaction of the potassium ion with the resin can be explained by its ionic diameter being 266 pm which enables it

to also fit into the into the cavity of the crown. The extraction equilibrium for potassium is shown below

$$K^+ + NO_3^- + DCH18C6 \rightleftharpoons K(NO_3)(DCH18C6) \qquad (3\text{-}2)$$

The curve in figure 3.3 shows that the extraction of strontium is initially significantly reduced by the presence of up to 250 mg of potassium but the effect decreases as the mass of potassium present increases above this value, since the gradient of the curve decreases. Even when the mass of potassium present was a thousand times that of strontium, 10 % of the strontium was still extracted, which implies that the resin has some degree of higher selectivity for strontium than potassium.

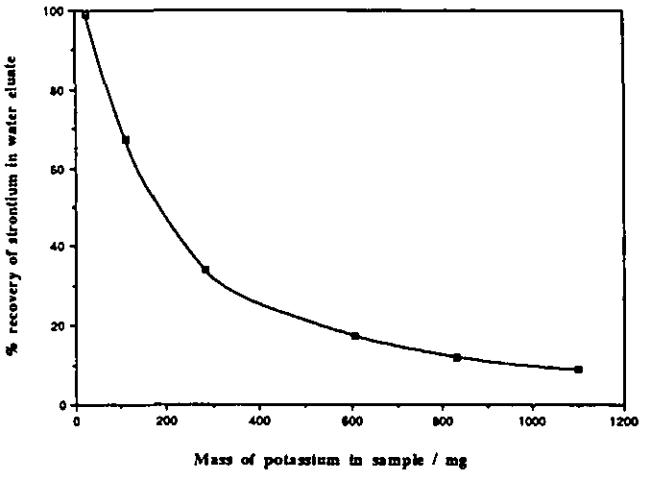


Figure 3.3 Effect of potassium on the extraction of strontium by the Sr.Spec columns

3.3.5 Determination of the loading capacity of the Sr.Spec columns for a variety of environmental samples

Since the interaction of strontium with the Sr.Spec columns depended on the volume of solution loaded and the presence of potassium in the sample, it was decided to determine the maximum amounts of different sample types that could be loaded

directly onto the columns. This would make it possible to establish to what degree the columns would be useful for environmental analysis of ^{90}Sr. The sample types used in the investigation were milk, cabbage, urine and fish. The samples were dried, then ashed at 550 °C overnight. The ash was then treated with nitric acid (s.g. 1.42) and re-ashed. The resulting residue was then digested in 3 M nitric acid for 1 hour. The samples were cooled, filtered to remove any insoluble residue and then diluted to 50 ml with 3 M nitric acid. Aliquots of the sample solutions were then removed, spiked with ^{90}Sr - ^{90}Y and diluted to 25 ml with 3 M nitric acid. The spiked samples were loaded onto Sr.Spec columns at the gravity flow-rate. The columns were then eluted with 6 ml of 3 M nitric acid to elute any residual cations, followed by 12 ml of HPLC water to elute the ^{90}Sr. The water eluates were then liquid scintillation counted.

Figures 3.4 - 3.8 show the variation in the recovery of ^{90}Sr with the quantity of sample analysed for milk, cabbage, grass, urine and fish respectively. In each case, the shape of the curves produced are similar to the curve for the strontium recovery as a function of potassium present. This further implied that the presence of potassium was the principal reason for reduced extraction of strontium by the Sr.Spec columns.

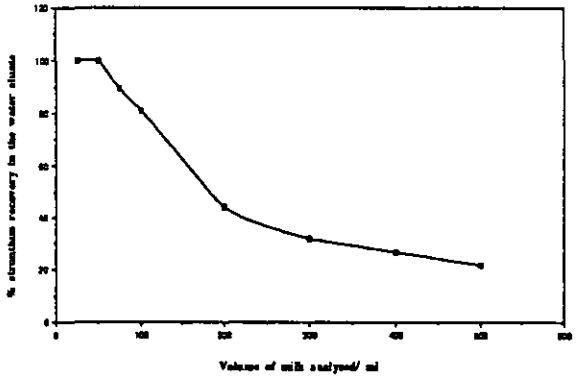


Figure 3.4 Effect of the amount of sample on the analysis of milk using the Sr.Spec columns

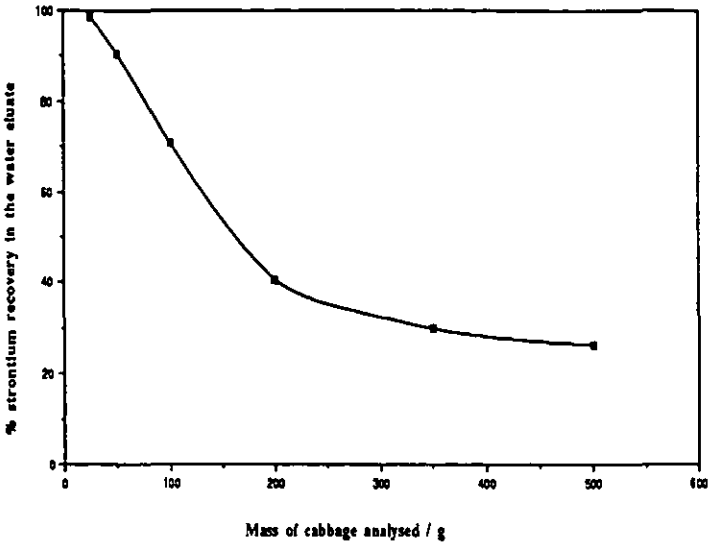


Figure 3.5 Effect of the amount of sample on the analysis of cabbage using the Sr.Spec columns

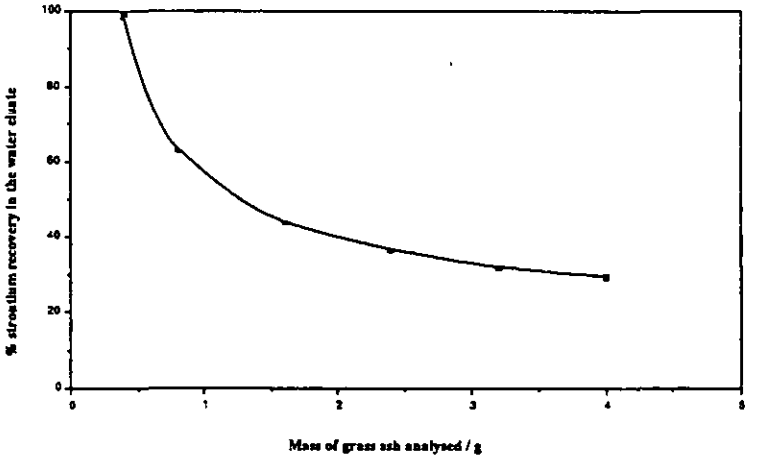


Figure 3.6 Effect of the amount of sample on the analysis of grass using the Sr.Spec columns

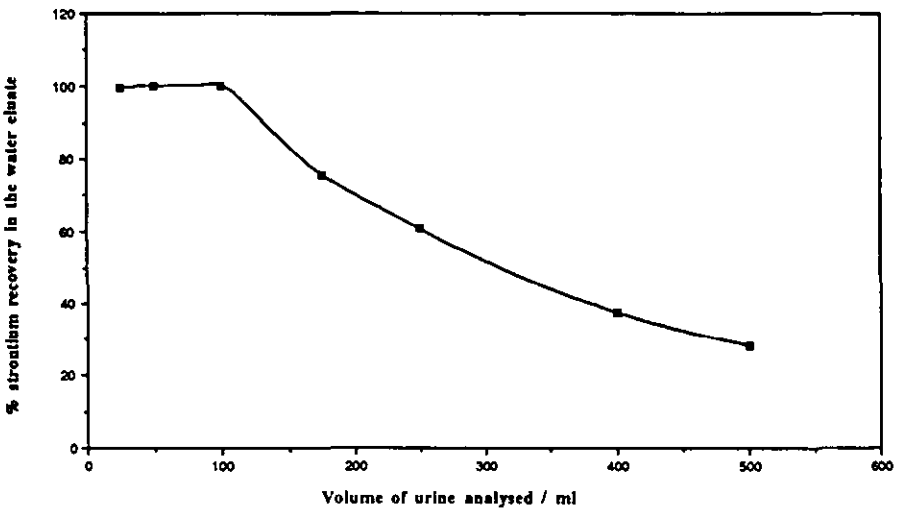


Figure 3.7 Effect of the amount of sample on the analysis of urine using the Sr.Spec columns

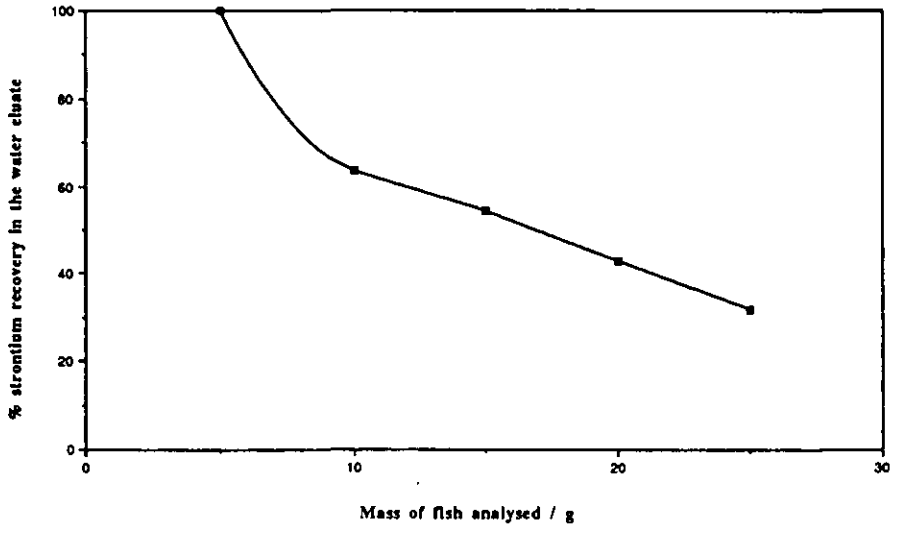


Figure 3.8 Effect of the amount of sample on the analysis of fish using the Sr.Spec columns

The approximate maximum amounts of the various sample types that permit the extraction and elution of ^{90}Sr from the Sr.Spec columns in greater than 90 % recovery are shown in table 3.7.

Sample	Amount of sample loaded for >90% recovery of ^{90}Sr
Urine	100 ml
Cabbage	50 g
Grass	60 g
Fish	5 g
Milk	50 ml

Table 3.7 The maximum amounts of sample that can be analysed by the Sr.Spec columns

The value quoted for grass is derived from the fact that approximately 8 g of the grass ash was equivalent to 1 kg of raw grass. The amount of milk that could be successfully analysed by the Sr.Spec columns was approximately 50 ml which was significantly less than the amount of milk that could possibly be directly analysed using the Dionex system. Thus there was no advantage in using these columns as a calcium clean-up step for the Dionex system.

A simple approach to increase the sample size that could be analysed using the Sr.Spec resin without including another pretreatment step was to increase the amount of resin used in a column. However, the cost of the Sr.Spec resin at the time of use was £1400 for 100 g and it was considered that the increase in the amount of resin required for the analysis of at least 500 ml of milk would give rise to an unacceptably high cost for routine analysis.

Another available option that was considered was the use of another resin available from EIChroM Industries, Inc. that is selective for lanthanides and actinides, which is available under the trade name TRU.Spec. Due to the chemical similarity between the lanthanides and yttrium, it was considered that this resin may provide the simple calcium clean-up step for the Dionex system required for milk analysis.

3.4 Studies using the TRU.Spec resins [92]

The TRU.Spec resin comprises octyl (phenyl)- N,N-diisobutyl-carbamoyl-methylphosphine oxide (CMPO) dissolved in TBP supported on Amberlite XAD-7. The CMPO is selective for lanthanides and actinides which are extracted as neutral nitrate complexes from nitric acid solutions ranging from 0.75 M to 6 M. Other cations are eluted from the resin with 2 M nitric acid and lanthanides and actinides are eluted using 0.05 M nitric acid. The extractant and extraction equilibrium for lanthanides are shown in figure 3.9 and equation (3-3) respectively.

$$Ln^{3+} + 3NO_3^- + 3CMPO \rightleftharpoons Ln(NO_3)_3(CMPO)_3 \qquad (3\text{-}3)$$

Although yttrium is chemically similar to the lanthanides, Horwitz reported that yttrium has a lower affinity for the resin than the lanthanides, but has a much higher affinity than alkali- and alkaline-earth metals [92]. Thus, although the resin may be used to extract ^{90}Y from an acid digested sample, losses of ^{90}Y could occur when eluting residual alkali- and alkaline-earth metals from the resin. Providing that the losses were low and consistent, the TRU.Spec resin could be used as the clean-up step for the Dionex system.

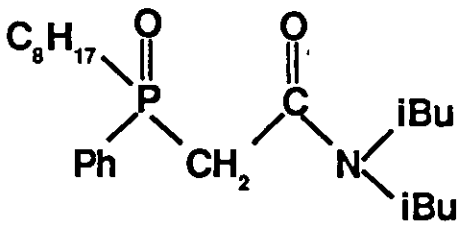


Figure 3.9 Structure of the extractant used in the TRU.Spec resins

In the experiments using these columns, prepackaged 2 ml columns were used. Since losses of yttrium from the columns were expected, the variation in losses of yttrium with increasing sample volume was investigated.

Test solutions were prepared by spiking varying volumes of 2 M nitric acid with either ^{90}Y or ^{45}Ca. The ^{90}Y was prepared by separating ^{90}Sr and ^{90}Y on the Dionex CC-1 column. The solutions were loaded onto the TRU.Spec columns at the gravity flow rate and the eluate was collected in 2 ml fractions and liquid scintillation counted. The column was then eluted with 2 ml aliquots of 2 M nitric acid until the count rate in the eluate was reduced to background. Figures 3.10 - 3.12 show the variation in the elution behaviour of the two radionuclides from the TRU.Spec column with the volume of nitric acid eluted for varying volumes of test solution loaded. Figure 3.13 shows a plot of ^{90}Y in the test solution eluate as a function of the volume of test solution loaded. Even when the volume of test solution loaded was 10 ml, at least 20 % of the ^{90}Y was eluted straight through the resin. Thus to minimize losses of ^{90}Y from the resin would require the volume of acid digested sample loaded to be small. This volume would be impractical for an acid digested 1 litre milk sample, since approximately 50 ml of 3 M nitric acid was required to keep the sample in solution.

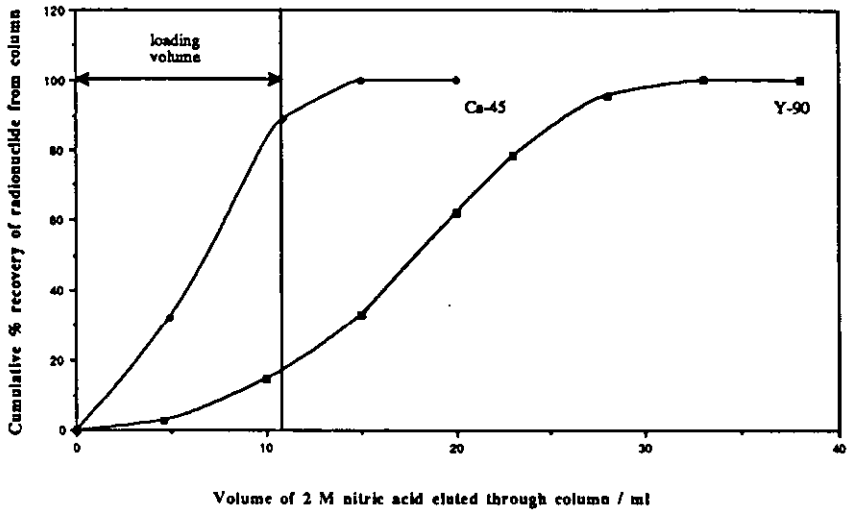


Figure 3.10 Elution behaviour of ^{90}Y and ^{45}Ca from a TRU.Spec column for a 10 ml loading volume

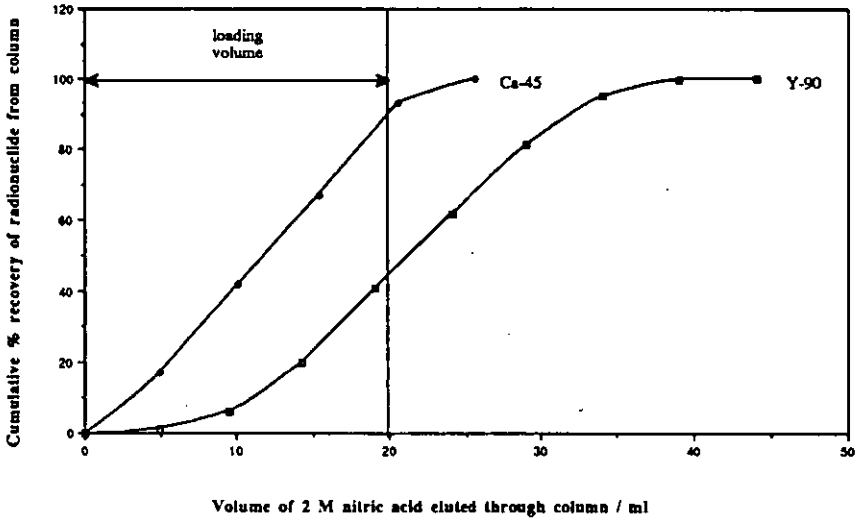


Figure 3.11 Elution behaviour of ^{90}Y and ^{45}Ca from a TRU.Spec column for a 20 ml loading volume

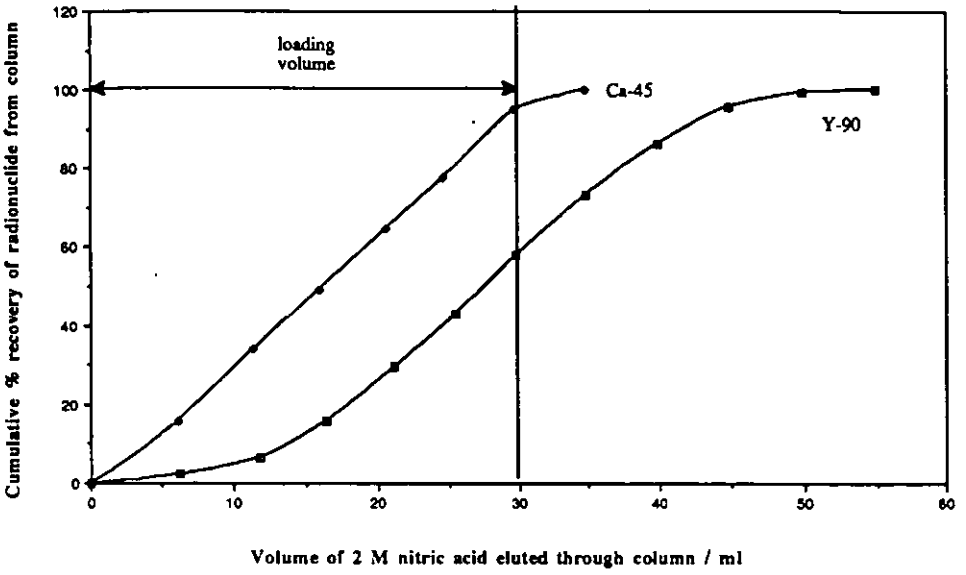


Figure 3.12 Elution behaviour of ^{90}Y and ^{45}Ca from a TRU.Spec column for a 30 ml loading volume

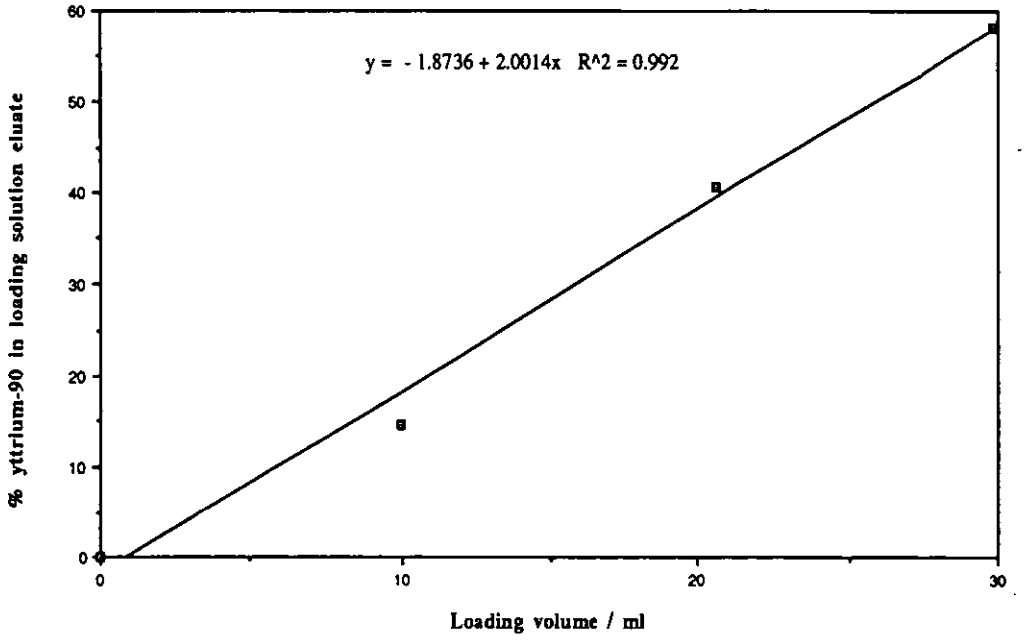


Figure 3.13 Variation in the recovery of ^{90}Y in the loading solution eluate for the TRU.Spec column with change in loading volume

3.5 Summary of the studies using the cation selective extraction resins

Both the Sr.Spec and the TRU.Spec columns appeared to be unsuitable as a single stage clean-up step for the analysis of milk using the Dionex system. The extraction of ^{90}Y by the TRU.Spec column required the loading volume to be small, otherwise significant losses of ^{90}Y occurred. Such small volumes would not be feasible for the analysis of a suitable milk sample size. The volume of solution that could be loaded onto the Sr.Spec columns was also limited, but to a significantly lesser extent than the TRU.Spec columns. However, the major factor reducing the effectiveness of the Sr.Spec columns for milk analysis was the presence of potassium. The levels of potassium in milk are such that a maximum of approximately 50 ml of milk could be successfully analysed by the column, otherwise significant losses of ^{90}Sr occurred. This volume of milk is less than the volume that could be directly analysed directly on the Dionex system. For either of these columns to be successful as a clean-up step, another pretreatment step would be required prior to the column in order to reduce the loading volume to a suitable size and the potassium to suitable levels. Comparing the two column materials, the Sr.Spec column permitted the loading of a larger volume of solution before losses of analyte occurred. It was also shown that the Sr.Spec column could tolerate calcium in quantities equivalent to 1 litre of milk. Thus, the Sr.Spec columns demonstrated more potential as the clean-up step providing that the levels of potassium could be reduced. Therefore, it was decided to investigate a clean-up step for the Sr.Spec columns. The approach that was selected was a co-precipitation step to reduce the levels of potassium that would be loaded onto the column.

Chapter 4

STUDIES USING A CO-PRECIPITATION STEP

4 STUDIES USING A CO-PRECIPITATION STEP

4.1 Co-precipitation step for ^{90}Sr in milk samples

Co-precipitation has been widely used as a preconcentration step in determinations of radionuclides in environmental materials. It provides a means of reducing a large sample size to one which can be manipulated more easily and also removes large quantities of the matrix elements present in the sample. In ^{90}Sr determinations, co-precipitants commonly used include carbonates[3,6], oxalates [6,31,45] and phosphates [3,6,43]. Co-precipitation of ^{90}Sr with calcium phosphate is particularly suitable for milk analysis due to the high calcium and phosphate concentrations inherently present. Therefore, the use of calcium phosphate to co-precipitate ^{90}Sr and reduce the levels of potassium present prior to the separation using the Sr.Spec resins was investigated for milk samples.

4.1.1 Determination of the optimum pH for co-precipitation of strontium with calcium phosphate

To eight portions of milk ash equivalent to 1 litre of milk, 2 ml of orthophosphoric acid (s.g. 1.7) and 1 mg each of strontium and yttrium (strontium nitrate and yttrium nitrate hexahydrate in 2 M nitric acid) were added. The samples were dissolved in 2 M nitric acid and made up to a volume of 100 ml and boiled at constant volume for 30 minutes. The pH of the resulting solutions was adjusted to different values by bubbling ammonia gas through them. The resulting precipitates were isolated from the supernatents on a 0.45 μm filter and then dissolved in 2 M nitric acid. Aliquots of the original sample solution, the dissolved precipitate and supernatent were analysed by ICP-AES to determine their cation composition. The content of the principal cations present in these solutions are shown in table 4.1.

pH at which calcium phosphate was precipitated	ORIGINAL SAMPLE Mass of principal cations present/mg						CALCIUM PHOSPHATE PRECIPITATE Mass of principal cations present/mg						SUPERNATENT Mass of principal cations present/mg					
	Ca	K	Na	Sr	Y	Mg	Ca	K	Na	Sr	Y	Mg	Ca	K	Na	Sr	Y	Mg
3.207	840	940	260	1.06	0.95	76	211	0.21	0.21	0.047	0.95	0.09	653	947	274	1.05	0.03	76
3.399	840	870	270	1.05	0.94	75	363	1.05	0.53	0.11	0.95	0.21	505	863	253	0.99	0.02	76
4.071	850	920	270	1.04	1.10	76	779	1.05	1.05	0.42	1.11	0.79	84	926	274	0.67	<0.01	76
5.127	880	960	270	1.05	0.96	79	884	1.05	1.05	0.69	0.95	19	17	986	274	0.40	<0.01	61
6.100	800	900	260	1.04	0.98	72	826	17.4	5.79	0.95	1.00	74	5.5	895	263	0.10	<0.01	1.8
7.384	1200	1100	380	1.08	1.05	100	1200	72.6	24.2	1.09	1.05	104	4.4	1073	358	0.03	<0.01	0.23
8.674	840	930	260	1.04	0.95	75	853	58.9	36.8	1.06	0.96	75	1.8	842	234	0.01	<0.01	0.10
9.829	1070	1040	340	1.07	0.93	93	1073	48.4	42.1	1.11	0.94	94	4.7	974	316	0.01	<0.01	0.10

Table 4.1 Variation in the recovery of strontium and principal cations on calcium phosphate as a function of pH

Precipitation was initially observed above pH 3 and the recovery of strontium on the precipitate increased with increasing pH and was quantitative for precipitation at pH 6.100 and above. Yttrium was essentially quantitatively recovered on the precipitate at all the pH values. The potassium present on the precipitate was negligible up to pH 5.127, but increased to a maximum of 73 mg at pH 7.384. According to figure 3.3, the Sr.Spec columns should be capable of tolerating this mass of potassium without interfering with the extraction of strontium. Therefore, since potassium was not co-precipitated sufficiently to interfere with the Sr.Spec columns, the major consideration was to maximize the recovery of strontium on the precipitate. The precipitation should therefore be performed above pH 7.

The recovery of calcium on the precipitate increased with increasing pH and was quantitative above pH 5. At the lowest pH value, 211 mg of calcium was present on the precipitate. This is approximately the maximum mass of calcium that could be present without significantly reducing the extraction of yttrium by the Dionex CC-1 column. At this pH, the recovery of yttrium on the precipitate was quantitative whereas the recoveries of potassium, sodium, magnesium and strontium were negligible. Thus, if the precipitate could be dissolved in the 2 M ammonium acetate solution used to adjust the sample pH for loading onto the Dionex system, then it was possible that the partial precipitation of calcium phosphate at low pH could be used as a calcium clean-up step directly for the Dionex system. The partial precipitation of calcium phosphate was therefore examined in more detail.

4.1.2 Study of the partial precipitation of calcium phosphate

4.1.2.1 Preliminary experiments

To ash equivalent to 500 ml of milk, 2 ml of orthophosphoric acid, 40 ng of yttrium (yttrium nitrate hexahydrate in 2 M nitric acid) and 8 Bq each of ^{90}Sr and ^{90}Y were

added. The ash was dissolved in 75 ml of 2 M nitric acid and boiled for 30 minutes at constant volume. The pH of the resulting solution was adjusted with ammonia gas until it initially became turbid, which occurred at approximately pH 3.7. The precipitate was isolated by filtration, dissolved in a minimum volume of 1 M nitric acid and diluted to 20 ml with HPLC water. The pH of the solution was adjusted to 5 by the addition of 2 M ammonium acetate. No re-precipitation was observed. Any ^{90}Y present was isolated on the Dionex CC-1 column and the nitric acid eluate was Cerenkov counted. The procedure was then repeated three times where the precipitation was performed at pH 3.7 and four times at pH 3.9. At the higher pH, a larger quantity of precipitate was visibly formed. The recoveries of ^{90}Y from the CC-1 column after co-precipitation are shown in table 4.2.

pH of sample	% ^{90}Y recovery
3.646	68
3.696	69
3.774	60
3.724	44
3.927	77
3.943	80
3.946	82
3.940	75
3.924	77

Table 4.2 Recoveries of ^{90}Y from the CC-1 column following partial precipitation of calcium phosphate

The recoveries of ^{90}Y were higher and more consistent when the precipitation was performed at the higher pH, even though more precipitate was actually formed. This could have been due to the smaller quantity of precipitate not being sufficient to quantitatively carry the ^{90}Y or that the losses of precipitate on manipulation were relatively more significant for the smaller quantities of precipitate. The recoveries of ^{90}Y at the higher pH were 75 to 80 % which would be acceptable for incorporating into the Dionex method providing that the recoveries were consistent. Apart from the losses of ^{90}Y on co-precipitation and manipulation, further losses could have occurred due to the calcium content of the precipitate being too high for the Dionex system. However, it was clear that not all the calcium present in the sample was precipitated, otherwise according to figure 2.24, the losses of ^{90}Y would have been much greater. The recovery of ^{90}Y therefore depended on a balance between precipitating sufficient calcium phosphate to permit co-precipitation of ^{90}Y in consistently high recovery, but not to precipitate too much calcium so as to significantly reduce the extraction of ^{90}Y by the Dionex system. Therefore control of the precipitation was required to permit the optimum quantity of precipitate to be formed which appeared to require careful control of the pH.

The precipitation procedure was repeated with the intention of performing the precipitation at a series of pH values to compare the recoveries of ^{90}Y. However, it was observed for the first sample analysed, that after the adjustment of the pH to approximately 3.9 and no further addition of ammonia gas, the pH of the solution began to decrease and was accompanied by the formation of a visibly larger quantity of precipitate than was formed in the experiments described above. The pH of the solution dropped until it became constant at approximately pH 3.2. The precipitate formed was isolated by filtration and then dissolved in a minimum volume of 1 M nitric acid and then Cerenkov counted. After counting, the solution was adjusted to

pH 5 with 2 M ammonium acetate and the ^{90}Y present was isolated on the Dionex CC-1 column and the nitric acid eluate was then Cerenkov counted. 98 % of the ^{90}Y added to the sample was recovered on the precipitate and the overall recovery after isolation on the CC-1 column was 75 %. This experiment demonstrated that there was a definite point where significant precipitation began, which was when the pH began to decrease. In this experiment, the initial point at which the pH decreased could have been passed in order to obtain pH 3.9 and as a consequence, excess precipitate could have been formed which could have affected the subsequent Dionex separation.

The partial precipitation procedure was repeated three times, such that the pH of the acid digested sample was initially adjusted to 3.0 with ammonia gas and then carefully adjusted by the dropwise addition of 6 M ammonia solution until the addition of one drop caused a decrease in pH and the formation of precipitate. The decrease in pH continued for approximately 20 minutes until it attained a constant value. The precipitate was then filtered, dissolved in a minimum volume of 1 M nitric acid and diluted to 20 ml with deionized water. The pH of the solution was adjusted to 5 with 2 M ammonium acetate and then loaded onto the CC-1 column. The nitric acid eluate was collected and Cerenkov counted. The results for this experiment, in table 4.3, show that although the pH at which the pH decrease started varied from sample to sample, ^{90}Y was recovered from the CC-1 column consistently and with a yield of greater than 80 %. Therefore, the point at which the pH begins to decrease could be used as the reference point to stop pH adjustment, rather than the adjustment to a specific pH.

pH at which pH drop began	pH at which pH drop stabilizes	% ^{90}Y recovery
3.771	3.165	84
3.174	2.737	84
3.236	2.803	83

Table 4.3 Recoveries of ^{90}Y from the CC-1 column following the partial precipitation step involving a pH decrease

4.1.2.2 Determination of the mass of precipitate formed

The partial precipitation process was performed on twelve portions of milk ash equivalent to 500 ml milk. Six of the precipitates were collected by filtration onto pre-weighed sintered glass crucibles thirty minutes after the point at which the pH decrease occurred and the other six precipitates were collected after standing in the solution for varying time intervals up to 24 hours. The precipitates were dried to constant mass at 105°C.

Table 4.4 shows that an approximately constant amount of precipitate (300 - 350 mg) was formed by the precipitation process and that the quantity of precipitate formed did not vary significantly with increasing amount of time standing in the solution. Although there was a slight variation in the mass of precipitate formed, there was no definite demonstration that standing time in the solution increased the mass of precipitate formed. There was also a slight variation in the pH at which the precipitation started from sample to sample, the range being from pH 3.085 to 3.477. The results implied that as the pH at which the precipitation started decreased, the mass of precipitate formed was increased.

Time precipitate left in solution /h	Mass of precipitate formed /g	pH at which pH decrease started	pH at which pH decrease stabilized
0.5	0.3218	3.225	2.901
0.5	0.3196	3.298	2.932
0.5	0.3229	3.205	2.861
0.5	0.3310	3.186	2.807
0.5	0.3186	3.314	2.916
0.5	0.3171	3.305	2.913
1	0.3216	3.225	2.896
2	0.3131	3.477	2.931
6	0.3405	3.106	2.760
12	0.3122	3.476	2.927
17	0.3024	3.477	2.861
24	0.3567	3.085	2.742

Table 4.4 Variation in the mass of precipitate formed with standing time in solution

Although slight variations in the mass of precipitate and the pH values were observed, the precipitation step appeared to be a consistent process for a constant milk sample size. Also, the precipitation process was essentially complete after the pH decrease had stabilized, which meant that it would be possible to allow precipitated samples to stand overnight without affecting the quantity of precipitate formed.

4.1.2.3 Determination of the structure of the precipitate

The precipitate was analysed by X-ray powder diffractometry to determine its structure, using monochromatic X-rays of wavelength 0.15405 nm produced using a copper filter. The d-spacings derived from the ten most intense peaks produced by the precipitate are shown in table 4.5 and are compared to the literature values for brushite syn, $CaHPO_4.2H_2O$ [93]. The observed d-spacings and relative intensities correspond closely with this compound and the structure is a reasonable one.

Assuming this structure was correct, it was possible to determine the mass of calcium present in a typical precipitate produced from 500 ml of milk.

Observed		Brushite syn.	
d-spacing	Intensity Order (1st = most intense)	d-spacing	Relative Intensity I/Io
7.39	1st	7.57	100
4.18	2nd	4.24	100
3.83	9th	3.80	7
3.43	6th	3.63	1
3.12	3rd	3.05	75
3.01	4th	2.93	50
2.85	5th	2.86	9
2.73	10th	2.62	50
2.55	8th	2.60	30
2.32	7th	2.43	15

Table 4.5 Comparison of the d-spacing values for the precipitate and the literature values for brushite syn[93] .

Approximately 300 to 350 mg of precipitate was formed by the partial precipitation process which meant that a maximum of approximately 100 mg of calcium would be present on the precipitate, approximately 20 % of that present in the original 500 ml milk sample. The mass of calcium present in the precipitate was therefore only half of the CC-1 column calcium limit which meant that ^{90}Y should be extracted from the precipitate after dissolution and pH adjustment with a greater than 90 % recovery. However, the results from table 4.3 show that the overall recoveries of ^{90}Y from the partial precipitation and CC-1 steps were approximately 84 % which meant that losses occurred from the partial precipitation step to the Dionex step. The calcium content derived from the mass of precipitate formed and its structure shows that it is

not due to the calcium present, but must be due to some other factor, possibly manipulation losses or the presence of significant quantities of trivalent cations on the precipitate, which would interfere with the extraction of ^{90}Y by the CC-1 column.

4.1.2.4 Determination of when ^{90}Y was isolated from ^{90}Sr

The results from the ICP-AES analysis of the calcium phosphate precipitation in table 4.1 demonstrated that yttrium was effectively quantitatively precipitated at all values above pH 3, whereas the precipitation of strontium was negligible below pH 4. Since the partial precipitation process occurs below pH 4, it was possible that the process separates ^{90}Y from ^{90}Sr. It was essential to know whether or not this occurred if the precipitation step was to be incorporated into a method for determining ^{90}Sr in milk using the Dionex system. If the precipitate contained only ^{90}Y, then the ^{90}Y decay time would begin when the precipitate was isolated from the sample solution, otherwise the decay time would begin at the midpoint of the loading of the sample onto the CC-1 column.

The precipitation process was performed on milk ash equivalent to 500 ml of raw milk as described previously. The precipitate was filtered and then dissolved in 1 M nitric acid and the resulting solution was Cerenkov counted at intervals over a period of three weeks. Figure 4.1 shows that the count rate decayed exponentially with time. Figure 4.2 shows a plot of the natural log of the count rate versus time, which is linear. The half-life derived from the gradient is 64.5 hours compared to the literature value for ^{90}Y which is 64.1 hours [8]. This demonstrated that ^{90}Y alone was present on the precipitate whereas ^{90}Sr was not. Therefore, the partial precipitation not only reduces the levels of calcium to a suitable level for the Dionex system, it also provides a means of separating ^{90}Y from ^{90}Sr. In terms of the Dionex based ^{90}Sr method, the ^{90}Y decay correction must be applied from the point when the precipitate is isolated from the sample solution.

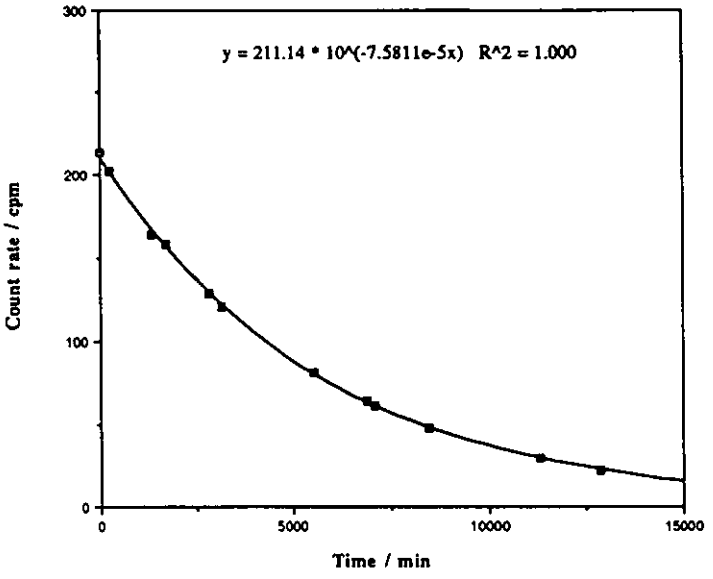


Figure 4.1 Variation in the count rate present on the $CaHPO_4.2H_2O$ precipitate with time

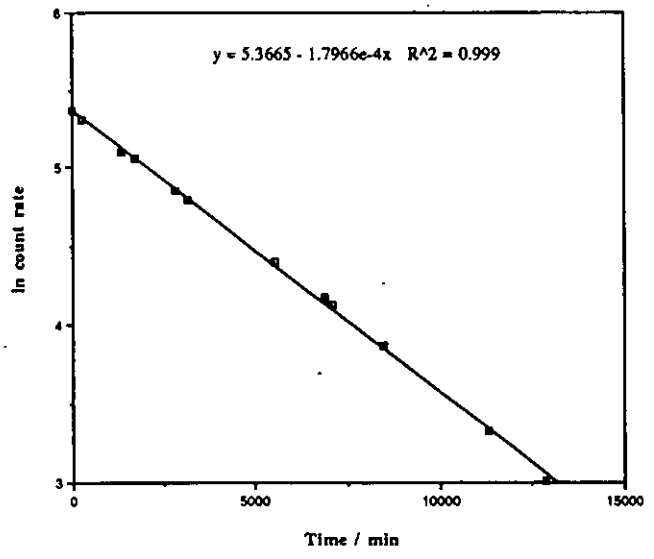


Figure 4.2 Plot of ln count rate versus time for the $CaHPO_4.2H_2O$ precipitate

4.1.2.5 Further studies of the partial precipitation step

A series of experiments were carried out to obtain further information on the partial precipitation process. The precipitation was carried out as described in section 4.1.2 on the following samples:

i) Ash equivalent to 500 ml of milk dissolved in and made up to 75 ml with 2 M nitric acid. No orthophosphoric acid was added;

ii) 2 ml of orthophosphoric acid made up to a volume of 75 ml with 2 M nitric acid;

iii) 2.9681 g of calcium nitrate tetrahydrate and 1.8223 g of potassium dihydrogen orthophosphate dissolved in and made up to 75 ml with 2 M nitric acid;

iv) 2.9460 g of calcium nitrate tetrahydrate and 1.9236 g of disodium hydrogenorthophosphate dissolved in and made up to 75 ml with 2 M nitric acid;

v) Ash equivalent to 500 ml of milk and 2 ml of orthophosphoric acid dissolved in and made up to 75 ml in 2 M nitric acid. The solution was not boiled for 30 minutes prior to precipitation;

vi) 2 ml of orthophosphoric acid and 30 mg of stable yttrium dissolved in and made up to 75 ml with 2 M nitric acid;

vii) Ash equivalent to 500 ml of milk, 2 ml of orthophosphoric acid and 30 mg of stable yttrium dissolved in and made up to 75 ml with 2 M nitric acid;

viii) Ash equivalent to 500 ml of milk and 2 ml of orthophosphoric acid dissolved in and made up to 75 ml with 2 M nitric acid. The precipitate was formed and isolated by filtration and the pH of the supernate was increased further by the addition of ammonia gas.

Any precipitates formed were analysed by X-ray powder diffractometry to determine their structure.

For samples i) - iv) the partial precipitation process was observed. For i), for duplicate samples, the pH decrease started at pH 3.522 and 3.621 and stabilized at pH 2.865 and 2.962 respectively. The masses of precipitate formed for the duplicate samples were 0.1560 and 0.1494 g. For ii), the pH decrease occurred from pH 3.630 to 2.970 and 0.1434 g of precipitate was formed. For iii), the pH decrease occurred from pH 4.128 to 3.427 and 0.0920 g of precipitate was formed. For iv), the pH decrease occurred from pH 4.191 to 3.405 and 0.0736 g of precipitate was formed.

For sample v), the solution became turbid at approximately pH 3, and a large quantity of precipitate was formed. No decrease in pH was observed until the pH was at 4.495, at which point the pH dropped to 4.326. The mass of precipitate produced was 1.2473 g, which was much greater than that formed for samples which were boiled in nitric acid prior to the partial precipitation.

For vi), the solution became turbid at pH 1.4332 and a gelatinous precipitate was formed. The pH was then adjusted to 2.068 and then filtered. The pH of the supernate was then further adjusted up to pH 7.914 but no further precipitation resulted.

For vii), the solution became turbid at pH 1.371 resulting in the formation of the gelatinous precipitate similar to vi). The pH was adjusted to 2.014 and the precipitate was then isolated by filtration. On further pH adjustment, the decrease in pH accompanied by precipitation was observed starting at pH 3.602 and stabilizing out at pH 3.021. The mass of precipitate formed was 0.3152 g.

For viii), after the precipitation accompanied by the decrease in pH occurred, and after further adjustment of pH of the supernate, the precipitation process recurred. The observations are summarized in table 4.6.

Precipitation	Mass of precipitate formed / g	pH at which pH decrease started	pH at which pH decrease stabilized
1st	0.3175	3.675	3.190
2nd	0.1830	3.666	3.312
3rd	0.1333	3.894	3.434
4th	0.1394	3.990	3.551
5th	0.3542	3.981	3.502
6th		3.885	3.623
7th		3.934	3.719
8th		3.892	3.715

Table 4.6 Effect of increasing the pH of the sample solution after the partial precipitation

The X-ray powder diffractometry study showed that precipitates from i) - iv) and viii) were $CaHPO_4.2H_2O$. For v), vi) and vii) the diffraction patterns produced did not possess well defined peaks and could not be related to a known structure.

The results for samples i) to iv) demonstrated that the partial precipitation process occurred whether the starting solution contained milk, H_3PO_4, $H_2PO_4^-$ or HPO_4^{2-} only. This was not unexpected since the precipitate was $CaHPO_4.2H_2O$ and its precipitation should depend on the concentration of HPO_4^{2-} present, which could be released into solution from all these starting materials.

If the solution was not boiled prior to precipitation, the precipitation step occurred at a higher pH than expected and large quantities of precipitate were formed before the pH decrease. Although the precipitate formed could not beconclusively identified, it could not have simply been $CaHPO_4.2H_2O$ since this produced a well defined X-ray powder diffraction pattern. It was likely that the precipitate formed in this case was a polyphosphate formed during the ashing procedure and the removal of the boiling step prevented its complete hydrolysis to a monophosphate species that would be required to be present to permit the precipitation of only $CaHPO_4.2H_2O$. Therefore if the precipitation step were to be included in the ^{90}Sr method, it would be essential that after dissolution of the sample ash in nitric acid, the resulting solution should be boiled prior to precipitation to ensure the complete hydrolysis of polyphosphates remaining from the ashing step, thereby permitting the precipitation step to occur.

The results for samples vi) and vii) showed that yttrium was precipitated from the acid digested milk sample solutions at a lower pH than that at which the precipitate was formed. The yttrium precipitate formed however, could not be conclusively identified, although it is likely that it was precipitated as a phosphate. It has previously been shown that yttrium was quantitatively precipitated on the $CaHPO_4.2H_2O$. The results here show that the reason for this could be due to all the yttrium being precipitated prior to the partial precipitation of $CaHPO_4.2H_2O$. Therefore in the determinations of ^{90}Sr, where a maximum of only 40 ng of yttrium is present, the calcium precipitate provides the small quantities of the yttrium precipitate formed a large surface with which it can co-precipitate, which allows the yttrium precipitate to be easily manipulated without significant losses occurring.

In addition to the above studies, it was found that the partial precipitation from the milk samples could be successfully achieved using ammonia solution or sodium hydroxide solution rather than ammonia gas to adjust the pH.

4.1.2.6 Discussion of the partial precipitation step

The studies described thus far using the partial precipitation step have demonstrated that ^{90}Y could be co-precipitated with $CaHPO_4.2H_2O$ precipitated from an acid digested milk sample. Thé start of precipitation is accompanied by a decrease in pH, which then stabilizes at a lower pH and precipitation ceases. The partial precipitation process produces consistent masses of precipitate, which for 500 ml milk samples to which 2 ml of orthophosphoric acid were added, contain approximately 100 mg of Ca^{2+}, which is approximately 20 % of the original content. The precipitation could also be performed from solutions containing calcium to which either H_3PO_4, $H_2PO_4^-$ or HPO_4^{2-} were added.

The precipitation of $CaHPO_4.2H_2O$ requires its solubility product, K_s, to be exceeded. Equating activities to concentrations, K_s can be approximated to

$$K_s = [Ca^{2+}] [HPO_4^{2-}] [H_2O]^2 \quad (4\text{-}1)$$

In the experiments described involving the partial precipitation, $[Ca^{2+}]$ was essentially kept constant, therefore the extent K_s was exceeded depended on $[HPO_4^{2-}]$ released into solution. This in turn is dependent on the pH of the solution according to the equilibria described in equations (4-2) and (4-3).

$$H_3PO_4 \rightleftharpoons H_2PO_4^- + H^+ \quad (4\text{-}2)$$

$$H_2PO_4^- \rightleftharpoons HPO_4^{2-} + H^+ \quad (4\text{-}3)$$

Figure 4.3 shows a speciation plot as a function of pH for pure solutions of the monophosphate species which was produced using the MINTEQA2 speciation modelling program, which is described in section 4.1.3.

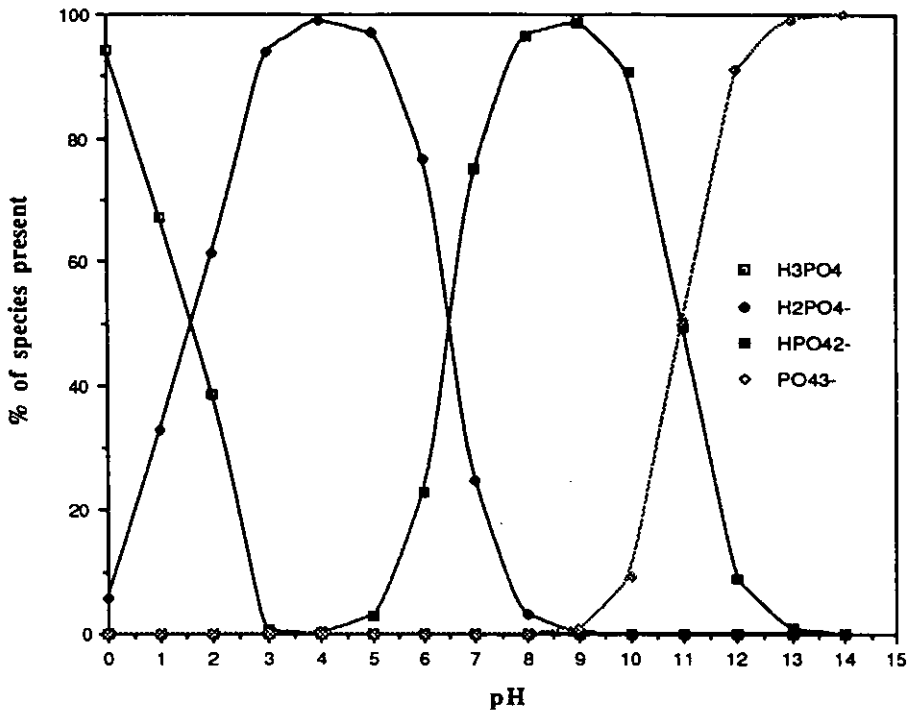


Figure 4.3 Speciation plot for monophosphates as a function of pH

Over the pH range where precipitation occurred, the dominant species present is $H_2PO_4^-$, whereas the concentration of HPO_4^{2-} present is negligible. However, the milk sample solutions are much more complex than the pure solutions used to produce the speciation plots and the presence of other cations in solution could affect the position of equilibrium in favour of the formation of HPO_4^{2-}.

The partial precipitation experiments were performed by pH adjustment of initially acidic solutions containing milk, H_3PO_4, $H_2PO_4^-$ or HPO_4^{2-}. For these strongly acidic initial conditions, according to the speciation plot, H_3PO_4 is likely to be the dominant monophosphate species present in solution, independent of the monophosphate species added. Therefore, the behaviour of the partial precipitation process could be viewed as being essentially a function of the concentration of H_3PO_4 initially

present. Therefore the effect on the partial precipitation process of varying the initial orthophosphoric acid concentration for solutions of constant [Ca^{2+}] was investigated using synthetic solutions. The use of synthetic solutions permitted the conditions used to be computer modelled to predict the chemical species present prior to and at the point precipitation occurred, thus providing further information to determine the chemistry of the process.

4.1.3 Synthetic studies of the partial precipitation step

Six sample solutions were prepared as follows: 1.83 g of calcium chloride dihydrate were dissolved in deionized water, 1 to 7 ml of orthophosphoric acid (sg 1.7) and 19.67 g of hydrochloric acid (sg 1.18) were added to each of the solutions, which were then diluted to 100 ml with deionized water. The solutions thus contained 0.5 g of Ca^{2+}, were 2 M in hydrochloric acid and the orthophosphoric acid concentrations varied from 0.173 M to 1.211 M.

The pH of the solutions was adjusted to 3.0 by the addition of sodium hydroxide pellets and then carefully adjusted to the decrease in pH by the dropwise addition of 6 M sodium hydroxide solution. The precipitates formed were isolated by filtration onto a sintered glass crucible, dried at 105 °C and weighed.

The precipitation process for two of the synthetic solutions was computer modelled, which enabled an estimation of the concentrations of the chemical species present at various pH values up to and at the point at which precipitation was expected to occur. The code used was MINTEQA2 which is a geochemical equilibrium speciation model developed by the United States Environmental Protection Agency [94]. The model is capable of computing equilibria involving dissolved, adsorbed, solid and gas phases. The database is based on reliable thermodynamic data accessed by

PRODAFA2, a program designed to create the required MINTEQA2 input file from the thermodynamic database. The conditions inputted into the program were for initial orthophosphoric acid concentrations of 0.173 M and 0.519 M Although the computer modelling of the synthetic solutions does not provide an entirely accurate representation of the precipitation from milk samples, it provides a reasonable approximation in which the modelling can be compared to known experimental parameters, whereas it would be significantly more difficult to model the precipitation from the more complex milk matrix. In this study, the synthetic solutions contained hydrochloric acid and sodium hydroxide rather than nitric acid and ammonia solution because nitrogen species cause problems for the computer modelling program.

The experimentally determined results are shown in figures 4.4 - 4.6.

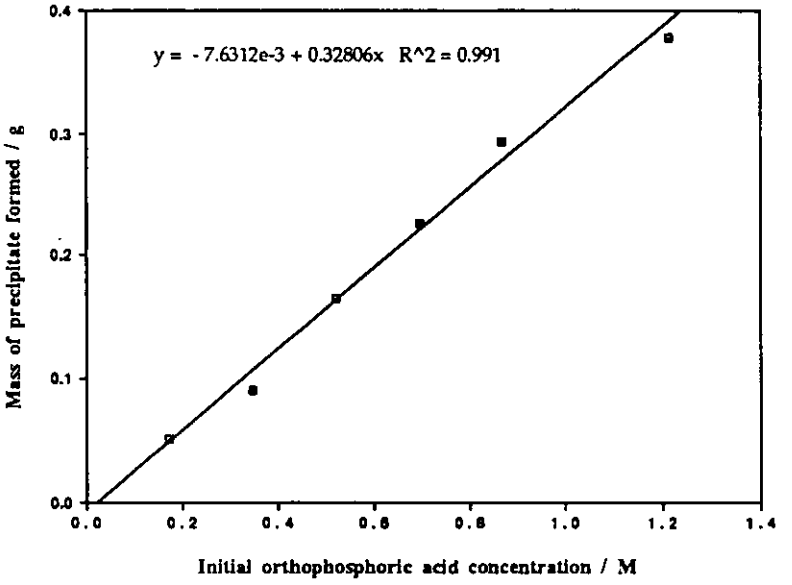


Figure 4.4 Variation in the mass of precipitate formed with initial orthophosphoric acid concentration

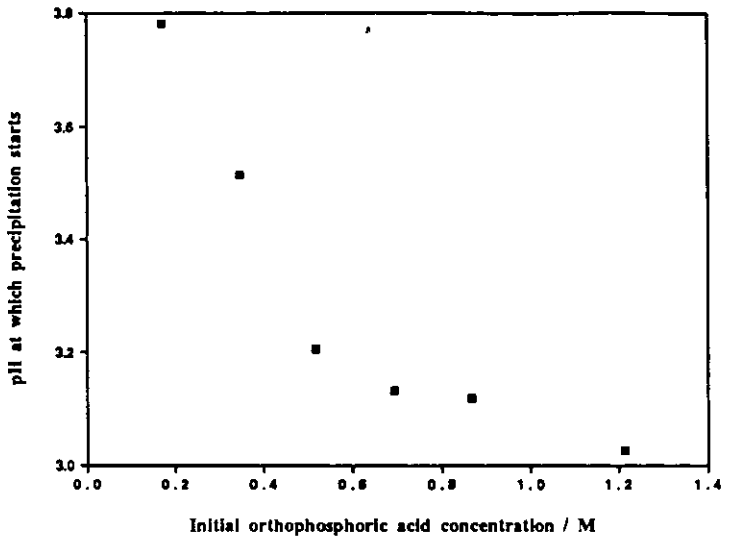


Figure 4.5 Variation in the pH at which precipitation starts with initial orthophosphoric acid concentration

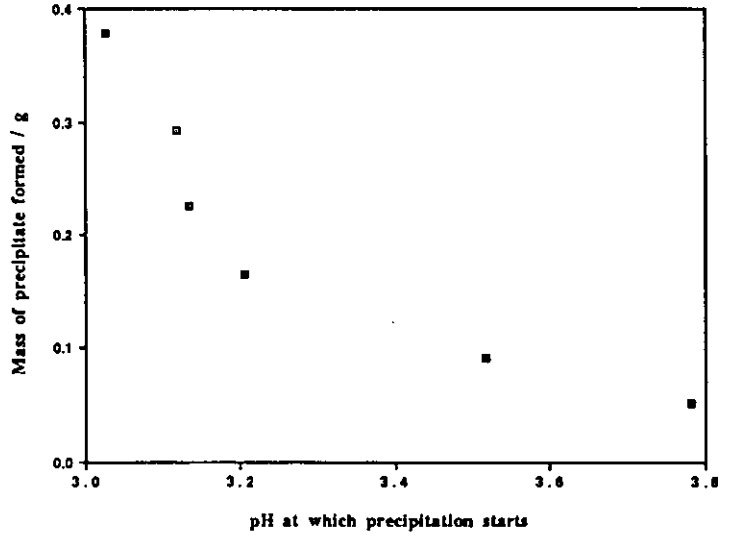


Figure 4.6 Variation in the mass of precipitate formed with the pH at which precipitation starts

Figure 4.4 shows that the mass of precipitate formed increases linearly with increasing initial orthophosphoric acid concentration. Figure 4.5 shows that the pH at

which the pH drop accompanied by precipitation occurs decreases as the initial orthophosphoric acid concentration increases. It follows that larger masses of precipitate are formed when the pH drop occurs at a lower pH, which is shown in figure 4.6.

The results from the computer modelling studies, shown in tables 4.7 and 4.8, show that the [HPO_4^{2-}] in solution at all the pH values is higher for the solution with the higher initial [H_3PO_4]. This was expected since at a given pH, the position of the equilibria given in equations (4-2) and (4-3) is constant. Thus the ratio of H_3PO_4:$H_2PO_4^-$:HPO_4^{2-} is constant, hence as the initial [H_3PO_4] increases, the [HPO_4^{2-}] in solution at a given pH also increases.

Species	Concentration of species present at given pH of solution / mol l^{-1}				
	pH0	pH1	pH2	pH3	pH4
PO_4^{3-}	6.008×10^{-23}	4.408×10^{-20}	1.568×10^{-17}	2.298×10^{-15}	2.414×10^{-13}
Ca^{2+}	1.262×10^{-1}	9.386×10^{-2}	5.334×10^{-2}	4.168×10^{-2}	4.009×10^{-2}
$H_2PO_4^-$	2.147×10^{-3}	1.575×10^{-2}	5.603×10^{-2}	8.209×10^{-2}	8.624×10^{-2}
H_3PO_4	3.011×10^{-1}	2.209×10^{-1}	7.860×10^{-2}	1.152×10^{-2}	1.210×10^{-3}
$CaOH^+$	3.115×10^{-14}	2.316×10^{-13}	1.316×10^{-12}	1.029×10^{-11}	9.894×10^{-11}
$CaPO_4^-$	2.183×10^{-17}	1.191×10^{-16}	2.407×10^{-16}	2.756×10^{-16}	2.785×10^{-6}
$CaH_2PO_4^+$	6.918×10^{-3}	3.774×10^{-2}	7.630×10^{-2}	8.734×10^{-2}	8.826×10^{-2}
HPO_4^{2-}	1.333×10^{-10}	9.799×10^{-9}	3.479×10^{-7}	5.096×10^{-6}	5.534×10^{-5}

Table 4.7 Species present predicted by computer model for synthetic solution with an initial orthophosphoric acid concentration of 0.173 M

Species	Concentration of species present at given pH of solution / mol l^{-1}				
	pH0	pH1	pH2	pH3	pH4
PO_4^{3-}	1.810×10^{-22}	1.448×10^{-19}	6.583×10^{-17}	1.070×10^{-14}	1.141×10^{-12}
Ca^{2+}	1.138×10^{-1}	5.592×10^{-2}	1.827×10^{-2}	1.186×10^{-2}	1.111×10^{-2}
$H_2PO_4^-$	6.465×10^{-3}	5.174×10^{-2}	2.352×10^{-1}	3.821×10^{-1}	4.077×10^{-1}
H_3PO_4	9.069×10^{-1}	7.258×10^{-1}	3.299×10^{-2}	5.360×10^{-2}	5.719×10^{-3}
$CaOH^+$	2.791×10^{-14}	1.372×10^{-13}	4.481×10^{-13}	2.910×10^{-12}	2.726×10^{-11}
$CaPO_4^-$	5.924×10^{-17}	2.330×10^{-14}	3.460×10^{-12}	3.650×10^{-10}	3.649×10^{-8}
$CaH_2PO_4^+$	1.878×10^{-2}	7.385×10^{-2}	1.097×10^{-1}	1.157×10^{-1}	1.156×10^{-1}
HPO_4^{2-}	4.014×10^{-10}	3.212×10^{-8}	1.460×10^{-6}	2.372×10^{-5}	2.531×10^{-4}

Table 4.8 Species present predicted by computer model for synthetic solution with an initial orthophosphoric acid concentration of 0.519 M

More unexpectedly, the computer modelling results also show that the $[Ca^{2+}]$ in solution is not constant over the pH range investigated and in fact decreases as the pH increases. This reduction in the $[Ca^{2+}]$ with increasing pH is principally due to the Ca^{2+} being bound as the complex $CaH_2PO_4^+$, the concentration of which increases as the pH increases. The $[Ca^{2+}]$ in solution is lower at all the pH values for the solution with the higher initial $[H_3PO_4]$. The reason for this is that the $[H_2PO_4^-]$ in solution available to bind with the Ca^{2+} to form the complex is higher at all the pH values for the solution with the higher initial $[H_3PO_4]$. The computer modelling therefore demonstrated that the availability of the Ca^{2+} and HPO_4^{2-} in solution were both dependent on the initial $[H_3PO_4]$ and it wasn't simply the availability of the HPO_4^{2-} in solution that was the controlling factor in the precipitation.

At the point precipitation occurs, the product of $[Ca^{2+}]$ and $[HPO_4^{2-}]$ must exceed K_s, which for $CaHPO_4.2H_2O$ at an ionic strength of zero is 2.63×10^{-7} mol^2 l^{-2} [95]. The experimentally observed results for the precipitation show that precipitation starts

between pH 3 and 4 for all the solutions investigated. From the computer modelling, the products of $[Ca^{2+}]$ and $[HPO_4^{2-}]$ at pH 3 and 4 for the 0.173 M solution are 2.12×10^{-7} mol^2 l^{-2} and 2.22×10^{-6} mol^2 l^{-2} and for the 0.519 M solution are 2.81×10^{-7} mol^2 l^{-2} and 2.81×10^{-6} mol^2 l^{-2} respectively. Thus at pH 3, K_s is just exceeded for the 0.519 M solution and is not exceeded for the 0.173 M solution, whereas at pH 4, K_s is exceeded for both solutions. The computer modelling therefore predicted that precipitation of $CaHPO_4.2H_2O$ should occur for both solutions between approximately pH 3 and 4, with the solution of higher initial $[H_3PO_4]$ precipitating at the lower pH. This is therefore in agreement with the experimentally observed results shown in figure 4.5.

From the information collected with respect to the precipitation process, a possible explanation for the chemistry of the process for milk samples is as follows:

In the initial acid digested milk sample solution, H_3PO_4 is the dominant monophosphate species present in solution, i.e. the position of equilibrium (4-2) is strongly to the left. As the pH of the solution is increased by the addition of ammonia, protons in the solution are removed which drives equilibrium (4-2) to the right resulting in the release of $H_2PO_4^-$. As the pH is further increased, equilibrium (4-3) is driven to the right, resulting in the release of HPO_4^{2-} into solution. The free $H_2PO_4^-$ in solution is also removed from solution by the formation of $CaH_2PO_4^+$ which also results in a reduction of the free Ca^{2+} in solution. In the pH range 3 to 4, the product of $[Ca^{2+}]$ and $[HPO_4^{2-}]$ in solution is sufficient to exceed K_s for $CaHPO_4.2H_2O$ resulting in its precipitation according to equation (4-4).

$$Ca^{2+} + HPO_4^{2-} + 2H_20 \rightleftharpoons CaHPO_4.2H_2O\downarrow \qquad (4\text{–}4)$$

As precipitation begins, the addition of ammonia is ceased. The removal of HPO_4^{2-} from the solution due to the precipitation results in equilibrium (4-3) being driven to the right, therefore further HPO_4^{2-} and protons are released. The HPO_4^{2-} released is consumed in the formation of more precipitate and since the protons released are not neutralized by the addition of ammonia, the pH of the solution decreases. As precipitation proceeds, the $[Ca^{2+}]$ and $[HPO_4^{2-}]$ in solution decreases, although for HPO_4^{2-} this is partially offset by the dissociation of $H_2PO_4^{2-}$ and for Ca^{2+} this is partially offset by dissociation of $CaH_2PO_4^{+}$ as the pH decreases. At some point, the balance between the reduction and release of Ca^{2+} and HPO_4^{2-} into solution becomes such that K_s for $CaHPO_4.2H_2O$ is no longer exceeded, therefore the precipitation ceases. This occurs at a lower pH than that at the start of precipitation due to the release of protons.

From this above explanation, the experimental observation that the mass of precipitate formed increased as the initial $[H_3PO_4]$ increased could be viewed as being due to the balance between the consumption and release of Ca^{2+} and HPO_4^{2-} after K_s has been exceeded being in favour of their release into solution as the initial $[H_3PO_4]$ increases.

4.1.4 Determination of the initial orthophosphoric acid concentration for the optimum recovery of ^{90}Y from the partial precipitation step

From the results from the synthetic studies of the partial precipitation step, it was clear that the partial precipitation was dependent on the initial $[H_3PO_4]$. It was therefore important for its incorporation into the Dionex procedure for ^{90}Sr determination to examine effect of the initial $[H_3PO_4]$ on the recovery of ^{90}Y on the precipitate. Six sample solutions were prepared as described in section 4.1.3 except that in this case, 40 ng of stable yttrium and 6.4 Bq each of ^{90}Sr and ^{90}Y were added to each of the solutions. The precipitation process was performed as described in

section 4.1.3. The precipitates were isolated by filtration, dissolved in 1 M nitric acid and the resulting solutions were Cerenkov counted.

Figure 4.7 shows that the recovery of ^{90}Y on the precipitate was greater than 90 % and showed little variation for the solutions with an initial $[H_3PO_4]$ of greater than 0.346 M. The recovery of ^{90}Y was significantly lower, approximately 70 %, when the initial $[H_3PO_4]$ was 0.173 M. Figure 4.4 shows that this corresponds to the formation of approximately 0.05 g of precipitate, which simply may not be sufficient to successfully scavenge the ^{90}Y from the sample solution, which would explain the lower recovery of ^{90}Y on the precipitate.

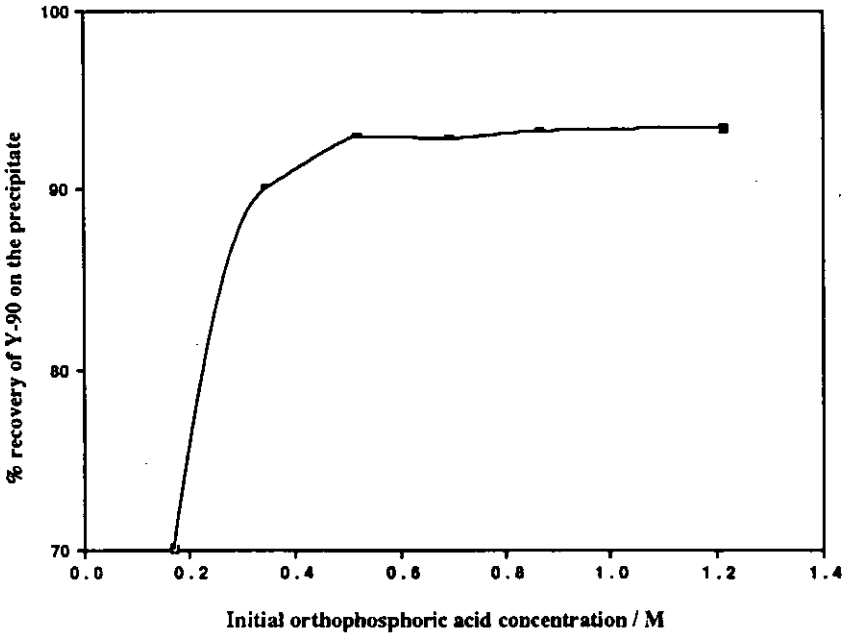


Figure 4.7 Variation in the recovery of ^{90}Y on the precipitate with initial orthophosphoric acid concentration

For the conditions previously used for the precipitation from 500 ml milk samples, i.e. 500 ml of milk and 2 ml of orthophosphoric acid in a total volume of 75 ml, typically 0.3 g of precipitate were formed. From figure 4.4 this corresponds to an initial orthophosphoric acid concentration of 0.938 M which was sufficient to ensure

a ^{90}Y recovery of greater than 90 %. 2 ml of orthophosphoric acid in a volume of 75 ml corresponds to a concentration of 0.461 M, therefore the concentration of orthophosphoric acid contributed by the milk is 0.477 M. Thus 500 ml of milk is approximately equivalent to 2 ml of orthophosphoric acid. The results from section 4.1.2.5 for the precipitation from solutions containing 2 ml of orthophosphoric acid only or 500 ml of milk only showed that in both cases approximately 0.15 g of precipitate were formed. This was therefore consistent with the observation described above for the synthetic solutions.

The recovery of ^{90}Y on the precipitate from solutions when the initial orthophosphoric acid concentration is 0.477 M is greater than 90 %, therefore it is not necessary to add orthophosphoric acid to a 500 ml milk equivalent in 75 ml of nitric acid to permit the high recovery of ^{90}Y on the precipitate. However, figure 4.7 shows that this initial orthophosphoric acid concentration may not quite provide optimum recoveries of ^{90}Y on the precipitate. It was therefore decided that in the validation of the method for milk samples that 2 ml of orthophosphoric acid would be added to the milk sample. In the validation, 1 litre milk samples were also analysed and the partial precipitation was carried out such that their concentrations in solution were identical to those for the 500 ml samples.

4.1.5 Behaviour of other elements during the partial precipitation step

The precipitation process was performed on three portions of milk ash, equivalent to 500 ml of milk as described previously. All the samples were spiked with a solution containing stable yttrium, strontium, uranium and a variety of lanthanides and two of the samples were also spiked with a solution containing cobalt, iron, nickel and ruthenium. The precipitates formed were dissolved in 1 M nitric acid and aliquots of this solution, the original sample solution and the supernate after precipitation were

analysed by inductively coupled plasma mass spectrometry (ICP-MS) or ICP-AES to determine the cations present. Tables 4.9 - 4.11 show the results for this experiment. As well as the transition metals added, the recoveries of some transition metals inherently present in the milk are also shown. The uncertainties associated with the analyses are in the order of 20 % for values significantly higher than the detection limit and increase as the values get closer to the detection limit. These uncertainties may partially explain why in some cases recoveries of significantly greater than 100 % were obtained.

The results confirmed that yttrium was essentially quantitatively recovered on the precipitate, whereas strontium was not recovered on the precipitate. The large quantities of potassium, sodium and magnesium originally present in the milk sample were not present on the precipitate. 14 to 20 % of the calcium originally present was precipitated, which was consistent with that calculated from the structure of the material determined by X-ray powder diffractometry which further indicated that $CaHPO_4.2H_2O$ was the correct structure of the precipitate. The masses of phosphorus present on the precipitate for the three samples were 52 mg, 45 mg and 53 mg respectively and the molar ratio of calcium : phosphorus was 0.95, 1.15 and 1.20 respectively, therefore they were approximately 1 : 1 which again was consistent with $CaHPO_4.2H_2O$ being the structure.

Element	Total present in sample / µg	Total on precipitate / µg	Total in supernate / µg	Total recovery / µg	% Recovery on precipitate wrt original amount present	% Recovery on precipitate wrt total amount recovered
†						
La	191	254	2	256	133	99
Ce	86	112	<1	112	130	100
Nd	100	105	<1	105	105	100
Sm	109	106	<1	106	97	100
Eu	86	88	<1	88	102	100
Gd	91	106	<1	106	116	100
Tb	81	105	<1	105	130	100
Y	91	109	1	110	120	99
U	100	42	44	86	42	49
*						
Co	70	<1	73	73	<1	<1
Fe	218	225	83	308	103	73
Ni	91	<1	99	99	<1	<1
Ru	91	63	<1	63	69	100
Sr	67	<1	64	66	<1	<1
Cr	28	4	30	34	14	12
Cu	14	3	17	20	15	21
Al	–	–	–	–	–	–
Y	79	96	2	98	122	98
*	/mg	/mg	/mg	/mg		
Ca	400	73	327	400	18	18
K	600	<1	481	481	<1	<1
Na	160	<1	127	127	<1	<1
Mg	45	<1	32	32	<1	<1

† ICP-MS Analysis

* ICP-AES Analysis

Table 4.9 Recovery of elements on $CaHPO_4.2H_2O$ for milk spiked with stable lanthanides and transition metals (i)

Element	Total present in sample / µg	Total on precipitate / µg	Total in supernate / µg	Total recovery / µg	% Recovery on precipitate wrt original amount present	% Recovery on precipitate wrt total amount recovered
†						
La	225	209	3	212	93	99
Ce	99	93	5	98	94	95
Nd	117	103	5	108	88	95
Sm	117	101	6	107	86	94
Eu	99	87	5	92	88	95
Gd	90	96	3	99	107	97
Tb	90	96	5	101	107	95
Y	89	93	11	104	104	89
U	117	48	68	116	41	41
*						
Co	76	<1	75	75	<1	<1
Fe	207	193	100	293	93	66
Ni	99	<1	98	98	<1	<1
Ru	99	48	<1	48	48	100
Sr	73	<1	73	75	<1	<1
Cr	36	3	34	37	8	8
Cu	16	1	16	17	6	6
Al	2160	1398	3000	4398	65	32
Y	86	93	2	95	108	98
*	/ mg	/ mg	/ mg	/ mg		
Ca	504	67	420	487	13	14
K	630	<1	600	600	<1	<1
Na	162	<1	170	170	<1	<1
Mg	41	<1	41	41	<1	<1

† ICP-MS Analysis

* ICP-AES Analysis

Table 4.10 Recovery of elements on $CaHPO_4.2H_2O$ for milk spiked with stable lanthanides and transition metals (ii)

Element	Total present in sample / µg	Total on precipitate / µg	Total in supernate / µg	Total recovery / µg	% Recovery on precipitate wrt original amount present	% Recovery on precipitate wrt total amount recovered
†						
La	207	201	3	204	97	99
Ce	90	87	1	88	97	99
Nd	99	99	1	100	100	99
Sm	108	101	1	102	94	99
Eu	99	90	1	91	91	99
Gd	87	96	1	97	110	99
Tb	90	98	1	99	109	99
Y	99	99	2	101	100	98
U	144	129	180	309	125	42
*						
Co	–	–	–	–	–	–
Fe	117	170	350	520	145	33
Ni	18	<1	19	19	<1	<1
Ru	–	–	–	–	–	–
Sr	73	<1	73	75	<1	<1
Cr	37	3	34	37	8	8
Cu	17	2	45	45	12	4
Al	3150	1705	500	2205	54	78
Y	85	96	<1	96	113	100
*	/mg	/mg	/mg	/mg		
Ca	410	85	333	418	21	20
K	600	<1	540	540	<1	<1
Na	170	<1	135	135	<1	<1
Mg	44	<1	36	36	<1	<1

† ICP-MS Analysis

* ICP-AES Analysis

Error in results approximately 10-20%

Table 4.11 Recovery of elements on $CaHPO_4.2H_2O$ for milk spiked with stable lanthanides

The lanthanides were quantitatively precipitated, which was expected since the lanthanides and yttrium would be expected to behave similarly. Only 40 - 50 % of the uranium added was recovered on the precipitate. Cobalt and nickel were not recovered on the precipitate whereas iron, ruthenium, chromium, copper and aluminium were recovered on the precipitate to varying degrees. The recoveries of iron and aluminium varied greatly, which could have been a consequence of reagent contamination of the analysed solutions. Although it is difficult to quantify the recoveries of iron and aluminium from these results with any great certainty, the fact that they were present on the precipitate could greatly affect the subsequent extraction of ^{90}Y by the CC-1 column, since the presence of only a few milligrams of these causes a reduction in the extraction of ^{90}Y, as demonstrated by figure 2.26. The presence of significant quantities of iron and aluminium on the precipitate could therefore be the explanation for ^{90}Y being recovered from the CC-1 column with a recovery of approximately 84 % after precipitation, even though recovery of ^{90}Y on the precipitate is almost quantitative.

The quantitative recovery of the lanthanides on the precipitate meant that the partial precipitation step could also be used as a clean-up step for the determination of lanthanide fission products in milk by the Dionex system as well as ^{90}Sr. Although consistent, the low recoveries of uranium on the precipitate would limit the suitability of the precipitation step as clean-up step for the analysis of uranium in milk.

4.1.6 Summary of the co-precipitation studies for ^{90}Sr in milk

A partial precipitation step has been developed in which ^{90}Y is co-precipitated from acid digested 500 ml milk samples onto $CaHPO_4.2H_2O$. The precipitation is such that only approximately 100 mg of Ca^{2+} is present on the precipitate and ^{90}Y is present in greater than 90 % recovery. After dissolution of the precipitate and pH adjustment of

the resulting solution, ^{90}Y can be isolated on the CC-1 column with a recovery of greater than 80 % and therefore the precipitation step provides a suitable calcium clean-up step for the analysis of milk samples using the Dionex system. The losses of ^{90}Y from the precipitation step to the Dionex step can be attributed to the small quantities of iron and aluminium being present on the precipitate, thus interfering with the isolation of ^{90}Y by the CC-1 column. For 500 ml samples, to which 2 ml of orthophosphoric acid were added, consistent masses of precipitate were formed and recoveries of ^{90}Y after separation on the Dionex system were also shown to be consistent. Lanthanides are also present on the precipitate in quantitative recovery and the partial precipitation step could also therefore be used in lanthanide radionuclide determinations from milk samples. The application of the partial precipitation step to the determination of ^{90}Sr and lanthanide radionuclides in milk samples is described in chapter 5.

4.2 Co-precipitation step for ^{90}Sr in urine samples

Having established a method for the determination of ^{90}Sr in water and milk samples, it was decided to develop a similar procedure for urine samples. The calcium content for a typical sample volume of 300 ml is not sufficient to interfere with the separation of ^{90}Y by the Dionex system. It was therefore considered possible that the urine sample could be prepared for the Dionex separation following a pretreatment procedure analogous to that for water samples described in section 2.5. i.e. evaporation, ashing, acid digestion followed by adjustment to pH 5 with 2 M ammonium acetate. However, it was found that the pH adjustment caused precipitation of salts present in the urine matrix. Redissolution of the material did not occur until the solution was diluted to approximately 300 ml. Using the Sr.Spec columns as a pretreatment step only permitted the analysis of approximately 100 ml of urine which was less than the required sample size.

The use of co-precipitation has been reported by Kramer and Davies [31] as a matrix clean-up step prior to solvent extraction for ^{90}Sr determinations in urine. The approach involved the co-precipitation of ^{90}Sr with calcium oxalate at pH 3, directly from the urine sample. For this investigation, a procedure based on this was followed, however, strontium oxalate was used since strontium has been previously shown to have a weaker interaction with the Dionex CC-1 column than calcium does and therefore should present less of an interference problem. For incorporation into a Dionex separation procedure, the oxalate would be converted to the carbonate by ashing, thus also destroying any organic materials present in the urine which may be brought down on the precipitate. The carbonate would then be dissolved in nitric acid and depending on whether ^{90}Sr alone or both ^{90}Sr and ^{90}Y were co-precipitated, would determine whether an ingrowth period would be required prior to separating ^{90}Y on the CC-1 column.

4.2.1 Determination of the optimum pH for co-precipitation of ^{90}Sr - ^{90}Y on strontium oxalate

To six 300 ml samples of urine, 20 mg of strontium, 40 ng of yttrium, 30 ml of nitric acid (s.g. 1.42) and 6.4 Bq each of ^{90}Sr and ^{90}Y were added. The samples were heated to 90 °C, with stirring, for 1 hour. The sample was then cooled and 30 ml of Sulkowitch reagent were added. This reagent comprises 33 g l^{-1} oxalic acid dihydrate, 33 g l^{-1} ammonium oxalate monohydrate and 67 ml l^{-1} glacial acetic acid made up to volume with HPLC water. The pH of the samples were adjusted to various values by the addition of 6 M ammonia solution to precipitate strontium oxalate. The oxalate was then ashed overnight at 550 °C. The residue was dissolved in 1 M nitric acid and then liquid scintillation counted. Figure 4.8 shows the count rate recovery as a function of pH.

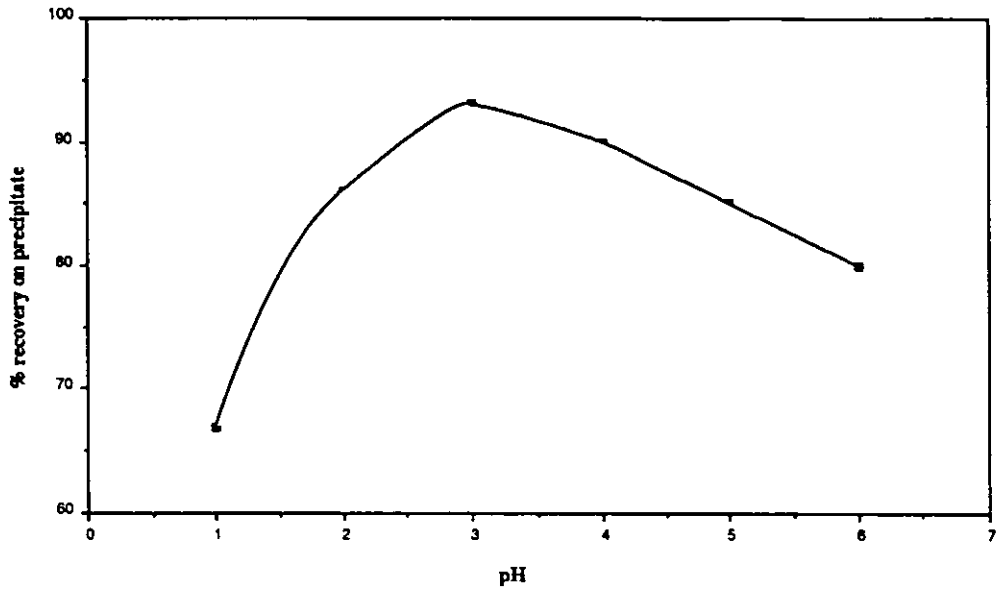


Figure 4.8 Variation in the recovery of ^{90}Sr - ^{90}Y on strontium oxalate precipitated from urine as a function of pH

The optimum pH, for which the recovery was greater than 90 % of the total count rate added, was at pH 3. This high overall recovery determined by liquid scintillation counting implied that ^{90}Sr and ^{90}Y were both co-precipitated in high recovery.

4.2.2 Determination of the recovery of ^{90}Sr - ^{90}Y on strontium oxalate at the optimum pH

The procedure described in 4.2.1 was repeated at pH 3 for three 300 ml urine samples. The final nitric acid solutions containing the ^{90}Sr and ^{90}Y were initially Cerenkov counted to estimate the recovery of ^{90}Y alone and then liquid scintillation counted to determine the total recovery of ^{90}Sr and ^{90}Y. The results for this are shown in table 4.12.

$^{90}Sr + {}^{90}Y$ added / Bq	Count rate added / cpm		Count rate recovered / cpm		% recovery	
	Liquid scintillation	Cerenkov	Liquid scintillation	Cerenkov	Liquid scintillation	Cerenkov
6.4	352.5	177.3	326.1	163.0	93.0	91.9
6.4	352.5	177.3	330.3	163.8	93.8	92.4
6.4	352.5	177.3	329.0	163.4	93.4	92.1
					mean = 93.4 ± 0.4	mean = 92.1 ± 0.3

Table 4.12 Recoveries of ^{90}Sr - ^{90}Y on strontium oxalate precipitated from urine samples at pH 3.

The Cerenkov results show that ^{90}Y was co-precipitated in greater than 90 % recovery. These combined with the liquid scintillation counting results which show that the total recovery of ^{90}Sr and ^{90}Y is greater than 90 %, implies that the ^{90}Sr and ^{90}Y were co-precipitated effectively in secular equilibrium and both in high recovery. The recoveries for the three samples were also reproducible and this step could therefore be included as the pretreatment stage for urine analysis. The co-precipitation of the two radionuclides means that no ingrowth period would be required prior to the isolation of ^{90}Y on the Dionex system. In the complete method, the nitric acid solution would be buffered to pH 5 with 2 M ammonium acetate and then loaded onto the CC-1 column. The method for the determination of ^{90}Sr in urine samples is described in chapter 5.

Chapter 5

METHODS AND VALIDATION

5 METHODS AND VALIDATION

5.1 Evaluation of β-counters for the low-level measurement of ^{90}Y

A requirement of the developed ^{90}Sr method was that the minimum detectable activity (MDA) should be less than 100 mBq l^{-1} of sample. The MDA is dependent on several factors:

i) the quantity of sample analysed;

ii) the chemical yield of the method;

iii) the detector background;

iv) the detector counting efficiencies;

v) the counting time.

i) and ii) are dependent on the separation procedure used. iii) and iv) are dependent on the counting technique used, and their determination is described below. v) is simply dependent on how long it is practically feasible to count the sample for routine analysis purposes. In the case of ^{90}Y, the length of the counting time has to be balanced against the relatively rapid decay of ^{90}Y.

The low-level β-counting of ^{90}Y was compared using three different counters that are currently in use at AEA Technology, Harwell. These were a Tennelec LB400 gas flow proportional counter, an LKB 1219 liquid scintillation counter and an LKB 1220 'Quantalus' liquid scintillation counter. The liquid scintillation counters were compared for both liquid scintillation counting and Cerenkov counting.

The ^{90}Y standards used in the evaluation were prepared by precipitating a known specific activity of ^{90}Y on yttrium hydroxide as described in section 2.3.2.2. After dissolution of the precipitate in a minimum volume of 8 M hydrochloric acid, the

resulting solution was diluted to 25 ml using the oxalate - diglycolate eluant used to elute ^{90}Y from the Dionex system. For the proportional counter, sources were prepared by evaporating 2 ml of the ^{90}Y standard onto stainless-steel planchets under an infra-red lamp and the background source was prepared by evaporating 2 ml of the oxalate - diglycolate eluant onto a stainless-steel planchet. For liquid scintillation counting, sources were prepared by adding 2 ml of the ^{90}Y standard to 10 ml of Hi-Safe III scintillant (which is routinely used in the Harwell laboratory) in 20 ml plastic scintillation vials. Background sources were prepared by adding 2 ml of the oxalate - diglycolate eluant to 10 ml of scintillant. For Cerenkov counting, the sources were 2 ml of the ^{90}Y standard diluted to 13 ml with deionized water and the background sources were 2 ml of the oxalate - diglycolate eluant diluted to 13 ml with deionized water.

The counting conditions for each of the counters were as follows:

i) For the proportional counter, the counting gas composition was 10 % methane and 90 % argon and was supplied at a flow rate of 0.15 cubic feet per hour;

ii) For liquid scintillation counting on the 1219 counter, the counting window was set from channel 150 - 900 and for Cerenkov counting from 25 - 400;

iii) For liquid scintillation counting on the 1220 counter, the counting window was set from channel 300 - 900 and for Cerenkov counting 100 - 400.

The full counting window for the two liquid scintillation counters are from channel 1 - 1000.

Each of the ^{90}Y and background sources were counted for 100 minutes. Tables 5.1 to 5.3 show the counting efficiencies and the minimum detectable activities for the three counters.

Source	^{90}Y added /dpm	Background corrected source count rate / cpm	Background count rate / cpm	% counting efficiency	MDA for 95 % confidence and 100 minutes counting / m Bq
1" ribbed stainless steel planchet	447.6	221.5	1.0	49.3	17
2" plain stainless steel planchet	895.2	410.4	1.0	45.7	18

Table 5.1 ß-counting of ^{90}Y using a Tennelec LB400 gas proportional counter

Counting method	^{90}Y added / dpm	Background corrected source count rate / cpm	Background count rate / cpm	% counting efficiency	MDA for 95 % confidence and 100 minutes counting / m Bq
liquid scintillation	1051.2	911.0	23.6	86.7	44
Cerenkov	1058.4	500.6	18.8	47.3	72

Table 5.2 ß-counting of ^{90}Y using an LKB 1219 liquid scintillation counter

Counting method	^{90}Y added / dpm	Background corrected source count rate / cpm	Background count rate / cpm	% counting efficiency	MDA for 95 % confidence and 100 minutes counting / m Bq
liquid scintillation	180.3	162.6	6.4	90.2	22
Cerenkov	182.6	94.7	1.8	51.9	21

Table 5.3 ß-counting of ^{90}Y using an LKB 1220 Quantalus liquid scintillation counter

The MDA values referred to in the tables were based on the definition of detection limit as given by Currie [96] and Lochamy [97]. The detection limit, L_d, is defined as the smallest quantity of radioactive material which can be detected with some specified degree of confidence. This is calculated using:

$$L_d = \frac{k^2}{T} + 2k\left(2\frac{R_b}{T}\right)^{1/2} \qquad (5\text{-}1)$$

where T is the counting time

R_b is the background count rate

and k is the one-sided confidence factor (For 95 % confidence limits k = 1.65)

The MDA values used in the tables were a modified value of L_d, taking into account the percentage counting efficiency of the counter for ^{90}Y, C, the percentage chemical yield of the separation procedure, Y, and the volume of sample analysed in litres, V. This gives:

$$MDA = L_d \times \frac{100}{CYV} \qquad (5\text{-}2)$$

therefore

$$MDA = \left[\frac{k^2}{T} + 2k\left(2\frac{R_b}{T}\right)^{1/2}\right] \times \frac{100}{CYV} \qquad (5\text{-}3)$$

The units of MDA defined here are those of specific activity. In tables 5.1 - 5.3, Y was set to 100 % and V was set to 1 litre. Thus the values quoted were minimum values, used simply to directly compare the counting techniques without taking into account the separation procedure.

The proportional counter provided the lowest MDA values of the three counters used, although these were not greatly lower than those achievable on the 1220 liquid scintillation counter by both liquid scintillation and Cerenkov counting. The MDA values for the 1219 liquid scintillation counter were significantly greater than the other two counters, particularly for Cerenkov counting.

All the counting techniques provided MDA values that were less than the required value of 100 mBq l^{-1} and therefore appeared to be suitable for counting ^{90}Y in the developed ^{90}Sr method. However, the actual MDA values would be greater than these when modified for chemical yield and sample size. The MDA values for the analysis of water, milk and urine are given in section 5.4.

The three counting techniques are subject to factors which would affect their respective counting efficiencies. However, each ^{90}Y fraction eluted from the CS5 column should be of essentially constant volume and chemical composition, therefore the effect the eluate has on the counting should also be constant from sample to sample. For example, the source thickness in proportional counting should be constant, any impurity quenching effect in liquid scintillation counting should be constant and any colour quenching effect in liquid scintillation and Cerenkov counting should be constant. Therefore, due to the consistency of composition of the ^{90}Y fraction, none of the counting methods should be significantly disadvantaged relative to the others.

In practical terms, the proportional counter has the disadvantage over the liquid scintillation counters in that more source preparation is required prior to counting since after fraction collection in scintillation vials, the ^{90}Y fraction from the CS5 column would be transferred to a planchet and evaporated to dryness. The major

advantage the proportional counter has over the liquid scintillation counters is that it permits the simultaneous counting of twelve samples, whereas the liquid scintillation counters can only count one sample at a time. The proportional counter therefore offers a potentially higher sample throughput for the same counting times or alternatively, the possibility of longer counting times for the same sample throughput. The advantage of the use of longer counting times is that it offers improved counting statistics and reduced MDA values. Thus, although the MDA values for the proportional counter and the 1220 liquid scintillation counter were equally suitable for the low-level counting of ^{90}Y, the proportional counter was the preferred form of counting due to it being able to simultaneously count twelve samples.

5.2 Methods for the determination of ^{90}Sr in liquid matrices

5.2.1 Method for natural water samples

40 ng of yttrium carrier are added to 1 litre of water, which is then acidified with 20 ml of nitric acid (s.g. 1.42) and evaporated to dryness. The residue is ashed at 550 °C in a muffle furnace overnight to destroy any organic material that may be present in the sample. The ashed residue is then dissolved in 25 ml of 1 M nitric acid. The pH of the resulting solution is then adjusted to 5 with an equal volume of 2 M ammonium acetate (pH 5.5) and if necessary, dropwise addition of 6 M ammonia solution. The sample is then loaded onto the Dionex chromatography system at a flow rate of 2 ml min^{-1} and the elution program described in table 2.5 is run, using 51 % water - 15 % diglycolate - 34 % oxalate as the final eluant. The time for the beginning of the ^{90}Y decay is taken from the midpoint of the loading of the sample onto the CC-1 column. The eluate from the CS5 separator column is collected in 2 ml fractions and the fraction containing ^{90}Y is β-counted. Figure 5.1 shows a summary of the method.

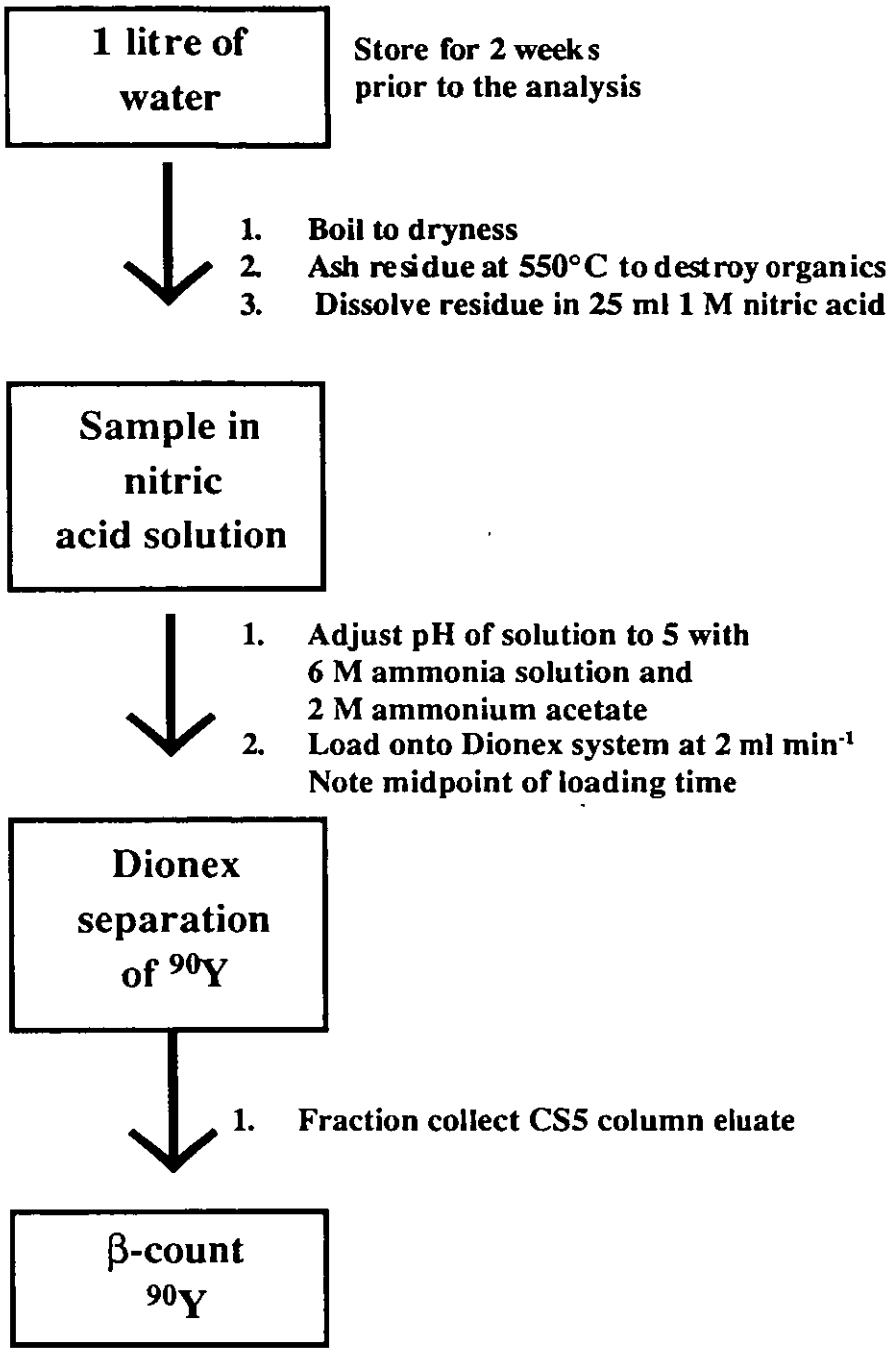


Figure 5.1 Summary of the method for the determination of ^{90}Sr in water samples

5.2.2 Method for milk samples

A milk powder sample equivalent to 500 ml of raw milk is ashed in a muffle furnace overnight at 550 °C. 10 ml of nitric acid (s.g. 1.42) is added and the mixture is evaporated to dryness. The residue is then re-ashed until it becomes white. 40 ng of yttrium carrier and 2 ml of orthophosphoric acid are added to the residue which is then dissolved in 100 ml of 2 M nitric acid. (For 1 litre equivalent milk samples, the volumes of orthophosphoric acid and 2 M nitric acid used are doubled). The resulting solution is then boiled at constant volume for 30 minutes and then cooled. The pH of the solution is adjusted to 3 by the addition of ammonia solution (s.g. 0.880) and then adjusted by the dropwise addition of 6 M ammonia solution, until the addition of one drop is followed by a decrease in pH accompanied by precipitation. At this point the addition of ammonia solution is ceased. After re-stabilization of the pH, the precipitate formed is then collected on a 0.45 μm filter. The time for the beginning of the ^{90}Y decay is taken at this point. The precipitate is then dissolved in a minimum volume of 1 M nitric acid and diluted to 20 ml with deionized water. The pH of the solution is then adjusted to 5 with an equal volume of 2 M ammonium acetate (pH 5.5) and if necessary, dropwise addition of 6 M ammonia solution. The sample is then loaded onto the Dionex chromatography system at a flow rate of 2 ml min^{-1} and the elution program described in table 2.5 is run, using 51 % water - 15 % diglycolate - 34 % oxalate as the final eluant. The eluate from the CS5 separator column is collected in 2 ml fractions and the fraction containing ^{90}Y is β-counted. Figure 5.2 shows a summary of the method.

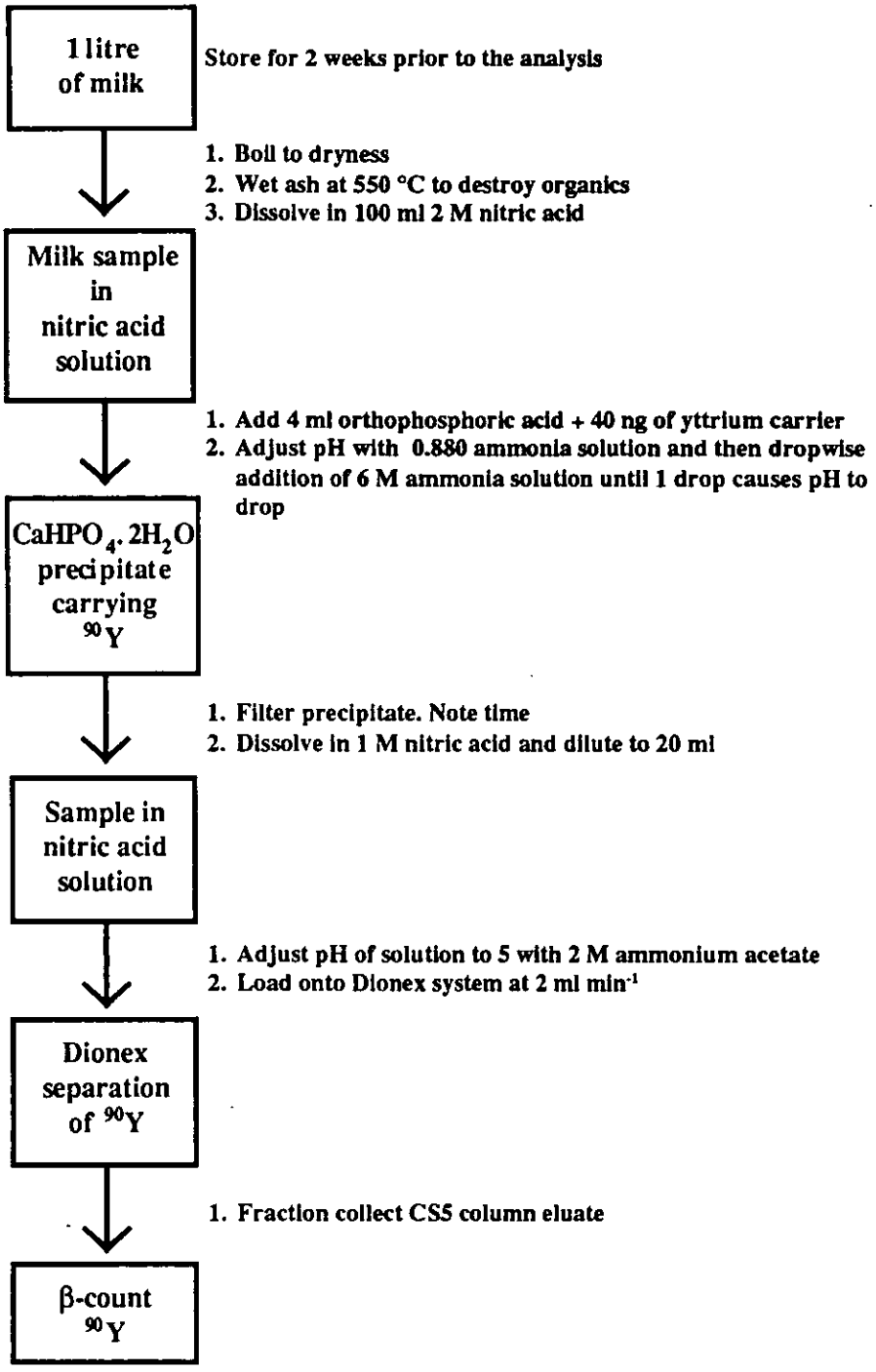


Figure 5.2 Summary of the method for the determination of ^{90}Sr in milk samples

5.2.3 Method for urine samples

20 mg of strontium carrier, 40 ng of yttrium carrier and 30 ml of nitric acid (s.g. 1.42) are added to 300 ml of urine. The sample is heated to 90 °C, with stirring, for one hour and after cooling, 30 ml of Sulkowitch reagent is added. The pH of the sample is adjusted to pH 3 to permit the formation of an oxalate precipitate. The precipitate is isolated by centrifugation at 3000 rpm for 10 minutes, transferred to a beaker with nitric acid (s.g. 1.42) and evaporated to dryness. The residue is then ashed at 550 °C in a muffle furnace overnight. The ashed residue is then dissolved in a minimum volume of 1 M nitric acid and diluted to 20 ml with deionized water. The pH of the solution is then adjusted to 5 with an equal volume of 2 M ammonium acetate (pH 5.5) and if necessary, dropwise addition of 6 M ammonia solution. The sample is then loaded onto the Dionex chromatography system at a flow-rate of 2 ml min^{-1} and the elution program described in table 2.5 is run, using 51 % water - 15 % diglycolate - 34 % oxalate as the final eluant. The time for the beginning of the ^{90}Y decay is taken from the midpoint of the loading of the sample onto the CC-1 column. The eluate from the CS5 separator column is collected in 2 ml fractions and the fraction containing ^{90}Y is β-counted. Figure 5.3 shows a summary of the method.

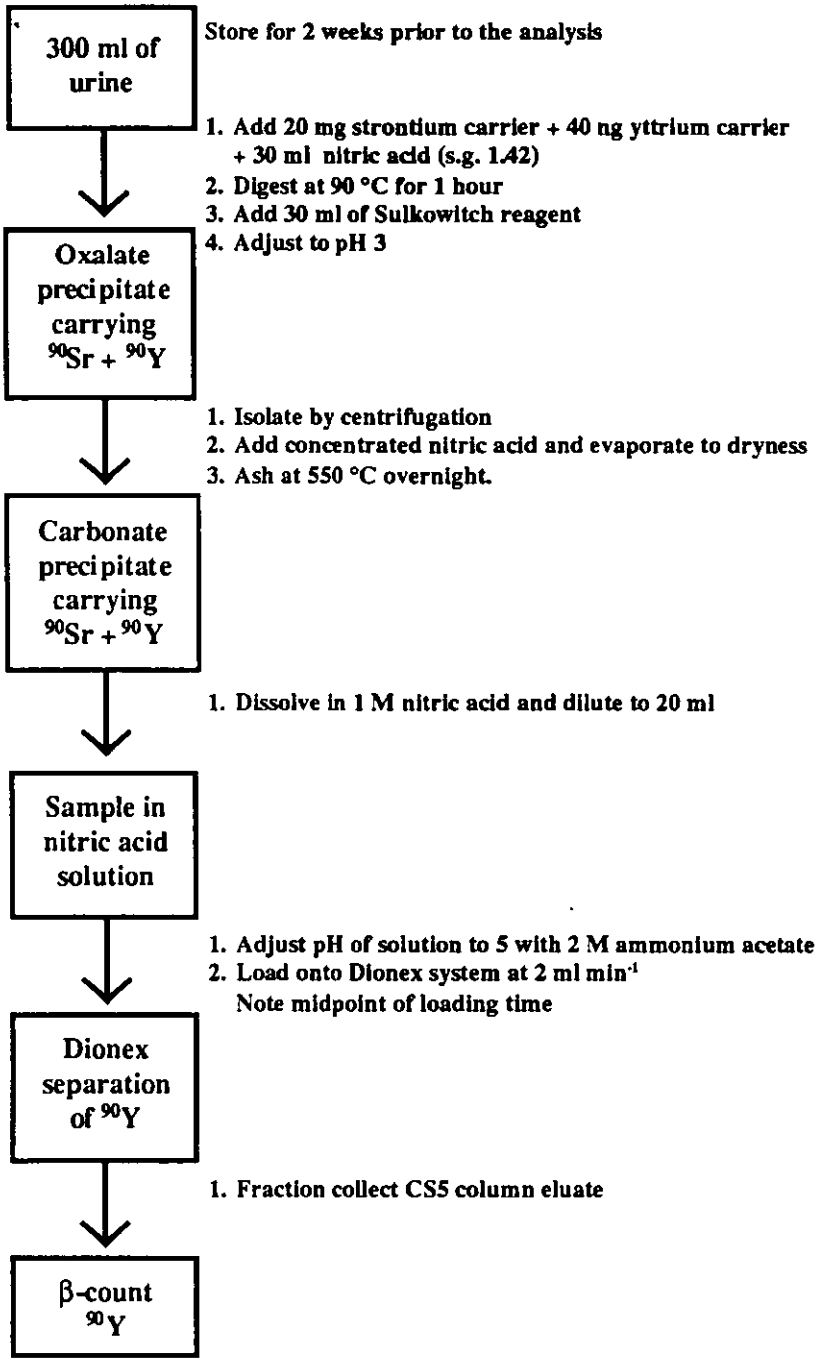


Figure 5.3 Summary of the method for the determination of ^{90}Sr in urine

5.3 Validation of the ^{90}Sr methods

The uncertainties quoted with the results in this section are for 95 % confidence limits.

For the determination of ^{90}Sr in reference materials that were used in the validation of the methods, the specific activities of ^{90}Sr present were calculated using the following equation:

$$A_{Sr} = \left[\frac{(C_Y - B)}{\exp(-\lambda_Y t_Y)}\right] \times \frac{100}{CYM} \qquad (5\text{-}4)$$

where A_{Sr} is the specific activity of ^{90}Sr present in Bq kg^{-1}

C_Y is the ^{90}Y source count rate in counts per second

B is the background count in counts per second

λ_Y is the ^{90}Y decay constant

t_Y is the time from when ^{90}Y was separated from ^{90}Sr to the mid point of the counting

C is the percentage counting efficiency for ^{90}Y

Y is the percentage chemical yield

M is the mass of sample analysed in kg

5.3.1 Validation of the method for natural water samples

The natural water samples used in the method validation were surface water collected from Moscar, Derbyshire, UK and rainwater samples collected by funnel collection in Loughborough, Leicestershire, UK over a period of several weeks. These samples were spiked with varying activities of ^{90}Sr and ^{90}Y in secular equilibrium. The ^{90}Y count rate for these samples was measured by Cerenkov

counting in the tritium channel of the LKB 1215 liquid scintillation counter. A National Physical Laboratory (NPL) Radioactivity Measurement Standard BG 030/92, Teddington, Surrey, UK was also used to validate the method. For this sample, the Tennelec LB400 gas flow proportional counter was used to measure the ^{90}Y count rate. Deionized water spiked with 6.4 Bq each of ^{90}Sr and ^{90}Y was used as a recovery monitor for this sample. Table 5.4 shows the recoveries of ^{90}Y for the spiked natural water samples.

Surface water				Rainwater			
^{90}Y activity added / Bq	^{90}Y count rate added / cpm	^{90}Y count rate recovered / cpm	% recovery	^{90}Y activity added / Bq	^{90}Y count rate added / cpm	^{90}Y count rate recovered / cpm	% recovery
5.00	129.6	119.6	92.3	5.00	129.6	120.6	93.1
5.00	129.6	118.1	91.2	5.00	129.6	119.7	92.4
5.00	129.6	116.9	90.2	5.00	129.6	118.2	91.2
5.00	129.6	118.5	91.4	2.50	64.8	59.0	91.1
2.50	64.8	59.8	92.3	2.50	64.8	59.7	92.1
2.50	64.8	60.5	93.3	2.50	64.8	59.8	92.3
2.50	64.8	59.6	92.0	1.25	32.4	29.9	92.3
1.25	32.4	29.6	91.2	1.25	32.4	29.8	92.1
1.25	32.4	29.5	91.1	1.25	32.4	29.3	90.4
1.25	32.4	29.9	92.3	1.25	32.4	29.9	92.3
		Mean = 91.7 ± 1.8				Mean = 91.9 ± 1.6	

Table 5.4 Recoveries of ^{90}Y from spiked 1 litre water samples

The mean recoveries were 91.7 ± 1.8 % and 91.9 ± 1.6 % for the surface water and rainwater samples respectively. Table 5.5 shows that the activity of ^{90}Sr in the NPL standard determined by the method was in good agreement with the value quoted by the NPL [98].

Sample	Mass of sample analysed / g	Certified ^{90}Sr specific activity / Bq kg^{-1}	Observed ^{90}Sr specific activity / Bq kg^{-1}
1	25	49.0 ± 0.2	46.4 ± 1.5
2	25	49.0 ± 0.2	47.5 ± 1.5

Table 5.5 Determination of ^{90}Sr in an NPL Intercomparison Standard

The analysis of this standard provided a good test for the method, since this was the only water sample analysed for which the ^{90}Sr content was not accurately known prior to the analysis.

5.3.2 Validation of the method for milk samples

The samples used in the validation of the method were milk powders obtained from several sources spiked with varying activities of ^{90}Sr and ^{90}Y in secular equilibrium. International Atomic Energy Agency (IAEA) reference materials A14 and IAEA-152, Vienna, Austria were also used. A mass of 100 g of these was approximately equivalent to 1 litre of raw milk. Spiked milk powders were used as a recovery monitor for the reference materials. Tables 5.6 and 5.7 shows that the recoveries of ^{90}Y from 500 ml and 1 litre milk samples.

Sample description	^{90}Y activity added /Bq	^{90}Y count rate added /cpm	Count rate recovered /cpm	% recovery
Marvel	8.4	217.9	185.9	85.3
Harwell	8.4	217.9	181.8	83.4
Harwell	8.4	217.9	179.6	82.4
KLIM	2.5	64.9	54.8	84.6
KLIM	2.5	64.9	54.1	83.4
Dairy Farms	8.4	217.9	188.9	86.7
KLIM	1.25	32.4	27.5	84.9
KLIM	1.25	32.4	27.7	85.6
Marvel	1.25	32.4	27.4	84.7
Marvel	1.25	32.4	27.0	83.2
				mean = 84.4 ± 2.6

Table 5.6 Recoveries of ^{90}Y from spiked 500 ml equivalent milk samples

^{90}Y activity added /Bq	^{90}Y activity added /cpm	Count rate recovered /cpm	% recovery
1.96	50.8	41.4	81.6
1.96	50.8	40.9	80.4
1.96	50.8	41.8	82.3
0.98	25.4	20.9	82.4
0.98	25.4	20.8	81.9
0.98	25.4	20.1	79.1
			mean = 81.3 ± 2.5

Table 5.7 Recoveries of ^{90}Y from spiked 1 litre equivalent milk samples

For the 500 ml samples, the mean recovery was 84.4 ± 2.6 % and for the 1 litre samples was 81.3 ± 2.5 %, thus the larger sample size produced a slight reduction in the recovery of ^{90}Y. Table 5.8 shows the results for the determination of ^{90}Sr in the IAEA reference materials.

Sample	Mass of milk powder used / g	Certified specific activity / Bq kg^{-1}	Confidence interval / Bq kg^{-1}	Observed specific activity / Bq kg^{-1}
A14	99.2162	1.32	1.17 - 1.38	1.41 ± 0.34
IAEA-152	99.7349	6.79	6.17 - 7.32	6.99 ± 0.51
IAEA-152	50.0762	6.79	6.17 - 7.32	6.47 ± 0.73

Table 5.8 Determination of ^{90}Sr in IAEA reference milk samples

The specific activities of ^{90}Sr determined by the method were in good agreement with the values quoted by the IAEA. The certified values quoted in the table are calculated values based on the specific activities of A-14 and IAEA-152 being 1.5 Bq kg^{-1} [99] and 7.7 Bq kg^{-1} [100] on 31st August 1987.

5.3.3 Validation of the method for urine samples

The samples used in the method validation were 300 ml aliquots of human urine spiked with varying activities of ^{90}Sr and ^{90}Y in secular equilibrium. The urine was collected over a two week period and bulked before spiking. The ^{90}Y count rate for these samples was measured in the tritium channel of the LKB 1215 liquid scintillation counter.

Table 5.9 shows the recoveries of ^{90}Y in the urine samples at the varying activity levels. The mean recovery was 90.0 ± 2.7 %.

^{90}Y activity added / Bq	^{90}Y count rate added / cpm	^{90}Y count rate recovered / cpm	% recovery
6.84	177.3	159.7	90.1
3.42	88.6	78.6	88.7
1.71	44.3	40.2	90.7
0.86	22.3	20.3	91.0
0.86	22.3	19.6	87.9
0.86	22.3	20.3	91.3
			mean = 90.0 ± 2.7

Table 5.9 Recoveries of ^{90}Y from spiked 300 ml urine samples

5.4 Discussion of the developed ^{90}Sr methods

The recoveries of ^{90}Y from the methods for the three liquid matrices were all high, greater than 90 % for the water and urine samples and greater than 80 % for the milk samples, and were also reproducible. The recoveries for milk showed a slight variation for the two sample sizes analysed, although they were reproducible for a specific sample size. From this, it was clear that the external standard run with each batch of samples as a yield monitor, should be of equivalent volume to the samples. The variation in recovery observed for the different volumes of milk analysed could be attributed to larger quantities of transition metals, especially iron and aluminium, being carried down on the precipitate for the larger sample volume during the partial precipitation step. The presence of these would have had a significant effect on the

subsequent Dionex separation of ^{90}Y.

From the recoveries, it was possible to estimate the MDA values for the three sample types. Substituting the counting parameters for the Tennelec LB400 gas flow proportional counter, and the recoveries and sample volumes above into equation (5-4), the MDA for water samples is 20 mBq l^{-1}, for 500 ml milk samples is 43 mBq l^{-1}, for 1 litre milk samples is 22 mBq l^{-1} and for urine is 60 mBq l^{-1}. Thus the methods provided MDA values significantly below the required value of 100 mBq l^{-1} using the proportional counter for a 100 minute counting time.

The determined ^{90}Sr levels in the NPL water standard and the IAEA milk standards were all within the uncertainties of the certified values which demonstrated the reliability of the methods for the determination of ^{90}Sr. The minimum activity of ^{90}Y actually measured in the validation was for the IAEA reference material A-14, which was 0.141 Bq for the 100 g sample (equivalent to 1 litre of milk). This therefore demonstrated that the method was reliable for the determination of ^{90}Sr at significantly below the Becquerel level and just above the required MDA value.

In terms of analysis time, the Dionex separation of ^{90}Y takes approximately 75 minutes for each sample, which meant that it was possible to run five samples and a standard on the Dionex system per day. The Dionex run time is split into 25 minutes for loading the sample onto the CC-1 column, 40 minutes to run the elution program and 10 minutes between each sample run for cleaning and re-equilibration of the columns. In addition to this, 30 minutes are required to equilibrate the columns with eluant prior to running samples through the system and 15 minutes are required to wash the columns with water prior to shutdown of the system. After separation, each of the separated ^{90}Y fractions from a days separation could be counted

simultaneously using the Tennelec LB400 gas flow proportional counter for a specified counting time, which could be carried out overnight. Both the Dionex separation and counting steps require little attention time by the analyst.

Of the sample pretreatment steps, the one for water samples was the simplest and required the least attention time. The evaporation of the water samples was carried out the day prior to the Dionex separation and the ashing stage overnight. For the urine samples, the precipitation step was carried out the day prior to the Dionex separation and the ashing stage again was carried out overnight. For water and urine samples, it was possible to process five samples in approximately one and a half days.

The sample pretreatment step for milk samples was marginally the most labour intensive of the three sample types. In the validation, the ashing of the milk powder was carried out overnight. The following day, the samples were acid digested in a batch of five, then one sample was taken straight through the partial precipitation step and the Dionex separation. While this sample was undergoing separation, the next sample was partially precipitated and so on. Alternatively, it would be possible to carry out the partial precipitation on a batch of samples and leave the precipitates in solution until they were ready for separation on the Dionex system. This approach however does not appear to reduce labour or analysis time. Using the method described above, five samples could be processed in one and a half days. This analysis time was for milk powder, which was used in the method development. If the original sample was liquid milk, a further step would be required involving either evaporation of the milk to dryness or freeze drying of the milk which would extend the analysis time by a further half day.

The total analysis time for milk was similar to that for water and urine. However, the partial precipitation step required a significant amount of attention time which made the milk method more labour intensive than the water and urine methods. It would be possible to reduce the labour intensity of the partial precipitation step by automating the process. This could be achieved using a computerized system which monitors the pH of the sample solution and has control over the addition of ammonia solution to the sample. Thus, after the addition of ammonia solution to the sample, the system monitors the pH after a suitable time interval. If the pH has increased or remains constant, the system permits the addition of further ammonia solution, if the pH decreases, the system ceases the addition of ammonia solution.

The three methods, as described above, permit the analysis of five samples and a standard within a maximum of two days. This however does not take into account that the samples should be stored for at least fourteen days prior to analysis, to ensure that ^{90}Sr and ^{90}Y are in secular equilibrium at the time of analysis. This therefore significantly extends the total analysis time from the time of sample collection, but has no effect on the labour intensity of the methods.

The developed methods are suitable for routine ^{90}Sr determinations and provide separations which are rapid and are not greatly labour intensive, which is largely brought about by the degree of automation provided by the Dionex system. The methods also provide MDA values below those that were required of the developed methods for 100 minute counting times, which is in part due to the high recoveries obtainable from the separation procedure.

The methods would not be particularly suitable for rapid determinations of ^{90}Sr in accident scenarios due to the ingrowth period being required. However, it may be possible to provide quick estimations based on shorter build up times of ^{90}Y in such

cases, providing that the ^{90}Y ingrowth could be accurately estimated. Another problem in these scenarios is that ^{91}Y is likely to be present. In order to eliminate its contribution in the proportional counting stage, β-absorbers would have to be used, resulting in reduced counting efficiencies and increased MDA values.

5.5 Comparison of the developed ^{90}Sr methods with current methods

Using the commonly used 'nitric acid' method permits the determination of ^{90}Sr in six samples in three to four days, excluding the period for ^{90}Y ingrowth, which is a substantially longer analysis time than the developed methods. This method also has the disadvantage that it contains many more steps than the developed methods, as summarized in table 1.3 and is consequently more labour intensive. Chemical recoveries for similar sample sizes are typically 70 - 80 % for the 'nitric acid' method and are therefore inferior to those for the developed methods. Another advantage of the developed methods is that they avoid the use of the highly corrosive fuming nitric acid.

One disadvantage of the developed methods relative to the 'nitric acid' method is that the presence the short-lived radionuclide, ^{91}Y, would interfere with the developed methods since ^{90}Y is directly extracted, whereas this is not a problem for the nitric acid method which initially involves the extraction of ^{90}Sr.

It was intended that the developed method should be a replacement for a method involving solvent extraction using HDEHP summarized in table 1.4. In terms of actual analysis time, this method and the developed methods are comparable. However, the solvent extraction stage is particularly labour intensive and as it stands, unlike the developed methods, it relies on lanthanide fission products such as ^{140}La, ^{141}Ce and ^{147}Nd being absent and also, as with the developed method, ^{91}Y would interfere. Further solvent extractions would be required to ensure that ^{90}Y was totally

separated from these, thus increasing the labour intensity of the method and the analysis time. The chemical yield for this method is typically 65 - 75 % and is therefore inferior to the developed methods.

An advantage that both the nitric acid and solvent extraction methods have over the developed methods is that they permit the use of internal chemical recovery monitors whereas the developed methods only permit the use of external recovery monitors. However, the consistency of the recoveries for the developed methods provide sufficient compensation for this.

Although the developed methods have weaknesses relative to the two established methods described, overall they appear to provide improved methods of routine ^{90}Sr analysis relative to both the 'nitric acid' and solvent extraction methods.

5.6 Determination of lanthanide radionuclides using the developed ^{90}Sr methods

The studies in chapter 2 demonstrated that the Dionex system could separate lanthanide radionuclides in almost quantitative recovery. Kramer and Davies [31] demonstrated that lanthanides could be co-precipitated with calcium oxalate in high recovery and the studies in chapter 4 demonstrated that lanthanides were almost quantitatively recovered on the $CaHPO_4.2H_2O$ precipitated from milk samples. It was therefore apparent that the developed methods could be used for the analysis of lanthanide radionuclides in liquid matrices. The methods described in section 5.2 were therefore applied, unaltered, for the analysis of lanthanide radionuclides in water, milk and urine. The lanthanides used were ^{141}Ce, ^{147}Pm and ^{152}Eu. ^{147}Pm was measured by liquid scintillation counting with a counting efficiency of 66.2 %. ^{152}Eu and ^{141}Ce were measured by γ-counting and the counting efficiency for ^{152}Eu was 60.4 %. The counting efficiency for ^{141}Ce was not determined because a reliable

standard was not available. The recoveries for the lanthanide radionuclides from 1 litre water samples, 500 ml milk samples and 300 ml urine samples are shown in tables 5.10 to 5.12 respectively.

i) ^{147}Pm

Activity added / Bq	Count rate added / cpm	Count rate recovered / cpm	% recovery
16.26	604.9	552.7	91.4
16.26	604.9	549.9	90.9
8.13	302.4	271.9	89.9
8.13	302.4	276.0	91.3
4.07	151.2	139.0	91.2
4.07	151.2	137.1	91.0
			mean = 91.0 ± 1.0

ii) ^{152}Eu

Activity added / Bq	Count rate added / cpm	Count rate recovered / cpm	% recovery
40.14	1449.4	1325.9	91.5
40.14	1449.4	1317.5	90.9
40.14	1449.4	1322.0	91.2
40.14	1449.4	1328.4	91.7
40.14	1449.4	1315.6	90.8
40.14	1449.4	1321.9	91.2
			mean = 91.2 ± 0.7

iii) ^{141}Ce

Activity added / Bq	Count rate added / cpm	Count rate recovered / cpm	% recovery
	1374.6	1253.1	91.0
	1374.6	1245.0	90.6
	1374.6	1261.4	91.8
	1374.6	1242.6	90.4
	1374.6	1249.8	90.0
	1374.6	1249.0	90.9
			mean = 90.9 ± 1.0

Table 5.10 Recoveries of lanthanide radionuclides from 1 litre natural water samples

i) ^{147}Pm

Activity added / Bq	Count rate added / cpm	Count rate Recovered / cpm	% recovery
16.26	604.3	504.3	83.5
16.26	604.3	507.1	83.9
8.13	302.2	257.8	85.3
8.13	302.2	256.0	84.7
4.07	151.1	126.2	83.6
4.07	151.1	128.0	84.8
			mean = 84.3 ± 1.5

ii) ^{152}Eu

Activity added / Bq	Count rate added / cpm	Count rate recovered / cpm	% recovery
40.14	1458.4	1227.0	84.1
40.14	1458.4	1213.6	83.2
40.14	1458.4	1223.1	83.9
40.14	1458.4	1241.4	85.1
40.14	1458.4	1233.8	84.6
40.14	1458.4	1209.0	82.9
			mean = 84.0 ± 1.7

iii) ^{141}Ce

Activity added / Bq	Count rate added / cpm	Count rate recovered / cpm	% recovery
	1378.9	1147.4	83.2
	1378.9	1135.7	82.4
	1378.9	1166.3	84.6
	1378.9	1175.3	85.2
	1378.9	1174.4	85.2
	1378.9	1145.1	83.0
			mean = 83.9 ± 2.4

Table 5.11 Recoveries of lanthanide radionuclides from 500 ml equivalent milk samples

i) ^{147}Pm

Activity added / Bq	Count rate added / cpm	Count rate recovered / cpm	% recovery
16.26	606.3	539.7	89.0
16.26	606.3	537.6	88.7
8.13	303.2	266.6	87.9
8.13	303.2	273.6	90.2
4.07	151.6	135.5	89.4
4.07	151.6	136.8	90.3
			mean = 89.3 ± 1.8

ii) ^{152}Eu

Activity added / Bq	Count rate added / cpm	Count rate recovered / cpm	% recovery
40.14	1439.6	1291.6	89.7
40.14	1439.6	1304.3	90.6
40.14	1439.6	1279.5	88.9
40.14	1439.6	1290.2	89.6
40.14	1439.6	1283.7	89.2
40.14	1439.6	1289.4	89.6
			mean = 89.6 ± 1.1

iii) ^{141}Ce

Activity added / Bq	Count rate added / cpm	Count rate recovered / cpm	% recovery
	1362.4	1209.5	88.8
	1362.4	1205.3	88.5
	1362.4	1207.0	88.6
	1362.4	1211.3	88.9
	1362.4	1223.7	89.8
	1362.4	1215.1	89.2
			mean = 89.0 ± 1.0

Table 5.12 Recoveries of lanthanide radionuclides from 300 ml urine samples

The recoveries for the three lanthanide radionuclides were similar to each other and to the recoveries obtained for ^{90}Y in the three liquid matrices. This was not unexpected due to the chemical similarity between yttrium and the lanthanides. These results therefore demonstrate the potential of the Dionex separation based methods for multi-radionuclide separations. However, it was demonstrated in chapter 2 that americium and plutonium co-eluted with promethium and europium respectively and would remain interferences in the determination of these lanthanide fission products using the Dionex system. Therefore, discrimination in the subsequent counting step would be required to reliably permit the determination of these lanthanide fission products as the method currently stands. If this counting discrimination could be achieved, it would be possible to measure americium and ^{147}Pm in the same eluted fraction and plutonium and ^{152}Eu in the same eluted fraction. In the case of plutonium, further investigation of its extraction by the CC-1 column would be required due to its strong interaction with the CC-1 column.

The use of the CS5 column in conjunction with the PDCA eluant system has been used for transition metal radionuclide determinations, therefore the Dionex based separation methods offer the potential for simultaneous ^{90}Sr, actinide, transition metal and lanthanide radionuclide determinations.

Chapter 6

CONCLUSIONS AND FURTHER WORK

6 CONCLUSIONS AND FURTHER WORK

6.1 Conclusions

The primary aim of the research was to develop a routine method for the analysis of ^{90}Sr in milk with an MDA value of less than 100 mBq l^{-1}, to replace the solvent extraction approach currently in use at AEA Technology, Harwell. This has been achieved not only for milk but also for water and urine, using a procedure involving an ion-chromatographic separation of ^{90}Y, in conjunction with gas flow proportional counting.

The approach provides an improvement over the solvent extraction approach mainly as a result of the degree of automation provided by the ion-chromatography system, which reduces the labour intensity of the approach relative to the solvent extraction approach. The system permits the analysis of water samples with a minimum of pretreatment and the analysis of urine is achieved by the inclusion of a strontium oxalate co-precipitation step prior to the ion-chromatographic separation. The presence of large quantities of calcium in milk prevented its direct analysis using the ion-chromatography system. However, this problem was overcome by the inclusion of a step involving the controlled partial precipitation of $CaHPO_4.2H_2O$ at pH 3 - 4. This precipitate carried ^{90}Y quantitatively and the levels of calcium precipitated were sufficiently low to permit the isolation of ^{90}Y using the ion-chromatography system. The three methods permit the analysis of five samples and one standard in one and a half to two days.

Advantages of the developed methods are:

i) They do not contain many steps and are relatively simple;

ii) They are not labour intensive, but the labour intensity varies with water analysis being the least labour intensive and milk analysis being the most labour intensive;

iii) They provide effective decontamination from other radionuclide interferences;

iv) The chemical recoveries are high and reproducible;

v) The MDA values are significantly below the required 100 mBq l^{-1} limit (They are 20, 22 and 60 mBq l^{-1} for water, milk and urine respectively).

Disadvantages of the methods are:

i) They rely on external standards to act as chemical recovery monitors, however, the reproducible recoveries compensate for this;

ii) The presence of ^{91}Y presents an interference problem, but this can be overcome at the counting stage.

The disadvantages of the developed methods are therefore overcome, and overall, the methods are an improvement on the solvent extraction approach currently in use. The reliability of the methods for ^{90}Sr determinations in milk and water has been validated using standard reference materials.

The developed ^{90}Sr methods have also been applied, unaltered, for the analysis of lanthanide fission products with similar chemical recoveries to ^{90}Sr. However, these are interfered with due to co-elution with actinides from the chromatography system.

The ion-chromatography system has also demonstrated that that it could separate actinides and transition metal radionuclides. The system has therefore demonstrated potential for multi-radionuclide analyses, which is potentially another advantage of the approach. Multi-radionuclide analyses should however be considered with caution, since co-elution of radionuclides from the system has been observed and alterations of the conditions may be required to successfully isolate radionuclides of interest.

Since the use of the chromatography system requires a fairly large initial financial outlay to purchase the system, it may not be feasible for many laboratories to use the developed methods. However, it may be possible to incorporate the the partial precipitation step developed for the milk method into an established method for ^{90}Sr determinations, since it could be used as a calcium clean-up step in such a method. If this is the case, then the research may prove to be useful in methods other than the developed methods.

Strontium selective crown ether resins were originally considered as a calcium clean-up step for the ion-chromatography system and they demonstrated potential for the isolation of ^{90}Sr in the presence of calcium levels equivalent to that present in a litre of milk. However, their applicability for the determination of ^{90}Sr in environmental samples was shown to be limited. This was principally due to the large concentrations of potassium present in these samples, which prevented the successful extraction of strontium by the resin due to potassium successfully competing for the crown ether sites. For these resins to successfully isolate ^{90}Sr from environmental materials would require the inclusion of a calcium phosphate or calcium oxalate co-precipitation step to reduce the potassium to suitable levels. Therefore the use of the resins as a simple calcium clean-up step for the ion-

chromatography system was negated, since a single co-precipitation step proved to be a suitable clean-up step for the chromatography system. The resins in conjunction with a co-precipitation step could be used for the determination of ^{90}Sr in environmental materials, but they do not appear to offer any advantage over the developed ion-chromatographic methods, since the procedures would contain similar numbers of steps.

6.2 Further work

Here, methods have been developed for the determination of ^{90}Sr in liquid matrices only, therefore the application of the ion-chromatographic approach to other environmental and biological matrices of interest, for example, vegetation, soil, foodstuffs, bone and faeces could be investigated. For these matrices, as with milk, a clean-up step prior to the ion-chromatography system will be required to reduce the levels of interfering matrix elements present. For vegetation, foodstuffs and bone it may be feasible to use the partial precipitation step used for milk, but adjusted to take into account the concentrations of calcium and phosphate present in the sample. For faeces and soil, the presence of large concentrations of iron would prevent the use of the partial precipitation step, hence an alternative clean-up step would have to be considered.

The use of the ion-chromatography system for multi-radionuclide analyses should be further investigated. Although co-elution and poor recoveries may cause problems for certain radionuclides, as in the case of the actinides, it may be possible to establish successful separations of certain radionuclides of interest. Therefore, it is important to establish which of these radionuclides in particular it would be feasible to analyse simultaneously in a single chromatographic separation. Once established, the behaviour of these radionuclides during the various sample pretreatment steps

should then be investigated to determine if these radionuclides could be successfully analysed in the various environmental materials. Currently, a more detailed investigation into the separation behaviour of ^{241}Am, which has been shown to be retained by the ion-chromatography system in high recovery, is being carried out.

Another area of future investigation which may be considered, is the possibility of automating the partial precipitation step as described in section 5.4. This step is currently the most labour intensive part of the milk method and automating this would provide a further improvement to the method.

REFERENCES

1. Eisenbud, M., *Environmental Radioactivity*, 3rd Ed., New York Academic Press, (1987).

2. Mackenzie, A.B., *Anal. Proc.*,**19**, 511, (1982)

3. International Atomic Energy Agency, *Measurement of Radionuclides in Food and Environment*, Technical Report. Series 298, IAEA, Vienna, (1989).

4. Pochin, E., *Monographs on Science, Technology and Society 2: Nuclear Radiation, Risks and Benefits*, Oxford University Press, (1985).

5. Volchock, H.L. and De Planque, G., (Eds), *Environmental Measurements Laboratory Procedures Manual*, 27th Ed., HASL-300, US Dept. of Energy, New York, (1983).

6. RADREM, *Sampling and Measurement of Radionuclides in the Environment*, HMSO Books, London, (1989).

7. Hassinsky M. and Adloff, J.P, *Radiochemical Survey of the Elements*, Elsevier Publishing, Amsterdam, (1965).

8. Lide, D.R., (Ed), *Handbook of Chemistry and Physics*, 71st Ed., CRC Press, Boca Raton, (1990).

9. International Commission on Radiological Protection, *Report of the Task Group on Reference Man*, ICRP Publication 23, Pergamon Press, Oxford, (1975).

10. Frielander,G., Kennedy, J.W., Macias, E.S. and Miller, J.M., *Nuclear and Radiochemistry*, 3rd Ed, John Wiley and Sons, (1981).

11. Emsley, J., *The Elements*, Clarendon Press, Oxford, (1989).

12. Browning, E., *Toxicity of Industrial Metals*, Butterworths, London, (1969).

13. International Commission on Radiological Protection, *Alkaline-Earth Metabolism in Adult Man,* ICRP Publication 20, Pergamon Press, Oxford, (1973).

14. International Commission on Radiological Protection, *Limits for Intakes of Radionuclides by Workers*, Pergamon Press ICRP Publication 30(2), Oxford,(1980).

15. Goldin, A.S., Velten, R.J. and Frishkorn, G.W., *Anal. Chem.*, **31**, 1490, (1959).

16. Wilken, R.D. and Joshi, S.R., *Radioactivity and Radiochemistry*, **2**, 14, (1991).

17. Wilken, R.D. and Diehl, R., *Radiochim. Acta*, **29**, 1578 (1987).

18. Willard, H.H. and Goodspeed, E.W., *Ind. Eng. Chem., Anal. Ed.*, **8**, 414, (1936).

19. Sundermann, D.N. and Meinke, W.W., *Anal. Chem.*, **29**, 1578, (1957).

20. Coryell, C.D. and Sugarmann, N., *National Nuclear Energy Series IV, Radiochemical Studies: The Fission Products*, M^{c} Graw-Hill, New York, (1951).

21. Weiss, H.D. and Shipman, W.H., *Anal. Chem.*, **29**, 1764, (1957).

22. Boni, A.L., *Anal. Chem.*, **35**, 774,(1963).

23. Eakins, J.D. and Gomm, P.J., *AERE R-4753*, (1964).

24. Bunzl, K. and Kracke, W. J., *J. Radioanal. Nucl. Chem. Art.*, **148**, 115, (1991).

25. Goldin, A.S. and Velten, R., *Anal. Chem.*, **33**, 149, (1961).

26. Velten, R. and Goldin, A.S., *Anal. Chem.*, **33**. 128, (1961).

27. Baratta, E.J. and Reavey, T.C., *J.Agric. Food Chem.*, **17**, 1337, (1969).

28. Zhu, S., Ghods, A., Veselsky, J.C., Mirna, A. and Schelenz, R., *Radiochim. Acta*, **51**, 195, (1990).

29. Petrow, H.G., *Anal. Chem.*, **37**, 584, (1965).

30. Bogen, D.C., *Health Physics*,**14**, 131, (1968).

31. Kramer, G.H. and Davies, J.M., *Anal. Chem.*, **54**, 1428, (1982).

32. Borcherding, J. and Nies, H., *J. Radioanal. Nucl. Chem. Art.*, **98**, 127, (1986).

33. AEA Technology, *The Radiochemical Determination of ^{90}Sr in Milk by Solvent Extraction*, Private Communication.

34. Toth, L., *J. Radioanal. Nucl. Chem. Lett.*, **59**, 245, (1983).

35. Koprda, V., Scasnar, V. and Galan, P., *J. Radioanal. Nucl. Chem. Art.*, **80**, 55, (1983).

36. Kimura, T., Iwashima, K., Ishimori, T. and Hamada, T., *Anal. Chem.*, **51**, 1113, (1979).

37. Lada, W.A. and Smulek, W., *J. Radioanal. Chem.*, **50**, 169, (1979).

38. Blasius, E., Klein, W. and Schon, U., *J. Radioanal. Nucl. Chem. Art.*, **89**, 389, (1985).

39. Mikulaj, V., Hlaty, J. and Vasekova, L., *J. Radioanal. Nucl. Chem. Art.*, **101**, 51, (1986).

40. Mohite, B.J. and Khopac, S.M., *Anal. Chem.*, **59**, 1200, (1987).

41. Vaney, B., Friedli, C., Geering, J. and Lerch, P.,*J. Radioanal. Nucl. Chem. Art.*, **134**, 87, (1989).

42. Wai, C.M. and Du,H.S., *Anal. Chem.*, **62**, 2412, (1990).

43. Horwitz, E.P., Dietz, M.L. and Fisher, D.E., *Anal. Chem.*, **63**, 522, (1991).

44. Horwitz, E.P., Chiarizia, R. and Dietz, M.L., *Solv. Extr. & Ion Exch.*, **10**, 313, (1992).

45. Vajda, N., Ghods-Esphahane, A., Cooper, E. and Danesi, P.R., *J. Radioanal. Nucl. Chem. Art.*, **162**, 307, (1992).

46. El-Dessouky and Sharaf El-Deen, A.N., *J. Radioanal. Nucl. Chem. Art.*, **125**, 481,(1988).

47. Stanley, C.W. and Kruger, P., *Nucleonics*, **14**, 114, (1959).

48. Bryant, E.A., Sattizahn, J.E. and Warren, B., *Anal. Chem.*, **31**,334,(1959).

49. Lerner, M. and Rieman, W., *Anal. Chem.*, **26**, 610, (1954).

50. Milton, G.M. and Grummitt, W.E.,*Can. J. Chem.*, **35**, 541, (1957).

51. Goodall, G., *UKAEA PG Report 815 (Ca)*, (1968).

52. Gregory, L.P., *Anal. Chem.*, **44**, 2113, (1972).

53. Natsume, H., Umezawa, H., Suzuki, T., Ichikawa, F., Sato,T., Baba, S. and Amano, H., *J. Radioanal. Nucl. Chem. Art.*, **7**, 189, (1971).

54. Amano, H. and Yanase, N., *Talanta*, **37**, 585, (1990).

55. Oravec, J. and Navarcik, I., *J. Radioanal. Nucl. Chem. Art.*, **121**, 331, (1988).

56. Cahill., D.F. and Lindsey, G.I., *Anal. Chem.*, **38**, 639, (1966).

57. Lamb., J.D., Nordmeyer, F.R., Drake, P.A., Elder, M.P., Miles, R.W. and Lash, R.P.,*J. Radioanal. Nucl. Chem. Art.*, **134**, 317, (1989).

58. Malcolm-Lawes, D.J, *Introduction to Radiochemistry*, Macmillan Press Ltd., London, (1979).

59. Birks, J.B., *The Theory and Practice of Liquid Scintillation Counting,Pergamon Press*, Oxford, (1964)

60. Horrocks, D.L., *J. Radioanal. Nucl. Chem. Art.*, **43**, 331, (1978).

61. Rundt, K., *On the Determination and Compensation of Quench in Liquid Scintillation Counting*, Ph.D. Thesis, Abo Akademi, Finland (1989).

62. Ross, H., Noakes, J.E,, and Spaulding, J.D., (Eds), *Liquid Scintillation Counting and Organic Scintillators*, Lewis Publishers Inc., (1991).

63. Benzi, P., Operti, L. and Volpe,P., *J. Radioanal. Nucl. Chem. Art.*, **126**, 245, (1988).

64. Ross, H.H., *Anal. Chem.*, **41**, 1260, (1969).

65. Regan, J.G. and Tyler, J.F.C., *Analyst*, **101**, 32, (1976).

66. Haddad, P.R. and Jackson, P.E., *J. Chromatogr.. Lib.*, **46**, 105, (1990).

67. Walton, H.F. and Rocklin, R.D., *Ion-Exchange in Analytical Chemistry*, CRC Press, Boca Raton, Fl, (1990).

68. Weiss, J., *Handbook of Ion Chromatography*, Dionex Corporation, Sunnyvale, CA,(1986).

69. Small, H., Stevens, T.S. and Baumann, W.C., *Anal. Chem.*, **47**, 1801, (1975).

70. Schmuckler,G., *Talanta*,**12**, 281, (1965).

71. El Sweify, F.H.,Shabana, R., Abdel-Rahman, N. and Aly, H.F., *Radiochim. Acta*, **38**, 211, (1985).

72. Denbleyker, K.T., Arbogast,, J.K. and Sweet, T.R., *Chromatographia*, **8**, 449, (1983).

73. Raja, R., *Am. Lab.*, **14**, 35, (1982).

74. Dionex Technical Note 25, (1990).

75. Kingston, H.L., Barnes, I.L., Brady, T.J. and Rains,T.C., Anal. Chem., **50**, 2064, (1978).

76. Riley, J.P. and Taylor, D., *Anal. Chim. Acta*, **40**, 479, (1968).

77. Dionex Technical Note 23, (1987).

78. Heberling, S.S., Riviello, J.M., Shifen, M. and Ip, A.W., *Res. and Dev.*, Sept., 74.(1987).

79. Bridle, D.A., Brown, G.R. and Hamacher, P., *Chemie im Kraftwerk*, , 40. (1989).

80. Cassidy, R.M. and Elchuck, S., *J. Chromatogr. Sci.*, **18**, 217, (1980).

81. Kragten, J., *Atlas of Metal-Ligand Equilibria in Aqueous Solution*, Ellis Horwood Ltd., Chichester, (1978).

82. Robb, P., *Some Aspects of the Assay of Technetium in Environmental Waters*, Ph.D Thesis, Loughborough University, UK, (1983).

83. Katz, J.J. and Seaborg, G.T., *The Chemistry of the Actinide Elements*, Methuen and Co. Ltd., London, (1957).

84. Baes, C.F. and Mesmer, R.E., *The Hydrolysis of Cations*, John Wiley and Sons, New York, (1976).

85. Freeman, A.J. and Keller, C., (Eds.), *Handbook on thePhysics and Chemistry of the Actinides*, Vol. 3, North-Holland, Amsterdam, (1985).

86. Martell, A.E. and Smith, R.M., *Critical Stability Constants, Volume 3: Other Organic Ligands*, Plenum Press, New York, (1977).

87. Martell, A.E. and Smith, R.M., *Critical Stability Constants, Volume 6: Second Supplement*, Plenum Press, New York, (1989).

88. Pederson, C.J., *J. Am. Chem. Soc.*, **89**, 2495, (1967).

89. M^{c}Dowell, W.J., Moyer, B.A., Case, G.N. and Case, F.I., *Solv. Ext. Ion-Exch.*, **4**, 217, (1986).

90. Horwitz, E.P., Dietz, M.L. and Fisher, D.E., *Solv. Ext. Ion-Exch.*, **8**,199, (1990).

91. EIChroM, *Extaction Chromatographic Material for Rapid, Single Separation of Strontium*, EIChroM Technical Note, (1991).

92. Horwitz, E.P., *New Chromatographic Materials for Determination of Actinides, Strontium and Technetium in Environmental, Bioassay and Nuclear Waste Samples*, Argonne, Illinois, (1992).

93. Smith, J.V.(Ed.), *X-Ray Powder Data File, 9-77*, American Society for Tesing Materials Special Technical Publication 48H, Philadelphia, (1959).

94. Allison, J.D., Brown, D.S. and Novo-Gradec, K.J., *MINTEQA2/PRODEFA2, A Geochemical Assesment Model for Environmental Systems, Version 3, Users Manual*, (1991).

95. Kotrly, S. and Sucha, L., *Handbook of Chemical Equilibria in Analytical Chemistry*, Ellis Horwood, Chichester, (1985).

96. Currie, L.A., *Anal. Chem.*, **40**, 586, (1968).

97. Lochamy, J.C., *The Minimum Detectable Activity Concept, NBS Special Publication 4566*, 169, National Bureau of Standards, Gaithersberg, Maryling, (1976).

98. Jerome, S.M., Woods, M.J., Lucas, S.E.M. and Hooley, A.C., *Environmental Radioactivity Intercomparison 1992*, National Physical Laboratory, (1993).

99. International Atomic Energy Agency, *Reference Sheet A-14, Milk Powder for Radionuclides*, IAEA, Vienna, (1988).

100. International Atomic Energy Agency, *Reference Sheet IAEA-152, Milk Powder for Radionuclides*, IAEA, Vienna, (1988).

APPENDIX

Statistical Methods

Where several replicate values were presented as results, an estimation of the true value was calculated using the arithmetic mean, $\bar{x}$. If the replicate values are denoted by $x_1, x_2, \ldots, x_i$, then the arithmetic mean is given by

$$\bar{x} = \frac{1}{N}\sum_{i=1}^{N} x_i \qquad \text{(A-1)}$$

where N is the number of replicate values obtained experimentally.

The error associated with x is the standard deviation, σ_x, which is given by

$$\sigma_x = \left[\frac{1}{N-1}\sum_{i=1}^{N} (x_i - \bar{x})^2 \right]^{1/2} \qquad \text{(A-2)}$$

The estimate of the true value was quoted as

$$\bar{x} \pm k\sigma_x \qquad \text{(A-3)}$$

where k is a two-sided confidence factor, which determines the magnitude of the uncertainty associated with the estimated mean.

For the results quoted in this thesis, k was set to 1.0 in the method development, which implies 68.27 % confidence limits and for the method validation, k was set to 1.96, which implies 95 % confidence limits.

Many of the results were derived from a single radioactive count, x. The standard deviation associated with a single count, σ_x, is given by

$$\sigma_x = x^{1/2} \tag{A-3}$$

Thus, the result from a single count is quoted as

$$\bar{x} = x \pm kx^{1/2} \tag{A-4}$$

In many cases, the results involved combining values, each with an associated uncertainty. The combined uncertainty for two values A and B, each with their own associated uncertainties ± a and ± b respectively is given by the following equations

$$(A \pm a) + (B \pm b) = (A + B) \pm (a^2 + b^2)^{1/2} \tag{A-5}$$

$$(A \pm a) - (B \pm b) = (A - B) \pm (a^2 + b^2)^{1/2} \tag{A-6}$$

$$(A \pm a) \times (B \pm b) = (A \times B) \pm (a^2B^2 + b^2A^2)^{1/2} \tag{A-7}$$

$$\frac{(A \pm a)}{(B \pm b)} = \frac{A}{B} \pm \left(\frac{a^2B^2 + b^2A^2}{B^4} \right)^{1/2} \tag{A-8}$$

Determination of Strontium-90 in Water and Urine Samples Using Ion Chromatography

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A semi-automated method was developed for the determination of ^{90}Sr in water and urine samples using ion chromatography. Yttrium-90 in secular equilibrium with ^{90}Sr was initially extracted from the sample solution buffered to pH 5 using a high-capacity iminodiacetate chelating resin. At this pH, transition metals, lanthanides and actinides were extracted by the resin. The extracted metals were then transferred on to a separator column where they were separated and eluted as weak acid anionic complexes. The transition metals were eluted first by using a pyridine-2,6-dicarboxylate eluent, then the lanthanides, actinides and ^{90}Y were eluted from the column by using an oxalate–diglycolate eluent. The fraction containing ^{90}Y was then collected and β-counted. For water samples, a minimum of sample preparation was required prior to chromatography, whereas an oxalate coprecipitation was included as a preconcentration step for urine samples. The derived recoveries for ^{90}Sr for surface water, rain water and urine samples were 91.7 ± 1.8, 91.9 ± 1.6 and 90.0 ± 2.7%, respectively, and the minimum detectable activity using gas flow proportional counting was 8 mBq.

Keywords: Strontium-90; yttrium-90; ion chromatography; water; urine

Introduction

The biologically hazardous radionuclide ^{90}Sr was released into the environment as a result of the nuclear weapons testing in the 1950s and 1960s and more recently as a result of the accident at Chernobyl in 1986. Strontium-90 is a pure β-emitter and its decay scheme is as follows:

$$^{90}Sr \xrightarrow[\text{half-life} = 28.8\ \text{years}]{\beta_{max}\ 540\ \text{keV}} {}^{90}Y \xrightarrow[\text{half-life} = 64.1\ \text{h}]{\beta_{max}\ 2280\ \text{keV}} {}^{90}Zr\ (\text{stable})$$

As the decay of ^{90}Sr and ^{90}Y is not accompanied by γ-emission, it is not possible to measure ^{90}Sr in the sample by a non-destructive method. Complex radiochemical procedures are therefore required to separate either ^{90}Sr or ^{90}Y from other interfering radionuclides and large amounts of inactive materials that may be present prior to β-counting.

The classical method for the determination of ^{90}Sr involves the precipitation of strontium nitrate from fuming nitric acid solution followed by subsequent ingrowth and separation of the ^{90}Y daughter.[1,2] The disadvantages of the method are that the analysis requires numerous steps and hazards associated with the use of fuming nitric acid. Alternative methods of analysis involve the use of liquid–liquid extraction,[3,4] ion-exchange[5,6] or a combination of both[7] to produce a purified fraction suitable for β-counting. Recently, the use of crown-ether impregnated resins has been reported.[8,9] An automated ion-chromatographic method for the determination of ^{90}Sr has been described previously[10] in which the ^{90}Sr is isolated and β-counted. However, with this approach, complications can arise in counting owing to the presence of ^{89}Sr and the ingrowth of ^{90}Y.

Experimental

The method described here is a semi-automated method utilizing ion chromatography to isolate the ^{90}Y daughter in a form suitable for subsequent measurement by β-counting. The method requires ^{90}Sr and ^{90}Y to be in secular equilibrium prior to analysis, but the isolation of ^{90}Y rather than ^{90}Sr simplifies the subsequent β-counting. The separation of ^{90}Y is achieved by using a three-column system which is commercially available from Dionex. Yttrium-90 is initially extracted from the sample solution on to a Dionex Metpac CC-1 column containing a high-capacity iminodiacetate chelating resin. It has been shown that this type of resin under certain pH conditions selectively concentrates transition metals and rare earths whilst having a low affinity for alkali and alkaline earth metals, which can easily be removed from the resin by elution with ammonium acetate solution.[11] The retained metals can then be eluted from the resin in dilute nitric acid for further separation. The separation of the transition metals and rare earths is achieved by anion-exchange of weak acid anionic complexes of the metals using a Dionex Ionpac CS-5 column.[12] Pyridine-2,6-dicarboxylate is used to elute transition metals and then an oxalate–diglycolate eluent is used to elute rare earths including the ^{90}Y. In the ion-chromatography system used, a third column is required to permit the adjustment of pH from the strongly acidic environment of the chelating resin to a level more suitable for the weak acid separator eluents. This column, the Dionex TMC-1 column, is a sulfonated cation-exchange resin.

Instrumentation

The following components were used in the Dionex ion-chromatography system: Metpac CC-1 concentrator column, TMC-1 column, Ionpac CS-5 separator column and Ionpac GC-5 guard column; two Dionex series 4000i gradient pumps (one of the pumps was used to deliver eluents to the CC-1 and TMC-1 columns and the other was used to deliver eluents to the CS-5 column); DQP sample pump; eluent de-gas module, to de-gas the eluents and to pressurize the eluent resrvoirs with helium at 7 psi; two Dionex inert high-pressure valves operated with air at 80 psi, to control eluent switching between the columns; variable-wavelength detector module, to detect stable metals eluted from the CS-5 column following post-column derivatization; reagent delivery module, for delivering post-column reagent; membrane reactor coil, for mixing post-column reagent with the CS-5 column eluate. Fig. 1

shows a schematic diagram of the columns and eluents used in the investigations.

Other instrumentation used included a Pharmacia LKB Redifrac fraction collector, an LKB Wallac 1215 Rackbeta liquid scintillation counter, a Philips PW4800 automatic gamma counter and a Tennelec LB400 gas flow proportional counter.

Reagents, Eluents and Samples

All reagents were of analytical-reagent grade and all solutions and eluents were made up in HPLC-grade water (Rathburn). All eluents were filtered through a 0.45 μm filter prior to use.

The following reagents were used: nitric acid (d = 1.42); ammonia solution (d = 0.88); yttrium carrier (40 ng ml^{-1} of yttrium in dilute nitric acid); strontium carrier (20 mg ml^{-1} of strontium in dilute nitric acid); Sulkowitch reagent (33 g l^{-1} of oxalic acid dihydrate, 33 g l^{-1} of ammonium oxalate monohydrate and 66 ml l^{-1} of glacial acetic acid); and Ecoscint A (National Diagnostics).

The eluents delivered to the CC-1 and TMC-1 columns were: HPLC-grade water; 2 mol l^{-1} ammonium acetate (pH 5.5); 2 mol l^{-1} nitric acid; and 0.1 mol l^{-1} ammonium nitrate (pH 3.5). The eluents delivered to the CS-5 column were: HPLC-grade water; pyridine-2,6-dicarboxylic acid (PDCA) eluent (6 mmol l^{-1} PDCA, 50 mmol l^{-1} sodium acetate and 50 mmol l^{-1} acetic acid); oxalate eluent (100 mmol l^{-1} oxalic acid and 190 mmol l^{-1} lithium hydroxide); and diglycolate eluent (100 mmol l^{-1} diglycolic acid and 190 mmol l^{-1} lithium hydroxide).

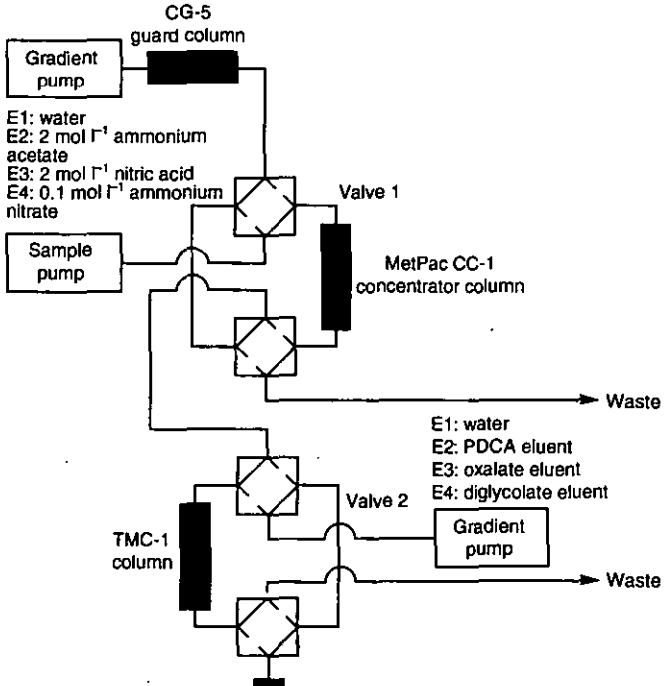

Fig. 1 Schematic diagram of the Dionex column system.

The radioactive spikes and samples used were: $^{90}Sr/^{90}Y$ (2.85 GBq mg^{-1}), ^{45}Ca (0.37 GBq mg^{-1}), ^{241}Am (8.42 kBq g^{-1}), ^{57}Co (260.5 GBq g^{-1}), ^{141}Ce (7.64 MBq mg^{-1}), ^{152}Eu (528.5 GBq g^{-1}), ^{63}Ni (360 GBq g^{-1}) and ^{99}Tc (629 MBq g^{-1}), Amersham International; ^{147}Pm (34.3 TBq g^{-1}), ICN Biomedicals; ^{229}Th (189 Bq g^{-1}), ^{232}U (4.08 kBq g^{-1}) and ^{242}Pu (143.9 MBq g^{-1}), AEA Technology. National Physical Laboratory (NPL) Radioactivity Measurement Intercomparison sample BG 030/93 was also used.

The surface water sample was collected from Moscar, Derbyshire, UK. Rain water was collected by funnel collection in Loughborough over several weeks. The human urine sample was collected over a 2 week period and bulked before spiking with radionuclides.

Method Development

Study of the interaction of a series of radionuclides with the CC-1 column

A series of sample solutions were prepared containing the radionuclides $^{90}Sr/^{90}Y$, ^{45}Ca, ^{141}Ce, ^{57}Co, ^{137}Cs, ^{152}Eu, ^{63}Ni, ^{147}Pm, ^{99}Tc, ^{242}Pu, ^{243}Am, ^{232}U and ^{229}Th. The solutions were prepared in water and buffered to pH 5 with ammonium acetate and made up to a final volume of 25 ml. The sample solutions were loaded on to the CC-1 column at a flow rate of 2 ml min^{-1}. The column was then eluted with 7 ml of 2 mol l^{-1} ammonium acetate, followed by 7 ml of 0.56 mol l^{-1} nitric acid. Aliquots of the sample solution, the sample eluate and the ammonium acetate and nitric acid eluates were collected and their radioactivity was measured by either liquid scintillation counting or γ-counting. Any radionuclides present in the nitric acid eluate would be eluted to the separator column for further separation and are therefore retained by the column system, whereas any radionuclides present in the sample eluate and ammonium acetate eluate would be eluted to waste and are therefore not retained by the column system.

Effect of pH of sample solution on retention of ^{90}Y on the CC-1 column

Sample solutions were prepared by spiking a 2 mol l^{-1} ammonium acetate solutions with ^{90}Sr and ^{90}Y in secular equilibrium. The pH values of the samples were adjusted with either 5 mol l^{-1} nitric acid or 0.88 g ml^{-1} ammonia solution. The volumes of the solutions were made up to a final volume of 25 ml with water and the pH values of the resulting solutions were measured. The sample solutions were loaded on to the CC-1 column at a rate of 2 ml min^{-1}. The column was then eluted with 2 mol l^{-1} ammonium acetate, followed by 0.56 mol l^{-1} nitric acid. The nitric acid eluate was collected and subjected to liquid scintillation counting.

Effect of matrix elements on the interaction of ^{90}Y with the CC-1 column

The effect of large concentrations of a monovalent, divalent and trivalent metal on the interaction of ^{90}Y with the concentrator column was investigated. Sample solutions were prepared by dissolving various amounts of either sodium, calcium of aluminium nitrate in water. The solutions were then spiked with ^{90}Sr and ^{90}Y in secular equilibrium and buffered to pH 5 with 2 mol l^{-1} ammonium acetate to a final volume of 25 ml. The sample solutions were loaded on to the CC-1 column at a rate of 2 ml min^{-1}. The column was then eluted with 2 mol l^{-1} ammonium acetate followed by 0.56

nol l^{-1} nitric acid. The nitric acid eluate was collected and ounted by liquid scintillation counting.

eparation of ^{90}Y from other radionuclides retained by the Dionex system

A series of radionuclides were individually loaded on to the CC-1 column and the elution programme described in Table 1 vas run. The CS-5 column eluate was then collected initially n 5 ml fractions to establish approximately the point at which ne radionuclides were eluted from the CS-5 column. The rocedure was then repeated collecting 0.33 ml fractions to etermine accurately the point at which the radionuclides vere eluted. The fractions were measured by either liquid cintillation counting or γ-counting.

In order to compare yttrium with other lanthanides, stable anthanide and stable yttrium standards were separated on the Dionex system. The CS-5 column was monitored at 520 nm sing an ultraviolet–visible detector, following post-column erivatization with 4-(2-pyridylazo)resorcinol.

Method for the Determination of ^{90}Sr in Water Samples

A 40 ng amount of yttrium carrier was added to 1 l of water vhich was then acidified with 20 ml of nitric acid (d = 1.42) nd boiled to dryness. The residue was ashed at 550 °C in a nuffle furnace overnight to destroy any organic material that nay be present in the sample. The ashed residue was then igested in 25 ml of 1 mol l^{-1} nitric acid. The pH of the olution was adjusted to 5 with an equal volume of 2 mol l^{-1} ammonium acetate (pH 5.5) and, if necessary, dropwise addition of 6 mol l^{-1} ammonia solution. The sample was loaded on to the Dionex chromatography system at a flow rate of 2 ml min^{-1} and the elution programme was run. The beginning of ^{90}Y decay time was taken from the mid-point of the sample loading on to the CC-1 column. The eluate from the CS-5-analytical column was collected in 2 ml fractions and the fraction containing ^{90}Y was β-counted.

Method for the Determination of ^{90}Sr in Urine Samples

For urine samples, buffering the sample solution to pH 5 with ammonium acetate caused precipitation to occur in the sample solution and therefore an alternative sample preparation procedure was used based on the approach developed by Kramer and Davies.[4] This involves the coprecipitation of $^{90}Sr/^{90}Y$ on strontium oxalate directly from the urine sample.

A 20 mg amount of strontium carrier, 40 ng of yttirum carrier and 30 ml of nitric acid were added to 300 ml of urine. The sample was heated to 90 °C with stirring for 1 h and, after cooling, 30 ml of Sulkowitch reagent were added. The pH of the solution was adjusted to between 3 and 4 to allow the formation of an oxalate precipitate. The precipitate was isolated by centrifugation at 3000 rev min^{-1} for 10 min, transferred into a beaker with concentrated nitric acid and evaporated to dryness. The residue was ashed at 550 °C overnight to convert the oxalate into carbonate. The carbonate was dissolved in the minimum volume of 1 mol l^{-1} nitric acid and diluted to 20 ml with de-ionized water. The pH of the resulting solution was adjusted to 5 with an equal volume of 2 mol l^{-1} ammonium acetate and, if necessary, dropwise addition of 6 mol l^{-1} ammonia solution. The resulting solution was loaded on to the Dionex system and the elution programme was run. The beginning of ^{90}Y decay time was taken from the mid-point of the sample loading. The CS-5 eluate was fraction-collected and the fraction containing ^{90}Y was β-counted.

Table 1 Dionex ion chromatography elution programme*

	Time/ min	Water (%)	2 mol l^{-1} ammonium acetate (%)	2 mol l^{-1} nitric acid (%)	0.1 mol l^{-1} ammonium nitrate (%)	Flow rate/ ml min^{-1}
GPM 1—						
Step 1	0.0	0	100	0	0	3.0
	0.1	0	100	0	0	3.0
	2.5	0	100	0	0	3.0
Step 2	2.6	72	0	28	0	3.0
	5.0	72	0	28	0	1.0
Step 3	5.1	0	0	0	100	3.0
	6.6	0	0	0	100	1.0
Step 4	6.7	0	0	100	0	3.0
	7.7	0	0	100	0	3.0
Step 5	7.8	0	100	0	0	3.0
	9.3	0	100	0	0	3.0
Step 6	9.4	100	0	0	0	3.0

	Time/ min	Water (%)	PDCA (%)	Oxalate (%)	Diglycolate (%)	Flow rate/ ml min^{-1}
GPM 2—						
Step 7	6.6	0	100	0	0	1.0
	18.6	0	100	0	0	1.0
Step 8	18.7	100	0	0	0	1.0
	23.6	100	0	0	0	1.0
Step 9	23.7	40	0	60	0	1.0
	27.6	20	0	80	0	1.0
Step 10	27.7	20	0	80	0	1.0
	36.6	51	0	26	23	1.0

* Step 1: elution of Group II metals from CC-1 column to waste; tep 2: elution of retained metals from CC-1 column to TMC-1 olumn; step 3: conversion of TMC-1 column from hydroxonium into ammonium form; steps 4, 5 and 6: regeneration of the CC-1 and TMC-1 columns; step 7: elution of TMC-1 and CS-5 columns with PDCA; step 8: washing of CS-5 column with water; step 9: elution of CS-5 column with oxalate; and step 10: elution of CS-5 column with oxlate–diglycolate.

Results and Discussion

The errors quoted in all the results presented in this paper are ±2 standard deviations.

Method Development

Table 2 shows the recoveries of radionuclides in the CC-1 column eluates. The recoveries for $^{90}Sr/^{90}Y$ show that

Table 2 Retention behaviour of radionuclides on the CC-1 concentrator column

Radionuclide	Count rate loaded in sample eluate and ammonium acetate eluate (%)*	Count rate loaded in nitric acid eluate (%)*	Total count rate loaded recovered (%)*
$^{90}Sr/^{90}Y$	48 ± 2	49 ± 1	98 ± 2
^{45}Ca	79 ± 3	19 ± 2	98 ± 2
^{141}Ce	—	97 ± 3	97 ± 3
^{57}Co	—	97 ± 2	97 ± 2
^{137}Cs	97 ± 2	—	97 ± 2
^{152}Eu	—	99 ± 4	99 ± 4
^{63}Ni	—	96 ± 2	96 ± 2
^{147}Pm	—	98 ± 1	98 ± 1
^{99}Tc	96 ± 3	—	96 ± 3
^{242}Pu	—	21 ± 1	21 ± 1
^{243}Am	6 ± 2	90 ± 3	96 ± 4
^{232}U	45 ± 3	48 ± 1	93 ± 3
^{229}Th	19 ± 2	77 ± 2	96 ± 3

* The values are the mean of three determinations.

approximately 50% of the count rate loaded was present in the nitric acid eluate and 50% was in the combined sample and ammonium acetate eluates. The variations in the count rates for the eluates were monitored for 20 d. The change in count rate in the ammonium acetate eluate was consistent with that for the ingrowth of ^{90}Y, indicating that ^{90}Sr was originally present in the eluate. The change in count rate in the nitric acid eluate was consistent with that of the decay of ^{90}Y, the calculated half-life being 64.8 h. The results showed that the CC-1 column separated ^{90}Sr from ^{90}Y because approximately 100% of the ^{90}Sr was removed from the column to waste, whereas approximatley 100% of the ^{90}Y was retained by the CC-1 column. Yttrium-90 can then be eluted from the column for further separation.

Fig. 2 shows the percentage of ^{90}Y retained by the CC-1 column as a function of sample pH. The optimum pH range for the retention of ^{90}Y is between 4.5 and 5.5. At lower pH values, interaction of ^{90}Y is reduced owing to protonation of the chelating sites on the iminodiacetate resin. Above pH 6, tripositive yttrium in solution begins to hydrolyse, forming reduced charge cationic species which have reduced interaction with the sites on the resin. All samples were therefore buffered to pH 5 with ammonium acetate prior to loading on the CC-1 column.

For the same conditions as those used for ^{90}Y, the trivalent lanthanide and divalent transition metal radionuclides were retained by the CC-1 column in almost quantitative recovery. The radionuclides ^{137}Cs and ^{99}Tc were not retained by the CC-1 column, the latter being due to it being present as the anion, TcO_4^-. Approximately 20% of the ^{45}Ca loaded on to the CC-1 column was retained by the column, which indicated that calcium has a reduced affinity for the column relative to the lanthanides and transition metals. The interaction of the actinides with the CC-1 column varied according to the particular actinide. Approximately 90, 77 and 40% of the loaded ^{241}Am, ^{229}Th and ^{232}U, respectively, was retained by the column. This indicated that the speciation of these elements was variable at the loading pH. In total, only 20% of the ^{242}Pu loaded was recovered in the CC-1 column eluates; the remaining plutonium was recovered by eluting the column with more nitric acid. This indicated that most of the plutonium was more strongly bound to the resin than all the other radionuclides used.

In summary, the results demonstrate that, to different extents, yttrium, lanthanides, transition metals, actinides and calcium are retained by the CC-1 column and further separation using the CS-5 column is required to produce a ^{90}Y source, free from other radionuclides, for counting.

Fig. 3 shows the effect of large amounts of Na^+, Ca^{2+} and Al^{3+} on the interaction of ^{90}Y with the CC-1 column. Up to 1 g of Na^+ had little effect on the interaction of ^{90}Y with the column, whereas no more than approximately 200 mg of Ca^{2+} and 2 mg of Al^{3+} could be present before ^{90}Y retention was reduced. The reduced retention of ^{90}Y in the presence of these metal ions limits the applicability of the Dionex system for analysing complex samples such as milk, soil and vegetation but, because of the amounts of Na^+, Ca^{2+} and Al^{3+} in water and urine samples, the use of Dionex columns should be useful for analysing these matrices.

Fig. 4 shows a chromatogram for the separation of radionuclides retained by the CC-1 column using the CS-5 column. The chromatogram shows that the divalent transition metal radionuclides, ^{45}Ca and ^{232}U, are eluted using PDCA as eluent. The other radionuclides are eluted using the oxalate–diglycolate eluent. Yttrium-90 is eluted from the column after 39 min and is well separated from the other radionuclides used but may co-elute with other lanthanides and actinides. Fig. 5 and 6 show chromatograms for the elution of a stable lanthanide standard including and excluding yttrium, respectively. These show that yttrium would be eluted with similar retention times to dysprosium and holmium. Neither of these lanthanides possesses a major long-lived β-emitting isotope which could interfere with the subsequent β-counting of ^{90}Y. Possible co-elution of ^{90}Y with actinides heavier than americium should also not be an interference problem as the half-lives of β-emitting actinides are usually very short and thin window proportional counting would exclude any contribution to the count due to α-emission. The Dionex system therefore provides a ^{90}Y fraction free from other potential radionuclide interferences which is suitable for β-counting.

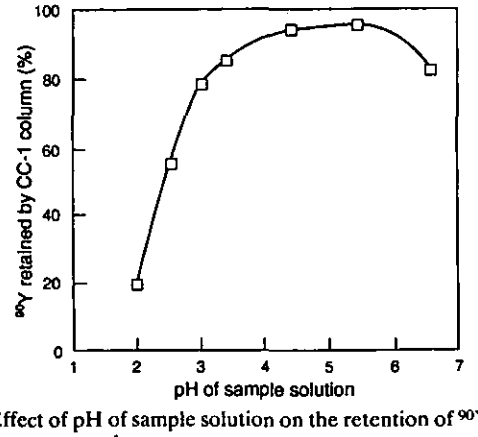

Fig. 2 Effect of pH of sample solution on the retention of ^{90}Y on the CC-1 concentrator column.

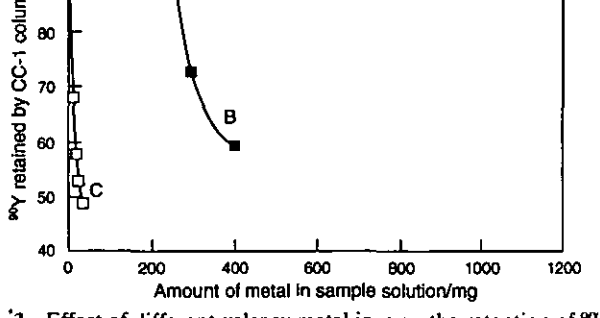

Fig. 3 Effect of different valency metal ions on the retention of ^{90}Y on the CC-1 column. A, Na^I; B, Ca^{II}; and C, Al^{III}.

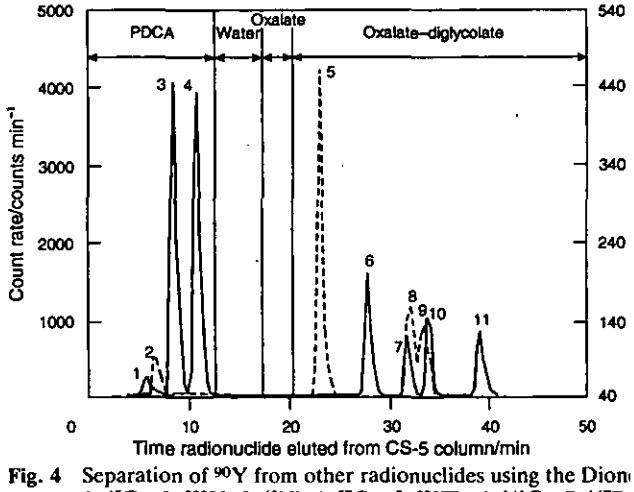

Fig. 4 Separation of ^{90}Y from other radionuclides using the Dionex system. 1, ^{45}Ca; 2, ^{232}U; 3, ^{63}Ni; 4, ^{57}Co; 5, ^{229}Th; 6, ^{141}Ce; 7, ^{147}Pm; 8, ^{241}Am; 9, ^{237}Pu; 10, ^{152}Eu; and 11, ^{90}Y.

Determination of ^{90}Sr in Water Samples

Table 3 shows the recoveries of ^{90}Sr in spiked natural water samples at various activity levels. The mean recoveries were 91.7 ± 1.8% (n = 10) and 91.9 ± 1.6% (n = 10) for surface water and rain water samples, respectively. The recovery of ^{90}Y from the ashing and dissolution steps was 95.9 ± 2.3% (n = 3). For the spiked samples the ^{90}Y was measured by Cerenkov counting in the tritium channel of the LKB 1215 Quid scintillation counter.

Table 4 shows the analysis of an NPL environmental standard. The activity of ^{90}Sr in the standard determined by the Dionex method was in good agreement with the value quoted by NPL. A spiked $^{90}Sr/^{90}Y$ water sample was used as a recovery monitor for the analysis and the ^{90}Y fraction was measured using a Tennelec LB400 gas flow proportional counter, which was the preferred method of counting for environmental samples. The minimum detectable activity using the proportional counter (with a background count rate of 1 count min^{-1} and 49% counting efficiency for ^{90}Y) for 95% confidence and for a 100 min counting time was 8 mBq. The run time from loading the sample on to the Dionex system and fraction-collecting the ^{90}Y fraction was approximately 90 min, which would permit the analysis of six or seven samples per day. Furthermore, the process is semi-automated, which means that little attention time is required by the analyst. The sample preparation steps prior to the Dionex system and the subsequent counting increase the analysis time but again do not require significant attention time by the analyst.

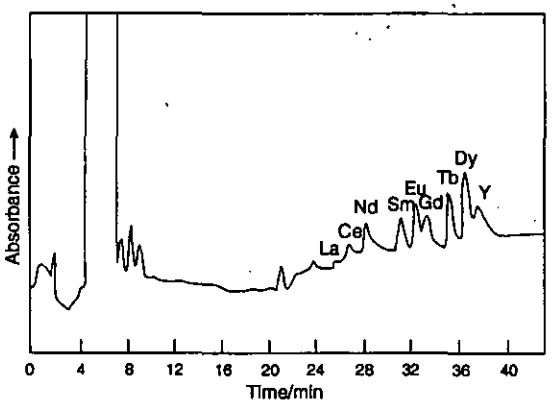

Fig. 5 Chromatogram of stable lanthanide standard including yttrium.

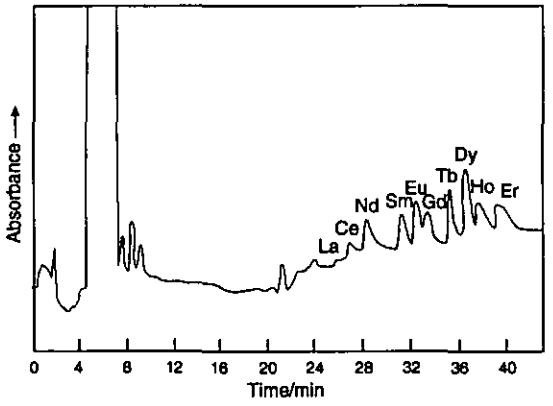

Fig. 6 Chromatogram of stable lanthanide standard excluding yttrium.

Determination of ^{90}Sr in Urine Samples

Table 5 shows that the mean derived recovery of ^{90}Sr in the urine samples at various activity levels was 90.0 ± 2.7% (n = 6). The recovery of a $^{90}Sr/^{90}Y$ mixture in secular equilibrium on the strontium oxalate precipitate was 93.4 ± 0.8% (n = 3). No significant change in count rate present on the precipitate with time was observed, indicating that the ^{90}Sr and ^{90}Y were effectively coprecipitated in equilibrium. The inclusion of the precipitation step prior to the Dionex system slightly increases the attention time and skill required by the analyst relative to that for the method used for the water samples.

Conclusion

The Dionex ion-chromatography system provides a semi-automated method for the determination of ^{90}Sr in water and urine samples. The recoveries of ^{90}Y are high for both water and urine samples and the ^{90}Y is separated from potential interfering radionuclides. A minimum of sample preparation is required for water samples and the inclusion of a single precipitation step permits the analysis of urine samples. The Dionex part of the separation takes a relatively short time but, more importantly, requires little attention time by the analyst, thus providing a significant improvement over many of the methods that are currently available.

The Dionex system is not suitable for analysing complex sample matrices that contain large amounts of calcium and trivalent metals; however, approaches to overcome the problems of these matrix types are being investigated.

In the work reported here, the Dionex system was applied to specific sample sizes. The system should be applicable to

Table 3 Determination of ^{90}Sr in natural waters

Surface water				Rain water			
^{90}Y activity added/Bq	^{90}Y count rate Added/counts min^{-1}	^{90}Y count rate recovered counts min^{-1}	Recovery (%)	^{90}Y activity added/Bq	^{90}Y count rate added/counts min^{-1}	^{90}Y count rate recovered counts min^{-1}	Recovery (%)
5.00	129.6	119.6	92.3	5.00	129.6	120.6	93.1
5.00	129.6	118.1	91.2	5.00	129.6	119.7	92.4
5.00	129.6	116.9	90.2	5.00	129.6	118.2	91.2
5.00	129.6	118.5	91.4	2.50	64.8	59.0	91.1
2.50	64.8	59.8	92.3	2.50	64.8	59.7	92.1
2.50	64.8	60.5	93.3	2.50	64.8	59.8	92.3
2.50	64.8	59.6	92.0	1.25	32.4	29.9	92.3
1.25	32.4	29.6	91.2	1.25	32.4	29.8	92.1
1.25	32.4	29.5	91.1	1.25	32.4	29.3	90.4
1.25	32.4	29.9	92.3	1.25	32.4	29.9	92.3
		Mean = 91.7 ± 1.8				Mean = 91.9 ± 1.6	

larger sample sizes although the recoveries may be affected by the increased amounts of matrix elements present. Hence, if larger samples are to be processed, the recoveries for these volumes should be established prior to analysis to determine whether they are different to those established for the samples analysed in the work reported here.

The system has potential for the determination of several radionuclides in a single separation; for example, it should be possible to analyse lanthanide fission products, although adjustment of conditions would be required to determine several actinides in a single step successfully, owing to the variation in interaction of the actinides with the CC-1 column.

Table 4 Analysis of NPL Environmental Radioactivity Intercomparison Standard (1992)

Sample	Amount of sampled used/g	Certified ^{90}Sr activity/Bq kg^{-1}	Observed ^{90}Sr activity/Bq kg^{-1}
1	25	49.0 ± 0.2	46.4 ± 1.5
2	25	49.0 ± 0.2	47.5 ± 1.5

Table 5 Determination of ^{90}Sr in urine samples

^{90}Y activity added/Bq	^{90}Y count rate added/counts min^{-1}	^{90}Y count rate recovered/ counts min^{-1}	Recovery (%)
6.84	177.3	159.7	90.1
3.42	88.6	78.6	88.7
1.71	44.3	40.2	90.7
0.86	22.3	20.3	91.0
0.86	22.3	19.6	87.9
0.86	22.3	20.3	91.3
		Mean =	90.0 ± 2.7

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References

1 Krieger, H. L., Martin, E. R., and Friskhorn, G. W., *Health Phys.*, 1976, **30**, 465.
2 Wilken, R. D., and Diehl, R., *Radiochim. Acta*, 1987, **41**, 157.
3 Baratta, E. J., and Revey, T. C., *J. Agric. Food Chem.*, 1969, **7**, 1337.
4 Kramer, G. H., and Davies, J. M., *Anal. Chem.*, 1982, **54**, 1428.
5 Bryant, E. A., Sattizhan, J. E., and Warren, B., *Anal. Chem.*, 1959, **31**, 334.
6 Amano, H., and Yanase, N., *Talanta*, 1990, **37**, 585.
7 Borcherding, J., and Nies, H., *J. Radioanal. Nucl. Chem.*, 1986, **98**, 127.
8 Horwitz, E. P., Dietz, M. L., and Fisher, D. E., *Anal. Chem.*, 1991, **63**, 522.
9 Dietz, M. L., Horowitz, E. P., Nelson, D. M., and Wahlgren, M., *Health Phys.*, 1991, **61**, 871.
10 Lamb, J. D., Nordmeyer, F. R., Drake, P. A., Elder, M. P., Miles, R. W., and Lash, R. P., *J. Radioanal. Nucl. Chem.*, 1989, **134**, 317.
11 Kingston, H. M., Barnes, I. L., Brady, T. J., Rains, T. J., and Champ, M. A., *Anal. Chem.*, 1978, **50**, 2064.
12 Dionex Technical Note TN23, Dionex, Sunnyvale, CA, 1987.

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Determination of Strontium-90 in Milk Samples Using a Controlled Precipitation Clean-up Step Prior to Ion-Chromatography

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Abstract

Strontium-90 may be determined by the beta-counting its yttrium-90 daughter following separation by ion-chromatography, using a three column system comprising a chelating concentrator column, a cation-exchange column and an anion-exchange separator column. The column system has previously been applied to the determination of strontium-90 in water and urine samples. The applicability of the system to the analysis of milk is hampered by the large concentrations of calcium present, which significantly reduces the extraction of yttrium-90 by the concentrator column. A maximum of approximately 200 mg of calcium can be present for the successful extraction of yttrium-90, which greatly limits the quantity of milk that can be analysed. The quantity of milk analysed can be increased by the inclusion of a controlled precipitation step prior to the ion-chromatographic separation. The precipitation is carried out on acid digested milk samples by the addition of ammonia solution until the addition of one drop causes a reduction in pH resulting in the precipitation of calcium hydrogenphosphate . Under these conditions, approximately 20 % of the calcium present in the original milk sample is precipitated, yttrium-90 is precipitated whereas strontium-90 is not precipitated. Dissolution of the precipitate, followed by separation of yttrium-90 using the ion-chromatography system facilitates the analysis of a litre of milk with recoveries of greater than 80 %.

Introduction

Strontium-90 is one of the most biologically hazardous radionuclides produced in nuclear fission processes. If introduced into the environment, it becomes incorporated into the calcium pool and the principal pathway followed to humans is: soil to plant to cow's milk to humans. On entering the body, strontium-90 becomes distributed throughout the volume of the mineral bone, where it emits its moderately energetic beta-particles with a half life of 28.8 years. It is therefore essential that the levels of strontium-90 in environmental materials and foodstuffs, particularly dairy products, are closely monitored.

The determination of strontium-90 in environmental materials may be achieved by the separation and beta-counting of strontium-90 or its yttrium-90 daughter. The separation procedures used can be divided into three general categories: selective precipitation methods [1,2], liquid-liquid extraction methods [3,4] and ion-exchange methods [5,6]. In some cases, combinations of these methods are required to produce a source suitable for beta-counting[7]. Disadvantages associated with these methods are that they tend to be time consuming and labour intensive.

Recently, a semi-automated method involving ion-chromatography was reported for the determination of strontium-90 in liquid matrices, which largely overcame the problems associated with the above procedures [8]. The ion-chromatography system used comprised a chelating resin to concentrate yttrium-90 from the sample solution, an anion-exchange resin for the separation of yttrium-90 from other interfering radionuclides retained by the column system using an oxalate-diglycolate eluent and a cation-exchange resin, which acts as an interface between the concentrator and separator columns to permit the change of their respective eluent systems. A major problem associated with this ion-chromatographic method was the inability of the chelating resin to concentrate yttrium-90 from solutions containing large concentrations of calcium. More than 200 mg of calcium per sample prevented the successful extraction of yttrium-90, which greatly limited the applicability of the system for the analysis of milk.

Here, the method has been further developed to permit the determination of strontium-90 in milk by the inclusion of a controlled calcium hydrogenphosphate precipitation step prior to the ion-chromatography system.

Experimental

Instrumentation

The following components were used in the ion-chromatography system: Dionex Metpac CC-1 concentrator column; Dionex TMC-1 column; Dionex Ionpac CS5 separator column and Dionex Ionpac CG5 guard column; Two Dionex series 4000i gradient pumps. One of the pumps was used to deliver eluents to the CC-1 and TMC-1 columns and the other was used to deliver eluents to the CS5 column; DQP sample pump; eluent degas module, to degas the eluents and to pressurize the eluent reservoirs with helium at 7 psi; two Dionex inert high pressure valves operated with air at 80 psi, to control eluent switching between the columns. Figure 1 shows a schematic diagram of the column system used in the investigation.

Other instrumentation used included a Pharmacia LKB Redifrac fraction collector, an LKB Wallac 1215 Rackbeta liquid scintillation counter and a Tennelec LB400 gas flow proportional counter.

Reagents, Eluents and Samples

All reagents were of analytical-reagent grade and all solutions and eluents were made up in HPLC grade water (Rathburn). All eluents were filtered through a 0.45 μm filter prior to use. The following reagents were used: nitric acid (s.g. 1.42, 1 M and 2 M); ammonia solution (s.g. 0.88 and 6 M); yttrium carrier (40 ng ml^{-1} of yttrium in dilute nitric acid).

The eluents delivered to the CC-1 and TMC-1 columns were: HPLC grade water; 2 M ammonium acetate (pH 5.5); 2 M nitric acid; 0.1 M ammonium nitrate (pH 3.5). The

eluents delivered to the CS5 column were: HPLC grade water; pyridine-2,6-dicarboxylic acid (PDCA) eluent (pH 4.8), which comprised 6 mM PDCA, 50 mM sodium acetate and 50 mM acetic acid; oxalate eluent (pH 4.8), which comprised 100 mM oxalic acid and 190 mM lithium hydroxide; diglycolate eluent (pH 4.8), which comprised 190 mM lithium hydroxide. The elution program used for the separation of yttrium-90 is shown in table 1. Before use, the CS5 column was equilibrated for 30 minutes with the PDCA eluent and between sample runs was equilibrated for a minimum of 10 minutes.

The samples used were milk powders from various sources in the UK which were spiked with known activities of strontium-90 and yttrium-90 in secular equilibrium. International Atomic Energy Agency (IAEA) reference materials IAEA-152 and A-14 were also used.

Procedure for the controlled precipitation process

The conditions used for the controlled precipitation process described in the following method permit the partial precipitation of calcium from acid digested milk samples. The pH of the acid digested milk sample is initially adjusted to pH 3 with ammonia solution (s.g. 0.88). The pH of the solution is then adjusted by the dropwise addition of 6 M ammonia solution until the addition of 1 drop causes the pH to decrease. This marks the onset of precipitation and at this point, the addition of ammonia solution is ceased. After approximately thirty minutes, the pH stabilizes at a lower value, marking the end of precipitation.

Method for the determination of strontium-90 in milk samples

A milk powder sample equivalent to 500 ml of raw milk was ashed in a muffle furnace overnight at 550°C. A 10 ml aliquot of nitric acid (s.g. 1.42) was added and the mixture evaporated to dryness. The residue was then re-ashed until it became white. A 40 ng amount of yttrium carrier and 2 ml of orthophosphoric acid were added to the residue

which was then dissolved in 100 ml of 2 M nitric acid. (For 1 litre equivalent milk samples, the volume of orthophosphoric acid and 2 M nitric acid used were doubled). The resulting solution was then boiled at constant volume for 30 minutes and then cooled. The pH of the solution was adjusted to 3 by the addition of ammonia solution (s.g. 0.88) and then adjusted by the dropwise addition of 6 M ammonia solution until the addition of one drop was followed by a decrease in pH accompanied by precipitation. At this point the addition of ammonia solution was ceased. After restabilization of the pH, the precipitate formed was then collected on a 0.45 μm filter. The time for the beginning of the yttrium-90 decay was taken at this point. The precipitate was then dissolved in a minimum volume of 1 M nitric acid and diluted to 20 ml with deionized water. The pH of the solution was then adjusted to 5 with an equal volume of 2 M ammonium acetate (pH 5.5) and if necessary, dropwise addition of 6 M ammonia solution. The sample was then loaded onto the ion-chromatography system at a flow-rate of 2 ml min^{-1} and the elution program outlined in table 1 was run. The CS5 column eluate was collected in polythene vials in 2 ml fractions. The yttrium-90 fraction which was eluted from the CS5 column with a retention time of 39 minutes, was then beta-counted.

Results and Discussion

Table 2 shows the variation in the mass of precipitate formed for the controlled precipitation process performed on 500 ml milk equivalent samples, to which 2 ml of orthophosphoric acid were added. Even though the pH at which precipitation started varied from sample to sample, an approximately constant mass of precipitate (300-350 mg) was formed in each case. Also, the mass of precipitate formed did not vary significantly with increasing standing time in solution. The precipitation process was therefore consistent for a constant sample size and the precipitation was essentially complete after the pH had restabilized.

The precipitate formed by the controlled precipitation process was analysed by X-ray powder diffractometry using monochromatic X-rays of wavelength 0.15405 nm

produced using a copper filter. Table 3 shows a comparison between the d-spacings derived from the ten most intense peaks produced by the precipitate and the literature values for brushite syn, $CaHPO_4.2H_2O$. Assuming that this structure was correct and the fact that 300-350 mg of precipitate were typically formed, meant that a maximum of 100 mg of calcium were present in the precipitate, approximately 20 % of that originally present in the original 500 ml milk sample. The mass of calcium present on the precipitate was also approximately half that which could be loaded onto the ion-chromatography system for the extraction of yttrium-90 in greater than 90 % recovery.

Figure 2 shows a plot of the variation in the natural log of the count rate present on the precipitate with time which was precipitated from for a 500 ml equivalent milk sample spiked with strontium-90 and yttrium-90 in secular equilibrium. The plot is linear and the half-life derived from the gradient was 64.5 hours, compared to that for yttrium-90, which is 64.1 hours. Therefore, the precipitation step not only reduced the calcium to suitable levels for the ion-chromatography system, but also separated strontium-90 from yttrium-90, since only the latter was present on the precipitate. Therefore in a method using the precipitation step the yttrium-90 decay time must begin when the precipitate is isolated from the sample solution.

Validation of the method for the determination of strontium-90 in milk

The uncertainties in the results quoted in this section are for 95 % confidence limits.Tables 4 and 5 show the recoveries of yttrium-90 from spiked 500 ml and 1 litre milk samples. For the 500 ml samples, the mean recovery was 84.4 ± 2.6 % ($n = 10$) and for the 1 litre samples was 81.3 ± 2.5 % ($n = 6$). The recoveries were high and reproducible, although the recoveries for the 1 litre samples were consistently lower than for the 500 ml samples. The variation in recovery observed for the two sample sizes could be attributed to larger quantities of transition metals, especially aluminium and iron, being carried down on the precipitate for the larger sample volume. The

presence of these have a significant effect on the subsequent ion-chromatographic separation of yttrium-90 [8]. Table 6 shows the results for the determination of strontium-90 in the IAEA reference materials. The specific activities of strontium-90 determined by the method were in good agreement with the values quoted by the IAEA and demonstrate the reliability of the method. The certified values quoted in the table are calculated values based on the specific activities of A-14 and IAEA-152 being 1.5 Bq kg^{-1} and 7.7 Bq kg^{-1} on 31st August 1987. Spiked milk powders were used as recovery monitors for the reference materials and the final yttrium-90 fraction was measured using the Tennelec LB400 gas flow proportional counter (background count rate of 1 count min^{-1} and 49 % counting efficiency for yttrium-90). The minimum detectable activity achievable using the method in conjunction with the proportional counter for a 100 minute counting time and 95 % confidence was 22 mBq l^{-1} for the analysis of a 1 litre sample.

Conclusion

The inclusion of the controlled calcium hydrogenphosphate precipitation step has permitted the analysis of strontium-90 in milk samples by ion-chromatography. The chemical recoveries of the method are high and reproducible and the ion-chromatographic separation gives the method a degree of automation, which provides reduced labour intensity relative to other currently available methods. The inclusion of the controlled precipitation step does not extend the analysis time to any large degree and is relatively simple. The analysis of reference materials has demonstrated the reliability of the method.

Acknowledgements

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References

1. R.D. Wilken and R. Diehl, Strontium-90 in Environmental Samples From Northern Germany Before and After the Chernobyl Accident. Radiochim. Acta, 134 (1987) 157-162.
2. International Atomic Energy Agency, Measurement of Radionuclides in Food and Environment, Technical Report. Series 298, IAEA, Vienna, 1989, pp 70-89.
3. E.J. Baratta and T.C. Reavey, Rapid Determination of Strontium-90 in Tissue, Food, Biota and Other Environmental Media by Tributyl Phosphate. J. Agric. Food Chem., 17 (1969) 1337-1339.
4. J. Borcherding and H. Nies, An Improved Method for the Determination of ^{90}Sr in Large Samples of Seawater. J. Radioanal. Nucl. Chem., 98 (1986) 127-131.
5. E.A. Bryant, J.E. Sattizahn and B. Warren, Strontium-90 by an Ion-Exchange Method. Anal. Chem., 31 (1959) 334-337.
6. H. Amano and N. Yanase, Measurement of ^{90}Sr in Environmental Samples by Cation-Exchange and Liquid Scintillation Counting. Talanta, 37 (1990) 585-590.
7. K. Bunzl and W. Kracke, A Simple Radiochemical Determination of ^{90}Sr in Environmental Samples. J. Radioanal. Nucl. Chem., 148 (1991) 115-119.
8. J. Cobb, P. Warwick, R.C. Carpenter and R.T. Morrison, Determination of Strontium-90 in Water and Urine Using Ion Chromatography. Analyst, 119 (1994) 1759-1764.

GPM 1

	Time /min	% water	% 2 M ammonium acetate	% 2 M nitric acid	% 0.1 M ammonium nitrate	Flow rate / ml min $^{-1}$
Step 1	0.0	0	100	0	0	3.0
	0.1	0	100	0	0	3.0
	2.5	0	100	0	0	3.0
Step 2	2.6	72	0	28	0	3.0
	5.0	72	0	28	0	1.0
Step 3	5.1	0	0	0	100	3.0
	6.6	0	0	0	100	1.0
Step 4	6.7	0	0	100	0	3.0
	7.7	0	0	100	0	3.0
Step 5	7.8	0	100	0	0	3.0
	9.3	0	100	0	0	3.0
Step 6	9.4	100	0	0	0	0.0

GPM 2

	Time /mins	% water	% PDCA	% oxalate	% diglycolate	Flow rate /ml min $^{-1}$
Step 7	6.6	0	100	0	0	1.0
	18.6	0	100	0	0	1.0
Step 8	18.7	100	0	0	0	1.0
	23.6	100	0	0	0	1.0
Step 9	23.7	40	0	60	0	1.0
	27.6	20	0	80	0	1.0
Step 10	27.7	20	0	80	0	1.0
	36.6	51	0	34	15	1.0

Step 1:	Elution of alkaline-earth metals from CC-1 column to waste
Step 2:	Elution of extracted metals from CC-1 column to TMC-1 column
Step 3:	Conversion of TMC-1 column from hydroxonium to ammonium form
Steps 4, 5 and 6:	Regeneration of the CC-1 and TMC-1 columns
Step 7:	Elution of TMC-1 and CS5 columns with PDCA eluant
Step 8:	Elution of CS5 column with water
Step 9:	Elution of CS5 column with oxalate eluant
Step 10:	Elution of CS5 column with oxalate - diglycolate eluant

Table 1 The ion-chromatography elution program

Time precipitate left in solution /h	Mass of precipitate formed /g	pH at which pH decrease started	pH at which pH decrease stabilized
0.5	0.3218	3.225	2.901
0.5	0.3196	3.298	2.932
0.5	0.3229	3.205	2.861
0.5	0.3310	3.186	2.807
0.5	0.3186	3.314	2.916
0.5	0.3171	3.305	2.913
1	0.3216	3.225	2.896
2	0.3131	3.477	2.931
6	0.3405	3.106	2.760
12	0.3122	3.476	2.927
17	0.3024	3.477	2.861
24	0.3567	3.085	2.742

Table 2 Variation in the mass of precipitate formed with standing time in solution for 500 ml milk samples

Observed		Brushite syn.	
d-spacing	Intensity Order (1st = most intense)	d-spacing	Relative Intensity I/Io
7.39	1st	7.57	100
4.18	2nd	4.24	100
3.83	9th	3.80	7
3.43	6th	3.63	1
3.12	3rd	3.05	75
3.01	4th	2.93	50
2.85	5th	2.86	9
2.73	10th	2.62	50
2.55	8th	2.60	30
2.32	7th	2.43	15

Table 3 Comparison of the d-spacing values for the precipitate and the literature values for brushite syn

Sample description	^{90}Y activity added /Bq	^{90}Y count rate added /cpm	Count rate recovered /cpm	% recovery
Marvel	8.4	217.9	185.9	85.3
Harwell	8.4	217.9	181.8	83.4
Harwell	8.4	217.9	179.6	82.4
KLIM	2.5	64.9	54.8	84.6
KLIM	2.5	64.9	54.1	83.4
Dairy Farms	8.4	217.9	188.9	86.7
KLIM	1.25	32.4	27.5	84.9
KLIM	1.25	32.4	27.7	85.6
Marvel	1.25	32.4	27.4	84.7
Marvel	1.25	32.4	27.0	83.2
				mean = 84.4 ± 2.6

Table 4 Recoveries of yttrium-90 from spiked 500 ml equivalent milk samples

^{90}Y activity added /Bq	^{90}Y count rate added /cpm	Count rate recovered /cpm	% recovery
1.96	50.8	41.4	81.6
1.96	50.8	40.9	80.4
1.96	50.8	41.8	82.3
0.98	25.4	20.9	82.4
0.98	25.4	20.8	81.9
0.98	25.4	20.1	79.1
			mean = 81.3 ± 2.5

Table 5 Recoveries of yttrium-90 from spiked 1 litre equivalent milk samples

Sample	Mass of milk powder used / g	Certified specific activity / Bq kg^{-1}	Confidence interval / Bq kg^{-1}	Observed specific activity / Bq kg^{-1}
A14	99.2162	1.32	1.17 - 1.38	1.41 ± 0.34
IAEA-152	99.7349	6.79	6.17 - 7.32	6.99 ± 0.51
IAEA-152	50.0762	6.79	6.17 - 7.32	6.47 ± 0.73

Table 6 Determination of strontium-90 in IAEA reference materials

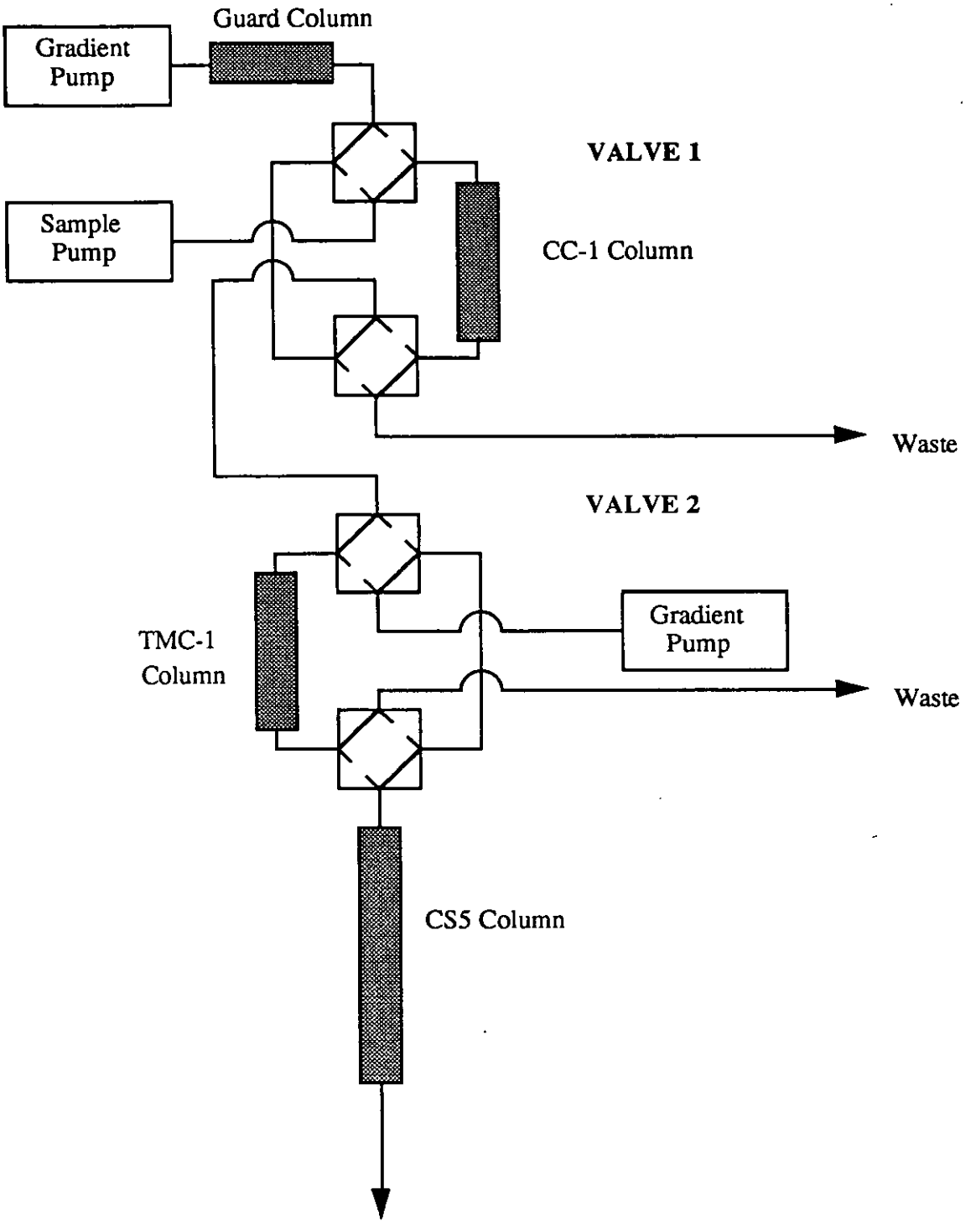

Figure 1 Schematic diagram of the ion-chromatography system

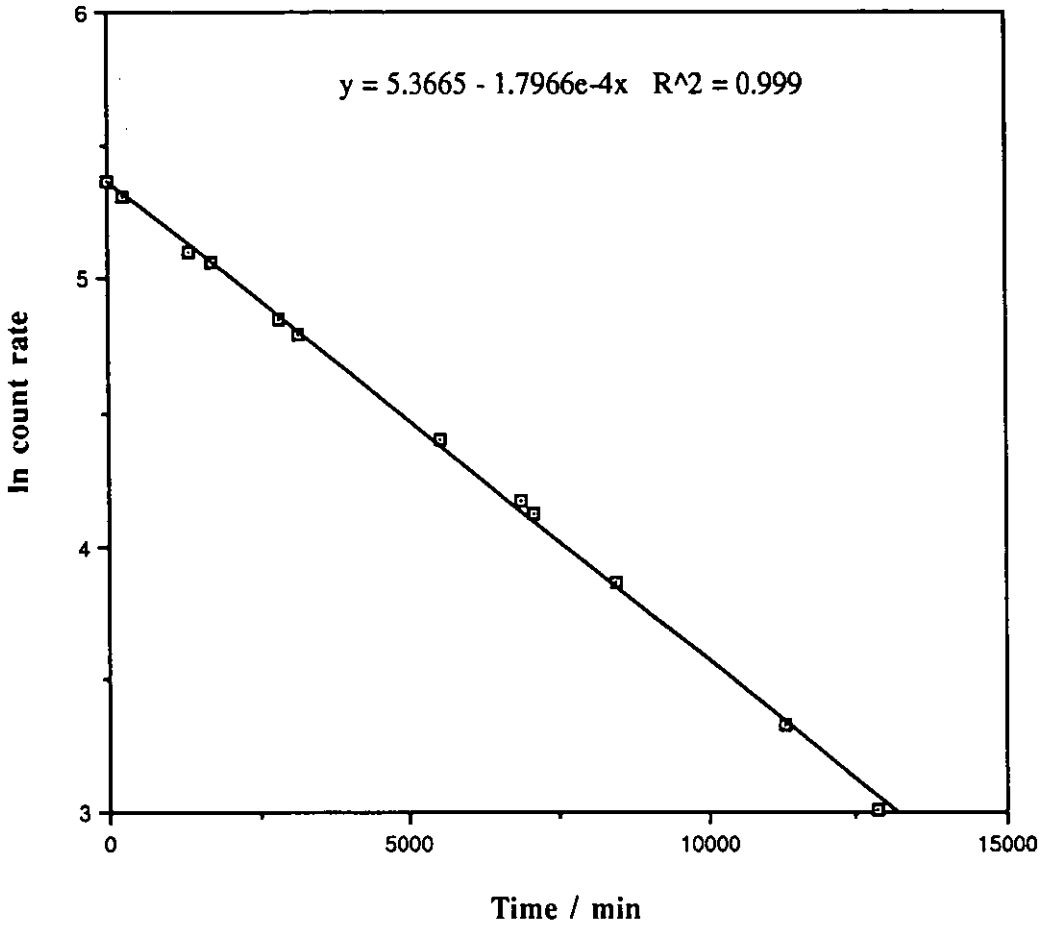

Figure 2 Variation in the natural log of count rate with time on the precipitate for a 500 ml milk sample spiked with strontium-90 and yttrium-90 in secular equilibrium