ANALYTICAL SEPARATION OF ZIRCONIUM-95 AND NIOBIUM-95 FROM URANIUM IRRADIATED BY THERMAL NEUTRONS

By

KAWTHER ABDUL-RAZZAK AL-ZUBAIDI

Thesis submitted for the
Degree of
Master of Philosophy

Department of Chemistry
The University of Aston in Birmingham

April 1980

TO MY HUSBAND

ABSTRACT

ANALYTICAL SEPARATION OF ZIRCONIUM-95 AND NIOBIUM-95 FROM URANIUM IRRADIATED BY THERMAL NEUTRONS

A thesis submitted for the degree of M Phil

in the University of Aston in Birmingham

April 1980

by

Kawther Abdul-Razzak AL-ZUBAIDI

Summary

The presence of zirconium and niobium in nuclear spent fuel is undesirable, both because these metals interfere seriously with later fuel reprocessing steps, and because of the high level of penetrating gamma radiation emitted by radioactive zirconium and its daughter niobium. In this thesis, after discussing the origin of the problem, methods for the separation of fission products have been reviewed. An investigation was conducted into the ability of silica gel, in a medium of hydrochloric acid, to separate zirconium and niobium from an irradiated uranium sample and from a non-radioactive sample.

Different procedures were then considered for the determination of zirconium and niobium; gamma ray detection, X-ray fluorescence and a colorimetric method using Alizarin Red-S. Alizarin Red-S was not found suitable for this research due to the interference of niobium, so the other techniques mentioned above were used.

The results are summarised in tables which show the percentage of each element in aqueous solution. From these results it is clear that, for certain specific column dimensions and flow rates, using several concentrations of hydrochloric acid, it is possible to separate zirconium and niobium both from each other and from other fission products. This method was not, however, found suitable for separation of other fission products e.g. ruthenium, cerium.

Key Words

Zirconium
Niobium
Silica gel
Hydrochloric acid
Adsorption

Acknowledgements

I would like to thank Dr E R Clark for his careful supervision and guidance during the period of the research. I would also like to thank Dr H Al-Sharistani for helpful and useful discussions and to express my gratitude to Rev. Dr J E Gregory, Dr G B Briscoe and many friends for their constant help and encouragement, particularly during the period of my illness.

Throughout the experimental work I have received much assistance from Mr W Harris and Mr D Peak, (both of Imperial Metal Industries, Witton, Birmingham), for which I am very grateful. For financial support and assistance whilst I was working there, I would like to thank the Iraqi Atomic Energy Organisation. I would also like to thank Sandra Baker for typing this thesis.

I also wish to thank my parents for their support and encouragement.

Finally, I wish to express my sincere gratitude and thanks to my husband for allowing me to continue my studies away from him and for his constant support and encouragement. Also, I must thank my daughter, Mayaseh, for letting me work away from her while she is so little and for always waiting patiently for my return.

TABLE OF CONTENTS

Page No.

Page No.

Page No.

CHAPTER 4 SPECTROPHOTOMETER DETERMINATION OF ZIRCONIUM USING ALIZARIN RED-S

CHAPTER 5 SEPARATION OF ZIRCONIUM AND NIOBIUM BY SILICA GEL ADSORPTION

Page No.

LIST OF FIGURES

LIST OF TABLES

Chapter One Introduction

1.1 Nuclear Fission and Nuclear Reactors

1.1.1 Brief History of Nuclear Fission

Nuclear fission was discovered by two German Chemists Hahn and Strassmann in 1938[1]. They and many other workers had been trying to make transuranic elements by bombarding uranium with slow neutrons, but in contrast to their expectation Hahn and Strassmann found that the products of their bombardments were not transuranic elements, but elements with much lower atomic weights, i.e. fission had occurred.

It was Fermi in Italy[2] who first suggested that a fission reaction which is induced by a neutron may itself become a source of more neutrons. Fermi put forward a hypothesis that, if this was true, it may be possible to start a chain reaction such that neutrons emitted by one fission reaction may start other similar reactions . This hypothesis was proved to be true in a controlled chain reaction using natural uranium and graphite to moderate or slow down the fission neutrons to energies at which they are easily captured by ^{235}U, at the University of Chicago in 1942[3].

The chain reaction of the type described above occurs only with the uranium isotope uranium-235 which is present only to the extent of one part in 139 of the natural uranium.

The major isotope uranium-238 if bombarded with neutrons behaves exactly as Hahn and Strassmann expected it to do, so it does give a short lived transuranic element (neptunium) which disintegrates radioactively to another transuranic element plutonium-239 which is also fissionable or fissile like uranium-235. Neptunium and plutonium were in fact the first artificially produced transuranic elements[4].

For a sustained chain reaction to be possible the nucleus must be capable of being fissioned by neutrons of any energy. ^{235}U is the only naturally occurring fissile isotope, but ^{233}U, ^{239}Pu and ^{241}Pu can be produced following neutron bombardment of ^{232}Th, ^{238}U and ^{240}Pu respectively. Isotopes such as ^{238}U which have a fission threshold at about 1.4 MeV cannot sustain a chain reaction due to competing reactions and the threshold energy being higher than the most probable energy of neutrons emitted in fission[5].

It was clear now that if uranium-235 or plutonium-239 could be obtained in sufficient quantity (in kilogram amounts) and in sufficiently pure state, a chain reaction with neutrons could be carried out at such a fast speed that an explosion may result. This fact was confirmed by the dropping of the well-known atom bombs over the Japanese cities of Hiroshima and Nagasaki[6].

Nuclear bombs are not the only results of research into nuclear fission. The development of nuclear power generation and the production of isotopes for medical and research purposes is also very important[7]. At the present time research is centred on the development of nuclear reactors, but the disposal of nuclear waste is becoming a big problem[8].

1.1.2 General Features of the Fission Process

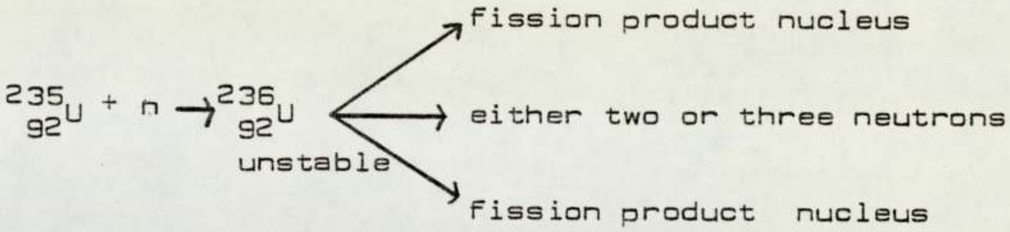
Nuclear fission is a process in which a heavy nucleus splits into two fragments, with the release of a considerable amount of energy in the form of radiation (light, heat, etc.) and is almost always accompanied by the emission of some neutrons[9]. Most of the nuclei with atomic number above 70 will undergo fission when bombarded with neutrons, charged particles (e.g. alpha-particles) or simply by excitation with electromagnetic radiation[10]. In all of these cases the energy of the particles in the radiation should be sufficient to overcome the fission threshold of the nucleus in question. For heavier nuclei, i.e. those with atomic number more than 92, the fission process may occur spontaneously without the presence of an external agent (for example $^{252}_{98}Cf$)[11]. As mentioned above, for induced fission the energy of the neutrons should be sufficient to overcome the fission threshold. However, for maximum fissioning of uranium-235 neutrons with high kinetic energy (i.e. travelling at high speed) have to be moderated since the fission cross section of uranium-235 is larger for moderated neutrons than for unmoderated neutrons, the increase being about 500 times between 2 MeV and $\frac{1}{40}$ eV[12]. For this purpose, in order to sustain a chain reaction in a nuclear reactor the neutron emitted from a fission reaction has to be slowed down before it induces another second fission process. This is usually done by using a moderator like heavy water, and the neutrons thus slowed down are called the 'thermal neutrons', having a most probable energy kT where T is the moderator temperature. [At room temperature kT = 1/40 eV][11][13].

Energy production in most nuclear reactors involves the use of thermal neutrons resulting from and sustaining a fission chain reaction in materials like uranium-235, uranium-233 and plutonium-239, since with thermal neutrons low enrichment fuel containing a high proportion of ^{238}U can be used. With graphite or heavy water as the moderator natural uranium can be used [1 part in 139 of ^{235}U][14].

1.1.3 The Nuclear Reactor - A Device for Controlled Fission

Most nuclear reactors consist of a core that contains the reactor fuel as well as neutron moderating and cooling materials. Uranium-235 is the most commonly used fuel, although uranium-233 and plutonium-239 may be used also. Each uranium-235 nucleus which undergoes fission emits on the average about 2.5 neutrons.

The reaction taking place in the reactor can be represented by:



The neutrons produced from the fissions have energies ranging from 0.1 to about 20 MeV. The most probable energy is about 0.72 MeV and the mean energy is about 2.0 MeV.

A few neutrons, however, arise from the fission of uranium-238 present in natural uranium and some from the interaction of gamma-rays with such materials as deuterium or beryllium that may be present. The maximum neutron flux that has been attained in nuclear reactors is about $10^{15} n/cm^2.sec$. The high energies with which neutrons are released in the fission process accounts for the extensive neutron moderator which serves to reduce the energies of the fission neutrons to thermal energies with a minimum of loss by neutron capture or by escape from the moderator. The neutron moderator is a low atomic-mass material such as water, heavy water, or graphite. The energetic neutrons resulting from fission collide with the nuclei of the moderator and are slowed down by a series of elastic collisions. This results in a more efficient fission process since the fission cross section of uranium-235 is larger for moderated neutrons than for unmoderated neutrons. Additional moderating material is placed around the core to further slow down and reflect the escaping neutrons. The core in most reactors is surrounded by a heavy thick-walled material such as concrete or immersed in a deep pool of water which serves as a radiation shield[15] [16].

Nuclear reactors designed for research have small highly enriched cores with high neutron leakage and are provided with facilities to allow samples to be irradiated for analysis and other purposes, such as research in activation analysis and health physics[17].

The most important features of a fission process in the nuclear reactor are:

(1) the high release of energy (up to 200 MeV per event)

(2) the emission of 2 or 3 neutrons from each fission process

(3) the successive radioactive disintegration gives rise to an array of new nuclei.

The nuclear fission reaction (whether it is induced or spontaneous) is said to proceed by the following stages[18] [19] (as shown in Figure 1).

(1) The heavy nucleus receives excitation energy such as the absorption of a neutron from outside. The excess binding energy caused by addition of the neutron causes the nucleus to undergo rapid changes of shape, oscillating from one form to another until finally it becomes elongated and takes the shape of a dumbell.

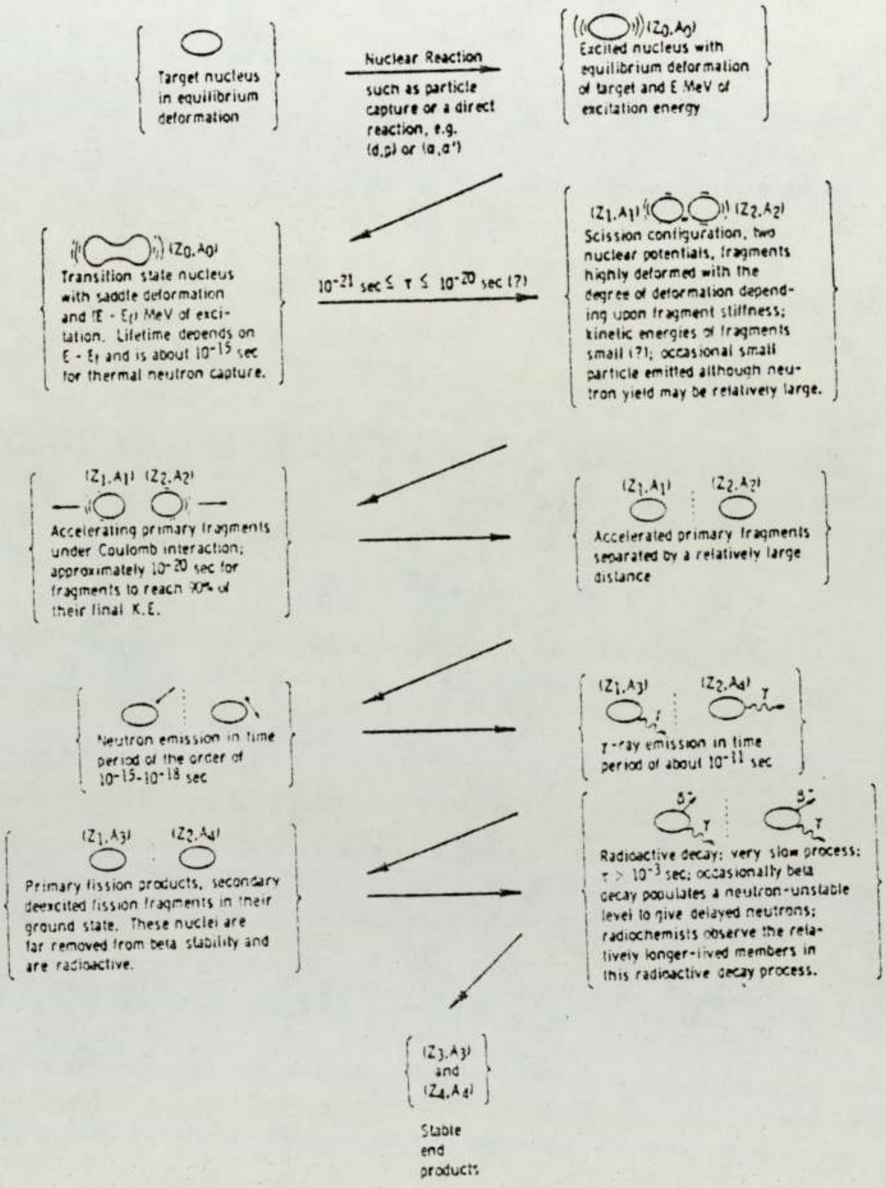


Figure 1 Schematic diagram of the fission process
Ref 18

(2) At this point (called the saddle point of the fission reaction), if the nucleus contracts slightly it might return to its oscillations, emitting the excess of energy in the form of gamma-radiation. On the other hand, if it stretches a little more, the forces holding the nucleus together would be overcome resulting in the breaking of the nucleus into two fragments accompanied with the release of some neutrons. This is the most common type of fission reaction and is known as binary fission. Less frequently the excited nucleus may break up into three fragments, the third part usually being an alpha particle or another isotope of helium. In such cases the reaction is known as ternary fission (20).

(3) The two fragments resulting in stage (2) have high internal excitation energy, which is lost by the emission of prompt neutrons.

(4) After emission of the prompt neutrons any excess internal energy is lost by the emission of prompt gamma rays.

(5) The fission fragments produced have always an excess of neutrons, and they are, as a consequence, unstable. In order to get rid of excess neutrons, most of the fission fragments decay by emission of beta rays (consisting of negative charged electrons that are produced when neutrons turn into protons) and occasional release of delayed neutrons.

The process from the original excitation of the nucleus to the emission of gamma rays will take about 10^{-14} seconds; this is the range quoted in the literature[11][18].

[6] As mentioned above, the fragments of the original nucleus then become radioactive elements, listed from zinc [Z = 30] to dysprosium [Z = 66]; these include representatives of each family of the periodic table, and are known as fission products. Then, over a period of time that may be only a few seconds or may be many years, successively disintegrate into other elements by the emission of X-rays, gamma-rays, beta-rays and sometimes delayed neutrons until they finally have no more excess energy left to disintegrate further, and turn into ordinary stable isotopes.

There are more than 30 different modes of fission, and in each of them a different pair of nuclei is formed. Besides barium and lanthanum, some of the other common nuclei formed are bromine, molybdenum, rubidium, antimony, tellurium, krypton, iodine, xenon and cesium[21]. However, because of the short half lives of some fission fragments, it is difficult to separate and identify them. Most of these fragments go through many β^- decays before becoming stable isotopes. A series of products with the same mass number A is a fission chain. More than 60 such fission decay chains have been established and one which is of interest is:

$$^{95}_{36}Kr \xrightarrow[2.5\ sec]{\beta^-} {}^{95}_{37}Rb \xrightarrow[0.36\ sec]{\beta^-} {}^{95}_{38}Sr \xrightarrow[26.0\ sec]{\beta^-} {}^{95}_{39}Y \xrightarrow[10.5\ min]{\beta^-}$$

$$^{95}_{40}Zr \xrightarrow[65d]{\beta^-} {}^{95}_{41}Nb \xrightarrow[35d]{\beta^-} {}^{95}_{42}Mo_{\text{stable}}$$

Some fission products such as ^{87}Br may decay either by ß decay to ^{87}Kr and so eventually to stable ^{87}Sr or alternatively by emission of a neutron to reach stable ^{86}Kr. These neutrons are delayed compared with fission neutrons on average by a time equal to the mean life of the precursor (79 s for ^{87}Sr) and are very important in reactor control since they slow down the rate of response to a change in multiplication[22].

1.1.4 Theoretical Aspects of Nuclear Fission

There is no single theory in existence today which could explain all the complex aspects of the process of nuclear fission, but various theoretical models have been put forward. Many of these theories are useful in the understanding of part of the process. The most important of these models are the liquid-drop model, the adiabatic model, and the statistical model[23][10].

The liquid-drop model likens the nucleus to a drop of an incompressible liquid having a uniform electric charge. The particles inside the drop all attract each other because of the nuclear force, but the attraction is one-sided only at the surface of the drop. This results in the skin of the drop being stretched by the force of surface tension. Now the positive charge of the protons produces a repulsive force acting in the direction opposite to that of the surface tension. Under normal circumstances the surface tension can overcome the opposing forces and keep the nucleus in one part. If an external energy is supplied to the nucleus, for example by bombardment with a neutron, the balance may be shifted. Under such circumstances, the disruptive forces may become so great as to break the nucleus into two fragments, with accompanying release of neutrons, and radiation.

The liquid-drop model takes the nucleus to be a blob of matter in which all the nucleons interact strongly with each other[19]. A variant of the nuclear drop model, called the shell-model, assumes that there is no interaction between individual nucleons. The adiabatic fission model combines some features of both types and has been useful in predicting the properties of fissioning nuclei up to the transition state[24].

The statistical model assumes that there are forces at work within the nucleus which are not adiabatic in nature and that the effect of these is to establish thermodynamic equilibrium between the different possible conditions of the nucleus at the point of breakage. Although the model as conceived originally has not been so useful, recent modifications have been a great improvement[19].

1.1.5 Fission Products and the Periodic System

Since elements in the same group of the periodic system have similar chemical properties, it is convenient to consider the fission products according to the group in which they appear. The treatment will be restricted to these isotopes formed in appreciable amount[8].

Group 0 : krypton and xenon

- Group I
  - A- rubidium and cesium
  - B- silver
- Group II
  - A- strontium and barium
  - B- zinc and cadmium
- Group III
  - A- yttrium and the rare earth elements, namely, lanthanum, cerium, praseodymium, neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium
  - B- gallium and indium
- Group IV
  - A- zirconium
  - B- germanium and tin

Sub-group IV A is important in the chemistry of processes of nuclear waste. The main radioisotope in fission products is zirconium-95 (half-life 65 days) formed in 6.3% yield. Both this isotope and its decay product niobium-95 (half-life 35 days) emit penetrating gamma radiation. For this reason and also because of its very diverse chemical properties and its high yield, zirconium is one of the most troublesome in the treatment of reactor fuel[16].

In its more common oxidation state IV, zirconium exhibits weak amphoteric behaviour, that is to say, the oxide (ZrO_2) has both basic and acidic properties. More detail is given in section 1.2.1.

A- niobium-95
Group V
B- arsenic and antimony

Niobium-95 (half-life 35 days), the decay product of zirconium-95, like its parent, has some amphoteric properties. Its frequently uncertain chemical behaviour combined with its high yield and gamma activity, makes the separation of niobium in particular one of the more difficult problems in separation processes[16].

A- molybdenum
Group VI
B- selenium and tellurium

A- technetium
Group VII
B- bromine and iodine

In subgroup VIIB iodine is the only one that is important in the fuel treatment, (half-life 8 days) and yield 2.8 %. Its significance lies in the fact that iodine is likely to be evolved in the elemental state as a vapour during processing and would thus create an air borne radiation hazard[5].

Group VIII (Transition Group): ruthenium, rhodium and palladium.

Only ruthenium is important in the chemical separation procedure relating to the reprocessing of the nuclear waste fuel, its decay product rhodium-106 emits highly energetic beta particles as well as some gamma radiation[16].

1.1.6 Mass Distribution of the Fission Products

The distribution of the mass of the fragments which originate from a fission reaction is an important characteristic of the fission process.

After the isolation of the two elements barium and krypton in the first reaction by Hahn and Strassmann in 1939, chemists were able to isolate a number of heavy fragments with the mass number between 130 and 145 together with a complementary light fragment having a mass number between 90 and 105. Conversely attempts to find isotopes of masses of

110 to 115 showed that the yields were very low, and this lead to the belief that the nuclear fission due to the neutrons appears to be a phenomenon which is essentially asymmetric. Later on it was found that this property is a characteristic of fission caused by thermal neutrons. However, when the energy of the neutron is increased the distribution is almost symmetrical; for example, when neutrons of energy 14 MeV are used the mass will distribute exactly symmetrically.

When the fission yield is plotted as a function of the mass number, a double-humped mass distribution curve is obtained as in Figure 2. The higher the peak/valley ratio, the more frequently occurring is the asymmetry of the fission events. The ratio is 650 in the case of uranium-235 when fission is caused by thermal neutrons, but it is only 65 when fission is caused by neutrons of 14 MeV as shown in Fig 2[16][11].

1.1.7 Fission Products Yield

The fission yield is the proportion (or percentage) of the total nuclear fissions that form products of a given mass number.

As mentioned earlier, the fission of uranium-235 by slow neutrons results in the emission of a large number of different products varying from zinc (A = 72, Z = 30) to dysprosium (A = 161, Z = 66). The yields are greatest in the mass ranges from 90 to 100 and 133 to 144, and they are quite small at extreme masses and at masses corresponding to nearly symmetrical fission (109 to 125).

Fission yields, of course, vary for different fissionable nuclei such as uranium-233, uranium-235 and plutonium-239. However, high-yield fission products correspond quite closely among the fissionable nuclei as low-yield fission products. The yields do not depend greatly on neutron energy over the spectrum encountered in reactor[25].

The percentage yields from thermal-neutron fission of uranium are given in Table 1.

From Table 1 Figure 2 it is clear that the percentage yields of zirconium-95 and its daughter niobium-95 are very high; as mentioned in section 1.1.5 these two elements have diverse chemical properties which cause difficulties in the reprocessing of spent fuel. This will be discussed later. It is therefore important to study the chemistry of both elements and the problems caused by them in order to find a method for separating these two elements from nuclear waste fuel.

1.2 Brief History and Basic Chemistry of Zirconium and Niobium

1.2.1 Zirconium

Martin Heinrich Klaproth, a German analytical chemist

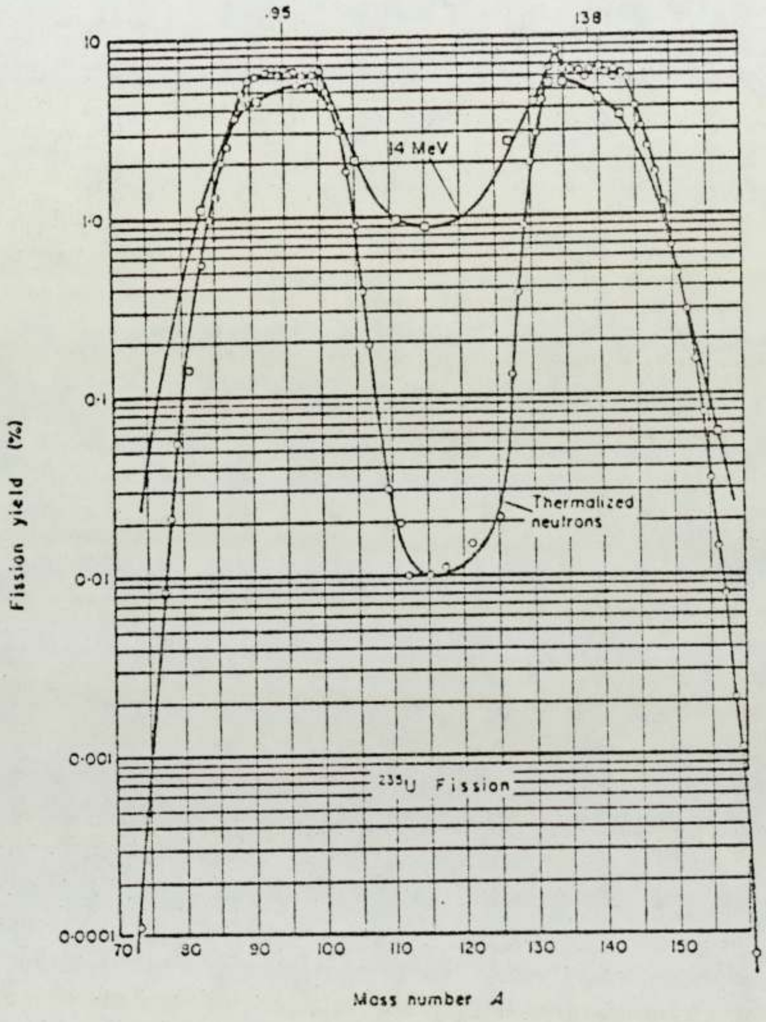
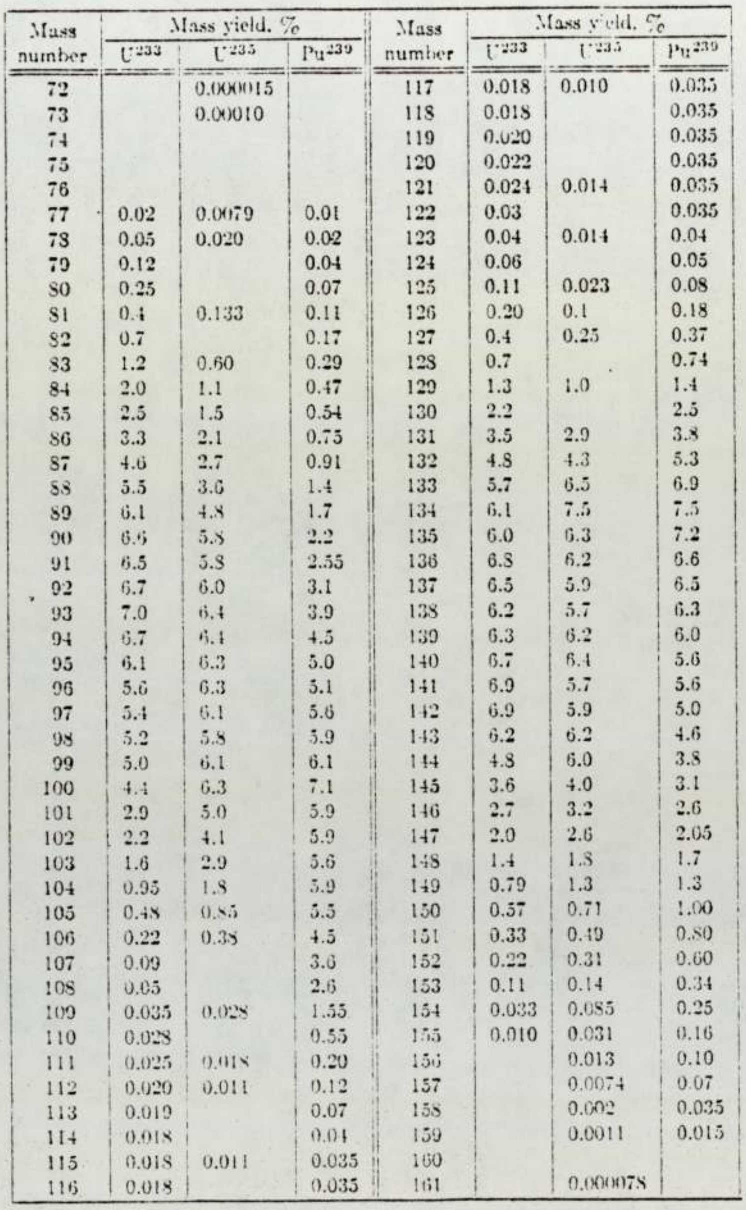


Figure 2 Mass yields for the fission of ^{235}U induced by slow neutrons and neutrons of 14 MeV Ref 11



Mass number	Mass yield, %			Mass number	Mass yield, %		
	U^{233}	U^{235}	Pu^{239}		U^{233}	U^{235}	Pu^{239}
72		0.000015		117	0.018	0.010	0.035
73		0.00010		118	0.018		0.035
74				119	0.020		0.035
75				120	0.022		0.035
76				121	0.024	0.014	0.035
77	0.02	0.0079	0.01	122	0.03		0.035
78	0.05	0.020	0.02	123	0.04	0.014	0.04
79	0.12		0.04	124	0.06		0.05
80	0.25		0.07	125	0.11	0.023	0.08
81	0.4	0.133	0.11	126	0.20	0.1	0.18
82	0.7		0.17	127	0.4	0.25	0.37
83	1.2	0.60	0.29	128	0.7		0.74
84	2.0	1.1	0.47	129	1.3	1.0	1.4
85	2.5	1.5	0.54	130	2.2		2.5
86	3.3	2.1	0.75	131	3.5	2.9	3.8
87	4.6	2.7	0.91	132	4.8	4.3	5.3
88	5.5	3.6	1.4	133	5.7	6.5	6.9
89	6.1	4.8	1.7	134	6.1	7.5	7.5
90	6.6	5.8	2.2	135	6.0	6.3	7.2
91	6.5	5.8	2.55	136	6.8	6.2	6.6
92	6.7	6.0	3.1	137	6.5	5.9	6.5
93	7.0	6.4	3.9	138	6.2	5.7	6.3
94	6.7	6.4	4.5	139	6.3	6.2	6.0
95	6.1	6.3	5.0	140	6.7	6.4	5.6
96	5.6	6.3	5.1	141	6.9	5.7	5.6
97	5.4	6.1	5.6	142	6.9	5.9	5.0
98	5.2	5.8	5.9	143	6.2	6.2	4.6
99	5.0	6.1	6.1	144	4.8	6.0	3.8
100	4.4	6.3	7.1	145	3.6	4.0	3.1
101	2.9	5.0	5.9	146	2.7	3.2	2.6
102	2.2	4.1	5.9	147	2.0	2.6	2.05
103	1.6	2.9	5.6	148	1.4	1.8	1.7
104	0.95	1.8	5.9	149	0.79	1.3	1.3
105	0.48	0.85	5.5	150	0.57	0.71	1.00
106	0.22	0.38	4.5	151	0.33	0.49	0.80
107	0.09		3.6	152	0.22	0.31	0.60
108	0.05		2.6	153	0.11	0.14	0.34
109	0.035	0.028	1.55	154	0.033	0.085	0.25
110	0.028		0.55	155	0.010	0.031	0.16
111	0.025	0.018	0.20	156		0.013	0.10
112	0.020	0.011	0.12	157		0.0074	0.07
113	0.019		0.07	158		0.002	0.035
114	0.018		0.04	159		0.0011	0.015
115	0.018	0.011	0.035	160			
116	0.018		0.035	161		0.000078	

Table 1 Recommended mass yield for thermal-neutron fission
Ref 8

discovered zirconium in 1789[26]. He published the results of his analysis of zircon by analyzing the semi-precious jewel.

Klaproth isolated an oxide which had properties different from any other known at that time. He proposed the name zirkonerde for the new oxide and the name zirconium was derived from zirkonerde. His discovery was soon confirmed by de Morveau Vangualen.

Both chemists were unsuccessful in isolating the pure metal until 1824, when Berzeluies[26] heated a mixture of potassium metal and potassium fluozirconate in a small closed iron tube placed inside a platinum crucible. After washing and drying the reaction products, he obtained metallic zirconium. Berzeluies determined the atomic weight of the metal and obtained a value of 89.46, as compared with 91.22, the modern value.

Zirconium has atomic number 40, maximum valency 4, and its maximum coordination number in its compounds is 8, melting point 1855 ± 15°C and density 6.5 g/cm^3 [27].

The known isotopes of zirconium are zirconium-86 to zirconium-99. Of these isotopes, ^{90}Zr, ^{91}Zr, ^{92}Zr, ^{94}Zr and ^{96}Zr are naturally occurring, none of these are radioactive, whilst the other isotopes are radioactive and not natural, but they are formed by atomic fission or by bombardment of suitable substance with neutrons or other high energy particles.

These isotopes have half lives of 1.1 × 10^6-yr ^{93}Zr, 65-day ^{95}Zr, and 17 hr ^{97}Zr. The isotope ^{93}Zr has such low activity to be of little concern and ^{97}Zr is ordinarily decayed by the time reactor products are processed. The 65-day isotope ^{95}Zr, however, with its high yield, intermediate half-life and high gamma energy is always of great concern, and its activity is enhanced and prolonged by the growth of its daughter, 35-day ^{95}Nb, i.e. zirconium-95 is one of the major products formed when uranium or plutonium undergo nuclear fission[27].

The chemistry of zirconium is complicated by the ability of its compounds to be covalent in nature and by the variety of different ways of bonding in the complexes formed. Some of these complexes, their oxidation states and sterochemistries are summarized below[28].

oxidation state	coordination number	geometry	examples
Zr^{II}, d^2	?	?	$ZrCl_2$
Zr^{IV}, d^0	4	tetrahedral	$ZrCl_{4(g)}$
Zr^{IV}, d^0	6	octahedron	$[ZrF_6]^{2-}$
Zr^{IV}, d^0	7	pentagonal-bipyramidal	$[ZrF_7]^{3-}$
Zr^{IV}, d^0	8	doecahedron	$[Zr(C_2O_4)_4]^{4-}$

Zirconium forms stable chelate complexes with many organic compounds in which coordination is usually through oxygen atoms. For instance -C=O, -COH or COOH groups are involved, the zirconium atoms often forming five or six membered ring systems.

Zirconium has a tendency to polymerize especially in solution. For example, $[Zr_4(OH)_8]^{4+}$ is thought to be present in aqueous solution and the degree of polymerization depends on the age of the solution, the pH, the temperature and the anion present.

Zirconium metal is fairly resistant to acids, and best dissolved in hydrofluoric acid. Zirconium will burn in air at high temperatures, reacting more rapidly with nitrogen than with oxygen to give a mixture of nitride, oxide and oxonitride(28).

1.2.2 Niobium

Niobium was discovered in 1801(29), after the examination of a heavy black mineral sent to the British Museum a number of years previously from Connecticut (USA).

It was Hatchett, a British chemist who examined the mineral and described it as a new acidic oxide of an element, who named it 'columbium' in honour of the state from which the ore came.

In the year following Hatchett's discovery, a Swedish chemist Ekeberg[30] discovered another new element which he proposed the name tantalum from the Greek "Tantalos". In 1844 Rose analyzed certain columbites which he named niobium from Niobe the daughter of Tantalos.

The name niobium, which was given by Rose for the metal, had been used abroad but not in the United States, where the name columbium has remained popular. The two names of the metal have lead to some confusion and have provided much discussion from time to time. However, in 1951 at the Amsterdam conference of the IUPAC, it was decided to call it niobium. Many metallurgists, engineers, businessmen, physicists and a few chemists in the United States resisted to change from the more familiar 'columbium' and the American Engineering Societies have voted to retain the name 'columbium'.

The atomic number of niobium is 41,the valencies are 2, 3, 4 and 5. The melting point of the metal is about 2468 ± 10°C and the boiling point is 5127°C, density 8.57 g/cm^3 [29].

The known isotopes of niobium are niobium-90 to niobium-99. Niobium-93 is non-radioactive and naturally occurring of capture cross section 1.1 barns. The others are radioactive and not natural. Niobium-95 is the result of the decay of zirconium-95 formed by the fission of uranium-235[29].

Niobium forms numerous anionic and neutral species. Examples, oxidation states and sterochemistries found in some of its compounds are summarised below[28].

oxidation state	coordination number	geometry	examples
Nb^{-I}	6	octahedral(?)	$[Nb(CO)_6]^-$
Nb^{I}, d^4		π complex	$[\pi\ C_5H_5]\ Nb(CO)$
Nb^{II}, d^3	?	?	NbO (?)
Nb^{III}, d^2	7	?	$NbCl_3$
Nb^{IV}, d^1	8	dodecahedral	$NbX_4(diars)_2$
Nb^{V}, d^0	6	octahedral	$NbCl_5$

Niobium metal is very resistant to acids. The best solvent is a mixture of nitric acid and hydrofluoric acid which gives fluoro complexes, but its resistance to alkalis is also poor.

1.3 Problem Caused by Zirconium-95 and Niobium-95 in Nuclear Waste Fuel Reprocessing

Most of the methods of reprocessing irradiated fuel are based on solvent extraction; this technique having been used widely for metal purification. Usually the metal of interest is extracted from an aqueous solution into an organic solvent, leaving many unwanted impurities in the aqueous phase.

In some cases, however, with particular metals some impurities will be transferred to the organic phase. This often happens in the reprocessing of nuclear waste fuel. Precipitation or ion exchange may be used for final purification of uranium and plutonium[25][31]. Depending on the composition of the spent fuel, different solvent and salting out agents are used. The most common separation processes are the 'redox' process which utilizes methyl isobutyl ketone for the extraction and the 'purex' process which employs tri-n-butyl phosphate (TBP) for the same function.

There are many variations of the 'purex' separation process. In the most common version the uranium and plutonium are extracted into an organic solvent. In the solvent extraction cycle most of fission products remain in the aqueous phase, so that with acid and counter extraction, complete separation cannot be achieved. However, two elements, zirconium and niobium are troublesome in the solvent extraction processes.

Zirconium, and its daughter niobium, create difficulties primarily because they react with small quantities of radiolytic and hydrolytic degradation products of TBP and of diluents and are retained in the solvent, reducing the decontamination factor and complicating solvent recycle[32].

In the case of these elements, because of similarity of their extraction behaviour with respect to uranium and plutonium they end up with the extraction cycle and part of them is found with the fissile materials. Because of the existence of polynuclear cationic species of zirconium, the chemical behaviour of the element in aqueous and organic phases is affected significantly.

The presence of even traces of zirconium is the cause of the formation of colloids. The adsorption of zirconium on colloidal particles can cause difficulties in separation processes[8].

As mentioned earlier, zirconium-95 is radioactive while zirconium-94 and zirconium-96 are not, therefore, the cooling of the reactor fuel will only cause the disappearance of zirconium-95 through its beta decay to niobium-95, whilst zirconium-94 and zirconium-96 will remain in the fuel and interfere with any chemical treatment of the fuel[27].

Another problem is caused by the fact that one of the isotopes of zirconium (i.e. Zr-95), as mentioned above, is highly radioactive and emits ß-rays and penetrating gamma rays with a half-life of 65 days and yield of 6.3%. This makes the disposal of the waste material obtained from the fuel reprocessing step a major problem[25].

For both reasons, it is important to develop a method for quantitative separation of zirconium and niobium from the spent fuel and to have available a sensitive analytical technique to assess the efficiency of the separation procedure.

In the present work, after studying the basic chemistry of zirconium and niobium, the methods published for the separation of fission products were reviewed. This was followed by a critical appraisal of the analytical techniques for the separation of the fission products. The chosen methods were evaluated by using stable isotopes of zirconium and niobium and then by extension of the technique to radioactive isotopes prepared at the Iraqi Nuclear Reactor.

1.4 Separation and Analysis of Fission Products - Brief Review

Many investigators have reported on the use of organic ion exchangers for the separation of fission products. Anion exchange resins of the Dowex type in conjunction with hydrochloric acid, nitric acid and sulphuric acid as eluants have been used. Solvent extraction using different organic solvents, for example, 8-hydroxyquinoline, etc. have also been used. The use of silica gel for separation of zirconium and niobium etc. in which various acids have been used has been extensively reported. Other techniques have also been investigated. Some of these findings are reviewed below.

Bunney et al[33] have studied the separation of different metal ions by the use of anion exchangers in the system Dowex 2-hydrochloric acid, Dowex 2-nitric acid and Dowex 2-sulphuric acid. Strontium, yttrium, cerium and americium showed no significant adsorption in any of these systems in solutions ranging from 0.1 M to concentrated acids. Molybdenum showed the greatest adsorption between 0.1 M and 1 M hydrochloric acid. Ruthenium in the oxidation state IV showed maximum adsorption at approximately 2 M hydrochloric acid. Minimum adsorption of niobium occurred below a concentration of 2 M hydrochloric acid. At approximately 8 M nitric acid thorium, uranium VI and zirconium showed maximum adsorption.

Wish[34] has reported that a rapid separation of neptunium, plutonium, uranium, zirconium, niobium and molybdenum isotopes in mixed fission products may be achieved by the use of anion exchanger Dowex 2 in conjunction with concentrated hydrochloric acid, hydrochloric-hydrofluoric acid and nitric acid mixtures. The methods described quantitative yields and satisfactory separations for molybdenum, zirconium, neptunium and uranium activities in the complex radionuclide mixture. The gamma ray purity of molybdenum and neptunium is greater than 99%. Zirconium and niobium fractions may contain gamma ray impurities which are easily tolerated by using gamma ray spectrometry. The uranium activity is mixed with tellurium-132, iodine-133 pair and usually requires further purification.

Freiling et al[35] have reported that cesium, strontium, cerium III, zirconium IV, tellurium IV, cerium IV, neptunium IV, niobium V, molybdenum VI and uranium VI fall into three groups in the adsorption on anion exchanger Dowex 2 resin using phosphoric acid solutions. The first group, cesium and tellurium IV show no significant adsorption even at concentrations of 0.1 M phosphoric acid. The second group composed of strontium, cerium III and cerium IV is weakly adsorbed at low phosphoric acid concentrations. The third group composed of zirconium IV, neptunium IV, niobium V, molybdenum VI and uranium VI is strongly adsorbed.

Huffman et al[36] have studied the behaviour of fluoride containing complex ions of zirconium, hafnium, niobium and tantalum by elution from anion exchanger Dowex 2 resin with mixtures of hydrochloric-hydrofluoric acids. They have reported that zirconium, hafnium, niobium and tantalum form complex chloro ions in strong hydrochloric acid which can be exchanged on anion exchanger resin.

Mathers et al[37] have described a semi-automatic apparatus for performing a five group separation of radio-elements by cation exchanger Dowex 50- x4 resin. Twelve samples were analyzed simultaneously, using five counting sources for each sample. By counting during an 8 hour day two samples may be analyzed. The radio-elements in these two samples were reported primarily to fall into the following groups. Group I, antimony, ruthenium zirconium, niobium. Group II, cesium. Group III, cobalt. Group IV, strontium and Group V, yttrium, rare earth elements.

Souka et al[38] have studied the conditions for the separation of protoactinium, niobium and zirconium by extraction with solution of tetraphenylarsonium chloride by using protoactinium-233, niobium-95 and zirconium-95 as tracers. Activities were measured with a NaI(Tl) detector and radiochemical purities were checked with a Ge(Li) detector. They found that the separation of protoactinium from niobium and zirconium could be achieved by selective extraction of protoactinium into 0.05 M of tetraphenylarsonium chloride in chloroform from a medium consisting of hydrobromic acid and 9 M sulphuric acid. Separation of niobium from zirconium was found to be possible by selectivly extracting niobium from a medium consisting of a mixture of 3 M hydrochloric acid and 9 M sulphuric acid.

Mukhovikova et al[39] report that they extracted a mixture of zirconium, niobium, iron and cobalt using 8-hydroxyquinoline solution in chloroform. Iron was first extracted at pH4 with 10 ml of 4% 8-hydroxyquinoline solution in chloroform, the organic phase is then diluted to 25 ml with chloroform and the absorbance of the organic phase is measured at 580 nm. In order to determine niobium, the solution was treated with 3% sodium tartrate solution and 5 ml of 0.1 M disodium salt of ethylenediaminetetraacetic acid. The pH was then adjusted to 6.0 with aqueous sodium hydroxide, the solution then extracted with 4% 8-hydroxyquinoline and the absorbance of the organic phase measured at 585 nm. To determine zirconium, a portion of the aqueous phase after the removal of niobium was treated with 3 ml of 1% gelatin solution, 0.1% Arsenazo III solution and sufficient 6 M hydrochloric acid to make the volume to 50 ml. The absorbance of the resulting solution was measured at 665 nm. To determine cobalt, the initial sample solution was treated with 20 ml of a solution stated to be an acetone buffer solution (pH 5.0) and sufficient 1 M sodium hydroxide to give a pH of 5.0. After development of the colour, 12 ml of sulphuric acid (1:5) was added plus water to make the volume up to 100 ml and the absorbance was measured at 560 nm.

Ejaz[40] has studied the use of 4-(5-nonyl) pyridine oxide and trioctylamine for the extraction of zirconium IV using successively nitric acid, hydrochloric acid, sulphuric acid solutions utilising a tracer technique. The influence of the concentration of salting out agents was described and the separation of zirconium from uranium fission products was achieved. In the nitric acid system zirconium is extracted over a wide range of acid concentration and the extraction is almost complete from 10 M nitric acid. In the hydrochloric acid system, the extraction of zirconium is generally similar to that in nitric acid system. In the sulphuric acid system, the extraction is at a minimum in the acidity range 0.1 - 1 M. The extraction of zirconium increases when the acidity increases above 1 M sulphuric acid.

Ejaz further reports that the addition of sodium nitrate to 0.25 M nitric acid, sodium chloride to 0.25 hydrochloric acid and sodium sulphate to 1 M sulphuric acid does not produce any increase in the distribution coefficient of zirconium extraction.

Schriver[41] has separated zirconium-95 from its daughter niobium-95 by shaking twice the aqueous solution containing these two elements [μ M in zirconium-95 - niobium-95 and made 4 M in perchloric acid] with equal volumes of 90 μ M ß isopropyltropolone in chloroform. He achieved the separation of 99.8% of the niobium in the organic phase and 80% of the zirconium remains in the aqueous phase. Schriver found that sulphate, oxalate and phosphate interfere even at m M concentration because they form complexes with the metal; chloride and nitrate [up to 3 M] do not interfere. Although thiocyanate is formed, a complex with zirconium enables a separation from niobium to be achieved.

Beachmann et al[42] have used a gas chromatographic technique for separation of the fission products by heating a sample at one end of the silica tube at temperatures up to 1100°C (generally at 600 - 700°C) in a stream of nitrogen containing carbontetrachloride at (80 Torr). Volatile products were condensed further along the tube and could then be transferred by heating to the condenser part of the tube. Separation of the radioactive chlorides e.g. iodine, tellurium, technetium, zirconium, niobium and molybdenum produced by heating fission products of ^{235}U in CCl_4 was carried out either in silica tubes packed with silica granules or in tubes having the walls and granule packing coated with KCl, NaCl or CsCl. The tubes were heated at various temperatures from 400°C to 800°C isothermally or with a temperature 'programmed' mode. He found that the separation was achieved more easily when using silica tubes packed with silica granules than that with the tubes coated with KCl, NaCl or CsCl.

At temperatures below 350°C within 2 hours iodine is eluted from the tube. At 359°C a separation of iodine, tellurium, niobium and molybdenum is achieved in less than 15 minutes; however, zirconium and technetium are not transported at all. At higher temperatures, zirconium and technetium are eluted, but only technetium and molybdenum can be separated from each other and from the rest of the elements present. It is remarkable that the separation of niobium and molybdenum is better at higher temperatures in spite of the fact that they have differing temperature dependence retention volumes.

Ahrland et al[43] have studied the ion exchange properties of silica gel. They showed that silica gel may be used as a sorbent for organic compounds, gases and for metal ions from water solution. They suggested that the silica gel acts as an ion exchanger of weakly acid type.

$$-\overset{|}{\underset{|}{Si}}-OH + Me^{+} \longrightarrow -\overset{|}{\underset{|}{Si}}-OMe + H^{+} \qquad Me^{+} = \text{a metal}$$

The sorption to and the affinity for the gel of sodium I, calcium II, barium II, uranium IV, gadolinium III, zirconium IV, niobium V, uranium VI and plutonium IV was also studied. They reported that at given acidity of the solution the distribution coefficient is larger for high valent ions e.g. zirconium IV than for low valent ions e.g. sodium I and the distribution coefficient between gel and solutions of different metals increases strongly with increasing pH. The affinity for the ion exchanger is given by the order:

$$\text{Zr IV} > \text{U IV} \approx \text{Pu IV} > \text{U VI} > \text{Gd III} > \text{Ca II} \approx \text{Ba II} \approx \text{Na I}$$

They have also reported that some species are sorbed very quickly and others more slowly and that the separation also depends on whether the ion is hydrolysed or not.

In another paper Ahrland et al[44] have studied the use of silica gel adsorption in the separation of plutonium and fission products in nitric acid solution produced from uranium which has been irradiated with thermal neutrons.

They found that uranium VI showed no adsorption in 0.1 M and 0.5 M HNO_3. Plutonium was adsorbed in the range of 0.1 - 0.5 M HNO_3 but at 0.1 M HNO_3 the distribution coefficient for plutonium is much larger than that at 0.5 M HNO_3. Zirconium adsorption in 0.1, 1.5 and 5 M nitric acid has been studied and the lowest acidity was found to be the maximum adsorption state. Yttrium and the lanthanum, neodymium, gadolinium and ytterbium showed no adsorption on silica gel under these conditions.

Caletka[45] has investigated a method for separation and purification of zirconium-95 and niobium-95 in hydrochloric acid and hydrochloric acid-methanol solution by batch equilibrium method and subsequent passage through a silica gel column. He used a stock solution mixture of zirconium-95, niobium-95, hafnium-175, 181 and a small quantity of ruthenium-103 . Solutions of zirconyl chloride and hafnyl chloride were used as a carrier. In a batch of equilibrium study he found that the distribution coefficient of niobium was approximately constant from 1 to 6 M HCl where after it decreased with increase in acid concentration. However, zirconium was less strongly adsorbed than niobium at low acidities but in concentrated hydrochloric acid very surprisingly the reverse occurred. He also found that with column adsorption using silica gel of small surface area and using 6 to 9 M hydrochloric acid solutions, niobium is strongly retained on the column, whilst zirconium is easily eluted. Niobium elution has been achieved by using concentrated hydrochloric acid. **Ruthenium** behaviour was also investigated and showed no adsorption by silica gel. Investigation for the separation of a mixture of ruthenium, zirconium, niobium and hafnium by mixed eluant (10 Vol % methanol and 90 Vol % 11.5 M hydrochloric acid) was found to be better in comparison with the aqueous solution.

El-Garhy et al[46] have investigated the separation of zirconium-95 and niobium-95 from the other fission products using silica gel adsorption. After conditioning the column with 6N HCl and 0.005N HNO_3, it is washed with distilled water until neutral to pH paper. They then passed the dissolved target material through the column and the effluent was found to contain all fission product activities except those of zirconium-95 and niobium-95. These latter nuclides were adsorbed on the silica gel column. The column was then washed with 5-10 ml of (6N HCl + 0.005N HNO_3) to remove any activities other than zirconium-95 and niobium-95. The zirconium-95 and niobium-95 were quantitatively eluted with approximately 10 ml of 0.5% W/V oxalic acid. In their work although El-Garhy et al were successful in separating zirconium-95 and niobium-95 from other fission products, they have presented no evidence to indicate whether they were able to separate these two metals from each other.

Akatsu et al[47] have reported a separation method for zirconium-95 from other radionuclides by silica gel adsorption in 2.0 M nitric acid medium. The yield of zirconium-95 is given as 98% and decontamination factors are over 500 for niobium-95, ruthenium - 103, antimony-124, cesium-137, molybdenum and uranium IV.

In another paper Akatsu et al[48] have reported their investigations of the adsorption behaviour of inorganic ions using zirconium phosphate, silica gel and charcoal as adsorbents. The aqueous phase were 0.01 - 10 M nitric acid and 0.01 - 10 M ammonium nitrate solution. The distribution ratio of about 50 chemical elements from sodium to curium were determined by batch methods using radioactive tracer techniques. Cesium shows the highest distribution ratio value in the zirconium phosphate system and most bivalent species are not adsorbed. It is worth noting that a few elements are adsorbed on silica gel from nitric acid solutions. High distribution ratio values are shown by zirconium and niobium and protactinium under the same conditions. In the charcoal system Akatsu found that most chemicals are adsorbed to some extent except those of the alkali and alkaline earth ions.

Tsaletka[49] studied the adsorption behaviour of zirconium and hafnium on silica gel as a function of perchloric, nitric, hydrochloric acids concentrations. He found that the adsorption of both zirconium and hafnium from solution of perchloric acid is the highest in comparison with the other acids. Zirconium and hafnium adsorption curves showed a minimum at 4 M perchloric acid concentration. In nitric acid solution the adsorption of zirconium corresponds to a curve with a flat minimum in the region of medium acid concentrations and is appreciably reduced in the concentration greater than 10 M. The adsorption of hafnium decreases almost linearly with increasing nitric acid concentration within the range 1 - 4 M and the adsorption curve showed a minimum at 4 M HNO_3. However, at the acid concentration greater than 6 M HNO_3, the adsorption remains practically constant. In comparison with perchloric and nitric acid media, the adsorption of both elements from hydrochloric acid is the lowest at a given concentration.

Hung-Chih [50] investigated the adsorption behaviour of ruthenium, cerium, zirconium and niobium on silica gel-nitric acid system by batch equilibrium studies and also by passage through a column using the same media. Both ruthenium and cerium showed no significant adsorption under these conditions. Zirconium showed an adsorption maximum at 1 M nitric acid but the adsorption of niobium increases with increasing nitric acid concentration from 0.1 to 15 M. 0.2 M oxalic acid have been successfully used for the elution. The chemical yield and radioactivity purity of zirconium-95 and niobium-95 is greater than 99% in this procedure.

1.5 Summary

As seen from the above survey of literature, silica gel has been used by many workers for the purpose of separating the fission products. In the work reported here silica gel was chosen in preference to other methods [e.g. ion exchange and solvent extraction techniques] because of the following reasons:

1. Solvent extraction techniques have the problem of sample handling and incomplete separation and the use of many reagents, therefore a column chromatographic technique is to be preferred.

2. Compared to the ion exchange resins, silica gel is cheap.

3. Whereas the radiochemical purities of the separated nuclides using ion exchange resin [e.g. Dowex 2 and Dowex 50] is doubtful, when silica gel is used, elements may be obtained in a fairly pure state.

4. Silica gel is not effected by radioactive species in solution.

5. Compared with ion exchange resins [e.g. Dowex 2 and Dowex 50 type] separation of fission products by silica gel adsorption might involve the use of less complicated acid mixtures or even simple acids for adsorption and desorption. The mixtures of strong acids as suggested by some workers should be avoided if possible for two reasons:

[i] The expense involved in the preparation of such strongly acid solutions

[ii] The hazards in the use of such mixtures.

It was therefore decided in the present work to develop a scheme for the separation of zirconium and niobium from fission products based on silica gel adsorption. Previously reported results with this media do not seem to be very conclusive. For example, workers are in disagreement regarding the recommended condition for the most efficient adsorption. Caletka[45] reported that in batch studies, the adsorption coefficient of niobium was approximately constant from 1 - 6 M hydrochloric acid, but it decreased with increase in acid concentration. However, zirconium was less strongly adsorbed than niobium at low acidities, but in concentrated hydrochloric acid the reverse happened. He also reported that when using a column separation, he was able to separate zirconium-95 by elution with 9 M hydrochloric acid solution, whilst niobium-95 was strongly retained on the column. This observation was not confirmed in our preliminary studies. In contrast to the work of El-Garhy et al[46] it was decided to embark on a separation of zirconium-95 and niobium-95 not only from other fission products but also from each other. Furthermore, it was decided to investigate the possibility of using simple acid solvents of varying strength and to avoid complicated acid mixtures as used by El-Garhy.

1.6 Choice for Methods of Trace Analysis of Zirconium and Niobium

In order to study the quantitative separation of zirconium and niobium from other nuclides (and from each other) a sensitive analytical method had to be selected. The following are the most important techniques available.

1.6.1 Atomic Absorption Spectrophotometry

The determination of metals by atomic absorption spectrophotometry is a well-established technique and has found many applications in many fields. It is an analytical technique in which the absorption of radiant energy by atoms is related to the concentration of the metallic species in a flame. Trace elemental analysis can be carried out by the technique. Although this is very useful for many metals, zirconium and niobium present some special problems. For example, the solvents used have to be extremely pure, otherwise high readings are observed. Also the method is not very sensitive for the two metals because zirconium and niobium give very stable oxide species in the flame which makes atomisation difficult. Electrothermal atomisation can also not be used to increase the sensitivity because of the formation of carbide at high temperatures[51][52].

1.6.2 X-Ray Fluorescence

X-ray fluorescence analysis is one of the most universally used analytical methods but the apparatus is very expensive and not usually available. It may be a non-'destructive' method when solids and powders are analysed. Liquid may be examined but the destruction occurs in the dissolution stage. Except in the case of some lighter elements analytical results are independent of the type of matrix in which the analyte is present.

X-ray fluorescence is based on the principle that when material is bombarded with charged particles or high energy photon inner shell electrons are ejected from different orbitals of the atom and the vacancies left are filled with electrons coming from the outer shells. As a result of the transition of electrons from higher energy levels to lower ones, energy in the form of X-rays is given out. Measurement of the X-ray characteristic energies and the intensities serve as the basic of qualitative and quantitative analysis. But the methods of target preparation involved, such as the digestion of the sample, are still a major problem in the case of many elements of interest. Also the method may give large background readings at very low concentration[53][54].

In the present work this method was evaluated (using stable isotopes) for possible use in the study of the separation of fission products. However, it was found that it could not be extended to radioactive isotopes because of the problems encountered in the handling of the sample. Even for stable isotopes individual fractions from the silica gel column could not be analysed because of the low sensitivity and small volume.

1.6.3 Colorimetric Methods

Colorimetric methods in general are easy to use and are of reasonable sensitivity. Also the instrumentation involved is usually not very expensive. Therefore, it was thought advisable to use the colorimetric method for the estimation and the determination of zirconium at least for preliminary work with the stable isotopes. A survey of the literature showed that Alizarin Red-S[27] has been frequently used for the colorimetric determination of zirconium but there are conflicting reports about the best conditions for the absorption measurements. There is some doubt about the stoichiometry of the metal-dye complex. For this reason the method was thoroughly studied before using it for the purpose of the study of column eluents. The results of this study are presented in Chapter Four.

1.6.4 Gamma Ray Detection Method

This method of analysis was used for the determination of radioactive isotopes in solutions which had been irradiated in the Iraqi Nuclear Reactor.

When a nuclear probe interacts with an atomic nucleus the reaction may result in radioactive nucleus emiting a variety of radiations. The radiations have important properties. They can in the first place be detected and measured with very great sensitivity, so minute traces of material can be studied. On occasions one can even observe the radiation from a single atom. Secondly, the radiations are characteristic of the atoms from which they arise, so that they can be used for identification purposes, as well as for quantitative determination.

All methods of detecting nuclear particles and radiations are based on the fact that charged particles cause ionization when passing through matter. The charge may be collected directly by electrical means as it is in the gas ionization counter and semiconductor counters, or it may be detected by the consequent emission of light quanta as in the scintillation counters.[55]

The right choice of suitable detector which satisfies the conditions and the aims at a specific project is one of the important steps in the research described in this thesis.

In the work the gamma spectrum was expected to be complex and gamma rays energies for zirconium-95 and niobium-95 are very close (756.6 KeV for ^{95}Zr, 765.8 for ^{95}Nb) which means there was requirement for good resolution. So a Ge(Li) detector was chosen as a satisfactory detector in this particular case. More detail will be given in Chapter Two.

1.7 The Present Work

In the present work i.e. that involving the separation of fission products using non-radioactive species for preliminary studies were carried out using (i) atomic spectrophotometer (ii) X-ray fluorescence and (iii) the Alizarin Red-S colorimetric method. The techniques were later extended to real samples from the Iraqi Nuclear Reactor. The atomic absorption method could not be utilised for analysing samples containing zirconium and niobium because of the low sensitivity for these two elements and difficulties with the availability of the instrument.

For the preliminary separation studies with the stable isotopes, the X-ray fluorescence and the Alizarin Red-S colorimetric methods were used and for radioactive isotopes the gamma detection methods were utilised.

Chapter Two Gamma Ray Detectors

2.1 Interaction of Gamma Radiation with Matter

Gamma radiation is the emission of energy from the nucleus of an atom when it falls either to a lower excited state or to the ground state. The energy levels being quantised the photons are of a precise energy of the order of 0.1 to 2.5 MeV, and the photons are more conveniently described by their energy in MeV than by their wave length or frequency.

Gamma rays in fact are hard, or high-frequency, X-rays. They penetrate relatively great thicknesses of matter before being absorbed. Instead of having a well-defined range, like alpha or beta particles, a beam of gamma rays loses a certain fraction of its intensity per unit distance travelled through matter; great thickness of air, water, concrete or lead is required to dissipate one-half the intensity of a beam of gamma rays.

Because of the penetrating nature of gamma radiation, overexposure of the body to it results in deep-seated organic damage. Of the three types of radiation from radioactive substances, gamma radiation is by far the most serious external hazard, and it thus requires heavy shielding and remotely controlled operations.

Because a photon has neither charge nor mass, the parent and daughter nuclides in a gamma radioactive transformation are nuclear isomers.

The origins of gamma rays are:

1. Gamma-rays produced as a result of the capture of an external nuclear particle by the nucleus.

2. Gamma-rays emitted by a fragment of the nucleus due to fission of the latter.

3. Gamma-rays produced by an inelastic scattering process.

4. Gamma-rays occurring simultaneously with the emission of the beta and alpha rays.

The absorption of gamma-rays by matter differs fundamentally from that of charged particles. The latter dissipate their energy continuously in the sequence of many ionization and excitation events. Gamma-rays, on the other hand, are absorbed or scattered in single events. Like other forms of electromagnetic radiation, absorption in matter of gamma radiation follows an exponential law, and if the thickness is described in terms of mass per unit area, the absorption coefficient [and hence the half-thickness] is almost independent of the nature of the adsorbing material for energies up to 2.5 MeV.

The mechanism of absorption of the photons may be any of three processes, the likelihood of any particular process depending principally on the energy of the photon[10]. At low energies (0 - 100 KeV) the photo-electric effect predominates and in this an electron is ejected from an atom or molecule and the whole of the photon energy is used to release the electron (the work function) and to provide kinetic energy. At higher photon energies (100 - 1000 KeV), only part of the energy is used to eject an electron and the residue remains as a photon of lower energy (Compton scattering). At photon energies greater than 1.02 MeV, the photon, in the field of a nucleus, may form a positron and a negatron which on separating will carry any energy in excess of 1.02 MeV as kinetic energy.

2.2 Detection Methods

Detection of any resulting particles or radiations can be utilised in nuclear methods of analysis. Some of the parameters needed to help in the identification of a product nuclide are:

1. Energy and nature of the emitted radiations.
2. Presence of coincident radiation.
3. Half-life.
4. Intensity of gamma-ray of the particles emitted.

Most nuclear analytical methods depend on the measurement of the gamma rays emitted by a nucleus and absorbed by one of the processes mentioned in 2.1 returning to its ground state.

2.3 Types of Detectors

The ionization produced in the medium which a particle or ray passes through can be detected by one of several methods.

Three main types of detectors are in widespread use, namely gas ionization detectors, scintillation detectors and solid state detectors(54).

Gas ionization detectors employ gas filled chambers containing two electrodes between which there is an electric field. When radiation causes ionization in the gas the electrons produced are drawn rapidly to the anode, while the heavy positive ions move more slowly to the cathode. The result is that current flows through the circuit and this is used to measure the amount of radiation causing the ionization. Detectors based on gaseous ionization are of limited use with gamma radiation. The chance of the photon being absorbed by the detectors is small - it will probably pass straight through; and the response of the detector will show no relationship to the energy of the photon. The two important types of these detectors are proportional and Geiger Muller.

In the scintillation detectors the ionization particles pass through certain substances and are ionized. Excited states are produced which, during their return to the normal state, emit light. This light is picked up by a photomultiplier tube and the resulting pulse of current out of the photomultiplier produces a signal and is then counted by the electronic counter. These detectors can be made in sizes up to several litres. This ensures the most complete absorption of the photons, but the process of conversion to light and back to an electrical pulse via a photomultiplier tube is at the best only 20% efficient. Response times are fast (10^{-9} sec) but energy resolution is relatively poor. Thallium activated sodium iodide detectors are by far the most important ones of this class.

In the semiconductor detectors the operational principle is similar to that of gas-filled detectors, except that the ionization is produced in a solid medium fabricated from single crystals of high purity semiconductor materials, mostly germanium and silicon. This detector will be explained in more detail in the following section.

2.4 Semiconductor Detector

Semiconductor detectors have revolutionised gamma-ray spectroscopy by providing energy resolution unattainable with previous methods. In these detectors the charge carriers produced by ionizing radiation are electron-hole pairs rather than ion pairs. The ionizing radiation lifts electrons into the conduction band and these electrons travel towards the positive electrode with high mobilities. The positive charge travels in the opposite direction by successive exchanges of electrons between neighbouring lattice sites. Two general types of semiconductor detectors are: lithium-drifted silicon detectors which are generally used for X-rays; and lithium-drifted germanium detectors which are used for gamma rays.

Lithium-drifted germanium was used during this work for the detection of gamma rays.

The lithium-drifted germanium spectrometer consists of a virtually windowless Ge(Li) crystal, a vacuum cryostat maintained by cryosorption pumping, a liquid-nitrogen Dewar and a preamplifier. The Ge(Li) crystal is fabricated by drifting lithium ions (a donor) into and through p-type germanium. This is performed under the influence of a high electric field at 400°C. This process results in compensation of all acceptors within the bulk material, yielding a very high resistivity region which acts like ultrapure germanium within the bulk material. The drifting process is discontinued whilst a layer of p-type germanium still remains. This intrinsic or compensated volume becomes the radiation-sensitive region. When ionizing radiation enters the intrinsic layer, electron-hole pairs are created, and the charge produced is rapidly collected under the influence of the bias voltage. The complete detector must be maintained at 77°K at all times to prevent precipitation of the lithium, since the lithium drift process is not stable at normal room temperature. At this low temperature thermal noise is greatly reduced and the resolution capabilities are vastly increased[56].

2.4.1 Advantages of Ge(Li) Detectors

The main advantages of the detectors are:

1. The higher density of the ionizing system.
2. The energy needed for the production of a pair of charge carriers is less by a factor of 8 - 10 in a Ge(Li) detector than in gases, and less by a factor of about 100 than that required to produce a photoelectron in scintillation counters.
3. The resolution of Ge(Li) detectors is a factor of 3 better than that which is obtainable from gas counters and a factor of 10 better than that which is obtainable from a scintillation counter.
4. Ge(Li) detectors have a good linear relationship between pulse height and incident energy.

5. Response times are fast (10^{-9} sec) for Ge(Li) detectors and equal those of sodium iodide.

2.4.2 Disadvantages of Ge(Li) Detectors

The Ge(Li) detector has some inherent disadvantages. These are[55]:

1. The volume of Ge(Li) detector is limited at the present time to 100 cc whilst for NaI scintillation counters crystal up to 20,000 cc have been made and detectors of 400 cc are common.

2. Ge(Li) detectors must always be kept at liquid nitrogen temperature because lithium can diffuse significantly at room temperature.

3. Low efficiency, therefore, is not satisfactory for quantitative analysis in low activity.

2.5 Choice of Detector

The right choice of suitable detectors which satisfy the conditions and the aims of a specific project is one of the important steps in the research. Different factors which influence the choice of gamma detector are:

1. The aim of the research, whether it is qualitative or quantitative.

2. The detection efficiency which dictates the source strength necessary for the measurement of the spectrum.

3. The resolving power which determines the complexity of the spectrum that can conveniently be analysed.

4. The simplicity of the arrangement and the ease of data accumulation.

According to the above factors, it seemed that the biggest drawback to the gas filled counters is their low sensitivity and the use limited to gamma rays having ranges within the dimension of the chambers, which leads to limitations on the energy of the photon to be detected. Scintillation counter detectors, on the other hand, have very high efficiency but do not have such good resolution as the Ge(Li) detectors.

In the present work, the gamma ray spectrum was expected to be complex which meant there was a requirement for good resolution. Also the activity to be observed was not very low, so high efficiency and sensitivity factor is not very important. So a Ge(Li) detector was quite a satisfactory detector in this particular case.

Chapter Three Reagents and Methods of Analysis

3.1 Introduction

After reviewing all the methods of analysis outlined in Chapter One, three techniques were selected as those most suitable for use in this research: X-ray fluorescence, colorimetric method using Alizarin Red-S, and gamma ray spectrometry using a Ge (Li) detector. These are described in more detail later in this chapter. As these methods require the use of a considerable number of reagents, and many more are needed for the experiments themselves, a complete list of all reagents used in this work is given below.

3.2 Reagents

Hydrochloric acid solution (SG 1.18)

Analar grade, BDH Chemicals Limited. Solutions of the requisite concentration were prepared by dilution with distilled water; the concentration of the acids was determined by titration.

Nitric acid (SG 1.42)

Analar grade, BDH Chemicals Limited.

Hydrofluoric acid solution

40%, supplied by Hopkin and Williams Limited.

Oxalic acid solution, 5×10^{-2} M

Dissolve 0.6304 g of oxalic acid $(COOH)_2 . 2H_2O$. ['Analar' Hopkins and Williams Limited] dissolved in a few mls of distilled water and dilute to 100 ml. Solutions of requisite concentration were prepared by dilution with distilled water to a certain volume.

Standard sodium hydroxide solution, 4M

Concentrated volumetric solution, BDH Chemicals Limited. The solution is obtained by diluting the contents of one vial to 500 ml.

Uranyl nitrate powder

Reagent grade, supplied by Hopkins and Williams Limited.

Standard zirconium solution, 1.1×10^{-2} M [1000 ppm Zr]

Dissolve 0.1766 g purified salt $[ZrOCl_2 . 8H_2O]$ [Hopkins & Williams] in distilled water and dilute to 50ml in a graduated flask. The zirconium content of this solution was determined gravemetrically as ZrO_2. The zirconyl octahydrate was purified by recrystallisation from concentrated hydrochloric acid, washed with acetone and dried to constant weight in air.

Standard niobium solution 0.1076 M [10000ppm Nb]

Dissolve 0.100 g niobium powder, 99%,Koch light laboratories contained in a Teflon beaker, in 0.5 ml of concentrated hydrofluoric acid and add, dropwise, concentrated nitric acid. Heat to dryness, then add a few mls of distilled water and heat to dryness again (this procedure is repeated three times), and then the solution is diluted to 10.00 ml in a graduated flask with distilled water. This solution was standardised gravimetrically by using 8 hydroxyquinoline as precipitant.

After standardisation of the niobium solution, it was found that the solution contained 10,000 ppm niobium. This means that the powder used is very pure and this method of dissolution is satisfactory.

Molybdenum solution (100 ppm)

Dissolve 0.1840 g of ammonium molybdate ($(NH_4)_6MO_7O_{24}.6H_2O$) 'Analar' Hopkins and Williams Limited) in a few ml of distilled water and dilute to 100 ml in a graduated flask.

Cerium solution (100 ppm)

Dissolve 0.3099 g of cerium (III) ($Ce(NO_3)_3.6H_2O$) (Hopkins and Williams Limited) in a few ml of distilled water and dilute to 100 ml in a graduated flask.

Alizarin Red-S solution 1.1×10^{-3} M

Dissolve 0.0376 g of purified Alizarin Red-S in 50 ml of hot distilled water and filter through paper pulp. Dilute to 100 ml with distilled water. The commercial dye (Hopkins and Williams Limited) was purified by extraction with aqueous alcohol and dried at 110°C. It assayed (by nmr and TLC) 99%.

Silica gel

The specification of silica gel used is (60 - 120) mesh size Fisons (S 10780) batch 34 laboratory reagent. The silica gel was digested before use by repeated washing with 5 M HCl at 80 - 90°C for 8 hours. The gel was then freed from the bound acid by washing it several times with distilled water. Finally, it was heated for 20 hours in an electric oven at 110°C.

3.3 Apparatus

The specifications of the apparatus used are listed below.

Spectrophotometers

A Unicam SP8-100 double beam recording spectrophotometer and a Unicam SP6-100 single beam spectrophotometer were used. 1 cm glass cells were used throughout this study.

pH meter

pH measurements were made using Electronic Instruments

Limited Model 23A Direct Reading pH meter at 25°C. The instrument was standardised by using buffer solution pH7.0 and pH4.0.

Ge[Li] Detector

The radioactivity was measured by a Ge[Li] detector with an active volume of 30 cm^3, 4096-channel pulse height analyser connected to hp 9640. A multiprogrammic system is shown in Fig. 3 . The efficiency of the detector at various energies was calibrated by standard sources:

^{57}CO[121.9 KeV], ^{203}Hg[279.1 KeV], ^{23}Na[511.0 KeV], ^{88}Y[898.0 KeV], ^{22}Na[1274.5 KeV], ^{88}Y[1836.9 KeV] as shown on page 60 .

Atomic-absorption spectrophotometry

Perkin Elmer model 460 atomic absorption spectrophotometer was used for the determination of molybdenum. The absorbences of the aspirated solutions were measured at 313.3 nm using N_2O/C_2H_2 as combustion gases.

A Perkin Elmer molybdenum hollow cathode lamp was used. Molybdenum standard solutions for calibration of the instrument, of requisite concentration, were prepared by diluting molybdenum standard solutions [1000 ppm] specifically made for atomic absorption spectroscopy by BDH Chemicals Limited, with distilled water to a certain volume.

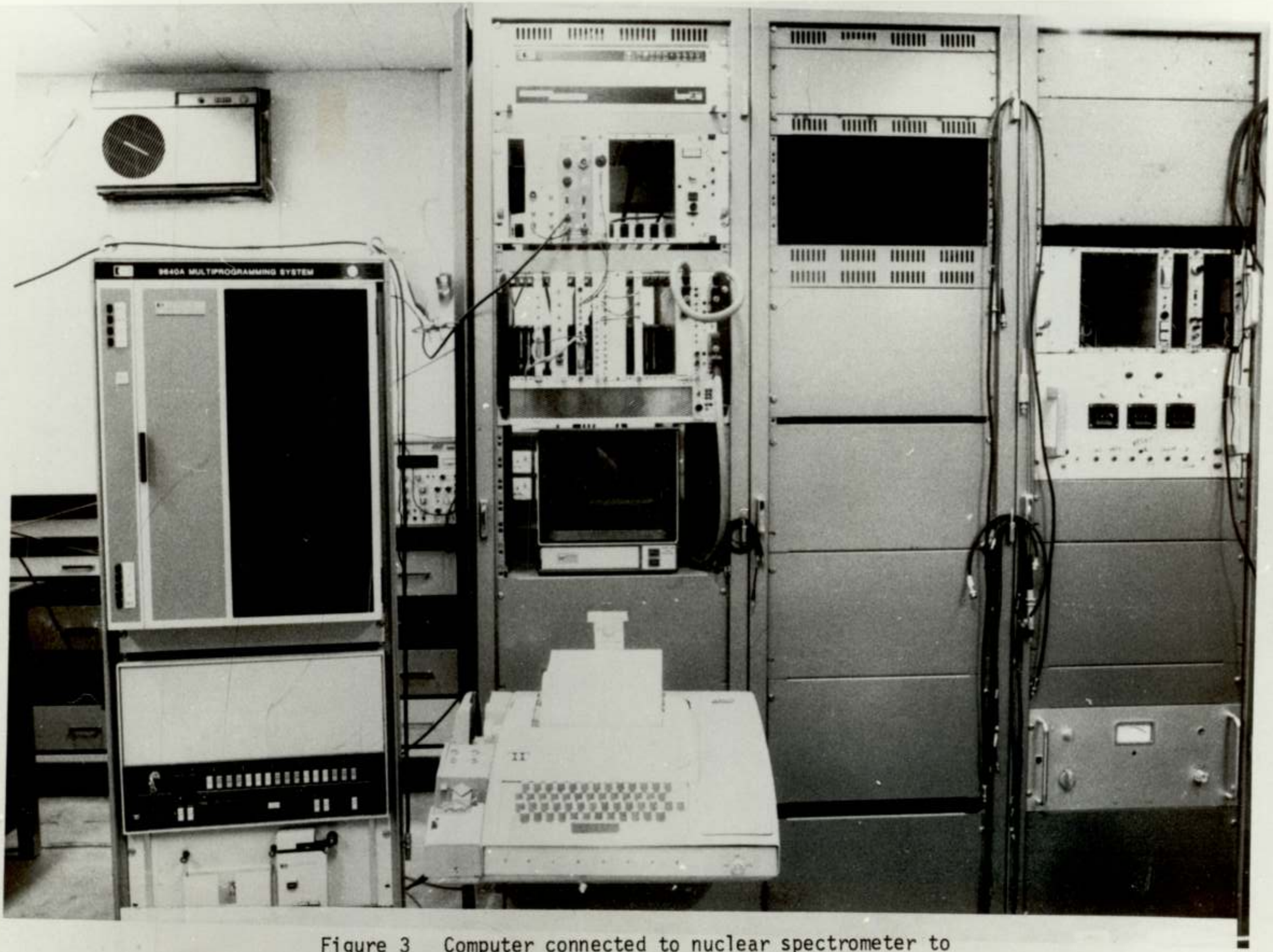


Figure 3 Computer connected to nuclear spectrometer to provide pulse height analysis

```
  START RUN       1
 END OF RUN     1
COM?
PK, 1
MAX POINT=      2000
MAX POINT=       400
MAX POINT=       400
MAX POINT=       200
 PEAK SEARCH AND FIT
 RUN NO.        1
 CHANNELS 1-4096
 ENTER EN(KEV) FOR PEAK IN CHANNEL    252

121.9
 EN=    121.90
 ENTER EN(KEV) FOR PEAK IN CHANNEL    558
279.1
 EN=    279.10
 ENTER EN(KEV) FOR PEAK IN CHANNEL   1008
511.
 EN=    511.00
 ENTER EN(KEV) FOR PEAK IN CHANNEL   1758
898.
 EN=    898.00
 ENTER EN(KEV) FOR PEAK IN CHANNEL   2487
1274.5
 EN=  1274.50
 ENTER EN(KEV) FOR PEAK I
                              N CHANNEL   3572
1836.1
 EN=  1836.10
 NO. OF CALIB. PKS.= 6
 COEF 1=-.80078E+01
 COEF 2= .51450E+00
 COEF 3= .51502E-06
   121.90    121.69    279.10    279.32    511.00    511.09    898.00    897.96
  1274.50  1274.40  1836.10  1836.16
 RMD IN KEV   .567E-01

NP NI  INI  NC  PEAK PO  ENERGY   FWHM    AREA      DELA/A     CHISQ    IT

 1  1  242  21   252.03   121.90  1.49  .668E+03  .797E-01  .222E+
                                                                01    4

 2  2  547  23   558.16   279.10  1.75  .861E+03  .634E-01  .192E+01  3

 3  3  996  26  1007.92   511.00  3.26  .614E+04  .268E-01  .314E+01  4

 4  4 1744  29  1757.83   898.00  2.24  .113E+04  .527E-01  .216E+01  4

 5  5 2472  31  2486.36  1274.50  2.57  .131E+04  .524E-01  .268E+01  4

 6  6 3555  34  3571.65  1836.10  2.81  .579E+03  .473E-01  .782E+00  3
COM?
JX
```

Print-out results of the standard sources

X-ray fluorescence

Philips model PW1212 X-ray fluorescence connected to a plotter was used throughout the study. [Figure 4, page 63].

Shaker

Stuart flask shaker was used in these experiments.

Auto-burette

DOFINAT E 535 auto-burette was used to standardise hydrochloric acid solution using 1 M and 4 M sodium hydroxide solution.

3.4 Analytical methods

3.4.1 Analysis of Zirconium and Niobium using X-ray Fluorescence

This method of analysis was used for non-radioactive samples. Samples may be submitted for analysis in a variety of forms; solids, powders, or liquids. [In this work the samples were in liquid form]. It is important that samples be presented to the spectrophotometer in a homogeneous state and in a manner which can easily be reproduced. In this work the following method was used.

Each sample was placed in a cylindrical plastic container which had a small hole in the bottom covered by a piece of tape. The top of the container was sealed. Four such samples were inverted and placed in a disc-shaped holder. The tape was then removed from the small hole in each container and a beam of x-rays from an x-ray tube was directed onto each sample in turn, producing x-ray fluorescence. A detector converted the X-ray photons into voltage pulses which were amplified and output on a graph plotter.

The energy of the fluorescence radiation which is emitted from the sample is the characteristic 'X'-ray of the elements present in the sample, e.g. $K\alpha$ for niobium = 21.37 KeV and for zirconium $K\alpha$ = 22.17 KeV.

In order to determine the quantity of the elements present in the sample (for this work, zirconium and niobium) standard samples, containing different known amounts of both elements, were analysed and the quantity of radiation emitted at a certain energy was plotted on the graph plotter connected to the instrument, as shown in Fig. 4 . The height of the resulting peak on the graph is directly proportional to the amount of the element involved. Thus, by comparing the height of the peak from the sample under test, one can deduce the amount of a certain element present in the test sample.

It is important to note that the standard samples must be prepared in the same way, i.e. in the same matrix, as the sample, with acid of the same molarity, because it is observed that the concentration of the acid affects the sensitivity of

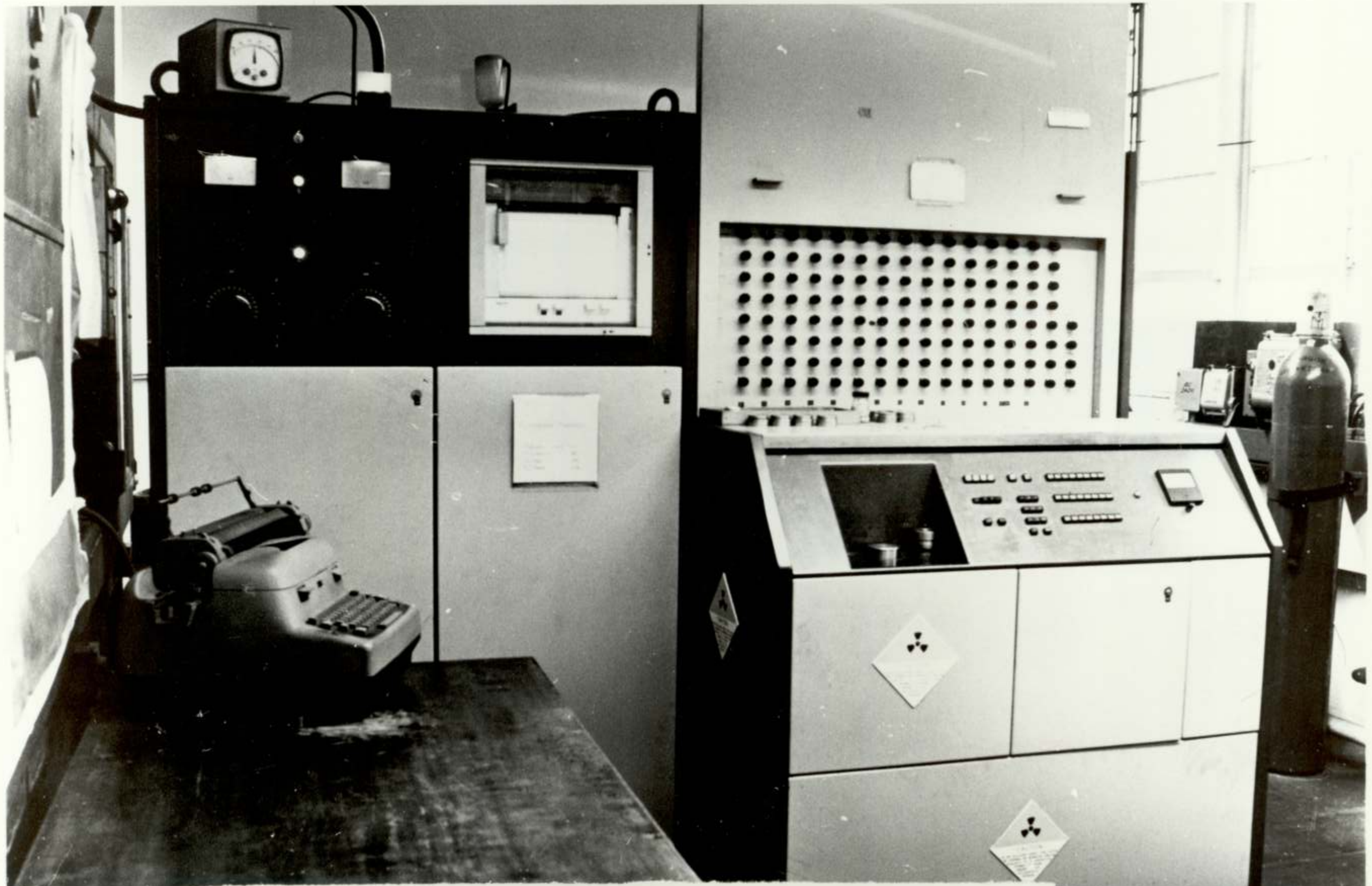


Figure 4   X-ray fluorescence spectrometer

the instrument, i.e. the height of the peak from a sample containing a given amount of an element decreases with increasing acid concentration. This matrix effect needs to be investigated further.

3.4.2 Analysis of Zirconium and Niobium using Nuclear Spectrometer

This method of analysis was used for radioactive samples and the detector which was used was a Ge(Li) detector.

Samples may be submitted for analysis in a variety of forms (solids, powders or liquids) and it is important that the sample is presented in a homogeneous state. (In this work the samples were in liquid and solid form).

In this work the basic procedure was as follows:

1.0 ml fractions (sample from the batch equilibrium studies and the eluant of the silica gel column) were placed in a 10 cm^3 glass tube situated in a specific geometry relative to the detector, as shown in Figure 5.

The gamma rays emitted from the sample are absorbed by the crystal producing positive holes and electrons in proportion to the energy of the incident photons. Migration of these ionization products across the depletion layer will result in voltage pulses which can then be amplified and analogued to a digital computer.

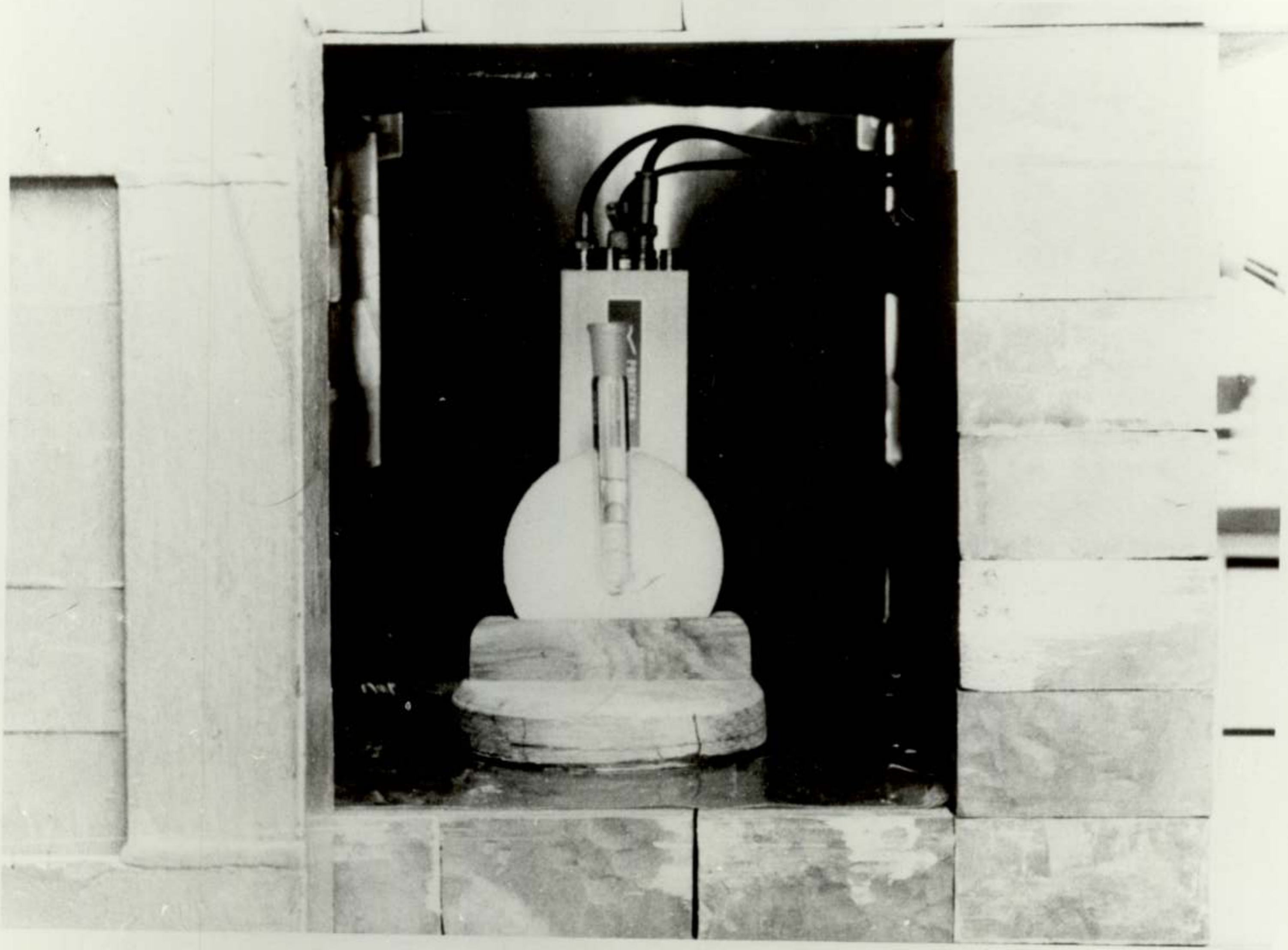


Figure 5 Orientation of sample relative to Ge(Li) detector

The nuclear spectrometer was connected to a digital computer to provide pulse height analysis, in which a special subroutine was used which is capable of both storing and processing data, as well as controlling the display and operation of the instrument. All this information was then given to a computer via a teletype, in the form of a comment. The spectrum of the gamma ray energies was transmitted on the video display. The result was output on the line printer. The relevant detail is shown on page 68.

Note: Before the irradiated sample is dissolved, the induced activity of the sample must be checked to ensure it is under the maximum permissible dose [**5rem/yr**] which is suggested by the International Commission on Radiological Protection [57].

3.4.3 Complex Formation of Zirconium-Alizarin Red-S

The complexation of zirconium with Alizarin Red-S was thoroughly studied and in contrast to what has been generally reported in the literature, it was found that zirconium forms a complex with Alizarin Red-S in the ratio 1:2. Evidence is presented to support this finding by using the well-known continuous variation, slope ratio, and the molar ratio techniques. Interference effects of niobium, cerium, oxalate, fluoride and nitrate were studied. It was found that the Beer Law is obeyed for zirconium concentrations of up to 6 μg/ml.

The basic working procedure was as follows:

To 0.2 ml of concentrated hydrochloric acid contained in a 50 ml volumetric flask, 2 ml of 100 μg/ml zirconium solution and 5 ml of 0.0011 M Alizarin Red-S solution were added. The volume was made up to 50.0 ml with distilled water. The dark cherry colour of zirconium Alizarin Red-S complex was formed. All subsequent measurements of the absorbance of zirconium Alizarin Red-S complex were carried out after 30 minutes at pH 1.3 against distilled water as reference solution in 1 cm cell at 525 nm. More detail is given in Chapter Four.

```
 SET RUN NO.
1
 SET ADC PARMS.
DE
 PRESET TIME
300.

RU
  START RUN      1
COM?
CT
200.
COM?
TI
    200.     149.     0
 PRST TIME   OR RUN STOP     1
 END OF RUN      1
COM?
PK,1
MAX POINT=      5000
MAX POINT=      2000
MAX POINT=         8
MAX POINT=        40
 PEAK SEARCH AND FIT
 RUN NO.       1
 CHANNELS 1-4096
 NO. OF CALIB. PKS.= 0
 COEF 1=-.79199E+01
 COEF 2= .50891E+00
 COEF 3= .53766E-06

NP NI  INI  NC  PEAK PO  ENERGY   FWHM    AREA      DELA/A    CHISQ   IT

 1  1  266  21   276.62   132.90  1.38  .268E+04  .309E-01  .148E+01  4

 2  2  290  22   300.30   144.96  1.40  .118E+05  .
                                                   311E-01  .314E+01  4

 3  3  960  22   971.67   487.13  1.59  .180E+03  .151E+00  .826E+00  5

 4  4  981  23   991.04   497.01  1.64  .323E+03  .256E-01  .140E+01  4

 5  5 1423  26  1435.68   723.93  1.83  .340E+04  .337E-01  .286E+01  4

 6  6 1486  23  1499.36   756.45  1.85  .400E+04  .355E-01  .331E+01  4

 7  7 1508  22  1517.11   765.51  1.80  .641E+04  .371E-
                                                        01  .635E+01  5

 8  8 3124  33  3139.87  1595.80  2.10  .904E+02  .126E+03  .329E+00  4
CCM?
```

Print-out results of 50λ of the stock solution [0.1g of irradiated uranyl nitrate dissolved in 1 M HCl]

Chapter Four Spectrophotometer Determination of Zirconium Using Alizarin Red-S

4.1 Introduction

This chapter describes preliminary work to determine zirconium in the separation and adsorption studies of these elements using silica gel and non-radioactive species.

It was found that the Alizarin Red-S method could be suitably adapted for the determination of zirconium.

The use of Alizarin Red-S as a spot test has been known for a long time[58] and the reagent has been suitably adapted for the quantitative determination of zirconium in such materials as clays and silicate rocks[59], magnesium alloys[60][61] and radioactive samples[62]. In spite of the success of these analytical methods, there is much divergence of views as to the optimum conditions for development of the colour. This may be explained in part as arising from differences in matrixes, but there is some disagreement concerning the stoichiometry of the reaction.

Mayer and Bradshaw[60] report that a 1.26:1.00 zirconium-Alizarin Red-S complex is formed and their calculations from the data given by Green[59] give a value of 1.24 but there is no indication about the purity of Green's Alizarin Red-S. Flagg et al[63] found a value between 1.0 and 1.4 using alcoholic alizarin whilst Drăgulescu et al[64] established optimum conditions by use of trichloro acetic acid to stabilise the zirconium followed by butanol extraction, and found that a 1:1 complex was formed .

After reviewing all the available literature (much of which is summarised later in the chapter), it was found that differing results were given for the optimum condition for formation of the zirconium-Alizarin Red-S complex. None of these papers has mentioned the possible interference of niobium with the reagent.

For this reason, it was decided to investigate the reaction thoroughly and at the same time re-examine the conditions for the development of the colour and the interference of niobium with Alizarin Red-S.

4.2 Experimental

All reagents and apparatus used in this experimental work were mentioned in Chapter Three.

4.2.1 Absorption spectra of the Zirconium Alizarin Red-S Complex (Fig. 6)

To 0.2 ml of concentrated HCl contained in a 50 ml

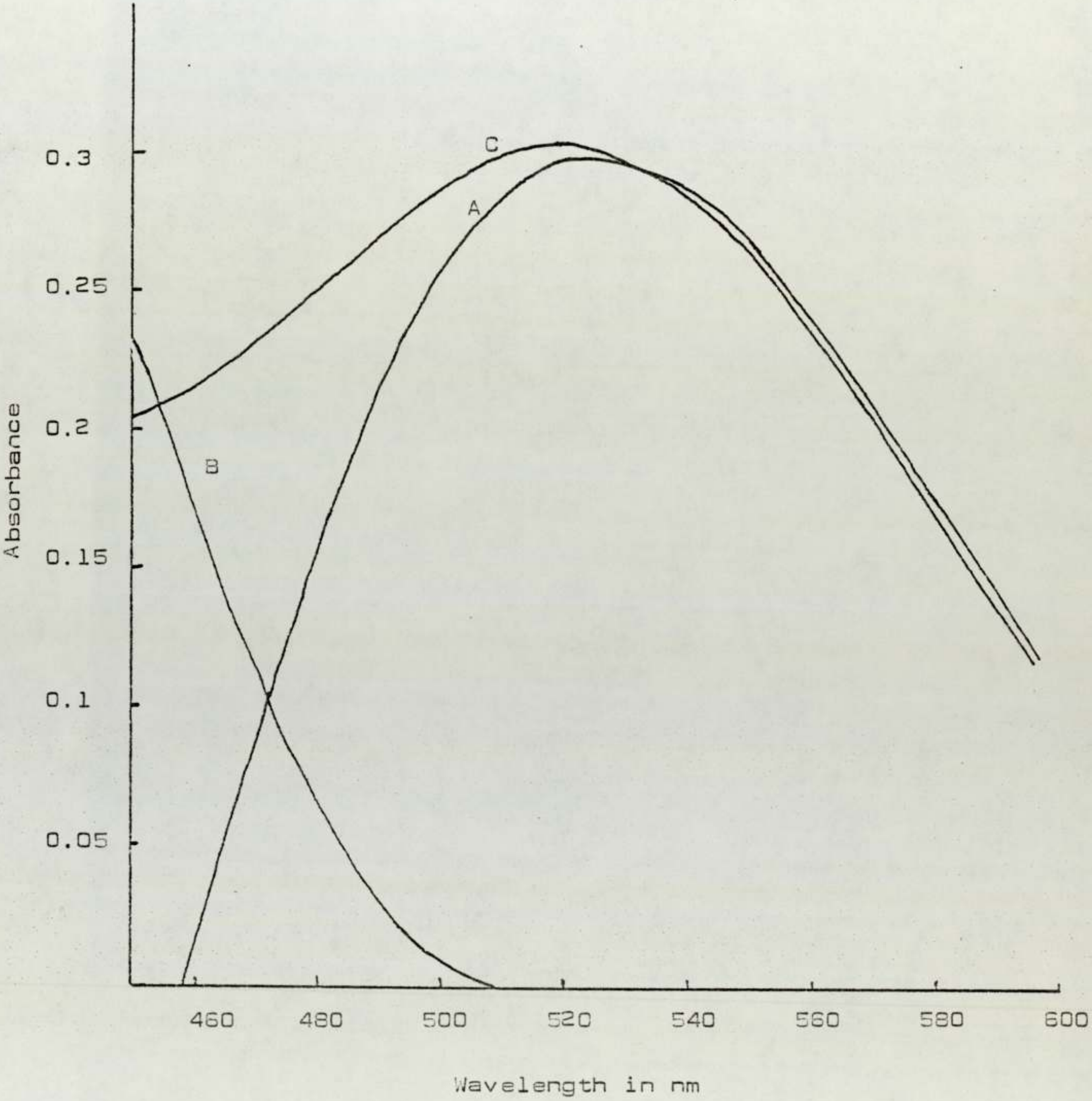


Figure 6 Absorption spectra

A. Zirconium-Alizarin Red-S lake against Alizarin Red-S in distilled water

B. Alizarin Red-S in water against distilled water

C. Zirconium-Alizarin Red-S lake against distilled water volumetric flask, 2 ml of 0.0011 M Zirconium solution and 5 ml of 0.0011 M Alizarin Red-S solution were added. The volume was made up to 50.0 ml with distilled water and the absorption spectra measured against Alizarin Red-S and distilled water. The absorption spectra of Alizarin Red-S was also measured against distilled water as reference solution. All subsequent measurements were carried out at 525 nm.

4.2.2 Conditions for the Formation of the Zirconium - Alizarin Red-S Lake (Fig. 7)

The influence of pH on the absorption of the zirconium-alizarin lake was examined by adding 5 ml of 0.0011 M Alizarin Red-S reagent to 200 μg quantities of zirconium, and diluting to 50 ml with varying quantities of hydrochloric acid. All absorption readings were made after 30 minutes. The optimum conditions were obtained at pH 1.3.

4.2.3 Colour Development and Stability (Fig.8)

The colour development at room temperature and by heating on a waterbath (as recommended by Mayer and Bradshaw(60) was studied at pH 1.3 by measuring the absorption of solutions produced by treating 200 μg Zr with 5 ml 0.05% Alizarin Red-S reagent and making up to 50 ml after addition of the appropriate amount (0.2 ml) of concentrated hydrochloric acid.

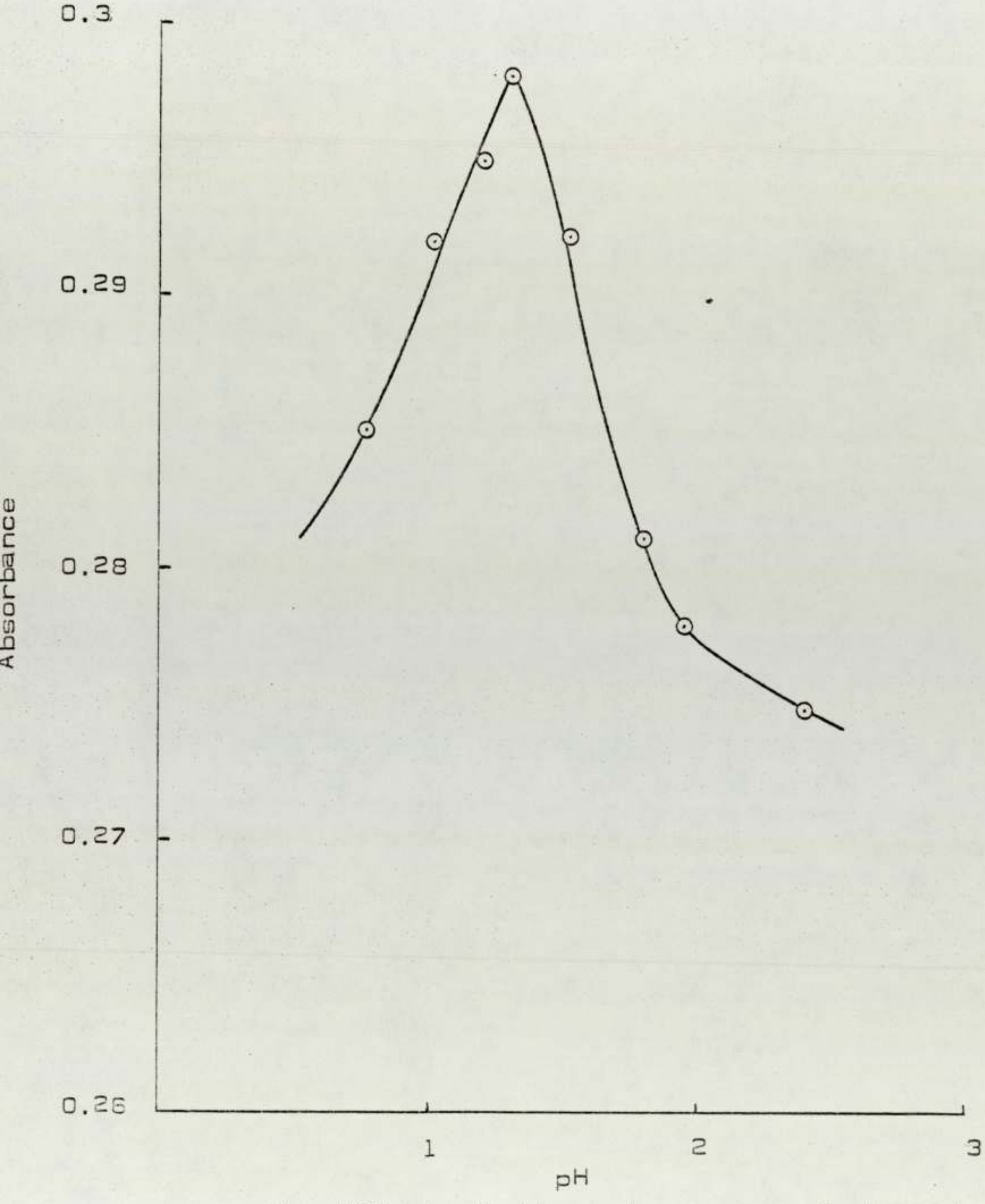


Figure 7 Effect of pH on absorbance of zirconium-Alizarin Red-S complex

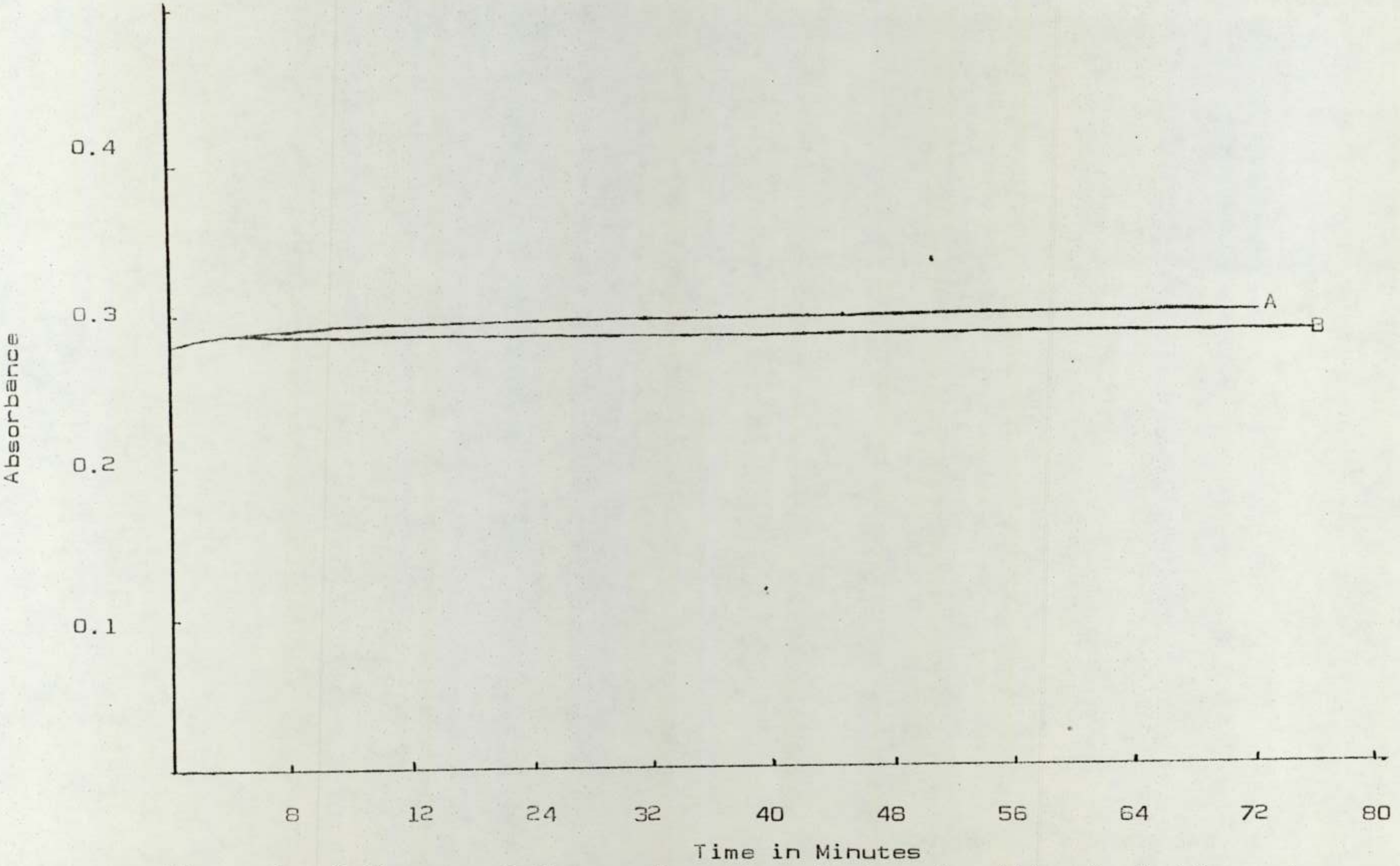


Figure 8 Influence of time on formation of zirconium-Alizarin Red-S complex

A. Formation of zirconium-Alizarin Red-S complex heating for 2½ minutes in boiling water bath

B. Formation of zirconium-Alizarin Red-S complex without heating

4.2.4 Influence of the Amount of Alizarin Red-S on the Formation of the Zirconium Alizarin Red-S Complex [Fig. 9]

The absorbance of solutions containing 200 µg Zr with various amounts of 0.0011 M Alizarin Red-S reagent all adjusted to pH 1.3 and diluted to 50 ml with distilled water were measured and it was found that 4 ml of reagent was sufficient to give the maximum absorbance with 200 µg Zr.

4.2.5 Effect of the Ageing of the Zirconyl Chloride Solution [Figs. 10 and 11]

The absorbance of the zirconium-Alizarin Red-S complex of solutions containing 200 µg Zr/50 ml, pH 1.3, was measured in solutions which had been allowed to age for various periods of time.

4.2.6 Beer's Law Studies [Fig.12]

The absorbance of solutions of the zirconium-Alizarin Red - S complex containing varying amounts of zirconyl chloride up to 600 µg Zr/50 ml at pH 1.3, showed that Beer's Law was obeyed up to 300 µg Zr/50 ml i.e. 6 µg/ml.

4.2.7 Composition of the Zirconium-Alizarin Red-S Complex [Figs.13,14, and 15]

Continuous variation curves, slope ratio and molar

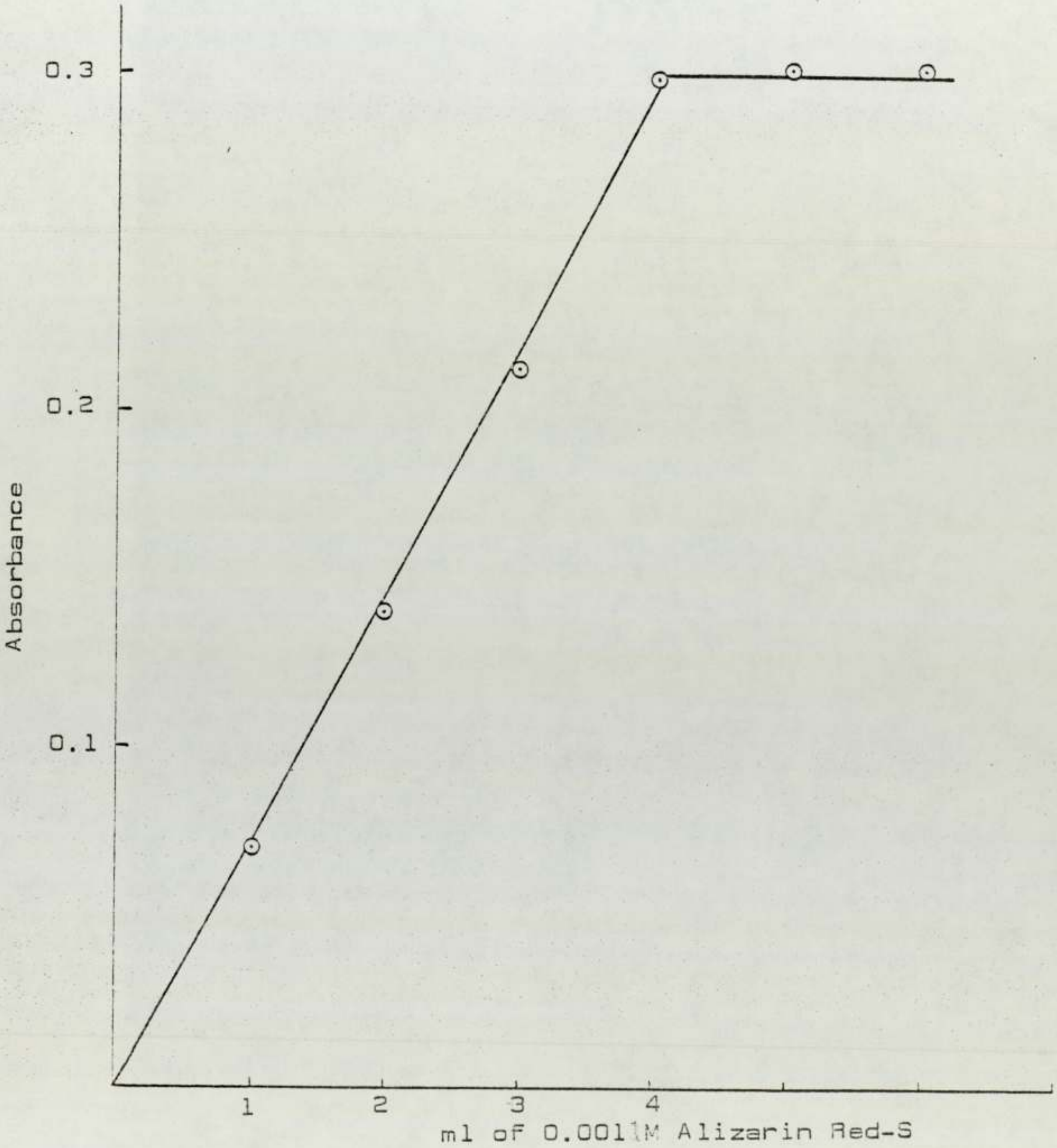


Figure 9 Influence of the amount of Alizarin Red-S on the formation of the zirconium-Alizarin Red-S complex

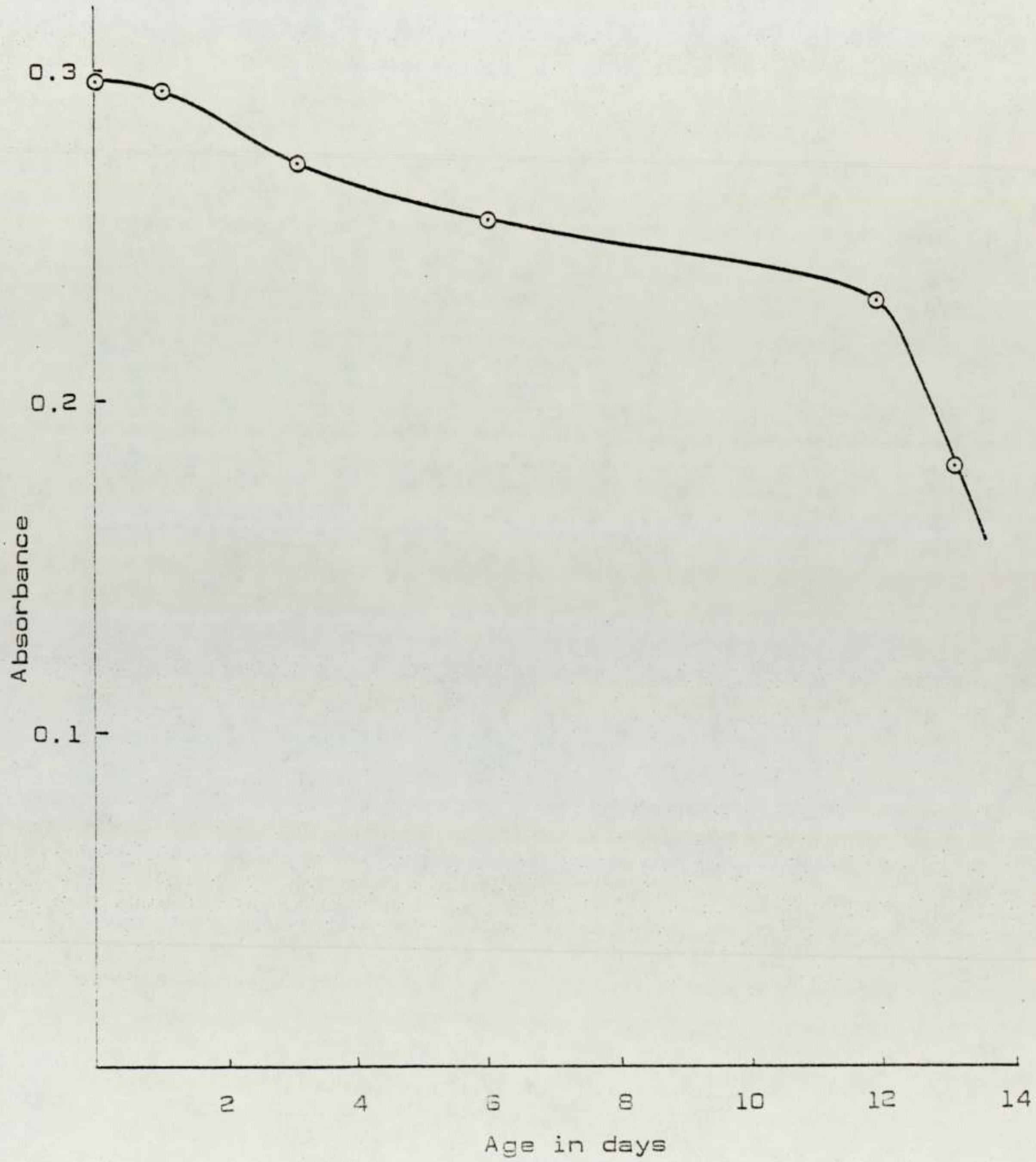


Figure 10 Effect of the age of zirconyl chloride solution on the absorbance of the zirconium-Alizarin Red-S complex

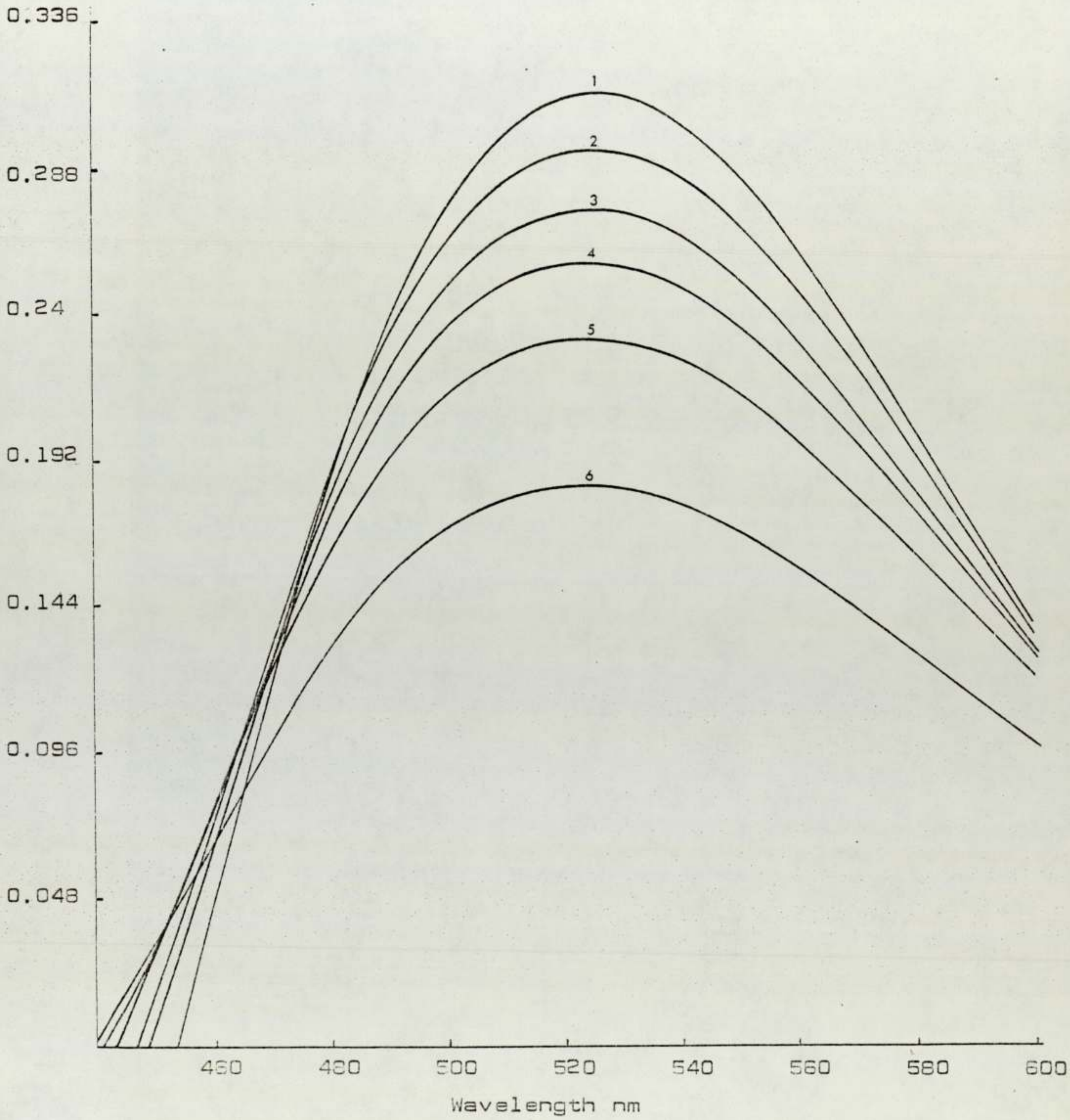


Figure 11 Absorption spectra of zirconium-Alizarin Red-S complex prepared from zirconyl chloride solution of varying age

1. Fresh solution
2. 1-day old solution
3. 3-day old solution
4. 6-day old solution
5. 12-day old solution
6. 13-day old solution

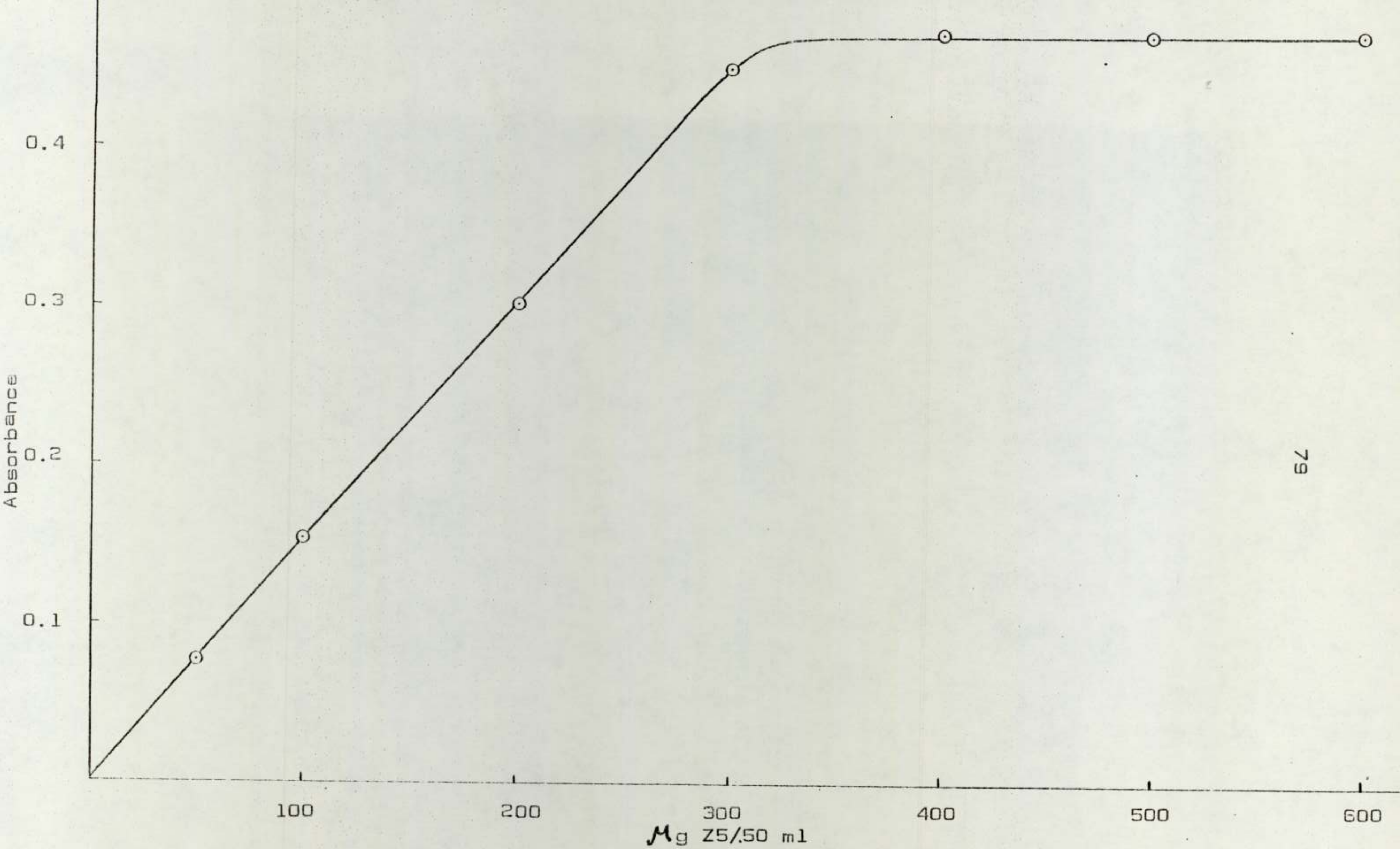


Figure 12 Beer's Law plot

ratio method were used to study the stoichiometry of the complex[64].

All solutions used in the stoichiometry study were adjusted to pH 1.3 and all absorbances were measured at 525 nm using 1 cm cells.

Continuous variations curves were obtained by mixing in different ratios 0.0011 M zirconium solution and 0.0011 M Alizarin Red-S solution and diluted to 50 ml (Fig. 13].

mls of 0.0011 M Zirconium solution	mls of 0.0011 M Alizarin Red-S
3.0	0.0
2.5	0.5
2.0	1.0
1.5	1.5
1.0	2.0
0.5	2.5
0.25	2.75
0.0	3.0

The slope ratio plots were obtained by using the following solutions:

(a) Various amounts of 0.0011 M zirconium solution (0.5,1.0, 1.5, 2.0, 2.5, 3 and 5) mls with 5 ml of 0.1% Alizarin Red-S (the constant component) the volume of each being made up to 50 ml (Line A, Fig. 14).

(b) Various amounts of 0.0011 M Alizarin Red-S solution (0.5, 1.0, 1.5, 2.0, 2.5 and 3.0) mls with 5 ml of 0.0011 M zirconium solution (the constant component) the volume of each being made up to 50 ml (Line B, Fig. 14).

Molar ratio plots were obtained by adding 2 ml of a 0.0011 M Zirconium solution to varying amounts of 0.0011 M Alizarin Red-S solution (1.0, 2.0, 3.0, 4.0, 5.0, 6.0 and 7.0) mls and making the volume up to 50 ml.
The results obtained are plotted in Fig. 15 .

4.2.8 Effect of Foreign Ions

The influence of some foreign ions on the colour development was investigated by adding up to 200 μg/50 ml of the possible interfering ion to fixed amounts of zirconium 200 μg/50 ml.

4.3 Results and Discussion

Slightly differing wavelengths for the absorption maximum have been reported by various workers. Mayer and Bradshaw(60) recommend 560 nm whilst Wengert(61) use 510 nm. From Fig. 6 it is clear that the absorption maximum occurs at 525 nm in agreement with the value quoted by Green(59) (520 nm). Manning et al(66) studied the differential spectrophotometric determination of zirconium in perchloric acid solutions and recommended 530 nm.

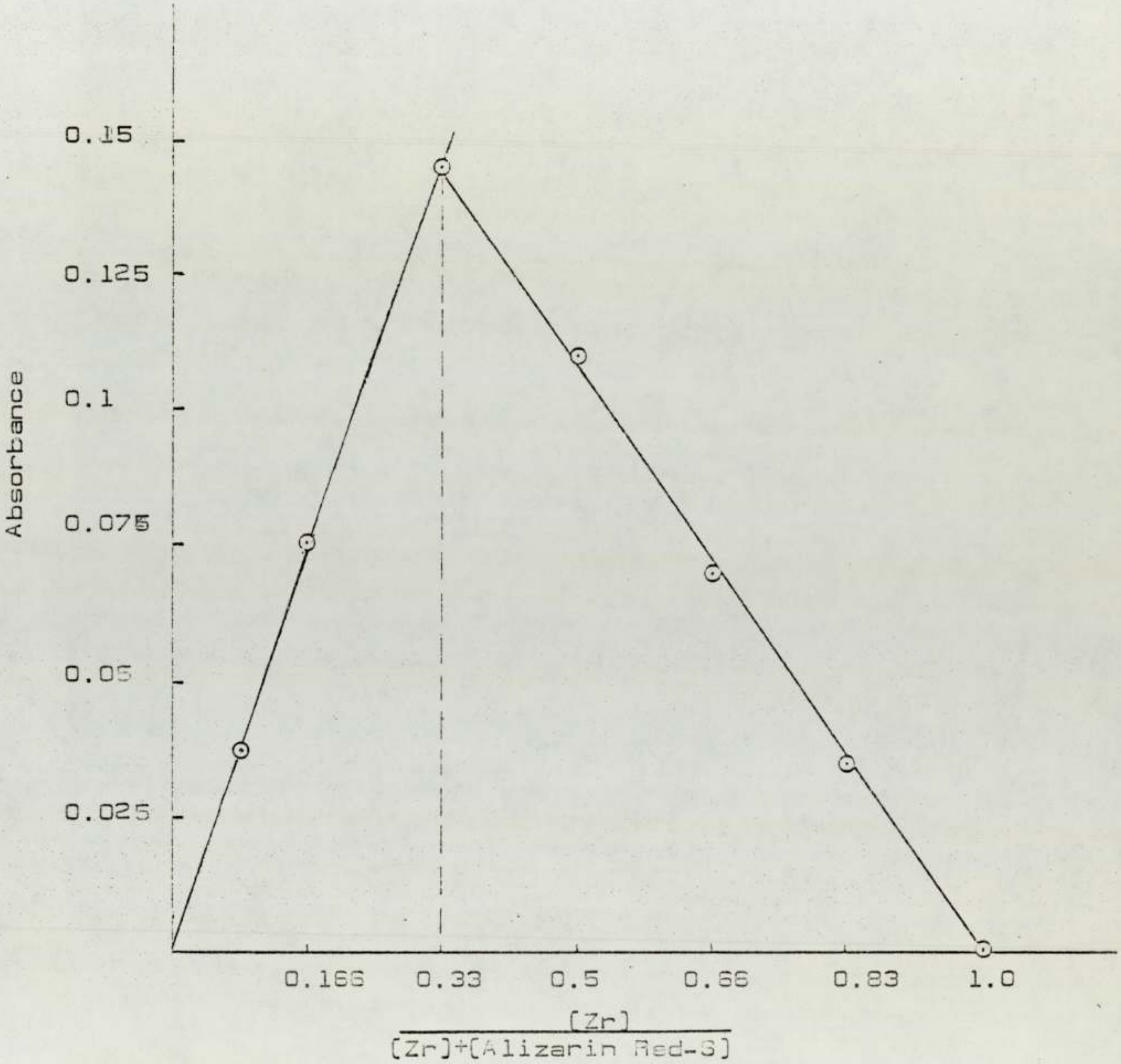


Figure 13 Continuous variation curves for various ratios of 0.0011 M zirconium solution and 0.0011 M Alizarin Red-S

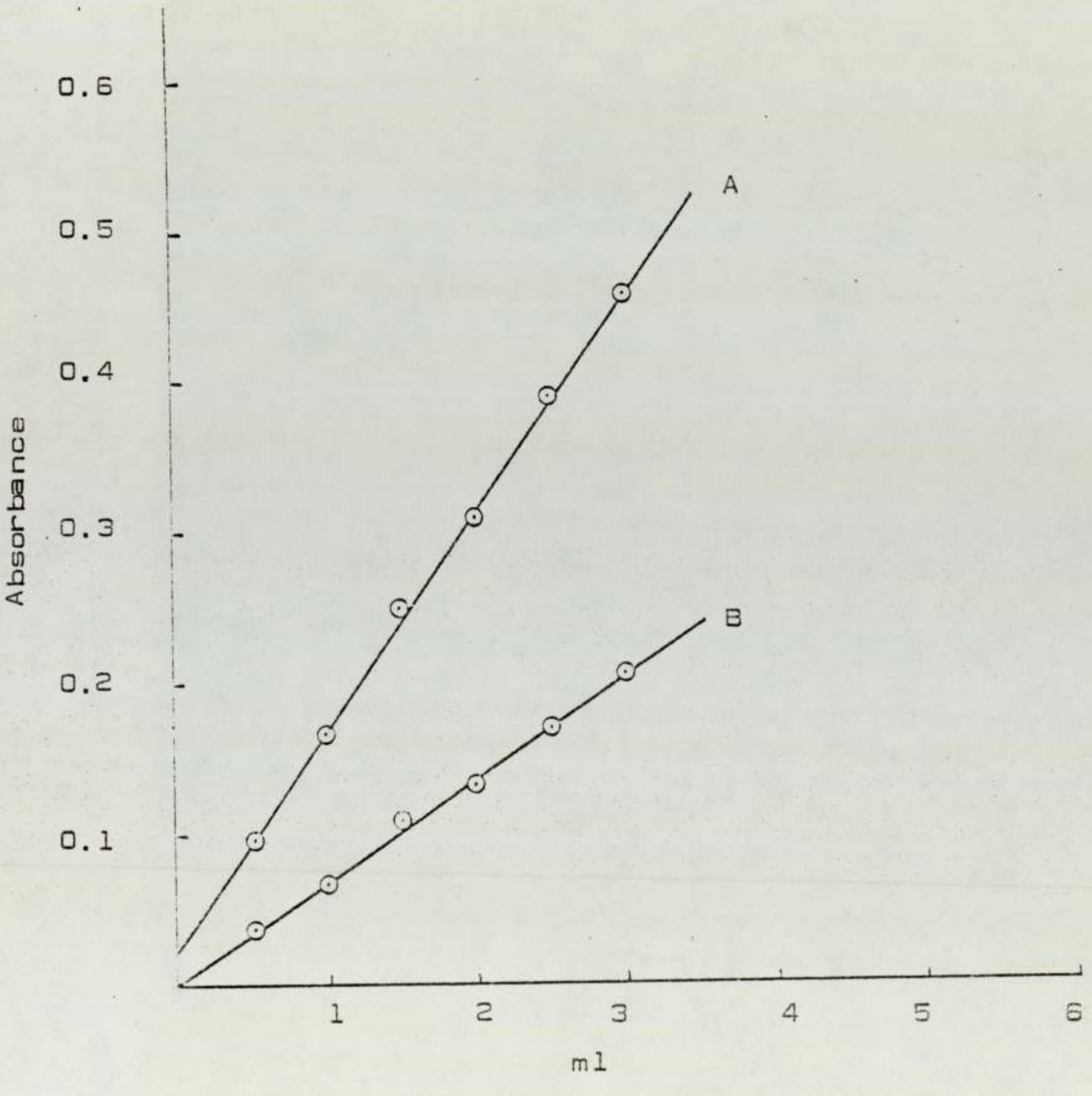


Figure 14 Slope ratio curves for zirconium-Alizarin Red-S complex

A. Various amounts of 0.0011 M zirconium solution with 5 ml of 0.1% Alizarin Red-S per 50 ml of solution
Slope A = 1.4×10^{-1}

B. Various amounts of 0.0011 M Alizarin Red-S with 5 ml of 0.0011 M zirconium solution per 50 ml of solution
Slope B = 6.8×10^{-2}

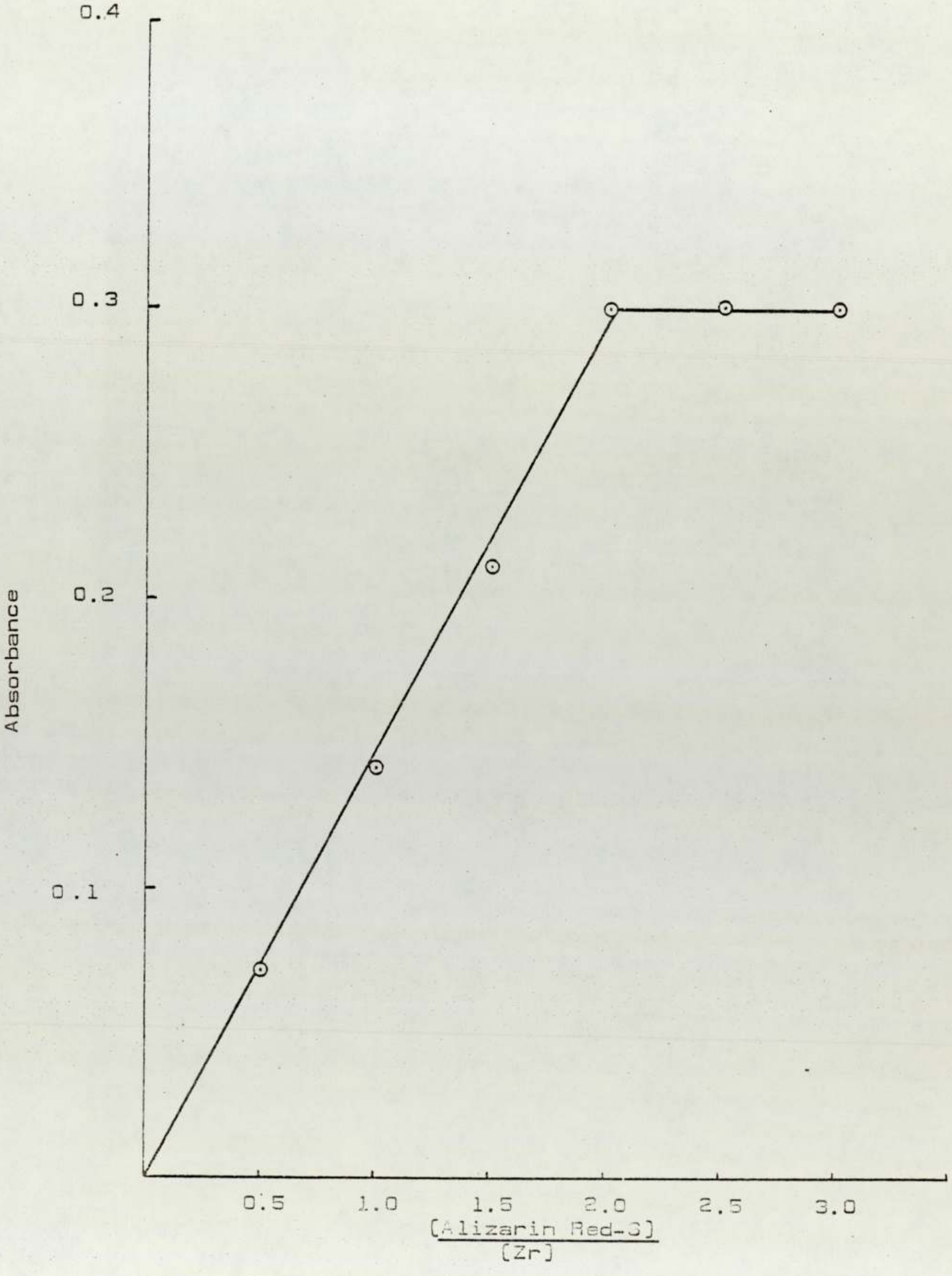


Figure 15 Molar ratio curves for zirconium Alizarin Red-S Complex

It is well established that above pH 2.8 zirconium solutions hydrolyse rapidly and that precipitation of the hydroxide occurs. Mayer and Bradshaw(60) have commented on the equilibria involved, and that 'it is not safe to boil a solution with an acid concentration of less than 0.5 M' (HCl). Their recommended procedure is to develop the zirconium Alizarin Red-S complex at 100°C for not less than 2½ minutes and not more than 3½ minutes. Green(59) recommends a pH of 1.1 and at least 20 hours for colour development. From Fig.7 it can be seen that the pH for colour development is critical. Higher concentrations of acid either decrease the absorbance of the complex or inhibit its formation because of the limitation of the dissociation of ligand (Alizarin Red-S) when insufficient alizarin ions will be available. Another competing reaction may be the formation of chlorozirconium species in strong acid solution. The optimum pH condition for the formation of the zirconium-Alizarin Red - S complex is 1.3 in hydrochloric acid solution. Manning and White(66), who use perchloric acid solutions note that 'the acidity generally used is in the pH range of 1 to 2' for colour development by other workers but they do not present any data for their own work recommending that the pH is critical. Drăgulescu et al(64) recommend the use of trichloroacetic acid to stabilise the lake in hydrochloric acid followed by butanol extraction over a large range of pH but they do point out that best pH conditions for the initial formation of the complex are limited to a very narrow pH range (optimum value 1.15). They also claim that a 1:1 complex is formed in aqueous solution, a point which we dispute. Green[59] states that 'the pH should be 1.1'.

Having established that the optimum conditions for colour development may be obtained at pH 1.3, all subsequent experimental work was carried out at this pH. We find that the reaction is complete within 30 minutes (Fig. 8) and that the colour is stable for at least 24 hours. Green[59] suggested that the colour development be allowed to proceed overnight or 20 hours. Mayer and Bradshaw[60] overcame all the difficulties of colour development by heating the reagents above 85°C for 2 minutes in 1.5 N acid which, it is claimed, increases the rate of reaction with alizarin and converts hydrolysed zirconium compounds to zirconyl ions. In the method of Drăgalescu et al, the addition of the trichloroacetic acid 'stabilises' the lake and enables extraction over a large range of pH.

The influence of varying amounts of Alizarin Red-S on the formation of the complex is shown in Fig. 9 4 ml of 0.0011 M Alizarin Red-S are sufficient to develop the colour for 200 μg Zr/50 ml.

It is well known that zirconium solutions polymerise and hydrolyse in acid solution. Connick and Reas[67] have studied the reaction in perchloric acid solutions of moderate acidity. In the colorimetric method any ageing or hydrolysis(60) of the zirconyl solutions prior to addition of the Alizarin Red-S reagent will be reflected in an absorbance lower than expected when the colour is finally developed. Even before precipitation occurs, hydrolysis takes place and to prevent this stock solutions of zirconium should be prepared in strong (1M) HCl. The effect of ageing of a zirconium solution is shown in Figs. 10 and 11 .

The Beer's Law plot of the zirconium Alizarin Red-S colour developed as in the recommended conditions (see Fig. 12) shows that the linear relationship is found up to 6 μg Zr/ml when 0.0011 M Alizarin Red-S is used.

As mentioned in the introduction, there is some disagreement concerning the stoichiometry of the reaction between zirconium and Alizarin Red-S. Our results show (Fig. 13 - continuous variation curve) (Fig. 14 - slope ratio method) and (Fig. 15 - molar ratio method) that the complex is 1:2. The experiments were carried out as described by Harvey and Manning(65).

The interferences in the alizarin method are well known and have been reported elsewhere(60)(61)(66). For our study, we were only interested in the effect of ions likely to be present in the particular application we are studying, viz., absorption studies on silica gel and the separation of zirconium from other elements. Ions which form stronger complexes with zirconium than does Alizarin Red-S, such as fluoride and oxalate interfere. Oxidising agents such as nitric acid which bleach the complex must also be absent. We find that up to an equimolar quantity of cerium does not cause a reduction in the absorbance of the zirconium-Alizarin Red-S complex, but niobium in even small amounts interferes.

4.4 Conclusion

As we will see in Chapter Five, separation of zirconium occurs in a medium of 5.5 M HCl. From section 4.2.2, we have found that optimum conditions for formation of the complex are attained at pH 1.3. Because of this, and because (from section 4.3) it was found that niobium, even in small quantities, interferes with the formation of the complex, Alizarin Red-S cannot be used for the determination of zirconium in this research.

Chapter Five Separation of Zirconium and Niobium by Silica Gel Adsorption

5.1 Introduction

Many workers have studied the behaviour of silica gel, with regard to its adsorption of zirconium and niobium from the fission products and as a medium for separation of the elements from each other (as mentioned in Chapter One). However, the work reported to date is not sufficiently detailed, and there are differences in the published results from paper to paper. It was therefore considered worthwhile to investigate the adsorption and desorption behaviour of silica gel using these elements and the reagents and methods of analysis outlined in Chapter Three.

It was decided to work initially with non-radiated samples, both to gain experience and to study the adsorption of zirconium and niobium by silica gel. Later, the work would be extended to irradiated uranyl nitrate samples from the Iraqi Nuclear Reactor.

5.2 Experimental

5.2.1 Preparation of samples

1. Non-radiated samples

The freshly prepared stock solution used in all experiments was 1.0 ml of niobium standard solution (10000 ppm), pipetted in a 25 ml volumetric flask. 5.0 ml of zirconium standard solution (1000 ppm) was then added and the solution made up to volume with distilled water.

14 samples of 1.0 ml of the stock solution were pipetted into a series of 20 ml volumetric flasks and different quantities of concentrated hydrochloric acid were added to each flask in order to produce solutions of 0.1 M, 0.5 M, 0.8 M, 1 M, 2 M, 3 M, 4 M, 5 M, 6 M, 7 M, 8 M, 9 M, 10 M and 11 M hydrochloric acid concentration. Each flask was then made up to volume with distilled water.

2. Irradiated samples

The tracer used in all experiments was 0.1 g of irradiated uranyl nitrate in the Iraqi Nuclear Reactor. The irradiation time was 24 hours with flux 2.4×10^{13} n/cm^2/sec and the cooling time was 100 days. The irradiated target was dissolved in 2 ml of concentrated nitric acid and 3 ml of concentrated hydrochloric acid. The solution containing the radioactivity was evaporated to dryness. The process of dissolution and evaporation was repeated three times in order to drive off gases and the volatile radioactive material from the matrix of the active solution. The residue remaining after the last evaporation step was taken up in 5 ml of 1 M hydrochloric acid, as a stock solution for further investigation.

50 γ of the stock solution was pipetted into a test tube and made up to 1 ml with distilled water and its activity was then measured by a Ge(Li) detector.

5.2.2 Batch equilibrium studies for silica gel adsorption

1. Non-radiated samples

Experiment A

In the batch equilibrium study, 1g samples of silica gel (14 samples) were shaken for 18 hours with 10 ml samples of 0.1 M, 0.5 M, 0.8 M, 1 M, 2 M, 3 M, 4 M, 5 M, 6 M, 7 M, 8 M, 9 M, 10 M and 11 M hydrochloric acid solutions (prepared as outlined in section 5.2.1 - 1) in plastic bottles (V = 50 ml). Then from each sample, after settling, 7 ml of solution was pipetted into a plastic container and the amount of zirconium and niobium was measured by an X-ray fluorescence technique, as described in Chapter Three. The results are shown in Table 2 Figure 16.

The amount of zirconium and niobium on the silica gel was obtained from the difference between the original amount of these two elements in the feed solution and the amount in the aqueous solution.

Experiment B

In the batch equilibrium study, 1g samples of silica gel (12 samples) were shaken for 18 hours, in plastic bottles,

Sample	Total μg Zr	% Zr	Total μg Nb	% Nb	Total μg Mo	% Mo
Stock solution loaded +	100.0	100.0	200.0	100.0	20	20
0.1 M HCl	5.0	5.0	8.0	4.0	20	20
0.5 M HCl	4.0	4.0	8.2	4.1	20	20
0.8 M HCl	12.1	12.1	8.0	4.0	20	20
1.0 M HCl	19.2	19.2	6.4	3.2	20	20
2.0 M HCl	41.0	41.0	7.0	3.5	20	20
3.0 M HCl	60.4	60.4	8.6	4.3	20	20
4.0 M HCl	79.6	79.6	8.5	4.25	20	20
5.0 M HCl	100.0	100.0	10.0	5.0	20	20
6.0 M HCl	100.0	100.0	12.0	6.0	20	20
7.0 M HCl	99.6	99.6	36.0	18.0	20	20
8.0 M HCl	99.4	99.4	76.0	38.0	20	20
9.0 M HCl	99.8	99.8	160.2	80.1	20	20
10.0 M HCl	100.0	100.0	195.0	97.5	20	20
11.0 M HCl	99.6	99.6	200.0	200.0	20	20

Table 2 Batch Equilibrium Study - Effect of hydrochloric acid on the adsorption of Zr, Nb, Mo on silica gel. In this table, figures for Zr, Nb and Mo in the columns refer to the percentages not adsorbed

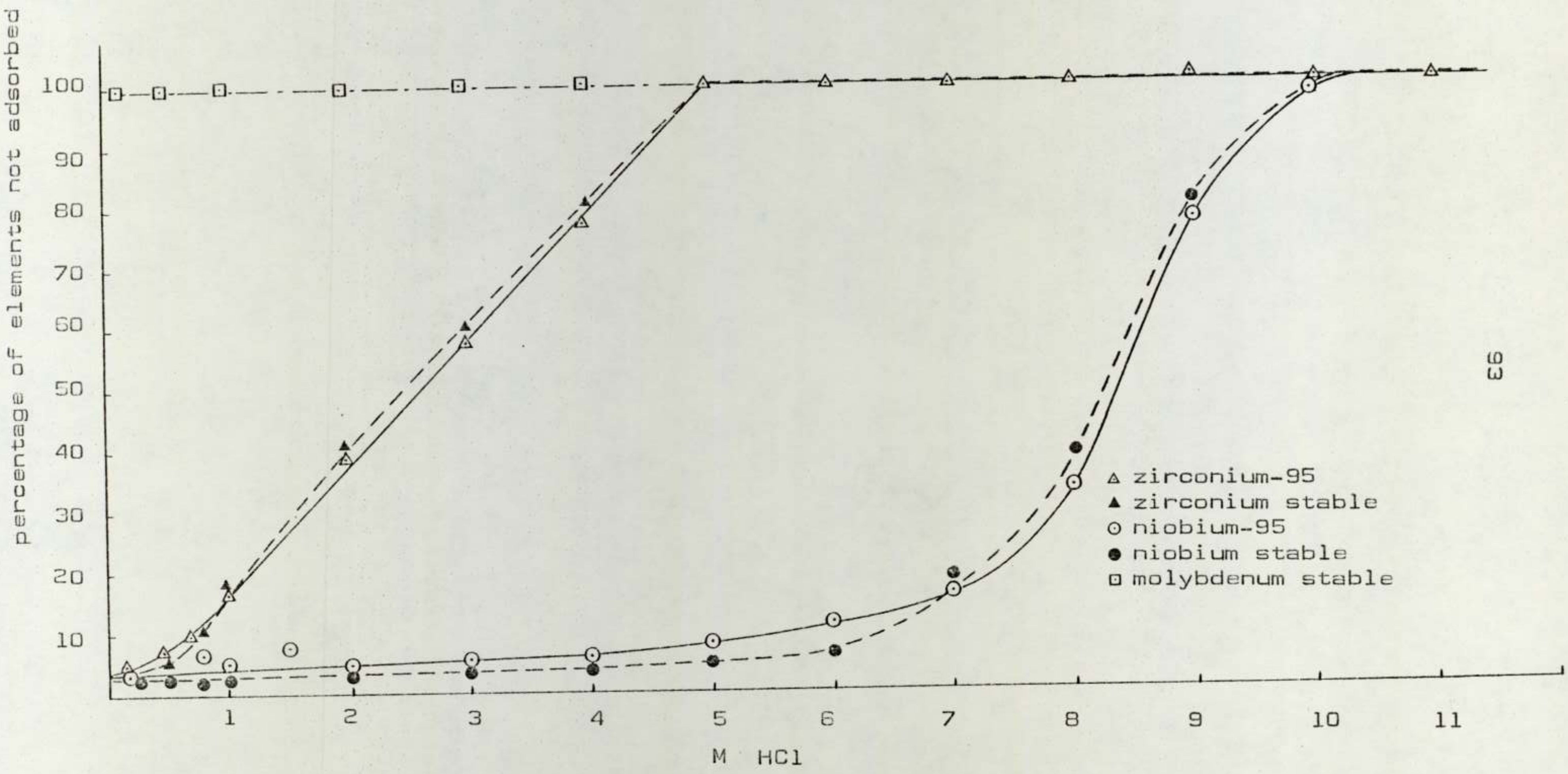


Figure 16 Batch Equilibrium Study - Effect of hydrochloric acid on the adsorption of zirconium, niobium and molybdenum

with 10 ml samples of 0.1 M, 0.5 M, 5 M and 6 M hydrochloric acid solutions (prepared as mentioned in section 5.2.1 - 1) together with oxalic acid of different molarities. The first group contained 0.01 M oxalic acid, the second group 0.025 M oxalic acid, and the third group 0.05 M oxalic acid. Then, after settling, 7 ml of each solution was pipetted into a plastic container and the amounts of both elements, zirconium and niobium, were measured as described above. Results are shown in Table 3.

Experiment C

In the batch equilibrium study, 1g samples of silica gel were shaken with 10 ml samples of 0.5 M hydrochloric acid solution (prepared as mentioned in section 5.2.1 - 1) in plastic bottles. Then, after settling, 7 ml of each solution was pipetted into a plastic container, and the amounts of both elements, zirconium and niobium, were measured as described above. The results are shown in Table 4 Figure 17.

All experiments were carried out at room temperature.

2. Non-radiated samples containing molybdenum

As mentioned in section 5.2.1 - 2, the cooling time of the irradiated samples was 100 days, i.e. there is a stable isotope of molybdenum with the radioactive nuclide.

Sample	Total μg Zr	% Zr	Total μg Nb	% Nb
Stock solution loaded	100	100	200	200
1. 0.01 M $H_2C_2O_4$ +				
0.1 M HCl	100	100	200	200
0.5 M HCl	100	100	200	200
5.0 M HCl	100	100	200	200
6.0 M HCl	100	100	200	200
2. 0.025 M $H_2C_2O_4$ +				
0.1 M HCl	100	100	200	200
0.2 M HCl	100	100	200	200
5.0 M HCl	100	100	200	200
6.0 M HCl	100	100	200	200
3. 0.05 M $H_2C_2O_4$ +				
0.1 M HCl	100	100	200	200
0.5 M HCl	100	100	200	200
5.0 M HCl	100	100	200	200
6.0 M HCl	100	100	200	200

Table 3 Batch Equilibrium Study - Effect of oxalic acid on the adsorption of Zr and Nb on silica gel. In this table, figures for Zr and Nb in the columns refer to the percentages not adsorbed

Sample	Shaking time in hours	Total µg Zr	% Zr	Total µg Nb	% Nb
Stock solution loaded		100.0	100.0	200.0	100.0
0.5 M HCl	2	89.0	89.0	178.4	89.2
0.5 M HCl	4	53.3	63.2	110.6	55.3
0.5 M HCl	6	26.6	26.6	54.0	27.0
0.5 M HCl	8	6.1	6.1	11.0	5.5
0.5 M HCl	10	5.6	5.6	10.8	5.4
0.5 M HCl	12	5.5	5.5	9.8	4.9
0.5 M HCl	14	5.1	5.1	10.4	5.2
0.5 M HCl	16	4.8	4.8	10.6	5.3
0.5 M HCl	18	5.0	5.0	10.4	5.2

Table 4 Batch Equilibrium Study - Effect of shaking time on the adsorption of Zr and Nb on silica gel. In this table, figures for Zr and Nb in the columns refer to percentages not adsorbed

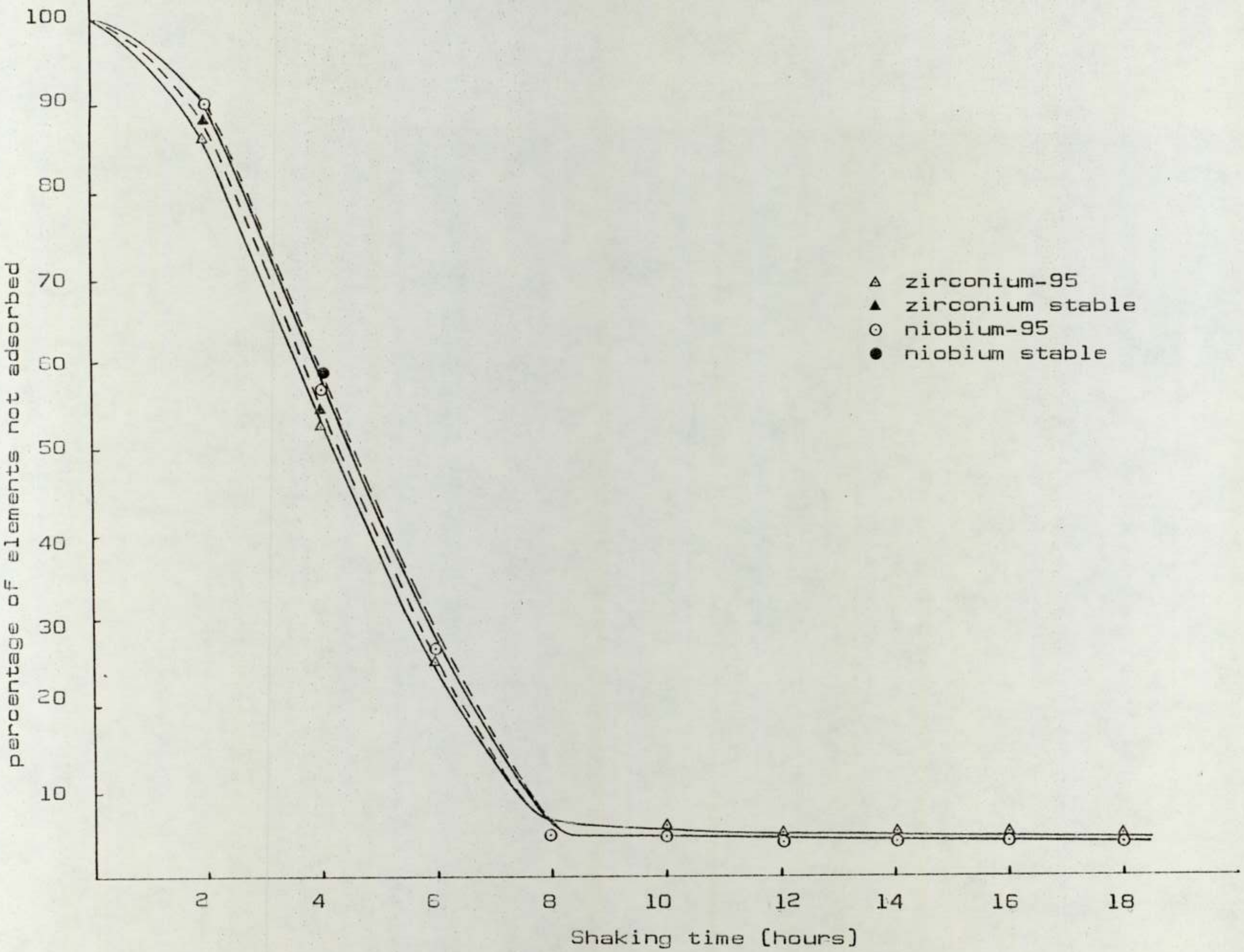


Figure 17 Batch Equilibrium Study - Effect of shaking time on the adsorption of zirconium and niobium

This stable isotope cannot be measured or detected by a Ge(Li] detector. For this reason, and to study the chemical purity of the separated nuclide, experiment A, which was carried out in section 5.2.2 - 1, was repeated, but with the addition of 2 ppm molybdenum. The results are shown in Table 2 Figure 16.

3. Irradiated samples

Experiment A

In the batch equilibrium study, 0.1g samples of silica gel [14 samples] were shaken for 18 hours with 5 ml solutions made up of 50γ from the stock solution [prepared as mentioned in section 5.2.1 - 2] and 0.1 M, 0.5 M, 0.8 M, 1 M, 2 M, 3 M, 4 M, 5 M, 6 M, 7 M, 8 M, 9 M, 10 M and 11 M hydrochloric acid solutions in plastic bottles [V = 50 ml]. Then, after settling, 1 ml of each solution was pipetted into a test tube and its activity was measured using a Ge[Li] detector. The results are shown in Table 5 Figure 16.

The activity on the silica gel was obtained from the difference in the activity of the feed solution and that of the aqueous solution. The amount of the activity adsorbed on the surface of the plastic bottles was found to be negligible.

All experiments were carried out at room temperature and in a glove box surrounded by lead blocks to minimize the danger from radioactive material.

Sample	754.0 KeV Zr-95	% Zr-95	764.0 KeV Nb-95	% Nb-95	133.4 KeV Ce-144	% Ce-144	497.27 KeV Ru-103	% Ru-103
Stock soln. [50γ]loaded +	0.55×10^4	100.0	0.78×10^4	100.0	0.33×10^4	100.0	0.46×10^4	100.0
0.1 M HCl	0.30×10^3	6.5	0.36×10^3	4.6	0.33×10^4	100.0	0.46×10^4	100.0
0.5 M HCl	0.48×10^3	8.9	0.6×10^3	7.7	0.33×10^4	100.0	0.46×10^4	100.0
0.8 M HCl	0.65×10^3	11.8	0.45×10^3	5.8	0.33×10^4	100.0	0.46×10^4	100.0
1.0 M HCl	0.1×10^4	18.2	0.75×10^3	9.6	0.33×10^4	100.0	0.45×10^4	100.0
2.0 M HCl	0.24×10^4	42.7	0.39×10^3	5.0	0.33×10^4	100.0	0.46×10^4	100.0
3.0 M HCl	0.32×10^4	57.3	0.43×10^3	5.6	0.32×10^4	100.0	0.46×10^4	100.0
4.0 M HCl	0.42×10^4	76.4	0.44×10^3	5.7	0.33×10^4	100.0	0.46×10^4	100.0
5.0 M HCl	0.55×10^4	100.0	0.65×10^3	8.3	0.33×10^4	100.0	0.46×10^4	100.0
6.0 M HCl	0.55×10^4	100.0	0.95×10^3	12.2	0.33×10^4	100.0	0.46×10^4	100.0
7.0 M HCl	0.55×10^4	100.0	0.13×10^4	16.6	0.33×10^4	100.0	0.46×10^4	100.0
8.0 M HCl	0.55×10^4	100.0	0.26×10^4	32.7	0.33×10^4	100.0	0.46×10^4	100.0
9.0 M HCl	0.55×10^4	100.0	0.6×10^4	76.9	0.33×10^4	100.0	0.46×10^4	100.0
10.0 M HCl	0.55×10^4	100.0	0.75×10^4	98.2	0.33×10^4	100.0	0.46×10^4	100.0
11.0 M HCl	0.55×10^4	100.0	0.78×10^4	100.0	0.33×10^4	100.0	0.46×10^4	100.0

Table 5 Batch Equilibrium Study - Effect of hydrochloric acid on the adsorption of Zr-95, Nb-95, Ce-144 and Ru-103 on silica gel. In this table, figures for Zr-95, Nb-95, Ce-144 and Ru-103 in the columns refer to the percentages not adsorbed

Experiment B

In a batch equilibrium study 0.1g samples of silica gel (12 samples) were shaken for 18 hours with 5 ml solutions made up of 50 γ of the stock solution and 0.1 M, 0.5 M, 5 M and 6 M hydrochloric acid solutions together with oxalic acid of different molarities, in plastic bottles. The first group contained 0.01 M oxalic acid, the second group 0.025 M oxalic acid and the third group 0.05 M oxalic acid. Then, after settling, 1 ml of each solution was pipetted into a test tube and its activity was measured as described above. The activity on the silica gel was found to be zero in each case. The results are shown in Table 6.

Experiment C

In the batch equilibrium study, 0.1g samples of silica gel were shaken with 5 ml solutions of 0.5 M hydrochloric acid, containing 50 γ of the stock solution in 8 groups, for 2, 4 6, 8, 10, 12, 14, 16 and 18 hours. Then, after settling, 1 ml of each solution was pipetted into a test tube and its activity was measured as described above. The results are shown in Table 7 Figure 17.

5.2.3 Column separation of zirconium and niobium using silica gel and hydrochloric acid as eluant

The filling of the columns required for this work was difficult as it took a long time to produce a satisfactory

Sample	754.0 KeV Zr-95	% Zr-95	764.0 KeV Nb-95	% Nb-95
Stock solution (50γ) loaded	0.74×10^4	100	0.11×10^5	100
1. 0.01 M $H_2C_2O_4$ + 0.1 M HCl	0.74×10^4	100	0.11×10^5	100
0.5 M HCl	0.74×10^4	100	0.11×10^5	100
5.0 M HCl	0.74×10^4	100	0.11×10^5	100
6.0 M HCl	0.74×10^4	100	0.11×10^5	100
2. 0.025 M $H_2C_2O_4$ + 0.1 M HCl	0.74×10^4	100	0.11×10^5	100
0.5 M HCl	0.74×10^4	100	0.11×10^5	100
5.0 M HCl	0.74×10^4	100	0.11×10^5	100
6.0 M HCl	0.74×10^4	100	0.11×10^5	100
3. 0.05 M $H_2C_2O_4$ + 0.1 M HCl	0.74×10^4	100	0.11×10^5	100
0.5 M HCl	0.74×10^4	100	0.11×10^5	100
5.0 M HCl	0.74×10^4	100	0.11×10^5	100
6.0 M HCl	0.74×10^4	100	0.11×10^5	100

Table 6 Batch Equilibrium Study - Effect of oxalic acid on the adsorption of Zr-95 and Nb-95 on silica gel. In this table figures for Zr-95 and Nb-95 in the columns refer to the percentages not adsorbed

Sample	Shaking time in hours	754.0 KeV Zr-95	% Zr-95	764.0 KeV Nb-95	% Nb-95
Stock solution		0.74×10^4	100	0.11×10^5	100.0
0.5 M HCl	2	0.64×10^4	86.4	0.99×10^4	90.0
0.5 M HCl	4	0.4×10^4	54.1	0.63×10^4	57.3
0.5 M HCl	6	0.19×10^4	25.6	0.29×10^4	26.4
0.5 M HCl	8	0.51×10^3	6.9	0.66×10^3	6.0
0.5 M HCl	10	0.44×10^3	6.0	0.56×10^3	4.0
0.5 M HCl	12	0.37×10^3	5.0	0.53×10^3	4.8
0.5 M HCl	14	0.38×10^3	5.1	0.53×10^3	4.8
0.5 M HCl	16	0.38×10^3	5.1	0.55×10^3	5.0
0.5 M HCl	18	0.37×10^3	5.1	0.54×10	4.9

Table 7 Batch Equilibrium Study - Effect of shaking time on the adsorption of Zr-95 and Nb-95 on silica gel. In this table, figures for Zr-95 and Nb-95 in the columns refer to the percentages not adsorbed

column. The silica gel must be packed in the column in such a way that no bubbles of air or water are present, as an unsatisfactory separation will occur if bubbles are present.

1. Non-radiated samples

The stock solution which was used in this experiment contained 100 μg zirconium and 200 μg niobium in a 1.0 ml sample. Niobium was separated from zirconium by the first silica gel column. The column was first conditioned with 5.5 M hydrochloric acid solution. The stock solution [1.0 ml] was then loaded onto the column and the column was washed with 35 ml of 5.5 M hydrochloric acid solution and finally the adsorbed niobium was eluted with 21 ml of concentrated hydrochloric acid solution. The washing and the eluant solutions were collected in 7 ml fractions [7 ml being the capacity of the special container used in the measurement]. The amounts of zirconium and niobium were measured by an X-ray fluorescence technique, as described in Chapter Three. The results are shown in Tables 8 and 9.

The washed solution from the first silica gel column, containing zirconium and 15.9% niobium, was evaporated to about 0.1 ml in a beaker and the residue was made up to 1 ml with 0.5 M hydrochloric acid solution and was then loaded onto the second column. The zirconium and the remaining 15.9% of the niobium were adsorbed at the second column.

Sample	Total μg Zr	% Zr		Total μg Nb	% Nb
1 ml of stock solution	100	100		200	100
7 ml	60.0	60.0	99.1	31.8	15.9
7 ml	31.2	31.2		-	-
7 ml	7.9	7.9		-	-
7 ml	-	-		-	-
7 ml	-	-		-	-

Table 8 Separation of niobium (stable) from 1 ml of the stock solution containing 100 μg Zr and 200 μg Nb from first silica gel column adsorption using 5.5 M hydrochloric acid solution as eluant

Sample	Total μg Nb	% Nb	% Nb*	
Nb on the column	168.2	100	84.1	
7 ml	149.6	88.9	74.8	83.3
7 ml	17.0	10.1	8.5	
7 ml	-	-	-	
7 ml	-	-	-	

Table 9 Elution of niobium (stable) from silica gel column using concentrated hydrochloric acid solution as eluant

* The last column in this table gives the amount of niobium as a percentage of the original amount loaded on the column (200 μg)

This column had been conditioned with 0.5 M hydrochloric acid solution and then washed with 14 ml of 0.5 M hydrochloric acid solution. The adsorbed zirconium was then eluted with 21 ml of 5.5 M hydrochloric acid solution. Afterwards, the adsorbed niobium was eluted with 14 ml of concentrated hydrochloric acid solution. The washing and the eluant solutions were collected in 7 ml fractions. The amounts of zirconium and niobium were measured as described above. The results are shown in Tables 10, 11 and 12.

This experiment was repeated several times in order to achieve optimum conditions for good separation. The diameter of both columns used was kept at 1 cm but the column length varied from 5 to 10 cm. The washing and the elution flow rates were changed from 0.04 to 0.4 ml/min. Also, the first column was conditioned and washed with 5.5 - 6 M hydrochloric acid solution and the second column was conditioned and washed with 0.1 - 0.5 M hydrochloric acid solution.

2. Irradiated samples

The sample used was 50 γ from the stock solution containing the fission products (prepared as mentioned in section 5.2.1 - 1). The niobium-95 was separated from the other radionuclides by the first silica gel column. The column was first conditioned with 5.5 M hydrochloric acid solution, then 50 γ from the stock solution was loaded onto

Sample	Total μg Zr	% Zr	% Zr*	Total μg Nb	% Nb	% Nb*
evaporated sample	99.1	100	99.1	31.8	100	15.9
7 ml	-	-	-	-		
7 ml	-	-	-	-		

Table 10 Adsorption of zirconium and niobium (stable) onto the second column using 0.5 M hydrochloric acid solution as eluant

Sample	Total μg Zr	% Zr	% Zr*
Zr on the column	99.1	100	99.1
7 ml	89.4	90.2 } 98.0	89.4 } 97.1
7 ml	7.7	7.8	7.7
7 ml	-	-	

Table 11 Elution of zirconium (stable) from the second column using 5.5 M hydrochloric acid solution as eluant

Sample	Total μg Nb	% Nb	% Nb*
Nb on the column	31.4	100	15.7
7 ml	30.0	95.5	15.0
7 ml	-	-	

Table 12 Elution of niobium (stable) from the second column using concentrated hydrochloric acid solution as eluant

* The starred columns in Tables 10,11,12 give the amount of zirconium and niobium as percentages of the original amounts loaded on the column (100 μg Zr) (200 μg Nb)

the column. The column was washed with 30 ml of 5.5 M hydrochloric acid solution and finally the adsorbed niobium-95 was eluted with 15 ml of concentrated hydrochloric acid solution, the washing and the eluant solution being collected in 1 ml fractions. The radioactivity of each ml fraction was measured by a Ge(Li) detector. The results are shown in Tables 13 and 14, Figures 18 and 19.

The effluent from the first silica gel column, containing zirconium-95 and 14.68% niobium-95 and the other fission products, was evaporated to about 0.1 ml in a beaker and the residue was made up to 1 ml with 0.5 M hydrochloric acid solution, then loaded onto the second column and washed with 5 ml of 0.5 M hydrochloric acid solution. The zirconium-95 and the remaining niobium-95 were isolated from the other fission products on this column. Finally, the adsorbed zirconium-95 was eluted with 15 ml of 5.5 M hydrochloric acid solution, thenthe adsorbed niobium-95 was eluted with 5 ml of concentrated hydrochloric acid solution and collected with the eluant of the first column. The radioactivity of each ml fraction was measured by a Ge(Li) detector. The results are shown in Tables 15, 16 and 17, Figures 20 and 21. A diagram illustrating the complete procedure is given in Figure 22.

This experiment was repeated several times to achieve good separation. The diameters of both columns were varied

Sample	754.0 KeV Zr-95	%Zr-95	764.0 KeV Nb-95	%Nb-95	133.0 KeV Ce-144	%Ce-144	497.0 KeV Ru-103	%Ru-103
Stock solution 50 γ loaded	0.78×10^{4}	100.0	0.18×10^{5}	100.0	0.69×10^{4}	100.0	0.49×10^{4}	100.0
1 ml	-	-	0.27×10^{3}	1.5	0.65×10^{3}	9.4	0.42×10^{3}	8.5
2 ml	0.92×10^{2}	1.2	0.14×10^{4}	7.7	0.44×10^{4}	63.7	0.3×10^{4}	61.2
3 ml	0.82×10^{3}	10.5	0.4×10^{3}	2.2	0.73×10^{3}	10.5	0.66×10^{3}	13.5
4 ml	0.99×10^{3}	12.7	0.27×10^{3}	1.5	0.46×10^{3}	6.7	0.39×10^{3}	8.0
5 ml	0.11×10^{4}	14.1	0.18×10^{3}	1.0	0.36×10^{3}	5.2	0.28×10^{3}	5.7
6 ml	0.1×10^{4}	12.8	0.13×10^{3}	0.72	0.26×10^{3}	3.8	0.16×10^{3}	3.2
7 ml	0.85×10^{3}	10.8						
8 ml	0.7×10^{3}	9.0						
9 ml	0.51×10^{3}	6.5						
10 ml	0.32×10^{3}	4.1						
11 ml	0.25×10^{3}	3.2						
12 ml	0.22×10^{3}	2.8						

Table 13 Separation of niobium-95 from 50 γ of the stock solution using the first silica gel column adsorption using 5.5 M hydrochloric acid solution

Sample	754.0 KeV Zr-95	%Zr-95	764.0 KeV Nb-95	%Nb-95	133.0 KeV Ce-144	%Ce-144	497.0 KeV Ru-103	%Ru-103
13 ml	0.17×10^3	2.2						
14 ml	0.13×10^3	1.7						
15 ml	0.96×10^2	1.2						
16 ml	0.76×10^2	0.97						
17 ml	0.71×10^2	0.91						
18 ml	0.68×10^2	0.87						
19 ml	0.63×10^2	0.81						
20 ml	0.5×10^2	0.64						
21 ml	0.3×10^2	0.38						
22 ml	0.21×10^2	0.2						
23 ml	0.2×10^2	0.2						
24 ml	0.2×10^2	0.2						
25 ml	0.12×10^2	0.15						

Table 13 (cont'd)

Sample	764.0 KeV Nb-95	% Nb-95	% Nb-95*
Nb-95 on the column	0.154×10^5	100.0	85.38
1 ml	-	-	-
2 ml	0.57×10^4	37.0	31.67
3 ml	0.42×10^4	27.2	23.33
4 ml	0.14×10^4	9.0	7.78
5 ml	0.91×10^3	6.0	5.06
6 ml	0.79×10^3	5.1	4.39
7 ml	0.70×10^3	4.9	3.89
8 ml	0.48×10^3	3.0	2.67
9 ml	0.29×10^3	2.0	1.61
10 ml	0.86×10^3	5.6%	4.78%
11 ml			
12 ml			
13 ml			
14 ml			
15 ml			

Table 14 Elution of Nb-95 from the first silica gel column using concentrated hydrochloric acid solution

* The last column in this table gives the amount of niobium as a percentage of the original amount loaded on the column

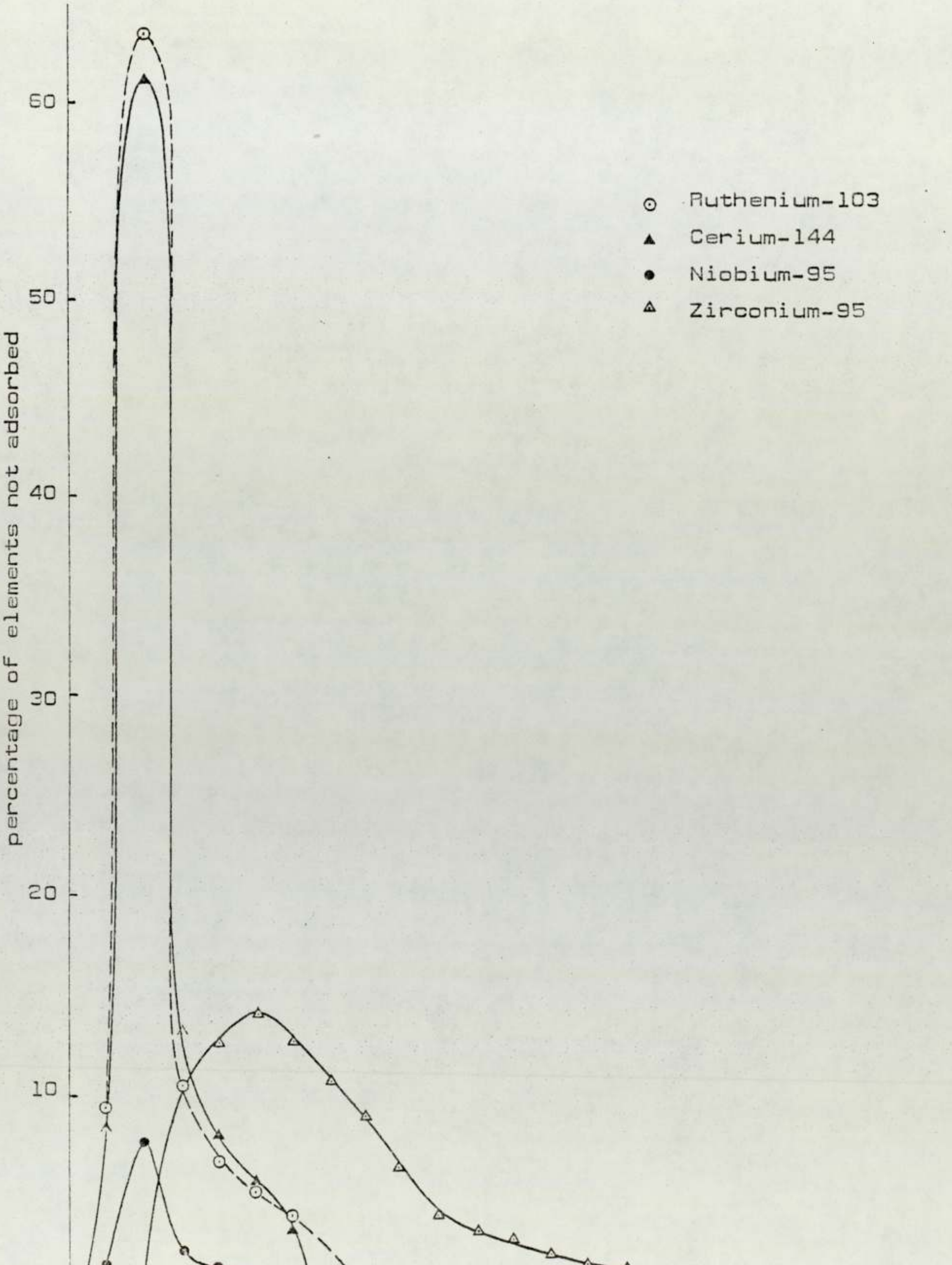


Figure 18 Separation of niobium-95 from other fission products in first silica gel column

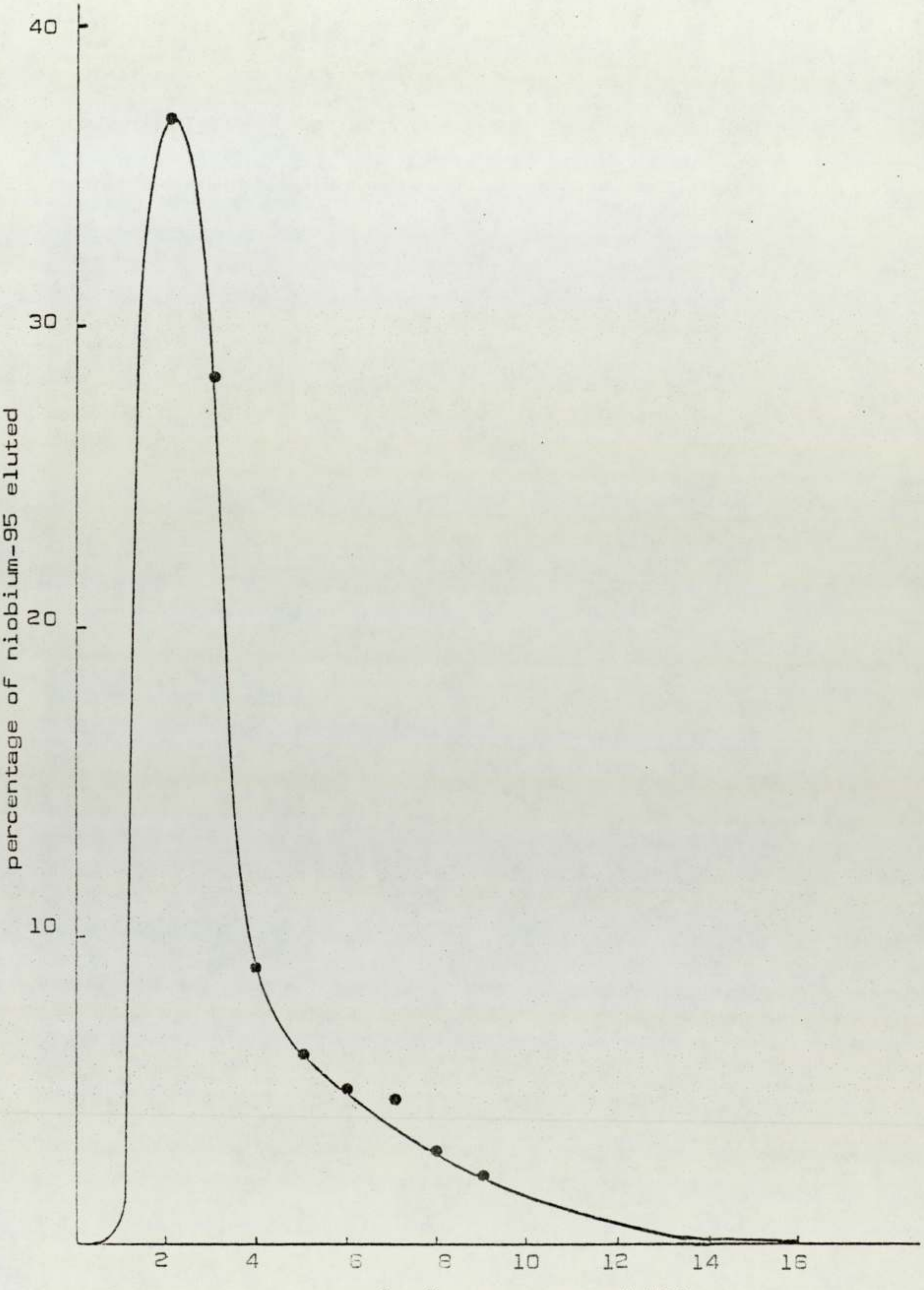


Figure 19 Elution of niobium-95 from first silica gel column

Sample	754.0 KeV Zr-95	%Zr-95	764.0 KeV Nb-95	%Nb-95	%Nb-95*	133.0 KeV Ce-144	%Ce-144	497.0 KeV Ru-103	%Ru-103
evaporated sample	0.77×10^4	100.0	0.26×10^4	100.0	14.6	0.67×10^4	100.0	0.48×10^4	100.0
1 ml	-	-	-	-	-	0.16×10^3	2.3	0.5×10^2	1.04
2 ml	0.17×10^2	0.22	0.72×10^2	2.8	0.4	0.32×10^4	47.8	0.24×10^4	50.0
3 ml	0.43×10^2	0.55	0.69×10^2	2.7	0.38	0.3×10^4	44.8	0.21×10^4	43.8
4 ml	-	-	-	-	-	0.31×10^3	4.6	0.23×10^3	4.8
5 ml	-	-	-	-	-	-	-	-	-

Table 15 Adsorption of zirconium-95 and niobium-95 onto the second column using 0.5 M hydrochloric acid solution as eluant

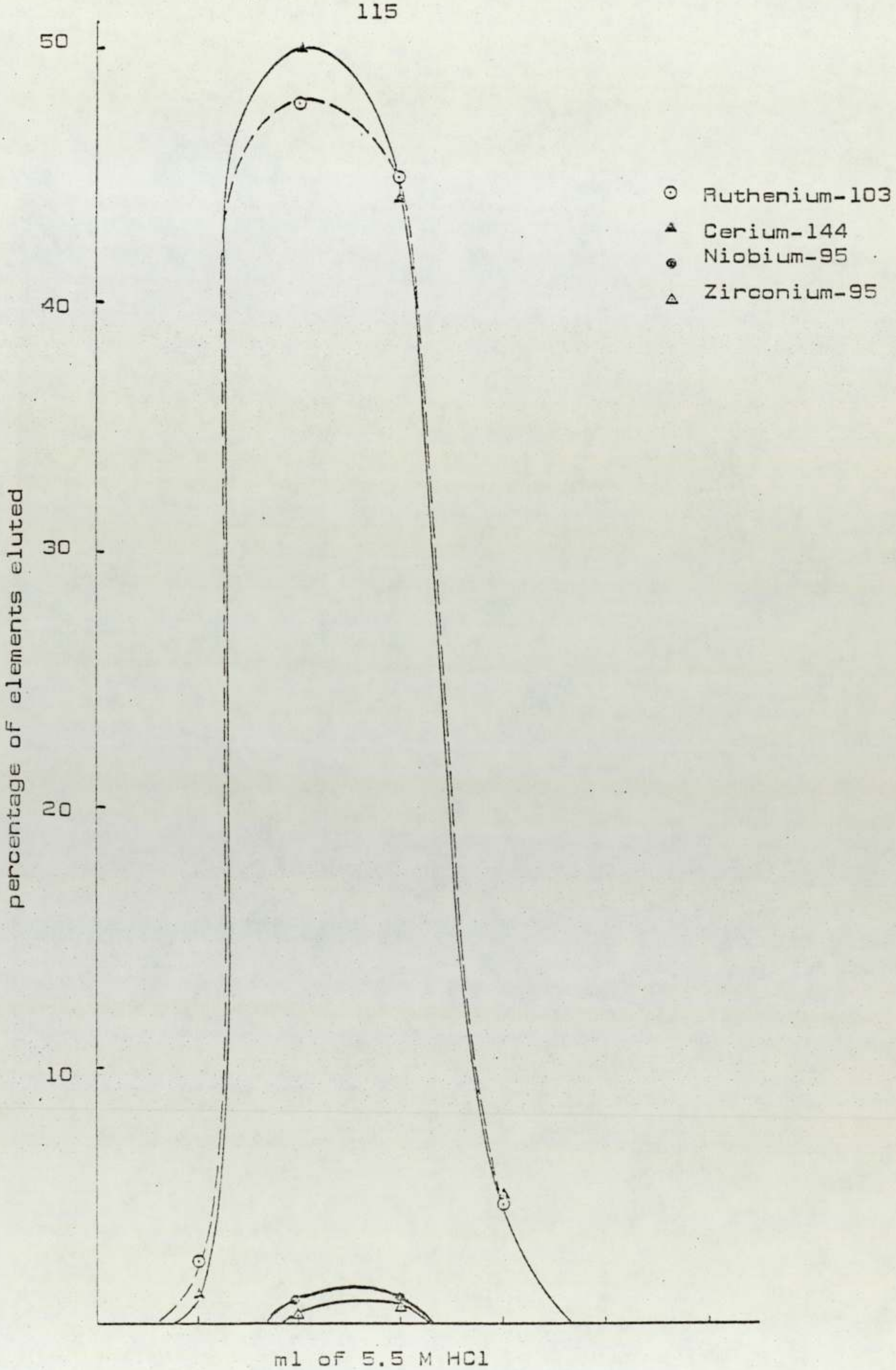


Figure 20 Separation of zirconium-95 and remaining niobium-95 from the evaporated solution in second silica gel column

Sample	754.0 KeV Zr-95	%Zr-95
Zr-95 on the column	0.77×10^4	100.0
1 ml	-	-
2 ml	0.79×10^2	1.1
3 ml	0.26×10^4	33.9
4 ml	0.21×10^4	27.4
5 ml	0.12×10^4	15.5
6 ml	0.51×10^3	6.6
7 ml	0.39×10^3	5.1
8 ml	0.24×10^3	3.1
9 ml	0.18×10^3	2.3
10 ml	0.39×10^3	5.1
11 ml		
12 ml		
13 ml		
14 ml		
15 ml		
16 ml	-	-

Table 16 Elution of zirconium-95 from the second column using 5.5 M hydrochloric acid solution as eluant

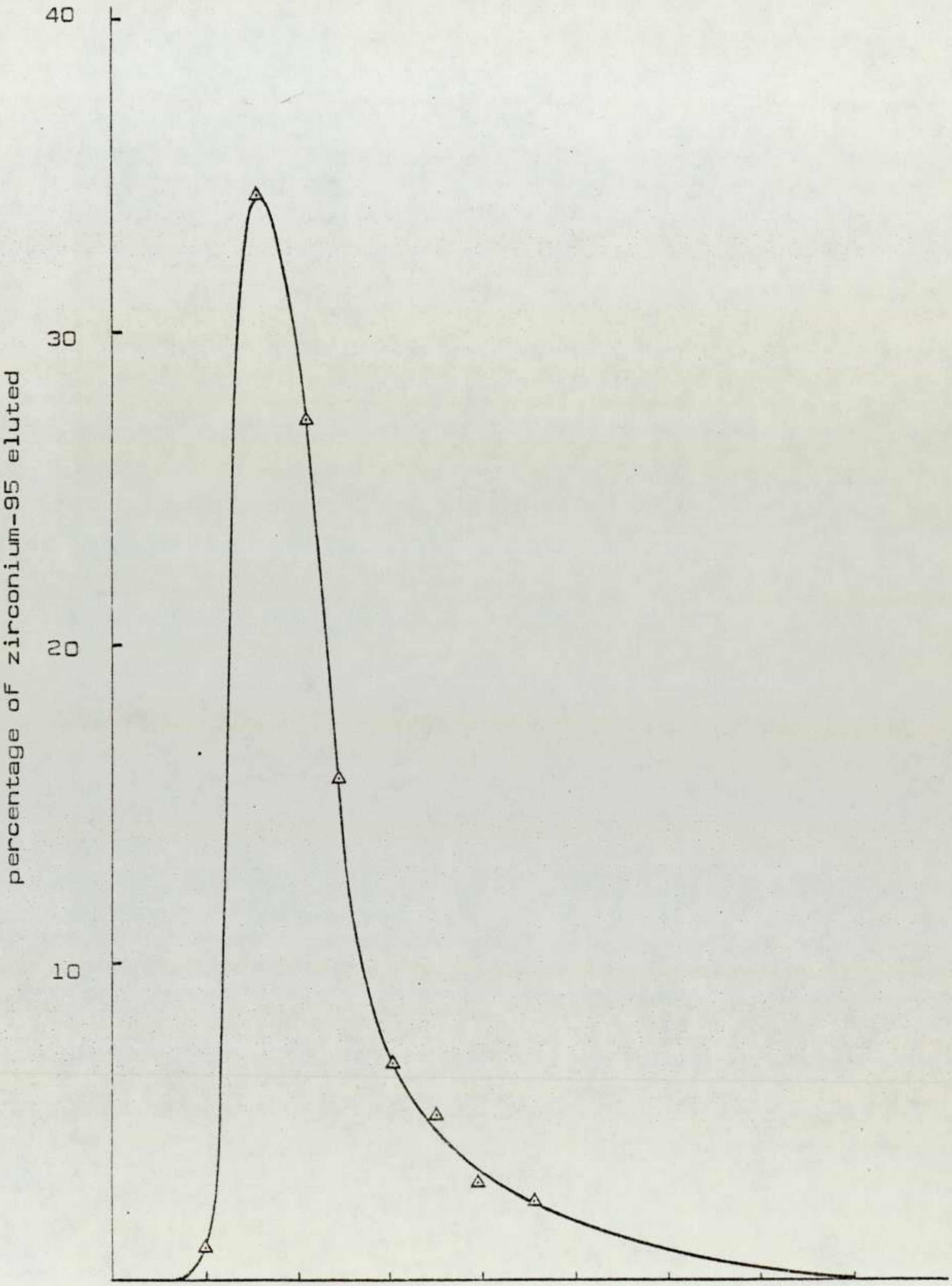


Figure 21 Elution of zirconium-95 from second silica gel column

Sample	764.0 KeV	%Nb-95	%Nb-95*
Nb-95 on the column	0.246×10^4	100.0	13.8
1 ml	-	-	-
2 ml	0.55×10^3	22.5	3.1
3 ml	0.19×10^4	77.3	10.7
4 ml			

Table 17 Elution of niobium-95 from the second column using concentrated hydrochloric acid solution as eluant

* The starred columns in Tables 15 and 17 give the amounts of niobium as percentages of the original amounts loaded onto the column

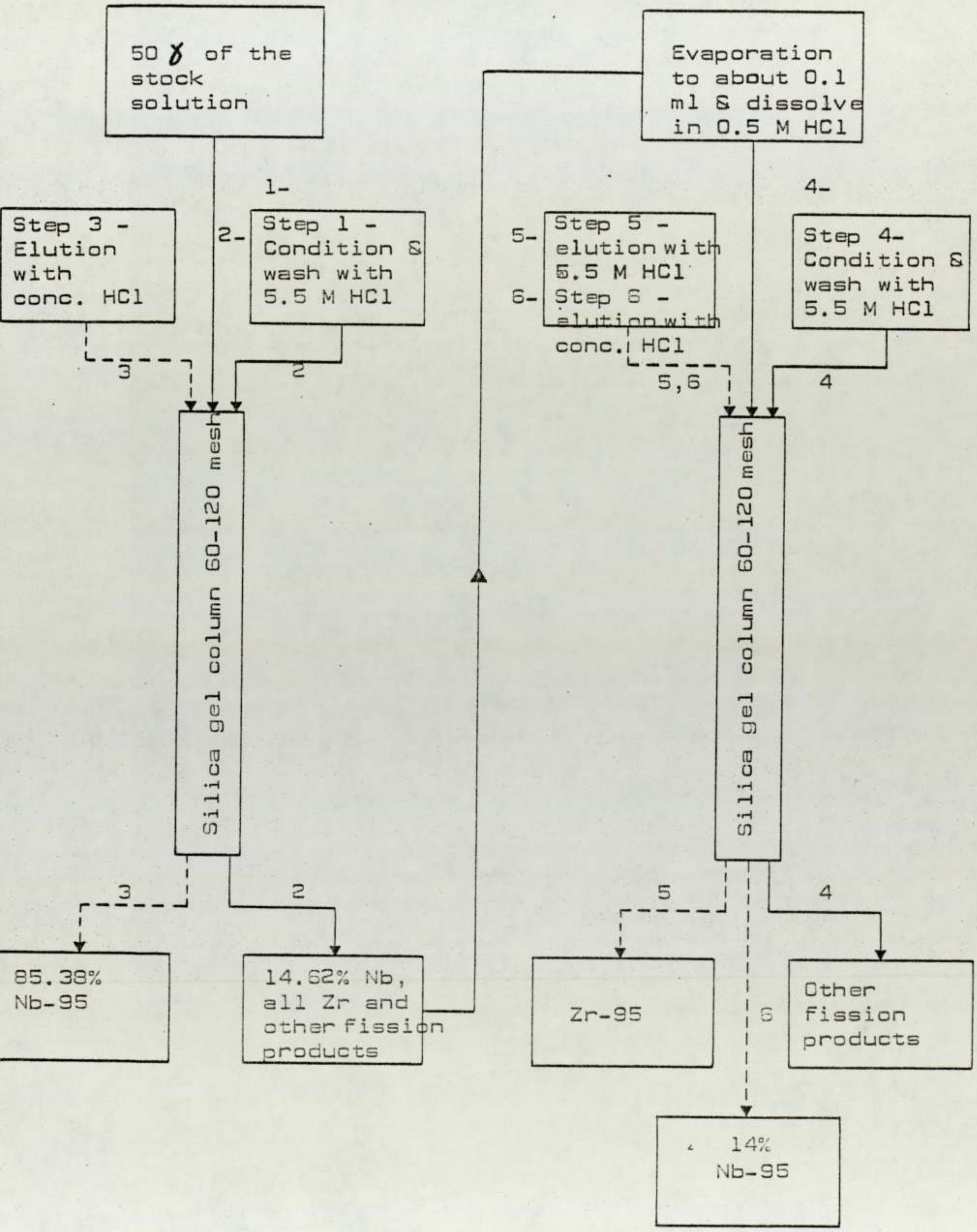


Figure 22 Schematic diagram of the separation process

from 0.4 - 0.7 cm, the length was varied from 5 - 10 cm and the washing and the elution flow rates were changed from 0.04 - 0.13 ml/min. Also, the first column was conditioned and washed with 5.5 - 6 M concentrated hydrochloric acid solutions and the second column was conditioned and washed with 0.5 M, 5.5 M and concentrated hydrochloric acid solutions.

5.2.4 Column separation of zirconium and niobium using silica gel and oxalic acid as eluant

Experiment 5.2.4 was carried out in the same way as experiment 5.2.3, except that the elution solution in this experiment was 0.05 M oxalic acid.

Identical results were obtained for the first column in both experiments (using stable and radioactive nuclide), but in the second column in experiment 5.2.3 zirconium was eluted with 5.5 M hydrochloric acid solution and then the remaining niobium was eluted with concentrated hydrochloric acid solution. In this experiment, zirconium and niobium were eluted together. However, one cannot obtain by this method pure zirconium. Therefore, hydrochloric acid solution is to be preferred as eluant.

5.3 Results and discussion

Silica gel adsorption has been successfully applied to separate zirconium and niobium both from each other and from other fission products, using only hydrochloric acid medium. The results obtained are summarised in Tables 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16 and 17 and detailed below.

5.3.1 Effect of hydrochloric acid concentration on the adsorption of the stable and radioactive nuclide

The percentages of elements not adsorbed, plotted as a function of hydrochloric acid concentration, for stable nuclides and radioactive nuclides, are shown in Tables 2 and 5, Figure 16.

The results indicate that zirconium [stable] and zirconium-95 show a maximum adsorption between 0.1 and 0.5 M hydrochloric acid concentration; then adsorption decreases rapidly with increasing hydrochloric acid concentration from 0.1 M to 5 M, and finally almost levels off. The adsorption of niobium stable and niobium-95 is at a maximum and is found to be approximately constant, from 0.1M to 6 M hydrochloric acid concentration, then it decreases with increasing hydrochloric acid concentration. It also almost levels off at 10 MHCl.In several respects these results differ from those of Caletka[45]; he found that zirconium was less strongly adsorbed than niobium at low acidities, and that the opposite occurred when using concentrated hydrochloric acid. The results described in this thesis also indicate that any other radioactive nuclide e.g.

ruthenium-103, cerium-144 and stable molybdenum, do not show any adsorption at any concentration of the acid, (see Tables 2 and 5 and Figure 16)

The results clearly show that the separation of stable zirconium and niobium and the separation of zirconium-95 and niobium-95 from the other fission products (ruthenium, cerium, etc.) and from each other, can be achieved in hydrochloric acid solution by the use of silica gel. This means that pure chemical and radiochemical separation for zirconium and niobium occurs. Other fission products, stable nuclides and radioactive nuclides, do not show any adsorption at any concentrations of hydrochloric acid.

5.3.2 Effect of oxalic acid concentration on the adsorption of zirconium and niobium - stable and radioactive nuclides

From Tables 3 and 6 it can be seen that in the presence of oxalic acid of various molarities (from 0.01 - 0.05 M), no adsorption occurs for zirconium and niobium on silica gel. This means that oxalic acid is a good eluant for both zirconium and niobium from silica gel. Similar results were found by El-Garhy et al[46].

5.3.3 Kinetics of adsorption

Ahrland[43] has reported that at the sorption of strongly hydrolysed elements such as zirconium or niobium the equilibrium is reached only slowly. In the work reported in this thesis, the adsorption rate of zirconium and niobium on silica gel in the medium of 0.5 M hydrochloric acid has been examined. Tables 4 and 7, Figure 17 shows that the adsorption for each nuclide is almost constant after 8 hours shaking; therefore, in this study a shaking time of 18 hours* is assumed sufficient to establish equilibrium.

5.3.4 The separation of zirconium and niobium from the fission products and from each other using stable and radioactive nuclides

Niobium adsorbs strongly at 5.5 M hydrochloric acid concentration; therefore, it can be retained in the column, whereas the other radionuclides and stable nuclides come out of the column. After separation from niobium, zirconium can be isolated from other radionuclides with a silica gel column at 0.5 M hydrochloric acid concentration. Also, it can be seen that hydrochloric acid solutions of strength 5 M to 11.5 M are good eluants for zirconium, and hydrochloric acid solutions of strength 10 M to concentrated are good eluants for niobium.

---

* In the work described in this thesis, the shaking of the samples was done overnight; hence the shaking time was 18 hours

1. Non-radiated samples

The optimum separation conditions for stable nuclides were obtained and are summarised as follows.

Niobium is adsorbed at 5.5 M hydrochloric acid and desorbed with concentrated hydrochloric acid. Zirconium is adsorbed at 0.5 M hydrochloric acid and desorbed with 5.5 M hydrochloric acid. The column parameters for both columns were 10 cm column length, 1 cm diameter, using a flow rate of 0.11 ml/min.

From Table 8 it can clearly be seen that when using the first silica gel column conditioned with 5.5 M hydrochloric acid,

84.1% of niobium is retained on the column and 99.1% of zirconium is removed from the column with 15.9% of the niobium.

From Table 9 it can clearly be seen that 99% of niobium is desorbed from the column with concentrated hydrochloric acid, therefore 1.6 μg of total niobium is retained on the column.

From Table 10 it can clearly be seen that when using the second silica gel column conditioned with 0.5 M hydrochloric acid,

all zirconium is retained on the column with all remaining niobium.

From Tables 11 and 12, it can clearly be seen that, 98% of zirconium is desorbed with 5.5 M hydrochloric acid and 95.5% of remaining niobium is desorbed with concentrated hydrochloric acid; therefore, 2 μg of zirconium is retained on the column and 1.4 μg niobium is retained on the column.

Thus, 97.1% of zirconium and 98.5% of niobium can be separated.

2. Irradiated samples

The optimum separation conditions for radioactive nuclides were obtained and are summarised as follows:

Niobium-95 is adsorbed at 5.5 M hydrochloric acid and desorbed with concentrated hydrochloric acid. Zirconium-95 is adsorbed at 0.5 M hydrochloric acid and desorbed with 5.5 M hydrochloric acid. Parameters of both columns were 10 cm column length, 0.4 cm diameter, with a flow rate of 0.11 ml/min.

From Table 13 Figure 18 it can clearly be seen that when using the first silica gel column conditioned with 5.5 M hydrochloric acid,

86.38% of niobium-95 is retained on the column and all zirconium activity is removed from the column, with 14.62% of niobium-95 and other fission products [e.g. ruthenium-103, cerium-144].

From Table 14 Figure 19 it is seen that concentrated hydrochloric acid desorbs all niobium-95 from the column; thus it is a good eluant for niobium.

From Table 15 Figure 20 it can clearly be seen that, 0.83% of zirconium-95 is removed from the column (i.e. over 99% of zirconium-95 is retained on the second column); also 0.78% of niobium-95 is removed from the column (i.e. 13.12% of the remaining niobium-95 will be retained on the second column).

All other fission products are removed from the column.

From this it may be seen that 0.5 M hydrochloric acid is the best strength of acid for the retention of zirconium-95 on the column.

From Tables 16 and 17 Figure 21 it is clearly seen that,

all zirconium-95 is desorbed with 5.5 M hydrochloric acid, and all the remaining niobium is desorbed with concentrated hydrochloric acid.

Thus, over 99% of both elements can be separated from the fission products and from each other.

The slight difference in the results for stable and radioactive nuclides is due to the low sensitivity of the X-ray fluorescence technique at low concentration.

These results differ from those of Caletka[45], who finds that in 6 M to 9 M hydrochloric acid solutions niobium is strongly retained on the column, while zirconium is easily eluted. We found that from 0.1 M to 0.5 M hydrochloric acid solution, both niobium and zirconium are retained on the column; from 0.1 to 5 M hydrochloric acid concentration, niobium is still retained on the column, but zirconium is gradually eluted with increasing acid strength reaching 100% elution at about 5 M hydrochloric acid solution. With solutions greater than 5 M hydrochloric acid, zirconium remains 100% eluted and niobium is gradually eluted with increasing acid strength reaching 100% elution at about 10 M hydrochloric acid.

Thus, we have a possible scheme of separation of zirconium and niobium from other fission products and from each other.

5.3.5 Sorption mechanism

The use of silica gel as a highly active adsorbent is now taking on increasing importance. The most interesting properties of silica gel include its ability to adsorb readily hydrolysed elements onto its surface from acid solutions, in particular, such typical representatives (of this group of elements) as zirconium and niobium. Only a few studies, the data of which are contradictory, have been devoted to the investigation of the mechanism of the sorption of readily hydrolysed elements. Ahrland et al[44] believe that silica gel behaves as a weak acid cation exchange resin and adsorption onto it occurs according to an ion exchange mechanism.

$$G(OH)_n + Me^{n+} \rightleftharpoons GO_nMe + n\,H^+ \quad \ldots (1)$$

where G is the framework of silica gel, which does not participate in the exchange, Me is a metal.

No evidence concerning the study of the sorption of zirconium and niobium by silica gel from hydrochloric acid media is available. However, in considering the sorption of zirconium by silica gel from nitric acid media, the following conclusions were reached[68]:

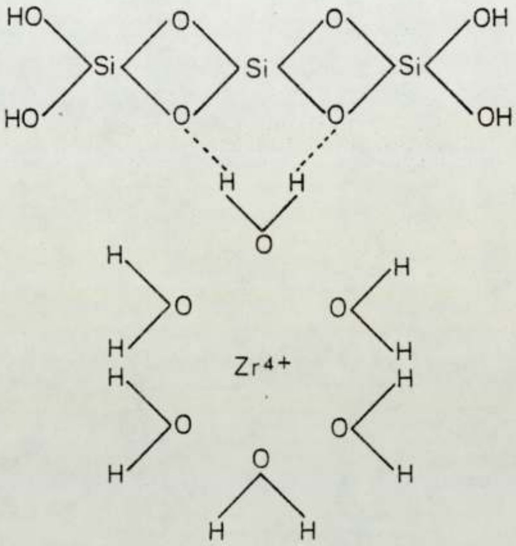
1) In weakly acid solutions (0.1 - 1 M) hydrolysed forms of zirconium are sorbed according to the mechanism of hydrolytic sorption, analogous to the mechanism proposed by Kohlschutter[69] for the sorption of aluminium

$$\equiv Si - OH + Al(OH)_3 \rightleftharpoons \equiv Si - OH/Al(OH)_3$$

2) from a solution approximately 2 M with respect to nitric acid, Zr^{4+} ions are sorbed either according to an ion exchange mechanism,

$$G(OH)_n + Zr^{4+} + (4-n)NO_3^- \rightleftharpoons GO_nZr{-}{-}{-}(NO_3)_{4-n} + n\,H^+$$

or on account of the formation of hydrogen bridges with the oxygen atoms of silica gel on the surface.



3] neutral complexes of zirconium are sorbed in 4 - 8 M nitric acid according to mechanism molecular sorption.

We think that the mechanism of the sorption of zirconium by silica gel in hydrochloric acid medium from a solution of 0.1 - 0.5 M hydrochloric acid concentration, is either due to process 1, or to process 2, and as shown in Figure 16 with increasing acid molarities from 0.5 M to 5 M, adsorption decreases. It is also apparent from Figure 21 that on elution with 5.5 M hydrochloric acid solution almost all the zirconium is eluted together from the column in the first few mls collected. This suggests that possibly a single species is being eluted in 5.5 M hydrochloric acid solution.

Thus, while the compound is held tightly by the silica gel, processes 1 and 2 (described above) apply, but as the protonating power of the medium increases, the equilibrium more likely follows equation (1) and the equilibrium is gradually shifted to the left. As the acid concentration increases still further, molecular adsorption alone becomes the predominant mechanism assisting release and passage of zirconium through the column.

Elution is fairly rapid at high acid concentrations because only molecular size is impeding progress of the substance. Also, at such low metal concentrations as have been employed in this work, the formation of cluster ions and polymerisation, which would lead to high molecular weight ions or compounds, is thought unlikely[67].

As can be seen from Figure 16 most of the niobium is retained on the silica gel surface until the concentration reaches 6 M. Examination of Figure 16 suggests that almost all the niobium adsorbed is eluted readily from the column with 10 M hydrochloric acid solution. It seems possible, therefore, that a more soluble niobium species is present in strong acid solutions, but that with the low acid concentrations used a less soluble niobium compound is adsorbed by the silica gel.

It is thought[50] that even at such low metal ion concentrations as have been used in this work, some degree of niobium polymerisation is possible and it may be that these clusters are only broken down in the stronger acid solution used in the final elution. Alternatively, the existence of the niobium species shown below is postulated - $Nb(OH)_x\,(Cl)_y^{5-x-y}$. This species might then be retained on the column and only eluted under strong acid concentrations in a manner exactly analagous to that previously discussed with regard to zirconium.

5.4 Conclusions

The main purpose of this research was to find a procedure which would enable separation of the elements zirconium and niobium from nuclear spent fuel. This problem is of particular interest because these two elements complicate the satisfactory decontamination of products in the reprocessing of irradiated fuel.

Initially, work was done, at Aston University, on non-radiated samples. After many attempts, a method was found which gave pure chemical separation of 97%. This process involved the use of silica gel as the stationary phase in glass columns, with hydrochloric acid of various molarities as eluant. It was found that with both zirconium and niobium, separation was complete for both metal species.

The work was then extended to include radioactive samples. The samples were irradiated at the Iraqi Nuclear Reactor, where this part of the research was conducted. The work was complicated by the gamma ray emission from the samples, which necessitated the use of a lead-shielded glove box.

It was found that the first silica gel column could not completely separate the niobium from the zirconium [this was also found with the stable isotopes] and other fission products, but when the solution containing the remaining niobium, the zirconium and the other fission products was loaded into a second column, complete separation was achieved of niobium and zirconium from the remaining fission products and from each other. Over 99% pure chemical separation was achieved.

As mentioned in section 1.1.5, ruthenium is important in the chemical separation process relating to the reprocessing of nuclear spent fuel. Therefore, it would be useful to be able to separate ruthenium. An attempt was made to separate ruthenium using the silica gel method, but this was not successful. Whilst the initial problem has been solved, and zirconium and niobium can now be separated chemically, it could be useful to do further work on the silica gel method, possibly involving the use of different mesh sizes for the silica gel, in order to compare the relative efficiencies of the different mesh sizes. For the separation of ruthenium, a careful study of existing literature suggests that one possibility might involve the use of anion exchange resin Dowex 50 × 8.

Overall, the results obtained in this study are very encouraging and indicate the feasibility of using silica gel for the separation of fission products for analytical purposes, and possibly also for large scale use in nuclear reprocessing steps.

Appendix One Recommended Schematic Procedure for the Separation of Zirconium and Niobium from Other Fission Products and from Each Other

1) Dissolve the spent fuel in a few mls of concentrated nitric acid and a few mls of concentrated hydrochloric acid, then evaporate to dryness. The process of dissolution and evaporation must be repeated three times in order to drive off gases and the volatile radioactive material from the matrix of the active solution. The residue remaining after the last evaporation step may be dissolved in 1 M hydrochloric acid solution.

2) Load a suitable volume of the above solution onto the silica gel column and wash the latter with 5.5 M hydrochloric acid, retaining the washings.

3) Elute niobium from the silica gel column with concentrated hydrochloric acid and keep the solution for later analysis.

4) Evaporate the washings from (2) above, until the volume is reduced to about 0.1 ml; make up to 1 ml with 0.5 M hydrochloric acid. Load this reduced volume of solution onto another silica gel column, washing the latter with 0.5 M hydrochloric acid. Ruthenium, cerium and other fission products are contained in the washings. If these elements are to be quantified, the washings may be retained.

5] Elute zirconium from the second column with 5.5 M hydrochloric acid and later elute any extra niobium with concentrated hydrochloric acid. Add the niobium solution to that obtained in [3] above. Analyse the two portions of eluants for zirconium and niobium by appropriate means.

NOTE: The amount of original sample, the aliquote loaded onto the first column, and the volume of eluants used, would depend on many factors e.g. the mesh size of the gel and the dimensions of the column.

For the application of the above method to a specific sample, it is recommended that studies be carried out to confirm the optimum conditions before attempting to deal with an actual sample. Any alteration of column size, flow rate of elution, silica gel pretreatment etc. may alter the optimum conditions recommended in this work.

LIST OF REFERENCES

1. Turner, L.A.
'Nuclear Fission'
Rev. Modern Physics Vol. 12 (1), 1940, 1-29

2. Halpern, I.
'Nuclear Fission'
Ann. Rev. Nucl. Sci. Vol. 9, 1959

3. 'Nuclear Fission'
The New Encyclopaedia Britannica Vol. 13, 15 (ed), 1974, 301-307

4. Hunt, S.E.
'Fission, Fusion and the Energy Crisis', Vol. I
Pergamon Press, Oxford, 1974

5. Glasstone, S.
'Principle of Nuclear Reactor Engineering'
Macmillan and Co Ltd., London, 1956

6. Lenihan, J.M.A.
'Atomic Energy and its Applications'
Sir Isaac Pitman and Sons Ltd., London, 1966

7. Fremlin, J.H.
'Applications of Nuclear Physics'
The English Universities Press Ltd., London, EC1, 1964

8. Peterson, S. and Wymer, R.G.
'Chemistry in Nuclear Technology'
Addison-Wesley Publishing Company, Inc. Pergamon Press, Oxford, 1963

9. Vandenbosch, R. and Huizenga, J.R.
'Nuclear Fission'
Academic Press, 1973

10. McKay, H.A.C.
'Principle of Radiochemistry'
Butterworths, London, 1971

11. Lefort, M.
'Nuclear Chemistry'
D. Van Nostrand Company Ltd., London, 1968

12. Burcham, W.E.
'Nuclear Physics: An Introduction' (2nd edition)
Longman Group Ltd., 1973

13. Lyon, W.S.
'Guide to Activation Analysis'
D. Van Nostrand Company Inc., 1964

14. Lenihan, J.M.A. and Thomson, S.J. (Ed.)
'Advances in Activation Analysis' Vol 1
Academic Press, London, 1964

15. Bowen, H.J.M. and Gibbons, D.
'Radioactivation Analysis'
Oxford at the Clarendon Press, 1963

16. Ellis, R.H.
'Nuclear Technology For Engineers'
McGraw-Hill Book Company, Inc., New York, 1959

17. Lenihan, J.M.A. and Thomson, S.J. (Ed.)
'Activation Analysis: Principles and Applications'
Academic Press, London, 1965

18. Yaffe, L. [Ed]
'Nuclear Chemistry' Vol. 11 Chap. 1 Nuclear Fission
Academic Press, 1968

19. Leachman, R.B.
'Nuclear Fission'
Scient. Am. 213, August 1965, 49-59

20. Halpern, I.
'Three Fragment Fission'
Ann. Rev. Nucl. Sci. 21, 1971

21. Benedict, M. and Pigford, T.H.
'Nuclear Chemical Engineering'
McGraw-Hill Book Company, Inc. New York, 1957

22. Arya, A.P.
'Fundamentals of Nuclear Physics'
Allyn and Bacon, Inc., Boston, 1966

23. Nix, J.R.
'Theory of Nuclear Fission and Superheavy Nuclei'
Preprint From Los Alamos Sci. Lab., 1972

24. Wilets, L.
'Theories of Nuclear Fission'
Oxford Univ. Press, London, 1964

25. Cooper, A.R.
'Chemical Processing in the Atomic Energy Industry'
Iliffe Books Ltd., London, 1964

26. Blumenthal, W.B.
'The Chemical Behaviour of Zirconium'
D. Van Nostrand Company, Inc. Princeton, 1958

27. Kolthoff, I.M. and Elving, P.J. (Ed)
'Treatise on Analytical Chemistry,' Vol 5 Part II
Interscience Publishers, New York, 1961

28. Cotton, F.A. and Wilkinson, G.
'Advanced Inorganic Chemistry (3rd ed)
Interscience Publishers. A division of John Wiley & Sons, New York, 1972

29. Kolthoff, I.M. and Elving, P. J. (ed)
'Treatise on Analytical Chemistry', Vol 6 Part II
Interscience Publishers, New York, 1964

30. Fairbrother, F.
'The Chemistry of Niobium and Tantalum'
Elsevier Publishing Company, Amsterdam, 1967

31. Martin, F.S. and Miles, G.L.
'Chemical Processing of Nuclear Fuels'
Butterworths Scientific Publications, 1958

32. Siczek, A.A. and Steindler, M.J.
'The Chemistry of Ruthenium and Zirconium in the Purex Solvent Extraction Process'
Atomic Energy Review, 164, 1978

33. Bunney, L.R., Ballou, N.E., Pascual, J., and Foti, S.
'Anion Exchange Behaviour of Several Metal Ions in Hydrochloric, Nitric, and Sulphuric Acid Solutions'
Anal. Chem., 31, (3), 1959, 324-326

34. Wish, L.
'Anion Exchange Behaviour in Mixed Acid Solutions and Development of a Sequential Separation Scheme'
Anal. Chem., 31, (3), 1959, 326-330

35. Freiling, E.C., Pascual, J., and Delucchi, A.A.
'Anion Exchange Equilibrations in Phosphoric Acid Solutions'
Anal. Chem., 31, (3), 1959, 330-331

36. Huffman, E.H., Iddings, G.M., and Lilly, R.C.
'Anion Exchange of Zirconium, Hafnium, Niobium and Tantalum in Hydrochloric Acid Solutions'
J. Amer. Chem. Soc., 73, 1951, 4474-4476

37. Mathers, W.G. and Hoelke, C.W.K.
'Semiautomatic Machine for Group Separation of Radioelements by Cation Exchange'
Anal. Chem., 35, (13), 1963, 2065-2071

38. Souka, N., Shabana, R., and Girgis, C.
'Protactinium Extraction from Mixed Mineral Acid Solutions, Separation Methods for Protactinium, Niobium and Zirconium'
Analyt. Abstr., 33, 1977, 588

39. Mulshomkova, N.P. Bulalov, M.I., and Vashukova, N.F.
'Extraction - photometric Determination of Zirconium, Niobium, Iron and Cobalt Present Together' (in Russian)
Analyt. Abstr., 35, 1978, 4D15

40. Ejaz, M.
'N-Oxides of 4(5-Nonyl) Pyridine and Trioctylamine as Extractents for Zirconium from Uranium and Fission Products'
Anal. Chem., 48, 1158-1161

41. Schriver, L.
'Separation of the Radionuclides Zirconium-95 and Niobium-95 by Liquid-Liquid Extraction in the Presence of β^- Isopropyltropolone' [in French]
Analyt. Abstr., 31, 1976, 18118

42. Beachmann, K. and Rudolph, J.
'Gas Chromatography of Inorganic Radioactive Halide Compounds'
J. Radioanal. Chem., 32, [2], 1976, 245-264

43. Ahrland, S., Grenthe, I., and Noren, B.
'The Sorption of Na^+, Ca^{2+}, Ba^{2+}, UO^{2+}, Gd^{3+}, Zr [IV] + Nb, U [IV] and Pu [IV]'
Acta Chem. Scand. 14, 1960, 1059-1076

44. Ahrland, S., Grenthe, I., and Noren, B.
'Separation of Plutonium and Fission Products From Irradiated Uranium'
Acta Chem. Scand. 14, 1960, 1077-1090

45. Caletka, R.
'Separation of ^{95}Zr and ^{95}Nb by Means of Sorption on Silica Gel from Hydrochloric Acid Solutions'
J. Radioanal. Chem., 6, 1970, 5-10

46. El-Garhy, M., Shehata, M.K.K., and El-Bayoumy, S.
'The Use of Hydrochloric Acid in Separating ^{95}Zr - ^{95}Nb Activity from Uranium Fission Products on Silica Gel'
J. Radioanal. Chem., 11, 1972, 175-178

47. Akatsu, E. and Aratono, Y.
'Separation of Zirconium from Fission Products in Silica Gel-Nitric Acid Systems'
Analytica Chimica Acta, 84, 1976, 347-353

48. Akatsu, E., Ono, R., Tsukuechi, K., and Uchiyama, H.
'Radiochemical Study of Adsorption Behaviour in Inorganic Ions on Zirconium Phosphate, Silica Gel and Charcoal'.
J. Nucl. Sci. and Tech., 2, (4), 1965, 141-148

49. Tsaletka, R.
'Adsorption of Zirconium and Hafnium from Solutions of Mineral Acids'
Radiokhimiya 12, (3), 1970, 448-455

50. Hung-Chih, L.
'Separation of Zirconium-95 and Niobium-95 from Irradiated Uranium by Silica Gel Adsorption'
Analyt. Abstr., 32, 1977, 3394

51. Thompson, K.C. and Reynolds, R.J.
'Atomic Absorption, Fluorescence and Flame Emission Spectroscopy - A Practical Approach' (2nd ed)
Charles Griffin and Company Limited, 1978

52. Price, W.J.
'Spectrochemical Analysis by Atomic Absorption'
Heyden and Son Ltd., 1979

53. Korte, F. (ed)
'Methodicum Chimicum' Vol 1 B
Academic Press, New York, 1974

54. Fifield, F.W. and Kealey, D.
'Principle and Practice of Analytical Chemistry'
International Textbook Company Ltd., 1975

55. Deme, S.
'Semiconductor Detectors for Nuclear Radiation Measurement'
Adam Hilger Ltd., London. 1971

56. Willand, H.H., Merritt, L.L. and Dean, J.A.
'Instrumental Methods of Analysis'(5th edition)
Van Nostrand Reinhold Company Ltd., New York, 1974

57. Meredith, W.J. and Massey, J.B.
'Fundamental Physics of Radiology'
John Wright, 1977

58. Feigl, F.
'Quantitative Analysis by Spot Test', p. 124-129
Nordemann Publishing Co., New York, 1939

59. Green, D.E.
'Colorimetric Microdetermination of Zirconium'
Anal. Chem., 20, (4), 1948, 370-372

60. Mayer, A. and Bradshaw, G.
'The Adsorptiometric Determination of Zirconium by means of Alizarin Red-S with Special Reference to Magnesium Alloys'
Analyst, 77, 1952, 476-483

61. Wengert, G.B.
'Photometric Determination of Zirconium in Magnesium Alloys'
Anal. Chem., 24, (9), 1952, 1449-1451

62. Cohen, Y.
'Views on Quality Tests of Radiopharmaceuticals'
J. Radioanalyt. Chem., 26, (2), 1975, 317-325

63. Flagg, J.F., Liebhalsky, H.A., and Winslow, E.H.
'A Spectrophotometric Study of Three Zirconium Lakes'
J. Amer. Chem. Soc., 71, 1949, 3630-3632

64. Drăgulescu, C., Simonescu, T., and Palice, S.
'Extraction of the Zirconium-Alizarin Red-S Complex with Butanol'
Talanta, 11, 1964, 747-755

65. Harvey, A.E. and Manning, D.L.
'Spectrophotometric Methods of Establishing Empirical Formula of Coloured Complexes in Solution'
J. Amer. Chem. Soc., 72, 1950, 4488-4493

66. Manning, D.L. and White, J.C.
'Differential Spectrophotometric Determination of Zirconium'
Anal. Chem., 27, (9), 1955, 1389-1391

67. Connick, R.E. and Reas, W.H.
'The Hydrolysis and Polymerization in Perchloric Acid Solution'
J. Amer. Chem. Soc., 73, 1951, 1171-1176

68. Caletka, R. and Kyrs, M.
'Zum Mechanismus der Zirconium Sorption Salpetersäuremenium' (in German)
Collection of Czeckoslov. Chem. Commun. 29, (5-6), 1964, 1150-1162

69. Kohlschutter, H.W.
'Zur Anwendung von Trennsäulen in der Analytischen Chemie' [in German]
Z. Anal. Chem. 166, 1959, 262-273