ALPHA-RADIOACTIVE ISOTOPES IN THE MARINE ENVIRONMENT

by

J.J.W. HIGGO

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Abstract

Various marine organisms collected from southern-hemisphere waters around Cape Town were analysed by radio-chemistry and alpha-spectrometry for Pu-239, 240. Many of these organisms were also analysed for Pu-238, Po-210 and those isotopes of thorium and uranium that are alpha-emitters. In some samples an estimate of the Ra-226 content was also made.

The Pu-239 concentrations are compared with the values reported in the literature for similar organisms found in the northern hemisphere and an attempt is made to relate the differences in concentration to differences in the quantity of fall-out Pu-239 delivered to the sea-surface in the two hemispheres. Within the limits of experimental error it appears that the Pu-239 content of recent fall-out is reflected in the Pu-239 concentration in many marine organisms.

The Pu-238/Pu-239 ratio was determined accurately on five samples and was surprisingly low when compared with the ratio in fall-out. It is postulated that Pu-239 might be selectively taken up by marine organisms in preference to SNAP-9A Pu-238.

Collateral determinations of a large number of alpha-emitting isotopes in a wide range of marine organisms were carried out. While no clearcut relationships between the elements emerged, the results gave many clues to the behaviour of these isotopes in the marine environment. Current theories about this behaviour, and the published data concerning these isotopes, are reviewed and discussed in the light of this work.

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PART I

BACKGROUND, RESULTS AND DISCUSSION

CHAPTER I

Introduction

During the past few years there has been increasing concern about the impact of man's activities upon the environment. In particular, the advent of the nuclear age has led to widespread anxiety about the dangers of introducing radioactive nuclides into the environment. Artificial radioactivity has always been very carefully contained and controlled and there is no doubt that the popular press takes a delight in exaggerating these hazards. Nevertheless, it is essential that a close watch should be kept upon environmental radioactivity.

In 1944 the discharge of effluent from the reactors at the Hanford atomic plant introduced radionuclides into the Pacific Ocean via the Colombia river. In July 1945 the first nuclear device was detonated in New Mexico (the Trinity test) and fallout began. Since then radioactive nuclides have been added to the oceans in wastes of various kinds and as a result of fallout from numerous nuclear explosions. The result of this has been a gradual build up of longer-lived nuclides in the biosphere.

Hopefully, atmospheric testing is on the decline but the utilization of nuclear energy for peaceful purposes is increasing rapidly and the oil crisis can only reinforce this trend. It seems certain, moreover, that even with improved waste-management techniques, some of this artificially produced radioactivity will find its way into the sea.

This radioactivity subjects marine organisms to doses of radiation over and above the natural background level and it is very important that we should have a clear understanding of the behaviour of the various nuclides in the oceans and of their transport along aquatic chains.

Early workers in the field of radio-ecology concentrated on the beta-emitting nuclides. This was because the major portion of the long-lived activity from a nuclear bomb blast is due to nuclides such as Sr-90, Cs-137 and Fe-55, all of which decay by a beta-process. Furthermore, the natural isotope K-40, which is also a beta-decay isotope, accounts for about 97% of the activity in sea water. However, during the last ten years many cases have been observed where the alpha-

emitting Po-210 contributes a major portion of the natural burden of ionising radiation (25, 43, 99). Indeed in a recent review Woodhead (150), after discussing the dose commitment from environmental radioactivity, has stated that: "The greater proportion of the background dose rate to ALL groups of organisms considered is due to incorporated radioactivity, alpha-emitting nuclides (principally Po-210) being the main source and K-40 delivering most of the remainder."

Of the alpha-emitting nuclides introduced into the environment by man the most important, by far, are the plutonium isotopes. It has been estimated that fall-out from nuclear explosions alone has introduced over 400 kCi of Pu-239 into the atmosphere (62). Furthermore, it has become evident that plutonium is concentrated significantly by many organisms in the sea (103, 107, 153, 150). As a result some of these organisms may receive appreciable doses of alpha-radiation from accumulated plutonium while the concentration of plutonium in water itself is still very low. In fact, it now appears that when the relative biological effectiveness of alpha-, beta- and gamma-radiation is considered, fall-out plutonium contributes more than fall-out Sr-90 or Cs-137 to the artificial radiation exposure of many marine species (103).

It is particularly important to learn as much as possible about the environmental distribution of plutonium in view of the increasing number of applications that are being found for its isotopes. Seaborg has estimated that the annual world production rate of Pu-239 will increase from about 20 000 kg in the 1970-1980 period to 80 000 kg in the period 1990-2000. He also visualized that the annual rate of production of Pu-238 could increase from the present 19-20 kg to 100 kg in 1980-1990 with the amount in use in power sources for mechanical heart pumps reaching perhaps 6 000 kg by the turn of the century (80).

Even if there were to be no further nuclear tests, it is inevitable that some of this vast amount of plutonium will find its way into the biosphere. Moreover, the half life of Pu-239 is $2{,}4 \times 10^4$ years; so the effects of any release of this isotope into the environment will be felt for thousands of years to come.

Up to the present time all determinations of plutonium in the marine environment have been carried out in the northern

hemisphere, where fall-out has been considerably higher than in the southern hemisphere. It was considered important therefore to establish the current levels of plutonium in the waters of the southern hemisphere before the inevitable growth of the nuclear industry resulted in further additions to the environment. The establishment of the base-line should be invaluable when assessing the significance of any subsequent increase in concentration.

Because of the difficulties associated with analysing sea water itself and because the real dangers arise out of the biological accumulation of radioactive isotopes, it was decided to concentrate on the analysis of a range of organisms. This would give us some insight into the way in which plutonium is carried up the food chains and would help us to decide which organisms would be most suitable for analysis during a projected long-term programme aimed at monitoring the marine environment.

Plutonium is a very toxic element. From the moment of its discovery its dangers have been emphasised to a degree which can almost be described as alarmist. Langham (75) contends that we know more about the physiology, toxicity and industrial medical control of plutonium than of any other element in the periodic table. The toxicity of plutonium is, of course, due to the fact that many of its isotopes are alpha-radioactive, and in assessing the danger of exposure to its isotopes it is important to consider their concentration relative to those of the other alpha-emitting nuclides present.

All natural materials are radioactive to some degree and all organisms are subject continually to a low level of radiation from within their tissues, from the immediate environment and from cosmic rays. About half the naturally occurring radionuclides are alpha-emitters and many of them are present in the environment at concentrations considerably higher than current plutonium levels. However, as Woodhead has pointed out, "While both natural and fall-out radio-nuclides have been measured in a great diversity of marine organisms there is not a single species or group for which a complete set of data is available" (150). It is becoming increasingly obvious that if we are to obtain a clear understanding of the role of the alpha-radioactive nuclides in the marine environment, it is essential that simultaneous measurements of the concentrations of as many alpha-

emitters as possible should be made on the same sample. Only in this way can we keep the importance of the different isotopes in perspective and only in this way can we gain some insight into the behaviour of the natural alpha-emitters as they decay through their complex chains.

Also, the alpha-emitting nuclides have great potential as oceanographic and geochemical tracers. The plutonium isotopes, with their known dates of introduction into the environment, could prove of great value in this way. The members of the three natural series have already been used for dating and as tracers (19, 67, 93) but considerably more information is still needed.

The purpose of the research described in this dissertation was primarily to establish the current levels of the plutonium isotopes in marine organisms in South African waters but, for the reasons given above, the analytical methods were extended to include as many alpha-emitting nuclides as possible. Thus, several organisms were analysed for various isotopes of plutonium, uranium, thorium and polonium, whilst plutonium and polonium only were determined on many more. An estimate of the Ra-226 content was also made for some samples.

Part I of this thesis contains all these results and they are presented and discussed in Chapters 4 and 5. Chapters 2 and contain, respectively, a description of the alpha-emitting nuclides and a review of published data concerning their occurrence and behaviour in the marine environment.

Part II is devoted to the experimental aspects of this project. In Appendix I alpha-spectrometry and the analytical chemistry of the alpha-emitters are discussed. The problems encountered during the development of the analytical methods are described. The final procedures adopted are outlined, the accuracy and precision of the results obtained are discussed and typical spectra are shown. Finally, in Appendix II detailed analytical procedures are given.

CHAPTER 2

The Alpha-Radioactive Nuclides

2.1 Introduction

The alpha-radioactive nuclides found in the environment can be classified into two main groups: those which occur naturally and those which are artificially produced.

Approximately half of all the naturally occurring radionuclides are alpha-emitting, and most of them belong to the three series of radioactive isotopes known as the uranium, thorium and actinium series. These groups consist of a series of elements which include thorium, uranium, radium, radon and lead. In the marine environment the mother-daughter equilibria in the series are frequently completely disturbed by the differing physico-chemical behaviour of the two isotopes. Apart from their intrinsic interest, these disequilibria and the general decay patterns have been used in the age determination of corals, shells and sediments and for the determination of sedimentation rates in the oceans. Some, e.g. radium and radon, are used as oceanographic tracers in the study of water-mass transport. Figure 2.1 shows the three decay series. The half-life of each isotope is given below each symbol. Some plutomium and uranium isotopes that are not naturally occurring are included out of interest. The alpha-particle energies are not shown here but Table 6.1 gives the energies of all the alpha-emitting nuclides that are likely to be found in the environment.

Naturally occurring radionuclides that are not members of the three series have been found in nature. Thus in 1972 Hoffman *et al.* (59) detected Pu-244 in a natural sample (a bastnasite) at a level of 10^{-18}g of Pu-244 per gram. The half-life of Pu-244 is $8,3 \times 10^{7}$ years. This is the shortest-lived naturally occurring alpha-emitter that has been detected in nature. Cherry and Shannon (29) have arbitrarily taken 8×10^{7} years as the cut-off for nuclides in the category Isolated alpha-radioactive nuclides with long half-lives. They list six such nuclides; none of them have been detected in the marine environment to date, but for completeness they are listed in Table 2.1.

Fig. 2.1 The Natural Radioactive Series

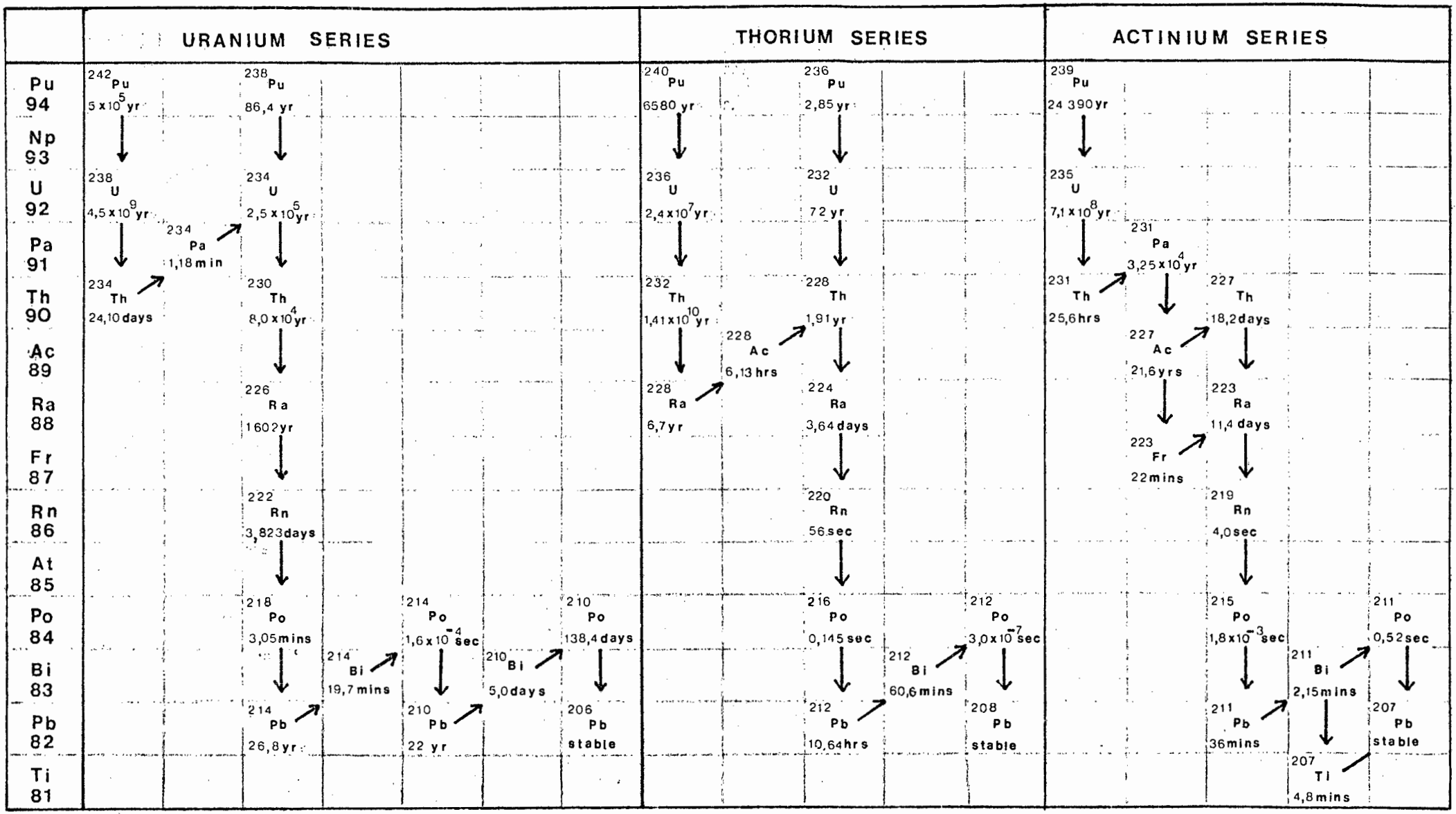


Table 2.1

Isolated alpha-radioactive nuclides with half-lives greater than 8×10^7 years

Nuclide	Half-life (years)
Pu-244	$8,3 \times 10^7$
Pt-190	6×10^{11}
Hf-174	3×10^{15}
Gd-152	$1,1 \times 10^{14}$
Sm-147	$1,1 \times 10^{11}$
Nd-144	2×10^{15}

The most important of the artificially produced alpha-radioactive nuclides are listed in Table 2.2.

Table 2.2

Some artificially produced alpha-emitting nuclides

Nuclide	Half-life (years)
Pu-242	$3,8 \times 10^5$
Pu-240	$6,58 \times 10^3$
Pu-239	$2,4 \times 10^4$
Pu-238	$8,64 \times 10^1$
Am-241	$4,58 \times 10^2$
Np-237	$2,1 \times 10^6$
Cm-242	$4,5 \times 10^{-1}$
Cm-244	$1,76 \times 10^1$

All the artificially produced and many of the naturally occurring alpha-emitting radionuclides belong to the chemical group of elements known as the actinides or the 5f transition series. This series consists of the fourteen elements which follow actinium (z = 89) in the periodic table. They result from the successive addition of electrons to the empty 5f orbitals of the precursor element and are analagous to the lanthanide or 4f transition series. The chemistry of the actinides is, however, far more complex than that of the lanthanides. This is because in the actinide series the energies of the 5f, 6d, 7s and 7p orbitals are comparable over a range of atomic numbers (especially U - Am) and the orbitals also overlap spatially. As a result the actinides in the early part of the series exhibit a variety of oxidation

states. Furthermore, they are prone to complex formation and readily form complexes with halides, sulphates and even certain π-bonding ligands. They hydrolyse readily; it has been established, for example, that the Pu^{4+} ion cannot exist in solution below 0,05 M in acid.

All this and the fact that these elements are present in the sea at infinitesmally low concentrations makes it very difficult to make predictions about the behaviour of the actinides in the marine environment from their chemical properties. In fact, it is hoped that information about the way in which they are absorbed and concentrated by marine organisms will give us some insight into the chemical and physical properties of the different isotopes in sea water.

Apart from the actinides, the three other elements that have alpha-emitting isotopes of interest are radon, radium and polonium.

Radon is a rare gas with typical rare gas chemistry. The half-lives of both Rn-222 (U-series, $t_{\frac{1}{2}}$=3.82 days) and Rn-220 (Th-series, $t_{\frac{1}{2}}$=56 sec) are short and no attempt has been made to determine the concentration of these isotopes in marine organisms.

Radium is the heaviest Group II element. The members of this group form a closely allied series in which the chemical and physical properties of the elements vary systematically with size. They are all highly electro-positive metals, readily losing their two external electrons for form divalent cations. It appears that approximately 90% of the calcium and magnesium present in sea water is ionic (49) and it seems likely therefore that the same applies to radium.

Polonium has been shown to be the most important contributor to the alpha-radioactive dose of many marine organisms (99,25, 43) and as such is of particular relevance to the present discussion. Unfortunately relatively little is known about the chemistry of polonium, largely because the intense alpha-radiation of Po-210, the longest lived polonium isotope ($t_{\frac{1}{2}}$= 138 days), makes it very difficult to study. In addition investigations into the solution chemistry of polonium have been complicated by the ease with which it hydrolyses and forms colloids. However, polonium is the heaviest member of the Chalcogen group of elements (O, S, Se, Te, Po) and there is a

close chemical resemblance of polonium to tellurium and also to bismuth, its neighbour in the periodic table.

The Chalcogens have the $ns^2\ np^4$ outer electronic configuration and are therefore predominantly non-metallic with gradually increasing metallic characteristics as one progresses down the group. Polonium itself is a typical metal and, as is to be expected from the electronic configuration, can exist in the stable oxidation states -2, +4 and possibly +6.

Polonium is present in sea water at incredibly low concentrations (3×10^{-17} M) but may be concentrated many thousands of times by marine organisms and, as with the actinides, it is possible that increased knowledge about this concentration process will enable us to make deductions about the chemical and physical forms in which polonium exists in the oceans.

A discussion of the various alpha-radioactive isotopes that are found in the environment and the inter-relationships between them now follows. For the purpose of discussion they will be classified into the following groups:-

1) Nuclides in the uranium series
2) Nuclides in the thorium series
3) Nuclides in the actinium series
4) Isolated nuclides with long half-lives (greater than 8×10^7 years)
5) Artificially produced nuclides with half-lives less than 10^8 years

2.2 The Uranium Series

At the head of this series we have U-238 and U-234 separated by the two much shorter-lived nuclides Th-234 and Pa-234. In the terrestrial environment they are generally found to be in radioactive equilibrium but in the marine environment the situation is more complicated. The disequilibrium between these two uranium isotopes is discussed in Chapter 3.

The typical U-238 concentration in rocks is about 2,8 ppm. In general, igneous rocks and granite contain higher concentrations than sedimentary rocks such as limestone and chalk, although some sedimentary rocks of marine origin do contain very high levels of uranium.

Traces of Ra-226, at a level of about 1 pCi/g, are

present in most geological materials. Ra-226 decays to the rare gas Rn-222, some of which is continuously emitted from land surfaces to escape into the atmosphere. This Rn-222 and its short-lived decay products constitute the main part of the radioactivity of ground-level air. The actual concentration of Rn-222 in the air varies considerably and depends upon the rate of emanation from soils, atmospheric thermal stability, local meteorological conditions, time of day and distance from the coast. Rn-222 has a half-life of 3,8 days and its daughter Po-218 decays rapidly to Pb-210, a beta-emitter. The half-life of Pb-210 (22 years) is much longer than its mean residence time in the troposphere, which is probably somewhere between one and four weeks (29, 140). A natural fall-out of Pb-210 and its daughters Bi-210 and Po-210 then results and these nuclides are incorporated into the biosphere and the geosphere.

The half-life of Bi-210 is only five days and its disequilibrium situation is relatively uninteresting. However, the half-life of Po-210 is 138 days and the Pb-210 - Po-210 disequilibrium has been intensively studied during recent years. Thus the Po-210/Pb-210 activity ratio in ground level air usually ranges between 0,05 and 0,30 but ratios of greater than unity are found in industrial regions. This implies that a significant amount of Po-210 is released from coal burning. It is estimated that in the latitude zone between 40°N and 60°N the quantity of artificial Po-210 is about 10%-20% of that arising naturally (140).

The deposition rate of Pb-210 in rain water is 3 mCi/km^2 p.a. The level in rain water is of the order of 1 - 5 pCi/l while that of Po-210 is five to ten times less. The concentrations in surface water are usually ten to a hundred times less than in rain water (140).

2.3 The Thorium Series

The Thorium series is headed by Th-232 and is made up of different isotopes of the same elements as the Uranium series. The equilibrium situation is, however, much simpler.

Like uranium, thorium is more abundant in basic than in acidic rocks. Both its terrestrial abundance on a mass basis and its half-life are approximately three times those of U-238. This means that on an activity basis the terrestrial abundance

of Th-232 is approximately the same as that of U-238.

Ra-226 and Ra-228 are generally present in soil at varying levels of radioactive equilibrium with their parents and have similar terrestrial abundances on an activity basis.

The gaseous element of this series is Rn-220. Rn-220 and its daughters behave in the atmosphere in the same way as Rn-222 and its decay products but the short half-life of Rn-220 (56 sec) prevents them from giving rise to any substantial fall-out like that resulting from the situation with Pb-210 - Bi-210 - Po-210. Thus although in normal emanation conditions the Rn-220 and Rn-222 concentrations one metre above ground level are of the same order, the distance covered by a Rn-220 atom between the point where it emanates from the ground and the point where it disintegrates is less than one metre. This means that fall-out from Rn-222 over the sea is negligible.

After Th-228 the series comes into secular equilibrium in less than three weeks and after Ra-220 within three days. These time scales are short and from the point of view of marine samples the only Thorium series nuclides that have provided data of interest are the trio Th-228, Ra-228 and Th-228.

2.4 Nuclides in the Actinium Series

The head member of this series is U-235, which constitutes about 0,7% by mass of natural uranium. Because of its shorter half-life its activity is approximately 4,5% of the U-238 activity. The gaseous element in the chain is Rn-219 but its very short half-life (4,0 sec) leads to an atmospheric activity of its decay products about 2000 times less than that of Rn-222.

Because of these low concentrations less attention has been paid to the members of this series than to nuclides of the other two series. In fact, only the nuclides at the top of the series (i.e. U-235, Pa-231, Ac-227 and Th-227) are of any interest in the marine environment.

2.5 Isolated Alpha-radioactive Nuclides with Long Half-lives

None of these nuclides (Table 2.2) have been detected in the marine environment and they will not be considered further.

2.6 Artificially Produced Radionuclides

The most important artificially produced radionuclides have been listed in Table 2.1. Of these the only isotopes that have been found in the marine environment in readily detectable quantities, on a global basis, are those of plutonium; these will now be considered in some detail.

2.6.1 Plutonium Isotopes

At present fifteen isotopes of plutonium are known but only Pu-239, Pu-240, Pu-238 and possibly Pu-242 are of interest to the ecologist. The half-life of Pu-239 is 2,4 x 10^4 years and therefore any Pu-239 that may have existed when the universe was first formed has long since decayed. However, Pu-239 has been detected in pitchblende and monazite ores in the ratio Pu-239/U = (0,7 to 2,0) x 10^{-11}. It is believed that this plutonium is formed from U-238 by the action of neutrons evolved as a result of spontaneous fission of U-238

$$\left[{}^{238}_{92}U\,(n,\gamma)\,{}^{239}_{92}U \xrightarrow{\beta^-} {}^{239}_{93}Np \xrightarrow{\beta^-} {}^{239}_{94}Pu \right]$$

and also during the fission of U-235 and through (α, n) reactions of the lighter elements.

The concentration of natural plutonium in the environment is however negligible and nature was virtually free from plutonium until the explosion of the first atomic bomb in July 1945. Since then the levels of plutonium in the environment have risen continuously (although at a decreasing rate in the last decade) mainly as a result of nuclear explosions.

Pu-239 is a significant component of worldwide fall-out, its activity in fall-out being approximately 2%-3% of the Sr-90 activity. Hardy (53) has calculated that 326 kCi of fall-out Pu-239 had been deposited on the earth by mid 1970.

Pu-240 is also present in fall-out in significant quantities. Unfortunately, the energies of the alpha-particles from Pu-239 and Pu-240 are not sufficiently different to be separated by alpha-spectrometry and it has become customary to report fall-out activities as the sum of the activities of Pu-239 and Pu-240. This practice has been followed here and wherever concentrations of Pu-239 are given one should actually read Pu-239 plus Pu-240.

Recently Noshkin and Gatrouss (105), using mass spectrometry, have distinguished fall-out Pu-239 from Pu-240 in aquatic

samples for the first time. Their results show no single characteristic Pu-240/Pu-239 ratio and the ratio on an atom basis varies from 0,11 to 0,24. The atom ratio in fall-out can vary from 0,02 to 0,36 but they calculate that the average ratio (up to 1973) in the middle latitudes must have been about 0,18. The authors feel that their results indicate that Pu-239 and Pu-240 may exist in different physical and chemical forms in fall-out and that selective concentration by surface organisms is occurring. A Pu-240/Pu-239 atom ratio of 0,18 implies an activity ratio of 0,66 or that Pu-240 accounts for about 48% of the Pu-239 + Pu-240 activity.

Higher mass isotopes such as Pu-242 were deposited in the Pacific following the MIKE thermonuclear explosion in 1952, in which a considerable quantity of transuranium isotopes was generated. However, this was an isolated event and these isotopes are at present of little interest to the radio-ecologist.

Pu-238 is formed during weapons testing in the approximate ratio Pu-238:Pu-239 = 1:20 and has been detected in marine samples and on land. A further quantity of Pu-238 was introduced into the environment in 1964 when a Transit Navigational Satellite was launched from California. The payload included a SNAP-9A generater (Systems for Auxilliary Power) containing 17 kCi or about 1 kg of Pu-238. The rocket failed to boost the satellite into orbital flight and the satellite re-entered the atmosphere in the southern hemisphere. By mid 1970 it was estimated that 95% of the SNAP-9A Pu-238 had been deposited on the earth's surface and that as a result of this accident the global deposit of Pu-238 had almost tripled. A similar device re-entered the atmosphere and fell into the Pacific Ocean in April 1970 but no information about any release to the environment is available. Another fell into the waters off the coast of California in May 1968 when a weather satellite exploded during launching but was later recovered. Thus the SNAP-9A accident is not an isolated case and the increasing use to which these generaters are put makes it likely that further such incidents will occur.

While most of the plutonium in the environment has been produced during weapons testing, small quantities have been released from other sources. Joseph (62) has given a detailed discussion of all sources of radioactive pollution. It appears

that plutonium reaches the seas as a result of underwater nuclear testing, from fuel reprocessing facilities and from accidents involving nuclear devices such as the SNAP-9A incident, the B-54 aircraft disaster near Thule in 1968 and the loss of the Thresher submarine. Thus increased plutonium levels have been reported in waters and marine life near test sites (e.g. Bikini in 1964), in the discharge area of the Windscale pipe line and near Thule.

At the moment very little plutonium reaches the oceans from nuclear reactors but the introduction of Fast Breeder Reactors may well change this. These reactors will breed Pu-239 from U-238. They will derive 80% of their energy output from Pu-239 fission and the other 20% from fast fission of U-238, while producing enough additional plutonium to provide fuel for new reactors. It was the proposed introduction of these reactors that led Seaborg to predict the rapid increase in plutonium production mentioned in Chapter I.

2.6.2 Plutonium Isotopes and Worldwide Fall-out

When discussing fall-out one must consider the effects of atmospheric circulation. The atmosphere can be divided into a surface (troposphere) and a bulk (stratosphere) circulation. In the stratosphere, zonal, or east-west, circulation is fast, requiring a week or ten days to circle the earth. Meridional, or north-south, circulation is much slower and is driven by the need to move heat from the equator to the poles. The air rising at the equator turns towards the poles, the lower layers moving faster than the upper layers. This poleward motion is not present above about 80 000 feet where the air is considered to be stagnant in the meridional plane. Understandably, there is little reason for this circulation to produce motion across the equator.

In the troposphere debris from an explosion also tends to be dispersed in an east-west band around the earth. Here dispersion is effected by the weather system and, in the middle latitudes in the upper troposphere, by jet steams. Again meridional circulation is slow because it depends on large scale eddy diffusion or mixing by turbulence associated with weather fronts.

Exchange between stratosphere and troposphere is small and occurs intermittently rather than continuously, chiefly in high latitudes in winter.

Thus, in both stratosphere and troposphere as well as in the wind driven ocean surface currents, there is a minimum of mixing across the equator and pollutants injected into one hemisphere are on the whole, slow to move into the other hemisphere.

Until 1968 most nuclear tests were carried out in the northern hemisphere and Hardy (53) estimated that up to 1970 about 80% of the total weapons fall-out had occurred in this hemisphere. The SNAP-9A accident on the other hand occurred in the southern hemisphere and he estimated that about 75% of the SNAP-9A Pu-238 was deposited in the southern hemisphere.

It should be of considerable interest to compare our results with those of northern hemisphere workers and to relate them to the deposition of fall-out plutonium in the different regions. Unfortunately data on fall-out plutonium is very sparse but it has been possible to make rough estimates of the relative amounts of plutonium that have been deposited in each hemisphere and of the Pu-238/Pu-239 ratio in this fall-out from the results reported by the United States Atomic Energy Commission Health and Safety Laboratory (H.A.S.L.).

H.A.S.L., in an attempt to follow the deposition of plutonium on a global basis, began measurements of Pu-239 in the stratosphere in 1953 but there were relatively few determinations in surface air before 1965. Measurements of Pu-238 also commenced in 1965 after the SNAP-9A accident. Some of the early data are suspect but from 1965 onwards their figures can be considered reliable.

Attempts to follow the ground deposition rates of Pu-238 at three stations using large area fall-out collection systems failed. This was because of contamination problems at H.A.S.L., New York, and incomplete removal of plutonium from the collectors at Melbourne. As a result ISPRA (Italy) is the only site from which continuous fall-out data are available.

In the circumstances a soil sampling programme was the only way to measure the accumulated deposit and from October 1970 to January 1971 sixty-five sites around the world were sampled and subsequently analysed. The results of this survey

have been reported by Hardy, Krey and Volchok (53), while the Pu-238 and Pu-239 concentrations in surface air are listed in various H.A.S.L. reports (55).

A useful check on the Pu-239 data is provided by the fact that the Pu-239/Sr-90 ratio in fall-out has remained virtually constant through the years and should continue to do so unless the pattern of weapon types changes. The Pu-239/Sr-90 ratio at the time of formation is 0,18. This ratio increases with time since Sr-90 decays at a rate of 2,5% per year; but, as long as the ratio at time of formation remains constant, the ratio

$$\frac{\text{Sr-90 in southern hemisphere}}{\text{Sr-90 in northern hemisphere}}$$

should equal the ratio

$$\frac{\text{Pu-239 in southern hemisphere}}{\text{Pu-239 in northern hemisphere}}$$

Table 2.3 shows the results of Hardy, Krey and Volchok's soil analysis programme, which gave reliable results for total cumulative fall-out throughout the world up to 1970.

Tables 2.4 and 2.5 summarise the figures in the H.A.S.L. reports. The H.A.S.L. network extends from about 75°N to 90°S. Air is filtered continuously at each station and the combined filters are composited into a monthly sample for analysis. Between 20 and 30 stations were involved in the plutonium programme.

In the absence of detailed knowledge about local conditions it has been possible to do no more than to average the results for the two hemispheres. Two stations, namely Thule, site of the B52 bomber crash, and Rocky Flats, where plutonium from leaking oil drums resulted in high local concentrations in surface air, were excluded.

Simple averaging has the disadvantage that excessive weight may be given to specific latitudes but as most of the stations were in the middle latitudes, where most of the marine organisms analysed were collected, this may be an error in the right direction. In actual fact it makes very little difference whether one averages the results for just the middle latitudes or for the whole hemisphere (see Table 2.4). The latter practice was, therefore, generally adopted as it makes it easier to compare with other workers - because of uncertainty

Table 2.3

Inventory of Pu-239 and Pu-238 in Fall-out

	Pu-239 mCi/km^2			Pu-238 mCi/km^2			Pu-238/Pu-239	
Latitude	S	N	S/N	S	N	S/N	S	N
0-90°	69 ± 14	256 ± 33	0,27 ± 0,07	12,4 ± 2,1	9,2 ± 1,1	1,3 ± 0,3	0,18 ± 0,047	0,036 ± 0,006
30°-40°	0,40 ± 0,12	1,8 ± 0,6	0,20 ± 0,07	0,07 ± 0,02	0,067 ± 0,020	1,0 ± 0,4	0,175 ± 0,072	0,037 ± 0,016

Table 2.4

Activities of Pu-239 and Sr-90 in in Northern and Southern Hemisphere Surface Air as calculated from H.A.S.L. Reports

Year	Plutonium-239 (+ Plutonium-240)				Strontium-90		
	Attocuries/ m^3				Femtocuries/ m^3		
	S	N	S/N	$\frac{S(16^\circ-40^\circ)}{N(25^\circ-44^\circ)}$	S	N	S/N
1966	58,83	81,92	0,72	0,67	1,70	4,17	0,42
1967	33,16	30,28	0,91	0,86	0,86	2,15	0,40
1968	13,61	63,15	0,22	0,19	1,04*	2,06*	0,50*
1969	17,63	45,29	0,39	0,46	0,77	1,74	0,74*
1970	34,9	57,87	0,60	0,58	1,20	2,80	0,58
1971	28,51	58,86	0,50	0,44	1,28	3,07	0,43
1972	27,51	29,14	0,94	0,93	0,88	1,06	0,71
1973	15,83‡	11,10	1,44	1,57	0,39	0,40	0,97
$\frac{1972S}{1969N}$			0,61				0,50
$\frac{1972S}{1970N}$			0,48				0,31
$\frac{1973S}{1969N}$			0,35				0,22
$\frac{1973S}{1970N}$			0,27				0,14

* Neglecting Portillo

‡ Neglecting Santiago

Table 2.5

Comparison of South/North Ratios Obtained From Different Sets of Figures

Year	Pu-239 in surface air.H.A.S.L(55)	Pu-239 in surface air. Harley (54)	Sr-90 in surface air.H.A.S.L.(55)	Annual deposition of Sr-90 (139, 140)
1966	0,72	0,94	0,42	0,66
1967	0,91	1,0	0,40	0,65
1968	0,22	0,18	0,50	0,53
1969	0,39	0,38	0,77	0,93
1970	0,60	0,67	0,58	0,62
1971	0,50		0,43	
1972	0,94		0,71	
1973	1,44		0,97	

about the effects of strong winds and surface currents and because in some years results from only three stations at the relevant latitudes are available.

Because we are interested in comparing our southern-hemisphere samples collected in 1972 and 1973 with northern-hemisphere samples collected in 1969 and 1970, various south/north ratios for these years are also included in Table 2.4.

Harley (54) has discussed the plutonium in fall-out up to 1970 and has tabled Pu-239 concentrations in surface air up to that date. Although he was working with H.A.S.L. data, his figures are very different from those given in Table 2.4 and were presumably obtained using sophisticated statistical techniques and bearing in mind local conditions of which we are unaware. However, south/north ratios calculated from his figures are virtually the same as those in Table 2.4 and it is, therefore, likely that the 1972 and 1973 ratios in Table 2.4 are also reliable.

Finally, Sr-90 has been studied in much greater detail than Pu-239 and figures for the annual deposition of Sr-90 are available up to 1970 (140, 143). South/north ratios have been calculated from these data and Table 2.5 shows these figures together with those calculated from Harley's data and, for ease of comparison, the ratios already given in Table 2.4.

On the whole, agreement between the four sets of figures is reasonably good certainly good enough for our purposes and we would expect the south/north ratio in marine samples to vary from the low 0,27 cumulative figure in sediments to as high as 1 in surface water and plankton depending on the time of sampling.

Table 2.6 shows the Pu-238/Pu-239 ratios in northern and southern hemisphere surface air as calculated from the H.A.S.L. figures. (A column showing the average concentration of Pu-238 in southern hemisphere surface air is also included but it should be noted that, as Pu-239 was determined in many more samples than was Pu-238, one cannot simply calculate the Pu-238/Pu-239 ratio by dividing the figures in this column by the Pu-239 - south figures given in Table 2.4. The ratios given in Table 2.5 are the averages of individual ratios).

Table 2.6

Pu-238/Pu-239 Activity Ratios in Surface Air as Calculated from H.A.S.L. Figures

Year	Average Pu-238 in southern hemisphere (atto curies/m^3)	Pu-238 / Pu-239	
		Southern Hemisphere	Northern Hemisphere
1966		0,64	0,11
1967	55,84	1,34	0,44
1968	21,01	1,69	0,33
1969	12,71	0,85	0,24
1970	12,46	0,35	0,11
1971	6,0	0,28	0,15
1972	5,2	0,175	0,16
1973	11,2	0,56*	0,27

* This figure unreliable. See discussion

These ratios are, on the whole, higher than those reported by Miyake and Sugemura (89), who claimed that the Pu-238/Pu-239 ratio in fall-out over Tokyo was between 0,10 and 0,16 during the years 1967-1969. Because of the sheer number of determinations made by H.A.S.L. more weight should be attached to their figures, but it is difficult to decide just how reliable they are.

From a qualitative point of view it is interesting to note the very different ratios in the two hemispheres and the peak in 1967/68. But a careful study of the original individual figures shows that they are of rather dubious value from a quantitative point of view. For example, the results of a more detailed look at the 1971-1973 southern hemisphere figures and calculated standard deviations are shown in Table 2.7.

Table 2.7

Pu-238/Pu-239 Activity Ratios in Surface Air in Southern Hemisphere

Year	No. of Determinations	Mean	Range
1971	96	0,276 ± 0,241	0,08 - 1,5
1972	44	0,175 ± 0,148	0,05 - 0,78 Neglecting one value of 8,5
1973	7	0,499 ± 0,326	0,04 - 0,92

The range in the 1973 Pu-238/Pu-239 ratios is extremely wide and as there were only seven determinations the 1973 mean must be regarded as suspect. This is particularly unfortunate because all five of the southern hemisphere marine organisms in which the Pu-238/Pu-239 ratio was determined in this project were collected in 1973.

For a proper evaluation of our results, therefore, it is important to find a more reliable figure for the 1973 ratio in southern hemisphere surface air. Extrapolation from the activitie of the two isotopes during the preceeding years should yield a better estimate. Figure 2.2, overleaf, shows how the southern hemisphere concentrations of Pu-238 and Pu-239 varied over the period 1966-73. Figure 2.3 is a graph of the Pu-238/Pu-239 ratio over the same period.

Fig. 2.2 Pu-239 and Pu-238 Activities in Surface Air in the Southern Hemisphere.

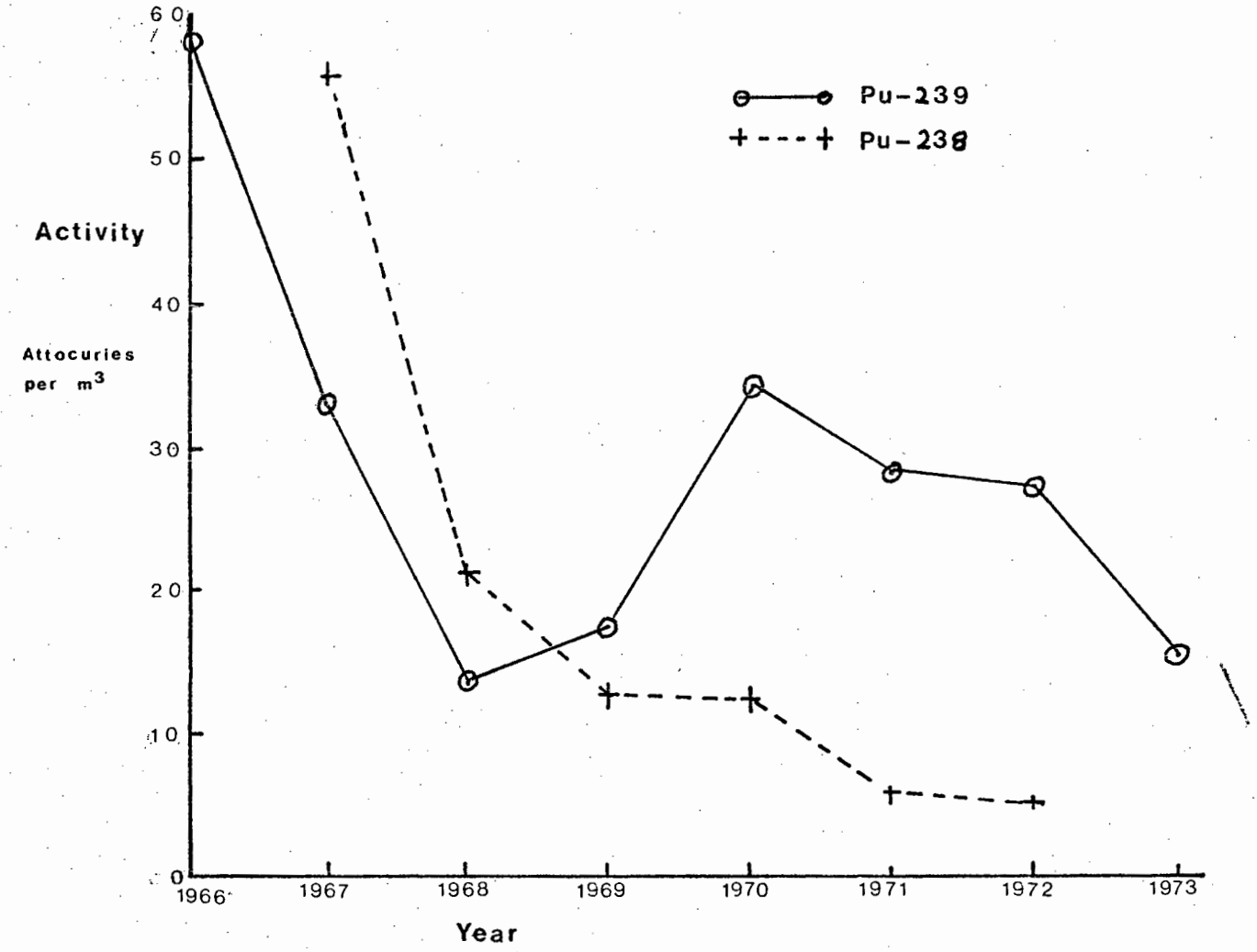
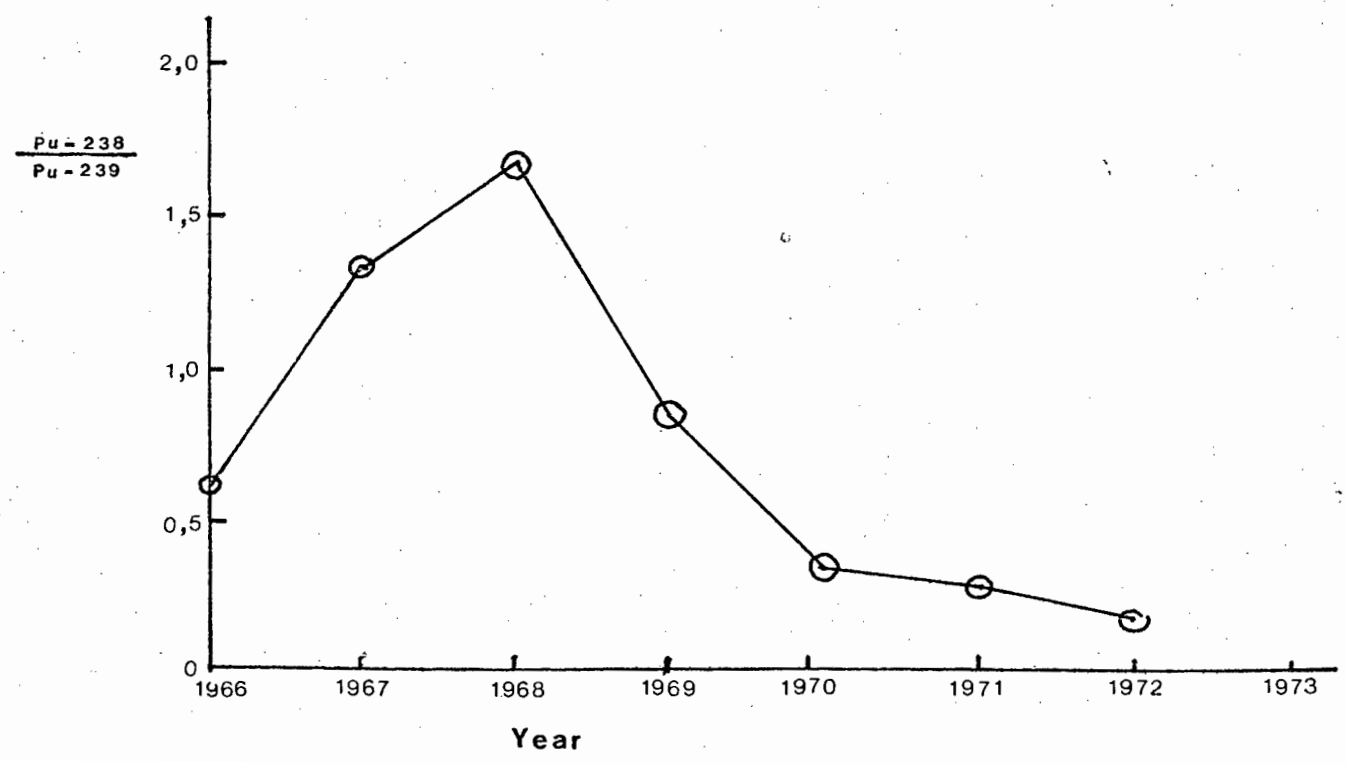


Fig. 2.3 Pu-238/Pu-239 Activity Ratio in Surface Air in the Southern Hemisphere.



No significant amounts of nuclear debris were injected into the atmosphere between 1963 and mid-1966 and the Pu-239 concentration in surface air therefore dropped steadily until 1968. In the last half of 1966 five nuclear devices were exploded above ground at the Tuamotu Islands in the South Pacific. Three were exploded in mid-1967 and several more in subsequent years. As a result the Pu-239 concentration in surface air rose and for the first time the Sr-90 and Pu-239 deposition was equally divided between the hemispheres. In 1973, however, the concentration of both these nuclides in surface air dropped to about half that of the previous year.

The Pu-238 concentration, on the other hand, dropped fairly steadily from the 1967 maximum, levelling out in 1971-1972. Thus in 1973, while the Pu-238 concentration probably dropped only slightly, the Pu-239 concentration was halved. This means that the Pu-238/Pu-239 ratio must have risen and was probably somewhere between 0,35 and the 1972 value of 0,175.

In this section an attempt has been made to obtain an overall picture of the way in which fall-out plutonium has been distributed between the two hemispheres. In Chapters 3 and 4 an attempt is made to relate the concentrations of Pu-239 and Pu-238 found in sea water and marine organisms to these fall-out figures.

2.6.3 Other Artificial Isotopes

Neptunium, americium and curium are also produced either during nuclear explosions or by the nuclear industry. Np-237 has been produced in bomb tests in quantities comparable with Pu-239 but no information on the occurrence of this isotope in the global marine environment is available. Presumably this is because the long half-life of Np-237 means that its environmental activity levels would be lower than that of Pu-239 by a factor of one hundred, making it difficult to detect by alpha-spectrometry.

Am-241 and Cm-242 have been detected in porphyra collected from the vicinity of Windscale and in the lagoon receiving the discharge from the Nuclear Fuel Services Inc. reprocessing facility. Am-241 was also released into the environment after the military aircraft disaster near Thule in 1968 (103). However, the quantities involved were very small and at the moment these isotopes are of little interest to the environmentalist.

CHAPTER 3

The Alpha-Radioactive Nuclides in Sea Water and Marine Organisms

3.1 Introduction

Cherry and Shannon in a recent review (29) have attempted to co-ordinate and systematise current knowledge about the concentration and distribution of alpha-radioactive elements in sea water and marine organisms. However, as they point out, the problem is not simple. "There are an enormous variety of organisms; they occupy various stages in the marine food chain; their function and/or physiology vary with their stage of growth and with their physico-chemical environment; the higher organisms possess different organs which will concentrate different nuclides to different levels. To make matters worse, the available data are patchy and usually unco-ordinated."

For the purpose of discussion they divided the organisms into the following categories:-

A1 : phytoplankton
A2 : macrophytes
B : zooplankton
C : marine invertebrates (excluding zooplankton)
D : fish
E : mammals

This classification will be followed here.

Frequent use is made of the term concentration factor. The concentration factor is a useful concept and is defined as the ratio of the concentration of the element or radionuclide in the organism or tissue to the concentration of the same nuclide in sea water.

The whole concept of concentration factors and the use of biological indicators presupposes that increased concentrations of an element in the water causes an increased concentration in the tissues of the organism. This is frequently the case and Polikarpov (110) has drawn up some "basic rules and principles on the dependence of processes of uptake and accumulation on concentration of chemical elements." His rule one is: "In the region of micro-concentrations (10^{-6} - 10^{-4} moles/l) under otherwise equal conditions the concentration of a chemical element in

the hydrobiont is directly proportional to such in water, that is, concentration factors are not dependent on concentration."

Whether or not the rule is obeyed depends upon both the element and the type of organism. Thus plankton are generally excellent biological indicators while, to take an example at random, in decapod crustaceans the concentration of zinc in the body is regulated and does not increase appreciably when the concentration in the water is increased from 1 to 10 µg/l, i.e. from $1,5 \times 10^{-5}$ to $1,5 \times 10^{-2}$ moles/litre. As a result the concentration factor for zinc in these animals is almost inversely proportional to the concentration in water.

Brown seaweeds on the other hand appear to be unable to regulate many trace metals. The metals appear to be adsorbed onto colloids present or combined with polysaccharides such as alginic acid or fucoidan. These polysaccharides are found in the cell walls and are ion-exchange materials. Very often binding is strong and seaweeds placed in clear water may be very slow to lose adsorbed metals. This limits their usefulness as monitors of short-term fluctuations in the concentration of pollutants. The brown seaweeds will be discussed in more detail in the next section.

With the exception of uranium all the alpha-emitters are present in sea water at micro-micro levels (Table 3.1) and will therefore probably not be physiologically regulated. Nevertheless a study of concentration factors may prove misleading particularly if short-term fluctuations in concentrations in sea water are involved.

Table 3.1

Typical Oceanic Concentrations of Some Alpha-emitting Nuclides in Sea Water

Nuclide	Typical Oceanic Level (29)	
	pCi/l	moles/l
U-238	1,1	$1,4 \times 10^{-5}$
Th-232	1×10^{-4}	4×10^{-9}
Pu-239	7×10^{-4}	4×10^{-14}
Po-210	$2,5 \times 10^{-2}$	3×10^{-17}

A study of published tables of concentration factors (15, 29, 79) shows that for any organism and metal the range is large. In fact one is tempted to say that the greater the number of determinations the greater the range in values reported. For this reason published values of concentration factors should be treated with caution particularly if ranges are not given. In particular very few determinations of the alpha-emitters in marine organisms have been made and the concentration factor may be based on a single determination, e.g. the value of 2600 for plutonium in phytoplankton (79) is based on the single determination of Pillai (107).

One reason for this variability may be that very little attention has been paid to seasonal variations although these are known to be appreciable for several bivalve grazers, for many algae and possibly for plankton . Thus, while it is always instructive to compare concentration factors with those of other workers, it is, except in a few thoroughly investigated cases, impossible to generalise from a few results.

In addition to the biological classification used by Cherry and Shannon (29) it is interesting to consider which of the three main classes of marine ecosystems (pelagic, benthic or near-shore) an organism inhabits. Pelagic animals are associated with the water, maintaining buoyancy by flotation mechanisms or by swimming. Benthic animals are associated with the ocean bottom. The benthic and pelagic regions merge at the edge of the sea, forming the near-shore environment.

In the open ocean, light intensity decreases rapidly with depth so that most photosynthetic plants are found in the near-surface waters in the photic zone. Animals in the aphotic zone must rely on food derived either directly or indirectly from primary production in the overlying photic zone.

In the benthic and near-shore environments the sediment-water interface plays a major role : resuspended bottom materials form a significant part of the diet of many invertebrates as well as providing a surface upon which radionuclides can adsorb. This may play an important role in both the concentration process and the removal of elements from the water. Organisms that ingest sediment particles may or may not remove

radionuclides from the sediment, depending in part on the pH of the digestive system and in part on the nature of the sediment particles.

Near-shore waters will tend to contain higher concentrations of most elements (even fall-out nuclides will be enriched in near-shore waters by land run-off) and are areas of relatively intense biological activity. Nutrients are abundant, there is sufficient light to support photosynthesis and the bottom is especially rich in biota supported by the photic zone just above it. Radio-activity introduced into this environment will be found later in water, sediment and biota in proportions depending on the pro-perties of sediment, biota and particular radionuclides.

Of the categories mentioned above plankton (A1 and B) and fish (D) contain members belonging in the pelagic region.

Nektonic animals such as tuna make long migrations through different water masses and the radioactivity they contain will depend on their individual histories. Bowen et al. (15) describe them as "averagers". Because of their size they generally have a high ratio of mass to surface area. They are therefore relatively ineffective at taking up radionuclides directly from the water and different isotopes will be concentrated in different organs to different extents.

Plankton, on the other hand, drift with the surface waters and equilibrate with them. They can therefore often be used as biological monitors of radioactivity in their environment. Smaller plankton are particularly quick to equilibrate and it is postulated (15) that surface sorption, including ion-exchange, may play an important part in the incorporation of trace elements into the food chains by phytoplankton.

Larger plankton, e.g. euphausiids and salps, effectively filter large volumes of water while feeding. They responded quickly to increased amounts of Zr-95 and Nb-95 after the 1961-1962 atmospheric nuclear test (106). Either the radioactive particles were absorbed on the mucous, were directly filtered or, most probably, became attached to phytoplankton and smaller zooplankton and were eaten.

Furthermore, plankton are of importance in marine geochemical cycles not only because they are able to concentrate large

quantities of elements but also because they can transport them in a variety of ways. These include the sinking of skeletal structures and organic detritus; the moulting of crustacean exo-skeletons; the zooplankton's vertical migrations across mixing barriers and the incorporation of elements into fast-sinking faecal pellets.

In spite of all this and in spite of their position at the head of the food chain, it will be seen from the following chapter that very few determinations of alpha-emitting nuclides have been made in plankton. This paucity of results reflects not only the difficulty of collecting large samples but also the problems associated with assessing the data obtained. Thus any given sample may contain species from a dozen phyla having different morphologies, ash contents, trophic levels etc. Each group of species can have a very different elemental content as each may have different means available for concentrating a particular element. The rates of uptake will depend upon various physical factors such as temperature, salinity, population turnover rate and the physiological state, e.g. age, of the organism.

Nevertheless before we can hope to undertake a detailed biogeochemical balance of the alpha-emitting nuclides in the marine environment, we will have to gain some insight into the role played by plankton. This means that considerably more data will have to be amassed.

The mechanisms by which the different organisms absorb radionuclides varies according to feeding habits and may be very complex. In some cases simple adsorption onto the surfaces of organisms such as the macrophytes or plankton may be involved. In most cases, however, the nuclides appear to be incorporated into the tissues of the organisms and adsorption across biological membranes must be involved.

Biological membranes can absorb metal ions by a number of mechanisms. Small molecules and ions may penetrate by passive diffusion under the combined influence of a concentration and an electrochemical gradient. Certain essential ions and molecules can be transported across membranes against

an electrochemical gradient. Such a process requires an expenditure of energy from the breakdown of carbohydrates and is known as active transport.

At present it is difficult to provide a satisfactory explanation of ion transport because we are still ignorant of many of the fundamental properties of ions. We still cannot answer with certainty such questions as: "To what extent are ions hydrated in water and sea water?" "What are the radii of the hydrated ions?" "What molecules are likely to complex with what ions?"

The polyvalent ions because of their small size and large charge are frequently surrounded by an inner layer of firmly held water molecules. Recently the number of molecules in the inner hydration sphere of several cations has been determined by nuclear magnetic resonance (3, 34). Hydration numbers of 6 were found for Al^{+++}, Ga^{+++}, Mg^{++} and Ni^{+} of 4 for Be^{++} and of 10 for Th^{4+}.

The large value for Th^{4+} is probably because of the large size of the Th^{4+} ion and if no other factors are involved one might expect the other alpha-emitting nuclides to have similarly high hydration numbers.

All mechanisms attempting to explain the transport of ions from low to high concentrations across membranes require selective complexing of the ion in question. The ion may be transported by a complexing substance or once inside the cell it may be complexed with material already present and effectively removed from solutions. Thus any explanation of the different concentration factors for different elements should involve the different complexing properties of the ions.

Some marine organisms, such as plankton or seaweeds, may concentrate radionuclides directly from the water but others, such as the marine invertebrates, presumably obtain the bulk of their trace elements from food. They may have relatively complex structures and different elements may be concentrated in different organs. It would be impossible, here, to give an account of the structure and biochemistry of all these organisms but it is important to note that minor and trace elements are frequently concentrated in either the digestive system or the

skeleton (or shell). As we learn more about the mechanisms involved, which of the two is the main repository for a particular nuclide may help us to understand its general behaviour in sea water.

From a geochemical point of view the shells of the marine invertebrates are of great importance and their structure and formation have been studied in detail. Furthermore the uranium series dating methods for sediments and fossil shells have led to considerable interest in the concentration of, and the mechanism by which, the natural alpha-emitters are incorporated into the structure of the shell.

For the above reasons a fairly detailed discussion of shell structure and formation now follows. The shells of three main groups will be considered:-

1) Mollusca (mussels) 2) Echinoderms (sea urchin, starfish) 3) Crustacea.

It is convenient to consider the shell-forming system as consisting of four compartments in a linear arrangement (Fig. 3.1). The first compartment represents the medium, i.e. sea water and adjoining this in order are the tissue compartment, i.e. the mantle, the entrapallial fluid compartment and the shell. The compartments are interconnected permitting ions to pass from the mantle to the shell and vice versa.

The calcium of the shell which normally comes from the medium may be supplied from solubilised calcium carbonate in the mantle and other tissues. The organic matrix of the shell, consisting mainly of protein and mucopolysaccharides, is secreted by the mantle cell into the extrapallial fluid, where it becomes part of the growing inner surface of the shell.

Clearly the incorporation of ions into the crystalline structure of the shell is directly dependent upon their concentration in the extrapallial fluid at the site of crystallisation. The extrapallial fluid concentration in turn depends upon the concentration in blood and tissues which are governed by the rate of intake from the medium, sediment and food as compared with the rate of excretion and movement to the medium.

While much more information is needed about the composition

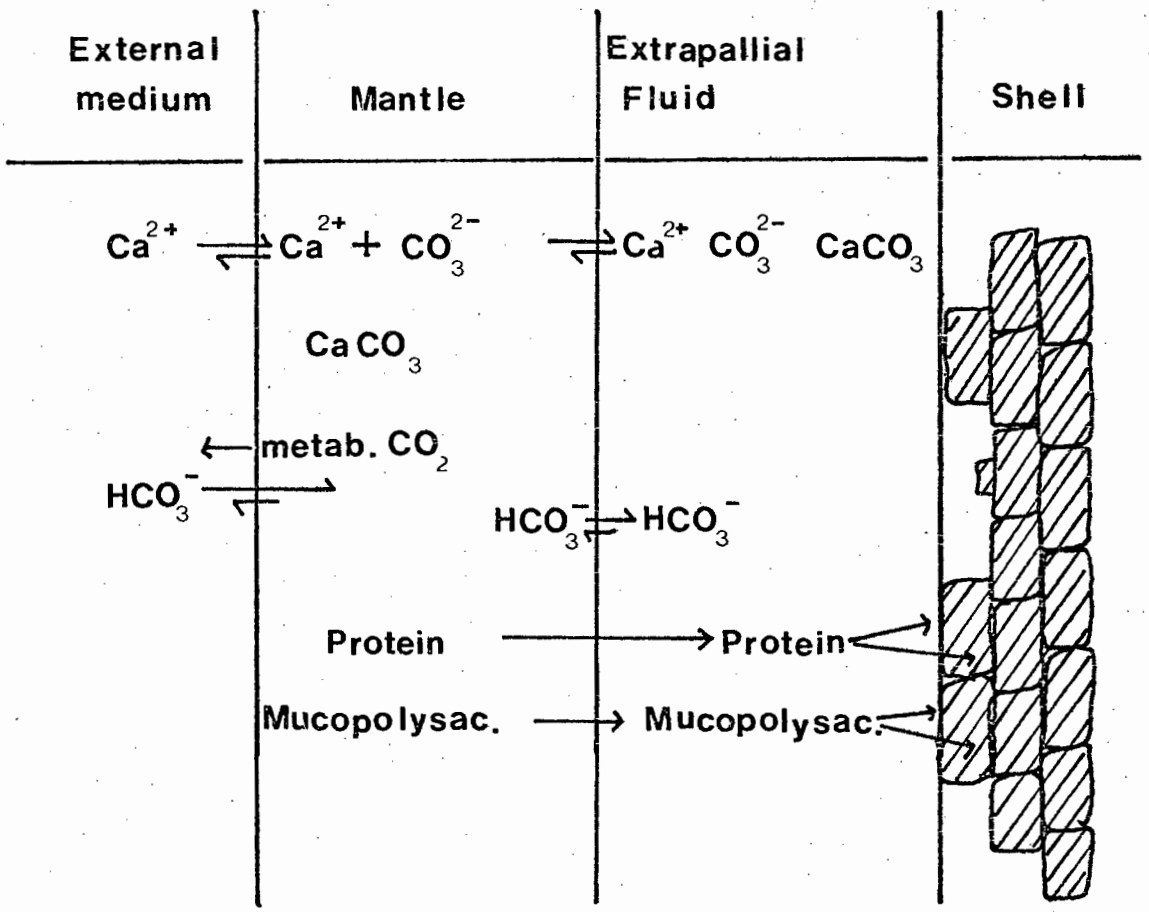


FIG. 3,1 Diagram of Compartments in Mollusks Showing Ions and Organic Compunds Compounds Concerned in Shell Formation [From K.M. Wilbur (23)]

of the extrapallial fluid it appears that it is slightly alkaline, the pH being between 7,33 and 7,41 (cf. sea water 7,8 - 8,2) and that it is saturated with respect to calcite and aragonite. It contains in addition numerous inorganic ions, proteins, mucopolysaccharides, glycoproteins and organic acids and there is evidence to suggest that crystal type is influenced by these organic constituents (23).

Calcification of the shell can be viewed as the result of two closely interrelated processes. The first is secretion of the extrapallial fluid by the mantle and the crystallisation of calcium carbonate from the fluid. The second involves the organic matrix and nucleation, crystal orientation and growth. These aspects of shell formation parallel those proposed for the formation of calcium phosphate in bone.

The type of crystals that form within an organism depend upon physical and chemical conditions and the cations involved. If the cationic radii are between 0,78 and 1,00 Å hexagonal crystals will be deposited and if the radii lie between 1,00 and 1,43 Å the crystals will be ortho-rhombic. The ionic radius of calcium is 0,99 and calcium carbonate occurs in the hexagonal form as calcite and in the ortho-rhombic form as aragonite.

Both crystal types are found in mollusc shells frequently in different layers in the same shell. Among the factors which influence the aragonite/calcite ratio and the development of aragonitic and calcitic layers in shells are temperature, salinity and the nature of the organic matrix.

The distribution of minor and trace elements in shell has frequently been examined for correlation with shell mineralogy. In particular the relationship between ionic size and the extent to which an ion is incorporated in the crystal lattice has been studied.

Table 3.2 gives some ionic sizes that are of interest. The second column is an attempt to summarise present views on the physical and chemical nature of the elements in sea water. Thus the alkaline earths are largely ionic (presumably hydrated).

Very little is known about the alpha-emitting nuclides and this problem has been emphasised throughout this thesis. The comments in Table 3.2 are conjecture rather than fact.

Table 3.2

Ionic Sizes of Cations and Probable Physical and Chemical Nature of the Elements in Sea Water

Element	Ionic Radius (Å)	Probable Physical and Chemical Form in Sea Water
Ca	0,99 (+2)	Ca^{++} (91%)
Mg	0,66 (+2)	Mg^{++} (87%)
Sr	1,13 (+2)	Sr^{++}
Ba	1,35 (+2)	Ba^{++} } probably 80-90%
Ra	1,40 (+2)	Ra^{++}
U	0,81 (+4) 1,11 (+3)	$[UO_2 (CO_3)_3]^{4-}$
Th	0,95 (+4) 1,14 (+3)	Precipitates as phosphates, hydroxides, etc. May be colloidal or attached to particulate matter.
Pu	0,93 (+4) 1,07 (+3)	Probably partly particulate. Associated with sinking particles.
Pb	1,20 (+2) 0,84 (+4)	Partly particulate. Also present as $Pb(OH)_2$, $[Pb\,Cl]^+$, $[Pb(Cl)_3]^-$.
Po	0,67 (+6) 1,02 (+4)	75% particulate. Probably colloidal and/or associated with particulate matter.

Calcitic shells contain about ten times as much magnesium as do aragonitic shells while generally speaking, aragonitic shells have a higher strontium content than calcitic shells. This is usually explained on the basis of easier substitution of the relatively small magnesium ion into the calcite lattice. Calcite is isostructural with magnesite ($Mg\,CO_3$). Similarly the larger strontium ion will fit more easily into the aragonite lattice which is isostructural with strontianite ($Sr\,CO_3$).

Thus, although other factors such as the chemical form of an ion in sea water and the conditions in the extrapallial fluid of an organism must frequently play a major part in deciding whether or not a particular element is incorporated into the

calcium carbonate lattice, it appears that in some cases ionic size is the deciding factor.

Certainly the large radium ion should fit more easily into an aragonitic than into a calcitic shell and one would therefore expect to find higher Th-228 concentration in aragonitic shells.

It has been suggested (40, 67) that uranium ions should fit more readily into the aragonitic lattice. However the ionic size of uranium is actually slightly smaller than that of calcium and at the moment the picture with regard to living shells is rather confused. (See section 3,4,2).

Uranium can be readily substituted into the apatite (calcium phosphate) structure and it has been reported that uranium in fossil fish bone is incorporated into the crystal lattice, while thorium is concentrated with hydrocarbons in the bone cavities (21,17) This difference in behaviour between thorium and uranium is probably due to the ionic nature of uranium as compared with the particulate or complexed nature of thorium in sea water.

Apart from uranium there are no published data on possible relationships between crystal structure and the extent to which the different alpha-emitting nuclides are incorporated into shells; but reference will be made to the above discussion when dealing with the results obtained in this project.

So far only molluscan shells have been considered. Some important differences exist between molluscan shells and the shells of other invertebrates and these will now be considered briefly.

The mineral part of the skeleton of the echinoderms is composed of magnesium calcite (71-95% calcium carbonate and 3-15% magnesium carbonate). This mineral forms a calcerous network whose pores can occupy more than 50% of the total volume. In the living organism these pores are filled with connective tissue.

We would expect therefore that if steric factors are important then a large ion would be less highly concentrated in a sea urchin shell than in a mussel shell. On the other

hand elements that complex readily with organic molecules might be concentrated in the pores.

Starfish also belong to this class but the martha asterias analysed in this project had relatively flexible skeletons when compared with the brittle sea urchin shell. It therefore seems likely that while the skeleton was also composed of magnesium calcite it contained a higher proportion of organic material such as chitin.

The shells of crustacea change with age. Thus little calcium is present in the epidermis of a lobster immediately after moult but it begins to accumulate as the shell hardens. In addition to calcification the protein component of the shell is hardened by sclerotisation. Calcified shell in crustacea cannot be classified as either aragonitic or calcitic. During calcification aggregates of micro-crystals usually radiating from a central point are formed. The mechanism of deposition appears to be a simple physico-chemical process depending upon salinity, alkalinity, etc. and the normal processes of co-precipitation could lead to the inclusion of trace elements.

A discussion of published data on the individual nuclides in sea water and marine organisms now follows. They will be dealt with in the same order as in Chapter 2.

With regard to units the example of Cherry and Shannon (29) will be followed. They have quoted all data in units of pCi/kg wet mass, as only in this way is it possible to reflect the in vivo situation. Where writers have reported activities per unit mass of dry or ashed sample they have converted all the data to a wet mass basis. Unless the experimental wet/dry factors are available in the original reference they have used the following conversion factors:-

Table 3.3: Wet to Dry Ratios

Phytoplankton: 21; Macrophytes: 7,5; Zooplankton: 15; Entire organisms in categories C and D: 3,7; Invertebrate shell (excluding crustacea): 1,2; Crustacean shell: 2,0; All soft tissue (excluding crustacean digestive glands): 3,7; Crustacean digestive glands: 2,7; fish and mammal bone and teeth: 1,2.

Ash to wet mass conversion factors used were phytoplankton: 55; zooplankton: 39; bone and teeth: 2,5.

3.2 Plutonium Isotopes

Several workers have determined plutonium in sea water and marine organisms. In this discussion only natural levels will be considered. Thus anomalously high local concentrations resulting from waste product disposal (103) or nuclear weapons incidents (1) have been excluded.

Apart from three sea water determinations by Bowen et al. (16) all determinations have been made in the northern hemisphere mainly at latitudes between 27° and 44°.

3.2.1 Sea Water

A summary of the available data on plutonium concentrations in sea water is given in Table 3.4 overleaf.

It is difficult to decide whether the variations in concentration are real or due to experimental error. The years 1962-1964 were years of exceptionally high fall-out, which explains the high plutonium concentrations found in 1963-1964. The mean of the 1967-1972 values is 7×10^{-4} pCi/l and this is the value reported by Cherry and Shannon (29) as typical for northern-hemisphere waters.

The only three Pu-239 determinations carried out in the southern hemisphere waters were reported by Bowen (16) in 1968, who remarks that they contained roughly half the amount found in northern hemisphere waters.

Unfortunately there is very little data on the Pu-238/Pu-239 ratio in sea water, although one would expect that the variations in fall-out described in Chapter 2 would be reflected in sea water.

Noshkin et al. (102) report that "six selected samples of water from Woods Hole Harbour (latitude 41° 30') collected during 1970 had a Pu-238/Pu-239 ratio of 0,12."

Miyake (88) in 1967, analysed thirteen samples obtained at latitudes between 24° and 44°. He found that the ratio varied between 0,07 and 0,28 with a mean of 0,14.

Table 3.4

Plutonium in Sea Water

Year	No. of Samples	Depth (m)	Location	Pu-239 pCi/l x 10^{-4} mean	Pu-239 pCi/l x 10^{-4} range	Pu-238/Pu-239 mean	Pu-238/Pu-239 range	Ref.
1963	1	0	44°N 41°W	14	-	-	-	16
1964	4	0	32°N 117°W	4	3-5	-	-	107
	2	0	27°-34°N, 129°-150°W	24	20-30	-	-	107
1967	1	0	56°N, 51°W	9	-	-	-	16
	10	0	24°N, 133°W	4	1-14	0,14	0,07-0,28	88
	3	0	35°N, 140°E	8	6-12			88
1968	3	0	27°N, 67° W	10	7-12	-	-	152
1968-69	2	0	36-37°N, 70°W, 0°E	9	6-15	-	-	16
	7	300-700	0-39°N, 63°W – 0°E	12	4-30	-	-	16
	7	1000-4500	25°N, 76°W	2	1-4	-	-	16
	2	1000-3000	33°N, 143°E	3	2-3	-	-	88
1969	4	0	36°N, 70°W	11	6-14	-	-	152
	1	0	36°N, 129°E	7,5	-	0,65	-	61
1968	6	0	Japan Sea	-	2-12	-	0,13-0,38	89
1970	6	0	41°N	-	-	0,12	-	102
1970	6	0	30°-42°N, 156-170°W	7,6	5,6-10,8	0,38	0-0,74	61
1971	1	0	27°N, 128°E	15,0	-	0,30	-	61
1972	1	0	36°N, 136°E	15,9	-	-	-	61
1968	3	0-100	18-28°S – 7°E	4	3-5	-	-	16

Finally Imai and Sakanou (61) analysed nine samples from the North Pacific. Their ratios varied from "Pu-238 scarcely detected" to the surprisingly high value of 0,74.

The analytical problems associated with the determination of such small quantities of Pu-238 in sea water are such that one must bear in mind that these results may not be too reliable. Certainly the wide variation in the values obtained by the latter two authors does not inspire confidence. Nor does the remark by Imai and Sakanou that recoveries varied from 3% to 68%. Furthermore, the spectra shown by Imai and Sakanou have "background" in the high energy ranges of the same order of magnitude as the Pu-238 peak. If only a small part of this background is due to Th-228 daughters then the Pu-238/Pu-239 ratios would be too high. (Th-228 and Pu-238 both emit alpha-particles with energies of 5,48 MeV).

In Chapter 2.1.2 some time was spent endeavouring to obtain accurate estimates of the Pu-238/Pu-239 ratio and the $\frac{\text{Pu-239 in the southern hemisphere}}{\text{Pu-239 in the northern hemisphere}}$ ratio in surface air and in total cumulative fall-out at different latitudes and times. We must now consider in what way these ratios can be expected to affect the corresponding ratios in sea water and marine organisms.

The residence time of fall-out in the troposphere is approximately 30 days (62, 139). Changes in the Pu-238/Pu-239 ratio will therefore be quickly reflected in the sea provided that the effect of such changes is not masked by the plutonium already present in the water.

Noshkin (104) reports that plutonium is rapidly depleted from the shallow water environment to bay sediments and that in deep water it appears to be associated with rapidly sinking particles. It is difficult to set a time scale to this depletion, but if this model is correct, then the upper mixed layer residence time is probably less than a year. If this is true then one would expect the Pu-238/Pu-239 ratio in surface waters to be nearly the same as that in surface air during the preceding months. Unfortunately there are too few published values for the Pu-238/Pu-239 ratio in sea water and these are too unreliable for it to be possible to test this theory by

comparison with the ratios in surface air.

Shallow water sediments, on the other hand, should contain almost all the plutonium that has been deposited through the years, and the Pu-238/Pu-239 ratio should therefore be the same as in total cumulative fall-out. Since fall-out has been low in recent years the values reported by Hardy et al. in 1971 (53) will have changed very little since his inventory was completed. Nowadays an isolated test can have a marked effect on the stratospheric inventory (because of the small amount of debris from earlier tests remaining in the atmosphere) but the effect on the global inventory is negligible.

It is impossible, given the sparse data available, to make any reliable estimate of the actual concentrations of plutonium that one might expect to find in surface waters. Nevertheless, for the reasons discussed above, it is reasonable to suppose that the regional variations in the concentration of plutonium in surface air would be rapidly reflected in the surface water. Thus the ratio $\frac{\text{Pu-238 in southern hemisphere}}{\text{Pu-239 in northern hemisphere}}$ should be similar in air and water at any given time. There must of course be a time lag but unless there were a sudden change in the air concentration this would probably not be noticeable.

Thus it is to be expected that at any given time both the S/N ratio and the Pu-238/Pu-239 ratio:-

1) Will be approximately the same in surface air and surface water.

2) Will be approximately the same in sediment as in total cumulative fall-out up to that date.

3) In organisms the ratios can be expected to vary according to whether the organisms obtain their plutonium from the water, the sediment or both. Thus the S/N ratio can be expected to vary between the cumulative figure of 0,27 and the ratio in surface air at the time of sampling. Similarly the Pu-238/Pu-239 ratio will vary between the cumulative figure for the latitude at which the sample was collected and the ratio in surface air at the time of collection.

If assumption number 1 is correct, it is a simple matter, given the fall-out figures and the north/south ratios in Table 2.4 to calculate the probable Pu-239 concentration in southern-hemisphere sea water during the years 1972 and 1973.

In Table 3.5 the 1967-1972 surface water concentrations from Table 3.4 are repeated. The next four columns show the calculated concentrations in southern-hemisphere water assuming that the N/S ratio in surface water was the same as the N/S ratio in surface air during the particular periods involved.

Apart from the high 1972 result (which is based on a single result from Japanese waters) the calculated Pu-239 concentration in southern-hemisphere waters for the years in question are surprisingly constant. The range within individual sets of northern-hemisphere results is wide and this is reflected in the ranges for the calculated southern-hemisphere values. Nevertheless the mean concentration of 4×10^{-4} pCi/l for 1972 and 2×10^{-4} pCi/l for 1973 are probably reasonable estimates of the Pu-239 concentration in southern-hemisphere surface waters.

These concentrations are used in Chapter 4 to calculate concentration factors and it must be emphasised that all figures calculated in this way can only be approximate. It is impossible to make a statistical estimate of the accuracy of these sea water values (so many figures of differing accuracy and so many assumptions are involved) but a subjective guess is ± 50%.

3.2.2 Plutonium in Marine Organisms

Whether or not organisms reflect integrated or recent fall-out patterns will depend upon the path by which they absorb plutonium. Thus it is to be expected that plankton, living in the open ocean, will reflect recent fall-out, while benthic organisms will experience and possibly absorb, the continually increasing total concentration of plutonium in the sediment.

In the following discussion of the published data on the concentrations of plutonium in marine organisms, particular attention has been paid to those organisms whose South African counterparts were analysed during this research. As far as possible organisms will be dealt with in the categories as listed in the introduction to this Chapter. Once again only samples reflecting natural levels will be considered and data

Table 3.5

Calculated Pu-239 Concentrations in Southern Hemisphere Sea Water During the Years 1972 and 1973

Year	Ref.	No. of Samples	Northern Hemisphere pCi/l (observed) mean	range	Southern Hemisphere 1972 pCi/l (calculated) mean	range	Southern Hemisphere 1973 pCi/l (calculated) mean	range
1967	16	1	9		8,2		4,7	
1967	88	10	4	1-14	3,6	1-13	2,1	0,5-7
1967	88	3	8	6-12	7,3	5-11	4,2	3-6
1968	152	3	10	7-12	4,3	3-5	2,5	2-3
1968	89	6	-	2-12	-	1-5	1,5	0,5-3
1968-69	16	2	9	6-15	4,6	3-8	2,6	2-4
1969	61	4	11	6-14	6,7	4-9	1,4	2-5
1969	89	1	7,5	-	4,6	-	2,6	-
1970	61	6	7,6	5,6-10,8	3,6	3-5	2,1	1,5-3
1971	61	1	15,0	-	7,0	-	4,0	-
1972	61	1	15,9	-	15,0	-	8,6	-
mean					4,3		2,2	

from areas of local contamination will be excluded. All the results described in this section were obtained from northern-hemisphere samples at latitudes between 30°N and 45°N.

A1 Phytoplankton

Because it is difficult to obtain sufficiently large samples of phytoplankton for plutonium analysis, Pillai (107) is the only author to report a value. He found a concentration of 0,276 ± 0,037 pCi/kg wet weight. This sample was taken in 1964, a year of high fall-out.

A2 General Macrophytes

This is an important group. Samples are easy to obtain and it is generally felt that seaweeds may be sensitive indicators of environmental plutonium levels. Concentration factors of over a thousand have been reported thus making analysis far easier than that of the surrounding water.

Table 3.6 summarises the results of various authors.

Wong, Hodge and Folsom (153) and Hoffman Hodge & Folsom (60) have studied the distribution of plutonium and polonium in various parts of the giant kelp, pelagophycus porra. Their early work showed first that, both elements tend to be concentrated at the surface of the plant and secondly that their concentrations varied with the age of the plant. Furthermore different regions of the plants contained different concentrations.

The question was immediately raised as to whether the plant itself was concentrating the nuclides or whether the various organisms that invariably live on the surface of seaweeds were responsible. They found that encrusting bryozoans were responsible for the accumulation of much of the polonium and postulated that even smaller organisms might be responsible for some of the remainder. The presence of bryozoans did not however appear to have a significant effect on the plutonium concentration although it still remains to be determined whether smaller organisms such as bacteria have any effect.

These authors also noted that on clean blades the activity ratio of Po-210 to Pu-239 was fairly constant at about 200

Table 3,6

Plutonium in Macrophytes

Year	No. of Samples	Pu-239 pCi/kg wet mass	Pu-238 / Pu-234	Type of Macrophytes	Concentration factor	Ref.
1964	1	0,65	-	Green Algae (Enteromorpha spp.)		107
1964	1	0,32	-	Giant Kelp (Macrocystis Pyrifera		107
1964	1	0,45	-	Palm Kelp		107
1970	1	0,09	-	Kelp	143	102
1970	1	0,18	-	Cadrium Fragile		102
1970	1	0,63	-	Fucus Vessaculosis		102
1970	2	0,57, 1,4	-	Ascophyllum Nidex		102
1970	1	0,35	-	Chondrus Crispus		102
1971	1	0,36	-	Kelp (Pelagophylus Porra)	600	153
1971	19	Mean 0,64	-	Mixed Algae	1060	103
12-1965	1	20,4	0,057	Sargassum sp. (Atlantic)		102
2-1966	1	84,0	0,035			102
5-1966	1	4,9	0,030			102
11-1968	1	2,8	0,026			102
7-1969	1	4,1	0,092			102
4-1970	1	9,0	0,051		15000	102
1971	2	0,28	-	Sargassum sp.(Pacific Coast)		103

which suggests that a similar mechanism might be bringing both the polonium and the plutonium to algal surfaces.

The concentration of both elements increased with the age of the blade, as shown by the fact that there was a five- to six-fold increase in the plutonium activity from youngest to oldest blades (both on a surface area and on a weight basis). This is probably due to the slow accumulation of plutonium, to the synthesis of more binding sites and possibly to surface contamination of older parts with fine particles.

This work shows clearly that if brown seaweeds are to be used to monitor changes in plutonium levels in sea water, extreme care must be taken with sampling. If the whole plant is sampled the actual time of the year will be important because the relative proportions of young and old tissues will change during periods of growth. Alternatively, since easily measurable plutonium has been found in young blades only a few days old, it might be possible to monitor rapid changes in coastal waters by carefully selecting these blades.

The high levels of plutonium in the North Atlantic sargasso weed are immediately noticeable (Table 3.6). If these results are correct, interesting speculations as to the possible reasons can be embarked upon. The various possibilities will be discussed in Chapter 4.

B Zooplankton

As for phytoplankton very few results have been reported; these are listed in Table 3.7. In spite of the importance of species identification all the samples apart from the 1958 salp sample are simply described as mixed zooplankton.

Table 3.7

Date	pCi/kg wet	Ref.	Sr-90 Deposition in Northern Hemisphere (MCi/yr.)
1950	0,023	103;107	-
1958	1,40	103	0,63
1961	2,03	103	0,35
1964	1,08	103;107	1,65

It would be too much to expect so few results to show a direct relationship between Pu-239 content and fall-out. So many other variables such as species, season of collection, etc. are involved. Nevertheless, figures for the annual Sr-90 deposition during the relevant years are included in Table 3.6, out of interest. (This should, of course, be proportional to the Pu-239 deposition.)

It can be seen that while the 1950 sample , collected before any significant fall-out had occurred, is very low. the other three samples are all relatively high in plutonium; but there is no direct relationship between the Pu-239 content and the Sr-90 deposition. Wong (152) has estimated that zooplankton concentrates plutonium by a factor of roughly two thousand relative to sea water but much additional data is needed before this figure can be accepted as general.

C Marine Invertebrates

Table 3.8 summarises the results reported in the literature for plutonium in marine invertebrates. The dividing line separates general samples from those species whose equivalents in South African waters have been analysed. All these organisms were taken from the near-shore regions and were thus subject to the complex environmental variables described at the beginning of this Chapter.

Most of these analyses were carried out by Noshkin et al. (102), who also analysed sea water and sediment. They found that the Pu-238/Pu-239 ratio in sea water was 0,12, while in sediment the ratio was 0,045. It can be seen that the Pu-238/Pu-239 ratio in all the organisms analysed lay between these two values. The authors were therefore able to conclude that those organisms with high ratios drew their Pu-239 mainly from the water while those with low ratios presumably obtained their Pu-239 mainly from the sediment. The implications of these results have been discussed at length in this Chapter and will be discussed further in Chapter 4.

Probably the most important marine invertebratesare the mussels. They are filter feeders subsisting on tiny organisms and organic detritus removed from suspension. Noshkin et al. found that the concentration factor from sea water to

Table 3.8

Plutonium Activities in Marine Invertebrates

Organism	Date	No. of Samples	Pu-239 (pCi/kg wet) Mean	Range	Pu-238/Pu-239	Ref.
Blue Mussel Body	1969-70	1	0,18			151
Blue Mussel Shell		1	0,26			151
Blue Mussel Body	1970	7	0,26	0,16-0,44	0,099 (1 sample only)	102
Blue Mussel Shell		3	0,42	0,40-0,45	0,081,0,095	102
Brown Mussel Body	1970	1	0,29		0,071	102
Californian Mussel Body	1964	1	0,11			107
Starfish (Asterias Forbesi)	1970	2	1,1 & 0,76		0,085,0,090	102
Marine Worm	1970	1	3,5		0,056	102
Sponge	1970	1	1,8		0,074	102
Shrimp	1967-68	5		0,9 - 3,8		102
Coral	1969	1	1,9		0,42	61
Soft Shell Clam	1970	1	0,38			102
Oyster Body	1970	2	0,12	0,045,0,14		102
Scallops Body	1970	3	0,45	0,35-0,59	0,041,0,057	102
Scallops Shell	1970	1	0,52		0,058	102
Whelk Body	1970	1	0,12			102
Whelk Shell	1970	1	0,25			102
Moonshell body	1970	1	0,58		0,093	102
Moonshell shell	1970	1	0,60		0,046	102

All samples collected in the northern hemisphere at latitudes between 30° and 50°.

mussels was fairly constant (between 250 and 350) and similar to that found by Pillai for the mussel mytilus californium. Furthermore the Pu-238/Pu-239 ratio was closer to the water value (0,12) than the sediment value (0,045). They therefore conclude that mussels regulate their plutonium content in relation to the concentration in water rather than to other sources such as sediments. Of course, the fact that the ratio is somewhere between the two values may mean that mussels are influenced by both water and sediment. In any case they conclude: "These results suggest that mytilus is an excellent biological indicator for plutonium in assessing environmental aquatic levels." This has also been found to be true for other radionuclides such as Mn-54, Co-60 and Zn-65 (154).

It is interesting to note that starfish contained some four times as much plutonium as the mussels on which they fed.

One marine invertebrate that does not appear in Table 3.4 is the lobster. No determinations of plutonium in lobsters collected from their natural habitat have been made, but Ward (148) kept some lobsters in sea water containing $6,5 \times 10^{-2}$ μCi/l Pu-239. She found that calcifying shell accumulated plutonium at a rapid rate and reports that 89,5% of the total plutonium absorbed lay in the calcified skeleton which accounts for approximately 43% of the total body weight of lobster. Approximate concentration factors after 50 days and after 200 days are given in Table 4.5, where they are compared with the results obtained in this project.

D Fish

Once again only a very limited amount of data is available (Table 3.9) and different workers have tended to analyse different organs.

Nevertheless it is possible to draw some tentative conclusions. Thus the high gut concentrations indicate that, as with mammals, plutonium is poorly absorbed from the intestinal tract. In fish such as tuna the plutonium is deposited in the bone and to a lesser extent in the liver. However, the cartilagenous skeleton of sharks concentrates much less plutonium than does the better calcified skeleton of bony fish. In sharks, however, where the skeleton is less available

Table 3.9

Plutonium Activities in Fish (pCi/kg wet)

Organism	Date	Backbone	Liver	Gut	Muscle	Whole Animal	Ref.
Bonito	1964					0,001	107
Thunnus Alalunga	1964		0,06				58
Thunnus Alalunga	1965		0,29				58
Thunnus Alalunga	1968		0,22				58
Thunnus Alalunga	1970		0,10				58
Thunnus Alalunga	1971		0,09				58
Blue Fin Tuna	1970	0,1			0,003		103
Blue Fish	1969	0,6	0,03		0,005		103
Blue Fish	1968-69	0,8			0,007		151
Blue Shark	1970	0,02-0,03	0,1-0,2		0,001-0,005		103
Mako Shark	1971	0,01-0,04			0,01		103
Dusky Shark	1971	0,05			0,003		103
Shark	1969-70	0,011	0,13				152
Shark	1969-70	0,016	0,10				152
Stripped Bass	1970	0,6	0,07	0,8			103
Blackback Flounder	1970	0,05	0,06	1,2	0,002		103
Tautog	1970	0,06	0,07	0,8			103

as a "repository" for plutonium the liver concentration is higher (103).

The concentration of plutonium in fish muscle is very low and it certainly appears that at the moment man is in little danger of accumulating plutonium as a result of eating fish. However, Noshkin has pointed out that such food items as anchovies and sardines, which are consumed whole, and fish protein concentrate, could represent an important transfer vector of plutonium into humans. However, this danger seems very slight when one bears in mind the fact that animal experiments indicated that only 0,002-0,05% of ingested plutonium is absorbed from the gastro-intestinal tract. This fact and the fact that the absorption of plutonium from soil through the root system is very limited was one of the main reasons that the subject of environmental plutonium was so long neglected. It was felt that the main hazard came from inhalation. Nevertheless, as most of the plutonium that is absorbed is deposited in the bone and this appears to be a continuing process, one must be cautious in discounting the dangers of long term exposure to low levels of plutonium.

3,3 The Naturally Occurring Radionuclides

Unlike plutonium the concentration of the naturally occurring alpha-radioactive isotopes has been affected very little, if at all, by the advent of the nuclear age and fall-out. Thus while different geological conditions may markedly affect local concentrations of these nuclides, the differences between the northern and southern hemispheres described for plutonium do not occur.

Up to the present time the main interest in uranium, thorium and protactinium isotopes in the marine environment has centred upon their use in the geological dating of sediments and corals (67, 11, 18) while radium and radon have proved of great value in the study of ocean mixing (97, 94, 33, 73). For this reason there is a substantial body of data on the concentrations of isotopes of these elements in sea water, sediments and to a lesser extent in shells but there is very little information on their concentration in marine organisms.

The biological accumulation of polonium, on the other hand,

has been intensively studied during the ten years since it was first pointed out (99, 25, 125) that a major part of the radioactive dose to marine organisms is due to Po-210.

The review by Cherry and Shannon (29) contains tables giving the range and typical levels of the various alpha-emitters in sea water and marine organisms. Their figures for the natural alpha-emitting nuclides have been condensed into Table 3.10. Table 3.11 has also been taken from their review and gives typical concentration factors from sea water to some marine organisms. It should be noted that some of the "typical" levels and concentration factors are based on very few results and may well not be representative of the whole population.

In sections 3.4-3.7 these figures are discussed element by element with particular attention being paid to the published data on organisms of which specimens of a similar type were analysed during this project.

3,4 Uranium Isotopes (U-238, U-235, U-234)

3,4,1 Uranium Isotopes in Sea Water

Uranium is relatively soluble in sea water where it exists as the complex $[UO_2(CO_3)]_3^{4-}$. The distribution of uranium is fairly uniform in well mixed oceanic surface waters and the mean concentration can be taken as 3,3 µg/l. There are however wide variations in coastal waters, there is a decrease with decreasing salinity and there may be local variations within isolated basins.

Thus values reported range from 1,0 to 6,0 µg/l in coastal waters (11, 12), from 1,5-3,8 µg/l in surface oceanic waters and from 2,0 to 5,0 µg/l in deep oceanic waters (90, 86, 87, 9).

On a mass basis naturally occurring uranium contains about 99,7% U-238; 0,3% U-235 and 0,01% U-234. A uranium concentration of 3,3 µg/l therefore implies a U-238 activity of 1,1 pCi/l.

Surprisingly, in view of the short half-lives of the two intermediaries, it has been shown that U-238 and U-234 are not in equilibrium in many environmental materials (87, 90, 11, 145) This appears to be due to a change in the oxidationstate of the

Table 3.10

Activities of Natural Alpha-Emitters in Sea Water and Marine Organisms

Category	Organism	U-238 (pCi/kg)		Typical Thorium (pCi/kg)			Ra-226 (pCi/kg)		Po-210 (pCi/kg)	
		Typ.	Range	232	230	228	Typ.	Range	Typ.	Range
A_1	Phytoplankton	11	9-13	2	3	30	100	5-1800	90	40-170
A_2	Marine Algae	30	2-105	2	-	-	8	0,3-30	40	16-300
B	Zooplankton	6	3-9,5	1-2	1-2	9	6	3-25	400	80-3000
C	Marine Shells	30	< 1-590	-	-	~ 1	50	3-210	300?	
C	Molluscan Soft Tissue	-	-	-	-	10	20	2-57	500	20-2000
D	Fish Entire	-	-	-	-	2	5	1,5-13,5	400	70-7000
D	Fish Muscle	0,07	0,07-7,0	-	-	1	3	0-58	50	< 1-500
D	Fish Liver	-	-	-	-	-	-	-	3000	100-30000
D	Fish Calcium	-	-	-	-	-	-	-	30000	9000-50000
Sea Water										
Oceanic		1,1	0,6-1,7	$1x10^{-4}$	$4x10^{-4}$	$16x10^{-4}$	0,1	0,01-0,16	$25x10^{-3}$	$8-64x10^{-3}$
coastal		1,1	0,33-2,1	$20x10^{-4}$	$40x10^{-4}$	$80x10^{-4}$	0,1	0,01-0,59	$3x10^{-3}$	

Table 3.11

Concentration Factors From Sea Water to Marine Organisms

	Organism	U-238	Th-232	Th-230	Th-228	Ra-226	Po-210	Pu-239
A	Phytoplankton	1×10^{1}	2×10^{4}	8×10^{3}	2×10^{4}	2×10^{3}	4×10^{3}	4×10^{2}
B	Zooplankton	5×10^{0}	2×10^{4}	4×10^{3}	6×10^{3}	1×10^{2}	2×10^{4}	2×10^{3}
D	Fish Muscle	6×10^{-2}	-	-	6×10^{2}	5×10^{1}	2×10^{3}	6×10^{0}

uranium as a result of the two beta-decays. In minerals and rocks the parent U-238 exists mainly in the +6 oxidation state but electrons are lost during the decay process and some of the U-234 ends up in the +4 state. These uranyl U-234 ions are more readily leached than the parent U-238 ions, presumably because they form strong carbonate complexes.

In sea water the U-234/U-238 ratio varies within very narrow limits and a mean activity ratio of 1,14 is in agreement with most of the data (68, 129). U-235 concentrations in sea water do not appear to have been determined but the U-238/U-235 isotopic ratio is usually assumed to be the same as that found on the continents. Thus Koide and Goldberg (68) assume that the U-238/U-235 activity ratio is 21,96 and use this value when calculating the U-235 contribution to the U-238 peak during alpha-spectrometry.

These ratios coupled with a mean oceanic concentration of 1,1 pCi/l imply a concentration of 1,2-1,3 pCi/l of U-234 and about 5 x 10^{-2} pCi/l of U-235.

3.4.2 Uranium Isotopes in Marine Organisms.

Categories A and B - Plankton

Miyake *et al.* (90) collected three phytoplankton and six zooplankton samples in the Western North Pacific off Japan. Their results are given below in Table 3.12.

It may well be significant that those samples containing a high proportion of diatoms (and hence silica) also tend to be high in uranium. Little is known about the uranium content of silaceous organisms and oozes but Sacket *et al.* (121) have found high uranium concentrations in sediments with a high biogenic silica component. They also report that Scott *et al.* found a similarly high uranium concentration in several cores which consisted largely of radiolaria and diatom oozes.

Up to date all attempts to perform a biogeochemical balance for uranium in the oceans have resulted in a large excess of input over output and it is possible that deposition with silaceous oozes may account for some of this discrepancy. Thus although Miyake (90) concludes from his results that biological effects can result in a variation in the uranium concentration in sea water of only a few per cent, the picture may

Table 3.12

U-238 Activities in Plankton (Miyake et al. - Ref. 90)

Species	pCi/kg dry	pCi/kg wet	U-234/U-238
Phytoplankton - Diatoms	-	-	1,11 ± 0,05
- Diatoms	251	11,9	1,15 ± 0,05
- Diatoms	191	9,1	1,18 ± 0,03
Zooplankton - Copepods	-	-	1,18 ± 0,04
- Euphausiids, Amphipods, Larvae	55	3,6	1,18 ± 0,10
- Thalids	112	7,4	1,18 ± 0,03
- Diatoms (###) and Euphausiids (##)	245	16,3	1,10 ± 0,04
- Copepods (###), Diatoms (##), Chaetognaths (+)	183	12,2	1,14 ± 0,06
- Copepods (###), Diatoms (##), Chaetognaths (+)	207	13,8	1,13 ± 0,04
- Radiolaria (+)			

Note These results were reported on a dry basis. The wet concentration values have been calculated using the conversion factors in Table 3.3.

well change if we concentrate on silaceous organisms only. Possibly deposition in association with silica is an important oceanic sink for uranium.

The association of uranium with calcium carbonate has been investigated more thoroughly than has the association with silica. Unfortunately no living calcerous plankton appears to have been analysed and analyses of the coccolith and foramen fractions of deep sea sediments give widely differing results. Ku (72) found between zero and 0,025 ppm U in the coccolith and foramen fractions of one Atlantic core, while Mo, Suttle and Sackett (121)report considerably higher concentrations in foramens from the Gulf of Mexico. They found that coccoliths contain 0,1 ppm foramens up to 0,5 ppm and pteropods up to 2,7 ppm uranium.

It is however dangerous to draw conclusions about living organisms from results obtained on fossils and there is evidence that the uranium content of shells increases during the years immediately after death (18). It should therefore be of great interest to extend the work of Miyake et al. by analysing carefully selected silaceous and calcerous plankton. Their effect on the biogeochemical balance of uranium may well be greater than expected.

Category A2 - Macrophytes

Edgington et al. (40) determined uranium, thorium and radium in a number of highly calcified marine algae and found a very significant correlation between the uranium content and the calcium content of the algae.

As the degree of calcification increases the proportion of organic matter decreases and hence protein nitrogen decreases. There was therefore a corresponding inverse correlation between uranium and protein nitrogen.

They report that in all the species of algae analysed the calcium carbonate was laid, and normally retained, as the ortho-rhombic crystalline form of aragonite. Because of this they remark that: "Surface exchange or co-precipitation of uranyl ions with calcium is therefore possible because there should be neither steric problems nor restrictions on the

formation of solid solutions due to ionic size."

Calcerous algae precipitate calcium as either calcite or aragonite and, in contrast to molluscan shells, no algae containing a mixture of the two minerals have been recorded (78). In view of the strong correlation between uranium and calcium observed by Edgington and in view of the conflicting opinions as to the effect of crystal structure on the uranium content of shells (see 3.1) it should be of great interest to study some calcitic algae.

Edgington et al. found that the uranium concentration in their calcified algae varied from 240-552 pCi/kg dry algae (or, using the conversion factor of 7,5, from 32-74 pCi/kg wet algae).

Sackett et al. (121) report even higher concentrations in calcerous algae collected in the Gulf of Mexico, viz. 975-1480 pCi/kg of (presumably) dry algae.

Miyake et al. (90) analysed several seaweeds without any bias towards calcified samples and found that the concentration of uranium varied between 13,5 and 791 pCi/kg dry seaweed (1,8-105 pCi/kg wet). They also determined the U-234/U-238 activity ratio in their samples. This ranged from 1,07 to 1,17 with an average value of 1,11 ± 0,03 and was the same as the ratio found in the surrounding sea water.

Category C - Marine Invertebrates

The determination of uranium in marine invertebrates has been exclusively devoted to shell and corals as various dating methods have been investigated. Although the tendency has been to analyse fossil rather than recent shells a large number of living shells have been analysed. In 1971 Kaufman et al. (67) collected the results from a number of workers and reported that the uranium concentration varied from less than 1 to 590 pCi/kg U-238 with an average value of around 30 pCi/kg. In fact 69 out of the 78 living shells studied contained less than 40 pCi/kg U-238.

Kaufman also reports that calcitic molluscs typically pick up about half as much U-238 as do aragonitic ones. Tatsumoto and Goldberg (135), on the other hand, analysed a range of calcerous organisms and found no preferential

association of uranium with the aragonitic structure. This difference of opinion is probably due to the fact that Kaufman et al. were considering shells of all ages and fossil marine molluscs typically contain much more uranium than do living ones. It appears that, after death, uptake occurs quickly and ceases after a few thousand years (18). It is likely that under these conditions the substitution of uranium into the aragonitic lattice is easer than into the calcitic lattice. In the living mollusc on the other hand the situation is much more complex and different factors may dominate the uptake of uranium ions.

For the purpose of comparison with the results obtained in this project it is of interest to look closely at the results of Tatsumoto and Goldberg (135) and they are summarised in Table 3.10.

Table 3.13

Uranium in Shells (from Tatsumoto and Goldberg (135))

No. of Samples	Type of Shell	pCi/kg U-238	Crystal Structure
2	Echinoderms	54-57	Calcitic
5	Molluscs (Gastropods)	3-9	Aragonitic only
8	Molluscs (Gastropods and Pelecypods)	1-15	Aragonitic and Calcitic mixed
1	Barnacle	13	Calcitic

3.5 Thorium Isotopes (Th-232, Th-230, Th-228 and Th-227)

3.5.1 Thorium in Sea Water Little is known about the chemistry of thorium in sea water. Both uranium and thorium isotopes enter the ocean from rivers as a result of weathering and land run-off. Uranium however remains in solution as the soluble carbonate complex, while thorium is rapidly removed from solution, probably as either the hydroxide or the phosphate.

The mechanism by which thorium precipitates out and settles to the ocean bottom is not well understood but it seems likely that the newly precipitated thorium forms charged colloidal particles which would be liable to co-precipitation and adsorption

onto the surface of both organic and inorganic particles. Bhat (9) found that the settling rate of Th-234 coincided closely with the settling rates of organic debris from the surface layers and concluded that thorium is adsorbed onto solids during precipitation.

Goldberg et al. (50) suggest that thorium phosphate is involved in biological cycles in which phosphate is regenerated by the decomposition of organic debris descending through the water column.

The fact that the Th-230 activity in sea water is less than 0,1% of the activity of the parent U-234 indicates that this isotope must settle very rapidly after its formation.

Estimates of the oceanic residence times of the thorium isotopes vary between 15 and 350 years (9, 129, 39, 50). In any case the residence time of all the thorium isotopes is less than the mixing time of the oceanic water masses. One would therefore expect to find regional variations in the thorium content of the oceans depending upon the rate of supply, sedimentation, etc. In fact, the variations reported are very wide (29) and this makes calculations of concentration factors and comparison of results from different regions very difficult.

Although Th-228 is a grand-daughter of Th-232 its activity in sea water is typically about fourteen times higher than that of its grand-parent. This appears to be because the intermediate Ra-228 is soluble in sea water and has a half-life of only 6-7 years. Th-232 decays to Ra-228 which then enters the oceans by horizontal transport from the continental shelf and slope regions and by upward diffusion from the bottom sediments (91, 95). To a lesser extent Ra-228 may be introduced from suspended particulate phases containing Th-232. This is likely to play a large part in coastal regions where the higher thorium concentrations are probably due to suspended inorganic material introduced from rivers etc. (129, 91).

The other natural alpha-emitting thorium isotope, Th-227, is of little interest. It has a short half-life (18,2 days) and is a member of the actinium series, all of whose members are present at very low levels in the environment. The few

estimates that are available for the concentration of Th-227 in sea water vary between $1,4 \times 10^{-2}$ and 2×10^{-3} pCi/l (119, 29).

3.5.2 Thorium in Marine Organisms

Very little data is available on the concentration of thorium isotopes in marine organisms. In fact there are so few figures that ranges are not quoted in Table 3.10. What little information there is will now be discussed category by category.

Categories A1 and B - Plankton

Cherry et al. (26) determined Th-228 in seven phytoplankton and forty-three zooplankton samples collected in South African waters. They used the total counting (pairs) method which, while it involves several assumptions, is extremely straightforward from the experimental point of view and should give reliable results. They found that Th-228 in phytoplankton varies from 8-57 pCi/kg wet plankton (70-900 pCi/kg dry plankton) with a mean of about 30 pCi/kg wet plankton. Concentrations in zooplankton were lower, ranging from 2-24 pCi/kg wet plankton (20-500 pCi/kg dry plankton) with an average of about 9 pCi/kg wet plankton.

These authors found that real variations appeared to exist in the Th-228 content of plankton from different water masses. Thus they found the highest concentration of Th-228 in plankton collected from the thorium rich waters of the Walvis Ridge. The lowest Th-228 values were associated with cold waters such as the Benguela Current and the waters at the convergence between sub-tropical and sub-antarctic surface waters.

They suggest that the fact that phytoplankton contains more Th-228 than zooplankton is possibly due to the calcium-rich nature of the phytoplankton. Thus Ra-228 might have been absorbed in association with the calcium and subsequently decayed to Th-228. On the other hand Ku (73) and Edmund (41) have concluded from a study of depth profiles that radium is incorporated into silaceous tests, sedimented to deep water and then redissolved. Their evidence suggests that calcium carbonate tests play a relatively minor role in the transport of radium. Obviously there is scope for further work here and interesting factors would surely emerge if the different types

of plankton could be analysed for the various alpha-emitting nuclides.

Shannon (126) also attempted to estimate the concentrations of Th-232 and Th-230 in some of his samples. He used a wet-extraction technique followed by alpha-spectrometry and estimated his recoveries from the Th-228 values obtained by the pairs technique. He was unable to make any estimate of the extent to which the Th-228 was supported by Ra-228 during the 12-27 months that elapsed between sample collection and chemical extraction. Nevertheless, while the errors in these results may be large, they are probably of the right order of magnitude and the "Typical values" given in Table 3.10 are based on these figures.

Category A2 - Marine Algae

No published values for the concentrations of the various Thorium isotopes in marine algae appear in the literature but Edgington et al.(40) and Strohal et al.(130) have determined the total thorium in a number of different algae. Their results are summarised in Table 3.14.

Table 3.14

Th-232 in Marine Algae

	Strohal (130)		Edgington (40)*	
	pCi/kg dry	pCi/kg wet	pCi/kg dry	pCi/kg wet
Green	2,0-72	0,12-3,2	5,4-30,5	0,7-4,1
Brown	1,2-19,6	0,08-2,7	14,2-24,0	1,9-3,2
Red	109-251	15,3-40,4	7,6-67,6	1,0-9,0

*Results reported on a dry basis only. Wet values calculated using the conversion factor of 7,5.

It can be seen that the results of both groups are of the same order of magnitude, although the tendency for the rhodophytes to be high in thorium is not as marked in Edgington's results as in those of Strohal.

Edgington found no correlation between the thorium and calcium contents of the algae analysed. There was however a positive correlation between radium and calcium in red and brown but not green seaweeds. It is a pity that an isotopic analysis of thorium could not be carried out as this would have shown to what extent this radium absorption affected the Th-228 concentration relative to sea water and the other isotopes.

Edgington, after a careful study of thorium-calcium discrimination factors, concluded that the main mechanism by which thorium and radium are concentrated by marine algae is ion-exchange or co-precipitation of the ion within the calcium carbonate matrix. In algae of low calcium content however, some form of complex formation with either proteins or other organic compounds may become significant.

Category C - Marine Invertebrates

Very little information is available on thorium isotopes in marine invertebrates. Even living shells have been neglected, which is rather surprising in view of the attention that has been paid to uranium series dating methods.

The Th-230/U-234 method has been particularly recommended for the dating of shells (13, 18, 65, 67) and is based on the measurement of the extent to which Th-230 has grown in as a result of the decay of uranium that was incorporated into the shell during its formation. A detailed discussion of dating methods would be out of place here and it is sufficient to say that several assumptions are involved which lead to inaccuracies in the final ages. The most important of these is probably the assumption that after growth there is no movement of uranium series isotopes into or out of the shell. Another important assumption that was made when the method was originally proposed was that the concentration of Th-230 in fresh shell is negligible in comparison with U-234.

Early workers who attempted to determine the concentration of thorium isotopes in fresh shells used insensitive methods and were happy to conclude that the latter assumption was valid (13, 144, 146, Table 3,14). It was soon shown however that a correction for the Th-230 initially present in shells has to be made (65, 67). This correction is normally based on the

assumption that the initial Th-230 is proportional to the initial Th-232 and the ratio at zero time, $R = \left(\frac{\text{Th-230}}{\text{Th-232}}\right)_o$ is usually taken to be somewhere between 1,3 and 1,7, although occasionally R- values ranging from 0,9 to 2,4 have been needed to bring Th-230/U-234 dates into line with the C-14 dates. The older the sample the less important this correction becomes. In "young" samples an error in this ratio can cause a substantial error in the estimated age.

The few values that are available for the concentration of thorium isotopes in shells are listed in Table 3.15 together with values for the important isotopic ratios.

Table 3.15

Thorium Activities in Living Marine Shells

Shell type	Th-232 pCi/kg	Th-230 pCi/kg	Th-228 pCi/kg	Th-230 / Th-232	Th-230 / U-234	Th-228 / Th-232
Gastropods Bivalues (109)	0±5-6±7		1±1-10±5		< 0,02 to 0,3	
Corals (183)	< 5,5	< 1,5			< 0,01	
Corals (184)	0,9-2,0 0,5-3,4		8,1-25,1 2,8-17	1,48 0,79		16 1-15

As in sea water the Th-228 content of shells is many times higher than that of the parent Th-232. This is presumably due partly to the fact that, owing to its high concentration in sea water, more Th-228 is available and partly to the fact that Ra-228 is also incorporated into shells during their formation. As mentioned (see section 3.1) radium is chemically similar to calcium, although it has a relatively large ionic radius. Typically the Ra-228 concentration in living shells is between 4 and 30 pCi/kg (38, 94) and the decay of this isotope ($t_{\frac{1}{2}}$ = 6,7 years) may contribute significantly to the Th-228 content of shells that are a few months old. Because of its large ionic radius one would expect radium to be more readily accepted into an aragonitic

lattice than into a calcitic one and hence one would expect Th-228 to be higher in aragonitic shells. There is however no published data on this point.

The ionic radius of thorium itself is very similar to that of calcium but this is probably not significant, as it seems likely that thorium is associated more with the organic matrix of shells than with the calcium carbonate crystals.

Category D - Fish

Virtually no information is available on the thorium content of members of this group.

3.6 Radium Isotopes (Ra-226, Ra-224, Ra-223)

The following figures (Table 3.16) for the concentration of Ra-226 in sea water are taken from the review by Cherry and Shannon (29).

Table 3.16

Ra-226 Activities in Sea Water

	pCi/l Ra-226
Range in coastal waters	0,01 - 0,59
Range in oceanic waters	0,024 - 0,182
Typical concentration in surface oceanic water	0,04 - 0,08
Typical concentration in deep oceanic water	0,08 - 0,16
Typical oceanic mean	0,1
Typical coastal mean	0,1

It can be seen that the concentration of Ra-226 in sea water varies over an even wider range than do the concentrations of the thorium isotopes and there is generally disequilibrium between Ra-226 and Th-230.

Ra-226 was the first alpha-emitting nuclide to be determined in marine organisms and the data are more abundant than for uranium and thorium. The relatively high concentration factors for Ra-226 shown by most organisms may be connected with its chemical similarity to calcium.

There is no direct information concerning the nuclides

Ra-224 ($t_{\frac{1}{2}}$ = 3,6 days) and Ra-227 ($t_{\frac{1}{2}}$ = 11 days). Presumably they are present at approximately the same activity levels as their immediate parents Th-228 and Th-227.

Ra-228 is a beta-emitter but it is important because, as the precursor of Th-228, it has a marked influence on the concentration of this isotope in sea water and many marine organisms. (See Sections 3.1 and 3.5).

3.7 Polonium Isotopes (Po-218, Po-216, Po-215, Po-214, Po-212, Po-211 and Po-210

The first five of these isotopes all have very short half-lives and it is reasonable to assume that they are in equilibrium with their parents in sea water and marine organisms. Po-210 ($t_{\frac{1}{2}}$ = 138 days) is of much more interest; it makes a significant contribution to the alpha-radioactive dose received by marine organisms and a rapid sensitive analytical method is available.

For these reasons a great deal of work has been done on Po-210 in the marine environment in recent years and there is now a vast profusion of published data.

Folsom et al. (43, 44) suggested that "since several living systems have been encountered in the marine environment that accumulate Pu-239 almost as efficiently as Po-210 something about the behaviour of plutonium in the environment might possibly be inferred from studies of polonium."

A glance at the periodic table gives one little reason to suppose that there will be much chemical similarity between Po and Pu (or the other actinides such as U, Th or Pa). However both polonium and plutonium can exist in a variety of oxidation states, are easily hydrolysed and readily form complexes, colloids, etc. Furthermore, being reactive, they are likely to become attached to any particulate matter in sea water. They are present in sea water at extremely low concentrations (typically 3×10^{-17} moles/litre Po and 4×10^{-14} moles/litre Pu) and it is possible that the similarity in such properties could lead to the postulated similarity in biological behaviour.

With the above arguments in mind it was decided to deter-

mine Po-210 (and Pb-210) in all the samples in which Pu-239 was determined. There is already a great deal of data available on the concentration of polonium in the various organisms and while it was not expected that anything new would emerge from the Po-210 data alone, it was hoped that the situation with regard to any relationship between plutonium and polonium might be clarified.

No attempt will be made here to review all the work that has been done on polonium in marine organisms. This has been discussed and summarised by Cherry and Shannon (29) and the typical values, ranges and concentration factors reported in Tables 3.6 and 3.7 are taken from this review. It is sufficient here to describe first the situation in sea water and then the general conclusions that have been drawn from the accumulated data on organisms. The work of Folsom et al. (43, 44) has already been described in section 3.2.2.

3.7.1 Polonium in Sea Water

As indicated in Table 3.6 there is a fairly wide variation in the Po-210 content of sea water (29, 128, 44, 153). The results of Shannon et al. are of particular interest because they were obtained in South African waters. They found that the polonium content in waters around the Cape of Good Hope during March 1969 varied between 8×10^{-3} and 41×10^{-3} pCi/l. Four samples collected off rocky beaches around the Cape Peninsula contained an average of 30×10^{-3} pCi/l.

Shannon also reported Pb-210 values ranging from 10×10^{-3} pCi/l to 135×10^{-3} pCi/l with a mean value of 38×10^{-3} pCi/l.

Bunn (20), also working in South African waters, found that the polonium concentration varied between 18 and 45 pCi/l and showed that as much as 75% of this polonium was associated with the particulate phase. He found that the proportion of particulate Pb-210 was lower - of the order of 20% to 25%. Langford (74) and Schell (123) have also presented data indicating that a significant proportion of the Po-210 and the Pb-210 in sea water is particulate.

3.7.2 Polonium in Organisms

Table 3.10 shows the range in values reported for Po-210 in various marine organisms. Cherry and Shannon (29) point out that three important general conclusions can be drawn from the data available. These are:-

1) Polonium is very efficiently concentrated by most marine organisms. In fact, although the molar concentration of polonium in sea water is considerably lower than that of any of the other alpha-emitters (Table 3.1), the concentration factor from sea water to marine organisms is higher than for any of the other alpha-emitters, with the possible exception of some thorium isotopes.

2) There is a clear increase in the polonium content of organisms as we move up the food chain from phytoplankton to zooplankton to entire fish. This is completely different from the situation for uranium, thorium, radium and plutonium where the trends tend to be in the reverse direction.

3) In marine invertebrates and fish polonium is very highly concentrated in the internal organs. Thus the hepatopancreas of shrimp and lobster and the livers, pyloric caeca and viscera of fish are all extremely high in Po-210. It is perhaps worth pointing out here that the retention of selenium and tellurium in animals is highest in the liver, kidney and spleen (85). Thus their chemical nature and possibly the type of complexes they form, must play some part in the pathways followed by these elements.

Finally brief mention must be made of Pb-210. With regard to this isotope the following general points have emerged.

1) Pb-210 is concentrated much less efficiently than is Po-210.

2) Pb-210 concentration does not increase up the food chain.

3) Various organs of fish such as the liver and viscera are sites of accumulation for Pb-210, as they are for Po-210, but the Pb-210 levels remain very much lower than for Po-210. Relatively speaking Pb-210 has a greater tendency to accumulate in bone.

CHAPTER 4

Plutonium Results

4.1 Introduction

In this chapter the results of plutonium determinations on organisms collected in South African waters are presented. A discussion of alpha-spectrometry and details of the analytical methods used are given in Part II of this thesis. Here it is sufficient to say that plutonium was isolated by ion-exchange, plated onto stainless steel discs and counted on semi-conductor alpha-spectrometers.

A Pu-236 tracer was used enabling an accurate assessment of the chemical recovery to be made. These recoveries are quoted for each determination and they tend to be between 50% and 90%. Exceptions to this are the kelp and stockfish samples. They were analysed before the plating technique had been perfected and recoveries were low. Low recoveries were also obtained when analysing shell. These analytical problems will be discussed in Appendix I.

Unfortunately the Pu-236 tracer contained some Pu-238 (approx. 6% of the Pu-236 activity). This made it impossible to determine the Pu-238/Pu-239 ratio unless either the tracer was left out or the plutonium content of a sample was extremely high. Thus estimates of this ratio were made on only five samples.

Wherever possible all samples were analysed in duplicate, that is, after drying they were ground, mixed and split into two identical portions which were then analysed separately.

Because of the difficulty of assessing wet weights accurately, all results are reported both on a wet and a dry weight basis. The errors quoted are standard deviations based purely on counting statistics.

4.2 Phytoplankton

No phytoplankton samples were available for analysis.

4.3 Macrophytes

Because of its possible importance as a biological indicator of plutonium levels in sea water, several samples of kelp were analysed at the outset. The samples were large

and consisted of the blade only. No attempt was made to distinguish between young and old plants or different parts of the blade.

Several other seaweeds with differing biological properties were analysed. In particular, in view of the work of Wong et al. (153), plants with different surface properties were chosen. Thus aoedes orbitosa is also a brown seaweed but it has a very "slimy" surface - possibly a good breeding ground for bacteria. Porphyra (a red seaweed) and ulva (a green seaweed) both have very high surface areas. The blades of porphyra are often only one cell thick. Furthermore they tend to be rough and should provide a suitable surface for bacteria and other minute organisms to inhabit. The blades of ulva on the other hand are smooth and glossy and are therefore probably less likely to harbour micro-organisms.

Sargassum heterophyllum was chosen because of its relationship to the sargassum sp. of the Sargasso Sea. Unlike its relative, however, it does not float but grows in clumps in rocky pools just below the low-tide mark. The plants are small and bushy and the whole plant was analysed. Because of the bushy nature of the plant it was difficult to ensure that no foreign bodies were present and small shell-fish, sand, etc., may well have been included in the samples. Older parts of the stem also tended to have small particles embedded in them. The other seaweeds were easy to clean and the samples contained no visible inclusions.

The results of these determinations are given in Table 4.1. Table 4.2 gives approx. concentration factors for the different seaweeds. Sea water values of 4 pCi/l Pu-239 for 1972 samples and 2 pCi/l for 1973 samples have been used (see Ch. 3.2.1).

The most striking fact to emerge from these tables is that sargassum heterophyllum contained significantly more plutonium than did the other seaweeds, although not nearly as much as the floating sargassum sp. analysed by Noshkin et al. (102). Thus the metabolism of the sargasso weed appears to be especially well suited to the concentration of plutonium. It would be interesting to study this species more carefully and an analysis of different parts of the plant and plants of different ages should prove fruitful. Other members of the family, e.g.

Table 4.1 -Pu-239 Activity in Macrophytes Collected in South African Waters

Organism	Sample No.	Collection date	Wet Weight(g)	Chemical Recovery %	pCi/kg Wet	pCi/kg Dry
Kelp (Ecklunia maxima)		1/8/72	1000g	22	0,13 ± 0,02	0,92 ± 0,14
				33	0,13 ± 0,02	0,92 ± 0,14
				26	0,15 ± 0,02	1,06 ± 0,14
				16	0,15 ± 0,02	1,06 ± 0,14
				19	0,14 ± 0,02	0,99 ± 0,14
Aoedes orbitosa	S -7	24/10/73	1070g	84	0,15 ± 0,01	0,72 ± 0,05
				86	0,15 ± 0,01	0,72 ± 0,05
Sargassum heterophyllum	S -3	3/6/73	970g	75	0,41 ± 0,06	1,7 ± 0,3
Porphyra	S -2	24/10/73	1000g	75	0,15 ± 0,02	0,79 ± 0,09
Ulva	S -5	3/6/73	935g	78	0,07 ± 0,01	0,43 ± 0,06
			935g	75	0,07 ± 0,01	0,43 ± 0,06

Table 4.2-Approximate Concentration Factors for Pu-239 inMacrophytes

Species	Year of Collection	Approx. Concentration Factor
Kelp	1972	350
Aoedes orbitosa	1973	750
Sargassum heterophyllum	1973	2000
Porphyra	1973	750
Ulva	1973	350

sargassum longifolium, which lives in deeper waters off the South African coast, might also be analysed.

In spite of their very different surfaces, kelp, aoedes and porphyra all contained about the same concentration of Pu-239. Thus there is no evidence of concentration at the surface either by the seaweed itself or by surface-living organisms.

Ulva contained less Pu-239 than the other macrophytes and this may be connected with the fact that it is the only green seaweed analysed. Generally, brown and red seaweeds appear to accumulate greater quantities of trace elements than do the green.

Concentration factors for macrophytes (other than sargassum sp.) reported in the literature vary between 100 and 1600 and it can be seen that (apart from sargassum heterophyllum) all the results in Table 4.2 are within this range.

Two other workers have reported concentration factors for kelp. Noshkin (102) found a concentration factor of 140 and Wong (153) found 600. Our value of 350 fits neatly in between these two figures. While this range in concentration factors is fairly wide, it is almost certainly due to differences in sampling procedure. If samples of the same age and tissue composition are taken the concentration factors may well prove to be more constant and kelp may be a very useful biological indicator. A concentration factor of around 300 is useful and large samples are easy to collect and to handle.

4.4 Zooplankton

Only two samples of zooplankton were analysed. The samples were collected at different times and were very different in biological composition. There is some doubt about the actual species present in the first sample (S-79) but it contained a large amount of acid-insoluble silica and therefore presumably included in its composition a proportion of either radiolaria or silaceous phytoplanktonic organisms. The second sample (S-82) was composed entirely of amphipods.

The results obtained are shown in Table 4.3.

If one calculates the sea water to zooplankton concentration factor (using the 1973 sea water value of 2×10^{-4} pCi/l

Table 4.3 - Pu-239 Activity in Zooplankton Collected in South African Waters

Organism	Sample No.	Collection Date	Wet Weight (g)	Chemical Recovery	pCi/kg	
					Wet Weight	Dry Weight
Silaceous zooplankton	S79	24/1/73	195g	68	0,13 ± 0,03	1,3 ± 0,3
				54	0,08 ± 0,02	0,8 ± 0,2
Amphipods	S82	24/10/73	376g	50	0,16 ± 0,02	0,8 ± 0,1
				58	0,13 ± 0,02	0,6 ± 0,1

Pu-239 calculated in Ch. 3.2.1) one obtains a value of between 400 and 850. This is lower than the value of 2000 given in the literature (29, 103, 152) but as this value was based on a single determination better agreement could hardly be expected.

It is difficult to compare these results with those of other workers who analysed samples taken from northern hemisphere waters during years of high fall-out and before Pu-239 was routinely determined in surface air. Nevertheless, using Sr-90 figures, it is possible to make a rough estimate of the likely plutonium deposition in the northern and southern hemispheres during the years in which the zooplankton samples were collected. Thus we find that the approximate ratio of northern hemisphere fall-out during the years 1958, 1961 and 1964 to 1973 southern hemisphere fall-out was:-

1958 - 15
1961 - 40
1964 - 10

The fact therefore that the two zooplankton samples analysed in this project contained between one-tenth and one-twentieth of the plutonium reported in samples collected during these years fits in satisfactorily with fall-out figures.

Zooplankton may well prove to be very suitable organisms for monitoring the plutonium content of surface oceanic waters. However much work still needs to be done on the effect of seasonal variations and of different species.

4.5 Marine Invertebrates (excluding zooplankton)

A number of marine invertebrates were collected from the near-shore environment and analysed. The plutonium concentrations found are listed in Table 4.4. A discussion of the organisms one at a time now follows.

4.5.1 Mussels

Black mussels cling to the rocks in the intertidal zone while white mussels burrow in the sand; but both are filter feeders and they appear to have concentrated plutonium to the same extent.

Calculation of sea water to mussel soft tissue concentration

Table 4.4

Pu-239 Activity in Marine Invertebrates Collected in South African Waters

Organism	Sample No.	Collection Date	Wet Weight	Chemical Recovery	pCi/Kg	
					Wet Weight	Dry Weight
Black Mussel Soft Tissue*	S-40	23/11/72	570	60	0,14±0,03	0,91±0,20
			570	27	0,14±0,03	0,91±0,20
White Mussel Soft Tissue*	S-47	23/11/72	570	82	0,15±0,03	0,71±0,14
			570	84	0,15±0,03	0,71±0,14
Black Mussel Shell	S-42	23/11/72	498	15	0,10±0,03	0,11±0,03
			498	21	0,07±0,02	0,08±0,03
White Mussel Shell	S-46	23/11/72	486	13	0,13±0,07	0,14±0,07
			486	49	0,09±0,03	0,10±0,03
Starfish - whole (Martha Asterias)	S-64	3/6/73	930	65	0,73±0,05	2,26±0,16
			930	57	0,70±0,05	2,17±0,16
Sea Urchin Shell	S-28	10/73	635	16	0,14±0,02	0,25±0,04
			635	54	0,12±0,02	0,22±0,04
Sea Urchin Digestive System	S-30	10/73	179	62	0,36±0,05	2,8 ±0,4
			179	67	0,27±0,05	2,1 ±0,4
Sea Urchin Gonads	S-29	10/73	212	72	0,13±0,03	0,89±0,20
			212	63	0,09±0,03	0,61±0,20
Sea Urchin Fluid	S-31	10/73	592	45	0,03±0,01	0,6 ±0,2
			592	-	0,01±0,01	0,2 ±0,2
Lobster Flesh (Jasus Lalandii)	S-9	31/1/73	780	89	0,017±0,005	0,07±0,02
			780	93	0,015±0,005	0,06±0,02

Continued/.....

Table 4.4 (continued)

Organism	Sample No.	Collection Date	Wet Weight	Chemical Recovery	pCi/Kg	
					Wet Weight	Dry Weight
Lobster Shell	S-11	31/1/73	213	27	0,73±0,10	1,02±0,14
		31/1/73	213	22	0,81±0,10	1,1 ±0,1
		16/10/73	393	71	0,15±0,02	0,39±0,05
Lobster Gills	S-17	31/3/73	67	73	0,88±0,14	3,52±0,56
Lobster Digestive Gland	S-14	31/1/73	180	74	0,27±0,04	0,57±0,09
		31/1/73	168	52	0,13±0,02	0,49±0,08
	S-78	28/6/73	280	41	0,07±0,02	0,16±0,05
Blood Worm	S-81	2/9/73	265	41	0,08±0,02	0,02±0,01
			265	34	0,16±0,03	0,04±0,01

*Note: Black Mussel - Chloromytillus Meridonalis.
White Mussel - Donax Serra.

factors gives values of 350 and 375 for black and white mussels respectively. This is in remarkable agreement with the values obtained by Noshkin et al. (250-350) and by Pillai (230-290). Thus three sets of mussels, widely separated by time and environment, give almost identical concentration factors. It has already been pointed out that mussels appear to regulate their plutonium content in relation to the concentration in sea water rather than other sources and the apparently constant concentration factor makes them an ideal biological indicator.

The Pu-239 content of mussel shell was, if anything, slightly lower than that of mussel meat. This is contrary to the findings of Noshkin et al. (102) who found that "in every case, where both body and shell were analysed the average concentration of Pu-239 in shell exceeded that in the body". However, this statement was based on a small number of observations and may be an over-generalisation. It is possible that something as simple as variations in wet weight determinations could account for our disagreement on this point.

It can be seen that the Pu-239 contents of mussel shell and sea urchin shell are very similar. This in spite of the fact that the former were probably mainly aragonitic while the latter were calcitic. So crystal structure appears to have little effect on the accumulation of plutonium and in view of the similar ionic sizes of Ca^{+2} and Pu^{+4} (Table 3.2) this is hardly surprising. In any event it is probable that plutonium is associated with the organic matrix rather than incorporated into the crystal structure of shells. In this context it is interesting to note that the plutonium content of lobster shell is much higher than that of the more highly calcified mussel and sea-urchin shells.

Because of their potential as biological indicators it would be worth trying to find answers to such questions about mussels as:-

i) Are there seasonal variations in the concentration factor?

ii) Is uptake continuous and does the plutonium concentration increase with increasing age of the animals? Experiments with other metals indicate that this is not the case but there is no information about plutonium.

iii) What is the mechanism by which plutonium is absorbed? In particular, do mussels absorb soluble as well as particulate plutonium? Mussels can filter off particles as small as bacteria and as plutonium in sea water may be largely particulate it is probable that it is absorbed via the normal feeding mechanism. On the other hand uptake could occur directly into the blood stream across the gill or mantle epithelia or the soluble form could be absorbed onto the mucous used in feeding and so become available for absorption from the digestive gland.

It would certainly be instructive to analyse the digestive gland separately in order to see whether, as with other invertebrates, plutonium is concentrated there. Useful information might be gained by following the practice of keeping mussels in filtered sea water for two days before analysis. This gives them time to eliminate undigested food material from their intestines.

4.5.2 Starfish

Noshkin *et al.* (102) found that starfish (*asterias forbesi*) contained roughly four times as much plutonium as the mussels on which they were feeding and concluded that "plutonium is concentrated up this simple food chain". Our starfish showed a similarly high plutonium concentration (in fact five times the concentration in mussels). They were not, however, living on mussel beds but in shallow rock pools among sea urchins. They appeared to be feeding on general detritus and periwinkles.

The fact that their concentration factor relative to mussels, and presumably therefore to sea water, is similar to that reported by Noshkin *et al.* may mean that starfish could also be used as indicators of plutonium levels in sea water. The higher concentration factor would make them very suitable for this purpose. They are easy to collect and the high plutonium concentration made it possible to determine the Pu-238/Pu-239 ratio even in the presence of our Pu-236 tracer.

4.5.3 Sea Urchins

Sea urchins have been attracting the interest of marine biologists in recent years. They consist almost entirely of a shell containing digestive organ and gonads, in about equal proportions, bathed in fluid. The effect of various marine pollutants on the fertilisation and development of sea urchin

eggs has been used as a sensitive indicator of marine pollution (63). (A similar study on the effect of some of the alpha-emitting isotopes should prove an entertaining project for some biologist).

It can be seen from Table 4.4 that the concentration of plutonium in shell and gonads is much the same as in mussels while the digestive system contains two to three times as much. Thus even in these simple animals plutonium appears to be retained in the digestive tract, although relatively more passes into the rest of the animal than is the case with fish or mammals.

The sea urchins were collected from the sea floor at a depth of about 20 metres. Their diet was mainly particles of kelp and there appears to have been very little concentration of plutonium up the food chain from kelp to sea urchin.

4.5.4 Marine Worm

Noshkin et al. reported a very high value for marine worm. Our bloodworm was found burrowing in sand at Langebaan, a lagoon 100 km north of Cape Town. The worms were completely full of sand and it was impossible to clean them effectively. (After digestion of the 265g samples about 20g of sand was filtered off each sample). This sandy sediment was presumably low in Pu-239, but Noshkin et al. report that their worm was found in sediment containing 28 pCi Pu-239/kg. Presumably they managed to separate worm and sediment but there was no change in concentration from sediment to worm. The results are therefore of little interest; the worms are unlikely to reflect sea water concentrations and it is easier to analyse sediments than to collect worms.

4.5.5 Lobster

The work of Ward (148) on lobsters has been described in Chapter 3. Ward was working with sea water concentrations more than 10^8 times our natural level and her plutonium was probably not in the same chemical and physical form as that found naturally. This makes a comparison of results difficult but there are obvious similarities as can be seen from Table 4.5, which compares our concentration factors with those of Ward after 50 days (before equilibrium) and after 300 days (after equilibrium). It can be seen that there is a striking

similarity in the order of preference of plutonium for the different organs although our concentration factors are much higher. Our high concentration factors are presumably due to the low levels of plutonium in sea water.

Table 4.5

Pu-239 Concentration Factors from Sea Water to Lobster

Organ	Concentration Factor		
	This Project	Ward after 50 days	Ward after 200 days
Shell	4000	100	110
Gills	4000	90	100
Digestive Gland	1000	10	100
Flesh	80	1	14

The concentration factor of 80 for lobster flesh is perhaps higher than might have been expected when compared with the typical value of six for fish muscle. The lobsters were collected early in 1973 and it is quite possible that the concentration of Pu-239 in sea water was higher than our calculated 1973 value of 2 pCi/l. Using the 1972 values of 4 pCi/l reduces the concentration factor to 40. This is still significantly higher than that for fish muscle, although there is no question of any health hazard.

4.6. Fish

Pu-239 concentration in stockfish and tuna caught in South African waters are shown in Table 4.6. These results support the conclusions reached in Chapter 3 - that plutonium is not highly concentrated by fish and appears to be immobilised in the gut as soon as it is absorbed. Any plutonium that does manage to enter the fish is deposited in the bone and liver.

Very high Po-210 levels (in excess of 10^4 pCi/kg) have been observed in the pyloric caecum of the tuna (43, 61) and in view of the suggestion (125, 153, 43) that something about the behaviour of plutonium might be inferred from studies of polonium it seemed worthwhile determining plutonium in this organ. However, it can be seen that no such spectacular concentration of plutonium occurs and the levels in caecum and

Table 4.6

Pu-239 Activity in Fish Caught in South African Waters

Organism	Collection Date	Wet Weight	Chemical Recovery %	pCi/kg	
				Wet	Dry
Stockfish - Muscle	1972	1500g	67	< 0,01	< 0,05
	1972	1000g	17	< 0,03	< 0,14
Bone	1972	975g	14	0,03 ± 0,01	0,09 ± 0,03
Liver	1972	167g	31	< 0,01	< 0,02
Gut	1972	327g	38	0,30 ± 0,05	2,64 ± 0,44
Tuna Pyloric Caecum	1973	464g	55	0,07 ± 0,01	0,43 ± 0,06
Tuna Pyloric Caecum	1973	429g	68	0,05 ± 0,01	0,30 ± 0,06
Tuna Liver	1973	210g	68	0,06 ± 0,02	0,18 ± 0,06
Tuna Stomach Contents	1973	125g	27	0,17 ± 0,05	9,66 ± 0,20
Tuna Stomach Contents	1973	182g	21	0,03 ± 0,01	0,12 ± 0,04
Tuna Stomach Walls	1973	415g	83	0,01 ± 0,005	0,05 ± 0,02

liver are approximately the same. The liver value is slightly lower than the concentration reported by Hodge et al. (59) probably because ours was a southern-hemisphere tuna. In Chapter 5 complete sets of polonium and plutonium data are given and the whole question of possible Po-Pu correlations is discussed.

One tuna had a relatively high plutonium concentration in the stomach contents, which appeared to contain whole anchovies among other things. Presumably this plutonium would have eventually been either retained in the gut or excreted.

4.7 World-Wide Fall-Out and Plutonium in Marine Organisms

Finally it is important to take a general look at the results obtained during this project and to see how they fit into the overall picture of world-wide fall-out and the Pu-239 and Pu-238 contents of northern-hemisphere samples.

In this chapter comparisons have already been made, where possible, between concentration factors reported for northern-hemisphere organisms and those observed in their South African counterparts. In general, agreement has been good, implying first that the organisms involved were good biological indicators and secondly that the values calculated for the Pu-239 concentration in southern-hemisphere sea water are of the right order (Chapter 3.2.1).

An alternative approach would be to calculate the southern hemisphere/northern hemisphere ratio for different pairs of organisms and to compare these ratios with the ratios in fall-out.

In practice it is very difficult to find comparable samples but Table 4.6 lists a few. In this table our southern-hemisphere samples have been compared with the northern-hemisphere samples reported in the open literature, mainly by Noshkin et al. (102 and Table 3.4).

All the southern-hemisphere samples were collected in the years 1972 and 1973, while the northern-hemisphere samples were collected during 1969 and 1970. Therefore, if the organisms obtain their plutonium primarily from the water, the south/north ratio should have a value between 0,27 and 0,61 depending upon the times of collection. (See Table 2.4). For organisms living

in the sediment the ratio should be close to the cumulative figure of 0,27. In actual fact all the organisms listed in Table 4.7 are more likely to be affected by the plutonium concentration in the water than in the sediment.

Unfortunately there are too few results for it to be possible to take the actual year of collection into account but it can be seen that apart from starfish all the ratios do lie within the expected range of 0,27 - 0,61. The northern- and southern-hemisphere starfish were different species living under different conditions and too much importance should not be attached to this high ratio.

We can therefore conclude that the ratio of plutonium in southern-hemisphere organisms to plutonium in northern-hemisphere organisms is in rough agreement with the ratio predicted from fall-out.

Table 4.7

Comparison of Pu-239 Concentrations in Southern- and Northern-Hemisphere Organisms

Organism	Pu-239 in Southern-Hemisphere Organisms (1972/73) / Pu-239 in Northern-Hemisphere Organisms (1969/70)
Mussel Soft Tissue	0,53
Mussel Shell	0,25
Starfish	0,83
Kelp	0,39
Other Mixed Algae	0,3
Tuna Liver	0,6

4.7.1 The Pu-238/Pu-239 Ratio

For convenience the relevant data have been extracted from Tables 2.6 and 2.3 and repeated in Table 4.8.

Table 4.8

The Pu-238/Pu-239 Ratio in Surface Air and Total Cumulative Fall-out

	Southern Hemisphere	Northern Hemisphere
Surface Air 1966		0,11
1967		0,44
1968		0,33
1969		0,24
1970		0,11
1971	0,28	0,15
1972	0,175	
1973	Between 0,175 and 0,35	
Cumulative Fall-out up to December 1970	0,18	0,037

For the purposes of this discussion the following assumptions will be made:-

1) During each year the Pu-238/Pu-239 ratio in surface water lies somewhere between the ratio in surface air for that year and the preceding year. Thus in 1972 the surface-water ratio in the southern hemisphere was between 0,175 and 0,28 while in 1973 it was between 0,175 and 0,35. (See Table 2.6).

2) The ratio in sediments is very similar to the ratio in cumulative fall-out.

Noshkin et al. (102) are the only authors to report the Pu-238/Pu-239 ratio in a significant number of organisms. Their results were obtained in the northern hemisphere and are reported in Tables 3.6 and 3.8. Noshkin also determined the ratio in sea water and sediment obtaining the following values:

water - 0,12 sediment - 0,045

All their samples were collected during 1970 and it can be seen that their water and sediment ratios fit in very well with assumptions 1 and 2 above.

A study of Tables 3.6 and 3.8 shows that in all the northern-hemisphere organisms analysed by Noshkin et al. (102) the ratio was somewhere between the sediment value of 0,045 and the water value of 0,12. Thus in benthic organisms such as marine worm the ratio was low while in mussels, which filter

sea water, the ratio was high. This variation in ratio enabled the authors to draw conclusions about the feeding habits of the various organisms.

It is, however, important to note that in all the samples analysed the ratio is significantly lower than the ratio in the water. This could possibly be ascribed to the fact that some of the plutonium was obtained from sediment rather than from the water. Thus filter feeders such as mussels could have ingested re-suspended sediment. However Noshkin et al. feel strongly that mussels regulate their plutonium content in relation to the concentration in water rather than other sources such as sediments. This argument is supported not only by the relatively high Pu-238/Pu-239 ratio but also by the fact that samples (including those analysed in this project) separated both by time and environment display similar concentration factors. Moreover their mussel samples were collected from rocks and piles well removed from bottom sediments.

The Pu-238/Pu-239 ratio in starfish was the same as the average value in the mussels on which they were feeding. Thus starfish, albeit indirectly, should also reflect the ratio in sea water.

Seaweeds should certainly regulate their plutonium concentration in relation to sea water rather than sediment and it is unfortunate that the only macrophytes on which Noshkin determined this ratio were the floating sargassum fluitans and sargassum natans. The Pu-239 content of these samples was very high while the ratios were low; they bear no relation to the ratio in surface air for the year of collection. Noshkin et al. suggest that the plutonium concentration may be more closely correlated with short-term changes in delivery patterns to the ocean surface rather than with water concentrations. This implies that the high plutonium concentrations may have been caused by accumulation immediately following some intense fall-out. If this were true then the ratio could be expected to be close to the normal weapons ratio of 0,04. This is indeed the case but it is difficult to believe that all six samples happened to be collected shortly after local tests, of which there appears to be no record.

An alternative explanation is that, as these sargasso

weeds are capable of vegetative regeneration by fragmentation and can exist in the floating state indefinitely, they may be reflecting cumulative rather than total fall-out ratios. This would also explain the high concentrations of Pu-239 that were found.

Finally the possibility exists that Pu-239 is selectively absorbed with respect to Pu-238. This theory will be discussed later in this Chapter.

No published values exist for the Pu-238/Pu-239 ratio in southern-hemisphere organisms and the presence of Pu-238 in the tracer used in this project made it impossible to determine Pu-238 in most of the samples analysed. Only three contained sufficient Pu-238 for an accurate estimate of the Pu-238/Pu-239 ratio to be made. These were two starfish samples and one sargassum heterophyllum sample. In addition two portions of sargassum heterophyllum were analysed without the addition of a tracer. This gave a figure for the ratio but not an absolute plutonium concentration. These ratios are listed in Table 4.9 and it can be seen that agreement is excellent.

Table 4.9

The Pu-238/Pu-239 Activity Ratio in South African Marine Organisms

Organism	Collection Date	Pu-238/Pu-239
Martha asterias	3/6/73	0,12 ± 0,02
	3/6/73	0,12 ± 0,02
Sargassum heterophyllum (No tracer)	3/6/73	0,11 ± 0,02
	3/6/73	0,09 ± 0,02
Sargassum heterophyllum	4/2/73	0,13 ± 0,04
	Mean	0,11 ± 0,02

All the spectra from which these values were obtained were of high quality, showing good resolution and low background and there can be little doubt that these figures are accurate. It is surprising, therefore, that the mean ratio of 0,11 ± 0,02 is so much lower than the estimated ratio in sea water of between 0,175 and 0,35. (Ch. 2.6.2).

As already mentioned, Noshkin et al. working in the

northern hemisphere also found that the Pu-238/Pu-239 ratio in organisms was invariably lower than the ratio in the surrounding sea water. Their ratio in sediments was even lower and they assumed that the low ratio in organisms was due to the influence of sediment - this despite the fact that many of the organisms they analysed are presumed to regulate their plutonium content in relation to the plutonium concentration in sea water rather than in sediment. In the southern hemisphere, however, no such simple explanation is possible, since the Pu-238/Pu-239 ratio in cumulative fall-out and hence in sediment, was 0,175 (i.e. approximately the same as in water and considerably higher than in organisms).

Admittedly there is some doubt about the reliability of the estimated Pu-238/Pu-239 ratios in surface air but on balance it seems unlikely that the ratio in southern hemisphere sea water could have been lower than 0,175 during 1973. It is desirable therefore to seek an explanation not based on the influence of sediment to account for the fact that in two sets of results (ours and those of Noshkin et al.) the ratio is lower in organisms than in the surrounding sea water. Fall-out Pu-239 and SNAP-9A Pu-238 have completely different origins and may well be in completely different chemical and physical forms. Thus the two isotopes might have quite different solubilities or tendencies to adsorb onto other particles or to form colloids, hydroxides etc. It is therefore quite possible that organisms might absorb a higher proportion of Pu-239 than of Pu-238. Selective concentration of this type would result in the ratio being lower in one organism than in the surrounding water and it may have been this, rather than the influence of sediment that led to Noshkin's low ratios, as well as our own.

It is interesting to note here that Noshkin and Gatrouss (105) after a study of the Pu-240/Pu-239 ratio reached a similar conclusion about Pu-240 and Pu-239. They found that the Pu-240/Pu-239 ratio in plankton was higher than could be predicted from fall-out and postulated that the Pu-240 is selectively absorbed in preference to Pu-239. We can therefore conclude that, if selective absorption is indeed taking place, the order of preference is

Pu-240 > Pu-239 > Pu-238 (SNAP-9A).

Of course, this refers only to SNAP-9A Pu-238. Pu-238 from weapons testing might well behave quite differently but its behaviour would have been masked by SNAP-9A plutonium during recent years.

The alternative hypothesis, that Pu-238 is more rapidly removed from the surface water than is Pu-239, would result in low ratios in water as well as in organisms. From the small amount of data available on the ratio in sea water this does not seem to be the case; selective absorption seems to be the most likely explanation for the low ratios in organisms.

A great deal more work will have to be done before the above theory can be confirmed or rejected and it is important that as much information as possible about the Pu-238/Pu-239 ratio should be amassed. The SNAP-9A Pu-238 has already proved of great value in helping us to understand air movements in the atmosphere and could well be of equal value as a bio-geochemical and oceanographic tracer.

Chapter 5

Uranium, Thorium, Polonium and Total Counting Results

5.1 Uranium and Thorium Results

Uranium and thorium were determined on fourteen samples, all belonging to one of the categories zooplankton, macrophytes or marine invertebrates. Because of the small number of samples and because of the many inter-relationships between the various isotopes no attempt has been made to stick rigidly to biological or elemental classifications in this discussion.

Tables 5.1 and 5.2 list the results obtained and a number of ratios of interest. All samples were analysed in duplicate and in order to give some idea of the precision of the analytical methods both uranium results are given in the table. Since the thorium figures were obtained from pairs of samples, one spiked and one unspiked, only one result can be given. The standard deviations quoted are based entirely on counting statistics. Because the ratios between isotopes of the same element can be calculated directly from the counts obtained, the standard deviation for these ratios is often much lower than for the absolute concentrations of the isotopes. Figures 5.1 and 5.2 are designed to show up qualitative relationships between the various isotopes. Within the limits of experimental error the U-234/U-238 ratio was a constant value of 1,14 and a graph for U-238 has therefore not been included.

The discussion that now follows is divided into two parts. Section 5.2 briefly compares these results with those of other workers described in Chapter 3, while Section 5.3 is a discussion of the various ratios and inter-relationships between different isotopes and organisms.

5.2 Comparison of Individual Uranium and Thorium Results with Published Values

5.2.1 Zooplankton:

Uranium It was suggested in Section 3.4.2 that there might be an association between the silica content of organisms and the extent to which uranium is absorbed. Thus Miyake *et al.* (90) found their highest uranium concentration in the plankton sample containing the highest proportion of diatoms (Table 3.12).

The two plankton samples analysed in this project support this theory. The silaceous sample contained seven times as much uranium as the amphipod sample on a wet weight basis (or thirteen times as much on a dry weight basis). For convenience these

Table 5.1

Activities of Uranium and Thorium Isotopes in Marine Organisms collected in vicinity of Cape Town

Sample No.	Sample Description	Wet wt. / Dry wt.	Chemical Recovery % Th	Chemical Recovery % U	pCi/Kg wet wt. Th-232	Th-230	Th-228	pCi/Kg wet U-238	U-234
S-79	Zooplankton - Silaceous	10,2	77 57	77 68	0,11±0,03	0,15±0,07	1,50±0,17	48,4±4,0 49,0±4,2	54,5±4,5 55,5±4,9
S-82	Zooplankton - Amphipods	4,8	63 70	37 57	0,41±0,05	0,40±0,04	3,4±0,27	7,2±0,7 6,8±0,6	8,3±0,8 7,5±0,6
S-7	Aoedes Orbitosa	4,8			0,3±0,1	0,5±0,1	1,1±0,2	<0,5	<0,5
S-3	Sargassum Heterophyllum	6,6	91 61	41	0,35±0,06	0,39±0,07	1,2±0,2	16,9±1,5	18,8±1,7
S-28	Sea Urchin Shell	1,8	97 92	70	0,32±0,05	0,27±0,05	2,8±0,3	24,7±2,3 24,3±2,3	27,8±2,6 28,5±2,7
S-46	White Mussel Shell	1,1	70 79	60	0,18±0,03	0,34±0,05	4,1±0,5	29,0±2,9 21,4±3,0	34,0±3,4 24,3±2,4
S-42	Black Mussel Shell	1,1	77 50		0,41±0,18	0,64±0,32	7,6±3,5	-	-
S-11/ 12	Lobster Shell	1,4		47	4,7±1,7	5,6±2,5	13,5±3,9	27,1±2,4 26,5±2,5	31,8±2,8 32,5±3,2
S-64	Starfish	3,1	59 85	80 80	0,16±0,03	0,22±0,04	2,0±0,3	65,8±5,5 68,3±6,0	74,2±6,2 77,5±6,8
S-30	Sea Urchin Digestive	7,9	20 35	70 62	7,7±4,1	10,5±5,5	10,9±5,5	20,6±1,8 18,2±1,5	22,8±2,0 20,3±2,0
S-29	Sea Urchin Gonads	6,7	78 78	71 76	0,23±0,10	0,23±0,10	1,5±0,4	25,5±2,2 26,9±2,5	29,2±2,6 28,6±2,7
S-31	Sea Urchin Fluid	21,2	44 48	76 71	0,32±0,05	0,36±0,05	0,9±0,2	2,3±0,3 2,2±0,3	2,3±0,3 2,5±0,3
S-47/ 48	White Mussel Soft Tissue	4,7	65 64	58 65	0,23±0,05	0,55±0,12	0,90±0,18	5,9±0,5 6,4±0,5	7,0±0,6 7,1±0,6
S-40	Black Mussel Soft Tissue	6,5			0,41±0,18	0,91±0,41	0,64±0,32	-	-
	Typical Seawater								
	Oceanic				$1x10^{-4}$	$4x10^{-4}$	$1,6x10^{-3}$	1.1	1.2(5)
	Coastal				$20x10^{-4}$	$40x10^{-4}$	$8,0x10^{-3}$	1.1	1.2(5)

Table 5.2

Uranium and Thorium Activity Ratios

Sample No.	Sample Description	$\frac{^{230}Th}{^{232}Th}$	$\frac{^{228}Th}{^{232}Th}$	$\frac{^{230}Th}{^{234}U}$	$\frac{^{232}Th}{^{234}U}$	$\frac{^{234}Th}{^{238}U}$	$\frac{^{238}U}{^{235}U}$
S-79	Zooplankton - Silaceous	1,5±0,6	15,2±4,8	0,003±,001	0,002±0,001	1,12±0,02 1,13±0,02	-
S-82	Zooplankton - Amphipods	1,0±0,1	8,1±0,7	0,05±0,01	0,05±0,01	1,14±0,2 1,12±0,02	20,8±0,6 23,2±0,6
S-7	Aoedes Orbitosa	1,6±0,1	3,8±0,1	-	-	-	-
S-3	Sargassum Heterophyllum	1,1±0,6	3,4±0,2	0,07±0,01	0,019±,003	-	-
S-28	Sea Urchin Shell	0,9±0,1	9,1±0,7	0,010±0,002	0,011±0,002	1,13±0,02 1,18±0,02	22,2±2,0
S-46	White Mussel Shell	1,8±0,2	21,9±1,6	0,012±0,002	0,006±0,002	1,17±0,04 1,14±0,05	21,7±2,0 19,1±2,5
S-42	Black Mussel Shell	1,6±0,2	11,5±0,9	-	-	-	-
S-11/12	Lobster Shell	1,2±0,1	2,9±0,4	0,17±0,07	0,15±0,05	1,12±0,03 1,16±0,04	-
S-64	Starfish	1,4±0,2	8,9±0,6	0,003±0,001	0,002±0,001	1,13±0,02 1,13±0,02	28,5±0,7 22,9±0,7
S-30	Sea Urchin Digestive	1,4±0,1	1,4±0,1	0,54±0,3	0,36±0,19	1,12±0,03 1,11±0,03	20,8±2,0
S-29	Sea Urchin Gonads	0,91±0,20	6,04±0,97	0,008±0,004	0,008±0,004	1,14±0,03 1,06±0,03	20,8±2,0
S-31	Sea Urchin Fluid	1,1±0,2	2,8±0,3	0,17±,03	0,13±,03	1,06±0,05 1,14±0,05	-
S-47/48	White Mussel Soft Tissue	2,4±0,2	3,8±0,3	0,08±0,02	0,03±0,01	1,13±0,04 1,11±0,04	-
S-40	Black Mussel Soft Tissue	2,2±0,2	1,2±0,2	-	-	-	-
	Typical Seawater						
	Oceanic	0,5-10,5	1,7-65			1,14	
	Coastal	0,6-20	1,0-9,1				

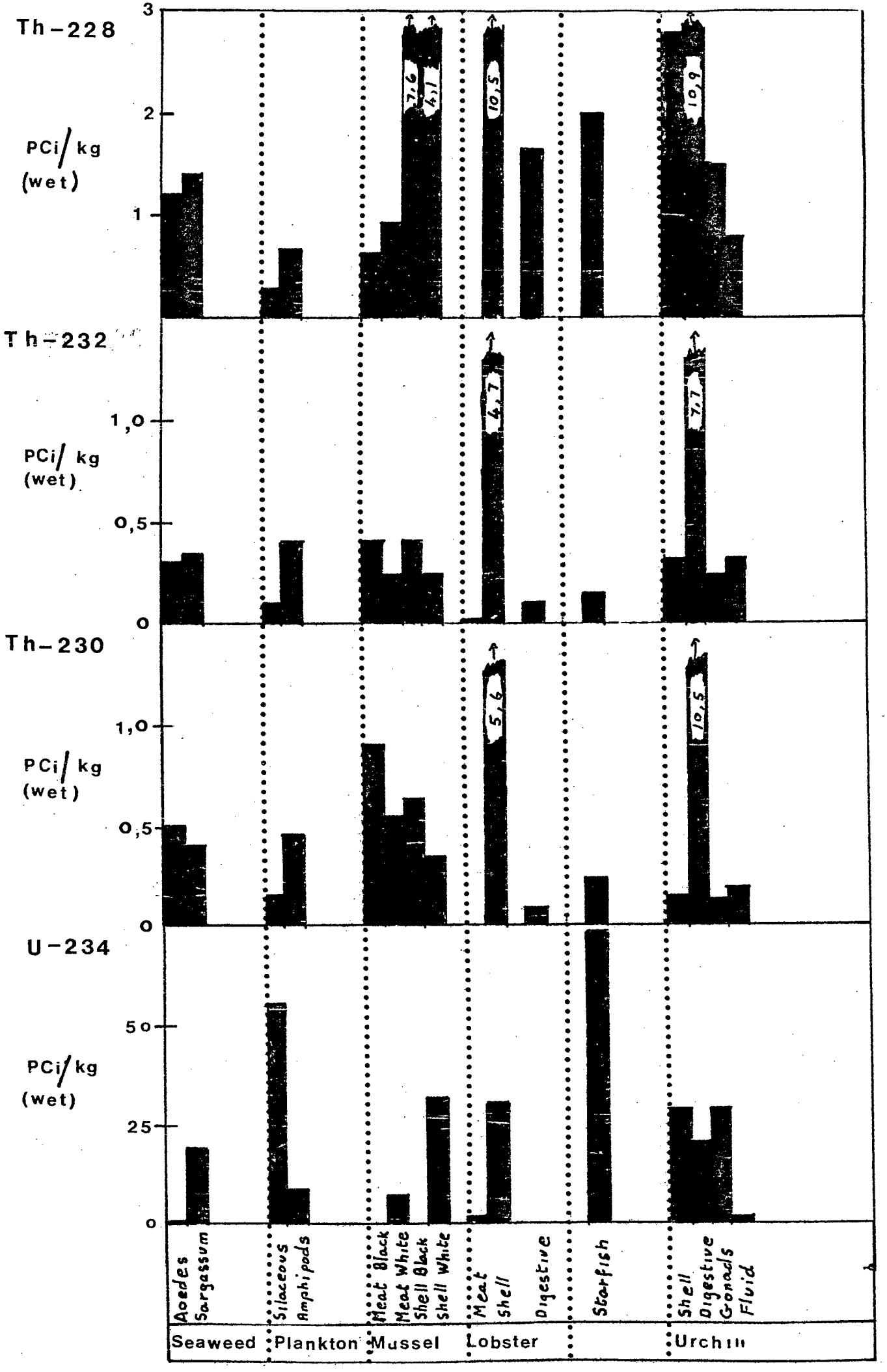


Fig 5.1 Thorium & Uranium Isotopes in Various Marine Organisms

results are repeated in Table 5.3 together with Miyake's lowest and highest sample.

Table 5.3

Uranium in Plankton

Sample Description	U-238 pCi/kg dry	U-238 pCi/kg wet
S-79 Silaceous Plankton	490	49
S-82 Amphipods	34	7
Miyake (30) Diatoms ###, Euphausiids ##	245	16,3
Miyake (30) Euphausiids, Amphipods, Larvae	55	3,6

It can be seen that our silaceous plankton sample was remarkably high in uranium - more than twice as high as Miyake's highest sample. Unfortunately we can make no estimates of the relative silica contents of the samples but the possibility of an association between uranium and silica is of great importance to geochemists and the determination of uranium in a large number of such organisms, possibly with collateral silica determinations, might lead to information of considerable value.

Thorium There are very few results with which to compare our thorium figures. However our plankton were caught in the same waters as those of Cherry and Shannon (26, 126) and therefore were presumably subject to similar oceanic concentrations of thorium. A comparison is given in Table 5.4.

It is interesting to note here that Shannon's lowest thorium values were found in plankton samples caught in the cold water of the sub-Antartic and the Benguela current. The two samples analysed in this project also came from the Benguela current and this may explain the fact that their thorium contents were at the lower end of the range reported by Shannon.

5.2.2 Macrophytes:

Table 5.5 compares the uranium and thorium concentrations in the two seaweed samples analysed in this project with the ranges reported by other workers (Chapter 3.5).

Table 5.4

Thorium Isotopes in Plankton

	Th-228 (pCi/kg)		Th-232 (pCi/kg)		Th-230 (pCi/kg)	
	dry	wet	dry	wet	dry	wet
S-79 Silaceous Plankton	15	1,5	1,1	0,11	1,5	0,15
S-82 Amphipods	16	3,4	2,0	0,41	1,9	0,40
Cherry and Shannon (59)	20-500	2-24	-	-	-	-
Shannon - Zooplankton (181)	22-236	2-20	0-36	0-3	0-36	0-3
Phytoplankton	174-1760	8-80	0-140	0-6	0-127	0-6

Table 5.5

Uranium and Thorium in Macrophytes

	U-238 (pCi/kg)		Th-232 (pCi/kg)		Th-230 (pCi/kg)		Th-228 (pCi/kg)	
	wet	dry	wet	dry	wet	dry	wet	dry
S-7 Aoedes Orbitosa	< 0,5	< 2,4	0,3	1,4	0,5	2,4	1,1	5,3
S-61 Sargassum Heterophyllum	16,9	111,5	0,35	2,3	0,39	2,6	1,2	7,9
Range in Literature	1,8-105	137-1480	0,08-2,7*	1,2-2,4*				

* Range for brown seaweed

Uranium Neither sargassum heterophyllum nor aoedes orbitosa are calcified and this may be connected with the fact that concentrations found tend to be at the lower end of the scale of published values. The very low value in aoedes orbitosa is surprising and needs confirmation.

Thorium The Th-232 values are within the range of published values.

5.2.3 Marine Invertebrates

As already mentioned the determination of uranium and thorium by other workers in marine invertebrates has been almost entirely confined to shells and the possibility of some relationship between the crystal structure and uranium content has been raised.

Uranium A comparison of Table 5.1 with the results described in Chapter 3.4 shows the following:-

1). Our value of 21-29 pCi/kg U-238 in mussel shell agrees well with Kaufman's mean figure of 30 pCi/kg (67). It is however higher than the values of between 1 and 15 pCi/kg U-238 reported by Tatsuomoto and Goldberg (135) for molluscan shells composed of aragonite or a mixture of aragonite and calcite.

2) Our value of 42 pCi/kg dry sea urchin shell is reasonably close to the 54-57 pCi/kg reported for echinoderm shells by Tatsuomoto and Goldberg. Furthermore, in spite of the calcitic nature of the sea urchin shell the uranium content appears to be higher than that of molluscan shells. This may well be something to do with the porous nature of echinoderm shells. It is interesting to note, here, that the uranium content of the single barnacle shell analysed by Tatsuomoto and Goldberg was similar to that of molluscan shells rather than echinoderm shells. Barnacle shells, while also calcitic, do not have the same porous structure as the shells of echinoderms.

From so few results it is impossible to draw any firm conclusions about the nature of uranium absorption by shells and even the suggestion that echinoderm shells contain higher concentrations of uranium than molluscan shells needs confirmation. Lobster shell was also relatively high in uranium and on balance it appears that in living shells, crystal structure is not the determining factor.

Sheldon (128A) found that in apatite, reduced uranium (+4)

substituted into the crystal lattice while uranyl (+6) ions were apparently adsorbed at the surfaces of the crystals. Under normal conditions uranium will be present in the +6 oxidation state. Therefore if a similar situation exists with calcium carbonates it is likely that uranium is adsorbed at the surfaces of the crystals whether they are aragonitic, calcitic, or simply aggregates of micro-crystals as is the case in crustacea. Thus the higher uranium concentration observed in echinoderm shells might well be due to the increased surface area available.

In sediments, on the other hand, reducing conditions often exist and this might explain the tendancy reported by Kauffman for aragonitic fossil shells to be higher in uranium than calcitic shells. When substitution is directly into the lattice it should be easier in aragonite than in calcite.

The very high uranium content of starfish (also an echinoderm) is intriguing. Unfortunately this organism was not dissected but it would be interesting to know how the uranium is distributed between shell and body. The similarity in concentration in sea urchin shell (wet) and sea urchin digestive organ and gonads indicates that distribution may be fairly even.

The increase in concentration from tissue to shell in mussels may be significant but it would be necessary to analyse the extrapallial fluid on its own before any deductions about the mechanism of transfer from tissue to shell could be made.

Thorium As can be seen from Table 3.10 there are so few published values for thorium in marine invertebrates that comparison with other workers is meaningless. All that can be said is that the thorium results obtained in this project are in general agreement with those of Blanchard (13) and that on the whole we found less thorium in our shells than did Dodge and Thompson in their corals (38).

The high thorium content of the lobster shell is interesting as is the high value in sea urchin digestive system, but until this trend is confirmed by further analyses it is pointless to speculate on its significance.

The different isotopic ratios and the effect of shell structure on these ratios are discussed in detail in Section 5.3.

5.3 Uranium and Thorium Isotopic Ratios

5.3.1 The U-234/U-238 ratio

The remarkable constancy of the U-234/U-238 ratio in sea water has been observed by many workers (29, 68, 129, 90, 87). Cherry et al. (29) state that a mean activity ratio of 1,14 is in agreement with most of the data and the range in this ratio seems to be small. The fact that this ratio remained constant in all the organisms analysed is of great interest and enables two important conclusions to be drawn:-

1) Since such a wide variety of organisms shows no sign of distinguishing between the two isotopes the generally held view that once in the sea both U-234 and U-238 are present in the same physical and chemical form, is almost certainly correct.

2) Since the U-234/U-238 activity ratio in sediments, sea sands, granite, etc. is 1,0 or lower it seems clear that the organisms all obtained their uranium either directly or indirectly from the water and not from re-suspended sediments etc. Thus all the organisms incorporated uranium as ionic $UO_2(CO_3)_3^{4-}$ into their structures or obtained their uranium from organisms which had done so.

5.3.2 Th/Th ratios

A study of Fig. 51 enables us to draw similar conclusions about the three thorium isotopes although not with the same degree of certainty. Thus all the thorium isotopes follow a similar "pattern" although, as in sea water, the activity of Th-228 is an order of magnitude higher than that of Th-230 and Th-232. The only exceptions to this are shells where the presence of Ra-228 has presumably resulted in exceptionally high Th-228 values.

This leads one to the conclusion that, where Ra-228 is not involved as an intermediary, all the isotopes must be absorbed by the same mechanism by a variety of organisms. And this implies that the three isotopes must be present in sea water in largely the same chemical and physical form. Of course, far more work will have to be done before this latter conclusion can be confirmed.

5.3.3 The Th-230/Th-232 Ratio

This similarity in behaviour is particularly clear for Th-232 and Th-230 and the Th-230/Th-232 ratio varies between the fairly narrow limits of 0,9-2,4 with a mean of 1,4. It seems likely moreover that the ratio in sea water was of the same order since although published values vary widely, figures between 1 and 3 are the most common.

The Th-230/Th-232 ratio in shallow sediments on the other hand tends to be much higher and is generally between 10 and 50 in the top 30 cm (21, 129, 9). This indicates that resuspended sediment is unlikely to have been a major source of thorium for the organisms analysed. Of course granite, sand, etc., newly introduced into the oceans, might have a Th-230/Th-232 ratio close to one but it is unlikely that this material could have been a major contributor of thorium to such a wide variety of organisms.

It is possible that the relatively high Th-230/Th-232 ratio in mussel meat is due to the fact that these creatures filtered off and retained some sediment particles. That the ratio is lower in the shell may indicate that these particles are not broken down and that this thorium is not absorbed into the blood stream and made available for transfer to the shell. It is quite likely that these particles of sediment may be excreted and unchanged. It would be interesting to check such theories by keeping mussels in clear water for a few days before analysing them.

The Th-230/Th-232 ratio in shells is of particular importance because it is necessary to make a correction for the Th-230 present in shells at zero age when dating shells and sediments by the uranium series method (Chapter 3). The world average for this ratio has been taken to be 1,5 although values ranging from 0,9 to 2,4 have been used (67). Since this dating method is frequently used for molluscan shells it is satisfying to note that the ratio in mussel shells was close to 1,5. The value of 1,5 for the silaceous plankton sample is also encouraging news for people engaged in dating diatomaceous oozes etc.

The low ratio in sea urchin shell may be significant. Kaufman et al (67) have reported that calcitic shells are less suitable than aragonitic shells for Th-230/U-234 dating. The reason he gives is that calcitic shells contain large amounts

of Th-232 relative to U-234. Of course, a high Th-232 concentration means a large correction for the Th-230 initially present in the shell and any error in the assumed $(Th\text{-}230/Th\text{-}232)_{t=0}$ ratio would lead to a very inaccurate date.

In actual fact there is no significant difference between the Th-232/U-234 ratio in our calcitic sea urchin shell and a (presumably) mainly aragonitic mussel shell. However the $(Th\text{-}230/Th232)_{t=0}$ ratio in sea urchin shell is very different to the "world average" figure of 1,5 used by Kaufman. It is therefore possible that errors in this value have contributed to the less satisfactory results obtained when dating calcitic shells.

5.3.4 The Th-230/U-234 Ratio

As already mentioned it is important for uranium series dating that the Th-230/U-234 ratio should be low in living shells. In all the samples analysed this was indeed the case. The only samples in which this ratio was above 0,1 were the lobster shell and the sea urchin digestive system (neither of which are likely to be dated). In both cases the high ratio was due to high Th-230 values.

5.3.5 The Th-228/Th-232 Ratio

Because of the wide range in the Th-228/Th-232 ratio and because of the small number of samples it is more difficult to analyse our results for the Th-228/Th-232 ratio. Before doing so it is worth considering what we would expect and the following points should be made:-

1) Any organism that concentrates radium will have a high Th-228/Th-232 ratio relative to the surrounding sea water since Ra-228 decays to Th-228 ($t_{\frac{1}{2}}$=6,7 yr). The value of this ratio can therefore be taken as a guide to the extent to which radium has been concentrated by the organism. Of course this effect would be more marked in an old sample than in a young one.

Shell and bone samples tend to contain relatively high concentrations of radium (29, 13, 18) and it is therefore to be expected that the ratio will be high in samples containing shell.

It has been postulated (29, 73) that radium is associated with silaceous organisms. One might therefore expect to find a higher Th-228/Th-232 ratio in silaceous plankton than in amphipods.

Because of its large ionic radius (Table 3.2)

radium should fit more readily into an aragonitic than into a calcitic lattice. Thus one would expect the Th-228/Th-230 ratio to be higher in mussel shell than in sea urchin shell.

2) Since no mechanism has been proposed by which Th-232 might be absorbed in preference to Th-228 the Th-228/Th-232 ratio in the surrounding sea water must be equal to or lower than that observed in organisms.

3) Typically the Th-228/Th-232 ratio is higher in oceanic than in coastal waters (29, 91, 26, 66). Therefore even without the influence of radium one would expect a higher ratio in plankton than in organisms collected in near shore waters.

In view of the above we can now take a closer look at the individual results. It must be borne in mind that these are single results and the possibility of analytical error or unrepresentative sampling cannot be ignored. All conclusions must therefore be regarded as tentative although it can be seen that in general they are in agreement with the expectations outlined above. Thus:-

1) In all three shell samples (mussel and sea urchin) the Th-228/Th-232 ratio was very high. Furthermore both the absolute Th-228 value and the Th-228/Th-232 ratio were lower in the calcitic sea urchin shell than in the aragonitic mussel shell. Thus radium does appear to be more readily accepted into the aragonite lattice.

Although the absolute Th-228 concentration (in pCi/kg dry weight) was the same in both plankton samples the ratio in the silaceous sample was double the ratio in the amphipod sample. This may be partly due to the fact that the amphipod sample was analysed immediately after collection, while the silaceous sample was kept for eight months before analysis, thus giving Th-228 a chance to grow in. On the other hand the silaceous nature of the latter sample might have led to increased radium absorption relative to thorium.

2) The Th-228/Th-232 ratio in coastal samples, other than shells, varied between one and six with a mean of around three. Therefore if assumption two above is correct, the ratio in sea water must have been close to one, or at any rate between one and three.

3) The Th-228/Th-232 ratio was indeed higher in plankton

than in coastal (non-shell) organisms. There is no way of telling to what extent the Th-228 content of the amphipod sample was enhanced by Ra-228 decay but we can say that the ratio in oceanic sea water was probably eight or lower.

5.3.6 The U-238/U-235 Ratio

Finally brief mention must be made of the U-238/U-235 ratio. This is difficult to determine because of the low concentration of U-235 and because of the spread in the energies of the alpha-particles emitted by U-235. Nevertheless, in six samples with high uranium concentrations and good spectra, it was possible to make a fairly accurate estimate of this ratio. The mean of the six ratios obtained is 21,7 ± 0,9 which is in agreement with the terrestial ratio of 21,96 used by Koide and Goldberg (68). Thus it appears that the U-238/U-235 ratio is the same on land and in the sea. There is no evidence of any discrimination between the two isotopes by marine organisms and it is therefore likely that they exist in the same chemical and physical form.

5.3.7 Thorium/Uranium Ratios

It can be seen from Fig.5.1 that there is very little similarity in the "pattern" shown by thorium and uranium. This is hardly surprising in view of the very different chemical and physical forms in which the two elements are presumed to exist in sea water. It is probably these differences that account for the very much higher concentration factors for thorium than uranium. Thus the concentration factor for uranium varies between six and fifty, while that for thorium is usually at least one thousand. This may be due to the fact that uranium has reached some sort of saturation value in many organisms but it is more likely that the particulate nature of the thorium isotopes and their tendancy to form complexes and associate with organic molecules results in more effective concentration.

5.4 Polonium Results

Table 5.6 gives the Po-210 and Pb-210 concentrations found in the various organisms analysed. For the purposes of comparison Pu-239 concentrations are also included in the table. Most of the results in this table are the mean of two determinations. While uranium and thorium results are not included

in the table, those samples in which they were determined are marked with an asterix and the figures can be found in Table 5.1.

Fig.5.2 is designed to show up any qualitative relationships between the isotopes Po-210, Pu-239 and Pb-210 and should be compared with Fig.5.1. Samples in which uranium and thorium isotopes were also determined are shaded in solid black, while the others are unshaded.

A study of Table 5.6 shows that the polonium and lead results contain no surprises. With one exception (the macrophyte ulva) all the values obtained were within the ranges reported as typical in Table 3.10. For this reason individual polonium results will be discussed only briefly. The usual classification into categories will be adhered to.

5.4.1 Category A2 - Macrophytes

Macrophytes, and the interesting work of Wong et al. (153) and Hoffman et al. (60) on the variation of the Po-210 content with distance from the surface of kelp blades, have already been discussed in Chapter 3. Thus there is evidence to suggest that much of the Po-210 found in macrophytes is in fact accumulated by small surface living animals.

The value of 4 pCi/kg found in ulva is very low although the difference between this and the values of 16-30 pCi/kg reported by Schell (123) may not be significant. Ulva has a high surface area but the blades are smooth and glossy and probably do not harbour many surface living animals.

Porphyra has an even larger surface area, the surface is rough and may well form a more suitable environment for encrusting animals. This may explain the relatively high Po-210 content of the porphyra sample. However, until a microscopic examination of the various seaweeds is made and the surface layers are analysed on their own no firm conclusions can be drawn from results such as these.

It is interesting to note that the Pb-210 content of the four seaweed samples is more constant than the Po-210 concentration. This means that the Po-210/Pb-210 ratio is high for porphyra, low for ulva with aoedes and sargassum heterophyllum in between. This would indicate that the mechanisms by

Table 5.6

Po-210, Pb-210 and Pu-239, 240 Activities in Marine Organisms

Sample No.	Sample Description	Wet / Dry	pCi/Kg Wet			pCi/Kg Dry			Po-210 / Pb-210	Po-210 / Pu-239	Pb-210 / Pu-239
			Po-210	Pb-210	Pu-239	Po-210	Pb-210	Pu-239			
Category A2											
S7*	Aoedes Orbitosa	4.8	158±14	38±3	0,15±,01	758	182	0,72	4,2	1053	253
S3*	Sargassum Heterophyllum	6.6	79±6	15±2	0,41±0,06	521	99	2,71	5,3	193	37
S2	Porphyra	5.1	215±14	24±4	0,15±0,02	1097	122	0,77	9,0	1433	160
S5	Ulva	6.1	4±5	33±3	0,07±0,01	24	201	0,43	0,1	50	471
Category B											
S-79*	Zooplankton - Silaceous	10.2	100±8	8±2	0,11±0,02	1020	82	1,12	12,5	909	73
S-82*	Zooplankton - Amphipods	4.8	1366±15	38±6	0,15±,02	6557	187	0,72	35,9	9107	253
Category C											
S-40*	Black Mussel Soft Tissue	6.5	869±34	54±5	0,14±,03	5642	351	0,91	16,1	6200	382
S-47*	White Mussel Soft Tissue	4.7	405±41	15±6	0,15±,03	1904	71	0,71	27	2700	100
	Oyster Soft Tissue	5.5	850±90	20±3	-	4675	110	-	43	-	-
S-42*	Black Mussel Shell	1.1	57±82	129±14	0,09±,03	63	142	0,10	0,4	(633)	1433
S-46*	White Mussel Shell	1.1	46±220	107±45	0,11±,08	51	118	0,12	0,4	(418)	973
	Oyster Shell	1.1	0±10	68±15	-	0±10	75	-	-	-	-
S-28*	Sea Urchin Shell	1.8	379±28	54±13	0,13±,02	682	97	0,23	7	2915	431
S-30*	Sea Urchin Digestive	7.9	586±34	38±3	0,32±,07	4629	300	2,53	15,6	1831	117
S-29*	Sea Urchin Gonads	6.7	117±8	7±4	0,11±,04	784	47	0,74	16,7	1064	64
S-31*	Sea Urchin Fluid	21.2	14±2	0±1	0,02±,01	297	0	0,42	-	700	0

Continued/.....

Table 5.6 (continued)

Sample No.	Sample Description	Wet / Dry	pCi/Kg Wet			pCi/Kg Dry			Po-210 / Pb-210	Po-210 / Pu-239	Pb-210 / Pu-239
			Po-210	Pb-210	Pu-239	Po-210	Pb-210	Pu-239			
S11/12*	Lobster Shell	1.4	158±64	8±3	0,77±,14	221	28	1,23	7,9	180	23
S-17	Lobster Gills	3.9	348±60	20±10	0,88±,14	1357	78	3,43	17,4	395	23
S-14	Starfish	3.1	468±22	90±15	0,72±,05	1451	279	2,2	5,2	650	125
S9*	Lobster Meat	4.1	38±17	0±2	0,016±0,007	156	0	0,07	-	2375	0
S-14	Lobster Digestive	2.3	8825±3514	57±10	0,2±0,04	20297	131	0,46	155	44125	285
S-13	Lobster Digestive	2.1	147±34	6±12	-	309	13	-	25	-	-
S-78	Lobster Divestive	2.3	6445±360	157±80	0,07±0,02	14824	361	0,16	41	92071	2243
S-81	Blood Worm (Arenicola loveni)	3.8	1169±37	73±6	0,12±0,02	4442	277	0,46	16	9742	608
Category D											
S-A	Tuna Caecum	6.1	12825±600	44±3	0,07±0,01	78233	268	0,43	291	183214	629
S-B	Tuna Caecum	6.0	7050±425	54±4	0,05±0,01	42300	324	0,30	131	141000	1080
S-C	Tuna Liver	3.0	2140±58	10±7	0,06±0,02	6420	30	0,18	214	35667	167
S-D	Tuna Stomach Walls	4.3	545±25	-	0,01±0,005	2344	-	0,04	-	54500	-
S-E	Tuna Stomach Content	3.7	1340±57	5±5	0,17±0,05	4958	19	0,6	268	7882	29
S-F	Tuna Stomach Content	3.7	1290±43	10±6	0,03±0,01	4773	37	0,11	129	43000	333
	Sea Water Typical										
	Oceanic		25×10^{-3}	50×10^{-3}	4×10^{-4} ‡				0,5	60	125
	Coastal		3×10^{-3}								

‡ Southern Hemisphere.

* U and Th isotopes determined on these samples as well as Po, Pb and Pu. See Table 5.1

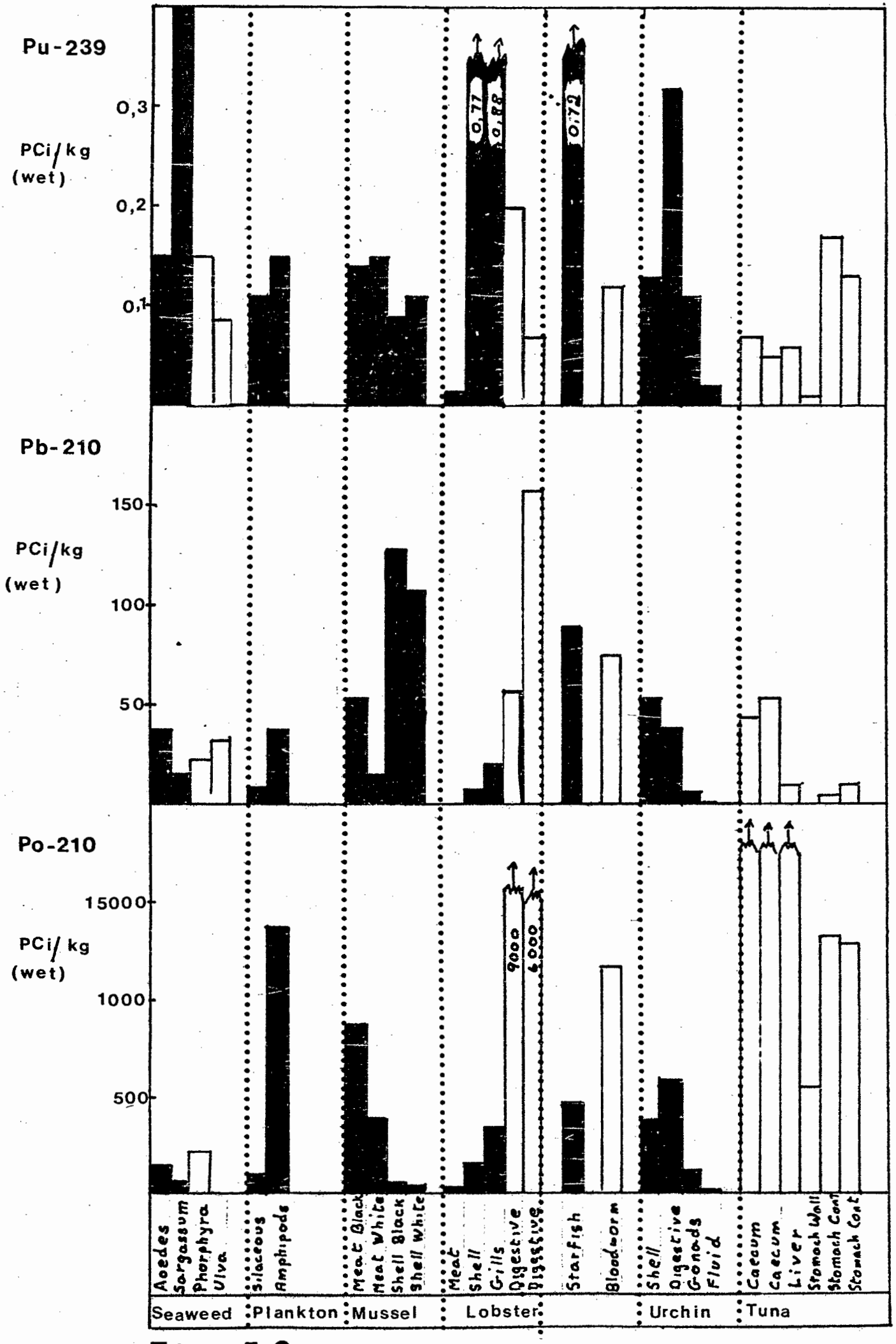


Fig 5.2 Pu-239, Pb-210 & Po-210 in Various Marine Organisms

which Po-210 and Pb-210 are accumulated are different. Generally speaking marine animals concentrate Po-210 to a much greater extent than Pb-210 and it may be variations in the quantity of surface animals that accounts for the variations in Po-210/Pb-210 ratio.

Although the Po-210/Pu-239 ratio is very different to the value of 200 reported by Hodge et al (149) the high values observed support the view that much of the polonium found in porphyra and aoedes orbitosa was in fact absorbed by surface animals which do not show a similar preference for plutonium and lead.

Sargassum heterophyllum is a special case in that it is high in plutonium. It has a lower surface area than aoedes orbitosa and porphyra and this may account for the slightly lower Po-210 values. These two factors combined, result in the low (relative to aoedes and porphyra) Po-210/Pu-239 ratios.

It is worth noting that in ulva which contained virtually no polonium the Pu-239 content is also low. Possibly Po-210 is absorbed by two different mechanisms:

1) Accumulation by surface organisms

2) Absorption by the seaweed itself

If one could separate the two effects a clearer relationship between Po-210 and Pu-239 absorption might emerge.

5.4.2 Category B - Zooplankton

In view of the fact that Po-210 is concentrated up the food chain and is very high in the various digestive organs, one would expect the larger more complex zooplankton to contain higher concentrations of Po-210 than the smaller less differentiated creatures such as radiolaria. Unfortunately, there is not yet enough data to establish any real interspecies variations in the polonium content of plankton. The work of Beasley et al (8) indicated that mysiids might be higher in Po-210 than euphausiids and micro-zooplankton but seasonal variations seemed to be as important as the species involved. Schell's (123) "salt water zooplankton" tended to be lower in Po-210 (but not in Pb-210) than his "salt water crustacea - euphasiids, mysiids and pasiphaea pacifica" but once again

there is some overlap.

Thus although it is tempting to ascribe the high Po-210 content of our amphipod sample relative to our silaceous zooplankton sample to its relatively high position in the food chain, many more samples will have to be analysed before general conclusions can be drawn. The fact that the two samples were collected at different times of the year could well be as important as the different species involved.

Plutonium on the other hand was approximately the same in both samples with the result that the Po-210/Pu-239 ratio for the two samples differed by a factor of ten. Clearly (unless the variation in Po-210 concentration is due to variations in the concentration of Po-210 in sea water) different mechanisms were involved in the absorption of the two isotopes.

5.4.3 Categories C and D – Marine Invertebrates and Fish

These are complex groups and it is very difficult to pinpoint any definite trends or relationships between the different isotopes.

The Po-210 values are all within the ranges reported by other workers. They are very high in digestive systems and relatively high in mussel meat. Probably if the digestive gland of the mussel were analysed on its own this value would be substantially higher.

The fact that Pu-239 does not appear to be preferentially concentrated in digestive organs to nearly the same extent as Po-210 means that wherever digestive organs are involved the Po-210/Pu-239 ratio is very high. On the other hand because Po-210 is relatively low in shell the ratio in shell is low.

Polonium is remarkably low in mussel and oyster shell. In fact when one considers the high Po-210 concentration in the bodies of these organisms it is clear that Po-210 must be actively discriminated against when transfer to the shell occurs. Possibly the Po-210 atoms are strongly complexed with large molecules that retain them firmly in the digestive tracts. All the other alpha-emitters are of the same order (or higher) in the shell as in the body indicating that polonium and the other alpha-emitters are transferred to shell by different mechanisms.

Sea urchin shell, on the other hand, contained a significant quantity of Po-210. The Po^{+4} ion is roughly the same size as the Ca^{+2} ion (Table 3.2) and crystal structure is unlikely to be important. However the porous nature of the sea urchin shell and the presence of organic connective tissue could well be the reason for the high polonium concentration relative to molluscan shells.

Thus in this category we find that Po-210 tends to be high in digestive organs and low in shell, while for all the other alpha-emitting isotopes the reverse if anything is the case. We are forced to conclude therefore that different mechanisms of absorption are probably involved and that the mechanism by which polonium is concentrated is exceptionally efficient.

5.5 - Total Counting Results

The technique of total alpha counting has provided some very useful information about the alpha-activity of environmental samples. Thus in 1964 Cherry (8) was able to show that plankton were subject to unexpectedly high radiation doses due to the presence of incorporated alpha-activity and that Po-210 was responsible for a substantial proportion of this activity. Subsequent interest in the subject of alpha-radioactivity in the marine environment was stimulated to a considerable extent by this early work.

At the close of this project it was considered worthwhile to determine the total alpha-activity of those samples on which all of the elements plutonium, uranium, thorium and polonium had been determined. It was hoped that this would provide a useful check and give some idea of the extent to which other elements contributed to the alpha-radioactivity of the organisms.

The total alpha-counting technique was essentially the same as that described by Turner *et al.* (136), Cherry (25, 27) and Shannon (126). The theory and limitations of this technique have been discussed in detail by these authors and only a brief summary of the principles involved is given in Appendix I (section 6.10.1). The total counting apparatus is described in Appendix II (section 7.2).

Basically the finely ground dried sample is packed into a ZnS phosphor system, left for 2-3 weeks in order to allow radon to regain equilibrium and then "total-counted". The main uncertainty

in the final answer is due to the fact that it is necessary to know the range of the alpha-particles in the sample material. This depends not only on the energy of the particular alpha-particle but also on the composition of the sample. Shannon (126) has discussed this problem in detail and has estimated the average range of alpha-particles in various marine organisms. His figures were used to calculate the results in Table 5.7.

Because most of the samples were several months old when they were total-counted it was necessary to correct for polonium decay. As the Po-210 content had already been determined this was a simple matter. The contribution of Th-228 to the total alpha-activity was relatively small in all cases and no attempt was made to correct for the decay of this isotope.

Before looking at the results it is worth studying the three natural radiation series (Fig. 2.1) to see which of the nuclides likely to contribute to the total alpha-radioactivity have not been chemically determined.

1) The Uranium Series:- The first three alpha-radioactive members of this series (U-238, U-234 and Th-230) and Po-210 were all determined chemically. However Ra-226 with its short lived daughters was not determined and may be an important contributor to the alpha-radioactivity.

2) The Thorium Series:- Th-232 and Th-228 were both determined. After Th-228 we have a series of short lived daughters and as all the samples were at least three weeks' old when they were analysed we can assume equilibrium. The contribution of the Thorium Series isotopes can therefore be taken to be approximately Th-232 + 5 Th-228. While this approximation is sufficiently accurate for the present purpose, it does assume that the ranges of the alpha-particles emitted by Th-228 and the four alpha-emitters below it in the series are the same. This is of course not true.

3) The Actinium Series:- Apart from U none of the members of this series were determined but it is reasonable to assume that this contribution is negligible. For the purpose of calculation it was assumed that the activity of the U-235 was 4.5% of the activity of U-238.

Table 5.7

Total Alpha-Counting Results

Sample No.	Sample Description	Collection Date	Total Counting Date	Total Alpha Activity: On counting date	Total Alpha Activity: Corrected for Po-210 decay to collection date (A)	Th-232+Th-230 +5Th-228+U-238 +U-234+U-235+Pu -239+Po-210 pCi/Kg wet (B)	Δ pCi/Kg wet (A - B)	Δ/4 Approximately equal to Ra-226 pCi/Kg wet
S-79	Zooplankton - (Silaceous)	24/1/73	26/10/73	203±14	278±30	210±10	66±32	16±8
S-82	Zooplankton - (Amphipods)	25/10/73	22/11/73	1213±42	1397±47	1399±15	-2±49	0±12
S-7	Aoedes Orbitosa	25/2/73	6/12/73	96±11	216±18	165±14	51±23	13±6
S-61	Sargassum Heterophyllum	3/6/73	30/11/73	118±8	165±10	123±7	42±12	11±3
S-28	Sea Urchin Shell	28/4/73	30/11/73	619±36	849±48	446±28	403±56	101±14
S-46	White Mussel Shell	25/1/73	24/11/73	909±47	947±225	122±220	825±315	206±79
S-42	Black Mussel Shell	23/11/72	3/12/73	730±47	779±95	-	-	-
S-11/12	Lobster Shell	31/1/73	24/10/73	457±73	573±98	296±66	277±18	69±6
S-64	Starfish	3/6/73	27/11/73	458±21	733±32	622±24	111±40	28±10
S-30	Sea Urchin Digestive	28/4/73	24/10/73	393±20	739±42	700±43	39±60	10±15
S-29	Sea Urchin Gonads	28/4/73	29/10/73	117±11	187±13	180±9	7±16	2±4
S-31	Sea Urchin Fluid	28/4/73	24/10/73	29±5	37±5	24±8	13±6	3±2
S-47/48	White Mussel - Soft Tissue	24/12/72	24/11/73	328±16	653±45	424±41	229±61	57±13
S-40	Black Mussel - Soft Tissue	23/11/72	6/12/73	305±11	1043±36	-	-	-

4) The contribution of artificial isotopes and isolated long lived natural isotopes may also be assumed to be negligible.

Thus any difference (Δ) between the total alpha-radioactivity and the sum of the activities chemically determined (Pu-239 + U-238 + U-234 + U-235 + Th-232 + Th-230 + 5 Th-228 + Po-210) is likely to be almost entirely due to Ra-226 and its three short lived daughters. In the following discussion it is assumed that Ra-226 = $\frac{1}{4}\Delta$ pCi/kg. (Once again this is only an approximation because it assumes that the range of Ra-226 and the four alpha-emitters below it in the series are the same).

In Table 5.7 the total alpha-activity both on the counting date and on the collection date is given. It can be seen that the correction due to Po-210 decay is, in some cases, very large. This total alpha-activity is then compared with the total activity due to the isotopes chemically determined and the approximate Ra-226 activity calculated.

Table 5.8 shows the approximate contribution made by the various groups of isotopes to the total alpha-radioactivity of each organism.

Shannon (126) and Cherry (25) determined the total alpha-radioactivity of a number of marine organisms. For the purposes of comparison their results are summarised in Table 5.9. It should be noted that in all cases the total alpha-activity observed in this project fell within the ranges reported by these authors.

A study of these tables shows that the total counting results, although only approximate, do provide interesting confirmation of the results and theories already discussed in this thesis. Thus in Chapter 5.3.5 it was concluded from the Th-228/Th-232 ratios that 1) shell samples are high in radium and that the aragonitic mussel shell contained more radium than the calcitic urchin shell

2) The silaceous plankton contained more radium than the amphipod sample.

Both these conclusions are strongly supported by the results in Table 5.7. In fact it is clear that in shells radium rather than Po-210 is the major contributor to the alpha-radioactivity. The fact that Δ for mussel shells is twice that for sea urchin shells is almost certainly significant and due to the different crystal structures. The even lower value for lobster shells may be due to the lack of a definite crystal structure.

Table 5.9 - Total Alpha-Activity in Marine Organism Reported by Shannon (184)

Organism	No. of Samples Analysed	Average Total alpha-activity (pCi/kg wet)	Range pCi/kg wet
Zooplankton	211	850	45 - 15,000
Seaweed	13	300	90 - 900
Mussel Shell	5	910	455 - 1400
Lobster Shell	9	430	200 - 2940
Starfish	1	1433	
Mussel Soft Tissue	5	1020	508 - 1740

The difference between the two plankton samples is striking. Thus there appears to be virtually no radium in the amphipod sample while approximately 24% of the alpha-radioactivity in the silaceous sample was due to radium.

Finally it is interesting to note that although the alpha-radioactivity of seaweed is low the contribution by radium appears to be relatively high (25% of the total) in spite of the fact that neither seaweed was calcified.

Table 5.8 shows clearly that with the exception of shell samples polonium is the main contributor to the alpha-radiation dose of marine organisms although uranium and radium frequently make significant contributions. In general thorium is relatively low and almost all the natural alpha-radiation in these organisms is due to uranium series isotopes. At present the alpha-radioactivity due to the artificial isotope plutonium-239 is negligible in comparison with that due to these natural isotopes.

5.6 General Discussion

This project was in the nature of a general preliminary survey and samples were analysed from the whole spectrum of marine life. This may well be the reason why so few similarities in behaviour have been observed among the different isotopes. The organisms analysed were complex, different absorption mechanisms were probably involved with different organisms and at different sites within each organism. A more detailed study of one particular category or sub-category such as plankton, macrophytes, molluscs or shells might reveal some consistent relationships.

Any such study should involve not only different members of a group but would have to include the effects of seasonal variations and age of the organisms. The organisms should be dissected and sites of accumulation identified. Finally some sort of biological input-output, balance could provide much useful information. A start on this type of approach has already been made by Cherry *et al.* (24) who determined Po-210 in whole Euphausiids (Meganyctiphanes norvegica) dissected material, and in faecal pellets moults and eggs. From this data they were able to estimate that the removal time of Po-210 from the upper mixed layer of the ocean due to zooplankton alone is about 0,9 years. If one compares this value with the figure of 0,6 years, the estimate for total removal time (128),

it is obvious that zooplankton metabolic activity plays an important role in the removal of Po-210 from the surface layers of the sea.

A similar approach applied to the other alpha-emitting nuclides should provide much valuable information. It should enable us to estimate the relative importance of the various biological removal routes for each nuclide. It should give us a better understanding of the general chemical and physical nature of the different elements in sea water and should provide essential data for the development of a quantitative bio-geochemical balance of alpha-emitters in the marine environment.

PART II

EXPERIMENTAL

Appendix I

Analytical Chemistry and Experimental Procedures

6.1 Introduction

In this chapter the general principles involved and the various problems encountered in the development of the analytical methods used in this project are discussed. Detailed instructions for carrying out the procedure finally adopted are given in the appendix.

The main aim of this project was to determine plutonium in marine samples and the perfection of a suitable plutonium method was the first objective. However for the reasons discussed in Part I it was also considered desirable to determine as many other alpha-emitting isotopes as possible. As soon as the plutonium method was working satisfactorily attention was therefore turned to possible means of extending it to include uranium, thorium, polonium and radium.

Finally a sequential method was developed for the determination of plutonium, uranium and thorium isotopes. Very large samples (200g-1000g) were required for the determination of plutonium, wet ashing was therefore impractical and all samples were dry ashed at 450-500°C. At these temperatures polonium is volatile and it was necessary to determine polonium on separate samples. Fortunately the specific activity of polonium is high and only small samples are required. Representative portions weighing 0,5-1,0g were therefore taken after grinding and before ashing and polonium was determined by the method of Flynn (42).

The main alpha-emitter of interest not determined directly was radium. The divalent radium ion is not easily complexed and most radium compounds are simple ionic salts. Radium compounds have very low solubilities in organic solvents and are not easily separated from other elements by ion-exchange. For these reasons the only practicable method that has been found for separating radium from large quantities of other elements is co-precipitation usually with sulphates or carbonates of barium or lead. Separation from the carrier metal is then difficult and indirect methods (e.g. counting of ingrown Pb-211 or Bi-212) or thick source counting of the Ba SO_4 precipitate are often used. The radon emanation method is rapid and accurate but specialised equipment is required.

Radium remained with the bulk of the sample throughout the Pu/Th/U analysis and a preliminary investigation showed that the development of a suitable method for its determination would not be easy. The lack of a suitable tracer only added to the difficulties and it was decided to concentrate on the other alpha-emitters. However a rough estimate of the radium content was obtained for some samples by determining the total alpha-activity and calculating the radium content by difference.

The final stage in the determination of the isotopes of plutonium, uranium and thorium was alpha-spectrometry and in section 6.2 this technique and the limitations that the use of this method imposes on the chemist are briefly discussed. In Appendix II (section 7.1) a detailed description of the apparatus used is given.

Section 6.3 is devoted to a discussion of plutonium and the factors which influenced the choice of plutonium method while section 6.4 shows how this method was extended to include uranium and thorium.

It is important to realise at the outset that when dealing with the very low concentrations that concern us here (1 dpm Pu-239 = $7,4 \times 10^{-9}$ ppm) and when the analytical procedures involve several stages it is impossible to achieve recoveries of 100%. It is therefore necessary to use tracers as yield determinants and in section 6.7 details of the various tracers used are given.

Sections 6.5 and 6.6 discuss the individual steps in the sequential Pu/U/Th method finally adopted while section 6.8 examines the quality of the results thus obtained. Typical spectra are shown and blanks, standard deviations and the calculations involved are considered.

Finally in sections 6.9 and 6.10 respectively the polonium method and total counting are discussed.

6.2 Alpha-Spectrometry

The kinetic energy of an alpha-particle is a specific value characteristic of the decay process involved. Table 6.1 lists (in order of increasing energy) the alpha-energies and half-lives of the most important naturally occurring nuclides as well as some of the artificial isotopes that may be found in the environ-

Table 6.1

Alpha-Radioactive Nuclides (from Lederer & Hollander (76))

Isotope	Series	Half-Life	Specific Activity pCi/µg	Alpha-Particle Energy MeV		
Thorium-232	Th	$1,41 \times 10^{10}$ years	$1,1 \times 10^{-1}$	4,01(76%)	3,95(24%)	
Uranium-238	U	$4,51 \times 10^{9}$ years	$3,3 \times 10^{-1}$	4,20(75%)	4,15(25%)	
Uranium-235	Ac	$7,1 \times 10^{8}$ years	2,1	4,58(8%)	4,40(57%)	4,37(18%)
Thorium-230	U	$8,0 \times 10^{4}$ years	$1,9 \times 10^{4}$	4,68(76%)	4,62(24%)	
Uranium-234	U	$2,47 \times 10^{5}$ years	$6,1 \times 10^{3}$	4,77(72%)	4,72(28%)	
Radium-226	U	$1,60 \times 10^{3}$ years	$9,4 \times 10^{5}$	4,78(95%)	4,60(6%)	
Neptunium-237		$2,14 \times 10^{6}$ years	$7,1 \times 10^{2}$	4,78(75%)	4,65(12%)	
Plutonium-242	U	$3,79 \times 10^{5}$ years	$4,0 \times 10^{3}$	4,90(76%)	4,86(24%)	
Protactinium-231	Ac	$3,25 \times 10^{4}$ years	$4,6 \times 10^{4}$	4,73-5,06		
Plutonium-239		24390 years	$6,2 \times 10^{4}$	5,16(88%)	5,11(11%)	
Plutonium-240		6580 years	$2,3 \times 10^{5}$	5,17(76%)	5,12(24%)	
Polonium-210	U	138,4 days	4×10^{8}	5,305(100%)		
Uranium-232		72 years	$2,1 \times 10^{7}$	5,32(68%)	5,27(32%)	
Thorium-228	Th	1,91 years	$7,9 \times 10^{8}$	5,43(71%)	5,34(28%)	
Radon-222	U	3,83 days	$1,4 \times 10^{10}$	5,49(100%)		
Americium-241		458 years	$3,3 \times 10^{6}$	5,49(85%)	5,44(13%)	
Plutonium-238		86,4 years	$1,7 \times 10^{7}$	5,50(72%)	5,46(26%)	
Radium-224	Th	3,64 days	$1,5 \times 10^{10}$	5,68(94%)	5,45(6%)	
Radium-223		11,4 days	$4,9 \times 10^{9}$	5,54-5,75		
Plutonium-236		2,85 years	$5,3 \times 10^{8}$	5,77(69%)	5,72(31%)	
Thorium-227	Ac	18,2 days	3×10^{9}	5,72-6,04		
Curium-243		32 years	$4,7 \times 10^{7}$	5,74-6,06		
Polonium-218	U	3,05 minutes	$1,1 \times 10^{12}$	6,00(100%)		
Bismuth-212	Th	60,6 minutes	$5,5 \times 10^{10}$	6,09(10%)	6,05(20%)	+β
Curium-242		162,5 days	$3,4 \times 10^{8}$	6,12(74%)	6,03(26%)	
Californium-252		2,646 years	$5,7 \times 10^{8}$	6,12(82%)	6,08(15%)	
Radon-220	Th	55,3 seconds	$3,6 \times 10^{12}$	6,29(100%)		
Polonium-216	Th	0,145 seconds	$1,4 \times 10^{15}$	6,78(100%)		
Polonium-214	U	$1,64 \times 10^{-4}$ seconds	$1,2 \times 10^{18}$	7,69(100%)		
Polonium-212	Th	$3,04 \times 10^{-7}$ seconds	$6,5 \times 10^{20}$	8,78(100%)		

ment or that have been used as tracers in the various analytical procedures.

Using alpha-spectrometry it is possible to count the number of alpha-particles emitted from a source and to determine their energies. From the spectrum thus obtained it is possible to make both a qualitative and a quantitative analysis of the source. Low backgrounds and high sensitivities are usual and, provided uniform thin sources were prepared, a resolution of 80-100 KeV (full width at half maximum) was generally obtained during this project. This meant that in practice two nuclides with energies differing by 0,2 MeV could be determined without appreciable mutual interference.

An important characteristic of the alpha-particle is its short range : of the order of tens of microns in solids for most alpha-particles emitted by radioactive nuclei. This means that sources prepared for alpha-spectrometry must be very thin and uniformly deposited. If this is not the case a serious loss of alpha-energy can occur within the deposit and a poor quality spectrum results. $100\,\mu g/cm^2$ is frequently quoted as the upper limit for an acceptable alpha-spectroscopic source.

Because of this requirement any alpha-emitter to be determined by alpha-spectrometry must be separated, not only from other alpha-emitters with similar energies, but also from virtually all other matter. The chemistry involved in preparing sources for alpha-spectrometry is therefore primarily concerned with the complete isolation of the element concerned, and the determination of an alpha-emitter by alpha-spectrometry usually involves several purification steps.

After purification the source itself is usually prepared by evaporation onto a planchette or electroplating although sublimation and electro-spraying have also been used successfully.

Producing a thin source by evaporation is very difficult. The solution must be essentially free of salts and any minute quantities of solid material that are present tend to deposit as crystals and aggregates that cause self-absorption of alpha-activity. Wetting agents can be added to reduce the surface tension and tetramethylene glycol, alcohol, lactic acid and zalpon (nitrocellulose in acetone) have all been used (141, 142). More satisfactory is the direct evaporation of organic solutions.

In particular very thin films can be prepared by the evaporation of benzene or toluene solutions of the T.T.A. complex (2-thenoyltrifluoroacetone). Such solutions spread when heated instead of forming drops as do aqueous solutions. If the planchette is heated from the outer edge while a cold spot or heat sink is in contact with the centre of the disc the solution is less likely to spread over the edge. Sources prepared in this way usually have very good energy resolution.

The method most widely used for the preparation of thin sources is electro-deposition. Very uniform thin films can be prepared by this method which is applicable to many elements. The apparatus needed is simple and numerous detailed methods have been published for the preparation of electroplated sources of the actinides (134, 77, 84).

Some difficulty has been experienced in obtaining consistently high yields by electroplating methods and small quantities of impurities in the plating solutions can result in low yields or in non-adherent deposits. However the ammonium sulphate method of Talvitie (134) has proved very successful for plutonium and, provided plating solutions are pure, should be equally satisfactory for uranium, thorium and americium.

6.3 The Determination of Plutonium

A large number of papers has been published describing methods for determining plutonium in environmental samples. The earlier ones were based on the fact that plutonium can be quantitatively co-precipitated with a wide variety of reagents (for a comprehensive list see Milyukova et al. (82)). Most popular were bismuth (and other) phosphates and lanthanum flouride. Frequently the lanthanum flouride precipitate was deposited on a plate and alpha-counted. Other workers dissolved the precipitate in $AlNO_3/HNO_3$ and then extracted the plutonium with 2-thenoyltrifluoroacetone (T.T.A.). Sources for alpha-spectrometry were then prepared either by evaporation of the T.T.A. layer or by back-extraction and electroplating (101, 77, 149, 112).

However, as more was learned about the ion-exchange properties of plutonium, it became obvious that ion-exchange separations were an attractive alternative to co-precipitation.

The work of Ryan and Wheelright (117) and Kressin and Waterbury (69) established the optimum conditions for isolation and purification of plutonium from impurities and more and more analysts turned to ion exchange procedures for separating plutonium from large quantities of sample material.

Using ion exchange procedures it is possible to separate plutonium completely from all other elements. It is possible to handle large samples more rapidly and less manipulative skill is required than is the case with the co-precipitation methods. For these reasons most of the later published methods use ion exchange (14, 22, 30, 133, 152).

In particular the work of Wong (152) was specifically directed towards the determination of plutonium in sea water and marine organisms and it was decided to use this method as a basis as far as possible. In practice it was found that with only a few minor changes the method worked very well. Furthermore uranium and thorium were separated from each other and from plutonium as a matter of course and it was a relatively simple matter to extend the method to include the determination of the alpha-radioactive isotopes of these two elements. How this was done can be seen by a study of Fig. 6.1.

6.4 Outline of the Sequential Method Used for the Determination of Plutonium, Uranium and Thorium

Figure 6.1 is a schematic diagram showing the main steps in the final procedure. After ashing, addition of tracers, and digestion these are as follows:-

I. Adsorption of plutonium, thorium and some uranium onto Bio-Rad AG X-8 resin (100 to 200 #) from 8N nitric acid.

II. (1) Elution of thorium with 12N hydrochloric acid.
(2) Elution of plutonium with 0,05M ammonium iodide in 12N hydrochloric acid.
(3) Elution of adsorbed uranium with 0,1N hydrochloric acid. This eluate is added to the bulk of the sample solution which passed through the column and contained most of the uranium.

III. Purification of the plutonium eluate by adsorption of the plutonium from 12N hydrochloric acid onto Bio-Rad AG X-8 resin. Once again elution is with ammonium iodide in 12N hydrochloric acid.

IV. Preparation of a plutonium source by electroplating.

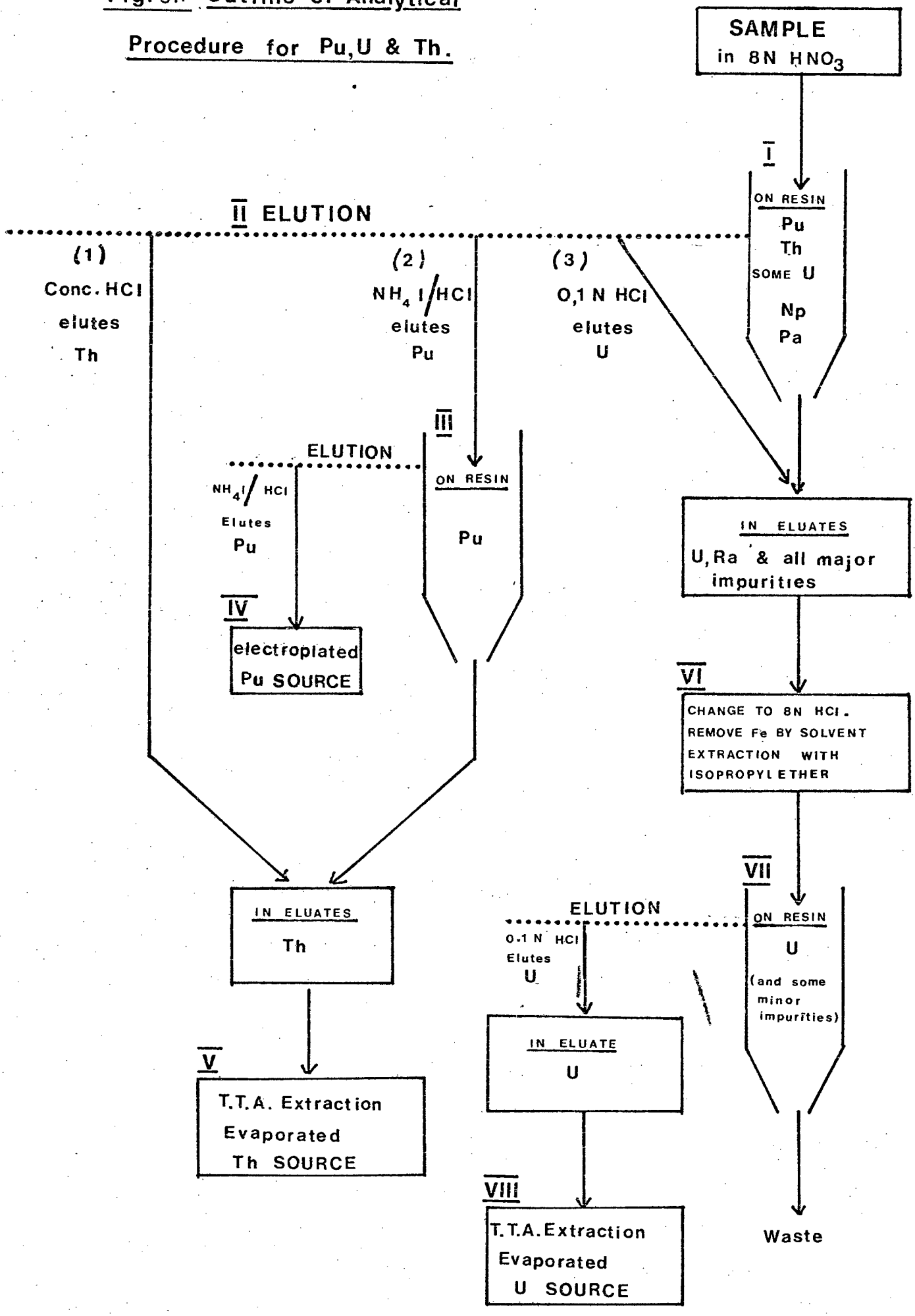
V. Preparation of a thorium source by T.T.A. extraction and evaporation.

VI. Adjustment of the uranium containing eluate from the first column II(3) to 8N hydrochloric acid and removal of iron by solvent extraction with isopropyl ether.

VII. Adsorption of uranium onto Bio-Rad AG X-8 resin from 8N hydrochloric acid and elution of uranium with 0,1N hydrochloric acid.

VIII. Preparation of uranium source by T.T.A. extraction and evaporation.

Fig. 6.1 Outline of Analytical Procedure for Pu, U & Th.



Note Bio-Rad AG X 8 Resin (100 - 200 #) in all ion-exchange columns.

6.5 Discussion of Individual Steps

6.5.1 Drying

It is the custom to report the concentrations of radionuclides in organisms in terms of wet weight. In this way we reflect the actual role of living organisms in concentrating chemical elements from aqueous solutions. Moreover calculation of internal radiation doses from incorporated nuclides is only possible from their concentration factors in relation to live weight (109).

However, it is frequently difficult to assess the wet weight accurately. Surface water may contribute significantly to the weight of plankton and seaweeds of large surface area. Organisms such as mussels and sea urchins contain quantities of fluid the volume of which may vary depending on the time of collection and the interval between collection and dissection. For this reason all samples were dried at 105°C and all results are reported both on a wet and on a dry basis.

6.5.2 Sample Dissolution

In order to achieve sufficient sensitivity it was necessary to take samples weighing about 1 kg where possible. This made wet ashing and/or total dissolution procedures impractical and some uncertainties were therefore introduced at the outset since all samples were dry ashed at 480°C and then digested in aqua-regia for four hours. There was frequently a large amount of insoluble residue which was filtered off.

Pillai (107) tested his procedure of wet ashing followed by three extractions of the residue with 8N nitric acid on an algal sample contaminated by waste effluent. The residue, still insoluble after this treatment, was finally decomposed and contained only 1,9% of the total plutonium activity.

Several workers have compared acid leaching and total dissolution procedures for the analysis of sediment samples (14, 152, 133) and it is generally concluded that more than 99% of the plutonium is removed by three successive acid leaches.

It must, however, be remembered that fall-out plutonium is likely to be fairly loosly bound in soil samples which may

not necessarily be the case in all biological samples. Nielson and Beasley (101) remark that "plutonium that has entered samples by metabolic processes is usually in a readily soluble form while lung tissues and faeces will likely contain insoluble plutonium. One cannot generally assume complete dissolution of plutonium in the latter samples unless HF is used as a complexing agent."

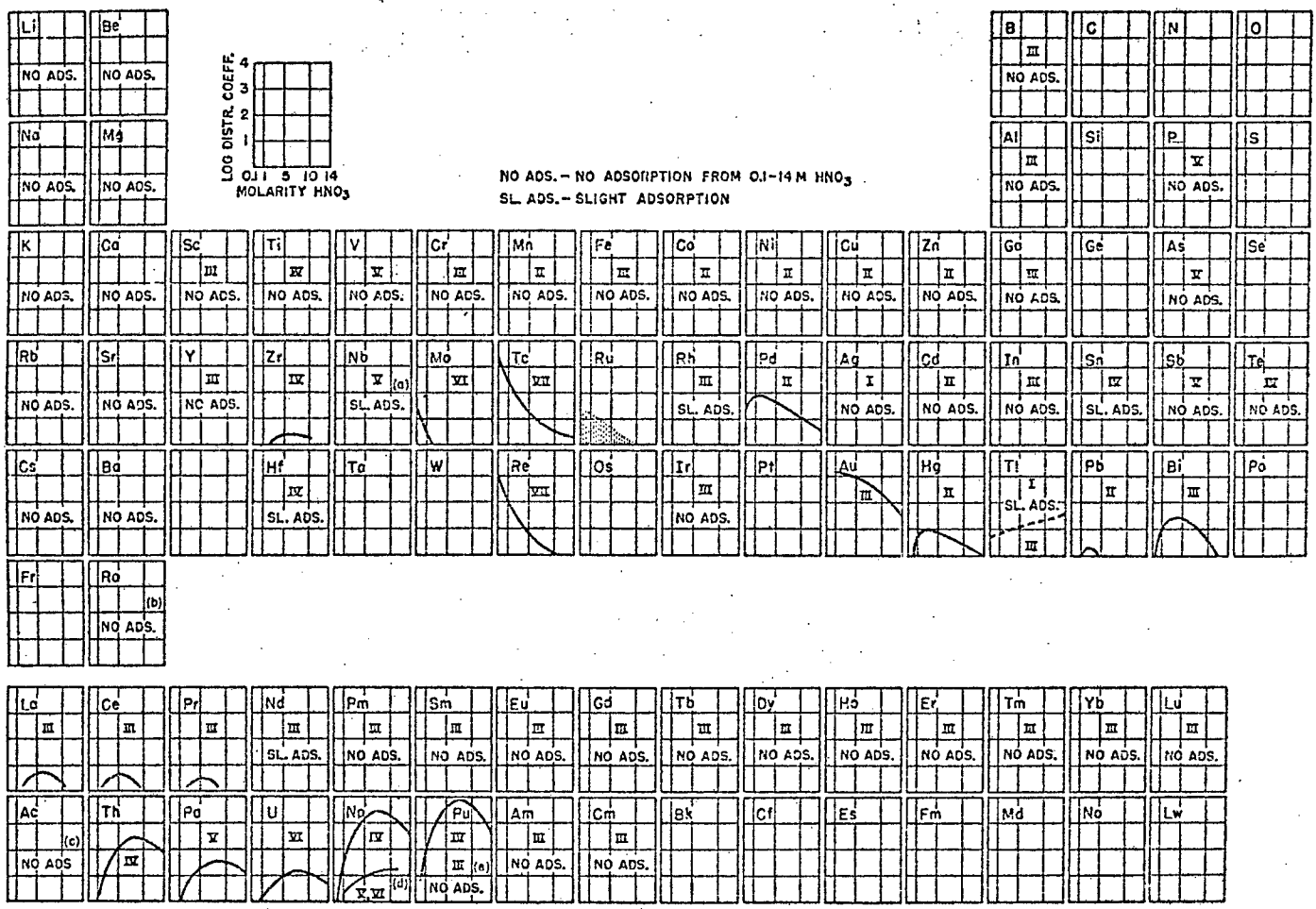
No attempt was made in the present work to compare the acid digestion method used with total dissolution methods. However, in the absence of evidence to the contrary it is reasonable to assume, in common with other workers in the field, that virtually all the plutonium is dissolved during the digestion.

It is less easy to be certain that all the thorium was dissolved. In fact, the undissolved portion of the sample is often mainly silica and it is not unlikely that insoluble minerals such as thorite ($ThSiO_4$) might also be present. For this reason thorium results should be treated with caution until such time as the acid digestion method has been compared with total dissolution. Most uranium minerals on the other hand are acid soluble and it is probable that all the uranium was dissolved although, here too, experimental verification is desirable.

6.5.3 Ion Exchange

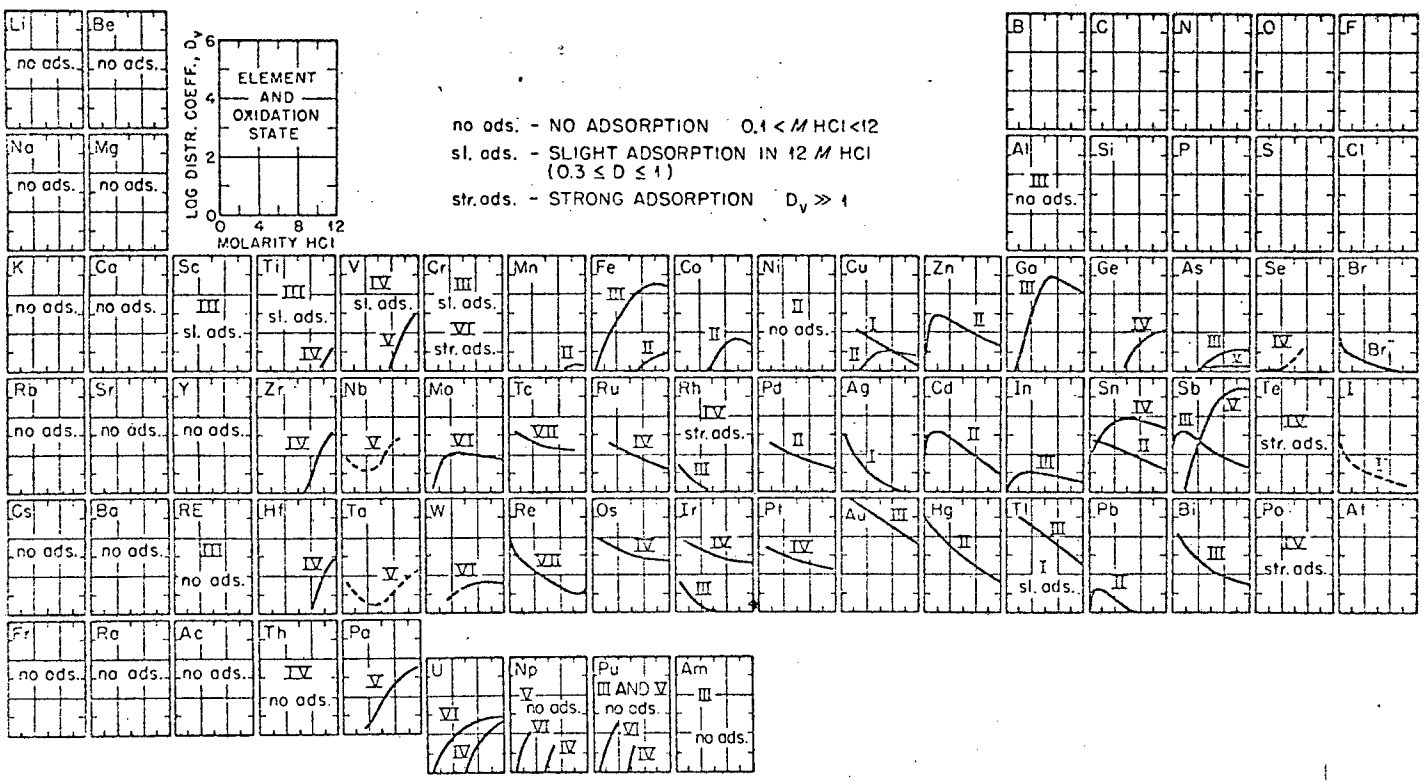
A very useful guide when considering ion-exchange separations are the tables prepared by Kraus et al. (68A) and Faris et al. (41A) Those for the adsorption of the elements from nitric acid and hydrochloric acid by a strong-base anion-exchange resin are reproduced in Fig. 6.2.

It can be seen that very few elements are adsorbed to any significant extent from nitric acid solutions. In fact a single ion-exchange separation from 7.5N nitric acid separates the alpha-emitting nuclides Th^{IV}, Pa^{V}, Np^{IV}, Pu^{IV} and some U^{IV} from almost all other elements. These elements are adsorbed because of their ability to form anionic complexes. Ryan (118) has shown that $Pu(NO_3)_6^{=}$, $Th(NO_3)_6^{=}$, $Np(NO_3)_6^{=}$ and $U(NO_3)_6^{=}$ are the species involved in the anion-exchange adsorption of the quadrivalent actinides. Goble et al. (46) suggest that protactinium



Removal from solution of elements in 0.1*M* to 14*M* nitric acid with strongly basic anion exchange resin

From Faris & Buchanan (41A)



Adsorption of the elements from HCl solutions by a strong-base anion-exchange resin, Dowex-1, as a function of HCl molarity.

From Kraus & Nelson (68A)

FIGURE 6.2

exists as the $PaO_2(NO_3)_4^-$ ion but there seems to be some doubt about this.

A careful study of the tables shows that none of the non-actinides will follow plutonium through both ion-exchange steps. Traces of rare earths and zirconium might follow thorium but these will be separated from thorium during the T.T.A. extraction. Separation of uranium is less complete and will be discussed at a later stage.

Of the five actinides adsorbed from 8N nitric acid

1) Protactinium and neptunium are of little importance because they are present in the marine environment at such low concentrations that they will not interfere.
2) Thorium is the only one not adsorbed from 12N hydrochloric acid, presumably because it does not form an anionic chloride complex. This makes it a simple matter to isolate thorium.
3) Since the adsorption coefficient of uranium on Dowex-I is only about ten, uranium is only partially adsorbed onto the resin. In fact, when a solution containing 200 dpm U-232 was taken through the plutonium method only 10% of the uranium was adsorbed. The remainder was found in the eluate that passed through the resin.

The uranium that is retained on the resin is separated from plutonium by control of the oxidation states of plutonium. Thus in both ion-exchange steps Pu^{IV} is selectively reduced to Pu^{III} and eluted under conditions where U^{VI} (and Np^{IV}) remain unaffected. Uranium and neptunium can subsequently be eluted with 0,1N hydrochloric acid. It is possible to elute neptunium separately from uranium with 4M HCl-0,1M HF (100).

Initially some difficulty was experienced with the elution of plutonium using the 12N HCl/NH_4I recommended by Wong but increasing the volume of eluate from 75 ml to 300 ml increased recoveries from zero to greater than 90%.

Note It is important that the plutonium should be present in the +4 oxidation state before ion-exchange. The chemistry of plutonium is complicated by the fact that it can exist in solution in several states of oxidation at the same time. However, plutonium

ions with a charge of +4 are the most stable and nitrite treatment of nitric acid solutions containing plutonium in several valency states results in all the plutonium being converted to the tetra-valent state. (With respect to Pu^{VI} the nitrite ion acts as a reducing agent. Pu^{V} formed by the reduction rapidly disproportionates and any Pu^{III} formed by the disproportionation is in turn oxidised to Pu^{IV} by the nitrite ions).

6.5.4 Isolation of Thorium and Uranium

From the foregoing discussion or a study of Figures 6.1 and 6.2 it can be seen that thorium is readily isolated during the course of the plutonium separation. It is adsorbed onto the AG I x 8 resin from 8N nitric acid and then eluted with 12N hydrochloric acid. Any traces that remain with the plutonium are recovered during the second ion-exchange step (Step III, Fig. 6.1).

Uranium on the other hand remains with the bulk of the sample and must be treated separately. Two possible methods of isolating uranium were considered. The extraction of uranyl nitrate from nitric acid by Tributylphosphate (T.B.P.) was attractive because the sample was already in the recommended 7,5 N nitric acid (2,98,122). On the other hand, T.B.P. extraction is normally used for much higher concentrations of uranium and most workers in the field of marine radioactivity (73,68,11,90) use anion exchange from 8N hydrochloric acid.

Accordingly both methods were tried simultaneously on seaweed samples. The T.B.P. method gave a recovery of 5%, while the ion-exchange method gave a recovery of 70%. The latter was therefore adopted without further investigation.

6.6 Source Preparation

As already discussed in section 6.2, sources for alpha-spectrometry must be thin and homogenous and the two most common methods of source preparation are direct evaporation and electrolytic deposition. Generally electroplating is preferred because films prepared by this method are thinner and more homogenous than those prepared by evaporation, particularly from aqueous solutions. However, unless plating solutions are extremely pure, thick non-adherent deposits will be formed and yields may be low.

The analytical procedures used here resulted in very

pure plutonium solutions and excellent plutonium sources were obtained by electroplating. However, the thorium and uranium fractions isolated by the ion-exchange procedures contained too many non alpha-radioactive impurities for plated sources to be made without further purification. For these elements a T.T.A. extraction followed by evaporation of the T.T.A. layer onto stainless steel planchettes was used.

6.6.1 Electroplating of Plutonium

Wong (152) used the ammonium chloride method first developed by Mitchell (84). However, using this method it was difficult to obtain reproducible quantitative yields despite a thorough study of the various variables. Thus the effect of plating time, current, stirrer design, temperature and pretreatment of the cathode were all investigated. Cooling the cell during plating dramatically decreased the deposition rate but apart from this none of the variables investigated had much effect. Working with pure solutions and using a plating time of one hour (instead of 15 mins.) and a current of 1,3 amps., it was possible to obtain a 90-100% recovery four out of five times but the occasional 50% recovery was annoying. Furthermore, recoveries were considerably lower when plating actual sample solutions. A second plating on these solutions showed that it was the plating itself that was inefficient.

At this stage a request to Dr. Bowen at Woods Hole Oceanographic Institute for advice produced the reply that they had abandoned the ammonium chloride plating in favour of Talvitie's (133) sulphate method. This method was therefore tried with immediate success. Recoveries were consistently 100% and sources were of an excellent quality. Sulphate plating was therefore used on all subsequent samples.

This sulphate plating method also worked extremely well on pure solutions of uranium and thorium (after the addition of a drop of H_2O_2 to dissolve insoluble thorium sulphate) but was not used on actual samples for the reasons discussed below.

6.6.2 Uranium and Thorium Source Preparation

As mentioned previously attempts to prepare plated uranium

and thorium sources immediately after the ion-exchange separations failed because of the presence of excessive impurities. It was therefore necessary to introduce an additional purification step.

In recent years 2-thenoyltrifluoroacetone (T.T.A.) has been widely used as a chelating agent in the solvent extraction of microgram quantities of the actinides (51, 64, 36, 37, 98, 111, 113). The T.T.A. complexes are soluble in non-polar solvents such as benzene and the equilibrium concentration of a particular chelate is a function of the acidity of the solution.

$$M^{+n}_{(aq.)} + nH(T.T.A.)_{(O)} \rightleftharpoons M(T.T.A.)_{(O)} + nH^{+}_{(aq.)}$$

where

M^{+n} = metal ion of oxidation number n.

(O) = organic phase

(aq) = aqueous phase

The stronger the complex formed the more acidic is the aqueous solution from which it can be extracted. Thus the optimum pH for carrying out the extraction varies over a wide range as can be seen from Table 6.2.

Table 6.2

Optimum pH for T.T.A. Extraction

Element	Optimum pH	Element	Optimum pH
Sr	> 10	Yb	3,4
Ca	8	U^{+6}	3
Y	> 6	Cf, Es, Fm	3,0
Be	> 6	Fe, Bi	2,0
Al	5,5	Sc, Po	1,5
Ac	> 5	Th	0,8
La	> 4,5		
Am, Cm	> 3,5	Pa	0
Tl, Cu	3,0	Np^{+4}, Pu^{+4}	-0,7
Eu	> 3,4	Hf, Zr	-0,8

In general an element will be separated from those above it in the Table but not from those below. Of course the further apart any two elements are the better the separation.

Thus Th will be separated from everything except Np, Pu, Pa, Hf and Zr, none of which are likely to be present. Uranium extracts however, may be contaminated with rare earths iron etc. It was therefore necessary to make quite sure that no iron was present before extraction.

If an aqueous solution of the extracted element is required it is a simple matter to back extract into a solution of low pH and a T.T.A. extraction followed by a back extraction and electroplating would almost certainly result in excellent uranium and thorium sources. However it was found that direct evaporation of the T.T.A./benzene layer onto heated stainless steel planchettes resulted in high quality uniform thin sources and there seemed little point in back extraction and electroplating. All uranium and thorium sources were therefore prepared by evaporation of the T.T.A./benzene extract. This was evaporated down to a volume of about 1 ml and then transferred dropwise onto the heated planchette. In order to prevent the solvent from spreading over the edges of the planchette a special ring heater which heated the outer edges of the planchette only was used (see appendix II, Fig. 7.3).

6.7 Tracers

6.7.1 Plutonium - 236

Recently it has been pointed out (70, 78A) that Pu-242 is a superior tracer to Pu-236. This is because the alpha-energy of Pu-236 is higher than that of both Pu-239 and Pu-238 and there is always the possibility that the degraded tail of the Pu-236 peak will contaminate the Pu-238 and possibly even the Pu-239 peak. Furthermore the ingrowth of the daughters of Pu-236 (U-232 and Th-228) can also lead to contamination of these peaks and a Pu-236 tracer should be periodically purified.

Pu-242 suffers from none of these disadvantages since its alpha-energy is lower than that of Pu-239 and its daughter U-238 has such a long half-life that its decay presents no problem. However at the commencement of this project Pu-242 was not available commercially and a solution of Pu-236 was purchased from Amersham. It was standardised by the suppliers, between 16/3/72 and 21/3/72. They reported that it had the following composition:-

Pu-236:- $(2,676 \pm 0,03) \times 10^{-4}$ dpm/ml

Furthermore of the total activity in the solution

Pu-236 accounted for (93,9 ± 0,5) %
Pu-238 accounted for (5,9 ± 0,2) %
Pu-239 accounted for (0,15 + 0,2) %
Higher energy alphas 0,02%

The Pu-236 tracer was prepared by diluting the standard solution 10^4 times with 1N nitric acid. Several sources were prepared from this tracer solution by evaporating 1 ml portions onto stainless steel planchettes. Within the limits of experimental error and assuming a counting efficiency of 36% the activity of the tracer was found to agree with the figures supplied by Amersham. Further sources were prepared at intervals of about 6 months and the activity remained "correct". Thus there was no sign of loss of Pu-236 by adsorption onto the walls of the glass flask in which the solution was stored.

It was unfortunate that the tracer contained Pu-238 as this made it impossible to determine the Pu-238/Pu-239 ratio in the samples unless the plutonium concentration was unusually high. Of all the samples analysed only two (sargassum heterophyllum and martha asterias) contained sufficient plutonium for an

estimate of this ratio to be made.

6.7.2 Uranium-232

A solution containing about 45 dpm/ml U-232 in equilibrium with Th-228 was available in the laboratory. Unfortunately it also contained about 45 dpm Pu-239 and it therefore had to be very carefully purified before it could be used in the analytical scheme. The plutonium and the thorium were both removed from the solution by anion exchange using the same principles as were used in the analysis of the samples. Briefly the method used was as follows:-

1) 100 ml of the U-232 solution were evaporated to dryness and the residue dissolved in 2 ml 9N hydrochloric acid plus 0,1 ml 1N nitric acid.

2) This solution was passed through a 3 cm x 1 cm column of AG1 X-8 resin (100-200 #) and washed with 1 ml 9N hydrochloric acid.

3) The plutonium was eluted with a mixture of 40 ml 9N hydrochloric acid and 2 ml 1N ammonium iodide.

4) The uranium was eluted with 40 ml 0,1N hydrochloric acid.

5) This U solution was evaporated to dryness, treated with nitric acid to remove the ammonium iodide and the residue redissolved in 2 ml 9N hydrochloric acid + 0,1 ml 1N nitric acid.

6) The entire ion-exchange procedure was then repeated two more times and the final U-232 solution diluted to 250 ml.

10 ml of this solution was spiked with Pu-236 and a plutonium determination carried out. The Pu-236 recovery was 80% and no counts of Pu-239 were detected in 72 hours. This solution was therefore standardised and used as a tracer thereafter.

Standardisation was difficult. Direct evaporation onto flat planchettes gave poor quality sources because salts were present in the solution and these deposited unevenly in spots. It was found however that evaporation in a concave planchette (prepared by depressing a 2 mm deep saucer shaped depression into a standard flat planchette) resulted in a fairly even deposition of salts and a higher quality spectrum.

The use of these concave planchettes reduced the sensitivity (by about 20%) because much of the source was further from the detector. Furthermore the geometry of such a source is complicated and concave planchettes were only used when relative

rather than absolute activities were of importance. However by adding a known amount of Pu-236 tracer to the U-232 tracer and evaporating the mixture in a concave planchette it was possible to make a reasonable estimate of the U-232 activity. Four such sources were prepared and the activity was found to be 4,9 ± 0,4 dpm U-232/ml.

6.7.3 Thorium Tracer

A sample of pure thorium nitrate was found which contained the isotopes Th-232, Th-230 and Th-228 in the activity ratio of approximately 1:10:1. A solution of this salt was prepared and standardised by evaporating 1 ml portions onto flat planchettes. The solution was fairly pure and reasonable spectra were obtained. In addition very accurate estimates of the Th-232:Th-230:Th-228 ratios were made by counting sources prepared by plating and by evaporation of T.T.A. extracts.

The activities and ratios in the thorium tracer were found to be:-

Th-232 = 3,9 ± 1,0 c/hr/ml ≡ 10,8 ± 2,8 dpm/ml
Th-230 = 35,2 ± 0,9 c/hr/ml ≡ 98,0 ± 2,5 dpm/ml
Th-228 = 2,1 ± 0,5 c/hr/ml ≡ 5,8 ± 1,4 dpm/ml

Th-232/Th-230 = 0,107 ± 0,012

Th-228/Th-230 = 0,060 ± 0,007

6.8 Results and Calculations

In order to give some idea of the accuracy and precision of the analytical methods used all the Tables of results in Chapters 4 and 5 include duplicate results, chemical recoveries and standard deviations based on counting statistics. A brief discussion of these figures and the results generally now follows.

6.8.1 Resolution and Typical Spectra

Figures 6.3-6.6 show typical spectra obtained during this project. It can be seen that the resolution of the evaporated uranium and thorium sources is as good as that obtained for the plated plutonium source. In general the resolution was between 75 and 100 KeV (full width at half maximum) and it was possible to sum the counts over 5-8 channels or 125-200 KeV. There was, therefore, virtually no interference due to overlapping peaks.

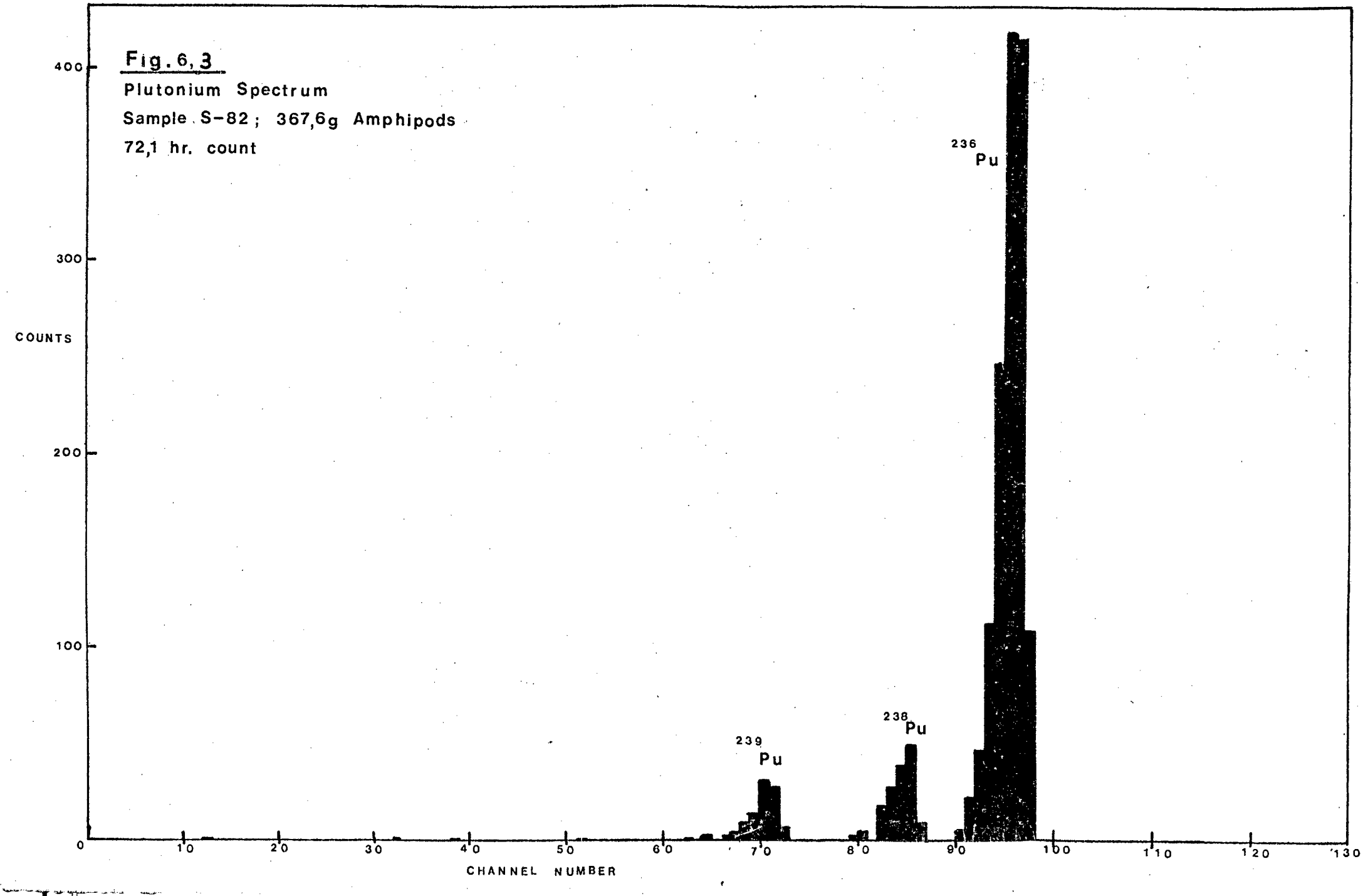


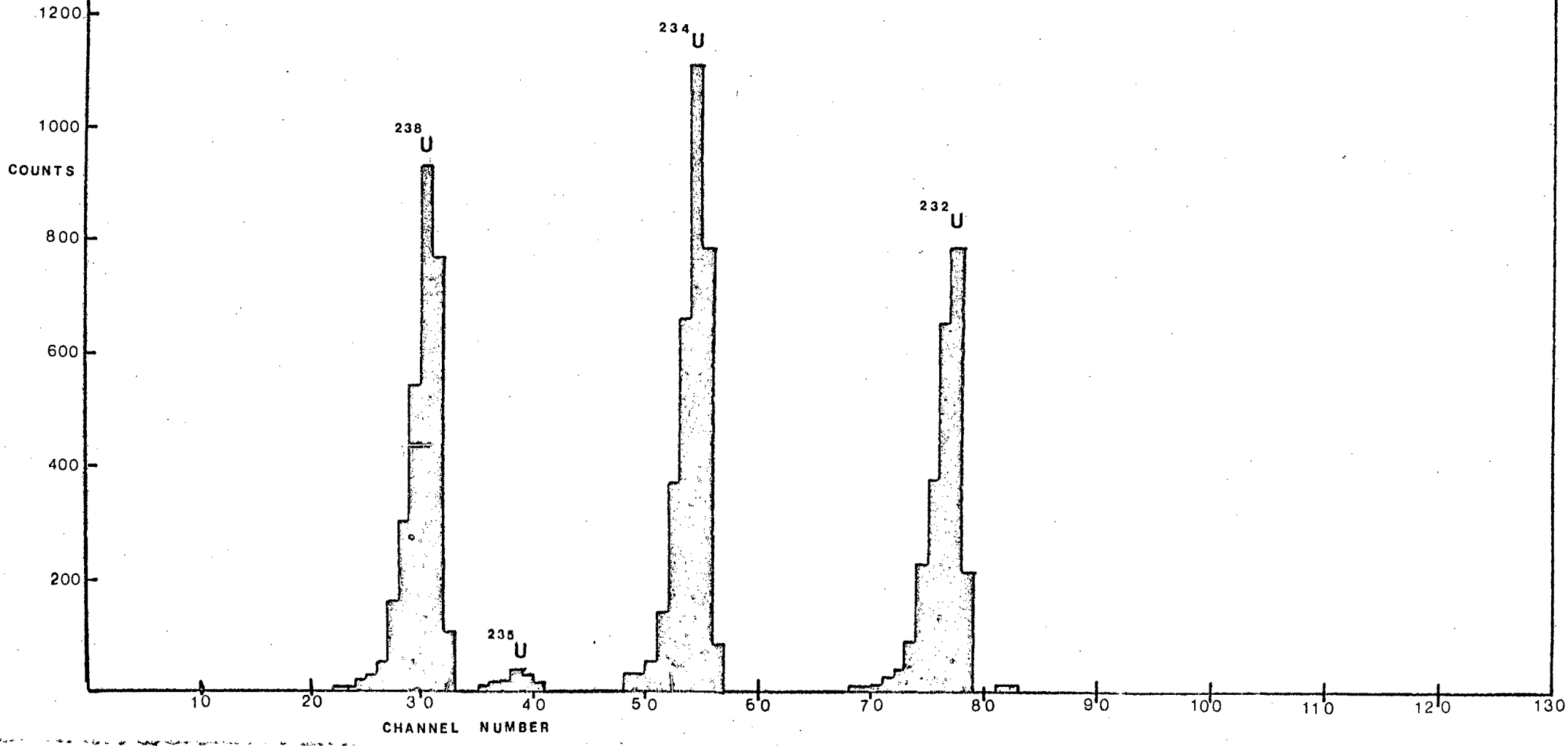
Fig. 6, 3
Plutonium Spectrum
Sample S-82 ; 367,6g Amphipods
72,1 hr. count
400
300
200
100
0
COUNTS
236 Pu
238 Pu
239 Pu
10
20
30
40
50
60
70
80
90
100
110
120
130
CHANNEL NUMBER

Fig. 6,4

Uranium Spectrum

Sample S-82; 376,4 g Amphipods

42,7 hr. count



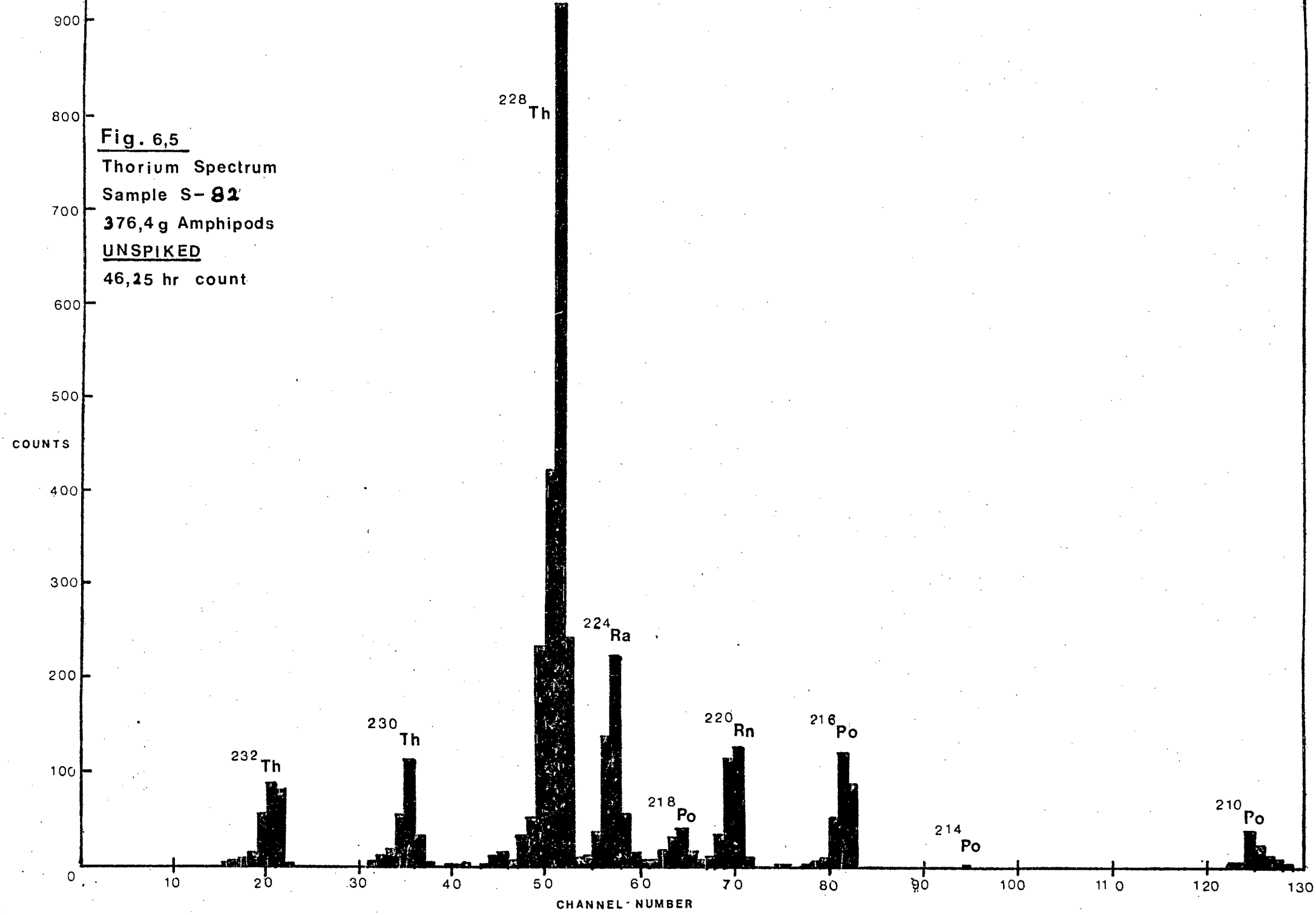


Fig. 6,5
Thorium Spectrum
Sample S-82
376,4 g Amphipods
UNSPIKED
46,25 hr count
COUNTS
CHANNEL NUMBER
0
100
200
300
400
500
600
700
800
900
10
20
30
40
50
60
70
80
90
100
110
120
130
232 Th
230 Th
228 Th
224 Ra
218 Po
220 Rn
216 Po
214 Po
210 Po

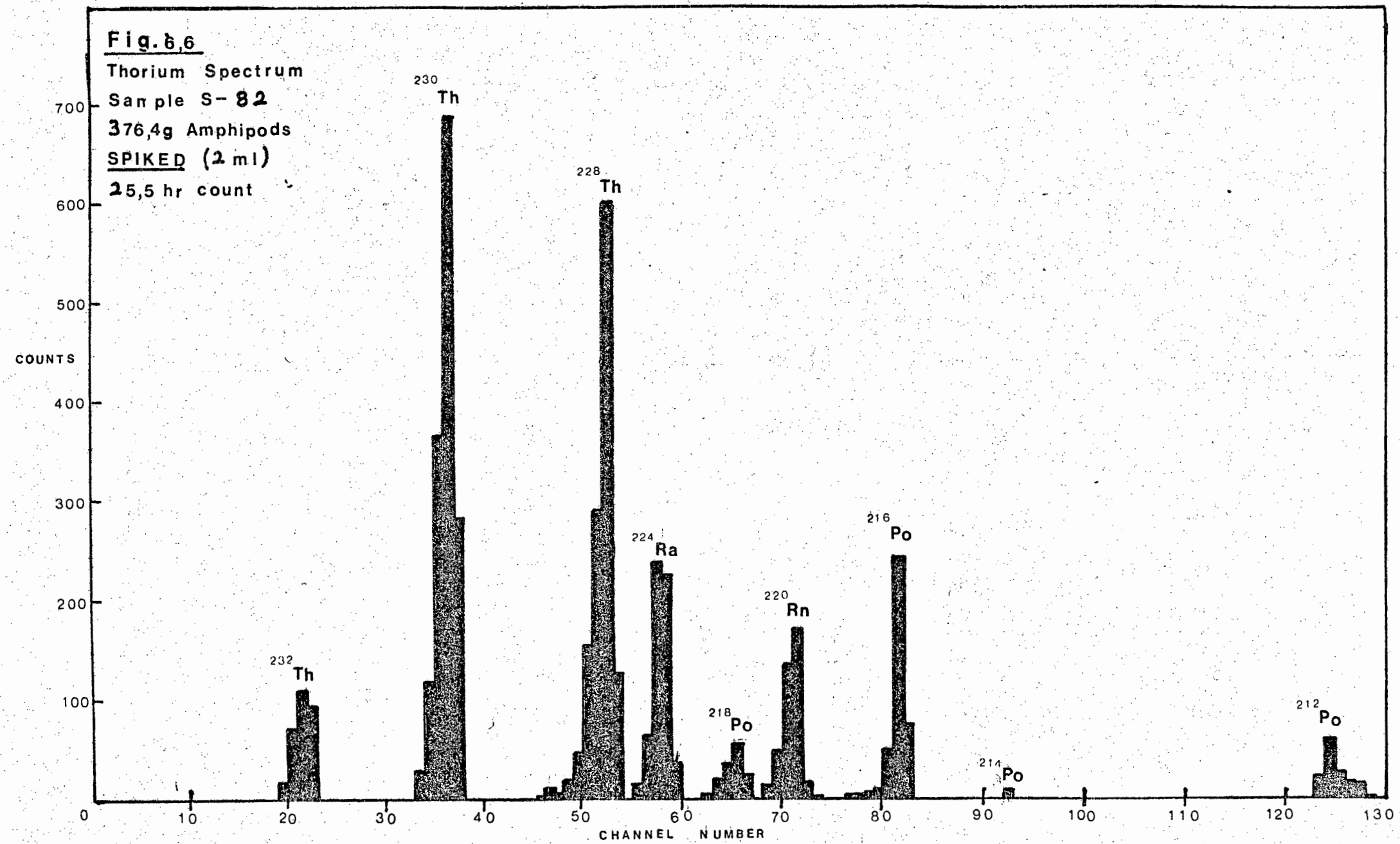


Fig. 6,6
Thorium Spectrum
Sample S-82
376,4g Amphipods
SPIKED (2 ml)
25,5 hr count
230 Th
228 Th
224 Ra
232 Th
218 Po
220 Rn
216 Po
214 Po
212 Po
COUNTS
CHANNEL NUMBER
0
100
200
300
400
500
600
700
10
20
30
40
50
60
70
80
90
100
110
120
130

It was however necessary to make a correction to the Th-228 count as 6% of the Ra-224 alpha-particles have an energy of 5,45 MeV. This makes them indistinguishable from the 5,48 MeV Th-228 alpha-particles.

6.8.2 Blank Count Rates

A blank was run with each set of three samples. In general they were very low compared with samples although sample count rates were always corrected for blanks. Average blanks are shown in Table 6.1. The last column in this table gives the calculated limits of detection assuming that:-

1) to be detectable the sample + blank count rate should be twice the blank alone
2) A 1 kg sample is available
3) The chemical recovery is at least 50%

Table 6.3

Blanks and Limits of Detection

Isotope	Blank (c/hr/200 KeV) Average	Range	Limit of Detection pCi/kg
Pu-239	0,04 ± 0,01	0,00 - 0,07	0,002
U-238	1,2 ± 0,2	0,7 - 2,0	0,06
U-237	1,4 ± 0,2	0,7 - 2,1	0,06
Th-232	0,8 ± 0,2	0,1 - 1,2	0,04
Th-230	0,8 ± 0,2	0,2 - 1,4	0,04
Th-228	3,5 ± 0,4	2,7 - 3,3	0,16

In most of the samples analysed in this project all the isotopes determined were well above the limit of detection and high blanks presented no problem.

Because of the low plutonium concentration in most organisms care was taken to use clean detectors for counting plutonium sources. The same did not apply to uranium and thorium sources because it was feared that they themselves might contaminate the detectors. Consequently the detectors themselves contributed about 1 c/hr to Th-228 and 0,1 - 0,2 c/hr to Th-232, Th-230, U-234 and U-238. The remainder of the blank count rates for uranium and thorium isotopes were presumably due to the presence of traces of uranium and thorium in the large volumes of reagents used.

6.8.3 Chemical Yields

Once the plutonium procedure had been perfected and the sulphate plating method adopted plutonium recoveries were generally good. They seldom fell below 60% and were often over 80%. Exceptions to this were shell samples where recoveries were always low. The reasons for this are not clear but losses appear to occur during the ion-exchange step.

Uranium and thorium recoveries did not appear to be affected by sample composition and averaged a satisfactory 65%.

6.8.4 Calculations and Counting Statistics

Plutonium and uranium calculations are to a very good approximation just a matter of simple proportion. Thus if there were $x \pm \sqrt{x}$ counts of the unknown isotope and $y \pm \sqrt{y}$ counts of the spike containing $(a \pm \alpha)$ dpm of tracer then

$$\text{dpm unknown} = \frac{x \pm \sqrt{x}}{y \pm \sqrt{y}} \times a \pm \alpha$$

where the errors are standard deviations in all cases and counts have been corrected for blank values.

Note An approximation arises here because the percentage of the total alpha counts which falls within "n" say channels is a function of the alpha energy. However since in practice the peaks were summed over a fairly wide energy range (125-200 KeV) a high percentage of the total counts for all energies should have been included. The error should therefore be negligible.

Plutonium Approximately 2 dpm of accurately standardised spike (2,76 ± 0,03 dpm; see section 6.7.1) were added to each sample. Sources were counted for between one and three days which meant that there were normally over a thousand Pu-236 counts. This meant that the relative standard deviation in y was less than 3%.

In order to reduce the relative standard deviation in the Pu-239 count to 10% sources were counted until 100 counts had been obtained wherever this was possible. However for many of the "low" samples this was impractical and counts of 30 were not unusual. This meant that the relative error in y and a was negligible in comparison with the relative error in x and explains the fact that the relative standard deviations quoted in the tables of results are often 20% or higher.

Uranium Most samples were fairly high in uranium and between 2 000 and 15 000 counts of U-238, U-234 and U-232 were usually obtained. As a result the counting statistics were good (relative standard deviations less than 3%) and the main contributor to the final calculated standard deviation was ∝ Some difficulty was encountered in standardising the U-232 spike (section 6.7.2) and the final value of 4,9 ± 0,4 dpm U-232/ml means that this term has a relative standard deviation of 8%. The relative standard deviation in most of the uranium results is therefore about 10%.

Thorium The situation with thorium was far more complex. The actual concentration of the isotopes in the samples had to be calculated from two sets of results obtained by analysing one spiked and one unspiked sample. The calculations were as follows:-

Assume that the concentration (in dpm or counts) in the spike and samples are as given in Table 6.2.

Table 6.2

Thorium Calculations

	Th (dpm present) 232	230	228	Th-228/Th-230	Th-232/Th-230
Spike	x'	y'	z'		
Unspiked Sample	x	y	z	$p = \frac{z}{y}$	$p' = \frac{x}{y}$
Spiked Sample	x+x'	y + y'	z + z'	$q = \frac{z + z'}{y + y'}$	$q' = \frac{x + x'}{y + y'}$

N.B. Whatever the chemical recoveries the observed ratios p and q are, of course, equal to the actual ratios in the samples

$$\text{i.e.} \quad p = \frac{\text{dpm Th-228 present}}{\text{dpm Th-230 present}} = \frac{\text{counts Th-228}}{\text{counts Th-230}}$$

Now $\frac{z + z'}{y + y'} = q$

$$\therefore z + z' = qy + qy' = q\frac{z}{p} + q\,y'$$

$$\therefore z - q\frac{z}{p} = q\,y' - z'$$

$$\therefore \quad z\left(1 - \frac{q}{p}\right) = y'\left(q - \frac{z'}{y'}\right)$$

$$\therefore \quad z = \frac{y'\left(q - \frac{z'}{y'}\right)}{1 - \left(\frac{p}{q}\right)^{-1}}$$

i.e. $$z = \frac{y' \text{ (ratio in spiked sample - ratio in spike)}}{1 - \left(\frac{\text{ratio in unspiked sample}}{\text{ratio in spiked sample}}\right)^{-1}} = \frac{y'\ A}{1-B} \text{ (say)}$$

It can be seen from the above that it is very important that the optimum amount of spike be added since:-

1) If too much spike is added the ratio in the spiked sample tends to the ratio in the spike and the errors in A become very large.

2) If too little spike is added the ratio in the unspiked sample tends to the ratio in the spiked sample and $(1 - B) \rightarrow 0$. Of course this could also happen if the ratio in the sample was actually the same as the ratio in the spike but this is most unlikely.

Note The above formula was derived for the pair of isotopes Th-228 and Th-230. In the same way it can be deduced that

$$x = \frac{y'\left(q' - \frac{x'}{y'}\right)}{1 - \frac{q'}{p'}}$$

The pair Th-232 and Th-228 was not often used because these two isotopes had the same concentration in the spike and concentrations in samples were often similar. However z and x were normally calculated independently and the mean of the two sets of results was reported.

For most samples well over one hundred counts were obtained for each isotope but because of the importance of choosing the optimum amount of spike, the standard deviations reported in Tables 5.1 and 5.2 vary widely. In general the influence of the amount of spike on the final calculated standard deviation was far greater than was the influence of the error in any of the individual terms.

Sample Calculation

Table 6.3

Results obtained from Zooplankton Sample S-82

	Observed c/hr (corrected for blank)			$\frac{\text{Th-228}}{\text{Th-230}}$	$\frac{\text{Th-232}}{\text{Th-230}}$
	Th-232	Th-230	Th-228		
376,4 g Sample	4,8±0,4	4,6±0,4	38,9±1,1	p=8,457±0,773	p^1=1,043±0,126
376,4 g Sample + 2ml Spike	11,3±0,7	54,5±1,4	45,8±1,4	q=0,840±0,034	q^1=0,207±0,014
				$\frac{q}{p}$=0,099±0,010	$\frac{q^1}{p^1}$=0,198±0,027

Note: For composition of Spike (i.e. values for x^1, y^1 and z^1) see Section 6.7.3.

1. Using Th-228/Th-230

$$z = \text{Th-228} = \frac{(70,4 \pm 1,8)\,[q - (0,060 - \cancel{0,020})]}{1 - \frac{q}{p}} \text{ c/hr}$$

0,087

$$= \frac{(70,4 \pm 1,8)\,[(0,840 \pm 0,034) - (0,060 \pm 0,020)]}{1 - (0,099 \pm 0,010)} \text{ c/hr}$$

$$= 60,94 \pm 2,94 \text{ c/hr}$$

% Recovery in Unspiked Sample = 63,83 ± 3,57.

2. Using Th-232/Th-230

$$x = \text{Th-232} = \frac{(70,4 \pm 1,8)\,[(0,207 \pm 0,014) - (0,107 \pm 0,012)]}{1 - (0,198 \pm 0,027)} \text{ c/hr}$$

$$= 8,78 \pm 1,61 \text{ c/hr.}$$

% Recovery in Unspiked Sample = 54,67 ± 11,03.

3. Weighted Mean of Recoveries = 62,95 ± 4,79.

4. Calculated c/hr assuming a recovery of (62,95 ± 4,79)% in the Unspiked Sample.

Th-232 = 7,6 ± 0,9 c/hr

Th-230 = 7,3 ± 0,8 c/hr

Th-228 = 61,8 ± 5,0 c/hr

6.9 The Determination of Polonium

An important characteristic of polonium is its ease of deposition either by chemical deposition onto less noble metals or by electrodeposition. Most of the commonly used separation procedures involve a deposition step either as the final step (e.g. plating onto a metal disc for counting) or as a means of concentrating polonium from relatively dilute solutions.

Polonium deposits readily onto silver from dilute nitric acid or hydrochloric acid solutions. During deposition a black film appears on the silver and this may consist either of the oxide or peroxide. Flynn (42) while determining low levels of Po-210 in environmental materials, made a careful study of possible interferences and the optimum conditions of pH etc. He has published a method in which no preliminary separations are required and essentially quantitative recoveries are obtained from samples containing as little as 0,02 pCi Po-210.

Flynn found that greatest plating efficiency could be obtained by plating from 50 ml of hydrochloric acid solution at pH 2 at a temperature of 85-90°C and in the presence of 0.5 g sodium citrate. The interference of iron (III), chromium (VI) and other oxidants is eliminated by the addition of hydroxylamine hydrochloride. The addition of sulphate prevents precipitation of thorium and the addition of 10 mg of bismuth carrier prevents the deposition of the Bi-212 decay product of Th-232.

Flynn's method was followed unchanged. The following points should be noted:-

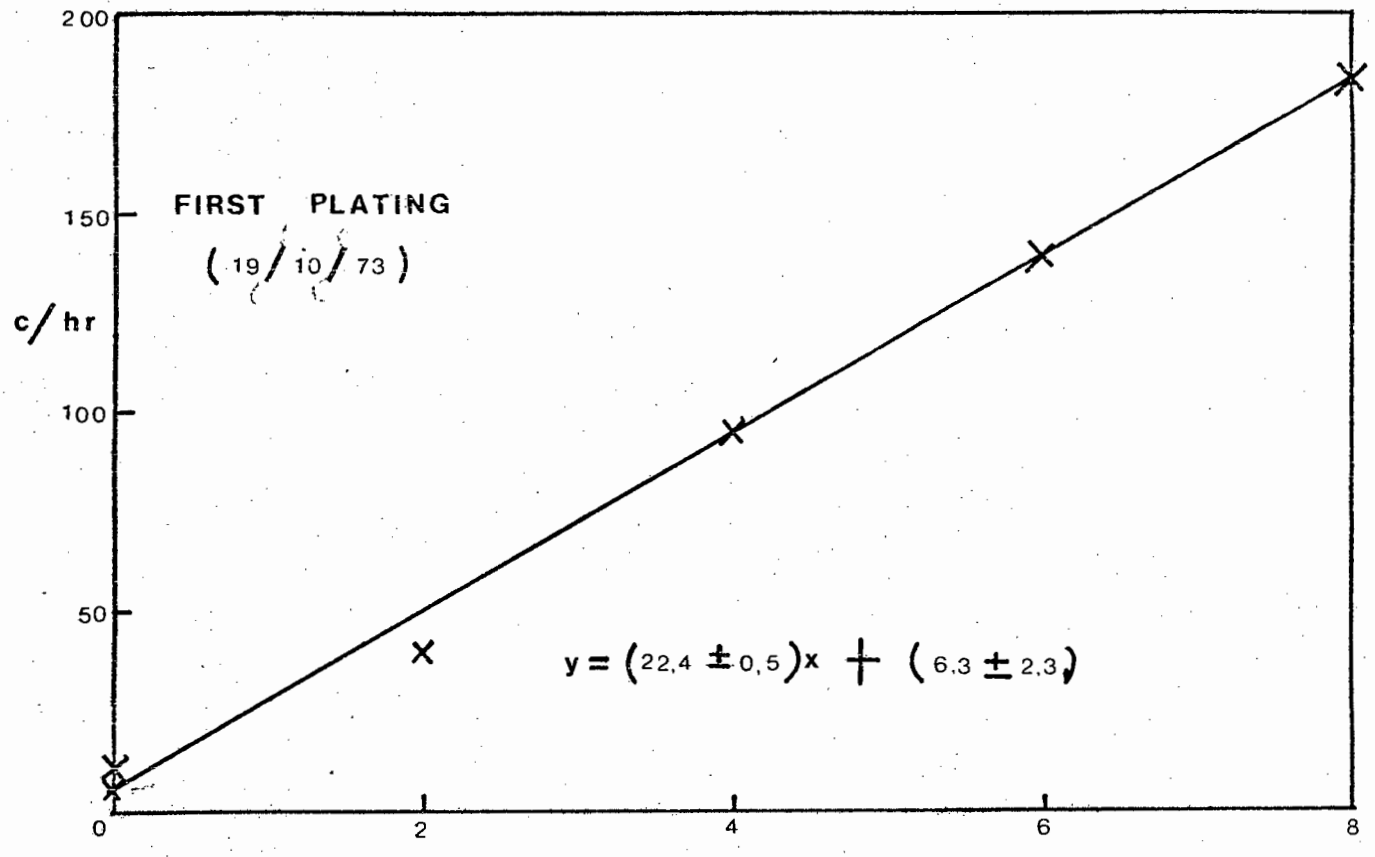
1) Polonium is strongly adsorbed onto glass and all standard solutions and sample solutions were kept in polythene bottles in 2N hydrochloric acid.

2) If the samples are not analysed immediately after collection the decay of Pb-210 ($t_{\frac{1}{2}}$ = 22 yrs) may contribute significantly to the observed level of Po-210. In order to correct for this the sample solutions were stored after plating for as long as possible (6-8 weeks) and a second plating then carried out. In this way the ingrown Po-210 was determined and the Pb-210 content and its contribution to the observed Po-210 concentration could be calculated.

3) Many workers in the field of environmental polonium have used Po-208 as a tracer when determining polonium (7, 43, 58).

Fig. 6,7 Po - 210 STANDARD ADDITION CURVES

on $\frac{1}{2}$g Samples of White Mussel Shell



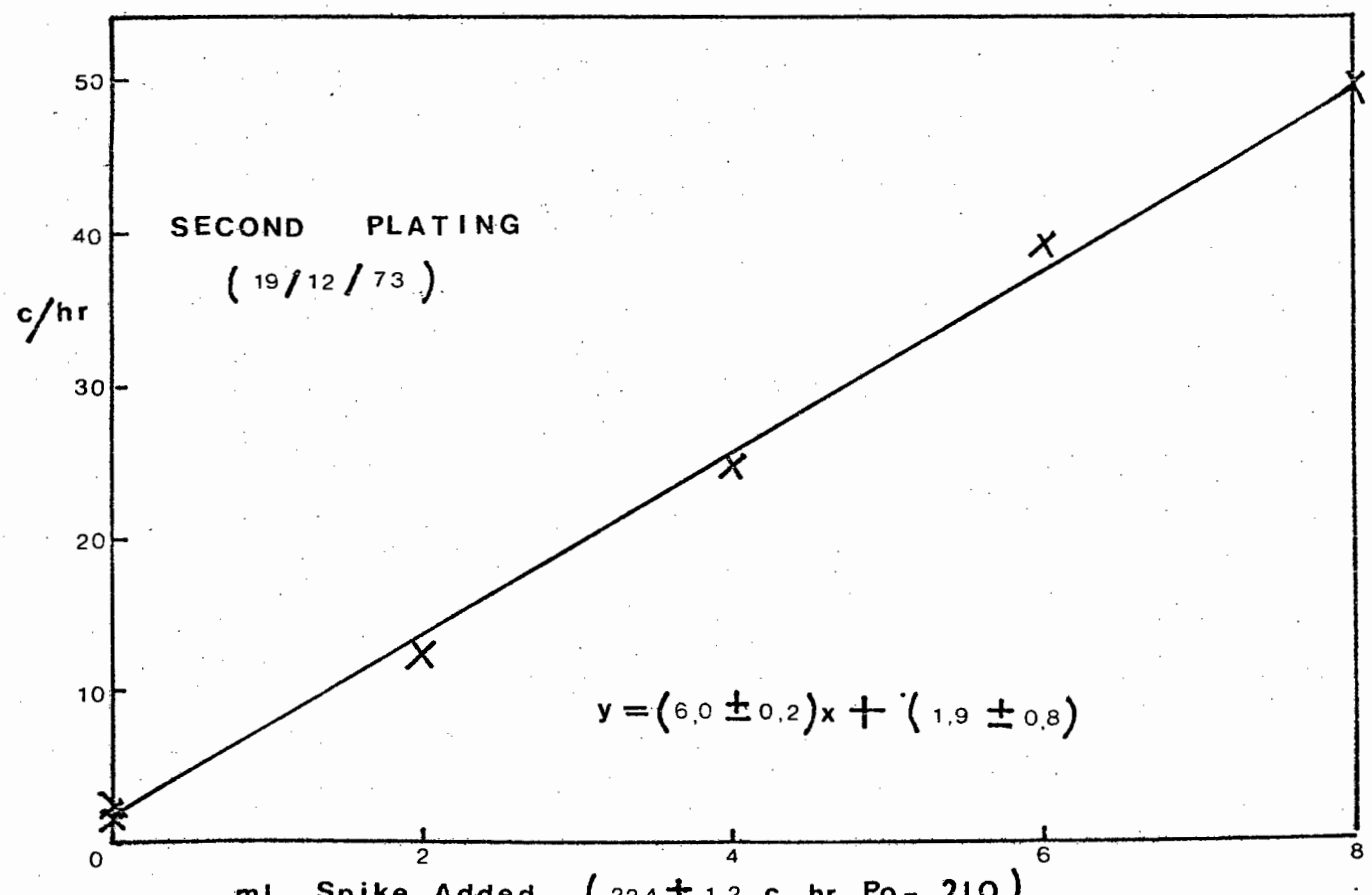
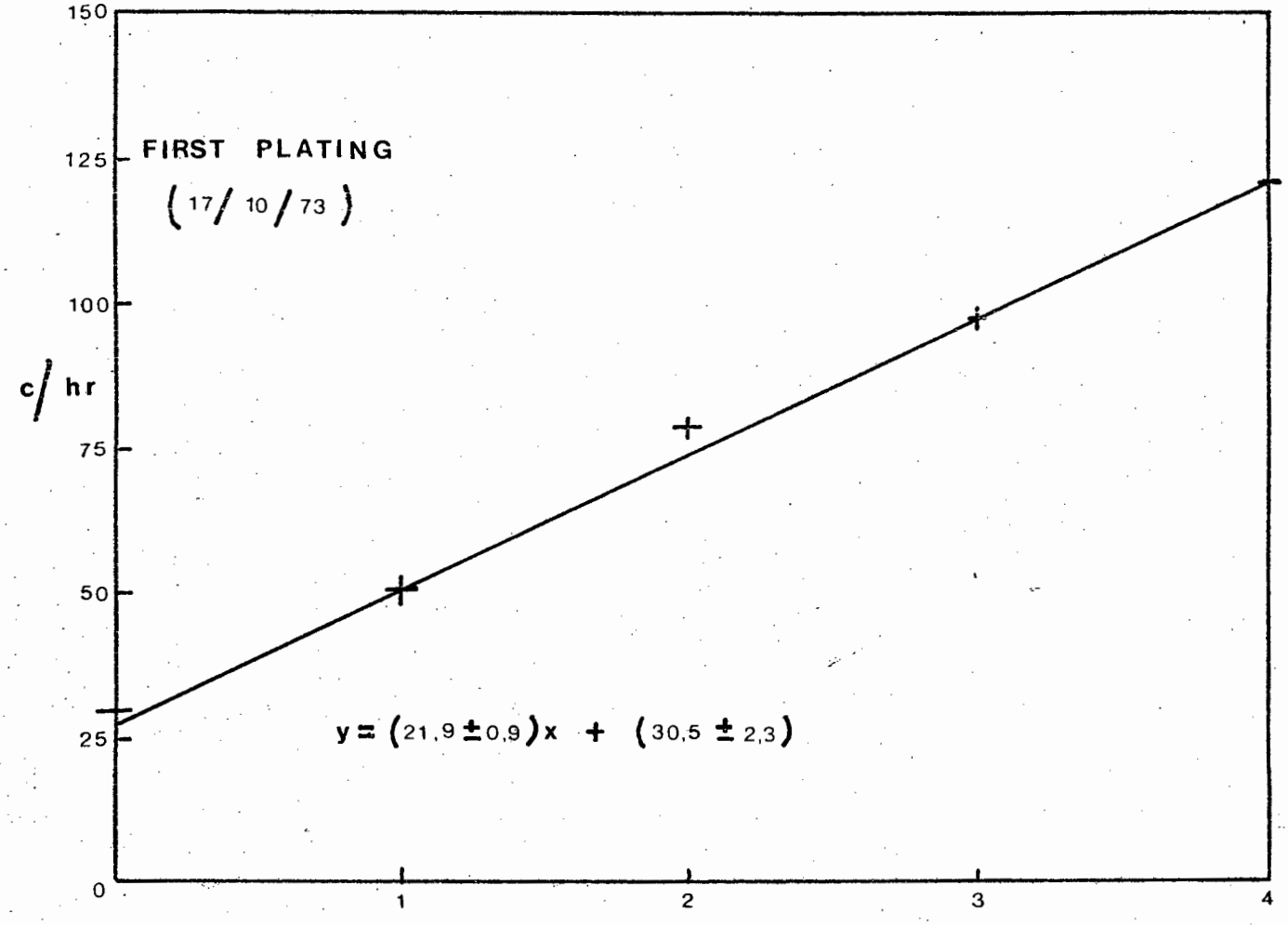
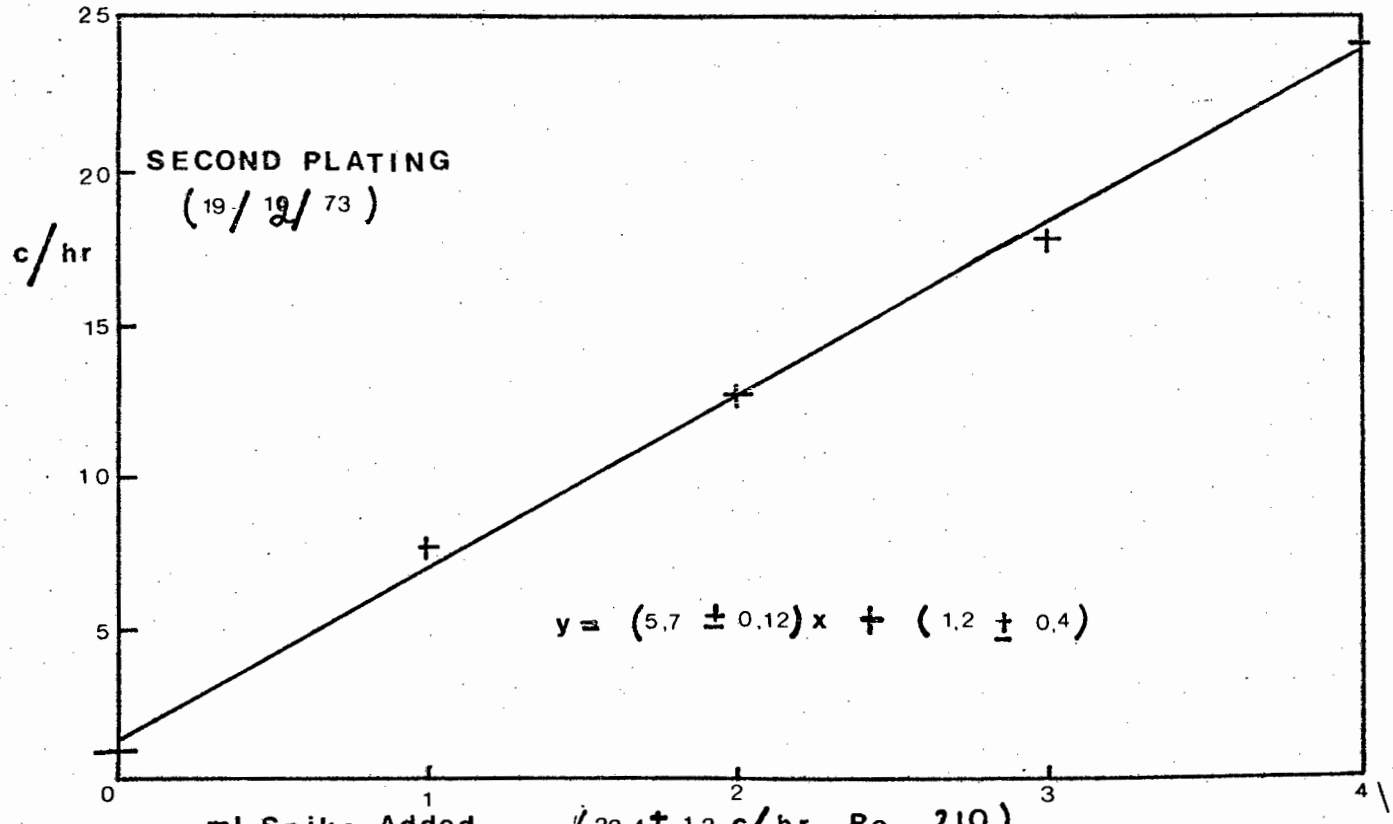


Fig. 6,8 Po- 210 STANDARD ADDITION CURVES

(on 1 g Samples of White Mussel Soft Tissue)





However, the determination of Po-210 is straightforward and recoveries are generally close to 100%. In fact when standard addition curves (Figs. 6.7 and 6.8) were prepared, by adding known amounts of a standardised solution of Pb-210 in equilibrium with Po-210, to samples of mussel shell and mussel meat the following recoveries were obtained:-

Mussel meat: 1st plating (98 ± 7) % 2nd plating (95 ± 7) %
Mussel Shell: 1st plating (100 ± 6) % 2nd plating (100 ± 6) %

For this reason it was considered unnecessary to use a tracer and polonium sources were counted on total alpha-counters rather than alpha-spectrometers.

6.10 Total Alpha-Counting

"Total" or "Thick Source" alpha-counting is a simple and sensitive method that can provide useful information about the total alpha-activity of a sample. A thick source is one whose thickness is greater than the range of the alpha-particles emitted by the nuclides in the sample. The energies of the alpha-particles emitted from such a source will range from zero to the theoretical maximum depending upon the distance travelled through the sample.

No preliminary chemistry is necessary and zinc sulphide scintillation counters can be used. These are simple to operate and give reliable results. Thus provided a reasonable number of counts can be obtained the margin for experimental error is small and the main limitations on the method are due to theoretical rather than practical considerations.

The theory of thick source counting and the approximations involved have been discussed in detail by several authors and is only briefly outlined in section 6.10.1 which now follows. Details of the experimental procedure are given in Appendix II (section 7.3

6.10.1 Total Counting - Theory and Approximations

The basic theory of thick source counting assumes that the alpha-emitters are homogenously distributed in the sample and that all alpha-particles down to zero energy are detected. Then provided that the area of the source is much greater than the square of the range of the alpha-particles and provided that the thickness of the source is greater than the range of the alpha-particles;

$$No = \frac{NRA}{4}$$

where No = the number of alpha-particles emerging from the source per unit time

N = Number of alpha-disintegrations per unit volume per unit time

R = Range of the alpha-particles in the sample

A = Area of the source.

Furthermore if the density of the sample is ρ then the alpha-radioactivity of the sample in pCi/kg is given by

$$S = \frac{No}{RA\rho} \times 30,08 \text{ pCi/kg}$$

Therefore if $R\rho$ is known and No is determined it is possible to calculate the total alpha-radioactivity (S) of the sample.

Much work has gone into attempting to evaluate $R\rho$ accurately for different materials but several assumptions are unavoidable. This is because the range depends both on the chemical composition of the sample and on the energies of the alpha-particles present.

In order to calculate $R\rho$ Shennon (126) used the semi-empirical formula

$$R\rho = 3,2 \times 10^{-4} R_o \frac{\sum f_i A_i}{\sum f_i Z^{2/3}}$$

where fi is the atom fraction of the element in the sample

Ai is the atomic weight of the element

Zi is the atomic number of the element

Ro is the range in standard air

He calculated the value of $\frac{\sum f_i A_i}{\sum f_i Z^{2/3}}$ for various marine organisms using the chemical composition figures given by Vindgradov (147). These calculated values are given in Table 6.4.

Table 6.4 - Stopping Power Terms

Organism	$\frac{\Sigma f_i A_i}{\Sigma f_i Z^{2/3}}$
Diatoms	3,65
Copepods	3,22
Amphipods	3,36
Seaweed	3,53
Mollusc (Soft tissue)	3,28
Mollusc (Shell)	4,42
Echinoderms	3,59
Decapods (Soft tissue)	3,45
Decapods (Shell)	4,44

Shannon assumed that the average range of the alpha-particles in "standard" air (Ro) is 4,51 for shells and 4,24 for zooplankton, macrophytes and the soft tissue of marine invertebrates and fish. He estimates that variations in the proportions of uranium and thorium series isotopes in the samples will not introduce an error of more than 10% into these figures. These values and the stopping power values in Table 6.4 were used to calculate the total alpha-activity of the samples analysed in this project.

The errors reported are standard deviations based entirely on counting statistics and take no account of errors that may have been introduced by uncertainty as to the exact value of the ranges.

Appendix II

Experimental and Analytical Detail

7.1 Plutonium, Thorium, Uranium Procedure

Special Apparatus

1) Counting Apparatus

Alpha-spectrometric measurements were made with 450 mm^2, 90 μm depletion depth, Ortec silicon surface barrier detectors operated in vacuum chambers. The detectors used in this project had a guaranteed resolution of better than 55 KeV full width at half-maximum.

However this resolution was obtained using a small very thin alpha-spectroscopic source and probably a source to detector separation equal to the detector diameter. Such resolution is achieved only at the expense of some efficiency and in practice resolution is usually sacrificed in favour of sensitivity. Moreover the sources obtained in practice from environmental samples are never as thin as the optimum sources used by detector manufacturers in measuring resolution. The detector mounts and planchette holders used at the University of Cape Town were especially designed to give maximum sensitivity (the counting efficiency is typically 37%) and in practice a resolution of 75-100 KeV was usually obtained.

Pulses from the detector were fed in turn to an Ortec Model 109 A preamplifier, an Ortec Model 485 amplifier and an Ortec Model 408 bias amplifier. The output pulses were analysed by means of a nuclear data (ND 110 or ND 555) 128 channel analyser coupled to a digital printout. An Ortec test pulser model 480 was included in the system for quick setting of gains and bias levels and for routine checks on the electronics.

2) Electrodeposition Apparatus

Figure 7.1 shows the electrodeposition apparatus used. Disposable electrodeposition cells were prepared by cutting the bottoms off 1 oz. plastic bottles. These were screwed into a brass base machined to fit the thread at the neck of the bottle. The external diameter of the necks of the bottles was 17,2 mm and the stainless steel cathodes therefore fitted neatly into the brass base. A neoprene gasket was inserted between the bottle and the plating disc to ensure a perfect seal.

In order to prevent evaporation a tightly fitting perspex

lid which also served as an anode holder was placed on the bottle. The platinum wire ($\frac{52}{1000}$ inches diameter) anode was fitted through the perspex holder and the wire formed into a circle approximately 1 cm in diameter. This portion of the electrode was positioned about 3 mm above the plating disc.

Electrolyses were conducted without stirring using a Heath Kit Battery Eliminator (Model I.P. 12). Two cells were plated in parallel, each with a rheostat and ammeter in series, so that the current in each could be controlled independently.

3) Ion Exchange Columns

The Ion Exchange Columns were of standard design. They were fitted with teflon taps throughout in order to avoid difficulties due to grease. The large columns (Fig.7.2) were attached to 1 litre reservoirs which were raised to a height of about 2 metres above the columns. This made handling of large sample volumes easier and speeded up flow through the fine resin.

Column dimensions were:-

Small size - 1,0 cm I.D. x 20 cm length
Large size - 1,5 cm I.D. x 30 cm length

4) Stainless Steel Planchettes and Heater for Preparing Evaporated Sources

The stainless steel planchettes fitted exactly into the semi-conductor assembly. They were flat discs, 2,5 cm in diameter, with vertical sides 2 mm high.

Before use they were electropolished in order to obtain the mirror finish essential for low level determinations by alpha-spectrometry.

For electropolishing the planchette was mounted in the electrodeposition cell (a 400 ml beaker) with the flat side facing out. The cell was half filled with an electrolyte composed of 100 ml glycerine, 80 ml phosphoric acid, and 20 ml

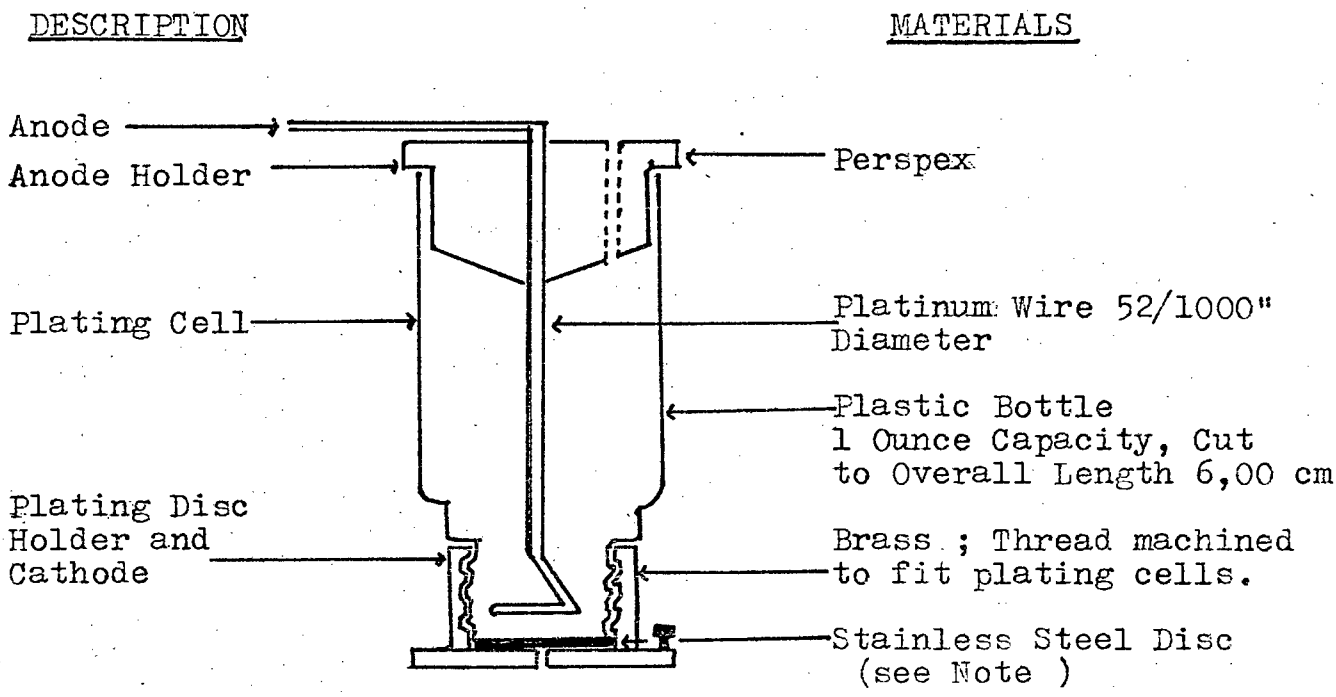
water. The temperature of the electrolyte was maintained at 90°-100°C. The cathode was a stainless steel plate approx. 4 cm x 6 cm. Electrolysis was conducted at a current of one amp. for about 15 minutes after which the planchette was thoroughly rinsed with distilled water and dried.

The heater was designed to heat the planchette from the circumference so that the centre was cooler than the edges (Fig. 7.3). The bimetallic strip was adjusted to give a temperature of about 120°C. At this temperature evaporation was rapid without spattering.

Reagents (All reagents analytical reagent grade)

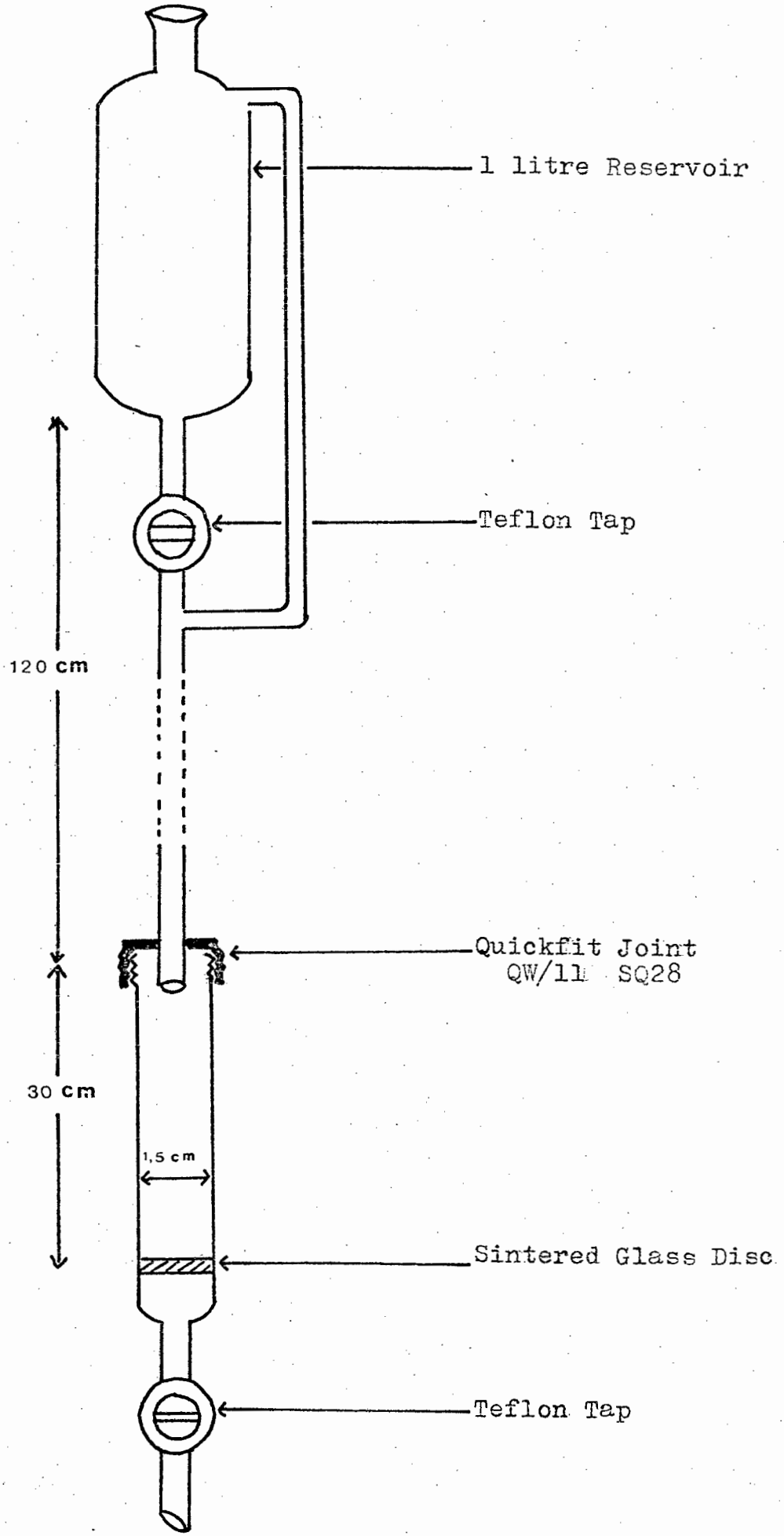
1) Nitric acid: 16N HNO_3.
2) Conc. Hydrochloric Acid: 12N HCl.
3) Conc. Ammonium Hydroxide: 15N NH_4OH.
4) Ammonium Iodide Solution: 1M NH_4I in water (freshly prepared)
5) Sodium Nitrite: Granular $NaNO_2$ crystals.
6) Anion Exchange Resin - AG 1 x 8, 100-200#, Bio-Rad.
7) n-octyl alcohol.
8) Iso-propyl ether.
9) 2-thenoyltrifluoroacetone: 0,5 M T.T.A. in benzene.
10) Hydrogen Peroxide: H_2O_2, 30% (100 vols.)
11) Pu-236 tracer, standardised 2-3 dpm/ml
12) U-232 tracer, standardised 4-6 dpm/ml
13) Thorium tracer: see Appendix I - Section 6.7.3
14) Perchloric acid: concentrated
15) Sulphuric acid: concentrated
16) Thymol blue indicator - 0,04%
17) Sodium Hydroxide: 1M NaOH
18) Benzene.
19) Acetone.
20) Glycerine.
21) Phosphoric Acid: concentrated
22) Sodium Dichromate.

FIG. 7.1 ELECTRODEPOSITION APPARATUS



Note : The stainless steel plating discs were 17 mm diameter x 0,5 mm thick, mirror finished on one side only; (Metallic Valve Co., 117-125 Bridge Street, Birkenhead, Cheshire, U.K.) Before use they were degreased with detergent and acetone and then immersed for 10 minutes in hot 4M nitric acid - 2% sodium dichromate, rinsed and stored under water until needed.

FIG. 7.2 ION EXCHANGE COLUMN AND RESERVOIR



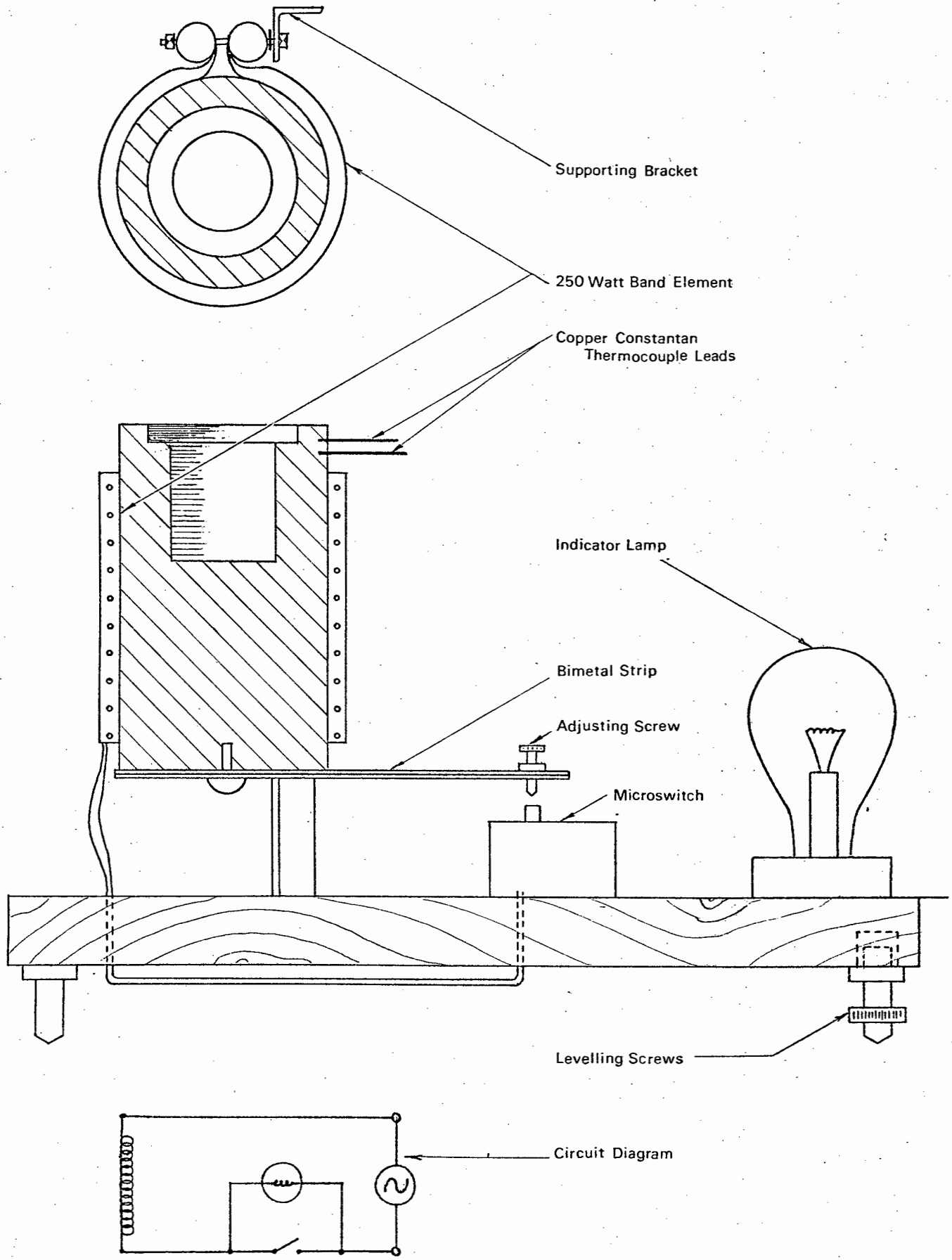


FIG. 7,3 PLANCHETTE HEATER

Analytical Procedure

(I) Sample Preparation

1) For thorium determinations two identical samples are required, one spiked and one unspiked. Therefore whenever possible 2 kg of soft tissue or 1 kg of shell should be taken. (More shell is difficult to handle because of the large quantities of salts present).

2) Dry the sample to constant weight at 105°C, grind finely and mix thoroughly by coning and quatering or by riffling. Remove a 5-10g representative sample and keep this for polonium analysis.

3) Divide the remainder of the sample into two identical portions in 600 ml Pyrex beakers. Place them in a muffle furnace and raise the temperature slowly to 480°C.

Note Oily samples tend to froth violently and unexpectedly at about 200°C. It was found that the addition of one gram of Dow-Corning Silicone anti-foaming agent considerably reduced this. However after a sophisticated temperature gauge was installed on the furnace it became possible to dispense with the anti-foaming agent by increasing the temperature very gradually over the critical 120°-300°C range.

(II) Dissolution

1) Transfer the ashed sample to a two litre beaker and moisten with distilled water.

2) Add the three tracers. For most samples 1 ml of each tracer is a suitable volume. The thorium tracer must be added to only one of each pair.

3) Carefully add 200 ml of 16N nitric acid and 100 ml of 12N hydrochloric acid. If foaming becomes appreciable the addition of a little n-octyl alcohol controls it.

Note Samples of shell require considerably more acid for complete dissolution. (500g $CaCO_3$ = 650g HNO_3). Therefore, for shell samples add 100 ml conc. hydrochloric acid and then carefully add nitric acid until the addition of more acid ceases to cause frothing. Now add another 200 ml nitric acid. For a 500g shell sample about 1 litre of 16N nitric acid is normally required.

4) Cover the beaker with a watch glass and digest at near boiling for two hours with occasional stirring.

5) Add 300 ml 1N nitric acid and 25 ml 30% hydrogen peroxide. Continue heating until the peroxide has decomposed.

6) Cool the sample, filter through glass fibre filter paper and wash the residue with 50 ml hot 1N nitric acid.

7) Return the residue to the original beaker. Add 200 ml 16N nitric acid and 100 ml 12N hydrochloric acid and repeat the entire digestion process (Steps 4-6).

8) Combine the filtrates and acid rinses and evaporate until salts begin to form. Estimate the volume, add an equal volume of 1N nitric acid and dilute to 1 litre with 8N nitric acid.

Note Frequently salts begin to form when the volume is more than 500 ml. If this happens continue evaporation until about 400 ml remain. Then add 200 ml 1N nitric acid and 400 ml 16N nitric acid. It is advisable to check the final acid concentration of such samples by titration with 1N sodium hydroxide. If necessary the nitric acid concentration can then be adjusted to between 7,5N and 8N.

(III) Ion Exchange Procedure

1) Add 5g solid sodium nitrite to the sample solution and leave for 30 minutes. (Only 5g are added because it is difficult to keep large quantities of sodium chloride in solution in 8N hydrochloric acid during the uranium determination).

2) Pass this solution through a large ion-exchange column containing 25 ml of anion exchange resin preconditioned with 8N nitric acid. The flow rate should be about 10 ml/minute.

3) Drain the solution carefully to the top of the resin. Rinse the reservoir and column walls with a few ml of 8N nitric acid and again drain carefully to the top of the resin. Repeat the rinse and draining step once. Elute the column with 75 ml 8N nitric acid and drain to the top of the resin. Keep the eluate (about 1100 ml) for the uranium determination.

4) Elute as above with 300 ml 12N hydrochloric acid. Keep this eluate for the thorium determination.

5) Elute the plutonium with a solution of 300 ml of 12N hydrochloric acid and 15 ml 1M ammonium iodide. Mix this eluant just before use.

6) Some uranium will have been retained on the column. Place the 8N nitric acid eluate from step 3 under the column and elute any uranium with 300 ml 0,1N hydrochloric acid (after two rinses as usual).

7) Now complete the purification and source preparation for each element as follows:-

(IV) Plutonium Isolation

1) Take the plutonium eluate from step III-5 and evaporate, below boiling, to dryness on a hot plate. Remove the ammonium salts by evaporation with several portions of 2-3 ml each of conc. nitric acid and hydrochloric acid. Rinse the walls of the beaker with each addition of acid. Finally add a rinse of 2-3 ml 12M hydrochloric acid and evaporate to dryness.

2) Add 5 ml 12N hydrochloric acid, warm the solution on a hot plate for a few minutes and transfer the solution to a 15 ml centrifuge tube. Rinse the beaker thoroughly with about 5 ml 12N hydrochloric acid combining the solutions.

3) Add approximately 100 mg sodium nitrite, stir with a glass stirring rod and allow to react for about 30 minutes. Centrifuge at low speed for 2-3 minutes.

4) Transfer the supernate to the top of a small ion-exchange column, loaded with 2 ml wet anion exchange resin (AG 1 x 8, 100-200 mesh) preconditioned with conc. hydrochloric acid. Place the beaker containing the hydrochloric acid/thorium eluate from step III-4 under the column and drain the solution to the top of the resin. Rinse the centrifuge and column walls twice with 1-2 ml portions of conc. hydrochloric acid, draining carefully to the top of the resin each time.

5) Wash the column with 80 ml conc. hydrochloric acid. Keep the combined hydrochloric acid fractions for the thorium determination.

6) Elute the plutonium with 20 ml conc. hydrochloric acid and 1 ml ammonium iodide; mix just prior to use.

7) Collect the plutonium eluate in a 50 ml beaker and slowly evaporate the solution as described in step IV-1.

Now prepare the plated source as follows:-

(V) Electroplating of Plutonium

1) Add 0,5 ml conc. sulphuric acid and heat until dense white fumes are visible. Allow the sulphuric acid to reflux on the walls of the beaker for a minute or two.

2) Remove the sample from the heat and allow it to cool to room temperature. Add exactly 5 ml of distilled water making certain to wash down the walls of the beaker.

3) Add two drops of 0,04% thymol blue indicator and 1 ml 14M ammonium hydroxide. The indicator should turn blue or at least yellow indicating a basic pH. If the solution is still pink add enough ammonium hydroxide to make the solution basic.

4) Neutralise the solution with 18M sulphuric acid and add one drop in excess. The solution should be slightly pink.

5) Transfer the solution to the plating cell rinsing the beaker twice with 2 ml portions of approx. 0,02M sulphuric acid (three drops of 36N sulphuric acid/100 ml water).

6) Adjust the pH to 2-3 using 2M ammonium hydroxide. The end point colour is salmon pink. The total plating volume should be 10 ± 1 ml.

7) Plate the samples for two hours at one amp per cell. (12V, filtered D.C. output from the battery eliminator).

8) At the end of the plating period add 1 ml 14M ammonium hydroxide to each sample. Mix, wait one minute and switch off.

9) Disassemble the cell as quickly as possible after plating. Wash the plated disc with distilled water and acetone. Dry and store for counting.

(VI) Thorium - Isolation and Source Preparation

1) Evaporate the hydrochloric acid eluate from steps III-4 and IV-4 down to about 5 ml. Transfer to a 50 ml beaker and add about 1 ml perchloric acid. Evaporate to dryness.

2) Wash down the walls with nitric acid and heat until no further fumes of perchloric acid are evolved. Repeat several times until no more perchloric acid remains.

3) Add 1 ml 1N nitric acid to the residue in the beaker. Warm for a few seconds. Transfer to a 100 ml separating funnel using about 9 ml of water.

4) Add 3 ml of 0,45M T.T.A. in benzene. Shake for half an hour. Allow the layers to separate.

5) Drain off the lower aqueous layer and run the benzene layer into a dry centrifuge tube. Centrifuge for a few seconds. Transfer the benzene layer to a dry 10 ml beaker and evaporate down to about $\frac{1}{2}$ ml.

6) Using a disposable dropper transfer the T.T.A./benzene onto a heated polished stainless steel planchette. Rinse the beaker and dropper twice with benzene.

7) Place the planchette in a muffle at 800°C for a few minutes until the organic matter has all burnt off and the metal is straw-coloured. Cool and store for counting.

(VII) Uranium - Isolation and Source Preparation

1) Evaporate the nitric acid eluate from steps III-3 and III-6 to near dryness.

2) Add a few ml conc. hydrochloric acid and heat until no further brown NO_2 fumes are evolved. Repeat several times until all the nitric acid has been removed.

3) Estimate the sample volume. Add an equal volume of 12N HCl and dilute to 1 litre with 8N HCl. (Note: add 8N HCl before 12N HCl as this prevents salts precipitating out). If all the salts do not dissolve decant the supernate and dissolve the salts in hot water. Then add enough conc. hydrochloric acid to give an 8N hydrochloric acid solution. Combine the two portions.

When the salts are all in solution it is advisable to check the normality by titrating a one ml aliquot with ~ 1N sodium hydroxide. The final volume is usually between 1 and 2 litres. Occasionally for shell samples it is preferable to use only half the sample solution rather than to battle with volumes of 3 litres or more.

4) Transfer the solution to a 2-3 l separating funnel and add 300 ml iso-propyl ether. Shake vigorously for five minutes. Allow the layers to separate and run the aqueous layer back into the original beaker. Discard the organic layer. Repeat this extraction once more.

5) Evaporate the sample solution down to about 600 ml. and then add 600 ml 10N hydrochloric acid. The acid concen-

tration should now be 8N.

6) Pass the sample solution through the large ion-exchange column containing 25 ml resin (AG 1-X8, 100-200 mesh) which has been pre-conditioned with 8N hydrochloric acid.

7) Wash the resin as in step III-3 with 2 rinses of 8N hydrochloric acid followed by 75 ml 8N hydrochloric acid. Discard the eluate.

8) Rinse the walls of the reservoir and column with a few ml of 0,1N hydrochloric acid and drain to the top of the resin twice. Now elute the uranium with 300 ml 0,1N hydrochloric acid.

9) Evaporate the eluate to dryness. If any iron is visible dissolve the residue in a few ml 8N hydrochloric acid and extract the iron with iso-propyl ether. Evaporate the aqueous layer to dryness.

10) Rinse the walls of the beaker with hydrochloric acid and add 1 ml perchloric acid. Fume to dryness as in step VI-2.

11) To the residue in the beaker add 1 ml 1N nitric acid. Warm to dissolve all the salts.

12) Transfer to a 100 ml separating funnel. Rinse the beaker with about 10 ml water containing a few drops of nitric acid.

13) Using a pH meter adjust the pH to between 3 and 3,5 with 1N sodium hydroxide.

14) Add 3 ml 0,45M T.T.A. in benzene and prepare a source exactly as described for thorium in steps VI-4 to VI-7.

7.2 Polonium-210 and Lead-210 Procedure

Special Apparatus

1) Counting Apparatus

The total counting apparatus used was essentially the same as that used by Shannon (126). Pulses are fed from an E.M.I. type 9530 B photomultiplier tube, having a photocathode diameter of 12,7 cm, to the pulse amplifier of an Ekco type N529 scaler. After amplification they are fed through a discriminator circuit with a variable bias; all pulses greater than the discriminator bias level are then counted by the scaler. It is an easy matter to adjust the discriminator bias and the E.H.T. supply voltage to the phtomultiplier tube in such a way that almost all the alpha-particles are counted while essentially all the beta and gamma rays and tube noise are rejected.

Zinc sulphide phosphors were prepared by stretching cellulose adhesive tape over perspex rings. Silver activated zinc sulphide powder was then sprinkled onto the sticky surface of the tape and the disc agitated until no more powder would adhere to the tape. The polonium source was then placed directly on the zinc sulphide layer and held in place with a cork disc.

2) Polonium Deposition Cell

Teflon holders especially designed to hold the 1" diameter silver discs were constructed. The directions of Flynn were followed exactly and Fig.7.4 is taken from reference 42.

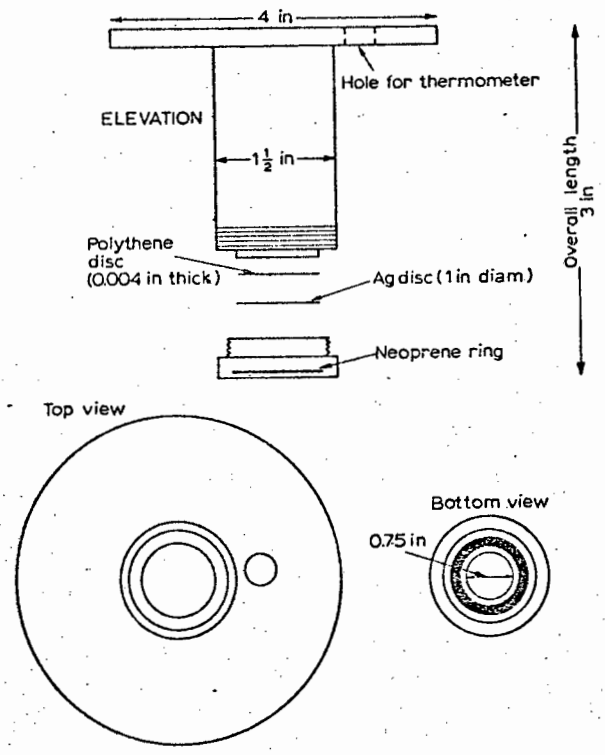


Fig. 7.4 Teflon Disc Holder

Reagents - (Analytical Reagent Grade in all Cases)

1) Nitric acid - concentrated
2) Perchloric acid - concentrated
3) Hydroxylamine hydrochloride - 20 w/v
4) Sodium citrate - 25% w/v
5) Bismuth carrier (10 mg Bi^{3+}/ml)
   2,32g of $Bi(NO_3)_3\ 5H_{20}$ dissolved in 5 ml concentrated nitric acid and diluted to 100 ml
6) Ammonium hydroxide - concentrated
7) 1" discs cut from silver foil

Procedure

1) Weigh out between 0,5 and 1,0g of dried sample into a 150 ml beaker.
2) Wet ash by adding 1 ml concentrated nitric acid and 3 ml concentrated perchloric acid. Wait until foaming subsides and then continue heating until no further fumes are evolved. Since polonium is volatile at 150°C it is important to use a cool hot plate (120°C) and not to "bake" the sample.
3) Add 10 ml 2 N hydrochloric acid and warm to dissolve the residue.
4) Add 5 ml 20% hydroxylamine hydrochloride
   2 ml 25% sodium citrate
   and 1 ml Bismuth carrier.
5) Using a pH meter adjust the pH to 2 with concentrated ammonia.
6) Dilute to 50 ml. Place on a hot plate magnetic stirrer and heat to 85°-90°C. Stir with a 1" teflon stirrer for 2-3 minutes to reduce any Fe^{3+}, or other oxidants that may be present.
7) Position the holder with the silver disc in the beaker and remove air bubbles by manipulating the stirrer.
8) Stir for 75 minutes at 85°-90°C.
9) Remove the disc, wash with distilled water and methanol, dry and count.
10) Insert a clean silver disc into the holder and plate for a further hour to make sure that no trace of Po-210 remains in the solution. Remove and discard this disc.
11) Transfer the plating solution to a plastic bottle washing out the beaker with about 3 ml concentrated hydrochloric acid.
12) Store this solution for at least two months to allow sufficient Po-210 to grow in as a result of the decay of Po-210.
13) Transfer the solution to a 150 ml beaker. Adjust the pH to 2 using concentrated ammonia and repeat the polonium plating as described in steps 6-9.

Calculations

Po-210 and Pb-210 activities at the time of sample collection may be calculated using the following formulae.

$$\text{Pb-210} = \frac{C_2}{E} \times \frac{1}{e^{-\lambda t_4}} \times \frac{1}{1-e^{-\lambda t_3}}$$

$$\text{Po-210} = \frac{1}{e^{-\lambda t_1}}\left[\frac{C_1}{E.e^{-\lambda t_2}} - Pb(1 - e^{-\lambda t_1})\right]$$

where

t_1 = time between collection and first plating

t_2 = time between first plating and counting

t_3 = time between first plating and second plating

t_4 = time between second plating and the corresponding counting

c_1 = activity measured at first counting

c_2 = activity measured at counting after second plating

λ = decay constant for Po-210

E = plating plus counting efficiency

Note In this project it was assumed that the plating efficiency was 100% and that counting efficiency was 46%, i.e. E = 0,46.

7.3 Total Counting Procedure

Apparatus The counting apparatus and zinc sulphide phosphors were exactly the same as those used for polonium (section 7.2). The area of the zinc sulphide phosphors was either 45,6 cm or 19,6 cm depending upon the amount of sample available.

Procedures

1) Pack the finely ground, dried sample firmly into the phosphor. Cover with a cardboard disc and seal with cellulose tape.
2) Allow to stand for three weeks.
3) Count until at least 200 counts have been obtained.
4) Correct count rate for background which is determined by counting blank phosphors for several days. (The black count rate normally varies between 1,0 c/hr and 1,3 c/hr depending upon the instrument used).
5) Calculate the total alpha-radioactivity using the formulae given in Appendix 1, Section 6.10.1.

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