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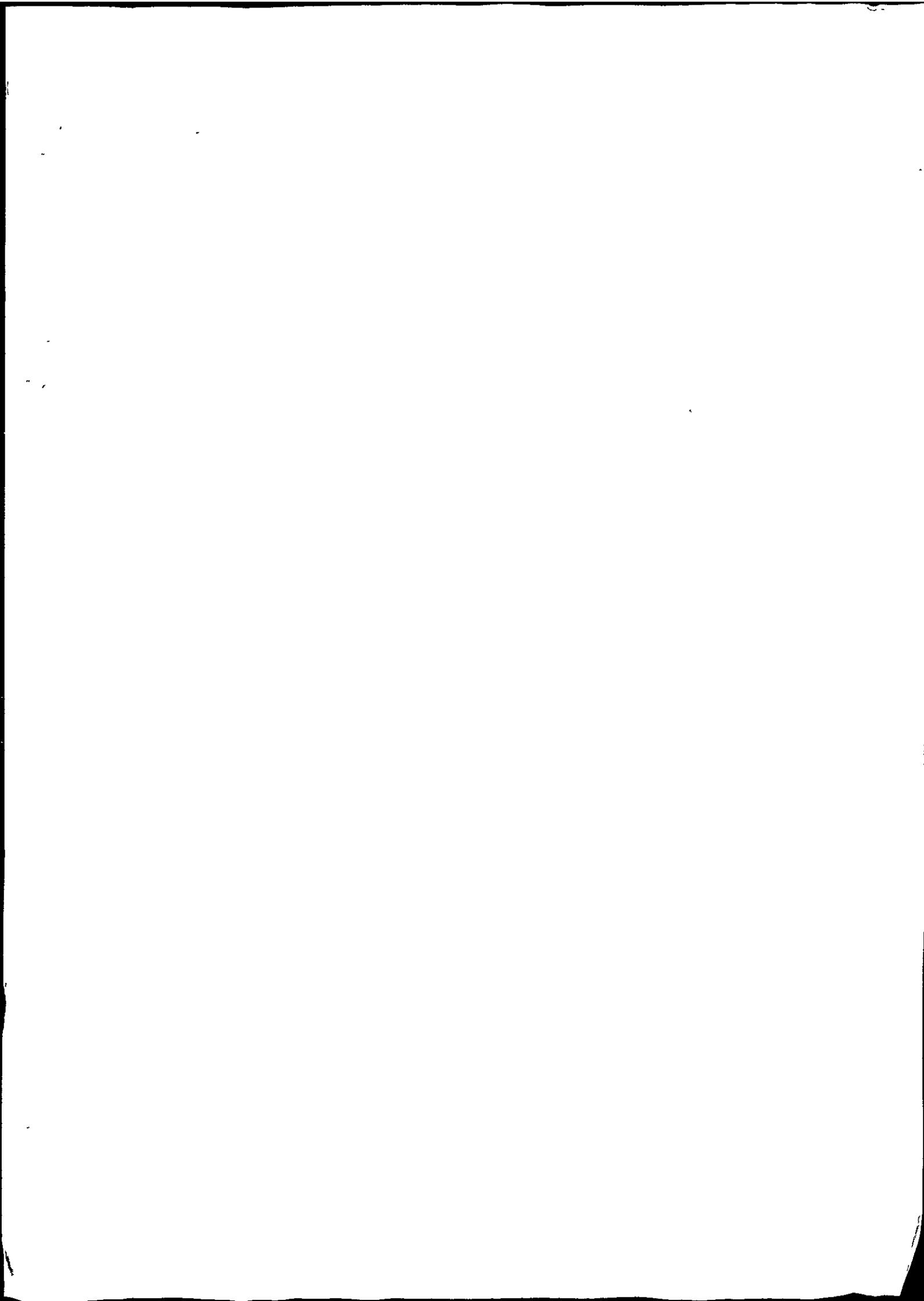
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MEASUREMENT AND MODELLING
OF URANIUM AND THORIUM
IN NATURAL WATERS

E. R. UNSWORTH

Ph.D. 2001



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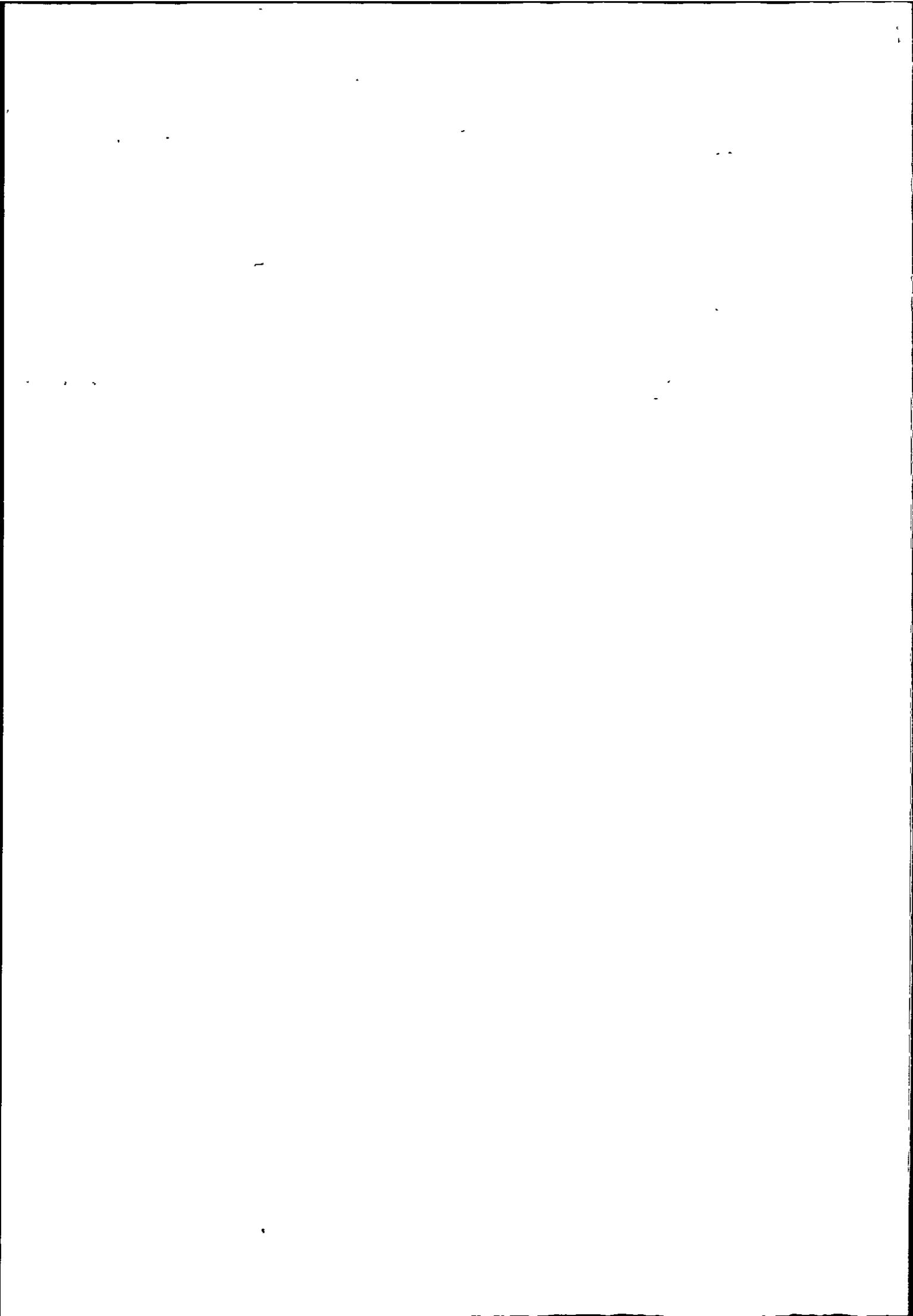
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**Measurement and modelling of uranium and thorium
in natural waters**

by

Emily Rachel Unsworth

A thesis submitted to the University of Plymouth
in partial fulfilment for the degree of

Doctor of Philosophy

Department of Environmental Sciences
Faculty of Science

In collaboration with the
British Geological Survey

2001

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Measurement and modelling of uranium and thorium in natural waters

Emily Rachel Unsworth

Abstract

Uranium and thorium are the only elements in the actinide series which naturally occur in the environment in sufficient amounts for practical extraction. They are both radiotoxic and chemotoxic to humans due to the effects of the ionising radiation produced by their radioactive decay, the decay of their daughter products, and due to the chemical toxicity resulting from absorption into the body. Thus it is important to be able to quantitatively determine the levels of uranium and thorium in the environment.

Measurement of low levels of uranium and thorium in the presence of high levels of inorganic and organic matrix components has been achieved by coupling on-line solid phase extraction (SPE) with inductively coupled plasma mass spectrometry (ICP-MS) detection. This allowed direct analysis of water samples without any sample pre-treatment offering detection limits of 0.01 ng ml^{-1} uranium and 0.006 ng ml^{-1} thorium.

However, in many studies not only do the total levels of uranium and thorium need to be determined, but also their speciation, since this can effect their toxicity and mobility in the environment. An on-line uranium speciation method has successfully been developed using a chelating resin micro-column attached to an ICP-MS. This method has been applied to the analysis of natural water samples (from Dartmoor, Devon, UK) and the results obtained indicate that the uranium-organic species such as those formed with humic substances are the major species present. A comparison of the pH and level of organic carbon (in a range of natural and synthetic water samples), with the level of uranium-organic species indicates that the organic carbon concentration is a controlling factor in determining the level of uranium-organic species formed. The kinetics of dissociation of uranium and thorium-humic substance species was also studied. The slow rate of dissociation observed indicates that once the uranium-humic species have formed these species could remain in the environment for some time. These studies also indicate that even if a change in environmental conditions affected the speciation, it would take time before the uranium and thorium-humic species dissociated and the system equilibrated to a new speciation profile.

Two computer programs (WHAM and PHREEQCI) were used to model uranium and thorium speciation in aquatic systems. The Nuclear Energy Agency Thermochemical Database Project (NEA-TDB) values were incorporated into both programs, as differences in the thermodynamic data provided with the two programs were found to have a major effect on the predicted speciation profiles produced by the two programs. Using the NEA-TDB values, both programs produced similar inorganic speciation profiles for a given aqueous system but when an organic carbon component was added to the system the two programs produced different predictions for the level of uranium-organic species. This reflected the different organic speciation components utilised within the two programs. WHAM uses a discreet site electrostatic humic substance model and PHREEQCI uses an analogy type model based on a 'model fulvic acid' dataset.

A comparison of model predictions with experimental data for the same water sample, indicates that the WHAM program produces closer predictions to the experimental results than the PHREEQCI program. A further study of the WHAM program, using synthetic water solutions with a range of pH, organic carbon and uranium concentrations, indicates that the program has a bias towards low predictions at high pH and low organic carbon concentrations ($\text{pH} > 7$, organic carbon $< 0.5 \text{ } \mu\text{g ml}^{-1}$), but will function satisfactorily within the range of conditions found in the natural (Dartmoor) water samples. The results of these studies should aid environmental investigation based on uranium and thorium where model predictions are to be used.

Author's Declaration

At no time during the registration for the degree of Doctor of Philosophy has the author been registered for any other University award.

This study was financed with aid of a studentship from the Engineering and Physical Sciences Research Council (EPSRC) and the British Geological Survey.

A program of advanced study was undertaken, which included a postgraduate course on Atomic Spectrometry and a course on Research Methods.

Relevant scientific seminars and conferences were regularly attended at which work was often presented and work has been published in a scientific journal.

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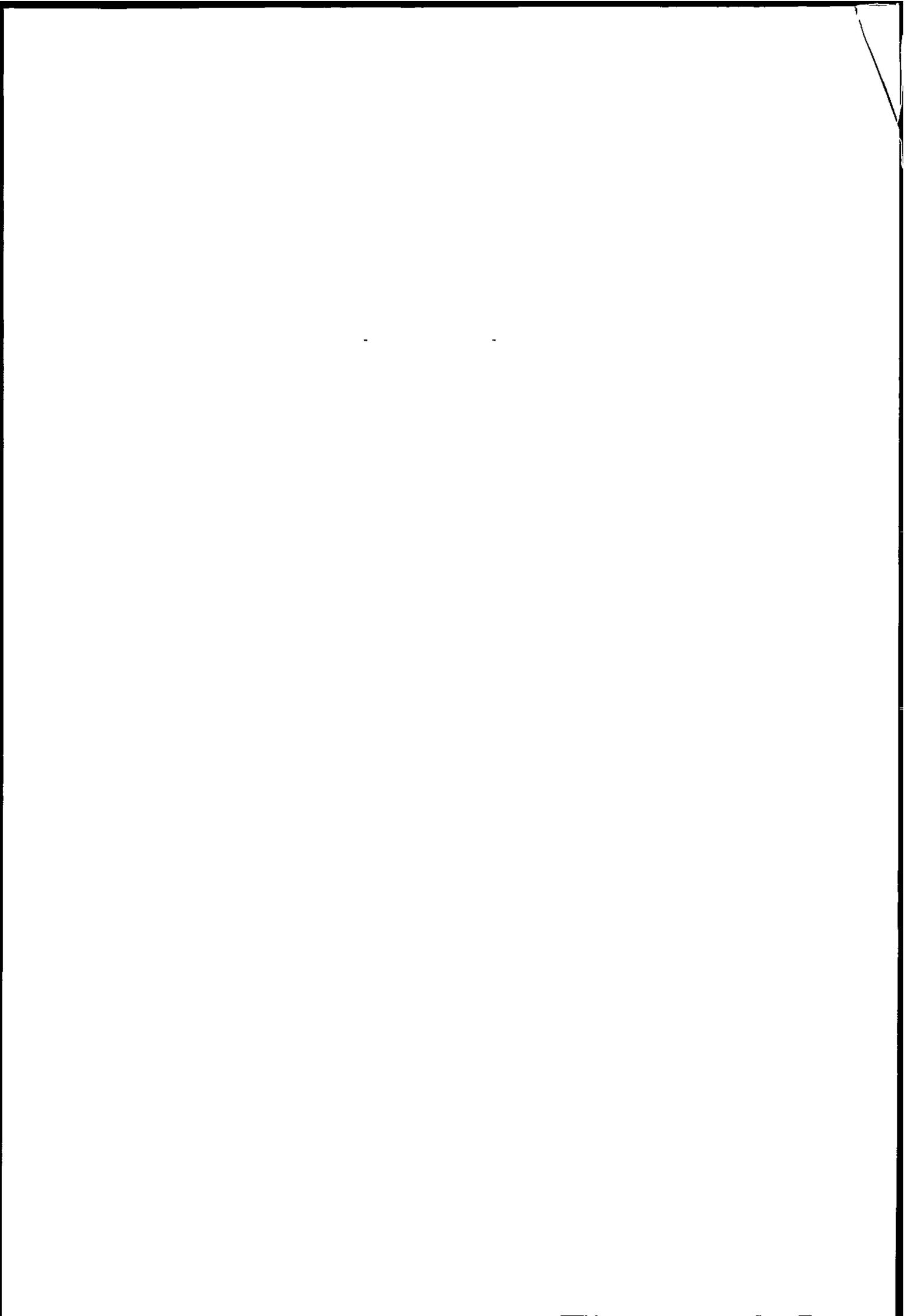
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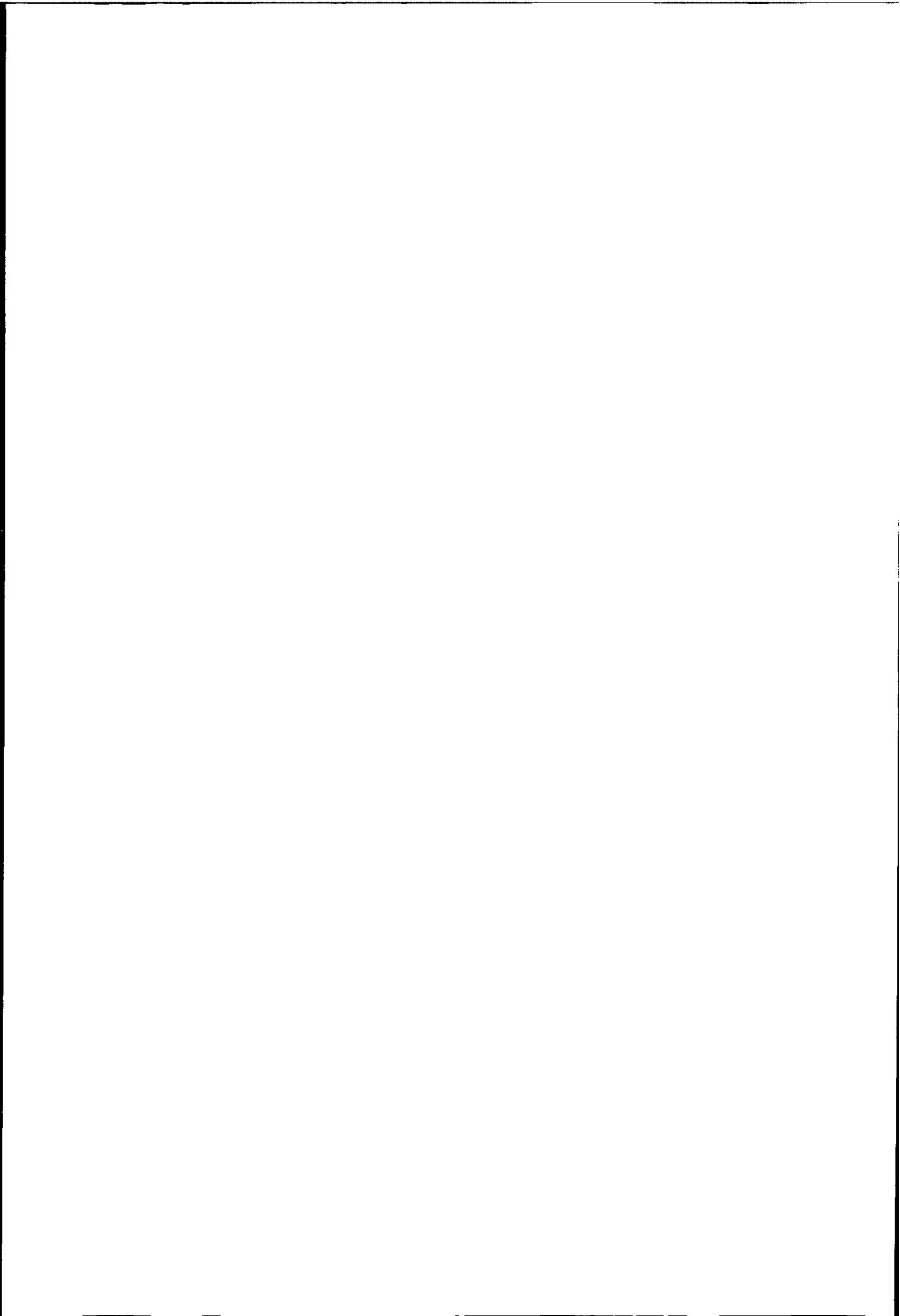
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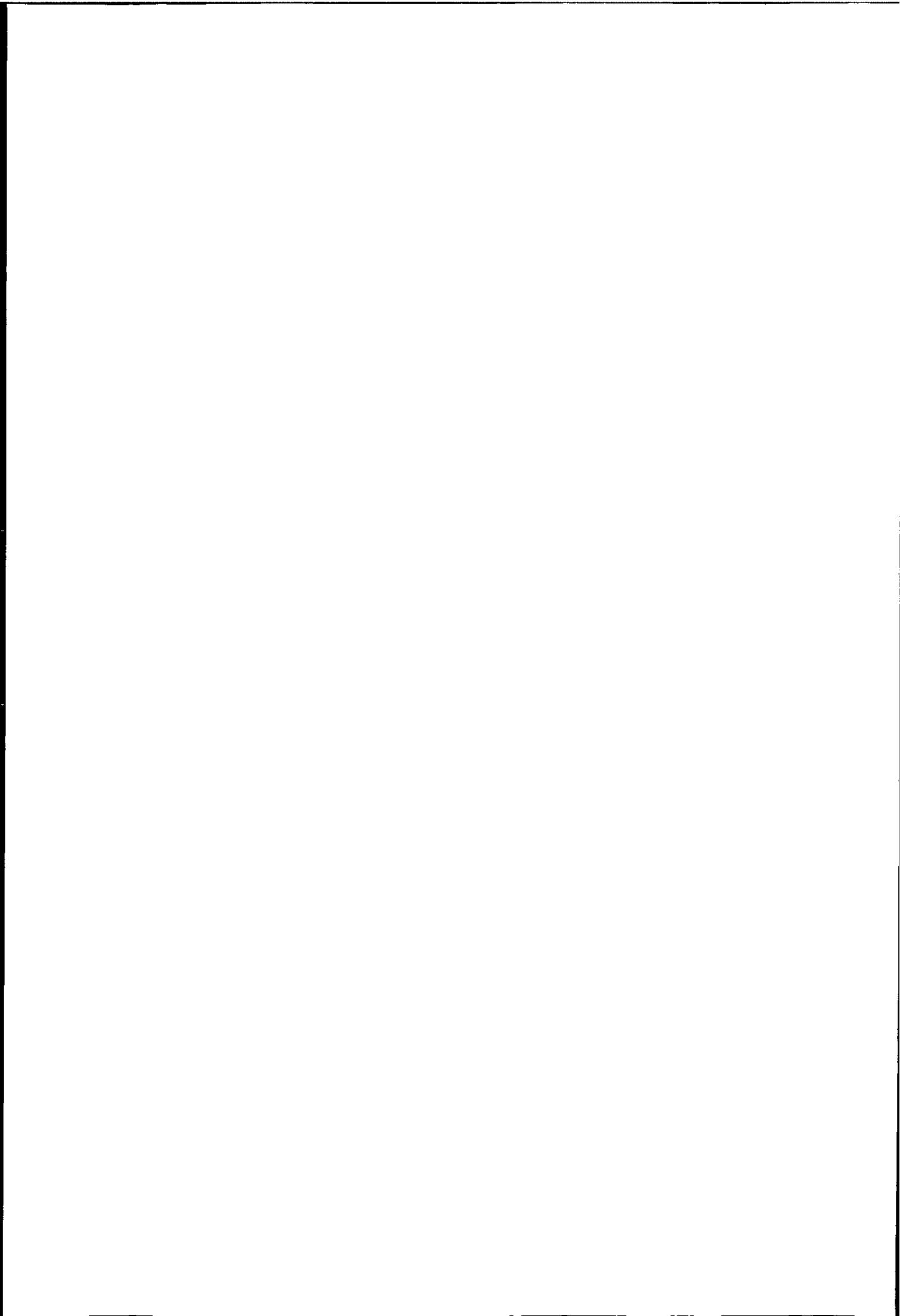
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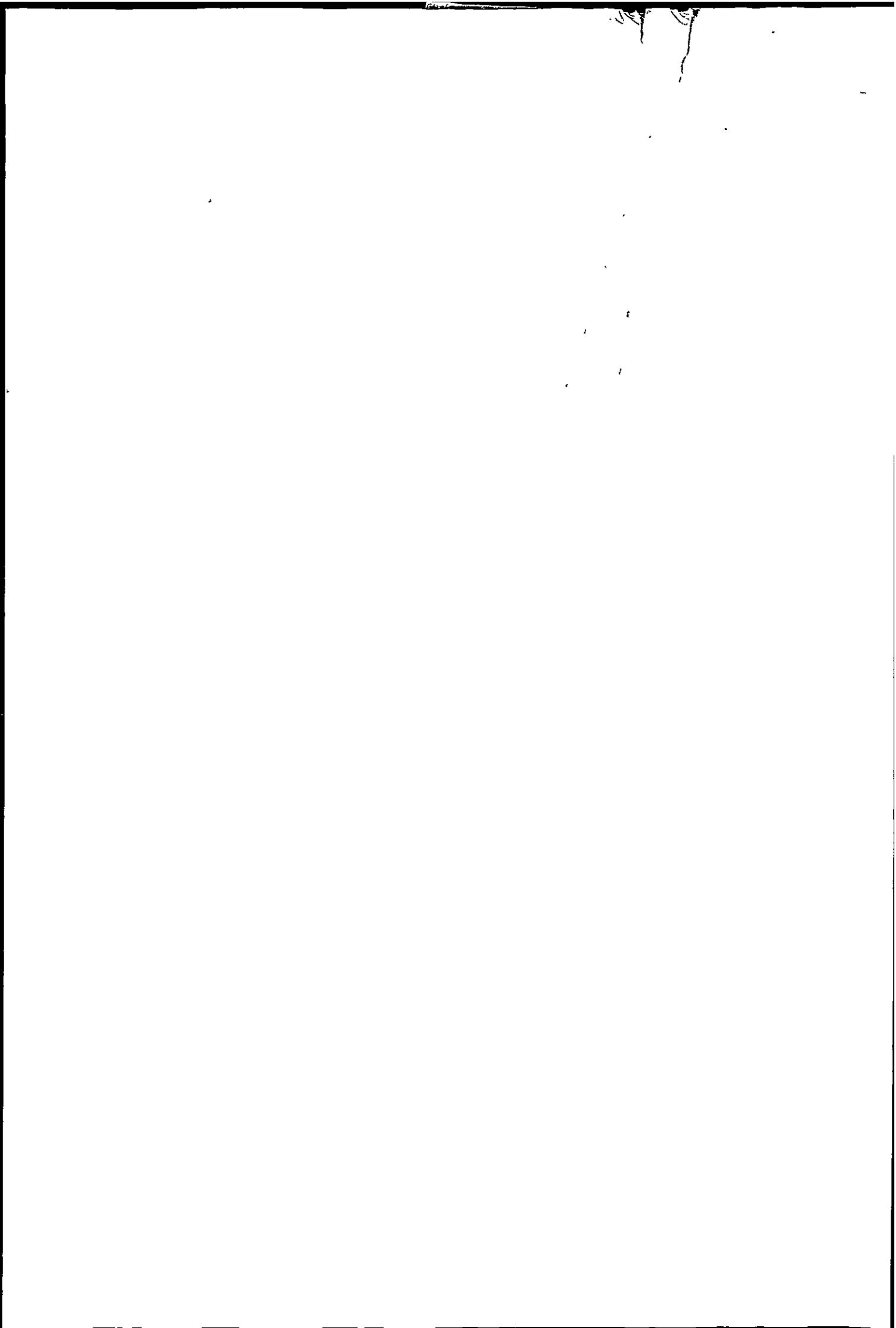


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Chapter One

1. Introduction

This study seeks to investigate the environmental behaviour of uranium and thorium, which occur naturally at low levels in the environment. Since their toxicity to man and other organisms is well documented, the measurement of these potentially dangerous radionuclides is crucial. However, information on both the total concentration and speciation of these two elements needs to be determined, in order to assess their impact in the environment. This study is concerned with their measurement in aquatic samples since this medium can facilitate their dispersion throughout the environment.

1.1 Uranium

Uranium was first discovered by M. H. Klaproth in 1789 in the uranium ore Pitchblend¹. It has an atomic number of 92 and is a radionuclide. It has two naturally occurring long lived isotopes, ^{238}U ($t_{1/2}$ 4.46×10^9 years) and ^{235}U ($t_{1/2}$ 7.04×10^8 years) which form the source of the uranium and actinide decay series. The natural abundance distribution of these isotopes is ^{238}U 99.2739%, ^{235}U 0.7204% and 0.0057% ^{234}U ($t_{1/2}$ 2.45×10^5 years) which is a daughter product of ^{238}U from the uranium decay series. This distribution can be altered by the introduction of uranium isotopes from anthropogenic sources such as nuclear power stations and radioactive waste repositories. There are a large number of uranium minerals, some of the more common ones being Pitchblend (U_3O_8), Uraninite (UO_2), Schoepite ($\text{UO}_2(\text{OH})_2 \cdot 2\text{H}_2\text{O}$), Gummite (UO_3) Coffinite (USiO_4) and Autunite ($\text{Ca}(\text{UO}_2)_2(\text{PO}_4)_2$)^{2,3}. Uranium has several oxidation states ranging from III to VI. The most common state is U(VI) and in acidic aqueous solution this is present as the uranyl ion (UO_2^{2+}). Under reducing conditions it is present in the U(IV) state and as the U^{4+} ion. In neutral conditions the uranyl ion forms hydrolysis products in aqueous solution. In

the presence of carbonate ligands uranium forms soluble carbonato complexes, and will also form sulphate and phosphate complexes in the presence of these ligands. Strong complexes are formed with fluoride ions but only weak complexes with the heavier halides. Uranium also forms complexes with carboxylates, for example oxalate ^{1,4}.

1.2 Thorium

Thorium was first discovered by J. J. Berzelius in 1828. It has an atomic number of 90 and is a radionuclide with one naturally occurring long lived isotope, ²³²Th ($t_{1/2}$ 1.39×10^{10} years). The main source of thorium is from monazite sands which are rare earth orthophosphates containing approximately 5% thorium ¹. Thorium is also found in mineral form as Thorianite (ThO₂), Thorite (ThSiO₄), and to a lesser extent Cerianite ((Ce,Th)O₂) and Thorbastnaesite ((Ce,Th)FCO₃) ^{5,6}. Thorium has a +4 oxidation state and exists as the Th⁴⁺ ion in acidic aqueous solution although it will hydrolyse above pH 3. It also forms strong aqueous complexes with fluoride, sulphate, phosphate, nitrate and carboxylate ligands and weaker complexes with the heavier halides. A general trend for the actinide elements is that the strength of the complexes increases $MO^{2+} < M^{3+} \approx MO_2^{2+} < M^{4+}$ so the thorium complexes will be stronger than the corresponding uranyl complexes ^{1,4}.

1.3 Toxicity

The toxicity of uranium and thorium is due to both radiotoxic and chemotoxic effects. The decay of these radionuclides and their daughter products produces ionising radiation which can have mutagenic, carcinogenic and teratogenic effects on humans ^{7,8}. ²³⁸U and ²³²Th produce alpha radiation (alpha particles have the same composition as helium nuclei) as they decay which would only have toxic effects when in close contact with the subject, for example after incorporation into the body. However their decay products are also toxic. One decay product of ²³⁸U is radon gas (²²²Rn), exposure to which can cause lung cancer ⁹. This is of particular concern in areas where housing is built on granite

bedrock (containing uranium) since radon gas can accumulate in cellars and areas with inadequate ventilation. This problem can also apply when granite is used as a building material and/or potable water is obtained from groundwater associated with granitic rocks.

The primary chemotoxic effect of uranium in humans is nephritis (kidney failure)¹⁰. This is caused by the precipitation of U(VI) in the proximal kidney tubules and the resulting tissue damage leads to kidney failure. Uranium also accumulates in the skeleton, replacing the calcium in the hydroxyapatite crystals in the bone matrix¹¹.

Although thorium is poorly absorbed in the digestive tract, the use of Thorotrast (a colloidal suspension of thorium dioxide) as a radiographic contrast medium has been found to have fatal long term effects¹². Such effects include fatal blood dyscrasia, bone sarcomas and chronic immune system dysregulation, thought to be due, at least in part, to close contact with low level alpha irradiation¹⁰.

Given these potentially lethal effects it is important to be able to monitor the levels of uranium and thorium and to be aware of the factors which can effect their fate in the environment.

1.4 Uranium and thorium in the environment

In the earth's crust uranium and thorium are enriched in silicate rich rocks, and thus granites have a higher uranium and thorium concentration than basalts. In some cases sedimentary rocks may exhibit high uranium concentrations due to secondary enrichment where a strongly reducing environment has caused U(VI) in solution to be deposited as U(IV) which is less soluble¹³.

The movement of uranium and thorium through the environment can be effected by factors such as weathering and leaching from rocks containing uranium minerals and uranium ore deposits. As they migrate through the environment both elements can become 'fixed' in humic rich areas such as peat bogs¹⁴, and billabongs^{15, 16}. Natural uranium and

thorium mineral deposits have been studied as 'natural analogues' to radioactive waste repositories¹⁷⁻¹⁹. Studying the transport of uranium and thorium from these sites by surface and groundwater can provide data on the environmental factors which could effect the mobilisation, or retard the dispersal of, radionuclides from radioactive waste repositories. A study on uranium movement from a river to a groundwater aquifer²⁰ reported seasonal changes in uranium concentration due to the binding, and subsequent release due to photoreductive reactions, of uranium to iron-oxyhydroxides. The transfer of uranium from one phase to another (e.g. solid (sediment) to aqueous) can be tracked using isotope ratio measurements. In an equilibrated system the ratio of parent to daughter isotopes in a decay series will be at a steady state (secular) equilibrium²¹. However transfer of radionuclides outside this system will result in disequilibrium occurring. This can be due to the fact that different isotopes in the decay series have different physio-chemical properties. For example, uranium and thorium have different solubility's in aqueous solution. The ^{238}U nuclide could transfer from the solid phase to the aqueous phase resulting in an increased $^{230}\text{Th}/^{238}\text{U}$ ratio in the solid phase and a decreased $^{230}\text{Th}/^{238}\text{U}$ ratio in the aqueous phase²². This would also apply to the $^{230}\text{Th}/^{234}\text{U}$ ratio. A change in the $^{234}\text{U}/^{238}\text{U}$ ratio can also be observed at rock-water interaction sites. ^{234}U is preferentially leached from the radiation damaged matrix lattice. This is due to the 'alpha recoil' which occurs as the radionuclide decays. The radionuclide recoils, when the alpha particle is ejected, with an energy which is inversely proportional to the radionuclide, alpha particle, mass ratio. This recoil damages the mineral lattice. This happens to a greater extent to the ^{234}U because it has a lower mass and shorter half than ^{238}U ^{21, 22}.

Typical levels of uranium found in natural waters range from 0.1 to 7 ng ml⁻¹ for streams and 2 to 4 ng ml⁻¹ in seawater¹³. Thorium is usually found at lower levels, for example 0.02 ng ml⁻¹ in Norwegian groundwaters²³. However these levels can be elevated due to input from anthropogenic sources such as nuclear power plants and radioactive

waste repositories. UK water quality standards do not include a limit on the level of uranium permissible in drinking water²⁴. Although the World Health Organisation has no set limit on the level of uranium permissible in drinking water (due to lack of chemical toxicity data) it recommends a limit of 140 ng ml⁻¹ based on radiochemical limits¹¹. Other 'commonly suggested limits' range between 14 and 160 ng ml⁻¹²³.

The nature of the environment can also effect the levels of uranium present and its speciation. For example, an increase in the carbonate concentration in water can produce uranium carbonate species which are more soluble than uranium hydrolysis species¹³. Anoxic conditions could reduce the uranium from the more soluble U(VI) oxidation state to the less soluble U(IV) oxidation state. The speciation of uranium can also effect its toxicity. A study on the effect of uranium speciation on bivalve (*Velesunio angasi*) behaviour reported that when groups of these bivalves were exposed to solutions containing the same total uranium concentration, but present as different uranium species, those exposed to inorganic species were more adversely affected than those exposed to organic uranium species^{25,26}. An in vitro study of uranium cytotoxicity reported greater toxic effects observed in cells exposed to uranium carbonate than in cells exposed to uranium citrate. This was due to the uranium citrate not penetrating the cell walls²⁷.

The significance of dissolved humic substances on heavy metal speciation and the formation of metal-organic species has been reported in a study on zinc, cadmium and lead speciation in natural waters²⁸. This study reported that metal-humic substance species were formed when the humic substance concentration exceeded 1 µg ml⁻¹. This level of dissolved humic substance is not typically present in seawater but is often found in rivers and lakes and hence could play a large role in heavy metal speciation. The study also reported that, in the case of the zinc species, fulvic acids had a lower binding capacity than humic acids and the level of metal-organic species formation was pH sensitive²⁸. The potential for dissolved humic substances to also effect uranium and thorium speciation can be seen in a study which

reported 80% thorium-organic species present in water from an old mine¹⁸. Another study using a computer model to predict the uranium speciation (but not determining it experimentally) reported 76% uranium-organic species in solutions containing humic substances²⁶. The interaction of actinides with 'naturally occurring organic compounds' is discussed more fully by Choppin and Allard²⁹.

1.5 Analysis

The presence of trace (ng ml^{-1}) amounts of the actinides in aquatic environmental samples can be determined using a number of techniques. Examples of these as reported in the literature include, radiochemical techniques such as alpha spectrometry^{30,31}, liquid scintillation counting³² and delayed neutron counting^{33,34}, spectrometric methods, uv-vis^{35,36}, inductively coupled plasma atomic emission spectrometry (ICP-AES)^{37,38} and inductively coupled plasma mass spectrometry (ICP-MS)³⁹⁻⁴⁷. The radiochemical techniques utilise the radioactive decay of uranium and thorium and can be sensitive techniques. However, complex sample pre-treatment may be required, for example the use of alpha spectrometry requires co-precipitation of the radionuclides with manganese dioxide, followed by separation using anion exchange chromatography and finally electrodeposition onto metal plates prior to measurement³¹. In other cases large amounts of sample may be required, as in the case of delayed neutron counting where one litre sample volumes may need to be preconcentrated³³. The sensitivity of radiochemical techniques is in part due to the long count times which can be required while analysing the sample, for example a 180 minute count time for a liquid scintillation method³². This does not facilitate rapid sample analysis. Spectrometric detection, when coupled with on-line preconcentration using an ion exchange column, can facilitate the detection of detect low (ng ml^{-1}) levels of uranium³⁶.

Table 1.1 Detection methods used for the determination of actinides in aqueous samples

Detection technique	Application	Ref. No
Alpha spectrometry	Water, soil and fertiliser samples.	30
Alpha spectrometry	Water, sediment and biological materials.	31
Liquid scintillation counting	Drinking water.	32
Delayed neutron counting	Natural waters.	33
Delayed neutron counting	Water and occupational health samples.	34
Spectrophotometric (UV-Vis)	Rock and water samples.	35
Spectrophotometric (UV-Vis)	Spiked water samples and ore leachates.	36
ICP-AES	Surface water samples.	37
ICP-AES	Uranium waste solutions.	38
ICP-MS	Urine samples.	39
ICP-MS	Environmental samples.	40
ICP-MS	Marine sediment pore waters.	41
ICP-MS	Pure water and seawater samples.	42
ICP-MS	Surface and seawater.	43
ICP-MS	Radioactive waste samples.	44
ICP-MS	Industrial waste-water.	45
ICP-MS	Urine samples.	46
ICP-MS	Groundwater samples.	47

ICP-MS is a technique which can provide rapid (e.g. 30 second acquisition time) and sensitive ($< \text{ng ml}^{-1}$ detection) analysis of samples containing uranium and thorium. The sample matrix can however give rise to interference effecting the detection of uranium and thorium. For example, high levels of an easily ionisable element such as sodium in the sample matrix can cause signal suppression of the analyte due to the plasma being 'saturated' by the ionised sodium and the resulting excessive electron density reducing the number of analyte ions⁴⁸. High levels of dissolved solids (e.g. $> 1\%$) in the sample can lead to a blocked nebuliser, torch and cones, as the dissolved solids come out of solution. This can in part be reduced by using a high solids nebuliser and a wide bore torch. However removing the analyte from the matrix would remove these problems and facilitate a more efficient analysis.

To remove the matrix interference may necessitate some form of sample pre-treatment. Sample dilution^{41, 46} will reduce the matrix effects but will also reduce the uranium and thorium concentration. Although low detection limits (0.1 pg ml^{-1}) have been obtained for diluted samples using a sector field ICP-MS⁴⁹⁻⁵¹, problems have been reported for studies using quadrupole ICP-MS. Even with diluted samples Roduskin and Ruth⁵¹ report in excess of 50% signal loss for a 10-fold dilution of NASS-4 seawater using a quadrupole instrument. A matrix removal technique such as solid phase extraction (SPE)⁵² separates the analyte from the matrix without reducing the analyte concentration and has the advantage, when coupled on-line, of only requiring a small sample volume. The use of a number of different resins for SPE (coupled with a range of different detection techniques) have been reported in the literature (see Table 1.2). These include cation exchange^{35, 36, 43}, reverse phase chromatography⁵³, chelating resins^{37, 38, 42, 54, 55}, and extraction type resins^{47, 56}. The extraction resin only has an affinity for actinides and hence a high selectivity towards the uranium and thorium present in a sample.

Table 1.2 Solid phase extraction (SPE) resins used for matrix removal with samples containing uranium and thorium

SPE resin	Application	Ref. No
Duolite C ₂₂₅ (H)	Cation exchange. Uranium in rock and water samples. Spectrophotometric detection.	35
Dowex 50-X8	Cation exchange. Spiked river water samples. Spectrophotometric detection.	36
Ion-Pac CG5 and CS5	Mixed cation and anion exchange resin. Surface water samples spiked with actinides. Low recoveries from samples containing humic acid. Flow-through scintillation detection.	78
Alumina	Exhibits cation exchange properties under basic conditions (used with 0.02M ammonium hydroxide). Surface and seawater samples. ICP-MS detection.	43
Brownlee OD-032	Silica base RPHPLC resin. Ground and surface waters. Low recoveries from uranium spiked peat bog waters thought due to uranium-organic complexes. Spectrophotometric detection.	53
Prosep	Iminodiacetate (IDA) on a controlled pore glass support. Pure water and artificial seawater samples. ICP-MS detection.	42

Chelex-100	IDA on a styrene divinylbenzene support. Low recoveries thought due to organic uranium species. Alpha counting detection.	77
Chelex-100	IDA on a styrene divinylbenzene support. Fresh and saline waters. Spectrometric and flurometric detection.	54
Hyphan	1-(2-hydroxyphenylazo)-2-naphthol on a cellulose support. Surface waters samples. ICP-AES and alpha counting detection.	37
TAR	4-(2-thiazolyazo)resorcinol on a styrene divinylbenzene support. Seawater and uranium waste effluents. ICP-AES detection.	55
TAR	4-(2-thiazolyazo)resorcinol on a styrene divinylbenzene support. Uranium waste solutions. Neutron activation analysis.	38
TRU spec	Octyl(phenyl)-N,N-diisobutyl carbamoylmethylphosphine oxide in tri-n-butyl phosphate (CMPO/TBP) on a polymeric base. Certified groundwater samples. ICP-MS detection.	47
TRU spec	CMPO/TBP on a polymeric base. Synthetic groundwater solutions. Alpha and gamma counting detection.	56

Analysis of the different uranium and thorium species present in a water sample presents further potential problems. For example, if the sample were acidified prior to storage and analysis this would alter the distribution of the species present (e.g. a higher proportion of the uranium could be present in the form of the uranyl ion once the sample was acidified than was present in the original water sample at natural pH). The use of different reagents in a separation technique could also effect the speciation. An example of this would be an oxalate eluent used with the TRU-spec solid phase extraction resin^{47,56} which would react with the uranium and thorium to form oxalate species. A number of different techniques reported in the literature for the determination of uranium and thorium species are listed in Table 1.3. Time-resolved laser-induced fluorescence (TRLFS) is a non-intrusive technique which can be used to determine uranium speciation in aqueous samples without affecting the nature of the species present^{57,58}. However matrix effects have also been reported as affecting this technique⁵⁹. Both cation and anion exchange resins have been reported as being used to separate different uranium oxidation state species^{60,61}. The anion exchange method used sealed apparatus to prevent oxidation of the U(IV) species. The use of a cation exchange resin has also been reported for the separation of inorganic and organic uranium species. In this case the inorganic uranium species are assumed to be in cationic form and hence retained on the resin⁶². Although the sequential extraction studies do not provide information on the uranium and thorium species in terms of chemical identity, they do provide speciation data in terms of bioavailable and residual species (each fraction from the extraction being a different species).

Table 1.3 Uranium and thorium speciation techniques

Speciation technique	Application	Ref. No
Time-resolved laser-induced fluorescence (TRLFS)	Influence of calcium concentration on uranium speciation in terms of the formation of calcium uranium carbonate species in 'natural seepage water'.	57
Time-resolved laser-induced fluorescence (TRLFS)	Uranium speciation in aqueous solutions and detection of uranium hydroxide and uranium phosphate species.	58
Time-resolved laser-induced fluorescence (TRLFS)	This technique has poor quantum efficiency in water and suffers from matrix effects.	59
Cation exchange separation using Dowex 50W-X8 (off-line)	Uranium oxidation state speciation in natural high carbonate waters.	60
Anion exchange separation using Dowex 1 (off-line)	Uranium oxidation state speciation in leachates from nuclear fuel pellets.	61
Cation exchange separation using Dowex 50X4 (off-line)	Separation of inorganic and organic species in synthetic aqueous solutions.	62
X-ray absorption spectroscopy	Determination of uranium oxidation state in contaminated soils.	63
X-ray absorption and X-ray fluorescence spectroscopy	Determination of uranium speciation in sand, clay and silt from soil.	64
Sequential leaching	Uranium and thorium speciation in suspended matter in marine waters.	65
Sequential leaching	Uranium speciation in particulate matter in seawater.	66
Sequential leaching	Uranium and thorium speciation in sediments from river beds.	67
Sequential leaching	Uranium in inter-tidal sediments, near a phosphoric acid plant.	68

1.6 Computer models

The term computer modelling is applied, in this study, to the use of computer programs to solve chemical equilibrium problems in aqueous systems by the application of physico-chemical principals. Computer models can be used to predict the speciation of an element within an aqueous system. By changing the input parameters 'what if' scenarios can be investigated in order to predict the potential changes in speciation due to, for example, the interaction of uranium with phosphate from fertiliser run-off or humic substances in bogs and settling ponds. Models can also be used to predict the speciation in situations where a sample is not available for analysis. However in this case the accuracy of the prediction would depend on the information available to model the system.

An early example of a computer program used to model the chemical equilibria of aqueous solutions is PATHI (1970), a mass transfer program modelling mineral-water interactions⁶⁹. An overview of early computer programs⁷⁰ (Table 1.4) covers programs which were developed to deal with specific situations such as acid mine drainage and waters from geothermal sources. Although programs such as PHREEQE were initially used for geochemical applications⁷¹⁻⁷³, more recently the use of these speciation programs has been applied to environmental situations^{20, 25, 26}. For example, studies to predict the effect of uranium speciation on toxicity have been reported using HARPHRQ (a modified version of PHREEQE) where the predicted speciation of uranium is linked to its effect on aquatic life forms^{25, 26}. A further study²⁰ used MINTEQA2 to model the chemical speciation and transport mechanisms of uranium in the aqueous environment following the infiltration of uranium from a river into a shallow aquifer. This type of work has required the addition of organic species into the programs, or the development of new programs to take into account the potential interactions of metals (for example uranium and thorium) with organic compounds (for example DOC) in order to provide a more complete picture of the potential

metal speciation in environmental situations. One such program is the Windermere Humic Aqueous Model (WHAM)^{74,75} which incorporates the earlier Tipping model V humic substance model⁷⁶.

Table 1.4 Computer programs used to predict metal speciation in aqueous systems

Program	Application
PATHI	1970 Mineral-water mass transfer interactions.
SOLMNEQ	1973 Waters from geothermal sources.
WATCHI	1982 Waters from geothermal sources.
RIVEQL	1982 Acid mine drainage interaction with rivers.
PHREEQE	1980 Modelling groundwater systems.
WATEQ3	1981 WATEQ2 rewritten to incorporate uranium speciation.
WATEQFC	1981 WATEQF updated for use in uranium ore exploration.
EQ3/6 PHREEQE HARPHRQ MINEQL	1992 Uranium and thorium solubility and speciation in groundwaters modelled using these programs produced a range of different results.
MINTEQA2	1994 Effect of speciation on the transport of uranium from a river to an aquifer.
HARPHRQ	1994 Predicting the impact of uranium species on fresh water biota and incorporating organic species into the program.
WHAM	1994 Modelling metal-humic substance species.

1.7 Aims and objectives

A key objective of this study was to develop an on-line SPE-ICP-MS method for the analysis of uranium and thorium in aqueous solutions. In order to achieve this, various resins needed to be evaluated. The resin required should provide a high degree of specificity toward the analytes and function in the presence of high levels of both inorganic and organic matrix components. One such resin offering potential for this study was TRU spec. It was also hoped that the use of this resin would overcome the problems associated with low recoveries due to the presence of dissolved organic carbon in the samples, which have been reported in the literature for methods using conventional chelating and ion exchange resins^{53, 77, 78}.

For most studies, not only is the determination of the total uranium and thorium concentration in a sample required, but information regarding the nature of their speciation is also important as this can effect a number of environmental factors such as their mobility and toxicity. Uranium and thorium speciation will be investigated in this study using two different approaches. The first is the experimental determination of the speciation and the second is the prediction of the speciation using computer models. The experimental results obtained in the former approach will provide an indication of the validity of the computer models for real samples.

The aim of the experimental methodology will be to separate the inorganic and organic uranium and thorium species using a chromatographic separation technique utilising ICP-MS detection. This technique would not be expected to facilitate the separation of individual inorganic species (e.g. hydroxide and carbonate species) as the nature of these species would be effected by changes in pH and/or mobile phase composition inherent in most chromatographic separations. However, it is the differentiation between inorganic and

organic species which is important in determining the overall toxicity of the sample²⁵⁻²⁷ and this will be the focus of this work.

The development of an experimental speciation method will allow the analysis of natural water samples from Dartmoor (Devon, UK), which is situated on granite bedrock. This will provide data on the level of uranium-organic species present in this type of sample and indicate whether these are a major species with regard to uranium speciation in environmental samples. This knowledge will also aid in the study of which factors may potentially influence the formation of uranium-organic species, such as, sample pH, organic carbon and uranium concentrations. A study of the kinetics of uranium-organic species dissociation, at uranium and organic carbon concentrations typically found in natural water samples, will also be undertaken to give an indication of the stability of such species in the environment.

The use of computer models will allow the prediction of uranium and thorium speciation in aquatic systems. Theoretical studies will be carried out modelling a synthetic surface-water system in order to assess which factors will affect the functioning of the computer programs in terms of predicted speciation. By modelling the speciation in 'real' Dartmoor water samples and by comparing the model predictions obtained with to the experimentally determined results an indication of the models ability to correctly predict uranium and thorium speciation may be evaluated. To predict the level of organic species, two different types of computer model will be used. These are, WHAM⁷⁴, which incorporates a discrete site electrostatic humic substance model in the program, and PHREEQCI⁷⁹, to which will be added the 'model fulvic acid' data set from ANSTO. Given the variation and lack of agreement for speciation results from different programs reported in the literature⁵, the functioning of the two programs will be compared and evaluated before they are used to model 'real' water samples. By modelling a range of different water samples with varying uranium and organic carbon compositions an insight into the

functioning of the programs may be obtained with a view to refine the models for future work.

In summary, the investigations carried out during this study and reported in this thesis may be broadly divided into four sections :-

- Development and characterisation of an analytical method for the determination of uranium and thorium in aqueous samples in the presence of inorganic and organic matrix components.
- Development and characterisation of a method to determine the speciation of uranium and thorium in natural water samples and the use of this method to investigate the factors effecting the formation of organic species.
- The use of computer models to predict uranium and thorium speciation in an aqueous system. An investigation of why different computer programs may produce different speciation results for the same system. The production of speciation models to illustrate the predicted effect of changes in component levels (e.g. carbonate concentration) on the speciation profile.
- A comparison of computer model predictions and experimental speciation results, using two different types of computer model to aid the development of new models for future work.

Chapter Two

2. Experimental

This chapter overviews the basic theory behind the analytical techniques used in this study and the specific parameters used in the methods developed and procedures used.

2.1 Inductively coupled plasma mass spectrometry (ICP-MS)

2.1.1 Background to the technique

An inductively coupled plasma (ICP) provides the ion source for elemental detection using the mass spectrometer (MS) to which it is attached. This coupling of the ICP to the MS was first achieved by Houk et al.⁸⁰. The temperature of the plasma is approximately 6000 to 8000K, which results in a complete breakdown of the sample into its constituent atoms followed by ionisation. The complete process from sample introduction to detection consists of the following stages^{81, 82}. The sample is introduced into the instrument in the form of a liquid. This is converted into an aerosol by the nebuliser. This aerosol is then carried by a stream of gas through the spray chamber which separates out the larger droplets. The smaller droplets pass through the spray chamber into the injector tube of the ICP torch and into the plasma 'fireball'. Here the aerosol is desolvated, decomposed and ionised by the plasma. The ions then pass through the sample and skimmer cones into the MS and are separated on the basis of their mass to charge ratio (m/z). These ions then pass into the detector (usually an electron multiplier) and the resulting signal is recorded by the data acquisition software. The overall configuration of these components in a typical ICP-MS instrument can be seen in Figure 2.1.

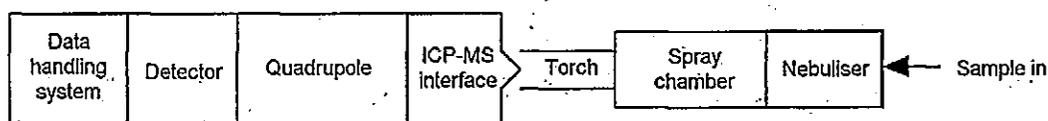


Figure 2.1 Schematic diagram of the components in an ICP-MS

Considering each of these stages in further detail :-

Sample introduction : The sample (solution or slurry) is pumped into the instruments sample introduction system, usually using a peristaltic pump. However sample may also be introduced to the instrument sample uptake capillary using, for example, flow injection or chromatographic systems. The sample introduction system used in this study will be discussed later in this chapter.

Nebulisation : There are a range of different types of nebuliser available, depending on the type of sample to be analysed. Typically a concentric nebuliser is used for samples with low levels of dissolved solids. In this case the flow of gas through the nebuliser creates a drop in pressure which draws the sample through the nebuliser by the Venturi effect (if it wasn't already being pumped into the nebuliser). The passage the sample and gas take through the nebuliser narrows towards the outlet, as seen in Figure 2.2, and it is at this point that the drop in pressure shatters the liquid into small droplets (the aerosol)⁸². The disadvantage of this type of nebuliser is that the very small (<1 mm) outlet can easily become blocked. To avoid this occurring a 'high solids' nebuliser can be used. In this study an Ebdon V-groove nebuliser was fitted to the instrument. With this type of nebuliser the sample passes through a relatively large outlet and down a V groove channel in the nebuliser (see Figure 2.3). This passes over a relatively small outlet through which the nebuliser gas passes. The high velocity of the nebuliser gas passing through the liquid shatters it, forming the aerosol. Since the liquid does not pass through a narrow orifice the nebuliser is not prone to becoming blocked.

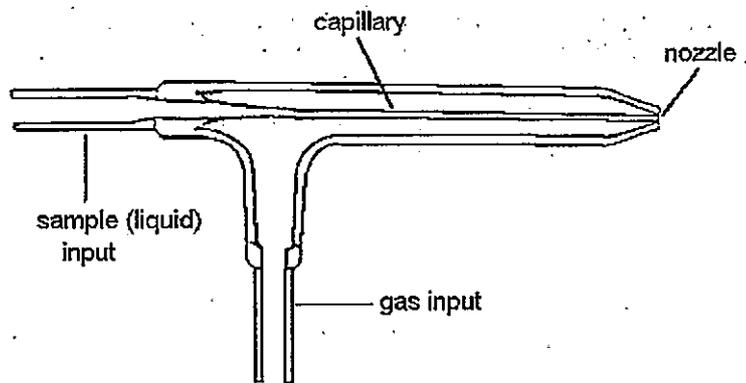


Figure 2.2 Concentric nebuliser

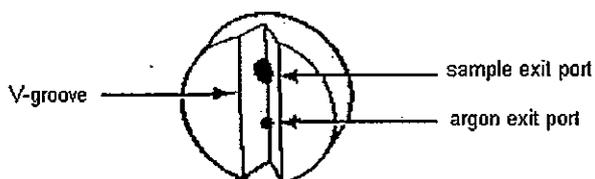


Figure 2.3 V-groove (high solids) nebuliser

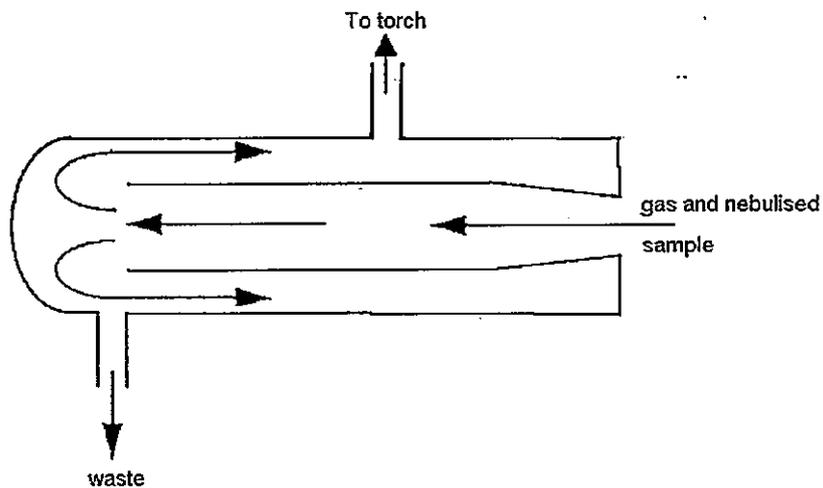


Figure 2.4 Scott double pass spray chamber

Spray chamber : A typical type of spray chamber⁸² and that used in this study, is the Scott double pass spray chamber (see Figure 2.4). The sample aerosol carried by the nebuliser gas flow passes through the spray chamber. The larger droplets in the aerosol are not carried around the 'U-bend' in the spray chamber by the nebuliser gas and collect in the bottom of the spray chamber to be drained to waste. Large droplets would produce a less homogenous aerosol and cause fluctuations in the plasma. A cooled spray chamber also causes solvent vapour carrier by the nebuliser gas to condense on the spray chamber walls. This reduction of the solvent vapour level entering the plasma reduces the formation of potential interferences such as ArO^+ ions (see spectroscopic interferences). The transport efficiency through the spray chamber is very low (typically 1%), i.e. the aerosol leaving the spray chamber contains approximately one percent of the sample present on introduction. The effect of the spray chamber on the aerosol is discussed in further detail by Sharp⁸³.

ICP torch : After the aerosol has passed through the spray chamber it enters the injector tube of the ICP torch. This is the innermost of three concentric tubes of which the torch is composed (see Figure 2.5). Typically the torch is quartz in composition but ceramic torches are occasionally used. The plasma gas (usually argon) flows through all three concentric tubes. The gas flow through the outer tube is the 'coolant' gas (13 to 15 l min⁻¹) and the middle gas flow is the 'plasma' gas (1 l min⁻¹). These two gases enter the torch tangentially causing the gas to spiral upwards through the torch. This replenishes the argon in the plasma and constrains the shape of the 'fireball'. This also results in a less stable weak spot to forming at the base of the plasma through which the nebuliser gas, coming through the injector tube, can punch through the plasma. The top of the torch is surrounded by a water cooled copper coil which carries the radio-frequency (RF) current used to sustain the plasma.

Plasma : A plasma is a mixture of positive ions, electrons and neutral species of an inert gas⁸⁴. It is created, in the case of an ICP, by coupling RF energy (27 MHz or 40 MHz), via an

induced magnetic field, into the plasma gas. The magnetic field is formed by the RF current, perpendicular to the RF coil. This magnetic field, along with the coolant gas, also holds the plasma away from the torch walls and thus preventing it from melting. To initiate plasma formation the gas is seeded with electrons by a spark from a tesla coil. These electrons are accelerated in the magnetic field and excite the plasma gas atoms ionising them, which in turn causes further atoms to be excited, this 'cascade effect' results in the plasma 'fireball'. The majority of the RF energy is coupled to the outer region of the plasma, known as the 'skin effect'. This results in the centre of the plasma being relatively cooler and being heated by conductive and radiative energy transfer from the outer 'skin' region. Overall the plasma is not in local thermal equilibrium⁸⁴. Collisions between atoms, ions and electrons disrupt the equilibrium between states resulting in the kinetic, excitation, ionisation, electron and rotational temperatures not all having the same value.

ICP's are typically formed using argon gas although they can be formed using other gases⁸⁵. Factors to be considered when selecting a plasma gas for analytical use include :-

High ionisation energy to facilitate sample ionisation and high thermal conductivity to allow heat transfer to the core of the plasma, but not so high that the plasma is hard to sustain due to cooling as heat is transferred out of the plasma into the surrounding environment.

At a typical usage rate of 15 l min⁻¹ an ICP can be expensive to maintain.

Ionisation energies for potential plasma gases are in the order He>Ne>Ar>N>Kr>O>H>Xe and thermal conductivity of the monoatomic gases in the order He>Ne>Ar>Kr>Xe⁸¹. This would indicate that helium would be a favourable plasma gas with a high ionisation energy.

However its high thermal conductivity would lead to a plasma which could be hard to sustain. Another possibility is neon. This has a lower thermal conductivity which should result in a more easily sustainable plasma but given that the cost of neon is at present approximately sixty times greater than that of argon it could be prohibitively expensive.

Argon has a high enough ionisation energy to ionise most elements and a thermal

conductivity which will heat the core of the plasma. Also its major isotope (^{40}Ar) has a 99.6% abundance which would reduce the level of spectroscopic interferences from other isotopes. Interferences will be discussed later in this chapter.

ICP-MS interface : The ICP operates at atmospheric pressure whereas the MS operates in a vacuum ($\sim 1.6 \times 10^{-6}$ mbar). This pressure differential is overcome by sequentially lowering the pressure at each stage between the plasma and the MS. At the interface the plasma is physically in contact with the surface of the sampler cone. The centre of the plasma is aligned with the hole in the centre of the sampler cone (~ 1 mm diameter) and the ions from the plasma pass into the 'expansion region' between the sampler and skimmer cones (see Figure 2.6). A rotary vacuum pump reduces the pressure in this region to ~ 2 mbar. This drop in pressure caused a supersonic, adiabatic, expansion of the ion beam⁸¹. The resulting shock wave is called the 'mach disc'. The region of expanding ions is known as the 'zone of silence'. The mach disc impacts on the skimmer cone which has a hole at its centre (~ 0.7 mm) axially aligned with the sampling cone.

Ion lenses : The resulting ion beam which emerges through the skimmer cone enters a vacuum chamber ($\sim 1 \times 10^{-4}$ mbar) containing the ion lenses which focus the beam onto the entrance of the MS⁸⁴.

Mass Spectrometer : The MS separates the ions based on their mass to charge (m/z) ratio. Since the ions from the plasma are usually singly charged the m/z is usually equivalent to the mass. The MS is typically a quadrupole instrument, as was the case in this study. This is composed of four metal rods with a hyperbolic cross section arranged as shown in Figure 2.7. This region of the instrument operates under a high vacuum ($\sim 1.9 \times 10^{-6}$ mbar). RF and DC voltages are applied creating an electric field between the rods⁸⁶. As the RF/DC ratio is changed the field between the rods allows ions with different m/z ratios to pass through. The path of the other ions through the quadrupole is disrupted and they do not reach the detector. By changing the RF/DC ratio incrementally a sequential scan of

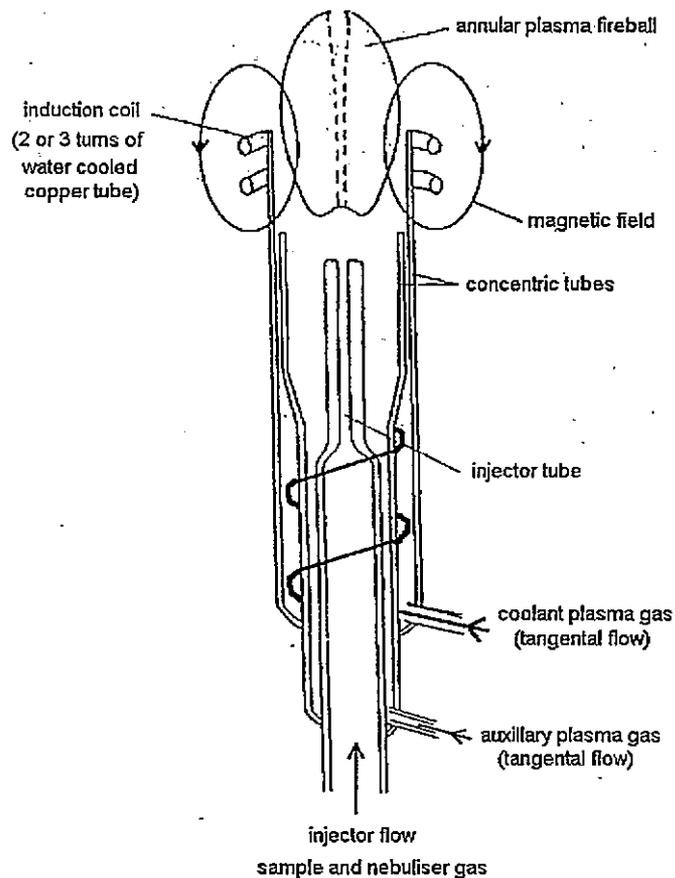


Figure 2.5 ICP torch

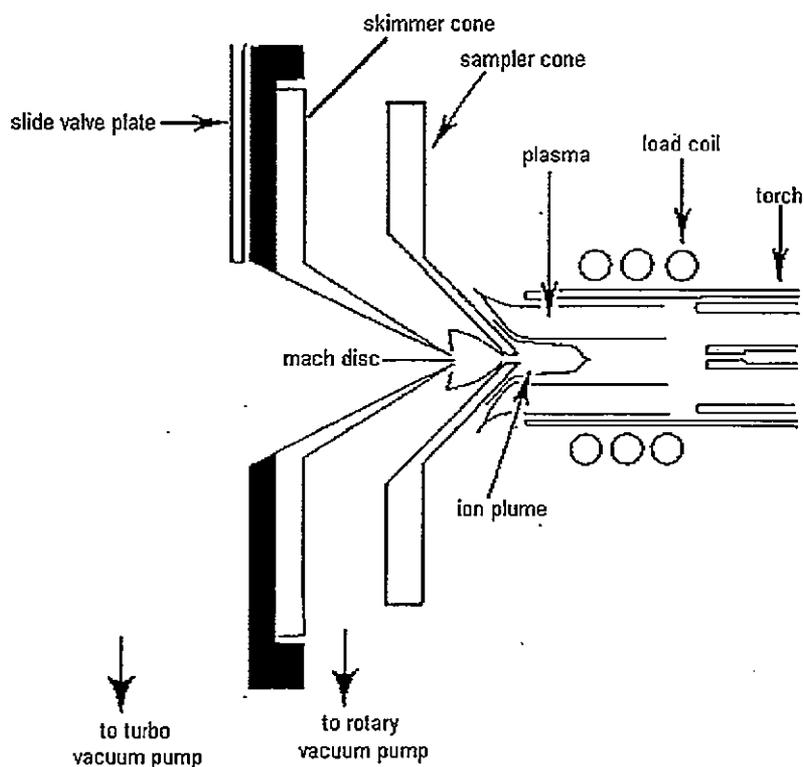


Figure 2.6 ICP-MS interface

increasing m/z ratios can be performed. Alternatively the RF/DC ratio could be changed to allow ions of a particular m/z to pass, jumping from a low m/z to a high m/z without allowing intermediate m/z ratio ions through. This 'peak jumping' mode can be used to detect specific elements without performing an entire m/z range scan. The range of m/z ions which can pass through the quadrupole for any given RF/DC ratio is typically 0.8 m/z . This allows for atomic mass unit (amu) resolution and separation of different elements but not of spectral interferences (e.g. Fe^+ m/z 55.9349, ArO^+ m/z 55.9572).

Detector : Once the ions of selected m/z ratio have passed through the quadrupole they enter the detector. The most common type of detector is the electron multiplier⁸¹. This is a curved horn shaped glass tube. The ions enter at the wide end and hit the sensitive coating on the inner wall of the tube. This in turn releases electrons which then travel further down the 'horn' colliding with the walls and releasing more electrons to give rise to a cascade effect (see Figure 2.8). The number of electrons detected at the end of the detector provide a greatly enhanced signal compared to that which originally entered the detector. This signal is recorded by the data acquisition software and reported as either counts per second (cps) or in the form of a chromatogram in the case of time resolved analysis (TRA) mode acquisition. Because the detector is also sensitive to light a photon stop is situated at the entrance to the quadrupole to block the passage of light into the instrument. Alternatively an 'S-bend' is placed at the end of the quadrupole before the detector through which the ions can be deflected but not the light.

A typical quadrupole ICP-MS instrument can provide rapid (30 s acquisition time), sensitive ($\text{LOD} < \text{ng ml}^{-1}$) sequential (almost simultaneous, 100 ms scan time) multi-element analysis, with a linear dynamic range of 10^7 in single, pulse counting, mode and 10^9 in dual, pulse counting and analogue, detection mode.

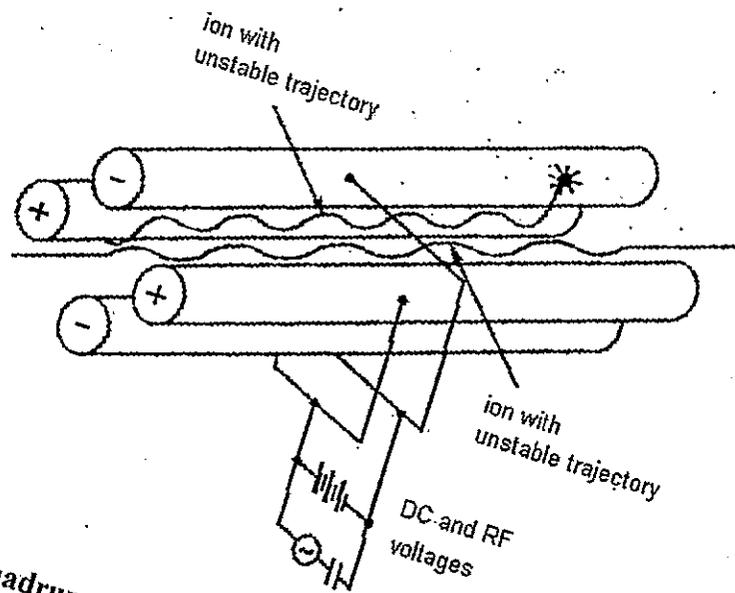


Figure 2.7 Quadrupole mass spectrometer schematic diagram

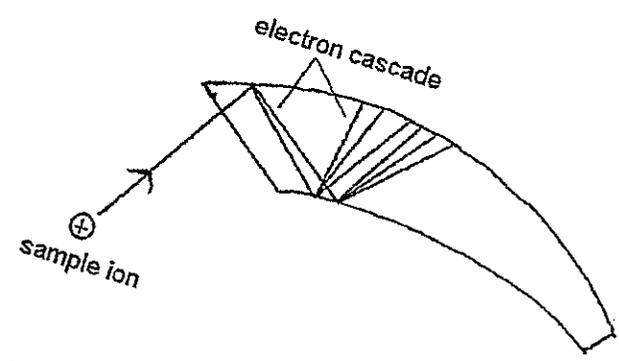


Figure 2.8 Electron multiplier detector

2.1.2 Interferences

Although ICP-MS is a rapid, sensitive, multi-element technique it does suffer from a number of interferences. These can be broadly divided into two categories, spectroscopic and non-spectroscopic.

Spectroscopic : These are caused by atomic or molecular ions with the same nominal m/z ratio as the analyte ion. This can be due to either overlapping isotopes of different elements, in which case a different analyte isotope could be measured, or alternatively due to molecular or polyatomic ions formed from the reaction of the plasma gas with the atmospheric gasses and water vapour⁸¹. These are an intrinsic part of the plasma process and will always be present to some extent. Molecular ions can also be formed by reactions of the plasma gas with the sample matrix. These can be reduced by, for example, changing the reagents used in the sample preparation (replace HCl with HNO₃ to reduce ArCl⁺ formation) or using a mixed gas plasma (thought to reduce polyatomic ions such as ArAr⁺ and ArO⁺ by reducing the ionisation temperature). Using an instrument with a higher resolution (such as a sector field instrument) could facilitate separation of the interfering ion from the analyte ion (e.g. Fe⁺ m/z 55.9349, ArO⁺ m/z 55.9372).

Non-Spectroscopic : In this case reduction or enhancement of the analyte signal is not caused by ions with the same nominal m/z ratio, but due to factors such as the effect of the sample matrix on transport efficiency, ionisation and blockages in the instrument due to the matrix. The sample matrix can effect the viscosity and evaporation rate of the sample which in turn effects its nebulisation and aerosol transport properties^{83, 87}. This can be accounted for to some extent by using matrix matched standards. A matrix containing a high level of an easily ionisable element (e.g. Na) can result in an excess of electrons and ions from the easily ionisable element in the plasma suppressing ion formation of the analyte atoms, resulting in a reduced analyte signal⁴⁸. The deposition of dissolved solids present in the

sample can result in partly or even total blockage of the nebuliser, torch and cones, and thus resulting in a drop in analyte signal⁸⁸. This can, to some extent, be alleviated by the use of a 'high solids' nebuliser and a wide bore torch (3 mm instead of 1.5 mm injector tube). Non-spectroscopic interferences can also be accounted for using an internal standard which should be effected by the interference in a similar manner and extent as the analyte, hence the ratio of the response of the analyte and internal standard would remain constant. In isotope dilution analysis⁸⁴ the sample is spiked with an enriched isotopic standard which is in effect an internal standard, and being the same element (although a different isotope) it would be effected in an identical manner to the analyte.

Alternatively the analyte could be separated from the matrix using some form of separation technique prior to analysis.

2.1.3 Total analyte measurement using the TRU-spec solid phase extraction

resin

This section describes the experimental parameters and procedures used with the on-line SPE-ICP-MS method developed for the determination of uranium and thorium in aqueous samples in the presence of high levels of inorganic and organic matrix components.

2.1.3.1 Chemicals and reagents

The solid phase extraction resin used was TRU-spec (EiChrom Europe, Paris, France), which consisted of octyl(phenyl)-N,N-diisobutyl carbamoylmethylphosphine oxide in tri-n-butyl phosphate (CMPO/TBP) on a polymeric base. This resin described by the manufacturers as an 'extraction resin' utilises reversed-phase partition chromatography as its mode of operation. The carriers used with the SPE column were prepared from concentrated nitric acid (Aristar, BDH, Poole, Dorset, UK) diluted to 2M with deionised water (18 M Ω , MiliQ system, Millipore S.A., Molsheim, France) and aluminium nitrate (AnalaR, BDH, Poole, Dorset, UK). The eluents were prepared from ammonium hydrogen oxalate (Sigma-Aldrich, Dorset, UK), ammonium oxalate and oxalic acid (AnalaR, BDH, Poole, Dorset, UK), made up to 0.1M in deionised water (18 M Ω , MiliQ system, Millipore S.A., Molsheim, France). A 1 ng ml⁻¹ bismuth and 1 ng ml⁻¹ thallium (Aristar, BDH, Poole, Dorset, UK) internal standard was added to the eluent. Synthetic seawater was prepared from sodium chloride, magnesium chloride, magnesium sulphate, calcium chloride, potassium chloride and sodium bicarbonate (AnalaR, BDH). Humic acid solutions were prepared by dissolving humic acid (Fluka, Dorset, UK) in deionised water (18 M Ω , MiliQ system). Fulvic acid was diluted from a stock solution (8000 μ g ml⁻¹, provided by the British Geological Survey) with deionised water (18 M Ω , MiliQ system) to a final concentration of 8 μ g ml⁻¹.

2.1.3.2 Standard and sample preparation

Uranium and thorium standards were diluted from stock solutions (Aristar 1000 $\mu\text{g ml}^{-1}$ standards, BDH) using 1% nitric acid to give final concentrations in the range of 0.1 to 10 ng ml^{-1} . Uranium and thorium standards were also prepared in synthetic seawater to assess recovery and method limit of detection. Solutions for recovery experiments were prepared by spiking the seawater, humic and fulvic acid solutions with 1 ng ml^{-1} U and Th. Humic and fulvic acid samples were left to equilibrate for four hours with the uranium and thorium before being acidified. Equilibration under acidic conditions would not be representative of the 'natural conditions' under which an environmental sample would have formed.

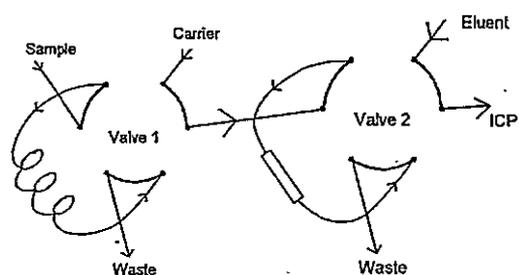
2.1.3.3 Column preparation

The TRU-spec extraction resin was slurry packed (0.1 g resin in 25 ml 1% nitric acid, 1.016 mm id peristaltic tubing, pump rate 1 ml min^{-1} , 10 rpm) into a small column made from Teflon HPLC tubing (2.4 x 50 mm), with 40 μm PTFE frits and 'flange free' end fittings. This produced a column volume of 0.226 cm^3 and a bed density of approximately 0.4 g cm^3 . In the initial stages of this study glass columns (Omnifit (Cambridge, England), 3 x 50 mm) were also packed. However the PTFE frits were not securely held in place in these columns resulting in them being displaced when the direction of the mobile phase flowing through the column was reversed.

2.1.3.4 Sample introduction manifold

The sample introduction manifold consisted of two six port valves (Type 50, Rheodyne, Cotati, CA, USA) connected in series and the SPE column. The outlet from this manifold was connected to the nebuliser inlet of the ICP-MS (PlasmaQuad 2+, VG Elemental, Winsford, Cheshire, UK). Several different manifold configurations were evaluated (Figure 2.9 to Figure 2.12). These allowed the carrier flow (loading the sample

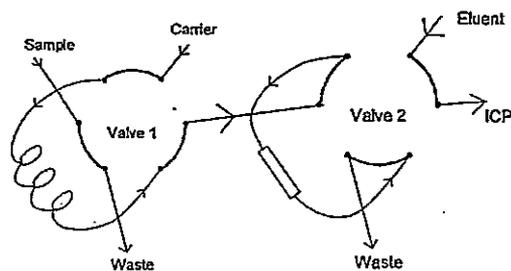
onto the column) and the eluent flow (removing the analyte from the column) to flow through the column in the same direction. Alternatively the eluent flow could be passed through the column in the reverse direction to that of the carrier flow. Different configurations were also used to either divert the carrier flow coming out of the column (containing the sample matrix) to waste or into the ICP-MS. Diverting the carrier flow through the ICP-MS during the method development stage of the work allowed for 'column breakthrough', that is analyte not being retained on the column, to be detected.



Step 1

Sample loop loaded.

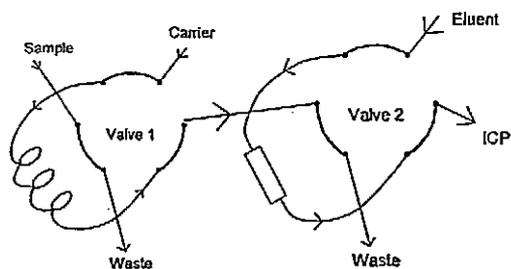
Column flushed with carrier.



Step 2

Sample loaded on to column.

Sample matrix diverted to waste.



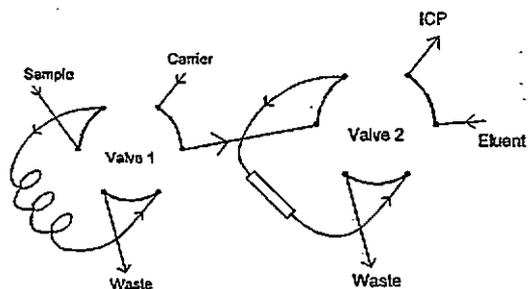
Step 3

Sample eluted off column.

Column outflow diverted to the ICP.

Loop flushed with carrier.

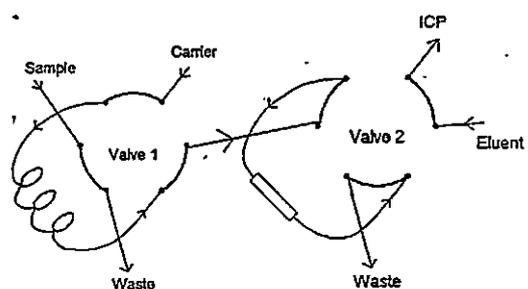
Figure 2.9 Injection manifold configuration for one direction column flow through with sample matrix diverted to waste



Step 1

Sample loop loaded.

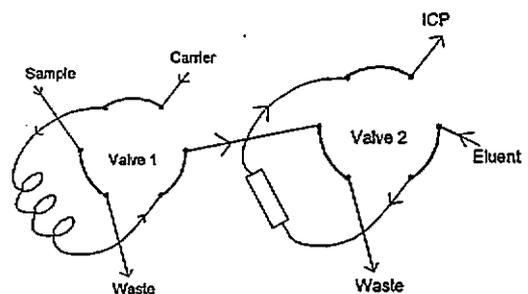
Column flushed with carrier.



Step 2

Sample loaded on to column.

Sample matrix diverted to waste.

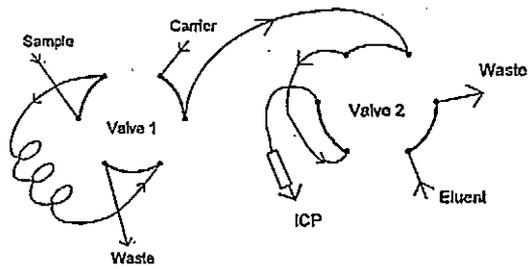


Step 3

Sample eluted off column with the eluent flowing in the opposite direction to the carrier flow.

Column outflow goes to the ICP.

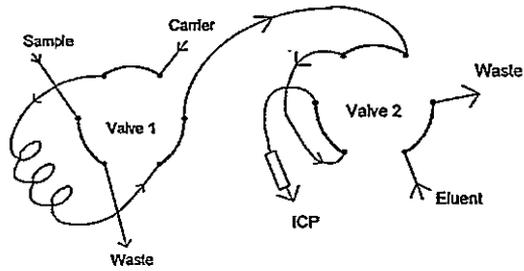
Figure 2.10 Injection manifold configuration for two direction column flow through with sample matrix diverted to waste



Step 1

Sample loop loaded.

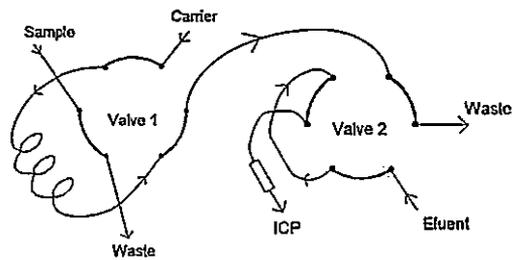
Column flushed with carrier.



Step 2

Sample injected on to column.

Sample matrix diverted to ICP.

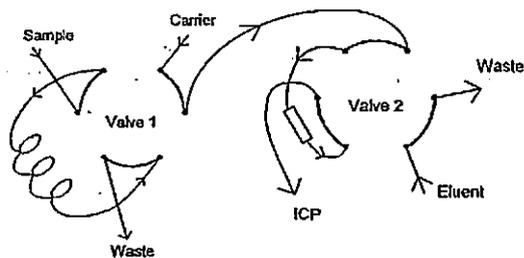


Step 3

Sample eluted off column.

Column outflow diverted to ICP.

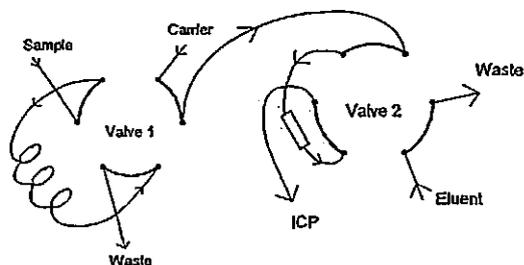
Figure 2.11 Injection manifold configuration for one direction column flow through with sample matrix diverted through the ICP



Step 1

Sample loop loaded.

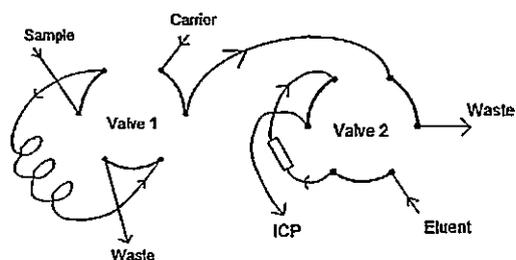
Column flushed with carrier.



Step 2

Sample injected on to column.

Sample matrix diverted to ICP.



Step 3

Sample eluted off column with the eluent flowing in the opposite direction to the carrier flow.

Column outflow goes to the ICP.

Figure 2.12 Injection manifold configuration for two direction column flow through with sample matrix diverted through the ICP

2.1.3.5 Instrument parameters

The instrumental parameters for the ICP-MS instrument and the use of the SPE column are detailed in Table 2.1 and Table 2.2.

Table 2.1 ICP-MS operating parameters for the determination of uranium and thorium with on-line solid phase extraction

Instrument	VG PlasmaQuad 2+
Plasma	Argon
Coolant flow	13 l min. ⁻¹
Auxiliary flow	1 l min. ⁻¹
Nebuliser flow	1 l min. ⁻¹
Nebuliser pressure	36 psi
Nebuliser type	V groove, high solids
Spray chamber	Scott double pass, water cooled, 10°C
Torch	Quartz, Fassel with wide bore (3 mm) injector
Power	Forward 1350 W, Reflected 0 - 2 W
Detector	Pulse counting mode Time resolved analysis data collection Data collection 1 second per slice Dwell time per AMU 107762.8 µs

Table 2.2 On-line solid phase extraction analysis parameters

Packing	TRU spec
Column	2.4 x 50 mm Teflon tube
Carrier	2 M HNO ₃
Eluent	0.1M (NH ₄)HC ₂ O ₄
Injection volume	500 µl
Flow rate	6 rpm (0.8 ml min. ⁻¹)
Runtime	load 2 minutes elute 3 minutes

2.1.3.6 Sample analysis procedure

The sample was loaded onto the column via the loop on the first Rheodyne valve with the acid carrier, the analyte being retained on the column whilst the matrix elements passed straight through. The analyte was then eluted with the oxalate eluent directly into the nebuliser of the ICP-MS instrument. The resulting ICP-MS data was collected using the time resolved analysis (TRA) mode which facilitated producing the results in the form of a chromatogram. Uranium and thorium concentrations were calculated using the ratio of the analyte peak area to the response of the internal standard in the eluent. This approach allowed for correction of changes in instrument response due to drift.

2.1.4 Sample speciation using DEAE cellulose anion exchange resin

This section describes the experimental parameters and procedures used to separate the inorganic and organic uranium and thorium species in water samples using an anion exchange resin.

2.1.4.1 Chemicals and reagents

The resin used was di-ethyl-amino-ethyl (DEAE) cellulose (DE52, Whatman, Maidstone, England). The eluent used was 0.5M sodium hydroxide, prepared from sodium hydroxide pellets (AnalaR, BDH) dissolved in deionised water (18 M Ω , MiliQ system). Fulvic acid was diluted from a stock solution (8000 $\mu\text{g ml}^{-1}$, provided by the British Geological Survey) with deionised water (18 M Ω , MiliQ system). Bismuth (Aristar 1000 $\mu\text{g ml}^{-1}$ standard, BDH) was used as the internal standard. A synthetic surface-water solution, for use as the sample diluent, was prepared from sodium bicarbonate, magnesium sulphate, calcium chloride, sodium fluoride and potassium dihydrogen orthophosphate (AnalaR, BDH).

2.1.4.2 Standard and sample preparation

Uranium and thorium standards were diluted from stock solutions (Aristar 1000 $\mu\text{g ml}^{-1}$ standards, BDH) using the fractions collected when a blank was run through the column, in order to provide a matrix matched diluent. Samples were prepared from a synthetic surface-water solution spiked with fulvic acid (8 $\mu\text{g ml}^{-1}$) and uranium and thorium (1 ng ml^{-1}).

2.1.4.3 Column preparation

An off-line separation method was used. The column was constructed using a 10 ml plastic syringe barrel with the tip blocked with a plug of glass wool. A slurry of the DEAE resin was prepared following the manufactures instructions and a 5 ml column bed was

formed in the 10 ml syringe barrel. Because an off-line method was employed there was no requirement for a sample introduction manifold to attach the column to the ICP-MS. The fractions collected from the column were aspirated into the ICP-MS using a peristaltic pump.

2.1.4.4 Instrument parameters

The ICP-MS instrument parameters used were the same as those detailed in Table 2.1 in section 2.1.3.5, except that the TRA data acquisition mode was not used.

2.1.4.5 Sample analysis procedure

The sample (5 ml) was applied directly to the top of the column and flushed through with 4 x 5 ml aliquots of deionised water (18 M Ω , MiliQ system). Mobile phase flow was under the effect of gravity (measured as 0.5 ml min⁻¹). The outflow from the column, the load fraction, was collected for subsequent analysis. Any sample bound to the resin was then eluted with 5 x 5 ml aliquots of 0.5M sodium hydroxide (AnalaR, BDH). This was collected as the elute fraction. Blank solutions were also run through the column, both to provide blank fractions for analysis and to provide solutions to be used as the diluents for matrix matched standards. These fractions were spiked with a bismuth (1 ng ml⁻¹) internal standard and were aspirated into the ICP-MS using a peristaltic pump. Data was acquired using the fully quantitative data acquisition mode.

2.1.5 Sample speciation using cellulose Hyphan chelating resin

This section describes the experimental parameters and procedures used to separate the inorganic and organic uranium and thorium species in water samples using a chelating resin.

2.1.5.1 Chemicals and reagents

The resin used was cellulose Hyphan (Riedel de Haën AG, Seeize, Germany) which consisted of 1-(2-Hydroxyphenylazo)-2-naphthol on a cellulose support. The carriers used with the Hyphan column were 0.01M ammonium acetate, 0.01M sodium acetate, 0.002M sodium citrate, and 0.001M and 0.01M sodium chloride (AnalaR, BDH) dissolved in deionised water (18 MΩ, MiliQ system). The eluent was 2M nitric acid diluted from concentrated nitric acid (Aristar, BDH) with deionised water (18 MΩ, MiliQ system). Thallium (Aristar 1000µg ml⁻¹ standard, BDH) was diluted to 1 ng ml⁻¹ with 2M nitric acid to provide the internal standard. Synthetic water solutions for use as diluents (see Table 2.3) were prepared from sodium chloride, magnesium chloride, magnesium sulphate, calcium chloride, potassium chloride, sodium bicarbonate, sodium fluoride and potassium dihydrogen orthophosphate (AnalaR, BDH). Humic acid (Fluka, Dorset, UK) was dissolved in deionised water (18 MΩ, MiliQ system). Fulvic acid was diluted from a stock solution (8000µg ml⁻¹, provided by the British Geological Survey) with deionised water (18 MΩ, MiliQ system).

2.1.5.2 Standard/sample preparation

Uranium and thorium standards were diluted from stock solutions (Aristar 1000µg ml⁻¹ standards, BDH) using synthetic surface and groundwater solutions as diluents, see Table 2.3 for diluent compositions. For the recovery experiment a standard was also prepared in a 0.01M sodium bicarbonate solution. For speciation experiments solutions

were prepared using the synthetic surface-water (without the sodium fluoride component) with humic substances added (1, 2 and 4 $\mu\text{g ml}^{-1}$), where the total humic substance concentration was composed of 10% humic acid and 90% fulvic acid, and spiked with uranium (0.1, 1 and 10 ng ml^{-1}). Samples were produced over a range of pH values using very dilute nitric acid or sodium bicarbonate to adjust the pH.

Table 2.3 Composition of synthetic water solutions used as diluents

Component	Surface water (mg l^{-1})	Groundwater (mg l^{-1})	Seawater (mg l^{-1})
NaCl	none added	none added	26300
$\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$	none added	none added	7400
KCl	none added	none added	700
$\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$	55	187	1500
NaHCO_3	46	135	200
$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	10	82	7400
NaF	0.6	6	none added
KH_2PO_4	0.2	1	none added

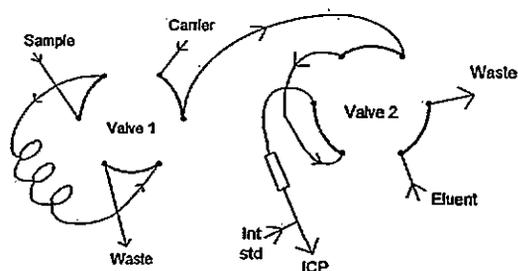
2.1.5.3 Column preparation

The Hyphan resin was slurry packed (0.1 g resin in 25 ml 1% nitric acid, 1.016 mm id peristaltic tubing, pump rate 1 ml min^{-1} , 10 rpm) into a small column made from Teflon HPLC tubing (2.4 x 50 mm), with 40 μm PTFE frits and 'flange free' end fittings.

2.1.5.4 Sample introduction manifold

The sample introduction manifold consisted of two six port valves (Type 50, Rheodyne, Cotati, CA, USA) connected in series, and the Hyphan column (Figure 2.13). The first valve, which held the sample loop and controlled the carrier flow, was connected

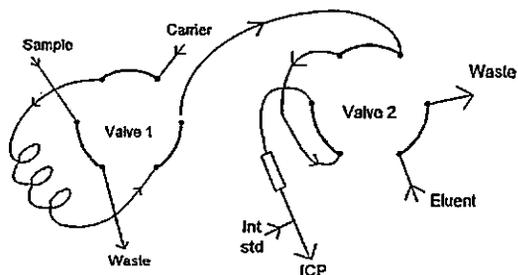
directly to the second valve which controlled the eluent flow. The outlet from the second Rheodyne valve was connected to the column which was in turn connected to the nebuliser inlet of the ICP-MS (PlasmaQuad 2+, VG Elemental, Winsford, Cheshire, UK). This configuration allowed both the carrier and eluent to pass from the column outlet into the ICP-MS in order to detect the organic related metal species in the carrier flow and the inorganic species in the eluent flow.



Step 1

Sample loop loaded.

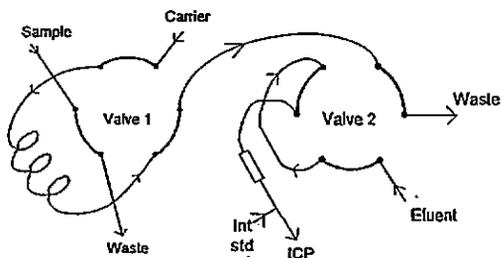
Column flushed with carrier.



Step 2

Sample loaded on to column.

Organic species pass through column into ICP.



Step 3

Eluent passes through column.

Inorganic species eluted off column into ICP.

Figure 2.13 Sample introduction manifold for on-line sample speciation

2.1.5.5 Instrument parameters

The instrumental parameters for the ICP-MS instrument and the use of the Hyphan column are detailed in Table 2.4 and Table 2.5.

Table 2.4 ICP-MS instrument parameters for on-line uranium speciation

Instrument	VG PlasmaQuad 2+
Plasma	Argon
Coolant flow	13 l min. ⁻¹
Auxiliary flow	1 l min. ⁻¹
Nebuliser flow	1 l min. ⁻¹
Nebuliser pressure	36 psi
Nebuliser type	V groove, high solids
Spray chamber	Scott double pass, water cooled, 10°C
Torch	Quartz, Fassel with wide bore (3 mm) injector
Power	Forward 1350 W, Reflected 0 - 2 W
Detector	Pulse counting mode Time resolved analysis data collection Data collection 1 second per slice Dwell time per AMU 107762.8 µs

Table 2.5 Parameters for on-line speciation analysis

Packing	Hyphan resin
Column	2.4 x 50 mm Teflon tube
Carrier	0.01M ammonium acetate
Eluent	2M nitric acid
Injection volume	500 µl
Flow rate	0.8 ml min. ⁻¹
Runtime	carrier 3 minutes eluent 2 minutes

2.1.5.6 Sample analysis procedure

Two procedures were used to analyse the samples, a batch technique and a column technique. For the batch technique the Hyphan resin was first equilibrated to the approximate pH of the sample by conditioning in an ammonium acetate solution over night. This solution was then decanted off and the resin mixed with fresh ammonium acetate solution for several hours. The resin was then filtered off and washed with deionised water prior to use. The batch procedure then involved mixing the resin with the sample (20 mg resin plus 10-ml sample, shaken for 30 seconds) after which the Hyphan resin was separated by filtration (0.45 μm cellulose acetate filter). The filtrate was retained as the fraction containing the organic species (this was acidified prior to analysis). The inorganic species bound to the Hyphan resin were then eluted by passing 2M nitric acid through the Hyphan retained on the filter paper. This produced the fraction containing the inorganic species. Both fractions were subsequently analysed by ICP-MS.

Using the column technique the column containing the Hyphan resin was attached to the sample introduction manifold and ICP-MS instrument. The sample was injected on to the column in a carrier stream (0.01 M ammonium acetate). The inorganic species were retained on the column whereas the organic species passed straight through the column into the instrument. The resulting ICP-MS data was collected using the time resolved analysis (TRA) mode which again produced the results in the form of a chromatogram. The organic species produced a peak in the first half of the chromatogram. The eluent flow was then switched through the column and the inorganic species eluted, producing a peak in the second half of the chromatogram. The ratio of the analyte peak area to the response of the internal standard was used in subsequent calculations. This allowed correction for changes in instrument response due to drift.

2.2 In-field sample collection

Water samples were collected and stored in plastic (polypropylene or polyethylene) bottles⁸⁹. Prior to use the bottles were acid washed (overnight in 10% nitric acid⁹⁰) and rinsed in triplicate with deionised water. Prior to collecting a sample the bottle to be used was rinsed out with the river water being collected. The samples were filtered on site (0.45µ cellulose acetate filter), the container being used for sample storage being rinsed out with filtered sample prior to use. Samples collected for analysis of total uranium and thorium concentrations were acidified (1% nitric acid) to preserve the solutions on storage⁹¹. Samples collected for speciation analysis were not acidified as this would effect the species present. These samples were analysed as soon as possible after collection. Samples for phosphate analysis (as part of the sample characterisation) had 1% chloroform added (to inhibit biological activity) and were refrigerated for storage⁹².

Temperature and pH measurements were taken in-situ at the sampling sites, and for the unacidified samples, taken again prior to analysis, to form part of the computer modelling parameters.

At the abandoned South Terras uranium mine, a background radiation count was taken using a Geiger counter. On the first sampling trip the background count next to the adit was 2.5 cps. After filtering two litres of water from the adit mouth the filter paper gave a count of 40 cps. On the second sampling trip water was not available from the adit mouth as an underground drainage pipe had been installed. The background radiation count was several hundred cps, probably due to the disturbed ground and mine waste exposed when the drainage pipe was installed and the lack of water shielding the waste from the air.

2.3 Characterisation of water samples

The composition of the water samples collected from Dartmoor (Devon; UK) was determined using a number of techniques. The techniques and procedures are detailed in the following sections.

2.3.1 Total organic carbon analysis

This technique is based on the combustion of the sample so that all the carbon in the sample is converted to carbon dioxide. This is then detected by a non-dispersive infra-red detector, the level of absorption being proportional to the carbon dioxide concentration. In order to quantify the levels of organic and inorganic carbon separately, two aliquots of the sample are required. The total carbon content of the first aliquot is determined. Acid is then added to the second aliquot, this reacts with the inorganic carbon in the sample producing carbon dioxide which is detected giving the level of inorganic carbon in the sample.

Subtracting this from the total amount of carbon in the sample gives the level of organic carbon in the sample by difference. If the proportion of organic carbon in the sample is very low relative to the total level of carbon in the sample then this can result in an inaccurate organic carbon result due to the small difference between the total and inorganic carbon results. An alternative procedure for determining the organic carbon level in the presence of a large inorganic carbon component, or if only the organic carbon concentration of the sample is required, is to use a non-purgeable organic carbon (NPOC) analysis. This involves adding acid to the sample prior to analysis and purging the sample with a carrier gas to remove the inorganic carbon. The analysis procedure is then the same as for total carbon analysis.

Since the water samples had been filtered the analysis in this study was based on the dissolved inorganic and organic carbon (DIC and DOC). The 'total carbon - inorganic carbon' procedure was used to measure the levels of both inorganic and organic carbon in

the samples. The instrument used was a Shimadzu TOC 5000A with ASI 5000A autosampler (Shimadzu corporation, Kyoto, Japan). Standards for the total carbon analysis were prepared from potassium hydrogenphthalate (Shimadzu corporation, Kyoto, Japan) dissolved in deionised water (18 M Ω , MiliQ system) and standards for the inorganic carbon analysis were prepared from sodium carbonate and sodium bicarbonate (Shimadzu corporation, Kyoto, Japan) dissolved in deionised water (18 M Ω , MiliQ system). Standard calibration was over the range 0 to 10 $\mu\text{g ml}^{-1}$ with the 'linear regression with zero shift' calibration option used to calculate the calibration plot and correct for the dissolved carbon content of the water used to prepare the standards.

2.3.2 Anion chromatography

Anion chromatography was used to separate and quantify the anions, F^- , Cl^- , NO_3^- and SO_4^{2-} in the water samples. The column used in this analysis was a strong anion exchange column consisting of latex particles with an alkanol quaternary ammonium group and a polyethylvinylbenzene / divinylbenzene stationary phase. A conductivity detector was used in conjunction with a suppresser unit (placed between the column and the detector) in order to reduce the background mobile phase conductivity. The operating parameters are detailed in Table 2.6. Standards were prepared from sodium fluoride, sodium chloride, sodium sulphate and potassium nitrate (AnalaR, BDH) dissolved in deionised water (18 M Ω , MiliQ system).

Table 2.6 Operating parameters for characterisation of water samples by anion chromatography

Column packing	IonPac AS4-SC (Dionex)
Column dimensions	4 x 250 mm
Mobile phase	1.8 mM Na ₂ CO ₃ / 1.7 mM NaHCO ₃
Flow rate	1 ml min ⁻¹ (LDC constaMetric 3000 pump)
Injection volume	20 µl (Rheodyne 7125 six port injection valve)
Suppresser	ASRS-ULTRA (Dionex)
Detection	Conductivity, sensitivity 0.01, base range 100 (Waters 431 detector)
Run time	16 minutes
Data handling	PE Nelson systems 900 series interface

2.3.3 Spectrophotometry

The phosphate content of the water samples was determined by reacting the sample with an acidic molybdate reagent in the presence of antimony which resulted in a phospho-molybdenum blue complex, the concentration of which was measured spectrophotometrically^{93,94}.

This was carried out using an automated nutrient analyser (Skalar, Breda, Holland) with air segmented flow analysis. The molybdate reagent was composed of 0.6% w/v ammonium molybdate (AnalaR, BDH), 0.023% w/v potassium antimony tartrate (AnalaR, BDH), 7% v/v sulphuric acid (Aristar, BDH) and 0.2% FFDS6 (Skalar Analytical, Holland), a surfactant and cleaning agent used to prevent sample build-up on the tubing walls of the instrument. A 1% w/v ascorbic acid solution was mixed with the molybdate reagent during the analysis. Standards were prepared by dissolving potassium dihydrogen orthophosphate (AnalaR, BDH) in deionised water (18 MΩ, MiliQ system).

2.3.4 Inductively coupled plasma atomic emission spectrometry

This technique was used to measure the major cations (Na^+ , K^+ , Ca^{2+} and Mg^{2+}) present in the water samples.

The inductively coupled plasma used in this technique is essentially the same as that used in ICP-MS except that the plasma torch is usually orientated vertically and the detector is situated perpendicular to the plasma instead of end-on as in ICP-MS. The level of analyte in the sample is determined by atomic emission spectrometry (also known as optical emission spectrometry since it is the UV-Vis region of the electromagnetic spectrum which is measured). The basic theory of emission spectrometry is that when energy is added to an atom (in its ground state) electrons are excited into a higher orbital (excited state atom). Since this is a less stable state the electron then drops back down to a lower orbital and in doing so emits energy in the form of light^{81,95}. The difference in energy between the upper and lower orbitals determines the wavelength of light emitted. Transitions between different excited states produces emissions at different wavelengths which result in an emission spectrum. Every element has its own unique emission spectrum thus the emissions from different elements in a sample can be differentiated from each other by monitoring each element at a different wavelength. The intensity of the emission (of the wavelength being monitored) is proportional to the concentration of the element present in the sample. In the case of a sequential detection instrument, the polychromatic radiation emitted by the sample in the plasma is focused on to a monochromator which uses a diffraction grating to separate the various wavelengths present. Each wavelength of interest is sequentially focused on to the detector allowing each element of interest to be detected in turn. The detector is usually a photomultiplier tube^{81,95}.

The work in this study was performed using a Liberty ICP-AES spectrometer (Varian Australia Pty Ltd). The instrument parameters used are detailed in Table 2.7.

Standards were diluted from stock solutions (Aristar $1000\mu\text{g ml}^{-1}$ plasma emission standards, BDH) with 1% nitric acid and a calibration plot generated for the concentration range 0 to $50\mu\text{g ml}^{-1}$.

Table 2.7 Instrument parameters for water characterisation by ICP-AES

Instrument settings	Element			
	Ca	Mg	Na	K
Wavelength (nm)	396.847	279.553	589.592	769.896
Order	1	2	1	1
Filter position	7	6	7	7
Viewing height (mm)	15	8	7	8
Background correction	Dynamic	Dynamic	Dynamic	Dynamic
PMT (V)	650	650	650	650
Integration time (s)	1	1	1	1
Replicates	3	3	3	3
Power (kW)	1	1	1	1
Plasma gas flow (l min^{-1})	15	15	15	15
Auxiliary gas flow (l min^{-1})	1.5	1.5	1.5	1.5
Nebuliser pressure (kPa)	150	150	150	150
Stabilisation time (s)	15	15	15	15

2.4 Computer modelling

The following computer programs and thermodynamic databases were used in this study :-

WHAM (version 1.0), [Computer Program], The institute of Freshwater Ecology, Ambleside, UK. Program provided by the British Geological Survey.

PHREEQCI (version 1.03.009, implements PHREEQC 1.6), [Computer Program], United States Geological Survey NWIS Program Office, Reston, VA, USA. This program was obtained as a free download from the USGS water resources web site. URL <http://water.usgs.gov/software>

Nuclear Energy Agency - Thermochemical Database Project (NEA-TDB) uranium database (OECD, Paris, France). This data has been published by the OECD ^{96,97}.

'Model fulvic acid' database (Australian Nuclear Science and Technology Organisation (ANSTO), Menai, Australia). This data has been published by ANSTO ⁹⁸.

WHAM has been written in the 'Turbo Basic' programming language and runs in the 'MS-DOS' operating system. Data is input in the form of a text file, an example of such an input file can be seen in Figure 2.14. The contents of the input text file can be edited via the 'Windows' operating system. The thermodynamic database can also be accessed and edited in the form of a text file.

PHREEQCI is written in the programming language 'C' and has a 'Visual Basic' graphical interface which provides access to the program in the 'Windows' operating system. An

example of the input window can be seen in Figure 2.15. The thermodynamic database can be accessed and edited in the form of a text file.

WATER	,Example 1	Description of model
Database	,water41	Database to be used in calculations
Database size	,400	
Precision %	,0.01	
Temp K	,293	
THA TFA g/l	,0.0008,0.0072	Humic and fulvic acid concentrations
pH fixed	,YES	
PHSTART	,6.0	
pCO2	,0.00035	CO ₂ pressure (in atmospheres)
No. mast. Sp.	,6	Number of species input in to the model
UO2	,22,4.2017E-9	
Th	,27,4.3103E-9	
Na	,3,1.7571E-3	
Ca	,7,1.2714E-3	
Cl	,52,1.2714E-3	
SO4	,54,3.3293E-4	

Species ID No Concentration (M l⁻¹)

Figure 2.14 Example input file for the WHAM program

SOLUTION - [EX1 -- Simulation 1/2]

Help

SOLUTION

Number: 1 through 1 Description: SEAWATER FROM NORDSTROM ET AL. (1979)

pH: 8.22 Equilibrium Sat. index: Charge balance

pe: 8.451 Equilibrium Sat. index:

Temperature: 25

Redox: 0(-2)/0(0)

Units: ppm 1.023

Individual element input

Element/State: 0(0) Concentration: 1 [EF] [G] Clear

Units: A: GPW:

Redox:

Phase equilibrium: 02(g) Sat. index: -0.7 Charge balance

List of elements

S(6)	2712		
N(5)	0.29	as NO3	
N(-3)	0.03	as NH4	
U	3.3	ppb	N(-3)/N(5)
0(0)	1	02(g)	-0.7

Delete Selected Entry

Figure 2.15 Data input window from the PHREEQCI program

Chapter Three

3. Determination of total U and Th concentration in water samples with a high matrix concentration using SPE-ICP-MS

3.1 Introduction

Uranium and thorium are usually present in natural waters at low ng ml^{-1} to pg ml^{-1} levels. ICP-MS provides a rapid sensitive technique for their determination. However, high levels of sample matrix can interfere with the analysis. Sample dilution will reduce the matrix effects^{41, 46} but will also reduce the U and Th concentrations. Solid phase extraction (SPE) separates the sample from the matrix without reducing the analyte concentration and has the advantage, when coupled on-line, of only requiring a small sample volume.

The aim of the work in this chapter was to develop an on-line SPE-ICP-MS method to analyse U and Th in aqueous samples with a high total dissolved solids (TDS) content. Although good recoveries from seawater are obtained using conventional chelating resins^{99, 100}, when dissolved organic carbon (DOC) is present in the sample low recoveries have been reported^{77, 78, 101}. Because of this, an actinide specific extraction resin was chosen for this work. A sample introduction manifold was developed and the suitability of the extraction resin for on-line separation investigated.

3.2 Method development

3.2.1 Manifold design

There are two main configurations for sample introduction manifolds^{43, 47, 102, 103}. In one arrangement the carrier and eluent flow through the column in the same direction whereas, in the other the carrier flows in one direction to load the sample on to the column and the eluent flows in the opposite direction when stripping the analytes from the column. The advantage of the two-directional flow configuration is said to be a reduction in the tendency for the column packing material to bed down and sharper peaks (less band broadening) because the analyte does not pass through the whole length of the column. Diagrams for these manifold configurations can be seen in the Experimental chapter.

During the development phase, the sample matrix was diverted through the ICP-MS to check for column 'breakthrough', that is U and Th not retained on the column. The resulting chromatogram consisted of two parts corresponding to: (i) the load phase (the first two minutes), where the sample was loaded on to the column, U and Th were retained on column while the sample matrix passed straight through, and (ii) the second phase where U and Th were removed from the column and passed into the ICP-MS. This applied to both the one and two directional flow configurations.

With the sample introduction manifold arrangement for two directional flow through the column, the reversal in flow direction caused the frits to become dislodged, resulting in the column becoming unpacked. In addition, the peak obtained had a low shoulder on the leading edge which could cause peak integration problems. This was not seen when the flow was uni-directional. Figure 3.1 and Figure 3.2 show chromatograms from both configurations. The retention time for the peak from the one direction flow configuration was longer because the eluent had to flow slightly further through the manifold before it reached the column.

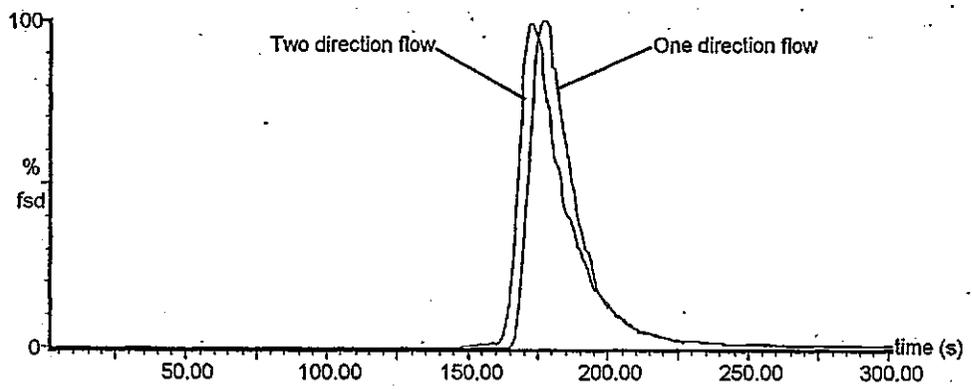


Figure 3.1 Chromatograms from one and two direction flow configurations

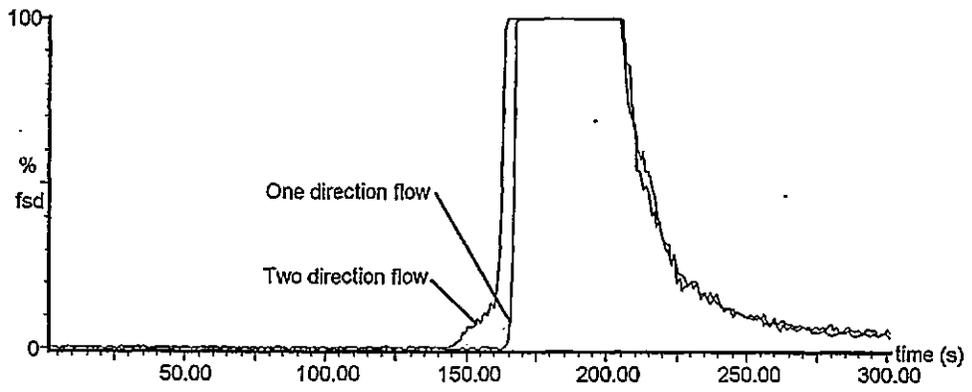


Figure 3.2 Chromatograms from one and two direction flow configurations on an expanded scale

3.2.2 Effect of carrier composition on resin capacity

The composition of the carrier and eluent used were investigated in order to ascertain the effect of changes in mobile phase composition on the chromatographic profile and hence optimise the system. Nitric acid is usually employed as the carrier with this resin⁵⁶; however the use of aluminium nitrate is said to increase the capacity of the resin¹⁰⁴. Nitric acid (0.01 to 2 M), aluminium nitrate (0 to 0.5 M) and combinations of both were tested and the capacity of the resin measured by adding the resin to a solution containing an excess of uranium and then measuring the amount of uranium left in solution. Figure 3.3 shows that the capacity of the resin increased with both higher nitric acid and aluminium nitrate concentrations, indicating that it was the nitrate concentration rather than the acidic conditions that facilitated the binding of uranium to the resin. However, if aluminium nitrate alone was used as the carrier, the U peak was broader than when nitric acid acted as the carrier, so the low pH did play some part in the procedure (see Figure 3.4). Since the U and Th concentrations in natural waters are normally very low it was not necessary to increase the loading capacity of the column by using aluminium nitrate, with the added benefit of reducing the level of dissolved solids in the carrier.

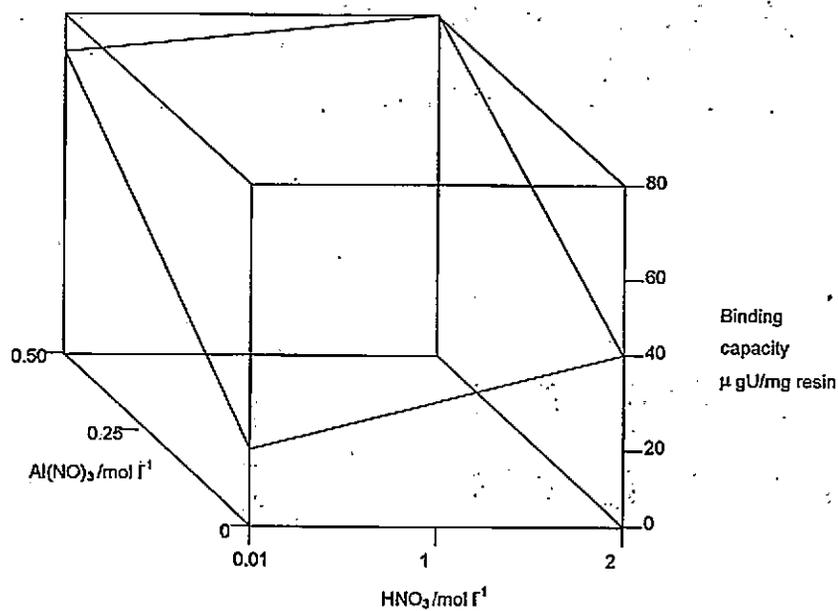


Figure 3.3 Effect of carrier composition on loading capacity of TRU spec resin

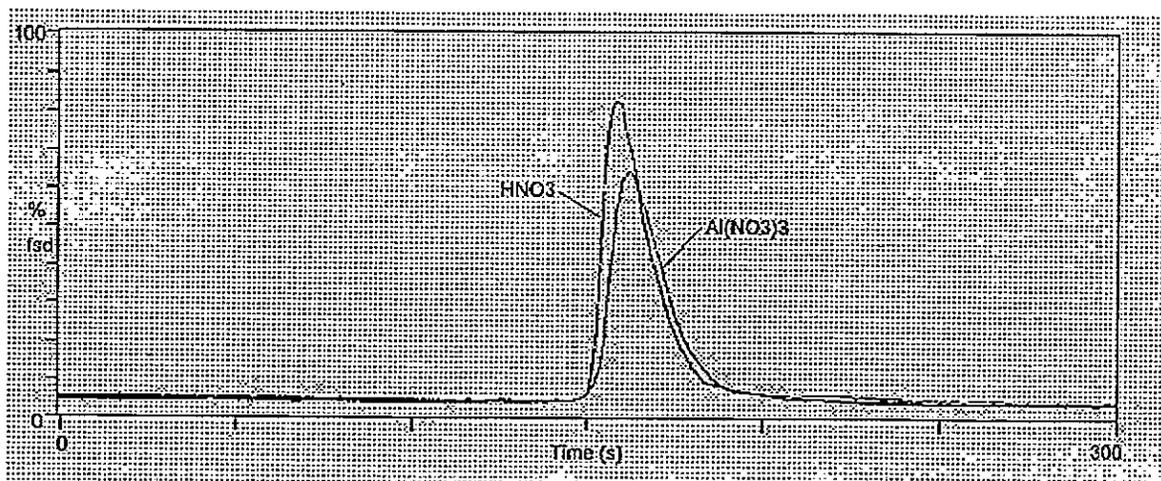


Figure 3.4 Effect of different carriers on peak profile

3.2.3 Effect of eluent pH on elution profile

The function of the oxalate eluent was to complex the U and Th and remove them from the column. The influence of eluent pH on peak profile was examined by using oxalic acid (pH 0.76), ammonium hydrogen oxalate (pH 2.30) and ammonium oxalate (pH 6.53) as eluent. The results can be seen in Figure 3.5. Oxalic acid produced a low symmetric peak whereas ammonium hydrogen oxalate produced a sharper more asymmetric peak and the ammonium oxalate produced a sharp peak but with increased tailing. The eluent pH did have an effect on peak profile, with higher pH causing a rapid elution of U, giving a sharper leading edge to the peak, but then tailing off to produce a more asymmetric peak. As a result of these observations ammonium hydrogen oxalate was used as the eluent in subsequent work.

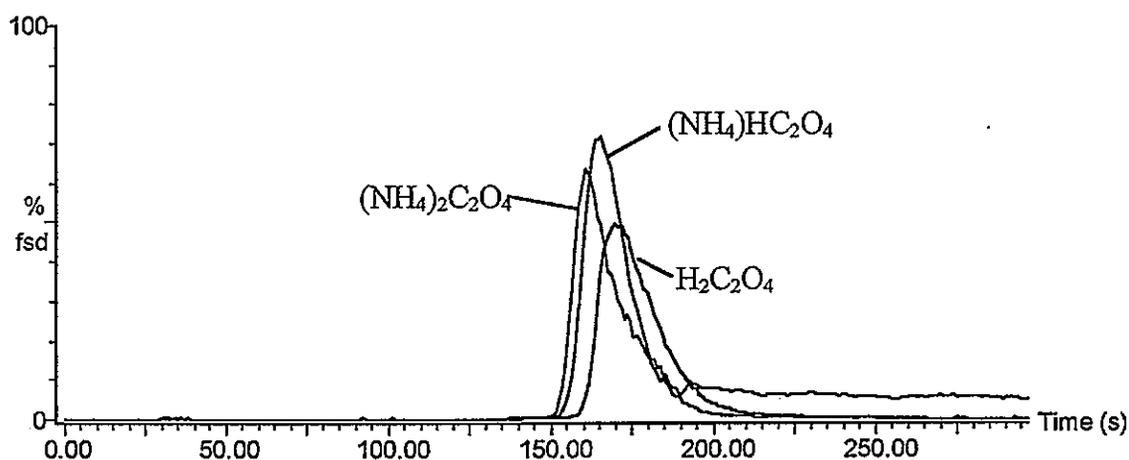


Figure 3.5 Effect of eluent pH on peak shape

3.2.4 Development of a system clean out procedure between injections

An evaluation of the baseline following a series of sample injections was performed by injecting a 'blank' (mobile phase going through system only). This resulted in a thorium peak clearly visible on the baseline which decreased in size with subsequent 'blank' injections. As nothing was injected while the carrier and eluent were run through the column to measure the baseline level of U and Th, this indicated that thorium was being retained in the system and then eluted by subsequent cycles of carrier and eluent. A protocol to flush the system was developed to overcome this. An increased elution time did not decrease the level of thorium carryover significantly but switching between the carrier and eluent in a shortened version of the complete injection cycle did reduce the carryover to an acceptable level (Table 3.1).

A second TRU spec column was also added to the system between the acid channel and the injection manifold to provide in-line acid carrier clean-up. This reduced the amount of uranium and thorium which was concentrated on column from the carrier in the load phase and seen as a peak in the elute phase of a baseline chromatogram (see Figure 3.6).

Table 3.1 Results for column flush procedures

Column flush method	% carryover in to baseline
Baseline run 5 minutes (x2)	2.1
Nitric acid and oxalate 2 minutes each (x2)	1.1
Nitric acid and oxalate 1 minute each (x2)	2.5

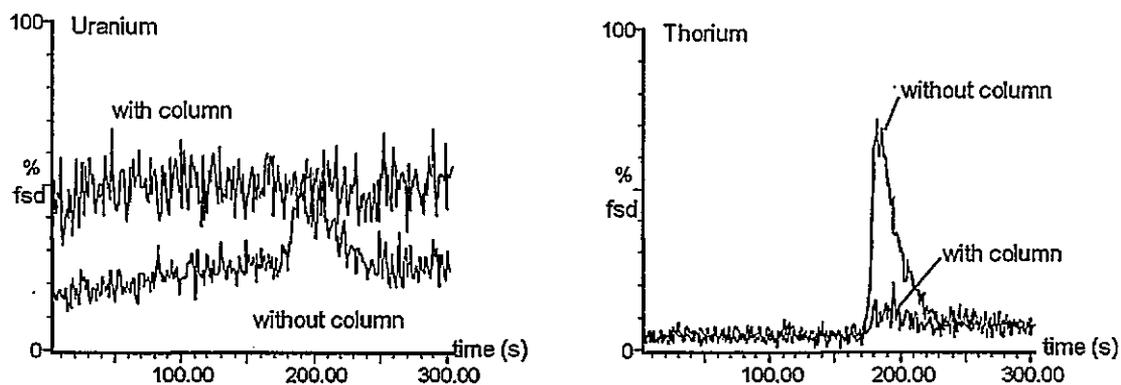


Figure 3.6 Effect of clean-up column on U and Th baseline levels

3.3 Method validation

3.3.1 Linearity, repeatability, limit of detection

Once the basic method parameters had been established the performance characteristics of the method were validated. The ability of the extraction resin to function in the presence of a matrix was confirmed using a synthetic seawater solution spiked with uranium and thorium. The ^{238}U and ^{232}Th responses were measured along with ^{44}Ca , to represent the sample matrix. Figure 3.7 shows the resulting chromatogram. The matrix (^{44}Ca) is seen as an unretained peak in the load phase and the ^{238}U and ^{232}Th as peaks in the elute phase.

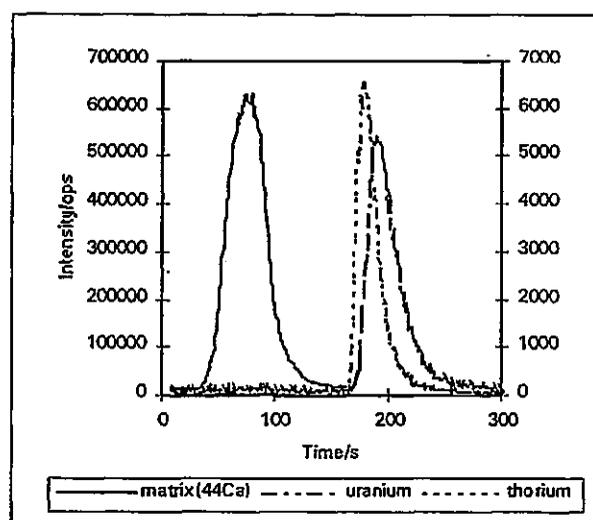


Figure 3.7 Separation of matrix from analyte using TRU spec column

The linearity of response was measured over the range 0 to 10 ng ml^{-1} (ppb) by ICP-MS and 1 to 10 $\mu\text{g ml}^{-1}$ (ppm) by ICP-AES (see Table 3.2 and Table 3.3 for results). The limit of detection (LOD) by ICP-MS was determined using standards made up in nitric acid and a seawater matrix to confirm that the presence of a matrix did not effect the results (see Table 3.4).

Table 3.2 Linearity and limit of detection by ICP-AES

	Uranium (385.958 nm)
Range	0 - 10 $\mu\text{g ml}^{-1}$
Correlation coefficient	0.9994
%rsd (n=6) at 1 $\mu\text{g ml}^{-1}$	4.7
LOD	0.05 $\mu\text{g ml}^{-1}$

Table 3.3 Linearity and repeatability results by ICP-MS

	^{238}U	^{232}Th
Range	0 - 10 ng ml^{-1}	0 - 10 ng ml^{-1}
Correlation coefficient	0.9997	0.9993
%rsd (n=6) at 1 ng ml^{-1}	4.3	5.8

Table 3.4 Limit of detection results by ICP-MS in nitric acid and seawater

	1% HNO ₃		Seawater	
	^{238}U	^{232}Th	^{238}U	^{232}Th
Correlation coefficient	0.9993	0.9982	0.9987	0.9992
LOD (ng ml^{-1})	0.013	0.006	0.015	0.006

The analyte response was derived from the peak area ratioed to the internal standard signal to take into account any variations or drift in signal from the instrument. In general an internal standard needs to have similar analytical characteristics to the analyte so that it will be effected by changes in the system in a similar manner and hence the ratio of response of the two would remain constant even if the intensity of response changed. The correlation of several different element responses to the uranium and thorium responses was measured to assess their ability to function as internal standards. Bismuth, thallium and lead have similar m/z and ionisation energies to uranium and thorium. The results obtained using these as internal standards and correlating their response to that of uranium and thorium can be seen in Table 3.5. All three internal standards show good correlation, compensating for variations in response as seen by the reduced %rsd when the analyte response is ratioed to the internal standard response (see Table 3.6 and Table 3.7). Another characteristic of an internal standard is that it should not already be present in the sample. This therefore excludes lead in this study but leaves bismuth and thallium. Initially bismuth was used but in later work this was found in some samples so the internal standard employed was changed to thallium.

Table 3.5 Correlation coefficients for each element response

	²⁰³ Tl	²⁰⁵ Tl	²⁰⁸ Pb	²⁰⁹ Bi	²³² Th	²³⁸ U
²⁰³ Tl		0.8927	0.9072	0.8736	0.8525	0.9054
²⁰⁵ Tl	0.8927		0.9354	0.9517	0.9190	0.9596
²⁰⁸ Pb	0.9072	0.9354		0.9521	0.8995	0.9496
²⁰⁹ Bi	0.8736	0.9517	0.9521		0.8980	0.9506
²³² Th	0.8525	0.9190	0.8995	0.8980		0.9361
²³⁸ U	0.9054	0.9596	0.9496	0.9506	0.9361	

Table 3.6 Response data for ²³⁸U, ²³²Th and each internal standard

	²⁰³ Tl	²⁰⁵ Tl	²⁰⁸ Pb	²⁰⁹ Bi	²³² Th	²³⁸ U
Mean	418	974	897	1012	1339	1332
sd	29	69	70	78	128	132
%rsd	6.83	7.08	7.83	7.68	9.55	9.90

Table 3.7 Relative standard deviation for ²³⁸U and ²³²Th responses when ratioed to each internal standard

	²⁰³ Tl	²⁰⁵ Tl	²⁰⁸ Pb	²⁰⁹ Bi	²³² Th	²³⁸ U
²³² Th	5.41	4.42	4.52	4.60		3.54
²³⁸ U	4.89	3.92	3.68	3.79	3.45	

3.3.2 Recovery from inorganic and organic matrixes

Uranium and thorium recovery was measured using spiked (1 ng ml^{-1}) synthetic surface, ground and seawater samples and a certified reference material, NASS-4 Open Ocean Seawater. The results can be seen in Table 3.8 and Table 3.9. The CRM was measured on two separate occasions to confirm the results.

Table 3.8 Recovery results from TRU spec column

Sample matrix	% recovery	
	Uranium	Thorium
Surface water	86.7	76.6
	102.5	94.1
Ground water	101.6	95.0
	103.5	99.2
Sea water	99.7	100.7
	107.6	103.7

Table 3.9 Recovery results from TRU spec column for NASS-4 CRM

NASS-4 Open Ocean Seawater Reference Material	
	(ng ml^{-1})
Certified U concentration \pm 95% CL	2.68 ± 0.12
Measured U concentration \pm 1 SD (n=4)	2.62 ± 0.08
	2.70 ± 0.09

Because the presence of dissolved organic carbon has been reported to cause recovery problems^{77, 78, 101}, samples spiked with uranium, thorium, and humic and fulvic acids were analysed. The results can be seen in Table 3.10. Good recovery was obtained except for thorium in humic acid which required an acid digest before complete recovery was obtained.

Table 3.10 Recovery from humic and fulvic acid samples

Sample	% recovery $\pm 1 \sigma_{n-1}$ (n=6)	
	Uranium	Thorium
Fulvic acid	108 ± 5	106 ± 14
Humic acid	101 ± 6	86 ± 6
Humic acid (acid digest)	101 ± 3	101 ± 3

Standards were also prepared in sodium hydroxide. This was for two reasons i) to see if it would be possible to analyse alkaline samples (ca pH 12) which had not been acidified and ii) in anticipation of speciation work involving DEAE cellulose which would result in samples in a sodium hydroxide matrix. Although it had been seen in section 3.3.1 that the TRU spec resin would function in the presence of a high level of dissolved solids the effect of above neutral pH on the resin was not known. Both acidified and unacidified samples were analysed and the results are presented in Figure 3.8 and Figure 3.9. It can be seen from these results that the above neutral pH did effect the recovery of uranium and thorium. The uranium recovery is much higher in the acidified samples but the thorium recovery, relative to the thorium standard, is low in all cases and not repeatable. The above neutral pH may have effected the thorium solubility reducing the residual level left in

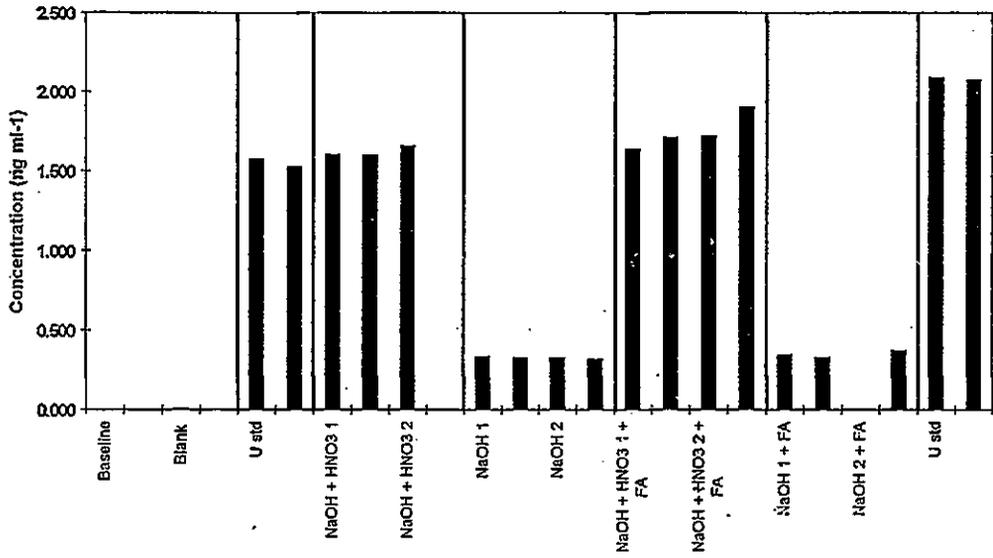


Figure 3.8 Uranium recovery from samples prepared in sodium hydroxide

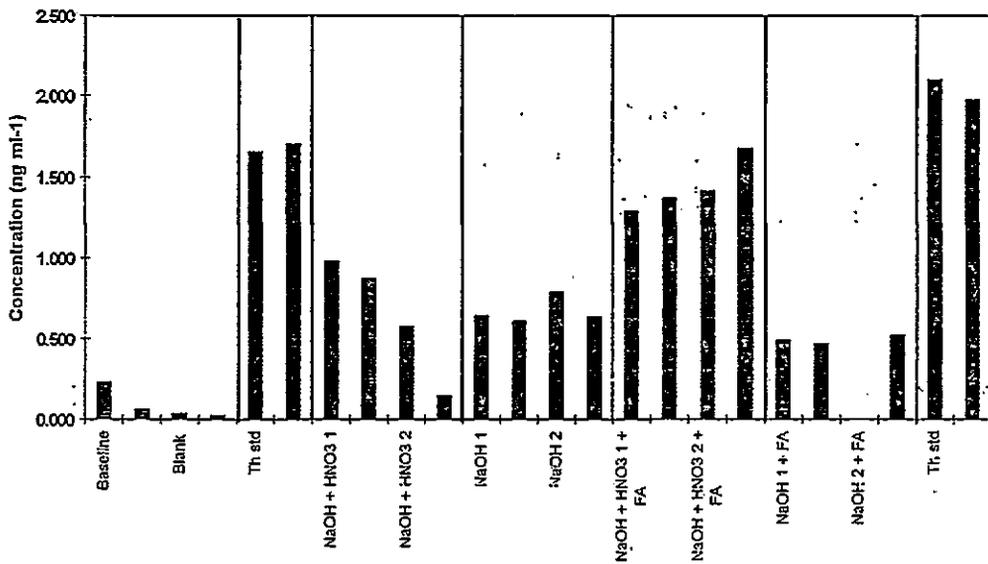


Figure 3.9 Thorium recovery from samples prepared in sodium hydroxide

containing fulvic acid (FA) gave the highest recoveries, possibly related to the formation of a more soluble thorium-fulvic acid complex.

3.3.3 Transfer of methodology

The TRU spec column and injection manifold developed at Plymouth were attached to the British Geological Survey (BGS) instrumentation at Keyworth in order to assess the transfer of the methodology between the two laboratories.

The linearity of response and limit of detection were determined (see Table 3.11 for results). Previous development work (section 3.3.1) had directed the sample matrix coming off the column into the ICP. For this work the manifold configuration was changed to direct the sample matrix to waste. This removed the sample matrix from the ICP-MS system and resulted in a constant oxalate flow through the spray chamber. This was done to allow the system to equilibrate to one set of conditions without having to re-establish equilibrium with each change from nitric to oxalate as the sample moves through the system. The constant flow of oxalate through the torch resulted in a build up of solid material at the point where the injector tube narrowed which could have lead to a blocked torch. This was remedied by using a torch with a wide bore injector in later work.

3.3.3.1 Cyprus groundwater samples

A number of high matrix concentration groundwater samples collected and analysed by the BGS were reanalysed using the TRU spec column and the results compared. For the original analysis the samples had been diluted to reduce the sample matrix concentration. The results can be seen in Table 3.12, and the sample compositions in Table 3.13.

The thorium results were all below the limit of detection (0.004 ng ml^{-1}) for the TRU spec column. This was however considerably lower than the original BGS limit of detection (1 ng ml^{-1}). The uranium results were similar to the original BGS results. This indicates that the TRU spec column will facilitate the analysis of this type of sample without

requiring any prior sample dilution. The TRU spec column and injection manifold functioned satisfactorily indicating that the method could be transferred between laboratories.

Table 3.11 TRU spec linearity and limit of detection on BGS instrumentation

	BGS result		Plymouth result	
	Uranium	Thorium	Uranium	Thorium
Correlation coefficient	0.9973	0.9983	0.9993	0.9982
LOD (ng ml ⁻¹)	0.0009	0.0040	0.0130	0.0056

Table 3.12 Comparison of results for groundwater samples

Sample ID	TRU spec results (ng ml ⁻¹)		BGS results (ng ml ⁻¹)	
	Uranium	Thorium	Uranium	Thorium
C1	0.07	<0.004	<0.1	<1
C2	0.14	<0.004	0.1	<1
C3	4.35	<0.004	4.3	<1
C4	10.02	<0.004	8.6	<1

**Table 3.13 Sample composition (major components, µg ml⁻¹)
for groundwater samples**

Sample ID	Ca	Mg	Na	Cl	SO ₄
C1	165	78	1239	1469	1285
C2	115	72	1096	1207	1261
C3	455	1468	12164	22394	3235
C4	676	85	190	248	1735

3.4 Analysis of natural water samples

Surface and groundwater samples from various locations in the S. W. of England were analysed using the TRU spec column. Dartmoor is situated on granite bedrock which leaches a low level of uranium into the environment. Samples were taken from the River Meavy and the River Plym on Dartmoor. Samples were also taken from the foreshore of Plymouth Sound at Devil's Point. South Terras is an abandoned uranium mine in Cornwall, where the rock is killas and greenstone with elvan dykes. The uranium was in the form of pitchblende with some autunite (a sample of copper autunite was found on the mine spoil heap during a sampling trip) and torbernite nearer the surface¹⁰⁵. Here samples were taken from the water coming out of the adit mouth, a drainage ditch south (downstream) of the adit mouth and a stream running north of the adit past the mine spoil heaps. The results for these samples can be seen in Table 3.14.

Table 3.14 U and Th results for water samples, obtained using the TRU spec column

Sample	U (ng ml ⁻¹)	Th (ng ml ⁻¹)
Dartmoor R. Meavy (acidified)	0.36	< 0.006
Dartmoor R. Meavy (not acidified)	0.35	< 0.006
Dartmoor R. Plym	0.17	< 0.006
Devil's Point pool	3.65	< 0.006
Devil's Point foreshore	3.03	< 0.006
South Terras adit mouth	8.95	0.009
South Terras drain S of adit	7.62	0.017
South Terras stream N of adit	0.37	0.017

Alkaline groundwater samples (acidified before analysis) with a high matrix concentration were analysed using the TRU spec method to determine the levels of uranium and thorium present. The results obtained were compared to those from analysis of the same samples (after a x20 dilution) at the BGS laboratory and the results are presented Table 3.15. A chromatogram obtained from one of the samples (Figure 3.10) with uranium quantified at 0.01 ppb shows that this level of uranium can be detected and quantitatively determined.

The uranium results from the TRU spec method could not be directly compared with the BGS results because all the BGS samples, except one, were below the BGS method limit of detection. The result for sample J10 (the only sample above the BGS limit of detection) is the same in both analysis. All the thorium results were below the limit of detection of both methods.

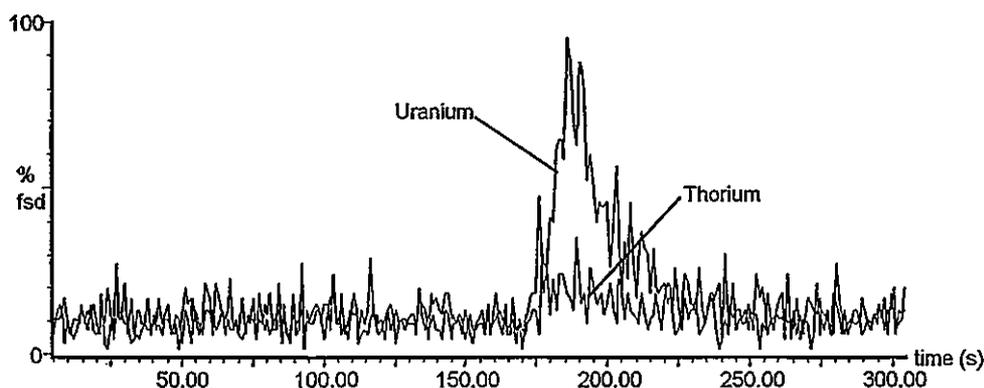


Figure 3.10 Chromatogram obtained from groundwater sample J4, demonstrating detection capability of $0.01 \text{ ng ml}^{-1} \text{ U}$

Table 3.15 Results for alkaline groundwater samples by TRU spec and BGS methods

Sample ID	TRU spec results		BGS results	
	U (ng ml ⁻¹)	Th (ng ml ⁻¹)	U (ng ml ⁻¹)	Th (ng ml ⁻¹)
J1	0.04	<0.006	<0.06	<0.1
J2	0.04	<0.006	<0.06	<0.1
J3	0.04	<0.006	<0.06	<0.1
J4	0.01	<0.006	<0.06	<0.1
J5	0.02	<0.006	<0.06	<0.1
J6	0.009	<0.006	<0.06	<0.1
J7	0.01	<0.006	<0.06	<0.1
J8	0.006	<0.006	<0.06	<0.1
J9	0.002	<0.006	<0.06	<0.1
J10	0.07	<0.006	0.069	<0.1
J11	0.03	<0.006	<0.06	<0.1
J12	0.07	<0.006	<0.06	<0.1
J13	0.002	<0.006	<0.06	<0.1

The unacidified portion of sample J10 was also run through the TRU spec column. When the load phase (containing the sample matrix and any other components not retained on the column) was directed through the ICP-MS a peak was seen in both phases of the chromatogram indicating that the uranium was not completely retained on the column under basic (pH 12) sample conditions (see Figure 3.11). Approximately 80% uranium was recovered in the elute phase. The mass balance (sum of both peaks) was in agreement with the result for the corresponding acidified sample.

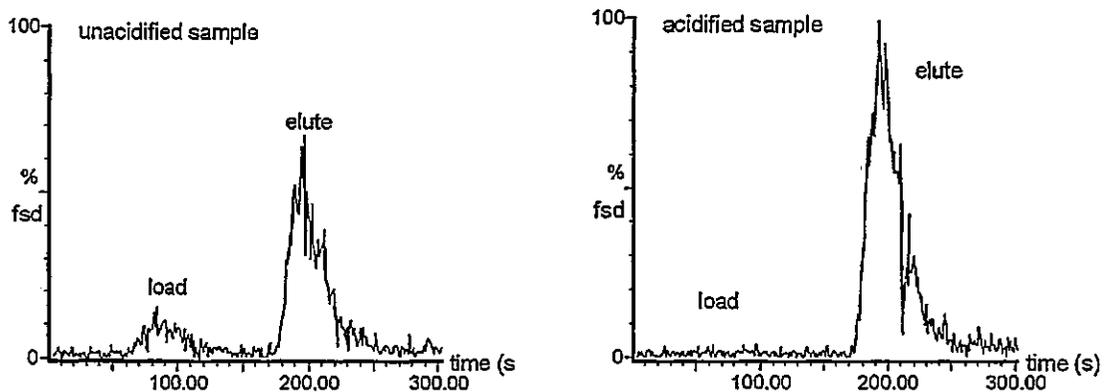


Figure 3.11 The effect of an unacidified sample (pH 12) on U retention on TRU spec

These results indicate that the TRU spec resin will function well in the presence of a natural sample matrix in acidic and neutral conditions but the analyte is not completely retained by the resin (during the load phase of the analysis) under basic conditions. For future work samples would have to be acidified or at least neutralised prior to analysis. However sample dilution would not be required.

3.5 Summary

Sample analysis was carried out using an in-line SPE column containing TRU spec, an actinide specific extraction resin, with a nitric acid carrier and ammonium hydrogen oxalate eluent. An acid clean-up column and system clean out protocol reduced thorium contamination. The TRU spec resin functioned well with acidified and neutral samples but alkaline samples required acidification before analysis to prevent low recovery. This method allowed analysis of samples with high dissolved solids content without prior sample dilution. Good recoveries (U 101-108%, Th 87-115%) were obtained from samples with high levels of inorganic and organic matrix components ($8 \mu\text{g ml}^{-1}$ humic substances). This was an improvement on conventional chelating resins which give low recoveries in the presence of organic carbon. A range of water samples were analysed and the methodology transferred to the BGS laboratory in Keyworth

Chapter Four

4. Separation of inorganic and organic uranium species

This chapter describes the work carried out to develop a separation method for inorganic and organic uranium and thorium species. This method was then applied to the analysis of natural water samples. Two different separation procedures were investigated. The principal behind the first procedure was to separate the sample by retaining the organic species on the resin while the 'free' inorganic species were not retained by the resin. This was carried out using an anion exchange resin, di-ethyl-amino-ethyl (DEAE) cellulose. The principal behind the second procedure was to separate the sample by retaining the 'free' inorganic species on the resin while the organic species were not retained. This was carried out using a chelating resin, Hyphan.

4.1 Use of DEAE cellulose anion exchange resin

The DEAE cellulose resin was packed in to a column and following the procedure outlined in the Experimental chapter (Chapter 2) samples with and without fulvic acid (FA) were run through the DEAE column. This was an off-line technique and the sample fractions from the load and elute phases of the separation procedure were collected for subsequent analysis by ICP-MS. The FA could be seen retained on the column as a brown band during the load phase, which was then removed during the elute phase. This was confirmed by comparing the UV spectra of the two phases with a standard containing FA.

The uranium and thorium, in the samples without FA, were expected to be in cationic form (sample at pH 5) and hence not retained on the anion exchange resin. This would result in uranium and thorium being recovered from the load fraction of the samples. In the samples containing FA, the uranium and thorium complexed with the FA were expected to be retained on the resin while the 'free' (not complexed with FA) uranium and

thorium passed straight through. The complexed uranium and thorium would then be removed from the resin in the elute phase of the separation. This would result in uranium and thorium being recovered in both the load and elute fractions of the sample. The uranium and thorium recovery results are presented in Figure 4.1 and Figure 4.2. These results indicated that for the samples without FA the uranium and thorium were not completely recovered in the load fraction of the sample. Although the remaining uranium from the sample was recovered in the elute fraction the remaining thorium was not. The results for the samples containing FA indicated that all the uranium was retained on the resin during the load phase and subsequently recovered in the elute phase of the separation. This could have indicated that all the uranium was complexed with the FA but, given the uranium recovery results for the samples without FA, this was not conclusive. The thorium recovery results indicated that the majority of the thorium was retained on the resin during the load phase of the separation but that this was not fully recovered during the elute phase, although the total thorium recovery was higher for samples containing FA than for those not containing FA.

This method was therefore not satisfactory since even the samples without FA were retained on the column. The incomplete thorium recovery in all of the samples was also unsatisfactory. The retention of 'free' uranium could be due to either incomplete washing of the column prior to elution or the presence of anionic uranium species. The uranium was thought to be in a cationic form ^{13, 25} but the literature can be inconsistent in its predictions of the nature of the species present.

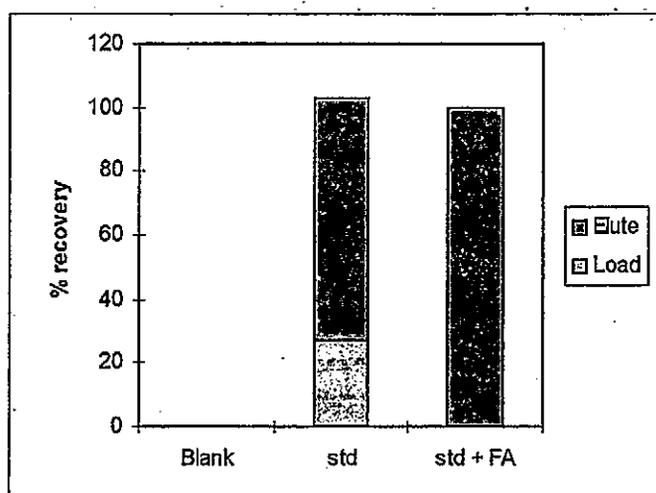


Figure 4.1 Uranium recovery from the load and elute fractions collected as the samples passed through the DEAE cellulose resin

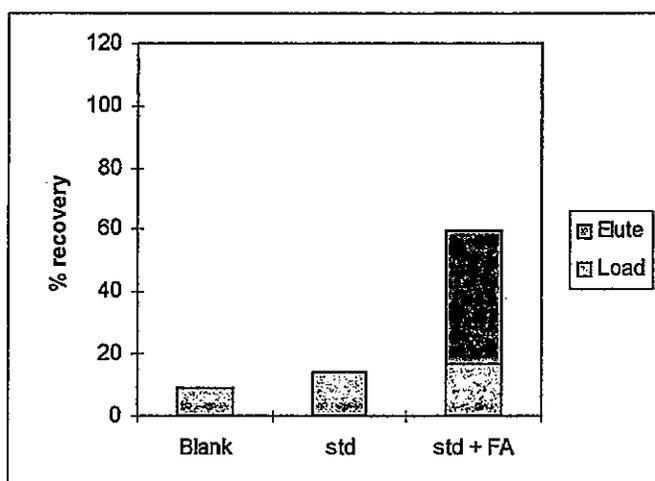


Figure 4.2 Thorium recovery from the load and elute fractions collected as the samples passed through the DEAE cellulose resin

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IN CANDIDACY FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

4.2 Use of Hyphan chelating resin

Hyphan is a cellulose based chelating resin which has been used for the recovery of uranium from water samples^{37,106,107,108}. Hyphan will bind uranium in neutral water samples but low recoveries have been reported in the presence of humic substances. This would suggest that the Hyphan resin does not bind uranium already complexed with humic/fulvic acids. While not suitable for total uranium determinations this property of the resin could be used to separate inorganic and humic/fulvic species in solution. The possibility of using the Hyphan resin to separate inorganic and organic uranium species was investigated in this work using two procedures, a batch method and a column method.

4.2.1 Batch method

The use of the Hyphan resin to chelate uranium^{37, 106} or transition metals^{107, 108} has been reported in the literature using a batch technique where the Hyphan resin is added directly to the sample. Recoveries of 80-95% have been reported using 0.1 to 0.5 mg Hyphan resin per 100 ml sample, with $t_{1/2}$ binding times of 10 seconds to 2 minutes and 70% elution in 30 seconds with acid. This gave the basis for the method used in this study. Sample pH values reported in the literature range from pH 4 to 8, so the samples were left at their near neutral pH for this study. The binding and elution times from studies reported in the literature also indicated that the Hyphan reaction kinetics were potentially fast enough to facilitate an in-line column separation method.

Following the procedure detailed in the Experimental chapter (Chapter 2) the initial findings from this study indicated that for a standard solution ($U\ 1\ ng\ ml^{-1}$) made up in synthetic surface-water the majority of the uranium was retained on the Hyphan resin and could then be recovered with an acid eluent. For a natural water sample (from the R. Meavy, Devon) most of the uranium was recovered from the water fraction. This was

thought to be due to the uranium being present in a uranium-organic form which was not retained on the Hyphan resin (see Table 4.1).

A comparison of the sum of the water and acid fractions, with the results from a determination of the total uranium concentration in the samples, indicated that complete uranium recovery had been obtained for the R. Meavy sample but that the recovery from the synthetic surface-water standard was slightly low. Further work on recovery and repeatability with a synthetic surface-water standard produced the results in Table 4.2. This study included a second extraction of uranium from the Hyphan resin with acid (labelled acid 2) to determine if low recovery was due to incomplete removal of uranium from the Hyphan resin in the first acid extraction. However this produced even lower recovery results than the previous work. The recovery level was not significantly increased in the second acid extraction. Thus if the uranium was not recovered from the water fraction, or extracted from the Hyphan resin into either acid fraction, then it is possible that it was irretrievably bound to the Hyphan resin (although this was thought unlikely given the higher recoveries obtained in the previous work and the recoveries reported in the literature), or it could have come out of solution and/or stuck to the sides of the plasticware and not been recovered. Although all the uranium in the R. Meavy sample had been recovered, the higher level of uranium in the synthetic surface-water sample may not have been entirely stable in that matrix, leading to recovery problems. Subsequent work (carried out after an investigation of a suitable diluent for preparation of standards at neutral pH, detailed in section 4.2.2) using standards prepared in a synthetic groundwater solution produced results with 97% total recovery (see Table 4.3).

Although the Hyphan resin can be used in a batch technique, developing an on-line column technique would offer the advantages of reducing the sample handling time required for the separation stage, the total analysis time and the volume of sample required.

Table 4.1 Initial uranium recovery results from the water and acid fractions of samples separated using the Hyphan resin

Sample	Water fraction (ng ml ⁻¹)	Acid fraction (ng ml ⁻¹)	Total uranium (ng ml ⁻¹)
River Meavy 1	0.34	0.05	
River Meavy 2	0.32	0.06	
R. Meavy (not separated)			0.35
Surface-water std 1	0.05	0.79	
Surface-water std 2	0.07	0.79	

Table 4.2 Recovery of uranium from synthetic surface-water using the Hyphan resin

Sample	Water fraction (ng ml ⁻¹)	Acid 1 fraction (ng ml ⁻¹)	Acid 2 fraction (ng ml ⁻¹)
Surface-water blank	0.00	0.00	0.00
Surface-water std 1	0.04	0.46	0.13
Surface-water std 2	0.03	no data	0.04
Surface-water std 3	0.00	0.32	0.10
Surface-water std 4	no data	0.47	0.05
Surface-water std 5	0.08	0.48	0.00
Surface-water std 6	0.13	0.47	0.03

Table 4.3 Recovery of uranium from synthetic groundwater using the Hyphan resin

Sample	Water fraction (ng ml ⁻¹)	Acid fraction (ng ml ⁻¹)	Water + Acid (ng ml ⁻¹)
Groundwater blank	0.00	0.02	0.02
Groundwater std 1	0.09	0.80	0.89
Groundwater std 2	0.16	0.84	1.00
Groundwater std 3	0.18	0.78	0.96
Groundwater std 4	0.08	1.00	1.08
Groundwater std 5	0.13	0.81	0.94
Groundwater std 6	0.13	0.82	0.95
Mean result	0.13	0.84	0.97

4.2.2 Column method

A small column was packed with the Hyphan resin following the procedure detailed in the Experimental chapter (Chapter 2). This column was then incorporated into the sample introduction manifold used to deliver the sample into the ICP-MS. This was the same manifold used with the TRU spec column in Chapter 3 and the details of the configuration of the column, manifold and ICP-MS can be found in the Experimental chapter. The on-line separation of the sample consisted of two stages: i) loading the sample on to the column with a neutral pH carrier, here the inorganic species would be retained on the column but the organic species would pass straight through the column and be detected as a peak in the first half of the resulting chromatogram and ii) eluting the inorganic species with an acidic eluent, these would then be detected as a peak in the second half of the chromatogram. Between injections an equilibration period was then used, when the carrier was switched back through the column, to allow the column pH to return to the original pH of the carrier before the acid had passed through the column. The length of time required to equilibrate the column was determined by measuring the pH of the carrier as it came out of the column, these results can be seen in Figure 4.3. A series of different carriers were investigated in order to determine which would provide an environment within the column at a similar pH value to that of a typical water sample when it was injected into the system and then return the column back to that pH value after the acidic eluent had passed through the column. Looking at the results in Figure 4.3 it can be seen that both the sodium chloride carriers failed to return to their original pH level and their pH values were still slowly drifting up after ten minutes. The acetate and citrate buffers displayed a rapid increase in pH which levelled off close to their original pH after five minutes. The acetate and citrate buffers would create a pH environment in the column similar to that of the samples which should aid in the repeatability of the method.

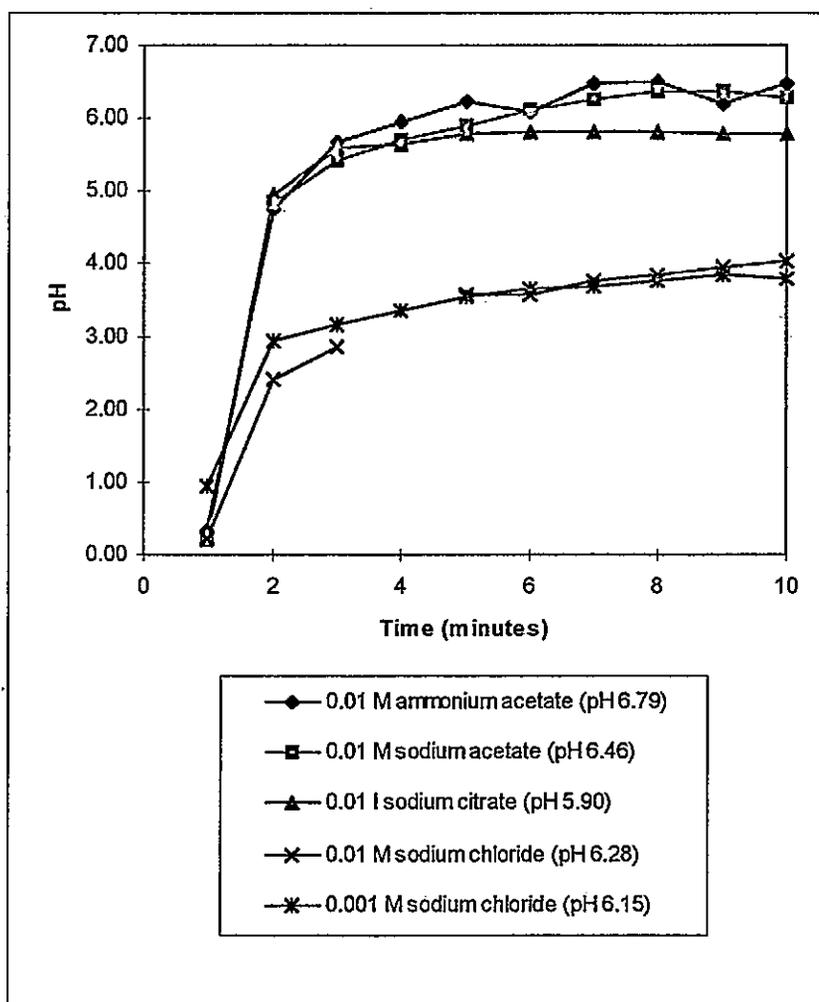
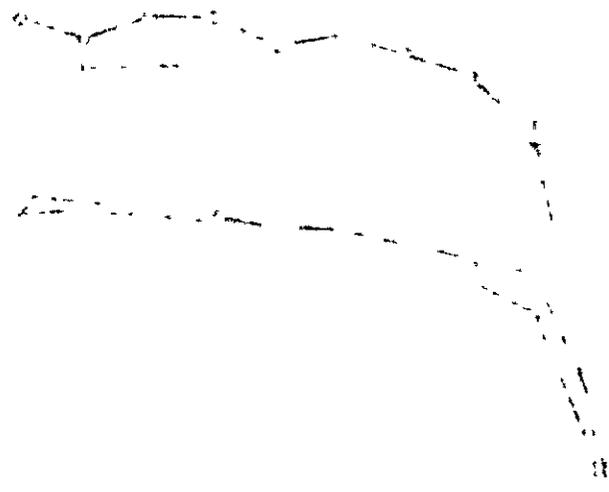


Figure 4.3 Change in carrier pH over time during passage through the Hyphan column after passage of the acidic eluent through the column



Time Value

A uranium standard, with no organic content, and a natural water sample containing dissolved organic carbon were analysed using the different carriers, with a five minute equilibration time before each sample injection. Representative chromatograms are displayed in Figure 4.4 and Figure 4.5.

The peak profiles were the same for each carrier, except citrate. Replicate injections ($n=3$) of standard and natural water sample gave reasonable repeatability for all of the carriers except sodium acetate.

Ammonium acetate 0.01M (pH 6.77) produced a chromatogram with one peak for the standard and two peaks for the sample (see Figure 4.4), the first peak being the organic species and the second the inorganic species.

Sodium acetate 0.01M (pH 6.22) produced a chromatogram with two peaks for the sample but, although the ratio of the two peaks remained constant, the peak size varied from injection to injection. This would not be suitable for a quantifiable method.

Sodium citrate solution with an ionic strength of 0.01 (pH 5.86) produced a chromatogram with two peaks for the sample but produced a chromatogram with three peaks for the standard; two in the first half and one in the second half (see Figure 4.5). The first peak in the standard chromatogram was an unretained peak coming off where the organic species would be expected. The second peak, which was also in the load phase of the chromatogram, was also where the organic species would be expected, but had been retained slightly on the column (Rt. 100s). The third peak was in the second part of the chromatogram, the elute phase, where the inorganic uranium species were expected. It is possible that although the standard was made up of inorganic species before it was injected, while in contact with the citrate carrier a fraction of the total uranium was converted in to a uranium citrate species which was not retained on the column. The slight retention of the second peak could be due to the uranium being retained on the column in its inorganic form,

then reacting with the citrate as the carrier passed through the column and subsequently being eluted as the citrate species.

Sodium chloride solutions at 0.01M and 0.001M (pH 5.47 and 5.82) produced chromatograms with one peak for the standard injection and two peaks for the sample injection, in the same manner as the ammonium acetate carrier. However the ratio of the two peaks was much lower, with more uranium being retained on the column with the sodium chloride carriers to form the second peak. This could be related to the pH of the carrier. Although it was measured as pH 5.5 before analysis, during the analysis the carrier pH dropped to 3.5 which could have effected the sample speciation and the separation.

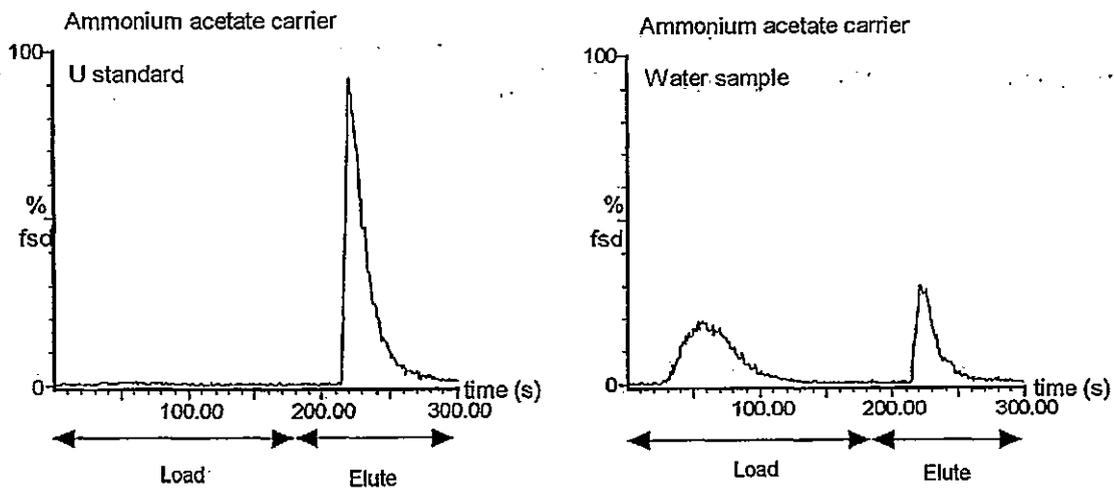


Figure 4.4 Chromatograms for a uranium standard and a natural water sample separated using the Hyphan column with an ammonium acetate carrier

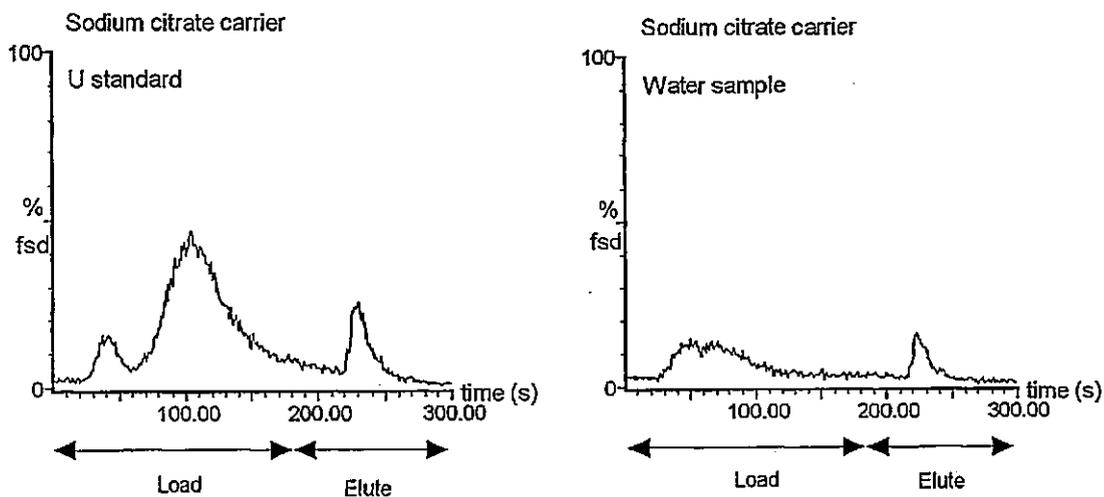


Figure 4.5 Chromatograms for a uranium standard and a natural water sample separated using the Hyphan column with a sodium citrate carrier

As the standards were not prepared in an acidic solution, since this would result in the uranium not being retained on the column, the diluent needed to be one which would maintain the uranium in solution (uranium is not very soluble in pure water at neutral pH but the addition of other components to the diluent would result in the formation of more soluble uranium species). The effect of different diluents on uranium recovery was therefore investigated. The results can be seen in Table 4.4. Standards were made up as 1 ng ml^{-1} uranium solutions. The use of natural river water as a diluent would have provided a similar matrix to that of the samples, but it did not provide complete recovery, nor did the use of synthetic surface-water as a diluent. The standard prepared using natural river water as a diluent had a higher uranium concentration than that found naturally in the river and it may be that this uranium concentration was too high to remain in solution under these conditions. The results indicated that the higher concentration of inorganic components in the synthetic groundwater solution was required to keep the uranium in solution.

Using the ammonium acetate carrier and standards prepared with the synthetic groundwater diluent, the linearity, repeatability and limit of detection of response were measured. The results are presented in Table 4.5.

An injection of a groundwater diluent blank produced the response shown in Figure 4.6. The response seen was from the internal standard which was added to the carrier stream at a 'T' join situated after the column and produced a constant signal. When a synthetic seawater blank was injected the response in Figure 4.7 was produced. Here there was a large drop in the internal standard signal, corresponding to the time period where the seawater matrix passed through the plasma (the plasma also went orange at this point due to the presence of sodium in the seawater). This demonstrated signal suppression (the internal standard signal being suppressed) due to the large amount of sample matrix in the plasma and hence the reason why the matrix separation method described in Chapter 3 was developed. Because when using the Hyphan column to separate the uranium species peaks

are seen in both the first part of the chromatogram (where the sample matrix effect is seen) and the second part of the chromatogram, the level of organic species could not be determined in seawater samples. This would have to be determined indirectly using the level of inorganic species, determined from the second peak in the chromatogram from the Hyphan column, subtracted from the total uranium concentration, determined using the TRU spec method detailed in Chapter 3, the difference representing the level of organic species. This procedure would not be required for surface or groundwater samples as the level of sample matrix would not typically be high enough to produce interference and hence the organic and inorganic species could be determined from the same chromatogram.

Table 4.4 Recovery of uranium from different diluents

Matrix	% recovery
Natural surface-water	85
Synthetic surface-water	79
Synthetic groundwater	97
Sodium bicarbonate 0.01M	68

Table 4.5 Linearity, repeatability and LOD for uranium on Hyphan column

Linearity (0 to 5 ng ml ⁻¹) correlation coefficient	0.9907
Repeatability (n = 6) % rsd 0.5 ng ml ⁻¹	6.3
Repeatability (n = 6) % rsd 0.1 ng ml ⁻¹	5.2
Limit of detection ng ml ⁻¹	0.002

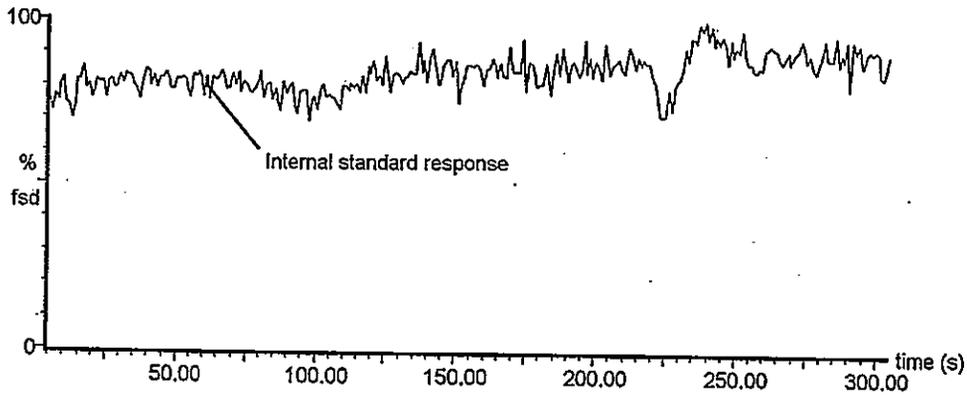


Figure 4.6 Effect of a groundwater blank injection on the internal standard response

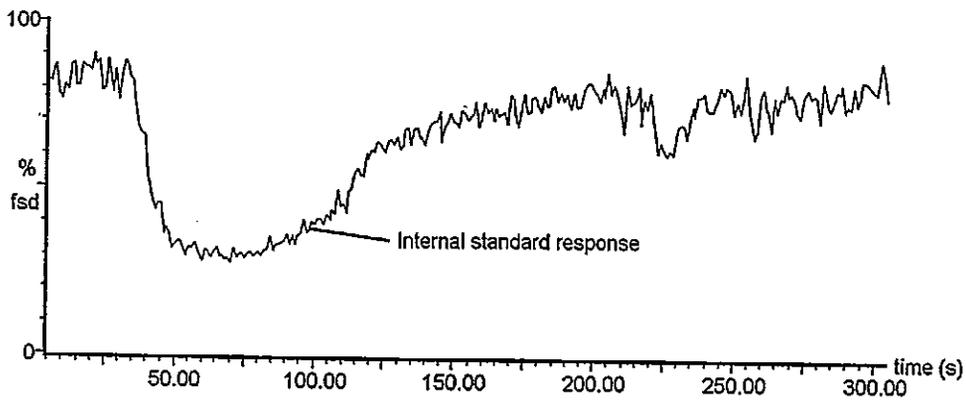
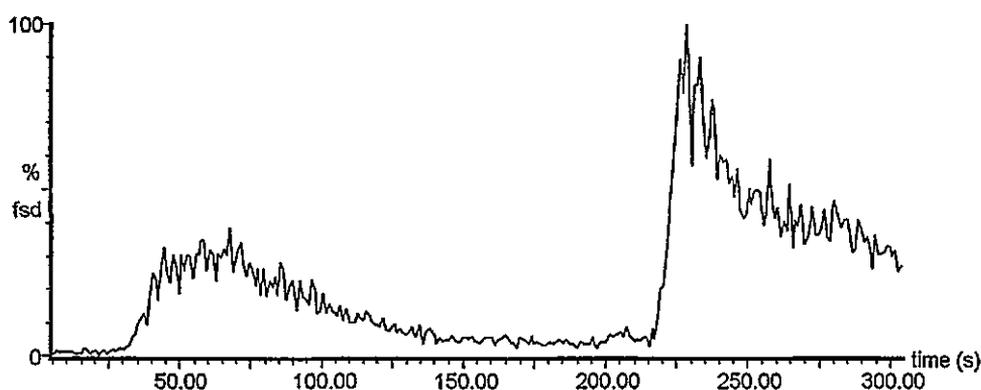


Figure 4.7 Effect of a seawater blank injection on the internal standard response

When a thorium standard, containing no organic carbon, was injected onto the column using the ammonium acetate carrier, two peaks were obtained, one in the load phase and one in the elute phase (Figure 4.8).

To determine whether this was due to thorium having little affinity for the Hyphan resin, or if the ammonium acetate was reacting with on the thorium in the same manner that the sodium citrate had reacted with the uranium in earlier experiments, the thorium standard was mixed with the Hyphan resin in batch mode. This was done to remove any effects due to the thorium reacting with the ammonium acetate, leaving only the thorium and the Hyphan resin to react. This resulted in the thorium binding to the Hyphan, thus indicating that it was the ammonium acetate which was effecting the thorium retention on the Hyphan column. This indicated that the in-line column technique would not be suitable for thorium speciation. Thus thorium speciation would have to be carried out using the batch technique or a different carrier found which would not react with the thorium.



**Figure 4.8 Thorium standard on Hyphan column
with ammonium acetate carrier**

4.3 Uranium speciation in natural water samples

Water samples were collected from a range of locations on Dartmoor, SW England. The location of these points are marked on the sketch map in Figure 4.9. From along the R. Plym these provided samples from near the source of the river at Ditsworthy warren, moving down through Cadover Bridge to Shaugh Bridge where samples were taken before and after the confluence of the R. Plym and R. Meavy and on to Plym Bridge. The R. Meavy locations provided samples before and after Burrator reservoir to see if this effected the samples. These samples were passed through the Hyphan column. The level of U-organic species obtained, as a percent of the total inorganic and organic species, can be seen in Table 4.6.

The September samples represent low water flow and the December samples high water flow in the rivers. All the samples had a high level of U-organic species which indicated that this was an environmentally important species. The level of U-organic species did not appear to be effected to any great extent by the increased water level in the December samples (see Table 4.7). Although the level of organic carbon had increased in the December samples this did not result in a corresponding increase in the level of U-organic species. Given the low uranium concentration and the relatively high organic carbon concentration it could be concluded that the samples had reached the maximum level of U-organic species which would form under the conditions present in the rivers at that time and an increase in organic carbon concentration would not increase the U-organic species level. This is further discussed in section 4.4.

Although there is little work in the literature on uranium and thorium speciation in natural water samples using chelating resins, there are results reported for a Swiss groundwater sample at pH 6 giving 83% U-organic species²⁰ and water from an old mine gallery in Morro do Ferro (Brazil)¹⁸ giving 80% Th-organic species at pH 6.5. These

Table 4.6 Experimental results obtained for uranium speciation of Dartmoor water samples

Location	% U-organic species	
	Sep. 2000	Dec. 2000
R. Plym, Ditsworthy Warren	83	no sample
R. Plym, Cadover Bridge	87	85
R. Plym, Shaugh Bridge	88	86
R. Plym + R. Meavy, Shaugh Bridge	84	81
R. Plym, Plym Bridge	85	79
R. Newleycombe Lake, above Burrator	79	76
R. Meavy, above Burrator	87	86
R. Meavy, Shaugh Bridge	80	79

Table 4.7 Characterisation of Dartmoor water samples

Location	Organic carbon ($\mu\text{g ml}^{-1}$)		Inorganic carbon ($\mu\text{g ml}^{-1}$)		pH		Total uranium (ng ml^{-1})	
	Sep. 00	Dec. 00	Sep. 00	Dec. 00	Sep. 00	Dec. 00	Sep. 00	Dec. 00
R. Plym, Ditsworthy Warren	1.91		0.71		6.38		0.11	
R. Plym, Cadover Bridge	2.82	3.83	0.88	0.56	6.45	6.26	0.12	0.11
R. Plym, Shaugh Bridge	3.12	4.19	1.12	0.87	6.55	6.28	0.14	0.12
R. Plym + R. Meavy, Shaugh Bridge	1.60	3.49	2.52	3.06	6.91	6.84	0.07	0.10
R. Plym, Plym Bridge	1.36	3.83	3.24	3.57	7.04	7.08	0.04	0.09
R. Newleycombe Lake, above Burrator	1.05	3.59	1.14	1.02	6.55	6.50	0.12	0.19
R. Meavy, above Burrator	1.41	4.75	1.30	0.47	6.58	6.22	0.11	0.15
R. Meavy, Shaugh Bridge	1.16	3.30	3.53	3.27	7.02	6.86	0.04	0.08

The levels of uranium and organic carbon, which give rise to the U-organic species in the samples, are detailed in Table 4.7. The high water level of the rivers in December could be expected to result in a lower level of uranium due to dilution of the river water, but the saturation of the land with water which occurred due to the high rain fall at this time of the year could increase the rate of dissolution of uranium out of the granite bedrock. The results in Table 4.7 indicate that the level of uranium was similar in both the September (low water flow) and December (high water flow) samples; i.e. the increased water flow does not appear to have a large net effect on the uranium concentration. Moving downstream (the R. Plym), the organic carbon level increased until the R. Plym meets the R. Meavy at Shaugh Bridge where there is a drop in the organic carbon level, as a result of the higher level in the R. Plym being diluted by the lower level in the R. Meavy. The sample pH values increased moving downstream as more inorganic carbon was picked up by the river. There was a large increase in pH and inorganic carbon when the R. Plym met the R. Meavy at Shaugh Bridge. The increase in pH and inorganic carbon in the R. Meavy was noted after Burrator reservoir. Thus the time spent in the reservoir effected the composition of the water. This increase in inorganic carbon, a potential competitor for uranium species formation, does not appear to have much effect on the level of U-organic species.

Analysing samples with a different water chemistry gave lower percent U-organic species results (see Table 4.8). These samples came from South Terras, an abandoned uranium mine in Cornwall, SW England. The southern sample comes from a drainage ditch fed by water from the adit mouth and the northern sample is from a stream running past the mine spoil heap. These samples have a higher uranium and inorganic carbon concentration and a higher pH. The lower level of U-organic species could be due to the higher level of inorganic carbon forming competing uranium carbonate species, and/or there not being sufficient organic carbon, relative to the increased uranium concentration, to form a greater amount of the U-organic species.

Table 4.8 Uranium speciation results for South Terras

	South Terras, South	South Terras, North
% U-organic species	62	69
Organic carbon ($\mu\text{g ml}^{-1}$)	5.54	3.77
Inorganic carbon ($\mu\text{g ml}^{-1}$)	8.88	12.47
pH	7.28	7.22
Total uranium (ng ml^{-1})	7.62	0.37

4.3.1 Speciation of synthetic water samples

In order to obtain data from samples with a wider range of organic carbon concentrations and pH values a series of synthetic surface-water samples were prepared with uranium ($0.1, 1, 10 \text{ ng ml}^{-1}$), humic substances ($1, 2, 4 \mu\text{g ml}^{-1}$) and pH (5.5 to 7.4). These were analysed in the same manner as the natural water samples. The results can be seen in section 4.4 where the level of U-organic species is correlated to the organic carbon (OC) concentration and the sample pH. The humic substance concentration of these samples was converted to organic carbon to match the DOC measurements of the natural samples. The humic substances were taken to be 50% carbon, so for example $1 \mu\text{g ml}^{-1}$ humic substances would be equivalent to $0.5 \mu\text{g ml}^{-1}$ organic carbon.

4.4 Comparison of the level of experimentally determined U-organic species to the level organic carbon and pH values of the samples

4.4.1 pH level

The Dartmoor and synthetic 0.1 ng ml^{-1} uranium samples show no relationship between pH and U-organic species level except for the sample at pH 7.4 with an organic carbon concentration of $0.5 \text{ } \mu\text{g ml}^{-1}$ (see Figure 4.10). To further investigate if this was an effect of pH or sample related, the results from the higher uranium concentration samples were processed to see if a similar trend could be found (see Figure 4.11). The same trend is seen, with a drop in U-organic species at pH 7.4 for the sample containing $0.5 \text{ } \mu\text{g ml}^{-1}$ organic carbon. This drop in the level of U-organic species is also seen for the sample containing OC $1 \text{ } \mu\text{g ml}^{-1}$ organic carbon (with more uranium present there is effectively less organic carbon per unit of uranium).

For the Dartmoor samples there was no correlation with pH. For the synthetic samples, pH only had an effect at high pH and in samples with a low organic carbon concentration.

4.4.2 Organic carbon level

The Dartmoor samples and the synthetic 0.1 ng ml^{-1} uranium samples show a similar trend indicating an increase in U-organic level with increasing organic carbon concentration (see Figure 4.12). However, a doubling of the organic carbon concentration from 1 to $2 \text{ } \mu\text{g ml}^{-1}$ does not produce a corresponding doubling of the %U-organic species. The main difference with the synthetic samples is that the samples at pH 7.4 show a much greater reduction in the level of U-organic species when the organic carbon concentration is below 1 ng ml^{-1} than any of the other samples with lower pH values. The synthetic samples with

higher uranium concentrations also show the same trend (see Figure 4.13), and the higher uranium concentration samples have a lower overall level of U-organic species. This is because although the organic carbon level is the same in these samples as in the lower uranium concentration samples, the higher uranium concentration effectively results in a lower level of organic carbon per unit of uranium. This leads to the possibility that the organic carbon/uranium (OC/U) ratio could be used to express a relationship between the organic carbon concentration, the uranium concentration and the level of U-organic species. This relationship is plotted in Figure 4.14 and Figure 4.15 for two sets of samples, those at around pH 6.5 and those at around pH 7.4 respectively. These graphs do show an increase in U-organic species with increasing OC/U ratio. Most of this effect is seen when the OC/U ratio is below 10, which in the case of the Dartmoor samples (or the $0.1 \text{ ng ml}^{-1} \text{ U}$ synthetic samples) would be equivalent to $1 \text{ } \mu\text{g ml}^{-1}$ organic carbon per $0.1 \text{ ng ml}^{-1} \text{ U}$. Thus the U-organic species would dominate even at a relatively low organic carbon concentrations under these conditions. It would appear that the level of U-organic species rapidly increases as organic carbon is added to the system but this then starts to slow down once the majority of the uranium is in the organic form. This then results in the trend seen in the Dartmoor samples, where the level of U-organic species only shows a small increase with a relatively large increase in organic carbon level. This could be due to the amount of U-organic species formed levelling off as the system approaches saturation with respect to organic carbon concentration.

A drop in the OC/U ratio in the samples produced a reduction in the U-organic level, but each set of data (at each uranium concentration) did not completely agree with the other data sets. Each data set produced a different slope indicating that although the overall trend was for an increase in the level of U-organic species with increasing OC/U ratio the degree to which this ratio had to increase to produce an increase in the level of U-organic species was different for each set of samples. This was most noticeable in the higher pH

samples, for example looking at the data in Figure 4.15, a uranium concentration of 1 ng ml⁻¹, and an OC/U ratio of 2, resulted in 70% U-organic species; whereas a uranium concentration of 0.1 ng ml⁻¹, and an OC/U ratio of 5, resulted in 66% U-organic species, a drop in the %U-organic species when moving from one data set to the other even though the OC/U ratio increased. The uranium concentration itself appears to be effecting the level of U-organic species formation, separately from the effect of organic carbon concentration.

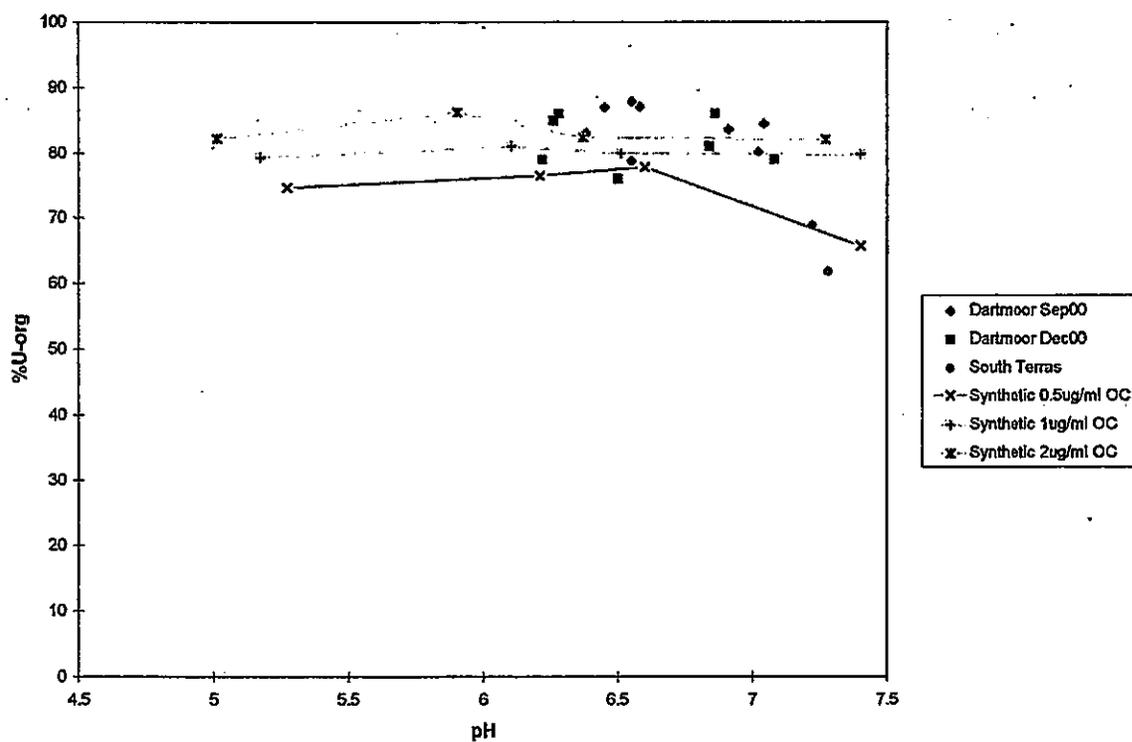


Figure 4.10 Correlation of %U-organic species with pH

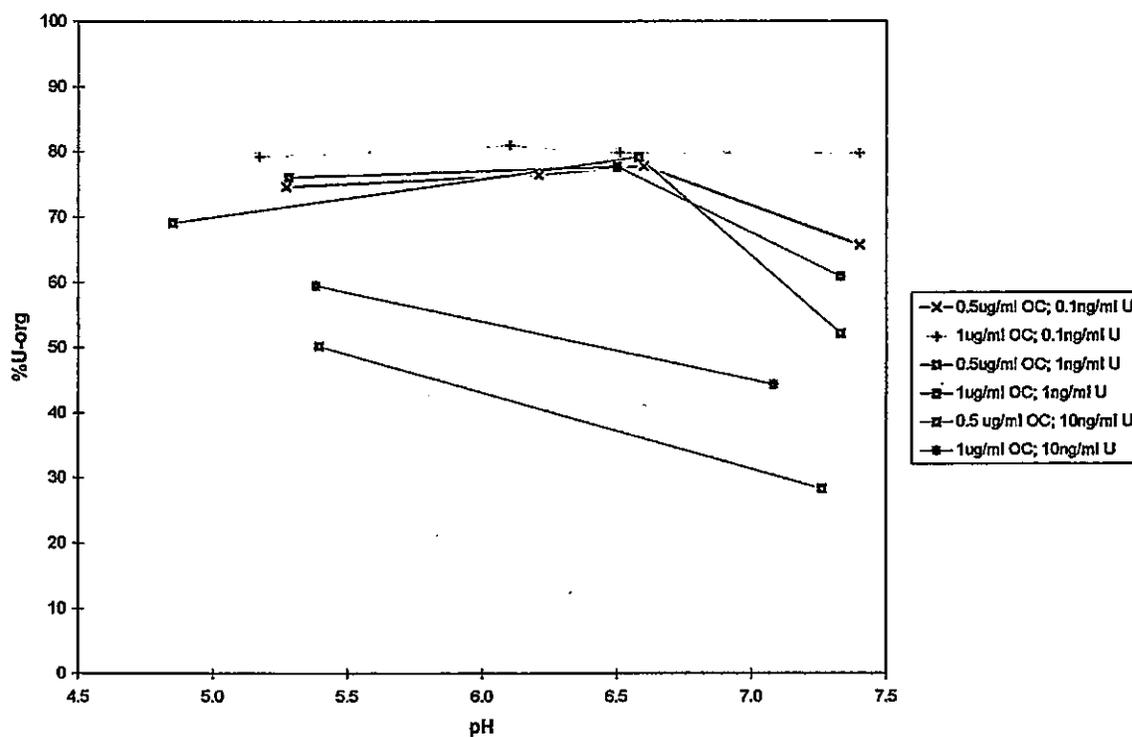


Figure 4.11 Correlation of %U-organic species with pH for synthetic water samples at various U concentrations

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1950

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1951

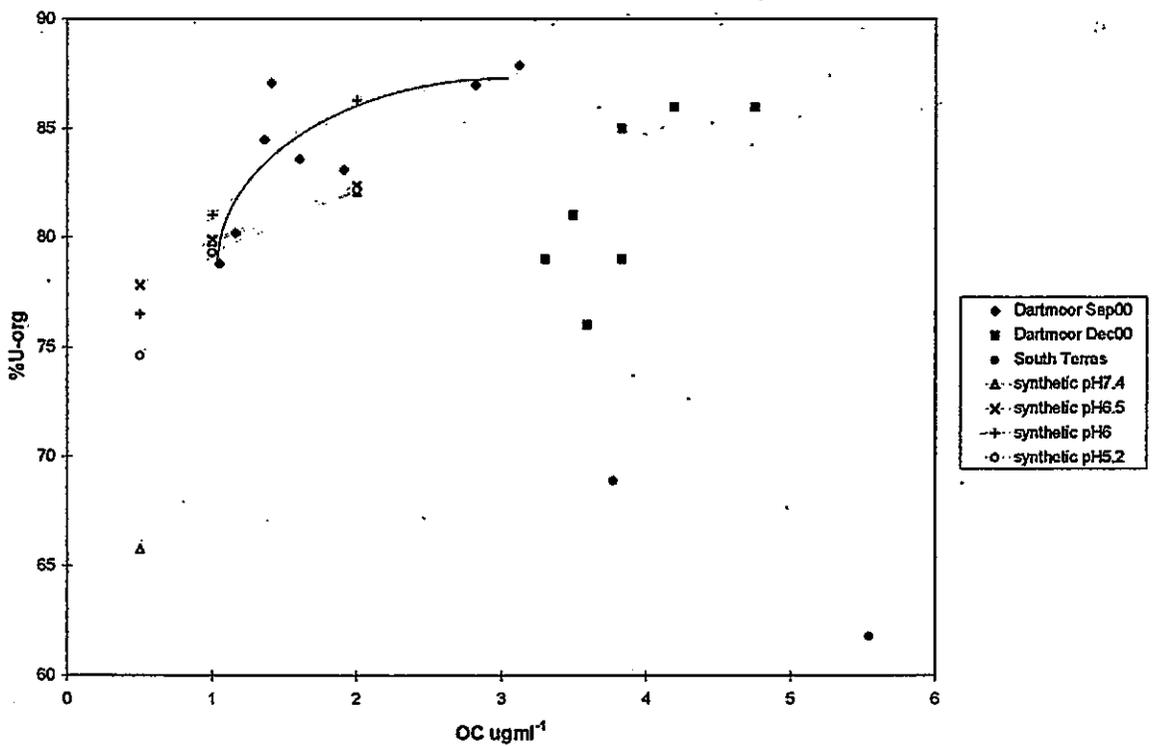


Figure 4.12 Correlation of %U-organic species with organic carbon concentration

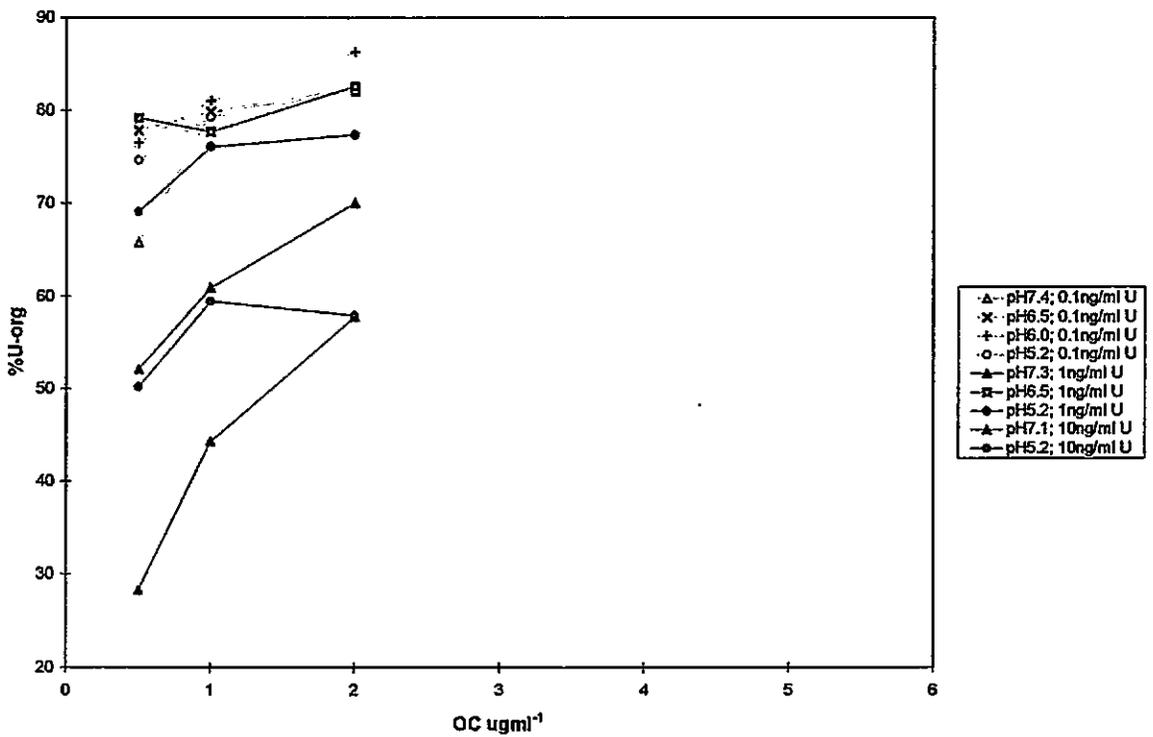


Figure 4.13 Correlation of %U-organic species with organic carbon concentration for synthetic water samples at various U concentrations

1

1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60 61 62 63 64 65 66 67 68 69 70 71 72 73 74 75 76 77 78 79 80 81 82 83 84 85 86 87 88 89 90 91 92 93 94 95 96 97 98 99 100

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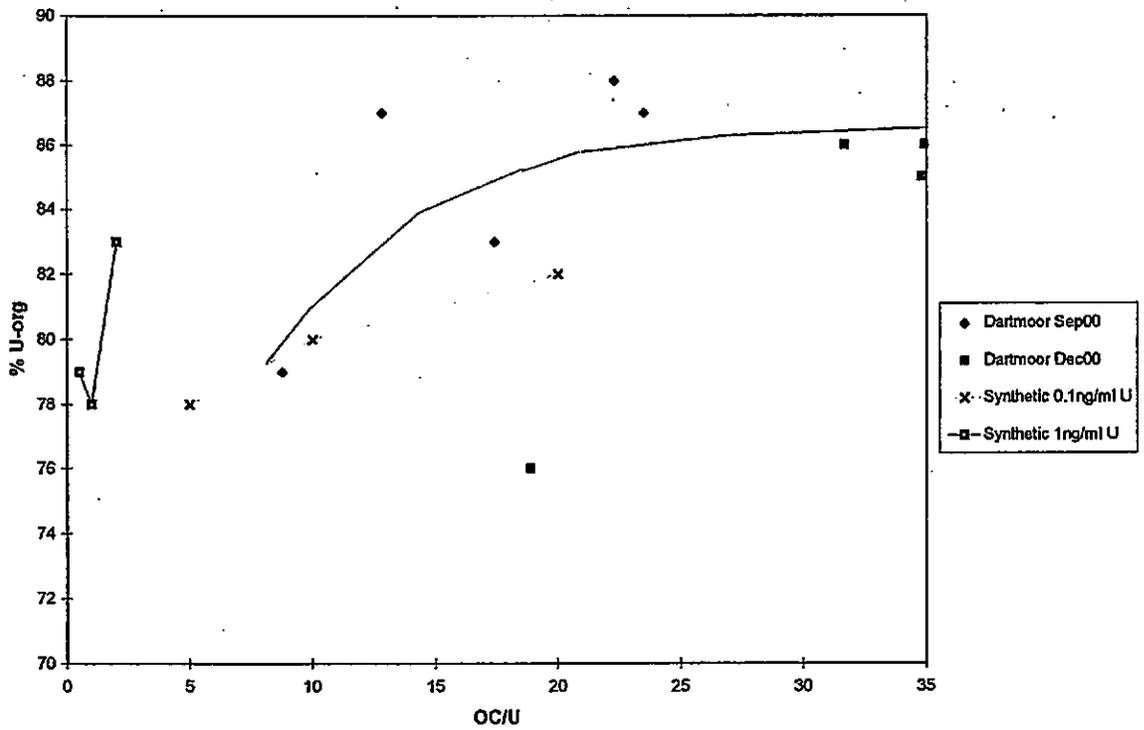


Figure 4.14 Correlation of %U-organic species with OC/U ratio for samples at ~pH 6.5

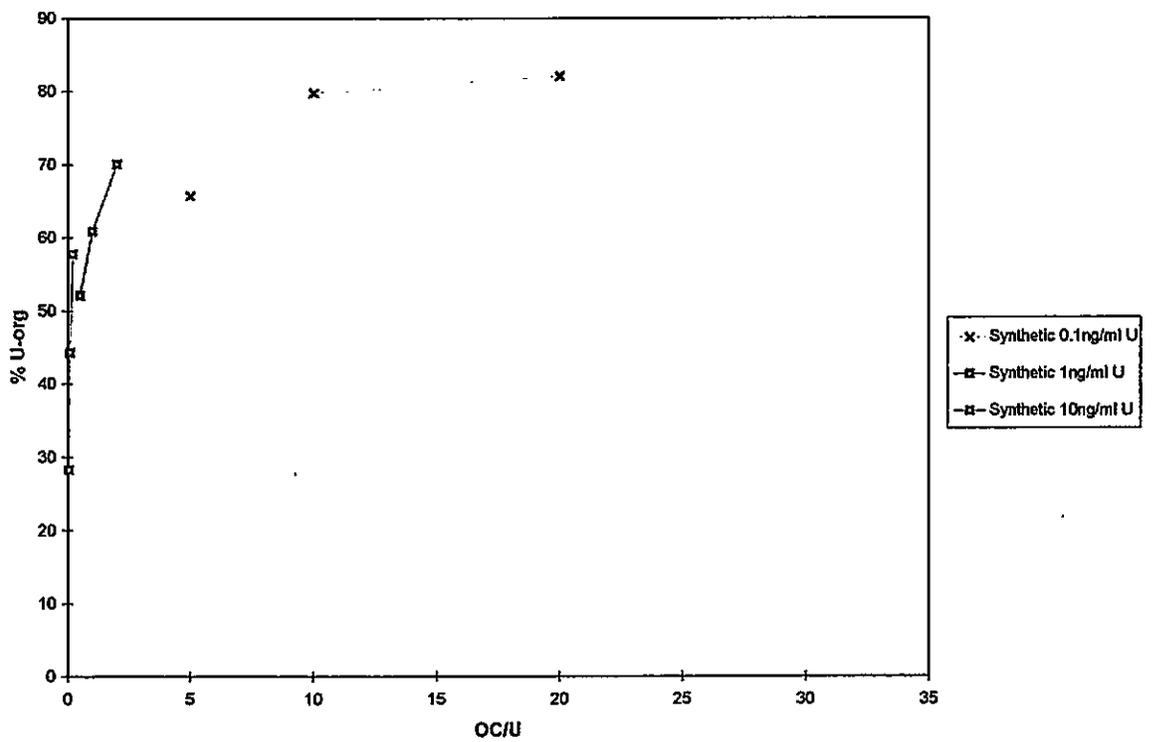


Figure 4.15 Correlation of %U-organic species with OC/U ratio for samples at ~pH 7.4

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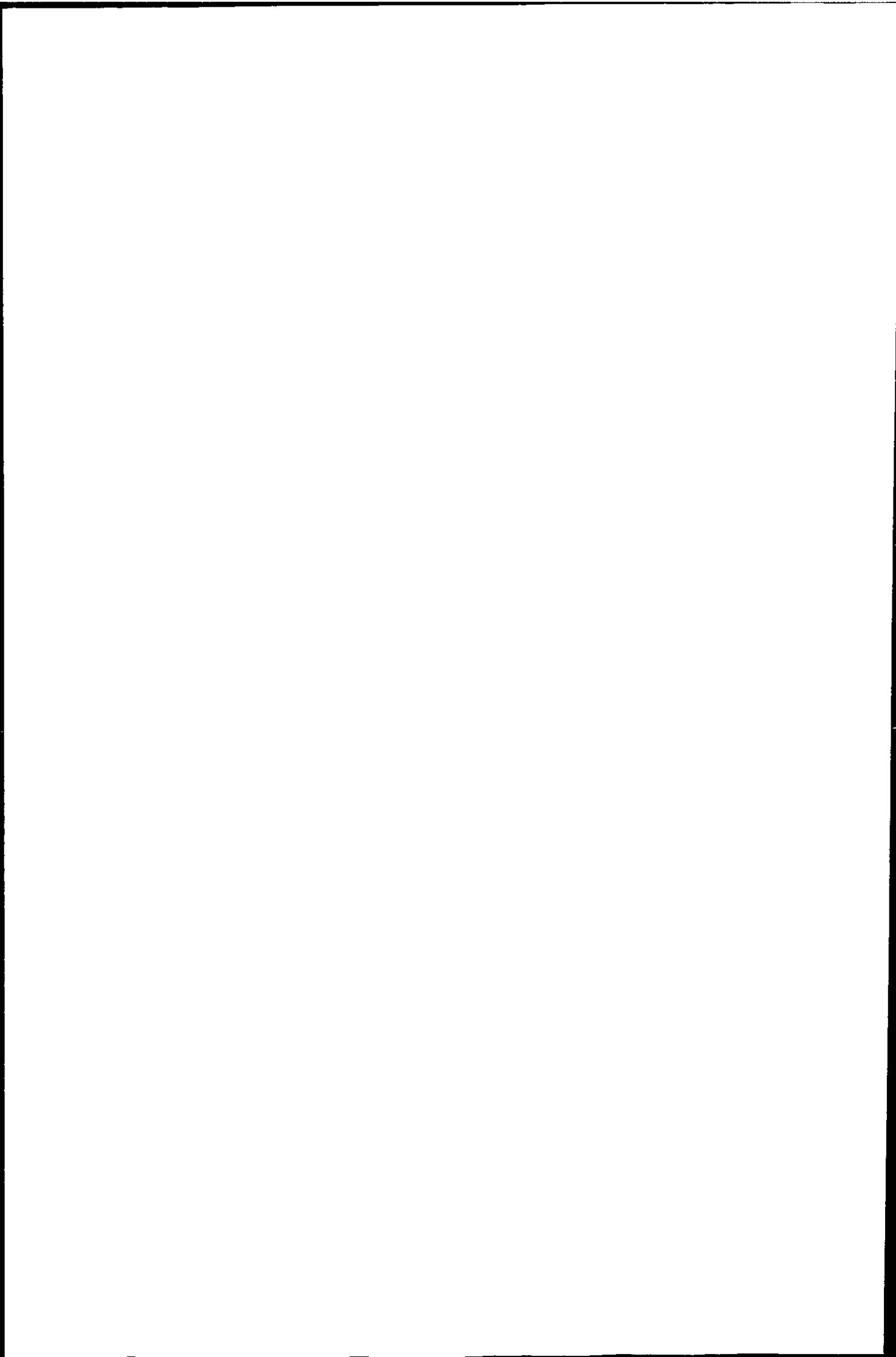
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4.5 Kinetics of uranium-humic substance dissociation

The dissociation rate of uranium-humic substance species was studied using a natural water sample from South Terras and a synthetic surface-water solution prepared in the laboratory. Thorium-humic substance species were also studied in the synthetic solution. Aliquots of the solutions were mixed with the Hyphan chelating resin. As the free (not bound to humic substances) metal was taken out of solution by being bound to the Hyphan resin, the metal-humic substance species dissociated to maintain the free metal, organically bound metal equilibrium. The metal-Hyphan reaction was considered to be irreversible under the conditions of the experiment. The level of uranium and thorium in solution and bound to the Hyphan resin was measured over a range of timepoints. The synthetic surface-water solution was left to 'age' for 1 day and 16 days before being used in the experiment, in order to investigate if this 'ageing' period would have any effect on the results. The South Terras sample contained $5.5 \mu\text{g ml}^{-1}$ DOC and the synthetic samples $4 \mu\text{g ml}^{-1}$ DOC, however the DOC in the synthetic samples was composed entirely of humic and fulvic acids.

The results obtained are presented in Figure 4.16 and Figure 4.17 displayed as percent metal-humic substance species (U-HS and Th-HS) left in solution over time. The samples, in particular the natural water sample, showed a rapid drop in the level of U-HS in solution occurring before the first timepoint. This was then followed by a much slower drop in the level of U-HS at subsequent timepoints. The synthetic solution displayed an overall slower rate of dissociation, possibly related to the DOC in this sample being composed of entirely humic substances. Both synthetic solutions displayed a similar rate of dissociation at the early timepoints. At the later timepoints (> 8 hours) the level of U-HS left in solution in the 16 day old synthetic solution appeared to level off, but the level of U-HS left in solution was still dropping at the end of the experiment in the 1 day old synthetic solution. This was possibly due to the age of the solutions, with the 16 day old solution having had time for the



uranium to bind to sites further within the HS molecule. Thus it could take longer to dissociate back out of the molecule, resulting in a slower rate of dissociation. The difference in dissociation rates between the natural and synthetic solutions could be due to a difference in the nature of the DOC in the samples. The synthetic solution was prepared with humic and fulvic acid (10% HA, 90% FA), whereas the DOC in the natural water sample, as well as being composed of HS, could also be composed of smaller organic acids. These, if they reacted with the uranium, may have formed much more rapidly dissociating species (seen as the rapid drop before the first timepoint) than the U-HS species. How long, and how much of, the U-organic species could remain in the environment would depend on the relative proportions of smaller organic molecules and HS which reacted with the uranium. In such cases the U-HS species could take much longer to dissociate than the smaller organic molecules and hence remain for a longer time period.

Rao, Choppin and Clark⁶² have proposed two types of metal-humate interaction, 'weakly' bound and 'strongly' bound metal. Their work was carried out on Eu(III) and UO_2^{2+} interactions with HA, using a polyelectrolyte binding model. The 'weakly' bound complexes were defined as where the metal was bound to sites on the surface of the HS molecule. Over time as the solution 'aged' the binding of the metal to the HS was then assumed to neutralise a portion of the anionic HS, allowing some folding and compaction of the HS due to the neutralisation of repulsion between anionic groups in the HS. This and migration of metal ions to less labile binding sites within the HS would result in less easily dissociated metal-HS complexes, termed 'strongly' bound. This theory could explain the experimental results with the 16 day old samples forming more 'strongly' bound U-HS complexes than the 1 day old samples leading to the difference in dissociation profiles seen in the latter half of the results.

When considering the thorium dissociation results a different trend is seen. Thorium does not display the rapid drop in HS species level seen in the uranium results, but displays

an approximate linear decrease in the level of Th-HS in solution over the whole 24 hour period of the experiment. The results are more scattered and there is a discontinuity in the results between the 4 and 8 hour timepoints. The results for the 1 day old synthetic solution could therefore be described as two sets of linear data but both with the same dissociation rate (slope). The level of Th-HS left in solution at the end of the experiment is higher than the corresponding level of U-HS left in solution, particularly for the 16 day old synthetic solution. This would indicate that in a natural environmental situation, once the Th-HS species had formed, a greater amount of more slowly dissociating Th-HS species would be present than the equivalent U-HS species. These species could remain in the environment a long time in this form. Even if a change in conditions in the environment could effect the speciation, it would take time before the Th-HS and U-HS species dissociated and the system equilibrated to the new speciation profile.

The difference in dissociation profiles between the uranium and thorium results could be due to the nature of the metal ions (thorium has a +4 charge and uranium has a +2 charge). The charge on the metal may effect its interactions with a HS molecule. The Th^{4+} ion could be more strongly attracted to the anionic charge of the HS. Uranium is also an oxycation (UO_2^{2+}). The size of the molecule could potentially effect the binding of uranium to sites within the HS molecule. The Th^{4+} ion, being smaller, could possibly bind to more sites within the structure of the HS and hence result in a higher level of Th-HS complexes which take longer to dissociate.

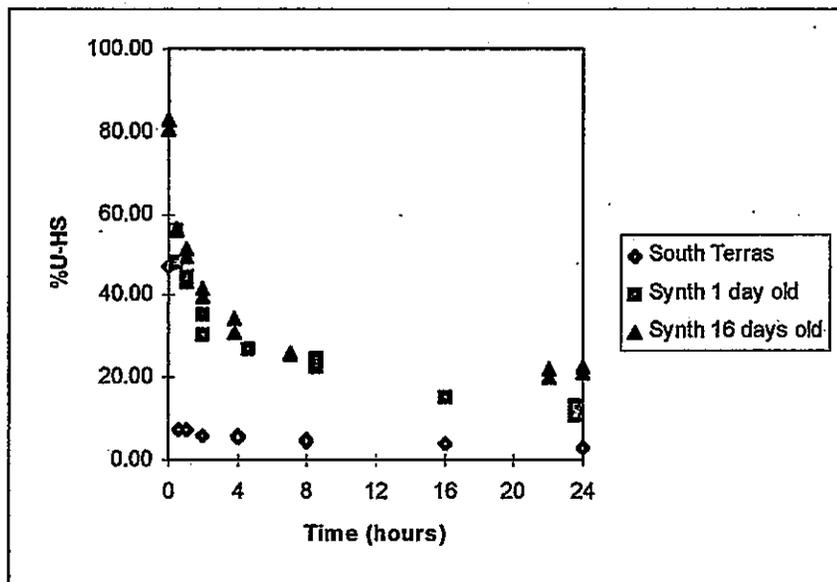


Figure 4.16 Experimental dissociation profile for U-organic species

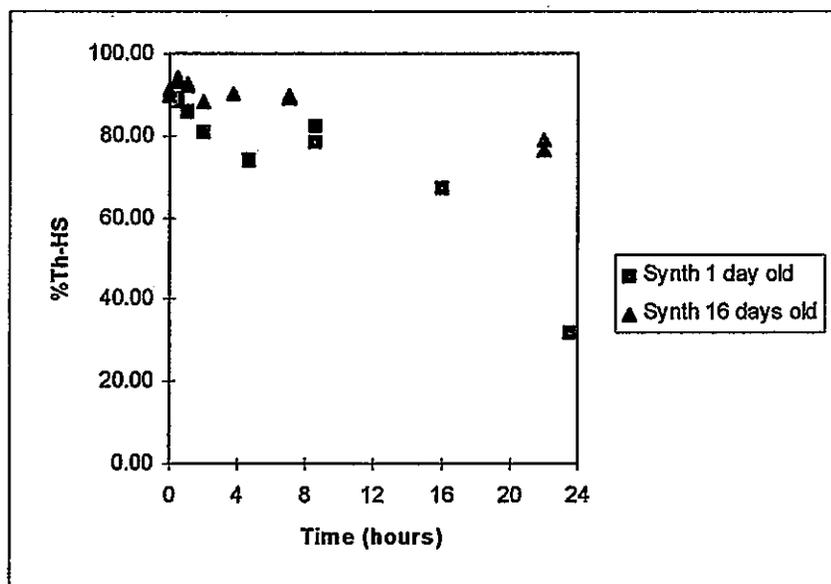


Figure 4.17 Experimental dissociation profile for Th-organic species

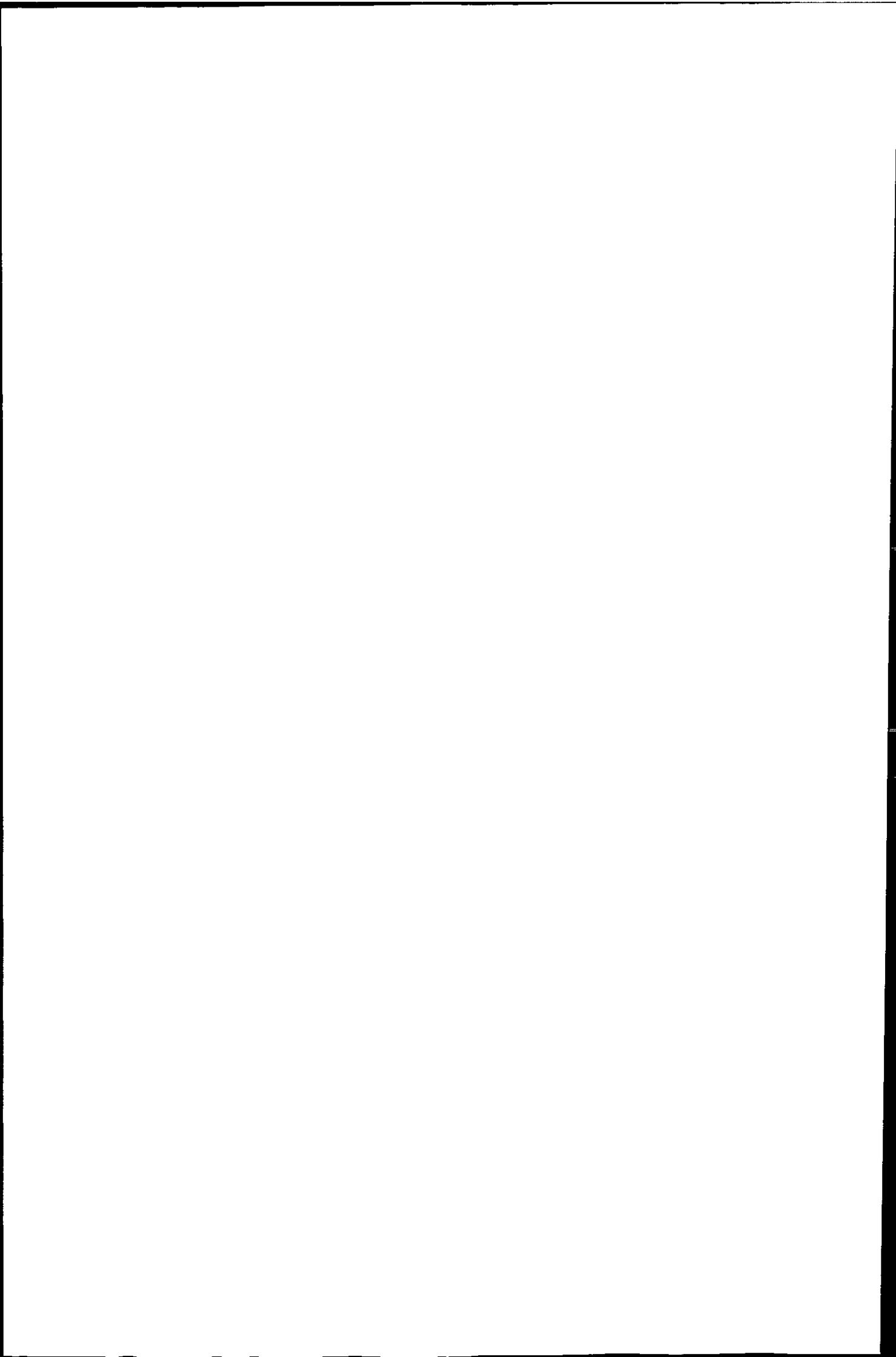
1. The first part of the document discusses the importance of maintaining accurate records of all transactions. It emphasizes that proper record-keeping is essential for the integrity of the financial system and for the ability to detect and prevent fraud. The text also notes that clear and concise reporting is necessary to ensure that all stakeholders have access to the information they need to make informed decisions.

2. The second part of the document focuses on the role of internal controls in ensuring the reliability of financial reporting. It describes how a strong system of internal controls can help to minimize the risk of errors and misstatements, and how it can provide a framework for the identification and management of risks. The text also discusses the importance of regular monitoring and evaluation of the internal control system to ensure that it remains effective and up-to-date.

4.6 Summary

An on-line uranium speciation method has been developed using a small column (0.24 x 5 cm) containing Hyphan, a chelating resin, coupled to an ICP-MS. The inorganic uranium species were retained on the column while the organic species passed straight through and were detected as the first peak in the chromatogram. The carrier flow was then switched over to the eluent which eluted the inorganic species, producing the second peak in the chromatogram. This in-line technique did not prove suitable for thorium speciation since two peaks were observed in the chromatogram for an inorganic thorium standard. The first peak was due to the thorium reacting with the carrier to form an acetate complex which was not retained on the column. The second peak was due to the inorganic thorium species. However, complete thorium recovery was obtained for an inorganic thorium standard using the same resin in a batch approach which involved no carrier, only the sample and the chelating resin. Thorium speciation could potentially be carried out in this manner.

The on-line speciation method for uranium was then used to analyse natural water samples from a range of locations on Dartmoor and South Terras. The results from the Dartmoor samples indicated levels of 79 to 88% U-organic species. The South Terras samples had a different water chemistry, with higher levels of inorganic carbon and uranium present. The results from these samples indicated 62 to 69% U-organic species. The difference between these sets of values was thought to be due to either the higher inorganic carbon concentration competing with the organic carbon to form uranium carbonate species or the increase in the uranium concentration relative to the organic concentration. To further investigate the effects of organic carbon concentration and pH on the U-organic species level, synthetic water samples were also prepared and analysed. The results from these samples indicated that levels from 28 to 86% U-organic species were present. Efforts to compare the results for the natural and synthetic water samples with their respective pH



values and organic carbon concentrations revealed no correlation between the % U-organic species present and the sample pH, except for the synthetic samples at the highest pH and lowest organic carbon concentration. A correlation of % U-organic species with organic carbon concentration did display a trend of increasing % U-organic species with increasing organic carbon concentration. A doubling of the organic carbon concentration did not however produce a corresponding doubling of the level of U-organic species. The level of U-organic species in the natural water samples only increased from 79 to 88% as the organic carbon concentration increased from 1 to 3 $\mu\text{g ml}^{-1}$. The synthetic water samples were found to display the same trend. The synthetic samples with higher uranium concentrations produced lower % U-organic levels. This was because the level of organic carbon, relative to the level of uranium, was much lower in these samples than in the samples with a low uranium concentration. Correlating the organic carbon / uranium ratio with the level of U-organic species did indicate a relationship between the two, but this was seen as three discontinuous sets of data for each of the three different uranium concentrations in the synthetic water samples. This indicated that there was a uranium concentration factor, separate to the organic carbon / uranium ratio factor, which effects the level of U-organic species formed.

The kinetics of dissociation of the U-organic species in natural and synthetic waters was also investigated. Previous work in this area reported in the literature is usually based on synthetic solutions at higher uranium concentrations than those typically found in environmental samples. For this study a natural water sample was used to produce results representative of the dissociation process as it would occur at the uranium concentration of an environmental sample. The natural water sample (from South Terras) dissociation plot consisted of an initial very fast dissociation of 88% of the U-organic species during the first 30 minutes of the experiment, followed by a much slower dissociation rate over the rest of the 24 hour experimental period. The synthetic water samples produced a much slower

dissociation rate in the early stage of the experiment. This was thought due to differences in the composition of the DOC (and hence the nature of the organic species) in the natural and synthetic water samples. The differences in dissociation plots for the 1 day and 16 day old synthetic samples was thought due to the formation of more 'strongly' bound U-HS and Th-HS species in the 16 day old sample which had a slower dissociation rate than the U-HS and Th-HS species formed in the 1 day old sample.

From the results presented in this chapter it can be seen that the presence of organic carbon and the formation of U-organic species are a major factor in uranium speciation.

Chapter Five

5. Computer modelling of uranium and thorium speciation in aqueous systems

5.1 Introduction

Computer modelling can be used to predict elemental speciation within a system (water sample) by utilising thermodynamic data, in particular the equilibrium constants for the components involved. Using these, the distribution of species which would lead to the most stable system under a defined set of conditions can be calculated. This speciation can effect the solubility and hence transport through the environment, and the toxicity of the metal. It also allows the investigation of 'what if' scenarios such as the addition of other components to the system which may change the speciation, or changes in conditions such as pH.

5.2 Use of thermodynamic data

The distribution of species in a system, at thermodynamic equilibrium, can be expressed using an equilibrium constant¹⁰⁹. For example for the system :-



where a, b, c and d are the concentrations or activities of the components A, B, C and D, the equilibrium constant can be expressed as :-

$$K = [C]^c [D]^d / [A]^a [B]^b \quad \text{Equation 5.2}$$

In equation 5.2 the square brackets denote concentration in moles per litre and K is a concentration equilibrium constant. Because the components (ions) in the system can interact with the solvent the value of the concentration constant will be affected by the ionic strength of the solution. The ionic strength (μ) is defined by equation 5.3 below :-

$$\mu = \frac{1}{2} \sum c z^2$$

Equation 5.3

where c represents the concentration of each individual ion and z represents the charge of the ion. Concentration equilibrium constants determined experimentally are quoted for systems at a particular ionic strength (typically 0.1). The standard state for equilibrium constants used in thermodynamic calculations is a system at infinite dilution. To take into account the ionic strength of the system concentrations are multiplied by an activity coefficient to give activities.

The equilibrium constant can be applied to calculating the solubility and speciation of uranium and thorium in water. For example :-



$$\Rightarrow K_s / [\text{OH}^-]^4 = [\text{Th}^{4+}] \quad \text{Equation 5.5}$$

The concentration of Th^{4+} in aqueous solution is dependent on the OH^- concentration which can be determined from the pH and ion product of water. Hence in this case the solubility is dependent on pH.

Carrying out further calculations to determine the solubility of the thorium hydrolysis species formed from the reaction of Th^{4+} with OH^- ligands will result in the solubility plot shown in Figure 5.1. The concentration of the soluble $\text{Th}(\text{OH})_4$ species does not change with pH.

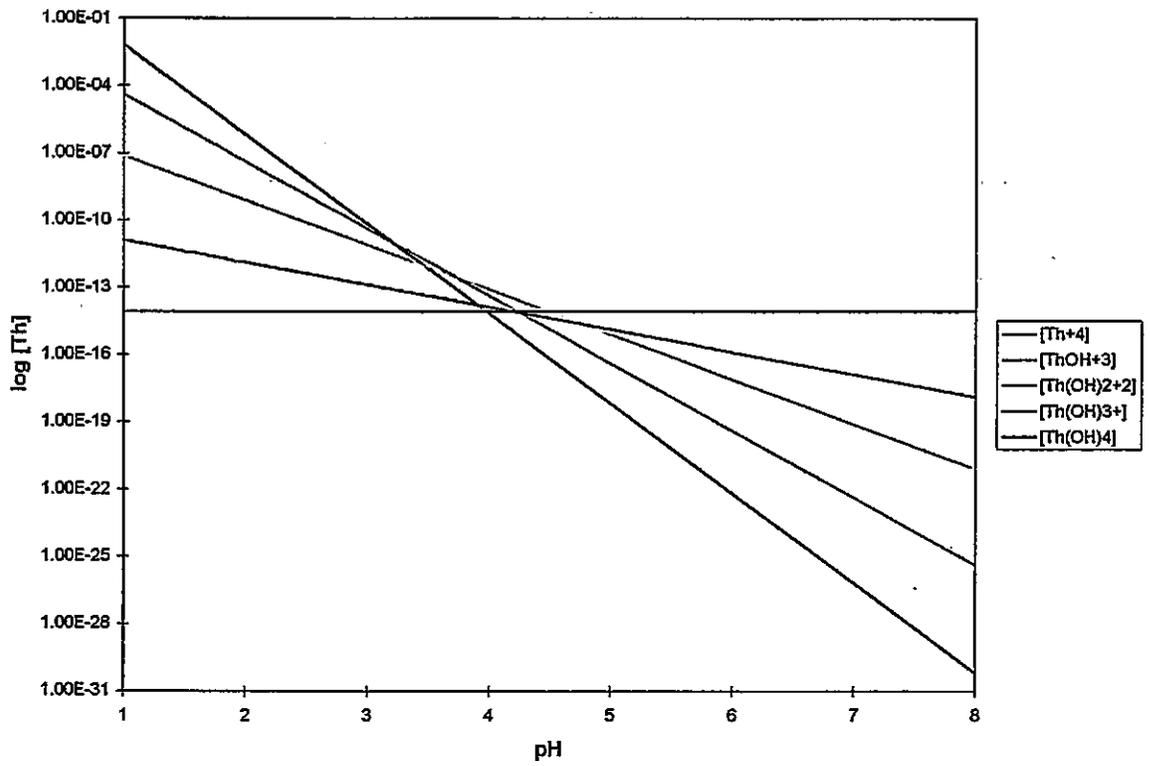


Figure 5.1 Solubility plot for thorium in water

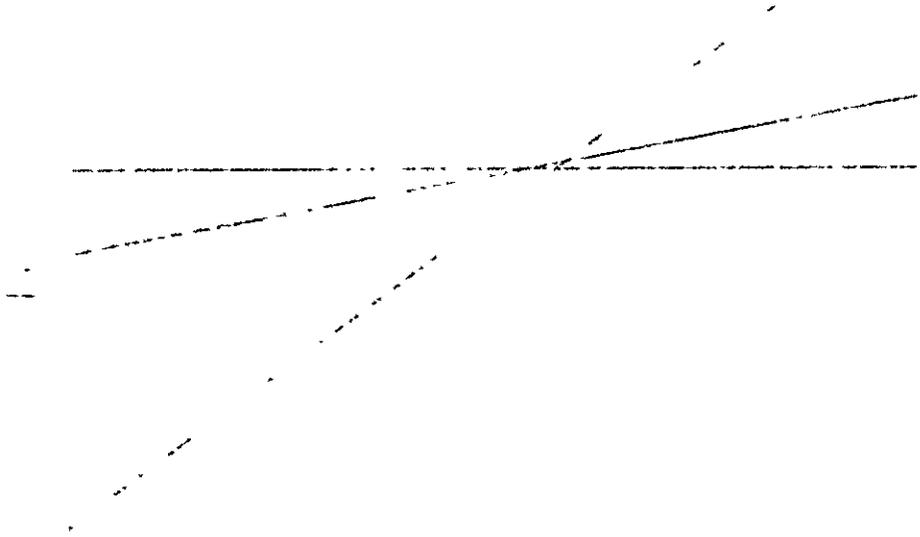


FIG. 1. A perspective view of a rectangular object with dashed lines indicating hidden edges.

Using equilibrium constants from the literature ¹¹⁰ the distribution of hydrolysis species can be calculated for a given thorium concentration and pH. For example, the synthetic surface-water sample used in the experiments in Chapter 3 contained 1 ng ml⁻¹ (4.31 × 10⁻⁹ mol l⁻¹) thorium. To simplify the calculations, if this amount of thorium was in a pure water system at pH 4 and the thorium species were represented in terms of concentration (not activity) then the species distribution would be as follows :-

$$\text{Ion product of water } K_w = [\text{H}^+] [\text{OH}^-] = 10^{-14}$$

$$\Rightarrow [\text{OH}^-] = K_w / [\text{H}^+] = 10^{-10} \quad \text{Equation 5.6}$$

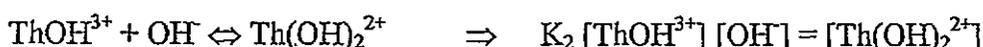
Complex formation



$$\Rightarrow K_1 [\text{Th}^{4+}] [\text{OH}^-] = [\text{ThOH}^{3+}]$$

$$K_1 = 10^{10.8}$$

$$\Rightarrow 6.31 [\text{Th}^{4+}] = [\text{ThOH}^{3+}] \quad \text{Eq. 5.7}$$



substituting [Th(OH)³⁺] with equation 5.7 gives

$$\Rightarrow K_2 6.31 [\text{Th}^{4+}] [\text{OH}^-] = [\text{Th(OH)}_2^{2+}]$$

$$\Rightarrow 11.75 [\text{Th}^{4+}] = [\text{Th(OH)}_2^{2+}] \quad \text{Eq. 5.8}$$

Carrying out the same procedure for K₃ and K₄ gives

$$2.0 [\text{Th}^{4+}] = [\text{Th(OH)}_3^+] \quad \text{Eq. 5.9}$$

$$1.26 [\text{Th}^{4+}] = [\text{Th(OH)}_4] \quad \text{Eq. 5.10}$$

Mass balance for equations 5.7 to 5.10 gives

$$[\text{Th}^{4+}] + [\text{ThOH}^{3+}] + [\text{Th(OH)}_2^{2+}] + [\text{Th(OH)}_3^+] + [\text{Th(OH)}_4] = 4.31 \times 10^{-9} \text{ M} \quad \text{Eq. 5.11}$$

Substituting equations 5.7 to 5.10 in to equation 5.11, to give everything in terms of $[\text{Th}^{4+}]$ gives

$$[\text{Th}^{4+}] = 1.93 \times 10^{-10} \text{ M} \quad \text{Eq. 5.12}$$

If the value obtained in equation 5.12 is then substituted into equations 5.7 to 5.10 the following values may be obtained :-

$$[\text{ThOH}^{3+}] = 1.22 \times 10^{-9} \text{ M} \quad 28.3\% \text{ total}$$

$$[\text{Th(OH)}_2^{2+}] = 2.27 \times 10^{-9} \text{ M} \quad 52.7\% \text{ total}$$

$$[\text{Th(OH)}_3^+] = 3.86 \times 10^{-10} \text{ M} \quad 9.0\% \text{ total}$$

$$[\text{Th(OH)}_4] = 2.43 \times 10^{-10} \text{ M} \quad 5.6\% \text{ total}$$

A comparison of the results obtained by the theoretical calculations above, with those calculated using the software package PHREEQCI⁷⁹ (a geochemical modelling program), can be seen in Table 5.1. Slight differences in the results may be due to the rounding of decimal places in the calculations, the calculation of ionic strength and the use of activities rather than concentrations by the computer program.

The formation of complex ions in solution can be represented as :-



where K is the stability (or formation) constant. If the stability constant were measured under conditions where Y^{m-} was not fully dissociated (e.g. $\text{HY}^{(m-1)-}$ present) then the level of Y^{m-} available to react with M^{n+} would be different and hence the value of K would be different. This value would be the conditional stability constant and would be dependent on the pH and composition of the solution.

When the system is at equilibrium the Th(OH)_4 species concentration is equivalent to the equilibrium constant K_{s4} , so if the Th(OH)_4 concentration was greater than the equilibrium constant then precipitation would occur to maintain at equilibrium within the system.

$$[\text{Th}(\text{OH})_4] > K_{s4}$$

$$2.43 \times 10^{-10} > 8.32 \times 10^{-15}$$

Equation 5.14

This can be expressed as a saturation index (SI) value.

$$\text{SI} = \log (\text{IAP}/K_s)$$

Equation 5.15

where IAP is the Ion Activity Product

When the system is at equilibrium, $\text{IAP} = K_s$, $\text{SI} = 0$.

A positive SI indicates an oversaturated system.

A negative SI indicates an undersaturated system.

An example of this can be seen in the SI results in Table 5.2. The speciation and SI of thorium and uranium in pure water was modelled using the PHREEQCI program. Thorium has a positive SI value indicating that the system is oversaturated with respect to thorium.

Thus, in a 'real' sample, this amount of thorium would not be soluble in pure water.

Uranium has a negative SI for each of the uranium solid phases in the model indicating that this system is undersaturated with respect to uranium. Using the model again, separately adding other components to the system which could potentially form complexes with thorium and uranium, the saturation index will change as the formation of other species affects the solubility of the thorium and uranium.

When modelling a natural water system further factors have to be taken in to account. One important factor is the presence of other components which may compete to form complexes with the metal of interest. In more concentrated systems the concentration values and activity values will differ. In order to take these factors into account more complex calculations are required. A multicomponent system would require the equations for each component to be solved simultaneously. Computer programs do this iteratively moving towards mass and charge balance for the whole system.

Table 5.1 Distribution of thorium species in pure water (% values)

Species	Theoretical calculation	PHREEQCI calculation
Th ⁴⁺	4.4	4.9
ThOH ³⁺	28.3	29.1
Th(OH) ₂ ²⁺	52.7	52.0
Th(OH) ₃ ⁺	9.0	8.6
Th(OH) ₄	5.6	5.4

Table 5.2 Saturation Index values for thorium and uranium calculated using the PHREEQCI program

Solid phase	Saturation Index (SI)		
	H ₂ O	H ₂ O + CO ₃	H ₂ O + PO ₄
Thorianite ThO ₂	4.45	no data	1.4
Uraninite UO ₂	-4.50	-4.90	-4.50
Gummite UO ₃	-8.54	-8.94	-8.55
Schoepite UO ₂ (OH) ₂ ·H ₂ O	-3.54	-3.94	-3.55
Pitchblende U ₃ O ₈	-7.88	-9.09	-7.91

5.3 Models used to simulate speciation with humic substances

It is generally accepted that trace metals in water will form complexes with humic substances (HS) to some degree. Therefore in order to obtain a more representative model for speciation, humic substances will have to be included in speciation calculations.

However HS are complex molecules and can not be treated in the same manner as inorganic ligands. To calculate metal-HS binding the concentration of reaction components would be needed; free metal in solution [M], HS in solution (HS) and metal-HS complex [MHS].

Because the HS is of unknown molecular weight it can only be expressed as g l^{-1} and not moles l^{-1} . In addition the stereochemistry of the reaction is not known. The value of a conditional stability constant determined experimentally would be dependent on the experimental conditions e.g. pH and the nature of the HS used. Thus the value obtained may not be valid under other circumstances.

An alternative approach is to create a computer model of a humic substance and have this react with the metal in the speciation program. In creating these models a number of assumptions are made about the HS and its reaction with the metal.

A simple model treats the HS as a simple organic acid and assumes :-

- i) There is only one type of binding site/functional group on the HS.
- ii) The metal only forms a 1:1 complex with the HS binding site.
- iii) The complexing capacity of the binding sites is constant.
- iv) There is no proton exchange on the functional groups within the pH range used.
- v) There are no electrostatic effects.

However humic substances have carboxylic and phenolic groups, both of which can act as binding sites^{111, 112}. A discreet multisite model would be more complex but would avoid the use of assumption i) and have several different types of binding site with different complexing capacities. A continuous distribution model would also avoid using assumption

i) but in this case replace the possibility of lots of different discrete binding sites with different complexing capacities, with a function for a continuous distribution about a mean value. A discrete site model is easier to incorporate into a geochemical speciation program.

In simple models the metal is assumed to bind only with deprotonated sites. This may work in situations where there is a high metal concentration but not at low metal concentrations¹¹¹. Since the work in this study will model uranium in natural water on Dartmoor (5×10^{-10} M) the model will need to function at low metal concentrations. More complex models include an empirical function to account for metal proton exchange reactions, thus removing assumption (iv). Another concept included in some models is a factor to take into account electrostatic effects. This can be used to account for the dependence of the conditional stability constant on pH and ionic strength. With this approach the concentration of protons and free metal ions close to the binding sites on the HS is different to that in the bulk solution. The overall charge on the HS affects the tendency of binding sites to co-ordinate or dissociate protons and metal ions. An increasing negative charge on the HS caused by progressive dissociation of HS functional groups as the pH increases makes it more difficult to dissociate protons and hence the change in the conditional stability constant.

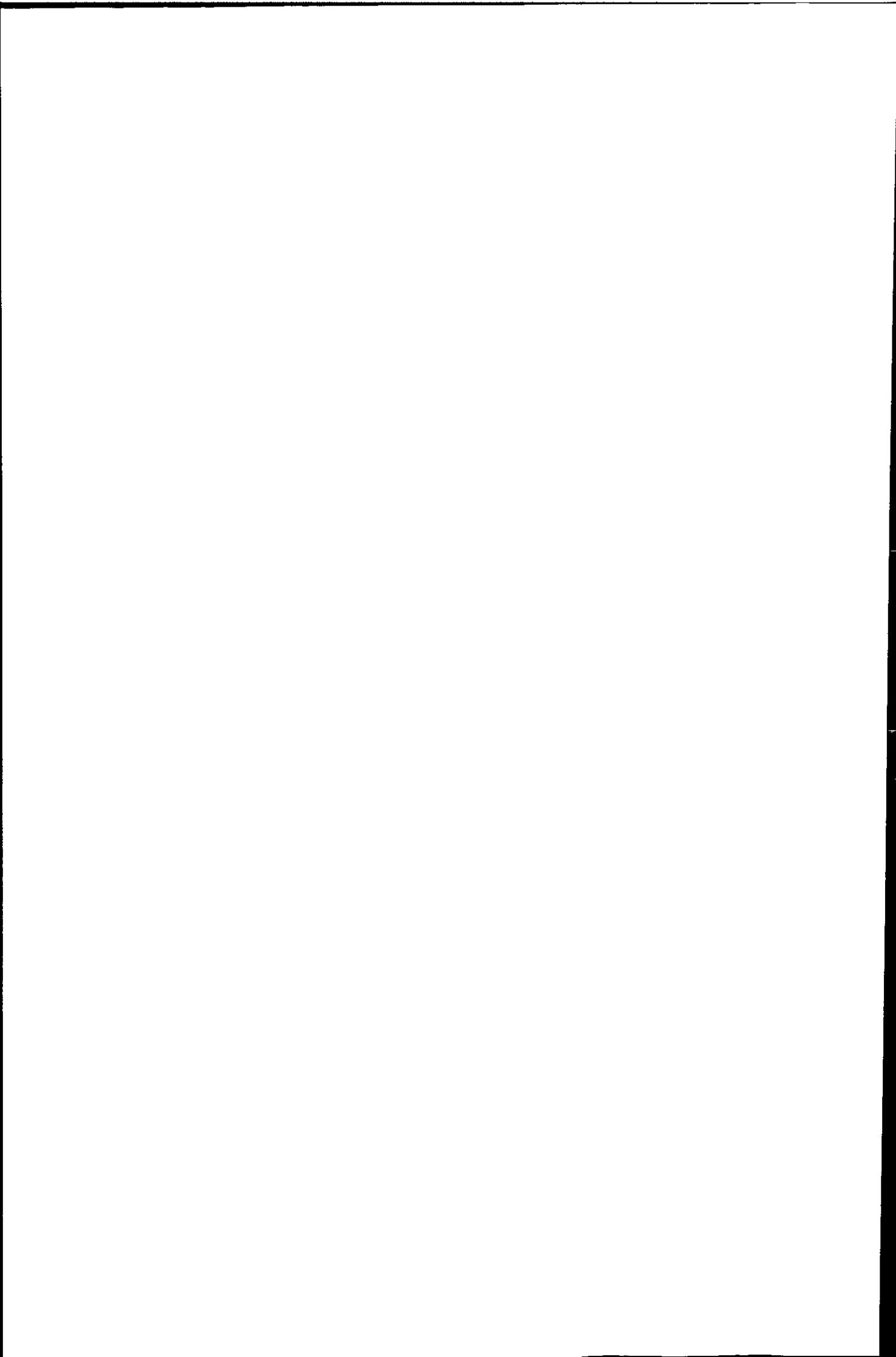
Overall, as the model becomes more complex, less assumptions are made but more data is required to describe the HS. If a HS was completely characterised and a model built it may be accurate but would only be relevant to that particular HS system. Other systems would vary to a greater or lesser extent. A more general model using averaged empirical functions to describe a 'local average HS' would be more widely applicable but is potentially less accurate in each specific case.

Various models have been reported and used in the literature, including :-

- MINTEQA2 : a computer speciation program with a 'humate ligand' added by the researchers²⁰ to the program's thermodynamic database. In this case the HS is being treated like a simple organic acid.
- HARPHRQ : a geochemical speciation program with a 'model fulvic acid' data set added^{25, 26, 98}. This model FA is an analogy based model and uses the equilibrium constants of several organic acids to represent FA. The relative amounts of each organic acid were changed by the researchers to match the results of the copper titration curves of different humic substances. The combination of acids provides different levels of acid dissociation over a pH range, a range of binding capacities and since they are known organic acids, log K values for various metal complexes are available. Little data on humic substances is required but electrostatic effects are not taken into account.
- WHAM⁷⁴ : This incorporates Tipping's Model V discreet multibinding site electrostatic model⁷⁶. This model of a HS uses 'intrinsic equilibrium constants'. It has two different types of binding site, with eight discreet binding sites altogether. It also includes factors for metal-proton exchange and electrostatic effects. A set of default values defining a 'global average HS' are included with the program.

For studies in this thesis, the WHAM program has been used, with some work using the PHREEQCI program with the 'model fulvic acid' dataset added, carried out as a comparison.

In the WHAM program, reactions between the Model V and the metal ions occur at eight proton dissociating groups. These are divided into two types, A and B. These can form either monodentate or bidentate ligands. Bidentate ligands are formed if two proton dissociating groups are close enough together. The probability of this happening is defined by the proximity factor f_{pr} .



Interactions are in terms of intrinsic equilibrium constants K_{int} for a hypothetical humic substance with zero charge and modified by an electrostatic term, $K_{int} e^{(2wZ)}$, for interactions with a charged humic substance, where w is a factor for electrostatic interaction and Z is the charge on the humic substance. The intrinsic equilibrium constants are entered into the program as pK_{MHA} and pK_{MHB} terms representing the negative log of the intrinsic equilibrium constant for type A and B binding sites. Since the pK_{MHA} is correlated to the pK_{MHB} ($pK_{MHB} = 1.38pK_{MHA} + 2.57$)⁷⁶ only the pK_{MHA} value need be entered. The smaller the pK_{MHA} value the stronger the metal binding capacity. The pK_{MHA} values supplied with the WHAM program have been derived by Tipping^{76, 113} from experimental data reported in the literature. To do this the proton dissociation characteristics of the humic substance used in the experiment (if known) or those for an 'average' humic substance were determined and used to define the Model V humic substance. From the experimental data sets in the literature the negative log ionic strength (pI), the negative log moles of metal bound per gram of humic substance (pv) and negative log concentration of free metal ($p[M]$) were used. The pK_{MHA} in the WHAM program was iteratively changed until the pv calculated by the program was close to the experimental pv . These results were then compared by Tipping to the equivalent equilibrium constants for similar reactions involving metal-proton exchange with smaller organic compounds such as lactate and acetate. Plots of pK_{MHA} for lactate and acetate versus pK_{MHA} for humic and fulvic acid complexes for a range of metals, including uranium and thorium¹¹³, indicated a correlation between the smaller organic compounds and the humic and fulvic acids and a trend in the linear free energy relationship. This relationship increased confidence in the pK_{MHA} values derived from the experimental data in the literature. The data used to produce the pK_{MHA} values for uranium and thorium were collected from experiments reported in the literature that had been carried out over the pH range 0.8 to 4.5. This is not representative of natural water conditions and so may have had an effect on the fitting of pK_{MHA} values to the data. The

thorium pK_{MHA} value came from two small data sets (5 to 6 points) but the uranium pK_{MHA} value was derived from larger datasets (27 points) which produced a smaller spread of pK_{MHA} values (0.96 to 1.22). The mean values from these results were provided in the database with the WHAM program. An indication of how well these values represent the formation of uranium and thorium humic complexes can be seen in Chapter 6 where model predictions produced using the WHAM program are compared to experimental speciation results, detailed in Chapter 4.

5.4 Comparison of results obtained from two different speciation programs

Two speciation programs (WHAM and PHREEQCI), in an unmodified form, were compared with respect to their ability to predict the uranium speciation of a surface-water sample containing 1 ng ml^{-1} ($4.2 \times 10^{-9} \text{ mol l}^{-1}$) uranium (see Table 5.3). The results obtained are presented in Figure 5.2. As can be seen, the results from the two programs were completely different, with each program predicting the presence of a different set of uranium species.

There could be several reasons for this :-

- i) Differences in calculation methods by the two programs.
- ii) Differences in the listed species in each program (i.e. the program cannot predict species it doesn't have data for).
- iii) Differences in the thermodynamic data provided with each program.

Uranium speciation studies in the literature also show a variety of results⁵ with the uranyl ion^{13,25}, carbonate¹¹⁴ or phosphate species¹⁷ predominating.

Looking at the thermodynamic databases provided with each of the programs, it could be seen that the PHREEQCI program contained data on phosphate species that was not provided in the WHAM program (see Table 5.4) and hence the WHAM program did not predict phosphate species. The data on phosphate species in the PHREEQCI program database could not be transferred in to the WHAM program database due to the different format of the two program. Thus a comparison of results from the two programs using the same thermodynamic data was not carried out at this point in the study.

Table 5.3 Components uses in surface-water computer models

Component	Concentration (mol l ⁻¹)
Na	2.74 x 10 ⁻⁴
K	5.90 x 10 ⁻⁵
Mg	1.71 x 10 ⁻⁴
Ca	3.75 x 10 ⁻⁴
Cl	2.20 x 10 ⁻⁴
CO ₃	9.51 x 10 ⁻⁴
SO ₄	3.85 x 10 ⁻⁵
F	1.58 x 10 ⁻⁵
PO ₄	1.05 x 10 ⁻⁶
NO ₃	2.00 x 10 ⁻³
U	4.20 x 10 ⁻⁹

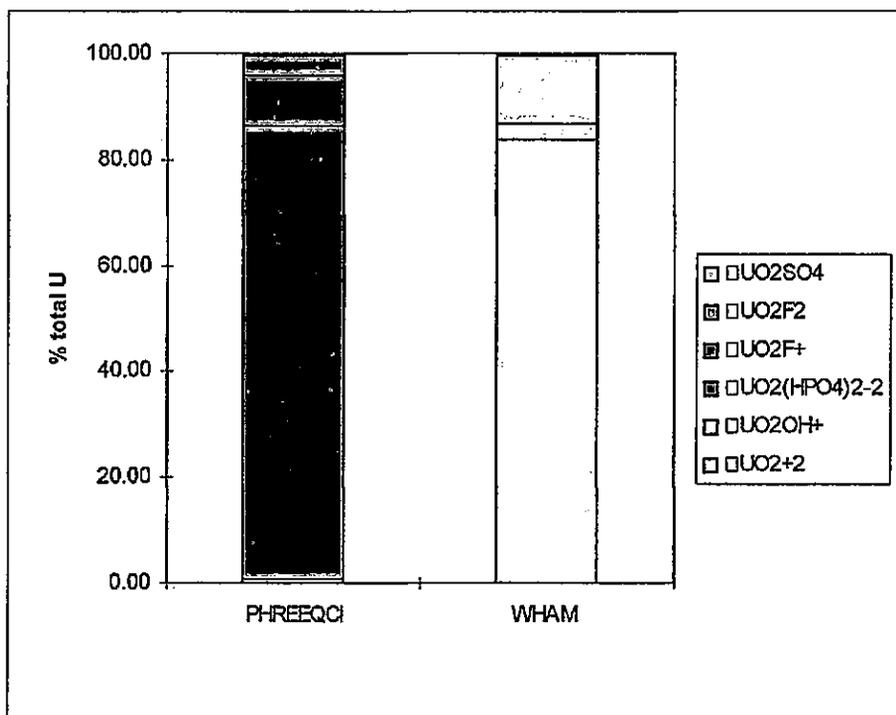


Figure 5.2 Uranium speciation results obtained from the PHREEQCI and WHAM speciation programs

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Table 5.4 Equilibrium constants provided with the WHAM and PHREEQCI programs

Species	PHREEQCI		
	WHAM $\log_{10} \beta$	WATEQ4F $\log_{10} \beta$	MINTEQ $\log_{10} \beta$
UO_2OH^+	8.8	-5.2	-5.09
$\text{UO}_2(\text{OH})_2$	16.1		
$\text{UO}_2(\text{OH})_3^-$	21	-19.2	
$\text{UO}_2(\text{OH})_4^{2-}$		-33	
$(\text{UO}_2)_2\text{OH}^{3+}$		-2.7	
$(\text{UO}_2)_2(\text{OH})_2^{2+}$	22.4	-5.62	-5.645
$(\text{UO}_2)_3(\text{OH})_4^{2+}$		-11.9	
$(\text{UO}_2)_3(\text{OH})_5^+$	54.3	-15.5	-15.593
$(\text{UO}_2)_3(\text{OH})_7^-$		-31	
$(\text{UO}_2)_4(\text{OH})_7^+$		-21.9	
UO_2CO_3	9.4	9.63	10.071
$\text{UO}_2(\text{CO}_3)_2^{2-}$	16.4	17	17.008
$\text{UO}_2(\text{CO}_3)_3^{4-}$		21.63	21.384
$(\text{UO}_2)_3(\text{CO}_3)_6^{6-}$		54	
UO_2SO_4	3	3.15	2.709
$\text{UO}_2(\text{SO}_4)_2^{2-}$		4.14	4.183
UO_2PO_4^-		13.69	
UO_2HPO_4		20.21	20.814
$\text{UO}_2(\text{HPO}_4)_2^{2-}$		43.441	42.988
$\text{UO}_2\text{H}_2\text{PO}_4^+$		22.87	22.643
$\text{UO}_2(\text{H}_2\text{PO}_4)_2$		44.38	44.7
$\text{UO}_2(\text{H}_2\text{PO}_4)_3^-$		66.245	66.245
$\text{UO}_2(\text{H}_3\text{PO}_4)^{2+}$		22.813	
UO_2F^+		5.09	5.105
UO_2F_2		8.62	8.92
UO_2F_3^-		10.9	11.364
$\text{UO}_2\text{F}_4^{2-}$		11.7	12.607
UO_2Cl^+		0.17	0.22
UO_2Cl_2		-1.1	
UO_2Br^+		0.22	

5.5 Effect of using different thermodynamic databases to predict uranium speciation

The PHREEQCI program comes with two different thermodynamic databases that contain uranium data. These are identified as WATEQ4F and MINTEQ. To investigate the effect of using different thermodynamic data sets on the prediction of uranium speciation, while using the same program (to eliminate different program calculation methods as a source of variation in results), the speciation of the same water sample was calculated using the two different databases provided with the PHREEQCI program. The results obtained show a 25% difference in the predicted major species (see Figure 5.3). This indicated that the predicted speciation was heavily dependent on the thermodynamic data used. Thus any comparison of results from different sources would be unreliable if the contents of the databases (i.e. the species included and their log K values) used in the calculations were not known to be the same in each case.

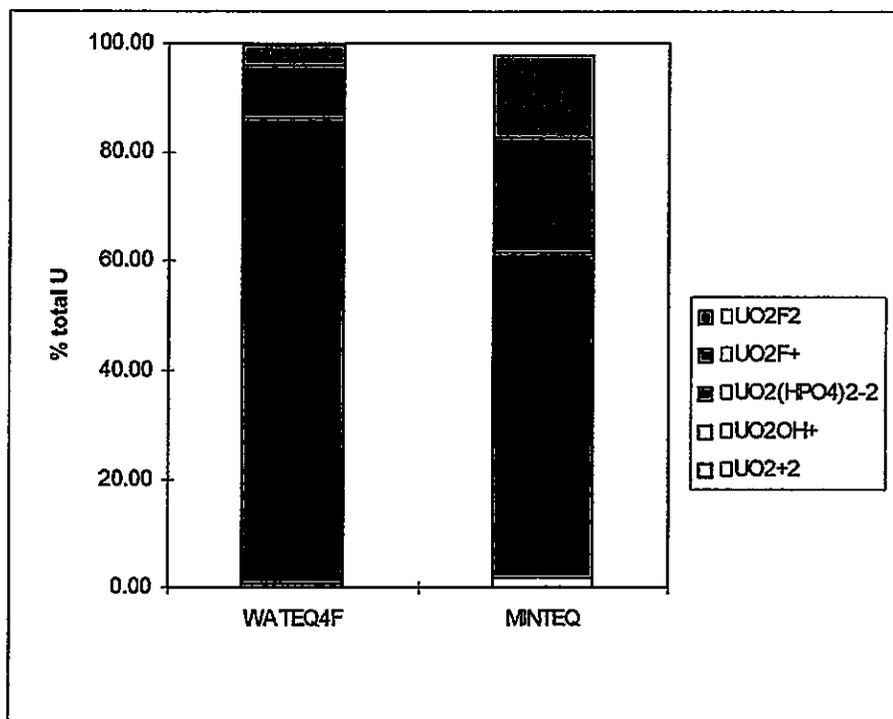
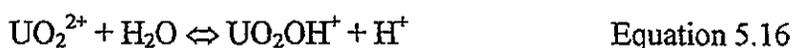


Figure 5.3 Effect of using different thermodynamic databases for uranium speciation

In order to address this problem several groups have prepared reviews and compilations of uranium thermodynamic data, such as CHEMVAL¹⁷ and HATCHES¹¹⁵. The Nuclear Energy Agency - Thermochemical Database Project (NEA-TDB) has produced a critical review of uranium thermodynamic data available in the literature. This has been compiled into a database containing log K values (at standard temperature and pressure and zero ionic strength) and ΔG_f° values⁹⁶. This database has also been used by other research groups^{20, 25, 26, 114}.

In this study, the NEA-TDB data was added to the PHREEQCI program but could not be directly inserted into the WHAM program. As noted earlier in Table 5.4 the log K values for the same hydrolysis species were completely different in the two programs. This was due to the way each species was represented. For example in PHREEQCI and the NEA-TDB data the species formation reaction was :-

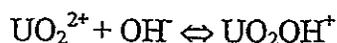


Alternatively the same species formation reaction could be represented as :-



as turned out to be the case with WHAM. The log K values for these two reactions would be different. In order to use the NEA-TDB data in the WHAM program the log K values for the uranium hydrolysis species had to be recalculated for reactions in the form of equation 5.15. This was carried out using the ΔG_f° values (supplied in the NEA-TDB database) for each component of the reaction to generate the ΔG_r° and then convert this value to a log K value using the Van't Hoff equation.

Example calculation :-



$$\Delta G_r^\circ = \Delta G_f^\circ \text{ products} - \Delta G_f^\circ \text{ reactants}$$

$$= -1160.009 - (-952.551 + -157.220)$$

$$= -50.238 \text{ kJ mol}^{-1}$$

$$\ln K = \Delta G_r^\circ / -RT$$

$$\Rightarrow \log K = \Delta G_r^\circ / -5.7079$$

$$= -50.238 / -5.7079$$

$$\log K = 8.80$$

The NEA-TDB data for phosphate species also had to be converted in this study for both the WHAM and PHREEQCI programs. The formation of uranium phosphate species is calculated, by the computer programs, as complex formation with phosphate ligands, whereas the data from the NEA-TDB is in terms of uranium reacting with phosphoric acid. The computer programs deal with phosphoric acid dissociation separately.

A comparison of results from the two programs (both using the NEA-TDB data) demonstrated that the two programs produce the same results (re. Section 5.4 point i) and that the different log K values (due to the different forms of species equations) produced the same results.

Comparing the results calculated with the NEA-TDB data with the results produced by both programs using their original thermodynamic data, indicated a complete change in the level of phosphate species (see Figure 5.4). The NEA-TDB database does contain phosphate species but the nature of these species and their log K values is different. This resulted in the loss of the phosphate species dominance seen in the PHREEQCI results calculated with the original PHREEQCI thermodynamic data. The original phosphate data in PHREEQCI was derived from a study which predicted the formation of $\text{UO}_2(\text{HPO}_4)_2^{2-}$ species¹¹⁷ (which dominated the PHREEQCI models run with this data). However the NEA reviewed and accepted later work by Tripathi which did not agree with the earlier interpretation of results and predicted the formation of the $\text{UO}_2(\text{H}_2\text{PO}_4)_2(\text{aq})$ and $\text{UO}_2(\text{H}_2\text{PO}_4)(\text{H}_3\text{PO}_4)^+$ species. The earlier work reported in the literature on uranium phosphate species was only carried out at low pH values however more recent work reported in the literature¹¹⁶ was carried out over a larger pH range (pH 3 to 9) and was

thus more representative of natural waters. The results from this indicated the formation of UO_2HPO_4 (aq) at pH 5.5 to 6.5 and UO_2PO_4^- at pH 6.5 to 9.

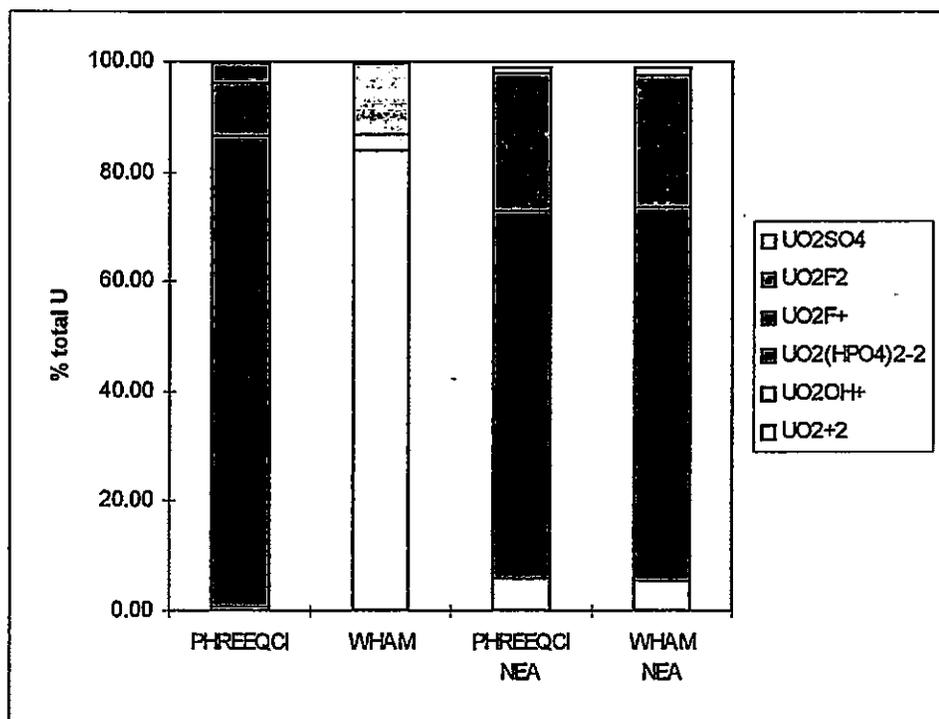


Figure 5.4 Uranium speciation calculated using the NEA-TDB thermodynamic data

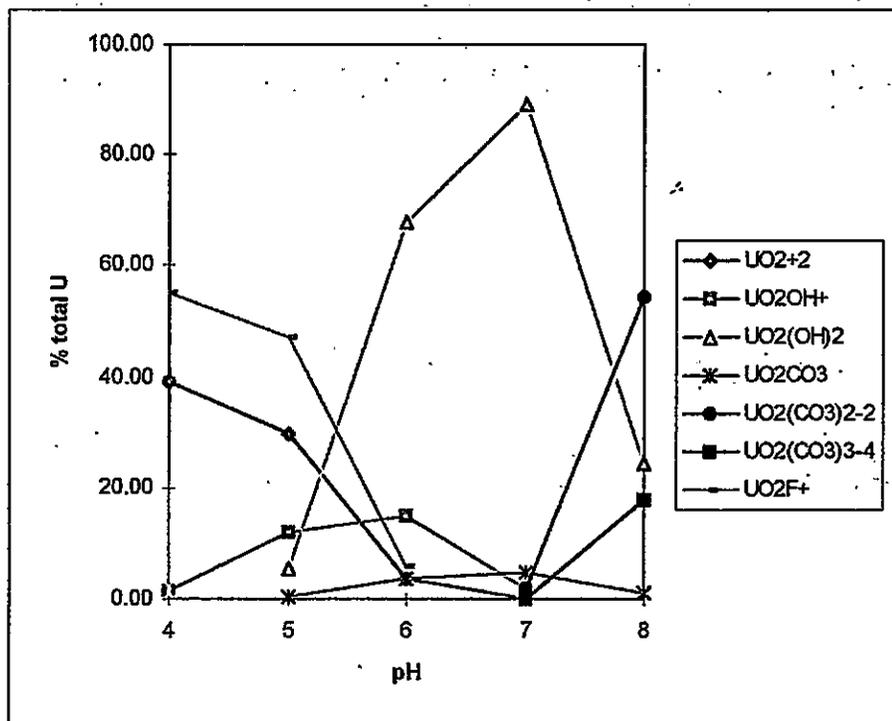


Figure 5.5 Predicted U speciation using NEA-TDB data at low carbonate concentration

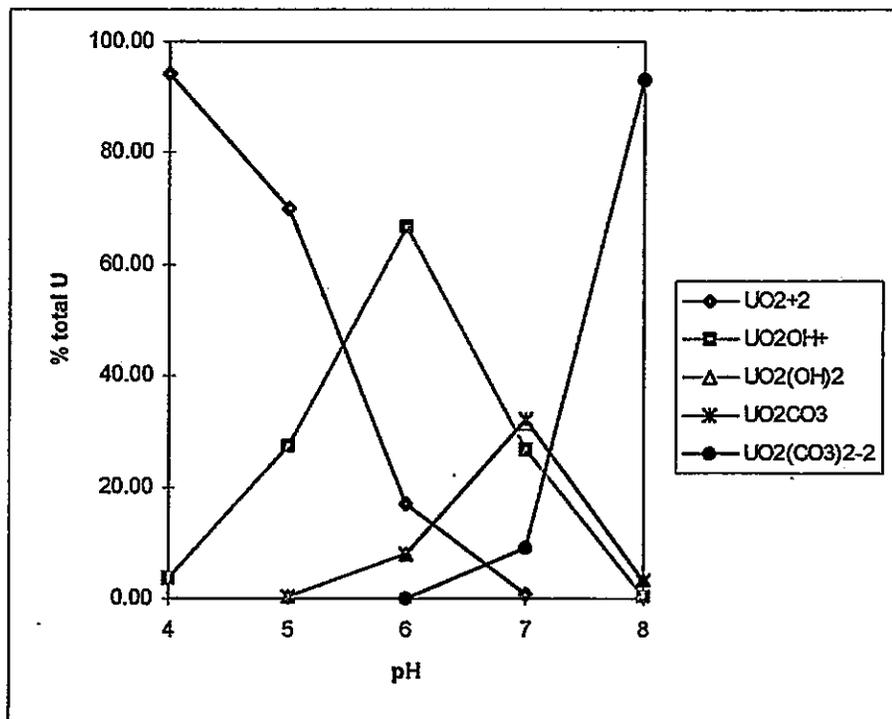
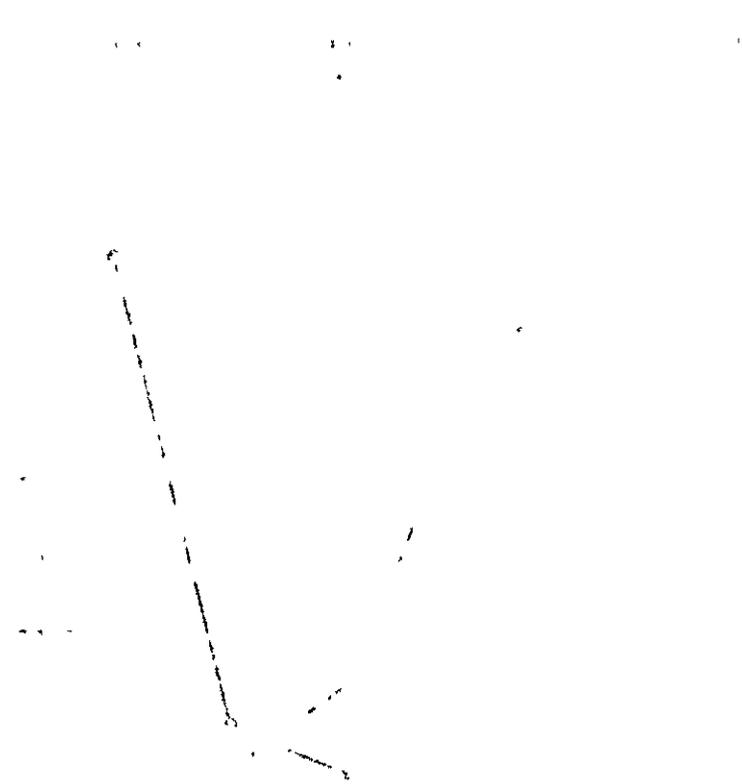


Figure 5.6 Predicted U speciation using original WHAM data at low carbonate concentration



1 2 3 4 5 6 7 8 9 10

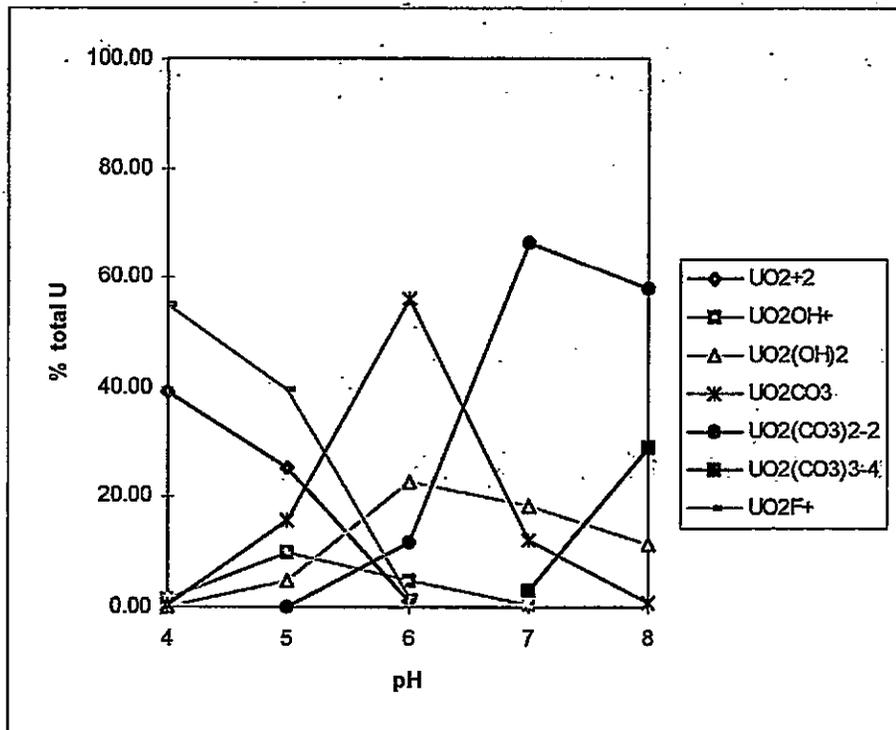


Figure 5.7 Predicted U speciation using NEA-TDB data at higher carbonate concentration

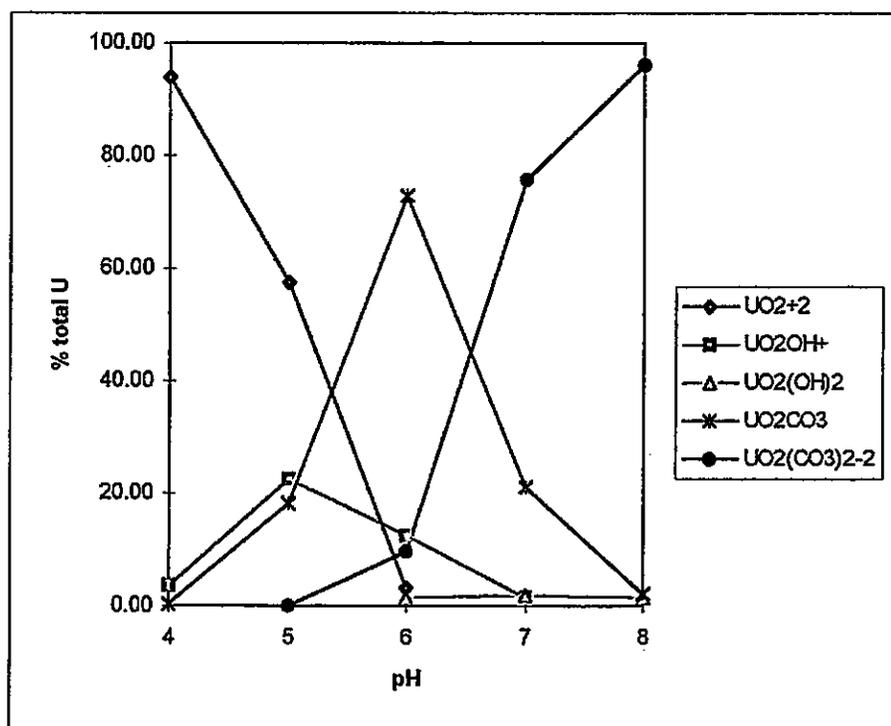
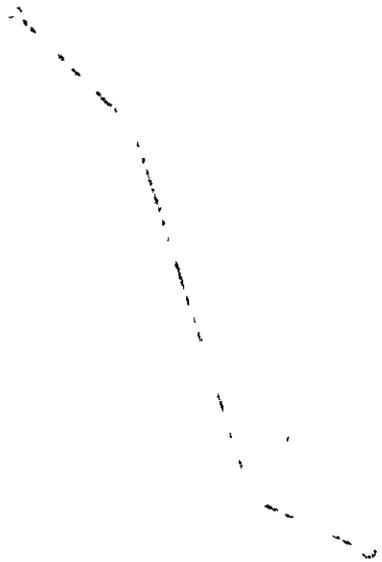
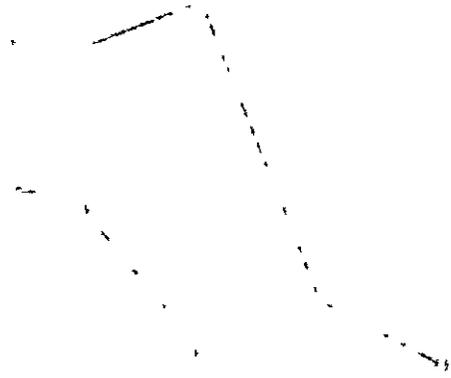


Figure 5.8 Predicted U speciation using original WHAM data at higher carbonate concentration



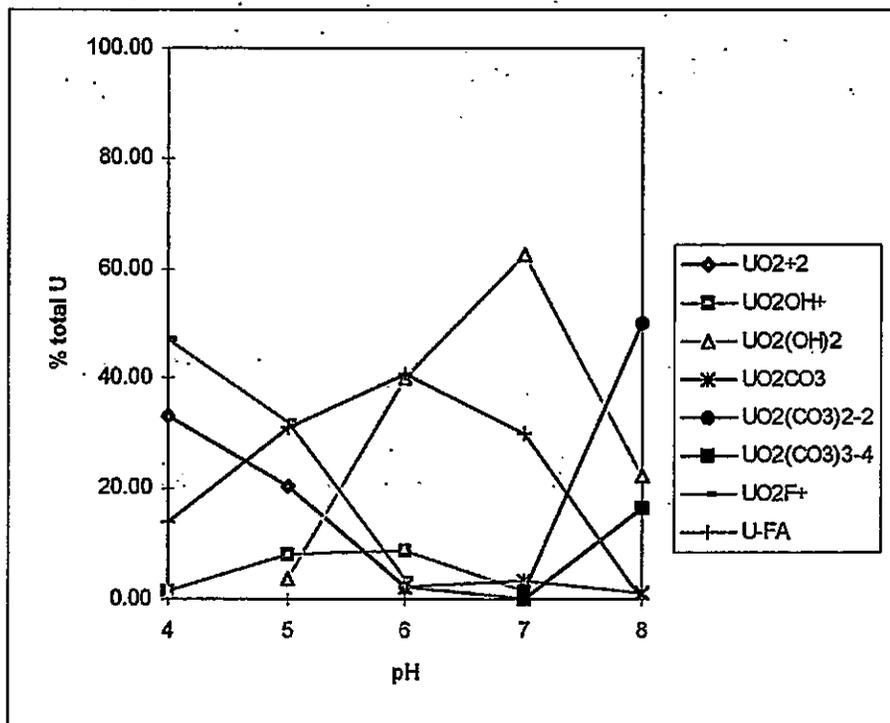


Figure 5.9 Predicted U speciation using NEA-TDB data at low carbonate concentration in the presence of fulvic acid

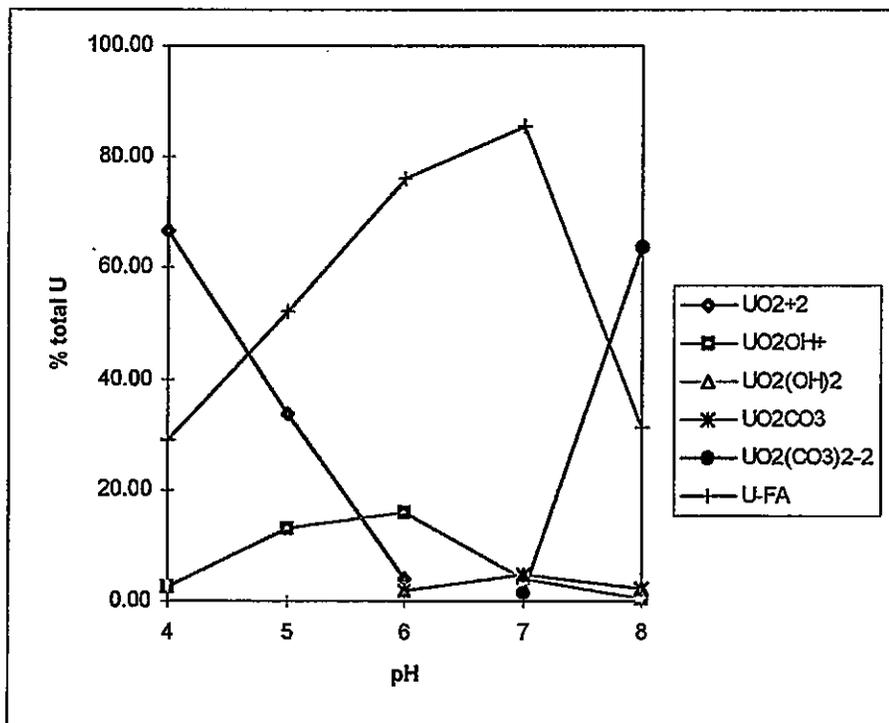
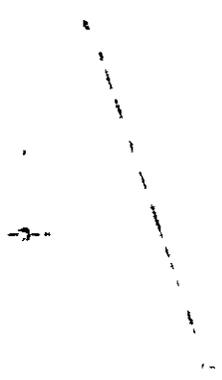
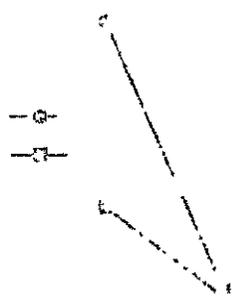


Figure 5.10 Predicted U speciation using the original WHAM data at low carbonate concentration in the presence of fulvic acid



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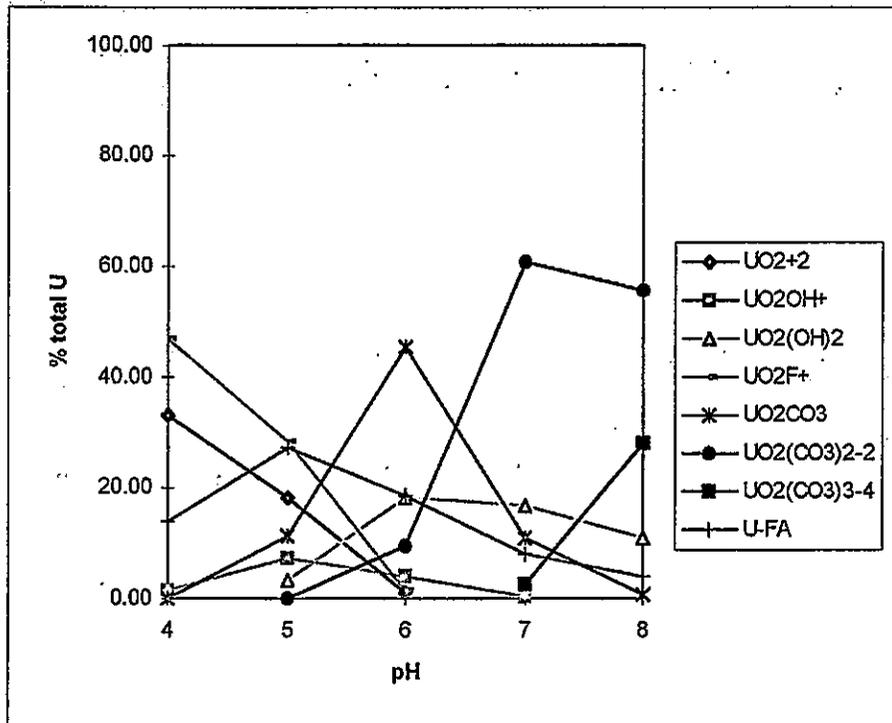


Figure 5.11 Predicted U speciation using NEA-TDB data at higher carbonate concentration in the presence of fulvic acid

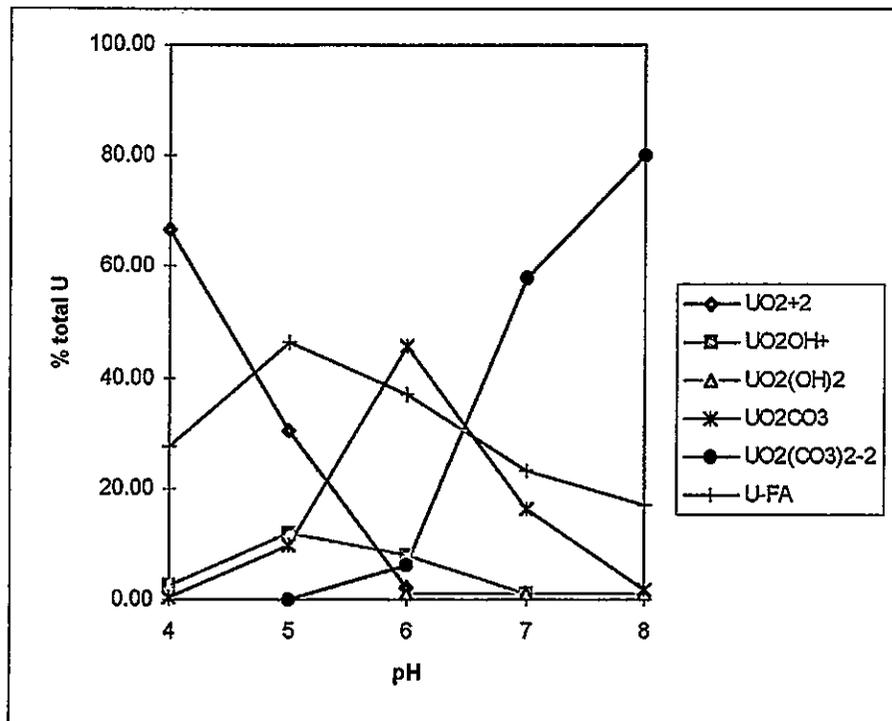


Figure 5.12 Predicted U speciation using the original WHAM data at higher carbonate concentration in the presence of fulvic acid



Consideration of the predicted thorium speciation reveals that the fluoride species completely dominates (>90%) at low pH. This level drops sharply above pH 5 and is completely replaced by the $\text{Th}(\text{OH})_4$ species at pH 6 and above (see Figure 5.13). If fluoride was not present in the water then the fluoride species would be replaced by a series of thorium hydrolysis products (Figure 5.14). Since thorium does not form carbonate species the model is not affected by an increase in carbonate concentration.

Adding FA to the system completely changes the predicted speciation, with the Th-FA species replacing the virtually insoluble $\text{Th}(\text{OH})_4$ species up to pH 7 (see Figure 5.15). Above this pH the $\text{Th}(\text{OH})_4$ species is once again the dominant species. Since there is no NEA data for thorium species, all calculations were carried out using the original data supplied with the WHAM program.

Models for groundwater with the same levels of uranium and thorium, but increased levels of the other inorganic components, produce similar results to those seen for the surface-water models. The main differences are the appearance of $\text{UO}_2\text{SO}_4(\text{aq})$ at low pH and a lower level of U-FA over the pH range modelled (Figure 5.16 and Figure 5.17). Thorium produced the same species but the Th-FA level dropped sharply below pH 5, although this did not happen in the surface-water models. This is possibly due to the increased fluoride level in the groundwater (Figure 5.18 and Figure 5.19).

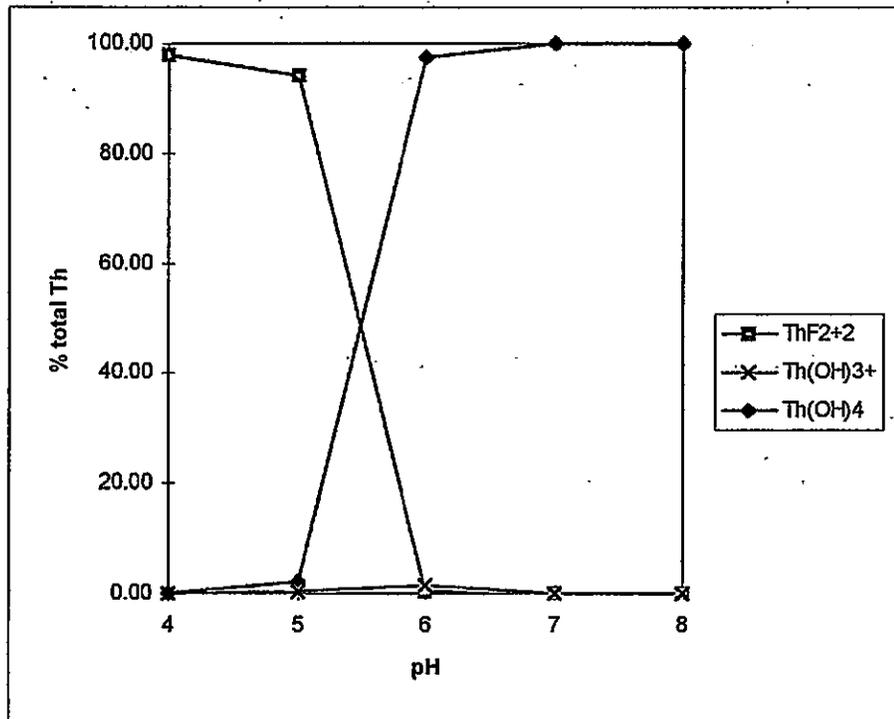


Figure 5.13 Predicted Th speciation in surface-water

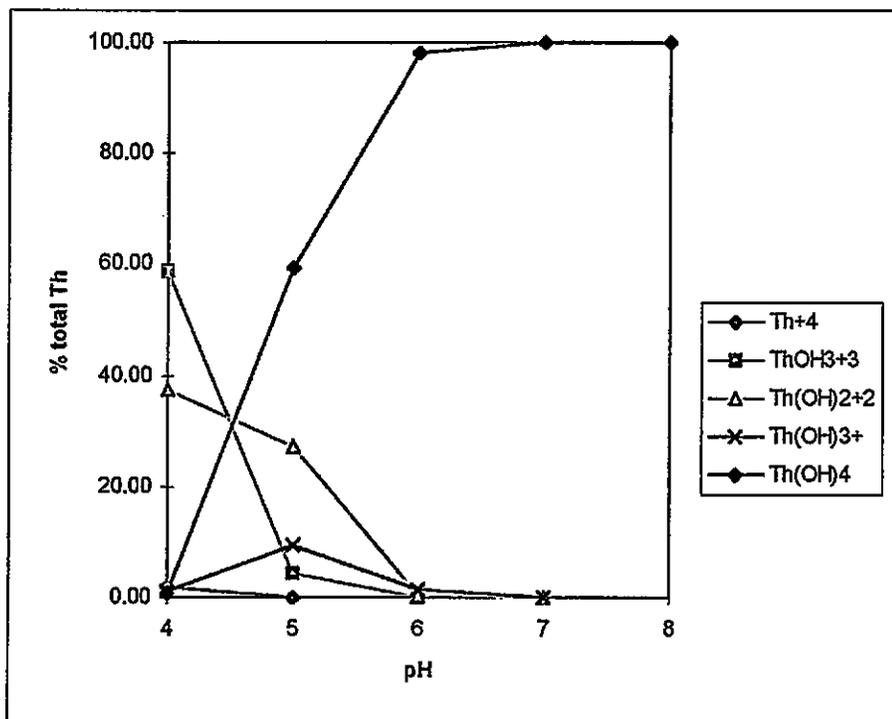
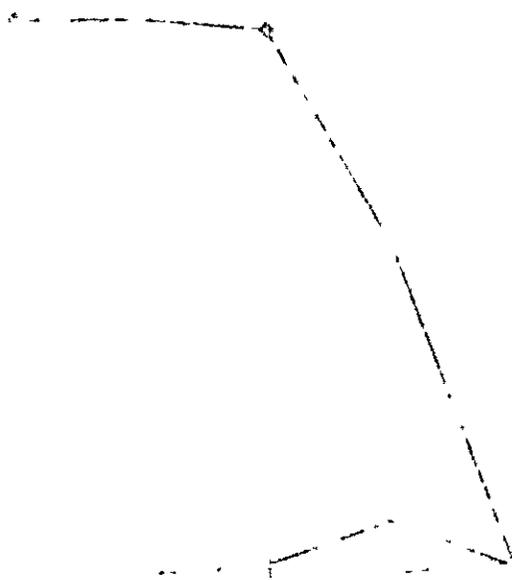
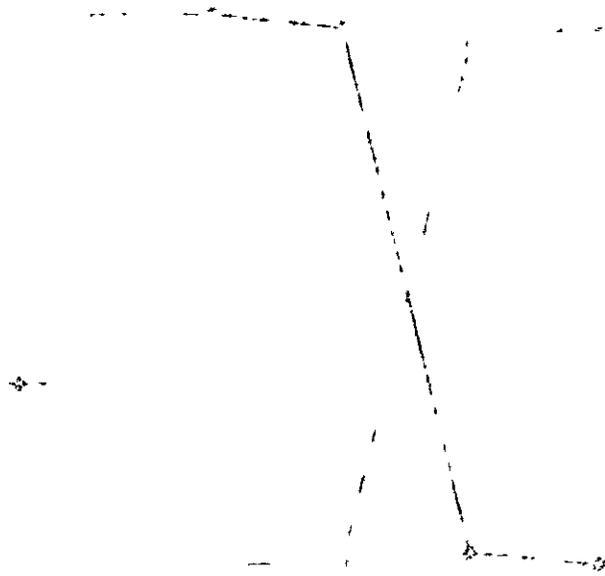


Figure 5.14 Predicted Th speciation in the absence of fluoride



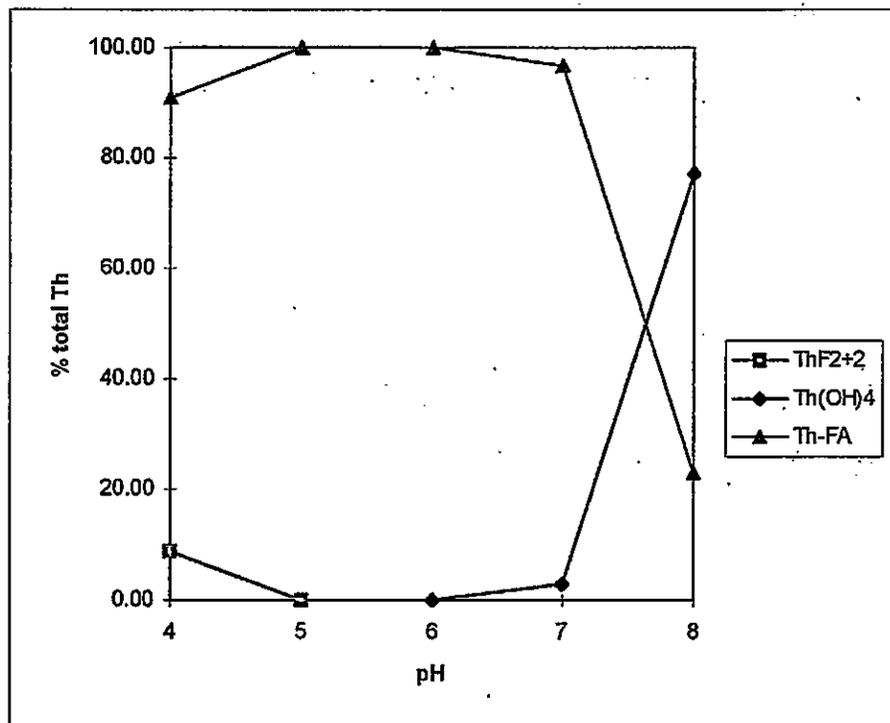


Figure 5.15 Predicted Th speciation in surface-water with fulvic acid present

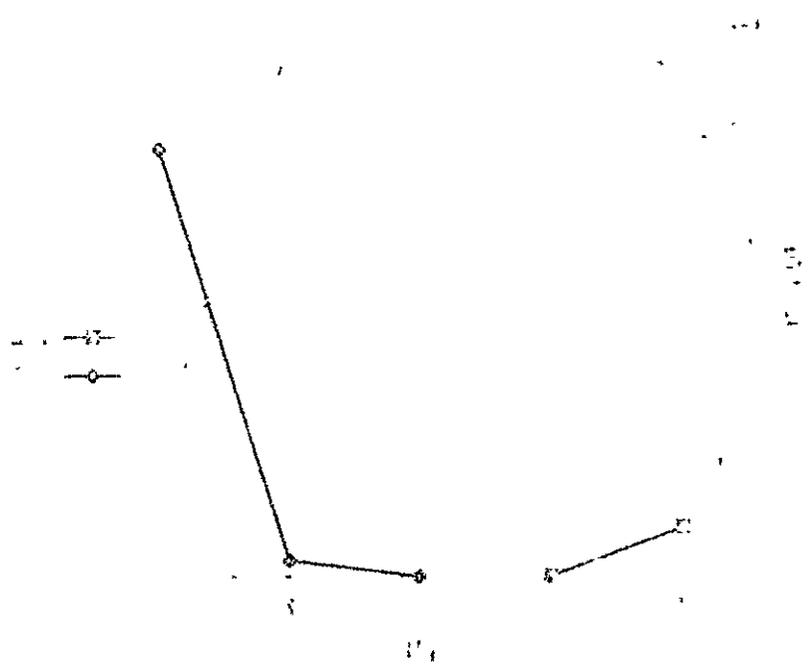


Figure 1. Comparison of the results of the two methods for the determination of the concentration of the substance in the sample.

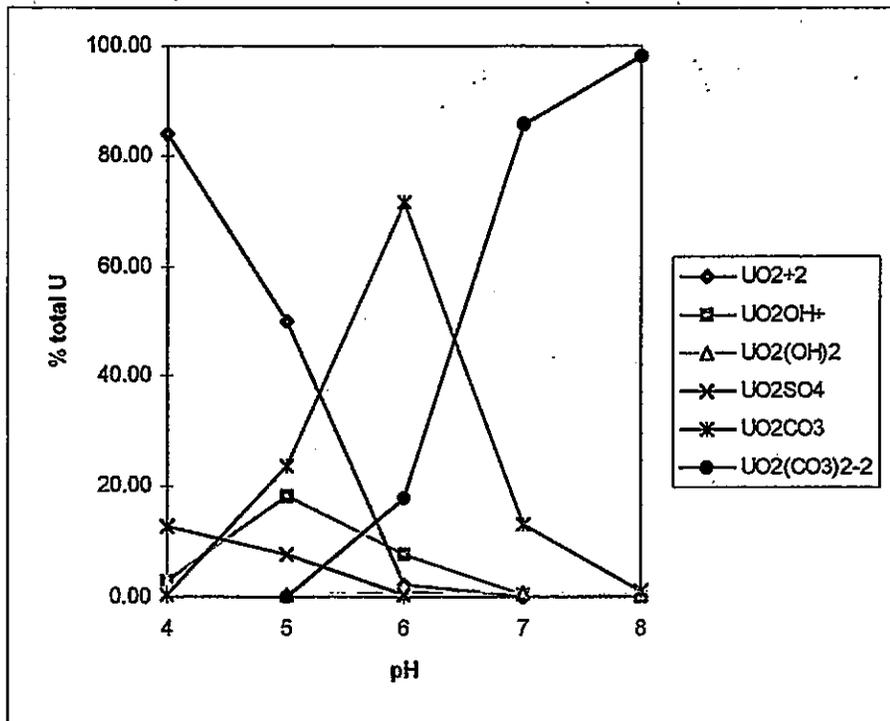


Figure 5.16 Predicted U speciation in groundwater

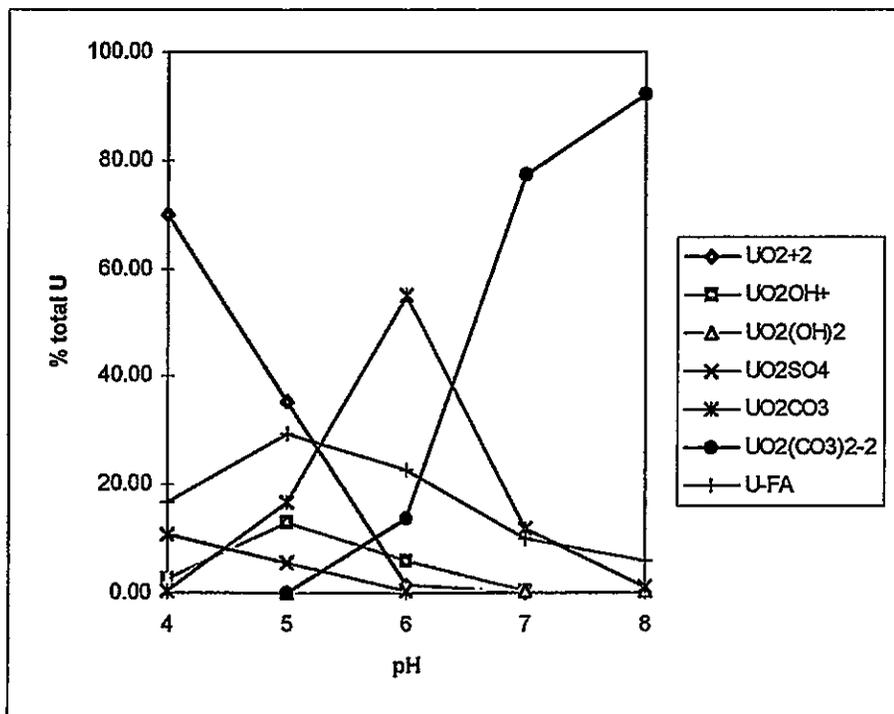


Figure 5.17 Predicted U speciation in groundwater with fulvic acid present

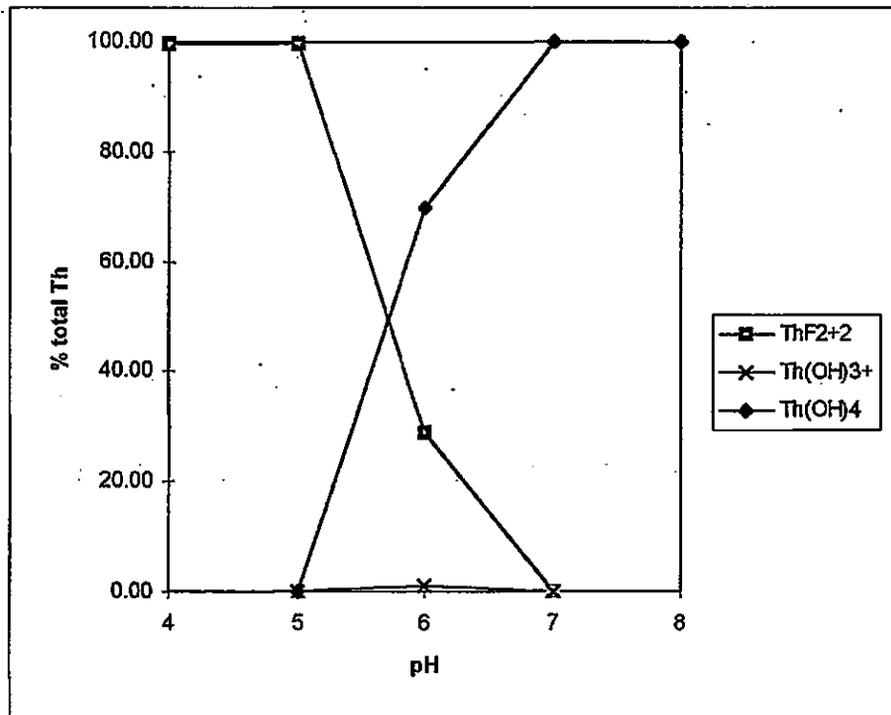


Figure 5.18 Predicted Th speciation in groundwater

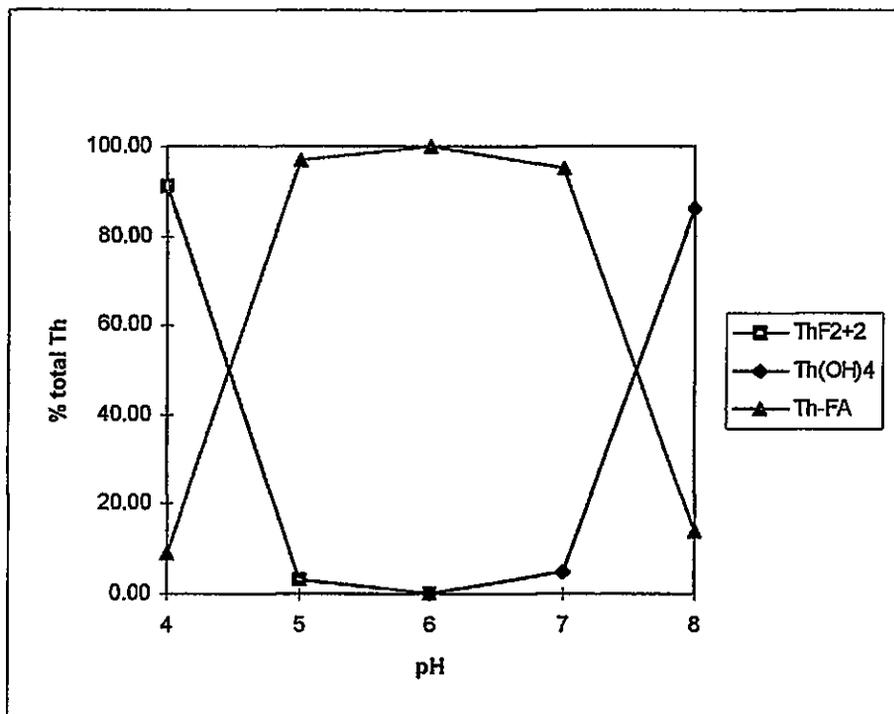


Figure 5.19 Predicted Th speciation in groundwater with fulvic acid present

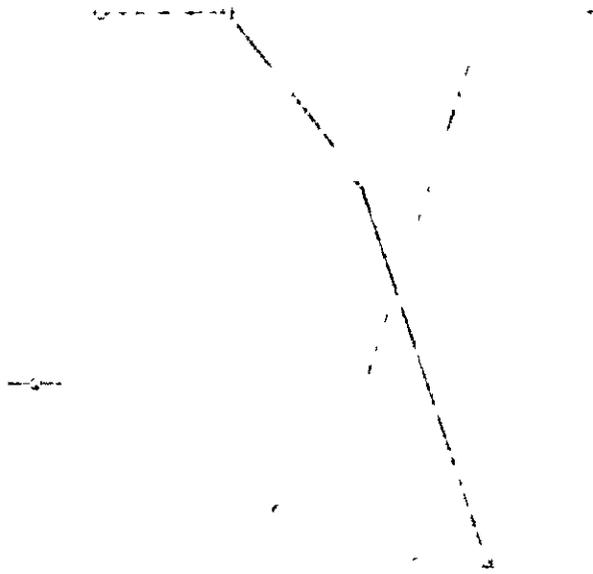


Figure 1. Comparison of two data series over time.

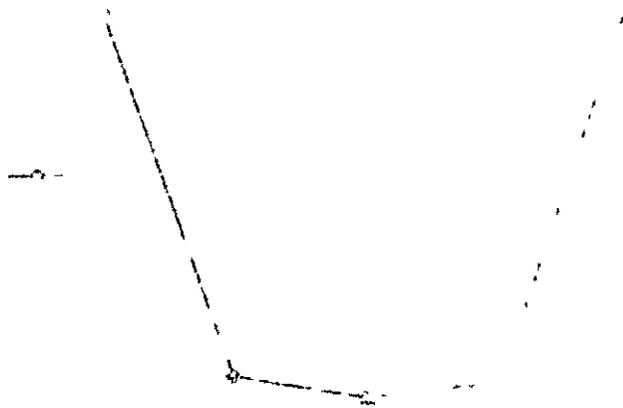


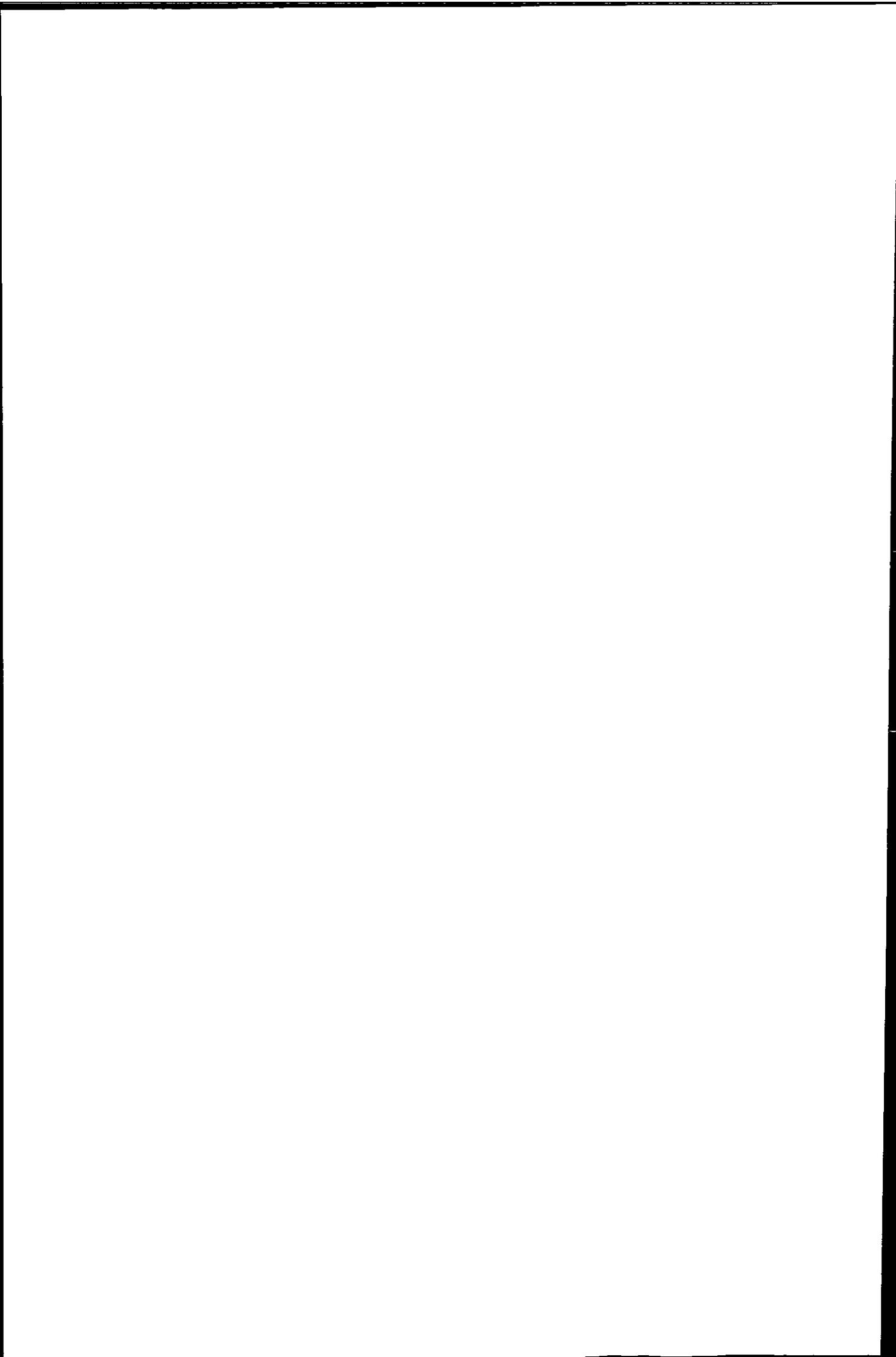
Figure 2. Comparison of two data series over time.

A comparison of the results obtained using these models to those in the literature, which include some form of humic species, shows that the WHAM program predicts the formation of uranium and thorium humic species above pH 6 whereas other models such as MINTEQA2 with a humate ligand²⁰, and PHREEQE with an unspecified organic component¹⁷, predict a sharp drop in the level of U-organic species above pH 6. The study reported using the PHREEQE model does not predict any specific organic species stating only that 'there is little evidence of organic complexation above pH 6'. Results reported for studies using the HARPHRQ program with a 'model fulvic acid' added^{25,26} predict a high (76%) level of U-FA species at pH 6 but results were not reported above this pH value.

The models using 'simple' humic ligands (MINTEQA2 and PHREEQE) predict a drop in U-humic species above pH 6 but the more complex WHAM humic substance model predicts U-humic species over the range pH 5 to 7. This difference in predictions could be related to the use of conditional stability constants, determined experimentally, in the 'simple' models. The value of the conditional stability constant used is dependent on the pH and nature of the HS used in the experiment. Hence, using this value to predict the speciation over a range of pH values could produce different results to those predicted by the WHAM program where, to some extent, the effect of pH is accounted for by the use of proton exchange and electrostatic factors. The HARPHRQ plus 'model fulvic acid' model uses several simple organic acids which dissociate over a range of pH values to take into account such effects.

In the literature thorium has only been modelled with simple organic ligands (oxalate and EDTA)¹¹⁰. These models predict thorium organic species to dominate up to pH 7, then a sharp drop in the level of organic species, similar to that seen in the WHAM model.

These results indicate the importance of including a humic substances in speciation models since they are predicted to play a large part in the interactions. The variety of



speciation scenarios predicted by these models indicates that there is a need for validation by comparison to experimentally determined speciation data.

5.7 Effect of other inorganic components on predicted uranium speciation

Various inorganic components in surface-water, some of which may be present at minor (ng ml^{-1}) levels, can interact with uranium to form additional uranium species. As the levels of these components change, the dominating uranium species may also change.

It has already been shown in the previous section (5.6), that the difference in carbonate concentration between 'soft' and 'hard' water also changes both the level of uranium carbonate species and U-FA species. In this part of the study, carbonate speciation was further investigated by modelling the U-H₂O-CO₃ system over a range of carbonate concentrations at pH 6 using the WHAM program with the NEA data. The results obtained are presented in Table 5.5. As the carbonate concentration is increased from just below the concentration found in 'soft' water samples ($1 \times 10^{-5} \text{ mol l}^{-1}$), to that typically found in high carbonate groundwater samples ($1 \times 10^{-2} \text{ mol l}^{-1}$), the level of uranium carbonate species also increases. The uranium carbonate species make up a significant part of the total uranium species at a carbonate concentration of $1 \times 10^{-4} \text{ mol l}^{-1}$ and are dominating the system (71%) at a carbonate concentration of $1 \times 10^{-3} \text{ mol l}^{-1}$, equivalent to the carbonate concentration in a typical surface-water sample. The carbonate concentration does not have to rise much above that found in a soft water sample to have an impact on the system.

With the NEA data, the domination by phosphate species seen in models calculated using the original PHREEQCI data, was eliminated. To investigate the role of phosphate species in a system defined by the NEA data, and to identify at what phosphate concentration they would become a major species, the U-H₂O-PO₄ system was modelled at

pH 6. The results obtained are presented in Table 5.6. As the phosphate concentration in the model is increased from the level seen in on Dartmoor ($1 \times 10^{-7} \text{ mol l}^{-1}$), to above that seen in a typical groundwater sample ($1 \times 10^{-4} \text{ mol l}^{-1}$) the phosphate species are only at 4% at $1 \times 10^{-6} \text{ mol l}^{-1}$ (equivalent to a typical surface-water level) and do not dominate the system until the phosphate concentration is at $1 \times 10^{-4} \text{ mol l}^{-1}$. Although phosphate dominates at a lower concentration than the carbonate does, in the equivalent U-H₂O-CO₃ system, there is a much lower phosphate concentration in the water to start with, hence it does not produce a major contribution to speciation under typical surface-water conditions. Also the $\text{UO}_2(\text{H}_2\text{PO}_4)_2(\text{aq})$ and $\text{UO}_2(\text{H}_2\text{PO}_4)(\text{H}_3\text{PO}_4)^+$ species which replaced the $\text{UO}_2(\text{HPO}_4)_2^{2-}$ species in the NEA database, form at a much lower pH. Data for the U-H₂O-PO₄ system over the pH range 4 to 8 at $1 \times 10^{-5} \text{ mol l}^{-1}$ can be seen in Table 5.7. $\text{UO}_2\text{HPO}_4(\text{aq})$ is the main species that forms at pH 5 to 6.

Fluoride became a major influence on uranium speciation at lower pH values when the NEA data was used to model surface-water in the previous section (5.6). The U-H₂O-F system was modelled in order to determine at what lower level the fluoride speciation would become insignificant. The results are presented in Table 5.8 and Table 5.9. At pH 6 the level of fluoride species is only 4% at $1 \times 10^{-5} \text{ mol l}^{-1}$ fluoride (the level found in a typical surface-water sample) but at pH 5, the fluoride species are at 43% for the same fluoride concentration. Reducing the fluoride concentration to $1 \times 10^{-6} \text{ mol l}^{-1}$, the fluoride species are at 7%, and do not become insignificant (< 1%) until $1 \times 10^{-7} \text{ mol l}^{-1}$ fluoride. Thus, although only a minor component ($< \mu\text{g ml}^{-1}$) in an average surface-water sample fluoride can play a major role in uranium speciation at lower pH values.

Table 5.5 Uranium speciation for the U-H₂O-CO₃ system at pH 6

Species (%)	Carbonate concentration (mol l ⁻¹)			
	1 x 10 ⁻⁵	1 x 10 ⁻⁴	1 x 10 ⁻³	1 x 10 ⁻²
UO ₂ ²⁺	3.49	2.96	1.06	0.06
UO ₂ OH ⁺	16.08	13.53	4.73	0.26
UO ₂ (OH) _{2(aq)}	78.29	65.69	22.74	1.21
Total OH	97.86	82.18	28.53	1.53
UO ₂ CO _{3 (aq)}	2.08	17.41	60.10	31.60
UO ₂ (CO ₃) ₂ ²⁻	0.00	0.32	11.30	65.90
Total CO ₃	2.08	17.73	71.40	97.50

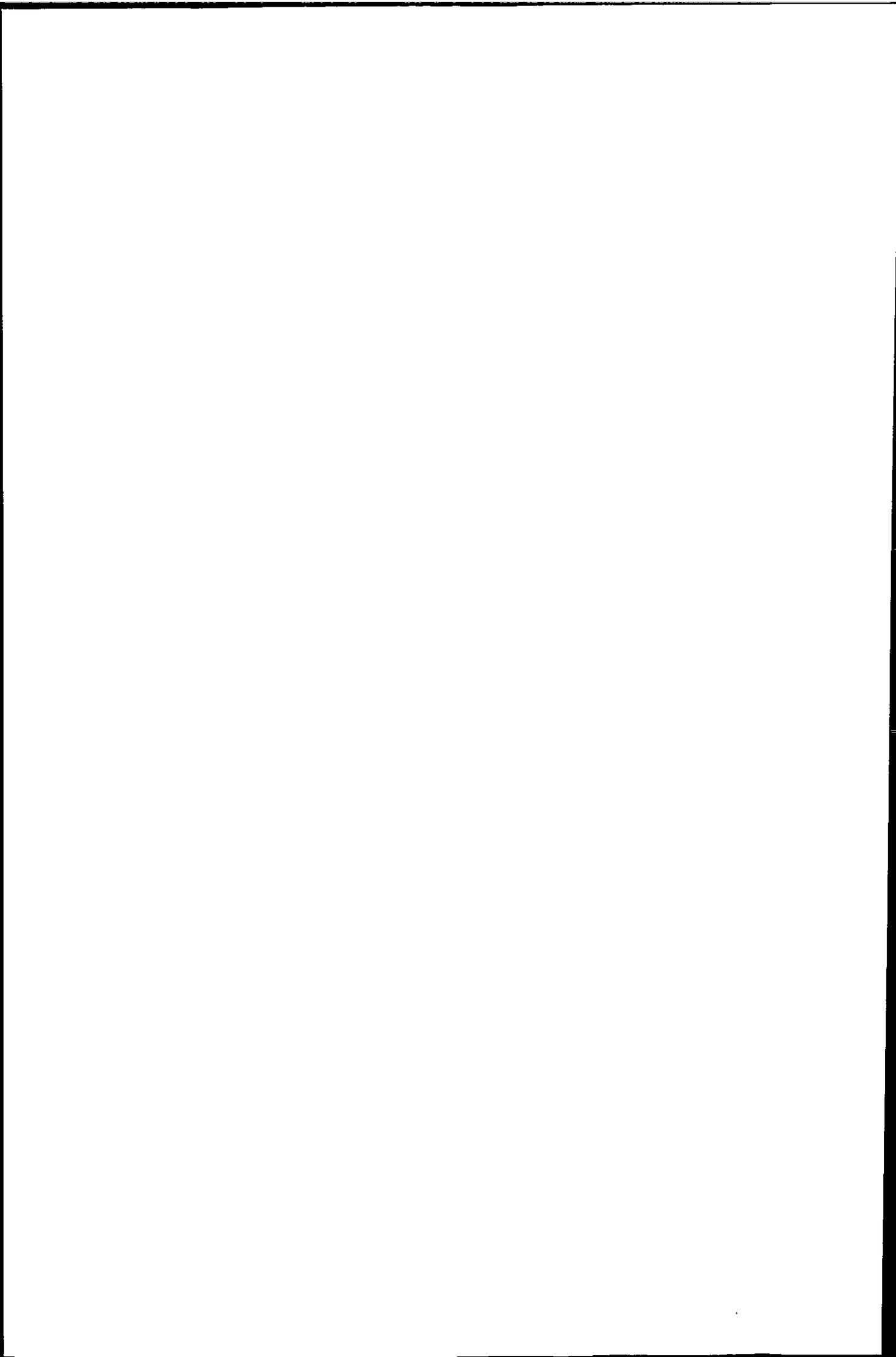


Table 5.6 Uranium speciation for the U-H₂O-PO₄ system at pH 6

Species (%)	Phosphate concentration (mol l ⁻¹)			
	1 x 10 ⁻⁷	1 x 10 ⁻⁶	1 x 10 ⁻⁵	1 x 10 ⁻⁴
UO ₂ ²⁺	4	3	2	1
UO ₂ OH ⁺	16	16	11	3
UO ₂ (OH) ₂ (aq)	80	76	55	14
Total OH	99	96	69	18
UO ₂ PO ₄ ⁻	0	1	9	23
UO ₂ HPO ₄ (aq)	0	3	22	58
Total PO ₄	0	4	31	82

Table 5.7 Uranium speciation for the U-H₂O-PO₄ system over the pH range 4 to 6

Species (%)	pH				
	4	5	6	7	8
UO ₂ ²⁺	87	37	2	0	0
UO ₂ OH ⁺	4	17	11	2	0
UO ₂ (OH) ₂ (aq)	0	8	55	86	90
Total OH	91	62	69	88	90
UO ₂ PO ₄ ⁻	0	1	9	9	2
UO ₂ HPO ₄ (aq)	8	36	22	2	0
Total PO ₄	8	37	31	12	2

Table 5.8 Uranium speciation for the U-H₂O-F system at pH 6

Species (%)	Fluoride concentration (mol l ⁻¹)			
	1 x 10 ⁻⁷	1 x 10 ⁻⁶	1 x 10 ⁻⁵	1 x 10 ⁻⁴
UO ₂ ²⁺	4	4	3	2
UO ₂ OH ⁺	16	16	16	10
UO ₂ (OH) ₂ (aq)	80	80	76	51
Total OH	100	100	96	63
UO ₂ F ⁺	0	0	4	28
UO ₂ F ₂ (aq)	0	0	0	9
Total F	0	0	4	36

Table 5.9 Uranium speciation for the U-H₂O-F system at pH 5

Species (%)	Fluoride concentration (mol l ⁻¹)			
	1 x 10 ⁻⁷	1 x 10 ⁻⁶	1 x 10 ⁻⁵	1 x 10 ⁻⁴
UO ₂ ²⁺	59	55	34	6
UO ₂ OH ⁺	27	25	16	3
UO ₂ (OH) ₂ (aq)	13	12	8	1
Total OH	99	93	57	10
UO ₂ F ⁺	1	7	41	69
UO ₂ F ₂ (aq)	0	0	1	21
Total F	1	7	43	90

5.8 Comparison of different humic substance models

As discussed earlier in this chapter, there are several different types of HS model which can be used to predict the level of U-HS speciation which may occur in water samples. To evaluate how the results from different models compare, the results for the speciation of a surface-water sample containing humic substances modelled using the WHAM program were compared to those for the same sample modelled using the PHREEQCI program. In order to use PHREEQCI to model HS interactions with uranium, 'model FA' data from the Australian Nuclear Science and Technology Organisation (ANSTO)⁹⁸ was added to the program for this study. This is an analogy type model where the HS is represented by a 'model FA' consisting of several relatively small organic acids. The nature of the reaction of uranium with these acids is known and a set of log K values have been compiled by ANSTO. The input parameters were the same as those used to produce the results in Figure 5.11. For the PHREEQCI program the FA concentration was converted, as shown below, to a COOH equivalent concentration using the COOH concentration data from ANSTO. This was then equally divided between the organic acids used to model the FA.

$$\text{COOH equivalent concentration} = 4.94 \mu\text{mol COOH per mg FA}$$

$$\begin{aligned} \Rightarrow 8 \text{ mg l}^{-1} \text{ FA} &= 8 \times 4.94 \\ &= 39.52 \mu\text{mol l}^{-1} \text{ COOH} \end{aligned}$$

Dividing this between the organic acids in the model FA.

$$39.52/5 = 7.90$$

and then converting this to an equivalent organic acid concentration.

$$\begin{aligned} 7.90/2 &= 3.95 \mu\text{mol l}^{-1} \\ &= 3.95 \times 10^{-6} \text{ mol l}^{-1} \text{ aspartic acid} \end{aligned}$$

The same procedure was followed for the other organic acids.

Models of a synthetic surface-water sample containing FA were constructed and predictions of the uranium speciation, at a range of pH values between pH 4 and 8, were obtained. The predicted uranium speciation from these models can be seen in Figure 5.20. The equivalent results produced using the WHAM program are given in Figure 5.21.

The PHREEQCI program predicted U-HS speciation to a much greater extent than that predicted by the WHAM program. Since both sets of results have been produced using the same thermodynamic data, except for the nature of the HS model, this would appear to indicate that it is the HS model that is causing the difference. Without further information, for example experimentally derived speciation data, it would not be possible to say which, if either, of these models was correct. For this reason a comparison of experimental results obtained in Chapter 4 and the corresponding computer model predictions was carried out and presented in Chapter 6.

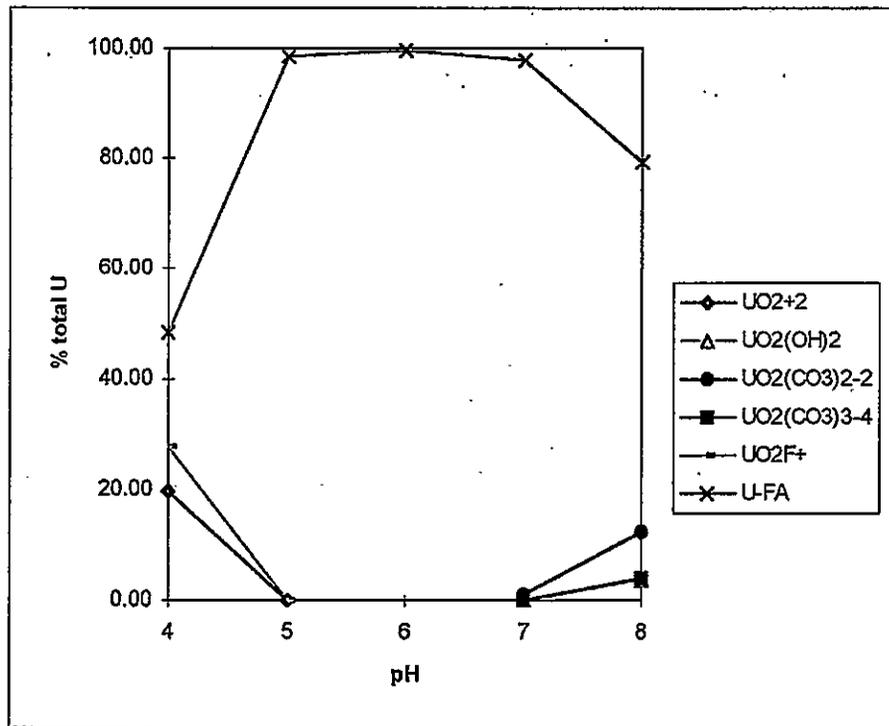


Figure 5.20 Predicted U-FA speciation using the PHREEQCI program

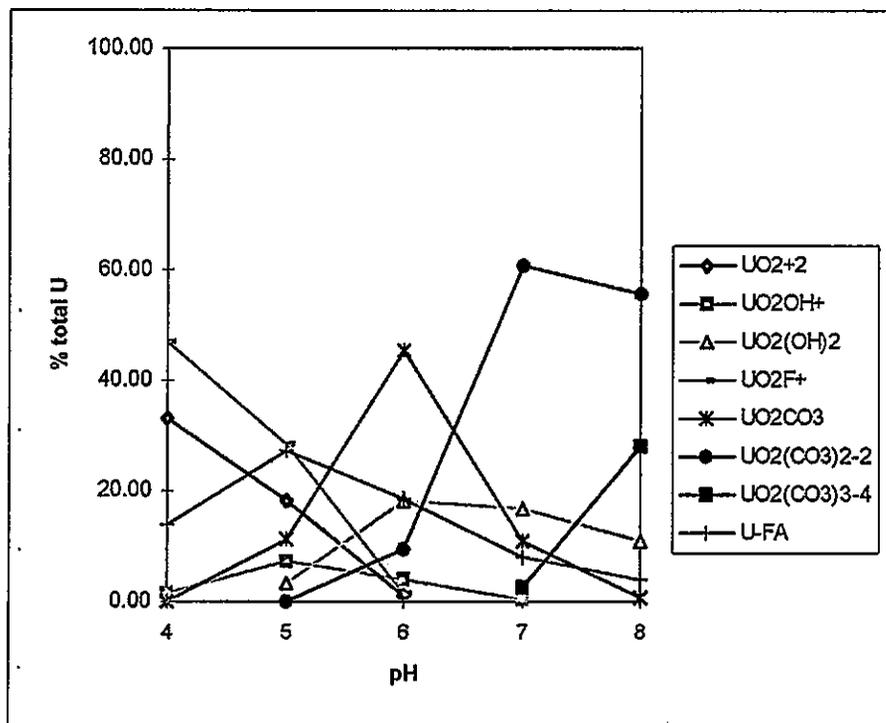


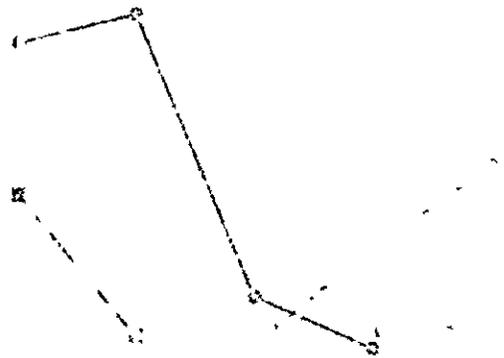
Figure 5.21 Predicted U-FA speciation using the WHAM program

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5.9 Summary

Variations in the thermodynamic data used to calculate uranium speciation in natural waters can have a major effect on the results obtained. In order to overcome this and allow comparison of results from different datasets a consistent database is required. The NEA-TDB have produced a critical review of uranium thermodynamic data in the literature. This database has been used in several projects and has been incorporated into the WHAM and PHREEQCI databases for work in this thesis.

Models of a 'soft' water system, produced using the original WHAM thermodynamic data, predicted uranyl species at low pH, UO_2OH^+ species at neutral pH and carbonate species above pH 7. The same model, calculated using the NEA thermodynamic data, predicted uranyl and fluoride species at low pH, $\text{UO}_2(\text{OH})_2$ species at neutral pH and carbonate species at pH 7. When the carbonate concentration in the model was increased, both the original WHAM and the NEA data predicted an increase in the level of carbonate species, displacing the hydrolysis species and being present from pH 5 upward. Thorium models were only produced using the original WHAM data as the NEA has not produced a thorium database. At low pH, thorium fluoride species were predicted to dominate the speciation and were almost entirely replaced by thorium hydrolysis species above pH 6. Since thorium carbonate species are not formed, the carbonate concentration in the model did not effect the predicted thorium speciation.

However, the nature of the interaction with humic substances still has to be considered. Being complex organic molecules which have not been fully characterised, humic substances cannot be treated in the same manner as simple inorganic ligands. Two possible techniques to overcome this are to either create a computer model of a HS and use this within the speciation program, or use an analogy type model where smaller organic acids with known reaction properties are added to the speciation program to represent the

HS. The WHAM program uses the former technique and the PHREEQCI program uses the latter. Simulations run using the two programs produced significantly different results. Models produced using the original WHAM thermodynamic data predicted 80% U-FA species. This level reduced to 40% when the NEA data was used to model the speciation. When the carbonate concentration in the model was increased the U-FA level dropped further to 20%. An equivalent model produced using the PHREEQCI program with the NEA data predicted 98% U-FA species. Thus, before the effectiveness of the programs to correctly predict U-HS speciation could be determined, the models required external validation by comparison to experimental (not computer generated) results. This has been carried out and details of the study and the results obtained are presented in Chapter 6.

Chapter Six

6. Comparison of experimental and computer modelled speciation

6.1 Introduction

Given the variation in the results which may be obtained when different computer models are used to predict uranium speciation in natural water samples, as demonstrated in Chapter 5, external validation, by comparison of the model predictions with experimental results, will give an indication of the effectiveness of these programs to correctly predict the uranium speciation. In this study, this comparison has been carried out by constructing computer models of the Dartmoor water samples, analysed in Chapter 4, using both the WHAM and PHREEQCI programs.

6.2 Characterisation of Dartmoor water samples

In order to construct computer models of the Dartmoor water samples previously analysed in Chapter 4, the major components of these water samples needed to be determined. This was achieved using several techniques as detailed in Chapter 2. The cations Na^+ , K^+ , Ca^{2+} and Mg^{2+} were determined by ICP-AES. The anions Cl^- , F^- , NO_3^- and SO_4^{2-} were determined by anion chromatography and total reactive phosphate was determined spectrophotometrically. Although fluoride and phosphate are typically only present in surface-waters at minor (ng ml^{-1}) levels, the models constructed in Chapter 5 indicate that these components can have a potentially large effect on the uranium speciation. Dissolved organic and inorganic carbon were determined by TOC analysis. Temperature and pH measurements were carried out in-field and again in the laboratory prior to analysis so that the models could be constructed using the same conditions as those found for the samples at the time of analysis (of uranium speciation). The results obtained are presented in

Table 6.1. The change in river water composition, moving from up stream to down stream sampling points, is more easily seen in Figure 6.1. In the R Plym, starting up stream at Ditsworthy Warren and moving down stream through Cadover Bridge to Shaugh Bridge, the level of the majority of the determinands remains fairly constant. At the confluence of the R Plym and the R Meavy at Shaugh Bridge there is an increase in the level of the inorganic components, including inorganic carbon (carbonate). This is due to the higher level of these components present in the R Meavy. There is however a decrease in the level of organic carbon in the R Plym after the two rivers have joined. These changes in the levels of the various components in the water samples could potentially effect the uranium speciation in the water samples.

Table 6.1 Results from the characterisation of Dartmoor water samples

Sample	Concentration ($\mu\text{g ml}^{-1}$)												
	U (ng ml^{-1})	TC	IC	OC	Na	K	Mg	Ca	F	Cl	NO ₃	SO ₄	PO ₄
R. Plym, Ditsworthy Warren	0.19	4.01	0.55	3.46	5.6	0.4	0.7	0.6	< 0.01	9.2	1.8	2.7	0.030
R. Plym, Cadover Bridge	0.12	4.22	0.56	3.65	5.9	0.6	0.8	1.0	< 0.01	8.9	1.3	2.8	0.035
R. Plym, Shaugh Bridge	0.18	4.05	0.54	3.51	6.1	0.6	0.9	1.2	< 0.01	9.1	3.2	6.1	0.035
R. Plym + R. Meavy, SB	0.09	5.35	2.23	3.12	8.0	1.8	1.6	5.4	< 0.01	10.2	7.6	5.4	0.110
R. Plym, Plym Bridge	0.10	5.43	2.73	2.70	8.5	1.7	2.2	8.0	< 0.01	10.7	10.5	5.9	0.096
R. Newleycombe Lake	0.17	2.06	0.09	1.97	5.8	0.8	0.9	1.2	< 0.01	9.2	1.5	4.1	0.031
R. Meavy, Burrator	0.23	2.84	0.77	2.07	6.5	0.2	0.9	1.5	< 0.01	10.3	3.2	4.0	0.033
R. Meavy, Shaugh Bridge	0.08	4.26	2.24	2.02	7.6	1.6	1.7	5.9	< 0.01	10.3	8.1	4.9	0.149

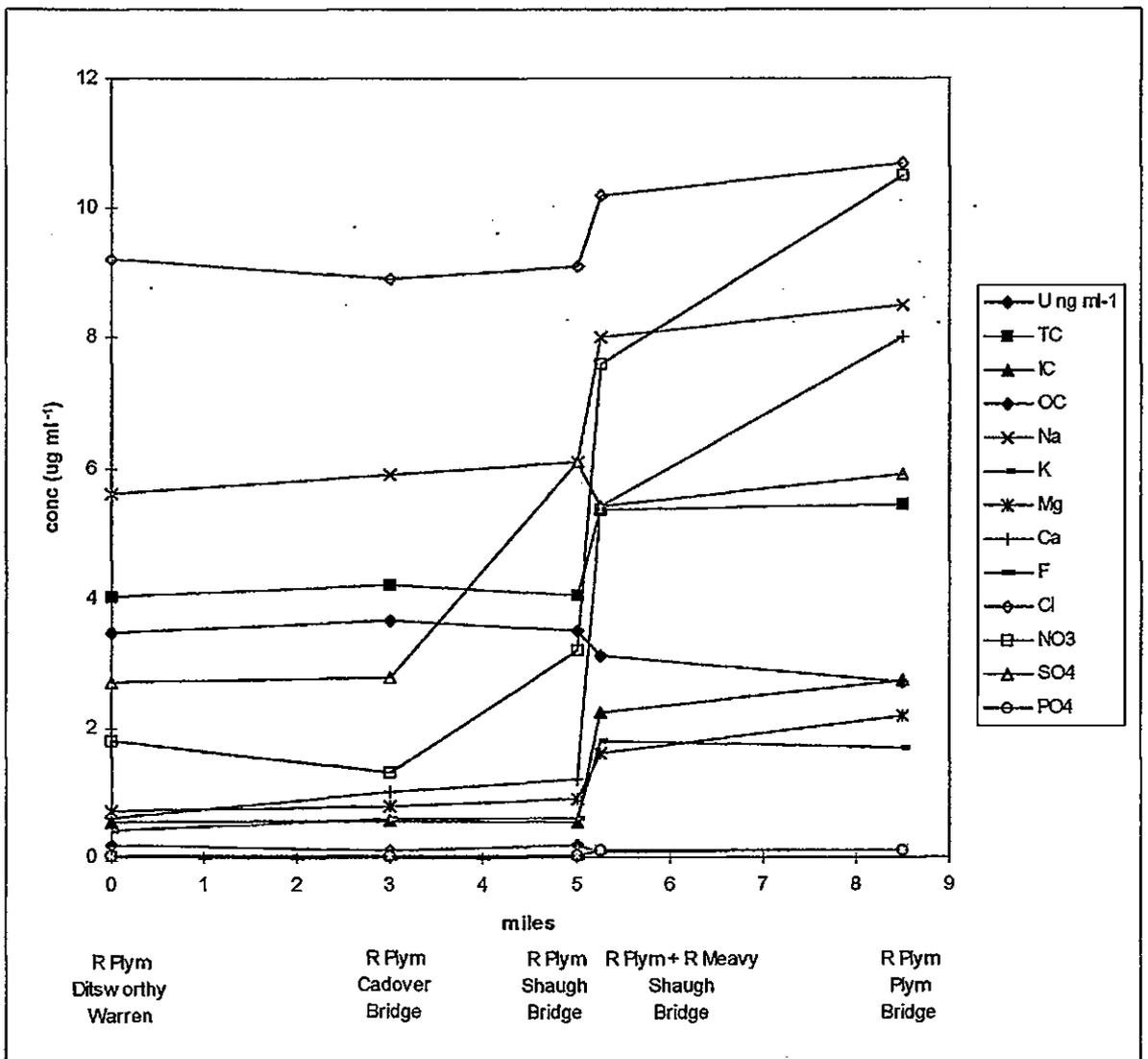
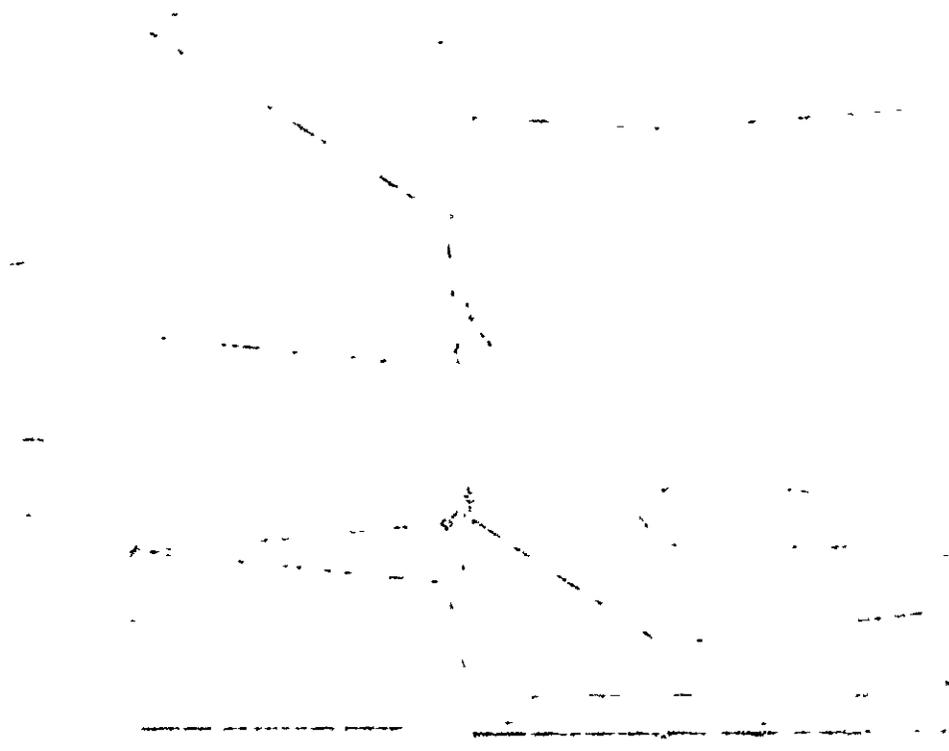


Figure 6.1 Change in water component levels along the length of the R Plym



6.3 Modelling uranium speciation in water samples using the WHAM program

Computer models were constructed using the WHAM program to predict the level of uranium-organic species for a series of natural water samples, collected from Dartmoor. The level of HS used in the models was derived from the experimental DOC results for these samples. Since humic substances are typically composed of approximately 50% carbon¹¹¹ the HS level would equate to twice the DOC level (i.e. $HS = 2 \times DOC$). However not all of the DOC in the water may necessarily be in the form of humic substances, a proportion is usually made up of simple lower molecular weight organic acids, carbohydrates and hydrocarbons¹¹⁸. For the purpose of this exercise the HS level was taken as being 50% of the total DOC concentration, in other words the HS level was taken to be equivalent to the DOC level ($HS = 2 \times DOC/2$).

In the initial models constructed of the Dartmoor water samples all the HS was modelled as fulvic acid (FA). The results for these 100% FA models, with both $HS = 1 \times DOC$ and $HS = 2 \times DOC$, were very low compared to the equivalent experimental results reported in Chapter 4 (see Table 4.6). Since humic substances in natural waters are composed of both fulvic and humic acids, the next step in this study was to add a humic acid (HA) component to the Dartmoor models. However, because the proportion of HA in river water samples can vary to comprise up to 20% of the total HS present^{98, 119, 120}, before adding an HA component to the Dartmoor models a study on the effect of adding HA to a synthetic surface-water system was carried out. This provided an overview of the effect of adding varying amounts of HA to the system over a range of pH values.

The models used in this study (on the effect of adding an HA component to a synthetic surface-water system) contained HS values of $4 \mu\text{g l}^{-1}$ of which 0 to 10% was HA, at pH values ranging from 4 to 8. The results obtained are presented in Figure 6.2

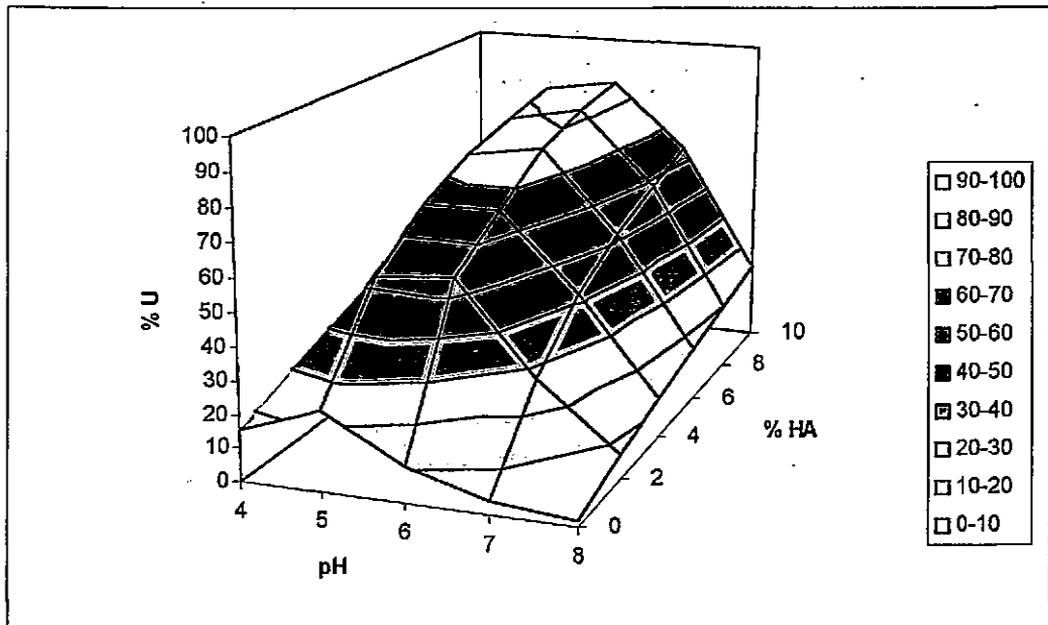


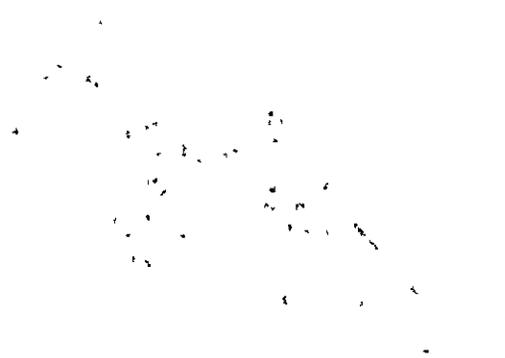
Figure 6.2 Predicted effect of changes in %HA on the level of organic uranium species

The pH values are plotted on the 'x' axis, the %HA on the 'y' axis, and the response to changes in these parameters, observed as an increase or decrease in the level of uranium-humic substance (U-HS) species, is plotted on the 'z' axis.

From Figure 6.2 it can be seen that at a level of 0% HA (100%FA), moving across the pH range from 4 to 8 the response profile of the U-HS species is the same as that seen in the model of surface-water with FA present presented in Chapter 5 (Figure 5.11). At 0% HA the profile displays an increase in the level of U-HS species as the pH increases from 4 to 5. This level of U-HS species then drops at pH values above 5 and continues to decrease up to pH values of 8. The pH range from 6 to 8 is where uranium-carbonate species are predicted, by the model, to form.

When increasing the HA concentration to 2% a large increase in the predicted level of U-HA species can be seen. Across the pH range at 2% HA there is also a change in the U-HS response profile. The level of U-HS species does not decrease above pH 5 but levels off, up to pH 6, before dropping between pH 6 and 7. The presence of competing carbonate

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ligands within this pH range appears to have less of an effect on the level of U-HS species when HA is present in the model.

Further increasing the concentration of HA leads to the same profile across the pH axis and the level of U-HS species continues to increase, although the increase in U-HS species with increasing HA level is less (the contour plot is less steep from 2 to 10% HA than it is from 0 to 2% HA).

In these models (Figure 6.2) the major effect of HA on %U-HS level was seen with the initial 2% addition of HA, causing a 40% rise in the U-HS level at pH 6. However at the extremes of the pH range (4 and 8) the level of HA had much less effect on the U-HS level. Based on the results obtained from these early models it was decided to construct further models of the Dartmoor water samples, first containing 2% HA, and then 10% HA. The results from these models can be seen in Figure 6.3. When using 10% HA in the models, 6 out of 8 of the model predictions were within 10% of the experimental results. Given the precision of the experimental method and the variations in modelled results due to differences in thermodynamic data, model predictions within 10% of experimental results were deemed acceptable.

Two samples gave differences between the modelled and experimental results greater than 10%, i.e. the R Meavy at Shaugh Bridge and the R Plym at Plym Bridge, both of which had pH values above 7. The trend observed for model predictions vs. pH value (Figure 6.5) indicates a drop in the level of U-HS species with increasing pH, although this is not seen in the experimental results.

These differences could be explained if the model had a low bias at high pH, and hence the low predictions for the samples above pH 7. An alternative explanation for the low model predictions could be that while the ratio of HA to FA is fairly constant in water samples^{119, 120}, the level of HS in the DOC can vary^{119, 121, 122}. A typical level of HS is 50% but it can be as low as 20% in some rivers. Lakes have a higher level, (70 to 80%) although

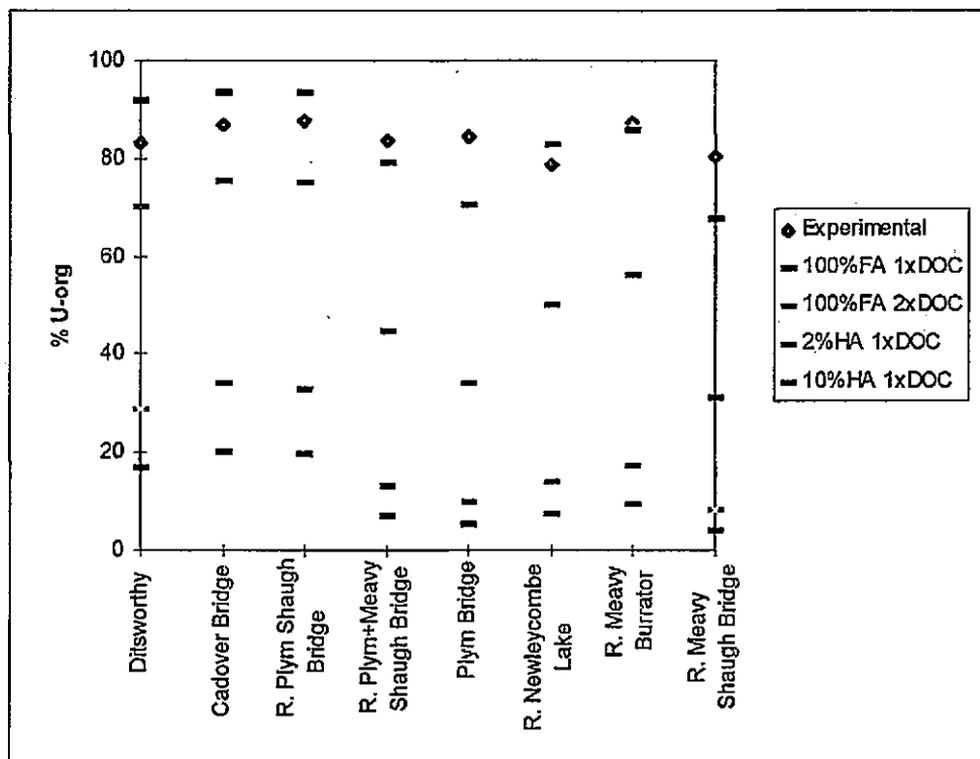


Figure 6.3 Experimental and computer modelled predictions of the level of uranium-organic species in Dartmoor water samples using computer models with different HS compositions

Year	1950	1951	1952	1953	1954	1955	1956
Production (1000 tons)	100	100	100	100	100	100	100
Consumption (1000 tons)	100	100	100	100	100	100	100
Stocks (1000 tons)	100	100	100	100	100	100	100
Exports (1000 tons)	100	100	100	100	100	100	100
Imports (1000 tons)	100	100	100	100	100	100	100

Production of goods and services in the economy is expected to increase by 10% in 1957. This is due to the fact that the government has decided to increase its spending on infrastructure projects. The increase in production is expected to be accompanied by a corresponding increase in the demand for raw materials and labor. The government is also planning to introduce new tax measures to encourage investment and production. It is expected that these measures will lead to a significant increase in the country's economic growth.

it is the residence time of the water in contact with soil, sediment etc. that effects the level of DOC and the proportion of HS in the DOC. The two samples which had the lowest model predictions (compared to the equivalent experimental results) were the R Meavy at Shaugh Bridge and the R Plym at Plym Bridge. The R Meavy at Shaugh Bridge is down stream of Burrator reservoir and the R Plym at Plym Bridge is downstream of the R Meavy joining the R Plym (these locations can be seen in Chapter 4, Figure 4.9). The residence time of the water in the reservoir could effect the proportion of HS in the DOC and hence the nature of the water samples down stream of the reservoir. It could therefore be possible that a different model is required for the R Meavy at Shaugh Bridge and the R Plym at Plym Bridge samples.

To investigate the effect of changing the level of HS in the DOC on the models prediction, a further set of models were constructed for HS = 25, 50, 75 and 100% of the DOC . The results, expressed as the difference between modelled and experimental results (a negative value indicating a low prediction by the model), can be seen in Table 6.2. As the proportion of HS in the DOC was increased the predicted level of U-HS increased. This happened to a greater extent in the downstream samples which had higher pH values. The WHAM program appears to be more sensitive to changes in input parameters at the higher pH and lower DOC levels (see Table 6.3). Considering the results for the HS = 75% DOC model in Table 6.2, the R Meavy at Shaugh Bridge and R Plym at Plym Bridge predictions are now within 10% of the experimental values. The upstream R Plym samples starting near the source at Ditsworthy and moving downstream through Cadover Bridge and Shaugh Bridge fit the 25 and 50% DOC models. Once the Plym joins with the Meavy at Shaugh Bridge the 50 and 75% DOC models fit, and at Plym Bridge the 75 and 100% models fit. The R Meavy and R Newleycombe Lake above Burrator fit the 50% DOC model and the R Meavy below Burrator at Shaugh Bridge fits the 75% DOC model. The 50% model can be used for all the samples except the R Meavy at Shaugh Bridge and the R Plym at Plym

Table 6.2 The difference between experimental results and computer model predictions produced using models with different humic substance levels based on the proportion of dissolved organic carbon (DOC) taken as humic substances (HS)

Sample	25% DOC	50% DOC	75% DOC	100% DOC
R Plym, Ditsworthy Warren	1.4	8.5	11.1	12.6
R Plym, Cadover Bridge	0.9	6.6	8.6	9.7
R Plym, Shaugh Bridge	-0.3	5.5	7.7	8.8
R Plym + R Meavy, SB	-18.2	-4.5	1.4	4.8
R Plym, Plym Bridge	-30.2	-14.0	-6.3	-1.8
R Newleycombe Lake	-8.5	3.9	8.9	11.8
R Meavy, above Burrator	-12.1	-1.3	3.0	5.5
R Meavy, Shaugh Bridge	-29.0	-12.5	-4.2	0.6

Difference = modelled value - experimental value

Table 6.3 Spread of predicted levels of U-organic species predicted by models with different levels of HS as related to sample pH and organic carbon (OC) concentration

Sample	Spread of results	pH	OC ($\mu\text{g ml}^{-1}$)
R Plym, Cadover Bridge	8.8	6.45	2.82
R Plym, Shaugh Bridge	9.1	6.55	3.12
R Plym, Ditsworthy Warren	11.2	6.38	1.91
R Meavy, above Burrator	17.4	6.58	1.41
R Newleycombe Lake	20.3	6.55	1.05
R Plym + R Meavy, Shaugh Bridge	23	6.91	1.60
R Plym, Plym Bridge	28.4	7.04	1.36
R Meavy, Shaugh Bridge	29.6	7.02	1.16

Spread = highest level of organic species - lowest level of organic species

Bridge which require the model in which HS make up 75% of the DOC.

Such changes in the models do make an assumption about the level of HS in the DOC. Although insufficient sample was available to experimentally fractionate the different types of organic carbon in the DOC, an indication of the relative amounts of HS in the different samples was obtained from UV absorption measurements. This technique is based on the composition of humic substances being more aromatic than the other organic carbon components of the DOC and hence exhibiting greater UV absorption. The ratio of absorption to mg DOC can be used to compare the relative levels of humic substances in water samples^{121, 123, 124}. The results of such measurements carried out on the Dartmoor samples are presented in Table 6.4. The absorption/DOC ratio can be seen to be greater for the R Meavy sample at Shaugh Bridge, below Burrator reservoir, than for the R Meavy sample taken above the reservoir. This indicates that there was a change in the nature of the DOC as the water passed through the reservoir. These results also indicate that there was a decrease in the absorption/DOC ratio of the samples collected at the confluence of the R Meavy and the R Plym at Shaugh Bridge. This was thought to be due to the lower absorption/DOC ratio present in the R Plym mixing with the higher absorption/DOC ratio observed in the R Meavy. By the time the R Plym had reached Plym Bridge the absorption/DOC ratio had increased back to that observed in the R Meavy before it joined the R Plym at Shaugh Bridge. This is reflected in the use of the 75% DOC model used for these two samples. A high absorption/DOC ratio is also seen in the R Newleycombe Lake sample taken above Burrator reservoir. As this river feeds in to the reservoir the nature of the DOC (reflected by the high absorption/DOC ratio) in this water could also have been responsible for the change in the nature of the R Meavy water during its passage through the reservoir.

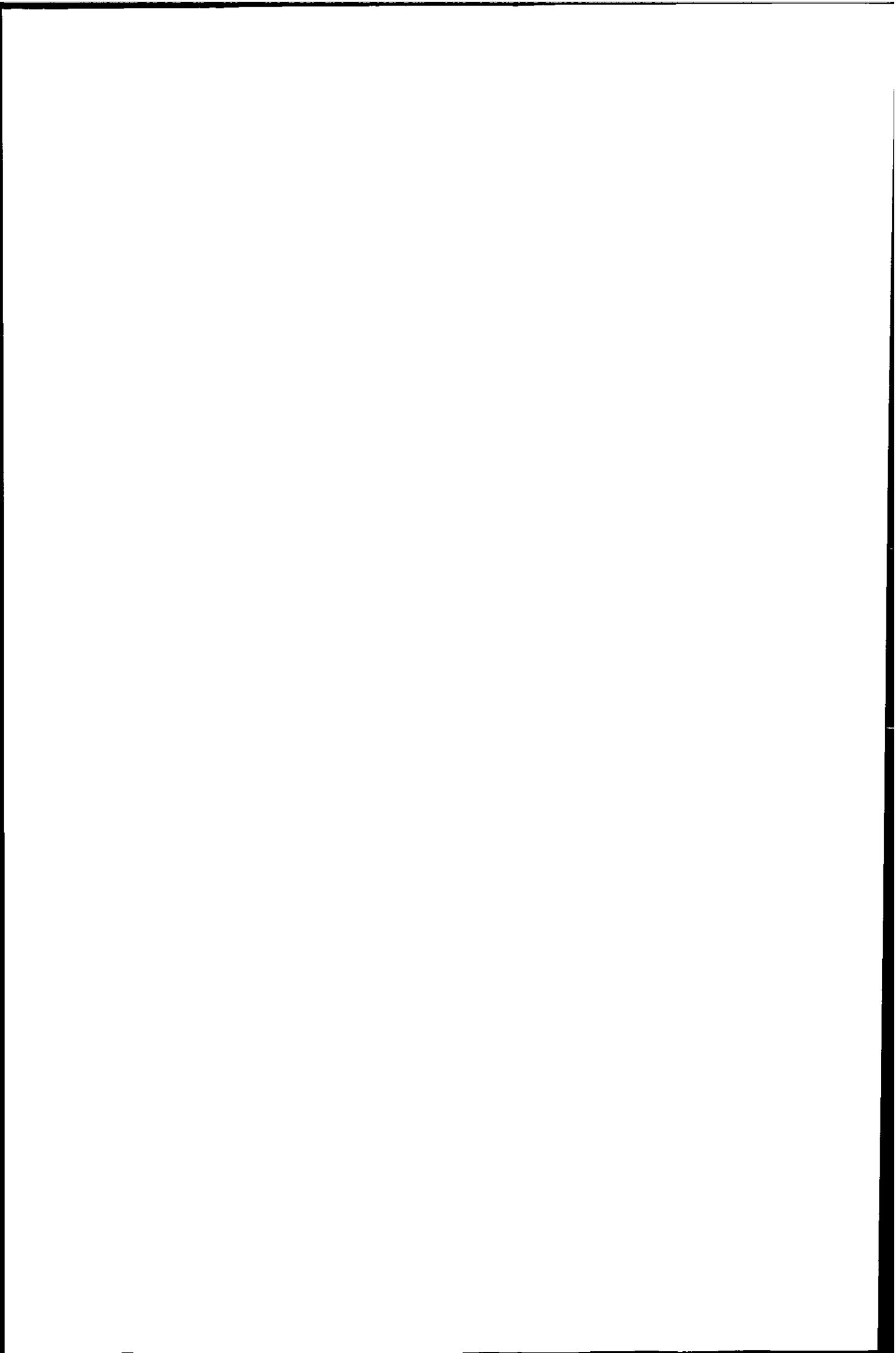


Table 6.4 Absorption/DOC ratios for Dartmoor water samples

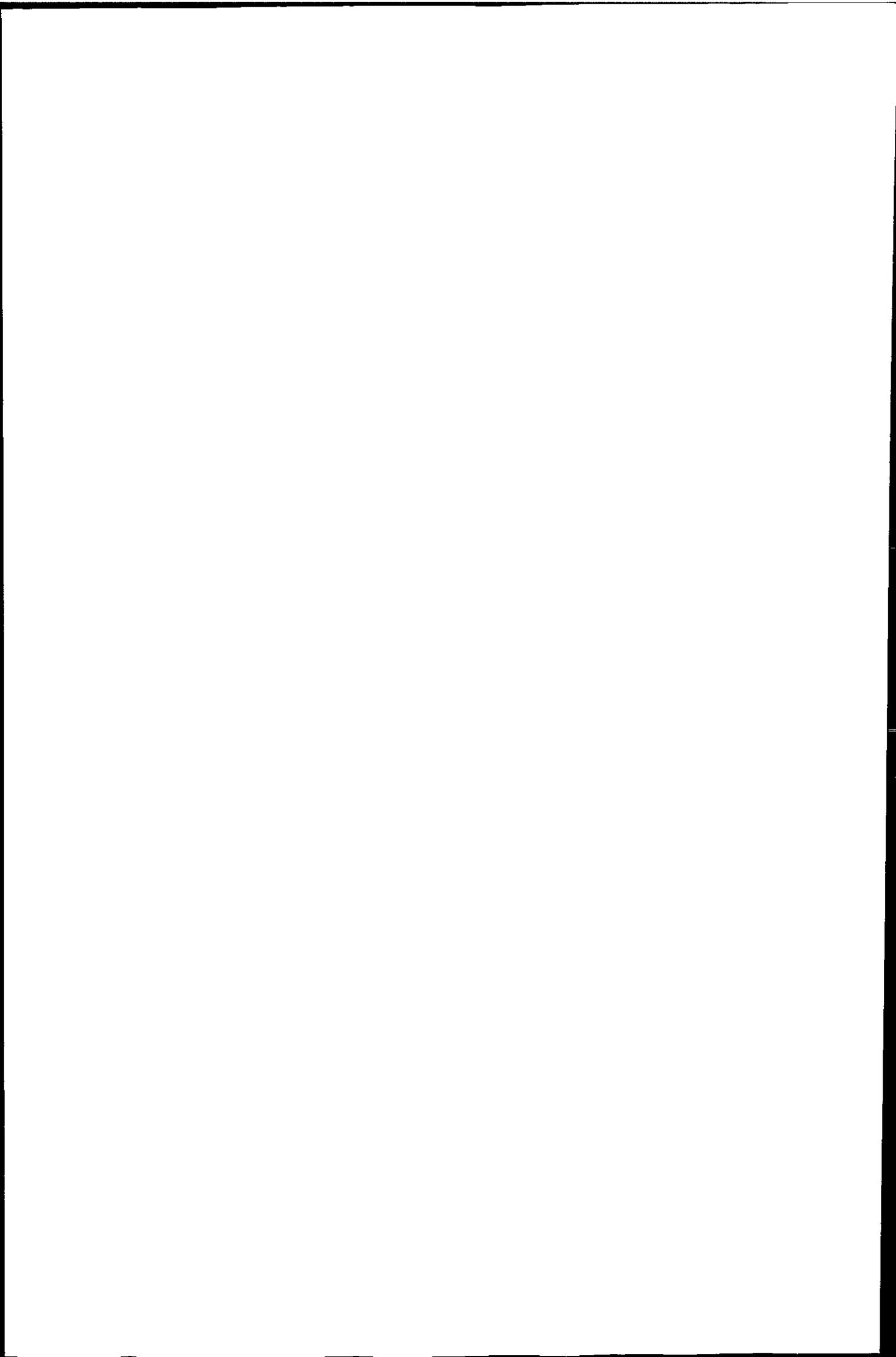
Sample	Absorption/DOC $\mu\text{g ml}^{-1}$	
	254 nm	340 nm
R Plym, Ditsworthy Warren	0.1410	0.0688
R Plym, Cadover Bridge	0.1337	0.0516
R Plym, Shaugh Bridge	0.0904	0.0493
R Plym + R Meavy, Shaugh Bridge	0.1564	0.0893
R Plym, Plym Bridge	0.1810	0.1023
R Newleycombe Lake, above Burrator	0.2412	0.1303
R Meavy, above Burrator	0.1592	0.0927
R Meavy, Shaugh Bridge	0.1856	0.1103
Fulvic acid solution	0.0808	0.0407
Humic acid solution	0.1150	0.0637

The higher the absorption/DOC ratio (at either wavelength) the higher the level of humic substances making up the total dissolved organic carbon content of the water.

6.3.1 Correlation of predicted uranium-humic substance species levels with organic carbon concentration and pH values for Dartmoor models

Comparing the computer model predictions of U-HS levels (as oppose to the experimental results correlation presented in Chapter 4) to the level of organic carbon, percent organic carbon and pH value of the samples can give an indication of how the model functions. How the model predictions vary for samples with different levels of organic carbon and with different pH values will indicate how sensitive the models are to changes in these parameters. As expected, it can be seen in Figure 6.4 that as the organic carbon concentration (represented by HS in the model) increases, the level of U-HS species also increases (R^2 model 0.75; experimental 0.73; model and experimental similar). When the percent organic carbon drops (inorganic carbon increases as a percent of the total carbon concentration) the U-HS species level also drops. This could be due to the model taking into account competition from carbonate ligands and/or due to the change in pH as the inorganic carbon level increases. The model appears to have a strong correlation to changes in pH, with decreasing U-HS species levels predicted as the pH increases (R^2 model -0.92; experimental -0.29), however this is not seen in the equivalent experimental results (see Figure 6.5).

When the proportion of HA introduced into the model is increased, the computer model predictions become closer to the experimental results. The trend indicated by these results, with respect to pH, also becomes slightly closer to that seen in the experimental results, that is, there is less of a drop in %U-HS species with increased pH seen in the 10% HA models than in the 2% HA models (2% HA model, 44% spread of results; 10% HA model, 25% spread of results; experimental, 9% spread of results). The electrostatic and proton exchange functions in the WHAM program are designed to take into account the effect of pH on the equilibrium constants and the predicted level of organic species



formation. Comparing model results to the experimental results this appears to be most successful when the level of HA in the model is increased.

JB Christensen and TH Christensen have reported using the WHAM program to predict the effect of pH on Cd, Ni and Zn complexation with DOC¹²⁵. When comparing their models with their experimental results they report that WHAM 'overestimated the pH dependence of metal-DOC complexation'. The main difference between their work and the work presented in this thesis is that their work was carried out at higher metal and DOC concentrations and that Cd, Ni and Zn displayed an increase in levels of organic species with increasing pH where as U displayed a decrease in organic species with increased pH. However, their models displayed a greater sensitivity to changes in pH than their experimental results did, which was the same effect that was seen with the uranium models and experimental results presented in this thesis.

Uranium-organic speciation has been modelled in groundwater by Higgo, Kinniburgh, Smith and Tipping using the Humic Ion-Binding Model V¹²⁶ (the Model V is the organic speciation part of WHAM). Their predictions were, for a system with $1 \mu\text{g ml}^{-1}$ HS at pH 7.6, 3% U-HS species and for a system with $7 \mu\text{g ml}^{-1}$ HS at pH 6.9, 40% U-HS species. These predictions are lower than the experimental results and model predictions produced in this thesis. Their pH 7.6 sample had a lower level of organic carbon than the samples modelled in this thesis, which could result in a lower level of the uranium-organic species. Their pH 6.9 sample had a higher level of organic carbon but also a higher level of inorganic carbon which could produce competition for uranium species formation. Another possible reason for their lower predictions this could be due to fulvic acid being modelled in their work rather than the humic and fulvic acid used together in this work.

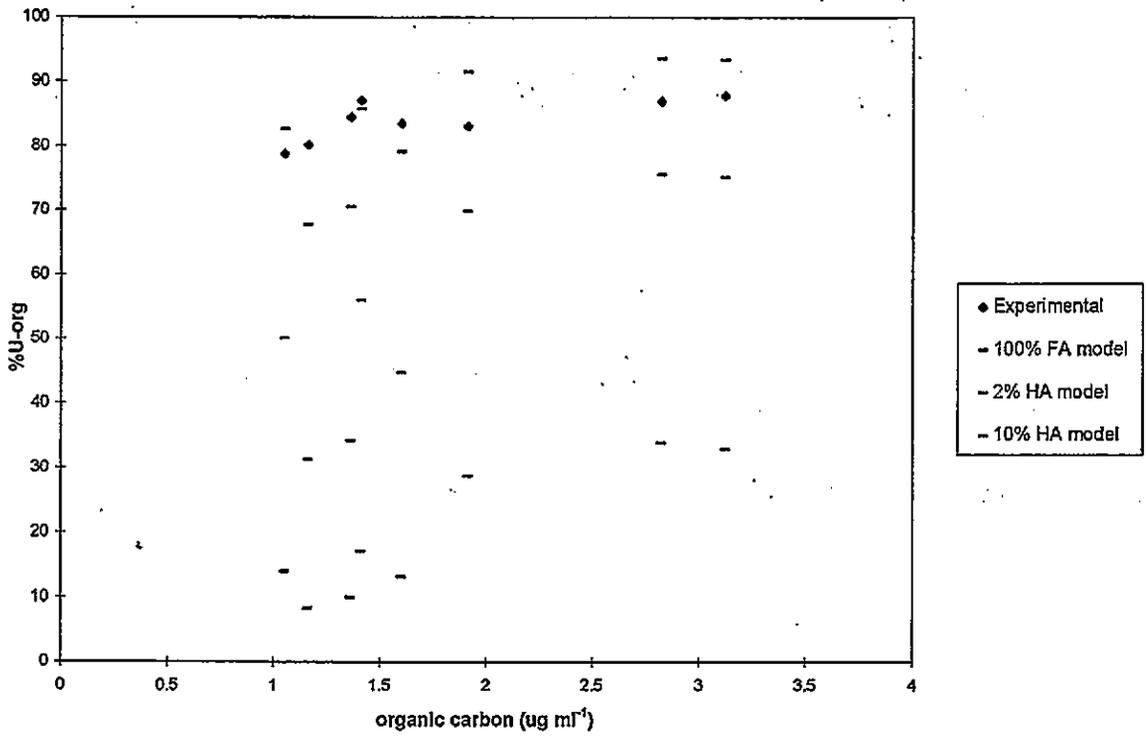


Figure 6.4 Correlation of modelled uranium speciation results with organic carbon level

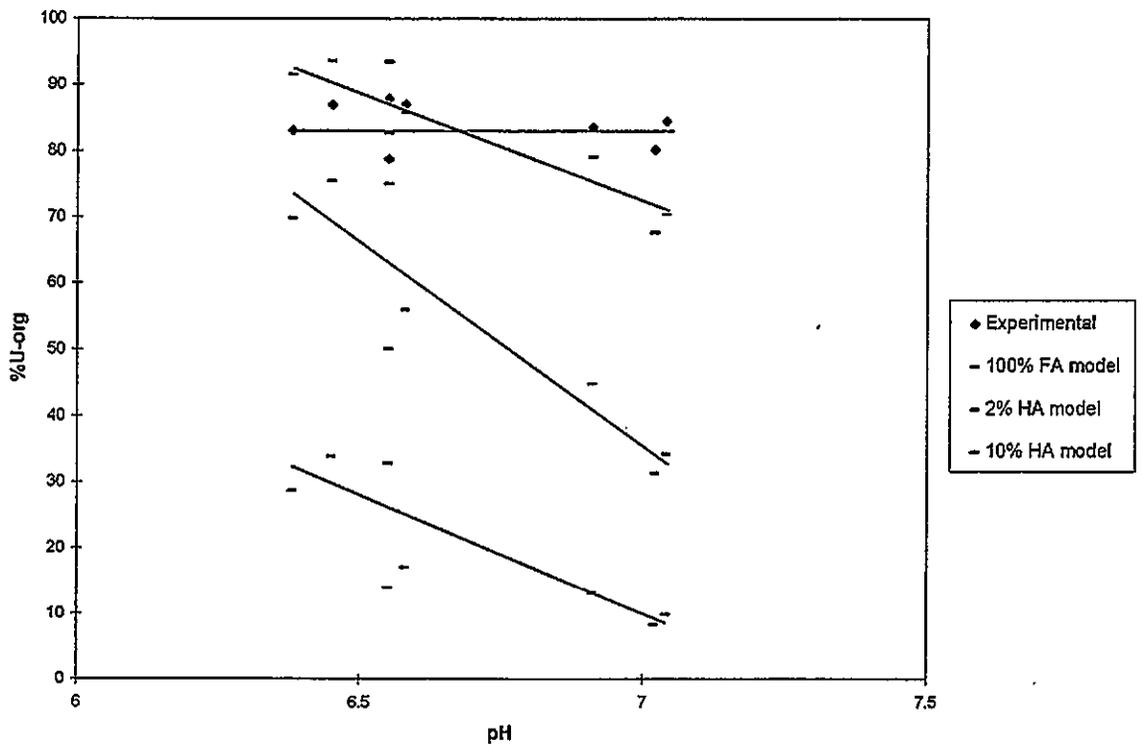


Figure 6.5 Correlation of modelled uranium speciation results with pH

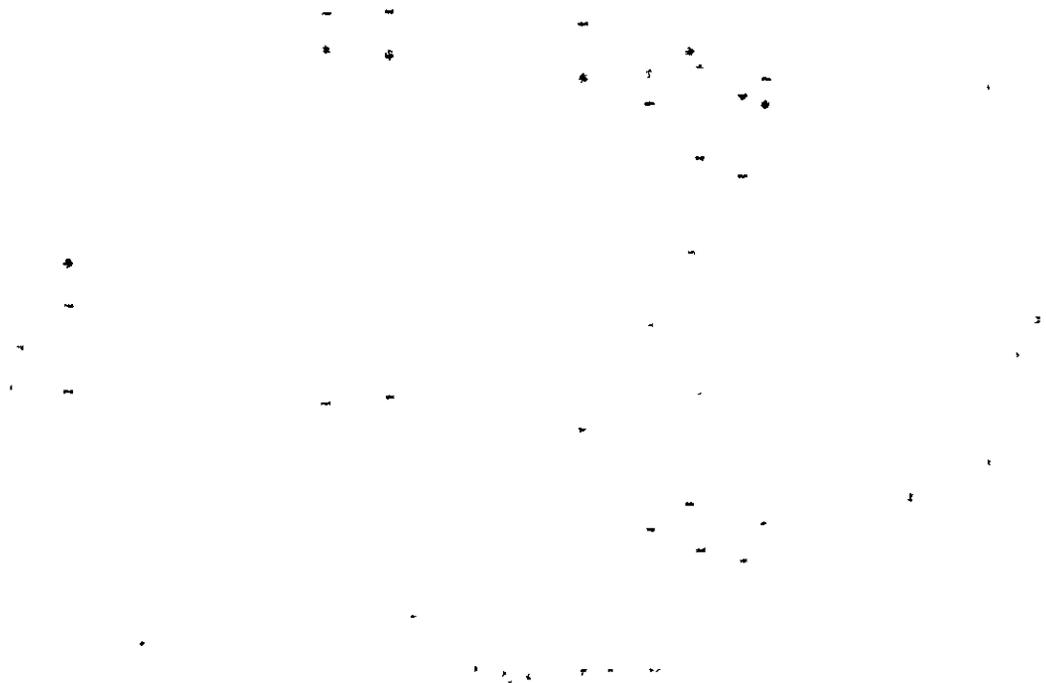


Figure 1. Scatter plot of $\ln(\text{rate})$ vs. $\ln(\text{time})$ for the data of Figure 1. The solid line is the fit to the data.

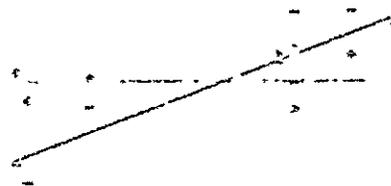


Figure 2. Scatter plot of $\ln(\text{rate})$ vs. $\ln(\text{time})$ for the data of Figure 2. The solid line is the fit to the data.

6.3.2 Correlation of predicted uranium-humic substance species levels with organic carbon concentration and pH values for synthetic surface-water samples

In order to explore the effects of uranium concentration, organic carbon concentration and pH on U-HS species formation, a set of synthetic surface-water samples were prepared with the U, OC and pH varying over a larger range than that seen in the Dartmoor water samples. The level of U-HS species was determined experimentally using the same method as used for the Dartmoor samples and these experimental results are presented in Chapter 4. This provided a set of experimental results for a set of samples of known HS composition which could then be used in comparison with the equivalent computer model predictions to assess the functioning of the computer program over a wider range of sample types.

A comparison of the experimental results and model predictions may be detailed as follows. Starting with the synthetic water samples at a uranium concentration of 0.1 ng ml^{-1} (equivalent to the Dartmoor samples), the experimental results display no correlation to pH except for a drop in the level of U-organic species for the synthetic sample with the highest pH and lowest organic carbon concentration. The model predictions are close to the experimental results for all these samples except for those at pH 7.4 where the predictions are up to 24% low. At this level of uranium (0.1 ng ml^{-1}) the models are exhibiting a low bias at high pH and also, to a lesser extent, the predictions are lower for the low HS concentration samples. These trends can be seen in Figure 6.6 where the differences between the model and experimental results are plotted vs. pH and HS concentration.

Moving onto the synthetic water samples at a uranium concentration of 1 ng ml^{-1} a different trend is seen. The model predictions are lower than the experimental results for the low HS concentration samples at each pH level (Figure 6.7).

For the synthetic water samples at a uranium concentration of 10 ng ml^{-1} all the model predictions were high (9 to 28% higher than the equivalent experimental results). The predictions were slightly lower at low HS concentration and high pH (Figure 6.8).

Overall the model predictions exhibit a pH bias, with lower predictions at high pH. The model also predicted lower values for samples with a low HS concentration compared to samples with a higher HS concentration. Models with a low HS concentration entered in to the program (rather than the models with a low HS/U concentration ratio), produced the low predictions. In addition, the predictions become higher, with respect to the experimental results, as the uranium concentration increases.

The model predictions are within 10% of the experimental results for samples with a uranium concentration of less than 10 ng ml^{-1} (0.1 and 1 ng ml^{-1} samples), a HS concentration of greater than $1 \text{ } \mu\text{g ml}^{-1}$ and a pH between 5 and 6.5.

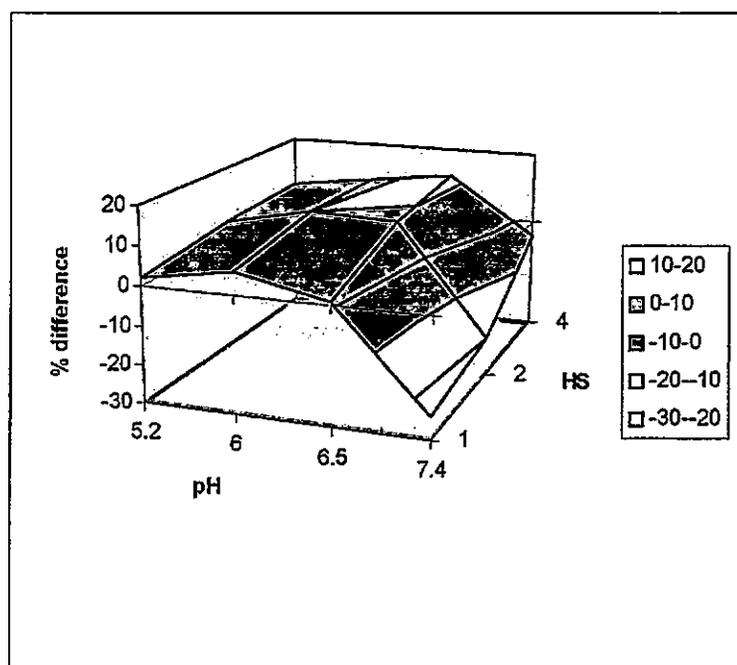


Figure 6.6 Difference between modelled and experimental uranium speciation results for 0.1 ng ml^{-1} synthetic uranium samples

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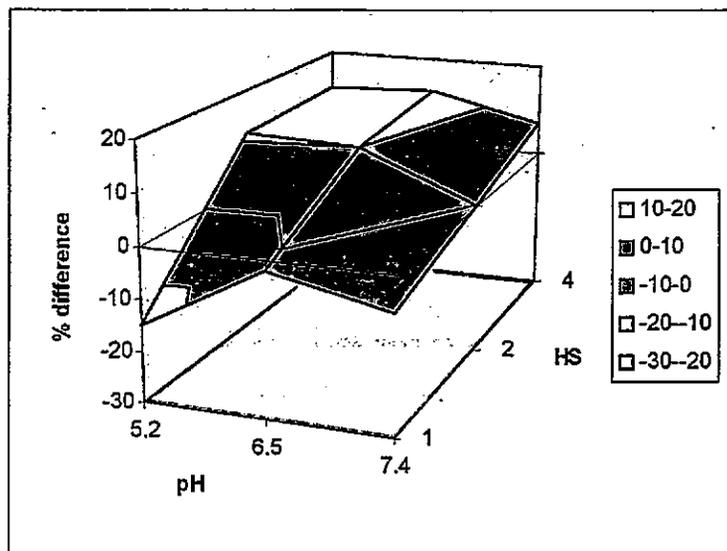


Figure 6.7 Difference between modelled and experimental uranium speciation results for 1 ng ml^{-1} synthetic uranium solutions

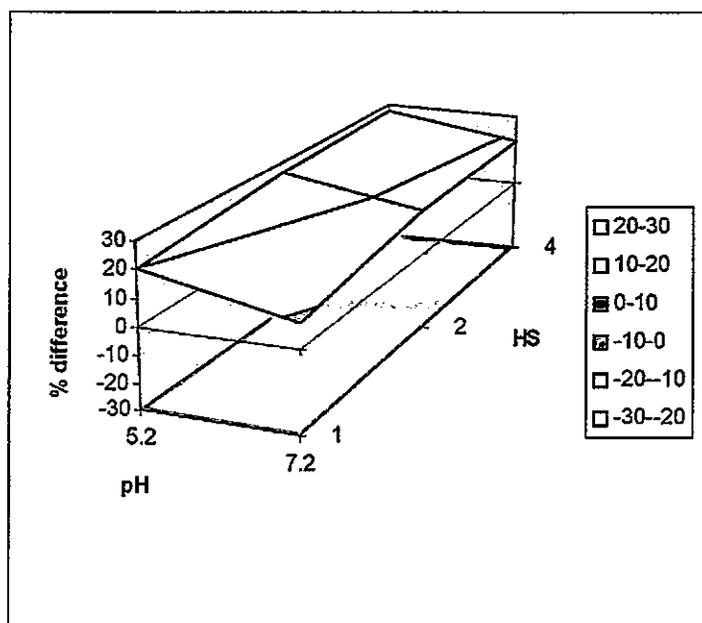


Figure 6.8 Difference between modelled and experimental uranium speciation results for 10 ng ml^{-1} synthetic uranium solutions

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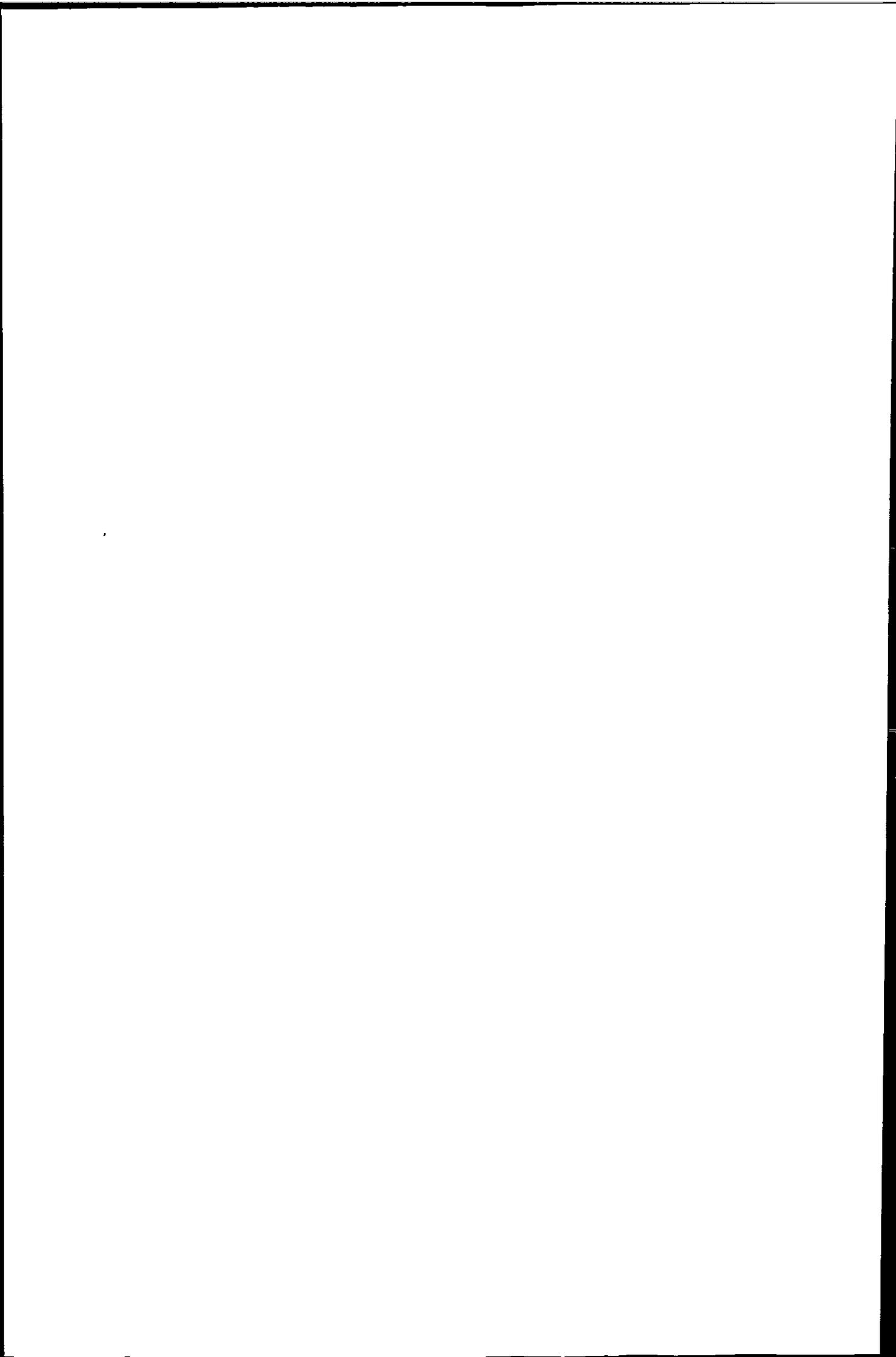
1000

6.4 Modelling uranium speciation in water samples using the PHREEQCI program

The Dartmoor water samples analysed in Chapter 4 and modelled in this chapter (section 6.3.1) using the WHAM computer program, were also modelled using the PHREEQCI computer program (with the model FA data from ANSTO added to the program) in order to provide a comparison of the results from natural water samples modelled with different types of HS model. The input parameters were the same as those used in the WHAM program except that the DOC concentration was converted into a COOH equivalent concentration which was then used to calculate the concentration of the organic acids which the 'model FA' was composed of. The levels of U-organic species predicted to be in the samples by the PHREEQCI program are presented in Table 6.5. All these results were high in terms of the predicted level of uranium-organic species compared to the experimentally determined level of uranium-organic species.

Table 6.5 Predicted uranium speciation of Dartmoor water samples using the PHREEQCI program

Sample	Predicted % U-organic species	Experimental % U-organic species
R Plym, Ditsworthy Warren	99	83
R Plym, Cadover Bridge	99	87
R Plym, Shaugh Bridge	99	88
R Plym + R Meavy, Shaugh Bridge	99	84
R Plym, Plym Bridge	98	85
R Newleycombe Lake, above Burrator	99	79
R Meavy, above Burrator	99	87
R Meavy, Shaugh Bridge	98	80



Because the results obtained were high and very similar, it was decided to use the PHREEQCI program to evaluate (and hopefully reproduce) a set of results from a study reported in the literature. This exercise would also give more confidence in the functioning of the PHREEQCI program with the incorporated 'model FA' data. The results from the study in the literature were reported as having been generated using the same 'model FA' data but incorporated in to the HARPHRQ program²⁶. Both the PHREEQCI and HARPHRQ programs are based on the original PHREEQE program, and using the same (NEA) thermodynamic database the results generated by the two programs were expected to be very similar. Using the input parameters reported in the literature a model was constructed with the PHREEQCI program. The results from this model, along with those reported for the HARPHRQ program are presented in Table 6.6. It can be seen that there are differences between the two sets of data. On closer review of the thermodynamic data used to produce the published HARPHRQ results it was noted that although the NEA-TDB uranium data had primarily been used, the $\text{UO}_2(\text{OH})_2$ stability constant was from a different source. The models constructed and presented in Chapter 5 have demonstrated the effect of using different thermodynamic databases on speciation predictions. In this case there was only one thermodynamic value which was different in the two programs but it appeared to have a large effect on the modelled data. This species ($\text{UO}_2(\text{OH})_2$) was represented by a different formation reaction in the database used with the HARPHRQ program, to that used in the database with the PHREEQCI program. Hence, the log K value could not be directly transferred in to the PHREEQCI program, which would have allowed the model to be re-run with the alternate $\text{UO}_2(\text{OH})_2$ log K value in order to ascertain if this would have reproduced the results reported in the literature.

Table 6.6 Uranium speciation predicted using the PHREEQCI and HARPHRO programs

Species	PHREEQCI %	HARPHRO %
UO ₂ ²⁺	0	0
UO ₂ OH ⁺	10	12
UO ₂ (OH) ₂	63	3
UO ₂ CO ₃	4	6
U-FA (total)	20	76

Table 6.7 Uranium speciation predicted using the WHAM program

Species	WHAM (NEA data) %	WHAM (original data supplied with the program) %
UO ₂ ²⁺	1	5
UO ₂ OH ⁺	7	35
UO ₂ (OH) ₂	74	9
UO ₂ CO ₃	3	8
U-HS (total)	14	43

As a further comparison, the model parameters reported in the literature were also input into the WHAM program and a model constructed using a 10% HA, 90% FA, humic substance composition. The speciation predictions were calculated using both the NEA data and the original thermodynamic data supplied with the WHAM program. These results are presented in Table 6.7 and illustrate both the effect of using a different HS model and a different thermodynamic database. Although predictions calculated by the WHAM and PHREEQCI programs for systems such as the Dartmoor water samples and the synthetic surface-water system used in Chapter 5 have been quite different, for this system the results are relatively close (WHAM, 14% U-organic; PHREEQCI, 20% U-organic). However neither set of the predicted results (Table 6.7) was close to those reported in the literature (Table 6.6). When the WHAM model was run with the original thermodynamic data provided with the program the predicted level of U-organic species was much higher, but still not as high as the literature value (WHAM 43% U-HIS, literature 76% U-FA), further indicating that it could be the $\text{UO}_2(\text{OH})_2$ log K value which was causing the difference between the PHREEQCI and HARPHRQ results. When the $\text{UO}_2(\text{OH})_2$ log K value had been obtained¹²⁷ in a format which could be used with the PHREEQCI program the model was then re-calculated using this data to produce the results presented in Table 6.8. The system in the literature had been modelled with and without the 'model FA' present and the same procedure was carried out in this work using the PHREEQCI program. The results for the system with no FA present were virtually the same for both programs, as would be expected from two similar programs using the same thermodynamic data. However once the 'model FA' was added to the system the PHREEQCI results were again lower than those reported for the HARPHRQ program (Table 6.8). In the HARPHRQ model the U-organic species are principally represented by the uranium-malonate (OHMal) and uranium-salicylate (OHSal) species. Using the PHREEQCI model, the OHSal species are not predicted to be present, thus resulting in a lower total level of U-organic (U-FA) species.

The PHREEQCI and HARPHRQ programs produced equivalent results for the inorganic system (no FA). Since the 'model FA' calculations follow the same procedure (except with different species and log K values) similar results would be expected from the two programs.

The NEA thermodynamic data for the $\text{UO}_2(\text{OH})_2$ species caused a lower level of U-organic species to be predicted by both the WHAM and PHREEQCI programs. For the WHAM program this was thought to be due to the predicted formation of a greater proportion of the $\text{UO}_2(\text{OH})_2$ species using the NEA data than with the original WHAM data. Since HS reactions are modelled with the UO_2^{2+} and UO_2OH^+ species, there would thus be less of these species present to react with the HS to form U-organic species. In the PHREEQCI program 'model FA' reactions are only modelled with the UO_2^{2+} species. Thus the formation of either of the hydrolysis species would not effect the level of U-organic species formed. However with the NEA data, a greater overall level of the hydrolysis species are formed, which would effect the level of UO_2^{2+} species which could then react with the 'model FA' to form U-organic species.

To investigate the level of formation of the OHSaI^- species, predicted by the HARPHRQ program to make up a significant proportion of the total U-organic species (but absent in the PHREEQCI predictions) a model was constructed containing only uranium and salicylic acid. This would effectively remove any potential competition effects from other components in the system. The results obtained are presented in Table 6.9. Even under these conditions the formation of the $\text{UO}_2\text{OHSaI}^-$ species is not thermodynamically favourable. Given the information available it has not been possible to reproduce the speciation results reported in the literature. This could either be due to the use of two different programs (PHREEQCI and HARPHRQ) or a difference in the incorporation of the 'model FA' in the two programs.

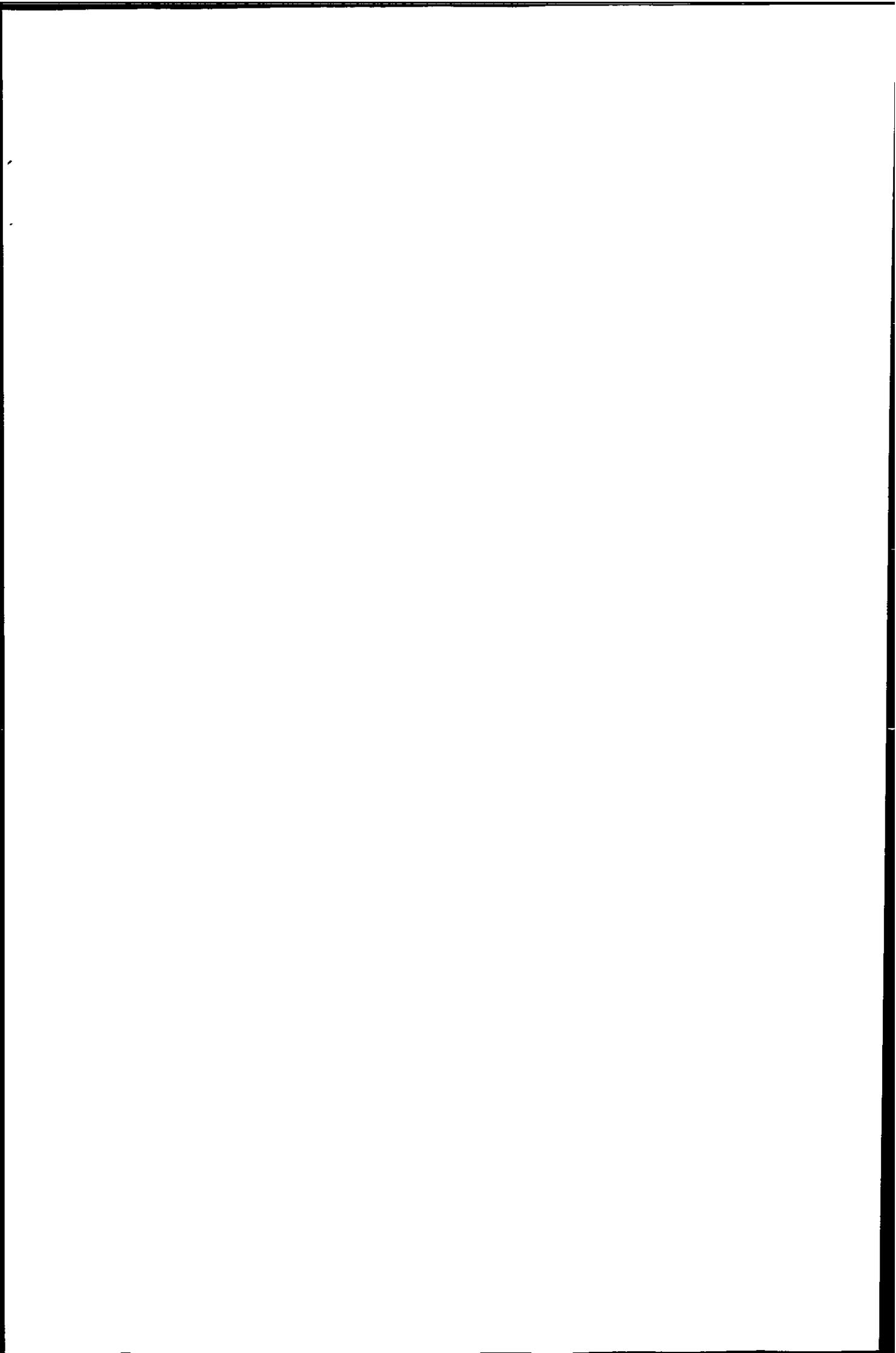
Table 6.8 Predicted uranium speciation as recalculated using the $\text{UO}_2(\text{OH})_2$ log K value reported used with the HARPHRQ program

Species	System without FA		System with FA	
	PHREEQCI	HARPHRQ	PHREEQCI	HARPHRQ
	% species	% species	% species	% species
UO_2^{2+}	9	10	4	0
UO_2OH^+	62	55	26	12
$\text{UO}_2(\text{OH})_2$	2	10	1	3
UO_2CO_3	26	25	11	6
$\text{UO}_2\text{OHMal}^-$			46	47
$\text{UO}_2\text{OHSal}^-$			0	17
UO_2Mal			9	9
UO_2Sal			1	3
Total U-FA			56	76

Table 6.9 Predicted uranium speciation using the PHREEQCI program for a system containing only uranium and salicylic acid

Species	% species
UO_2^{2+}	12
UO_2OH^+	72
$\text{UO}_2(\text{OH})_2$	3
UO_2Sal	9
$\text{UO}_2\text{OHSal}^-$	4

From the study carried out to compare the different HS models in the WHAM and PHREEQCI programs models constructed using the same input data and calculated using the same thermodynamic databases produced different uranium speciation predictions. The PHREEQCI model predictions were higher, in terms of the level of U-organic species, than the WHAM model predictions. The degree of variance between the predictions from the two programs depended on the system being modelled. The results from the WHAM and PHREEQCI models of the system reported in the literature²⁶ were much closer to each other than the results from the models utilising data from the Dartmoor samples and the synthetic water samples. However where the model results could be compared to experimental results the WHAM model predictions were closer to the equivalent experimental results than the PHREEQCI model predictions. This indicates, that for this type of system (Dartmoor water samples) at least, we can have a greater degree of confidence in the WHAM program models than the PHREEQCI program models for uranium speciation predictions.



6.5 Summary

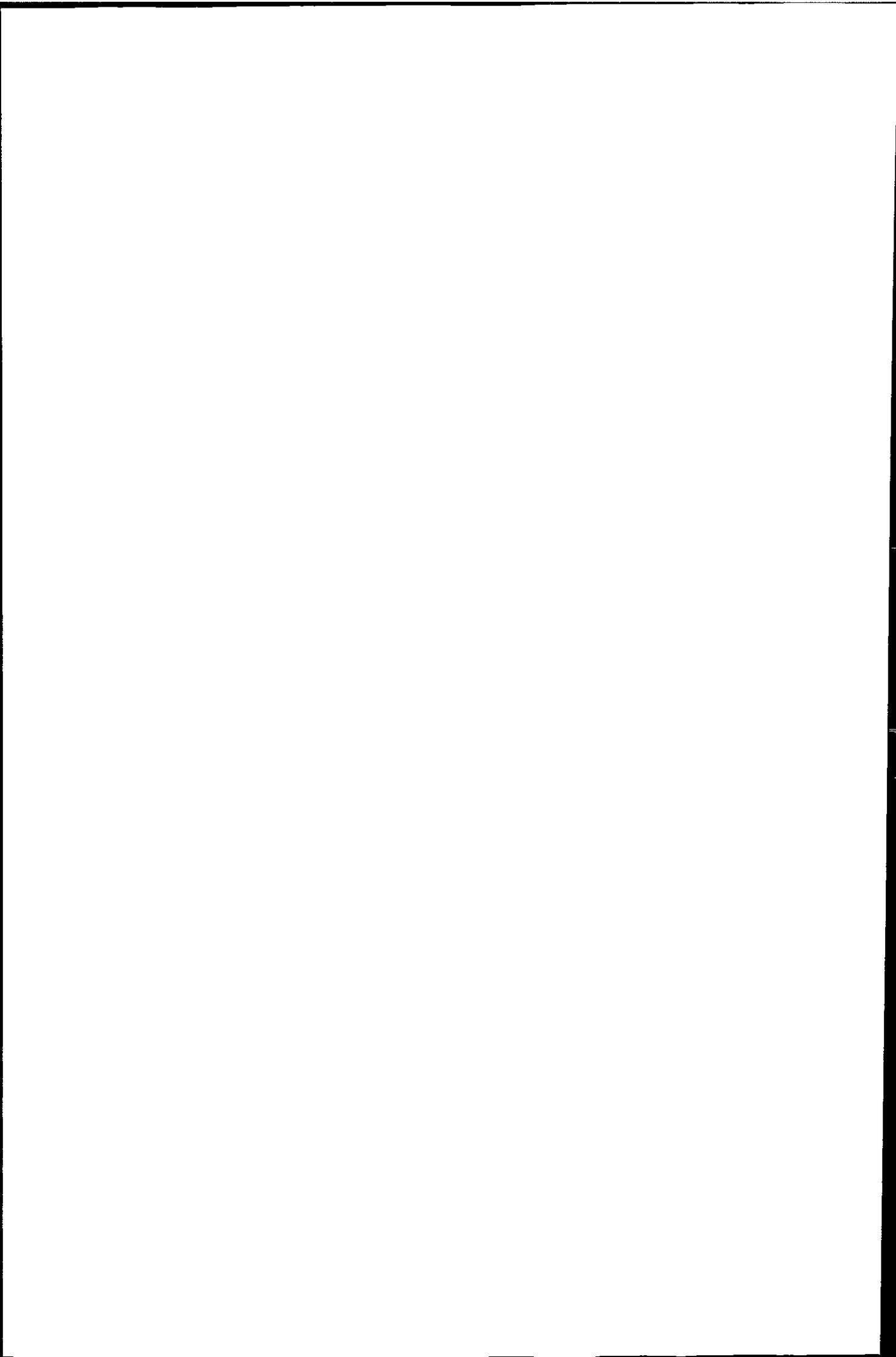
Computer models for uranium speciation based on data from a range of Dartmoor water samples and a set of synthetic water samples were constructed using the WHAM and PHREEQCI speciation programs. When using the WHAM program the HS can be input as both a FA and HA. The initial models generated in this study, which were created with the HS input entirely as FA, produced low U-HS predictions. Once a fraction of the total HS concentration was input as HA the predicted level of U-HS species increased. As the proportion of HA input in to the model was increased from 0 to 2% a large increase in the level of U-HS species was observed. A further increase, although not so great, was observed as the level of HA was increased up to 10% HA. With models constructed for the Dartmoor samples using 10% HA, 6 out of 8 of the model predictions were within 10% of the experimental results. The HS composition used in these models (10% HA, 90% FA, DOC=50% HS) was selected as typical of DOC compositions reported in the literature for river waters. The models which continued to predict low U-HS levels were for downstream samples with slightly higher pH values and this was thought to be due to either a model bias at higher pH values or a difference in the nature of the DOC in the downstream samples since these samples contained water which had passed through Burrator reservoir. The DOC from lake water can consist of a higher proportion of HS than river water^{155, 156, 158}. The absorption/DOC ratio found for the downstream samples was higher than the upstream samples indicating that they could contain a higher proportion of aromatic compounds (such as HS). When the proportion of DOC which was modelled as HS in the model was adjusted to 75%, the resulting predictions for the downstream samples were within 10% of the experimental values.

When correlating the model predictions with changes in the level of organic carbon and pH of the samples, an increase in the level of organic carbon in the model was found to

produced an increase in the level of U-HS species. The model predictions also had a strong correlation with pH, with the level of U-HS species dropping as the pH increased. This trend was not however seen in the experimental results. Using the synthetic water samples which consisted of wider range of uranium and organic carbon concentrations and pH values, the difference between the model predictions and experimental results for these samples was evaluated with respect to sample composition. At a low uranium concentration the WHAM models predicted low results at high pH and low HS concentration. Increasing the uranium concentration produced model predictions which were lower (although not below 10% of the experimental results) at low HS concentration at all pH values. With the uranium concentration input at 10 ng ml^{-1} all the model predictions were high, although they were lower at high pH and low HS concentrations. The WHAM model therefore appeared to exhibit a bias at high pH and low HS concentrations to give low values.

The WHAM model was however successful at predicting U-organic speciation for samples with a uranium concentration between 0.1 and 1 ng ml^{-1} , a HS concentration of greater than $1 \text{ } \mu\text{g ml}^{-1}$ and a pH between 5 and 6.5. This is important since these are the conditions that apply to most of the moorland water samples analysed.

When using the PHREEQCI program, the DOC concentration of the samples was converted to a COOH equivalent concentration which was then used to calculate the concentration of the 'model FA' incorporated into the program database. All the model predictions produced when using this program were high (98 to 99%). To further investigate the functioning of the PHREEQCI program a model was again generated to reproduce results from the literature which had also been generated by a program with a 'model FA' dataset. This program, HARPHRQ, is derived from the PHREEQE program and so would be expected to function in a similar manner. However, although the PHREEQCI model did reproduce the results reported in the literature for a system without FA, the PHREEQCI model for the system with FA predicted a lower U-FA level than that



reported in the literature (Table 6.8). The $\text{UO}_2\text{OHSal}^-$ component of the total U-FA level reported in the literature was not found to be present in the PHREEQCI model results. In addition, modelling the system with only uranium and salicylic acid did not predict this species.

When comparing the different HS models in the WHAM and PHREEQCI programs (using the same input values and thermodynamic data) the predictions from the WHAM models were found to be closer to the experimental results than those from the PHREEQCI models. This provided a greater degree of confidence in the predictive capability of the WHAM program which will allow it to be used in future work to further study uranium speciation in environmental aqueous systems.

Chapter Seven

7. Summary, conclusions and future work

7.1 Summary and conclusions

An on-line SPE-ICP-MS method has been developed for the determination of uranium and thorium in the presence of high levels of matrix components. Good recoveries were obtained from samples with high levels of both inorganic and organic matrix components and thus results are an improvement on those obtained using conventional chelating resins which have been reported in the literature as giving low recoveries for samples containing organic carbon.

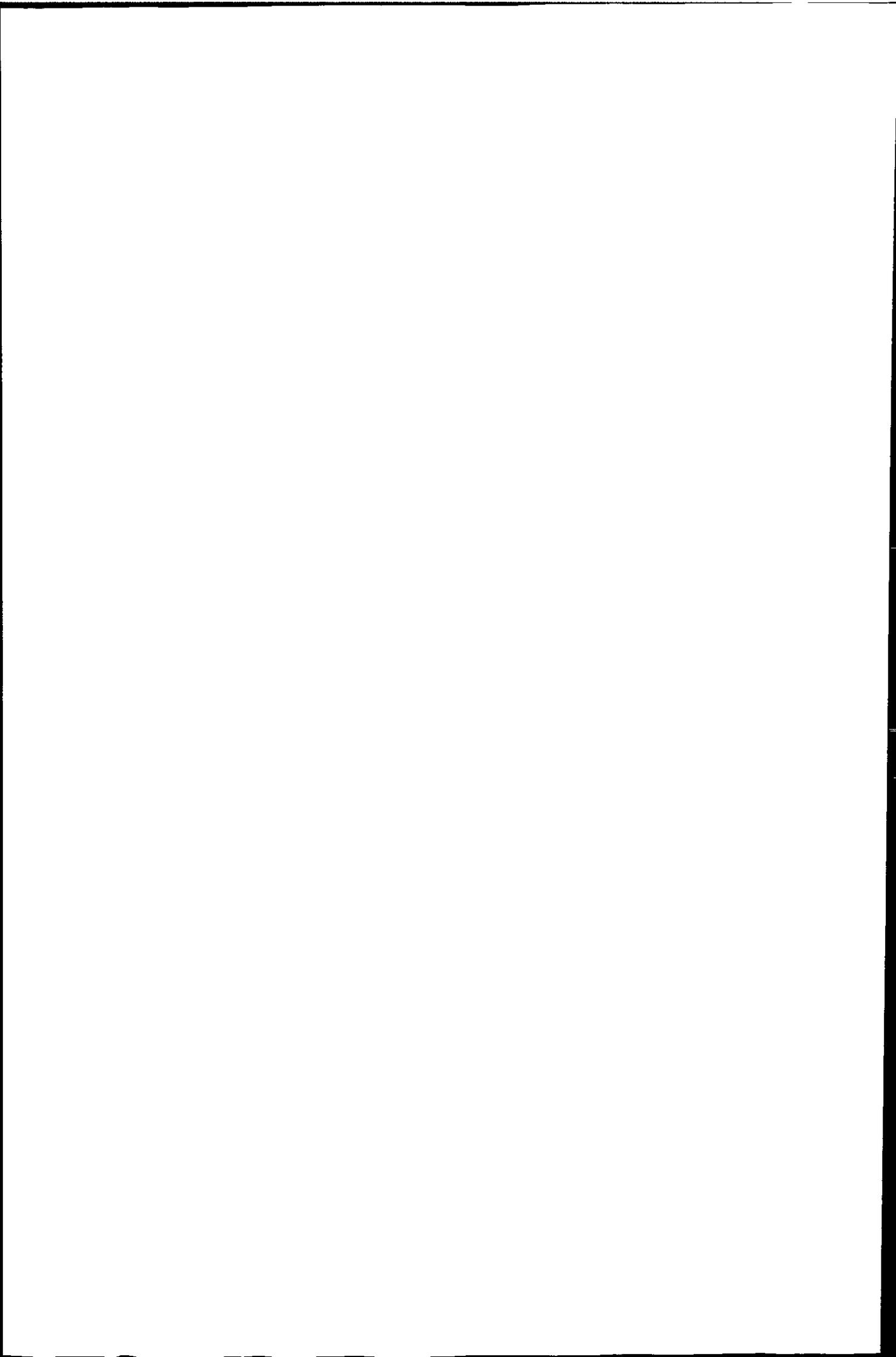
Inorganic and organic uranium species were successfully separated using a chelating resin column attached on-line to an ICP-MS instrument. Thorium speciation required an off-line technique (using the same resin) since the thorium reacted with the carrier used in the on-line technique resulting in changes to the inorganic/organic species distribution. The developed methodology was applied to natural water samples from Dartmoor, Devon, UK. From the results obtained it can be concluded that uranium-organic species form a major proportion (80%) of the total dissolved uranium present. Thus when considering speciation scenarios for environmental samples uranium-organic species need to be taken into consideration.

A set of synthetic water samples, with a range of different uranium, organic carbon and pH value compositions, were analysed in order to ascertain the effect these factors would have on organic bound uranium speciation. The results obtained indicated that the level of organic bound uranium species varied from 28 to 86%. Comparing the organic carbon and pH levels in the samples with the level of organic bound uranium species revealed no correlation between pH and percent uranium-organic species. The results did

however display a correlation between increasing organic carbon concentration and increasing uranium-organic species. The level of organic carbon appears to be the controlling factor in determining the extent of uranium-organic species formation.

The kinetics of dissociation of the uranium-organic and thorium-organic species were investigated in order to provide an indication of the stability of these species in the natural environment. The 1 day old and 16 day old water samples displayed similar dissociation rates at the early timepoints during the experiment but at later timepoints (>8 hours) the 16 day old sample displayed a slower dissociation rate than the 1 day old sample. This was thought due to the formation of more 'strongly' bound U-HS complexes which had formed in the 16 day old sample. The thorium-organic species produced a wider spread of results which were best fitted to a single linear plot. A much greater level (~50%) of the thorium-organic species than the U-organic species were still undissociated after 24 hours. The implications of this are that a small level of relatively stable uranium-organic species, and a higher level of relatively stable thorium-organic species, could remain in this form in the environment for some time.

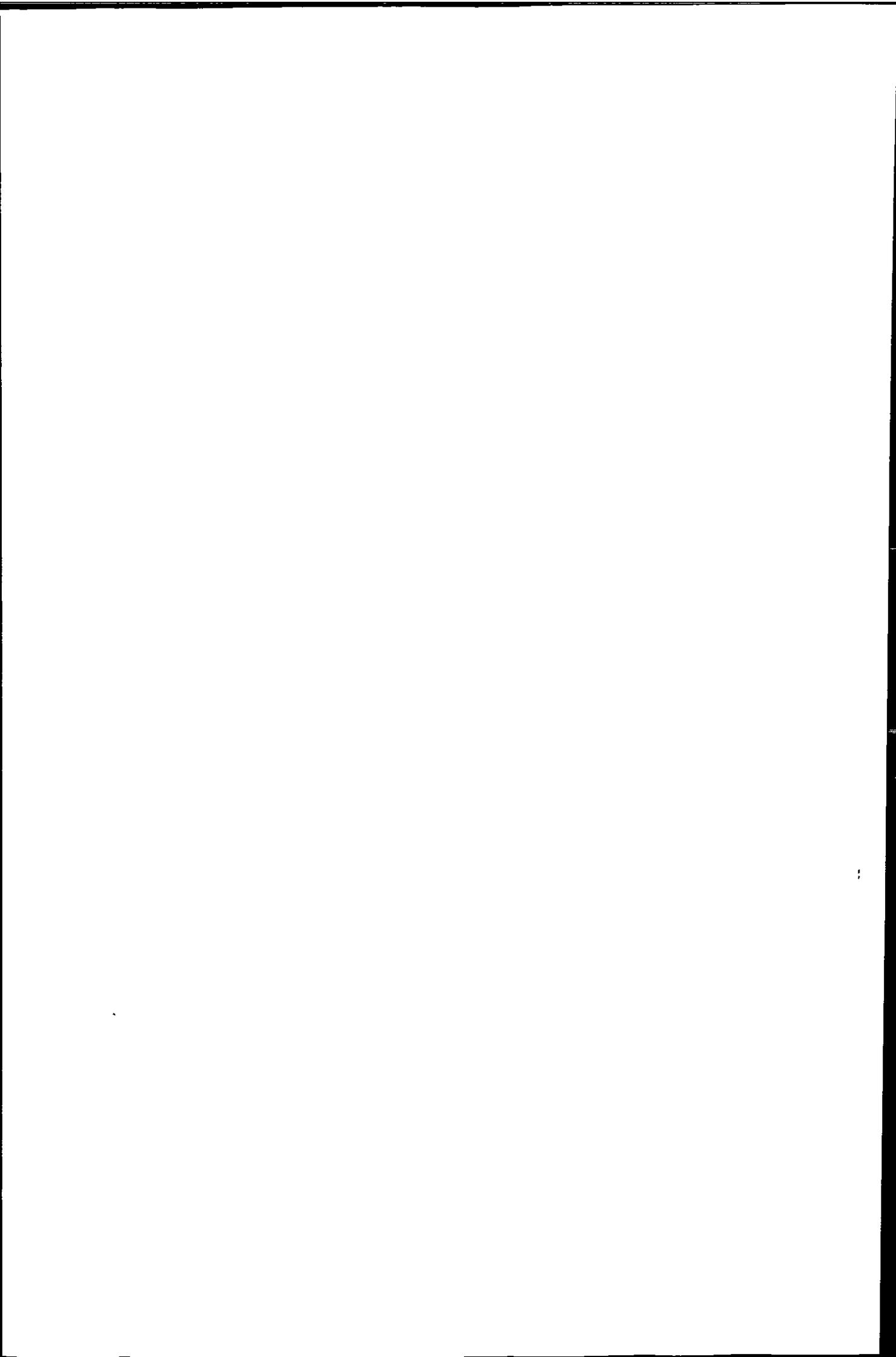
Differences in the thermodynamic data provided with the two computer modelling programs used in this study to predict uranium and thorium speciation in aqueous systems, resulted in large differences in the predicted speciation profiles. In order to compare results from the two programs a single comprehensive thermodynamic database was required. This was achieved by using the Nuclear Energy Agency Thermochemical Database Project (NEA-TDB) values. Various surface-water systems were modelled. In a 'soft' water system with no organic carbon present hydrolysis species predominated. In a 'hard' water system the hydrolysis species were displaced by carbonate species at pH values above 5. Uranium-phosphate species only became a major component in the system at phosphate concentrations much greater than those seen in typical surface-water systems. This was in complete contradiction to the domination of uranium-phosphate species which had been



seen in models constructed using the original phosphate data supplied with the PHREEQCI program (and rejected by the NEA-TDB). When a system containing organic carbon was modelled the uranium-organic species were a major component of the system over the pH range 5 to 7. The thorium-organic species dominated the system over the pH range 4 to 7.5. This demonstrated the importance of including organic species when constructing speciation models.

A number of computer models were constructed (using the WHAM program) for the natural water samples collected from Dartmoor. By varying the proportions of humic and fulvic acid in the humic substance component of the model, it proved possible to successfully predict the level of uranium-organic species. These predictions were within 10% of the experimentally derived results. Predictions obtained from the PHREEQCI models were all high when compared to the experimental results.

To investigate the functioning of the WHAM program over a wider range of conditions, models were constructed for synthetic water samples with varying uranium, organic carbon and pH value compositions. These models displayed a stronger correlation between changes in uranium-organic species level to changes in pH and organic carbon level than the experimental results. When comparing these predictions to the experimentally derived results the models were found to exhibit a low bias at high pH (7.5) and low organic carbon concentration ($0.5 \mu\text{g ml}^{-1}$) and a high bias at high uranium concentrations (10 ng ml^{-1}). However under the conditions prevalent in the natural water samples collected from Dartmoor, the WHAM models were successful at predicting the levels of uranium-organic species present.



7.2 Future work

Future experimental work on the humic/fulvic acid proportions in the humic substances present on Dartmoor would give further validity to the assumptions made when modelling these samples. If the distribution of humic and fulvic acid did not turn out to be that expected, the effect of these differences on the model predictions could be further investigated. The proportion of DOC that comprised of humic substances could also be determined, following on from the absorption/mg DOC work reported in this thesis. It should be noted that there are published methods for the fractionation of DOC which involve the use of XAD or DEAE resins.

A greater range of water systems could be investigated in order to obtain a greater understanding of the factors which effect uranium and thorium speciation. Although synthetic samples were analysed in this study, results from a range of 'real' water systems would provide further data from which to draw conclusions about the nature of uranium and thorium speciation in the environment. Such systems could include at a local level, South Terras (abandoned uranium mine), which has a killas geology rather than the granite of Dartmoor, and further afield, the sand ironstone area of Northhamptonshire, or an anthropogenic source of radionuclides such as Sellafield..

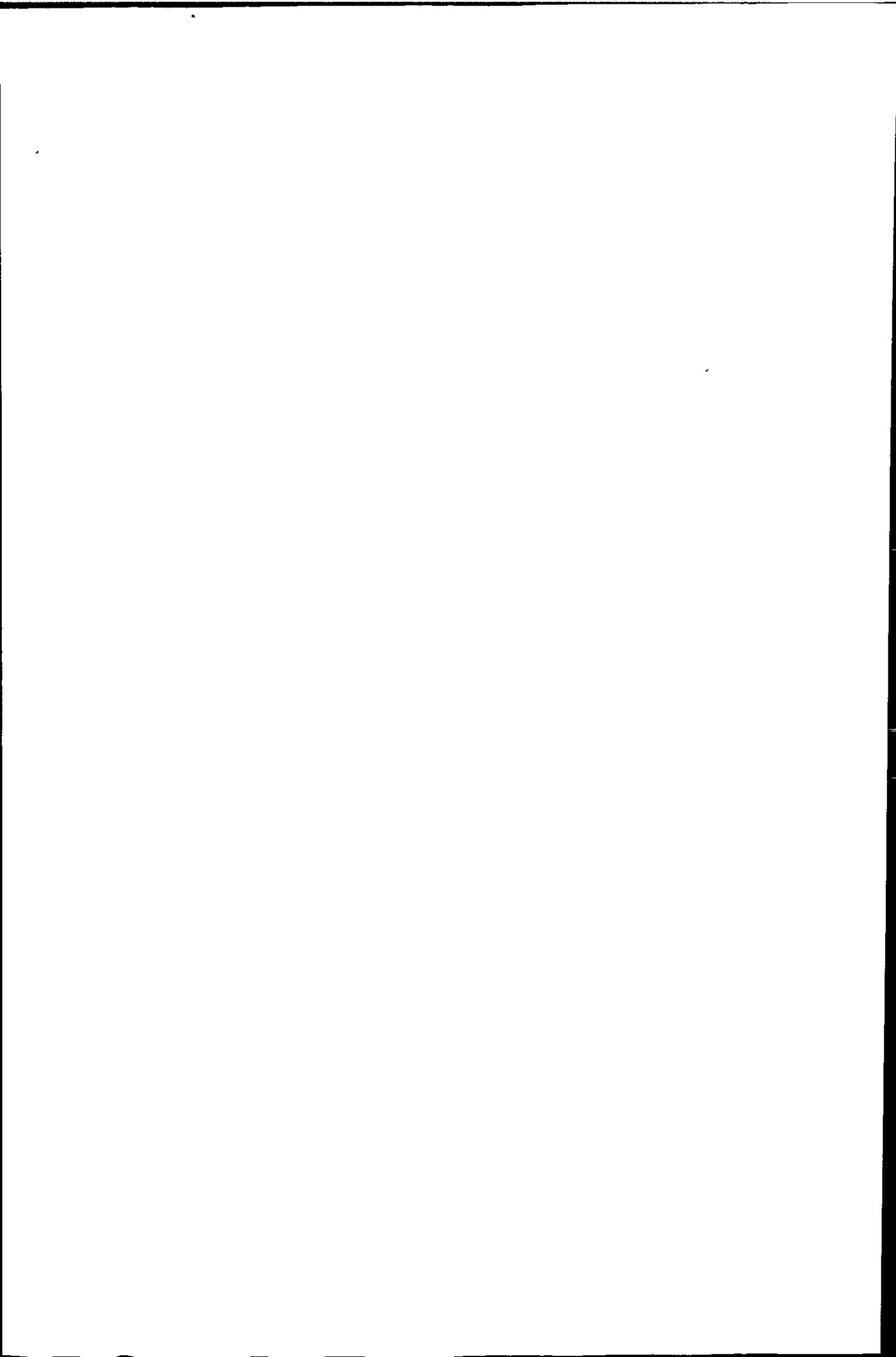
Further analytical development on the thorium speciation could be carried out using the chelating resin used in this study but utilising a batch technique to avoid the carrier effects seen when using the on-line procedure. There is less information available in the literature on thorium speciation, however since it is a Th^{4+} cation, and reflecting on the kinetics results from this study, there are indications that the binding of organic species could be even more significant in thorium speciation than in uranium speciation.

The effect of competition from other metals on the formation of organic species could also be investigated both experimentally and via modelling. This could relate to the

type of situation found in mine waste run-off where high levels of other metals may reduce the levels of uranium and thorium-organic species formed.

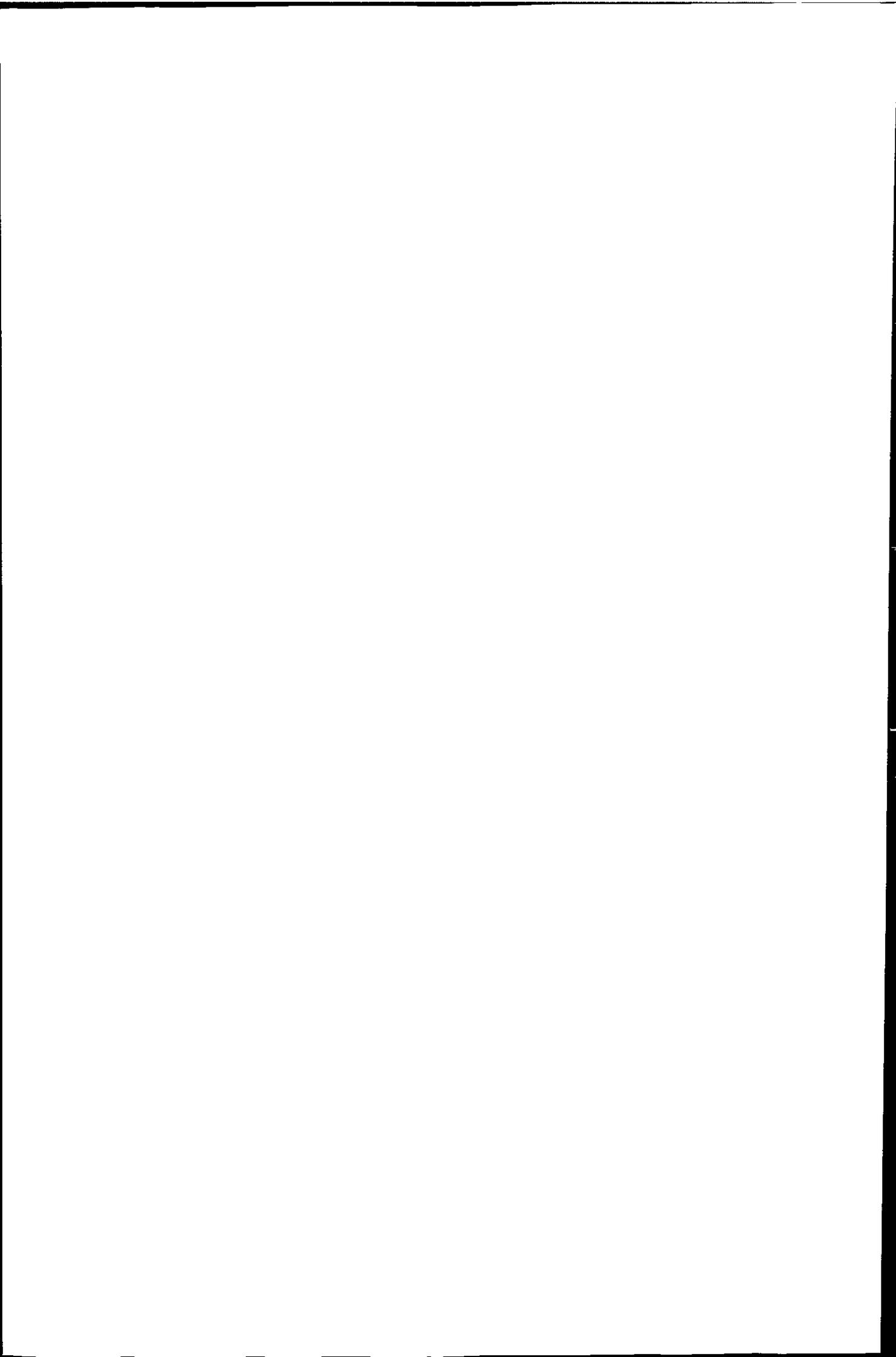
Not only are uranium and thorium present in the aqueous environment but also in the solid phase (rock, soil or suspended particles). Thus isotope ratio disequilibrium could be used to determine if transfer from one phase to another is occurring and if so, whether at significant levels. Sector field ICP-MS has the specificity and sensitivity to measure low levels of the different uranium and thorium isotopes, however using on-line SPE to preconcentrate the analyte could also be carried out to further utilise quadrupole ICP-MS.

Finally, it is hoped that this work described in this thesis will prove a useful aid to those currently studying uranium and thorium in the environment, and that the analytical methodology will provide a useful tool in this difficult and demanding area of analysis.



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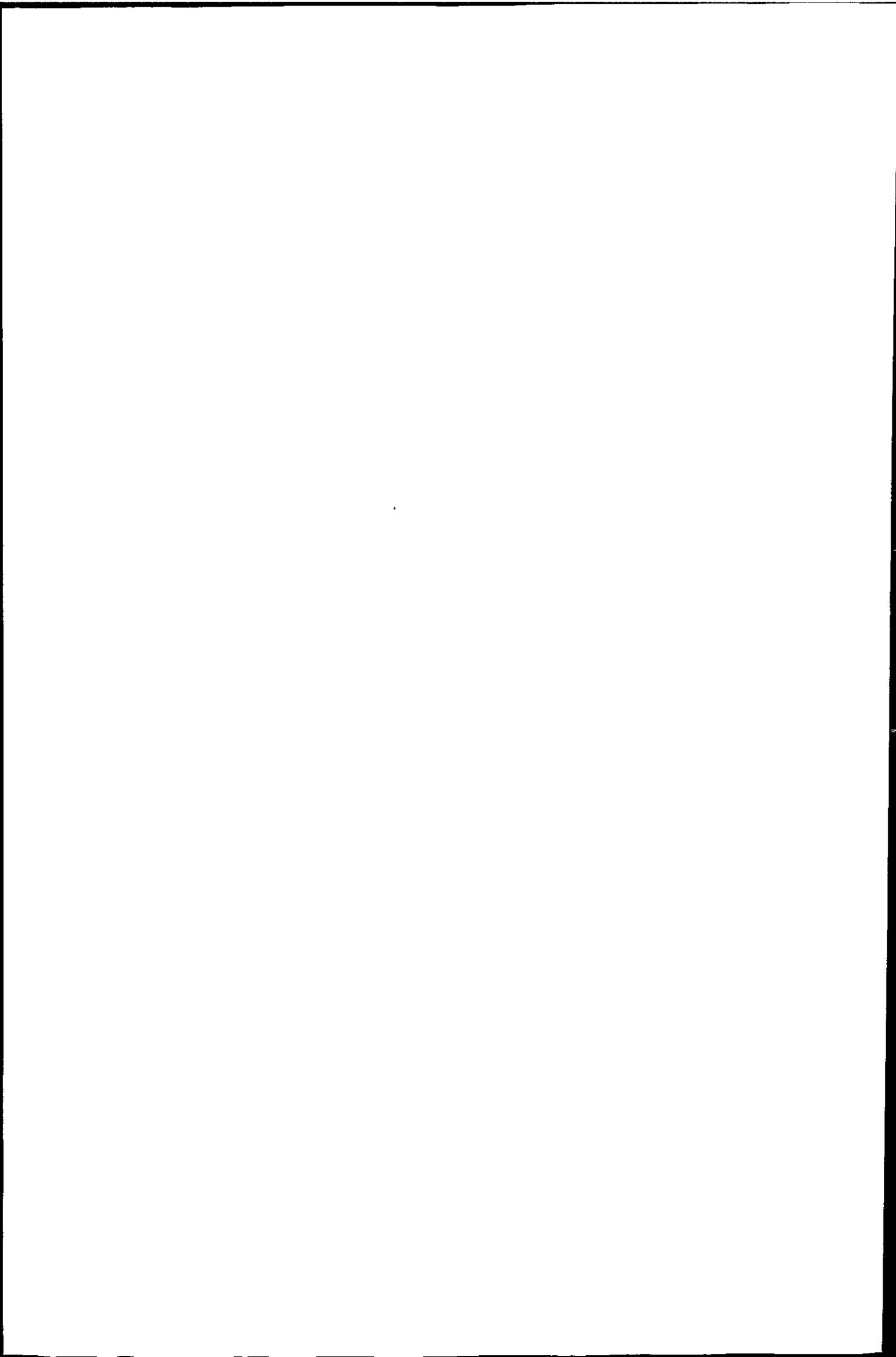
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Appendices

9.1 Appendix 1 : Professional Development

9.1.1 Conferences and meetings attended

European conference on Plasma Spectrochemistry, 1999, (Pau, France), Poster presentation.

9th Biennial National Atomic Spectroscopy Symposium (BNASS), 1998, (Bath, UK).

10th Biennial National Atomic Spectroscopy Symposium (BNASS), 2000, (Sheffield, UK),
Poster presentation.

35th Research and Development Topics in Analytical Chemistry, 1998, (Durham, UK).

36th Research and Development Topics in Analytical Chemistry, 1999, (Greenwich, UK),
Poster presentation.

37th Research and Development Topics in Analytical Chemistry, 2000, (Manchester, UK),
Poster presentation.

Royal Society of Chemistry, Atomic Spectroscopy Group meeting, 1998, 'The relevance of chemometrics in atomic spectroscopy' (Nottingham, UK).

Royal Society of Chemistry, Peninsular section, 1998-1999 and 1999-2000 lecture series (Plymouth, UK).

Royal Society of Chemistry, Young Analytical Chemists Network meeting, 1999, (Plymouth, UK).

EiChrom 'UK User's Group meeting', 1998, (Manchester, UK).

University of Plymouth, Department of Environmental Sciences, Departmental seminars, 1998, 1999, 2000. Oral presentations.

9.1.2 Courses attended

MSc Short Course in Analytical Atomic Spectroscopy, 1998.

Research Methods course, 1998.

Teaching Skills for Graduate Teaching Assistants, 1998.

Writing for Publication, 2000.

Evaluation of Uncertainty in Atomic Spectrometry, 2000.

9.1.3 Teaching experience

Demonstration of instrumentation and supervision of students during undergraduate Environmental Science laboratory practicals, 1998, 1999, 2001.

9.1.4 External collaboration

Two weeks (summer 1999) spent at the British Geological Survey laboratories (Keyworth, Nottingham, UK.). Work included an oral presentation of work already carried out at Plymouth and transfer of methodology developed at Plymouth to the Keyworth laboratories. Work already carried out at Plymouth and future areas of study were discussed with various members of staff.

9.2 Appendix 2 : Publications

Determination of uranium and thorium in natural waters with a high matrix concentration using solid-phase extraction inductively coupled plasma mass spectrometry

Unsworth ER, Cook JM, Hill SJ, *Analytica Chimica Acta*, 442, 2001, p141-146



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Determination of uranium and thorium in natural waters with a high matrix concentration using solid-phase extraction inductively coupled plasma mass spectrometry

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Abstract

An on-line solid-phase extraction method, linked to inductively coupled plasma mass spectrometry has been developed to overcome the problems of a high sample matrix concentration interfering with the determination of low levels of uranium and thorium in aqueous samples. Using an actinide-specific extraction resin (TRU-spec), in a small column incorporated into the sample introduction manifold, recovery of the analytes (U^{101} – 108%, ^{87}Th 115%) was obtained from seawater (NASS-4 seawater CRM, $2.68\text{ ng ml}^{-1} U$), ground water ($0.1\text{ ng ml}^{-1} U$ in $3000\text{ }\mu\text{g ml}^{-1}$ total dissolved solids) and samples containing significant levels of dissolved organic carbon ($1\text{ ng ml}^{-1} U/Th$, $8\text{ }\mu\text{g ml}^{-1}$ humic and fulvic acids). This is an improvement on conventional ion exchange and chelating resins which give low recoveries in the presence of dissolved organic carbon. The samples were injected directly on to the column, with no prior dilution. Figures-of-merit obtained were R^2 : U 0.998, Th 0.999, for 0 to 10 ng ml^{-1} , R.S.D.: U 4.3%, Th 5.8%, and limits of detection: U 0.015 ng ml^{-1} and Th 0.006 ng ml^{-1} in a synthetic seawater matrix. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Uranium; Solid-phase extraction; ICP-MS; Dissolved organic carbon; Thorium

1. Introduction

Uranium and thorium are usually present in natural waters at low nanogram to picogram per milliliter levels. There are a number of techniques available to analyse such samples but they often require complex sample pre-treatment. One example is the co-precipitation of radionuclides with manganese dioxide, followed by separation using anion exchange and electrodeposition onto metal plates with measure-

ment by alpha spectrometry [1]. In other cases large amounts of sample may be required as in the case of delayed neutron counting where 1 l sample volumes may need to be pre-concentrated [2]. Other approaches such as liquid scintillation with count times of 180 min do not provide rapid results [3]. However, inductively coupled plasma mass spectrometry (ICP-MS) provides a rapid and sensitive technique for the determination of these elements, although high levels of sample matrix can produce interferences in the plasma which result in a suppression of analyte ionisation [4], or block the nebuliser or torch due to the deposition of dissolved solids coming out of solution. This necessitates some form of sample pre-treatment. Sample

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dilution will decrease the matrix effects [5,6] but will also decrease the U and Th concentrations. Although low detection limits have been obtained for diluted samples using sector field ICP-MS [7–9], problems have been reported using quadrupole ICP-MS, even with diluted samples. Roduskin and Ruth [9] report in excess of 50% signal loss for a 10-fold dilution of NASS-4 seawater using a quadrupole instrument. Solid-phase extraction (SPE) separates the sample from the matrix without reducing the analyte concentration and has the advantage, when coupled on-line, of requiring only a small sample volume.

The aim of this study was to develop an on-line SPE-ICP-MS method to analyse for U and Th in aqueous samples with a high total dissolved solids (TDS) content. Although good recoveries from seawater have been obtained using conventional chelating resins [10,11], when samples containing dissolved organic carbon (DOC) have been analysed, low recoveries have been reported for U, Th [12,13] and other heavy metals [14]. Because of this, an actinide-specific extraction resin was employed which may be less affected by the presence of DOC in the samples. A sample introduction manifold was developed and the suitability of the extraction resin for on-line separation investigated. The ability of the resin to function in the presence of a high sample matrix concentration was ascertained using a seawater certified reference material, groundwater samples and, because of the recovery problems reported in the presence of DOC, samples spiked with humic and fulvic acids.

2. Experimental

2.1. Reagents

The carriers were prepared from concentrated nitric acid (Aristar, BDH, Poole, Dorset, UK) diluted to 2 M with deionised water (18 M Ω , MilliQ system, Millipore S.A., Molsheim, France) and aluminium nitrate (AnalaR, BDH). The eluents were prepared from ammonium hydrogenoxalate (Sigma-Aldrich, Gillingham, Dorset, UK), ammonium oxalate and oxalic acid (AnalaR, BDH), made up to 0.1 M in deionised water (18 M Ω , MilliQ system). A 1 ng ml⁻¹ bismuth (Aristar plasma emission standard, BDH) internal standard was added to the eluent.

The TRU-spec extraction resin (EiChrom Europe, Paris, France) was slurry packed into a small column made from PTFE HPLC tubing (2.4 mm \times 50 mm), with 40 μ m PTFE frits and 'flange free' end fittings.

2.2. Sample preparation

Uranium and Th calibration standards were diluted from stock solutions (1000 μ g ml⁻¹ Aristar plasma emission standard, BDH) with 1% nitric acid and synthetic seawater to give final concentrations of 0.1–10 ng ml⁻¹. Synthetic seawater was prepared from sodium chloride, magnesium chloride, magnesium sulphate, calcium chloride, potassium chloride and sodium hydrogen carbonate (AnalaR, BDH). Humic acid solutions were prepared by dissolving humic acid (Fluka, Gillingham, Dorset, UK) in deionised water (18 M Ω , MilliQ system). Fulvic acid was diluted from a stock solution (provided by the British Geological Survey) to a final concentration of 8 μ g ml⁻¹. Solutions for recovery experiments were prepared by spiking the seawater, and humic and fulvic acid solutions with 1 ng ml⁻¹ U and Th.

2.3. Analysis procedure

The sample introduction manifold consisted of two six port valves (Type 50, Rheodyne, Cotati, CA, USA) connected in series (Figs. 1–3). The first held the sample loop and the second the column. During its operation, the sample was loaded onto the column with the acid carrier, the analyte being retained whilst the matrix elements passed straight through. The analyte was then eluted with an oxalate eluent directly into the nebuliser of an ICP-MS instrument (PlasmaQuad 2+, VG Elemental, Winsford, Cheshire, UK). The ICP-MS

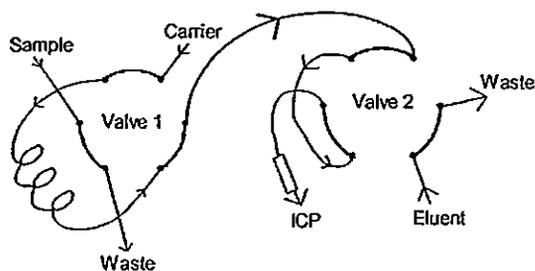


Fig. 1. Rheodyne valves set-up for one-directional flow, sample matrix diverted to ICP.

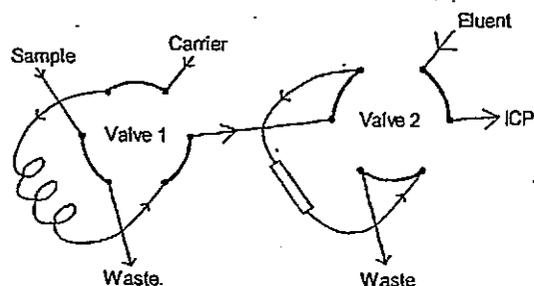


Fig. 2. Rheodyne valves set-up for one-directional flow, sample matrix diverted to waste.

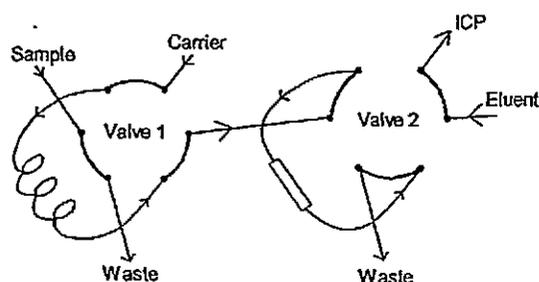


Fig. 3. Rheodyne valves set-up for two-directional flow, sample matrix diverted to waste.

data was collected using the time resolved analysis (TRA) software in the form of a chromatogram. Results were calculated using the peak area ratio to the response of the internal standard in the eluent. This allowed correction for changes in instrument response due to drift. The instrument and column parameters used are given in Tables 1 and 2, respectively.

Table 1
ICP-MS instrument parameters

Instrument	VG PlasmaQuad II
Plasma	Argon
Coolant flow	13 l min ⁻¹
Auxiliary flow	1 l min ⁻¹
Nebuliser flow	0.85 l min ⁻¹
Nebuliser pressure	36 psi
Nebuliser type	V-groove, high solids
Spray chamber	Scott double pass, water cooled, 10°C
Torch	Fassel
Power	Forward 1350 W, reflected 0–2 W
Detector	Pulse counting mode; time resolved analysis data collection

Table 2
SPE column parameters

Packing	TRU, spec
Column	5 × 0.24 cm Teflon tube
Carrier	2 M HNO ₃
Eluent	0.1 M NH ₄ HC ₂ O ₄
Injection volume	500 µl
Flow rate	6 rpm (0.8 ml min ⁻¹)
Run time	load, 2 min; elute, 3 min

There are two main configurations for sample introduction manifolds [15–18]. In one arrangement, the carrier and eluent flow through the column in the same direction whereas in the other, the carrier flows in one direction to load the sample on to the column and the eluent flows in the opposite direction when stripping the analytes from the column. The advantage of the two-directional flow configuration is said to be a reduction in the tendency for the column packing material to bed down, and sharper peaks (less band broadening) because the analyte does not pass through the whole length of the column. Figs. 1 and 2 show the one-directional flow configuration; Fig. 1 has the matrix diverted into the ICP-MS instrument to check for column breakthrough during development work. Fig. 3 shows the two-directional flow configuration. Both of these configurations were evaluated.

The composition of the carrier and eluent used were investigated. Nitric acid is usually employed as the carrier with this type of resin [19]; however, the use of aluminium nitrate is said to increase the capacity of the resin [20]. Nitric acid (0.01 to 2 M), aluminium nitrate (0 to 0.5 M) and combinations of both were tested and the capacity of the resin was measured by adding the resin to a solution containing an excess of uranium and then measuring the amount of uranium remaining in solution. The effect of eluent pH on peak profile was examined by using oxalic acid (pH 0.76), ammonium hydrogenoxalate (pH 2.30) and ammonium oxalate (pH 6.53) as eluent.

Once the system parameters had been optimised, the effectiveness of the procedure was assessed using a certified reference material (NASS-4, open ocean seawater, National Research Council, Ottawa, Ont., Canada) and standards spiked with humic and fulvic acids.

3. Results and discussion

During the development phase, the sample matrix was diverted through the ICP-MS to check for column 'breakthrough', i.e. U and Th not retained on the column. The resulting chromatogram consisted of two parts corresponding to (i) the load phase (the first 2 min), where the sample was loaded on to the column, U and Th were retained on column while the sample matrix passed through, and (ii) the second phase where U and Th were removed from the column and passed into the ICP-MS.

With the sample introduction manifold set-up for two-directional flow through the column, the reversal in flow direction caused the frits to become dislodged, resulting in the column becoming unpacked. In addition, the peak obtained had a low shoulder on the leading edge of the peak which could cause peak integration problems. This was not seen when the flow was unidirectional.

The capacity of the resin for uranium was measured while using nitric acid, aluminium nitrate and mixtures of both as carriers. Table 3 shows that the capacity of the resin increased with both higher nitric acid and aluminium nitrate concentrations, indicating that it was the nitrate concentration rather than the acidic conditions that facilitated the binding of uranium to the resin. However, if aluminium nitrate alone was used as the carrier, the U peak was broader than when nitric acid acted as the carrier, indicating that the low pH is also beneficial. Since the U and Th concentrations in natural waters are normally very low it was not necessary to increase the loading capacity of the column by using aluminium nitrate, with the added benefit of reducing the level of dissolved solids in the carrier.

The function of the oxalate eluent was to complex the U and Th and remove them from the column.

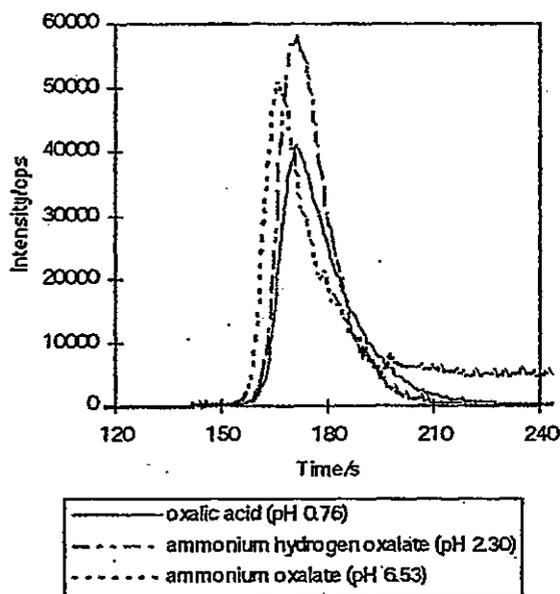


Fig. 4. Effect of eluent on peak shape.

The influence of eluent pH on this process can be seen in Fig. 4. Oxalic acid produced a low symmetric peak whereas ammonium hydrogenoxalate produced a sharper more asymmetric peak and the ammonium oxalate produced a sharp peak but with increased tailing. The eluent pH did have an effect on peak profile, with higher pH initially eluting the uranium off more quickly, giving a sharper leading edge to the peak, but then tailing off to produce a more asymmetric peak. As a result of these observations ammonium hydrogenoxalate was used as the eluent in subsequent work.

A chromatogram to evaluate the baseline following a standard injection (1 ng ml^{-1} in 1% nitric acid) produced a thorium peak in the eluted phase which decreased in size with subsequent runs, indicating that

Table 3
Change in resin binding capacity with variations in carrier composition

Experiment No.	Carrier concentration (M)		Binding capacity ($\mu\text{g U/mg resin}$)	
	Nitric acid	Aluminium nitrate	Experimental	Calculated
1	2	0.50	83	89
2	2	0.00	40	39
3	1	0.25	66	56
4	0.001	0.00	16	22
5	0.001	0.50	73	72

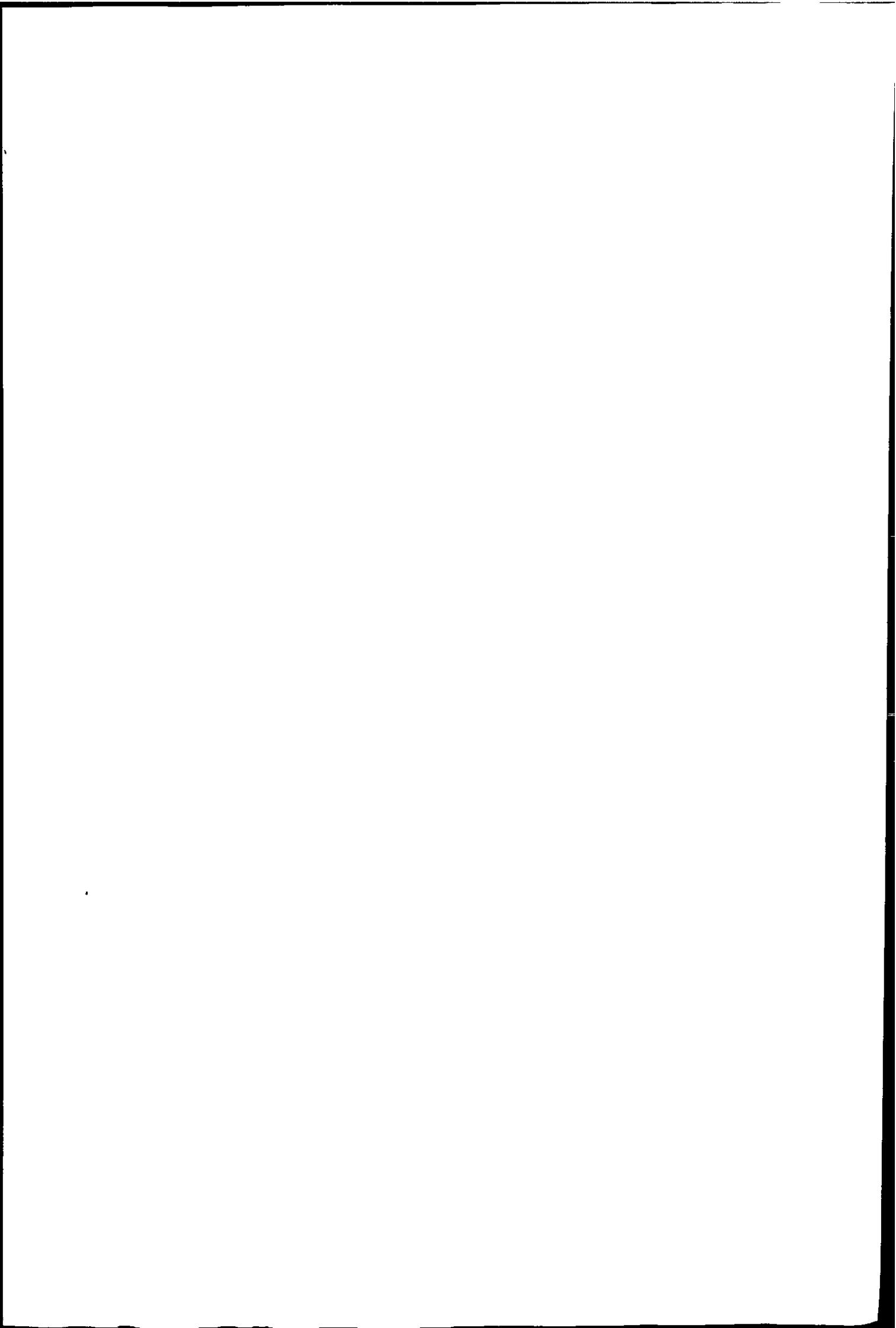


Table 4
Results for column flush procedures

Column flush method	Percentage carry-over to baseline
Baseline run 5 min ($\times 2$)	2.1
Nitric acid and oxalate 2 min each ($\times 2$)	1.1
Nitric acid and oxalate 1 min each ($\times 2$)	2.5

thorium was being retained in the system and then eluted by subsequent cycles of carrier and eluent. A protocol to flush the system was developed to overcome this. An increased elution time did not decrease the level of thorium carryover significantly but switching between the carrier and eluent in a shortened version of the complete injection cycle did reduce the carryover to an acceptable level (Table 4).

Fig. 5 shows the response for an injection of a standard made up in a synthetic seawater matrix. The peak in the load phase was due to the sample matrix passing straight through the column (^{44}Ca was measured to represent the sample matrix component) while the U and Th were retained. The peaks in the elute phase are the U and Th coming off the column. This demonstrated that the column functioned in the presence of a high sample matrix concentration and separated the analytes from a seawater matrix.

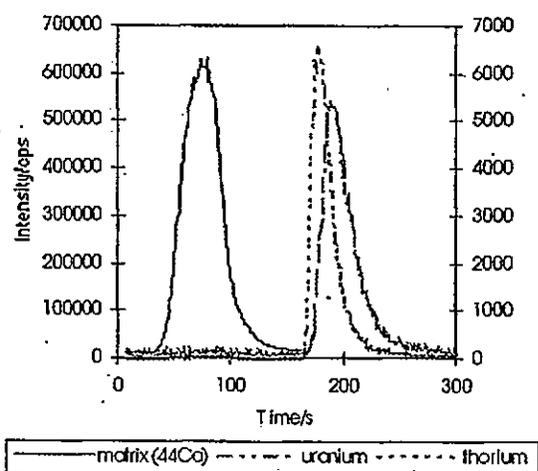


Fig. 5. Chromatogram showing the separation of uranium and thorium from the sample matrix. (Left-hand scale for the matrix, right-hand scale for the analyte).

Table 5
Uranium recovery results from seawater CRM

NASS-4 open ocean seawater reference material (ng ml^{-1})	
Certified U concentration \pm 95% C.L.	2.68 ± 0.12
Measured U concentration \pm 1 S.D. ($n = 4$)	2.62 ± 0.08
	2.70 ± 0.09

Table 6
Analysis of groundwater samples with and without use of SPE

Sample	Results from TRU-spec column (ng ml^{-1})		Results from diluted samples (ng ml^{-1})	
	Uranium	Thorium	Uranium	Thorium
1	0.07	<0.004	<0.1	<1
2	0.14	<0.004	0.1	<1
3	4.35	<0.004	4.3	<1

Sample recovery was assessed using a certified reference material (NASS-4, open ocean seawater) and a series of groundwater samples which had previously been analysed after dilution because of their high total dissolved solids content (0.4–4% TDS). These results can be seen in Tables 5 and 6, respectively. The thorium concentrations in the groundwater samples were below the limit of detection of the method.

To investigate the effect of DOC on recovery, humic and fulvic acid solutions spiked with U and Th were injected onto the column along with sample blanks. Full recovery was obtained for all samples except thorium in the humic acid solution (Table 7). An acid digest was required before complete recovery was obtained for Th in the presence of humic acid. The recovery values from fulvic acid solution were slightly high and could not be explained by the level of U and Th in the sample blanks (U 0.03 ng ml^{-1} , Th 0.02 ng ml^{-1}).

Figures-of-merit for the method are given in Table 8. The linearity and repeatability of response was measured over the range 0 to 10 ng ml^{-1} with

Table 7
Uranium and thorium recoveries from spiked humic and fulvic acid solutions

Sample	% recovery \pm 1 S.D. ($n = 6$)	
	Uranium	Thorium
Fulvic acid	108 ± 5	106 ± 14
Humic acid	101 ± 6	86 ± 6
Humic acid (acid digest)	101 ± 3	101 ± 3

Table 8
Figures-of-merit for the SPE method

	Uranium	Thorium
Correlation coefficient ($n = 5$)	0.9984	0.9994
Repeatability (% R.S.D., $n = 6$)	4.3	5.8
Limit of detection (ng ml^{-1})	0.015	0.006

standards prepared in 1% nitric acid. The limit of detection in the presence of a seawater matrix was taken as three times the standard deviation of the baseline response.

4. Conclusions

The use of SPE in an on-line configuration allowed a relatively rapid (5 min run time) analysis of U and Th in samples which would have otherwise required some form of sample pre-treatment. The actinide-specific resin selectively bound and released U and Th, separating these elements from the sample matrix, and facilitated on-line coupling to ICP-MS detection. Complete recovery of U from a seawater CRM and samples containing DOC showed that this method can be used for 'real' samples with a high total dissolved solids content. The resin exhibited an improvement in performance over conventional ion exchange and chelating resins in the presence of dissolved organic carbon.

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