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New methods for the speciation analysis of radioactive iodine in aqueous samples

by

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ABSTRACT

FACULTY OF ENGINEERING, SCIENCE AND MATHEMATICS

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NEW METHODS FOR THE SPECIATION ANALYSIS OF RADIOACTIVE IODINE IN AQUEOUS SAMPLES

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Radioactive iodine in the environment comes both from nature and as a result of human activities. Understanding its behavior and fate in the environment, to enable assessment be made of its environmental impact, requires knowledge of its chemical form (speciation). The aim of this research work was to develop new analytical methods for the identification and measurement of radioactive iodine species, with an emphasis on the measurement of iodate and iodide in aqueous samples.

A new derivatisation-solid phase extraction (DSPE) method was developed based on the conversion of iodine species to 4-iodo-*N, N*-dimethylaniline (IDMA) which was then extracted from the aqueous sample by using solid phase extraction. Stable iodine could be measured by HPLC determination of IDMA, giving a detection limit of ~1μmol L^{-1} for both iodide and iodate when a sample size of 250 mL was employed. DSPE methods could also be adapted to collect individual ^{129}I species as radioactive IDMA, with final measurement by liquid scintillation counting (LSC). The mean recoveries from determining $^{129}I^-$ (~9.2 Bq g^{-1}) and $^{129}IO_3^-$ (~0.52 Bq g^{-1}) in water were 96.5±2.6 % and 94.6±0.8 %, respectively. These adapted methods were applied to the speciation analysis of ^{129}I in an effluent from a nuclear facility without pre-separation. The inorganic forms of ^{129}I in the effluent were iodide, iodate and elemental iodine.

To overcome salt-derived interferences during DSPE analysis of seawater, an anion exchange approach was developed to pre-separate and enrich iodide and iodate from seawater (1 litre) prior to re-enrichment using the DSPE method. Total yields of iodide and iodate obtained from this combined approach were 81.6±1.8% and 79.1±7.7%, respectively. The concentration-based detection limit could be improved by using ICP-MS detection. Whilst the combined methods could enrich the concentrations of inorganic iodine species in seawater by 200-fold, some incomplete separation of iodide from iodate was however observed. Both methods were shown to offer simple and selective approaches to the speciation analysis of both stable and radioactive iodine in a variety of sample types.

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DECLARATION OF AUTHORSHIP

I, Supamatthree Bunprapob, declare that the thesis entitled:
New methods for the speciation analysis of radioactive iodine in aqueous samples and the work presented in the thesis are both my own, and have been generated by me as the result of my own original research. I confirm that:

- this work was done wholly or mainly while in candidature for a research degree at this University;
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- where I have quoted from the work of others, the source is always given. With the exception of such quotations, this thesis is entirely my own work;
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- none of this work has been published before submission.

Signed:……
Date:……

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ABBREVIATIONS

AMS	Accelerator mass spectrometry
Bq	Becquerel
DMA	*N*,*N*-dimethylaniline
DOI	Dissolved organic iodine
DOC	Dissolved organic carbon
DSPE	Derivatisation solid phase extraction
FIA	Flow injection analysis
GC	Gas chromatography
GC-MS	Gas chromatography-mass spectrometry
HPLC	High performance liquid chromatography
HPGe	High purity germanium
IBZ	2-iodosobenzoate
ICP-MS	Inductively coupled plasma mass spectrometry
IDD	Iodine deficiency disorder
IDMA	4-iodo-*N*,*N*-dimethylaniline
K_d	The solid-liquid distribution coefficient
LLW	Low level radioactive waste
LSC	Liquid scintillation counting
MBL	Marine boundary layer
MS	Mass spectrometry
NAA	Neutron activation analysis
NOCS	National Oceanography Centre, Southampton
PE	Polyethylene
ppb	Part per billion
ppm	Part per million
ppt	Part per trillion
SQPE	Spectral quench parameter (external)
SPE	Solid phase extraction
TMAH	Tetramethylammonium hydroxide
UV	Ultra violet
WHO	World Health Organization
XANES	X-ray absorption near-edge structure spectroscopy

INTRODUCTION

CHAPTER 1 A review of iodine chemistry

1.1 Overview of iodine chemistry

Iodine, a halogen, is a purple-black solid which can be sublimed at standard temperature. The estimated abundances of iodine in the continental crust and in surface seawater are 0.45 mg kg^{-1} and 60 μg L^{-1}, respectively[1] Although, it is a minor component in the environment, it is important for biological activity and has a high mobility in the environment. It is widely distributed being found in most samples that have been studied (**Table 1.1**).

Table 1.1 The estimated iodine contents of environmental samples[2].

Types of sample	Iodine content
Marine fish	1 mg kg^{-1}
Recent marine sediment	5-200 mg kg^{-1}
Seawater	58 μg L^{-1}
Marine plants	50 mg kg^{-1}
Smoke from burning fossil fuels	1-200 mg kg^{-1} (in soot)
River water	1-10 μg L^{-1}
Vegetation	0.5 mg kg^{-1}
Soil	2-15 mg kg^{-1}
Extrusive igneous rocks	0.24 mg kg^{-1}
Ore minerals	1.4 mg kg^{-1}
Metamorphic rocks	(0.3) mg kg^{-1}
Intrusive igneous rocks	0.24 mg kg^{-1}
Sandstones	0.80 mg kg^{-1}
Shales	2.3 mg kg^{-1}
Limestones	2.70 mg kg^{-1}
Atmosphere	1 μg kg^{-1}
Rain water	1-6 μg L^{-1}
Volcanic gases	(2) mg kg^{-1} (in condensate)

Values in brackets are from few data.

The isotopes of iodine

There are more than 30 isotopes of iodine, but only ^{127}I is stable. The radioisotopes of iodine found in the environment occur both naturally and from man-made activities. The longest lived radioisotope of iodine is ^{129}I ($t_{1/2}$ =1.57x10^7 years). The main anthropogenic source of radioactive iodine in the environment is nuclear activities such as leakage from nuclear reactors during normal operation, the detonation of nuclear weapons, fallout from nuclear reactor accidents[3], discharge from nuclear fuel reprocessing plants[3-4] and waste from medical institutes[5-6]. Radioactive iodine has similar physical and chemical properties to stable iodine, but radioactive iodine decays to other elements with time. Iodine reacts easily with other chemicals, and radioactive iodine is found as compounds rather than as the pure elemental nuclide[7]. Information on some of the iodine isotopes is shown in **Table 1.2**.

Table 1.2 The nuclear properties of some iodine isotopes[8].

Isotope	Atomic mass or weight[a]	Half-life	Decay mode	Emax (keV)	Main γ-X-ray (keV) (abundance)
^{123}I	122.90559	13.27 h	EC^+ β^+	1074.9 (97%, EC)	159(83%)
^{124}I	123.90621	4.18 d	EC^+ β^+	2557(25%, EC), 3160 (24%, EC), 1535 (12%, β^+),	602.7 (63%), 723 (10%), 1691 (11%)
^{125}I	124.90463	59.41d	EC	2138 (11%, β^+) 150.6 (100%)	35.5 (6.68%), 27.2 (40%), 27.5 (76%)
^{126}I	125.90562	13.11 d	EC^+ β^+, β^-	869.4 (32%, β^-), 1489 (29%, EC), 2155 (23%, EC)	338.6 (34%), 666.3 (33%)
^{127}I	126.90447	Stable			
^{128}I	127.90581	24.99 m	β^-, EC^+ β^+	2449 (80%, β^-)	442.9 (17%)
^{129}I	128.90498	1.57x10^7 y	β^-	154.4 (100%)	39.6 (7.5%), 29.5 (20%), 29.8 (38%)
^{130}I	129.90667	12.36 h	β^-	587 (47%), 1005 (48%)	536 (99%), 668.5 (96%), 739.5 (82%)
^{131}I	130.90613	8.02 d	β^-	606 (90%)	364.5 (82%)
^{132}I	131.90800	2.30 h	β^-	738 (13%), 1182 (19%), 2136 (19%)	667.7 (99%), 772.6 (76%)

Table 1.2 (continued)

Isotope	Atomic mass or weight[a]	Half-life	Decay mode	Emax (keV)	Main γ-X-ray (keV) (abundance)
^{133}I	132.90779	20.8 h	β^-	1240 (83%)	529.9 (87%)
^{134}I	133.90974	52.5 m	β^-	1307 (30%)	847 (95%), 884 (65%)
^{135}I	134.91005	6.57 h	β^-	970 (22%), 1388 (24%)	1260 (29%)

m = minutes, h = hours, d = days, y= years, β- = beta emission, β+ = positron emission, EC = electron capture. [a]Atomic weight or mass of iodine radioisotopes from Lide[1].

The properties of radioactive iodine are exploited in the fields of nuclear medicine and environmental studies. Iodine-129 is utilized as an environmental tracer because of its long half-life[9]. Iodine is involved in the cycling of organic matter in all surface environments and the $^{129}I/^{127}I$ ratio has been usefully employed as a tracer of terrestrial organic matter [10-11] and for dating and tracing in the hydrosphere[10, 12-13]. The ratio of $^{129}I/^{127}I$ has also been used to monitor the source and dispersal of ^{129}I from nuclear activities by comparing the pre-anthropogenic ratio with the post-anthropogenic ratio[14-16]. Other radioisotopes of iodine are widely used in nuclear medicine. For example, ^{123}I ($t_{1/2}$ = 13.2 hours) and ^{131}I ($t_{1/2}$ = 8.02 days) have been used for imaging neoplasm in the thyroid[17]. Positron emission tomography has employed ^{124}I ($t_{1/2}$= 4.18 days) for evaluating the dosimetry of radioactive iodine treatment for thyroid diseases[18]. For malignant tumors, encapsulated ^{125}I ($t_{1/2}$ = 59.4 days) has been used for treatment[19].

1.2 Iodine and human Health

Iodine, mainly as iodide, can enter the body through the consumption of food and water. Organic iodine compounds are converted to iodide before being absorbed via the gastro-intestinal tract into the blood stream. In the body, iodine is present as iodide (1%) and iodinated amino acids (80%) such as monoiodotyrosine (MIT), diiodotyrosine (DIT), thyroxine (T_4), 3,5,3′ triiodothyronine (T_3), 3,3′ diiodothyronine (T_2) and 3,3′,5′ triiodothyronine (reverse-T_3), as shown in **Figure 1.1**.

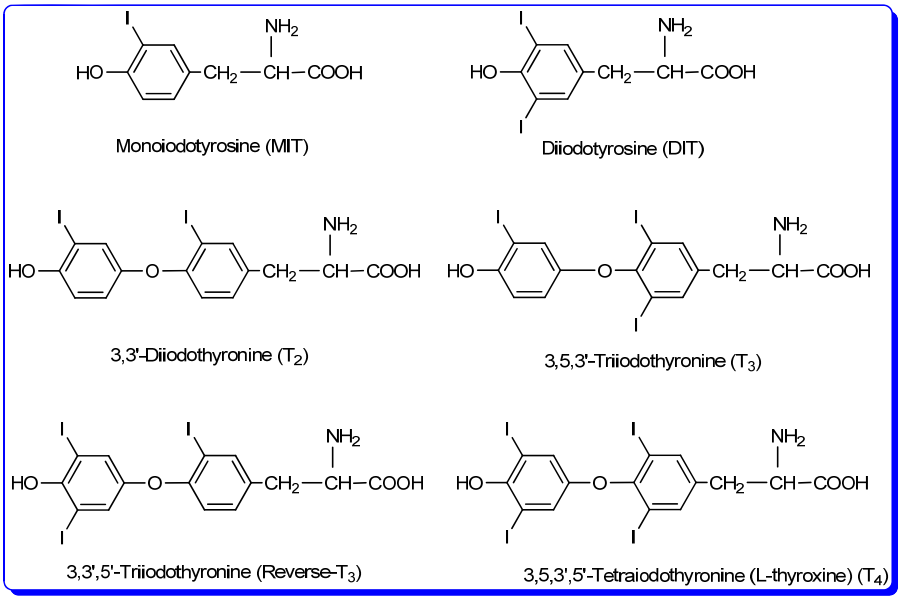

Figure 1.1 Thyroid hormones and iodinated amino compounds (adapted from Munkner[20]).

Most of the ingested iodide can be removed from the blood by the thyroid gland, and kidneys. Minor quantities can also be removed by the salivary, gastric and mammary glands. Accumulation of iodide can occur in the salivary glands, the gastric mucosa and the mammary gland. The thyroid hormones are important for the development of the brain and the nervous system, body growth and several metabolic activities in the body. The major way that iodide is lost from the body is by being trapped in the thyroid gland to produce thyroid hormones or by being excreted from the kidneys[20].

The whole body iodine retention in the human body is 12 days and 120 days for the thyroid. The recommended daily iodine intake for humans is considered to be: 50 μg day^{-1} for infants, 90 μg day^{-1} for children, 120 μg day^{-1} for school children, 150 μg day^{-1} for adults and 200 μg day^{-1} for pregnant and lactating women[21]. Excess iodine intake can cause goitre, hypothyroidism, hyperthyroidism and as an increased risk of thyroid papillary cancer in humans. For animals death can result from the intake of 200 -500 mg iodine day^{-1}. The maximum tolerated daily intake of iodine according to the World Health Organization (WHO) is equal to or less than 1 mg day^{-1} for most people [22].

Thyroid dysfunction can be from over-activity, under-activity and iodine deficiency. If the iodide concentration is reduced, and the thyroxine concentration increases, this causes hyperthyroidism. If the concentration of iodide increases and the concentration of thyroxine reduces, this will cause hypothyroidism. Where there is a deficiency of iodine, the iodide concentration reduces without an increase in thyroxine concentration[23].

The effect of radioactive iodine on human health

Radioactive iodine can enter the human body via inhalation of the vapours it releases into the atmosphere and by ingesting contaminated food and water. Acute exposure to radioactive iodine is harmful to body cells and to organs such as the thyroid, stomach, salivary glands, breast, kidneys and bladder, gonads and liver where iodide can be concentrated. The uptake of radioactive iodine by a baby's thyroid is found to be quicker than for an adult because of the difference in thyroid mass which increases with age. The physical half-life of the radioisotope is an important factor in thyroid radiation dosages in humans[23]. Examples of thyroid problems from being exposed to radioactive iodine include children and adolescents who lived in the contaminated areas of Belarus, Russia and Ukraine who were found to have thyroid cancer after the Chernobyl accident. An iodine deficiency increased the risk of getting thyroid cancer[24]. The problem came principally from the consumption of ^{131}I –contaminated milk. The thyroid doses in people who lived in these contaminated areas varied with age, location of residence and their milk consumption rate[25]. The risk of thyroid neoplasms and autoimmune thyroiditis increased in children who lived in the contaminated area for up to 30 years after their exposure to radioactive iodine[26].

When radioactive iodine enters the body, it changes its chemical form to become iodide and then accumulates in the thyroid gland and other organs of the body as stable iodine; any excess being removed by excretion. Potassium iodide (50 – 100 mg for an adult) has been proposed as a means of protecting the thyroid from radioactive iodine exposure after a nuclear accident; the stable iodide reducing the accumulation of radioactive iodine in the thyroid gland. The most efficient time to take the potassium iodide is 2 days before or 8 hours after exposure to the radioactive iodine[27].

1.3 The speciation and behavior of iodine in the environment

Iodine species in the environment

Iodine has six major oxidation states (-1, 0, +1, +3, +5 and +7). Its chemical properties are similar to the other halogens but it is less active than F, Cl and Br and it is found in a wide range of inorganic and organic species. Understanding changes of form is critical to our understanding of the movement and environmental significance of this element in the environment.

Based on thermodynamic calculations, the dominant inorganic forms of iodine in water can be predicted (**Figure 1.2)**. In most natural water samples, iodide (I^-) and iodate (IO_3^-) are predicted to be the dominant iodine forms.

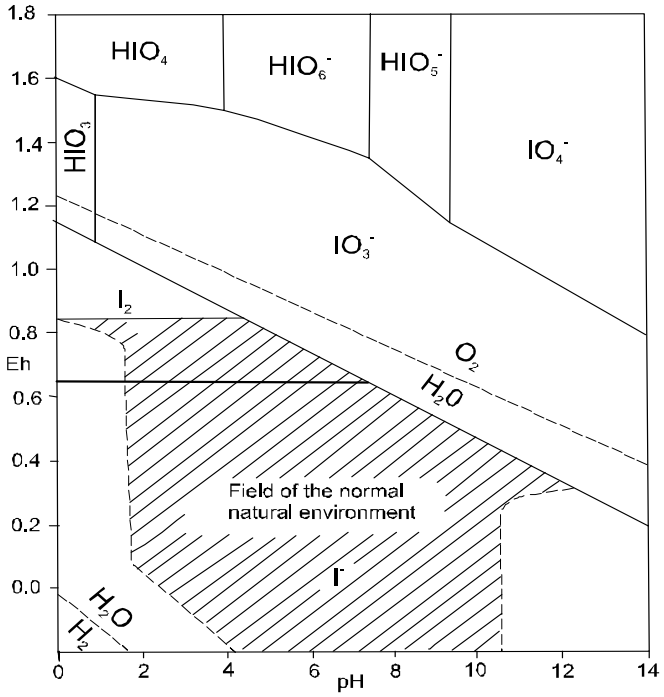

Figure 1.2 The major chemical forms of iodine in aqueous solutions (after Vinogradov and Lapp[28]).

In nature, iodine can however also occur as organoiodine compounds such as thyroxine and related compounds in animals, organic iodine compounds in marine plants, seawater and atmosphere[29] and alkyl iodide in soil[30] due to a number of biogeochemical processes.

1.3.1 Speciation and behavior of iodine in the aquatic environment

In fresh water

The concentrations of iodine in surface water and ground water can vary seasonally. Flood and erosion of the top soil is an important iodine input to groundwater[31] and the concentrations of iodine in stream and ground water are found to correlate with the concentrations of dissolved organic carbon (DOC)[32]. Iodide and iodate were found to be the major species of dissolved iodine in all types of fresh water collected from the English Lake District. The reduction of iodate and the oxidation of iodide occurred in the lakes with various temporal distributions. The former process was found in the summer, influenced by the biological activity. Oxidation by molecular oxygen at the water surface occurred in the winter[33]. The iodine content of rivers commonly decrease with distance from the sea[34]. Under aerobic conditions of fresh water, iodine is lost to the sediment. In contrast it remains in solution under anaerobic conditions and a small portion of the iodine is lost from water to the atmosphere[35]. There are other influences on the speciation of iodine in natural anaerobic environments, for example ferric iron and/or sulfate reducing bacteria which can reduce iodate to iodide[36]. Humic substances can attach to iodide in the natural aquatic environment. During water processing, the removal of humic substances can result in the co-removal of iodine, reducing the iodine content of drinking and mineral water to trace levels[37].

In estuarine water

An estuarine system is complex because its characteristics come from mixing river water and seawater and the presence and distribution of iodine species depends on the hydrological temporal profiles of the locations. Iodate, iodide and organic iodine were the major chemical forms of iodine found in the Nile River Estuary. The concentrations of each iodine species varied with the salinity and flow period but iodide was the dominant species in the surface and bottom waters of the estuary. Organic iodine could be found both at the surface and in bottom waters[38]. In the saline layers (salinity > 10), the concentrations of iodide and iodate were more stable than those in the upper brackish and interfacial layers. There was a seasonal change in the distribution of iodate and iodide in the brackish layer arising from freshwater phytoplankton and organic matter[39].

For humic-rich estuarine water, the total iodine concentrations are not varied by seasonal change. The concentration of iodate correlates linearly with the salinity while the iodide concentration is related to the dissolved phosphorus during the summer. Iodate is not detectable at low salinity and it is converted to organic iodine due to the reducing sediments and low dissolved oxygen concentrations. In the case of iodide, the biological activity influences its concentration. The organic iodine is produced in water where there is low salinity and the highest concentration of dissolved organic carbon[40].

Salinity has been found to influence the dissolved organic iodine (DOI), iodide and iodate contents of coastal, inshore and estuarine waters. The total iodine content does not change during estuarine mixing but iodate can be converted to iodide and then to DOI in the estuary[41]. Photosynthesis and autotrophic and heterotrophic respiration are the most important processes varying the concentrations of iodide and iodate in an estuarine system. Other processes, such as photooxidation or photoreduction to I_2 and release from sediments, are less important[42].

In marine water

Iodate can be reduced to iodide in surface ocean waters[43]. Spokes and Liss[44] suggested that the photochemical production of iodide was not from biological mediation, but came from organic matter which was the limiting species for the reduction[44]. The speciation of ^{127}I and ^{129}I in seawater collected from the North Sea and English Channel has been studied by Hou et al[45]. The results showed that the La Hague nuclear fuel reprocessing plant had influenced the distribution of ^{129}I in surface water of the North Sea. There was iodide oxidation and the iodate reduction (for ^{127}I and ^{129}I) in seawater during its transport to the European continental coast[45]. The different concentrations of iodate in surface waters collected from offshore, inshore and subsurface water might be from iodate-reducing substances in terrestrial run-off. The concentration of iodate was not found to vary at depths greater than 200 m[46]. In the oxic zone, the concentration of iodate was found to be depleted at the surface. The concentration of iodate increased from depths between 100 m and 1200 m before decreasing at depths below 1200 m. Iodide was only found in depths above 200 m. In anoxic areas, iodate depletion occurred with nitrate depletion. The remineralization of biogenic

particles in the sediments and in the anoxic water column might be a source of iodide in deep water[47]. Seasonal variations influence the redox conditions of dissolved iodine in deep water because of the variation in oxygen content[48].

The DOI in the euphotic zone is related to biogeochemical activities[49]. The concentration of DOI is 40% of total iodine in coastal waters, whilst its concentration in surface water decreases with depth and increases shoreward[50]. Brandao et al[51] reported that sunlight did not change iodine speciation, but an intense (artificial) UV- radiation source could alter the iodine speciation. The photosynthesis and respiration of phytoplankton and zooplankton in sea water can produce 5-8 nmol L^{-1} h^{-1} of iodide and iodate per day[51]. Iodide in inshore water can be produced from the decomposition of DOI by solar radiation[52]. Sherill et al[53] studied the effect of ozonation on the iodine speciation in artificial seawater and found that it could induce iodide conversion to iodate and DOI conversion to iodide or iodate (or both)[53].

The distributions of iodine species in various locations are different. Compos et al[54] studied the cycling of dissolved iodine at the Bermuda Atlantic and Hawaii Ocean time-series stations. Iodate was found to convert to iodide due to biological processes at both sites. However, the concentration of iodide in the upper 100 m at the Hawaii Ocean station was twice that found at the Bermuda Atlantic station. The biological iodate reduction was found to be 100 times faster than the combination of iodide with particulate organic carbon[54].

The role of biological activity in the speciation of iodine

Biological activity plays an important role in the iodine speciation and distribution in the marine environment. Moisan et al[55] studied iodate uptake by marine phytoplankton. For the duration of high and low tide, rates of iodate depletion were 0.26 and 0.08 nmol IO_3^- (μg chlorophyll a)$^{-1}$ h^{-1}, respectively. From their estimation, the phytoplankton could take up 3% of the iodate pool per day[55]. The nitrate reductase activity is an indicator of nitrate uptake by phytoplankton and iodate reduction and the iodide production are found to correlate with this nitrate reductase activity[56]. Phytoplankton also release biogenic volatile iodated

hydrocarbons into the open ocean and coastal surface waters[57]. The reduction of iodate by various phytoplankton, including cold water diatoms varies with species[58]. The reduction of iodate in seawater samples collected from depths between 200 m and 600 m (within the oxygen minimum zone) were studied by Farrenkopf et al[59] with results which showed that marine bacteria could reduce iodate to iodide[59].

The speciation and concentration of iodine in seaweed is found to vary between species. In aqueous leachates, the orders of iodine species contents are iodide> organic iodine> iodate. The species of seaweed and its bioavailability influence the iodine enrichment mechanism[60]. The iodide and total iodine in various types of edible seaweed was studied by Moreda-Pineiro et al[61]. Brown seaweed accumulated iodine as iodide at about 90%. The iodide percentages for accumulating green and red seaweeds were found to be less than 80% and 30%, respectively[61]. All brown seaweeds emit organic iodine, mainly as CH_2I_2. A number of seaweeds however emit $CHIBr_2$ and CHI_2Cl. Incidental light was found to stimulate the halocarbon production of seaweed. Short-lived organic iodine such as CH_2I_2 and $CHIBr_2$ diminish in surface seawater because of photolysis as reported by Carpenter et al[62]. Seaweed also emits gaseous elemental iodine during the daylight hours and at low tide[63].

1.3.2 The speciation and behavior of iodine in other environmental systems

In the atmospheric environment

The presence of iodine species in the atmosphere can be from various sources such as the sea, the land and biological activity. Its distribution mechanisms and pathways are of particular interest because iodine species can be the precursors of new atmospheric particles and the cause of ozone depletion. Iodine in the atmosphere can be categorized into 4 major groups: inorganic iodine gas, organic iodine gas, particulate iodine and precipitate iodine[64]. The concentrations of particulate iodine, inorganic iodine and organic iodine in the atmosphere along the coast of Ibaraki in Japan were found to be 0.3-3.4, 1.2-3.3 and 7.8-20.4 ng m^{-3}, respectively. About 90% of the iodine in the atmosphere was gaseous in an organic form[65]. For air samples collected from the northern and southern hemispheres,

iodide was found in both fine and coarse particles, whereas iodate was either lower than the detection limit or undetectable[66].

Deposition is the main route for iodine removal from the atmosphere to the Earth's surface, and it is also a source of iodine in soils and plants. The average iodine concentration in rainfall is found to be 1.55 μg L^{-1} as reported by Neal et al[32]. Iodine concentrations in UK rainfall were found to depend on the quantity of rainfall and they were not related to seasonal changes. Iodate was approximately one half of the total iodine concentration[67]. The organic iodine compounds (average 56%) were the dominant iodine species in rain and snow, followed by iodide (27%). Iodate was not found in the snow samples studied by Gilfedder et al[68-69]. The chemical forms of ^{131}I in Japanese rain after the Chernobyl accident were identified using an isotope exchange method and it was found to be 59% iodate and 35% iodide[70]. For the ^{129}I species in precipitation collected from Denmark, the major chemical form of ^{129}I was found to be iodide whilst iodate was the major chemical form of ^{127}I. Seasonal changes varied the total ^{129}I concentration and its species, with high concentrations occurring in the spring and low concentrations in the summer and autumn. A source of ^{129}I in the precipitation was the re-emission of ^{129}I from the surface water of the English Chanel, Irish Sea, North Sea and Norwegian Sea[71].

A number of organoiodine compounds in the marine boundary layer (MBL), such as CH_2ICl, CH_2BrCl and CH_2Cl_2, are produced by the photolysis of the CH_2I_2, CH_2IBr, C_2H_5I, CH_3I, C_3H_7I or CH_2ICl present in seawater[72-73]. CH_3I in the open sea is produced from a light dependent pathway that is indirectly dependent on biological activity[74]. CH_2I_2, $CHClI_2$ and CHI_3 are produced from the reaction between marine dissolved organic matter and hypoiodous acid (HOI) /molecular iodine (I_2) that HOI is the product from the oxidation of iodide by ozone[75]. Abiotic sources of polyhalogenated iodo- or bromocarbon, via the reaction of HOI and/or HOBr with humic materials on the quasi-liquid layer above sea ice/snowpack can produce CHI_3 and CH_2I_2[76]. Other compounds, such as IBr, ICl or I_2, can be produced by aqueous phase chemical reactions and then be released back to the gas phase[72]. The formation of iodine oxide nanoparticles occurs as a result of the

photooxidation of gaseous I_2 and O_3 at the coastal MBL area. The product of iodine oxide (IO) self reaction was IOIO which then dissociated to OIO and I. New particles will be then formed as stable I_2O_3 and I_2O_5 [77-78]. A simplified overview of the chemistry of iodine in the atmosphere derived from the ocean is shown in **Figure 1.3**.

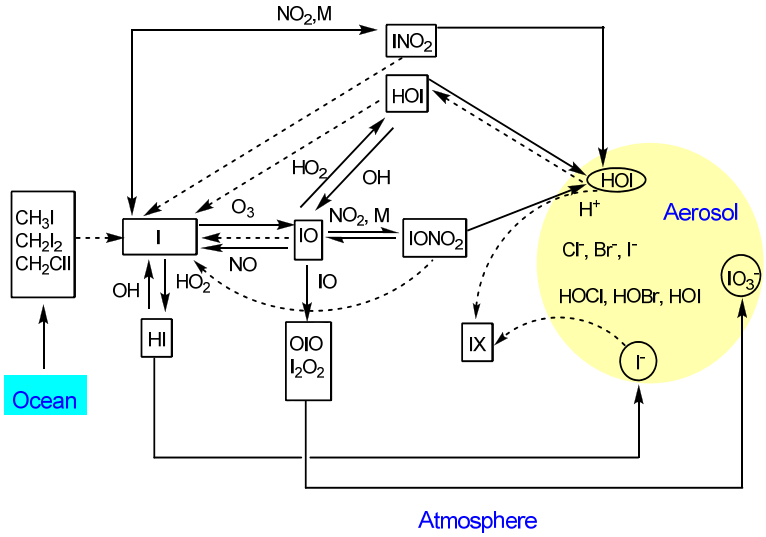

Figure 1.3 A simplified scheme showing atmospheric iodine chemistry resulting from oceanic inputs to the atmosphere. Dashed lines are photolyses, dotted line are volatilization from aerosol and IX is ICl, IBr or I_2 (after Carpenter[79]).

Gaseous organic iodine, especially CH_3I and C_2H_5I, can be released from volcanoes[80]. Ectomycorrhizal fungi in soil are another source for methyl halide emission to the atmosphere. The emission rate of methyl halide depends on the species of fungi[81]. The production of alkyl iodides: iodomethane, iodoethane, 1-iodopropane, 2-iodo-propane, 1-iodobutane and 2-iodobutane in soil were from the oxidation of organic matter by Fe^{3+} as illustrated in **Figure 1.4** [30].

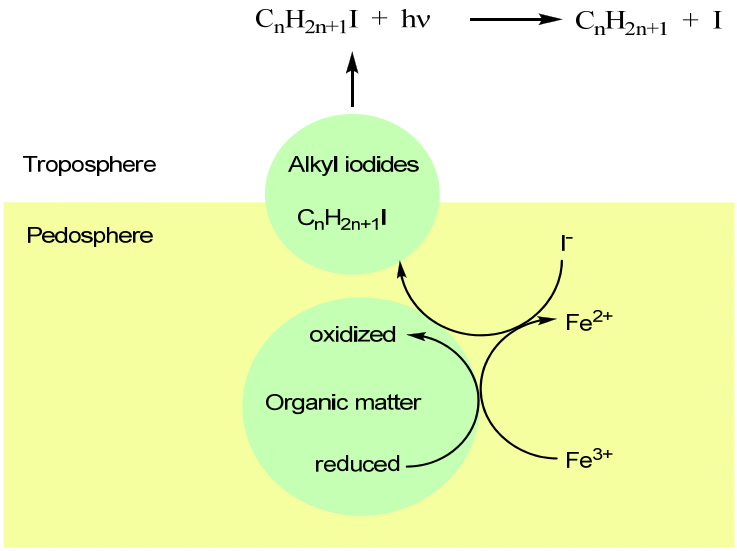

Figure 1.4 The model of alkyl iodide production from soil and release to the atmosphere (after Keppler et al[30]).

In soil and sediment

Most of the iodine in soil is derived from the oceans via the atmosphere and the concentration of iodine in soil is correlated to the total annual deposition of iodine from rain[82]. Little of the iodine in soil is water-soluble and any high iodine content is believed to be associated with organic matter, clays and aluminum and iron oxides. The removal of iodine from the soil can occur by many processes including volatilization, crop-harvesting and leaching into rivers and groundwaters[2, 83]. The uptake of iodine by plants is another way to transfer iodine from soil. The typical concentration range of iodine in plants is 0.03 to 12 μg g^{-1} (dry weight)[84]. With the concentration of iodine in vegetables increasing with the soil concentration, the enrichment of iodine in vegetables differs between vegetable types and in different parts of the same vegetable[85].

Iodine in soil can be separated into four fractions: organic iodine bound to humic acids[86], organic iodine bound to fulvic acids, iodate and iodide[87]. Soil conditions are a significant factor for the presence of iodine. Flooding of soil results in anoxic conditions but this can be converted to oxidizing conditions by a change in the soil water level. Insoluble iodine associated with soil solutions can be transformed to water soluble iodide under the reducing condition resulting from flooding. Iodate is

however found to be the dominant form of iodine in soil solutions under non-flooded oxidizing conditions[88].

Microbial processes influence the speciation and movement of iodine in soil. For example, some soil iodine is methylated by aerobic soil bacteria using an enzyme with an S-adenosyl-L methionine methyl donor and volatized as CH_3I. Iodine-volatilizing bacteria are pervasive in soil environments[89-90]. The reducing conditions (low Eh) for desorbing iodine in flooded soil can be enhanced by microbial activity. The concentrations of iodine in lowland soils, especially those used for rice cultivation, might be decreased by evaporation of biogenerated methyl iodide from the soil-plant system[91]. Filamentous fungi also significantly influence the mobility and speciation of iodine in soil through volatilization and accumulation[92].

The loss of iodine from solution in organic and carbonated sandy soils can be decreased by the presence of chloride and the remaining iodine is then associated with the dissolved organic carbon (DOC) at a slow rate[93]. The interaction of radioactive iodide and radioactive iodate in the soil was studied and the grain size of the soil was found to influence the distribution coefficient of radioactive iodate. The iodate adsorption mechanism was found to be a simple ion exchange, whilst that of iodide was more complex. The uptake of both species was found to decrease over the pH range 3.2 – 10.6 [94]. Schegel et al[95] reported that the organic iodine bound to humic acids and fulvic acids were stable in deep aquifers[95]. Peatland may be a major reservoir of iodine in the terrestrial environment from the last glacial period. The inorganic iodine in peat is transformed into organic iodine compounds by humification. This organic iodine is then stored and remains in the area[96].

The sorption of iodide on the inorganic components of sediment depends on the specific surface area of the minerals and on the salinity. Carboniferous particles, organic substances and microorganisms play role as iodine traps in the sediment with irreversible sorption. The amount of reactive organic materials and microorganisms in those traps and the specific activity of radioactive iodine influences the competence of radioactive iodine sorption by those traps[97]. The

concentrations of ^{129}I in a Spanish sediment core were found to vary with depths[98]. The reduction of iodate to iodide can occur from the mediation by Fe (II) in clay minerals. The sorption and transportation behavior of different iodine species in sediment collected from various depths are different because of their different physico-chemical properties[99].

1.4 Contamination of the environment with radioactive iodine

Many radioactive isotopes of iodine are produced by the fission of uranium atoms during the operation of a nuclear reactor. These include ^{129}I, ^{131}I, ^{132}I, ^{133}I, ^{134}I and ^{135}I. Most are short-lived isotopes, but ^{129}I and ^{131}I, cause a longer term exposure problem. Radioactive iodine forms as gaseous fission products within the fuel rods of the reactor and can leak into the environment as a result of corrosion of the rods. It will then mix with reactor coolant water and will leave the reactor as airborne, liquid and solid wastes. Nuclear reprocessing plants are an additional source of ^{129}I release into the environment. ^{129}I can be released as airborne, liquid and solid forms during the dissolution of spent fuel rods in strong acid[7].

Both of these radioisotopes will disperse and accumulate in the environment until they decay. Some information on the sources and inventory/releases of ^{129}I and ^{131}I are summarized in **Table 1.3**. A nuclear power reactor can produce huge quantities of ^{129}I and ^{131}I but these should not be released during normal operation. Nuclear reactor accidents and leakage from the reactor system can however disperse radioactivity into the environment.

The contamination of the environment with radioactive iodine is of interest due to the large quantity of radioactive iodine (^{129}I and ^{131}I) that has been released (**Table 1.3)**. Weapon testing has been an important pathway for the distribution of fission products throughout the World. Short lived radioactive iodine (especially ^{131}I) from the detonation can reach to the stratosphere, but decays before it reaches the troposphere. Dry and wet deposition remove radioactive iodine from the troposphere to the Earth's surface[100]. The emissions of gaseous radioactive iodine from nuclear reactor accidents such as there that occurred at Chernobyl, Windscale and the Three Mile Island, and those from nuclear fuel reprocessing plants, are the

main anthropogenic sources of radioactive iodine into the atmosphere. Their dispersal depends on weather conditions such as wind direction and speed.

Table 1.3 Sources and inventory/releases of ^{129}I and ^{131}I.

Source	Inventory/release (Bq)	
	^{129}I	^{131}I
Nuclear weapon tests	$3.59x10^{11}$	$7.8x10^{20}$
Chernobyl accident	$8.18x10^{9}$	$1.3x10^{18}$
Production from nuclear reactor	$4.28x10^{14}$ (a)	$2.8x10^{18}$ (b)
Windscale accident	-	$5.9x10^{14}$
Marine discharge from European nuclear fuel reprocessing plant until 2007	$3.27x10^{13}$	-
Atmospheric release from European nuclear fuel reprocessing plant until 2007	$2.77x10^{12}$	-
Nature	$1.57x10^{12}$	-

The estimation of ^{129}I inventory/releases is adapted from Hou et al (2009)[8] by converting the quantity of ^{129}I (kg) to activity (Bq) and calculated by using specific activity of ^{129}I ($1.7x10^{-4}$ Ci g^{-1}). The information of ^{131}I releases from nuclear detonation and nuclear reactor accidents are decay corrected to 3 days after shutdown or detonation (from Betti, 2000[101]). [a]An estimated quantity of ^{129}I was been produced in nuclear power reactors between 1980 and 2005. [b]The activity of ^{131}I is from the production of a nuclear power reactor at a power level of 3000 MW thermal in operation for 1 year.

The quantity of ^{129}I in the oceans has been increased by releases from nuclear activities such as weapon testing, nuclear fuel reprocessing discharge, the nuclear accident at Chernobyl and authorized or non-authorized dumping of radioactive waste. The discharge of low level waste from nuclear fuel reprocessing plants at La Hague and Sellafield into the sea is the most important anthropogenic source of ^{129}I into the oceans[102]. Radioactive iodine is believed to affect the global cycle of stable iodine due to the similarity of their chemical and physical properties. Some examples of studies in which radioactive iodine has been monitored from nuclear fallout are as follows.

After a nuclear accident at the JCO Uranium Fuel Company in Japan, environmental samples such as soil, mugwort, dry leaves and pine needles from the surrounding area were collected and measured by gamma ray spectrometry. Iodine-131 and iodine-133 could be detected in mugwort samples, with concentrations which varied according to their distance from the facility and when they were collected. The activity concentrations of ^{133}I in mugwort samples that had been collected at the boundary of the facility were greater than 1 kBq kg^{-1} at the time of the accident[103]. Iodine-129 in milk and vegetation samples from Sellafield were determined by using neutron activation analysis (NAA). The concentration of ^{129}I in the milk was found to range from undetectable to 16.1 mBq L^{-1}, whilst the concentrations of ^{129}I in vegetation samples were in the range of 162 to 705 mBq kg^{-1} [104]. Bowlt et al[105] studied the activity concentrations of ^{125}I and ^{129}I in sheep thyroids which were collected in Birmingham in the UK. Some sheep thyroid samples were found to contain ^{129}I that might have originated from the Sellafield nuclear reprocessing site. From 37 thyroid samples, the activity concentrations of ^{129}I in only six thyroids were found to be more than 10 mBq g^{-1}. The ^{125}I in sheep thyroids (4.5 – 14.1 mBq g^{-1}) might however have originated from hospital, research establishments and manufacturers releasing into rivers in the East Midlands and in the Thames Valley[105].

1.5 The global iodine cycle

In the environment as a whole iodine speciation is diverse and dependant on environmental conditions. In the aquatic environment, the presence and distribution of iodine species differs in various water types. The important factors of those are the hydrological and temporal profiles of the location and biological activity. Iodine species can be released from the water resources, especially oceans, to the atmosphere via many pathways including biological activity, photolysis and ozonation. The gaseous organic iodine emitted from biogeochemical processes in soil is another input of iodine to the atmosphere. These iodine species can be the precursors of new atmospheric particles and a cause of ozone depletion. Dry and wet depositions are the major routes of removal of iodine from the atmosphere to the Earth's crust. The accumulation and transportation of iodine species in soil and lithosphere depend on the physico-

chemical properties of iodine species, microbial process and depths. Iodine can associate with organic matter, aluminium, iron, and clay. The removal of iodine from soil occurs by volatilization, crop-harvesting and leaching into rivers and ground waters. Plants can take up iodine from soil, accumulating it in specific parts. The ingestion of these plants is a major route by which iodine enters animals. Many biogeochemical processes: volatilization, accumulation, reduction, oxidation and sorption of iodine are influenced by microorganisms. The anthropogenic radioactive iodine, such as the ^{129}I released from nuclear facilities, can contaminate both the environment and humans by entering the global cycle of iodine. Amachi[106] summarized the biogeochemical cycle of iodine in the global environment as illustrated in **Figure 1.5**.

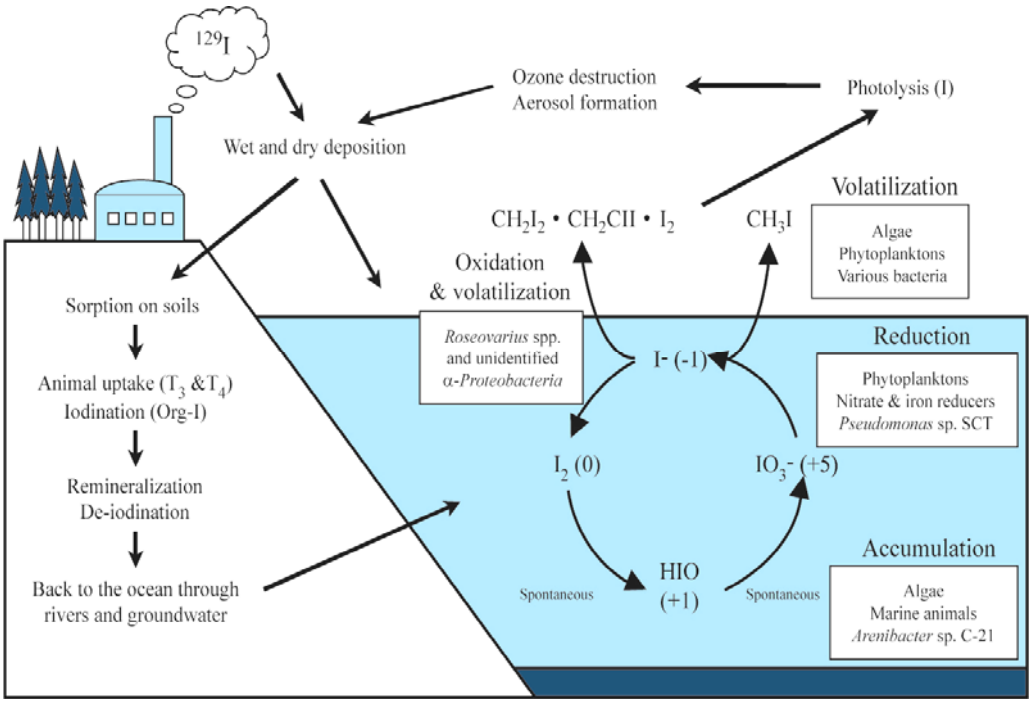

Figure 1.5 The biogeochemical cycling of iodine in the global environment including ^{129}I. The oxidation states of iodine are in parenthesis (after Amachi[106]).

1.6 Conclusion

Iodine and its isotopes are present in the environment by natural occurrence and man-made activities. Iodine is an essential element for the synthesis of thyroid hormones in animals and its radioisotopes are widely used in the field of nuclear medicine and environmental study. Iodine can be present as organic or inorganic

forms. Iodate and iodide are the most important inorganic forms of iodine in an aqueous system. The behavior of iodine is considerably complex with various processes in the environmental system. Different iodine species have different behavior. The releases of radioactive iodine from nuclear activities have to be of concern because of the long lives of some isotopes (^{129}I and ^{131}I). Due to their similar physico-chemical properties to the stable isotope, the environmental behavior of radioisotopes of iodine is believed to be similar to the stable iodine. It implies that the contamination by radioactive iodine may have a significant influence on the global cycle of stable iodine. Knowledge of behavior of radioactive iodine is therefore required to assess its environmental impact.

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CHAPTER 2 The measurement of iodine

Although the total concentration of iodine in a sample is more commonly determined, it can be present as many chemical forms (species) depending on conditions in the system. A knowledge of the total iodine concentration is therefore not sufficient to explain its reactions or behavior and the analysis of iodine species has been therefore introduced. A chemical species has been defined as a specific form of an element such as its isotopic composition, molecular or complex structure and/or oxidation state. Speciation analysis is therefore identification and measurement of the quantities of one or more individual chemical species in a sample[1].

A number of analytical methods are currently available for the measurement of iodine and its isotopes. Understanding the behavior of stable and radioactive iodine has required the development of analytical methods to identify and measure their chemical forms. The speciation analysis of radioactive iodine is often more difficult than that of stable iodine due to its presence at trace levels in the environment. Analytical techniques and separation methods which have been used in the measurement and monitoring of stable and radioactive iodine species are reviewed in this Chapter

2.1 Analytical techniques for the measurement of stable iodine and its species

2.1.1 Spectrophotometric and spectrofluorometric methods

The chemical forms of iodine in a variety of sample types can be identified and measured by using spectrophotometric and spectrofluorometric methods. The various iodine compounds such as I^-, I_3^-, I_2, I_2Cl^- and ICl_2^- which were simultaneously present in a brine solution was determined by using a spectrophotometer. The concentration of each iodine compound could be calculated by using its absorbance at the appropriate wavelength[2]. Other chemical forms of iodine such as periodate and iodate could be analyzed by spectrofluorometric method. Periodate (IO_4^-) in kelp samples could be determined by spectrofluorometrically after reaction of the periodate with paracetamol, giving a detection limit of $4x10^{-8}$ mol L^{-1} [(3)]. For the determination of iodate in salt

samples, a resonance scattering spectral method was introduced. The reaction of iodate with excess iodide under acidic conditions produced triiodide, which then combined with rhodamine 6G for measuring with a spectrofluorometer. The intensity of the resonance scattering intensity was proportional to the concentration of iodate. The detection limit of this method was 5.25 μg L^{-1} for iodate[4].

2.1.2 Flow injection analysis

Flow injection analysis (FIA) has been applied to the determination of iodide, iodate, periodate and iodine. For example, iodate and periodate in aqueous samples were simultaneously determined by using FIA with spectrophotometric and spectrofluorometric detection. The injected sample was split into two streams. In the first stream, periodate selectively oxidized Alizarine Navy Blue to a fluorescent product. In another stream, periodate and iodate were reduced by iodide to iodine which could then be determined spectrophotometrically. The detection limits of this method were 0.7 mg L^{-1} and 0.1 mg L^{-1} for periodate and iodate, respectively[5]. FIA with amperometric detection has also been developed for the determination of iodate in iodized table salt, giving a detection limit of 0.5 mg L^{-1} iodate[6].
The sensitivity of the FIA can be improved to determine iodine and iodide at the ppb level. For example, continuous flow and stopped flow injection could determine total iodine in urine sample based on the catalytic effect of iodine on the reaction between Ce (IV) and As (III). The detection limits of continuous and stopped-flow injection systems were 2.3 μg L^{-1} and 3.0 μg L^{-1}, respectively[7]. High sensitivity can be achieved with a chemiluminescence detection system based on acidic potassium permanganate. The detection limit of this method was 12.7 μg L^{-1} of iodide[8].

2.1.3 Electrochemical techniques

Electrochemical techniques such as cathodic stripping voltammetry, differential pulse polarography and differential pulse voltammetry have been employed for the determination of iodate, iodide and organic iodine in seawater[9-11]. Cathodic stripping voltammetry can be employed for the determination of iodine in biological samples using zephiramine as an ion association agent. The detection

limit of this method was 0.1 mg L^{-1} [12]. Amperometric detection, using electrodes such as a modified platinum electrode[13] and a silver-based solid carbon paste electrode[14], has been used with ion exchange chromatography for the determination of iodide in samples such as milk, wastewater, vegetables, iodinated drugs and table salts. Another chemical form of iodine, elemental iodine, in aqueous solution could be determined by using adsorptive stripping voltammetry after liquid-liquid extraction of the iodine, followed by conversion to iodoform. The detection limit of this method was 20 nM (or 2.5 µg L^{-1})[15].

2.1.4 Chromatographic techniques

Chromatographic techniques are widely used for the separation and measurement of iodine species. Liquid chromatography has been employed for the isolation and determination of iodate, periodate, iodide and organic iodine. High performance liquid chromatography (HPLC) using a C_{18} column, with a mobile phase consisting of acetronitrile and 0.1% of aqueous phosphoric, has been developed for the separation and measurement of periodate, iodate and iodide and also applied to determine iodine species from the oxidative cleavage of the steroid 4-androstene-3,17-dione[16]. Pre-column derivatisation of iodide to 4-iodo-2,6-dimethyphenol gives good HPLC performance by introducing a chromophore and the method was applied to determine iodide in natural water, iodized salt, milk, seawater and pharmaceuticals, with a detection limit of 5 µg L^{-1} [17].

An ion-pair chromatography is a type of ion chromatographic method that has been used to analyze the chemical species of iodine such as iodide in surface seawater. This method was achieved by using C_{18} reversed-phase column coated with 1 mmol L^{-1} of cetyltrimethylammonium in a mixture of water and methanol (56:44%, v/v). Sodium chloride was used as a mobile phase and a detection system was an UV or amperometric detection without an interference from high concentration of salt[18]. Ion Chromatography using Dionex AS-11 column has also been employed for the determination of iodine species such as iodide in ground water and soil[19], and iodide, iodate and organic iodine in seawater[20].

A number of other chromatographic methods have been applied to the determination of iodine species. For example, size exclusion chromatography with UV detection has been developed to determine iodide in seawater and urine. This method was based on the oxidation of iodide followed by forming a complex with starch, giving a detection limit of 0.2 μg L^{-1} [21]. Gas chromatography (GC) is commonly applied to the determination of volatile iodine species for instance iodine in soil[22] and organic iodine compounds in air samples, seawater samples[23] and humic substances[24]. Precolumn derivatisation has been used with the GC to analyze inorganic forms of iodine; for example iodide is converted to pentafluorophenoxyethyl iodide, a detection limit of 2.7 nmol L^{-1} can be achieved[25].

The sensitivity and selectivity of chromatographic techniques for the determination of iodine species can be improved by coupling with other analytical techniques. For example, three chromatographic techniques coupled with an inductively coupled plasma-mass spectrometry (ICP-MS) were employed to study iodine species in commercially available commonly consumed seaweeds. The association of iodine with various molecular weight fractions was investigated by separating inorganic iodine from organically bound iodine and analyzing by the size-exclusion chromatography coupled with ICP-MS. There were the associations of iodine with high and low molecular weight fractions in two commercial seaweed sample types. Anion exchange chromatography (coupled with ICP-MS) was used for the speciation of inorganic iodine species and it showed that iodide was the predominant form in the seaweed samples. The major species of iodine in enzymatic extracts from the seaweed samples were iodide, monoiodotyrosine and diiodotyrosine which were identified by reversed-phase HPLC with ICP-MS detection[26].

2.1.5 Mass spectrometry

Mass spectrometric methods are employed to analyze iodine and its isotopes with high sensitivity. Inductively coupled plasma-mass spectrometry (ICP-MS) has been used to determine trace stable and radioactive iodine in various samples. There is however a systematic problem in the use of this technique arising from a

memory effect of iodine. The technique has however been employed to determine iodine in natural and tap water samples without separation and preconcentration achieving a detection limit of 10 ng L^{-1} [27]. Isotope dilution mass spectrometry, another type of mass spectrometric technique, has been developed to study iodine species such as particulate iodine, iodide, iodate, HI, I_2, HOI and organic iodine in aerosol samples[28-30]. The electrospray-mass spectrometry of iodine can be carried out in i-C_3H_7OH:H_2O:$CHCl_3$ (8:2:0.5, v/v) with a detection limit of ~0.1 µg L^{-1} [31].

2.1.6 Neutron activation analysis

Neutron activation analysis (NAA) is a nuclear analytical technique that has high sensitivity and accuracy for iodine analysis. However, the disadvantages of this technique are that it is slow, has high running costs, and requires special skills and apparatus. Separation methods are necessary pre- or post-irradiation to remove interferences. Although, this technique has been commonly used to determine the concentration of total iodine in a variety of environmental samples, many researchers have also developed this technique for studying the chemical species of iodine. For the determination of iodine in biological and nutritional samples by NAA, a sample preparation step has been developed using microwave acid digestion followed by co-precipitation with bismuth sulfide. The detection limit of this method was low being 5 ng of iodine[32]. A polymer inclusion sorbent was introduced for the enrichment of iodine species prior to analysis. This method could be applied to the determination of iodate, iodide and total iodine in milk and milk powder[33]. An anion exchange method was used to separate iodide and iodate from aqueous samples and then applied to the determination of iodide and iodate in urine, milk and seawater, gave a detection limit of 10 ng for iodine[34].

2.2 Measurement of radioactive iodine

2.2.1 Analytical techniques for the measurement of radioactive iodine

The half-lives and the nature and energy of the emissions of radioisotopes of iodine vary significantly and are important factors to be considered when choosing which analytical techniques to employ. Radioactive iodine can be measured

directly in the field using portable survey instruments such as those based on Geiger-Mueller detector, sodium iodide scintillation detector and gamma ray spectrometers. In the laboratory, the commonly used analytical techniques are radiochemical methods employing γ-ray spectrometry and β-γ coincidence scintillation techniques, neutron activation analysis (NAA) and mass spectrometry[35].

As the most significant radioisotope of iodine in the environment, ^{129}I was chosen for initial investigation using the newly developed methods in this research work. The characteristics and appropriate analytical techniques for measuring ^{129}I are therefore only described in this Section.

The characteristics of ^{129}I

Iodine-129 ($T_{1/2}$ = 15.7x10^6 years) occurs naturally when high energy particles interact with xenon in the upper atmosphere and through spontaneous fission of ^{238}U in the lithosphere. It can be also produced from the fission of ^{235}U or neutron irradiation of Te. Its specific activity is 6.29x10^7 Bq g^{-1} [36]. The radiation data of ^{129}I in general use for radiochemical analysis is summarized in **Table 2.1**[37].

Table 2.1 The major emissions from ^{129}I (from Kocher[37])

Type of the emission	Energy (keV)	Intensity (%)
Beta	152.4	100
Gamma	39.6	7.5
$K_{\alpha 1}$ X-ray	29.8	37
$K_{\alpha 2}$ X-ray	29.5	20
K_{β} X-ray	33.6	13.2
L-1 Internal, conversion electrons	34.1	10.7

The decay scheme and beta spectrum of ^{129}I were studied by Mateosian and Wu[38]. Iodine-129 emitted beta particles at 150±5 keV to an exited level of 39 keV. Then, ^{129}I emitted 39 keV gamma rays converting to ground state ^{129}Xe. Iodine-129 also emitted Xe K X-rays (K_{α} and K_{β} lines) and a L conversion line from the internal

conversion of gamma ray emission. The decay scheme of ^{129}I is illustrated in **Figure 2.1.**

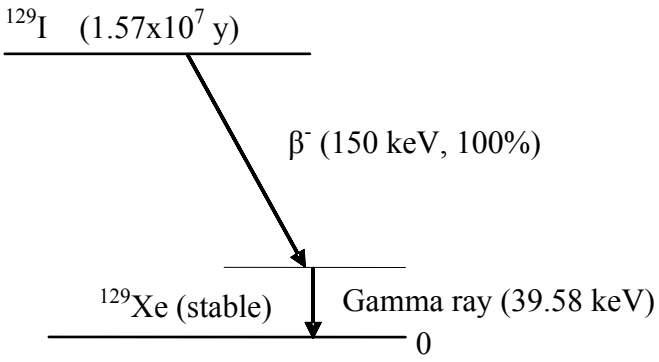

Figure 2.1 The major decay pathways of ^{129}I (after Eldridge et al[39]**)**

The analytical techniques for the measurement of ^{129}I

The radiometric methods that have been commonly used for ^{129}I measurement are liquid scintillation counting (LSC) and low energy gamma ray spectrometry. The radiation characteristics and low specific activity of ^{129}I cause self absorption in low energy decays, and it needs a long time for counting. Gamma ray spectrometers, using detectors based on NaI(Tl), Ge(Li) and high purity germanium (HPGe) have been used to detect the gamma rays or X-rays arising from ^{129}I. For example, Eldridge et al[39] proposed a high resolution Ge(Li) well detector to measure the K_α X-rays at 29.7 KeV and K_β X-rays at 33.6 keV for ^{129}I. The absolute detection efficiency at 29.7 keV was 72% and the detection limit for the K_α X-rays was 0.01 Bq [39]. Liquid scintillation counting is an alternative practical method for efficiently measuring the beta emission of ^{129}I. This method can also detect auger and conversion electrons from gamma radiation. Separation methods are however required to remove impurities and other radionuclides from the ^{129}I when analyzing environmental samples by liquid scintillation counting and gamma ray spectrometry.

NAA has been used to determine ^{129}I via the ^{129}I $(n,\gamma)^{130}I$ ($T_{1/2}$ =12.4 hours) reaction. A radiochemical separation such as ion exchange[40], alkaline fusion[41] and pyrohydrolysis followed by solvent extraction[42] is necessary to purify the ^{129}I from Cs, U, Te and Br which are the main interferences of this method. The ^{129}I in a

sample can be expressed as either total activity or total mass. Mass spectrometry, such as inductively coupled plasma- mass spectrometry (ICP-MS) and accelerator mass spectrometry (AMS), can be used to analyze ^{129}I. Hou et al[43] reviewed and compared radiochemical and mass spectrometric methods for the determination of ^{129}I as summarized in **Table 2.2**.

Table 2.2 A comparison of radiochemical and mass spectrometric methods for the determination of ^{129}I in environmental, biological and nuclear waste samples

Techniques	Advantages and disadvantages
Radiochemical methods	
Gamma ray spectrometry (HPGe detector)	Low counting efficiency, low gamma-ray abundance, high background, high detection limit (20-200 mBq for waste samples[44])
Liquid scintillation counting	Lower detection limit than gamma ray spectrometer (approximate 10 mBq for seaweed samples[45])
Radiochemical neutron activation analysis (RNAA)	Low background and low detection limit (1 μBq for environmental samples[46])
Mass spectrometric methods	
Accelerator mass spectrometry	Low background and low detection limit (10^{-9} Bq for environmental samples[47])
Inductively coupled plasma-mass spectrometry	Low ionization efficiency, isobaric and molecular ions interferences, memory effect and low abundance sensitivity (detection limit = 37 μBq mL^{-1} for water samples without preconcentration[48])

Table 2.2 (Continued)

Techniques	Advantages and disadvantages
Secondary ion mass spectrometry	Direct and in vivo analysis but high detection limit (5 Bq for thyroid samples[49])

2.2.2 Examples of the determination of radioactive iodine

Radioisotopes of iodine can sometimes be directly measured in environmental samples but separation techniques are frequently necessary when there is a low level activity of radioactive iodine, or there is a high level of interference. Some examples of separation methods and analytical techniques for measuring radioactive iodine in various sample types will now be described.

In air samples

Iodine-129 was measured in air samples collected from the plutonium-uranium extraction plant of the Hanford site during its operation and after closure. Stack samples were collected using silver-impregnated zeolite cartridges and analyzed using a low background high purity germanium diode gamma ray spectrometer. Vapour phase air samples were collected by drawing air through a glass fiber pre-filter to remove particulates and then through a chemically treated, low background petroleum-based charcoal cartridge. The air samples were prepared using several purification steps and then measured with AMS and NAA. Measurements at different distances from the source indicated that the ^{129}I in the locality came from atmospheric emission from the Handford site[50]. I-129 in atmospheric samples collected from Spain was investigated by collecting from air with a triethylenediamine-activated charcoal filter. These filters were extracted and then iodine precipitated as AgI before AMS was employed to measure the ^{129}I. The range of concentrations of ^{129}I was (0.71 - 4.28) $x10^{-16}$ g m^{-3} [(51)]. Another radioisotope of iodine, ^{131}I, was studied in the atmosphere of New York by collecting with an activated charcoal canister and measuring by gamma ray spectrometry. A detection limit of $2.3x10^{-11}$ g m^{-3} was achieved[52].

In biological materials

For the determination of ^{129}I in seaweeds, the samples were prepared by combustion, anion exchange disk extraction and solvent extraction. These samples were then measured by AMS and NAA with detection limits (as $^{129}I/^{127}I$ ratio) of 10^{-14} and 10^{-8}-10^{-9}, respectively[53]. The NAA was employed for determining ^{129}I in milk and vegetation samples. Iodine-129 in the milk samples was extracted onto anion exchange resins prior to irradiation. The vegetation samples were prepared by digestion under an alkaline reflux followed by anion exchange extraction. After being irradiated, iodine from the samples was removed from the resin and then precipitated as AgI. The detection limits of this method were found to be below 10 mBq L^{-1} for milk and 10 mBq kg^{-1} for vegetation[40].

In water samples

Iodine-129 contents and its behavior in various types of water sample have been studied by many analytical methods. For example, the distribution and sources of ^{129}I in Swedish rivers was investigated by Kekli et al[54]. Iodine-129 in the water sample was extracted, precipitated and then measured by AMS. The routine detection limit of ^{129}I was 2.14×10^{-15} g L^{-1} for a 100 mL sample. The concentrations of ^{129}I were found to be related to the concentrations of Cl and other chemical parameters. An important source of ^{129}I in Swedish rivers was from atmospheric fallout and volatilization from seawater, which came from atmospheric and liquid discharges from the Sellafield and La Hague nuclear fuel reprocessing plants[54]. The concentrations of ^{129}I in Northern European precipitation and surface water samples were determined by AMS. These samples were prepared by using chemical extraction followed by precipitation as AgI. The results showed that ^{129}I concentrations were 10^8-10^9 atoms L^{-1} ((2.14 - 21.4) $\times 10^{-14}$ g L^{-1}) in precipitation and (2-5) $\times 10^8$ atoms L^{-1} ((4.28 - 10.7) $\times 10^{-14}$ g L^{-1}) in surface water samples[55].

In soil & sediment

For the determination of ^{127}I and ^{129}I in sediment collected from an Irish lake, sediment samples were prepared by drying and grinding to a fine powder. Iodine was extracted from the sample by combustion followed by precipitation. The AgI precipitate was then measured by AMS. The total inventory of ^{129}I in the lake

sediment was found to be approximately 29 mBq m^{-2}. The accumulation of ^{129}I in the lake sediment could used to retrospectively search for evidence of the 1957 Windscale fire in North East of Ireland and it showed that it was a negligible contribution to an increase in the ^{129}I concentrations in this area[56]. An ICP-MS with hexapole collision cell can be employed to determine the $^{129}I/^{127}I$ isotope ratio in soil samples. Iodine-129 in the soil was introduced into the ICP-MS by thermal desorption from solid material and online into the system via a gas phase. The direct measurement of ^{129}I gave a detection limit of $3x10^{-11}$ g g^{-1} [(57)]. NAA was employed to determine ^{129}I in soil and grass samples from areas surrounding the reprocessing plant. The samples were prepared by wet oxidation using chromic acid, distillation and anion exchange. Radioisotope ratios of $^{129}I/^{127}I$ were (0.1 - 6.12)$x10^{-6}$ for the soil samples[58].

2.3 Measurement of radioactive iodine species

As with the stable iodine, radioactive iodine can be presented as organic or inorganic forms. The analytical methods used for determining only total activity or the concentration of radioactive iodine may not be suitable to analyze its species. Although the speciation analysis of radioactive iodine has increased in the last decade, few research works have investigated new methods for this approach. Examples of speciation analyses of radioactive iodine will now be described.

In environmental samples

Tracer experiments have been used to determine the chemical forms of radioactive iodine in water and soil samples. Muramatsu et al[59] proposed isotope exchange and anion exchange methods for this approach. The results showed that iodate in rain water (unfiltered) and milk changed to iodide, whereas iodide in seawater and tap water was converted to iodate. The chemical forms of ^{131}I in Japanese rain collected after the Chernobyl accident was studied and it was found to be 59% iodate and 35% iodide[59]. The interaction of radioactive iodide and radioactive iodate in the soil could be studied by using a radiotracer. Soluble and suspended fractions of soil samples were measured using a liquid scintillation counter. The pH conditions were found to affect the uptake of both radioactive iodine species. The concentration of iodine carrier influenced the solid-liquid distribution

coefficient (K_d) of both radioactive iodine species, but the grain size of the soil was only found to influence the K_d of radioactive iodate. The adsorption mechanism of iodate onto soil was found to be a simple ion exchange, whilst that of iodide was based on more than one sorption mechanism[60].

An anion exchange method has been employed to separate radioactive iodine species from water samples. This analytical method was developed for the determination of ^{129}I and ^{127}I species in seawater collected from Kattegat and Baltic Sea. Iodate, iodide and total inorganic iodine were isolated from seawater by an anion exchange method and then concentrated by solvent extraction. The iodine species were then precipitated as LiI for analyzing by NAA giving the detection limits of 7 nmol L^{-1} and $2.3x10^{-15}$ mol L^{-1}, for ^{127}I and ^{129}I, respectively. The concentrations of ^{127}I and ^{129}I species were found to be different between depths and locations[61]. The isotopic ratios of ^{129}I /^{127}I as various species in estuarine surface water has been studied by Schwehr et al[62]. The chemical forms of ^{129}I as iodide, iodate and total iodine were isolated by using anion exchange methods. Each species was then extracted by liquid extraction and then precipitated as AgI for analysis by AMS. The concentration of dissolved organic iodine (DOI) could be calculated from the difference between the total iodine and the sum of total iodide and iodate. The isotopic ratio of $^{129}I/^{127}I$ as dissolved organic iodine could be used as a terrestrial organic carbon tracer in the estuarine surface water[62].

In samples from nuclear activities

The speciation of ^{129}I in spent solvent (tributyl phosphate/odourless kerosene) from nuclear fuel reprocessing was studied from its x-ray absorption near-edge structure (XANES). The XANES spectrum of solvent samples showed that iodine was most probably present as an organoiodide species, when compared with eight reference compounds containing iodine in oxidation states from -1 to +7 [63]. The presence of radioactive iodine species in a boiling water reactor was studied by Lin[64]. He modified the exchange-extraction procedure for the isolation of radioactive iodine species from various sample types. All radioactive samples were measured with a gamma ray spectrometer using a Ge(Li) detector. Iodide and possibly hypoiodous acid (HIO) were the predominant forms in reactor water and condensate samples under normal operation, whilst iodate was found to be the major species during a

reactor shutdown. Organic iodine was the predominant species in an off-gas sample[64]. An ion chromatographic method has been developed for the isolation of iodate, iodide and molecular iodine from aqueous samples. Conductivity and Cs(I) scintillation detectors simultaneously measured for both stable and radioactive iodine species, and the radioactivity measurement was suitable for the study of carrier free samples. This method could be applied for determining radioactive iodine species in the cooling water of a nuclear power plant[65].

2.4 Aim and scope of study

In order to assess the contamination of radioactive iodine in the environment, many analytical techniques have been developed. Information as to the total quantity of radioactive iodine may not be sufficient for evaluating its effects on the environment and its bioavailability. Knowledge of the distribution mechanisms and pathways to the biogeochemical processes is necessary for understanding the fate of radioactive iodine in the environment. This will lead to the possibility of making an assessment of its safety and its impact on the environment. Radioactive iodine can change to various chemical forms in the environment. Therefore, a speciation analysis of radioactive iodine is required to obtain information that is not yet available.

The concentration of radioactive iodine in the environment is generally much lower than that of stable iodine which is present at ppb level. For example, the pre anthropogenic $^{129}I/^{127}I$ ratio is approximately 10^{-12} in marine sediments[66]. The post anthropogenic $^{129}I/^{127}I$ ratio has increased to be higher than 10^{-12} and it varies in different environmental samples[67]. The implication is that the concentration of ^{129}I in the environment has been increased by Man's activities. The speciation analysis of radioactive iodine requires the development of techniques that are different from those employed to study stable iodine.

The aim of this study is therefore to develop new analytical methods for the identification and measurement of radioactive iodine species in aqueous environmental samples. ^{129}I which is generally considered to be the most significant radioisotope of iodine released from nuclear facilities sites, especially

the discharge from nuclear fuel reprocessing plants, was chosen for this study. The main chemical forms of radioactive iodine for which speciation analysis is required in aqueous environmental samples, are iodate and iodide.

The main objectives of this study are therefore: 1) Select the appropriate methods for the identification and measurement of radioactive iodine species in aqueous samples and initially develop the new method by using the stable iodine species (to minimize unnecessary exposure of radioactive materials). 2) Adapt these methods to collect and measure individual ^{129}I species in the aqueous samples and 3) apply the developed method to the determination of ^{129}I species in aqueous environmental samples.

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EXPERIMENTAL

CHAPTER 3 The development of a derivatisation-solid phase extraction procedure for iodine speciation

3.1 Introduction

Many conventional analytical techniques have been developed to detect iodide and iodate in water samples. Some analytical approaches, particularly those employing electrochemical techniques, can measure iodide and iodate in water directly through such procedures as differential pulse polarography and cathodic square wave voltammetry[1]. These analytical techniques are not however suitable for measuring radioactive iodate and radioactive iodide. An approach involves derivatisation of iodide and iodate to iodo-derivatives that can then be collected in an extraction/preconcentration step and then measured. Derivatising agents such as 2,6-dimethylphenol[2], acetone[3], 2-(pentafluorophenoxy) ethyl 2-(piperidino) ethanesulfonate[4], *N,N*-dimethylaniline[5], 2,6-dimethylaniline[6-7] and alcoholic KOH solution[8] have all been used. Such procedures can possibly be adapted and developed for collecting the radioactive iodine species present in water samples.

The conversion of inorganic iodine species to 4-iodo-*N, N*-dimethylaniline (IDMA) has been chosen as the basis of new approaches to the determination of stable and radioactive iodine species in water. Its reaction is both fast and selective for three iodine species; namely iodate, iodide and elemental iodine. This chapter describes the development of a new approach to the determination of stable iodine species (iodate and iodide) that exploits this derivatisation chemistry. The increased sensitivity of this method is an important factor for the determination of trace levels of iodine. After the derivatisation, solid phase extraction (SPE) was to be employed for the enrichment step with the collected IDMA being determined by HPLC with UV detection.

3.2 Chemicals and apparatus

Water used in all experiments was purified (resistivity > 5MΩ.cm at 25 °C) using an ELGASTAT OPTION 4 Water Purifier. Sodium hydroxide (laboratory reagent

grade), acetonitrile, tetrahydrofuran (THF) and methanol (HPLC grade) were purchased from Fisher Scientific (Leicestershire, UK). Disodium hydrogen orthophosphate (anhydrous, analytical grade), potassium iodate (analytical grade), sulfuric acid (98%, w/v, analytical grade), acetic acid (analytical grade), potassium dihydrogen phosphate (analytical grade) and L-ascorbic acid (analytical grade) were purchased from VWR (UK). 2-iodosobenzoic acid (97%) was purchased from Alfar Aesar (Lancashire, UK). *N,N*-dimethylaniline (ReagentPlus^{TM} 99%) and DSC-18 (Supelco: 6 mL and 500 mg adsorbent) solid phase extraction (SPE) cartridges were purchased from Sigma-Aldrich (Poole, UK). Isolute^{TM}-C18 SPE cartridges (Biotage: 10 mL and 500 mg adsorbent) were purchased from Kinesis Ltd (Cambridgeshire, UK).

A sodium 2-iodosobenzoate (IBZ, $1.5x10^{-2}$ mol L^{-1}) solution was prepared by stirring 400 mg of 2-iodosobenzoic acid with a slight molar excess of sodium hydroxide (7.6 mL of 0.2 mol L^{-1} sodium hydroxide), diluting to 100 mL with water and filtering through a 0.45 μm membrane filter (Whatman). This solution was reported to be stable for at least 4 months at ambient temperature[5]. A *N, N*-dimethylaniline solution (DMA, $1.58x10^{-2}$ mol L^{-1}) was prepared by adding 200 μL of DMA to 100 mL of methanol.

Standard iodate and iodide solutions were prepared by dissolving appropriate quantities of potassium iodide and potassium iodate respectively in water. The phosphate buffer (pH 6.4) was prepared by dissolving 2 g of potassium dihydrogen orthophosphate and 1.59 g of disodium hydrogen orthophosphate in 50 mL of water, and the pH was adjusted to 6.4. Ascorbic acid solution (0.1 mol L^{-1}) was prepared by dissolving 881 mg of ascorbic acid in 50 mL of water. Acetic acid solution (1% v/v) was prepared by adding 1 mL of glacial acetic acid to 50 mL of water and diluting to 100 mL with water.

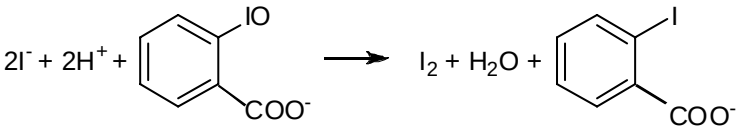
A Perkin-Elmer, Lambda 25 UV/VIS spectrophotometer was used to obtain absorption spectra of IDMA in acetonitrile. IDMA was measured by reverse-phase HPLC with isocratic elution. The HPLC system used in this study was a Beckman Module 126 progammable solvent delivery system with a Module 166 programmable ultraviolet detector set at 266 nm. Manual injection was employed

using a Rheodyne 7125 injector fitted with a 50 μL loop. The column was a 5 μm SymmetrySheild RP8 column (3.9x150 mm). The mobile phase was acetonitrile:water (55:45) at a flow rate of 1.5 mL min^{-1}. Data was processed using Beckman System Gold Chromatography Software (version 8.1) and output onto an Epson FX-800 printer.

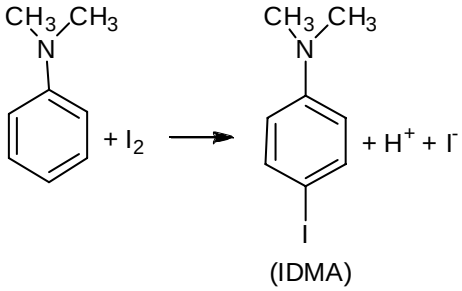
3.3 Derivatisation of iodine species to 4-iodo-*N,N*-dimethylaniline (IDMA)

The derivatisation of iodine species to 4-iodo-*N,N*-dimethylaniline (IDMA), was adapted from the procedure described by Mishra et al[5].

Iodide (I^-) is oxidized by excess 2-iodosobenzoate (IBZ) at pH 6.4 (**Equation 3.1)**. The released iodine then reacts with *N,N*-dimethylaniline (DMA) to give IDMA (**Equation 3.2**). The iodide that is formed will then re-enter **Equation 3.1** leading to the quantitative conversion of all iodide to IDMA. The IDMA that is formed can then be extracted by SPE and determined by HPLC.



(3.1)

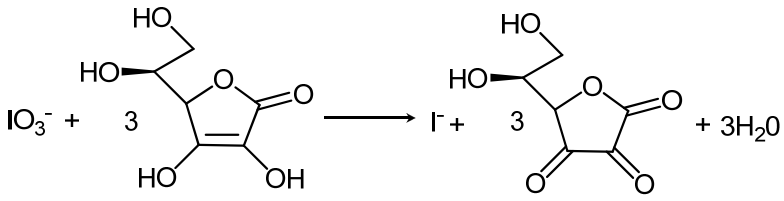


(3.2)

This derivatisation method can be used to determine elemental iodine in the absence of the IBZ reagent (**Equation 3.2**).

Iodate (IO_3^-) does not produce iodo-derivatives under the same derivatisation conditions used for iodide. Iodate has first to be reduced by ascorbic acid to iodide (**Equation 3.3**) in an acidic medium. The resulting iodide is then oxidized by IBZ and the iodine iodinates the DMA to IDMA (**Equation 3.1 and 3.2**). Any

remaining ascorbic acid must be oxidized by excess 2-iodosobenzoate to avoid the iodine being reduced by residual ascorbic acid[2, 5].



(3.3)

The redox potential of 2-iodosobenzoic acid at 25 °C is reported to be 1.21 V at pH 1.1, 1.08 V at pH 2, 0.53 V at pH 4 and 0.48 V at pH 7[9], and its selectivity as an oxidizing agent for iodide has been already reported[5, 10-11]. Only iodine, with a redox potential of 0.54 V[12], is therefore produced under pH neutral or feebly acidic conditions. Mishra et al[5] also reported that bromide, which is found in seawater, did not interfere with these reactions (**Equation 3.1&3.2**). Bromide could only be oxidized to bromine (redox potential = 1.06 V [12]) by using IBZ reagent under acidic conditions, so there was no bromine to convert iodide to iodate, or to brominate DMA to bromodimethylaniline. In the case of chloride, the redox potential of chlorine was 1.39 V[12] and chloride was not therefore oxidized by the IBZ reagent at a pH between 5 and 7[6].

Other oxidizing agents such as permanganate[13], peroxymonosulfate[14] and chloramine T[15-17], which have been used to oxidize iodide and bromide, were not suitable for this purpose because either iodide would be converted to iodate or bromine would be produced from bromide which would then convert iodide to iodate.

DMA was chosen to be the iodine scavenger as iodination occurs only at the *para* position due to steric hindrance of the 2 *ortho* positions by the large dimethylamino group[18]. The oxidation of iodide and iodination of DMA could occur at pH between 5 and 7, but the optimum pH was 6.4. When DMA and IBZ reagents were mixed at pH 6.4, there were no reports of obvious reactions[5].

Mishra et al [5] studied potential interferences by derivatising iodide (20 μg L^{-1}) in the presences of a number of foreign substances. The potentially influencing factors of the analysis were:

(a) Organic compounds such as aniline and phenol could be iodinated like DMA. Such organic compounds had to be removed before the derivatisation.
(b) A large quantity of IBZ reagent had to be employed to avoid the IBZ reagent being depleted by the ascorbic acid.
(c) Quantities of chloride, bromide, nitrate, phosphate, perchlorate, sulfate, hydrogencarbonate, ammonium, calcium, magnesium, zinc, cobalt and cadmium greater than those of the iodide by a factor of 1000.
(d) Quantities of sulfide, thiosulfate, sulfite, thiocyanate, nitrite, iron (II) and manganese (II) were produced at more than six times that of the iodide.

The synthesis of IDMA

4-iodo-*N,N*-dimethylaniline (IDMA) was synthesized using a procedure reported by Adimurthy et al[19]. First, 1.03 g of potassium iodide and 0.66 g of potassium iodate were dissolved in 30 mL of water. After stirring until it dissolved, 5 mL of methanol was added to the mixture, stirred for a while and 1.1 mL of *N, N*-dimethylaniline (DMA) was added to the mixture. Next, 9 mL of hydrochloric acid (1 mol L^{-1}) was slowly added over 45 minutes and then the mixture was continually stirred for 3 hours. The solution was diluted with 50 mL of deionized water and extracted 3 times with 25 mL of dichloromethane. The organic phase was washed with 100 mL of sodium thiosulphate (5% w/v), 100 mL of deionized water and 100 mL of brine. After drying with anhydrous sodium sulphate, the product was concentrated under reduced pressure to give a thick oil. Further purification was carried out by crystallization from cold hexane to afford a pale blue crystalline product.

The nuclear magnetic resonance spectrum of the product was recorded using a Bruker AV300/2 NMR spectrometer and was the same as that reported by La Clair [20]. ^{1}H NMR (300MHz, $CDCl_3$) δ 7.47 (2H,d, CH=CNCH, J = 8.85 Hz), 6.5(2H, d,

CH=CICH, *J* =8.85 Hz, 2H) and 2.93 (6H, $(CH_3)_2N$, s). ^{13}C NMR (75 MHz, $CDCl_3$) δ 40.36, 115.1, 137.56 and 150.03. Positive ion electrospray mass spectrometry gave a major peak at 248 m/z [$M+H^+$].

3.4 The measurement of IDMA by HPLC

3.4.1 Appropriate conditions of HPLC detection system

This section describes the optimization of the HPLC system, taking into account column choice, eluent components and flow rate for the separation of IDMA from other sample components.

Experimental procedure and results

The chemical properties of IDMA were firstly tested. It was found that IDMA dissolved well in moderate polarity solvents such as acetonitrile and methanol. IDMA dissolved in acetonitrile had a UV absorption maximum at 266 nm that was adopted for the HPLC detection system.

Initial separations were carried out on a Hichrom Spherisorb S5ODS1 C-18 column (250x4 mm i.d.) at room temperature and eluted with 1.5 mL min^{-1} of acetonitrile:water. Stock solutions of IDMA and *N,N*-dimethylaniline solution (DMA) were prepared in acetonitrile, and diluted with 50% (v/v) acetonitrile:water to better match the HPLC eluent composition.

The DMA and IDMA were resolved, but the peaks tailed. The retention times of IDMA using a variety of acetonitrile: water eluents are shown in **Table 3.1**

Table 3.1 The retention of IDMA on a Hichrom Spherisorb S5ODS1 C-18 column.

Ratio of acetonitrile:water	Retention time of IDMA (min)
40:60	18.42
50:50	7.75
60:40	4.26
80:20	2.27

Improved performance was achieved using a 5 μm phenyl-3 column (Phenomenex, 150x4.6 mm i.d.) at room temperature and eluted at 1.5 mL min^{-1} with varying ratios of acetonitrile:water. The DMA and IDMA were resolved well with a good peak shape. The retention times of DMA and IDMA, using a mobile phase of 40% (v/v) acetonitrile:water, were 3.98 and 8.96 min, respectively (**Table 3.2**). These conditions were adopted for the determination of IDMA.

Table 3.2 The retention of IDMA on a 5 μm phenyl-3 column.

Ratio of acetonitrile:water	Retention time of IDMA (min)
35:65	14.29
40:60	8.96
50:50	4.17
65:35	2.90
80:20	1.57

Over time, the efficiency of the 5μm phenyl-3 column decreased and a replacement was required. A 5μm SymmetryShield RP8 column (150x3.9 mm i.d.) was found to be suitable when eluted at 1.5 mL min^{-1} with 55% (v/v) acetonitrile:water. DMA and IDMA were well resolved giving retention times of 2.65 and 4.72 min, respectively (**Table 3.3**).

Table 3.3 The retention of IDMA on a 5 μm SymmetryShield RP8 column.

Ratio of acetonitrile:water	Retention time of IDMA (min)
40:60	27.96
45:55	11.21
55:45	4.72
70:30	2.39

Discussion and Conclusions

Three reversed phase columns: (1) Hichrom Spherisorb S5ODS1 C-18, (2) Phenyl-3 and (3) SymmetryShield RP8 with various ratios of acetonitrile:water as the mobile phase were investigated for the separation of IDMA. Although the Hichrom Spherisorb column could resolve the IDMA and DMA, the peak shapes exhibited

tailing. Phenyl-3 and SymmetryShield RP8 columns could both resolve IDMA and DMA very well, so both columns were used for the resolution of IDMA. The optimum conditions for the determination of IDMA by HPLC are to use a 5 μm SymmetrySheild RP8 column (3.9x150 mm) eluted with acetonitrile and water (55:45) at a flow rate of 1.5 mL min^{-1}. The column eluate was monitored by UV detector set at 266 nm.

3.4.2 Calibration graphs for various concentration ranges of IDMA

Calibration was carried out using external standards prepared from synthetic IDMA. A typical calibration graph for the IDMA determination by HPLC is shown in **Figure 3.1**. This linear calibration graph (from five concentration levels) was obtained for 6.75 to 54 μmol L^{-1} of IDMA with a coefficient of determination (R^2) of 0.9995.

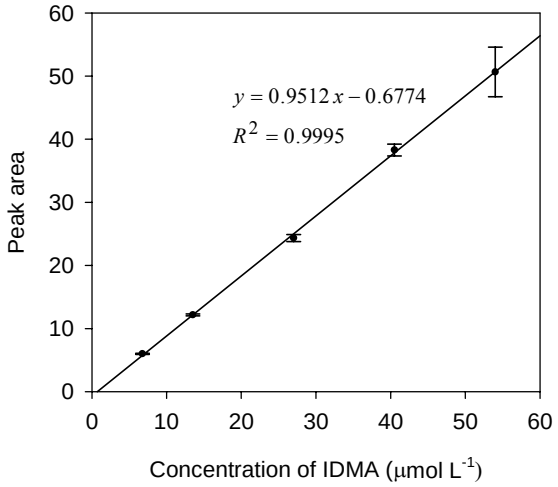


Figure 3.1 A typical calibration graph from the determination of 4-iodo-*N,N*-dimethylaniline (IDMA) by HPLC.

The HPLC system could determine IDMA concentrations below 1 μM. A linear calibration graph was obtained for 0.12 to 0.8 μmol L^{-1} of IDMA with a coefficient of determination (R^2) 0.9927 (**Figure 3.2**). The estimated detection limit from slope of this calibration graph was 0.08 μmol L^{-1} IDMA.

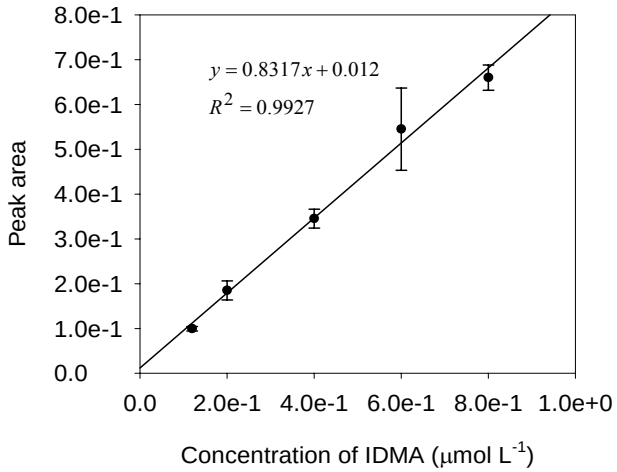


Figure 3.2 A calibration graph for HPLC determination of 4-iodo-*N,N*-dimethylaniline (IDMA) at concentrations below 1 μmol L^{-1}.

3.5 Solid phase extraction (SPE) of IDMA

An extraction method is required for separating IDMA from the other organic compounds which might occur from the derivatisation and interfere with the analysis. Liquid-liquid extraction[5], solid phase microextraction and single drop microextraction[7] have been used to extract IDMA from aqueous samples. This research work has introduced solid phase extraction (SPE) for the extraction of IDMA because it is a simple method, which can simultaneously extract and enrich IDMA from aqueous samples, and it can reduce the volume of organic solvent from the extraction.

SPE is widely used for sample clean up, enrichment and phase transfer. SPE is performed in a mini-column packed with a suitable sorbent. The SPE can perform offline sequence or online-coupling with other analytical techniques[21-22]. This research has chosen and used the C_{18} silica-based reversed phase sorbent for adsorbing the IDMA from aqueous samples. The fundamentals underlying SPE are the same as reverse phase liquid chromatography. The sorbent which is packed in the SPE cartridge is a stationary phase. An aqueous sample is passed through the SPE cartridge resulting in organic compounds of moderate to low polarity being retained on the sorbent. An appropriate organic solvent is then used to desorb the

organic compound from the sorbent. The organic compound in an eluate from the SPE cartridge can then be determined by using appropriate analytical techniques.

3.5.1 An appropriate organic solvent for the elution of IDMA

The partitioning of IDMA between a C_{18} bonded HPLC stationary phase and its eluting solvent is governed by the same principles as the IDMA partitioning between the SPE adsorbent and its eluent. Information derived from the HPLC of IDMA on a C_{18} column could be therefore be usefully employed in the development of conditions under which 4-iodo-*N,N*-dimethylaniline (IDMA) could be extracted and released from SPE cartridges containing C_{18} silica. The first stage was to identify appropriate organic solvents with which to elute the IDMA from the C_{18} sorbent of the SPE cartridge.

Experimental procedure and results

First of all, the Isolute^{TM}-C18 SPE cartridge was prepared by activating with 5 mL of methanol and equilibrating with 5 mL of water. It was connected to a peristaltic pump to collect the IDMA from the water by passing the aqueous solution through the SPE cartridge at a flow rate of approximately 0.7 mL min^{-1}. The peristaltic pump was then removed from the SPE cartridge and the IDMA on the SPE sorbent was then recovered for measurement by gravity elution using 5 mL of acetonitrile (as shown in **Figure 3.3)**. The eluted IDMA was diluted to 10 mL with water and then determined by HPLC.

Figure 3.3 The apparatus for collecting the IDMA from the SPE sorbent.

A mean recovery of 70.8±3.0 % (n = 5) was achieved for the enrichment of 1 μmol L^{-1} IDMA from water (100 mL).

A problem was encountered with the recovery of IDMA when DSC-18 SPE cartridges were used instead of Isolute^{TM}-C18 SPE cartridges. Whilst these cartridges are superficially similar, the volume of acetonitrile needed for the quantitative elution of IDMA from the DSC-18 SPE cartridge was four times greater than was required for the elution of IDMA from the Isolute^{TM}-C18 SPE cartridge.

Hexane, ethyl acetate, tetrahydrofuran (THF) and methanol were then evaluated for the recovery of IDMA from the DSC-18 SPE cartridge and the Isolute^{TM}-C18 SPE cartridge. THF and methanol were found to be more suitable than hexane and ethyl acetate.

The volume of methanol and THF needed to elute IDMA from the DSC-18 SPE cartridge was investigated. 5 mL aliquots of methanol or THF were used to elute the IDMA from the DSC-18 SPE cartridge at a flow rate of approximately 2 mL min^{-1}. 15 mL of methanol eluted the IDMA from the cartridge with a recovery of 69.9±14.9%, while only 5 mL of THF was needed to elute the IDMA giving a recovery of 75.1±10.1%.

THF (5 mL) was then evaluated for the elution of IDMA from both types of SPE cartridge. The mean recovery of IDMA from the DSC-18 SPE cartridge was 93.6±4.8% (n = 3) and from the Isolute^{TM}- C18 SPE cartridge was 94.8±1.0% (n = 3).

Discussion and conclusions

Initially, acetonitrile was employed to elute IDMA from Isolute^{TM} C-18 SPE cartridges, but this gave a poor mean recovery of only 70%. The volume of acetonitrile required to elute IDMA from the DSC-18 SPE cartridge was four times higher. This difference is believed to be due to minor differences between the SPE sorbents.

The Isolute™ C-18 silica is not end-capped but the DSC-18 silica is (**Figure 3.4**). Non end-capped C-18 sorbents have the high surface density of secondary silanol groups. These are blocked in the end-capped materials, leading to both higher loading and greater overall hydrophobicity. Hence, IDMA loaded onto a non end-capped C-18 sorbent could be eluted by acetonitrile more readily than IDMA which had been loaded on an end-capped C-18 sorbent.

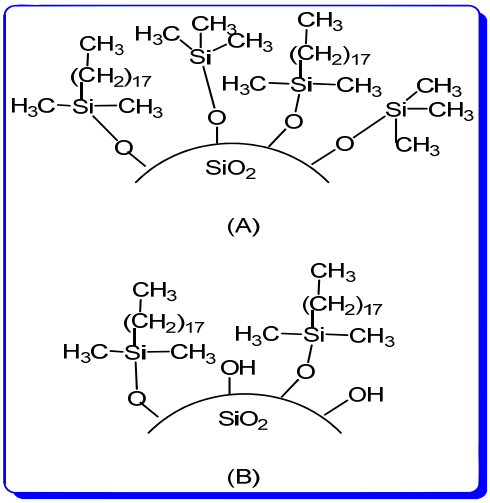


Figure 3.4 Chemical structures of (A) end-capped C-18 silica particles and (B) non end-capped C-18 silica particles.

Of the organic solvents (hexane, ethyl acetate, methanol and THF) tested to elute IDMA from both types of SPE cartridges, THF was found to be the most efficient with only 5 mL being required to elute IDMA from both types of SPE cartridges.

3.5.2 The optimum flow rate for loading IDMA onto the SPE cartridge

Flow rate is a critical factor in determining the efficiency with which IDMA can be extract from water. This factor was therefore studied.

Experimental procedure and results

A stock standard solution of IDMA (1.1 mmol L^{-1}) was prepared by dissolving 12.3 mg of IDMA in 50 mL of THF. IDMA solutions ($1.6x10^{-5}$ mol L^{-1}) were prepared by transferring 0.4 mL of IDMA (1.1 mmol L^{-1}) to 25 mL volumetric flask and diluting to the mark with water. These solutions of IDMA ($1.6x10^{-5}$ mol

L^{-1}) were extracted, as in the procedure above, but with a varying flow rate. 5 mL of THF was used to elute the IDMA from the SPE cartridges and the eluate volumes were adjusted to 10 mL with water. These solutions were analyzed by HPLC.

The IDMA recoveries were 93.4±4.4%, 91.3±6.5% and 95.7±5.6%, respectively for flow rates of 1.11, 2.18 and 3.43 mL min^{-1}.

Discussion and conclusions

IDMA could be loaded on the SPE sorbent with recoveries of better than 90% using any of the tested flow rates. A flow rate of 2.18 mL min^{-1} was chosen for further studies.

The optimized procedure for the extraction of IDMA from water

The trial procedure for the extraction of IDMA using solid phase extraction (SPE) was as follows. The aqueous sample solution was passed through the SPE cartridge using peristaltic pump to pull the sample solution through the SPE cartridge at a flowrate of 2.18 mL min^{-1}, and the eluate was discarded. In the case of samples obtained from the derivatisation, a phosphate buffer (pH 6.4, 5 mL) was used to wash the SPE cartridge after passing the sample through it, and the eluate was then discarded. The PVC pump tubing was removed from the SPE cartridge and the IDMA was eluted from the SPE cartridge (under gravity) with 5 mL of THF. The eluate was collected, adjusted to 10 mL with water and analyzed by HPLC.

3.6 The determination of iodide

Iodide in aqueous solution can be oxidized by 2-iodosobenzoate (IBZ) to iodine at pH 6.4, and the released iodine can then be used to derivatise *N,N*-dimethylaniline (**Equation 3.1&3.2)**. The iodide that is formed will then re-enter **Equation 3.1,** leading to the quantitative conversion of all iodide to IDMA. The IDMA that is formed can then be extracted by SPE and determined by HPLC.

3.6.1 Optimum time for the oxidation of iodide

The rate of iodide oxidation was an important factor for producing a high yield of iodine, which would be a precursor for the next reaction in the derivatisation step. The optimum time for this oxidation would be then investigated.

Experimental procedure and results

First, the method for the conversion of iodide to IDMA reported by Mishra et al[5] was modified as follows.

To a 25 mL volumetric flask was added 10 mL of iodide solution ($4x10^{-5}$ mol L^{-1}), 0.5 mL of the phosphate buffer (pH 6.4), 0.4 mL of sodium 2-iodosobenzoate (IBZ, $1.5x10^{-2}$ mol L^{-1}) and 0.5 mL of *N,N*-dimethylaniline solution (DMA, $1.58x10^{-2}$ mol L^{-1}). The volume was adjusted to the mark with water, shaken and kept for 30 minutes. The IDMA was extracted by SPE and determined by HPLC. The mean recovery of IDMA from this method was 48.4±1.8% (n = 3).

Next, the rate of the oxidation of iodide was studied in more detail. Sample solutions were prepared by transferring 10 mL of iodide (2.2×10^{-5} mol L^{-1}), 0.5 mL of phosphate buffer (pH6.4) and 1 mL of IBZ to 25 mL volumetric flasks. The samples were shaken and kept for various time periods (2, 5, 10, 20, 30, 40, 50 and 60 minutes). 0.5 mL of DMA was then added to each sample and the volume of the sample was adjusted to the mark with water. After shaking and keeping for 30 minutes, the IDMA was extracted by SPE and determined by HPLC. This was ***Method A***. The results are shown in **Figure 3.5.**

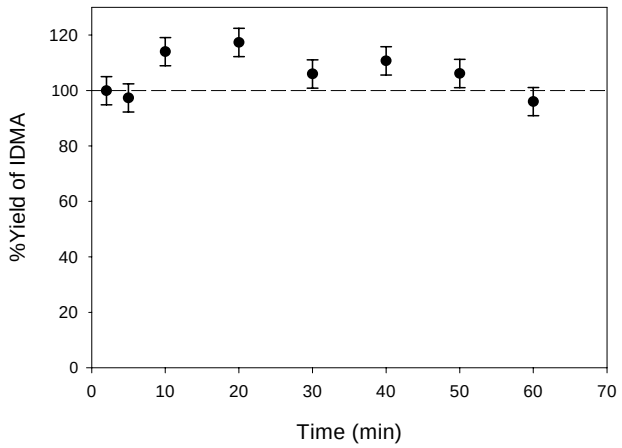


Figure 3.5 The rate of iodide oxidation (error bars represent three standard deviations).

***Conclusion*s**

The oxidation of iodide to iodine by IBZ reagent at pH 6.4 could be completed within 2 minutes, and for this research the time allowed for iodide oxidation was therefore set at 5 minutes.

3.6.2 Optimum time for the iodination

In the conversion of iodide to IDMA, the iodination of DMA was also important (**Equation 3.2**). The optimum time for this reaction was investigated by fixing the time for the oxidation of iodide at 5 minutes.

Experimental procedure and results

The rate of the iodination was investigated by fixing the time for iodide oxidation at 5 minutes. To a 25 mL volumetric flask was added 10 mL of iodide (2.4×10^{-5} mol L^{-1}), 0.5 mL of phosphate buffer (pH6.4) and 1 mL of IBZ. The flask was shaken and kept for 5 minutes. 0.5 mL of DMA was then added and the volume of each sample was adjusted up to the mark with water. The samples were shaken and kept for varying times (1, 5, 10, 20, 30, 50, 60 and 90 minutes) before the extraction of the IDMA and its determination by HPLC. The results are shown in **Figure 3.6.**

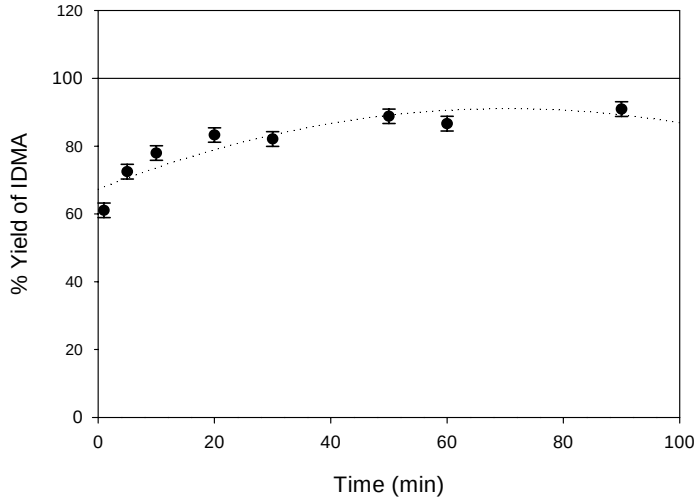


Figure 3.6 The rate of iodination of DMA (error bars represent three standard deviations).

Discussion and conclusions

The iodination of *N,N*-dimethylaniline (DMA) was relatively slow requiring approximate 50 minutes to complete iodination. These results showed that the iodination of DMA could not be completed in the 1 minute specified by Mishra et al[5]. This might be from differences in the experimental conditions between of this research and that of Mishra. This research used SPE for the IDMA extraction and a HPLC as the detection system, whilst Mishra's research used a liquid-liquid extraction for the IDMA extraction and a GC-MS for the detection system. For this research, 60 minutes was therefore the time chosen for the iodination of the DMA.

3.6.3 Adaptation to lower concentration samples

In order to reach the low concentrations of iodide found in many aqueous environmental samples, the concentration-based detection limit of the derivatisation-solid phase extraction procedure had to be decreased. This aim was achieved by increasing the sample volume.

Experimental procedure and results

250 mL of iodide (1.2 μmol L^{-1}) was mixed with 33 mL of phosphate buffer (pH 6.4), 10 mL of IBZ reagent and shaken for 5 minutes. 5 mL of DMA was added and shaken for 60 minutes. This solution was extracted using SPE, eluted and then

the IDMA determined by HPLC, using the conditions as described in section 3.4. The mean yield of IDMA was 110.8±9.7% (n = 3).

Discussion and conclusions

Method A could be successfully adapted to the determination of lower concentrations of iodide by increasing the sample volumes to 250 mL. A good mean recovery of IDMA was obtained from this adapted method with an enrichment factor of 25 times. Sample volumes larger than 250 mL could potentially improve the detection limit further. This method is judged to be suitable for use as the standard method for the determination of iodide in aqueous samples. A chromatogram of IDMA from the determination of iodide in water (250 mL) is shown in **Figure 3.7**.

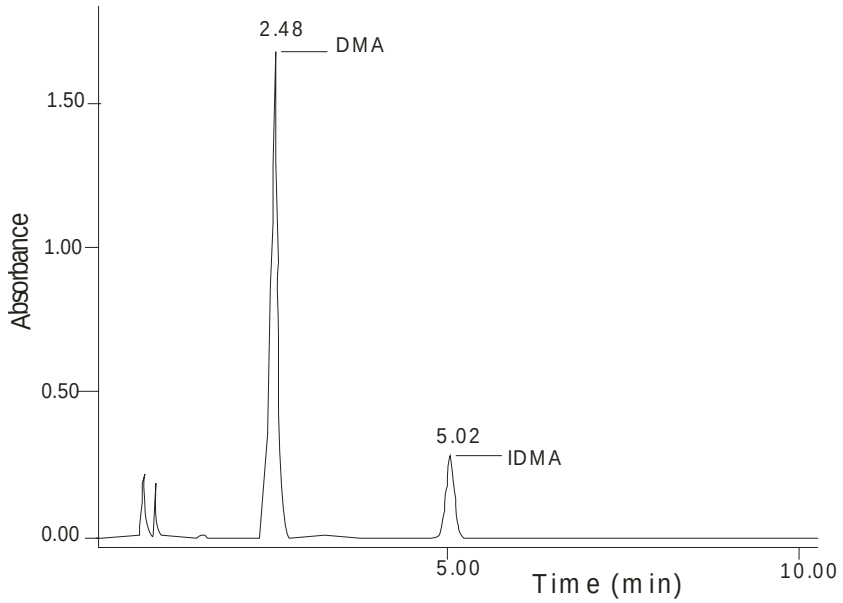


Figure 3.7 A chromatogram of a 1.2 μmol L^{-1} iodide (250 mL sample) derivatised to 4-iodo-*N,N*-dimethylaniline (IDMA, retention time 5.02 minutes) showing its resolution from residual *N,N*-dimethylaniline (DMA, retention time 2.48 minutes).

3.7 Determination of iodate

Iodate can be reduced with ascorbic acid in acid medium to iodide (**Equation 3.3**) and then determined as in ***Method A*** (**Equations 3.1&3.2**). ***Method A*** and the derivatisation method for the determination of iodate as reported by Mishra et al[5]

have been modified and developed for the extraction and preconcentration of IDMA using SPE and analysis by HPLC.

3.7.1 The iodate reduction

The collection of iodate as IDMA using SPE would require it to be first reduced to iodide by ascorbic acid. The impact of residual ascorbic acid on the other derivatisation reactions (iodide oxidation and DMA iodination) had therefore to be evaluated.

Experimental procedure and results

In an initial study, two samples of iodide solution were tested. 0.5 mL of ascorbic acid (0.01 mol L^{-1}) was added to 10 mL of iodide solution (~ $4x10^{-5}$ mol L^{-1}), kept for 30 minutes and then iodide was measured using ***Method A***. This reduction-derivatisation method was named ***Method B***. The time allowed for the iodination of the DMA was set to 30 minutes for one sample and 120 minutes for the other sample.

At this stage both ***Method A*** and ***Method B*** had been tested for the extraction-preconcentration of iodide but not for iodate. When 10 mL of iodide solution (~$4x10^{-5}$ mol L^{-1}) was measured using ***Method A*** (i.e. without ascorbic acid), the yield of IDMA after the DMA addition at 30 minutes was 83.4±2.8% and after 120 minutes was 87.8±1.3%.

No IDMA had formed using the 30 minutes reaction time but a 73.5±0.4% yield was obtained when left for120 minutes from testing with ***Method B***. From this result, it was evident that the iodination of DMA was slow and not completed within 30 minutes, but was so within two hours. It was deduced that ascorbic acid decreased the rate of iodide oxidation, due to the IBZ concentration having been reduced by the ascorbic acid.

10 mL of iodate solution (~$4x10^{-5}$ mol L^{-1}) was then tested by using ***Method A*** and ***Method B*** and the time allowed for the iodination of the DMA was set to 30 minutes for one sample and 120 minutes for another sample. No yield of IDMA

was found from using the ***Method A*** with setting the iodination time at 30 minutes or 120 minutes. The results obtained from using ***Method B*** showed that the yields of IDMA were 78.1±1.6% for 30 minutes and 97.6±2.2% for 120 minutes.

Ascorbic acid reduction of iodate to iodide is reported to be favored by acid conditions. Another method for the extraction of iodate was therefore developed using an acidic medium. This ***Method C*** was adapted from the procedure reported by Mishra et al[5]. Details of ***Method C*** are;

To a 25 mL volumetric flask, 10 mL of iodate (4×10^{-5} mol L^{-1}), 1 mL of acetic acid (1%v/v) and 0.5 mL of ascorbic acid (3 mmol L^{-1}) were added, shaken and kept for 30 minutes. Then, 0.5 mL of phosphate buffer (pH6.4) and 0.4 mL of IBZ (1.5×10^{-2} mol L^{-1}) were added. The sample was shaken and kept for 30 minutes. 0.5 mL of DMA (1.58×10^{-2} mol L^{-1}) was added and the volume of the sample was adjusted up to the mark with water. After keeping for 30 minutes, the IDMA was extracted by SPE with flow rate of 2.18 mL $min^{-1}$and analyzed by HPLC. The yield of IDMA was 73.5±7.2%.

Discussion and conclusions

The determination of iodate was investigated using ***Method A*** and the Mishra derivatisation method, ***Method C***. Ascorbic acid was used to reduce the iodate but it also reduced the IBZ reagent[9]. This could cause incomplete iodination of DMA or decrease the rate of reaction of iodide and IBZ. Hence, the concentration of the IBZ reagent had to be higher than that of the ascorbic acid to avoid this problem. Any excess ascorbic acid was then oxidized by the IBZ reagent to avoid the iodine being reduced by the residual ascorbic acid[5, 9-10, 23]. The rate of iodination of DMA was sluggish after adding ascorbic acid. The derivatisation time was therefore extended to two hours to give a good recovery. Furthermore, the concentration of ascorbic acid used for the reduction of iodate under acid condition could be decreased (***Method C***).

3.7.2 Improvement of system sensitivity

To decrease the concentration-based detection limit of the determination, a large volume/ lower concentration iodate sample was introduced, and an optimization of the conditions was sought. The acidity of the solution was important to iodate reduction by the ascorbic acid, but it was not necessary to scale up the volume of ascorbic acid to react with the low quantity of iodate. Any remaining ascorbic acid had to be oxidized by excess IBZ, so that sufficient IBZ was available to form the iodine (I_2). ***Method C*** was therefore adapted for large volume iodate samples.

Experimental procedure and results

250 mL of iodate solution (1.22 μmol L^{-1}) was mixed with 0.5 mL of ascorbic acid (0.1 mol L^{-1}) and 7 mL of acetic acid (1% v/v). After keeping for 30 minutes, 33 mL of the phosphate buffer (pH 6.4) and 10 mL of IBZ (1.5 x 10^{-2} mol L^{-1}) were added, shaken and kept for 30 minutes. 5 mL of DMA (1.58 x 10^{-2} mol L^{-1}) was then added. The mixture was shaken and kept for 120 minutes. This sample was extracted by SPE at a flow rate of 3.43 mL min^{-1}, the IDMA recovered and analyzed by HPLC. It gave a mean yield of 103.0±18.2% (n = 3). The concentration of IDMA measured in blank was high to 0.296±0.004 μmol L^{-1}.

*Discussion and conclusion***s**

Method C could be adapted to decrease the concentration-based detection limit for the determination of iodate by using a larger volume of the sample. The preconcentration factor of iodate with these samples was 25 times and the mean recovery of IDMA using this method was approximately 100%. Therefore, the detection limit of this derivatisation method could be reduced by a factor of 25 times with good repeatability and recovery. This method was therefore the one to use as the standard method for the determination of iodate in aqueous samples. The IDMA found in the blank might be from iodine contamination in the reagents which their quantities were also increased in the method improvement.

3.8 The minimization of iodine contamination in reagents

When the large volume of the sample was introduced so as to decrease the detection limit of the whole procedure, IDMA was found in the blank solution

extracted from the SPE. The iodine impurities could have been from the reagents. When these developed methods enriched the concentrations of iodide or iodate in the sample, they also enriched the concentration of any iodine in the reagents. Sources of iodine contamination in system were therefore investigated.

Experimental procedure and results

The iodine contamination of reagents was studied by varying the volume of each reagent. The results showed that iodine contamination was present in both the IBZ reagent and the acetic acid. Procedures were proposed to minimize the iodine impurities in the reagents.

(1) Purification of acetic acid

Most acetic acid is nowadays manufactured by the carbonylation of methanol and/or methyl acetate with a rhodium or iridium catalyst and through a methyl iodide intermediate[24-25]. A small amount of iodide remains in the acetic acid after production. This research proposed fractional distillation to remove the iodide from the acetic acid.

The purified acetic acid was tested using the standard method for the determination of iodate (250 mL). The concentration of IDMA in the blank was found to have dropped from 0.296±0.004 μmol L^{-1} to 0.148±0.002 μmol L^{-1} (a decrease of about 50%).

(2) Purification of the 2-iodosobenzoate (IBZ) reagent

A re-crystallization method was adapted from that reported for the production of iodosobenzoic acid by Isao[26].

250 mg of 2-iodosobenzoic acid was dissolved in a minimum quantity of NaOH (0.01 mol L^{-1}) to achieve complete dissolution. This solution was acidified using acetic acid (0.1 mol L^{-1}), kept overnight in a fume cupboard and then one hour in a refrigerator. The resulting suspension was filtered and rinsed with cold water. The white powder dried in a vacuum desiccator. This powder was then used to prepare the IBZ reagent.

The purified IBZ reagent was employed to improve the standard method for the determination of iodide (250 mL). The IDMA in blank was found to be 0.073±0.008 μmol L^{-1}.

Discussion and conclusions

The iodine-contamination was from both the acetic acid and the IBZ reagent. These iodine impurities could be minimized by the fractional distillation of the acetic acid and re-crystallization of the 2-iodosobenzoic acid, but small quantities of iodine remained in both reagents. This might be a significant problem for the determination of trace quantities of stable iodine species but should not influence the measurement of radioactive iodine.

3.9 Conclusion

The oxidation of iodide using IBZ combined with DMA iodination at pH 6.4 can be used to convert iodide to an organic derivative that can be extracted by SPE and then determined by HPLC. The iodide oxidation can be completed in 5 min. Iodate can also be derivatized to IDMA by its initial reduction to iodide and then by following the oxidation/ iodination/ SPE route.

The collection and release of IDMA from the Isolute^{TM}-C18 SPE cartridges has been optimized for the collection of iodine species from water. Initially the elution of IDMA from the C-18 SPE sorbent was only 70.8±3.0 % (n = 5) with 5 ml of acetonitrile, but a reinvestigation of elution solvents identified tetrahydrofuran (THF), which gave a mean recovery of IDMA of 94.8±1.0% (n = 3).

Many factors combine to ensure the quantitative conversion of the initial inorganic iodine species to IDMA. The full conversion sequence for iodate involves stages in which reducing and oxidizing agents are added in sequence and each stage requires its own optimum pH. At each stage of the conversion both redox and pH conditions have therefore to be controlled with the 2-iodosobenzoate (IBZ) oxidant being employed to destroy residual ascorbic acid.

The yield of IDMA was related to the rate of iodination with DMA. One hour was sufficient for this reaction unless ascorbic acid was present. Iodate was not converted to IDMA without ascorbic acid, but the addition of this reagent slowed the DMA iodination. The concentration of ascorbic acid could be reduced below 0.01 M, but acidification was then required. From the progress in the development of techniques for the selective collection of iodine species onto reverse phase sorbent of solid-phase extraction (SPE) cartridge, two main approaches were investigated to develop the extraction.

Method A for the collection of iodide-derived iodine is based on the following sequence

$$I^- \xrightarrow{IBZ} I_2 \xrightarrow{DMA} IDMA$$

Method C for the collection of iodide and/or iodate and/or iodine. In this method oxidized iodine species are reduced with ascorbic acid in the acid medium and then the sample is made to undergo the reaction sequence of ***Method A***.

Both ***Methods A & C*** have been successfully adapted and evaluated for both iodide and iodate. Assuming that iodine can be present in any combination of I^-, IO_3^- and I_2 in environmental samples and I_2 can be measured directly through its reaction with DMA (***Method D***), then speciation of individual iodine forms can be measured.

$$\textbf{\textit{Method A}} \Rightarrow [I^-] + {}^1/_2\,[I_2] = C_A$$

$$\textbf{\textit{Method C}} \Rightarrow [IO_3^-] + [I^-] + {}^1/_2\,[I_2] = C_B$$

$$\textbf{\textit{Method D}} \Rightarrow {}^1/_2\,[I_2] = C_D$$

Then:

$${}^1/_2\,[I_2] = C_D$$

$$[I^-] = C_A - C_D$$

$$[IO_3^-] = C_B - C_A$$

The sample concentration based detection limit for the measurement of iodide and iodate as IDMA has been improved by using a large volume of the sample.

Methods A & C were developed and applied to 250 mL of iodide and iodate samples, respectively. Both developed methods gave mean yields of 110.8±9.7% (n = 3) for iodide and 103.0±18.2% (n = 3) for iodate. The preconcentration factor of using large sample volumes was 25 times. The developed methods have, therefore, been used as the standard methods for the determination of iodide and iodate in aqueous samples.

When large sample volumes were employed to increase the sensitivity of ***Methods A & C***, some problems arose from there being iodine contamination of the IBZ reagent and the acetic acid. Re-crystallization and fractional distillation, respectively reduced the iodine contamination of the IBZ reagent and of the acetic acid.

Methods have been developed for the selective collection-preconcentration of iodate, iodide and iodine from aqueous solutions onto reverse phase solid-phase extraction media. The derivatisation-solid phase extraction procedures reported here will be adapted for the collection of the corresponding ^{129}I species and their activities can then be measured by β-γ coincidence scintillation techniques and gamma or X-ray spectrometry.

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Chapter 4 Adaptation of derivatisation-solid phase extraction for radioactive iodine speciation

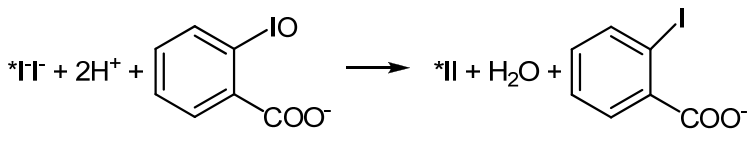
4.1 Introduction

Derivatisation-solid phase extraction (DSPE) methods have been developed (Chapter 3) that have appeared to be promising for testing both stable iodide and iodate in aqueous solution. The next approach taken in this study was to adapt the DSPE methods to the determination of radioactive iodide and iodate, so that they could be use in a speciation analysis of the radioactive iodine in environmental samples. As it is the most significant radioisotope of iodine released from nuclear facilities into the environment, ^{129}I was chosen for study in the initial adaptation of the DSPE methods. The investigation optimized conditions for the extraction and assessed appropriate detection systems for the measurement of ^{129}I species as its radioactive iodo-derivative.

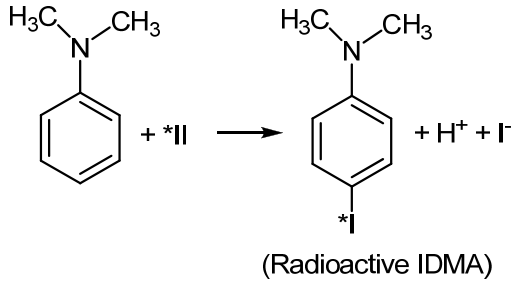
Derivatisation of ^{129}I species

The derivatisation of stable iodine species to 4-iodo-*N,N*-dimethylaniline (IDMA) (described in Section 3.3) is employed for use with ^{129}I species. The details of the derivatisation of radioactive iodine species are as follows.

The radioactive iodide will be converted to radioactive iodine by 2-iodosobenzoate reagent (IBZ) at pH 6.4 (**Equation 4.1**). The released radioactive iodine will then iodinate DMA to radioactive 4-iodo-N,N-dimethylaniline (**Equation 4.2**). The free radioactive iodide will re-enter **Equation 4.1&4.2** until depletion. The radioactive IDMA will be extracted by SPE and then measured by LSC.



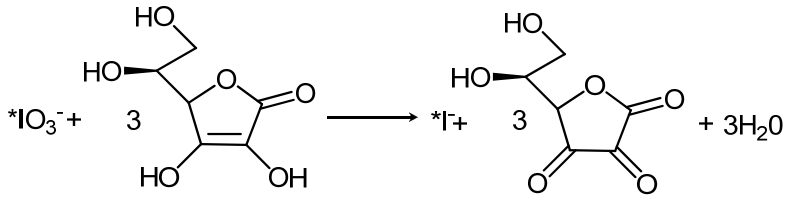
(4.1)



(4.2)

Where *I = radioactive iodine

Radioactive iodate, will be first reduced by ascorbic acid to radioactive iodide in acid medium (**Equation 4.3**).



(4.3)

This radioactive iodide will be oxidized to iodine and then converted to radioactive IDMA (**Equation 4.1&4.2**). In addition, radioactive iodine that is present as elemental iodine can be derivatised to radioactive IDMA in the absence of the IBZ reagent (**Equation 4.2**).

4.2 Chemicals and apparatus

The chemicals used for the DSPE procedure were specified in Chapter 3. Nitric acid (70%, w/v, analytical grade), sodium formate (99.0+%, Certified AR), hydrochloric acid (37%, w/v, analytical grade) and sodium hypochlorite (available chlorine ≥ 8%) were purchased from Fisher Scientific (Leicestershire, UK). The Gold Star liquid scintillation cocktail was purchased from Meridian Biotechnologies (Surrey, UK). Eichrom anion exchange resin (1 x 8, Cl^- form, 100-200 mesh) was purchased from Eichrom Europe Laboratories (France). The standard solution of ^{129}I (as iodide, 4600 Bq g^{-1}) solution was purchased from Amersham International (Buckinghamshire, UK).

The following solutions were prepared. Iodide solution (0.08 mol L^{-1}) was prepared by dissolving 0.332 g of potassium iodide in 25 mL of water. Nitric acid (HNO_3, 3 mol L^{-1}) was prepared by adding 18.75 mL of concentrated HNO_3 to 70 mL of water in a 100 mL volumetric flask and diluting to the mark with water. Sodium hypochlorite (NaOCl, 0.8%, v/v) was prepared by transferring 8 mL of NaOCl to 50 mL of water in a 100 mL volumetric flask and diluting up to the mark with water. Sodium formate (33.3%, w/v) was prepared by dissolving 50 g of sodium formate in 100 mL of water.

A Quantulus 1220 Ultra Low Level Liquid Scintillation counter (Perkin-Elmer) was used for measuring the beta particle emission from ^{129}I. This instrument is suitable for counting low levels of alpha and beta radiation, Cerenkov radiation, X-rays, Auger electrons, gamma radiation and luminescence. Two photomultiplier tubes were used for background event detection and further two separate photomultiplier tubes in the sample detector were used for counting the sample. The natural background is removed by coincidence event detection, without affecting the sample detection. The beta spectrum is discriminated by a pulse shape analyzer which can be used for background reduction in beta counting to cut out a slow fluorescence event background. The WinQ user interface, protocol editor and data acquisition program is used to control the performance of the LSC. The sample spectrum was analyzed by the Easy View spectrum analysis program (Version 1.0.3.4)[1].

Gamma ray spectrometry using a Canberra low energy germanium (LEGe) detector was employed to measure the gamma ray or X-ray radiation from ^{129}I. The configuration of the LEGe consisted of a vertical dipstick cryostat with Be window and 30 L Dewar, pulsed optical feedback or resistive feedback preamplifier with cooled FET and 3 meter bias, signal and power cables. The spectral deconvolution program Fitzpeaks (version 3.58, JF Computing) was used to analyze the gamma spectra. For the measurement of ^{129}I, standard solutions of ^{129}I in the same matrix and geometry as the sample solution were employed for calibration.

4.3 The measurement of ^{129}IDMA by LSC

Radiochemical and mass spectrometric methods have been used for determining ^{129}I in various sample types (**Table 2.2)**. Whilst mass spectrometry, particularly AMS and RNAA are high sensitivity methods for measuring ^{129}I in the environmental samples, their running costs are high and special skills and apparatus are required. A low energy gamma ray spectrometer and LSC were therefore employed for developing new methods in this research work. LSC was chosen for the initial development of the DSPE procedure because it offered high counting efficiency, specificity for radioactive iodine and low running costs. Its detection limit for measuring ^{129}I was also lower than that of low energy gamma ray spectrometry.

Important factors to be considered when liquid scintillation counting ^{129}I

There are two important factors to be considered:

(i) The liquid scintillation cocktail

The selection of a suitable liquid scintillation cocktail is an important aspect of the preparation of samples for analysis by LSC. The sample should dissolve homogeneously in the cocktail to ensure an efficient transfer of energy from the sample to the cocktail. There are three major components of the cocktail:

1. An organic aromatic solvent: toluene, xylene, pseudocumene (1,2,4-trimethylbenzene), diisopropylnaphthalene (DIN or bis (isopropyl) naphthalene), phenylxylylethane (PXE or 1,2-dimethyl-4-(1-phenylethyl)benzene) and dodecylbenzene (LAB or tetrapropylene-benzene)

2. A scintillator (or fluor): two scintillators are usually added in cocktails: 2, 5-diphenyloxazole (PPO) is used as the first scintillator and p-bis-(o-methylstyryl) benzene (bis-MSB) is used as the secondary scintillator.

3. An emulsifier (or surfactant): dioxane and methyleneglycol is added to the cocktail for the determination of water or aqueous samples to improve the dispersion of water in the aromatic solvents.

Liquid scintillation cocktails based on bis (isopropyl) naphthalene, 1,2-dimethyl-4-(1-phenylethyl)benzene, tetrapropylene benzene, benzyl toluene and 2-phenylethane are both higher performanced and safer than the classic cocktail. The safer cocktail has a high flash point, low release of volatiles, low toxicity, easy transport and storage and less hazardous[2-3]. With commercial liquid scintillation cocktails, the manufacturers often do not show detailed compositional information. Some examples of liquid scintillation cocktails used for the determination of ^{129}I are as follows.

In 1965, Rhodes[4] prepared 8 different scintillation solutions for the counting of ^{129}I (as iodide). The results showed that all the scintillation solutions could be used for counting ^{129}I with counting efficiency range of 96 - 121%[4]. Ross and Stockton[5] investigated an extractive-reactive scintillator based on cyclohexane for the low level determination of ^{129}I in environmental samples. ^{129}I was converted to elemental iodine which would then rapidly react with olefins in the cocktail under visible or ultraviolet photon excitation. This reaction produced diiodocyclohexane which has been thought to minimize quench in the cocktail. This method could determine 0.004 Bq of ^{129}I with a counting time of 5 minutes[5]. The Quicksafe-A cocktail was used for the identification of ^{129}I as iodoorganic compounds in kerosene from a nuclear fuel reprocessing plant. A solid phase extraction was used to separate ^{129}I from other fission product and the purified kerosene sample was then separated by HPLC and measured by LSC. The results showed that there were polar and non polar iodoorganic compounds in the kerosene. This commercial cocktail is based on DIN [6].

This study used a Gold Star multi-purpose liquid scintillation cocktail for mixing with the ^{129}IDMA derived from the DSPE methods. Gold Star scintillation cocktail is based on DIN which is a biodegradable and non-hazardous solvent. Its characteristics are low photo- and chemiluminescence, a high flash point of 144

˚C, no smell, low vapor pressure (1 mm Hg at 25 ˚C) and low toxicity (LD50 5,600 mg kg^{-1} oral rat)[7].

(ii) Quench and quench correction

The counting efficiency of LSC can be reduced by quenching which is produced from various chemical or physical processes in the sample solution mixed with the liquid scintillator. The quench reduces the light photon output of the scintillation solution and also the counts per minute (CPM) detected by LSC. It shifts the position of radionuclide emission peak to lower channels. The effect of quench on the counting efficiency of radionuclides is found to be greater in the lower energy of a beta emission. There are two main types of quench phenomena in LSC: chemical quench, in which nuclear radiation is absorbed by a chemical quencher instead of the solvent before converting to light; and a colour quench, in which coloured substances in the sample or scintillator absorb light in the wavelength range emitted from the scintillator (**Figure 4.1**)[3, 8]. In addition, there are ionization quench phenomena that occur as a result of interactions between a charged particle and the liquid scintillator. This quenching causes a non-linearity between the fluorescent emission and the energy deposition by the charged particle[9-10].

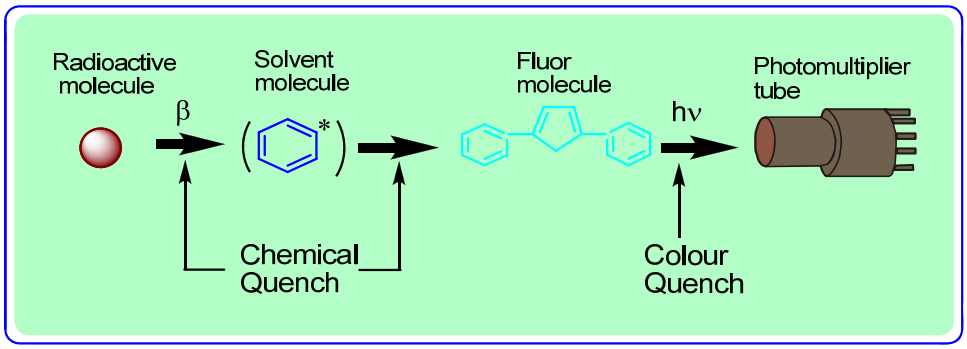


Figure 4.1 Quench phenomena in LSC (after Thomson[8]).

Many methods have been used for quench correction and those that are available depend on the instrument manufacturer. For the Wallace 1220 Quantulus ultralow level liquid scintillation counter, the quenching index of this instrument is determined by using a Spectral Quench Parameter (External), abbreviated as SQPE. An external gamma ray standard (^{152}Eu) is employed to study the quench in a sample by placing it close to the sample and this external standard produces the

Compton electron spectrum in the scintillation cocktail. The Compton electron spectra from the sample with and without the external standard are measured in equal interval time. The SQPE is therefore defined as the endpoint or uppermost channel of the Compton electron spectrum which is obtained from the subtraction of two Compton electron spectra. The advantages of this quench index are that it provides a fast, easy and nondestructive evaluation of the quench. For analysis of an unknown activity sample by LSC, its SQPE value is determined by the instrument and its counting efficiency is then determined from the calibration graph of the counting efficiency versus the SQPE value. The absolute sample activity is obtained from its calculating counting efficiency[1, 3]. The absolute activity of sample (DPM) is calculated as follows.

$$DPM = \frac{CPM}{E}$$

Where DPM = the sample activity in disintegrations per minute

CPM = the count rate of the unknown sample

E = the counting efficiency obtained from the calibration curve (expressed as a decimal)

4.3.1 The counting efficiency and SQPE for measuring ^{129}IDMA

Optimum conditions for the measurement of ^{129}IDMA by LSC had to be identified before LSC would be used in the adaptation of the DSPE methods to the measurement of ^{129}I species. The first step of this optimization involved investigating the impact of the components of the IDMA on the counting efficiency and SQPE of the LSC measuring system.

Experimental procedure and results

The eluate from the solid-phase extraction (SPE) step, ^{129}IDMA in 5 mL of tetrahydrofuran (THF) could be mixed with the scintillant cocktail without the addition of water. The SQPE for various concentrations of stable IDMA in THF was therefore studied.

5 mL of IDMA solutions in THF (0, 5.7, 11.4, 17, 22.7 and 28.4 μmol L^{-1}) were transferred to 22 mL polyethylene (PE) scintillation vials and 15 mL of Gold Star

scintillant was added. These sample mixtures were measured by LSC with the counting window channels being set from 1 to 1024. The SQPE measurement decreased slightly as the concentration of stable IDMA increased (**Figure 4.2**)

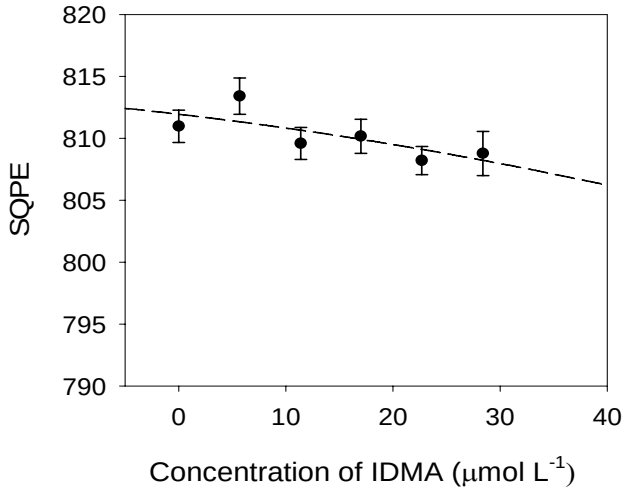


Figure 4.2 The SQPE measurement of various concentrations IDMA.

The volume of THF used for eluting IDMA from the SPE cartridge varied the SQPE values and the counting efficiency of ^{129}I in various volumes of THF was then investigated. Sample solutions were prepared by transferring 0, 1, 2, 3, 4, 5, 6 and 7 mL of THF to 22 mL PE scintillation vials. Then, these samples were spiked with 10 μL (ca 46 Bq) of $^{129}I^-$ solution and adjusted to 20 mL with the Gold Star scintillation cocktail. These samples were then measured by LSC, counting channels 1 to 1024 channel. It was found that the SQPE value and the counting efficiency decreased as the volume of THF increased, as shown in **Figure 4.3**.

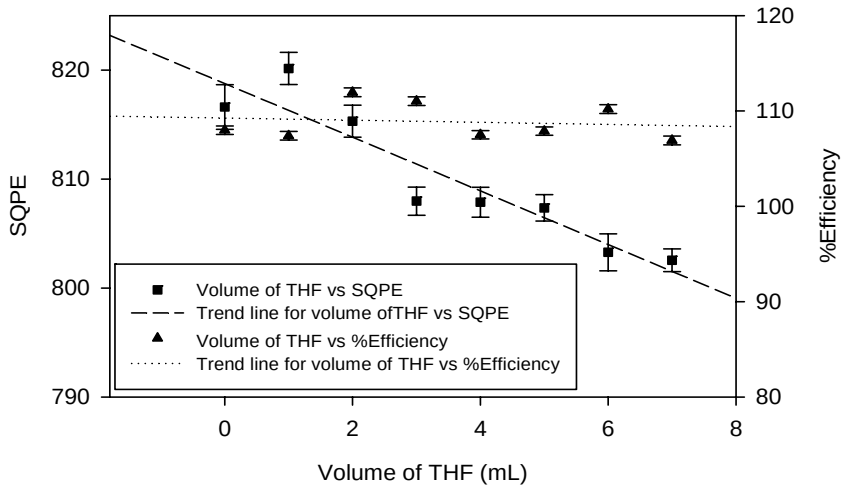


Figure 4.3 The SQPE values and the counting efficiencies of ^{129}I in samples containing various concentrations of THF.

The effect of SQPE on the counting efficiency of ^{129}I in various volumes of THF was studied by plotting the SQPE versus the counting efficiency (**Figure 4.4**). There was no apparent trend. The counting efficiencies of ^{129}I were higher than 100%, although the SQPE values decreased.

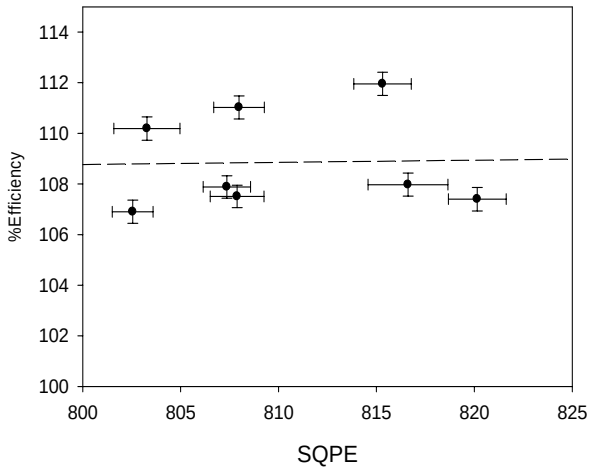


Figure 4.4 The effect of SQPE on the counting efficiency of ^{129}I for various volumes of THF

Discussion and conclusions

As a result of testing various concentrations of stable IDMA in 5 mL of THF by LSC, the SQPE values were found to decrease slightly as the concentration of IDMA increased. It showed a minor quenching impact on the counting. SQPE

values decreased slightly when the volume of THF increased. The counting efficiency of ^{129}I in various volumes of THF fluctuated between 106% and 112% but was likely higher than 100% for the various SQPE values (**Figure 4.4**). This might due to the detection of its beta particles, X-rays, gamma rays, Auger electrons and conversion electrons from gamma radiation. Therefore, this detection system could accept 1 to 7 mL of THF for the analysis of ^{129}IDMA without significantly impacting on the composition of the sample solution and the Gold Star liquid scintillation cocktail.

The results from this experiment was in good agreement with Rodes' research work[4]. He studied the liquid scintillation counting of ^{129}I in 8 different prepared scintillation solutions. From the optimization of conditions, the apparent counting efficiencies of ^{129}I in various scintillation cocktails were between 96% and 121%.

This reference also confirmed that an appropriate liquid scintillation cocktail could be used to obtain high counting efficiency. This study employed the commercial Gold Star scintillation cocktail based on di-isopropyl naphthalene, a scintillation cocktail that mixed well with the sample solution and suffered from only minor quench problems.

4.3.2 The liquid scintillation spectrum of ^{129}I

A typical liquid scintillation spectrum obtained from a solution prepared by diluting ^{129}I in 5 mL of THF with 15 mL of Gold Star scintillant is shown in **Figure 4.5**. The liquid scintillation spectrum of ^{129}I showed two overlapping peaks, the liquid scintillation counter detecting a small fronting peak separated from a large peak. The main peak maximum corresponds to the 152 keV energy beta emission from ^{129}I. The small fronting peak may be from X-rays, gamma rays and electrons due to their high emission probabilities that could be detected by the LSC.

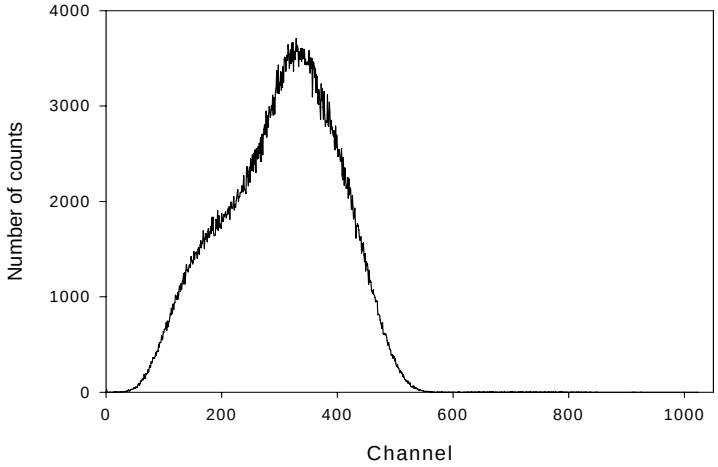


Figure 4.5 The liquid scintillation spectrum of ^{129}I (iodide form, 460 Bq) in 5 mL of THF mixed with the Gold Star liquid scintillation cocktail.

4.4 Preparation of a stock solution of $^{129}IO_3^-$

Only ^{129}I certified iodide (I^-) is commercially available but for this research ^{129}I as iodate (IO_3^-) was also required. The preparation of $^{129}IO_3^-$ was therefore investigated.

4.4.1 Basis of the preparation

Iodide (I^-) and elemental iodine (I_2) can be removed from dilute acid, neutral and alkaline solutions on a column of anion exchange resin. Sodium hypochlorite (NaOCl), a strong oxidizing agent, has been used as an eluent to remove iodide from the column by oxidizing iodide to iodate (**Equation 4.4**)[11].

$$I^- + 3ClO^- \longrightarrow IO_3^- + 3Cl^- \qquad (4.4)$$

From the above method, this study has adopted the information from reference 11 to prepare and separate $^{129}IO_3^-$ from the other species of ^{129}I.

Experimental procedure and results

An anion exchange column was prepared by packing an Eichrom anion exchange resin slurry (1 x 8, Cl^- form, 100-200 mesh) into a polyethylene column (0.9 cm,

i.d and 12 cm, length.). The volume of resin packed in column was approximately 3 mL. This column was then washed with 5 mL of deionized water.

The preparation of $^{129}IO_3^-$ was carried out as follows. 1 mL of a stable iodide (0.08 M) carrier, 5 mL of water and 1 mL of $^{129}I^-$ solution (approximate 4600 Bq) were added to a 22 mL PE scintillation vial. This solution was shaken well and passed through the anion exchange column followed by 20 mL of water. The eluate was discarded. The column was then washed with 20 mL of NaOCl (0.8%). The eluate was collected and decomposed by adding 1 mL of sodium formate (33%, w/v), evaporating until dryness on a hotplate and then continuing evaporation in an oven at 120 °C overnight. The white residue was re-dissolved in 5 mL of water. This solution was then passed through another anion exchange column, which was prepared in the same manner as the previous column, to remove other species of ^{129}I such as iodide or elemental iodine. The eluate was collected and 1 mL was transferred to a pre-weighed 22 mL PE scintillation vial. This solution was weighed and then mixed with 19 mL of Gold Star liquid scintillation cocktail and counted by LSC. The activity of $^{129}IO_3^-$ was found to be 248.8±1.1 Bq/g (n = 3).

For measuring $^{129}IO_3^-$ by using LSC, the composition of water was considered similar to the sample solution. Quenching during the counting of ^{129}I in various volumes of water was therefore investigated. The experiment was the same as the previous experiment for $^{129}I^-$ in THF. The SQPE values decreased and the counting efficiency was consistently higher than 100% for various volumes of sample solutions (1 to 5 mL). Hence, there was a minor quenching effect from sample solutions and water.

Discussion and conclusions

The $^{129}IO_3^-$ solution was prepared by passing the $^{129}I^-$ solution through the anion exchange column. NaOCl was used to convert $^{129}I^-$ to $^{129}IO_3^-$ which was then eluted from the column. For purifying the $^{129}IO_3^-$ solution, a second anion exchange column was employed which removed other residual ^{129}I species which had remained in the $^{129}IO_3^-$ solution.

The destruction of excess NaOCl in the eluate was necessary as *N,N*-dimethylaniline (DMA) could be chlorinated by NaOCl and acetic acid giving 2-chloro-dimethylaniline or 2,4-dichloro-dimethylaniline[12]. These products could be a serious problem during the iodination derivatisation procedure resulting in the formation of chlorinated DMA rather than IDMA.

Sodium formate was therefore used to destroy excess NaOCl on evaporating[13-15]. The hypochlorite (OCl^-) was found to be rapidly reduced by the formate at 90 -100 °C [15].

4.4.2 The purity of the $^{129}IO_3^-$ stock solution

After preparing the $^{129}IO_3^-$ solution, the purity of this solution was tested using the DSPE procedure for the determination of stable iodide described in Section 3.6. The activity of radioactive 4 iodo-*N,N*-dimethylaniline or ^{129}IDMA would be measured by LSC instead of HPLC.

Experimental procedure and results

A sample solution was prepared by spiking 50 μL (approximate 13 Bq) of $^{129}IO_3^-$ in 25 mL of water. 3.3 mL of phosphate buffer (pH 6.4) and 1 mL of IBZ were added. The sample solution was shaken and kept for 5 minutes. 0.5 mL of DMA was added followed by shaking well and setting aside for 60 minutes. The sample solution was extracted using the SPE procedure as described in Chapter 3. The activity of the SPE eluate sample was measured by transferring 1 mL of solution to a 22 mL PE scintillation vial, mixing with 19 mL of Gold Star liquid scintillation cocktail and measuring by LSC. The mean yield of ^{129}IDMA from this test was 0.7±0.2% (n = 3) of the added activity.

Discussion and conclusions

The DSPE procedure for the determination of iodide was chosen to test the purity of $^{129}IO_3^-$ solution because of its being selective for iodide and elemental iodine. A very small activity of ^{129}IDMA was detected in the SPE eluate sample. Therefore, there was only a very small impurity level present in the $^{129}IO_3^-$ solution, and this solution could therefore be used for the verification of the DSPE procedure.

4.5 The determination of inorganic ^{129}I species

4.5.1 The determination of $^{129}I^-$

This experiment was carried out by using $^{129}I^-$ as radioactive iodide agent to investigate the possibility of the adaptation of DSPE method. The reagents in the derivatisation step which were contaminated with stable iodine would also be used for the analysis of ^{129}I species.

Experimental procedure and results

Three surrogate samples were prepared by spiking 50 μL (approximate 230 Bq) of $^{129}I^-$ solution into 25 mL of water. 3.3 mL of phosphate buffer (pH 6.4) and 1 mL of IBZ were added to each sample solution. After shaking and keeping for 5 minutes, 0.5 mL of DMA (1.58×10^{-2} M) was added and the sample solution was shaken well and kept for 60 minutes. The SPE procedure (as described in Chapter 3) was then used to extract the radioactive IDMA from the sample solution. The radioactive IDMA extract was transferred to a 22 mL PE scintillation vial and mixed with 15 mL of Gold Star scintillant. The mixture was measured by LSC. The mean recovery of ^{129}IDMA was 96.5±2.6% (n = 3).

Discussion and conclusions

The conversion of $^{129}I^-$ to ^{129}IDMA was found to be more than 90% efficient. It implied that the stable iodine-contaminated reagents were a minor problem for the analysis of $^{129}I^-$. Consequently, the DSPE method was an interesting method that could be adapted to the collection and measurement of $^{129}I^-$ in aqueous samples.

4.5.2 The determination of $^{129}IO_3^-$

The $^{129}IO_3^-$ solution, the preparation of which was described in section 4.4, was employed to find out whether the DSPE method could be used for the determination of iodate.

Experimental procedure and results

Three surrogate samples were prepared by spiking 50 μL (approximate 13 Bq) of $^{129}IO_3^-$ solution in 25 mL of water. 50 μL of ascorbic acid (0.1 mol L^{-1}) and 0.7 mL

of acetic acid (1%,v/v) were added. After shaking and keeping for 30 minutes, 3.3 mL of phosphate buffer (pH 6.4) and 1 mL of IBZ were added. Next, the sample solution was shaken, kept for 30 minutes and then 0.5 mL of DMA ($1.58x10^{-2}$ mol L^{-1}) was added. After shaking and keeping for 120 minutes, the sample solution was extracted using the SPE procedure (as described in Chapter 3). The IDMA extractant was transferred to a 22 mL PE scintillation vial and mixed with 15 mL of Gold Star liquid scintillation cocktail. The mixture was measured by LSC, giving a mean yield of ^{129}IDMA of 94.6±0.8% (n = 3).

Conclusion

A known activity of $^{129}IO_3^-$ was converted to ^{129}IDMA and extracted using the procedure developed for stable iodate. A good recovery of ^{129}IDMA was achieved and the DSPE method could be suitable for the determination of $^{129}IO_3^-$ in aqueous samples.

4.6 Conclusion

The derivatisation-solid phase extraction (DSPE) procedures for the determination of stable iodide and iodate have been adapted to the collection and measurement of radioactive iodine species. Gamma ray spectrometry, liquid scintillation counting, NAA and mass spectrometry would all have been suitable methods for measuring the collected ^{129}I. For this study, liquid scintillation counting was chosen, however, because of its high counting efficiency and inexpensive running costs.

Investigations were carried out to optimize conditions for the determination of ^{129}IDMA by LSC. Gold Star liquid scintillation cocktail based on DIN was introduced to the ^{129}IDMA measurement. Increasing the concentration of the IDMA could slightly decrease the SQPE value, but had only a minor impact on the measurement. Increasing the volume of THF (1 to 7 mL) also decreased the SQPE value. The counting efficiency was consistently higher than 100%, possibly due to the detection of X-rays, gamma-rays, Auger electrons and conversion electrons from gamma radiation. Hence, the Gold Star scintillant could be used for the measurement of ^{129}IDMA with only a minor quench problem.

A $^{129}IO_3^-$ stock solution had to be prepared for this study because no available commercial solution existed. The preparation of this solution was based on the conversion of $^{129}I^-$ to $^{129}IO_3^-$ by using NaOCl, and an anion exchange method was used to purify the $^{129}IO_3^-$ solution. Excess NaOCl was destroyed to prevent it chlorinating DMA in the derivatisation step of the DSPE method. Less than 1% of iodide/iodine impurity was found to remain in the $^{129}IO_3^-$ solution.

Water (25 mL) spiked with $^{129}I^-$ and $^{129}IO_3^-$ was initially used to investigate the adaptation of DSPE methods to radioactive iodine measurement. Good recoveries were obtained from testing with both ^{129}I species. The DSPE methods could therefore be adapted to determine inorganic ^{129}I species in aqueous solutions without additional adjustment.

Iodine-contaminated reagents used in the derivatisation step were found to be a problem for the trace analysis of stable iodine species but for the measurement of ^{129}I species, these interferences were not found to have an impact.

The inorganic ^{129}I species: iodate, iodide and iodine can all be present together in environmental samples. These adapted DSPE methods were advantageous for determining all inorganic species of ^{129}I in the sample as follows. Total inorganic form of ^{129}I can be determined by using the adapted DSPE method for the determination of iodate (***DSPE 1***), whilst iodide and elemental iodine forms of ^{129}I can be collected and measured by using the adapted DSPE method for the determination of iodide (***DSPE 2***). The elemental iodine form of ^{129}I can be determined by missing out the IBZ oxidant from the DSPE method (***DSPE 3***) for iodide. Iodate and iodide can be determined from the different activities of these adapted DSPE methods.

$$\textit{DSPE 1} \Rightarrow {}^{129}I_2 + {}^{129}I^- + {}^{129}IO_3^-$$

$$\textit{DSPE 2} \Rightarrow {}^{129}I_2 + {}^{129}I^-$$

$$\textit{DSPE 3} \Rightarrow {}^{129}I_2$$

Then

$$^{129}I_2 = \textit{DSPE 3}$$

$$^{129}I^- = \textit{DSPE 2 - DSPE 3}$$

$^{129}IO_3^-$ = ***DSPE 1- DSPE 2***

In addition, stable and radioactive iodine are normally present together. The DSPE method could simultaneously collect both stable and radioactive iodine from the sample. A suitable detection system would then be chosen to measure individually either stable or radioactive iodine species.

The adapted DSPE methods can be applied to the identification and measurement of the activity inorganic ^{129}I species in aqueous samples. For the determination of low level ^{129}I species in the aquatic environment, further work is required to improve the sensitivity of the methods.

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Chapter 5 The combination of the anion exchange and DSPE methods for the determination of iodine species in seawater

5.1 Introduction

Iodine is a trace element in the marine environment where it is present predominantly as iodide and iodate. Many parameters influence the speciation of iodine including biological activities[1-3], dissolved oxygen[4] and ozone[5] (as described in Chapter 1). Typical concentrations of iodide and iodate in the oceans are approximately 22.5 μg L^{-1} and 63 μg L^{-1}, respectively[6]. In the case of ^{129}I, it is naturally occurring and remains in the oceans until decay all. Discharge from nuclear activities can increase the concentration of ^{129}I in the oceans. The concentrations of ^{129}I in archived seawater (from 1969 to 1981) are considerably low in a range of $1.57x10^{-12}$ g L^{-1} to $3.21x10^{-15}$ g L^{-1} [(7)]. Knowledge about ^{129}I speciation in the ocean is limited and little research has focus on the development of methods to determine ^{129}I species. The concentrations of ^{129}I found in ocean waters as iodide and iodate are in the ranges of $2.57x10^{-13}$ g L^{-1} to $4.71x10^{-11}$ g L^{-1} and $2.94x10^{-14}$ g L^{-1} to $6.67x10^{-11}$ g L^{-1}, respectively[6].

In measuring the concentrations of stable and radioactive iodine species in seawater, there are many other anions, cations and compounds, such as Cl^-, Br^-, F^-, SO_4^{2-}, HCO_3^-, Na^+, K^+, Mg^{2+}, Ca^{2+}, $MgSO_4$ and H_3BO_3 that must be considered[8]. There are many other radionuclides such as ^{40}K, ^{32}Si, ^{26}Al ^{90}Sr, ^{137}Cs, ^{239}Pu, ^{87}Rb, ^{3}H and ^{14}C in the oceans which come from different sources: (i) natural occurrence, (ii) nuclear explosion, nuclear detonation, nuclear power plant and nuclear fuel reprocessing plant or (iii) both natural and man-made occurrences [9]. These stable constituents and radionuclides in seawater can interfere in the direct measurement of both stable and radioactive iodine species. The analysis of stable and radioactive iodine without these interferences can be achieved by isolating and enriching iodine, especially ^{129}I, from marine water.

This chapter describes the development of methods for the speciation and enrichment of iodine in seawater that might be applied with stable and radioactive iodine. Initially, the DSPE method was tested for a speciation analysis of iodine in

large volume seawater samples. A significant drawback of the DSPE method was found to arise from the precipitation of calcium phosphate which clogged the SPE cartridge. A citrate-phosphate buffer and EDTA were unsuccessfully introduced to solve this problem and an anion exchange method was therefore adopted to pre-separate and enrich the iodide and iodate from large volume seawater samples. The eluent from the anion exchange method could then be derivatised and re-enriched using the DSPE method. A radioisotope tracer was employed in the development of these methods.

5.2 Chemicals and apparatus

All chemicals used in the development of the derivatisation-solid phase extraction (DSPE) methods and adapting those methods to the radioactive iodine species have been described in the previous chapters. Trisodium citrate (analytical reagent), potassium nitrate (analytical reagent) and iodine (resublimed, general purpose reagent) were purchased from VWR (UK). Citric acid monohydrate (assay 95%) was purchased from Hogg (Birmingham, UK). Ethylenediaminetetraacetic acid (disodium salt, dehydrate, 99%), Amberlite® IRA-400 resin strong basic anion exchanger (Cl^- form, gel type) and sodium bisulfite (ReagentPlus^{TM}, ≥99%) were purchased from Sigma-Aldrich (Poole, UK)

Phosphate buffer (pH 6.4, 6 M) was prepared by dissolving 27.218 g of potassium dihydrogen orthophosphate and 28.392 g of disodium hydrogen orthophosphate in 100 mL of water. The citrate buffer was prepared by dissolving 0.375 of citric acid monohydrate and 28.885 g of trisodium citrate in 50 mL of water. Both of these buffers were adjusted pH to 6.4 by NaOH (6 mol L^{-1}) and HCl (1 mol L^{-1}) and then mixed together with the ratio 1:1 to give the citrate-phosphate buffer (pH 6.4). Ethylenediaminetetraacetic acid (EDTA, 0.2 mol L^{-1}) was prepared by dissolving 7.478 g of ethylenediaminetetraacetic acid (disodium salt) in 100 mL of water. Iodine solution was prepared by dissolving approximately 0.01 g of iodine in 25 mL of iodide solution (6.63 mmol L^{-1}).

Diluted sodium hypochlorite solution (20%, v/v) was prepared by transferring 20 mL of sodium hypochlorite (NaOCl) to 50 mL of water in a 100 mL volumetric flask and diluting to the mark with water. Potassium nitrate solution (KNO_3, 2 mol

L^{-1}) was prepared by dissolving 50.55 g of KNO_3 in 250 mL of deionized water. Sodium bisulfite (0.27 mol L^{-1}) was prepared by dissolving 0.7129 g of sodium bisulfite in 25 mL of water. Hydrochloric acid (HCl, 1.2 mol L^{-1}) was prepared by transferring 5.2 mL of concentrated HCl to 30 mL of water in a 50 mL volumetric flask and diluting to the mark with water.

A seawater sample (salinity approximately 33.8, temperature 13.9 °C) was collected from Southampton at Lat 50° 48.998W, Long 1° 17.221W. This seawater was filtered through a Fisherbrand glass microfiber filter (MF300) to remove suspended solids and then stored at 4°C in a cold room.

A Quantulus 1220 ultra low level liquid scintillation counter (PerkinElmer) was employed to measure the beta-particle emission from the ^{129}I, whilst X-ray and gamma ray radiation from ^{129}I was measured by gamma ray spectrometry using a Canberra low energy germanium (LEGe) detector as described in Chapter 4.

An X-SERIES 2 ICP-MS (Thermo Fisher Scientific, Bremen, Germany) which was a facility of the Geochemistry Group, NOCS, was also employed for the measurement of ^{129}I. It was set up in the standard configuration, using an ASX-510 autosampler (Cetac, Omaha, Nebraska, USA). The instrument was tuned for optimum sensitivity. High purity reagents and ultra pure water of resistivity >18 MΩ cm (Milli-Q) were used. The built-in PlasmaLab software was used to construct the calibration of the standards and blank in the unknown samples. Data was acquired in peak-jumping mode (4 x 45 second repeats per sample/standard/blank analysis). After each sample analysis the system was washed with an appropriate solution until the signal returned to background levels. The reproducibility was typically better than 1% RSD for 4 repeats. From this system any abnormal results could be noted and re-run at the end of the procedure. Processing of the run data occurred simultaneously within the PlasmaLab using inputted data and correction factors as designated at the start of the experiment.

5.3 Problems with the direct determination of iodine species in seawater using DSPE method

The DSPE approach was initially employed to measure iodine species in seawater without any pre-separation. This Section describes the difficulties encountered in the analysis and the unsuccessful solutions tried out for these problems.

5.3.1 Preliminary measurement of iodide in seawater

The DSPE method was initially employed to measure iodide in a relatively large volume of seawater.

Experimental procedure and results

Two samples of seawater (250 mL) were tested directly with the DSPE method for the determination of iodide as described in Section 3.6.3. One of the samples was spiked with 3 mL of iodide solution (10^{-4} mol L^{-1}) and another sample was left unspiked. After completing the derivatisation, white precipitates formed in both samples and these precipitates clogged the SPE cartridge. A Philips X'Pert Pro X-ray diffractometer using a copper X-ray tube at the National Oceanography Centre in Southampton (NOCS) was used to study the chemical composition of these precipitates. The X-ray diffraction pattern identified the white precipitates as brushite ($CaHPO_4.2H_2O$).

Discussion and conclusions

Blockage in the extraction step meant that the DSPE method could not be applied to the direct determination of iodine species in large volumes of seawater. The precipitates were presumed to arise from the calcium (Ca^{2+}) or magnesium (Mg^{2+}) in the seawater reacting with the phosphate buffer. Several forms of calcium phosphate could have been formed such as calcium hydroxyapatite ($Ca_5OH\ (PO)_4$), octacalcium phosphate ($Ca_8H_2(PO_4)_6.5H_2O$), tricalcium phosphate ($Ca_3(PO_4)_2$) and brushite or dicalcium phosphate dihydrate ($CaHPO_4.2H_2O$). Which of these had occurred would depend on factors such as the temperature, the kinetics of reaction and the presence of any growth inhibitors[10]. Magnesium phosphate forms such as newberite (MgHPO4.3H2O), bobierite ($Mg_3(PO_4)_2.8H_2O$) and struvite ($MgNH_4PO_4.6H_2O$) might also have been present. Magnesium could inhibit the

growth of the calcium phosphate crystals by surface adsorption[11-12]. From its X-ray diffraction pattern, the precipitate from this experiment was found to be principally brushite ($CaHPO_4.2H_20$).

5.3.2 Using a citrate-phosphate buffer in the DSPE method

The precipitation was an unavoidable problem in the direct determination of iodide in seawater by the phosphate buffered DSPE method. A citrate-phosphate buffer was therefore chosen to control the pH of the oxidation of iodide, instead of the pure phosphate buffer. The hypothesis was that the calcium in the seawater might react with the citrate to generate calcium citrate preventing the formation of calcium phosphate.

Experimental procedure and results

Owing to the difficultly of adjusting the pH of the seawater for the oxidation of the iodide, the optimum pH was re-investigated. Stable iodide solutions ($1x10^{-5}$ mol L^{-1}, 25 mL) were tested with the DSPE method for the determination of iodide (described in Section 3.6.3) and various pH values (6.0, 6.3, 6.6 and 7.0) of phosphate buffer were used. The recoveries of IDMA were 107.6±3.5%, 106.9±3.4%, 107.2±3.6% and 105.6±2.5%, respectively.

Next, citrate-phosphate buffers (pH 6 and 7) were used instead of the phosphate buffers for the determination of iodide in the above procedure. The mean recoveries of IDMA from this method using citrate-phosphate buffer (pH 6 and7) were 99.5±2.6% (n = 3) and 106.6±0.8% (n = 3), respectively. The oxidation of iodide by IBZ could be efficiently performed over the pH 6 to 7 of citrate-phosphate buffers.

The optimum volumes and concentrations of citrate-phosphate buffer were then investigated using 100 mL seawater samples. It was found that 15 mL of citrate-phosphate buffer prepared from citrate buffer (pH 6.4, 2 mol L^{-1}) and phosphate buffer (pH 6.4, 4 mol L^{-1}), in a 1:1 ratio, was optimal for adjusting the pH of the seawater to approximately 6.4.

Seawater samples (100 mL) with and without spiking with 0.3 mL of stable iodide ($1.16x10^{-4}$ mol L^{-1}) were tested. The mean yield of IDMA from spiked seawater samples was 29.8± 5.8 %. (n = 3).

Discussion and conclusions

The pH of seawater could not be easily adjusted to 6.4 by phosphate buffer. The cause of this problem was that seawater is a weak buffer with a high salt content. When sea salts are added to a phosphate buffer, the pH of the buffer shifts due to the precipitation of buffer components a such as the calcium and magnesium assisted by the high ionic strength of the solution[13]. The optimized range of pH for the oxidation of iodide was therefore reinvestigated and it was found that the oxidation of the iodide by IBZ could occur at any pH between 6 and 7.

When a citrate-phosphate buffer was adopted to determine iodide in seawater using the DSPE method, the mean recovery of IDMA was below 50%. The low yields of IDMA might be from the loss of iodine during the derivatisation through a reaction of iodine and citrate. This reaction is found to occur in the dark at a slow rate. A small quantity of an unknown compound was produced immediately, however, when citrate and iodine were mixed together[14-15]. Hence, the citrate-phosphate buffer was not appropriate for controlling the pH of iodide oxidation in the DSPE method for the determination of trace iodine species.

5.3.3 Masking cations in seawater using a chelator

Ethylenediaminetetraacetic acid (EDTA) is a chelator widely used in analytical chemistry either for direct titration or as part of an indirect sequence of reactions[16]. EDTA was employed to solve the precipitation problem. In theory, EDTA should bind the calcium and magnesium that are present in seawater, potentially masking their presence and preventing the phosphate precipitation of alkaline earth metals (**Equation 5.1**).

$$Ca^{2+} + Y^{4-} \rightleftharpoons CaY^{2-} \qquad (5.1)$$

Where Y^{4-} = EDTA at alkaline conditions

Experimental procedure and results

For this reaction to be useful there would need to be no reaction between iodine and EDTA. This hypothesis was tested by adding 2 mL of EDTA (0.2 mol L^{-1}) to iodine solution. The colour of solution instantaneously changed from dark brown to colourless.

Discussion and conclusions

The occurrence of colour change implied that the iodine could react with EDTA. As the EDTA could react with both the calcium and the iodine, it would be not be appropriate to use EDTA to solve the precipitation problem.

5.4 The isolation of iodine species from seawater by using an anion exchange method

In order to solve the precipitation problem encountered in the DSPE method, an alternative approach based on an anion exchange method was developed. This method could both simultaneously separate and enrich iodine species from seawater. The seawater was deoxygenated by passing nitrogen through it to minimize iodide oxidation by dissolved oxygen in the water. The optimum conditions for separating iodide and iodate from seawater were investigated using an $^{129}I^-$ tracer. NaOCl, a strong oxidizing agent for iodide under slightly acid conditions, was employed as an eluent in this study. The concentration of NaOCl was 20% (v/v), which had been adopted from a draft working document from the UK Environment Agency (EA) for measuring ^{129}I.

The anion exchange separation of iodine species

The basic principle underlying the separation of ^{127}I and ^{129}I species from seawater has been adapted in this study from work reported by Hou et al[17-18]. Iodide in seawater strongly binds to anion exchange resins which are initially in their nitrate form.

$$R_A^+NO_3^- + I^- \rightleftharpoons R_A^+I^- + NO_3^- \qquad (5.2)$$

Where R_A^+ = anion exchange resin

Iodate, dissolved organic iodine, cations and neutral species in seawater will pass through the anion exchange column. The appropriate eluent is then used to elute iodide from the anion exchange column.

The other main inorganic iodine species in seawater, iodate, can also be isolated using an anion exchange column. Under acid conditions, the iodate in seawater is reduced by bisulfite to iodide. There are 3 reactions associated with this conversion. The bisulfite (HSO_3^-) initially slowly reduces some iodate to iodide (**Equation 5.3**).

$$IO_3^- + 3HSO_3^- \longrightarrow I^- + 3SO_4^{2-} + 3H^+ \quad (5.3)$$

Iodate rapidly oxidizes this iodide to iodine (**Equation 5.4)**.

$$IO_3^- + 5I^- + 6H^+ \longrightarrow 3I_2 + 3H_2O \quad (5.4)$$

This iodine is then reduced rapidly by bisulfite to iodide (**Equation 5.5**). The last reaction is continued until all the bisulfite ions are oxidized. So excess bisulfite has to be used to prevent the occurrence of I_2[19].

$$I_2 + HSO_3^- + H_2O \longrightarrow 2I^- + SO_4^{2-} + 3H^+ \quad (5.5)$$

This iodide derived from the iodate is then collected using an anion exchange column. The iodate-derived iodide is eluted from the column with the appropriate eluent, derivatised and then extracted by the same DSPE method used for iodide.

The choice of anion exchange resin

Anion exchange resins are normally prepared by chloromethylating cross-linked copolymers of styrene and divinylbenzene and then treating with a tertiary amine. Strongly basic anion exchangers have generally been used to remove halogens from aqueous solution. The strongly basic anion exchange resins can be separated into Type 1 and Type 2 having slightly different structures (**Figure 5.1)**. Some properties of Type 1 resins are different from those of Type 2 resins. For example,

the basicity of Type 1 resins is higher than that of Type 2 resins. The Type 1 resins operate over a wider range of pH values than the Type 2 resins[20].

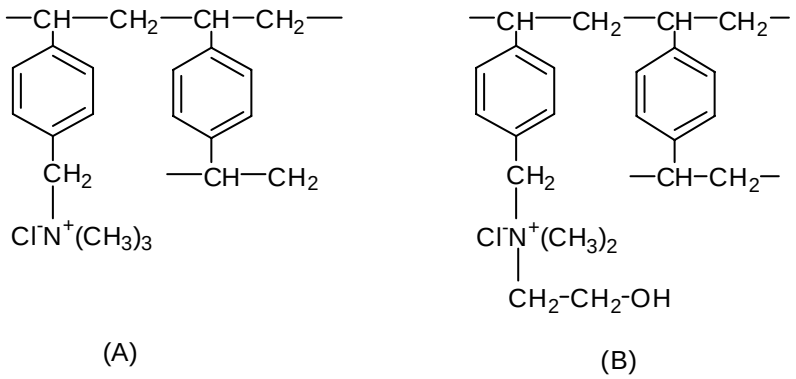

Figure 5.1 Chemical structures of the strongly basic anion exchange resins (Cl^- form): (A) Type 1 and (B) Type 2 (after Korkisch[20]).

The anion exchange resin which has been used in this study is Amberlite® IRA-400. It is a strong base gel-type resin (Cl^- form, Type 1). The characteristics of the Amberlite® IRA-400 resin are as follows. The matrix of this resin is a polystyrene divinylbenzene copolymer with quaternary ammonium functional groups. The degree of cross-linkage in the resin is 8%. The total exchange capacity of the resin is 1.4 meq mL^{-1} (wet bed volume) and 3.8 meq g^{-1} (dry weight). The particle size of resin is 16-50 mesh. Its moisture holding capacity is 40 to 47%. This resin can be used between pH 0 and 14[21-22].

The selectivity of the Amberlite® IRA-400 resin was investigated by Kunin et al[23]. The affinities of various anions for this resin were in the order: citrate > sulfate > oxalate > iodide > nitrate > chromate > bromide > thiocyanate > chloride > formate > hydroxyl > fluoride > acetate.

The affinities of iodide and iodate for the IRA-400 resin are different and this material can therefore be used to separate iodide and iodate from each other. Exploiting this selectivity, iodide has been separated from protein-bound ^{131}I isolated from patients with thyroid cancer[24]. For studying the binding affinity to the B4 allotype in rabbit anti-dinitrophenyl antibodies, IRA-400 resins were employed to remove unbound iodine remaining from the radiolabelling of proteins

with $Na^{125}I$ [25]. This resin has also been used to remove free iodine from ^{131}I thyroxine stock solutions[26]. Therefore, the IRA-400 resin can be used to separate iodide and iodate from other cations, some anions, neutral species and various organic iodine species.

Preparation of the anion exchange column

15 g of anion exchange resin was purified by soaking in hydrochloric acid (1.2 mol L^{-1}) overnight. The resin slurry was then packed in a glass column (1.8 cm, i.d. and 12.5 cm, length) connected to a 500 mL reservoir as shown in **Figure 5.2**. This resin slurry was washed with water until the pH of the eluate was neutral. The resin was then converted into its nitrate (NO_3^-) form by passing 50 mL of KNO_3 (2 mol L^{-1}) through the column at a flow rate of 1-2 mL min^{-1} and then washing the column with 30 mL of water to remove excess NO_3^-.

Figure 5.2 The anion exchange columns utilized for this research.

5.4.1 The effect of sample pH on the elution of iodide

Iodine species in seawater could be separated from the other interferences using the anion exchange column. The elution of iodide from the anion exchange column might be affected by the pH of sample solution. This factor was then studied.

Experimental procedure and results

6 g of Amberlite® IRA-400 resin (NO_3^- form) was initially used in this experiment. Two samples of seawater (50 mL), spiked with ca 230 Bq of $^{129}I^-$, were tested. One sample was acidified by using a little concentrated HCl to a pH below 2 and then 0.1 mL of sodium bisulfite (0.27 mol L^{-1}) was then added to

convert all the inorganic forms of iodine to iodide. This step was adopted from the separation of iodate from seawater as reported by Hou et al[18]. Another sample was left untreated. The samples were passed through anion exchange columns followed by 10 mL acidified water (pH <2, for acidified seawater sample) or 10 mL of water (for the non-acidified seawater sample). The flow rate for loading and washing was 3 to 5 mL min^{-1}. The eluates were collected and measured using a gamma ray spectrometer. No activity was found in either eluates. Iodine-129 was eluted from each column by eluting with 6 mL of NaOCl (30 mL), allowing the hypochlorite to soak in the column for about 5 minutes before continuing with the elution. The columns were then washed with 10 mL of water; the eluate and washing water being collected in the same bottle. Excess NaOCl in the eluate was destroyed by adding sodium formate and evaporating until 10-15 mL of sample solution was left. The volume of sample solution was adjusted to 25 mL with water. 1 mL of the solution was transferred to a 22 mL PE scintillation vial and mixed with 19 mL of Gold Star liquid scintillation cocktail. This mixture was measured by LSC. The recovery of ^{129}I from the acidified seawater and treated with bisulfite was 100.3±0.1% and the non- acidified seawater sample was 61.4±0.4%.

Acidified seawater spiked with ca 230 Bq of $^{129}I^-$ (50 mL), but with no added bisulfite was then tested using the same anion exchange column procedure as before. A small quantity of ^{129}I (0.6±0.2%) was found in the effluent obtained during the sample loading and washing. The recovery of ^{129}I from the NaOCl elution was 85.4±0.5%.

Discussion and conclusions

Iodide is retained strongly by the Amberlite® IRA-400 resin but its removal from the resin is very slow. The NaOCl elution of iodide from the acidic column was found to perform better than that from the neutral column. The acidification of seawater sample might increase the rate oxdiation of the iodide by the NaOCl.

Some iodide in the acidified seawater sample without bisulfite addition might react with chloride in acidified seawater to give iodochloride (ICl), which might not be retained on the column. With the acidified seawater to which had been added

bisulfite, no ^{129}I activity was found in the eluate obtained as the sample was passed through the column. This was from the conversion and preservation of all chemical forms of iodine as iodide in the acidified seawater sample by bisulfite. All the iodide was therefore retained on the anion exchange column.

Consequently, acidification of the seawater sample could increase the rate of NaOCl elution. This condition however produced a neutral species of iodine which would not bind to the anion exchange resin. This product was unavoidable for the separation of iodide from seawater, but it was negligible.

5.4.2 The breakthrough capacity of a 15 g resin column

The capacity of a 15g anion exchange resin column was tested for use with larger volume seawater sample.

Experimental procedure and results

An anion exchange column (**Figure 5.2**) was packed with approximately 15 g of resin and 20 mL of acidified seawater, spiked with approximately 230 Bq of $^{129}I^-$, was passed through the column at a flow rate of 3 to 5 mL min^{-1}. Further portions of unspiked seawater were passed through the anion exchange column and 20 ml aliquots of eluate were collected separately in 22 mL PE scintillation vials. There were measured using a gamma ray spectrometer. Iodine-129 activity could be detected once 1280 mL of seawater had passed through the column (0.75±0.41 Bq).

Discussion and conclusions

Breakthrough factor of the anion exchange column was detected after 1280 mL of the seawater had passed through the column. This anion exchange column was therefore suitable for loading iodide from seawater samples having volumes less than 1280 mL. This anion exchange column could therefore be used to separate iodine species from other ions in 1 litre of seawater.

5.4.3 The optimization of elution conditions

To improve the elution of iodide from the IRA-400 resins, the loading, washing and the optimum volume of NaOCl to elute most of iodide from the anion exchange column were studied.

Experimental procedure and results

An anion exchange column packed with 15 g of resin was used to collect 230 Bq of $^{129}I^-$ from 50 mL of acidified seawater. After loading and washing the column with 25 mL of acidified water, the loading and washing eluates were collected together (Fraction 1) and the receiving vessel was changed. NaOCl (20%, 100 mL) was then used to elute the $^{129}I^-$ from the column in four steps, adding 25 mL of NaOCl (20%), soaking for 1 hour and collecting each eluate separately in a new receiving vessel (Fraction 2 to 5). The anion exchange column was then washed with 25 mL of water and this fraction was collected in the same receiving vessel as Fraction 5. All fractions of eluates (Fraction 2 to 5) were separately decomposed by adding sodium formate and evaporating until 5- 10 mL of sample solution was left. The volume of each sample solution was adjusted to 25 mL with water. 1 mL of each fraction was transferred to each 22 mL PE scintillation vials, mixed with 19 mL of Gold Star liquid scintillation cocktail and measured by LSC.

Very little quantity of ^{129}I (0.9±0.3%) was found in Fraction 1 and almost quantitative recovery of ^{129}I (92.1±0.5%) was found in the first 25 mL of NaOCl (Fraction 2), as shown in **Figure 5.3**.

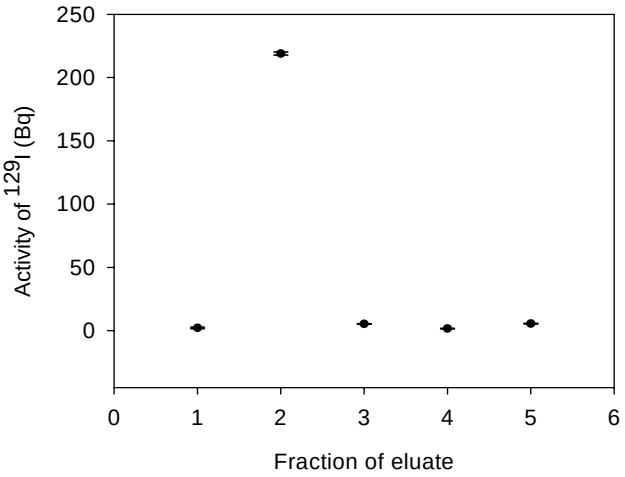

Figure 5.3 The loading, washing and elution behavior of iodide in seawater on a IRA-400 resin column using $^{129}I^-$ tracer. (Fraction 1 = loading and washing fraction, Fraction 2-5 = NaOCl elution fractions)

Discussion and conclusions

The optimum time for the oxidation of iodide by NaOCl was studied by Takayanagi and Wong[27]. To a series of 25 mL of iodide solutions (0.25 μmol L^{-1}) in a 0.5 mol L^{-1} NaCl/4 mmol L^{-1} $NaHCO_3$ medium, was added 0.2 mL of NaOCl (0.2%). These solutions were kept for various time periods. Above 92% yield was found at 20 minutes or longer. Iodide (0.5 μmol L^{-1}) in 0.5 mol L^{-1} NaCl/0.8 mmol L^{-1} KBr/4 mmol L^{-1} $NaHCO_3$ medium was also tested with NaOCl and gave similar results. 30 minutes was chosen for the optimum reaction time[27]. This information was adopted for this anion exchange method. In the initial study, an anion exchange column packed with 15 g of resin was used. The oxidation time and volume of NaOCl for each elution (Fraction 2-5) were set at one hour and 25 mL, respectively. From **Figure 5.3**, it can be seen that most of the activity could be eluted from the column with 25 mL of NaOCl (Fraction 2). One hour was possibly sufficient for the oxidation of iodide by NaOCl. The small activity of ^{129}I remaining (Fraction 3-5) on the column was eluted slowly. This might be from the increase of pH of anion exchange column via the NaOCl elution because the NaOCl solution was alkaline.

5.4.4 The separation of iodide from seawater

Having obtained a good quantitative recovery of iodide from 50 mL of seawater, the anion exchange method was adapted to isolate iodide from a larger volume of seawater.

Experimental procedure and results

A volume of acidified seawater (1 litre) spiked with approximately 230 Bq of $^{129}I^-$ was passed through the anion exchange column packed with 15 g of resin (NO_3^- form) at a flow rate of 3-5 mL min^{-1}. The column was then washed with 100 mL of acidified water. The eluate from passing the sample through the column, and washing with the acidified water, were then mixed together (Eluate 1). The elution was performed by partially eluting with 30 mL of NaOCl (20%, 60 mL), leaving the solution to soak in the resin bed for about 1 hour. This column was then washed with 25 mL of water. The eluate and washing water were pooled (Eluate 2). Excess NaOCl in Eluate 2 was decomposed by adding sodium formate and then evaporating on a hotplate until 25 mL of solution was left. The volume of the sample was finally adjusted to 50 mL with water. 1 mL of each eluate were transferred to 22 mL PE scintillation vials, mixed with 19 mL of Gold Star liquid scintillation cocktail and measured by LSC. A small quantity of ^{129}I (4.5±5.4%, n = 3) was found in Eluate 1. The mean recovery of $^{129}I^-$ in Eluate 2 was 92.2±2.0% (n = 3).

The stability of the eluted iodate was also investigated in case the eluate had to be stored prior to its analysis. A synthetic eluate was prepared by mixing 60 mL of NaOCl (20%) with 25 mL of water and then spiked with approximately 13 Bq of $^{129}IO_3^-$ in a 250 mL PE bottle. This synthetic eluate was then stored in a refrigerator. After 4 months, 1 mL of this solution was transferred to a 22 mL PE scintillation vial, mixed with 19 mL of Gold Star scintillation cocktail and measured by LSC. The recovery of $^{129}IO_3^-$ from three measurements was 88.4±5.0%.

Discussion and conclusions

Iodide could be extracted from a relatively large volume of seawater using a column of IRA-400 resin (15 g). Based on the results reported in Section 5.4.3, the elution using NaOCl was adjusted. Twice eluting with 30 mL of NaOCl should be sufficient for the removal of most iodide from a column. The mean recovery of iodide obtained from this method was approximately 90%. The results showed that a tiny amount of iodide was not collected by a column of IRA-400 resin. This might be from the reaction between iodide and chloride in acidified seawater to produce neutral compound as discussed in Section 5.4.1. Due to the larger volume of the seawater sample, the other cause might be that some bromide and chloride in the seawater sample was retained on the anion exchange resin column instead of iodide. From the affinities of bromide and chloride on the IRA-400 resin[23], their affinities were lower than that of nitrate. Iodide could be more selective than bromide and chloride, but bromide showed a relatively high affinity and chloride was high concentration in seawater. Bromide and chloride might reduce the binding sites of the anion exchange resins which were available for iodide[17-18].

In addition, the recovery of $^{129}IO_3^-$ from the storage of eluted iodate was approximately 90%. A little loss of iodate might be from adsorbing on the surface of the PE bottle. Therefore, the eluted iodate could be stored in the refrigerator about 4 months with a minor loss of iodate.

5.4.5 The isolation of iodate from seawater

The collection of iodate from seawater onto a column of IRA-400 resin was investigated.

Experimental procedure and results

To 1 litre of acidified seawater (pH <2) spiked with approximately 50 Bq of $^{129}IO_3^-$, was added 1.5 mL of sodium bisulfite (0.27 mol L^{-1}) to convert all the inorganic forms of iodine to iodide. This sample solution was loaded onto the column (15 g of resin) and analyzed by using same procedure for the separation of iodide from seawater (Section 5.4.4)

The mean recovery of ^{129}I from this method (Eluate 2) was 89.4±8.7% (n = 3). A low level activity of ^{129}I (2.5±5.0%, n = 3) was however found in the Eluate 1, obtained from passing sample solution and washing water through the column.

An acidified sample of seawater (1 litre), spiked with approximately 50 Bq of $^{129}IO_3^-$, was later tested with the procedure for the collection of iodide using the IRA-400 column. The mean recoveries of $^{129}IO_3^-$ in Eluate 1 (from passing sample through the anion exchange column followed by acidified water) was 89.7±4.6% (n = 3). Eluate 2 (from NaOCl elution and wash water) was found to contain 8.5±0.8%, (n = 3) of the $^{129}IO_3^-$ activity.

Discussion and Conclusions

The conversion of iodate in seawater to iodide by bisulfite was suggested by Hou et al[17-18]. He showed that the addition of excess bisulfite at a pH below 2 was necessary to convert iodine to iodide. The quantity of bisulfite used in this experiment was 4.05×10^{-4} mole which was an excess for the conversion of iodate. This approach has now been shown to be useful in the isolation of iodate from seawater onto a IRA-400 resin column. With a mean recovery about 90%, this method could also be applied to elute total inorganic iodine from seawater.

The anion exchange approach for the separation of iodide from seawater was also tested on 1 litre of acidified seawater spiked with $^{129}IO_3^-$ (approximate 50 Bq). It was found that approximately 9% of the iodate was probably converted to the iodide retained on the column. This may occur because of the reaction between iodate and chloride in acidified seawater produces iodide and Cl_2 (**Equation 5.6 & 5.7**).

$$IO_3^- + 6HCl \longrightarrow ICl + 5Cl^- + 3H_2O \qquad (5.6)$$

$$ICl + Cl^- \rightleftharpoons I^- + Cl_2 \qquad (5.7)$$

Another source of $^{129}I^-$ in this test might be from the $^{129}IO_3^-$ stock solution which contained very small impurity of other inorganic forms of ^{129}I.

Hence, this anion exchange method might not completely separate iodide from iodate when there is present in seawater. Small quantities of iodate might be converted to iodide and retained in the column. This might exaggerate the quantity of iodide found. The procedure for the separation of iodine species from seawater using the anion exchange method is shown in **Figure 5.4**

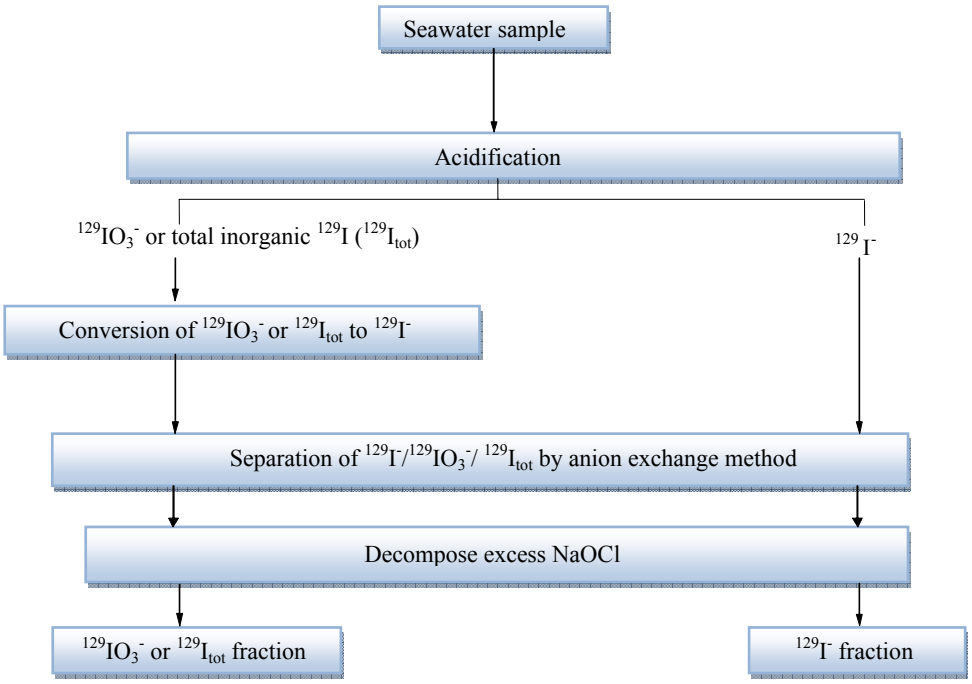

Figure 5.4 A procedure for the collection of iodine species from seawater.

5.5 Linking the DSPE method with the anion exchange preconcentration for the determination of iodine species

To increase the enrichment of the iodine species from the seawater sample, the DSPE method for the determination of stable iodate was introduced. The DSPE method was adapted and then tested with an eluted iodate after the excess NaOCl had been decomposed. The $^{129}IO_3^-$ tracer was used for this study.

Experimental procedure and results

The pH of each reaction step in the derivatisation is critical and the pH of the eluted iodate (after decomposition of excess NaOCl) was first tested. It was found to be pH 9. This eluted iodate was diluted with water prior to analysis.

Synthetic eluate from the anion exchange method was prepared. A mixture of 60 mL of NaOCl (20%) and 25 mL of water was reduced by adding sodium formate (33.3%, w/v) and evaporating on the hotplate (90-100 ˚C) until 25 mL of solution remained. This solution was then adjusted to 50 mL with water. This synthetic eluate was spiked with approximately 13 Bq of $^{129}IO_3^-$ and then diluted to 100 mL with water. 2 mL of HCl (0.5 mol L^{-1}), 5 mL of acetic acid (10%) and 0.2 mL of ascorbic acid (0.1 mol L^{-1}) were added. After shaking and leaving for 30 minutes,15 mL of phosphate buffer (pH 6.4, 2 mol L^{-1}) and 4 mL of IBZ were added. This solution was kept for 30 minutes. 2 mL of DMA was then added and the solution was shaken and kept for 120 minutes. This solution was extracted using the SPE procedure described in Chapter 3. All eluate was transferred to a 22 mL PE scintillation vial and mixed with 15 mL of Gold Star liquid scintillation cocktail. The mixture was measured by LSC giving a mean yield of 88.5±0.2 % (n = 3) as radioactive 4-iodo-*N,N*-dimethylaniline (^{129}IDMA).

Discussion and conclusions

The DSPE method was introduced to enrich and extract the iodine species collected by the anion exchange method. The pH of the derivatisation was very important for the adaptation of the DSPE method. The eluted iodate had to be pH adjusted before derivatisation because it was an alkaline. The dilution and the addition of acid were used to neutralize the pH of the eluted iodate solution.

In the derivatisation step, the acetic acid (10%, v/v) and the phosphate buffer (pH 6.4, 2 mol L^{-1}) were employed to control the pH of the iodate reduction and the iodide oxidation, respectively. Testing the eluted iodate using the DSPE method gave a good recovery of $^{129}IO_3^-$. The DSPE method for the determination of iodate could, therefore, be adapted to enrich and extract the iodine species collected from the anion exchange method.

5.6 Measurement of iodine species using both the anion exchange and the DSPE methods

The collection of iodide and iodate from seawater by anion exchange, followed by solid phase extraction of the iodate as 4-iodo-*N,N*-dimethylaniline (IDMA) was

studied by the addition of radioactive tracers ($^{129}I^-$ and $^{129}IO_3^-$). These proposed methods would enrich the concentrations of stable and radioactive iodine in seawater about 200 times. The total recoveries of iodide and iodate from these methods could be estimated by combining the yields from the individual steps, as shown in **Table 5.1**.

Table 5.1 Iodide and iodate recoveries from seawater using a combination of anion exchange and DSPE approaches.

Chemical species	Yield (%)		
	Anion exchange method	DSPE method	Calculated whole procedure
Iodide	92.2±2.0	88.5±0.2	81.6±1.8
Iodate	89.4±8.7	88.5±0.2	79.1±7.7

In addition, the isolation of iodide from seawater by both these methods was tested.

Experimental procedure and results

Two samples of acidified seawater (1 litre) spiked with approximately 230 Bq of $^{129}I^-$ were tested using the anion exchange method for the isolation of iodide from seawater (Section 5.4.4). The eluates from the anion exchange method were then analyzed using the adapted DSPE method, as described in Section 5.5. The mean recovery of ^{129}I from the whole procedure was 73.5±11.2% (n = 2). The limit of detection from LSC (one hour counting) was 0.03 Bq g^{-1} (4.03 μg L^{-1}).

Discussion and conclusions

The recovery of iodide from the whole procedure was approximately 74%. When this recovery was compared to the total recovery from the calculation as shown in **Table 5.1**, it was slightly less than that from the calculation. This might be from the loss of iodide during the process.

5.7 Sample preparation for analysis by ICP-MS

Due to the trace level of ^{129}I in seawater, the sensitivity of LSC might not be sufficient for measuring the ^{129}I obtained by using the combined anion exchange/ DSPE method. ICP-MS was then employed for this approach. Some optimization of conditions had to be carried out before the analysis could be performed.

Inhibition of memory effect with the ICP-MS

Many researches have encountered a systematic problem when employing ICP-MS for the measurement of iodine. This is a memory effect in which iodine is difficult to flush from the system. The iodine oxidation state is an important factor in the problem and nitric acid has generally been adopted as a wash-out solution. The slow removal of iodine from the system prolonged the time required for the signal to return to its blank level.

Many reagents have been introduced to prevent the vaporization of the iodide. For example, ammonia solution has been used to react with I_2 or HI to give NH_4I which has a lower tendency to be adsorbed by organic polymer tubing than I_2 or HI[28-31]. A reducing agent such as Na_2SO_3[32] , $Na_2S_2O_3$[33] and ascorbic acid[34] has been used to stabilize iodine as iodide. Tetramethylammonium hydroxide (TMAH) was another choice of reagent demonstrated to inhibit this effect. It reacted with iodide to produce the tetramethylammonium (TMA) iodide salt. TMAH has been used by directly adding it to water samples for the determination of iodide and iodate[35] or used to digest biological materials instead of acid[36-37]. A high concentration of TMAH was not suitable because carbon black could be produced in the plasma. 1% or 2% (v/v) TMAH was recommended for analysis[38]. This reagent was chosen to use in this research work to inhibit the memory effects of iodine on the ICP-MS.

5.7.1 The removal of THF from the sample solution

The direct injection of organic solvent into the ICP-MS could cause systematic problems. Kishi et al[39] proposed a dynamic reaction cell ICP-MS using pure NH_3 as the reaction gas to reduce argon- and carbon-based polyatomic spectral interferences from organic solvents such as isopropyl alcohol, N-methyl pryyrolidone, propylene glycol monomethyl ether acetate, propylene glycol methyl

ether and methyl methoxy propionate. This method could be applied to determine semiconductor elements with good spike recovery and precision[39].

Other organic solvents such as propane-2-ol have been found to cause signal reduction[40]. Methanol and acetone could effect the efficiency of nebulization and transport [41]. There was however no investigation of the effect from injecting the THF used in this work to elute IDMA from the SPE cartridge. To avoid the deposition of carbon residues in the ICP-MS, THF was removed from the samples by evaporation. The loss of iodine from this procedure was therefore investigated.

Experimental procedure and results

Radioactive IDMA (^{129}IDMA) solution was prepared as follows. 20 mL of water, spiked with 236.44 Bq of $^{129}I^-$, was added 2.64 mL of phosphate buffer (pH 6.4, 0.5 mol L^{-1}) and 0.8 mL of IBZ reagent. After keeping 5 minutes, this solution was added 0.4 mL of DMA and kept 1 hour. This solution was then extracted by SPE procedure as described in Chapter 3. 2 mL of this extract was transferred to a 25 mL volumetric flask and its volume was adjusted to the mark with THF. After mixing well, 1 mL of this solution was transferred to a 22 PE scintillation vial, mixed with 19 mL of Gold Star liquid scintillation cocktail and measured by LSC. The activity concentration of ^{129}IDMA solution was 3.224±0.030 Bq mL^{-1}.

2 mL of ^{129}IDMA solution (approximately 6.45 Bq) was transferred to a 20 mL glass vial. This solution was evaporated in a water bath (70 °C) until dryness. The residue was dissolved by adding 0.2 mL of nitric acid (8 mol L^{-1}) followed by 2 mL of TMAH (1 mol L^{-1}). The volume of sample was then adjusted to 4 mL by adding 1.8 mL of water. 1 mL of this solution was then transferred to a 22 mL PE scintillation vial and mixed with 19 mL of Gold Star liquid scintillation cocktail. This mixture was measured by LSC for 1 hour. A mean recovery of ^{129}I from this sample preparation was 66.2±3.5% (n = 5).

The counting efficiency and SQPE for this sample matrix was investigated prior to analysis by LSC. To a 22 ml PE scintillation vial, 1 mL of nitric acid (8 mol L^{-1}), 10 mL of TMAH (1 mol L^{-1}) and 9 mL of water were added. This solution was

mixed well. Sample solutions were prepared by transferring 1, 2, 3, 4 and 5 mL of this solution to 22 mL PE scintillation vials. These samples were spiked with 10 μL (approximate 46 Bq) of $^{129}I^-$ solution and then the volume was adjusted to 20 mL with Gold Star scintillant. These samples were measured by LSC.

The counting window was set from 150 to 550 channels because there was a chemiluminesence effect at the front of LSC spectrum. The results showed that the SQPE values and the counting efficiencies decreased when the volume of sample solution increased, as shown in **Figure 5.5**. The correlation between SQPE and efficiency in this sample solution was studied by plotting SQPE versus counting efficiency (**Figure 5.6)**. It showed that the counting efficiency decreased as the SQPE values decreased.

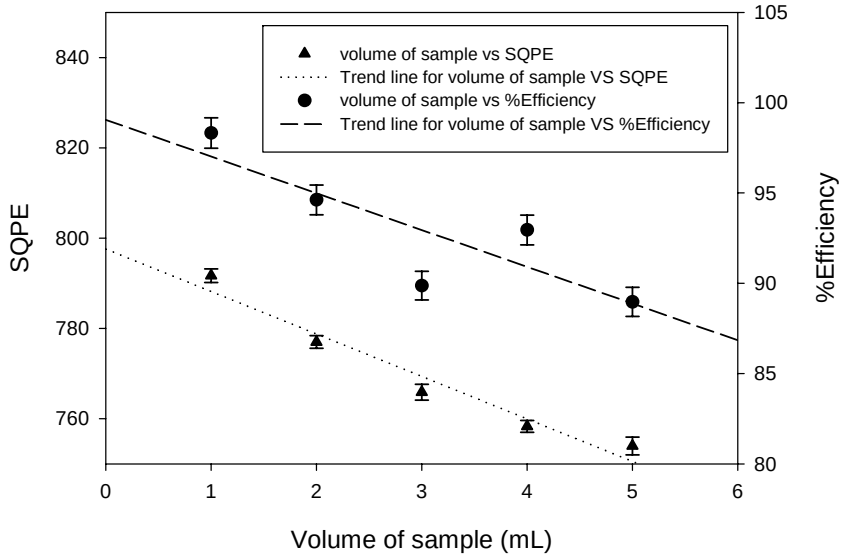

Figure 5.5 The SQPE values and the efficiencies of ^{129}I sample containing various volumes of solution having a similar matrix to that obtained from the dissolution of IDMA residues.

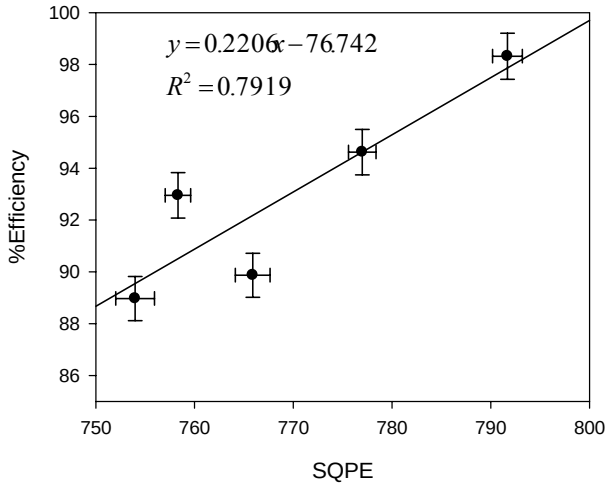

Figure 5.6 The effect of SQPE on the counting efficiency of ^{129}I for various volumes of solution in a similar matrix to that obtained from the dissolution of the IDMA residue.

The stability of the dissolved iodine solution was also tested by transferring 0.5 mL of nitric acid (8M), 5 mL of TMAH and 4.49 mL of water to a 22 mL PE scintillation vial. This solution was spiked with $^{129}I^-$ (44.62 Bq) and mixed well. The vial was closed tight and kept in a fume cupboard (at room temperature) between analyses. Periodically, 1 mL of this solution was transferred to a 22 mL PE scintillation vial, mixed with 19 mL of Gold Star liquid scintillation cocktail, shaken well and then measured by LSC for one hour.

The variation in measured activity over time is illustrated in **Figure 5.7**.

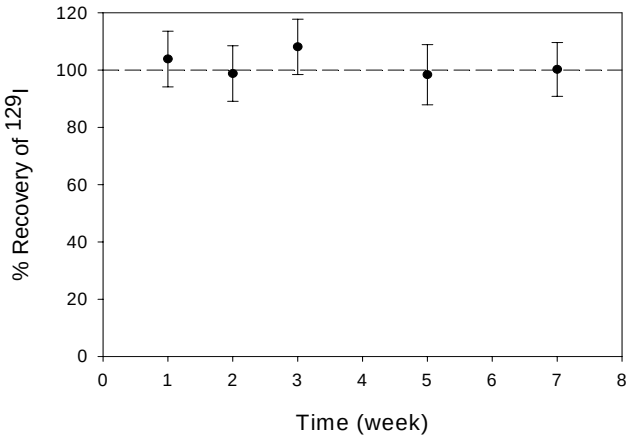

Figure 5.7 The stability of ^{129}I in the synthetic dissolved iodine solution (error bars represents two standard deviations).

Discussion and conclusions

The boiling point of IDMA is 263.7 ºC at 760 mmHg [42] and as the evaporation temperature was set at 70 ºC, only THF (boiling point = 66 ºC) should have evaporated from the sample solution. The IDMA solid was therefore exported to remain in the glass vial.

On addition of nitric acid iodine was released from the IDMA. Excess TMAH was then added to prevent the volatilization of the iodine and also to neutralize the pH of the sample solution. After dissolution of the IDMA, the pH of this sample solution was found to be above 11 and the TMAH content in the sample solution was 4.5% (v/v). The loss of iodine from this procedure was about 33.8%.

TMAH reacted with $^{129}I^-$ to give $TMA^{129}I^-$ which was found to decompose very slowly at room temperature (**Figure 5.7**). After storing for 7 weeks, the activity of ^{129}I in the synthetic solution was stable. Hence, the iodine-dissolved solution could be stored at room temperature more than one month before analysis by ICP-MS with no significant loss of iodine.

This method would be used to prepare samples from the DSPE method for the determination of ^{127}I and ^{129}I by ICP-MS. The calculated total recoveries for the determination of ^{127}I and ^{129}I species in water samples by using the anion exchange followed by the DSPE methods combine with this sample preparation procedure are shown in **Table 5.2**. A mean recovery of ^{129}I from the removal of THF was not good, so the calculated total recoveries of iodine species from the whole procedure dropped to approximately 50%.

Table 5.2 Recoveries of iodide and iodate from seawater using a combination of anion exchange, DSPE and removal of THF procedures.

Chemical species	Yield (%)		
	Anion exchange &DSPE method (from calculation)	Removal THF	Calculated all procedures
Iodide	81.6±1.8	66.2±3.5	54.0±3.1
Iodate	79.1±7.7	66.2±3.5	52.4±5.8

5.7.2 Effect of dissolved iodine solution on system

In order to prevent the iodine memory effect shown by the ICP-MS, TMAH was used in the sample preparation as described in Section 5.7.1. To confirm its effectiveness, surrogate solutions having similar chemical properties to the final solution of the THF removal process were tested.

Experimental procedure and results

A stock solution of ^{127}I was prepared by dissolving 0.0166 g of potassium iodide (pre-dried in an oven (100 °C) for one hour) in 20 mL of water. The stock solution was then diluted to 1.71 mg L^{-1} with water. Solutions of ^{127}I (0.87, 5.82, 11.8, 21.9 and 43.8 μg L^{-1}) were prepared by transferring the appropriate amount of ^{127}I stock solution to 22 mL pre-weighed PE scintillation vials, weighing and adding 0.5 mL of HNO_3 (8 mol L^{-1}) and 5 mL of TMAH. The volume of the ^{127}I solutions were adjusted to 10 mL with water and weighed. These ^{127}I solutions were analyzed by ICP-MS. The results from injecting ^{127}I solutions into the ICP-MS, including wash-out time, are shown in **Figure 5.8**.

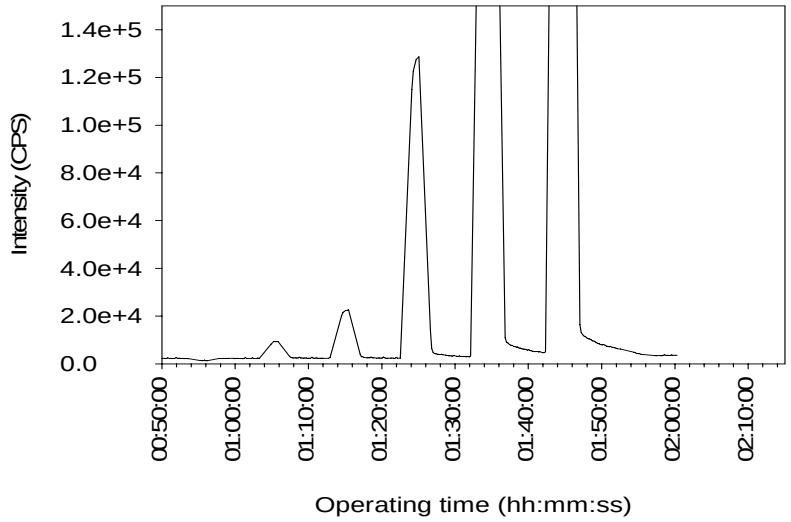

Figure 5.8 The analysis of ^{127}I solutions having a similar matrix to the dissolved iodine solution by ICP-MS.

Discussion and conclusions

After injecting an ^{127}I solution into the ICP-MS, residual iodine was found to be easily washed-out by water. The quantity of TMAH in ^{127}I solution did not have any effect on the ICP-MS system. The wash-out time depended on the concentration of ^{127}I. Hence, this sample solution could be directly determined by ICP-MS without a memory effect from iodine.

5.8 Conclusion

The concentration of ^{127}I and ^{129}I species in the marine environment is of interest for understanding their behavior and distribution. In this research work, the DSPE method was initially applied to determine stable iodide in 250 mL of seawater, but precipitation of calcium phosphate clogged the SPE cartridge. The adoption of a citrate-phosphate buffer and a masking EDTA chelator failed due to the reactions of the reagents with iodine.

An anion exchange separation was then introduced to pre-isolate and enrich iodide and iodate from seawater. The anion exchanger chosen for this study was Amberlite® IRA-400, a strongly basic anion exchange resin. This resin could separate iodide and iodate from each other and organic iodine compound are

reported to not be retained on this resin. The eluent used to remove the iodide from the resin was NaOCl (20%, v/v) with the collected iodide being oxidized to iodate and therefore released from the resin.

15 g of IRA-400 resin was found to be suitable for adsorbing iodide from 1 litre of seawater. The acidification of seawater sample increased the rate of NaOCl elution but it also produced small quantities of some neutral species of iodine which did not retain on the anion exchange column.

The collection of iodide from 1 litre of acidified seawater using the IRA-400 resin column was effective. Most collected iodide was released from the resin by using 60 mL of NaOCl (20%,v/v). The removal of the collected iodide onto the resin was performed by soaking the resin with 30 mL of NaOCl in the column for about 1 hour and then repeating it. When the iodide collection method was used to collect iodate from acidified seawater (without adding bisulfite), approximately 9% of the iodate converted to iodide which could retain on the column. Hence, this anion exchange method might not completely separate iodide and iodate and the concentration of iodide from this separation might be overestimated from the conversion of iodate.

For the separation of iodate from seawater, bisulfite was added to convert iodate to iodide. A good mean recovery was obtained and this method could then be applied to determine the concentrations of total inorganic iodine and iodate in seawater. The eluted iodate could be stored in the refrigerator for about 4 months with minor loss of iodate.

The DSPE method for the determination of stable iodate was employed to extract and re-enrich iodine species from the anion exchange method. The DSPE method was adapted to obtain a high recovery. The calculated recoveries of iodide and iodate from the combination of the anion exchange and the DSPE method were approximately 80%. The recovery of this combination method was however found to slightly decrease when tested for collecting iodide from acidified seawater.

Due to the trace levels of ^{129}I in seawater, the sensitivity of the detection might be improved by using ICP-MS. The problems ICP-MS exhibit from organic solvents and memory effect by iodine were considered. Tetramethylammonium hydroxide (TMAH) was employed to inhibit the iodine memory effect and evaporation was proposed to remove THF from the analyte solution. The mean recoveries of iodide and iodate from the whole procedures decreased to approximately 50%.

In conclusion, the anion exchange followed by DSPE methods could isolate and enrich iodine species (iodide, iodate and total inorganic iodine) from seawater. These methods could also be applied with stable and radioactive iodine species by using suitable detection systems for the measurement. The possibility of incomplete separation of iodide from iodate should however be considered.

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Chapter 6 Applications of new analytical procedures

This chapter describes the applications of the newly developed derivatisation-solid phase extraction (DSPE) and anion exchange methods to the speciation analysis of iodine in a variety of types of sample. The DSPE method was first applied to the determination of stable iodate and iodide in iodized table salt, validating the method by comparing the results obtained using the new method with standard addition and against a standard titration method. The main application of the speciation analysis of radioactive iodine was the determination of ^{129}I species in an effluent from the nuclear facility site at Sellafield. This sample was analyzed using the DSPE method to determine radioactive iodine species, anion exchange followed by precipitation and ICP-MS. The last application of this study combined the anion exchange method to collect iodine species followed by a determination step based on the DSPE method. This method was applied to the isolation and enrichment of ^{127}I and ^{129}I species (as iodide and iodate) from coastal and river water samples collected from Cumbria, UK. Three detection systems: HPLC, LSC and ICP-MS were used for the validation.

6.1 Determination of iodide/iodate in iodized table salt

6.1.1 Introduction

Iodine is an essential micronutrient for animal organisms which enters the body by ingestion. Once in the thyroid gland, iodide is converted to the organic iodine which synthesizes thyroid hormones using tyrosine[1]. These hormones are important for the growth and development of the brain and nervous system and they also control several metabolic processes in the body. Iodine deficiency disorder (IDD), which is globally a grave nutritional problem, can cause goitre, cretinism, brain damage, mental retardation, and hypothyroidism. Iodine supplements or iodized table salt have been used to solve the IDD problem, but can cause hyperthyroidism, a side effect of excessive iodine intake[2]. The recommended daily iodine intake for humans, according to the World Health Organization (WHO) is: 50 μg day^{-1} for infants, 90 μg day^{-1} for children, 120 μg day^{-1} for school children, 150 μg day^{-1} for adults and 200 μg day^{-1} for pregnant and lactating women. The amount of iodine in iodized table salt (1 kg) should amount to 20-40

mg of iodine or 34-66 mg of potassium iodate[3]. Excess iodine in the body is harmful to humans and the provisional maximum tolerable daily intake of iodine, recommended by the WHO, is 1 mg per day[4].

The geological distribution of iodine may influence the levels of IDD within a country. In Turkey, for example, the levels iodine deficiency and goiter tend to be worse in mountain areas and better in urban areas[5]. The people who live in the wet zone of Sri Lanka were generally found to have IDD diseases as a result of leaching of iodine from the soil by weathering, strong downward movement of the ground water and goitrogens[6].

Iodized table salt is produced by adding potassium iodate or potassium iodide to salt, in the quantities recommended by the WHO, to prevent IDD. Potassium iodide is less stable than potassium iodate because it can be oxidized to iodine by sunlight, excessive heat under neutral or acidic conditions, and by air[7]. Potassium iodate can however be converted to iodine by reducing agents in salt such as ferrous ions, sulfate and sulfite. After removing the reducing agents from salt, the iodine in iodized salt becomes stable[8]. Iodine loss of about 20% can occur during transportation from the manufacturers to the household. Another loss of iodine (20%) occurs during cooking[3]. Moisture was found to be the most important parameter governing the stability of iodine in iodized salt and the choice of packaging material had affected the stability. High-density polyethylene and low-density polyethylene bags were found to be effective. Salts produced in different countries have different iodine stabilities due to their inherent impurities and physical characteristics, but their iodine contents also depend on how the bulk salt was processed[9].

Several procedures have been developed for the determination of iodate or iodide or iodine in salt based on spectrophotometric[10-11], electrochemical [12-15] or flow injection with amperometric detection[16-17] approaches. Approaches based on HPLC [18] and GC-MS [19] offer high sensitivity. This study introduces the DSPE method followed by HPLC-UV detection to directly determine iodide or iodate in iodized table salts as 4-iodo-*N,N*-dimethylaniline (IDMA).

6.1.2 Chemicals and apparatus

The chemicals and apparatus used in the DSPE method were as described in Chapter 3. Sodium thiosulfate pentahydrate (analytical grade) was purchased from Fisher Scientific (Leicestershire, UK). Vitex indicator for the iodine titration was purchased from John D Bolton (Essex, UK). Sodium sulfite (anhydrous, analytical reagent grade) was purchased from VWR (UK).

For the titrimetric determination of iodide and iodate in iodized table salts[20], the following reagents were prepared. Water in this method was boiled, deionized water. Sodium thiosulfate (0.005 mol L^{-1}) was prepared by dissolving 1.24 g of sodium thiosulfate pentahydrate in 1 L of water. This solution was standardized with iodine solution[21].

Sulfuric acid (4 mol L^{-1}) was prepared by adding 5.56 mL of concentrated sulfuric acid to 90 mL of water and then adjusting the volume to 100 mL with water. Methyl orange indicator was prepared by dissolving 0.01 g of methyl orange in 100 mL of water. Bromine water was prepared by transferring 1 mL of bromine to 40 mL of water and then making up the volume to 50 mL with water. Phenol solution was prepared by dissolving 5 g of phenol in 100 mL of water. Sodium sulfite solution was prepared by dissolving 1 g of sodium sulfite in 100 mL of water. Potassium iodide solution was prepared by dissolving 10 g of potassium iodide in 100 mL of water.

Commercially marketed iodized table salts were studied. There had been produced in four countries: England, Kazakhstan, Thailand, and the Ukraine.

6.1.3 A comparison of iodide/iodate measurements using DSPE and titration

The DSPE methods for the determination of stable iodide or iodate were applied to determine the quantities of iodide or iodate in iodized table salt and the results of these methods were compared to those obtained by titration.

Experimental procedure and results

(i) Determination of iodine species using DSPE methods

Determination of iodide

An accurately weighed sample (1 g) of iodized table salt was dissolved in 25 mL of water. 3.3 mL of phosphate buffer (pH 6.4) and 1 mL of 2-iodosobenzoate (IBZ) reagent were added to the salt solution. After shaking well and keeping for 5 minutes, 0.5 mL of *N,N*-dimethylaniline (DMA) solution was added. The solution was shaken and kept for 60 minutes. The solution was then extracted by the solid phase extraction (SPE) procedure and analyzed by HPLC (as described in Chapter 3). For the standard addition evaluations, 0.5 mL of iodide solution (1 mmol L^{-1}) was added to the salt solution prior to its analysis.

Determination of iodate

1 g of iodized table salt was dissolved in 25 mL of water. 0.05 mL of ascorbic acid (0.1M) and 0.7 mL of acetic acid (1%, v/v) were then added. After shaking and keeping for 30 minutes, 3.3 mL of phosphate buffer (pH 6.4) and 1 mL of IBZ were added. This solution was shaken and kept for 30 minutes. 0.5 mL of DMA was then added and the solution was stored for 2 hours. The solution was then extracted using the SPE procedure and IDMA was then measured by HPLC (as described in Chapter 3). A standard addition of 0.5 mL of iodate solution (1 mmol L^{-1}) was also added to a portion of the salt solution.

A typical calibration for determination of iodide/iodate in iodized table salt samples by HPLC is shown in **Figure 6.1**. The relative standard deviations were 0.30% - 3.05% for 5 replicate injections of IDMA standard solutions.

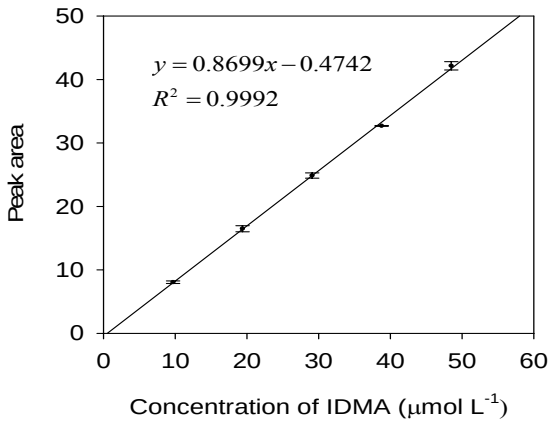

Figure 6.1 A typical calibration graph for determination of iodide/iodate in iodized table salt as IDMA by using HPLC.

A peak of iodide/iodate as IDMA from HPLC chromatogram was well resolved from the other peaks as shown in **Figure 6.2**.

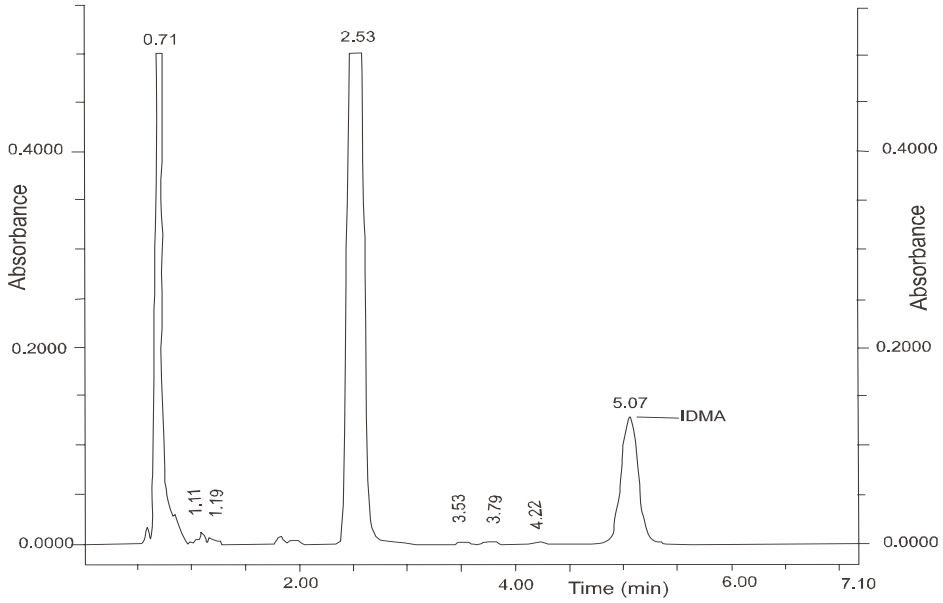

Figure 6.2 A chromatogram of iodide (22 ppm) in English salt derivatised to 4-iodo-*N,N*-dimethylaniline (IDMA), retention time 5.07 minutes.

The results obtained from the DSPE methods and standard addition to the DSPE methods are tabulated in **Table 6.1**.

(ii) Determination of iodine species by titration

Determination of iodate

To a 250 mL Erlenmeyer flask with stopper, 10 g of iodized table salt was dissolved in 50 mL of water. 1 mL of sulfuric acid (4 mol L^{-1}) and 5 mL of potassium iodide (10%, w/v) were added to the solution. The colour of this solution changed to yellow if significant quantities of iodine were present. The flask was closed and kept in the dark for 10 minutes. The liberated iodine was then estimated by titration with sodium thiosulfate (0.005 mol L^{-1}) using 0.3 to 0.5 g of Vitex indicator, added near to the end point of the titration.

Determination of iodide

10 g of iodized table salt was dissolved in 50 mL of water in a 250 mL Erlenmeyer flask. 6 drops of methyl orange indicator were added and the colour of the solution turned pale orange. Sulfuric acid (4 mol L^{-1}) was added (one drop or until colour

changed from orange to pink). 0.5 mL of bromine water was added and the colour of the solution turned yellow. Sodium sulfite solution was added until the colour of the solution turned pale yellow. The flask side was washed down with water. After adding 3 drops of phenol solution, the colour turned colourless. 1 mL of sulfuric acid (4 mol L^{-1}) and 5 mL of potassium iodide solution were then added and the colour turned to yellow. The liberated iodine was estimated by titration with sodium thiosulfate (0.005 mol L^{-1}) adding 0.3 to 0.5 g of Vitex indicator near to the end point of the titration.

The results from the determination of the iodide/iodate in iodized table salts using the titration are shown in **Table 6.1.**

Table 6.1 Concentrations of iodate or iodide found in iodized table salts.

Salt and manufacturer	Manufacturer's declaration	Amount of iodate or iodide present (ppm)		
		DSPE method		Titration[b]
		No standard addition[a]	Standard addition[a]	
Iodated salt				
Kazakh salt: "the cookery food salt, first grind" (Araltuz, Almaty, Republic of Kazakhstan)	KIO_3 40±15 ppm (Iodate = 32.7 ppm)	20.8±1.9	23.8±1.9	32.1±0.7
Thai salt: "Prung thip iodized refined salt" (Thai Refined Salt Co, Ltd, Nakonrachasima, Thailand)	Iodine 0.005% (Iodate = 68.9 ppm)	86.9±0.6	96.3±6.3	96.8±3.2
Ukrainian salt: "Artyomsol iodized salt" (Artyyomsol, Soledar, Donetsk region, Ukraine)	KIO_3 40±15x10^{-4}% (Iodate = 32.7 ppm)	43.5±0.3	46.2±7.9	55.8±0.6

Table 6.1 (continued)

Salt and manufacturer	Manufacturer's declaration	Amount of iodate or iodide present (ppm)		
		DSPE method		Titration[b]
		No standard addition[a]	Standard addition[a]	
Iodided salt				
English salt: "Cerebos extra fine iodized table salt"[c] (Cerebos, Middlewich, Cheshire, England)	KI ≥ 1150 µg per 100 g (Iodide ≥ 8.8 ppm)	22.7±1.3	25.7±1.4	26.1±1.9

[a]Each result is the mean of three determinations. [b]Each result is the mean of five determinations. [c]Cerebos iodized salt contains the anti-caking agents: magnesium carbonate and sodium hexacyanoferrate.

Discussion and conclusions

The four iodized table salt samples were from different manufacturers. The quantities of iodate or iodide in Thai and English salts were found to be quite a lot higher than was indicated on the packaging. This might be from a particular batch in the iodization process. For the determination of iodate content in Kazakh salt, the results obtained from the DSPE method, with or without standard addition, were less than from the titration. The iodide or iodate contents in all salt samples were, however, found to be at the recommended level for preventing IDD.

Both analytical methods could determine iodide or iodate in salt samples with good precision. The lack of correlation between the results obtained using the DSPE method and the titration may have been due to the heterogeneity of the solid sample. The quantity of iodized table salt tested by the DSPE method was one order of magnitude lower than that used for the titration. The variation of iodine content with depths of container was also reported by Dasgupta et al[22]. The iodine contents of the Kazakh salt, measured using the two methods, were found to be significantly different at the 95% confidence level (t-test).

6.1.4 The heterogeneity of iodized table salt

As no correlation had been obtained using the DSPE and titration methods, the Kazakh salt was chosen for a study of sample heterogeneity.

Experimental procedure and results

50 g of the Kazakh salt was dissolved in 250 mL of water. This salt solution was divided for analysis by the DSPE method and titration. 50 mL of the salt solution was analyzed by titration. 5 mL of the same salt solution was diluted to 25 mL and analyzed using the DSPE method (as described in Section 6.1.3).

The iodate contents of the Kazakh salt from using the DSPE method was 22.38±0.03 ppm and the titration result was 28.9±0.2 ppm.

Discussion and conclusions

The lack of agreement between the results obtained from the two methods was not therefore caused by the heterogeneity of the Kazakh salt. Due to the repeatability of both methods, the DSPE method was more precise than the titration. This disagreement might be from small quantities of chemicals that are normally added during salt production. Most iodized salts contain calcium, magnesium, strontium, sulfur, bicarbonate and carbonate. Some iodized salts also contain barium, potassium, iron and carbonate[23]. Ogur et al[24] studied the composition of salt sold in Turkish markets. He reported that sodium aluminium silicate was the preferred anti-caking additive in Turkish salts. Small amounts of potassium were found in all salts and some also contained small amounts of fluoride and magnesium. An anti-caking food additive is usually added to salt to prevent it from forming lumps, during storage. The types of anti-caking agent used depend on the manufacturer. Thai and Ukrainian salts used ferrocyanide or potassium hexacyanoferrate[25-26], but no information was provided on the anti-caking agent in the Kazakh salt. Impurities may, therefore, have interfered with the sensitivity of the DSPE method as shown by the standard addition results.

6.1.5 Conclusion

The new HPLC based DSPE methods for the determination of stable iodine species as 4-iodo-*N,N*-dimethylaniline (IDMA) were applied to the determination of iodide and iodate in iodized table salts without pre-separation. The iodide or iodate contents in iodized table salt samples were found to be in the recommended levels. These new methods were compared to a conventional titration approach. There was poor correlation of results obtained by the DSPE methods and the titration. This problem was not due to the heterogeneity of iodize table salt. It might possibly be from the food additives in the iodized table salt or impurities interfering with the derivatisation step of the DSPE method. The advantages of the DSPE methods were in its being simple, selective and precise, but a pre-separation step might be required to improve the accuracy of these methods.

6.2 Determination of ^{129}I species in an effluent from a nuclear fuel reprocessing site

6.2.1 Introduction

To minimize the release of ^{129}I from the nuclear facilities into the environment, the concentration of ^{129}I in radioactive waste is of interest. Many different analytical approaches have been employed to determine ^{129}I in radioactive waste (with or without the use of radiochemical separation methods) due to the low specific activity of ^{129}I and interference from other radionuclides. For example, the ^{129}I in waste-water from pressurized nuclear power reactors has been determined by separating it from ^{99}Tc using anion exchange, purifying by liquid-liquid extraction and measuring by LSC. The detection limit of this method was 5 Bq L^{-1} for ^{99}Tc and ^{129}I [27]. Gamma ray spectrometry has been used to determine ^{129}I in the radioactive waste streams from Spanish nuclear power plants, with and without radiochemical separation. For the direct measurement by gamma ray spectrometry, the detection limit was 0.2 Bq after 60 hours counting. In another method, two precipitation steps were used for sample preparation prior to measurement by gamma ray spectrometry. The detection limit was 0.02 Bq with 5 hours counting; one order of magnitude lower than the former method[28]. Neutron activation analysis (NAA) has been employed in the determination of ^{129}I in low level

radioactive wastes such as evaporator concentrate, sludge and spent ion exchange resin. A radiochemical separation was used to purify the ^{129}I. Its results were compared to other detection systems such as liquid scintillation counting (LSC) and its detection limit was found to be worse than the results from NAA[29]. Mass spectrometry, which is another high sensitivity technique, was used for the determination of ^{129}I in radioactive waste. Katayama et al[30] had introduced accelerator mass spectrometry (AMS) for the determination of ^{129}I in waste. Isolation of iodine was achieved using a solid phase extraction disk and this method was successfully used for testing liquid wastes from nuclear facilities in Japan.

To fully understand the transport of ^{129}I from radioactive waste to the environment, a knowledge of the speciation of ^{129}I in liquid waste is required. In this section, the speciation analysis of ^{129}I in an effluent sample from the nuclear facility at Sellafield was investigated by comparing the results obtained from two methods. The first method was the derivatisation-solid phase extraction (DSPE) method for the determination of radioactive iodine with detection by liquid scintillation counting. Another method that was applied was anion exchange followed by precipitation, with a low energy gamma ray spectrometer being employed for detection. ICP-MS was also employed for comparison.

6.2.2 Chemicals and apparatus

The chemicals for use in the DSPE method and the anion exchange method as described in Chapters 3, 4 and 5. Hydroxyammonium chloride was purchased from Merck (UK). Polyvinyl acetate, sodium metabisulfite (97%, ACS reagent), palladium (II) chloride (ReagentPlus, 99%) and tetramethylammonium hydroxide (1 M in water, ACS reagent) were purchased from Sigma-Aldrich (Poole, UK).

The chemicals for the precipitation of ^{129}I with palladium chloride were prepared as follows. Iodide solution (10 mg mL^{-1}) was prepared by dissolving 2.9529 g of sodium iodide (NaI) in 250 mL of water. Hydroxylamine hydrochloride solution (1 mol L^{-1}) was prepared by dissolving 6.95 g of hydroxylamine hydrochloride in 100 mL of water. This solution has to be prepared on the day it is to be used. Sodium

metabisulfite solution (1 mol L^{-1}) was prepared by dissolving 1.9002 g of sodium metabisulfite in 10 mL of water (this solution should also be freshly prepared on the day of use). Nitric acid (HNO_3, 8 mol L^{-1}) was prepared by transferring 50 mL of concentrated HNO_3 to 45 mL of water in a 100 mL volumetric flask. This solution was diluted to the mark with water. Hydrochloric acid (HCl, 2 mol L^{-1}) was prepared by transferring 87 mL of concentrated HCl to 400 mL of water in a 500 mL volumetric flask and diluting to the mark with water. Palladium chloride solution (1%, w/v in 0.05 mol L^{-1} HCl) was prepared by dissolving1.0 g of palladium chloride in 50 mL of water and then adding 0.50 mL of concentrated HCl. This solution was mixed well and then transferred to a 100 mL volumetric flask finally being diluted to the mark with water. Polyvinyl acetate in methanol was prepared (approximately 3% and 10%, w/v).

The apparatus used for the DSPE and anion exchange methods are as described in Chapters 4 and 5. High energy gamma emitting radionuclides in the effluent were measured using a Canberra well-type high purity germanium (HPGe) gamma spectrometer. This detector was calibrated against a matrix-matched mixed radionuclide standard of identical geometry (QCYK8563). The efficiency of the detector at 1332 keV was 40%. The spectral deconvolution program Fitzpeaks (version 3.58, JF Computing) was used to analyze the gamma spectra.

6.2.3 Characteristics of the effluent

The effluent was collected from a waste stream of the nuclear facility site at Sellafield. The effluent (250 mL) was consigned by LGC Limited, Middlesex, UK. The principal radionuclides in the sample were ^{137}Cs and^{129}I. Its activity was 50 kBq and had UN material number: UN2910.

As an initial safety screen, radionuclides in the effluent were checked by transferring 20.9678 g of the effluent to a 22 mL PE scintillation vial and measuring high gamma energy radionuclides using a well-type HPGe gamma ray spectrometer. The only significant radionulide found in this sample was ^{137}Cs (166.3±8.7 Bq g^{-1}).

The effluent was tested with the LSC by transferring 1 mL of the effluent to a 22 mL polyethylene (PE) scintillation vial and mixing with 19 mL of Gold Star liquid scintillation cocktail. There are overlaps of several peaks in the liquid scintillation spectrum of the effluent (**Figure 6.3**).

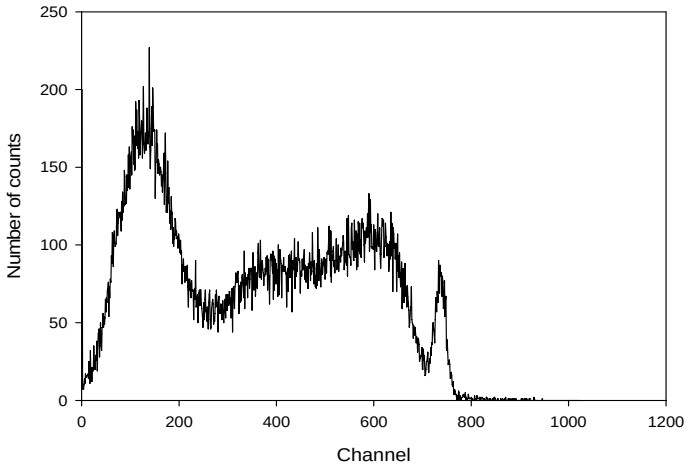

Figure 6.3 Liquid scintillation spectrum of the effluent sample prior to separation.

6.2.4 Determination of ^{129}I species in the effluent by various methods

For determining ^{129}I species in the Sellafield effluent, various analytical methods were employed: (i) DSPE method, (ii) anion exchange followed by precipitation and (iii) ICP-MS. These methods were used to evaluate the accuracy of analytical results because there was presently no available certified reference materials for ^{129}I in water.

Experimental procedure and results

(i) Determination of ^{129}I species using the DSPE approach

Determination of $^{129}I^-$

1 mL of sample was weighed, diluted to 100 mL with water and then subjected to a derivatisation solid phase extraction. 13.2 mL of phosphate buffer (pH 6.4) and 4 mL of IBZ reagent were added to the sample solution. After keeping for 5 minutes, 2 mL of DMA was added. This solution was shaken well and kept for 60 minutes. The SPE procedure was employed to extract the ^{129}IDMA. The eluate was finally transferred to a 22 mL PE scintillation vial, mixed with 15 mL of Gold Star liquid scintillation cocktail and measured by LSC over one hour.

Determination of total inorganic ^{129}I

1 mL of the sample was weighed and diluted to 100 mL with water. 0.2 mL of ascorbic acid (0.1 mol L^{-1}) and 2.8 mL of acetic acid (1%) were added. This solution was shaken and kept for 30 minutes. 13.2 mL of phosphate buffer (pH 6.4) and 4 mL of IBZ reagent were then added to this solution. After shaking and keeping for 30 minutes, 2 mL of DMA reagent was added. This solution was shaken, kept for 120 minutes and then extracted using the SPE procedure. The extract was transferred to a 22 mL PE scintillation vial, mixed with 15 mL of Gold Star liquid scintillation cocktail and its activity was measured by LSC over one hour.

Determination of elemental ^{129}I

1 mL of sample was weighed and diluted to100 mL with water. 13.2 mL of the phosphate buffer (pH 6.4) and 2 mL of DMA were added. This solution was shaken well and kept for 60 minutes. This solution was then extracted by the SPE procedure. The extract was transferred to a 22 mL PE scintillation vial, mixed with 15 mL of Gold Star liquid scintillation cocktail and then counted by LSC for one hour.

The working standard solution of ^{129}I was prepared by transferring a known activity of certified activity ^{129}I solution (4600 Bq.g^{-1}, iodide form) to a 22 mL PE scintillation vial and mixing with 5 mL of THF followed by 15 mL of Gold Star liquid scintillation cocktail.

All results are summarized in **Table 6.2**. The detection limits for the determination of $^{129}I^-$ and total inorganic ^{129}I were 0.095 and 0.080 Bq g^{-1}, respectively.

(ii) Determination of ^{129}I species using anion exchange followed by precipitation

The anion exchange methods for the separation of iodine species from seawater described in Chapter 5 were applied to determine the ^{129}I species in the effluent. ^{137}Cs in the effluent was separated from the ^{129}I by the anion exchange method. $PdCl_2$ was added to the anion exchange eluate to precipitate PdI_2. The activity of the precipitate was then measured by gamma ray spectrometry.

Determination of $^{129}I^-$

2 mL of the effluent sample was weighed and diluted to 50 mL with water and then acidified to below pH 2 using concentrated HCl. An anion exchange column (15 g of resin) was prepared as described in Chapter 5. After passing the sample through the anion exchange column, the resin bed was washed with 100 mL of acidified water (pH <2). The eluate and wash water were collected to be used for the determination of $^{129}IO_3^-$. 60 mL of NaOCl (20%, v/v) was then used to elute $^{129}I^-$ from the column. This was performed in two stages, adding 30 mL aliquots of NaOCl and allowing it to soak the column from about 1 hour. The column was then washed with 25 mL of water. The eluate and wash water were collected in the same receiving vessel.

The precipitation of ^{129}I using $PdCl_2$ was adapted from unpublished work carried out by the Geoscience Advisory Unit (GAU), NOCS. The procedure was carried out as follows. The combined eluate and wash water from the anion exchange column was acidified by adding 13.34 mL of HNO_3 (8 mol L^{-1}). Once effervescence had ceased 10 mL of hydroxylamine hydrochloride solution (1 mol L^{-1}) was added. After 5 minutes, 10 mL of sodium metabisulfite solution (1 mol L^{-1}) was added. This solution was kept for 5 minuntes, then transferred to a hot-plate and gently heated for about 10 minutes. 3 mL of HCl (2 mol L^{-1}) and 3 mL of iodide carrier solution (10 mg mL^{-1}) were added to the solution, followed immediately by 5 mL of $PdCl_2$ solution. Gentle heating of this solution was continued until coagulation of the PdI_2 precipitate occurred. The mixture was covered and allowed to cool overnight. The precipitate was filtered onto a pre-weighed filter paper and washed with methanol. The precipitate was dried in an oven at 100 °C for 20 min and then cooled to room temperature in a desiccator. The precipitate was weighed to determine the amount of PdI_2[1] and then was

[1] The percent iodide yield could be calculated from:

$$Y = \frac{W1x100}{W2xCF}$$

Where W1 = Weight of PdI_2 precipitate (mg)

W2 = Weight of iodide added (mg)

mounted onto an aluminium planchette. A solution of 10% polyvinyl acetate was used to secure the filter paper and a solution of 3% polyvinylacetate was used to seal the filter onto the planchette. Cling film was used to cover the planchette. The precipitate after preparation is shown in **Figure 6.4**. Its activity was measured by placing it face down on the LEGe detector for 4 hours.

Figure 6.4 The precipitate of ^{129}I as palladium iodide ($PdI_{2)}$ on a filter sealed on the aluminium planchette.

Determination of total inorganic ^{129}I

2 mL of the effluent sample was weighed and diluted to 50 mL with water. This solution was acidified to a pH < 2 by using concentrated hydrochloric acid. 1.5 mL of sodium bisulfite (0.27 mol L^{-1}) was added to the solution followed by 3 mL of stable iodide carrier solution (10 mg mL^{-1}). This sample solution was analyzed by using the anion exchange procedure followed by precipitation (as described for the determination of $^{129}I^-$) but without the further addition of iodide carrier solution.

Determination of $^{129}IO_3^-$

To the iodate fraction from the anion exchange separation was added 1.5 mL of sodium bisulfite (0.27 mol L^{-1}) and 3 mL of iodide carrier solution (10 mg mL^{-1}). The solution was then analyzed by anion exchange followed by the precipitation method, as described for determining of $^{129}I^-$. The iodide carrier was not however added in the precipitation procedure.

All results are presented in **Table 6.2**.

CF = Conversion factor for correcting measured activity of ^{129}I in sample which its geometry was different from that of standard source

50 mL of water spiked with $^{129}I^-$ (193.2 Bq) was used to test the method for the determination of iodide and a recovery of 101.7±5.5% was obtained. The mean recovery of stable iodide carrier was 94.8±4.2% (n = 3).

(iii) Determination of ^{129}I by ICP-MS

The activity concentration of inorganic ^{129}I in the effluent sample (measured by the anion exchange followed by precipitation) of approximately 39 Bq.g^{-1} corresponds to ca.6 mg L^{-1}. Four dilutions of the effluent sample were therefore prepared by transferring the appropriate quantities to 20 mL volumetric flasks and weighing them. These samples were mixed with 4.4 mL of TMAH (1 mol L^{-1}) and filled up to the mark with water. These samples were then weighed.

In this experiment, TMAH was added to the samples, blanks, working calibration standards and the rinsing solution to achieve a final concentration of 2% (v/v) of TMAH. A stock standard solution of $^{129}I^-$ with a certified activity of 4600 Bq g^{-1} contains 0.7 g L^{-1} of $^{129}I^-$. This standard solution was diluted to give working standard solutions (0.01, 0.05, 1.08 and 2.85 µg L^{-1}). In 50 mL of each standard solution, it was mixed with 11 mL of TMAH (1 mol L^{-1}) and water for diluting to the mark. These standard solutions were then weighed.

The linear calibration graph for the determination of ^{129}I by ICP-MS is shown in **Figure 6.5.**

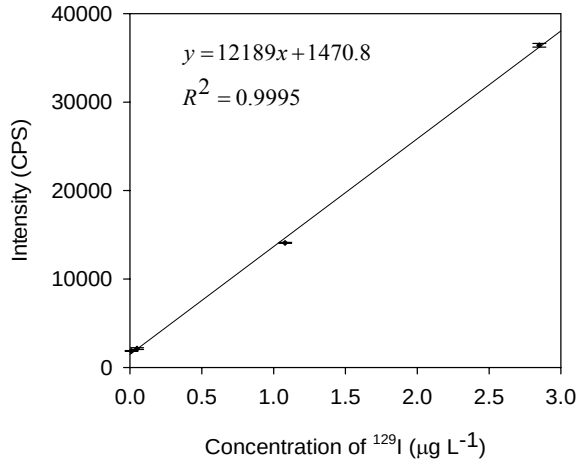

Figure 6.5 A calibration curve for the determination of ^{129}I.

The mean activity concentration of ^{129}I in the effluent sample (by ICP-MS) was 45.7±2.9 Bq g^{-1} (n = 4).

The accuracy of the analytical method could be evaluated by using a certified reference material having a matrix similar to that of the sample but such reference materials for ^{129}I and its species in water are not currently available. Three analytical methods are therefore used for validation. The results obtained from the DSPE methods, anion exchange followed by precipitation and ICP-MS are summarized in **Table 6.2**.

Table 6.2 The mean activity concentrations of ^{129}I species (Bq g^{-1}) in the effluent sample.

Chemical species	DSPE methods (n = 3)	Anion exchange followed by precipitation (n = 3)	ICP-MS (n = 4)
Total inorganic iodine (TII)	40.1±4.5	38.9±1.6	45.7±2.9[a]
Iodide (I^-)	27.4±0.7	22.9±2.0	-
Iodate (IO_3^-)	-	11.0±1.1	-
Elemental iodine (I_2)	0.22±0.02	-	-
TII-I^- = IO_3^-	12.7±4.6	-	-
I^--I_2 = absolute I^-	27.2±0.7	-	-

[a] *This value is the total quantity of ^{129}I in the effluent sample.*

Discussion and conclusions

Iodine-129 species in effluent determined by DSPE

The pH of the effluent sample was checked prior to analysis and its pH value was found to be 11. This would cause incomplete derivatisation of the ^{129}I species to radioactive IDMA (^{129}IDMA) and incomplete separation of the ^{129}I from the ^{137}Cs in the sample. This problem was solved by diluting the sample 100-fold with water prior to analysis.

From the determination of elemental ^{129}I by the DSPE method, the other inorganic forms of ^{129}I (as iodate and iodide) in the effluent sample would not retain on the SPE cartridge. To check this hypothesis, waste from the SPE step employed in the

determination of elemental ^{129}I were collected and then re-tested with the DSPE method. One of wastes was analyzed for $^{129}I^-$ and another waste was analyzed for total inorganic ^{129}I. The activity concentrations of $^{129}I^-$ and total inorganic ^{129}I in the wastes from the SPE step were found to be 24.5±0.1 Bq g^{-1} and 38.0±0.1 Bq g^{-1}, respectively. Therefore, the other inorganic forms of ^{129}I in the effluent could be separated from the elemental ^{129}I by using the DSPE method for the determination of elemental iodine.

The DSPE method could therefore identify and measure the inorganic species of ^{129}I in the effluent sample. The major inorganic form of ^{129}I in the effluent sample was iodide. The concentration of elemental iodine (^{129}I) in the effluent was negligible (**Figure 6.6)**. The activity concentration of $^{129}IO_3^-$ could be calculated as the difference between total inorganic ^{129}I and $^{129}I^-$.

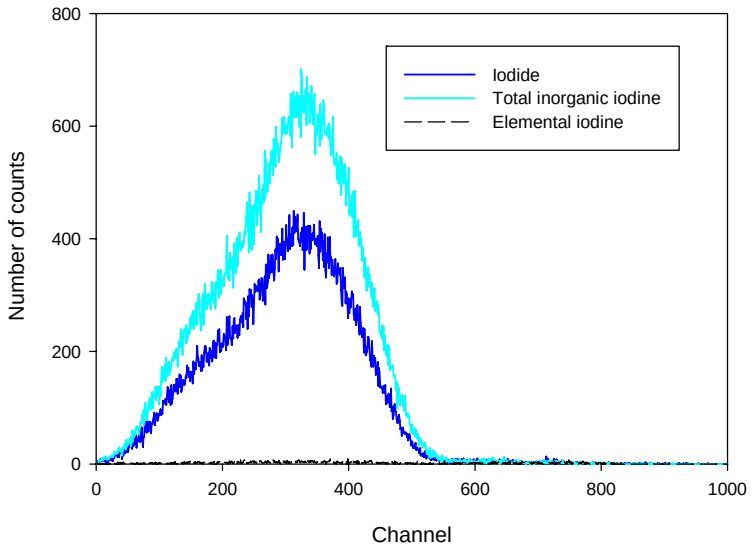

Figure 6.6 The liquid scintillation spectra of ^{129}I species in the effluent sample from analyses using the DSPE methods.

Iodine-129 species determined by anion exchange followed by precipitation

These anion exchange methods were used to isolate and collect iodate, iodide and total inorganic iodine forms of ^{129}I from the effluent sample. ^{137}Cs should not absorb on the anion exchange resin, so these methods could also separate ^{129}I from ^{137}Cs.

The major inorganic form of ^{129}I in the effluent sample was found to be iodide. For the determination of $^{129}I^-$, when a stable iodide carrier solution was added to the effluent sample prior to the anion exchange separation, the colour of the sample changed from colourless to brown and there was some brown vapour. This is believed to arise from $^{129}IO_3^-$ in the effluent sample reacting with excess of iodide carrier and $^{129}I^-$ in acid condition to produce iodine (**Equation 6.5**). This iodine changed to tri-iodide (I_3^-) later.

$$IO_3^- + 5I^- + 6H^+ \longrightarrow 3I_2 + 3H_2O \qquad (6.5)$$

To avoid this conversion, the stable iodide carrier solution had therefore to be added to the sample after the anion exchange step, when precipitating the iodine for the determination of $^{129}I^-$.

The analyses of other ^{129}I species (total inorganic iodine and iodate) did not have the problem from adding iodide carrier at the anion exchange step because all ^{129}I species were converted to $^{129}I^-$ by adding bisulfite.

^{129}I in the effluent determined by ICP-MS

The concentration of ^{129}I in the effluent sample could be determined by ICP-MS without prior chemical separation. The effluent sample was diluted to an appropriate level by predicting from the results obtained from the anion exchange followed by precipitation. The results obtained by ICP-MS were the total quantity of ^{129}I in the effluent sample.

Comparison of results obtained from three analytical methods

The general agreement among the three analytical methods was poor. The contents of total ^{129}I in the effluent sample obtained, from both the DSPE and anion exchange/precipitation methods were not statistically different at the 95% confidence level. Results obtained from the DSPE and anion exchange/precipitation method were statistically different (at the 95% confidence level) from the ICP-MS results.

The activity concentration of $^{129}I^-$ in the effluent sample obtained from the DSPE method for the measurement of $^{129}I^-$ did not agree with results obtained from the anion exchange/precipitation. Iodine-129 iodide may have been lost during the anion exchange process due to reaction of $^{129}I^-$ with $^{129}IO_3^-$ under acidic conditions.

Other inorganic forms of ^{129}I (iodate and elemental iodine) in the effluent sample were determined using the DSPE method and the anion exchange followed by precipitation. The DSPE could indirectly determine $^{129}IO_3^-$ by calculating the difference between total inorganic^{129}I and $^{129}I^-$. The activity concentration of $^{129}IO_3^-$ obtained from the anion exchange followed by precipitation was slightly less than that from the DSPE method. The low activity concentration of ^{129}I elemental iodine could be only measured by the DSPE method.

6.2.5 Conclusion

The DSPE methods for the determination of radioactive iodine species could be applied to determine ^{129}I as total inorganic iodine, iodide, iodate and elemental iodine in the effluent sample, whilst the anion exchange followed by precipitation method could be applied to determine ^{129}I as total inorganic iodine, iodate and iodide. The results obtained from the two methods and ICP-MS showed the presence of ^{129}I species in the effluent as iodate, iodide and elemental iodine. The predominant species of ^{129}I in the effluent sample was iodide. Both proposed analytical methods for the determination of ^{129}I species were simple, selective and provided good precision. However, the selectivity of the anion exchange method should be improved. The results from this study could, therefore, be useful for understanding the behavior of ^{129}I in the effluent released from nuclear facilities. If this effluent is released to the aquatic environment, the behavior of ^{129}I species will be predicted to be similar to that of stable iodine species.

6.3 Determination of ^{127}I and ^{129}I species in Cumbrian water samples

6.3.1 Introduction

The West coast of Cumbria (UK) is the location of the important nuclear facilities at Sellafield and Drigg, the environmental monitoring of which is of interest.

Sellafield is the site comprised of a nuclear reprocessing plant and Calder Hall nuclear power station. The main activities at the Sellafield site are reprocessing and conditioning of irradiated nuclear fuel and storing nuclear materials and radioactive waste. Low level liquid radioactive wastes from Sellafield are discharged, under authorization, into the Irish Sea by a 2.1 km long pipeline[31]. After a revised authorization in 1994, and the operation of a new thermal oxide reprocessing plant, the annual discharge of ^{129}I in low level liquid radioactive wastes into the Irish Sea was increased from 0.4 TBq to 2 TBq. The increased discharge of ^{129}I was however found to have very low radiological significance[32]. The liquid discharge of ^{129}I from the Sellafield nuclear fuel reprocessing plant into the Irish Sea until 2007 was 1,400 kg [33].

The Drigg waste disposal site is situated near the Cumbrian coast and at a distance of about 6 km from Sellafield. It is used for the disposal of low level radioactive waste (LLW). Most of the waste is from the Sellafield site. The location of LLW disposal in trenches 1-7 and vaults 8 is shown in **Figure 6.7**. The leachates from the trenches and vault initially discharge to a stream at Drigg which runs for about 2 km from the discharge point to its confluence with the Irt River. The discharge of leachates into the Irish Sea was changed in 1988. There is no information about the ^{129}I discharge and contamination from the Drigg waste disposal site[34-35].

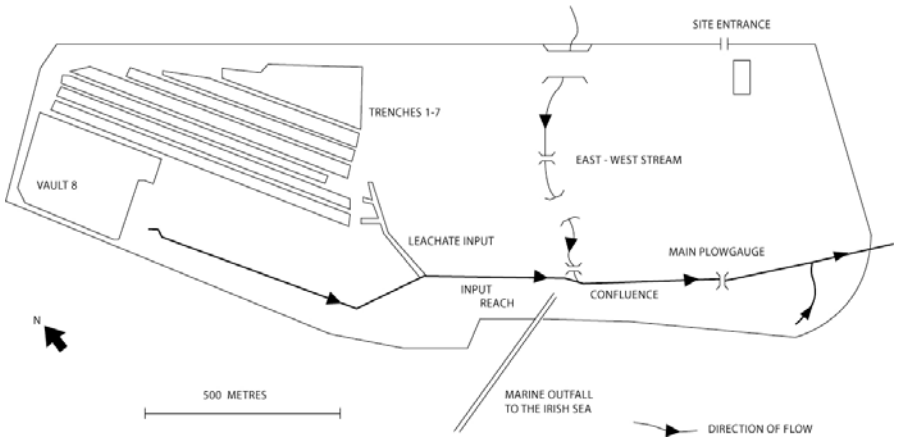

Figure 6.7 The location of disposal operation at the Drigg site (after Murdock[34]).

The distributions of ^{127}I and ^{129}I species in the environment are required to get a better understanding of the pathways into the biogeochemical processes. This information will be useful for the monitoring the transportation of ^{129}I and for assessing its environmental impact. For this purpose, a few researchers have

studied the speciation of ^{129}I in seawater using the high sensitivity techniques of AMS or NAA [36-37].

In this section, the anion exchange followed by DSPE method reported in Chapter 5 was used to separate and enrich ^{127}I and ^{129}I species from Cumbrian water samples. Owing to the very low concentration of ^{129}I in the aquatic environment, this proved to be quite a challenge using the apparatus available. Three detection systems: HPLC, LSC and ICP-MS were used for the validation because there were no available certified reference materials for ^{129}I and its species in water.

6.3.2 Chemicals and apparatus

The chemicals used for the determination of stable iodine species as IDMA by using HPLC were the same as described in Chapter 3. The chemicals used for the anion exchange followed by the DSPE methods were as described in Chapters 4&5. Millipore membrane filters (HA type, 0.45 μm) were purchased from Millipore (UK). Nitric acid (ARISTAR® grade) used to prepared sample for the determination of ^{127}I and ^{129}I species by ICP-MS was purchased from VWR (UK). The apparatus used to determine ^{127}I and ^{129}I species in Cumbrian water samples was the same as described in Chapter 3, 4 and 5.

6.3.3 Sampling sites and sample preparation

Details of sampling locations

Coastal surface water near the Sellafield nuclear reprocessing site and Irt river water from the Drigg disposal site in Cumbria, UK were collected. The details and related information about the sampling in this study are summarized in **Table 6.3**.

Table 6.3 The details of locations for collecting Cumbrian water samples.

Location	Latitude Longitude	Distance from Sellafield nuclear site (km)	Sampling time
River water Drigg	54°22′16.46″N 3°26′31.13″W	6.51 (1.305 km from LLW Repository)	11:45, 5/10/2008

Table 6.3 (continued)

Location	Latitude Longitude	Distance from Sellafield nuclear site (km)	Sampling time
<u>Seawater</u>			
Drigg	54°22′21.29″N 3°28′50.36″W	5.36 (1.608 km form LLW Repository)	11:30,5/10/2008
Nethertown	54°26′56.77″N 3°33′43.63″W	5.25	12:45, 5/10/2008
Parton	54°34′16.43″N 3°34′54.42″W	17.69	13:30, 5/10/2008

LLW = low level radioactive waste

Sampling and sample preparation

The Cumbrian coastal surface water samples and river water sample were taken by bucket from each location as shown in **Figure 6.8** and stored in 10 L polyethylene (PE) containers**.**

Figure 6.8 Sampling sites of this study: locations 1-3 = coastal water from Parton, Nethertown and Drigg areas, respectively and 4 = river water from the Drigg area. (Image reproduced from the Ordnance Survey map data with kind permission of Ordnance Survey and Ordnance Survey of Northern Ireland)

The Cumbrian water samples were collected at low tide. The water samples were stored in the PE containers and nothing was added to preserve the ^{127}I and ^{129}I species. All the water samples were filtered by using a 0.45 μm Millipore

membrane filters (HA type) to remove suspended particles and any microorganisms[38] before analysis. These samples were then stored in a cold room at 4-5°C until analysis.

The anion exchange followed by the DSPE methods (as described in Chapter 5) were used for the separation and enrichment of ^{127}I and ^{129}I species (iodide and iodate) from the Cumbrian water samples. Before analysis, the water samples were deoxygenated by passing nitrogen and the pH of the water samples was adjusted to below 2 by adding drops of concentrated HCl.

The pre-separation and enrichment of iodine species by the anion exchange method

Iodide in seawater

An acidified water sample (1 L) was passed through the anion exchange column followed by 100 mL of acidified water at a flow rate 3-5 mL min^{-1}. The effluent and acidified wash water were collected and combined together. 60 mL of NaOCl (20%) was used to elute $^{127}I^-$ and $^{129}I^-$ from the column in two steps; each 30 mL of NaOCl (20%) being left to soak into the column for about 1 hour. This column was then washed with 25 mL of water (flow rate of 2 mL min^{-1}). The combined hypochlorite and wash water fraction was collected and excess NaOCl was decomposed by adding sodium formate (50%, w/v) and evaporating on a hot plate (90 – 100 ˚C) until 25 mL of solution was left. This solution was adjusted to 100 mL by adding water.

Iodate in seawater

The combination of effluent and acidified wash water from passing the Cumbrian water sample through the anion exchange column was treated with 1.5 mL of $NaHSO_3$ (0.27 mol L^{-1}) . Next, this combined fraction was passed through another anion exchange column for the separation of $^{127}IO_3^-$ and $^{129}IO_3^-$ as iodide from the water sample. The anion exchange column was then washed by 100 mL of acidified water. The eluate and acidified wash water were discarded. Other steps of anion exchange procedure were same as the isolation of iodide from seawater by using the anion exchange method.

The re-enrichment of iodine species by the DSPE method

Both the iodide and iodate fractions of ^{127}I and ^{129}I were derivatised to 4-iodo-*N,N*-dimethylaniline (IDMA) and then enriched by solid phase extraction as follows.

2 mL of HCl (0.5 mol L^{-1}), 5 mL of acetic acid (10%) and 0.2 mL of ascorbic acid (0.1 mol L^{-1}) were added. This solution was shaken and kept for 30 minutes at room temperature. 15 mL of phosphate buffer (pH 6.4, 2 mol L^{-1}) and 4 mL of IBZ were added. After 30 minutes, 2 mL of DMA was added. This solution was shaken well. After 120 minutes, this solution was extracted onto a SPE cartridge and eluted with 5 mL of THF.

The analytical procedure for the determination of ^{127}I and ^{129}I species (iodide and iodate) in Cumbrian water samples is depicted in **Figure 6.9**.

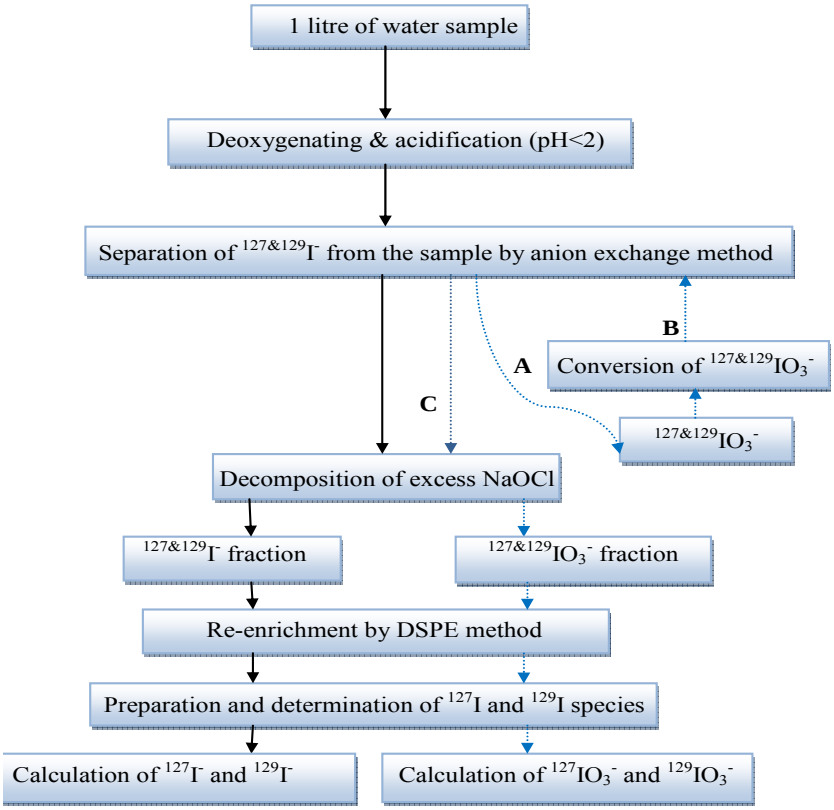

Figure 6.9 Analytical scheme of ^{127}I and ^{129}I species in Cumbrian water samples. (A = acidified seawater and acidified wash water passed through the column, B = iodine species in water sample was converted and passed through another column, C = eluate and wash water from the second anion exchange column)

6.3.4 Determination of ^{127}I and ^{129}I species in water samples using three detection systems

After preparing water samples by the anion exchange followed by the DSPE methods, each Cumbrian water sample solution was divided into three fractions for analysis of ^{127}I and ^{129}I species by HPLC, LSC and ICP-MS. As there was no available certified reference materials for ^{129}I and its species in water, the analytical accuracy was evaluated by comparing results obtained from the three analytical techniques.

Experimental procedure and results

(i) Determination of ^{127}I species by HPLC

1 mL of each extract was transferred to a 22 mL PE scintillation vial, mixed with 1 mL of water and then injected into the HPLC system. A stock standard solution was prepared by dissolving a specified amount of IDMA in THF and then diluting to the working standard solutions (1, 5.1, 10, 15.2 and 25.3 μmol L^{-1}) using THF (50%). The chromatographic conditions were as described in Chapter 3.

A calibration of various concentrations IDMA versus peak area gave a coefficient of determination (R^2) of 0.9985. For the quality control, the relative standard deviation was 5.67% for 6 replicate injections of the IDMA standard solution (50.52 μ mol L^{-1}).

A chromatogram of $^{127}IO_3^-$ in Cumbrian water which was derivatized as IDMA is shown in **Figure 6.10**. There were several unknown peaks but a peak of IDMA in water sample was resolved well from the other peaks. The peak shape from the IDMA was broadened. This may have been due to an incompatibility of the sample matrix with the mobile phase.

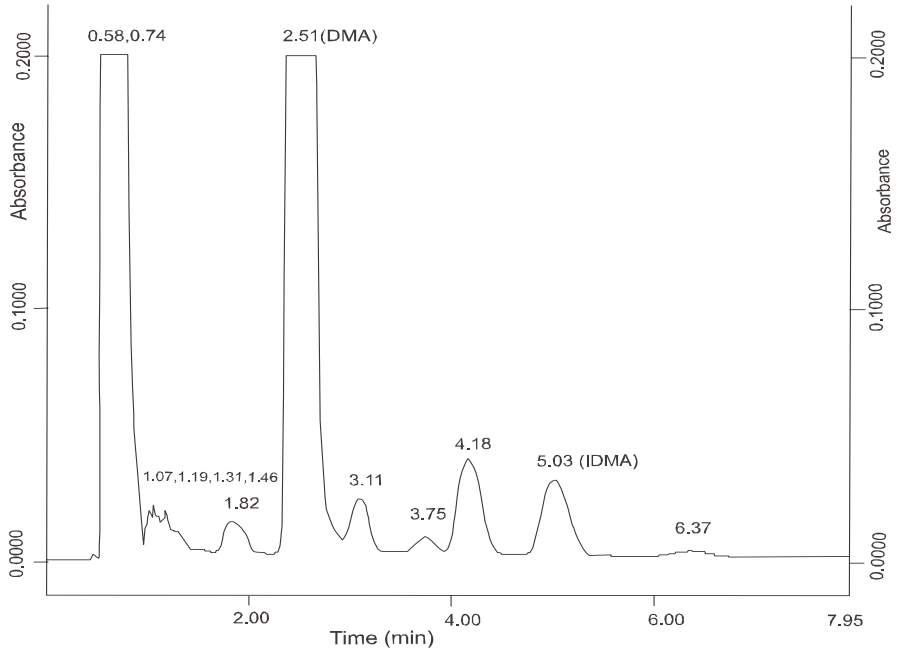

Figure 6.10 A chromatogram obtained from determination of $^{127}IO_3^-$ in Parton coastal water sample.

The results obtained from the determination of ^{127}I species in Cumbrian water samples are tabulated in **Table 6.4**.

Table 6.4 The concentrations of ^{127}I species (μg L^{-1}) in Cumbrian water samples.

Location	$^{127}I^-$	$^{127}IO_3^-$
1	9.6±1.3	10.1±0.7
2	9.3±1.1	7.8±2.5
3	9.1±2.4	10.8±4.0
4	<7.6	<7.7

Each result is a mean of three determinations.

(ii) Determination of ^{129}I species by LSC

1 mL of each extract was transferred to a 22 mL pre-weighed PE scintillation vial. This sample was then weighed and mixed with 19 mL of Gold Star liquid scintillation cocktail. A standard solution was prepared by spiking 0.05 mL of certified activity ^{129}I (4600 Bq g^{-1}) into a 22 mL pre-weighed PE scintillation vial and mixed with 1 mL of THF and 19 mL of Gold Star liquid scintillation cocktail. The standard, samples and blank were measured by LSC for 8 hours.

The activity concentrations of $^{129}I^-$ and $^{129}IO_3^-$ in Cumbrian water samples were found to be lower than the detection limit of the LSC (8.4 mBq g^{-1} for $^{129}I^-$ and 9.1 mBq g^{-1} for $^{129}IO_3^-$).

(iii) Determination of ^{127}I and ^{129}I species by using ICP-MS

Before analysis, THF had to be removed from the extracts and were prepared as described in Section 5.7.1. The stock standard solution of ^{129}I used in this experiment has a certified activity of ^{129}I as iodide (4600 Bq g^{-1}). Its concentration activity was equal to 0.7 g L^{-1}. This stock standard solution was diluted to gave working standard solutions (0.54, 1.14, 5.32, 17.6, 55, 109 and 543 ng L^{-1}) by transferring the appropriate quantities to a 22 mL PE scintillation vial. These working standard solutions were weighed and then mixed with 5 mL of TMAH (1 mol L^{-1}) and 0.5 mL of HNO_3 (8 mol L^{-1}). The volumes of the working standard solutions were adjusted to 10 mL with water and weighed.

The determination of ^{127}I species by HPLC had shown the concentrations of $^{127}I^-$ and $^{127}IO_3^-$ in the water samples to be in the ppb level. In order to protect the mass spectrometer, all the samples were diluted100 times as follows. 0.1 mL of each dissolved iodine solution was transferred to a 22 mL PE scintillation vial. 5 mL of TMAH (1 mol L^{-1}), 0.5 mL of HNO_3 (8 mol L^{-1}) and 4.4 mL of water were added. These sample solutions were analyzed for ^{127}I by ICP-MS.

A stock standard solution of ^{127}I was prepared by dissolving 0.0166 g of potassium iodide (pre-dried in the oven at 100 °C for one hour) with 20 mL of water. This was diluted to give working standard solutions (0.87, 5.82, 11.8, 21.9 and 43.8 μg L^{-1}). These standard solutions were mixed with 5 mL of TMAH (1 mol L^{-1}) and 0.5 mL of HNO_3 (8 mol L^{-1}), adjusted to 10 mL with water and weighed.

A calibration graph for the determination of ^{129}I in the Cumbrian water samples is shown in **Figure 6.11**.

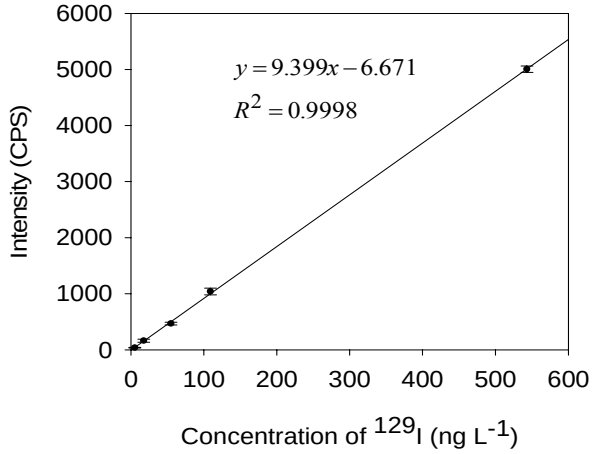

Figure 6.11 A calibration graph for determination of ^{129}I in Cumbrian water samples.

The results showed that the concentrations of ^{129}I species in Cumbrian water samples were below the detection limit (0.98 ng L^{-1}) related to the standard solutions.

A calibration graph for the determination of ^{127}I species in Cumbrian water samples is shown in **Figure 6.12**

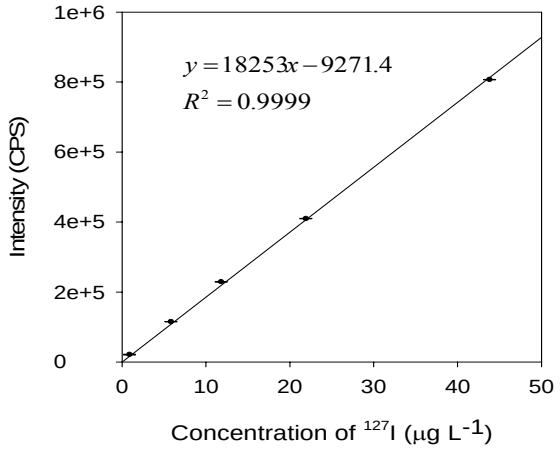

Figure 6.12 A calibration graph for the determination of ^{127}I in Cumbrian water samples by ICP-MS.

The quantities of ^{127}I in all samples and blanks were found to be much higher than the expected values and were out of calibration. The estimated concentrations of ^{127}I species in Cumbrian water samples were at ppm levels.

Discussion and conclusions

The concentration of ^{127}I species in water samples from analysis by HPLC

The concentrations of $^{127}I^-$ in coastal surface water samples from various sampling sites were found to be approximately 9 μg L^{-1}, whilst the concentrations of $^{127}IO_3^-$ were in range of 7.8 to10.8 μg L^{-1}. The concentrations of ^{127}I species in river water samples were found to be lower than the detection limit of the methods. The incomplete separation of iodate and iodide from seawater by anion exchange had to be considered. The concentrations of both iodine species might be incorrect.

The quantities of ^{127}I species in river water samples collected from the English Lake District were studied by Jones and Truesdale[39]. The concentrations of $^{127}I^-$ and $^{127}IO_3^-$ in river samples were 0.2 to1.9 μg L^{-1} and 0.4 to 3.3 μg.L^{-1}, respectively [39]. Atarashi-Andoh et al[40] reported that the concentration of total ^{127}I in the river out of Wastwater was 1.25±0.05 μg L^{-1} [(40)]. This study collected the surface water of the Irt River which was run from Wastwater to the Irish Sea. The sampling was carried out at low tide, so it was not intruded by seawater. The concentrations of $^{127}I^-$and $^{127}IO_3^-$ in the river water might be similar to those referenced above (39 & 40). Their contents in the river water were however found to be lower than the detection limit of the methods used.

The concentrations of $^{127}I^-$ and $^{127}IO_3^-$ species in seawater samples collected along the Eastern coast of the Irish Sea, were studied by Truesdale[41]. The spatial variation of $^{127}I^-$ and $^{127}IO_3^-$ concentrations (at salinity = 35, in late September, 1977) were approximately 0.16 and 0.39 μmol L^{-1} (20.3 and 68.2 μg L^{-1}), respectively. Atarashi-Andoh et al[40] reported that the concentration of total ^{127}I in seawater collected from Parton was approximately 34 μg L^{-1}[(40)]. The concentrations of ^{127}I species in seawater samples of this study were much lower than those were observed by Truesdale[41] and Atarashi-Andoh et al[40]. Some parameters might influence the concentrations of both ^{127}I species. The relationship between concentrations of $^{127}I^-$ and $^{127}IO_3^-$ and some parameters in coastal surface water samples collected from Alexandria was studied by Mahmoud and El Deek[42]. The concentrations of $^{127}I^-$ (13.29 - 41.51 μg L^{-1}) were found to be three times higher than the concentrations of $^{127}IO_3^-$ (4.98 - 14.98 μg L^{-1}). The concentrations

of $^{127}I^-$ correlated with chlorinity and $^{127}IO_3^-$ contents, but nitrite, organic matter and pH did not influence the $^{127}I^-$ contents[42]. For this study, the $^{127}IO_3^-$ content in seawater sample collected from Nethertown was found to be slightly lower than that collected from Parton and Drigg which were further from Sellafield than Nethertown. The concentrations of $^{127}I^-$ colleted from three sites were approximately 9 μg L^{-1}. Due to the complicated hydrographic transport pattern of the Irish Sea, many parameters influenced the distribution of iodine species in this area. An interpretation is therefore very difficulty requiring further work to clear it up.

Determination of ^{129}I species in water samples by LSC

The detection limit (approximate 9 mBq g^{-1}) of LSC for the determination of ^{129}I was approximately equal to 1.4 μg L^{-1}. The ratios of $^{129}I/^{127}I$ in surface water of the English Lake District were studied by Atarashi-Andoh et al[40]. The AMS which has the high sensitivity for ^{129}I detection required was employed in his study. From Atarashi-Andoh's results, the concentration of total ^{129}I in surface water of Parton collected in March, 2005 was approximately 0.27 ng L^{-1} [40]. The proposed method for sample preparation could enrich the concentration of ^{129}I species in Cumbrian water samples about 200 times. From this information, the concentrations of ^{129}I species at Parton obtained from this study would have been two orders of magnitude lower than the detection limit of LSC.

The concentration activities of $^{129}IO_3^-$ and $^{129}I^-$ in Cumbrian water samples were found to be below the detection limit of the LSC. Therefore, the anion exchange followed by the DSPE methods might not sufficiently enrich the activity concentration of ^{129}I species in the Cumbrian water samples for measuring by LSC.

The determination of ^{127}I and ^{129}I by ICP-MS

The concentrations of ^{129}I species in Cumbrian water samples were found to be below the detection limit. The sensitivity of ICP-MS might not be sufficient to determine ^{129}I species in the extracts prepared by the proposed method. The loss of ^{129}I species from the samples during the anion exchange process, as discussed in Section 6.2.4, might be another cause of this problem.

Very high concentrations of ^{127}I were found in the sample solutions and blanks. This might be from the reagents used in the process. The IBZ reagent was found to retain on the SPE cartridge which could be then eluted from the SPE cartridge with the IDMA by using THF.

Failure to separate residual IBZ reagent from the extract injected into the ICP-MS would result in elevated iodine levels being detected by ICP-MS. Therefore, the major cause of iodine interference for the determination of ^{127}I species in Cumbrian water samples was from the IBZ reagent.

This problem could potentially be solved by improving the elution at the SPE stage with an appropriate eluent eluting the IBZ and other impurities prior to the elution of IDMA from the SPE cartridge. Another idea for solving this problem would be an online coupling of HPLC with the ICP-MS. The IDMA in the sample solution would be first separated by HPLC from residual IBZ before being analyzed by the ICP-MS.

6.3.5 Conclusion

Anion exchange followed by the DSPE was introduced to separate and enrich ^{129}I species from Cumbrian water samples at trace levels. This proposed method could enrich the concentration of ^{127}I and ^{129}I in water sample to 200-fold. Owing to the reaction of iodate with iodide to produce iodine under the acid condition, iodine might be lost during the anion exchange stage (Section 6.2.4). Three detection systems: HPLC, LSC and ICP-MS were employed for the validation as there were no certified reference materials available for ^{129}I and its species in water. The ^{129}I contents in all Cumbrian water samples were found to be lower than the detection limits of LSC and ICP-MS. The preconcentration factor of the proposed method for the sample preparation should be improved for the determination of ^{129}I species in water samples.

A comparison of the results obtained from the three analytical techniques failed. The concentrations of ^{127}I species could be determined by HPLC, but ICP-MS

encountered a major iodine interference from the IBZ reagent to determine ^{127}I species.

Consequently, the determination of ^{127}I and ^{129}I species in Cumbrian water samples was not successful. Some drawbacks of the analyses were discovered. Further work will be required to improve on this proposed method. Some information and ideas from this study may be useful for future work.

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CHAPTER 7 Overall conclusions and suggestions for future work

The aspiration of this work was to develop new analytical methods for the identification and measurement of radioactive iodine species, especially iodate and iodide, in the aquatic environment. These newly developed methods will be useful in the study of iodine speciation in the aquatic environment and in assessing the environmental impact of radioactive iodine releases.

The derivatisation-solid phase extraction (DSPE) and anion exchange methods were both chosen for development due to their abilities to isolate and enrich inorganic forms of both stable and radioactive iodine from aqueous samples without requiring special apparatus. The two enrichment steps from combining both methods offered the potential for isolating specific iodine species from complex matrices and at the same time achieving the large enrichment factors necessary for ultra-trace analyses.

7.1 The development of the derivatisation-solid phase extraction (DSPE) method

The DSPE method was initially developed using stable iodide and iodate. This method was based on the conversion of iodine species to 4-iodo-*N,N*-dimethylaniline (IDMA) which was then extracted and enriched by solid phase extraction (SPE) before being measured by HPLC. Optimization of SPE and HPLC conditions resulted in good mean recoveries of IDMA from the analysis.

Many factors controlled the quantitative conversion of iodide and iodate to IDMA. The oxidation of iodide could be completed in 5 minutes, but the rate of iodination of DMA influenced the yield of IDMA. When measuring iodate, its reduction by ascorbic acid showed the rate of the subsequent *N,N*-dimethylaniline (DMA) iodination due to iodine reduction by residual ascorbic acid. Excess 2-iodosobenzoate (IBZ) had to be used to neutralize this residual ascorbic acid. Once optimized, the mean recoveries of iodide and iodate (~1 μmol L^{-1} in 250 mL of water) were 110.8±9.7% (n = 3) and 103.0±18.2% (n = 3), respectively.

The DSPE methods could be readily adapted to collect individual ^{129}I species as radioactive IDMA (^{129}IDMA) and final measure by liquid scintillation counting (LSC). The mean recoveries obtained from spiking $^{129}I^-$ (~230 Bq) and $^{129}IO_3^-$ (~13 Bq) in water (25 mL) were 96.5±2.6 % (n = 3) and 94.6±0.8 % (n = 3), respectively.

The DSPE methods could identify and measure the inorganic forms of stable and radioactive iodine as iodate, iodide, elemental iodine and total inorganic iodine.

7.2 The pre-separation and enrichment of iodine species from seawater by an anion exchange method

An anion exchange separation was introduced to solve preconcentration problems from directly determining inorganic iodine species in seawater using DSPE methods and to provide an additional analyte preconcentration step to improve concentration-based detection limits. The optimum conditions of the anion exchange followed by DSPE methods were investigated using radiotracer. The Amberlite® IRA-400 resin (15 g) was employed to pre-separate and enrich iodide and iodate from acidified seawater (1 litre). Two approaches were developed for the collection of iodide and iodate, both being based on iodide collection by the resin. NaOCl (20%, v/v) elution stripped the collected iodide from the anion exchange resin but excess NaOCl had to be destroyed to prevent the chlorination of DMA. Before collecting on the anion exchange column, iodate was converted to iodide using bisulfite. The approach for collecting iodate could be used to collect total inorganic iodine from seawater. An incomplete separation of iodide from iodate was however observed.

The DSPE method for the determination of iodate was then adapted to re-enrich the eluted iodate from the anion exchange column. Total yields of iodide and iodate from combining two methods were 81.6±1.8% (n =3) and 79.1±7.7% (n = 3), respectively. The inorganic forms of iodine that could be therefore determined by these developed methods were iodate, iodide and total inorganic iodine.

ICP-MS was chosen as an alternative higher sensitivity detection system for measuring the sample prepared from the anion exchange followed by DSPE methods. The sample preparation had to be adapted to prevent problems with the analyses of organic solvent and an iodine memory effect with the ICP-MS. The overall recoveries for the determination of iodine species in seawater dropped to 50%. Iodine-127 measurement by ICP-MS could not be carried out on extracts resulting from the DSPE procedure due to the presence of residual ^{127}IBZ.

7.3 Application of the new methods to various sample types

The inorganic forms of stable or radioactive iodine in some sample types were determined using the methods developed in this research work. The new HPLC based DSPE methods could be used to determine stable iodide/iodate in iodized table salts, with good selectivity and precision. The iodate/iodide contents of these iodized table salts from different countries were within the recommended limits for iodine.

The inorganic forms of ^{129}I in an effluent from nuclear facility could be identified and measured using the DSPE methods followed by LSC and the anion exchange followed by precipitation using gamma ray spectrometer detection. The results obtained from those methods were compared to those obtained by ICP-MS. The results showed that the inorganic forms of ^{129}I present in the effluent were iodide, iodate and elemental iodine and the predominant form of ^{129}I in the effluent was iodide.

The last application was the determination of ^{127}I and ^{129}I species in Cumbrian water samples. The concentrations of ^{129}I species in the Cambrian water samples were considerably lower than those of ^{127}I species. The anion exchange followed by the DSPE methods was employed to separate and enrich ^{127}I and ^{129}I as iodide and iodate from the water samples prior to analysis by HPLC, LSC and ICP-MS. The concentrations of $^{127}I^-$ and $^{127}IO_3^-$ from coastal water samples were approximately 9 μg L^{-1} and 7.8 – 10.8 μg L^{-1}, respectively, whilst the concentrations of both ^{127}I species in a river water sample were lower than the detection limits of methods. Failures and problems were discovered from LSC and

ICP-MS. All concentrations of ^{129}I from measuring Cumbrian water samples by LSC were found to be below the detection limit. The ICP-MS did also not achieve to measure ^{129}I in Cumbrian water samples and the iodine interference from IBZ reagent was discovered for analyzing ^{127}I. Further work is required to solve these problems.

7.4 Suggestions for future work

The analytical methods which have been developed in this work and their applications are useful for broadening the speciation analysis of stable and radioactive iodine. Future work is however required to improve these developed methods and to increase the versatility of their applications.

- The SPE step in the DSPE method should be improved to include an appropriate eluent to remove interferences from a SPE sorbent prior to elute the IDMA. This is particularly true for IBZ, residues of which currently prevent the use of this enrichment for ^{127}I measurement by ICP-MS.

- The DSPE methods may be adapted to collect and measure the other radioisotopes of iodine species such as ^{131}I. The idea of this adaptation is based on the gamma ray emission of ^{131}I. In this approach, the radioactive IDMA (^{131}IDMA) will not be eluted from a SPE cartridge, but will be retained on the SPE cartridge and measured directly using a gamma ray spectrometer.

- Due to the drawback of there being an incomplete separation of iodide and iodate from seawater, the anion exchange method requires further work to improve this separation.

- From the determination of ^{127}I and ^{129}I species in Cumbrian water samples by ICP-MS, it is evident that the removal of THF from IDMA solution should be improved to get a better recovery by using the other appropriate procedures.

- For ultra-trace analyses, the enrichment factors must be improved so that lower concentration-based detection limit can be achieved. Adaptation of the reported methods should result in the collection of all the iodine from litre quantity samples into a final extract, the entirety of which can be counted.

Appendices

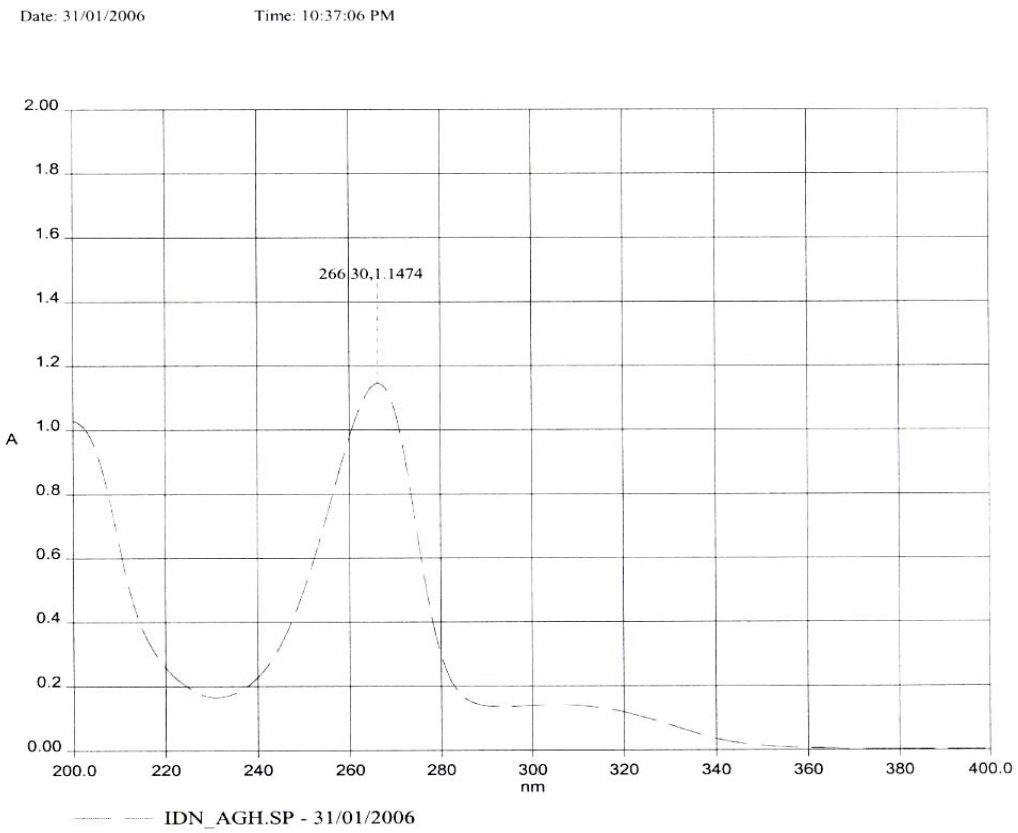


Figure A1 The absorption spectrum of IDMA (4.6 mmol L^{-1}) in acetonitrile.

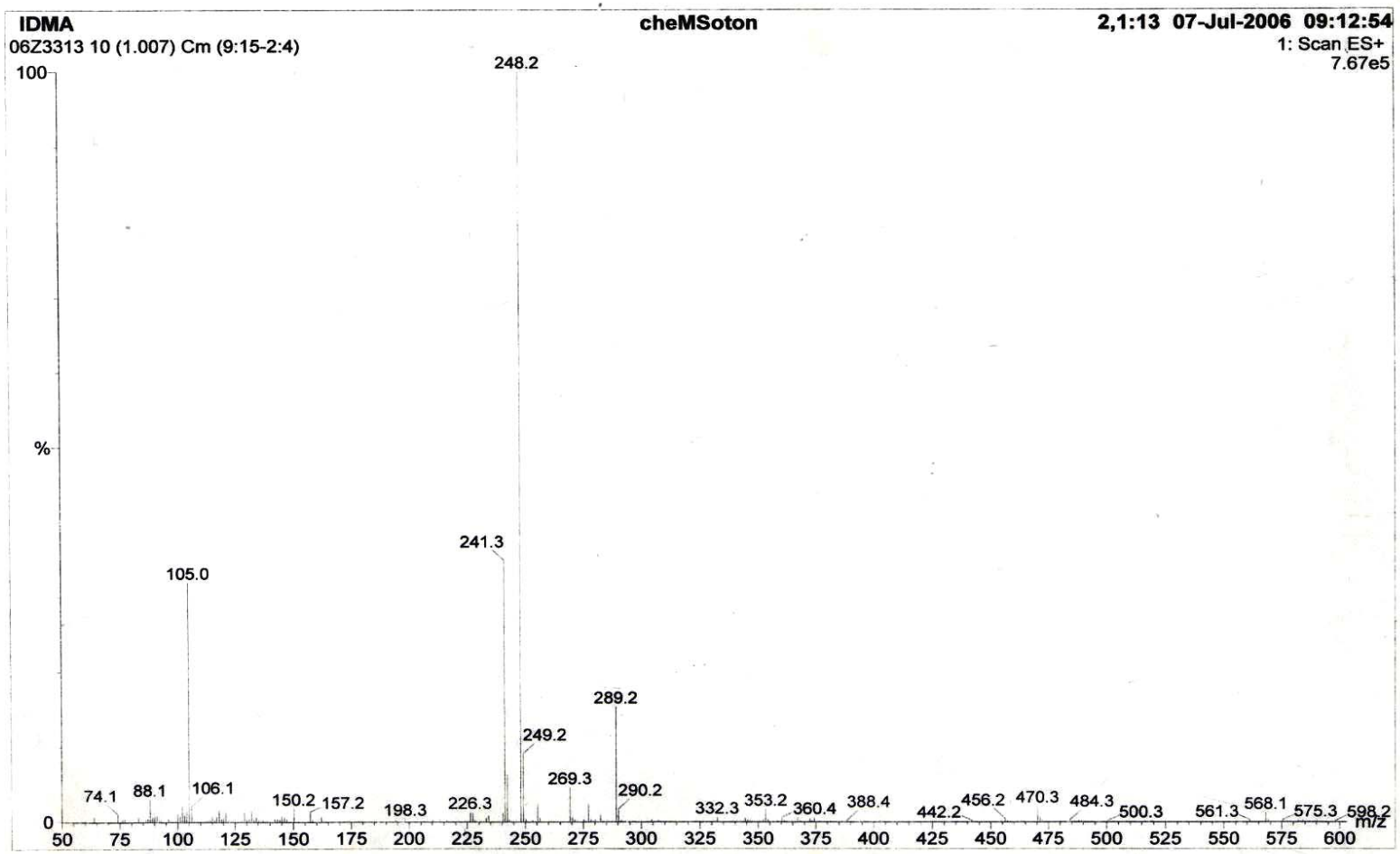
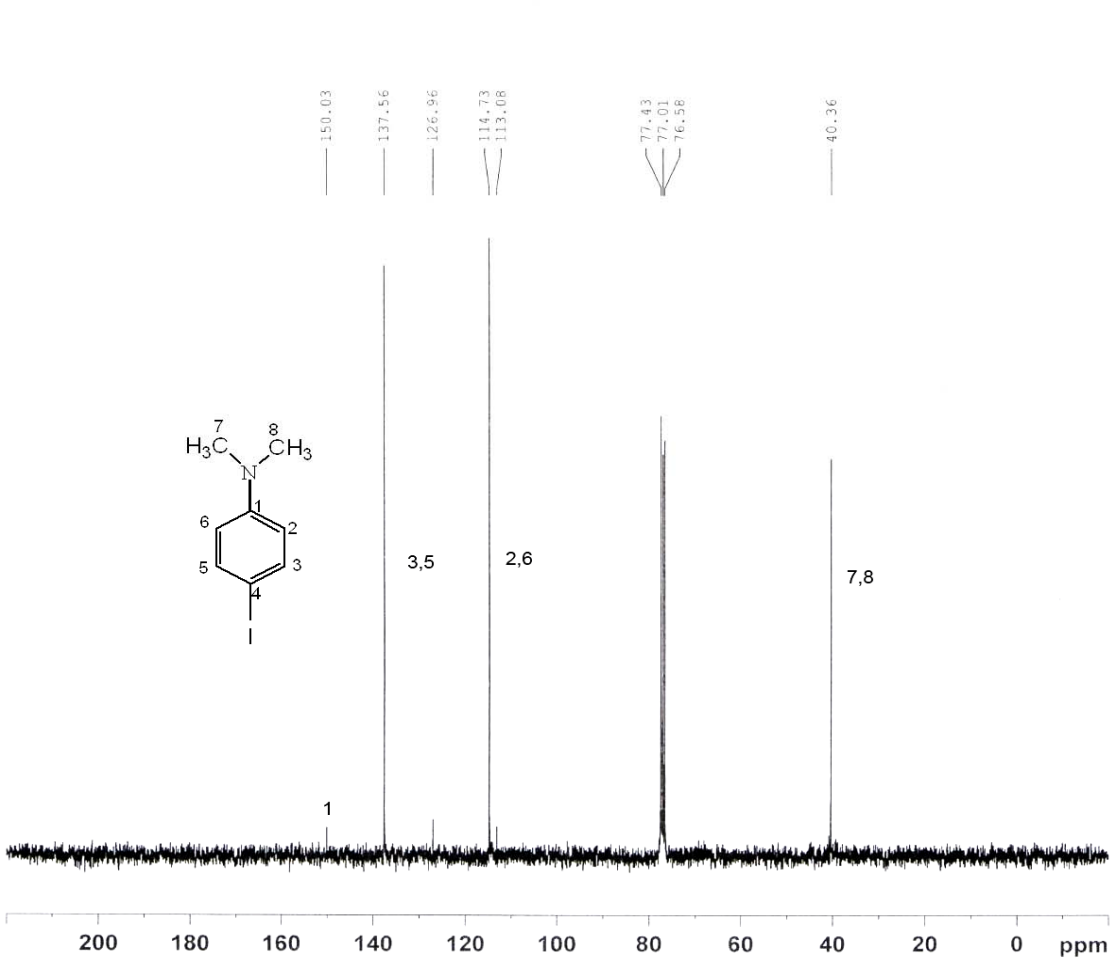


Figure A2 The positive ion electrospray mass spectrum of IDMA in acetonitrile.

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PROCNO                  1

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TD                  65536
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NS                    512
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FIDRES          0.276427 Hz
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RG                  574.7
DW                 27.600 usec
DE                  7.50 usec
TE                 300.0 K
D1              1.00000000 sec
d11             0.03000000 sec
DELTA           0.89999998 sec
MCREST          0.00000000 sec
MCWRK           0.01500000 sec

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P1                    8.00 usec
PL1                  -1.60 dB
SFO1           75.4752958 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                   1H
PCPD2                80.00 usec
PL2                  -2.00 dB
PL12                 16.00 dB
PL13                 16.00 dB
SFO2          300.1315007 MHz

F2 - Processing parameters
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Figure A3 ^{13}C NMR spectrum of IDMA in $CDCl_3$.

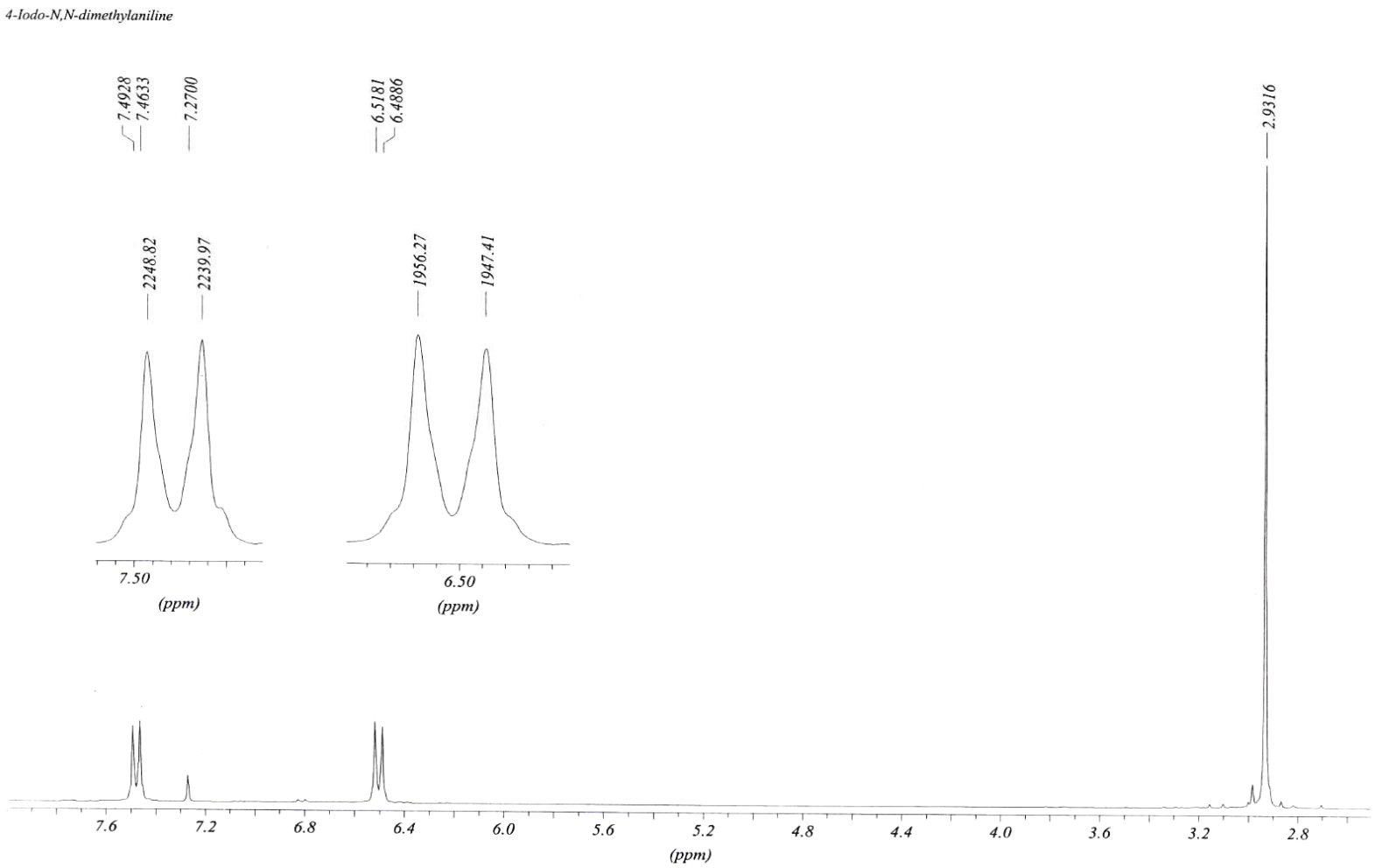

Figure A4 ^{1}H NMR spectrum of IDMA in $CDCl_3$.

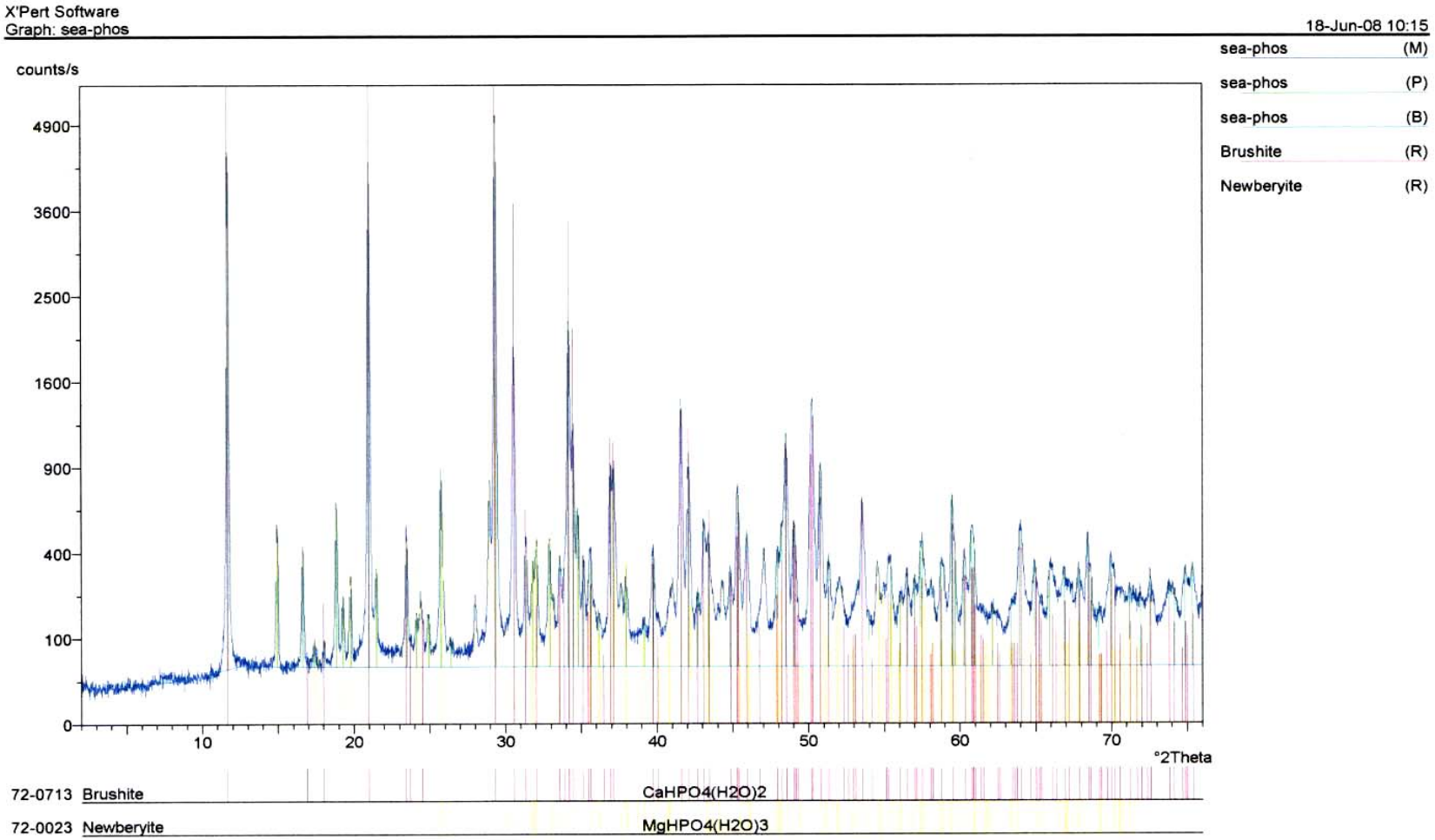

Figure A5 A X-ray diffraction pattern of precipitate from determining iodide in seawater (250 mL) by DSPE method.