DETERMINATION OF ^{237}Np IN LARGE VOLUME SAMPLES
OF SEA WATER BY A RADIOCHEMICAL PROCEDURE

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A radiochemical procedure followed by alpha spectrometry has been developed for the determination of ^{237}Np present at low activity concentrations in seawater. The analytical procedure is based on concentration of actinides from 1800 l sea water samples by hydroxide precipitations. Neptunium is isolated by ion exchange, fluoride precipitation and extraction with TTA (thenoyl-trifluoroacetone). As a radiochemical yield determinant ^{239}Np or ^{235}Np is used. Neptunium is electroplated onto stainless steel discs before alpha-spectrometry for about 10 days. The procedure allows for sequential separation of plutonium, americium, technetium and radiocaesium together with neptunium. The radiochemical yield for neptunium is only 20–50%, but the procedure has been applied with success on several samples contaminated with ^{237}Np at fallout or close to fallout levels.

Introduction

Neptunium–237 has been released to the environment mainly from nuclear weapon tests and nuclear fuel reprocessing plants. The total world integrated deposition from nuclear weapon tests is estimated at 2500 kg and the ^{237}Np/$^{239+240}$Pu activity ratio at 0.0050. [1,2]. There is an increasing interest in ^{237}Np, because, together with ^{99}Tc, it is one of the most important radionuclides remaining after long term storage of nuclear waste.[3]

Due to analytical difficulties our knowledge of neptunium in the environment is limited. In the present work a method has been developed for determining ^{237}Np in environmental samples, with particular emphasis on large-volume samples of seawater. There are radiochemical methods described in the literature for the determination of ^{237}Np in environmental samples [4, 5, 6], some of them combined with neutron activation analysis[7] or using mass spectrometry[2], but none of these was applied to large-volume seawater samples contaminated with fallout or close to fallout levels of ^{237}Np.

Experimental

Reagents and Apparatus

All reagents used are of analytical grade. A O.5.M. Thenoyl-
trifluoroacetone (TTA) solution is prepared by dissolving 11.1 g in 100ml
xylene. Dilute acids such as 10M HCl, 9M HCl, 4.5M HCl/0.1M HF mixture, 1M
HCl, 10M HNO$_3$, and 0.2M H$_2$SO$_4$ are prepared by dilution of concentrated acids
with H$_2$O. Other reagents used are La-carrier, FeSO$_4$, 0.3M Na$_2$SO$_4$, saturated
H$_3$BO$_4$ solution, saturated NaOH solution, ammonia, thymol blue indicator, 1M
NH$_4$I and H$_2$O$_2$ (30%). Neptunium-239 (T$_{1/2}$=2.35 d) obtained from ^{243}Am
(T$_{1/2}$=7950 a) or ^{235}Np (T$_{1/2}$=410 d) is used as the radiochemical yield
determinant. Large precipitation tanks (1800 l), stainless steel discs,
electrolysis vials, and an electrolysis apparatus are used for sample and
source preparations.

Preparation of ^{239}Np-yield determinant

Neptunium-239 is the daughter product of ^{243}Am. Take about 5-10 Bq of
^{243}Am from a stock solution. Evaporate and dissolve in 10 ml 10M HCl.
Prepare a small anion exchange column (Ø=0.5 cm. height=5cm, Dowex 1x4,
100-200 mesh). Precondition the column with 15 ml 9M HCl. Add 1 ml 1M NH$_4$I
to the ^{243}Am solution. Let the sample pass the column at a speed of about 1
ml min^{-1}. Wash the column with 20 ml 9M HCl. Collect the effluent and the
wash, which will contain ^{243}Am. After a week this solution can be newly
recycled for the recovery of ^{239}Np. Elute ^{239}Np with 20 ml 0.5M HNO$_3$.
Evaporate the solution to 1-2 ml. Take aliquots from this solution and add to
the samples to be processed.

Sample Preparation

Transfer 1000-2000 l of seawater to a conical tank. Acidify to pH 1-2
with HCl and add the radiochemical yield determinant ^{239}Np (~ 2 Bq) or ^{235}Np
(~ 0.5 Bq). Also add other yield determinants such as ^{242}Pu, ^{243}Am, ^{99}Tc^m,
and ^{134}Cs, if analysis of plutonium, americium and/or americium technetium or
radiocaesium will be carried out on the same sample. Mix mechanically or by
air bubbling for 1-2 hours. Precipitate actinides with mixed hydroxides and
carbonates of calcium and magnesium (naturally present in sea water). By

adding NaOH solution until the sample has a pH of 9-10. The supernant will contain technetium. Collect the precipitate (the tank should have a tap at the bottom). Dissolve the precipitate with HCl and perform a reprecipitation with ammonia (pH=9-10). Discard the aqueous phase or combine it with the previous aqueous phase if analysis of ^{99}Tc and/or radiocaesium will be performed. Centrifuge and dry the precipitate.

Ion Exchange

Prepare a column with ion exchange resin (0=1 cm, height=15-20 cm, Dowex 1x4 100-200 mesh). Precondition the column with 100 ml 9M HCl. Dissolve the sample in 10M HCl (200-300 ml) and a few drops of H_2O_2 during heating. Cool the sample, centrifuge and discard the remaining solids. Add 1 ml 1M NH_4I per 10 ml of 10M HCl used. Heat gently a few minutes. (This will reduce Np and Pu to the +4 and +3 oxidation states respectively.) Let the sample pass the column at a speed of 2-3 ml min^{-1}. Wash the column with 75 ml of 9M HCl. (The effluent and the wash will contain Pu, Am, Th.) Elute Np with 200 ml 4.5M HCl-0.1M HF. Add 20 mg of La to the Np-eluate and add HF until LaF_3 precipitate forms. Centrifuge and discard the aqueous layer, and wash the precipitate with distilled water.

Solvent Extraction

Dissolve the LaF_3 precipitate in 10 ml conc. HCl and 2 ml saturated H_3BO_4 solution. Heat and take to dryness. Dissolve the sample again in HCl and precipitate hydroxides with ammonia. Centrifuge and wash the precipitate. Dissolve the sample in 1M HCl (5 ml) and add about 100 mg $FeSO_4$ in order to keep Np in the +4 oxidation state. Transfer the sample to a separation funnel with 5 ml 1M HCl. Extract Np with 7 ml 0.5M TTA in xylene and shake for 2 minutes. After separation of the phases, wash the organic phase with 10 ml 1M HCl. Back-extract Np with 2x7 ml 10M HNO_3, leaving any iron in the organic phase. Wash the aqueous phase with 10 ml xylene in another separation funnel.

Electrodeposition

The procedure is the same as has been described earlier for other actinides.[8]

Briefly, neptunium is electrodeposited onto stainless steel discs ($0=20$ mm) mounted in polyethylene scintillation vials. Add 1 ml 0.3M Na_2SO_4 to the sample and evaporate to dryness on a hot plate. Add 0.3 ml conc. H_2SO_4 and heat gently. Add 4 ml H_2O and adjust pH to about 2-3 with ammonia, using thymol blue as indicator. Transfer the sample to the scintillation vial with 5 ml 0.2M H_2SO_4. Adjust pH to 1.9-2.1 using indicator paper. Electrolyze at 1A for 2 hours. Add 1 ml ammonia just before switching off the current. Dismount and rinse the planchet with 1% ammonia solution and acetone.

Yield Determination

The radiochemical yield is determined by gamma-spectrometry (Ge detector) or beta-counting. By gamma-counting higher activities of yield determinant should be used due to the generally lower detector efficiency. For gamma-counting of ^{239}Np the 106 keV transition and its characteristic K-x-rays) from Pu are used.

Neptunium-235 is mainly emitting low-energy L-x-rays from uranium. A planar Ge detector is the most suitable devise. However, a conventional GM-beta-counter which is sensitive for these low-energy photons can also be used to advantage.

Measurement of ^{237}Np

Neptunium-237 is measured by alpha-spectometry for about 10 days. (min alpha-energy emitted = 4.64 MeV, max alpha-energy emitted = 4.87 MeV). Correct for any ^{234}U present by subtracting the ^{237}Np peak with 1.14 times the ^{238}U (4.15, 4.20 MeV) peak. Calculate the activity using the actual detector efficiency.

Results and discussion

The method described is suitable for determining ^{237}Np in large-volume seawater samples. The major problem with a measurement of ^{237}Np by alpha-spectrometry is the interference of ^{234}U. This problem is particularly important for seawater samples, which usually contain 44 mBql^{-1} of ^{234}U. The levels of ^{237}Np from global fallout can be estimated at about 6.5×10^{-5} mBql^{-1}, if it is assured that the concentration of ^{239,240}Pu is about 13×10^{-3} mBql^{-1} and the integrated fallout activity ratio (^{237}Np/$^{239+240}$ Pu) is 0.0050.

In seawater from the Sellafield nuclear fuel reprocessing plant area, the [237]Np concentration was 9 mBq l[-1] in 1984 with a [237]Np/[239+240]Pu activity ratio of 0.40.[7]

The distribution-factor, K_D, (ratio between radioactivity concentration per kg of dry suspended matter and the activity concentration per liter in sea water) is smaller for neptunium (10^3-10^4) than for plutonium (10^5-10^6).[10] This means that the residence time for neptunium is longer, which would give a higher ratio to plutonium than what is found in integrated fallout.

Several steps in the analytical procedure prevent interference from uranium. In the column operation, neptunium is eluted by fluoride complexation. This does not affect uranium, which mainly remains on the resin. Uranium is not carried in the LaF_3 precipitation step and the extraction coefficient of U (+6) with TTA is only 3×10^{-5} compared to 10^4 for Np (+4). In spite of this, for some samples fully satisfactory removal of uranium was not obtained. This makes the corrections too large and the results statistically poor.

Protactinium-231 also has one of its alpha-energies (4.73 MeV) in the same region as [237]Np. However, concentrations of [231]Pa are low in seawater (4×10^{-3} mBq l[-1]), and [231]Pa is also eliminated in the fluoride precipitation step.

If preconcentration of the samples is carried out on board a ship, a more long-lived isotope than [239]Np, such as [235]Np must be used as radiochemical yield determinant. If analysis of [241]Am is to be carried out on the same sample, the [239]Np contains traces of [243]Am which are large enough to disturb the accurate yield determination of americium. However, the [235]Np yield determinant we used contained some [237]Np, for which correction is necessary. The activity concentration of [237]Np present in the [235]Np solution was determined by a similar procedure, as described, and using [239]Np as radiochemical yield determinant. As a result, in July 1985, we obtained an activity ratio [237]Np/[235]Np of 1.7×10^{-3}. This ratio increases with time. A [235]Np standard containing negligible amounts of [237]Np is now available.

We have analyzed 16 samples from the Barents, Greenland, and North Seas, collected in 1985 and 1981, respectively. To three of the samples no yield

determinant was added, in order to assure that no foreign radioactive elements would influence the count rate in our GM-gas flow counter when the yield determination was made.

The results are shown in Table 1. The samples originating from the Barents and Greenland seas are expected to contain slightly higher activities than representative for fallout levels, due to nuclear waste from European fuel reprocessing facilities. Our results, which show ^{237}Np levels within the expected ranges, demonstrate the possibility of employing the present method for such studies. However, the correction for ^{234}U was between 20–60% of the total counts in the ^{237}Np region and for 2 samples the results became negative, including the correction for presence of ^{237}Np in the ^{235}Np yield determinant. One sample from 71°N gave as result a ^{237}Np/$^{239+240}$Pu activity

Table 1
Activity concentrations of $^{239+240}$Pu and ^{237}Np in surface water
from the North, Barents and Greenland Seas (mBq m^{-3})

Collect. date	Position	Vol (1)	$^{239+240}$Pu	^{237}Np	^{237}Np/$^{239+240}$Pu
81-11	60°00'N, 2°00'W	750	34*	10.5	0.31
81-11	61°30'N, 2°00'E	750	17*	8.0	0.47
81-11	61°00'N, 4°10'E	750	16*	4.0	0.25
85-07-04	58°20'N, 5°00'E	1800	7.7	No Np yield determinant	
85-07-06	63°15'N, 6°00'E	1800	9.0	–	–
85-07-07	68°23'N,13°10'E	1800	5.7	No Np yield determinant	
85-07-08	71°08'N,21°00'E	1800	6.5	2.6	0.41
85-07-09	73°45'N,19°05'E	1700	12.3	No Np yield determinant	
85-07-10	75°13'N,17°42'E	1850	8.4	1.1	0.13
85-07-11	77°55'N, 8°18'E	1800	11.8	0.82	0.07
85-07-13	78°27'N, 1°55'E	1800	9.8	0.36	0.04
85-07-16	78°59'N, 5°16'W	1800	11.4	0.40	0.04
85-07-21	80°00'N,11°00'W	1750	7.0	0.34	0.05
85-07-23	80°00'N, 3°00'W	1800	11.5	0.86	0.07
85-07-24	80°00'N, 4°25'E	1800	8.3	1.06	0.13

*Values for $^{239+240}$Pu obtained from Kautsky[11].
One sample from 85-07-14, 79°02'N, 0°52'W failed both for Pu and Np.

ratio much higher than expected. The final purified neptunium fraction could conveniently be used for other measurement techniques, such as neutron activation analysis or mass-spectrometry.

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