A direct determination of ^{239}Pu in femtomole range in aquatic solution*

J. I. Kim, W. Scheibner, F. Baumgärtner, and R. Schwankner

Institut für Radiochemie, TU München, D-8046 Garching, Federal Republic of Germany

Direkte Bestimmung von ^{239}Pu in wäßriger Lösung im Femtomol-Bereich mit Hilfe der Neutronenaktivierung

Zusammenfassung. Es wird eine Methode vorgestellt, die die direkte Bestimmung von ^{239}Pu in wäßriger Lösung über die (n,f)-Reaktion mit Reaktorneutronen und mit anschließender gammaspektrometrischer Messung ohne chemische Aufbereitung ermöglicht. Spurenverunreinigungen der im Wasser enthaltenen Schwermetallelemente werden gleichzeitig über ihre (n,γ)-Reaktionen erfaßt. Durch die Messung der Spaltproduktpaare ^{132}Te/^{132}I oder ^{140}Ba/^{140}La wird bei dieser Methode eine Nachweisgrenze von $1{,}6 \times 10^{-15}$ mol/l ^{239}Pu erreicht. Die bestimmten Spurenverunreinigungen im Bereich von 10^{-8} bis 10^{-13} mol/l geben einen Einblick in das chemische Verhalten von Pu in einem vorliegenden Wasser. Der natürliche Urangehalt spielt auf der einen Seite eine einschränkende Rolle bei der Pu-Bestimmung, trägt aber auf der anderen Seite zum Verständnis des chemischen Verhaltens von Pu bei.

Summary. A method is presented which facilitates the direct determination of ^{239}Pu in aquatic solution by the (n,f) reaction with reactor neutrons and subsequent gamma spectrometry without chemical elaboration. Trace impurities of water constituent heavy metal elements are simultaneously determined through their (n,γ) reactions. The sensitivity attained by this method is 1.6×10^{-15} mol/l ^{239}Pu by measuring the fission product pairs ^{132}Te/^{132}I or ^{140}Ba/^{140}La. The trace impurities determined in the range of $10^{-8} \sim 10^{-13}$ mol/l give an insight into the chemical behaviour of Pu in a given water. The natural uranium concentration plays a role to limit the Pu determination on the one hand and to help understanding the chemical behaviour of Pu on the other hand.

1. Introduction

A global fallout distribution of ^{239,240}Pu on the surface soil due to nuclear weapon testings is known to be 4.5 ~ 22.5 femto Curie (fCi) per gram soil [1]. In Atlantic and Pacific oceans, the dissolved Pu concentration ranges from 0.14 ~ 1.8 fCi/l [2] and 0.06 ~ 0.42 fCi/l [3], respectively. In addition to the fallout Pu, the runoff of nuclear industry increased the Pu concentration in a certain area, e.g. Irish sea, to the range of 45 ~ 450 fCi/l [4]. The observation of chemical behaviour and natural transport of thus spread Pu in the environment is, although the concentration is many orders of magnitude lower than the maximum permissible level (8.2 nCi/l) [5], of significant importance for understanding its environmental pathways to the human being. Such a study requires an appropriate method to determine Pu for the concentration range down to femtomoles (fM). For the fallout Pu consisting of 60% to 40% for ^{239}Pu/^{240}Pu activities [5], an extensive chemical elaboration of large volume samples is necessary to determine its concentration in soil, water etc. Subsequently a sensitive α-detection method is required.

A commonly used detection technique is α-spectrometry with a surface barrier detector. Because of its low background and high energy resolution, the determination of Pu concentrations down to 10 fCi, equivalent to 0.7 fM ^{239,240}Pu, in aqueous solution is possible [5]. Other detection methods, like low background liquid scintillation counting [6], fission track counting [7] etc. are also sensitive enough to determine fM concentrations, nevertheless they are negated by poor energy resolution or incapacity of isotopic distinction. A recent development of laser photoionization spectrometry [8] is capable of ^{239}Pu detection as low as 3.6 fCi, i.e. 10^8 Pu atoms. This has an advantage of isotope specific detection. The high sensitivity of those methods discussed here is attainable for environmental samples only at the expense of an extensive chemical separation as well as preconcentration and subsequently preparation of a particular α-detection target.

In this paper we report a direct method of ^{239}Pu determination in aquatic solution, using the ^{239}Pu (n,f) reaction and subsequently measuring selected fission products. The method obviates chemical elaboration and preparation of a special detection target. At the same time it facilitates a simultaneous determination of trace constituents of water, which are usually present in much higher concentrations than ultratrace amounts of Pu under investigation. As a result the chemical behaviour of dissolved Pu can be anticipated indirectly by observing the behaviour of its chemical homologues among trace elements present in aqueous sample. The influence of uranium present in natural water imposes a limitation to the sensitivity of Pu determination. However, the nondestructive procedure of the method provides the possibility of studying its chemical behaviour in natural aquatic solutions in the concentration range of picomoles or less. The inclusion of preseparation, if necessary, may enable the method to attain a sensitivity in the fM range.

* Dedicated to Prof. Dr. K. H. Lieser on the occasion of his 65th birthday

Offprint requests to: J. I. Kim

Fresenius Z Anal Chem (1986) 323:821 – 826
© Springer-Verlag 1986

2. Experimental

Plutonium used in this experiment has an isotopic composition (as of May 2, 1983): ^{238}Pu (0.015%), ^{239}Pu (99.9714%), ^{240}Pu (0.270%), ^{241}Pu (< 0.0001%) and ^{242}Pu (< 0.0001%). The oxide (PuO_2) is dissolved in 1.4 M HNO_3, prepared by dilution of 'suprapur' HNO_3 in bidistilled water, in a 'suprasil' quartz flask to result in a concentration of 1.2×10^{-9} mol/l, which is then used as a stock solution throughout. The α-activity originates mainly from ^{238}Pu (4.13%) and ^{239}Pu (95.87%). To ascertain the sensitivity of the method, an experiment is first carried out for pure water spiked with Pu in the concentration range from 10^{-11} mol/l down to 10^{-15} mol/l. These solutions are adjusted to pH ~ 2 in order to obviate the sorption of dissolved Pu on vessel walls. For natural waters, e.g. river water and groundwater, their original pH values are maintained while spiking Pu. In these waters, it is found that Pu does not tend to be sorbed on vessel walls.

The Pu containing solution is irradiated in a specially prepared 'suprasil' quartz flask of 250 ml volume covered by a cap made of the same material. In the center of this volumetric flask, a quartz capillary (2 mm inside diameter), containing pieces of Al-Au-alloy (0.1274 ± 0.0004% Au) and Al-Co-alloy (0.0925 ± 0.0008% Co) wires of 0.5 mm diameter, is installed in order to monitor the neutron flux and resonance spectrum index at the irradiation position. A whole irradiation system has been described elsewhere previously [9, 10]. The irradiation is carried out in the FRM reactor (Forschungsreaktor München) at a special position which is constructed for activating a large volume of water sample [9]. The maximum neutron flux attainable at this position is 1.25×10^{-13} n s^{-1} cm^{-2}. The irradiation time is maintained from 4 h to 48 h depending on the total impurity concentration in samples under investigation, keeping a longer irradiation time for pure water and shorter for groundwater. However, there is no upper limitation for the irradiation time, since the gas generated by radiolysis reactions can be released from the sample flask during irradiation without an inflow of reactor water [9].

After irradiation, the sample solution is transferred to counting vessel made of plexiglas, having the optimal counting geometry to a given Ge(Li)-detector [9]. The efficiency calibration of the detector is made for the same geometry using a mixed liquid standard (Amersham QCY-44) composed of nine nuclides: ^{109}Cd, ^{139}Ce, ^{57}Co, ^{60}Co, ^{137}Cs, ^{203}Hg, ^{113}Sn, ^{85}Sr and ^{88}Y. A polynomial fitting is used to establish a efficiency curve from 100 keV up to 2 MeV. The flux monitors, Al-Au-alloy and Al-Co-alloy wires, are dissolved in 6 M HCl, diluted to 0.5 M HCl and measured in a plexiglas vessel at the same geometry as the sample. The gamma spectrometric measurement is made by a Canberra-80 multichannel analyser coupled to a PDP-11/73 computer and the activity evaluation is performed with the help of a spectrum-F program (Canberra).

Among fission products produced, ^{132}Te (78 h) and ^{140}Ba (12.8 d) are chosen for measurement, because these are not overlapped by the (n,γ) reaction products of trace impurities and have appropriate half-lives, high fission yields and many gamma energies with favorable intensities. These fission products undergo secular equilibria with the daughter nuclides, ^{132}I (2.28 h) or ^{140}La (40.3 h), which are easily detectable by gamma spectrometry. For the purpose of comparison or for some solutions with extremely low concentrations of Pu, a simple chemical process is applied to separate ^{132}Te or ^{140}Ba from irradiated samples. The irradiated water is acidified to 1 M HCl, to which 20 mg Te in 2 ml of 2 M HCl is added. Te in the solution is first oxidized with 150 mg KMO_4, then reduced by hydrazine chloride and filtered. The precipitate is redissolved in HNO_3 for gamma spectrometry. For the separation of ^{140}Ba, the irradiated solution is concentrated to about 30 ml, to which 150 mg $BaCl_2$ is added. With an excess addition of conc. HCl, $BaCl_2$ is precipitated, filtered and redissolved in H_2O for gamma spectrometry. The thus separated ^{132}Te or ^{140}Ba are found to be free from bulk activities of fission and activation products, being pure enough to eliminate gamma spectrometric interferences. Separations are found to be quantitative.

For the analysis of trace constituents in water, the mono-standard method [11, 12] is applied, using relevant nuclear data [11] compiled already in the computer for all nuclides in question. A number of gamma spectra for each sample measured repeatedly with appropriate time intervals are taken into consideration for quantitative evaluations.

3. Results and discussion

3.1 Determination of ^{239}Pu by the (n,f) reaction

The thermal fission cross section (σ_f) and resonance integral (I_f) of the ^{239}Pu (n,f) reaction are known to be 744.4 ± 1.7 b and 2,156 ± 57 b [13], respectively. Its effective cross section ($\hat{\sigma}_f$) for a given irradiation condition can be calculated in accordance with Wescott [14]:

$$\hat{\sigma}_f = \sigma_f[g(T) + r\sqrt{T/T_0}\,s_f] \quad (1)$$

where $s_f = (2/\sqrt{\pi})\,(I_f/\sigma_f)$, $g(T)$ is a factor adjusting to the temperature dependent Maxwellian distribution of cross section within the 1/v range [14, 15] and $r\sqrt{T/T_0}$ represents the fraction of the epithermal neutron flux in the total neutron flux, which can be determined by a combination of Au and Co monitors used in this experiment [11]. This value for the present irradiation position in the FRM is determined to be 0.012 ± 0.003. The $g(T)$ value for the same position in the reactor pool water (approximately 30 °C) is known to be 1.055 [15]. Based on these data the effective cross section of Eq. (1) is evaluated to be 814.5 b.

The selection of fission products for the determination of ^{239}Pu is based on the following criteria. They are produced solely by the (n,f) reaction, not by the (n,γ) reaction of water constituent impurities. They must have appropriate half-lives, neither too short nor too long, in order to facilitate the optimization of measuring sensitivity and accuracy. They must have a high fission yield. Under these criteria, there are two isobars that appear most favourable:

$$^{132}\text{Te} \xrightarrow[76.3\,\text{h}]{\beta^-} {}^{132}\text{I} \xrightarrow[2.3\,\text{h}]{\beta^-} {}^{132}\text{Xe (stable) (5.15\% yield [16])} \quad (2)$$

$$^{140}\text{Ba} \xrightarrow[12.75\,\text{d}]{\beta^-} {}^{140}\text{La} \xrightarrow[40.27\,\text{h}]{\beta^-} {}^{140}\text{Ce (stable) (5.58\% yield [16])}. \quad (3)$$

Neither ^{132}Te nor ^{132}I is interfered by the (n,γ) reaction products of impurities in water, whereas ^{140}La is overlapped by the ^{139}La (n,γ) reaction. However, the half-life difference between ^{140}Ba and ^{140}La (7.6 to 1) makes it possible to use

Table 1
Determination of ^{239}Pu in pure water by the (n,f) reaction and gamma spectrometry of fission products

Pu concentration (mol/250 ml)			Fission isobar used	Remarks
Spiked	Found	(Mean value)		
4.52×10^{-11}	4.36×10^{-11}		Te/I	dm[a]
	4.37×10^{-11}		Te/I	dm
	3.55×10^{-11}		Te/I	dm
	4.78×10^{-11}		Ba/La	dm
	5.26×10^{-11}		Ba/La	dm
	4.18×10^{-11}		Te/I	cs
	4.89×10^{-11}	$(4.48 \pm 0.56) \times 10^{-11}$	Te/I	cs
1.51×10^{-11}	1.55×10^{-11}		Te/I	dm
	1.40×10^{-11}		Te/I	dm
	1.15×10^{-11}		Te/I	dm
	1.38×10^{-11}	$(1.37 \pm 0.17) \times 10^{-11}$	Ba/La	dm
3.01×10^{-12}	3.20×10^{-12}		Te/I	dm
	3.13×10^{-12}		Te/I	dm
	2.56×10^{-12}		Te/I	dm
	3.14×10^{-12}	$(3.01 \pm 0.30) \times 10^{-12}$	Ba/La	dm
3.01×10^{-13}	2.98×10^{-13}		Te/I	dm
	2.43×10^{-13}		Te/I	dm
	2.91×10^{-13}	$(2.77 \pm 0.30) \times 10^{-13}$	Ba/La	dm
6.02×10^{-14}	6.47×10^{-14}		Te/I	dm
	4.56×10^{-14}		Te/I	dm
	7.55×10^{-14}	$(6.19 \pm 1.51) \times 10^{-14}$	Ba/La	dm
3.01×10^{-14}	2.27×10^{-14}		Te/I	cs
	3.71×10^{-14}	2.99×10^{-14}	Ba/La	cs
1.51×10^{-14}	1.89×10^{-14}		Te/I	dm
	2.27×10^{-14}	2.08×10^{-14}	Te/I	dm
4.52×10^{-15}	4.70×10^{-15}		Te/I	cs
9.03×10^{-16}	1.58×10^{-15}		Te/I	cs
Blank solution	$(3.60 \pm 1.62) \times 10^{-16}$		Te/I	cs

[a] *dm* directly measured; *cs* measured after chemical separation (see text)

this isobar chain, provided an appropriate decay time is adjusted before the activity measurement.

With the knowledge mentioned above, it is possible to assess the sensitivity for the (n,f) reaction in comparison with an α-spectroscopic measurement of ^{239}Pu. The former proceeds with a reaction rate : $\phi \hat{\sigma}_f$ (ϕ = neutron flux), with the fission yield of a nuclide f_i and its decay constant λ_i, whereas the latter follows only the decay process with λ_α of ^{239}Pu. A relative comparison of the two detection possibilities can be made by taking consideration of ^{132}Te (fission yield = 5.15 ± 0.11%) for an irradiation time of 40 h,

$$N \lambda_\alpha (^{239}Pu) = 5.5 \times 10^{11} \text{ Bq mol}^{-1} \quad (4)$$

$$N \phi \hat{\sigma}_f f_i (1 - e^{-\lambda t}) = 9.6 \times 10^{13} \text{ Bq mol}^{-1}. \quad (5)$$

Under normal measuring conditions, α-spectrometry with a surface barrier detector has a considerably lower background (3.7×10^{-4} Bq for a 2 cm diameter detector in our laboratory) than gamma spectrometry with the Ge(Li)-detector used in this experiment (3.7×10^{-3} Bq for the peak at 667.7 keV). Taking account of these backgrounds, the ^{239}Pu determination by the (n,f) reaction may provide a sensitivity of 3.8×10^{-17} mol which is superior to the value of 6.7×10^{-16} mol by the α-spectrometric detection. Since the present method involves also an extra background arising from activated impurities in a given water, the practical sensitivity is somewhat lower than the theoretical estimation (see below).

Experimental determinations of ^{239}Pu in pure water are summarized in Table 1. The concentration maintained in the experiment at 250 ml sample solution is directly given in this table in order to demonstrate the actual working condition. The Pu concentration is successively lowered from the starting concentration of 4.52×10^{-11} mol/250 ml down to 9.03×10^{-16} mol/250 ml. The experimentally attainable sensitivity for a direct irradiation and measurement is evaluated to be

3×10^{-15} mol/250 ml of ^{239}Pu

which corresponds to 45 fCi or 1.8×10^9 atoms of ^{239}Pu. With lowering the background activity of the sample solution, which arises from trace impurities present, the sensitivity can be improved as

4×10^{-16} mol/250 ml of ^{239}Pu

by simple chemical separation of a desired fission product, e.g. Te or Ba. This value is about ten times inferior to the theoretical estimation discussed above and equal to 6 fCi or 2.4×10^8 atoms of ^{239}Pu, which is comparable to the sensitivity attainable by α-spectrometry after chemical separation and preconcentration.

Table 2
Determination of ^{239}Pu in groundwater (RCM-01) by the (n,f) reaction and gamma spectrometry of fission products

Pu concentration (mol/250 ml)			Fission isobar used	Remarks
Spiked	Found	(Mean value)		
3.01×10^{-11}	2.88×10^{-11}		Te/I	dm[a]
	2.57×10^{-11}		Te/I	dm
	3.06×10^{-11}		Ba/La	dm
	2.58×10^{-11}		Te/I	cs
	3.53×10^{-11}	$(2.92 \pm 0.40) \times 10^{-11}$	Ba/La	cs
2.26×10^{-12}	2.22×10^{-12}		Te/I	dm
	2.35×10^{-12}		Ba/La	dm
	2.36×10^{-12}	$(2.30 \pm 0.09) \times 10^{-12}$	Te/I	cs
Blank solution	$(3.30 \pm 0.81) \times 10^{-13}$		Te/I	cs

[a] *dm* directly measured; *cs* measured after chemical separation (see text)

3.2 Determination of ^{239}Pu in natural aquatic solution

Because of the ubiquitous presence of uranium in natural aquatic solution, use of the (n,f) reaction for the determination of ^{239}Pu is immediately limited by uranium concentrations in solutions under investigation. They differ considerably from one natural water to another: $10^{-11} \sim 10^{-8}$ mol/l in surface water [17, 18] and an average of 1.4×10^{-8} mol/l in seawater [18]. Obviously the fission of ^{238}U in a reactor neutron spectrum is insignificant and the (n,f) reaction is important only for ^{235}U. This nuclide has a thermal fission cross section of 582.2 ± 1.3 b [19], resonance integral of 268 ± 4 b [20] and $g(T) = 0.973$ [15] at 30° C. Under the present experimental condition, the same amount of U and Pu gives rise to the production rate of the isobar chain 132 for U being inferior to Pu by a factor of 4.2×10^{-3}.

The determination of ^{239}Pu in one groundwater taken as an example is demonstrated in Table 2. The experiment with a blank solution manifests the limitation for the ^{239}Pu determination due to the ^{235}U fission reaction involved. This value infers the presence of 1.8×10^{-10} mol/l U in this groundwater, which is corroborated by the U determination made by the (n,γ) reaction product (^{239}Np). The sensitivity of ^{239}Pu detection shown in this table (3.3×10^{-13} mol/250 mol) is, however, about 50 times superior to α-spectrometry of an ordinary liquid scintillation counting [5], in which only a limited solution volume can be counted. The preconcentration and chemical separation provides an improvement of the sensitivity in the α-spectrometric measurement. The same is also valid for the present method. The major benefit of the method under discussion is the possibility of investigating the chemical behaviour of Pu in the range of picomole or less by observing the behaviour of water constituent trace elements, particularly chemical homologues, in aqueous solutions in question. This subject is further discussed below.

Table 3. Determination of water constituent tracer elements in different aqueous solutions by monostandard neutron activation analysis (MS-NAA)

Element	Concentration (mol/250 ml)		
	Bidistill. water	Isar river[a,b]	Groundwater[a,c]
Ag	2.4×10^{-11}	$(1.7 \pm 0.2) \times 10^{-10}$	$(1.3 \pm 0.3) \times 10^{-10}$
Au	5.0×10^{-13}	$(1.9 \pm 0.2) \times 10^{-12}$	$(8.5 \pm 0.7) \times 10^{-12}$
Ba	$< 3.7 \times 10^{-10}$	$(3.4 \pm 0.8) \times 10^{-8}$	$(2.0 \pm 0.5) \times 10^{-8}$
Br	1.3×10^{-11}	$(4.4 \pm 0.4) \times 10^{-8}$	$(4.9 \pm 0.4) \times 10^{-7}$
Ca	$< 8.9 \times 10^{-8}$	$(4.8 \pm 1.4) \times 10^{-4}$	$(7.7 \pm 2.3) \times 10^{-5}$
Ce	9.5×10^{-12}	$(1.1 \pm 0.1) \times 10^{-11}$	$(3.3 \pm 0.3) \times 10^{-9}$
Co	1.9×10^{-11}	$(6.9 \pm 0.5) \times 10^{-10}$	$(1.1 \pm 0.1) \times 10^{-9}$
Cr	6.5×10^{-11}	$(5.1 \pm 0.7) \times 10^{-9}$	$(3.6 \pm 0.4) \times 10^{-8}$
Cs	7.5×10^{-13}	$(2.8 \pm 0.3) \times 10^{-11}$	$(5.0 \pm 0.7) \times 10^{-11}$
Eu	3.3×10^{-13}	$(2.0 \pm 0.4) \times 10^{-12}$	$(8.2 \pm 0.7) \times 10^{-11}$
Fe	5.5×10^{-10}	$(7.6 \pm 0.7) \times 10^{-8}$	$(1.8 \pm 0.1) \times 10^{-6}$
Hf	1.4×10^{-12}	$(4.7 \pm 1.8) \times 10^{-12}$	$(4.4 \pm 0.4) \times 10^{-10}$
Hg	3.1×10^{-12}	$(1.4 \pm 0.4) \times 10^{-11}$	$< 1.1 \times 10^{-11}$
Ir	3.5×10^{-13}	$(3.2 \pm 0.4) \times 10^{-13}$	$(4.6 \pm 0.5) \times 10^{-13}$
K	7.3×10^{-10}	ND	ND
La	5.4×10^{-12}	$< 7.5 \times 10^{-12}$	$(1.4 \pm 0.3) \times 10^{-9}$
Lu	$< 1.8 \times 10^{-13}$	$(3.7 \pm 0.9) \times 10^{-12}$	$(2.8 \pm 0.4) \times 10^{-12}$
Na	2.9×10^{-9}	$(9.0 \pm 0.6) \times 10^{-5}$	$(3.0 \pm 0.2) \times 10^{-3}$
Nd	4.3×10^{-12}	ND	$(2.4 \pm 0.3) \times 10^{-9}$
Rb	$< 5.3 \times 10^{-12}$	$(2,9 \pm 0.4) \times 10^{-9}$	$(3.9 \pm 0.4) \times 10^{-9}$
Sb	3.5×10^{-12}	$(4.3 \pm 0.4) \times 10^{-10}$	$(1.4 \pm 0.1) \times 10^{-10}$
Sc	1.1×10^{-13}	$(1.5 \pm 0.1) \times 10^{-11}$	$(1.8 \pm 0.1) \times 10^{-9}$
Se	3.6×10^{-11}	$(4.4 \pm 0.7) \times 10^{-10}$	$< 1.3 \times 10^{-10}$
Th	1.3×10^{-12}	$(7.3 \pm 0.7) \times 10^{-11}$	$(5.7 \pm 0.5) \times 10^{-10}$
U	1.8×10^{-12}	$(1.6 \pm 0.1) \times 10^{-9}$	$< 1.1 \times 10^{-10}$
Yb	1.6×10^{-12}	$(1.0 \pm 0.3) \times 10^{-11}$	$(7.3 \pm 1.0) \times 10^{-11}$
Zn	2.5×10^{-10}	$(2.9 \pm 0.2) \times 10^{-8}$	$(9.7 \pm 0.7) \times 10^{-8}$
Zr	1.6×10^{-10}	$< 5.2 \times 10^{-9}$	$(5.5 \pm 0.6) \times 10^{-8}$

ND not determined
[a] After filtration at 400 nm filter pore size
[b] Sampled at Garching
[c] Deep groundwater near Gorleben (ca. 100 m)

3.3 Water constituent trace elements

The method under discussion enables a simultaneous determination of Pu as well as trace elements present in samples through their (n,f) and (n,γ) reactions, respectively. Since a large volume of solution can be activated without limitation of irradiation time and since neither preconcentration nor post chemical elaboration is required, both sensitivity and accuracy of determination for each element can be very high [21]. A typical example of water analyes is shown in Table 3, in which natural concentrations of water constituent trace elements are demonstrated. Particularly interesting elements are Fe, rare earth elements (REE) and tetravalent elements, like Hf, Zr, Th, which are common to hydrolysis reactions in near neutral solution and hence to generate pseudocolloids in natural aquatic systems [22, 23]. The chemistry of

Table 4. Concentration changes in filtrates from ultrafiltration (Isar river at Garching)

Element	Concentration (mol/250 ml) in filtrates from		
	∅ 400 nm filter	∅ 3 nm filter	∅ 1 nm filter
Fe	$(7.6 \pm 0.7) \times 10^{-8}$ (100%)[a]	$(6.0 \pm 0.6) \times 10^{-8}$ (78.9%)	$(1.6 \pm 0.1) \times 10^{-8}$ (21.1%)
Pu	$(3.0 \pm 0.1) \times 10^{-11}$ (100%)	$(1.9 \pm 0.3) \times 10^{-11}$ (63.3%)	$(5.0 \pm 0.8) \times 10^{-12}$ (16.7%)
U	$(1.6 \pm 0.1) \times 10^{-9}$ (100%)	$(1.6 \pm 0.1) \times 10^{-9}$ (100%)	$(1.2 \pm 0.1) \times 10^{-9}$ (75.0%)

[a] Values in percent relative to initial concentration (100%)

these elements is quite comparable to that of Pu(III) and Pu(IV) in natural water.

Even in pure water there is always a picomole range or more of heavy metal ions ($> 10^{-12}$ mol/l) which may influence directly the chemical behaviour of equivalent or less concentration of Pu ($< 10^{-12}$ mol/l), because their hydrolysed species are chemically homologous. Whatever the purification method used, the impurities are resulting always from the surface bleeding of a vessel which contains the water under normal laboratory conditions.

In the river water investigated in this experiment, the heavy metal impurities, apart from major constituents: Ca, Na, etc., are at $> 10^{-8}$ mol/l. The Fe concentration appears to be an important contribution, which exceeds theoretical estimation known from available thermodynamic data [24]. This may be attributable to the generation of Fe(III) pseudocolloids in natural water under oxidic conditions [22]. A large fraction of the Fe concentration can be, as shown in Table 4, separated by ultrafiltration. By an ultrafiltration at 1 nm pore size, about 79% Fe is filtered. A similar extent of filtration is also observed for Pu which is spiked in this water at 3×10^{-11} mol/250 ml: 83% Pu is separated by ultrafiltration at 1 nm pore size. This result reflects that Pu is probably sorbed on Fe pseudocolloids and hence follows the chemical behaviour of Fe in this water. Such a behaviour of Pu is already observed in groundwater [22], in which the generation of Pu pseudocolloids is confirmed. Whereas Pu follows closely the chemistry of Fe(III), the uranyl ion remains less filterable under the same condition. At 1 nm ultrafiltration, only a small fraction of U is separated, implying that the hexavalent ion tends to be more stable in neutral solution. For the determination of ^{239}Pu in filtrates, the contribution of the ^{235}U (n,f) reaction to the subjected fission product, i.e. ^{132}Te/^{132}I, is corrected appropriately. The difference in filtration properties of Pu and U suggests that the predominant Pu species in this river water is probably the tetravalent state that has a strong tendency to form colloids, either realcolloids or pseudocolloids [25]. Because of the oxidic condition and neutrality of the water, Pu(III) is certainly oxidized to Pu(IV) [26]. On the other hand, Pu(V) may not be affected by filtration (cf. Np(V) [27]). The presence of Pu(VI) is also unlikely for the reason mentioned above. However, a close observation of the filtration behaviour of other trace heavy metal impurities, e.g. Th, Zr, REE etc., will give more information about the chemical behaviour of Pu in this water. This study is still in progress for the moment.

In the deep groundwater, as shown in Table 3, there are much more trace impurities than in the river water, particularly heavy metal elements. Because of an agelong contact time, the dissolution equilibrium of surrounding geomatrices in groundwater can be sustained and hence higher concentrations of REE, Th, etc. are expected. Since the concentrations of heavy metal elements are many orders of magnitude greater than Pu concentrations studied in this groundwater (cf. Table 2), undoubtedly their influences on the chemical behaviour of Pu must be significant. Experiment has shown that the heavy metal elements in groundwater are present mostly as groundwater colloids [22]. Such colloids readily absorb hydrolysed Pu ions of tetravalent state and thus generate pseudocolloids of Pu in groundwater [22]. The colloid generation is in general much more pronounced in groundwater than in river water. The preliminary results indicate that the filtration effects on Fe and Pu in this groundwater are in concordance with one another and much more pronounced than the results shown in Table 4 for the river water. Since the present work is confined to the analytical subject, further details on chemistry and colloid generation of Pu in groundwater shall be given elsewhere.

Whereas Pu introduced in groundwater shows a strong tendency to generate pseudocolloids by its sorption on groundwater-colloids, the uranyl ion present originally in this water remains less affected by these colloids. Such different properties may be useful for the separation of Pu from U in groundwater simply by ultrafiltration or ultracentrifugation. This procedure can be beneficial for the determination of ^{239}Pu by the method described here and in addition for understanding of chemical behaviour of Pu in natural water.

Acknowledgements. This work is financially supported by the Bundesministerium für Forschung und Technologie (BMFT). Thanks are due to Mr. G. Birement for technical assistance and also to Mrs. M.-L. Schäffel for secretarial help.

References

1. Hardy EP (1974) Fallout program quarterly summary report, USAEC, HASL-286, pp 2–10
2. Bowen VT, Wong KM, Noshkin VE (1971) J Mar Res 29:1
3. Miyake Y, Sugimura Y (1976) Transuranium nuclides in the environment, IAEA, STI/PUB-410, pp 91–104
4. Hetherington JA, Jefferies DF, Michell NT, Pentreath RJ, Woodhead DS (1976) Transuranium nuclides in the environment, IAEA, STI/PUB-410, pp 139–156
5. Schüttelkopf H (1981) Report KfK-3032, p 13
6. Harrock DH (1974) Application of liquid scintillation counting. Academic Press New York
7. Sohnius B, Denschlag HO (1982) Nucl Instrum Methods 197:449
8. Peuser P, Hermann G, Rimke H, Sattelberger P, Trautmann N, Ruster W, Ames F, Bonn J, Kluge H-J, Krönert U, Offen E-W (1985) Appl Phys, in print
9. Kim JI, Stärk H, Fiedler I (1980) Nucl Instrum Methods 177:557
10. Kim JI, Fiedler I, Born H-J, Lux D (1980) J Environ Anal Chem 10:135
11. Kim JI (1981) J Radioanal Chem 64:121
12. Kim JI, Lux D, Fiedler I (1982) Mikrochim Acta I:137
13. Kim JI, Beck R, Gryntakis EM, Zaghloul R (1979) Nucl Instrum Methods 165:565
14. Westcott CH (1960) Report AECL-1106

15. Gryntakis EM, Kim JI (1975) Radiochim Acta 22:128
16. Crouch EAC (1977) At Data Nucl Data Tables 19:417
17. Langmuir D, Herman JS (1980) Geochim Cosmochim Acta 44:1753; Langmuir D (1978) Geochim Cosmochim Acta 42:547
18. Whitfield M (1981) Interdiscipl Sci Rev 6:20
19. Neutron Cross Sections (1973) Report BNL-325, 3rd Ed Vol 1
20. Gryntakis EM, Kim JI (1983) J Radioanal Chem 76:341
21. Kim JI, in preparation
22. Kim JI, Buckau G, Baumgärtner F, Moon H, Lux D (1984) Mat Res Soc Symp Proc 26:31
23. Kim JI, Treiber W, Lierse Ch, Offermann P (1985) Mat Res Soc Symp Proc 44:359
24. Baes Jr CF, Mesmer RE (1976) The hydrolysis of cations, Chapt 10, John Wiley, New York
25. Kim JI (1985) CEC-Report, EUR 10023, Chap 1
26. Lierse Ch (1985) Dissertation, Tech Univ Munich
27. Lierse Ch, Treiber W, Kim JI (1985) Radiochim Acta 38:27

Received January 4, 1986