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A Laboratory Simulation Research Method for Speciation Distribution of Ultratrace Pu in Groundwater and Its Application

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Abstract: The migration rate difference of various Pu species in contaminated groundwater can be up to 3 orders of magnitude. Accurately obtaining speciation distribution of Pu is the first problem to be solved in site safety assessment. However, the in-situ chemical properties of groundwater are easily affected by the external environment, and Pu content in the contaminated groundwater is usually at ultra-trace level, the existing sampling-laboratory analysis method cannot directly determine the speciation distribution of Pu. Here a laboratory simulation research method for speciation distribution of ultratrace Pu in groundwater was established, in which a nitrogen assisted sampling and storage device was designed and employed to sample groundwater, and the groundwater sample was transported and kept in Anaerobic Glove Box, into which spiked Pu was added and the speciation distribution of Pu were monitored at various aging time by series speciation analysis techniques we improved and integrated. Using the method, the in-situ chemical properties of groundwater are well maintained, and the speciation distribution of ultratrace Pu in a contaminated groundwater from a granite area, NW China was obtained successfully. The results were basically consistent with the modelling results by geochemical software and/or analysis results by related instruments. Not only the method can continuously be used in the field of speciation distribution of Pu in contaminated water, but also can be used in other fields such as the treatment of waste liquor from Nuclear Plant, Reactor study, and so on.

1. Introduction

As a hypertoxic radionuclide in HLW, plutonium (Pu) is an indispensable research subject [1-3] with regard to its transport in groundwater from radioactive contaminated site. The speciation distribution of Pu in contaminated groundwater is one of most important impact factors for its migration rate. Pu can exist in various physicochemical forms, ranging from simple Pu(IV) and Pu(V) cations, PuO₂(*am*, *hy*), to complex Pu polymers and Pu colloids [4,5]. The migration rate difference of various Pu species can be up to 3 orders of magnitude [5-7]. So, accurately obtaining speciation distribution of Pu is the first problem to be solved in assessing Pu migration behavior. However, The Pu content of groundwater in the polluted area belongs to ultra-trace level and the speciation of Pu can easily be affected by the physicochemical parameters of the groundwater, including Eh, pH, and especially the content of colloids [8-9]. Meanwhile, in-situ hydrochemical properties of groundwater are easily affected by the external environment after groundwater sample was collected. Therefore, the existing sampling-laboratory analysis method cannot directly determine the speciation distribution of ultratrace Pu in the groundwater from radioactive contaminated area. In this work, a simulation technology



system of Pu morphology in water was established based on Pu(IV) tracer, nitrogen protection and quasi-static simulation technology. Through integrating and improving related speciation analysis technology for Pu, we also established a synchronous analysis process for Pu speciation based on colloid ultrafiltration classification, sequential extraction and solvent extraction. Using the method, we determined the speciation distribution of Pu in groundwater from a monitoring well in Dunhuang region, NW China. The research results for Pu speciation were verified by the modelling technology using related geochemical software.

2. Materials and Methods

2.1. Materials, Reagents and Instruments

2.1.1. Materials and reagent. PTFE (F46) tubes. Ultrafiltration tube of 10kD and 100kD, 0.45 μm and 0.22 μm Millipore filter; HCl, HNO_3 , HF, HClO_4 , TTA-Dimethylbenzene and HDEHP-Dimethylbenzene solution; ^{239}Pu stock solution: 1 $\mu\text{g/g}$, Pu(IV) of ~95%, checked by solvent extraction technique and purified using anion exchange resin DOWEX 1 $\times$ 4 to remove the decay products and other impurities. Ultrapure-water.

2.1.2. Instruments Inductivity Coupled Plasma Mass Spectrometry. Ion Chromatography; Inductivity Coupled Plasma Atomic Emission Spectroscopy; pH and Eh meter; Multi-parameter controller; Anaerobic Glove Box; Nitrogen-Assistant Sampling Equipment; Thermostatic Oscillator; High speed centrifuge(>8000rpm);

2.2. Protective method of situ-groundwater

pH and Eh are two important factors affecting the speciation distribution and transformation of Pu in groundwater [10]. So it is essential to maintain pH and Eh of the groundwater as stable as possible during sampling, transportation as well as the experimental process. In this study, groundwater sample (100 m underground) of ~5L was collected into a protective sample container by a self-designed Nitrogen-Assistant Sampling Equipment from a monitoring well in Dunhuang region, NW China, and kept in an Anaerobic Glove Box in Lab for next experiment as shown in Figure 1. Sampling process as following: a, Fill the Protective Sample Container with ultra-pure water; b, Open interface A and charge nitrogen from interface B; c, Close interface A and interface B after all the water in the container flows out; d, When there is water flowing out of the Wateroutlet of Nitrogen-Assistant Sampling Equipment, open interface A and B, connect the wateroutlet with interface A; d, Close interface A and B when the container is filled full with groundwater; f, Bring the container back to the laboratory and place it in the anaerobic glove box for your experiment under the atmosphere without oxygen.

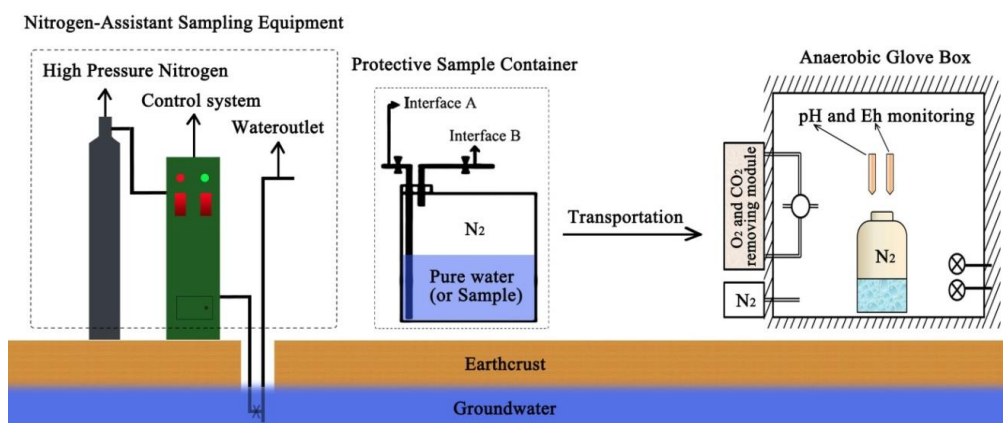


Figure 1. Sketch of sample collection, transportation and storage

The sample was kept away from air in the whole sampling, transportation and experiment process, and was characterized as soon as it was collected. The results showed that the water is a weak reductive ($E_h = -75$ mV), with high ionic strength (8.7 mol L^{-1}) and mineralization (21 g L^{-1}) as demonstrated in Table 1.

Table 1. Content of main chemical components (mg L^{-1}) and parameters of the groundwater

Ca^{2+}	Mg^{2+}	Na^+	K^+	HCO_3^-	SO_4^{2-}	Cl^-	Fe^{2+}
$(5.68 \pm 0.17) \times 10^2$	$(2.58 \pm 0.08) \times 10^2$	$(5.73 \pm 0.17) \times 10^3$	64.3 ± 1.6	$(1.15 \pm 0.04) \times 10^2$	$(1.49 \pm 0.05) \times 10^3$	$(1.01 \pm 0.03) \times 10^3$	<0.05
Free CO_2	COD_{Mn}	Sulfide	pH	Eh/mV	Ionic Strength (mol L^{-1})	Mineralization (g L^{-1})	Alcalinity (CaCO_3)
9.2 ± 0.2	0.61 ± 0.02	<0.02	7.3 ± 0.1	-75 ± 2	$(8.7 \pm 0.2) \times 10^{-2}$	21 ± 1	$(1.47 \pm 0.03) \times 10^2$

2.3. Laboratory simulation research method for speciation distribution of Pu

2.3.1. Preparation of samples containing spiked Pu. To resolve the problem of unobtainable speciation distribution of ultratrace Pu in groundwater. After the groundwater was collected and transferred into the Anaerobic Glove Box, into which spiked Pu(IV) was added as soon as possible and the sample containing Pu of content you wanted was obtained. The experiment was conducted with PTFE (F46) tubes to decrease the adsorption effect. Then the speciation distribution of Pu was monitored at various aging time by series speciation analysis techniques. The speciation of Pu inspected in this paper includes the colloid fraction, the colloid particle size and chemical bonding forms as well as the valence distribution of dissolved Pu.

2.3.2. Analysis of chemical bonding forms of colloidal Pu. A modified sequential extraction procedure based on Tessier procedure [11,12](see Table 2) was employed and improved to extract various species in colloidal Pu, by which colloid-associated Pu was divided into five fractions: Exchangeable(F1), Carbonate(F2), Fe/Mn Oxides(F3), Organic(F4) and Residual(F5). In this work, the Pu retained by 10 kD ultrafiltration tube was regarded as colloidal Pu. But it could not be separated from the 10 kD ultrafiltration tube due to the low colloids content ($\sim 0.06 \text{ mg}$ in 4 mL original groundwater and even lower after aging). So the extraction was conducted in situ by adding extraction agent into the inner pipe of the 10 kD Ultrafiltration tubes.

Table 2. Extraction procedure for chemical speciation analysis of colloid-associated Pu

Species	Sequential extraction procedures
Exchangeable	2 mL 1 mol/L MgCl_2 (PH=7) solution was added to the inner pipe of 10 kD Ultrafiltration tube, then the tube was shaken for 1 h at room temperature, centrifuged 8 000 r/min for 30 min.
Carbonate	2 mL 1 mol/L NaOAc (adjusted pH=5 with HOAc) solution was added to inner pipe of 10 kD Ultrafiltration tube, then the tube was shaken for 5 h at room temperature, centrifuged 8 000 r/min for 30 min.
Fe/Mn Oxides	2 mL 0.04 mol/L $\text{NH}_2\text{OH HCl}$ and 25% HOAc solution was added to inner pipe of 10 kD Ultrafiltration tube, then the tube was shaken for 6h at 96°C , centrifuged 8000 r/min for 30 min.
Organic	0.5 mL 0.02 mol/L HNO_3 and 1 mL 30% H_2O_2 (pH=2) solution was added to inner pipe of 10 kD Ultrafiltration tube, and the tube was shaken 3 h at 85°C , centrifuged 8000 r/min for 30min; then 1 mL 3.2 mol/L NH_4OAc and 20% HNO_3 solution was added and the tube was shaken for another 0.5 h at room temperature, centrifuged 8000 r/min for 30 min.
Residual	0.5 mL concentrated HClO_4 0.5 mL concentrated HF and 1 mL concentrated HNO_3 were added to inner pipe of 10kD Ultrafiltration tube, then the tube was shaken for 3 h at 70°C , centrifuged 8 000 r/min for 30 min.

2.3.3. Measurement of particle size distribution of colloidal Pu. The particle size distribution of colloidal Pu was measured by Filter Membrane Fractionation Technique, in which 4 mL of sample solution containing Pu were passed through $0.45 \mu\text{m}$ and $0.22 \mu\text{m}$ Millipore filters, and 100 kD and 10 kD ultrafiltration tubes (Amicon Ultra-4mL, Millipore) in order. The concentrations of Pu in each filtrate were determined using 8 M HNO_3 digestion and ID-ICP-MS method to calculate the particle size distribution of the Pu. The particle size of colloidal Pu would be divided into five partitions.

2.3.4. Analysis of the valence distribution of dissolved Pu. Valence distribution of dissolved Pu is an important topic of speciation study of Pu, which affects the migration of Pu in groundwater greatly [13]. In this study, The Pu permeated through the 10 kD ultrafiltration tube was regarded as dissolved Pu. The valence state distribution of Pu was determined by solvent extraction technique as described in related publications [14,15]. Briefly, samples containing Pu were adjusted to 1M HCl solution. Pu(IV) and Pu(IV+VI) in the solution were extracted with TTA-Dimethylbenzene and HDEHP-Dimethylbenzene solutions, respectively. The concentrations of Pu(IV), Pu(IV) and Pu(VI) could be calculated through determination of remaining Pu in the aqueous phase after exactions by ICP-MS.

2.3.5. Sample pretreatment for ^{239}Pu determination. A great number of sample solutions containing Pu (dissolved and/or colloidal Pu) were to be analyzed for Pu content at each predesigned monitoring time to obtain the speciation distribution of Pu in the groundwater. Due to the presence of colloids, the samples must be digested first. Three digestive acid mixtures were compared for sample pretreatment: 0.2 mL concentrated $\text{HNO}_3 + \text{HF} + \text{HClO}_4$ ($V_{\text{HNO}_3} : V_{\text{HF}} : V_{\text{HClO}_4} = 2:1:1$) complete dissolution, 0.2 mL 8 mol L^{-1} HNO_3 leaching for 2 h, and 0.1 mL concentrated $\text{HNO}_3 + 0.1$ mL concentrated HF leaching for 2h. After the treatment, the solutions were filtered and adjusted to 2% HNO_3 system for measurement of Pu content by ID-ICP-MS. The results showed that almost a same Pu content was obtained with a RSD<6% for three methods (see Figure 2). To simplify the pretreatment procedure and improve the experimental efficiency, the 8 mol L^{-1} HNO_3 2 h leaching was employed in this work for sample pretreatment due to its simplicity and short digestion time.

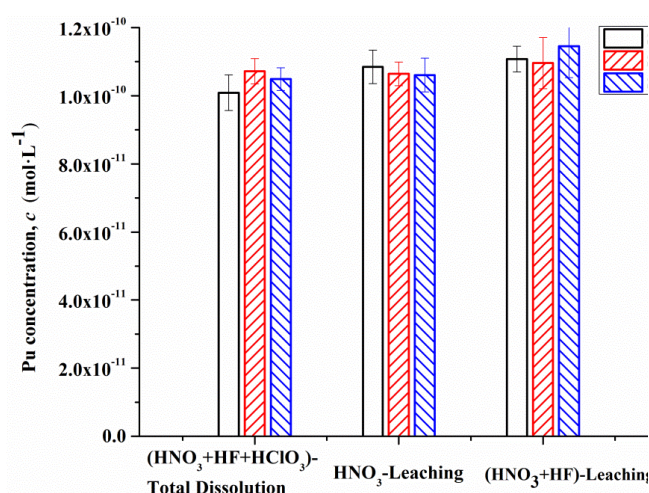


Figure 2. Comparison of three sample pretreatment methods for groundwater samples containing colloidal Pu

3. Verification and application of the method

3.1. Verification on effectiveness of the sample protective method.

A geochemistry software, Visual MINTEQ ver. 3.1 was also employed to simulate the effect of the air on Pu species in the groundwater under the condition of Pu initial concentration of 10 ng g^{-1} and the chemical composition as showed in Table 1. The results (see Figure 3 and Figure 4) showed that although the concentrations of Pu^{3+} and Pu^{4+} decreased with the increasing of pH under the atmosphere of either anaerobic or aerobic, the concentrations of PuO_2^+ and $\text{PuO}_2(\text{c})$ can maintain a steady level under anaerobic atmosphere. So we believe that the protective measurement during sampling and experiment process is in fact indispensable for our study. To verify the effectiveness of the sample protective measurement, both changes of pH and Eh of the groundwater were monitored during 120 d as shown by Figure 5. It showed that the pH and Eh changed little under the protective measurement. The changing area of pH (7.5 ~ 7.8) and Eh (-70 ~ -50 mV) under the protective measurement was featured in Eh-pH diagrams of Pu (see Figure 6). It is seen that this changes makes little influence on the speciation distribution of Pu.

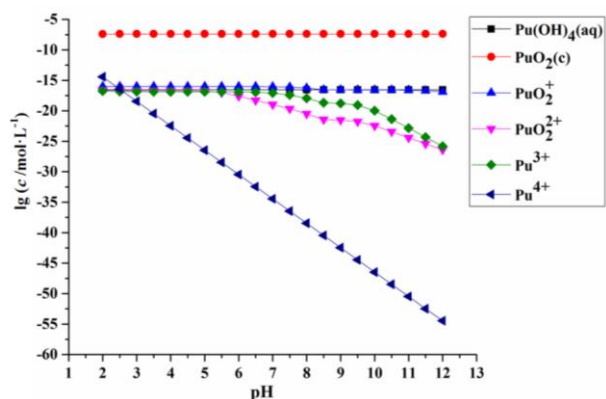


Figure 3. The effect of pH on the speciation distribution of Pu under anaerobic atmosphere by Visual MINTEQ ver. 3.1 ($c_{\text{Pu}} = 10 \text{ ng g}^{-1}$)

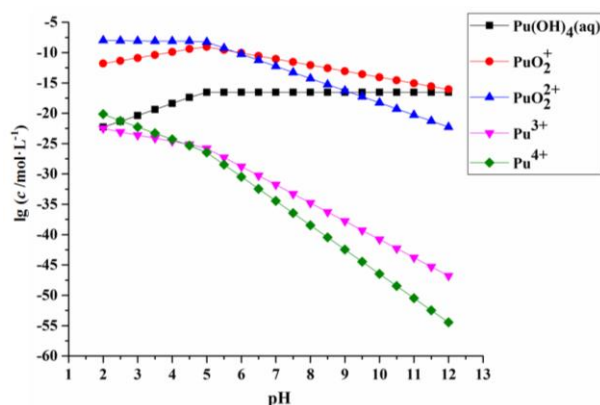


Figure 4. The effect of pH on the speciation distribution of Pu under aerobic atmosphere by Visual MINTEQ ver. 3.1 ($c_{\text{Pu}} = 10 \text{ ng g}^{-1}$)

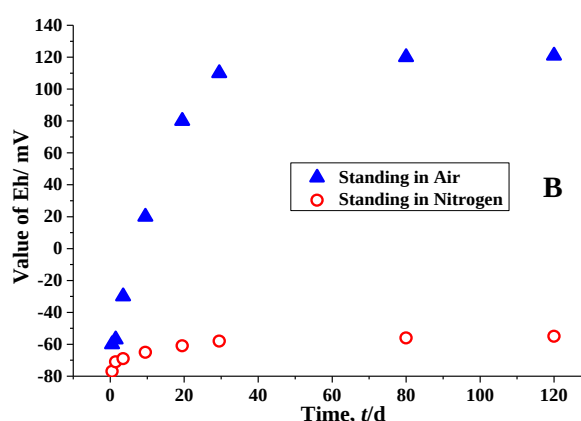
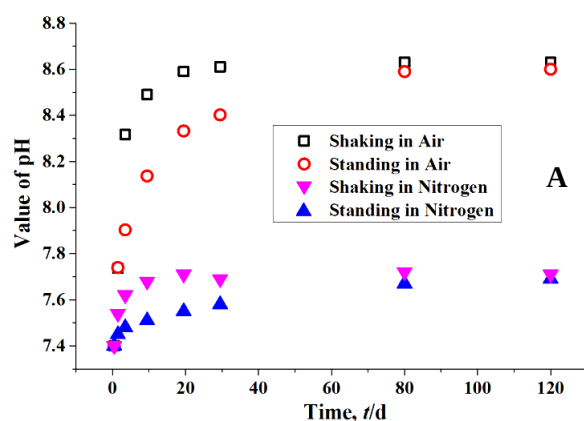


Figure 5. Comparison of changes of pH (A) and Eh (B) value in Air and in Nitrogen atmosphere

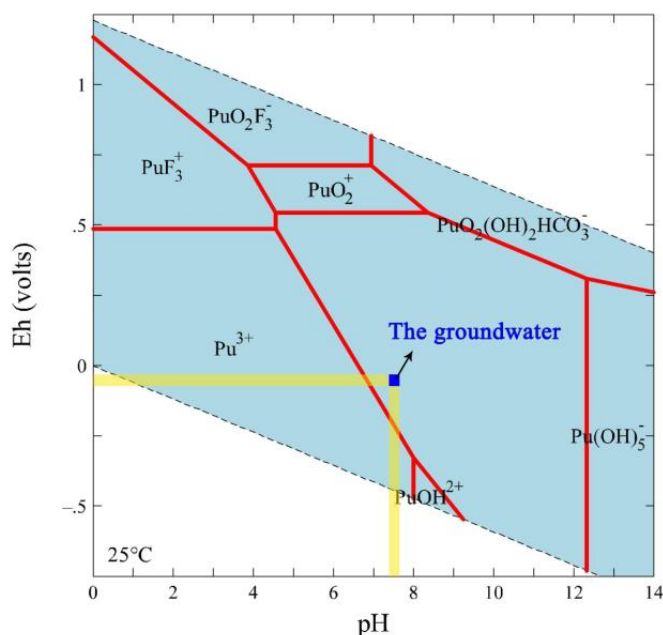


Figure 6. Eh & pH change range of the groundwater under the protection in the Eh-pH diagrams of Pu, which was drawn for 15 °C and a species activity of 10^{-9} M for Pu in the groundwater employing PHREEQC ver. 3.3.12 simulation with LLNL database

3.2. Analysis of impact factors for Pu determination

The impact factors for Pu determination include uniformity of Pu concentration and the adsorption of outer tube of Ultrafiltration Tube and filter membrane. These impact factors were carefully examined in this work.

3.2.1. Uniformity of Pu concentration. Pu colloids may have a vertical distribution when the groundwater samples are stood in Glove Box for long time, so the uniformity of Pu concentration in the groundwater must be examined to specify the error arising from small sample volume. Pu concentrations at various layers and points in a sample containing Pu of 300 pg g^{-1} were determined when the sample was stood for 6 months. A better uniformity of Pu concentrations was observed within uncertainty of 10% as shown in Table 3.

Table 3. Pu concentrations at various points in a sample container, pg g^{-1}

Sampling layer	Centre	periphery				Average
		0 °	90 °	180 °	270 °	
Surface	3.05 ± 0.11	2.84 ± 0.09	2.75 ± 0.08	2.83 ± 0.09	2.72 ± 0.10	2.84 ± 0.06
Middle	2.94 ± 0.09	3.01 ± 0.10	2.82 ± 0.08	2.98 ± 0.09	3.00 ± 0.11	2.95 ± 0.05
Bottom	2.81 ± 0.08	3.24 ± 0.12	3.09 ± 0.09	3.01 ± 0.11	3.04 ± 0.11	3.04 ± 0.07
Average	2.93 ± 0.07	3.03 ± 0.12	2.89 ± 0.10	2.94 ± 0.07	2.92 ± 0.10	2.95 ± 0.04

3.2.2. Adsorption of the outer tube of Ultrafiltration tube and filter membrane for Pu. In the process of ultrafiltration separation of colloidal Pu from dissolved Pu, neutral filtrate containing Pu was placed in the outer tube of ultrafiltration tube for about 2 h before Pu was analyzed, and the filter membrane might adsorb a fraction of Pu. So adsorption of the outer tube of Ultrafiltration tube and filter membrane for Pu was checked to understand the loss of Pu during the experimental process. Pu concentrations in two Ultrafiltration tubes (marked as Tube A and Tube B) were determined at various times (see Figure 7), and Pu concentration changes were checked before and after the second filtration for Pu solution with another new ultrafiltration tubes (see Table 4). It can be seen from Figure 5 and Table 4 that there were little changes of Pu concentrations in two experiments. The adsorption of the outer tube of Ultrafiltration tube and filter membrane for Pu could be neglected in this work.

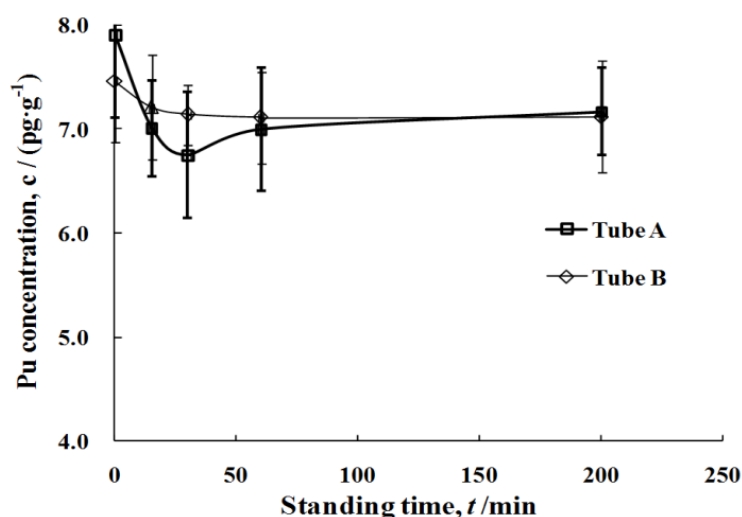


Figure 7. Changes of Pu concentration in the outer tube of Ultrafiltration tube

Table 4. Pu concentration changes before and after the second filtration

Pore size of filter	Pu concentrations before the second filtration, c_1 /(pg g ⁻¹)	Pu concentrations after the second filtration, c_2 /(pg g ⁻¹)	Adsorption loss/%
10 kDa	8.65±0.21	8.33±0.20	3.7
	8.36±0.20	8.11±0.18	3.0
100 kDa	8.58±0.21	8.35±0.21	2.7
	8.90±0.22	8.96±0.23	-0.7
0.45 μm	9.82±0.26	9.57±0.25	2.6
	9.16±0.24	8.96±0.22	2.2

3.3. Application results of the method

The method was successfully employed to determine speciation distribution of Pu in the groundwater from a granite region, NW of China. The results showed that Pu(IV) spiked was rapidly transformed to colloidal Pu which then formed precipitation on the container walls. Thus about 90% of Pu was lost from the water phase after 30 d. For the minority of Pu (~10%) remaining in the water phase (see Figure 8), most of it was dissolved species dominated by Pu(V) and Pu(VI) valence states, and the other part was colloidal Pu dominated by carbonates (~80%) with particle size greater than 300 nm. All of this applied results were presented in our previous study [16] and were basically consistent with the modelling results by geochemical software (Figure 9 was one of modelling figures for valence distribution of Pu in groundwater by Visual MINTEQ ver. 3.1) and/or analysis results by related instruments. The method can also be used to analyze the speciation distribution of Pu in waste liquor from Nuclear Plant and/or related reactor research.

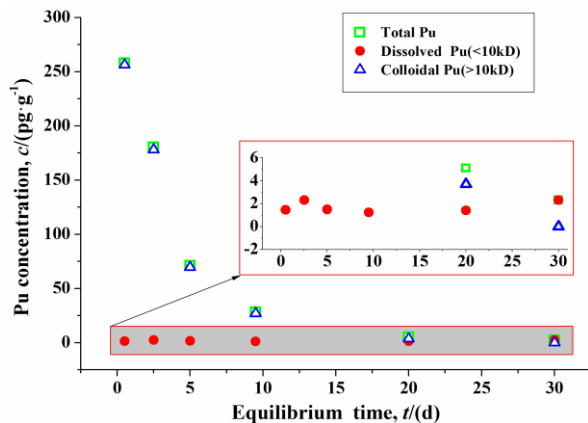


Figure 8. Concentration change profiles of Pu in different speciation states with aging time under Initial Pu concentration of ~0.3 ng g⁻¹ and without shaking the sample

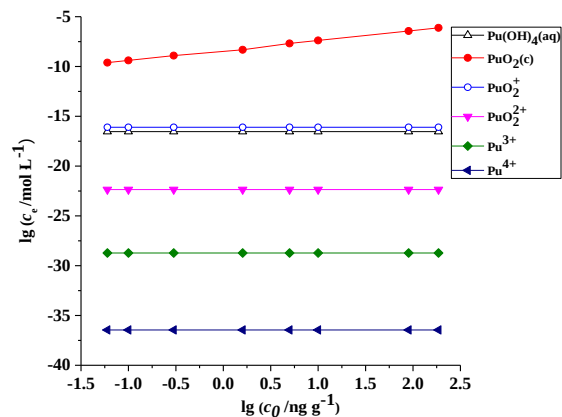


Figure 9. Simulation of equilibrium Pu concentration c of different speciation forms as functions of initial Pu concentration c_0 by Visual MINTEQ ver. 3.1

4. Conclusion

A laboratory simulation research method for speciation distribution of ultratrace Pu in groundwater was established, in which a nitrogen assisted sampling and storage device was designed and employed to sample groundwater, and the groundwater sample was transported and kept in Anaerobic Glove Box, into which spiked Pu was added and the speciation distribution of Pu were monitored at various aging time by series speciation analysis techniques. Using the method, the groundwater samples were kept away from air in the whole sampling, transportation and experiment process, and the speciation distribution of ultratrace Pu in a contaminated groundwater from a granite area, NW China was

obtained successfully. The results showed that Pu(IV) spiked was rapidly transformed to colloidal Pu which then formed precipitation on the container walls. Thus about 90% of Pu was lost from the water phase after 30 d. For the minority of Pu (~10%) remaining in the water phase, most of it was dissolved species dominated by Pu(V) and Pu(VI) valence states, and the other part was colloidal Pu dominated by carbonates (~80%) with particle size greater than 300 nm. All of this results were basically consistent with the modelling results by geochemical software and /or analysis results by related instruments. Not only the method can continuously be used speciation distribution of Pu in groundwater, but also can be used in other fields such as the treatment of waste liquor from Nuclear Plant, Reactor study, and so on.

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