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On the quality control for the determination of ultra-trace level ^{236}U and ^{233}U in environmental samples by accelerator mass spectrometry

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ABSTRACT: Our recent attempt to determine ultra-trace level ^{236}U and ^{233}U in small volume seawater samples was challenged by high and unstable procedure blanks in our environmental radioactivity laboratory, which used to be a spent fuel research facility. Through intercomparison experiments with different laboratories and background checks on the chemical reagents and laboratory dust, the resuspended U-bearing dust was identified as the dominating source of the ^{236}U and ^{233}U contamination. With the implementation of background control (especially dust control) measures, the procedure blanks and detection limits of ^{236}U and ^{233}U for the radiochemical separation procedure has been significantly improved by three orders of magnitudes. With well-controlled blanks, the analytical precision for ^{236}U and ^{233}U predominantly relies on the AMS counting statistics. Background check and dust control are strongly recommended before the analyses of environmental level long-lived radionuclides (such as ^{236}U and ^{233}U) that are conducted in the former or active nuclear facilities, even if clearance of radioactivity relevant for radioprotection was achieved.

The long-lived uranium isotope ^{236}U ($t_{1/2} = 23.4$ Myr) has become a popular tracer in oceanic studies because of improved measurement techniques by accelerator mass spectrometry (AMS) and its excellent properties, including high solubility, long residence time, and conservative features.¹⁻⁴ Besides a minor amount of naturally produced ^{236}U ,⁵ the majority of environmental ^{236}U was released through anthropogenic nuclear activities, including atmospheric nuclear weapon tests,^{1,6-8} authorized discharges of nuclear reprocessing plants⁹ and nuclear accidents¹⁰⁻¹². The pulse injection of anthropogenic ^{236}U

results in a wide scale of $^{236}\text{U}/^{238}\text{U}$ atomic ratios (10^{-13} - 10^{-6}) in the global oceanic systems (Figure 1),^{1,7,13–29,29,30} which roughly corresponds to a range of (10^3 - 10^9) atoms/kg for ^{236}U concentrations in seawater. This makes ^{236}U a suitable transient tracer to investigate the oceanic circulation patterns, water masses mixing, and transit time.

Recent developments of the AMS technique enable the measurement and tracer application of another long-lived anthropogenic uranium isotope ^{233}U ($t_{1/2} = 0.16$ Myr) in the environment.^{3,30,31} Different from ^{236}U , the only massive emission of anthropogenic ^{233}U occurred during the global fallout of nuclear weapons testing (GF). In contrast, little ^{233}U is produced by nuclear reactors and released from reprocessing plants or nuclear accidents.³ The representative level of the $^{233}\text{U}/^{236}\text{U}$ atomic ratio in natural reservoirs exposed to GF is estimated to be $(1.40 \pm 0.15) \times 10^{-2}$ by a recent study on a peat core (Black forest, Germany),³ while the documented levels in the discharges of the nuclear reprocessing plant at La Hague are 10^{-7} - 10^{-6} (HELCOM MORS Discharge database).³² In the Irish Sea, an average $^{233}\text{U}/^{236}\text{U}$ atomic ratio of $(0.12 \pm 0.01) \times 10^{-2}$ was measured in the seawater and sediments close to the nuclear reprocessing plant at Sellafield.³ Based on the production mechanisms of anthropogenic ^{233}U and ^{236}U , the $^{233}\text{U}/^{236}\text{U}$ atomic ratio only depends on the features of the nuclear fuel and neutron spectrum.³ This makes the $^{233}\text{U}/^{236}\text{U}$ atomic ratio a robust signature to identify the emission sources of anthropogenic uranium and allows the precise quantification of GF's contribution in multiple-source systems, demonstrated by the recent studies in the Danish Straits and Greenland coast.^{3,30}

AMS, together with the preceding radiochemical separation of uranium, is the only possible method to determine ultra-trace level ^{236}U and ^{233}U in the environmental samples. As a sufficiently low detection limit (LOD) of the analytical method is critical, the instrumental sensitivity of AMS and the levels of ^{236}U , ^{233}U , and interferences present in the procedure blank are therefore the most important parameters. The effective radiochemical separation and the physical processes involved in the AMS setup, mostly the stripping process, allow a high suppression of the molecular isobars, especially the ones coming from the naturally-occurring neighbouring isotopes (i.e. ^{235}U in the ^{236}U case and ^{232}Th in the ^{233}U case). Hence, the major limitations to overall LODs are the ^{236}U and the ^{233}U in the procedure blank introduced during the radiochemical procedure.³¹ In previous studies,^{19,23,25–27,33} the procedure blanks for 3 - 20 L of water samples were reported to contain 40 - 1000 ag (corresponding to 1.0×10^5 - 2.6×10^6 atoms, and 1 ag = 10^{-18} g) of ^{236}U , and the major contributions were from the ^{233}U spikes,^{26,29,34} reagents,^{5,24} labwares²⁹ and cross-contamination^{1,25}. However, few researches were concerned about the levels and sources of ^{233}U in procedure blanks since it was mainly utilized as a yield tracer for ^{236}U . It must, however, be investigated for the ^{233}U analyses in environmental samples considering its extremely low concentrations. From the representative levels of $^{236}\text{U}/^{238}\text{U}$ (10^{-9}) and $^{233}\text{U}/^{236}\text{U}$ atomic ratios for GF signature in modern ocean

surface waters,⁷ a $^{233}\text{U}/^{238}\text{U}$ atomic ratio of about 1.4×10^{-11} and a ^{233}U concentration of about 1.2×10^5 atoms/kg can be estimated in the open sea.

Besides procedure blank, precision is also vital for the determination and tracer application of ^{236}U and ^{233}U . For instance, the Atlantic Waters in the Arctic Ocean are labeled by the ^{236}U and ^{129}I discharged from two European reprocessing plants (RP). RP-derived $^{129}\text{I}/^{236}\text{U}$ atomic ratios have been adopted to estimate the age of Atlantic Waters.^{19,25–27,27,35,36} Lower measurement uncertainties of ^{236}U are favorable for the precise estimation of the transit time. Furthermore, the measured $^{129}\text{I}/^{236}\text{U}$ atomic ratios in Atlantic Waters could be significantly biased by the additional GF-derived ^{236}U along the transport pathway,¹⁶ which could be corrected by the simultaneous determination of ^{233}U .^{3,30} Such a subtraction also requires acceptable precision of ^{233}U to avoid introducing large uncertainties. For example, Greenland seawater consists of about 30% and 70% of GF- and RP-derived ^{236}U according to the $^{233}\text{U}/^{236}\text{U}$ atomic ratios,³⁰ and a relative uncertainty of 30% for ^{233}U will contribute a relative uncertainty of 13% for RP-derived ^{236}U . The reported ^{236}U analyses enabled the precise measurement of $^{236}\text{U}/^{238}\text{U}$ atomic ratios (within 10% of relative uncertainty) in 1 - 2 L seawater samples with the lowest value of 10^{-9} ^{17,21,22,27} and 3 - 20 L with 10^{-10} ^{1,7,15,17,19,24–27,29,33,35,37}. Even though limited experience exists for the ^{233}U analyses, unavoidably large uncertainties can be expected due to its extremely low concentrations in environmental samples, restricting its application on sources discrimination. Naturally, larger sample volumes are needed for the lowest-level samples to improve precision, but this leads to less sampling efficiency, higher cost for sample transportation and storage during the scientific expeditions,³⁸ as well as higher costs for the laboratory analyses. Hence, finding out the key parameters affecting the measurement uncertainties of ^{236}U and ^{233}U and optimizing them to obtain the desirable uncertainties are a pre-requisite for sampling plan and AMS measurement.

In this work, the aspects of quality control on laboratory background and analytical uncertainty are discussed by introducing our recent attempt to analyze ^{236}U and ^{233}U with 2 L of seawater samples, which was challenged by relatively high and unstable levels of ^{236}U and ^{233}U in procedure blanks prepared at an environmental radioactivity laboratory that used to be a spent fuel research facility. The sources of uranium isotopes presented in procedure blanks during the radiochemical preparation were systematically investigated. Background control measures were implemented, and the major contributors to combined uncertainties of ^{236}U and ^{233}U were analyzed. Two sets of seawater samples were utilized for the demonstration of background control and uncertainty analysis.

EXPERIMENTAL SECTION

Standards and Reagents. Uranium standard solutions (10 µg/mL in 2% HNO₃, Labkings) were used to establish the standard curve for the inductively coupled plasma mass spectrometry (ICP-MS) measurement. Chemicals with different purity grades and suppliers (as summarized in Table S1) were utilized at the different laboratories involved in this work, including the Department of Environmental Engineering in Technical University of Denmark (DTU-ENV), the National Institute of Aquatic Resources in Technical University of Denmark (DTU-AQUA), and the Vienna Environmental Research Accelerator facility in University of Vienna (VERA). At DTU-ENV and DTU-AQUA, 37% HCl and 65% HNO₃ solutions were distilled by an acid sub-boiling system before usage to remove uranium and other major matrix components.²⁴ 0.05 g/mL Fe solution was prepared by dissolving FeCl₃·6H₂O (analytical grade, Sigma-Aldrich) in 3 M HNO₃, and then purified with a UTEVA[®] resin column (100-150 µm, Triskem International) to remove uranium isotopes. At VERA, all of the chemicals were SuperPure[®] grade and directly utilized without any purification. Ultrapure water (18 MΩ·cm at 25 °C) was consistently used for reagent preparation in all laboratories.

Separation of Uranium from Seawater. An optimized radiochemical separation procedure was modified and utilized to separate uranium from 2 L water samples for the determination of ²³⁶U and ²³³U by AMS.²⁴ After filtration with filter paper (Grade 00K, Munktell Filtrak), 2 L of water sample was acidified to pH = 2 with 65% HNO₃. After adding 200 mg of Fe³⁺ as a carrier and bubbling for 10 min, 25% NH₃·H₂O solution was gradually added to the water sample while stirring until pH = 8-9 to co-precipitate uranium with Fe(OH)₃. The Fe(OH)₃ precipitate was allowed to settle down for 0.5 h. The supernatant was discarded, and the slurry was centrifuged at 3000 rpm for 10 min. The precipitate was dissolved with 1 mL of 37% HCl, and 5 mL of 65% HNO₃ was added. The solution was diluted with ultrapure water to a final concentration of 3 M HNO₃ and then loaded to a 2-mL UTEVA[®] resin column pre-conditioned with 20 mL of 3 M HNO₃. After washing the column with 2 × 20 mL of 3 M HNO₃ and 20 mL of 6 M HCl, uranium was eluted with 10 mL of 0.025 M HCl. 2 mg of Fe³⁺ was added to the eluate, and pH was adjusted to 8-9 for co-precipitating uranium with Fe(OH)₃. The precipitate was dried at 90 °C for 4 h and then baked at 800 °C for 12 h. Finally, the sample was pressed into an aluminum sputter target holder to measure ²³⁶U/²³⁸U and ²³³U/²³⁸U atomic ratios by AMS at VERA. Different from other AMS laboratories, no metallic powder was added to the uranium sputter material, even though it can increase the ionization yields and ion currents. On one hand, adding binders may introduce additional uranium isotopes to the procedure blanks, which is avoided as far as possible in this work (especially for ²³³U). On the other hand, during tuning the beam before stripping process, the often-used copper and silver binders give rise to molecular anions in the mass range around 250 amu, which interfere with the UO⁻

ions. In fact, any new element in the matrix will make the molecular spectrum more complex in the heavy mass range, which will increase the effort of method validation.

Measurement of ^{238}U , ^{236}U , and ^{233}U by ICP-MS and AMS. To obtain the chemical yield of the radiochemical procedure and calculate the ^{236}U and ^{233}U concentrations in water samples, 100 μL aliquots of original water and uranium eluate were taken and diluted 10-50 and 100-10000 times with 0.5 M HNO_3 respectively for the measurement of ^{238}U concentration by a triple-quadrupole ICP-MS (8800, Agilent). The detailed determination method for $^{236}\text{U}/^{238}\text{U}$ and $^{233}\text{U}/^{238}\text{U}$ atomic ratios and setup description for the AMS at VERA have been provided in the Supporting Information and reported elsewhere.^{3,31} The AMS system's overall detection efficiency for uranium atoms is about 5×10^{-4} ,³ assuming complete consumption of the sputter material. As no pure ^{238}U material without any ^{236}U or ^{233}U is available as machine blank, the instrumental LODs of AMS for $^{236}\text{U}/^{238}\text{U}$ and $^{233}\text{U}/^{238}\text{U}$ can only be estimated to be in the order of 10^{-14} and 10^{-16} , respectively.^{3,31}

It is noteworthy that the actual $^{236}\text{U}/^{238}\text{U}$ or $^{233}\text{U}/^{238}\text{U}$ atomic ratio in the original sample ($R_S^{236(233)}$) is obtained by a correction of AMS measurement result according to eq 1 to subtract ^{236}U or ^{233}U contained in the procedure blank.

$$R_S^{236(233)} = \frac{(m_m^{238} R_m^{236(233)} - m_b^{238} R_b^{236(233)})}{m_m^{238} - m_b^{238}} \quad (1)$$

where $R_m^{236(233)}$ and $R_b^{236(233)}$ are the $^{236}\text{U}/^{238}\text{U}$ or $^{233}\text{U}/^{238}\text{U}$ atomic ratios measured in the sample and blank targets; m_m^{238} and m_b^{238} are the corresponding ^{238}U contents. It should be noted that AMS can only quantitatively determine the isotopic ratios, but not the absolute amounts of ^{238}U since ionization yield might change between cathodes. As the chemical yield for the target preparation step is quantitative ($Y_{\text{target}} > 99\%$),²⁴ the ^{238}U content in the sample or blank target is assumed to be equal to that in the eluate and can be calculated by eq 2.

$$m_{m(b)}^{238} = m_{m(b),\text{eluate}} C_{m(b)}^{238} Y_{\text{target}} \approx m_{m(b),\text{eluate}} C_{m(b)}^{238} \quad (2)$$

where $m_{m,\text{eluate}}$ or $m_{b,\text{eluate}}$ is the mass of sample or blank eluate; C_m^{238} or C_b^{238} is the ^{238}U concentration in the eluate of sample or blank measured by ICP-MS. With R_S^{236} and R_S^{233} , the $^{233}\text{U}/^{236}\text{U}$ atomic ratio ($R_S^{233/236}$) in the water sample is calculated as $R_S^{233/236} = R_S^{233} / R_S^{236}$.

Blank Sample Preparation. To quantify ^{236}U and ^{233}U introduced during the radiochemical separation, procedure blanks (n=6, named as DTU-ENV Batch) were prepared at DTU-ENV with 2 L of ultrapure water following the aforementioned procedure. The whole procedure was conducted in the fume hood, where water samples were usually treated at DTU-ENV. For comparison, another three batches of

procedure blanks were prepared in a fume hood at VERA (n=4, named as VERA Batch), a fume hood at DTU-AQUA (n=4, named as DTU-AQUA Batch), and a laminar flow bench (Safe 2020, Thermo Fisher Scientific) at DTU-ENV (n=3, named as DTU-ENV-LFB Batch).

Based on m_b^{238} and $R_b^{236(233)}$, the ^{236}U or ^{233}U contents in the sputter targets of procedure blanks could be calculated by $m_b^{236(233)} = m_b^{238} \times R_b^{236(233)} \times 236(233) / 238$. Hence, the overall LOD of the analytical method for the $^{236}\text{U}/^{238}\text{U}$ or $^{233}\text{U}/^{238}\text{U}$ atomic ratio ($\text{LOD}(^{236(233)}\text{U}/^{238}\text{U})$) is deduced from eq 3.

$$\text{LOD}(^{236(233)}\text{U}/^{238}\text{U}) = \frac{\overline{m_b^{236(233)}} + 3 \times \sigma_b^{236(233)}}{C_s^{238} \times V \times Y} \times \frac{238}{236(233)} \quad (3)$$

where C_s^{238} is the ^{238}U concentration in the water sample; V is the sample volume; Y is the chemical yield for the chemical procedure; $\overline{m_b^{236(233)}}$ and $\sigma_b^{236(233)}$ are the average values and uncertainties (1 standard deviation) of ^{236}U or ^{233}U contents in the sputter targets of the procedure blanks.

Source Identification of ^{236}U and ^{233}U Contamination. To identify the sources of ^{236}U and ^{233}U present in the procedure blanks prepared in the fume hood usually used for processing seawater samples at DTU-ENV, the levels of ^{236}U and ^{233}U in chemical reagents and airborne dusts were investigated. The consumption amounts of different reagents for a blank in DTU-ENV Batch during the radiochemical procedure were calculated, as summarized in Table S2. Two ‘total reagent’ samples (named as DTU-TR samples, Table S4) were prepared by mixing equivalent amounts of these reagents. The DTU-TR samples were subjected to the entire radiochemical procedure starting from the first $\text{Fe}(\text{OH})_3$ co-precipitation step to determine the total contents of ^{236}U , ^{233}U , and ^{238}U in the mixture of reagents, which represent the contribution from chemical reagents to the procedure blank. A corresponding blank (named as DTU-TR-bk, Table S4) for DTU-TR samples was also prepared to deduct the extra ^{236}U , ^{233}U , and ^{238}U introduced during the radiochemical procedure. The entire procedure was conducted in the laminar flow bench to exclude the influence of airborne dusts.

To evaluate the contribution from airborne particles, four aerosol samples (1000-1700 m^3 of air volume) were collected by a high volume air sampler (Staplex[®]) with glass microfiber filters (0.45 μm , Staplex) in different laboratories of DTU-ENV and the field outside the laboratory building (as summarized in Table S3). A dust sample (DTU-BD-kemi3-fh) was also collected on a sheet of paper placed on the fume hood desktop, where water samples were previously treated. The aerosol samples and the dust sample were digested with 120 mL of *aqua regia* by heating on a hot plate at 150 $^\circ\text{C}$ for 0.5 h and then 200 $^\circ\text{C}$ for 2 h to leach uranium. The leachate was filtrated with glass microfiber filters (grade GF/A, Whatman), and the residue was washed with 10 mL of 0.5 M HNO_3 three times. The washing solution was combined into the leachate, and 100 mg of Fe^{3+} was added to each sample as a carrier. The

samples were processed starting from the first $\text{Fe}(\text{OH})_3$ co-precipitation step. All aerosol samples were prepared at VERA using VERA's reagents, while the dust sample was prepared in the laminar flow bench at DTU-ENV using DTU's reagents.

RESULTS AND DISCUSSION

Laboratory Background at DTU-ENV, DTU-AQUA, and VERA. The analytical results of ^{236}U , ^{233}U , and ^{238}U contents, together with $^{236}\text{U}/^{238}\text{U}$, $^{233}\text{U}/^{238}\text{U}$, and $^{233}\text{U}/^{236}\text{U}$ atomic ratios, in all procedure blanks are shown in Table S4. In the comparison of procedure blanks prepared at DTU-ENV, DTU-AQUA, and VERA (Figure 2), the DTU-ENV Batch shows about 2 - 4, 1 - 2, and 1 - 2 orders of magnitudes higher ^{236}U , ^{233}U , and ^{238}U contents than the DTU-AQUA Batch, and 3 - 5 and 1 - 2 orders of magnitudes higher ^{236}U and ^{238}U contents than the VERA Batch, respectively. The comparison indicates that typical high contamination of ^{236}U , ^{233}U , and ^{238}U occurred in the radiochemical procedure in the DTU-ENV batch. Specifically, the total amount of ^{236}U present in DTU-ENV-bk-1 ($(2.66 \pm 0.36) \times 10^7$ atoms) is much higher than the procedure blanks for 3 - 20 L of seawater samples (1.0×10^5 - 2.6×10^6 atoms) reported in other studies.^{19,23,25–27,33} Moreover, the highest $^{236}\text{U}/^{238}\text{U}$ atomic ratio ($(4.94 \pm 0.59) \times 10^{-6}$) in DTU-ENV Batch even exceeds the reported level in the Irish Sea water sample (IAEA-443, 2.45×10^{-6})³⁹ that is highly contaminated with ^{236}U discharged from the Sellafield Nuclear Reprocessing Plant. This excludes the possibility of cross-contamination as no sample with such a high level of $^{236}\text{U}/^{238}\text{U}$ atomic ratio has been treated at DTU-ENV based on our record. The results indicate that blanks prepared at DTU-ENV were randomly contaminated from a “hot” source with varying high $^{236}\text{U}/^{238}\text{U}$ atomic ratio. Considering that the same reagents and labware were used for the DTU-ENV Batch and the DTU-AQUA Batch, the source term should not be related to chemical reagents or labware but to the laboratory environment.

Sources of ^{236}U , ^{233}U , and ^{238}U in DTU-ENV Blanks. The measured contents of uranium isotopes and their ratios in the aerosol, dust samples, and reagents are summarized in Table S4. For the aerosol samples collected in various localtions of DTU-ENV, the highest air-volume-normalized ^{236}U content of $(1.60 \pm 0.36) \times 10^4$ atoms/ m^3 is observed in the sample collected in the fume hood of Kemi3 Lab (DTU-AS-kemi3-fh), where the environmental water samples were previously prepared. In comparison, no count was detected for ^{236}U in the aerosol sample collected in the field, suggesting that negligible ^{236}U is from the natural environment. High ^{236}U , ^{233}U and, ^{238}U contents of $(4.57 \pm 1.92) \times 10^9$ atoms, $(3.57 \pm 2.07) \times 10^6$ atoms, and (378 ± 158) ng, respectively, are also found in the dust sample collected in the same fume hood (DTU-BD-kemi3-fh, 0.16 g), which are higher than the DTU-ENV Batch (2.26×10^5 - 2.66×10^7 atoms, $(1.45 - 6.1) \times 10^4$ atoms and 0.37 - 6.27 ng, respectively). On the contrary, the ^{236}U , ^{233}U and, ^{238}U contents in the DTU-TR samples ($< 3.23 \times 10^3$ atoms, < 139 atoms, and $< 6.04 \times 10^{-2}$ ng, respectively)

are much lower than the DTU-ENV Batch. These results indicate that the unknown contamination of uranium isotopes in DTU-ENV Batch likely originates from aerosol particles and dust in the fume hood rather than from reagents.

In addition, the $^{233}\text{U}/^{236}\text{U}$ atomic ratios can also be utilized to identify the source terms of anthropogenic uranium isotopes. Low $^{233}\text{U}/^{236}\text{U}$ atomic ratios are found in the dust sample (DTU-AS-kemi3-fh, $(0.08 \pm 0.03) \times 10^{-2}$) and a procedure blank in the DTU-ENV Batch (DTU-ENV-bk-1, $(0.05 \pm 0.05) \times 10^{-2}$) (Figure 2), which are consistent with the presence of irradiated uranium with depleted $^{233}\text{U}/^{236}\text{U}$ atomic ratios.³ Even though large uncertainties exist in the results for $^{233}\text{U}/^{236}\text{U}$ atomic ratios in DTU-TR samples (Table S4), their lower limits are still higher than the expected global-fallout ratio of 1.4×10^{-2} .³ This supports our conclusion that the high and unstable level of ^{236}U observed in DTU-ENV Batch must be mainly attributed to aerosols and dust in the laboratory bearing anthropogenic uranium isotopes with thermal-reactor signature.

The building hosting the laboratories for ^{236}U and ^{233}U analyses at DTU-ENV has been used for researches related to spent fuel from the local research reactors. We assume that some ^{236}U -associated particles were generated during the spent fuel treatment process. These “hot particles” were released into the atmosphere, dispersed to the whole building, and deposited on the building's inner surface, including the ventilation system. Even though the building was renovated before it was repurposed to environmental radioactivity research, complete clearance was hard to achieve because of the difficulties in analyzing low-level long-lived radionuclides, such as ^{236}U . The contamination of dust from the ventilation system was likely to randomly happen during the column separation step in the fume hood, when the columns were exposed to the atmosphere.

Background Control. As the contamination may occur in any step of the procedure for the analyses of ^{236}U and ^{233}U , including sampling, storage, radiochemical separation, target preparation, and AMS measurement, background control measures have been implemented at DTU-ENV.

Purification of reagents: Purification of reagents and utilization of high-purity-grade chemicals containing very low contents of uranium isotopes are widely applied in ^{236}U studies.^{18,21,22,25,28–30,33,37} Our previous work demonstrated that distillation of acids and purification of Fe solution as detailed in the Experimental Section significantly reduced the ^{236}U contents in the procedure blanks for 10 L water analysis from $(3.35 \pm 2.40) \times 10^4$ ag (corresponding to 8.5×10^7 atoms) to $(6.5 \pm 5.6) \times 10^2$ ag (around 1.7×10^6 atoms) and thus improved the LOD.²⁴

Labware and cleaning: The replacement of the ordinary glassware with Teflon® and disposable labware has proven useful for reducing potential cross-contamination.²⁹ All the reusable labware (e.g., beaker, the

only glassware, and Teflon[®] centrifuge tubes) are boiled with 6 M HCl for 2 h and rinsed with ultrapure water after each usage to remove any adsorbed uranium.

Limitation of spike usage: In our radiochemical procedure, ²³⁸U is used as an intrinsic chemical yield tracer instead of ²³³U, which allows us to determine the ²³³U content of the sample and avoids the introduction of ²³⁶U potentially present in the ²³³U spike. For instance, 5×10^{-4} of ²³⁶U/²³³U atomic ratio has been reported in a ²³³U spike.²⁹ In addition, the isotopic equilibrium problem when using ²³³U spike is also eliminated.²⁴

Dust control: As the aerosols and dusts are identified as the primary source of ²³⁶U, ²³³U and ²³⁸U in DTU-ENV Batch, dust control has become a critical part, especially for ultra-low level samples. A new independent laminar flow bench has been installed and utilized at DTU-ENV to create a dust-free environment for the radiochemical separation and target preparation with the specially designed downward flow.⁴⁰ The built-in HEPA filter in the laminar flow bench is widely utilized in the nuclear industry,⁴¹ which can remove more than 99.99% of the 0.3 µm particles, including any inherited “hot particles”. Besides, dust-protection measures are also applied during the storage and transport of samples and glassware.

Improvement of Laboratory Background. A significant reduction of background is observed in the procedure blanks (DTU-ENV-LFB Batch) prepared after dust control (Figure 2). The contents of ²³⁶U, ²³³U, and ²³⁸U in DTU-ENV-LFB Batch are reduced by 3 - 4, 3, and 1 - 2 orders of magnitudes to $(2.09 - 3.79) \times 10^3$ atoms, 50 - 162 atoms and 0.06 - 0.18 ng, respectively, and are comparable with those in DTU-AQUA Batch, VERA Batch and DTU-TR samples. The ²³³U/²³⁶U atomic ratios in DTU-ENV-LFB Batch $((2.17 - 4.17) \times 10^{-2})$ are comparable with the GF signature, similar to the DTU-TR samples. This means that the aerosol and dusts contributed >90% of ²³⁸U and >99.9% of ²³⁶U and ²³³U present in DTU-ENV Batch, now eliminated by using laminar flow bench. The current dominating source of ²³⁶U and ²³³U in DTU-ENV-LFB Batch stems no longer from aerosols or dusts but reagents.

Improvement of Detection Limit. According to eq 3, the LODs of the analytical method based on the previous procedure blanks are estimated to be 3×10^{-9} and 8×10^{-12} for ²³⁶U/²³⁸U and ²³³U/²³⁸U atomic ratios, respectively, in open sea water samples (assuming $V = 2$ L, $Y = 80\%$, $C_s^{238} = 3$ µg/kg.). The previous LOD for ²³⁶U/²³⁸U atomic ratio could only enable the analyses of samples (2 L) collected from high-level areas such as the Irish Sea and part of the North Sea (Figure 1). With the reduced procedure blanks, the LODs for ²³⁶U/²³⁸U and ²³³U/²³⁸U atomic ratios are significantly improved to 4×10^{-13} and 2×10^{-14} for open sea water. Such low LODs theoretically enable the determination of ²³⁶U/²³⁸U and ²³³U/²³⁸U atomic ratios in most of the marine regions with 2 L of sample volume (Figure 1). Still, the analyses of low-level

samples typically have large uncertainties due to the limitations of AMS performance, and therefore an uncertainty analysis and optimization of measurement conditions are needed.

Uncertainty Analysis. The uncertainty of a measurement is a parameter that characterizes the dispersion of the measurement results that could be reasonably attributed to the analyte.⁴² Sources of uncertainty can exist at any step of the analysis and vary from laboratory by laboratory. In this work, all the major uncertainty components contributing to the combined uncertainty of the background-corrected $^{236}\text{U}/^{238}\text{U}$ or $^{233}\text{U}/^{238}\text{U}$ atomic ratios ($u(R_s^{236(233)})$) are illustrated by a fishbone chart (Figure S1). For $R_s^{236(233)}$ calculated from eq 1, the combined uncertainty can be derived with eq 4 according to the law of uncertainty propagation, which contains several independent uncertainty components, including the uncertainties of ^{238}U contents in the eluates of sample and blank ($u(m_m^{238})$ and $u(m_b^{238})$) determined by ICP-MS and the uncertainties of determined $^{236}\text{U}/^{238}\text{U}$ or $^{233}\text{U}/^{238}\text{U}$ atomic ratio in the eluates of sample and blank ($u(R_m^{236(233)})$ and $u(R_b^{236(233)})$) determined by AMS.

$$u(R_s^{236(233)}) = \sqrt{\left[\frac{\partial R_s^{236(233)}}{\partial R_m^{236(233)}} u(R_m^{236(233)})\right]^2 + \left[\frac{\partial R_s^{236(233)}}{\partial R_b^{236(233)}} u(R_b^{236(233)})\right]^2 + \left[\frac{\partial R_s^{236(233)}}{\partial m_m^{238}} u(m_m^{238})\right]^2 + \left[\frac{\partial R_s^{236(233)}}{\partial m_b^{238}} u(m_b^{238})\right]^2}$$

$$= \sqrt{\left[\frac{m_m^{238}}{m_m^{238} - m_b^{238}} u(R_m^{236(233)})\right]^2 + \left[\frac{m_b^{238}}{m_m^{238} - m_b^{238}} u(R_b^{236(233)})\right]^2 + \left[\frac{m_b^{238}(R_b^{236(233)} - R_m^{236(233)})}{(m_m^{238} - m_b^{238})^2} u(m_m^{238})\right]^2 + \left[\frac{m_m^{238}(R_m^{236(233)} - R_b^{236(233)})}{(m_m^{238} - m_b^{238})^2} u(m_b^{238})\right]^2} \quad (4)$$

The calculation of $u(m_m^{238})$ and $u(m_b^{238})$ is detailed in the Supporting Information, and here we focus on the discussion of $u(R_m^{236(233)})$ and $u(R_b^{236(233)})$. For the detection of ^{236}U and ^{233}U by AMS, the significant contributions to $u(R_m^{236(233)})$ and $u(R_b^{236(233)})$ are from counting statistics and measurement repeatability. The counting statistics determine the best achievable instrumental uncertainty by AMS for $^{236}\text{U}/^{238}\text{U}$ or $^{233}\text{U}/^{238}\text{U}$ atomic ratio. Poisson statistics predict a relative standard deviation (RSD) of 100% / $\sqrt{N^{236(233)}}$, where $N^{236(233)}$ is the number of ^{236}U or ^{233}U counts. 33%, 10%, and 3.3% of RSDs are yielded from 10, 100, and 1000 counts of ^{236}U or ^{233}U , which correspond to 2×10^4 , 2×10^5 , and 2×10^6 atoms of ^{236}U or ^{233}U sputtered from the sample target with the ultimate counting efficiency of 5×10^{-4} . The repeatability may vary from measurement to measurement due to unexpected instrumental issues of the complex equipment. Hence, it is assessed for every sample batch by repeated measurements on the samples and interleaved measurements on several reference materials. Even though the drifts of the current amplifiers for the ^{238}U measurement or the detector efficiency are accounted, the obtained repeatability is typically <5%, which is quadratically added to the uncertainty from counting statistics.

The contribution from the repeatability to $u(R_m^{236(233)})$ and $u(R_b^{236(233)})$ is usually less significant with <100 counts (typical for blanks) but dominating above >400 counts. However, cross-contamination during target preparation may also cause reduced repeatability, which cannot be detected in the AMS measurement of a single sample but replicates of the same samples or inserted procedure blanks. For the samples with very small uranium content, ^{234}U instead of ^{238}U is utilized for normalization, as introduced in Supporting Information. As the amounts of ^{236}U and ^{233}U are also small for such environmental samples and procedure blanks, ^{234}U counting statistics and a possible disequilibrium of $^{234}\text{U}/^{238}\text{U}$ do not substantially contribute to the uncertainty.

Four scenarios based on different laboratory backgrounds (Table S5) were designed to identify the major uncertainty compounds to $u(R_s^{236(233)})$. In each scenario, the contributions from $u(R_m^{236(233)})$, $u(R_b^{236(233)})$, $u(m_m^{238})$, and $u(m_b^{238})$ to $u(R_s^{236(233)})$ were calculated for the seawater samples ($C_s^{238} = 3 \mu\text{g/kg}$) with different levels of $^{236}\text{U}/^{238}\text{U}$ atomic ratios ($R_m^{236} = 1 - 100 \times \text{LOD}$) (Table S6). In all scenarios, when $R_m^{236(233)}$ is ten times higher than the corresponding LOD, contributions of $u(R_b^{236(233)})$, $u(m_m^{238})$ and $u(m_b^{238})$ can be ignored (less than 5% in total) and thus $u(R_s^{236(233)})$ is mainly from the measurement uncertainty of AMS. However, for the low-level samples (e.g., $R_m^{236(233)} = \text{LOD}$), $u(R_b^{236(233)})$ and $u(m_b^{238})$ also have considerable contributions to $u(R_s^{236(233)})$ and introduce extra uncertainty other than $u(R_m^{236(233)})$. As the levels of $^{236}\text{U}/^{238}\text{U}$ atomic ratios in most parts of the ocean (Figure 1) and estimated $^{233}\text{U}/^{238}\text{U}$ atomic ratio in modern surface ocean waters (1.4×10^{-11}) are at least ten times higher than the improved LODs of the analytical method for 2 L seawater samples (4×10^{-13} and 2×10^{-14}), the major contribution for $u(R_s^{236(233)})$ will result from the measurement uncertainty of AMS (mainly counting statistics).

The discussion above indicates that the best uncertainty of AMS measurement is determined by $N^{236(233)}$, which is relevant with the adopted sample volume, ^{236}U or ^{233}U concentration in the sample, and counting time for ^{236}U or ^{233}U . At DTU-ENV, $u(R_s^{236(233)})$ is predicted by an estimation of $N^{236(233)}$ before sampling and AMS measurement, which applies to the VERA setup and is utilized to optimize the related parameters, as detailed in the Supporting Information.

Demonstration of Real Samples. Two seawater samples provided by the Federal Maritime and Hydrographic Agency of Germany (2018184, Baltic Sea) and Swiss Federal Institute of Technology in Zurich (SW 49-57, Mediterranean Sea) were utilized to demonstrate the effectiveness of background control and reproducibility of analytical results. Four replicates of each sample with different sample

volumes (1, 2, 4.5, and 9 L) were prepared following the aforementioned radiochemical procedure except for the first $\text{Fe}(\text{OH})_3$ co-precipitation step, during which proportional amounts of reagents were used based on the sample volume. To obtain an unbiased estimation of the AMS performance, these replicates were included in a large batch of routine environmental samples, and the staff operating AMS was not informed on the purpose of these samples, which was encouraged by the VERA research group. The background-corrected $^{236}\text{U}/^{238}\text{U}$ and $^{233}\text{U}/^{238}\text{U}$ atomic ratios ($R_s^{236(233)}$) and their combined uncertainties ($u(R_s^{236(233)})$) are shown in Table S7. The calculations for weighted mean value (WMV) of $R_s^{236(233)}$ and its corresponding uncertainty are provided in the Supporting Information.

For all replicates of both 2018184 and SW 49-57, ^{236}U and ^{233}U present in the corresponding blanks is negligible compared to those in the samples, and background correction would, in principle, be not necessary with well-controlled procedure blanks. Consequently, $u(R_s^{236(233)})$ is equal to $u(R_m^{236(233)})$ and dominated by the number of counts detected by AMS for ^{236}U or ^{233}U . The reproducibility of analytical results of 2018184 and SW 49-57 is satisfactory with sample volume varying from 1 L to 10 L, and larger volume and/or longer detection time is favorable to achieve larger numbers of counts and thus lower uncertainties.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Setup description for the VERA and methods for ^{233}U and ^{238}U measurement. Calculation of the uncertainties of ^{238}U contents in the eluates of sample and blank. Optimization of Measurement Parameters for AMS measurement. Calculation weighted mean value and its corresponding uncertainty. Fishbone chart for the major components pertaining to the combined uncertainty of $^{236}\text{U}/^{238}\text{U}$ or $^{233}\text{U}/^{238}\text{U}$ atomic ratio. Summary of consumed chemical reagent at DTU and VERA, and consumption of chemical reagents for a procedure blank in DTU-ENV Batch. Information of aerosol and dust samples collected at DTU-ENV. The overall results for the ^{236}U , ^{233}U and ^{238}U masses, and $^{236}\text{U}/^{238}\text{U}$, $^{233}\text{U}/^{238}\text{U}$ and $^{233}\text{U}/^{236}\text{U}$ atomic ratios of blank, reagent and aerosol/dust samples. Description of 4 assumed scenarios with different laboratory background and the contributions of different uncertainty compounds to the combined uncertainty in these 4 scenarios. Results of $^{236}\text{U}/^{238}\text{U}$ and $^{233}\text{U}/^{238}\text{U}$ atomic ratios for the replicates of two seawater samples. (PDF)

AUTHOR INFORMATION

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Author Contributions

M.L. performed the experiment work and drafted the manuscript. J.Q. and X.H. designed the overall research. R.G., K.H., and P.S. implemented the AMS measurement. J.X., X.H., P.S., and K.H. revised the manuscript. All authors have given approval to the final version of the manuscript.

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Figure 1 Comparison of the $^{236}\text{U}/^{238}\text{U}$ atomic ratios in global oceanic systems. The red and green bars represent the detection limits of the analytical method for 2 L seawater (with ^{238}U concentrations of 1 - 3 $\mu\text{g}/\text{kg}$) based on the previous and improved procedure blanks, respectively.

Figure 2 Comparison of ^{236}U , ^{233}U and ^{238}U contents (A), and $^{236}\text{U}/^{238}\text{U}$, $^{233}\text{U}/^{238}\text{U}$ and $^{233}\text{U}/^{236}\text{U}$ atomic ratios (B) in the procedure blanks prepared at DTU-ENV, DTU-AQUA and VERA.

Background control → ^{236}U and ^{233}U analysis