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Method for ^{236}U Determination in Seawater Using Flow Injection Extraction Chromatography and Accelerator Mass Spectrometry

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ABSTRACT: An automated analytical method implemented in a flow injection (FI) system was developed for rapid determination of ^{236}U in 10 L seawater samples. ^{238}U was used as a chemical yield tracer for the whole procedure, in which extraction chromatography (UTEVA) was exploited to purify uranium, after an effective iron hydroxide coprecipitation. Accelerator mass spectrometry (AMS) was applied for quantifying the ^{236}U/^{238}U ratio, and inductively coupled plasma mass spectrometry (ICPMS) was used to determine the absolute concentration of ^{238}U; thus, the concentration of ^{236}U can be calculated. The key experimental parameters affecting the analytical effectiveness were investigated and optimized in order to achieve high chemical yields and simple and rapid analysis as well as low procedure background. Besides, the operational conditions for the target preparation prior to the AMS measurement were optimized, on the basis of studying the coprecipitation behavior of uranium with iron hydroxide. The analytical results indicate that the developed method is simple and robust, providing satisfactory chemical yields (80−100%) and high analysis speed (4 h/sample), which could be an appealing alternative to conventional manual methods for ^{236}U determination in its tracer application.
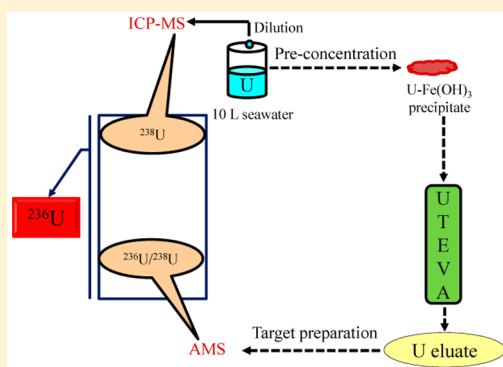
Uranium-236 is mainly produced from the omnipresent ^{235}U by thermal neutron capture via (n, γ)-reactions but can also be produced by ^{238}U (n, 3n) ^{236}U reactions with fast neutrons. On the surface of the earth, a very minor amount of ^{236}U (ca. 35 kg) is produced naturally, mainly in uranium ores,[1] while the majority of ^{236}U in the current environment is produced by anthropogenic processes, e.g., nuclear weapons testing and nuclear power reactors.[2]

It has been estimated that global fallout input of ^{236}U could be constrained in the range of 1000 to 1400 kg, and the direct release of ^{236}U from the two European reprocessing plants (Sellafield and La Hague) is about 115−250 kg.[2] The potential application of ^{236}U as an environmental tracer has been promisingly recognized, since ^{236}U/^{238}U atomic ratios carry key signatures of different sources.[3,4] In recent years, many researchers have been devoting efforts to explore ^{236}U as a new oceanographic tracer.[1,2,5−8]

For its tracer application, reliable, robust, and simple analytical methods for ^{236}U determination are needed to meet the workload for processing a large number of samples. Many methods have been developed for uranium determination in environmental samples and applied to current ^{236}U oceanographic studies.[1,3,8−15] However, key parameters affecting the effectiveness of uranium preconcentration from a large volume of seawater are still not yet clear to ensure constant and quantitative recovery of uranium. In addition to the laboratories handling samples/materials with a high ^{236}U/^{238}U ratio, relatively high ^{236}U background was also found in those

laboratories working exclusively with low-level environmental radioactivity.[15] It is still a difficult and challenging issue for many researchers to tackle the requirement of low method detection limit (i.e., low procedure blank) in determining ultratrace ^{236}U for most marine samples. Besides, all the methods reported in the literature are operated in manual fashion which is somehow labor intensive and less efficient.

With the development of automation technology, many researchers are becoming interested in applying semiautomated vacuum box systems or fully automated flow/sequential injection systems to improve the analytical efficiency and reduce the labor intensity in radioassays.[16−28] Although the application of these automated techniques offers great advantages in radiochemical assays, at present, their application is still limited to a few laboratories, especially the flow/sequential injection techniques. Moreover, the reported flow/sequential injection-based analytical methods are mainly for Tc, Pu, and Sr, and their application in U determination, especially for ^{236}U, have not been explored yet.

To tackle the aforementioned challenges, we aimed to develop a rapid analytical method based on the application of flow injection (FI) techniques for ^{236}U analysis in relatively large volumes of seawater (10 L). A fit-for-purpose FI automated system was designed, which was capable of

simultaneous multisample (namely, four) processing by extraction chromatography (UTEVA). ^{238}U was used as an intrinsic tracer for ^{236}U, whereupon extra addition of uranium isotopic tracer and the corresponding isotope equilibrium problem is avoided. Inductively coupled plasma mass spectrometry (ICPMS) was used for the direct measurement of ^{238}U after suitable dilution of the original seawater, while the measurement of $^{236}U/^{238}U$ atomic ratio in the purified target was carried out with accelerator mass spectrometry (AMS) and consequently the absolute concentration of ^{236}U in the seawater can be obtained.

■ EXPERIMENTAL SECTION

FI-Based Setup. The automated flow injection (FI) system (see Figure 1) consisted of one four-channel peristaltic pump
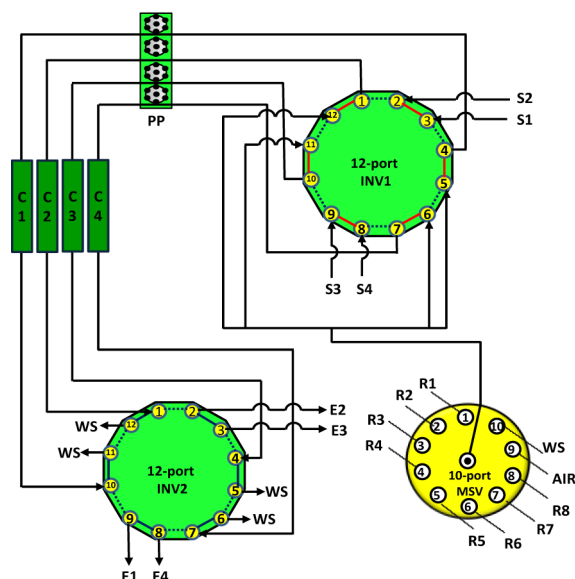

Figure 1. Schematic illustration of the multisample processing FI system for determination of ^{236}U in 10 L of seawater (AIR, port for air aspiration; C1−4, extraction chromatographic columns; E1−4, U eluates; INV1-2, injection valves no. 1−2; MSV, multiposition selection valve; PP, peristaltic pump; R1−8, reagents for column separation; S1−4, samples no. 1−4; WS, waste).

(Watson-Marlow Inc. Wilmington, MA), one 10-port multiposition selection valve (MSV, Valco Instruments, Houston, TX), and two 12-port injection valves (INV1-2). All outlets of the MSV were connected through PEEK (polyether ether ketone) ferrules and fittings with rigid PTFE (polytetrafluoroethylene) tubing of 2.4 mm i.d./3.2 mm o.d., while all outlets of INV1-2 were connected with PTFE tubing of smaller diameter (0.8 mm i.d./1.6 mm o.d). Four Econo-Columns (0.5 cm i.d. × 10 cm length (2 mL), Bio-Rad Laboratories Inc., Hercules, CA) packed with UTEVA resin (100−150 μm particle size, Triskem International, Bruz, France) were integrated in the flow system through PEEK ferrules and fittings. The chromatographic purification of uranium was controlled automatically via the aid of the user-friendly FIAlab software (FIAlab Instruments, Bellevue, WA).

Standards, Reagents, and Samples. A standard solution of uranium (1.000 g/L $UO_2(NO_3)_2$ in 2 mol/L HNO_3) was purchased from NIST (Gaithersburg, MD), which was used after suitable dilution as a standard in the ICPMS measurement for quantifying ^{238}U in seawater. All reagents used in the

experiment were of analytical reagent grade and prepared using ultrapure water (18 MΩ·cm). Surface seawater samples were collected from the Greenland coast in 2012 and the western coast of Jutland, Denmark in 2013 (see sample information details in the Results and Discussion). The collected seawater was filtered through a 0.45 μm membrane and reserved in a polyethylene container in normal laboratory circumstances until analysis.

Purification of Chemicals. In order to reduce the procedure blank of ^{236}U, all chemicals except $NH_3 \cdot H_2O$ were purified thoroughly in different ways. The purification of Fe (as $FeCl_3$) was performed using an 8 mL UTVEA column (1.0 cm i.d. × 5 cm length), whereupon 0.1 g/mL $FeCl_3$ was prepared in 3 mol/L HNO_3 and passed through the UTEVA column. To diminish any remaining absorbed Fe, the column was rinsed with 10 mL of 3 mol/L HNO_3 after loading every 10 mL of $FeCl_3$ solution and all effluents were combined. Thus, the actual concentration of $FeCl_3$ solution after purification was diluted to 0.05 g/mL. The UTEVA column was repacked with fresh resin after purifying 120 mL of 0.1 g/mL $FeCl_3$ solution. Concentrated HNO_3 and HCl were purified by distillation. 6 mol/L HCl and 0.025 mol/L HCl was prepared by dilution of purified concentrated HCl.

Sample Pretreatment. To establish an optimal sample pretreatment protocol, different parameters (the amount of Fe added, acidification condition, use of N_2 bubbling or mechanic stirring, organic matter decomposition protocol) were investigated during the method development. The detailed selection of these parameters is presented in the Results and Discussion section. In general, to 10 L of filtrated seawater, concentrated HNO_3 was added to adjust pH to 2 and then 10 or 20 mL of 0.05 g/mL Fe solution was added. The sample was vigorously stirred with N_2 bubbling or a stirring rod for 10 min. 10 % $NH_3 \cdot H_2O$ was slowly added to adjust the pH to 8−9. The sample was kept still for 0.5−1 h, and the major supernatant was decanted by siphoning. The sample slurry was centrifuged at 4000 rpm for 5 min, and the supernatant was decanted. The hydroxides precipitate was dissolved with 20 mL of concentrated HNO_3 and digested under 200 °C to decompose organic substances. The sample was then subject to a second $Fe(OH)_3$ coprecipitation or was directly evaporated to near dryness. The precipitate/residue was finally dissolved with 15 mL of 3 mol/L HNO_3 for the automated chromatographic separation performed in the FI system.

FI-Based Chromatographic Separation. The FI extraction chromatographic procedure for uranium purification consists of four steps as follows: I. Precondition the UTEVA columns with 20 mL of 3 mol/L HNO_3 at 2.0 mL/min; II. Load sample solution (ca. 30 mL) onto the UTEVA column at 1.0 mL/min; III. Rinse the UTEVA column with 40 mL of 3 mol/L HNO_3, followed by 20 mL of 6 mol/L HCl at 1.5 mL/min; IV. Elute uranium from UTEVA with 10 mL of 0.025 mol/L HCl at 1.0 mL/min.

Detection with ICPMS and AMS. The concentrations of ^{238}U were determined by an X Series^{II} ICPMS (Thermo Fisher Scientific, Waltham, MA) equipped with an Xt-skimmer core and a concentric nebulizer under hot plasma conditions. Indium (as $InCl_3$) was used as an internal standard and added into each sample to a final concentration of 1.0 μg/L for measurement efficiency calibration. The analytical sensitivities ranged between 1 and 5 × 10^6 cps per μg/L for ^{238}U.

Due to the relatively high concentration of salt in seawater, for quantifying ^{238}U in the raw seawater, each sample was

diluted with 0.5 mol/L HNO_3 by a factor of 20–50 and directly analyzed with ICPMS for measurement of ^{238}U. For quantifying ^{238}U in the uranium eluate from the extraction chromatographic separation, thus to calculate the chemical yields of uranium, a 100 μL aliquot was taken from the uranium eluate and diluted with 0.5 mol/L HNO_3 by a factor of 10 000 to ensure the measured values remain within the linear correlation range (0.01–100 ng/L). A 0.5 mol/L HNO_3 solution was used as a washing solution between consecutive assays. The typical operational conditions of the instrument have been given elsewhere.[29] It is important to note that the instrumental parameters were optimized each time when the instrument was initialized.

The AMS measurement of the $^{236}U/^{238}U$ atomic ratio was carried out by the 3-MV tandem accelerator facility VERA (Vienna Environmental Research Accelerator) at the University of Vienna, Austria. To prepare a solid sample material for AMS measurement, Fe^{3+} (as $FeCl_3$ solution) was added to the uranium eluate, and the sample was adjusted to pH 10 with 10% $NH_3 \cdot H_2O$ to coprecipitate uranium. To optimize the target preparation, investigations were carried out to select the optimal amount of Fe added (1 or 3 mg), precipitate settlement time (0–3 h), and composition of washing solution (H_2O or diluted ammonia solution (pH 10)) (see details in Table 2), respectively. The precipitate was dried in an oven under 100 °C and was then baked in a furnace for at least 4 h at 800 °C to convert the hydroxides to Fe_2O_3 and uranium oxides. The sample was ground to fine powder, mixed with a similar volume of silver powder, and pressed into aluminum target holders suitable for the cesium sputter ion source of VERA. The detailed AMS instrumental conditions have been reported elsewhere.[30]

Briefly, uranium was sputtered as UO^-. After a first mass separation, acceleration, and gas stripping, charge states of 5+ (5% yield for $^{238}U^{5+}$ using O_2 as stripper gas) or 3+ (25% yield for $^{238}U^{3+}$ using He as stripper gas) were chosen.[31] After separation by the "high-energy" mass spectrometer, the particle energy is measured in an ionization chamber, which allows the separation of background ions with lower charge states.

■ RESULTS AND DISCUSSION

Optimization of Procedure for Preconcentration and Chemical Purification of Uranium. For uranium preconcentration from 10 L of seawater, a simple $Fe(OH)_3$ coprecipitation was employed. To establish the optimal and simplest analytical protocol, investigations were carried out to study the effect of acidification, N_2 bubbling, and amount of Fe added on the coprecipitation efficiency of uranium. For uranium chemical purification, a UTEVA column was used to remove the interferences. During the coprecipitation, organic substances (e.g., organic colloids, algae) contained in seawater could possibly be wrapped into the $Fe(OH)_3$ floccules and could remain in the uranium fraction. These organic substances may be competitively absorbed onto the UTEVA column and thus deteriorate the chemical yields of uranium. Therefore, experiments were also performed to investigate the effect of possible wrapped organic substances in coprecipitation on the UTEVA separation performance. The overall results are discussed below.

Effect of Acidification and Bubbling on Uranium Preconcentration. It is known that uranium has a high residence time in the open sea because of the formation of uranyl complexes with carbonate.[32] Acidification is often used

to release uranium as free ions via the decomposition of uranyl carbonate complexes which are unstable in acidic solution. However, no details so far have been reported to indicate the importance of stirring or bubbling operation for the release of uranium ions. Our results (Table 1) demonstrate clearly that

Table 1. Effect of Acidification and Bubbling on the U Coprecipitation

sequence no.	experimental operation	loss of U in the supernatant, %	calculated chemical yield of U, %
1	no acidification, no stir, no bubbling	49.72 ± 4.97	50.28 ± 5.03
2	acidify to pH = 2, stir for 10 min, no bubbling	43.95 ± 4.40	56.05 ± 5.61
3	acidify to pH = 2, N_2 bubbling for 10 min	4.24 ± 0.42	95.76 ± 9.58

the chemical yield of uranium is barely 50% when the $Fe(OH)_3$ coprecipitation was performed directly without any previous acidification and bubbling or stirring (sequence no. 1, Table 1). In addition, an acidification (pH 2) with stirring for 10 min, but without bubbling, cannot sufficiently release uranium ions either, since uranium chemical yield is merely 56% under this condition (sequence no. 2, Table 1).

The explanation is probably that, under pH 2, uranyl carbonate complexes $(UO_2[CO_3]_x^{2(x-1)-})$ are dissociated into uranyl ion and carbonic acid, wherein the carbonic acid is unstable and thus can be further decomposed into H_2O and CO_2 as indicated in eq 1.

$$UO_2[CO_3]_x^{2(x-1)-} + 2xH^+ = UO_2^{2+} + xH_2CO_3$$
$$= UO_2^{2+} + xH_2O + xCO_2\uparrow \tag{1}$$
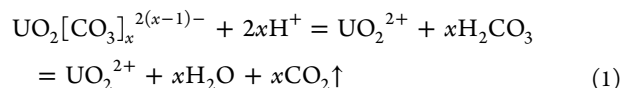
Nevertheless, due to the relatively large sample volume (10 L with the height of 30–40 cm), the diffusion of CO_2 gas from the water body into the atmosphere is probably very slow. Therefore, whenever pH was adjusted to 8–9 during the $Fe(OH)_3$ coprecipitation step, the remaining CO_2 would form carbonate ions $(CO_2 + 2OH^- \leftrightarrow H_2O + CO_3^{2-})$ which may complex with uranium again. On the other hand, with N_2 bubbling, the removal rate of CO_2 gas from the water body to the atmosphere is significantly enhanced, so carbonate was effectively eliminated, leading to the formation of stable UO_2^{2+} ions in the sample solution. Our results (sequence no. 3, Table 1) confirm that both acidification and N_2 bubbling are key operations ensuring quantitative (>90%) preconcentration of uranium in the coprecipitation step.

Effects of the Amount of Fe Added for Uranium Preconcentration. Sufficient addition of Fe is very crucial to ensure high chemical yields of uranium, while excessive Fe will increase the procedure background of ^{236}U (and ^{238}U) and thus worsen the detection limit of the method, as well as impose difficulties in the following chemical purification, especially for UTEVA column separation. From the results in Figure 2, it is apparent that only 60% of uranium is recovered when 0.5 g of Fe is added for coprecipitation, while when the Fe addition is increased to 1 g, the uranium chemical yields are quantitative (>95%). Therefore, in the following experiment, 1 g of Fe (equal to 0.1 g Fe/L seawater) was always used in the preconcentration step for 10 L seawater analysis.

Effect of Organic Substances on Chemical Purification of Uranium. For the chemical purification of uranium,
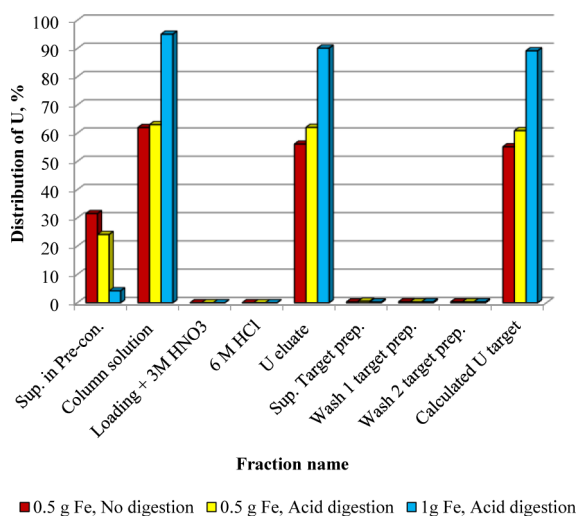
Figure 2. Distribution of uranium among fractions in the analysis under different conditions (namely, with 0.5 or 1 g of Fe addition in U preconcentration, with or without acid digestion prior to UTEVA column separation). Uncertainties for all values are less than 10%.

UTEVA resin was chosen due to its superior selective adsorption of uranium as per previous investigation and simple separation sequence during the chromatographic separation.[13,33] Our analytical results (Figure 2) also indicate that the chemical yields of uranium are not significantly affected regardless of whether an acid digestion was applied prior to the UTEVA column separation. The chromatographic separation profiles are very similar for both conditions with or without acid digestion, indicating that UTEVA is probably not very sensitive to organic substances coprecipitated with uranium under our experimental condition.

However, we have observed that, whenever an acid digestion was not performed beforehand, the viscosity of the sample solution obtained by directly dissolving the $Fe(OH)_3$ precipitate with 3 mol/L HNO_3 was very high. As a consequence, the flow rate for the UTEVA column separation was extremely slow (<0.2 mL/min) when the automation system was not used. Besides, some brown color was also observed on the top of the UTEVA column which is assumed to be related to the adsorption of organic substances. Therefore, an acid digestion was always performed in this work to avoid any blockage of the UTEVA column by organic substance coprecipitation.

Optimization of AMS Target Preparation. The target preparation is an important step to ensure the quantitative collection of purified uranium without significant dilution with Fe and thus to get optimal signal in the AMS measurement. Several key parameters affecting the efficiency of target preparation including the Fe amount, $Fe(OH)_3$ settlement time, and washing solution for $Fe(OH)_3$ precipitate as well as potential organic material bleeding from UTEVA resin were investigated in this work. The results in Table 2 indicate that uranium can be quantitatively (>95%) coprecipitated when the addition of Fe ranges from 1 to 3 mg and that the loss of uranium in the supernatant is slightly reduced from 3% to <1% with an increase in the amount of Fe added (see results of Test a in Table 2). The coprecipitation of uranium with $Fe(OH)_3$ is a very rapid process, and uranium is scavenged immediately by the $Fe(OH)_3$ floccus within a very short time. Therefore, prolonged settlement time is not necessary for $U-Fe(OH)_3$ coprecipitation. With the same amount of Fe added, the chemical yields (85−100%) of uranium after washing with H_2O are comparable to those using diluted $NH_3 \cdot H_2O$ (pH = 10) (see results of Test b in Table 2). Again, addition of sufficient

Table 2. Optimization of Target Preparation for AMS Measurement

Test a: Effect of Fe Addition Amount and Equilibrium Time			
sample ID	equilibrium time, h	Fe addition, mg	proportion of U in the supernatant, %
1(a)	0	1	2.32
1(b)	0	3	0.78
2(a)	0.5	1	2.45
2(b)	0.5	3	0.29
3(a)	1	1	1.21
3(b)	1	3	0.34
4(a)	2	1	2.06
4(b)	2	3	0.56
5(a)	3	1	2.55
5(b)	3	3	0.71

Test b: Effect of Wash Solution Composition						
sample ID	wash solution	Fe addition, mg	% U in 1st wash	% U in 2nd wash	% U in 3rd wash	sum of % U in three washes	% U in residue
1(a)	H_2O	1	3.05	2.33	4.33	9.71	85.96
1(b)	H_2O	3	0.89	0.99	0.90	2.78	97.96
2(a)	H_2O with $NH_3 \cdot H_2O$ (pH = 10)	1	3.31	2.02	3.30	8.64	85.77
2(b)	H_2O with $NH_3 \cdot H_2O$ (pH = 10)	3	0.99	1.17	0.93	3.09	98.00

Test c: The Effect of the Organic Material Bleeding from UTEVA			
sample ID	eluent from TEVA	Fe addition, mg	% U in the supernatant
6(a)	1st 10 mL 0.025 M HCl	1	1.68
6(b)	1st 10 mL 0.025 M HCl	3	0.52
7(a)	2nd 10 mL 0.025 M HCl	1	1.28
7(b)	2nd 10 mL 0.025 M HCl	3	0.54

amount of Fe is important to ensure high chemical yields of uranium in the target.

Since the function group and the matrix material of the UTEVA resin is composed of organic compounds (function group: diamyl, amylphosphonate (DAAP)), some organic compounds might bleed into the eluate during the elution of uranium with 0.025 mol/L HCl, which could hamper the coprecipitation efficiency of uranium in the target preparation. To investigate the effect of possible organic compounds bleeding from the UTEVA column, 10 mL of 0.025 M HCl was used to flush a clean UTEVA column and then ^{238}U was spiked into the effluent which thereafter was coprecipitated with $Fe(OH)_3$. It can be seen (results in Test c, Table 2) that the loss of uranium in the supernatant after the $Fe(OH)_3$ coprecipitation is negligible (<2%), which means the UTEVA resin does not impose deterioration during elution and therefore any influence in the sputter target preparation step.

Analytical Performance. *Laboratory Background.* ^{236}U/^{238}U ratios as high as 10^{-6} have been measured in chemical reagents and standard materials,[4] which makes it difficult to accurately determine the amount of anthropogenic ^{236}U, especially for low-level environmental samples. For example, an unexpectedly high laboratory background of around 10^8 atoms ^{236}U per sample has been reported in the literature.[15]

Similarly, in the beginning of method development for this work, an elevated ^{236}U level was observed in procedure blanks. As indicated in Table 3, the average mass of ^{238}U in procedure

Table 3. Improvement of Laboratory Background and Limit of Detection

date obtained	sample ID	U mass, μg^a	^{236}U, fg^a
Oct 2013	BK-1	0.27	25.91
	BK-2	0.28	21.56
	BK-3	0.46	69.00
	BK-4	0.23	17.37
	average ± SD	0.31 ± 0.10	33.46 ± 23.95
	^{b}LOD$_{inst}$ of ^{236}U/^{238}U atomic ratio = 1×10^{-14}		
	^{c}LOD$_{meth}$ of ^{236}U/^{238}U atomic ratio = 2.8×10^{-9}		
Nov 2014	BK-5	0.0027	0.99
	BK-6	0.0024	0.68
	BK-7	0.0027	0.85
	BK-8	0.0005	0.07
	average ± SD	0.0021 ± 0.0019	0.65 ± 0.56
	^{b}LOD$_{inst}$ of ^{236}U/^{238}U atomic ratio = 1×10^{-14}		
	^{c}LOD$_{meth}$ of ^{236}U/^{238}U atomic ratio = 6.6×10^{-11}		

^{a}Uncertainties for all values are −50%/+100%. ^{b}LOD$_{inst}$ refers to instrumental limit of detection. ^{c}LOD$_{meth}$ refers to method limit of detection calculated on the basis of eq 2 and assuming average $C_{238_U} = 3 \mu g/L$ and $Y = 85\%$.

blanks ($n = 4$) are 0.31 ± 0.10 μg, which is nearly negligible compared to the U content (25−30 μg) in the sputter targets. However, the mass of ^{236}U in the procedure blanks ($n = 4$) is 33.46 ± 23.95 fg (around 8.5×10^7 atoms), which is similarly high as previously reported values.[15]

To reduce the uranium level in the blank, purified chemicals (namely, iron and acids) as detailed in the Experimental Section were used throughout the analytical process, and an evaporation was used after acid digestion to reduce the sample volume instead of a second $Fe(OH)_3$ coprecipitation. For the purification of nitric and hydrochloric acids, sub-boiling

distillation as a classical acid purification method was employed in this work. The optimized analytical procedure for ^{236}U determination in 10 L of seawater is illustrated in Figure 3. The results (Table 3) indicate that, with this series improvement, the ^{236}U blank was significantly reduced to 0.65 ± 0.56 fg (around 1.7×10^6 atoms), 50-fold lower than before.

Considering the high adsorption of uranium on UTEVA resin, it might also be a possible alternative method for acid purification whenever a sub-boiling distillation system is not available. Therefore, we attempted to purify 3 mol/L HNO_3 and 6 mol/L HCl by directly passing them (ca. 500 mL of each) through a fresh 8 mL UTEVA column, respectively. However, it was found that uranium was unexpectedly removed from the column (2 mL UTEVA) in the chromatography separation when using the purified 6 mol/L HCl as a washing solution. This might be a consequence of an overuse of the 8 mL UTEVA column during the HCl purification process; thus, the organic function group grafted on the UTEVA resin might bleed into the purified 6 mol/L HCl. When this 6 mol/L HCl was used to wash the UTEVA column, the adsorbed uranium on the column was extracted to the organic compound of the function group in the 6 mol/L HCl solution. Therefore, sub-boiling distillation is recommended for purifying acids.

Limit of Detection. Using AMS at VERA, Vienna, the instrumental detection limit for the ^{236}U/^{238}U ratio is theoretically below 10^{-14} (although the lowest material encountered so far was 10^{-12}). Considering the procedure blank of ^{236}U and ^{238}U mentioned above, the detection limit of the ^{236}U/^{238}U ratio for the developed method can be calculated as follows:

$$\text{LOD}_{^{236}U/^{238}U} = \frac{3\text{SD}_{^{236}U} \times 238}{C_{^{238}U}VY \times 236} \tag{2}$$

where $\text{LOD}_{^{236}U/^{238}U}$ is the detection limit of the ^{236}U/^{238}U atomic ratio, $\text{SD}_{^{236}U}$ is the standard deviation of the ^{236}U mass in procedure blanks, $C_{^{238}U}$ is the mass concentration of ^{238}U in the samples, V is the sample volume used for the measurement, and Y is the chemical yield of U in the analytical procedure.

On the basis of the improved laboratory blank, using $3\text{SD}_{^{236}U}$ = 1.68 fg, V = 10 L, and assuming an average $C_{^{238}U}$ = 3 $\mu g/L$, and Y = 85%, the corresponding detection limit for the ^{236}U/^{238}U atomic ratio reaches down to 6.6×10^{-11}, which could provide sufficient accuracy and reliability for anthropogenic ^{236}U measurement in different type of waters. It is clear that using high-purity chemical reagents and reducing the amount of chemicals added are critical for the determination of ^{236}U in low-level samples.

Determination of ^{236}U in Coastal Surface Seawater from Greenland and Denmark. A set of samples collected from Greenland and the Danish coast were analyzed using the developed method. As indicated in Table 4, relatively low ^{236}U/^{238}U atomic ratios (($1.98−4.54) \times 10^9$) as well as ^{236}U concentrations (($1.58−3.65) \times 10^7$ atom/L) were observed in Greenland seawater compared to Danish seawater (^{236}U/^{238}U atomic ratios and ^{236}U concentrations ranging within ($7.34−17.64) \times 10^9$ and ($4.33−13.21) \times 10^7$ atom/L, respectively). This might reflect the strong influence of the reprocessing discharged ^{236}U from nuclear reprocessing plants at Sellafield (UK) and La Hague (France) in the Danish water compared to the Greenland water. The ^{236}U data for Danish seawater are very comparable to the values reported by Christl et al.[34] for seawater samples collected from the North Sea in 2009, which
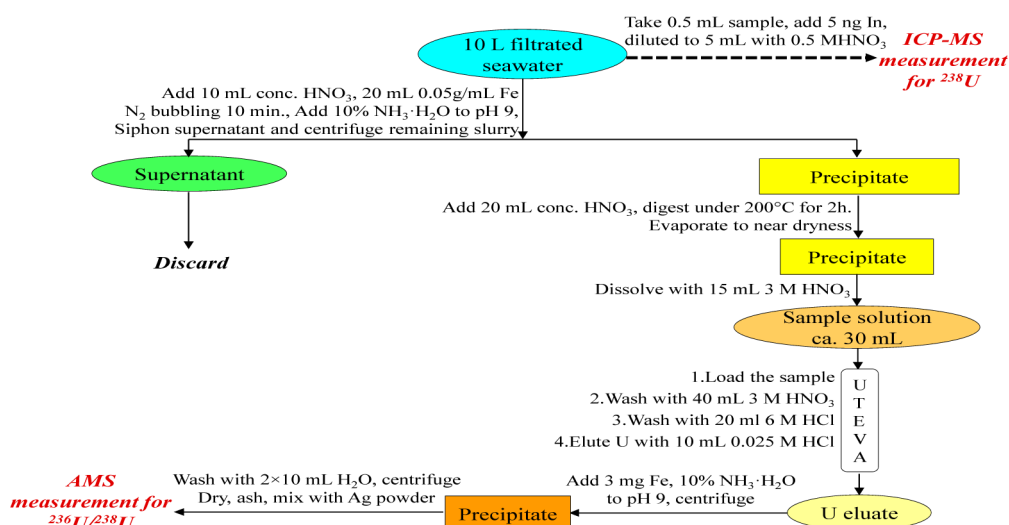
Figure 3. Optimized analytical procedure for ^{236}U determination in 10 L of seawater.

Table 4

sampling area	sample ID	location lat., °N	lon., °E	^{238}U, µg/L	^{236}U/^{238}U atomic ratio, ×10^9	^{236}U, ×10^7 atom/L
Western Greenland	2012-0535	64.99	−53.89	3.18 ± 0.32	4.54 ± 0.41	3.65 ± 0.33
	2012-0536	62.52	−51.42	2.78 ± 0.28	3.83 ± 0.35	2.70 ± 0.25
Eastern Greenland	2012-0542	67.54	−27.29	3.09 ± 0.31	2.56 ± 0.24	2.00 ± 0.19
	2012-0543	72.96	−13.05	3.15 ± 0.32	1.98 ± 0.18	1.58 ± 0.14
Danish coastal seawater	Jyl-1	56.81	10.28	2.33 ± 0.23	7.34 ± 0.13	4.33 ± 0.08
	Jyl-2	57.35	10.52	2.65 ± 0.27	10.70 ± 0.20	7.18 ± 0.13
	Jyl-3	57.73	10.52	2.8 ± 0.28	8.66 ± 0.28	6.14 ± 0.20
	Jyl-4	57.59	9.99	2.85 ± 0.29	7.58 ± 0.12	5.47 ± 0.09
	Jyl-5	57.12	8.63	2.92 ± 0.29	10.93 ± 0.26	8.08 ± 0.19
	Jyl-6	56.71	8.22	2.96 ± 0.30	17.64 ± 0.61	13.21 ± 0.46
	Jyl-7	56.00	8.12	2.25 ± 0.23	17.20 ± 0.61	9.79 ± 0.35

indicates the reliability of our results. For example, they have obtained the ^{236}U/^{238}U atomic ratio of 8.9 × 10^9 and the ^{236}U concentration of 7.20 × 10^7 atom/L at station 23 (55.00° N, 7.35° E), which is close to the sampling area in this work.

Analytical Merit of the Automated FI Network. In the developed method, the single step Fe(OH)$_3$ coprecipitation provides simple and expeditious preconcentration of uranium from a relatively large volume of seawater, which can be completed within 2 h. Combining the automated chemical purification, which takes less than 2 h, the analytical turnover time is further shortened to merely 4 h/sample. This endows our method with rapid analytical ability for ^{236}U seawater assays. The optimized Fe(OH)$_3$ coprecipitation conditions ensure quantitative (>95%) recovery of uranium in the preconcentration, and the superior affinity of uranium onto the UTEVA column maintains satisfactory chemical yields (>80%) of uranium for the whole procedure.

With the merit of automated chromatographic separation in the entirely closed FI network, the labor intensity as well as external contaminations from air, dust, or chemical splashes are notably reduced compared with the conventional manual methods. As a consequence of the four-sample simultaneous processing manner with controllable flow rate, any column blockage or fluctuation of flow rate caused by variable density/viscosity of sample solutions would be avoided; thus, enhanced analytical repeatability and constant sample throughput are

obtained. The developed FI system is compact and mobile and performs stably and robustly within a long-term continuous operation, suggesting its potential application in field studies for processing a large number of samples. As long as sufficient signal of ^{236}U in the sputter targets can be obtained by AMS measurement, the proposed method is also promisingly applied to other volumes of seawater as well as other types of water samples with minor modifications.

■ CONCLUSIONS AND PERSPECTIVES

An automated ^{236}U seawater analysis method was developed on the basis of the use of FI-extraction chromatography (UTEVA) and combined AMS-ICPMS detection. The analytical performance of the proposed method was thoroughly optimized and evaluated for the first time on account of series investigations upon several crucial experimental parameters. Bearing the strong complexation property of uranium with carbonates in mind, it is very important to use both acidification and N$_2$ bubbling in the preconcentration to achieve the quantitative scavenger of uranium. Besides, attention should be paid to the purification of chemical reagents and reducing as much as possible the use of chemicals in the procedure, in order to improve the method detection limit and thus to extend the method applicability to different types of low-level environmental water samples.

The proposed analytical method is simple and effective, which was successfully applied to processing Greenland and Danish coast seawaters. In connection with the application of FI-automated chromatography, the sample throughput is notably improved compared to traditional manual methods. The miniaturized feature of the developed FI system makes it also attractive in field studies to investigate the transit and geochemical cycling of ^{236}U in different environmental regions.

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Notes

The authors declare no competing financial interest.

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