

## **RiO5 METHOD (9)**

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**$^{236}\text{U}$  — UTEVA — seawater**

**U extraction from seawater samples**

### **Disclaimer**

It is the responsibility of the analyst to follow established safety and health practices. Although each laboratory identified as the source has tested the methods, each user should perform an individual validation procedure.

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## 1 SCOPE

This method describes the radiochemistry of  $^{236}\text{U}$  in seawater samples. It covers the radiochemistry of a seawater sample from right after its collection to the final preparation of the cathode (target) before its measurement with Accelerator Mass Spectrometry (AMS). One should note that every AMS system has its own targets and thus final steps of this method should be adapted.

## 2 EQUIPMENT and CHEMICAL REAGENTS

### 2.1 Equipment and consumables

- 250 mL centrifuge bottles
- Silicon tubes
- 2L and 1L plastic bottles.
- 50 mL syringe
- 0,2 and 0,45  $\mu\text{m}$  filters (adapted to the syringes)
- UTEVA cartridges
- Stopcocks (simple –two positions- and double –three positions-)
- Eichrom vacuum box
- 50 mL centrifuge tubes
- Conical targets
- Tools for the target preparation (including hammer, niobium, spatules, etc.)

### 2.2 Tracers

- $^{233}\text{U}$  Spike (32.06 +/- 0.11 pg/g).

### 2.3 Chemical reagents

- Methanol
- $\text{HNO}_3$  suprapure
- $\text{NH}_3$  suprapure
- $\text{H}_2\text{O}_2$
- Oxalic acid

### 2.4 Solutions

- $\text{HNO}_3$  8M (1 L = 555 mL  $\text{HNO}_3$  65% suprapure + 445 mL  $\text{H}_2\text{O}$  milliQ)
- $\text{HNO}_3$  2M + 0,05M oxalic acid (1 L = 139 mL  $\text{HNO}_3$  suprapure + 6.3035g. oxalic acid)
- 0,01M  $\text{HNO}_3$  (1 L= 1 mL  $\text{HNO}_3$  suprapure)

- Fe<sup>2+</sup> solution (50 g/L) in HNO<sub>3</sub> 3M

### 3 PROCEDURE

#### 1. Sample weight and acidification

- Take the weight of the closed canister before spiking (note in lab book!).
- Acidify sample with HNO<sub>3</sub> concentrated (1 mL/L of sample) ) + 1 mL H<sub>2</sub>O<sub>2</sub> (sp).

#### 2. Spike sample

- Take spike bottle out of the refrigerator about ½ hour before you start.
- Remove ParaFilm cover and condensed water from bottle.
- Fill estimated amount of spike in a small (e.g. Eppendorf) vial (this will be in contact with the pipette tip, not the original bottle containing the spike solution).
- Take about 2 ml from the 2M HNO<sub>3</sub> and fill into a cleaned 15ml centrifuge tube.
- Take the weight of the closed tube (weight 3-5 times → lab book)
- Add the U-233 to the spike by weighting 1 time

IMPORTANT: 3pg of U-233 is a typical amount of spike per sample.

Note: to get 3 pg of U-233 0,1 mL of spike (concentration 32.06 +/- 0.11 pg/g) were pipetted.

- Transfer the spiked solution to the canister and rinse the tube several times (min 3x) with 0.2 HNO<sub>3</sub> so that no spike is left in the tube and let it rest for >0.5 hours.

#### 3. U preconcentration

- Add the cleaned iron solution to the sample, about 500 mg of Fe (10 mL). Add always this amount of Fe, independently of the volume of the initial sample.
- Cover the sample and shake it, let it rest for >0.5 hours so that the spike and the iron equilibrate with the sample water (one night).
- Precipitate the sample by adding NH<sub>4</sub>OH (sp); check pH: should be between 8.5 and 10.
- Let it settle for 1 night.
- Use long silicon tubes to remove the supernatant.
- Transfer the iron precipitates to smaller bottles (1L or 2L) and finally to a 250 mL centrifuge bottle.

#### 4. Centrifuging and salt removal

- Centrifuge samples at 3000 rpm during 5-10 minutes.

IMPORTANT: the maximum volume for centrifugation is about 200 ml!

- Discard the supernatant.

- Use about 5-10 mL HNO<sub>3</sub> 8M to dissolve the precipitates.
- Once iron hydroxides are dissolved, evaporate samples overnight using the aluminium blog. (80°C during 1 night).
- Once dry, add 20 mL of 8M HNO<sub>3</sub> to dissolve it. Sample is ready to go to the column step.

Comment: *The sample can be stored in the bottles until the column step.*

## 5. Radiochemical separation UTEVA cartridges

### *Sample preparation*

- Filter sample at 0,45 µm. Rinse syringe with other 5 mL HNO<sub>3</sub> 8 M. Use the same syringe for columns.

### *Resin preparation and preconditioning*

- Prepare UTEVA columns as shown in the picture (Figure 1).
- Pre-condition columns with 20 mL HNO<sub>3</sub> 8 M.

### *Uranium radiochemical purification*

- Load the sample (25 mL) on the column.
- Check that this is running at 1 mL/min approximately.
- Rinse beaker and columns with 10+10 mL HNO<sub>3</sub> 8M.
- Np removal step: add 8 mL (4 CV) of 2M HNO<sub>3</sub>+oxalic acid solution.

Note that:

- Until here it is all discarded
- Change stopcocks for U collection!
- Elute U with 15 mL HNO<sub>3</sub> 0,01 M.
- Wash column with 10 mL milliQ water (collect it together with the U fraction).
- Collect the last two fractions in a 50 mL centrifuge tube.

## 6. Target preparation

- Add 1.25 mg Fe from the uranium cleaned iron solution

Note: 0,025 mL of Fe(NO<sub>3</sub>) solution 50 mg/mL.

- Precipitate with NH<sub>4</sub>OH (sp)
- Centrifuge and wash once with methanol
- Transfer into quartz crucible using methanol and dry on hotplate at 50°C
- Oxidize in the oven at 650°C
- Mix with about 1-3 mg Nb powder and press into a Tandy target holder. Use the spatula to do so.

## 4 REFERENCES

Casacuberta, N., M. Christl, J. Lachner, M. R. van der Loeff, P. Masque, and H. A. Synal (2014), A first transect of U-236 in the North Atlantic Ocean, *Geochim Cosmochim Acta*, 133, 34-46, doi:Doi 10.1016/J.Gca.2014.02.012.

López-Lora, M., E. Chamizo, M. Villa-Alfageme, S. Hurtado-Bermúdez, N. Casacuberta, and M. García-León (2018), Isolation of <sup>236</sup>U and <sup>239,240</sup>Pu from seawater samples and its determination by Accelerator Mass Spectrometry, *Talanta*, 178(Supplement C), 202-210, doi:<https://doi.org/10.1016/j.talanta.2017.09.026>.

## 5 IMAGES



Figure 1: Initial Fe precipitation to extract Uranium isotopes from

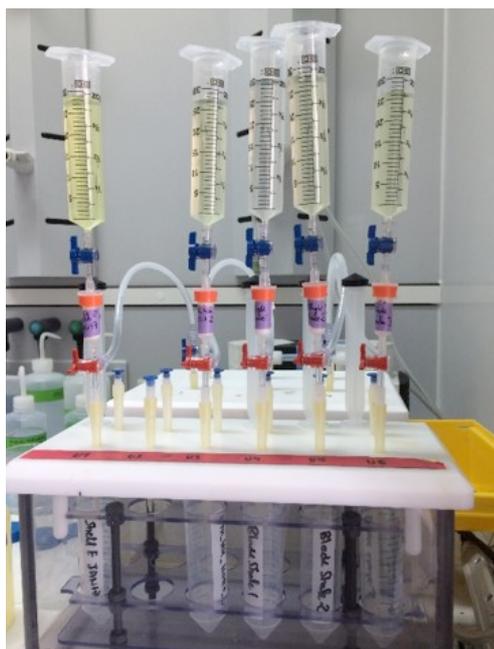


Figure 2: Uranium extraction using UTEVA resins coupled to a vacuum box system

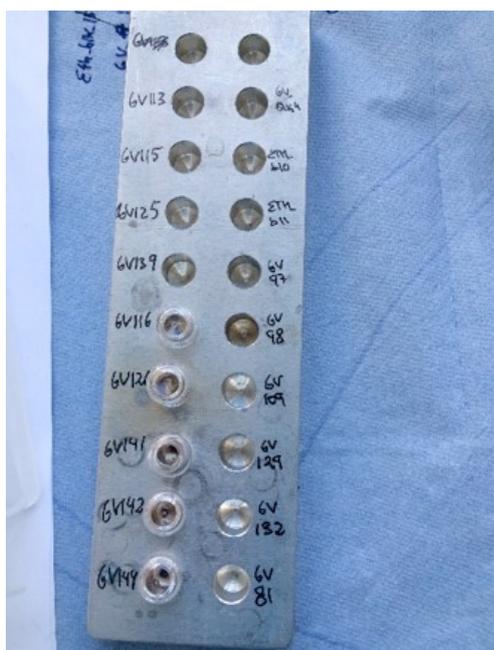


Figure 3: Quartz crucibles. Final iron hydroxides are heated in the oven at 650°C in this quartz crucibles placed on a quartz rack.