A radiochemistry laboratory exercise: determination of uranium in tap water by solvent extraction and liquid scintillation counting

Gabriele Magugliani[1] · Eros Mossini[1] · Maddalena Negrin[1] · Francesco Galluccio[1] · Andrea Santi[1] · Marco Giola[1] · Elena Macerata[1] · Mario Mariani[1]

Abstract

Environmental radiochemistry is a key pillar of the education of nuclear engineering students and young professionals. Teaching the fundamentals of this multidisciplinary field is best performed also through well-designed hands-on experiments. A simple and fast radiochemical procedure has been developed to determine uranium in tap water by liquid scintillation counting. The proposed method provides reliable and repeatable results, with accuracy and precision within 5%. It can be proficiently executed by undergraduate students, who have appreciated the engagement and got acquainted with standard analysis protocols, from sample collection and manipulation to radiometric measure and data analysis.

Keywords Hands-on exercise · Natural radioactivity · Uranium · Co-precipitation · Solvent extraction · Liquid scintillation counting

Introduction

Several challenges related to the civil use of nuclear technologies can be addressed by radiochemistry. These issues are not limited to the energy sector, namely nuclear fuel cycle, decommissioning of facilities and radioactive waste management, but they include a wider range of civil applications of nuclear technologies, such as nuclear medicine, environmental monitoring, food irradiation, nuclear forensics, and broader research activities [1]. In this perspective, it is crucial to build the background knowledge of future scientists and professionals to avoid a shortage of radiochemistry experts [2–4]. To this scope, it is important to recruit students for bachelor and specialistic academic programmes by improving their awareness and interest about nuclear topics [5]. A valid and engaging approach relies on delivering Massive Open Online Courses (MOOCs) or developing virtual/augmented reality educational tools, which favour the involvement of younger people [6, 7]. Europe-wide awareness of the importance of this topic is confirmed by dedicated H2020 projects like MEET-CINCH (grant agreement No 754972) and A-CINCH (grant agreement No 945301). Moreover, most EU-funded projects allocate a significative budget to education and training, like EURAD (grant agreement No 847593) and PREDIS (grant agreement No 945098), just to mention few of the most recent ones.

As a crucial step in the learning process, it is important to guarantee active participation of students to class activities. Passive learning, where students only receive information through lectures or written materials, might in fact not be sufficient to develop the necessary skills for radiochemistry: the connection between theory and practice is crucial, and university laboratories play a vital role in bridging this gap [8]. More advanced learning methods have therefore been proposed, and two prominent ones are cooperative and active learning. The latter engages students with the material being presented, refocusing their attention and enabling a better retention of concepts. On the other hand, collaborative learning fosters teamwork, essential for future careers in radiochemistry and other multidisciplinary fields. By implementing cooperative learning strategies through university laboratories, instructors can maximize the benefits of teamwork, promoting problem-solving skills and effective communication among students. This fosters essential interpersonal skills for successful collaboration in the context of radiochemistry research and applications. Incorporating Bloom's Taxonomy into the context of active

✉ Eros Mossini
  eros.mossini@polimi.it

1 Department of Energy, Politecnico Di Milano, Piazza L. da Vinci 32, 20133 Milan, Italy

and cooperative learning further enhances the educational experience [9]. The combination of these dynamic learning approaches equips students with the necessary skills for success in radiochemistry and beyond.

In this work, an original experimental laboratory experience on radiochemistry topics has been designed and tested with students of Politecnico di Milano (Italy) within their graduate and undergraduate training programmes. The students, organized in small sub-groups of two or three people, autonomously carried out the experiment under the guidance of a tutor, coherently with the principles of active and cooperative learning. The scope of the hands-on activity consisted in the determination of uranium in tap water by Liquid Scintillation Counting (LSC). Although long-lived radionuclides are proficiently measured by non-radiometric techniques [10], in this work a radiometric technique was chosen to get the students familiar with the execution of some preliminary radiochemical steps for analyte pre-concentration and purification.

The experiment was conceived in compliance with the educational objectives described in Bloom's taxonomy[1] [9, 11, 12]. Firstly, students were provided with exhaustive lab notes describing the aim and the main experimental steps of the proposed activity in order to *remember* and *understand* the topics previously encountered in the frontal classes and to prepare them to the practical laboratory session. This activity spans approximately three hours and was conceived to *apply* some theoretical concepts concerning sample pretreatment, analyte purification, source preparation and measurement. Afterwards, the students were requested to *analyse* the radiometric data and *evaluate* the measured values of uranium in tap water with respect to literature and reference measurements determined via mass spectrometry. Eventually, the students may be asked to *create* a modified protocol aimed for example at determining other radionuclides. The present article describes the experimental procedure adopted during the hands-on laboratory.

The students were requested to estimate the characteristic limits and the total concentration of U, under the hypothesis of secular equilibrium and unperturbed natural isotopic abundance. Alternatively, spectral deconvolution could also be applied to accurately estimate the isotopic ratios [13]. In order to verify the reliability of the proposed simplified protocol, a validation was performed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) prior to involving students in the activity.

The proposed exercise successfully aims at getting the students familiar with standardized test methods and with the concepts and the best practices of the environmental

radiological characterization, such as sample collection, pre-concentration, radiochemical separation, activity measurement by LSC, and data analysis.

Experimental

The experimental methodology has been adapted from literature [14], with the goal of achieving ease of implementation in a didactic laboratory setting without negatively impacting the analytical quality of the obtained results. Weighed amounts of tap water samples ("test samples", approximately 500 mL from Milan public water distribution network) were collected and acidified with 2 mL of concentrated HNO_3 [15, 16]. The experimental activity may be also performed with surface or groundwater samples. In this case, a filtration step may be necessary to remove suspended matter prior to acidification.

LSC sample preparation: co-precipitation

The test sample can be employed as-is or be subjected to a preliminary pre-concentration step to achieve higher analytical sensitivity. The parallel adoption of these two approaches between different student subgroups can be adopted to familiarize with the concept of detection limit (DL), and how sample preparation methods directly influence analytical sensitivity.

Standard ISO protocol [14] for U determination in water via LSC suggests the adoption of a pre-concentration step via evaporation (1:10 volume reduction) to reach adequate analytical sensitivity. In the present exercise, a calcium phosphate co-precipitation was instead selected [10], as it provides for higher student involvement and is better suited to didactic demonstrations in limited timeframes. Co-precipitation is also preferable when water samples with high salinity (> 500 mg/L) are considered, as evaporation may result in a large amount of precipitate which may be difficult to recover as it tends to adhere also to the walls of the container. Furthermore, co-precipitation provides for a preliminary radiochemical purification step, in which alkali metal (radio)nuclides, as well as dissolved anions and Rn, are separated from the analyte.

The employed co-precipitation procedure is adapted from a standard protocol [17]. A simplification of the reference procedure was required to perform the whole experiment within the typical duration of a didactic laboratorial session, *i.e.* approximately 3 h. The test sample is heated to 60 °C under stirring on a hot plate. Then, the following reagents are added stepwise:

- 0.5 mL of 1.25 M $Ca(NO_3)_2$.
- 1 mL of 3.2 M $(NH_4)_2HPO_4$.

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[1] The hierarchical categories of the revised Bloom's taxonomy are hereafter reported in italics.

- few drops of phenolphthalein indicator.

Few mL of concentrated NH_3 solution are added under mixing, until the solution reaches a pH value of 9–10. The pink colour given by the indicator evidences the approaching of the endpoint. Under these conditions, Ca phosphate precipitate formation can be observed, with the consequent co-precipitation of uranium by non-isomorphic substitution [18]. The suspension is kept under mixing for 15 min to allow for equilibrium. After cooling to room temperature, the supernatant is separated from the precipitate containing the analyte and discarded, *e.g.* by centrifugation. The precipitate is resuspended in water for a washing step. After centrifugation, the supernatant is again discarded, and the precipitate is dissolved by 20 mL of HNO_3. Variable nitric acid concentrations were tested for this step during the validation of the method in order to identify optimal conditions for the following solvent extraction step.

LSC sample preparation: solvent extraction

Since calcium phosphate co-precipitates several contaminants (alkaline earth metals, transition metals and other actinides) and it is not selective for uranium, a further purification step is required. In particular, considering the expected radioactivity content in potable waters, uranium must be selectively separated from its daughter nuclides which may interfere with the LSC measurement. This operation can be performed by several methods, *e.g.* solvent extraction and extraction chromatography [17]. During this laboratory exercise, the former method was adopted, as it provides better student engagement and is more cost- and time-effective. At the end of this purification step, the analyte must be mixed with the LSC cocktail to allow its radiometric measurement. Several methods have already been proposed to directly extract uranium into an organic phase measurable by LSC [19, 20]. Hence, the present laboratory activity also possesses some practical relevance which can be useful in directly enriching the technical competence of students.

Similarly to what is described in ISO 13169 [14], uranium may be directly extracted in a suitable lipophilic cocktail by means of a selective ligand dissolved in the cocktail itself. According to spent nuclear fuel reprocessing experience [21] and reagent availability in most radiochemistry laboratories, tributyl phosphate (TBP) was chosen as selective extractant for uranium. In fact, TBP can be easily dissolved in a lipophilic scintillation cocktail immiscible with an aqueous phase, like Maxilight (Hidex Oy). Hence, Maxilight cocktail + TBP mixture was used as a combined extracting/measurement solution. The concentration of the ligand was also optimized to achieve quantitative extraction of U.

The aqueous sample coming from the previous co-precipitation step is contacted with 10 mL of extracting cocktail and thoroughly mixed for at least 2 min, to allow the achievement of extraction equilibrium. The concentration of nitric acid in the aqueous phase directly influences the distribution ratio of U in the organic phase [22], hence the need for its optimization. The organic phase is collected after phases de-mixing by centrifugation and transferred to a LSC counting vial. Afterwards, a second extraction is performed from the same aqueous sample by means of additional 10 mL of fresh extracting cocktail. After centrifugation, the organic phase is collected and transferred to the same LSC counting vial. This second extraction allows to maximize the recovery of uranium [2]. As reported in the following section, under optimized experimental conditions the yield of the procedure is essentially quantitative. Hence, the use of a tracer is not necessary, thus proving beneficial for the cost effectiveness of the didactic procedure, as well as negating radiation protection concerns. During phase separation, it is important to avoid the recovery of aqueous solution along with the organic phase, that would affect the subsequent radiometric measure. Moreover, quantitative recovery of the organic phase is also essential to achieve the highest yield.

A blank sample was prepared following the same protocol using ultrapure water as a test sample.

LSC measurement

LSC measurement was performed with a Hidex 300 SL super low level (425–020, Hidex Oy) in the alpha counting window. Alpha/beta discrimination was implemented according to manufacturer instructions. For the adopted counting conditions, alpha detection efficiency was determined as > 99% via the triple to double coincidence ratio method [23]. For modern LSC and cocktails of other brands and manufacturers, very similar alpha counting efficiencies are expected. Hence, if necessary, the measurement of an efficiency calibration standard sample can be avoided to improve the cost effectiveness of the experiment with no significant impact on the accuracy of the results. In this case however, students must already be familiar with the concepts of detection efficiency and instrument calibration.

The characteristic limits of the measurement were determined according to ISO standards [24]. With the reported sample size of approximately 500 mL and considering a blank alpha count rate of 0.15 cpm, a counting time of 4 h can be adopted for all samples. This is more than sufficient to achieve adequate measurement uncertainty and a DL compatible to any likely analyte content in the test sample. However, counting time may need to be adapted in case of very high blank count rate and/or for very low analyte content (< 0.1 ppb).

Table 1 Variation of U yields for LSC analysis with respect to nitric acid and TBP concentration

HNO$_3$ (M)	TBP (wt%)	Yield (%)
0.7	4	22 ± 9
1.2	4	52 ± 3
3	1	24 ± 8
3	2	60 ± 5
3	4	98 ± 3

ICP-MS sample preparation and measurement

ICP-MS analysis was undertaken to provide reference values for U concentration in the same test samples used for LSC analysis. When necessary, sample dilutions were performed with 1 wt% ultrapure nitric acid. ICP-MS analyses were carried out with a NexION 2000 (PerkinElmer Inc.). Instrument calibration was performed with certified standard solutions (Inorganic Ventures) over the analyte concentration range of interest.

Results and discussion

Validation of LSC method

Chemical yield of the LSC analysis protocol was determined by performing preliminary measurements on an ultrapure water sample traced with a standard solution containing known U concentration of certified abundance. For this scope, 20 ppb of total U were employed, *i.e.* roughly 10 times the expected natural concentration in potable waters of Milan, in order to achieve good precision. As mentioned in the previous section, variable concentrations of both nitric acid (for the precipitate dissolution step) and TBP (for solvent extraction step) were tested. Resulting U yields are reported in Table 1.

From reported data, it can be seen how for a fixed TBP content in the organic extractant, higher HNO$_3$ concentrations resulted in higher yields. This is coherent with the known variation of U distribution ratio with respect to this parameter [22]. Fixing acidity at 3 M HNO$_3$, quantitative yield can be reached with a minimum TBP concentration of 4 wt% These latter conditions were therefore identified as optimal and were adopted uniformly across all repetitions of the practical exercises involving students.

A detection limit of ≈4 mBq/L was recorded under optimal conditions (500 mL test sample, 4 h measuring time, 3 M HNO$_3$ and 4 wt% TBP). Such DL is compliant with technical proficiency requirements indicated by Italian legislation for the radiological screening of potable waters [25]. The method is therefore well applicable to the determination

of U in potable waters where analyte concentrations are in the parts per billion range (tens of mBq/L). As already mentioned, the adaptation of experimental conditions (increased test sample size or longer measurement times) may need to be considered in case of very low U concentrations.

Prior to student involvement, the LSC analysis method under optimal extraction conditions was then employed for the determination of U in 5 tap water samples of unknown analyte content. Reference measurements of total uranium concentration were performed on the same test samples via ICP-MS. LSC results presented 5% precision and 3% accuracy with respect to mass spectrometry values.

Student results

The presented laboratory activity was tested by more than 50 students, both of graduate and undergraduate level, at the Radiochemistry and Radiation Chemistry Laboratory of Politecnico di Milano over two academic years.

Other than performing the reported procedure for LSC analyses, students were also requested to compare the results obtained from the radiometric (LSC) and non-radiometric (ICP-MS) techniques on the same test samples. Secular equilibrium between ^{238}U and ^{234}U and natural isotopic abundance can be reasonably postulated to this scope in tap water samples.

For each didactic laboratory campaign LSC measurement results were above the DL, thus confirming the adequacy of the analytical conditions for the test samples considered. Figure 1 illustrates relative biases between values of total U concentration obtained by students via LSC and corresponding reference values determined via ICP-MS. The laboratory activity involved 18 independent student groups. Considering a maximum acceptable relative bias on analyte concentration of ±15% [26], results obtained by 14 out of 18 groups were acceptable both in terms of accuracy and precision (blue markers), while 3 of them failed one of the statistical tests (orange markers). Only the result from 1 student group (red marker) was unacceptable for both figures of merit [27]. This confirms that the presented laboratory activity can be performed effectively—and mostly independently—also by student groups not yet possessing robust academic background and practical skills in radiochemistry.

Suggested additional activities

The present laboratory activity is well suited to incorporate variations in experimental conditions to provide a more extensive laboratory exercise for advanced students and stimulate critical thinking. Some examples of possible variations in experimental conditions and expected outcomes are reported in Table 2.

Fig. 1 Relative bias between U concentration values determined by students via LSC and reference values obtained by ICP-MS. Blue lines represent a maximum acceptable relative bias on analyte concentration of $\pm 15\%$
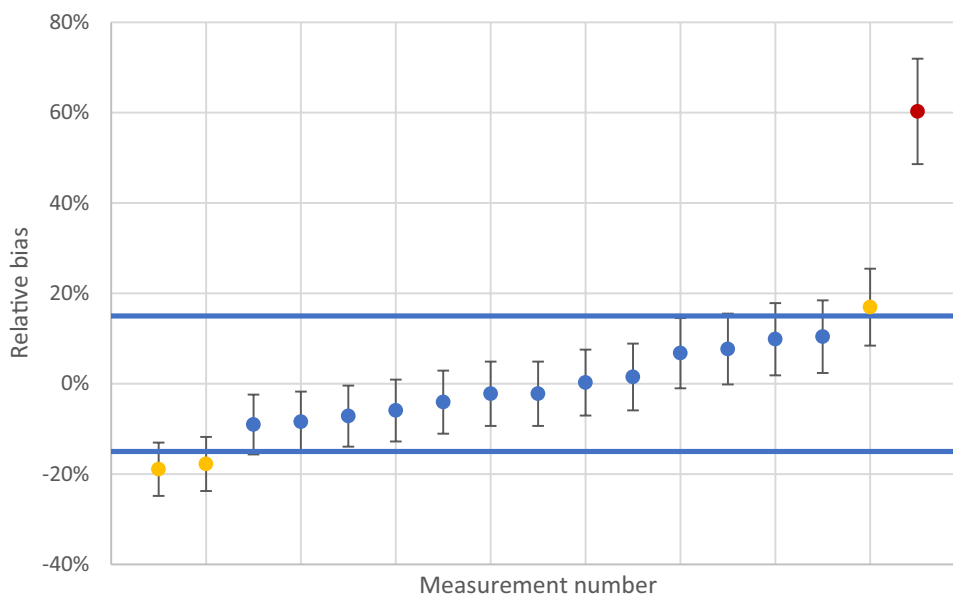

Table 2 Suggested variations in experimental conditions and expected outcomes

Action	Expected outcome
Analysis of test samples containing a sediment or suspended matter. Adoption of: (a) initial acidification prior to filtration (b) initial acidification after filtration	Higher analyte content in case a), due to its desorption/dissolution from particulate matter
Perform analysis with no pre-concentration of test sample (direct solvent extraction after acidification)	Detrimental impact on DL. Analyte may not be quantifiable due to insufficient sensitivity. Rn activity will also contribute to the count rate since it will be extracted by the organic cocktail
Perform solvent extraction 1 week after co-precipitation	Ingrowth of Rn and Rn daughters will occur. Rn will be extracted by the cocktail and contribute to the count rate, resulting in analyte overestimation
Perform sample counting 1 week after solvent extraction	No effect is expected

Furthermore, a discussion on experimental aspects should be promoted by the tutor, also exploiting a flipped-classroom didactic approach. Some examples of relevant questions to be presented to students to stimulate critical thinking may include:

- How to optimize counting time, in order to achieve a pre-established DL;
- How to optimize counting time, in order to achieve the DL attainable by ICP-MS;
- Identify which U daughters are removed by the co-precipitation step and the solvent extraction step, respectively;
- Discuss how a non-natural isotopic abundance of U may influence the accuracy of the results, and how this information is necessary to assess total analyte mass concentration from a radiometric measurement;

- Suggest how the present procedure may be adapted to quantify Pu in water samples, and possible sources of interference.

Conclusions

The present laboratory experience was completed by all student groups with minimal aid from tutors and all participants were actively involved. A copy of detailed lab notes describing the whole activity will be made freely available on NucWik (https://nucwik.com/). The laboratory exercise can be easily implemented and is very cost-effective since minimal amounts of reagents and no radiotracers need to be employed. Direct comparison between radiometric (LSC) and reference non-radiometric techniques, *e.g.* mass

spectrometry, can provide additional didactic value, but is not mandatory, hence limiting instrumental requirements.

Besides the positive didactic considerations, the developed protocol provided satisfactory results in terms of precision, accuracy, DL, and reproducibility. Hence, it could be used in routine analysis, especially if mass spectrometry is not available.

Data availability Additional data can be made available upon request.

Declarations

Conflict of interest The authors declare that they have no known competing interests that could have influenced the work reported in the present paper.

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