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Determination of uranium content in water using cathodic stripping voltammetry and gamma-spectrometry

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Two different techniques for the evaluation of uranium content in four water samples are compared. The results obtained and reported in this paper show the good agreement between the two techniques used. This comparison looks as a good method to test the reliability of the measurements performed.

Introduction

In the framework of an interdisciplinary project, funded by the University of Insubria, a collaboration between the Department of Chemical and Environmental Sciences and Physics and Mathematics was started, aiming at the estimation of radionuclide content in water samples. In connection with the presence of abandoned uranium mines in the region surrounding the town of Como, the attention was focused on uranium content, determined by using both a chemical method, based on cathodic stripping voltammetry, and a physical technique, i.e., gamma-spectrometry. The first one is an innovative low-cost method for trace water analysis, but it provides only total uranium content and is based on a destructive technique. After the development of the Baradello Underground Laboratory, a station for the measurement of low level radioactivity,[1] we started analyzing the same water samples using gamma-spectrometry, which allows to distinguish between different uranium isotopes and to evaluate the concentration of other radionuclides by means of a non-destructive technique. In view of this comparative work, the two methods were previously tested using the same uranium standard solution, as described in this article. The results of the analysis carried out on different water samples are also presented.

Experimental

The two different methods used for the determination of uranium content in water samples are based on gamma-spectrometric measurements, carried out in the underground site of the Baradello Laboratory, and on cathodic stripping voltammetry (CSV). Both methods were tested using the same standard solution of known uranium content.

The chemical method

For uranium analysis, a 250 ml aliquot of the sample was vacuum filtered on a 0.45 μm membrane (Millipore, nitrocellulose) using an all plastic (LDPE – Low Density Polyethylene), acid-cleaned system. Filtered and unfiltered samples were acidified to pH 2 with high purity hydrochloric acid (Fluka Traceselect, 36%). All the foregoing handling was performed under a laminar flow hood in order to minimize contamination.

UV-digestion was employed during the optimization method. A Metrohm 705 UV-Digester equipped with a 500 W high-pressure mercury lamp was used. Samples were transferred in acid cleaned, Teflon capped quartz tubes and digested for one through three hours. All investigated raw and UV digested samples gave undistinguishable results, probably because of the low organic matter content.

Uranium concentrations were determined by cathodic stripping voltammetry using a Metrohm VA 757 Computrace stand connected via VA computrace interface module to a personal computer (see Reference 2 for a general description of stripping techniques and Reference 3 for details about the method used for uranium determination). A standard three electrode configuration was used with a hanging mercury drop electrode (HMDE) as a working electrode, a double junction Ag/AgCl (3M KCl, saturated AgCl and a 3M KCl bridge) as a reference electrode and a platinum wire as a counter electrode.

Optimization

Uranium standard solutions were prepared by appropriate dilution of a standard solution (957 mg/l U in HNO_3, Aldrich), and acidified to pH 2 with HCl (Fluka Traceselect, 36%). A stock solution of chloranilic acid 2.5 mM (99%, Aldrich) was prepared in 0.01M HCl. A 10 ml sample aliquot was transferred into the

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voltammetric cell, 80 μl of chloranilic acid solution was added and the solution purged with nitrogen for 5 minutes. The UO_2^{2+}–chloranilic acid complex was adsorbed onto the mercury drop for 60 seconds at an accumulation potential of +0.1 V. Differential pulse scan from 0.05 to –0.15 V was then started with the following analytical parameters: pulse amplitude 50 mV, potential step 4 mV, pulse time 40 ms. Uranium concentration in the sample is proportional to the peak height measured with this scan. In order to minimize the matrix effect, quantification was carried out by the standard addition method with a limit of linearity (LOL) of 10 μg/l: samples with higher concentrations were properly diluted in order to remain within the limit of linearity. A sample analysis with standard addition is shown in Fig. 1.

The limit of detection (LOD) was calculated with the IUPAC method[4] with a 120-second accumulation time: it resulted to be 0.10 μg/l.

The method of validation was checked again to reach accuracy and precision. 8 repetitions of uranium standard solution at 2.00 μg/l were analyzed. The results are reported in Table 1.

Table 1. Replicate measurements of uranium standard solutions in CSV

Replicate	Expected [U], μg/l	Measured [U], μg/l
1	2.00	1.99 ± 0.03
2	2.00	1.97 ± 0.04
3	2.00	2.03 ± 0.05
4	2.00	2.03 ± 0.04
5	2.00	2.01 ± 0.05
6	2.00	2.03 ± 0.04
7	2.00	2.04 ± 0.05
8	2.00	2.01 ± 0.03
Mean:	2.00	2.01 ± 0.04

The uranium concentration mean value is 2.01±0.04 μg/l and this indicates the absence of any analytical bias and very good precision of the analytical protocol at trace concentrations (% RDS = 1.99%).

The uncertainty in the analysis results is reported as ±1 standard deviation, which was calculated from the standard addition calibration data (see Reference 5 for a detailed description of the procedure).

Gamma-spectrometry and the Baradello Laboratory

The Baradello Laboratory is situated in an artificial cave under the homonymous hill housing the water purification plant of the city of Como. In this site the natural background due to cosmic radiation is attenuated by a cover of about 100 m of rocks, corresponding to about 300 m water equivalent, allowing high sensitivity measurements. The gamma-spectrometric setup consists of an HPGe detector[6] with an active volume of 148 cm^3 and 33% relative efficiency at 1.33 MeV, shielded from all sides by 20 cm of electrolytic copper, as schematically shown in Fig. 2.

Thanks to the combined effects of the rock and the copper shielding, the natural radioactive background is lowered by about two orders of magnitude compared to that attainable in above ground sites[7] (Fig. 3).

The water samples were put into Marinelli beakers in order to maximize geometric efficiency and measured for at least two weeks. In one case uranium concentration resulted under the minimum detectable amount (MDA) level,[8] so we needed to perform the separation of uranium from the aqueous matrix by cation-exchange using Chelex-100 resin.[9]

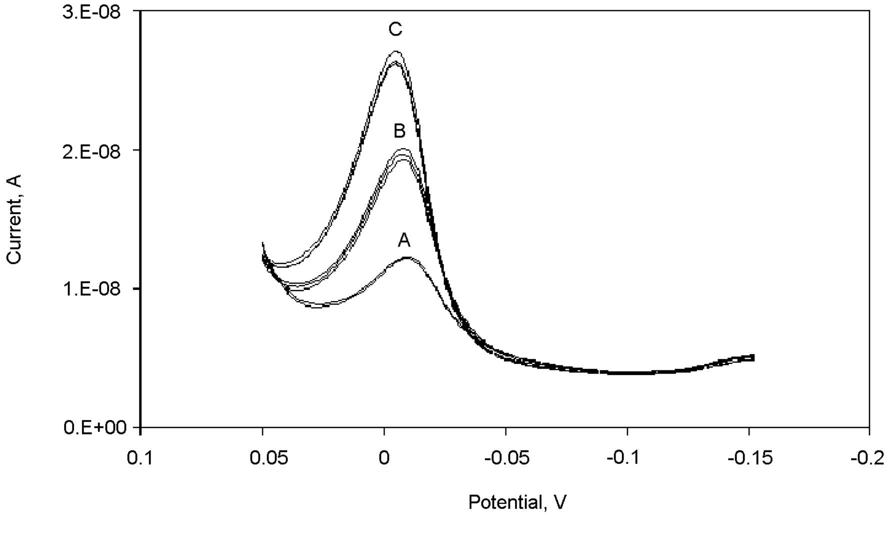

Fig. 1. Analytical signal of UO_2^{2+} ion in CSV; A – sample; B – after addition of 2 μg/l of uranium standard solution; C – after a second addition of 2 μg/l of uranium standard solution

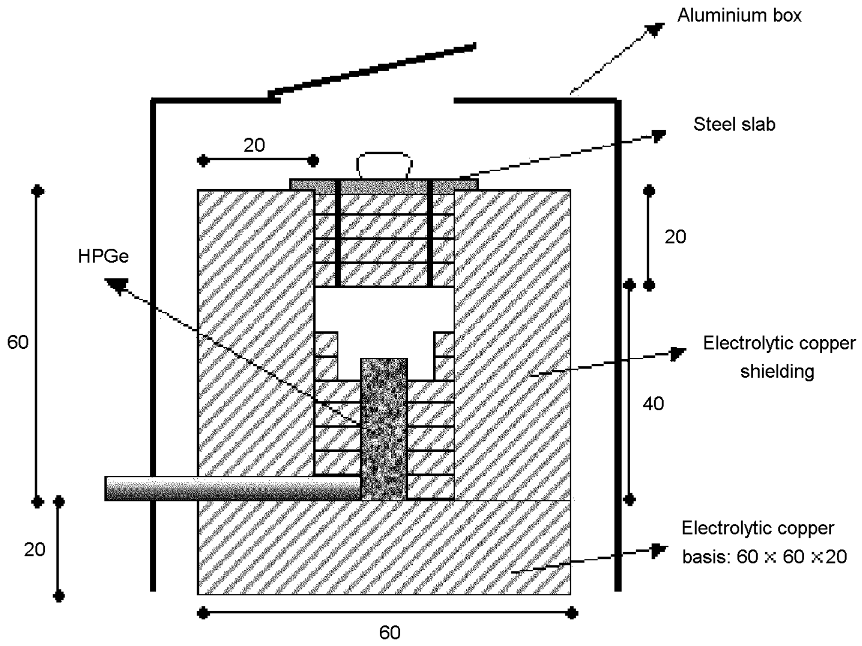

Fig. 2. Scheme of the shielding (dimensions in cm)

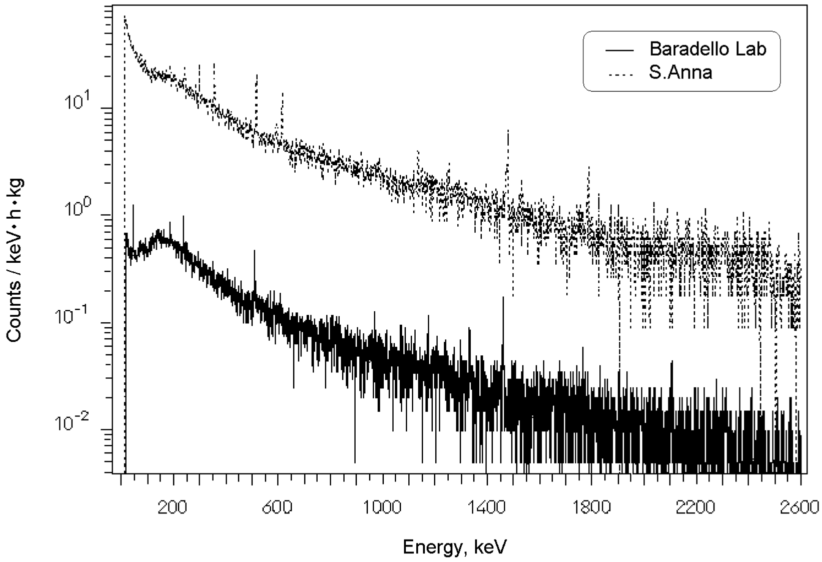

Fig. 3. Comparison of two background spectra acquired with HPGe detector at the Baradello Laboratory and with an HPGe detector, shielded by 10 cm of pure lead from all sides, at the Operating Unit of Health Physics (S. Anna Hospital, Como)

To determine the ^{238}U activity, the ^{234}Th γ-emissions at 63 keV (branching ratio 3.7%) and 93 keV (branching ratio 5.58%) and the ^{234m}Pa γ-emission at 1001 keV (branching ratio 0.837%) can be used in principle. The selected peaks in the gamma-spectra were fitted to Gaussian functions in order to get the count rate *C*, from which the background contribution was subtracted; ^{238}U specific activity (Bq/l) was then calculated according to the following expression:

$$A\left[\mathrm{Bq/l}\right]=\frac{C}{\varepsilon\cdot b\cdot T\cdot V}$$

where *ε* is the peak efficiency (calculated by means of Monte Carlo simulations, as explained in the next section), *b* is the branching ratio, *T* is the acquisition time, *V* is the water sample volume. The method was previously tested using the same standard solution of known uranium content used for the optimization of the chemical method.

Table 2. Comparison between calculated and certificated activities

Energy, keV	Type of geometry					
	0.5 l in Marinelli		1 l in Marinelli		0.5 l in bottle	
	Cert.,* Bq/l	Calc.,** Bq/l	Cert.,* Bq/l	Calc.,** Bq/l	Cert.,* Bq/l	Calc.,** Bq/l
63	12074	11990 ± 160	6037	6560 ± 90	12074	12950 ± 100
93	12074	12040 ± 102	6037	5890 ± 45	12074	11970 ± 60
1001	12074	11550 ± 120	6037	6590 ± 80	12074	13150 ± 130

* Certified activities.
** Activity calculated using Monte Carlo code.

Efficiency calibration of the HPGe detector

We used Monte Carlo code based on GEANT4 library to simulate the detector efficiency.[10] In order to test the results of the simulations, we made an efficiency calibration at the energies of interest (63, 93 and 1001 keV) using the same uranium standard solution that was used in the case of the chemical method optimization (957 mg/l U in HNO_3, Aldrich). The pure solution was analyzed with gamma-spectrometry at the Baradello Laboratory in three different geometries in order to reproduce the possible configurations used during measurements: (1) 0.5 l of standard solution diluted at 50% with distilled water in Marinelli beaker in order to obtain 1 liter of sample; (2) 0.5 l of standard solution in Marinelli beaker; and (3) 0.1 l of standard solution in bottle.

Table 2 summarizes the results with the uncertainties: we do not indicate the uncertainty on certified activities because it is not reported on the certificate.

Concerning the calculated activity we report the statistical uncertainties only, induced by the Poissonian fluctuation of the count number in the relevant energy region of the spectra. By comparing certified and calculated activities reported in Table 2, we can then extrapolate a maximum systematic uncertainty of about 10%, induced by the imperfect knowledge of the configuration of source and detector (which is used as an input for the Monte Carlo simulation).

Sample collection

We analyzed four water samples: two samples came from two different springs situated around an abandoned uranium mine in Val Vedello (Sondrio, Italy, see Reference 11 for more detailed data); a third sample came from the aqueduct of a village situated nearby the town of Como. The fourth sample, named “Carlazzo”, came from a mountain spring sited in the hills surrounding the Lake of Como.

All samples were collected in low-density polyethylene bottles (LDPE, Nalgene). The bottles were previously cleaned by soaking in hot detergent for 24 hours followed by soaking in 5M hydrochloric acid for one week, and then rinsed with several portions of ultrapure MilliQ water (Millipore MilliQ System, 18 MΩ·cm resistivity) under a laminar flow hood and stored filled with MilliQ water acidified to pH 2 with pure hydrochloric acid (Fluka Traceselect, 36% w/v).

Results and discussion

In Table 3 we report uranium concentration values found in the four water samples analyzed: these results show the good agreement between the two methods used in all the considered cases.

For the gamma-spectrometry results, we indicate only the statistical uncertainties in the table, pointing out that a systematic effect, related to Monte Carlo configuration, plays an important role resulting in a 10% systematic uncertainty, as stated above.

For gamma-spectrometric analysis we used the 93 keV ^{234}Th line for all the samples, due to the relatively low uranium activity which forbade the use of other lines with lower branching ratio. We put all the samples into Marinelli beakers except for the one coming from the aqueduct: in this case, due to the low uranium content, we needed to perform cation-exchange resin (Chelex-100), as previously announced.

In order to make a correct comparison between the two methods we must consider that cathodic stripping voltammetry gives results on total uranium content, i.e., ^{238}U plus ^{235}U, while gamma-spectrometry allows to distinguish between the two uranium isotopes.

Table 3. Uranium concentration and uncertainties (in the case of gamma-spectrometry a 10% systematic uncertainty must be added) found in the four water samples analyzed using gamma-spectrometry and cathodic stripping voltammetry

Sample	^{238}U (γ-spectrometry), μg/l	[U] (CSV), μg/l
Val Vedello (sample 1)	93 ± 7	97 ± 3
Val Vedello (sample 2)	30 ± 2	28.6 ± 0.4
Carlazzo	4.74 ± 0.83	5.28 ± 0.1
Aqueduct	4.26 ± 0.24	3.5 ± 0.06

Nevertheless the relative isotopic abundance of ^{238}U and ^{235}U are 99.28% and 0.71%, respectively. This implies a negligible influence of this circumstance on our results, in connection with the relatively low activities measured. To give an idea of the importance of this mechanism we separated the contribution of ^{238}U and ^{235}U to the total uranium concentration evaluated with the cathodic stripping voltammetry in the case of the sample with the highest uranium content, i.e., 97±3 μg/l. We obtained the following results: 96.3 μg/l for ^{238}U, 0.7 μg/l for ^{235}U. This example shows that the difference between total uranium and ^{238}U concentration is widely within the estimated uncertainties.

Conclusions

We applied two different techniques (chemical method based on stripping voltammetry and gamma-spectrometry) in order to evaluate the uranium content in four water samples. In all considered cases the two methods gave results which are compatible within the calculated experimental uncertainties.

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