
Determination of isotopic ratios of uranium (U-235/-U238) for the characterization of reverse osmosis compared with conventional tap water treatment in order to determine the source of a water leak

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Determinación de las relaciones isotópicas de uranio (U-235/-U238) para la caracterización de ósmosis inversa en comparación con el tratamiento de agua de consumo convencional con el fin de determinar el origen de una fuga de agua

Determinació de les relacions isotòpiques d'urani (U-235/-U238) per a la caracterització d'osmosi inversa en comparació amb el tractament d'aigua de consum convencional per tal de determinar l'origen d'una fuga d'aigua

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RESUMEN

La adecuación de la técnica analítica ICP-MS (plasma acoplado inductivamente con determinación por espectrometría de masas de cuadrupolo) se ha llevado a cabo para la determinación y caracterización de la relación isotópica mayoritaria del uranio, U-235/U-238 en las aguas de consumo. La metodología desarrollada se ha validado obteniéndose una elevada precisión ($RSD \leq 0,3 \%$) necesaria en la realización de este tipo de estudios. Los resultados obtenidos confirman un leve aumento en la proporción isotópica del uranio U-235/U-238 para el agua tratada mediante ósmosis inversa con respecto al agua tratada con tecnología convencional. Esta metodología de análisis y los resultados obtenidos para el agua osmotizada fueron utilizados para caracterizar los distintos orígenes de agua tratada en la red de distribución de la ciudad de Barcelona y su área metropolitana con el fin de determinar el origen de una importante fuga de agua sospechosa de provenir de la red de distribución, siendo la primera vez que esta aplicación isotópica es utilizada por una compañía de distribución de agua para resolver este tipo de problema.

Palabras clave: agua potable, determinación isotópica del uranio, tratamiento por osmosis inversa, identificación de una fuga de agua, agua subterránea.

SUMMARY

An analytical technique for the determination of the isotopic ratio of U-235/U-238 in waters by a classical technique based on a quadrupole ICP-MS has been implemented. A high precision ($RSD \leq 0.3 \%$) has been obtained, which is strictly necessary in these circumstances. The methodology developed was validated and the results obtained

confirmed a slight increase in the uranium isotopic ratio U-235/U-238 for the treated water using reverse osmosis with respect to conventionally treated water. This analytical methodology was applied to characterize different origins of treated water in the Barcelona Area in order to determine the origin of an important water leak. To the best of our knowledge, it is the first time that this isotopic application is used by a tap water distribution company to solve this kind of problem.

Key words: Drinking water; uranium isotopic determination; reverse osmosis; water leak identification; groundwater.

RESUM

L'adequació de la tècnica analítica ICP-MS (plasma acoblat inductivament amb determinació per espectrometria de masses de quadrupol) s'ha portat a terme per a la determinació i caracterització de la relació isotòpica majoritària de l'urani U-235/U-238 a les aigües de consum. La metodologia desenvolupada s'ha validat obtenint-se una elevada precisió ($RSD \leq 0,3 \%$) necessària per a la realització d'aquests estudis. Els resultats obtinguts confirmen un lleu augment a la proporció isotòpica del urani U-235/U-238 per a l'aigua tractada mitjançant osmosis inversa respecte a l'aigua tractada amb tecnologia convencional. Aquesta metodologia d'anàlisi i els resultats obtinguts per l'aigua osmotitzada van ser aplicats per caracteritzar els diferents orígens de agua tractada a la xarxa d'abastament de la ciutat de Barcelona i la seva àrea metropolitana amb la finalitat de determinar l'origen de una important fuga d'aigua sospitosa de provenir de la xarxa

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de distribució, sent la primera vegada que aquesta aplicació isotòpica es utilitzada per una companyia de distribució d'aigua per resoldre aquest tipus de problema.

Mots clau: aigua potable, determinació isotòpica del urani, tractament per osmosis inversa, identificació d'una fuita d'aigua, aigua subterrània

1. INTRODUCTION

The Drinking Water Distribution System of Barcelona and its Metropolitan Area (Spain, NE) has more than 40,000 km of pipelines, being one of the largest water supply networks in Southern Europe, with an overall consumption of about 850,000 m³ of drinking water per day. In such a huge system leaks of all kind are frequent, and the Laboratory carries out analyses in order to determine the origin of a water sample suspicious of being a water leak from our water distribution system. Frequent causes for the leaks are natural or modified groundwater, leaching from sewers or other natural or anthropogenic causes (1). Indeed, a precise methodology is required to identify the most likely origin of flooded water and for its characterization.

There are a number of methodologies to confront this analytical problem, such as the determination of the characteristic metals or the ionic concentration ratios of major elements present in the sample (1, 2). However, in most cases the results obtained are not conclusive for the final identification of water origin, especially when the sample shows a chemical pattern compatible with a mixture of different origins, changing the concentration of characteristic metals and ionic ratios of major elements (1, 2, 3).

The isotopic studies using different isotopic ratios showed good results in similar environmental problems, due to their great stability over time which allows the univocal characterization of an environmental sample (3, 4).

Most of the isotopic analytical techniques in water samples involve the determination of stable isotopes of both components of water, oxygen and hydrogen (3, 5, 6, 7), or also the determination of a common element, such as isotopes of nitrogen (2). These elements are very difficult to determine because they are very sensitive to contamination, so very specific laboratory conditions in addition to complex and expensive techniques are necessary for their quantification. In the ICP-MS field, other stable isotopes, such as B-10/B-11 (4), S-32/S-34 (6), Sr-86/ Sr-87 (8), and Pb isotopes (9), have also been used successfully. However, in the majority of publications the technology applied, high resolution ICP-MS, is unaffordable for most environmental laboratories. Moreover, the results achieved in many of these investigations involving isotopic ratios showed a very high similarity in the final value obtained for most environmental samples around the world, this limitation being the main reason for the extensive use of high resolution equipment, which is capable of achieving very high accuracy and especially a very high precision of the isotopic ratio measurement, given that in most cases it is necessary to compare different environmental samples (10-13).

There are actually a few publications dealing with a simple and lower cost technique, such as single quadrupole ICP-MS, with or without reaction cell (14,15).

Among the different isotopes studied, uranium isotopes are one of the most frequently evaluated, principally taking advantage of their different radioactivity properties and working with their activity determination (16-21). In the ICP-MS field, there are many publications focusing on this element. Despite the radioactivity environmental problems, this element has also been studied in regular water samples with very promising results (12, 13, 15).

Working with water samples, the study with uranium isotopes presents two important advantages with respect to other elements: uranium can be quantified in a reasonable concentration range and, in case of using low resolution ICP-MS, all isotopes of this element are free from matrix interferences. In addition, other distortion effects, such as repulsion by major elements present in the sample in the low mass isotopic elements, such as boron, are avoided. (22-24). The main disadvantage is the different proportion of major isotope U-238 with respect to the second one, U-235; an exhaustive control of background noise is thus recommended, mainly working with low resolution quadrupole ICP-MS equipment.

Therefore, following the advice previously published by M. Resano *et al* (14) with some modifications, a methodology to evaluate the isotopic ratio of U-235/U-238 from the different water origins has been applied in the most important water leak occurred in Barcelona's tap water distribution system on 2012, in order to characterize deduce its possible source. Different samples from the tap water system near anearby the water leak were analysed every 15 days for 5 months. T and the results obtained, with a high precision (RSD \leq 0.3 %) necessary in these studies and working with a classical technique based on quadrupole ICP-MS (7500 cICP-MS Agilent), showed a slight but significant difference in the isotopic ratio of U-235/U-238 between the different water origins studied; reverse osmosis origin and conventional treatment, with that allowed to resolve the most probable origin of the water leak. To the best of our knowledge, it is the first time that the determination of uranium isotopic ratio for membrane treated water has been performed and used for its characterization.

2. EXPERIMENTAL

Chemicals

Standard solutions for quantitative determination of uranium concentration U (depleted uranyl nitrate hexahydrate) 1000 mg L⁻¹ HNO₃ 1 % were purchased from Inorganic Ventures (Christiansburg, VA). Other reagents, such as concentrated nitric acid and some of individual standard 1000 mg L⁻¹ such as Na, Mg, Ca, K, Si were obtained from Carlo Erba (Rodano, Italy), and Merck (Darmstadt, Germany), respectively. The internal standard used for quantitative determination of uranium concentration was terbium, Tb (1000 mg L⁻¹ HNO₃ 2 %) and it was also purchased from Merck (Darmstadt, Germany). Water from the Milli-Q® purification system (Millipore Corp., Bedford, MA) was used.

Sampling

Samples were collected from all origins of treated water in the Barcelona Area (Spain) as shown in Figure 1. The different origins were: **WTP 1**, San Joan Despi Water treat-

ment Plant (WTP; partial treatment by Reverse osmosis (25) ; RO); **WTP 2**, Cardedeu WTP with conventional treatment; **FT**: Font Santa Tank, Blend treated water from Abrera plant (WTP 3, partial treatment by electrodialysis reversal, EDR) and El Prat reverse osmosis sea water plant (WTP 4). WTP 1 and FT are located on the Llobregat River Zone (Llobregat Zone) whereas WTP 2 are located on the Ter River Zone (Ter Zone). For details and location see Figure 1A.

For the study and characterization of flood water, the samples were collected from different points inside the tap water distribution system near the flooded water, suspicious of being a water leak from the tap water distribution system. For details and location see Figure 1B.

Water samples were always taken after a 5-minute purge, acidified, and in 250 mL high density polyethylene (HDPE) containers. The samples were analysed at the laboratory and maintained refrigerated until their analytical determination.



Figure 1; Sampling collection;
A) The Different Origins of the Water Distribution System of Barcelona and its Metropolitan Area

WTP 1: San Joan Despi Water Treatment Plant (partial treatment by Reverse Osmosis; RO). Llobregat River Zone
WTP 2: Cardedeu Water Treatment Plant with conventional treatment. Ter River Zone
FT: Font Santa Tank. Blend treated water of Abrera plant; WTP 3 (partial treatment by Electrodialysis Reversal; EDR) and El Prat Reverse Osmosis Sea Water Plant WTP 4. Llobregat River Zone

B) Different possible origins of the water leak

Black: Natural Origin (Rainfall infiltration or groundwater upwelling)

Red: Tap water leak from "Ter Zone" (Origin WTP2 provides less than 10% of tap water in the affected zone)

Yellow: Tap water leak from "Llobregat Zone" (Origins WTP 1 and FT provide more than 90% in the affected zone)

Instrumentation and Methodology

The determination of the uranium concentrations and their isotopic ratios in the different samples was analysed with an ICP-MS 7500cx fitted with collision-reaction cell (helium and hydrogen system). The system configuration for uranium isotopic ratio determination was established following the advice previously published (14) and applying the modification inherent to the different equipment used.

Helium (4 ml/min) as collision gas was used in order to optimize background noise. The nebulization was performed with concentric nebulizer and the analytical parameters selected for uranium ratio determination are presented in Table 1.

Table 1. Instrumental setting for uranium isotopic ratios determination by cICP-MS

| Instrument Agilent 7500cx | | He mode | |
|--|--|----------------------|-------------|
| RF power | 1500 W | Cell gas | 4 mL/min He |
| Analyzer pressure | 3.33 x 10 ⁻³ Pa | Cell entrance | -30 V |
| Carrier argon | 0.9 L/min | QP focus | -10 V |
| Makeup argon | 0.1 L/min | Cell exit | -42 V |
| Plasma argon | 15 L/min | OctP bias | -18 V |
| Auxiliary argon | 0.9 L/min | QP bias | -16 V |
| Ion optics and collision/reaction cell | | Sample introduction | |
| Extract 1 | 0.0 V | Concentric nebulizer | 0.3 mL/min |
| Extract 2 | -170 V | Quartz spray chamber | 10 °C |
| Omega bias | -16 V | Peristaltic pump | 0.1 r.p.m |
| OctP RF | 170 V | Sampling depth | 8 mm |
| Data acquisition conditions | | | |
| Number of acquisition point | 1 | | |
| Acquisition time per mass | 20s (U-234, U-235, m/z233, m/z=236) 5s (U-238) | | |
| Replicate measurements | 12 | | |

The total uranium concentration was determined using a standard calibration regression curve (depleted uranyl nitrate hexahydrate; 1000 mg L⁻¹ HNO₃ 1 %) with internal standard correction of terbium (I.S. m/z 159; Tb 1000 mg L⁻¹ HNO₃ 2 %), whereas the U-235/ U-238 ratios were determined directly from total accounts obtained by every mass scanned for a determined volume of sample introduced in the plasma, so the results are presented as % in mass (not as % atom number)(26,27)

Additionally to the U-235 and U-238 determination, other m/z, such as minor uranium isotope U-234 and m/z = 233 and m/z = 236, were also scanned as background noise control, in order to apply a correction as described in formula (1)

$$U235/U238 (\% \text{ in mass}) = 100 \cdot ((U235-F)/(U238-F)) \quad (1)$$

Where *F* is a correction factor to diminish the effect of background noise as described in formula (2)

$$F = (m/z233 + m/z236)/2 \quad (2)$$

Most of the times differences between both 233 and 236m/z scanned were less than 30%. In the few cases where difference was greater than 30%, *F* value was discarded and uranium ratio determination was repeated.

Working in these conditions, as explained in Table 1 and applying the correction factor *F*, a very high precision, equal to or lower than 0.3 % (RSD), was achieved in U-235/ U-238 ratio evaluation, necessary in these studies.

3. RESULTS AND DISCUSSION

The objective of this work was to characterize different treated water origins to identify the source of a water leak

in the distribution area. One of the best analytical methodologies for unambiguous characterization is the determination of the isotopic ratios of one or more elements present in the samples. The applicability of this method would depend on whether its accuracy and principally its precision are good enough to be successfully applied. Indeed, previous quality parameters, such as precision, and a further validation of the data obtained, have to be performed to confirm the usefulness of the method.

Study of the Precision and Evaluation of the Methodology
Given the aim of the study, the most important quality parameter of the method was its precision, which was evaluated using the conditions explained above. Therefore, four replicates of Llobregat Zone treated water (WTP 1; partially RO treated) were analysed consecutively for three days, obtaining an RSD = 0.3%, which is an acceptable value necessary for our purpose and working with quadrupole ICP-MS. Results are presented in Table 2.

Table 2. Evaluation of the precision obtained for U-235/U-238 ratio (% in mass) working in reproducibility conditions (n=4 x 3 different days)

| n | Osmosis treated water from Llobregat River; WTP 1 (U = 0.5 µg/L) |
|--------------------|--|
| 1 | 0,71453191 |
| 2 | 0,71365461 |
| 3 | 0,71263641 |
| 4 | 0,71758441 |
| 5 | 0,71765035 |
| 6 | 0,71358437 |
| 7 | 0,71750340 |
| 8 | 0,71534652 |
| 9 | 0,71443590 |
| 10 | 0,71281914 |
| 11 | 0,71913550 |
| 12 | 0,71452401 |
| Mean value | 0.715 |
| RSD (%) | 0.31 |
| Standard Deviation | 0.0019 |

WTP: Water Treatment Plant. WTP location in Fig. 1

Additionally, to evaluate the feasibility of the procedure in other real samples, a comparison with different treated water origins was performed working in the same conditions of repeatability. The different mean and RSD% values obtained are given in Table 3. To compare these results, mean values of uranium ratios from different treated water origins were statistically evaluated using the Student's t-test and were compared with the international mean accepted

value of U-235/U-238 ratio = 0.711% in mass (26,27). The significance values (P) are given in Table 3.

As was expected, for conventional treated water from WTP 1 and WTP 2 the uranium ratios obtained were not significantly different, with respect to the reference value and between the results obtained with both conventional treated waters, with a P value >0.05 in all cases. However, a statistical difference (P<0.05) was shown in uranium ratios obtained for RO treated water from the Llobregat Zone, demonstrating a very slight increase in U-235/U-238 ratios when the membrane treatment was used, an increase sufficient to be statistically distinguished from conventional waterworks treated water. The results obtained demonstrated the feasibility of the methodology and the possibility of its use to identify different treated water origins.

Uranium Ratios (U-235/ U-238) Obtained for Different Treated Waters. Comparison of Results

Once the feasibility of the method had been established, different treated water origins were measured to be characterized. For this purpose, different grab samples for every origin were analysed every 15 days from September to December 2012. Mean results of uranium concentration and isotopic ratios obtained are presented in Table 4.

Table 4. Characterization of the different origins of the Water Distribution System of Barcelona and its Metropolitan Area using the U²³⁵/U²³⁸ ratio evaluation

| Origin | Mean Concentration (µg/L) ^a | Isotopic ratio U-235/ U-238 (% in mass) ^a |
|-------------------------------|--|--|
| WTP1 (60 % reverse osmosis) | 0.5 | 0.715 |
| WTP1 (conventional treatment) | 1.0 | 0.710 |
| FT (70 % desalinated water) | 0.4 | 0.717 |
| WTP2 (conventional treatment) | 0.9 | 0.711 |

^a Mean values obtained from different grab samples analyzed every 15 days from September to December 2012. WTP: Water Treatment Plant. WTP location in Fig. 1

WTP 1: San Joan Despí WTP (partial treatment by RO). Llobregat River Zone.

FT: Font Santa Tank. Blend treated water of Abrera plant; WTP 3 (partial treatment by EDR) and El Prat Reverse Osmosis Sea Water Plant (WTP 4). Llobregat River Zone.

WTP 2: Cardedeu Water Treatment Plant (conventional treatment). Ter River Zone

Table 3. Validation of the methodology with respect to the mean value accepted for U-235/U-238 ratio (% in mass)^a

| Treated Water Origin | Mean | RSD(%) n=4 x3 | Significant differences between mean values and reference value ^a (P-value) ^b | Significant differences between mean values of different treatments (P-value) ^b |
|--|-------|------------------|---|--|
| Llobregat River (conventional treatment from WTP 1) | 0.710 | 0.28 | 0.053 | 0.259 |
| Ter River Origin (conventional treatment from WTP 2) | 0.711 | 0.30 | 0.801 | 0.259 |
| Llobregat River (60% Reverse osmosis from WTP 1) | 0.715 | 0.31 | 0.00003 | 0.004 |

^a U-235/U-238=0.711 % in mass (0.720% in atomic number) [

^b Estimated at 95% confidence value

WTP: Water Treatment Plant. WTP location in Fig. 1

The results obtained show that membrane treatments in the Llobregat Area (WTP1 and FT) produce a slight but significant increase in the U-235/U-238 ratio. This effect was also previously described with respect to other elements, such as boron (22, 24) and also has been also observed in our samples, due to the different isotopic stability in the geometries of two major species, borate (main species in the rejection effluent) and boric acid (main species found in the permeate) (4, 22, 298). For uranium, it is difficult to explain a possible mechanism of this effect. Thus, J. Farrell *et al* (29) studied the different species of uranium in water with two main species, reduced U (IV) and oxidized form U (VI), which is more soluble, and their equilibrium with soluble carbonates. Two main carbonated species with different chemical structure, neutral UO_2CO_3 and anionic $\text{UO}_2(\text{CO}_3)_2^{-2}$ species, at neutral-acidic conditions (pH = 6-7), could help to explain (at least partially) the different uranium isotope ratios observed in the membrane treatment. In fact, the slight solubility increase of U-235 with respect to U-238 (30) is well known for oxidized uranyl forms in water (U (VI) forms), which is the major soluble species under working conditions in water treatment by membranes.

Therefore, the uranium isotopic ratio U-235/U-238 is shown to be a very useful tool to distinguish between different water treatment origins.

Application to a Real Case. Study of a Water Leak.

Once all treated water origins had been characterized, the results obtained were applied to discern an important water leak in the north of the city of Barcelona. The zone is principally fed with treated water from the Llobregat Zone (above 90%, see figure 1 B).

For the study of the water leak, several grab samples were collected from September to December 2012 from specific points of the drinking water system near the zone of the water leak location. The isotopic uranium ratios were determined and were compared with those obtained from the water leak and with the other different origins previously characterized. Additional groundwater from every origin zone (Llobregat and Ter Areas) was collected to compare with the leak. The results are shown in Figure 2.

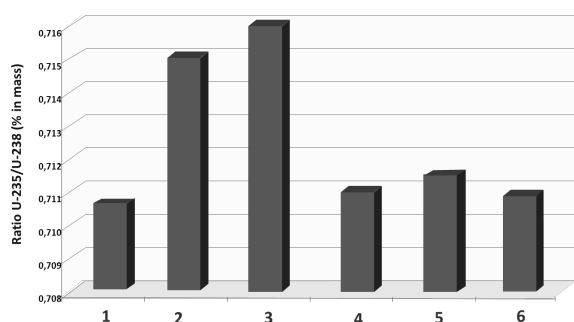


Figure 2: Uranium ratios (U -235/ U-238) obtained in flooded water zone. Comparison from different origins

1) Groundwater from Llobregat Zone; **2)** Treated water from Llobregat Zone (WTP1); **3)** Tap water near water leak; **4)** Water leak; **5)** Treated water from Ter Zone (WTP 2); **6)** Groundwater from Ter Zone.

The results obtained show that the water leak has the typical values from natural groundwater as well as conventional treated water from the Ter Zone (WTP 2). In fact, the water leak presented a high silicon content of about 8 mg/L, which indicates that the water experienced a long underground transit before the appearance point. As expected, the uranium isotopic ratios found for the treated water near the flooded water were from the Llobregat Zone, from Font-santa Tank (FT), with a high proportion of desalinated sea water. Therefore, the results obtained for all samples studied show that the leak was not coming from the nearby drinking water system, which was mostly fed by water treated from the Llobregat Zone.

4. CONCLUSIONS

A high precision methodology ($\text{RSD} \leq 0.3\%$) for the determination of the isotopic ratio U-235/U-238 using classical quadrupole technique with collision cell was successfully used for characterization of waters and identification of their origin. Uranium isotopic ratios (U-238/U-235) in waters from the two main distribution areas in Metropolitan Barcelona are statistically different: about 0.716 in the Llobregat Zone after partial membrane treatment, and about 0.711 in the Ter Zone once conventional treatment has been used for water potabilization.

The results obtained for U-235/U-238 in the different water distribution areas allows the identification of the most probable origin of important flooded water suspicious of being a network water leak.

The results obtained allow it to be concluded that the methodology presented can be a helpful tool for environmental or technical problems, such as the identification of the origin of a water leak.

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