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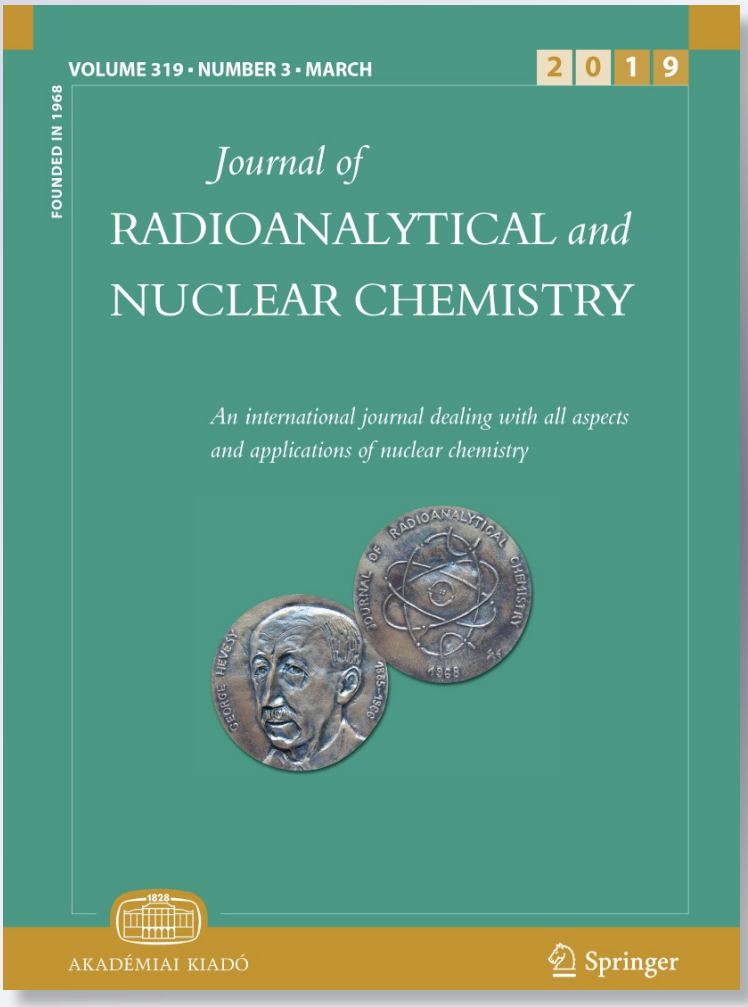
Journal of Radioanalytical and Nuclear Chemistry
An International Journal Dealing with All Aspects and Applications of Nuclear Chemistry

ISSN 0236-5731
Volume 319
Number 3

J Radioanal Nucl Chem (2019)
319:1345-1349
DOI 10.1007/s10967-018-6317-z



Springer

Journal of Radioanalytical and Nuclear Chemistry (2019) 319:1345–1349
https://doi.org/10.1007/s10967-018-6317-z

Uranium and radium isotopes in some selected thermal, surface and bottled waters in Vietnam

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Received: 29 August 2018 / Published online: 9 November 2018

Abstract
Uranium and radium isotopes were measured in 17 water samples (6 thermal, 3 stream and 8 commercial bottled waters) using LSC and alpha spectrometer after chemical separation. The thermal and stream water samples were collected from Kim Boi spa Hoa Binh, North Vietnam. The measured radioactivity ranged $\leq 0.5 \div 9.0$ mBq/L for ^{238}U, $1.60 \div 18.6$ mBq/L for ^{234}U, $\leq 5 \div 29.2$ mBq/L for ^{226}Ra. For the bottled water ^{234}U was ≤ 3 mBq/L and ^{238}U undetected, the ^{226}Ra ranged $5 \div 202$ mBq/L and ^{228}Ra $\leq 20 \div 115$ mBq/L. For studied thermal water the increasing tendency of Ra concentration with depth water formation is observed.

Keywords Uranium and radium · Thermal-water · Surface water · Bottled water · Kimboi spa · North-West Vietnam

Introduction

Water resource is an essential thing for sustaining life and society of human beings. Freshwater is needed for diet, as well as for industrial, agricultural, energy production, treatment and leisure activities. Nowadays, the consumption of mineral and spring water has also increased in various countries as well as in Vietnam. Natural water including surface and ground water usually contain useful elements, but heavy metals and radionuclides can be also present.

The knowledge of natural radionuclides concentration in drinking, mineral and therapeutic water is important to human health. For example, the radium isotopes have similar chemical behavior as calcium and therefore replaced Ca it in the body. For this reason both Ra isotopes in drinking water has relatively high dose factors for ingestion [1]. Therefore the presence and behavior of radionuclides in water sources have been studied in many countries and are controlled following the provisional WHO guideline for drinking water [2].

Numerous countries investigate and monitor the natural radionuclides in drinking water [3–17]; in groundwater [18–23]; and in thermal and spring water [24–29].

This study presents the ^{234}U, ^{238}U, ^{226}Ra, ^{228}Ra concentration of 6 thermal and 3 stream water samples from the famous mineral and thermal water resource in Kim Boi, Hoa Binh, Northwest mountain region of Vietnam, and 8 commercial available bottled waters in Vietnam.

Sampling area

In North Vietnam, Hoa Binh province is known to have very useful thermal and therapeutic waters. Every year several hundred thousand people use medical treatments, and tourists use the water for wellness holidays. The province is a hilly area situated between mountains and the Red River delta, with the area about 4660 km^2, and longitude 104°48′E–105°50′E, latitude 20°17′N–21°08′N. This area is composed mainly of limestone, sandstone, conglomerate, aphyric basalt, tuffaceous sandstone and black clay shale [30].

The water samples were taken in Sao Bay village located in the Boi River basin, Kim Boi district, Hoa Binh province, with an area about 18.42 km^2. According to Cao et al.

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[30] this studied area is composed of three main formations (Fig. 1): the first is the Dong Giao formation (T2a dg) which is distributed in the center and northeast area. This formation is composed of massive limestone, light-colored massive limestone marl, marl dolomitized limestone, and cherty limestone. The second is Suoi Bang formation (T3n-r sb) distributed in the southern part and built from sandstone, siltstone, conglomerate, clay shale and coal seams or lenses. The third part is the Quaternary sediments (Q), generally consisting of gravels, sands with interlaying of red-brown clay and silt constituting alluvial and fluvial deposits with depth up to 7 m [31].

In the studied area the NW–SE fault system including the F1 and F2 faults plays a major role governing the geological-geomorphologic characteristics of the studied area [30]. The expanded Dong Giao formation with widely cracked limestone forms as mineral water storage reservoir. On the other hand the SW–NE fault system including the F3 fault expands only in Suoi Bang formation playing only minor role in the mineral water forming processes [30].

From hydrogeological point of view the groundwater chemical characteristics are controlled by the Dong Giao limestone formations [30]. The magmatic suite is located in the western part of the study area. In consequence of the magmatic activity not only the Dong Giao limestone formation was transformed but also the several important elements for the mineral water were created [30]. The geological structure forms the high potential of the mineral and thermal water and in fact, the water has been exploited since beginning of Twenty Century for medical treatments and tourism. The average temperature of the thermal waters in the sampling area amount to 41 °C with 1100 mg/L mineralization, which compose of 534 mg/L SO_4^{2-}, 236 mg/L HCO_3^-, 238 mg Ca^{2+}, 26 mg Mg^{2+} and rest Cl^-, Fe^{3+}, K^+ and H_2SiO_3 [30].

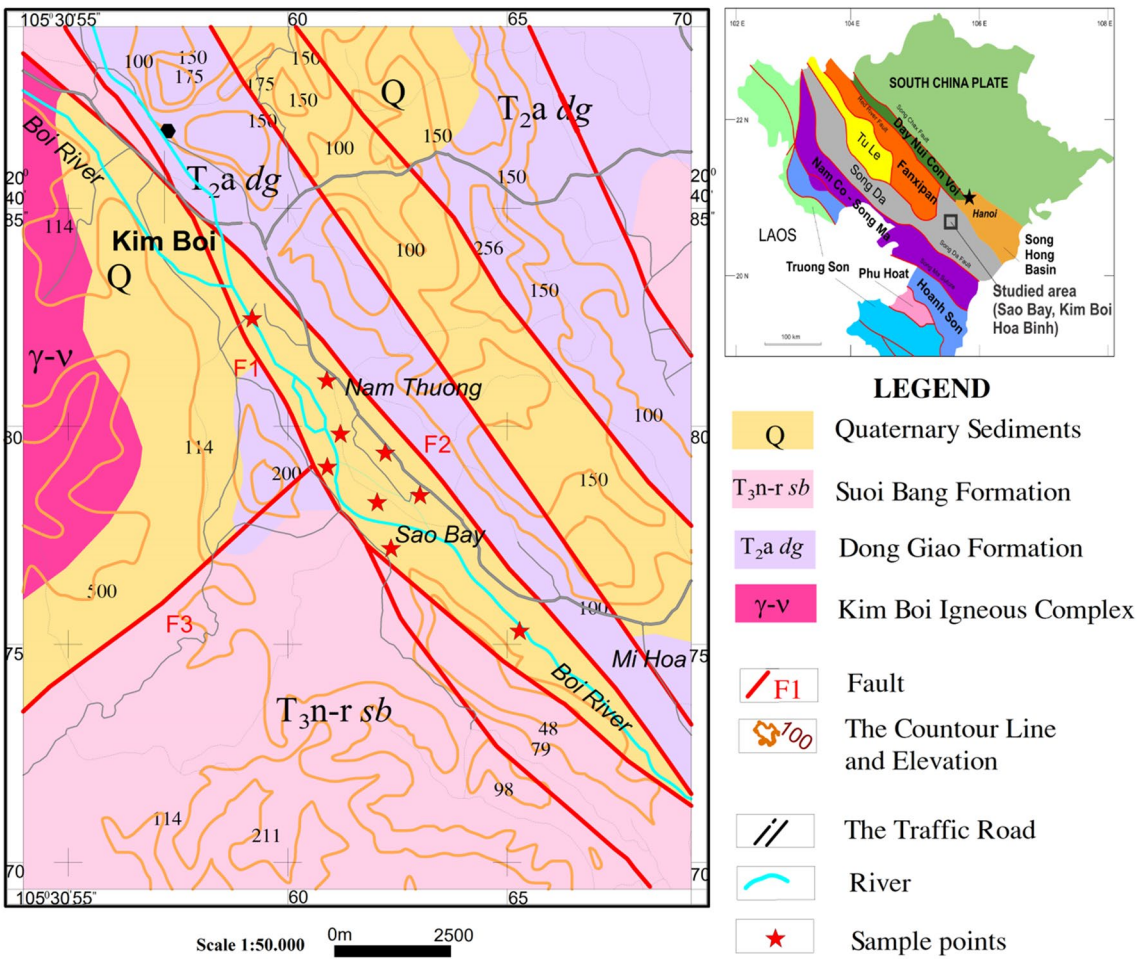

Fig. 1 Geological sketch of the sampling area (modified from Hoa Binh map 1:200,000)

Methods

Determination of radium isotopes (^{226}Ra and ^{228}Ra) concentrations in water samples

^{226}Ra and ^{228}Ra isotopes in water sample are determined using the radiochemical procedure and α/β liquid scintillation spectrometer as given in [32]. The radiochemical procedure involves the separation of radium isotopes from water sample in sulphate compound together with barium carrier. In order to eliminate the interfering isotopes occurring in the precipitate such as ^{210}Pb and ^{210}Po, the precipitate is dissolved up in EDTA solution and again precipitated as $Ba(Ra)SO_4$ after lowering the pH of the solution by addition of acetic acid. Finally the obtained precipitate is washed with distilled water and centrifuged, placed in a glass vial and then mixed with a gel forming scintillation cocktail Insta-Gel Plus Perkin Elmer™ and measured using α/β with 1414 Wallac Liquid Scintillation Counter® [33, 34].

To eliminate the background radiation originating from the chemical reagents, cosmic and electronic noise, the background sample from the distilled water is prepared together with a series of the investigated water samples. Standard sample ^{226}Ra is used to determine the efficiency of the applied chemical procedure and to control the value of the PSA parameter.

Every sample is measured daily for 2 h until the expected equilibrium between ^{226}Ra and its short-lived products is established (above 21 days). The contents of the ^{226}Ra and ^{228}Ra in the measured water sample are estimated using the dependence of the net measured intensities in α and β channels on the time elapsed from the precipitation of radium from the water sample (the net count rate) [32]. The relative uncertainty of the method depends on the concentration of Ra isotopes in the studied water sample and ranges from 3 up to 15%.

Determination of uranium isotopes (^{234}U, ^{238}U) concentrations in water samples

The determination of the uranium isotopes in water sample requires a radiochemical method. The well-known amount of the ^{232}U tracer is added to water sample at the very beginning of the chemical procedure, then the uranium isotopes are precipitated together with MnO_2 through adding ammonia, $KMnO_4$ and $MnCl_2$ to the water sample. The precipitate is washed with distilled water. The obtained precipitate is dissolved in HCl 9 M and the obtained solution is transferred through the chromatographic column with Dowex 1 × 8, 100–200 mesh. The absorbed uranium fractions are removed into plastic cup by distilled water from column then dried and dissolved in HCl acid. To the obtained liquid sample, neodymium and HF acid are added and then the suspended compound containing uranium was filtered off the liquid by passing through a plastic filter with 0.1 µm porosity. The obtained sample is dried and measured using alpha spectrometer Canberra 7401™ with silicon semiconductor detector PIPs, which resolution amounts to 17 keV at 5.5 MeV line of ^{241}Am.

The measuring time for every sample is chosen so that the uncertainty of the count rate at ^{232}U peak is below 2%. To eliminate the background derived from the chemical reagents, electronic noise or alpha particles emitted from the surrounding, the background sample from the distilled water is also prepared and measured. The relative uncertainty of the used method is equal to the 3%.

Results and discussions

The measured uranium and radium concentrations in bottled, thermal and stream water samples are summarized in Table 1. In thermal water samples the activity concentration is from ≤ 0.5 to 8.95 mBq/L for ^{238}U, from 1.60 to 18.63 mBq/L for ^{234}U and from ≤ 5 to 29.2 mBq/L for ^{226}Ra, the ^{228}Ra is below 20 mBq/L. In the case of stream water from ≤ 0.5 to 1.9 mBq/L for ^{238}U, 1.71 to 7.82 mBq/L, both ^{226}Ra and ^{228}Ra were not detected. ^{238}U in the bottled water samples is below 1 mBq/L, and ^{234}U below 4 mBq/L. The ^{228}Ra fluctuated between the low limit of detection (20 mBq/L) to 115 mBq/L, and ^{226}Ra ranges from below 5 mBq/L (LLD) to 202.1 mBq/L. The low concentration of uranium and radium isotopes in thermal water is connected with the low uranium and thorium concentration in the limestone aquifer and shallow water bearing formation. However an increase of ^{226}Ra with depth of well or borehole was observed (Fig. 2). When ^{238}U values are increasing, also ^{234}U shows the same tendency (Fig. 3). These observations can be the consequence of longer duration of interactions between groundwater and rock formation in very deep and therefore old water reservoirs. The absence of radium isotopes and very low uranium in surface water can be connected with no, or very weak drainage of groundwater into the stream.

The uranium and radium in the commercial bottled waters excluding the Alba water are very low, so the bottled water can origin from surface or spring waters occurring in the crystal rocks. This suggestion should be checked through analyzing of chemical and biological compositions of the measured commercial bottled waters.

Table 1 The uranium and radium concentrations in thermal, stream water samples in Kim Boi, Hoa Binh and commercial bottled waters in North Vietnam

STT	Name of sample	^{238}U (mBq/l)	^{234}U (mBq/l)	^{226}Ra (mBq/l)	^{228}Ra (mBq/l)	Depth
Thermal water						
1	Groundwater	LLD	LLD	≤5	≤20	2 m
2	Groundwater	0.68	2.73	8.70	≤20	3 m
3	Groundwater	≤0.50	1.60	10.1	≤20	6 m
4	Groundwater	≤0.50	LLD	13.7	≤20	38 m
5	Groundwater	3.66	18.6	16.5	≤20	157 m
6	Artesian aquifer	8.95	14.8	29.2	≤20	uk[a]
Stream water						
1	Stream water	≤0.50	1.71	≤5	≤20	Surface
2	Stream water	1.89	7.82	≤5	≤20	Surface
3	Stream water	1.76	3.34	≤5	≤20	Surface
Bottled water						
1	Alba	0.77	2.38	202	115	–
2	Aquafina	≤0.50	3.86	≤5	≤20	–
3	Danisa	≤0.50	LLD	≤5	≤20	–
4	Ion-lite	≤0.50	1.42	6.40	40.3	–
5	Lavie	≤0.50	1.19	≤5	≤20	–
6	Wow-luxury	≤0.50	≤0.50	≤5	≤20	–
7	Hanoi water	≤0.50	3.40	18.3	≤20	–
8	Vinh Dong	≤0.50	≤0.50	16.0	29.8	–

[a]Unknown

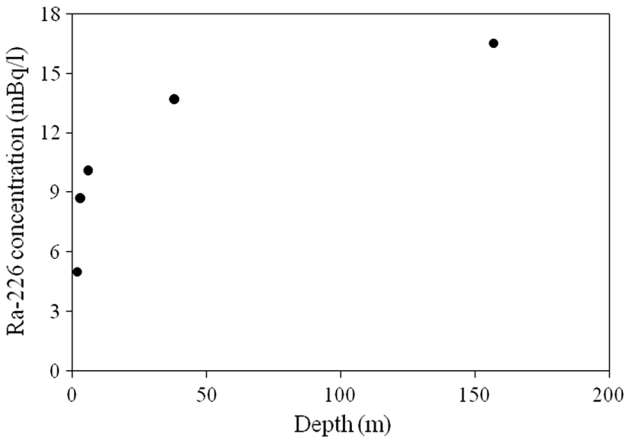

Fig. 2 The correlation between ^{226}Ra concentrations in thermal water with depth

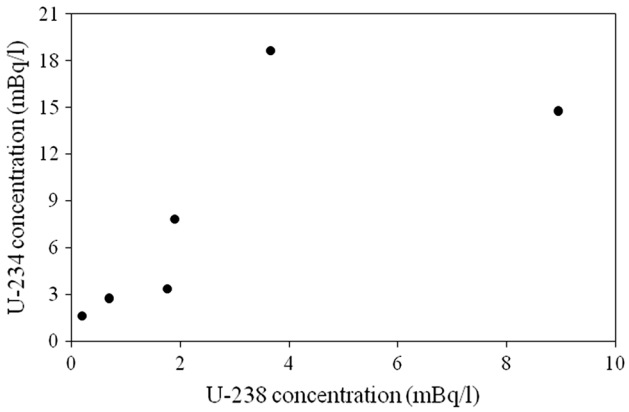

Fig. 3 The relation between ^{234}U and ^{238}U concentrations

Conclusions

The ^{238}U, ^{234}U, ^{226}Ra, and ^{226}Ra activities of studied samples from Kim Boi, Hoa Binh, Vietnam, vary from LLD to few tens mBq/L. The observed increase of radium isotope concentration in thermal water with depth reservoir is evidence of interaction between water and rock. The low concentration of radium and uranium in the water is showing: (1) connection with limestone reservoir formation, which is prevailing in the studied region; and (2) there is no radiological hazard resulting from the use of the studied water for drinking, medical treatment and tourism activities as well as for diet, and industrial and agricultural applications.

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