UDC 628.1.033:543.06
66.061.34:546.791
APTEFF, 36, 1-266 (2005)
BIBLID: 1450–7188 (2005) 36, 135-141
Original scientific paper

DETERMINATION OF INORGANIC COMPOUNDS IN DRINKING WATER ON THE BASIS OF HOUSEHOLD WATER HEATER SCALE

Part 2. Application of fractional extraction method for the determination of uranium origin

Miloš B. Rajković, Mirjana D. Stojanović,
Gordana K. Pantelić and Dragan V. Tošković

The concept of fractional extraction from sediment – in our analyses it is scale, is based on the assumption that uranium with a solid substance can form bonds of different strength and that these bonds can be gradually fractionated by the action of reagents of increasing dissolving power, whereby the separated phases of extraction are defined according to their function or the type of bond in that substance.

The advantage of this analytical procedure is that it enables simultaneous observing of different forms of uranium emergence in sediment (solid substance), which cannot be achieved by using individual extraction methods.

Using the method of fractional analysis, it has been found that uranium is mostly connected with mobile fraction – manganese and iron oxides (94.20 and 87.96 wt.%) which represents the fraction that is potentially accessible to human organism.

KEYWORDS: Household water heater scale; fractional extraction method; uranium; strontium; drinking water

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Dr. Miloš B. Rajković, Assoc. Prof., Institute of Food Technology and Biochemistry, Faculty of Agriculture, 11080 Belgrade-Zemun, Nemanjina 6, P.O.Box 14, e-mail: rajmi@agrifaculty.bg.ac.yu; Dr. Mirjana D. Stojanović, Head of System Quality and Characterization Laboratory, Institute for Technology of Nuclear and Other Mineral Raw Materials (ITNMS), 11000 Belgrade, 86 Franchet d'Esperey, P.O.Box 390; Gordana K. Pantelić, M.Sc., Research Associate, Section Head of Radiology, KCS Institute of Occupational and Radiological Health "Dr Dragomir Karajović", Belgrade, Serbia and Montenegro; Dr. Dragan V. Tošković, Assoc. Prof., Faculty of Technology, University of Serbian Sarajevo, 76000 Zvornik, Karakaj b.b., Republic of Srpska, Bosnia and Herzegovina

INTRODUCTION

The concept of fractional extraction from sediment is based on the opinion that uranium with a solid substance can form bonds of different strength and that these bonds can be gradually fractionated by reagents of increasing dissolving power, the separated extraction phases being defined according to their function or the type of bond in that substance (1).

The advantage of this analytical procedure is that it enables simultaneous observing of different forms of a metal (in our case of uranium) included in the sediment (solid substance), which cannot be achieved by using individual extraction methods.

Tessier et al. (2) were among the first to establish the systematized model of fraction extraction, which stems from the hypothesis that in solid phase (soil), as well as in sediments, according to their relation, under the influence of different ecological factors, there exist the following fractions of metals:

1. **Water soluble and exchangeable adsorbed metals**. The quantity of metals in this fraction is defined by the processes of adsorbtion-desorption, according to the law of matter action (establishing a balance between ions of different charge in the soil (sediment) and the solution). This fraction is extracted with 1 mol/dm^3 magnesium chloride in a neutral medium (pH = 7.0);
2. **Specifically adsorbed metals and metals bound to carbonates**. The content of metals in this fraction largely depends on the pH value of the solid substance – sediment. This fraction is obtained with 1 mol/dm^3 sodium acetate at pH 5.0;
3. **Metals occluded on manganese and iron oxides**. The fraction of occluded metals is under the influence of chemical (Eh potential) changes, that is, thermodynamically unstable in anaerobic conditions. The determination is performed with $NH_2OH{\cdot}HCl$, concentration 0.04 mol/dm^3 in 25 vol.% acetic acid at a pH of about 3.0, at the temperature of 96±3°C;
4. **Metals bound to organic matter**. The oxidation conditions lead to higher mineralization of organic matter, releasing thus the soluble metal forms. The determination is performed by the extraction with HNO_3, concentracion 0.02 mol/dm^3 and 30 wt.% H_2O_2, at a pH 2.0 and at a temperature of 85±2°C;
5. **Metals structurally bound in silicates**. This fraction represents the part of metal content which has the strongest bonds in the sediment, and under conditions that normally exist in sediment it is not expected to be released. This fraction is obtained by the destruction in a mixture of acids HF and $HClO_4$.

The analytical method of fractional extraction has a multiple application: in the analysis of possible contamination of soil with heavy metals (3,4), analysis of metal conduction in the soil (sediment) when using waste sludge (5), in the analysis of natural forms of metals in soil, that is, their mobility and fixation ability (6-8), etc.

In all above cases, this method gives a possibility of better understanding of chemistry of heavy metals in soil, and the main aim is the most complete realization of its accessibility for plants.

Tessier at al. (1) determined that:

1. high concentrations of heavy metals connected to manganese and iron oxides, as well to organic matter, clearly indicate that these compounds have great affinity to heavy metals. As metals from these fractions represent an important source of potentially accessible forms, their occurrence must be taken into account, especially in the assessment of certain metals;

2. high relative ratio of heavy metals in the residual fraction, that is, high level of primary and secondary minerals in crystal structures, clearly indicates the impossibility of exact determination of its origin (natural or artificial) by determining only their total contents.

Fractional extraction was first applied to the determination of uranium origin in different soils and in barren soil of Kalna mine (9). The results obtained confirmed the presumption of its origin.

The analysis of the scale originated from drinking water in the house water heater showed the presence of heavy metals including also uranium (10-15) in the amounts that are not alarming, but on a long run the drinking of such water can affect human health (16).

The aim of this paper was a qualitative analysis of different forms of uranium, using fractional extraction method, to determine its origin in drinking water.

EXPERIMENTAL

Two samples of scale, formed by precipitation on water heater surface during a time period of 6 months, have been used for this experiment. The scale originated from the water present in the water-supply system of the city of Belgrade - Upper Town of Zemun (sample 1) and town of Pančevo-Krnjača (sample 2). Content of total solids, which actually represents the scale, was determined by heating 1.0 dm^3 of drinking water to boiling and evaporating it to obtain dry residue.

Composition of the scale was determined on an AAS Perkin Elmer 703 atomic absorption spectrophotometer, according to the methods DM 10-0/4, 0/6, 0/7, 0/8, 0/9, 0/10, 0/11, 0/12, 0/13 and 0/17.

Quantitative content of uranium was assayed by fluorometric method based on linear dependence of the fluorescence intensity of the uranium solutions on their concentration. Linear dependence exists in a very large range of low concentrations (to the power of four). Reduction of the fluorescence intensity is brought to the least possible amount by the technique of ”standard addition” after the extraction of uranium with the synergistic mixture of TOPO (tri-*n*-octal phosphine oxide) and ethyl acetate. Fluorescence intensity was determined on a Jarrel Ash Division Fluorimeter 26-000 (Fisher Scientific Company, Waltham).

Fractional extraction is based on the theory that metals with solid phase form bonds of different strength (17) which can be gradually fractionated by the reagents of increasing dissolving power (2).

It should be emphasized that resources for fractional analysis are not standardized, so it cannot be claimed with absolute certainty that some forms of uranium really exist in the scale. The basic criterion for the evaluation of its accessibility is statistic correlations.

RESULTS AND DISCUSSION

The results of the analysis of scale samples on the presence of heavy metals and radioactive elements of uranium and strontium (18), based on the triple measurements, are shown in Table 1.

Table 1. Uranium and strontium contents in the scale samples

Samples	**Uranium (in ppm)**	**Strontium (in wt. %)**
sample 1	1.38 ± 0.03	0.05 ± 0.0001
sample 2	1.11 ± 0.02	–

The content of strontium in the first sample (sample 1) is relatively high, reflecting the presence of strontium in drinking water. In the second sample, the presence of strontium was confirmed and determined only by the special method for chemical separation of strontium (isotope ^{90}Sr) (19), which gave the measured activity of 0.72±0.11 Bq/kg.

Depending on the origin of uranium, it can be accessible to a higher or lower degree. Uranium in the scale originating from geochemical sources is in less accessible forms (carbonates, oxides, phosphates, sulphides, and silicates) (17). On the other hand, uranium which comes to water through different anthropogenic activities, most often in such forms (exchangeable in the soil solution and specifically adsorbed) from which it is more accessible to living organisms. According to the regulations (20) the content of uranium in drinking water is limited to 0.05 mg/dm^3, which remains as a maximum allowed concentration in drinking water during the state of emergency (21).

As uranium present in scale can be of natural but also of artificial origin, the aim of this paper was to determine its origin using the method of fractional extraction.

The results of the fractional extraction method, on the basis of triple measurements in the scale are shown in Table 2.

Table 2. Content of uranium in household water heater scale obtained from drinking water

Fraction	**Scale**	**Sample 1**		**Sample 2**	
	Uranium	U, ppm	% from U_{total}^{*}	U, ppm	% from U_{total}^{*}
	Total uranium content in the scale	1.38	100	1.1	100
Fraction I	Water-soluble and measurably adsorbed	< 0.01	0.72	0.02	1.85
Fraction II	Specifically adsorbed and connected with carbonates	0.08	8.33	0.09	8.33
Fraction III	Connected with manganese and iron oxides	1.3	94.20	0.95	87.96
Fraction IV	Connected with organic matter	< 0.01	0.72	< 0.01	0.93
Fraction V	Structurally connected in silicates	< 0.01	0.72	< 0.01	0.93

* Content, in %, individual fractions of total uranium content in the scale

It can be seen that the largest part of uranium is in the third fraction, which clearly indicates that such solutions have great affinity towards uranium, and also suggests its antropogenic origin. As manganese and iron represent the important source of potentially available forms, this must be taken into account, especially in the estimation of uranium bioavailability.

The mass concentration of iron (as Fe_2O_3) in drinking water (0.54 (sample 1) and 5.62 mg/dm^3 (sample 2)) and manganese (as MnO), (0.06 (sample 1) and 0.05 mg/dm^3 (sample 2)) (18), does not mean that the content of absorbed uranium is very low, but that it is not to be underestimated.

As there is a relative high portion of uranium in the residual fraction, i.e. in the crystal structures of primary and secondary minerals it is clear that a correct identification of its origin (natural or artificial) is not possible on the basis of determining only its total content.

The obtained results clearly indicate that uranium in water is of anthropogenic origin, which is in agreement with the to literature data (7,9).

CONCLUSIONS

The analysis of the household water heater scale taken from waterworks of the city of Belgrade, showed the presence of heavy metals and of radioactive elements uranium (isotope ^{238}U) and strontium (isotope ^{90}Sr). Unlike strontium (which is an α-emitter), whose presence is not such to affect substantially the health of drinking water consumers, uranium is more dangerous because of its chemical toxicity in addition to its radioactivity.

The question is how much the amount of scale can influence increasing radioactivity of the space around the household water heater.

Using the method of fractional extraction, it is determined that uranium is mostly bound with potentially accessible and mobile fraction – manganese and iron oxides (94.20 and 87.96 wt.%), which represents the fraction that is potentially accesible to human organism.

The method of fractional extraction proved to be suitable for the determination of uranium origin in sediments, which could be very useful in some future analyses.

ACKNOWLEDGEMENTS

The work was supported by the Ministry of Science and Environmental Protection
of the Republic of Serbia (Grant No 1941).

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ОДРЕЂИВАЊЕ НЕОРГАНСКИХ ЈЕДИЊЕЊА У ВОДИ ЗА ПИЋЕ НА БАЗИ КАМЕНЦА

Део 2. Примена методе фракционе екстракције за утврђивање порекла урана у каменцу

Милош Б. Рајковић, Мирјана Д. Стојановић,
Гордана К. Пантелић и Драган В. Тошковић

Принцип фракционе екстракције из седимента, у случају наших испитивања каменца, заснива се на схватању да уран може да формира са чврстом супстанцом везе различите јачине и да те везе могу бити поступно раскинуте, деловањем реагенаса растуће јачине, при чему се појединачне фазе екстракције дефинишу на основу њихове функције или облика везаности у тој супстанци.

Предност овог аналитичког поступка је у томе што омогућава истовремено сагледавање различитих облика појављивања урана у седименту (чврстој супстанци), што се не може постићи применом појединачних екстракционих метода.

Методом фракционе екстракције, примењеном у овом раду, утврђено је да је уран највише везан за потенцијално-приступачну и мобилну фракцију – оксиде гвожђа и мангана (94,20 одн. 87,96%), што представља фракцију која је потенцијално приступачна људском организму.

Received 3 September 2004
Accepted 20 June 2005