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NATURAL RADIONUCLIDES IN UNDERGROUND WATER IN UKRAINE

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ABSTRACT. Ukrainian national radiation regulations for potable underground water establish the following maximum values: natural uranium at 1.0 Bq/L; ^{226}Ra at 1.0 Bq/L; ^{228}Ra at 1.0 Bq/L; and radon at 100.0 Bq/L. We use liquid scintillation counting (LSC)-based technology for monitoring natural radionuclides in underground water. The current routine sample analysis procedure includes 10 mL of water and 10 mL of a water-immiscible, toluene-based cocktail for radon measurement, tributyl phosphate (TBP) in toluene extraction of natural uranium from a 1-L sample, preconcentration and a water-immiscible, toluene-based cocktail for ^{226}Ra by radon measurement in Teflon® vials after 7–10 days of equilibration. Preconcentration and LSC using OptiPhase HiSafe® 3 after 1 day is used for total alpha and total beta measurement. ^{228}Ra measurement in water is performed in case of elevated ^{226}Ra levels or when an unknown beta activity is present. The ^{228}Ra testing procedure includes gamma spectroscopy or coprecipitation from a 1- to 2-L sample and ^{228}Ac measurement by LSC using OptiPhase HiSafe 3. ^{210}Po and ^{210}Pb were found in some waters when high levels of uranium and/or ^{226}Ra were present. Details of spatial distribution of water radioactivity are described.

INTRODUCTION

We have performed analyses of natural radionuclides in water since 1988, when we installed a liquid scintillation (LS) spectrometer, Quantulus™ 1220. Initially, we followed the Salonen (1988, 1989) approach: 20–50 mL of water was preconcentrated to 2–4 mL, put into a Teflon® vial and OptiPhase HiSafe® 3 (PerkinElmer Inc.) was added. Two measurements are required, following 1 day and 30 days after preparation, respectively. The counting time was 3 hr. In the second measurement, ^{214}Po could be seen as separate peak corresponding to ^{226}Ra (as in equilibrium), and the unresolved alpha peak comprises ^{226}Ra (in equilibrium with ^{222}Rn and ^{218}Po) and total uranium. Thus, we could resolve ^{226}Ra and uranium. In total, we made statistical estimations for more than 500 samples collected in various regions of Ukraine (Zelensky et al. 1993).

We also take into account the high values of ^{234}U/^{238}U isotope ratios observed for 100 samples of underground water collected within Ukraine using precise measurements based on ICP-MS (Shiraishi et al. 1994). The Ukrainian Radiation Safety Regulation appeared in 1997 (NRBU-97) and set guidelines for radionuclides in water from drilled wells. The upper limits of activity concentrations are ^{222}Rn at 100 Bq/L, ^{226}Ra at 1.0 Bq/L, ^{228}Ra at 1.0 Bq/L, and total U at 1.0 Bq/L. When starting commercial measurements, we understood that the applicability of selective and highly sensitive methods for measuring the respective radionuclides is very important.

METHODS

For ^{222}Rn, we measured a 10:10 mL mixture of water sample and toluene-based cocktail, while our U measurement was based on tributyl phosphate (TBP) extraction and liquid scintillation counting (LSC). For ^{226}Ra, a 100–200 mL sample was preconcentrated to 10 mL and we measured ^{222}Rn that had grown in during 7–10 d (72–84%) in a toluene-based cocktail and Teflon vial. The total duration of sample analysis is 8–12 d. Only in cases where we found elevated levels of ^{222}Rn, uranium, or ^{226}Ra would we perform additional measurements of ^{228}Ra, ^{210}Pb, and ^{210}Po.

Uranium. For us, uranium isotopes were the most important nuclides to be analyzed. We used 1–2 L of water and performed a hydroxide precipitation followed by TBP extraction and LSC. These are

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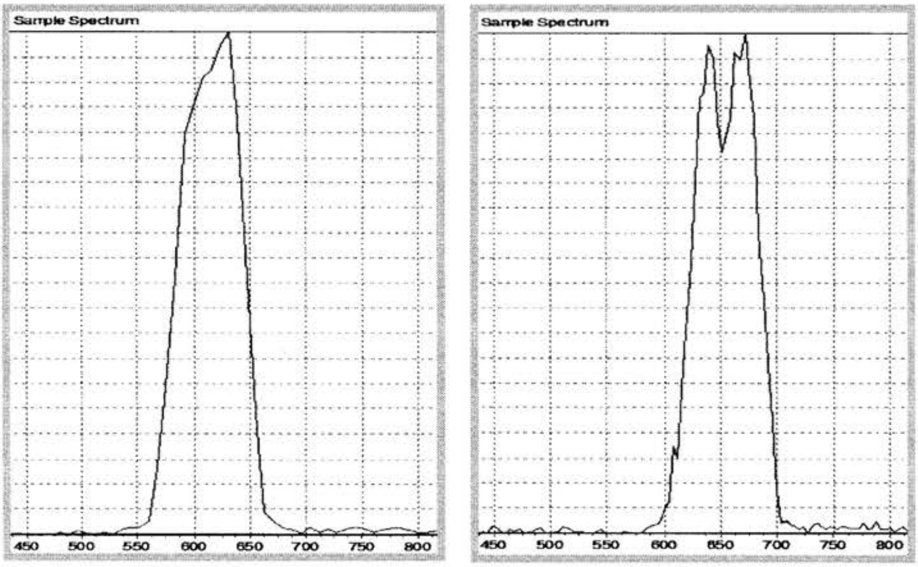
the steps in detail: water + 4 mL $FeCl_3$ (10 mg/mL Fe^{3+}) + 4 mL HNO_3 > heat and boil to remove CO_2 + ammonium hydroxide to pH 9 + wait for precipitation for 2 hr > filtration under vacuum > dissolution adding 40 mL 6M HNO_3 > add 10 mL 20% TBP in toluene for extraction + neutralization by adding ammonium nitrate (20 mL 6M NH_4NO_3) + bubbling with argon + toluene-based scintillation cocktail > LS counting. Special attention should be paid to the sample neutralization procedure after extraction and the argon bubbling, both resulting in a better spectrum resolution. The effect of argon bubbling is obvious (see Figure 1). Sample spectra could be decomposed for ^{238}U and ^{234}U. We had a 65 ± 3% chemical yield (checked systematically) and additionally we made a correction for the loss of extracting agent that is individually determined for each sample, depending of the amount of soluble matter in the water.



a)

b)

Figure 1 Uranium spectra: a) conventional spectrum and b) high-resolution spectrum when argon bubbling is used during sample preparation.

Ra and Rn. We actually measured ^{222}Rn when determining both ^{222}Rn and ^{226}Ra. We did not wait for ^{214}Po accumulation when we measured radon, i.e. we already measured 10 min after sample preparation using ^{222}Rn and ^{218}Po in equilibrium with ^{222}Rn counting rate for calculation. We used plastic vials. Next, a sample of 100–200 mL water was preconcentrated to 10 mL for ^{226}Ra measurement. The radium sample is equilibrated in a Teflon vial over 7–10 d and then measured. Calculations were performed taking into account ^{222}Rn, ^{218}Po, and ^{214}Po and the equilibration level.

^{228}Ra and ^{224}Ra determination is performed by HPG gamma spectroscopy in a 1-L water sample after ^{222}Rn is removed by air bubbling (^{228}Ra using 911 keV, MDA = 0.05 Bq/L; ^{224}Ra by ^{212}Bi at 727 keV; MDA = 0.3 Bq/L; both for 12-hr counting). Measurement of total alpha activity and total beta activity was performed using a 50-mL water sample preconcentrated to 4 mL and LSC using OptiPhase HiSafe 3 and a Teflon vial after 1 day. These methods were used as a check for any unexpected nuclides.

^{210}Po and ^{210}Pb. We adopted for LS counting the method based on thermostimulated deposition onto metal disks (Buzinny 2009), described by Bakhur et al. (2009). It allows the simultaneous measure-

ment of 2 radionuclides: ^{210}Po and ^{210}Pb by ^{210}Bi. Both Teflon and plastic vials are applied. The preliminary sample preparation for water includes precipitation and storage for equilibration ^{210}Pb to ^{210}Bi; 1–2 mL of HCl is added to 1 L of water sample and boiled for 20 min. Then, 25 mg of Fe (FeCl) is added and precipitated using a 25% ammonia solution under a condition of pH 8–9. The precipitate is dissolved in a minimal volume of HCl (1:4). The solution is then evaporated until dry on a sand bath. Drops of HCl solution are added to the precipitate and evaporation is repeated. The glass container is covered and stored for 25 d for equilibration. After equilibration, the dry residue is processed with 2 mL of HCl. Then, 50 mL of distilled water is added and heated. The metal disk target is placed in a vertical position by a Teflon holder into a glass container with 50 mL of liquid sample (Figure 1). The glass container is then placed onto an electric plate and heated for 2 hr. Some hot distilled water is periodically added to the sample solution to keep a stable volume. We use small-diameter disks that fit into the vial. After deposition, the metal disk is washed by distilled water and then dried. Finally, the target is fixed by metal clips into an LS vial and filled with LS cocktail. To allow reuse of the metal disk, it is boiled in 0.5M HNO_3 for 1 hr.

INTERCOMPARISON

From the IAEA World Wide Open Proficiency Test results, we learned that we systematically overestimated the counting efficiency and the background for our ^{210}Po measurement in water samples, see Table 1 (WWOPT 2007).

Table 1 Lab results of ^{210}Po activity measurements in water samples (Bq/L) in the framework of IAEA-CU-2007-09 World Wide Opened Proficiency Test (IAEA 2007).

Sample	Target value	Lab value	Precision	Acceptance
1	52.8 ± 1.4	43.0 ± 5.4	Yes	Yes[a]
2	101.6 ± 2.8	75.8 ± 7.9	Yes	No[a]
3	52.8 ± 1.4	42.2 ± 5.3	Yes	Yes[a]
4	101.6 ± 2.8	82.9 ± 8.9	Yes	Yes[a]
5	0.1 ± 0.01	0.41 ± 0.06		No[b]

[a] Systematic shift (overestimation of counting efficiency).

[b] Overestimated background because of radon in toluene.

An intercomparison of natural radionuclides measured in water (2007) showed corresponding results with the laboratory of the Swedish Radiation Regulatory Authority, when measuring uranium, ^{226}Ra, ^{210}Po, and ^{210}Pb in natural and spiked samples prepared in both labs (Buzinny et al. 2007).

A recent intercomparison for ^{222}Rn, uranium, ^{226}Ra, ^{210}Pb, and ^{210}Po measurements in 5 Ukrainian laboratories using natural water samples (Los' et al. 2008) showed good agreement for ^{222}Rn and uranium measurement (Table 2). Agreement for ^{210}Pb results is achievable on a second stage for HCl-stabilized samples. ^{226}Ra and ^{210}Po results show high uncertainty and irreproducibility; therefore, a standardization of the applied methods will be necessary.

RESULTS

Most drinking waters measured in recent years were sampled from 4 regions: Kiev, Zhytomyr, Vinnitsa, and Chernihiv (Table 3). The first 3 of these regions belong to the Ukrainian Crystalline shield, thus showing higher U and Rn values. Smaller numbers of samples analyzed from 4 other regions gave only weak statistics (see Table 3).

Table 2 Comparison of radionuclide concentrations in water samples measured by Ukrainian laboratories (2008), in Bq/L.

	^{222}Rn			Uranium			^{210}Pb		
Sample	Average	SD	%	Average	SD	%	Average	SD	%
1	1000	104	10%	0.71	0.09	12%	5.00	0.82	16%
2	470	33	7%	0.15	0.05	18%			
3	360	14	4%	3.54	0.27	8%			
4	1190	181	15%	1.55	0.09	6%	0.75	0.11	14%
5	420	54	13%	2.84	0.09	3%			

Table 3 Radionuclide data (Bq/L) measured in water supply systems based on drilled wells.

		^{222}Rn				^{226}Ra				Uranium			
Region	N	Avg	SD	Min	Max	Avg	SD	Min	Max	Avg	SD	Min	Max
Kiev	178	24.3	82.3	0.3	705	0.04	0.10	0.001	0.81	0.12	0.40	0.002	3.7
Zhytomyr	123	60.5	83.1	0.9	500	0.32	0.71	0.004	3.64	0.27	0.81	0.002	8.1
Vinnytsa	75	21.1	21.3	0.7	105	0.02	0.02	0.003	0.12	0.43	1.82	0.009	15.3
Chernihiv	27	3.2	2.3	1.0	12	0.02	0.01	0.001	0.05	0.03	0.05	0.002	0.21
Zaporizhzha	23	7.7	8.3	0.5	29	0.12	0.32	0.01	1.42	0.04	0.08	0.004	0.3
Luhansk	20	9.3	15.5	1.0	62	0.02	0.04	0.003	0.2	0.09	0.13	0.003	0.42
Mykolaiv	18	4.4	2.3	0.5	8	0.02	0.02	0.007	0.09	0.04	0.04	0.003	0.15
Poltava	13	9.1	7.9	1.3	25	0.05	0.05	0.010	0.22	0.01	0.01	0.004	0.02

DISCUSSION

When analyzing the origin of higher levels of natural radionuclides in water, it is clear that higher levels are linked to the initial high-level source (rock, crack, and water chemistry), to inactive to highly active water, or to a violation of the treatment system. Recently, we suggested as applicable different approaches for the national limitation of radionuclide concentrations in bottled water, namely for sources of surface water: 0.1 Bq/L for total alpha activity and 1.0 Bq/L for total beta activity; and for groundwater sources: 1.0 Bq/L for ^{226}Ra, ^{228}Ra, and total uranium activity, and 100 Bq/L for ^{222}Rn; according to the possibility of their implementation.

The most interesting result is an example of systematic remediation undertaken over 20 yr in the Myronivka District (Kiev region) under the control of the sanitary station. Water sources were switched between deep-drilled wells (depth ~100 m) to other, shallower ones (depth ~20–50 m). The change in activity concentration levels is obvious: ^{222}Rn 300–1000 Bq/L, now below 100 Bq/L; ^{226}Ra 0.5–10.0 Bq/L, now below 1.0 Bq/L; uranium 0.5–10.0 Bq/L, now below 1.0 Bq/L. We did not see any exceeding of health standards for all radionuclides in all sources after remediation.

Prospects for future work include the measurement of natural radioactivity in water, public information provisions, propagation of modern analytical equipment, and development and adaptation of measurement methods to cover problems of water purification throughout the state. Our contribution will organize information support for the population and other laboratories via the Web site http://safewater.narod.ru, as well as to provide information on development and adaptation of measurement methods, training of personnel, and establish an intercomparison of results.

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