

NATURAL RADIONUCLIDES IN UNDERGROUND WATER IN UKRAINE

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Uranium isotope ratio $^{234}/_{238}$

Ca. 100 samples of Ukrainian water was examined for uranium $^{234}/_{238}$ isotope ratio during 1992-1993 using ICP MS technique. It shows most values exceeding **5.0** and even **30.0 and 43.0** for some of the samples.

Application of calorimetric or luminescence methods for analyzing U-alphas on base of (^{238}U) – under-estimation of the total activity of uranium is of 2.0 to 10-15 times.

K. Shiraishi, Y. Igarashi, Y. Yamamoto, T. Nakajima, I.P. Los, A.V.Zelensky and M.G. Buzinny. Concentration Of Thorium And Uranium in Freshwater Samples Collected In Former USSR. Journal of Radioanalytical and Nuclear Chemistry, Articles, Vol.185, N.1 (1994)157-165.

Measurement approach

Since 1988, when we get Quantulus, we studied natural radioactivity of underground water following Salonen i.e. 30 day for each sample.

LSC-92 : Zelensky A.V., Buzinny M.G., Los' I.P. Measurement of Radium-226, Radon-222, and Uranium-238, 234 in Underground Water of the Ukraine with Ultra Low-Level Liquid Scintillation Counter. In Liquid Scintillation Spectrometry 92. Proc. of Int. Conf. on Advances in LSC, LSC 1992. Vienna, Austria, 14-18, 1992. Eds. J.E. Noakes, Franz Schönhofer & H.A. Polach. Radiocarbon. Tucson 1993, pp. 405-411.

After a while (since 1997) for routine analyses we use **uranium after TBP extraction**, **Rn-222** by its extraction in toluene, **Ra-226** by Rn extraction in toluene, using pre-concentrated (100-200 ml) samples in Teflon vial after 7-10 day equilibration (72%-84%).

In case we find elevated levels of **Rn-222**, **U**, **Ra-226** we do measurements of **Ra-228**, **Pb-210** and **Po-210**.

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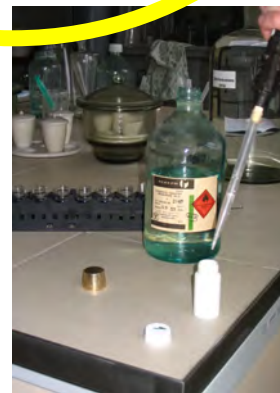
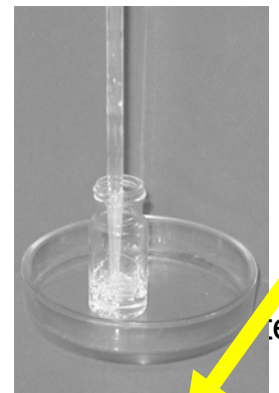
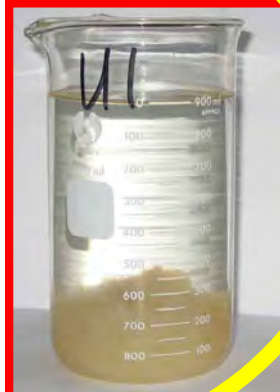
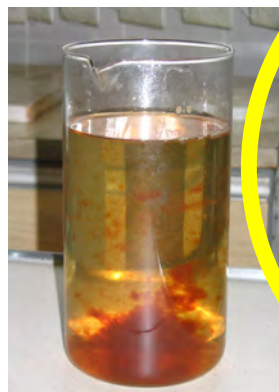
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Trace of sample in lab today: U-analyze



Water + FeCl + HNO₃ > Heat (boiling) + ammonium hydroxide +
wait for precipitation > filtrate > solubilize > TBP in toluene
extraction + neutralization by adding ammonium nitrate + bubling +
toluene based scintillator > **counting**

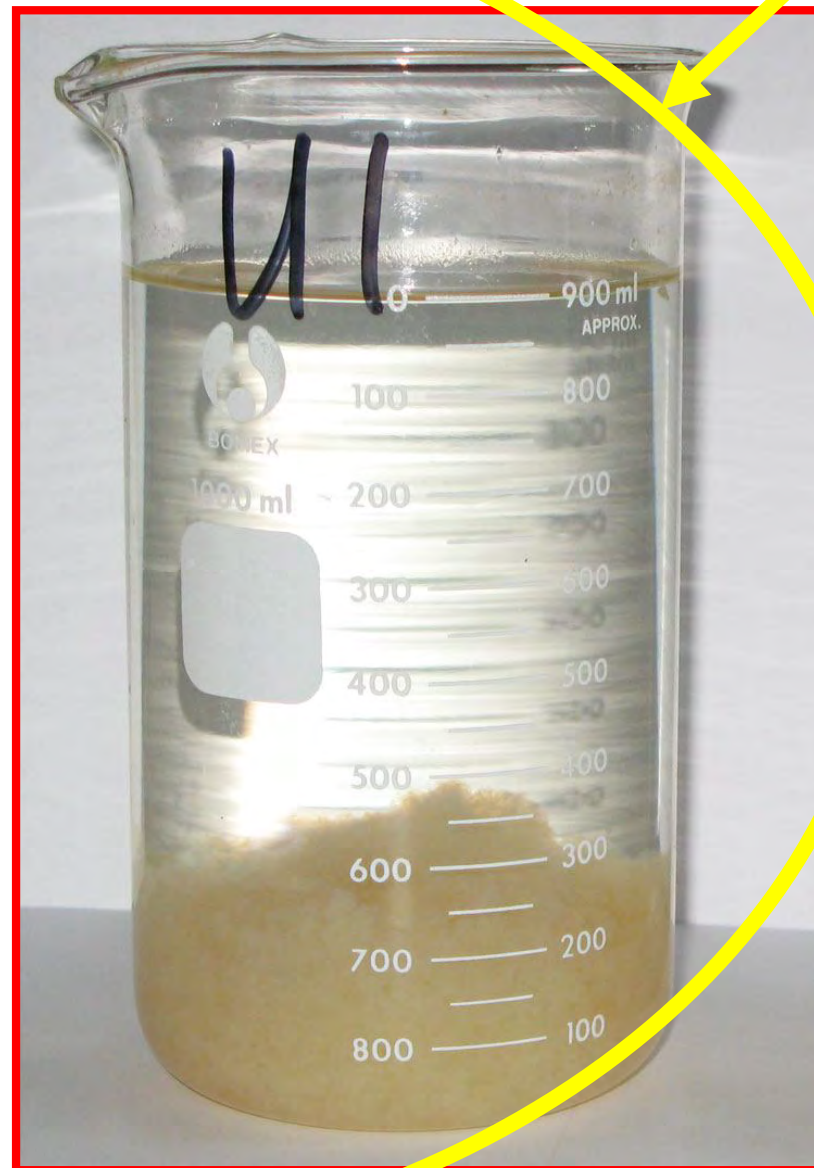


Conventional sample



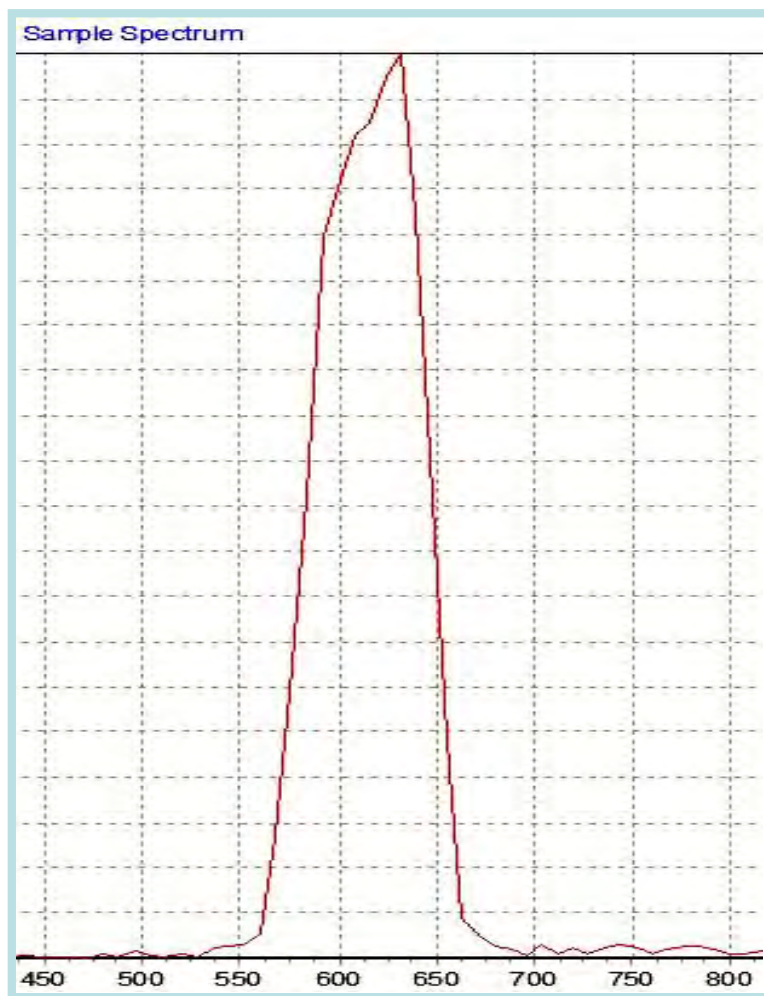
LSC-2010, Paris

Rare sample (1%)

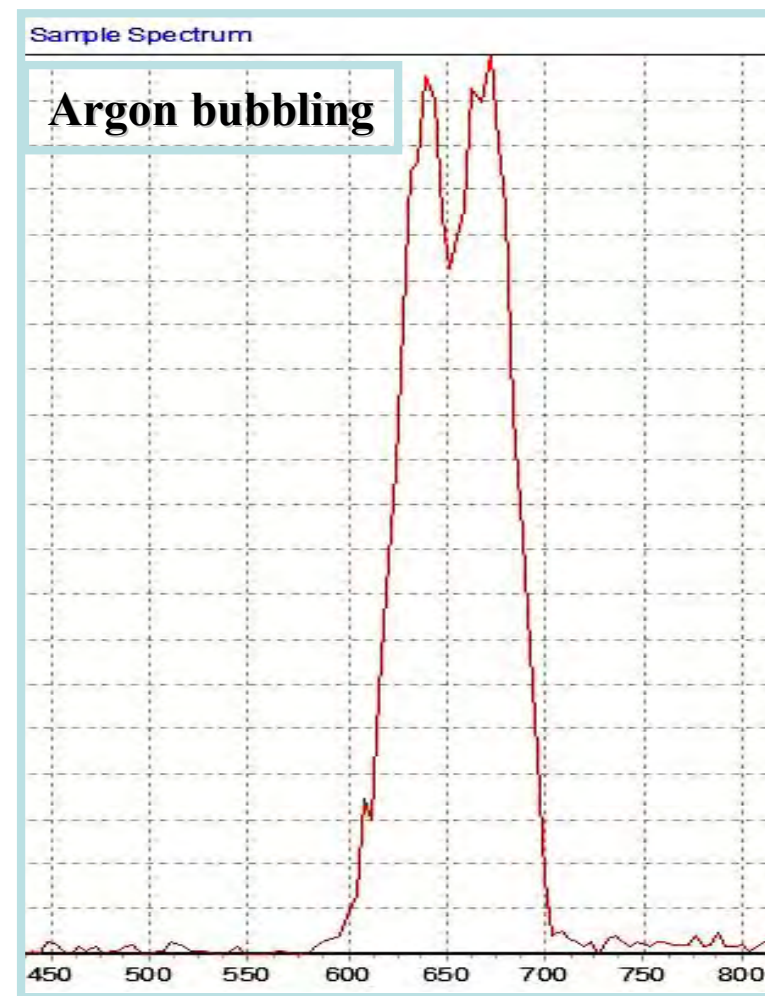


6-10 September, 2010

U spectra in toluene based cocktail measured in Teflon vial



a) Conventional spectrum of Uranium



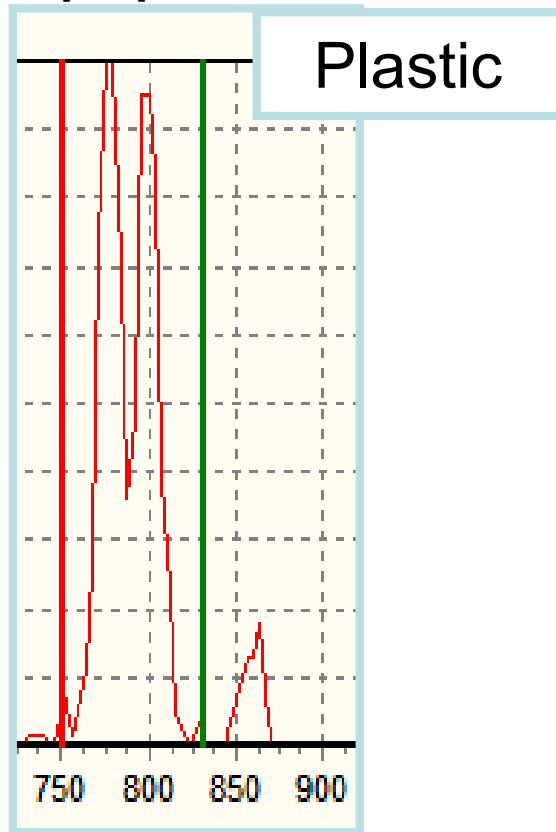
b) High resolution spectrum of Uranium

^{222}Rn & $^{226}\text{Ra}(^{222}\text{Rn})$ measurement

(10 ml water (solution) + 10 ml toluene based LS cocktail)

$^{222}\text{Rn} + ^{218}\text{Po}$

10+ minutes
after sample
preparation



LSC-2010, Paris

Solution:

Preconcentration of
100-200 ml !!!!!

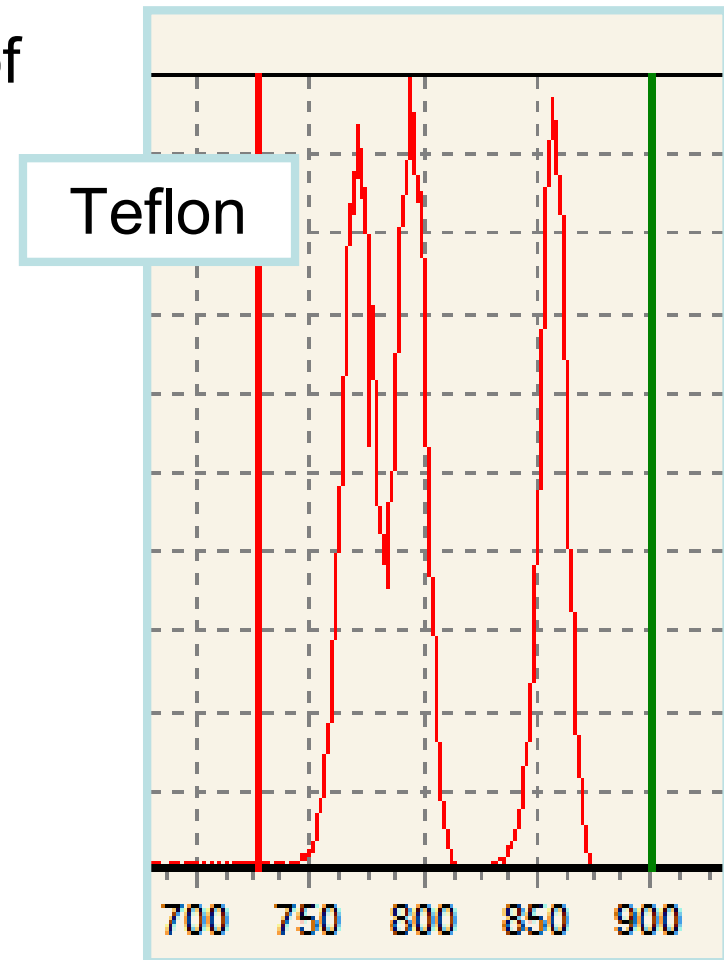
^{222}Rn growth

7-10 days

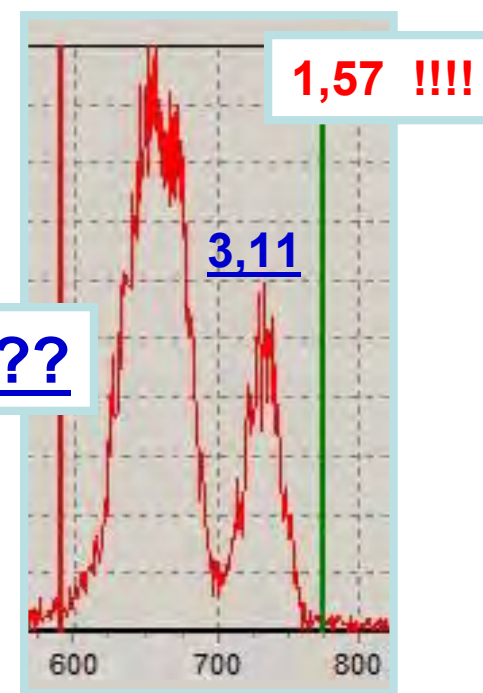
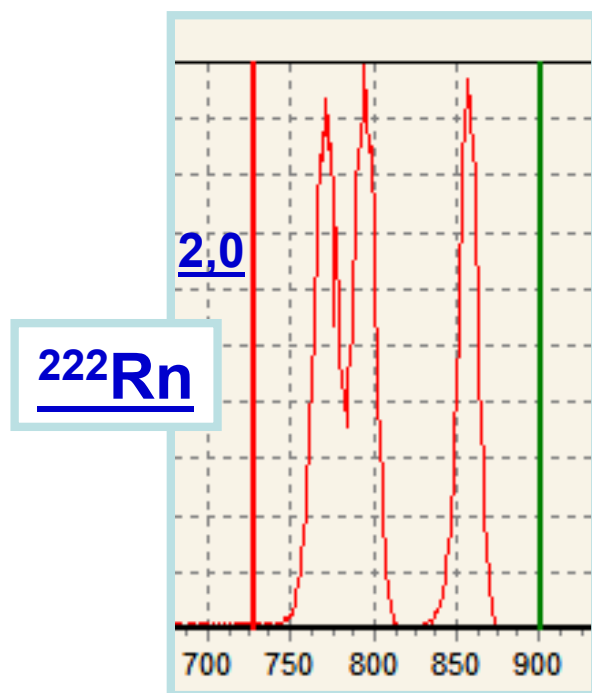
or

72% to 84%

$^{222}\text{Rn} + ^{218}\text{Po} + ^{218}\text{Po}$



6-10 September, 2010



| Sample | | II | III | I | II/I | Eq | II | III | II III | | I | Over |
|-------------|-----------|--------------|--------------|-------------|-------------|--------------|-------------|-------------|-------------|---|-------------|-------------|
| S1.9 | 8 | 133,5 | 174 | 40,5 | 3,30 | 76,6% | 7,45 | 7,15 | 7,30 | | 4,41 | 1,66 |
| S2.9 | 8 | 72,5 | 96 | 23,5 | 3,09 | 76,6% | 4,05 | 3,94 | 3,99 | | 2,56 | 1,56 |
| S3.9 | 8 | 5,3 | 7 | 1,7 | 3,12 | 76,6% | 0,30 | 0,29 | 0,29 | | 0,19 | 1,58 |
| | | | | | | | | | | | | |
| <u>S1.9</u> | <u>10</u> | <u>144,7</u> | <u>191,3</u> | <u>46,6</u> | <u>3,11</u> | <u>83,7%</u> | <u>7,39</u> | <u>7,19</u> | <u>7,29</u> | - | <u>4,64</u> | <u>1,57</u> |
| S2.9 | 10 | 76,9 | 103,8 | 26,9 | 2,86 | 83,7% | 3,93 | 3,90 | 3,91 | | 2,68 | 1,46 |
| S3.9 | 10 | 5,45 | 6,94 | 1,49 | 3,66 | 83,7% | 0,28 | 0,26 | 0,27 | | 0,15 | 1,82 |
| <u>S4</u> | <u>4</u> | <u>25</u> | <u>31</u> | <u>6</u> | <u>4,17</u> | <u>51,6%</u> | <u>2,07</u> | <u>1,89</u> | <u>1,98</u> | - | <u>0,97</u> | <u>2,04</u> |

$^{210}\text{Pb}(\text{Bi}) + ^{210}\text{Po}$ on metal disk

Thermostimulated deposition onto metal disk

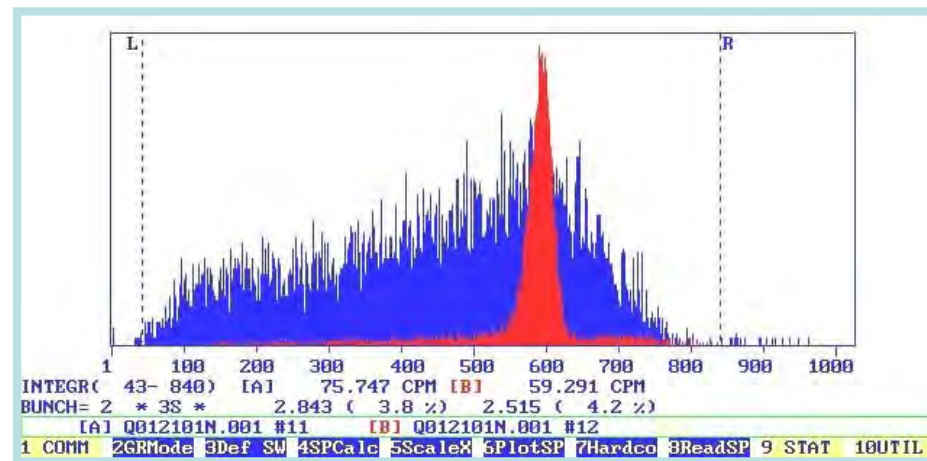


Measurement approach for LSC



A.E. Bakhur, L.I. Manuilova, T.M. Ovsjannikova. Po-210 and Pb-210 in environment. Methods of determination. ANRI. N.1. 2009. p. 29-39. (In Russian)

Buzinny M. Simultaneous determination of ^{210}Po and ^{210}Pb using LS technique. International Topical Conference on Po and Radioactive Pb isotopes. Sevilla, Spain, October, 26-28, 2009: Book of Abstract, 2009. – P. 45.



Intercomparison

Lab results of comparison ^{210}Po activity measurement in water samples (Bq/L) in frame 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 * |
| 2 | 101.6 ± 2.8 | 75.8 ± 7.9 | Yes | No * |
| 3 | 52.8 ± 1.4 | 42.2 ± 5.3 | Yes | Yes * |
| 4 | 101.6 ± 2.8 | 82.9 ± 8.9 | Yes | Yes * |
| 5 | $0,1 \pm 0.01$ | 0.41 ± 0.06 | | No ** |

* Systematic shift (overestimation of counting efficiency)

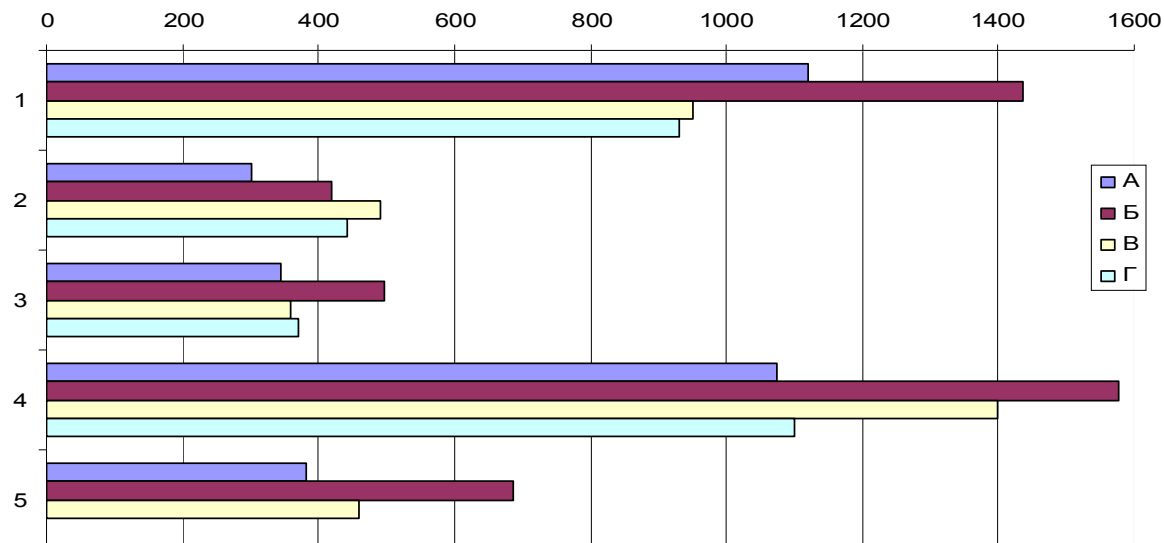
** Overestimated background because of radon in toluene

Intercomparison for uranium, radium and lead-210 in water samples

| IHME | | | | | | |
|------------------|---|------------------|---------------------|-------------------|---|-----------------|
| Sample \ Nuclide | Total alpha (beta) | U by TBP | Ra by Salonen 50 ml | Emanation 200 ml | Po/Bi placed on disk | Pb-210 by gamma |
| U | $0,65 \pm 0,07$ | $0,72 \pm 0,07$ | $<0,05$ | $<0,001$ | | |
| Drinking water: | $6,98 \pm 0,72$ | $5,25 \pm 0,73$ | $0,076 \pm 0,010$ | $0,078 \pm 0,007$ | $1,10 \pm 0,25$ $1,19 \pm 0,25$ | |
| Radium | $0,68 \pm 0,07$ | | $0,55 \pm 0,05$ | $0,64 \pm 0,08$ | $0,71 \pm 0,08$ $0,50 \pm 0,15$ | |
| Po-210 Pb-210 | $0,55 \pm 0,06$ | | $0,015$ | $<0,001$ | $0,54 \pm 0,09$ $0,57 \pm 0,09$ | $0,68 \pm 0,09$ |
| SSM | | | | | | |
| Sample \ Nuclide | Total alpha Total beta | U, Salonen | Ra-226 | | Po-210 Pb-210 | Pb-210 by gamma |
| U | | $0,76 \pm 0,007$ | $<0,05$ | | | |
| Drinking water: | $\alpha 7,51 \pm 0,08$ $\beta 5,81 \pm 0,06$ | $7,31 \pm 0,07$ | $0,2 \pm 0,002$ | | $\beta 2,35 \pm 0,02$ | |
| Radium | | | $0,52 \pm 0,005$ | | | |
| Po-210 Pb-210 | | | | | $\alpha 0,67 \pm 0,007$ $\beta 0,75 \pm 0,008$ | $0,71 \pm 0,1$ |

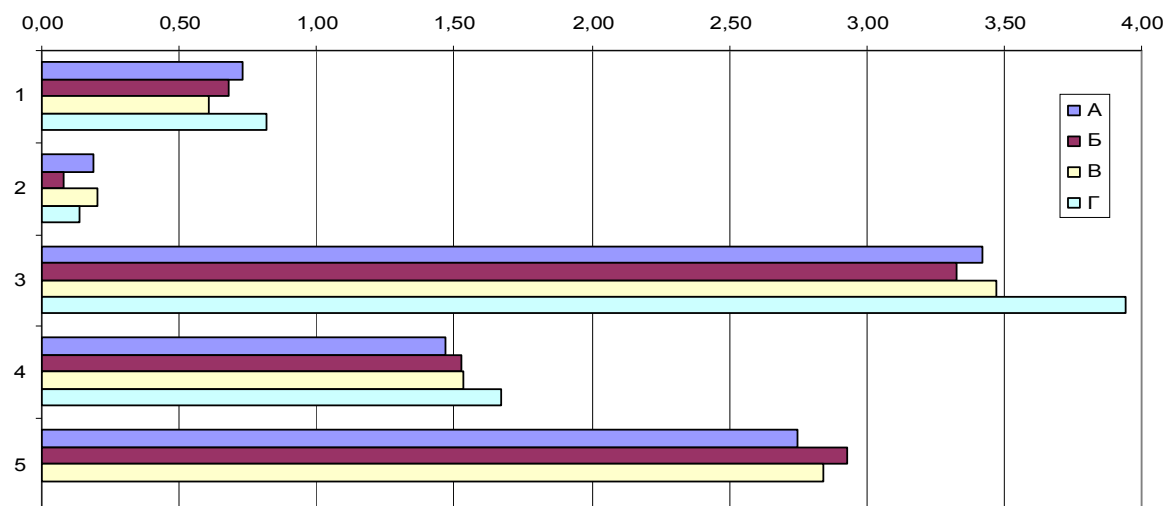
Lab Intercomparison for natural radionuclides in water

Radon



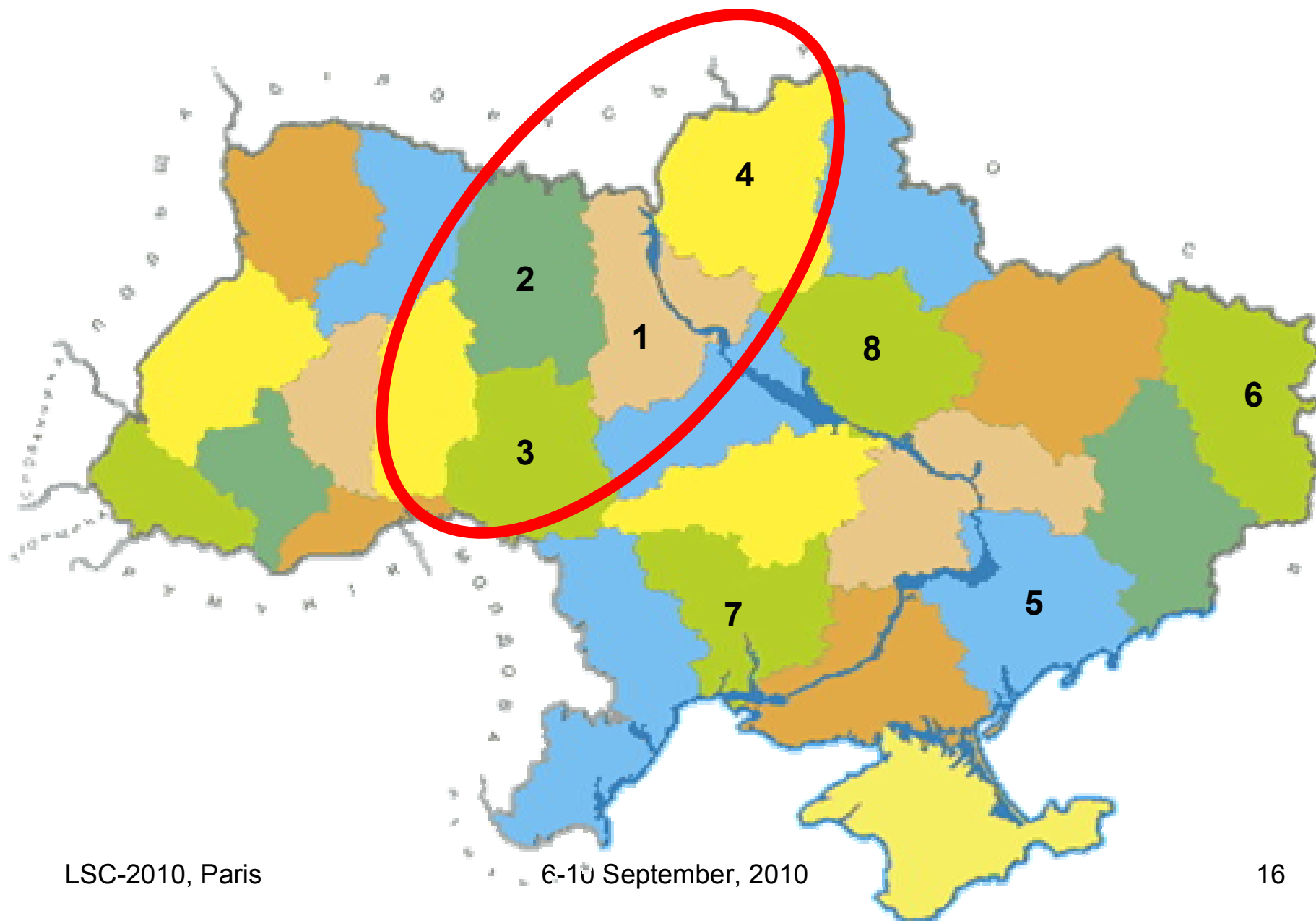
| Average | SD | % |
|---------|-----|-----|
| 1000 | 104 | 10% |
| 467 | 33 | 7% |
| 359 | 14 | 4% |
| 1191 | 181 | 15% |
| 422 | 54 | 13% |

Uranium



| Average | SD | % |
|---------|------|-----|
| 0,71 | 0,09 | 12% |
| 0,15 | 0,05 | 18% |
| 3,54 | 0,27 | 8% |
| 1,55 | 0,09 | 6% |
| 2,84 | 0,09 | 3% |





Data obtained

(drinking water)

| Region | N | Rn-222 | | | | Ra-226 | | | | Uranium | | | |
|---------------------|------------|--------|------|-----|------------|--------|------|-------|-------------|---------|------|-------|-------------|
| | | 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 |
| Zaporizhzhia | 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 |

Radionuclides high levels?

- **Initial high level source (rock, crack, water chemistry),**
- Violation of working conditions of well,
- Violations of the sampling,
- No action or violation of treatment.

RADIATION REGULATION FOR WATER

(bottled water)

Surface water:

- Total alpha - activity
0.1 Bq/L
- Total beta - activity
1.0 Bq/L
- Isotope analyses in case.

Wells, drilled wells:

- **^{226}Ra** - **1.0 Bq/L**,
- **^{228}Ra** - **1.0 Bq/L**,
- **^{222}Rn** - **100 Bq/L**;
- **Uranium** (total activity) – **1.0 Bq/L**

INDUSTRIAL IMPACT:

(mines, production of uranium, rare earth, fertilizers)

Uranium:

Water in vicinity of uranium processing sites:

- Underground – wells, local drilled wells (1.0 – 1500 Bq/L),
- Surface - reservoirs, rivers (0,1 – 10 Bq/L)

Mine waters up to 50 Bq/L.

Radium:

- Up to 5-10 Bq/L for mine waters.

Example of systematic remediation

Myronivka district, Kiev region

(Myronivka town and surrounding villages)

Initially for consumption was used water mostly deep drilled wells, ca 100+ m):

Rn-222 – 300-1000+ Bq/L, (100 Bq/L)

Ra-226 – 0.5-10.0 Bq/L, (1.0 Bq/L)

U – 0.5-10.0 Bq/L. (1.0 Bq/L)

After 20 years

All the sources was switched to water of 20-50 m wells,
and **no problem now (Radiation)**.

PERSPECTIVE

Directions of safewater (natural radioactivity):

- Measure natural radioactivity of water,
- Information provision,
- Propagation of modern analytical equipment,
- Development and adaptation of methods,
- Cover problems of water purification,
- Cover all territory of Ukraine.

Our contribution - organization of laboratory information support: <http://safewater.narod.ru>, development of measurement methods, training of personnel, intercomparison of results.

Acknowledgements

We thank Sergei Zvarich for initiation of our U by TBP method for LSC.

We thank Sanitary stations staff of Kiev, Zhytomyr, Vinnytsa, Chernihiv, Lugansk, Mykolaiv, Poltava regions for help.

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I thank SSM for support of attending the Conference.

Literature

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An aerial photograph of Kyiv, Ukraine, taken from a high vantage point. The foreground is dominated by a dense, lush green forest. Beyond the trees, the Dnipro River flows through the city. Several bridges are visible, including a large suspension bridge in the distance. The city skyline is visible in the background, featuring a mix of residential and industrial buildings. The sky is blue with scattered white clouds.

THANK YOU

Kiev 2010