

## LSC-BASED APPROACH FOR WATER ANALYSES AROUND THE CHERNOBYL NPP

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**ABSTRACT.** Water leakages and water flow inside and around the “shelter” covering the 4th reactor of the Chernobyl NPP were studied using radioactive tracers: <sup>3</sup>H, <sup>90</sup>Sr, and <sup>137</sup>Cs. We use the liquid scintillation (LS) technique to analyze tritium, <sup>90</sup>Sr, and <sup>137</sup>Cs concentration in water for a wide range of activities and ratios. Different sample preparation and measurement techniques were applied to cover the high range of mixture variation: direct counting, distillation, and extensive multiple ion-exchange procedures for tritium; direct LS counting, Cerenkov counting, and LS beta spectroscopy for strontium; and beta spectroscopy and gamma spectroscopy for cesium.

### INTRODUCTION

Water radioactivity analyses for tritium, <sup>90</sup>Sr, and <sup>137</sup>Cs have been provided for hydrogeological monitoring around the Chernobyl nuclear power plant (NPP) since 1997 (Panasjuk et al. 1998, 1999; Onyshenko et al. 1999; Buzinny 2001b), including surface and underground waters as well as high-activity water sources that are in contact with irradiated fuel and construction materials. Radionuclide concentrations for the analyzed samples varied greatly: tritium, 1.5–25,000; <sup>90</sup>Sr, 0.1–1.0 × 10<sup>7</sup>; and <sup>137</sup>Cs, 0.1–1.0 × 10<sup>7</sup> Bq/L. The tritium results are of the greatest interest, since tritium is used as a tracer of water flow inside and around the shelter covering the 4th reactor of the Chernobyl NPP and also as a tracer for radioactive leakages. Because radionuclide ratios vary greatly for different samples, some tritium samples could be measured immediately without any preparation, some required purification by distillation, and others required multiple ion-exchange procedures in order to be pure enough for tritium counting. Our <sup>90</sup>Sr measurements are well tested and can be widely applied using our modification of the Cerenkov counting method, which allows direct counting without sample preparation, even for colored waters (Buzinny 2001a; Buzinny et al. 1996). For most <sup>137</sup>Cs measurements, we applied direct gamma spectroscopy, but for a few samples of interest we used water pretreatment on 3–5 L.

### METHODS

The aim of this work was to determine the content of tritium and <sup>90</sup>Sr in both low- and high-activity water samples and <sup>137</sup>Cs in high-activity samples. High-energy beta emitters influence the measurement of tritium; thus, tritium measurements require complicated sample pretreatment and caution in all steps. We pay particular attention to describing the procedures applied for tritium measurements.

#### Tritium

##### *Low-Activity Water Samples*

Water samples of lower activity were collected using 1- to 2-L polyethylene bottles and transported to the lab without any pretreatment. Water samples were stored for 5–10 days. All samples were then filtered using a paper filter. Most of the water samples became completely clear after storage and filtration; however, some samples ranged from dark yellow to brown and remained colored for a long time, even after filtration. To prepare the samples, we acidified and heated them until boiling to allow coagulation of the organic matter present in the sample. All low-activity water samples under-

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went a distillation process for tritium measurement to avoid even a minor influence from  $^{90}\text{Sr}$  and/or  $^{137}\text{Cs}$ .

#### *High-Activity Water Samples*

Most of the beta activity in the water samples was caused by  $^{137}\text{Cs}$  and  $^{90}\text{Sr}+^{90}\text{Y}$ . Thus, highly radioactive water samples were collected and delivered to the laboratory in smaller volumes of 20–50 mL each due to their high  $^{137}\text{Cs}$  and  $^{90}\text{Sr}+^{90}\text{Y}$  concentrations. Distillation and ion-exchange procedures were tested for water sample purification, and ion-exchange technology was found to be more suitable because it controls the contamination of disposable vials, as well as a portion of the ion-exchange resin. Resin was first decontaminated and made ready for safe usage after being highly contaminated by  $^{137}\text{Cs}$  and  $^{90}\text{Sr}+^{90}\text{Y}$ . Water sample distillation requires highly efficient procedures for decontamination of the equipment used for evaporation and would be difficult for small-volume samples (20–50 mL).

The sample purification procedures applied for measuring tritium are illustrated in Figure 1. A 1-g portion of finely milled (0.1–0.2-mm grade) cation-exchange resin Dowex-50 was added to each 20-mL water sample in a corresponding plastic vial. Ion-exchange resin preparation includes transferring to  $\text{H}^+$  form, drying, and then milling. After the water sample was mixed with the cation exchanger for 2–3 hr, it was filtered using filter paper.

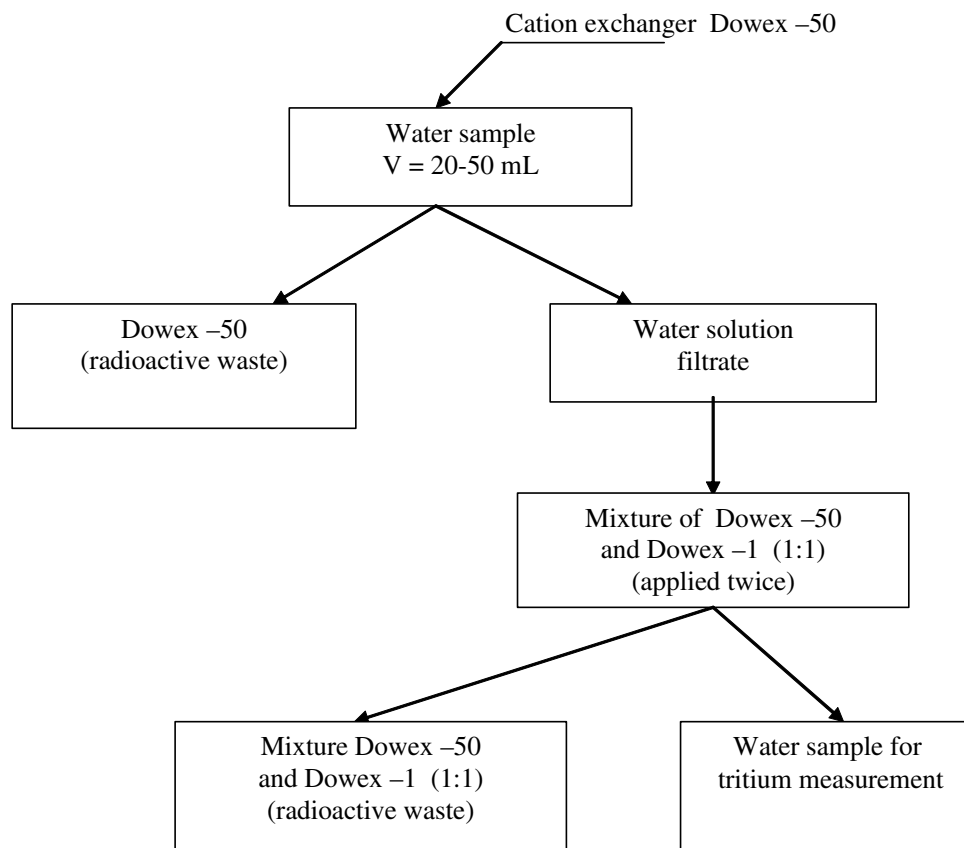


Figure 1 Chemical sample preparation scheme for tritium measurement applied to high-activity water samples

To perform the second stage of purification for a water sample, 1-g ion-exchange resins—a mixture of equal parts of cation exchanger (Dowex-50) and anion exchanger (Dowex-1)—were added to the resulting filtrate. Dowex-1 ion-exchange resin preparation includes the transfer to  $O^-$  form, drying, and milling to a fine 0.1–0.2-mm-grade fraction. High-activity waters have varying Cs/Sr activity ratios (see Figure 2). The water sample was mixed with the resin mixture for 2–3 hr and was filtered using filter paper. The second stage of water purification was not enough for some samples; residues of  $^{90}Y$  and even  $^{90}Sr$  after decay of prevailing  $^{90}Y$  are clearly identified in the sample spectra (see Figure 3). Thus, for some samples the second stage of water purification was performed twice to obtain a water sample pure enough for tritium counting. Surprisingly, after 2 steps of water purification, we found a second strong, beta-like peak in the sample spectra for most of the high-activity waters, with a different ratio to tritium each time a sample was prepared (see Figure 3).

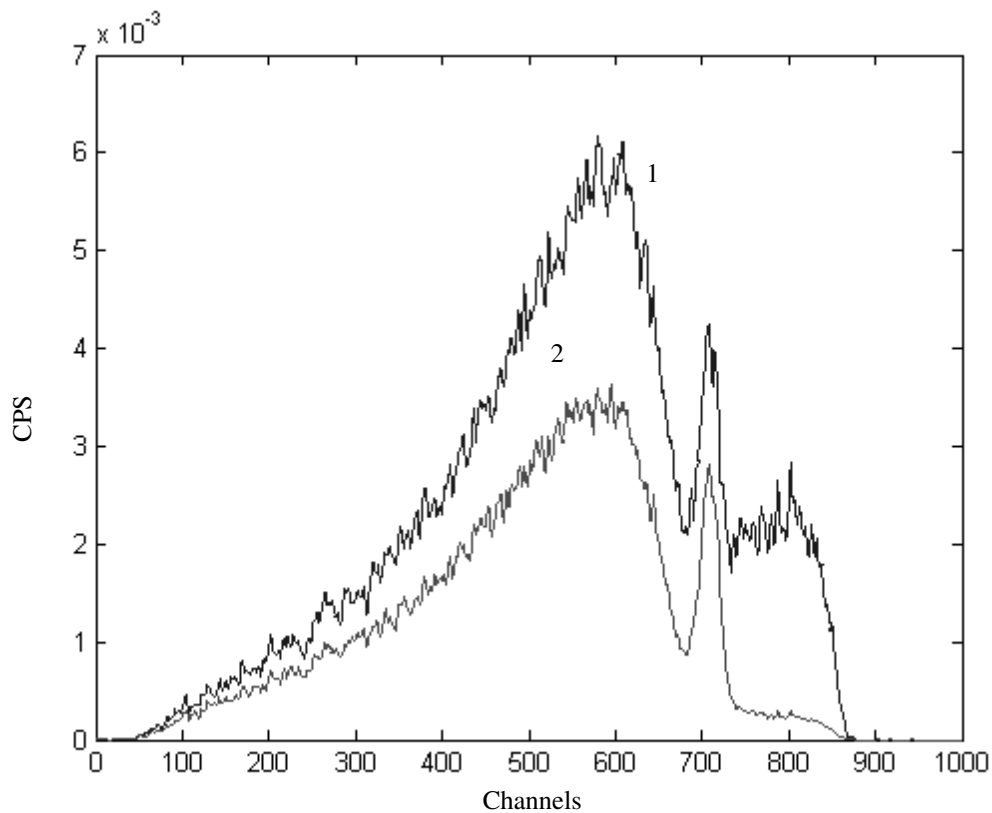


Figure 2 Beta spectra for highly radioactive waters. The corresponding  $^{137}Cs$  to  $^{90}Sr$  ratio is 2 (for spectrum 1) and 20 (for spectrum 2).

#### *Tritium Measurement Approach*

The tritium activity range for water samples of 1.5 to 25,000 Bq/L was wide enough to require the combination of different methods. We used polyethylene disposable vials for all sample measurements and measured low-activity samples using the maximum efficiency achieved for 8 mL of water and 12 mL of OptiPhase HiSafe 3 (Buzinny 2001a). When we measured the high-activity samples, we aimed for high sensitivity for tritium with relative decreasing sensitivity for counting high-energy beta emitters that could possibly interfere. The common figure of merit optimization

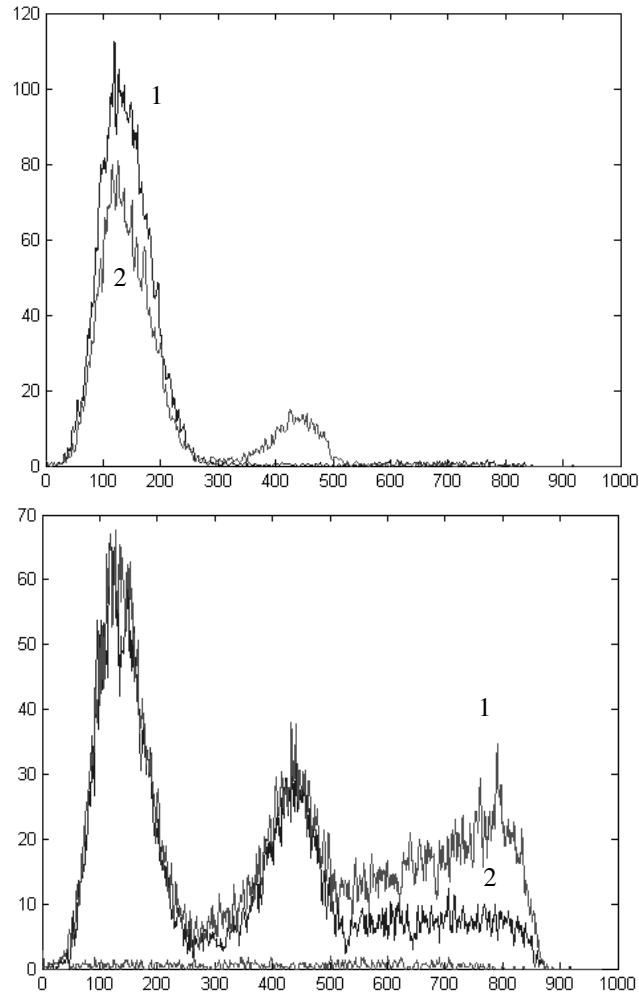


Figure 3 Upper: Liquid scintillation (LS) water samples spectra for tritium (1) and tritium and its unknown short-lived companion (2). Lower: Tritium and its unknown short-lived companion followed by  $^{90}\text{Y}$  (1) in the same sample at different conditions of  $^{90}\text{Y}$  decay (2). For both figures, the y axis is counts per second, and the x axis represents the channels.

approach, expressed in Equation 1, allows us to find a more sensitive combination for 4 mL of water and 16 mL of OptiPhase HiSafe 2 (see Table 1):

$$FOM = \frac{E^2 V^2}{BG} \quad (1)$$

where  $FOM$  is the figure of merit,  $E$  is the counting efficiency,  $V$  is the sample volume, and  $BG$  is the counting background.

Table 1 Approach used for sample volume optimization.<sup>a</sup>

| Volume | <sup>3</sup> H, Eff (%) | FOM            |           | Relative FOM ratios |           | Ratio (high beta vs. <sup>3</sup> H) |
|--------|-------------------------|----------------|-----------|---------------------|-----------|--------------------------------------|
|        |                         | <sup>3</sup> H | High beta | <sup>3</sup> H      | High beta |                                      |
| 1      | 45                      | 2025           | 2000      | 12.64               | 64        | 5.1                                  |
| 2      | 40                      | 6400           | 8000      | 4.00                | 16        | 4.0                                  |
| 4      | 35                      | 19,600         | 32,000    | 1.31                | 4         | 3.1                                  |
| 8      | 20                      | 25,600         | 128,000   | 1.0                 | 1.0       | 1.0                                  |

<sup>a</sup>Background for tritium is assumed to be 1 cpm; the background for high-beta is 5 cpm, with an efficiency of 100%.

### Strontium Measurement

For Sr measurement, most water samples that were measured did not require any pretreatment. For low-activity samples, we applied Cerenkov counting, which determines the activity calculation even for colored samples (Buzinny et al. 1996). Disposable polyethylene 20-mL vials were filled with water. Different <sup>90</sup>Sr and <sup>137</sup>Cs migration peculiarities in soil water flow cause a large difference in the corresponding specific activity levels. Fortunately, in observed situations <sup>137</sup>Cs activity was 2–3 orders of magnitude lower than <sup>90</sup>Sr activity. On the other hand, Cerenkov counting efficiency for <sup>137</sup>Cs was ~40 times lower than for <sup>90</sup>Sr. No other radionuclides could interfere with <sup>90</sup>Sr activity measurement using Cerenkov counting in surface water in the Chernobyl vicinity, excluding <sup>40</sup>K or other natural occurring radionuclides because their activities did not exceed 4–5 Bq/L.

For measuring high-activity water samples, we combined beta spectroscopy (Buzinny et al. 1993) with our modification of the Cerenkov counting method (Buzinny 2001a; Buzinny et al. 1996). We used only 1 mL of water, and added a liquid scintillation (LS) cocktail and/or distilled water.

### Cesium Measurement

We measured <sup>137</sup>Cs using beta spectroscopy (Buzinny et al. 1993), comparing the results with those obtained by a direct gamma spectroscopy method. The corresponding calibration for gamma spectroscopy [well-type NaJ(Tl)] was performed for the same sample placed into a 20-mL LS vial.

## RESULTS

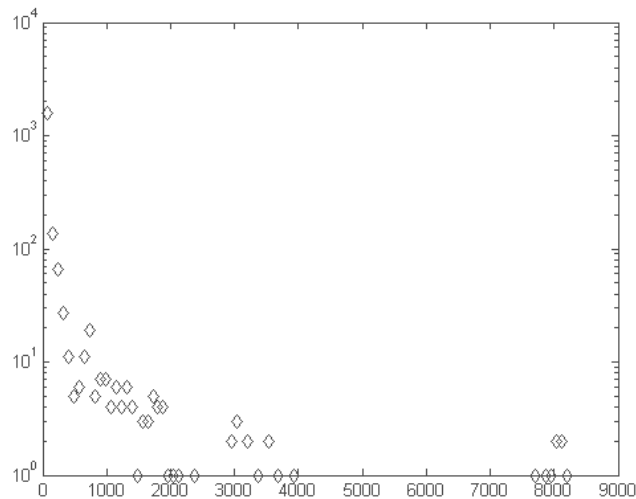
Tritium monitoring inside and around the Chernobyl shelter has been performed since 1997. Tritium concentration in high-activity water inside the shelter ranges from 1.0 Bq to 25.0 kBq/L. The seasonal variation of tritium levels reflects the water balance inside the reservoirs of the shelter. Precipitation flow brings “tritium-free water” into the shelter, forming a corresponding water border at the tritium level close to background (10 to 29 Bq/L). High-activity waters from inside the shelter have greatly contrasting ratios for all radionuclides of interest (see example in Table 2).

Water samples outside the shelter were collected in wells and drilled wells. The frequency distribution of data representing tritium activity is plotted on Figure 4 in a logarithmic scale. Corresponding tritium activities were in the range of 1.5 to 8200 Bq/L and were grouped as follows:

- Waters of low-activity levels in the range of 1.5–27 Bq/L;
- Waters of anomalous sampling wells that cover aquifers that are deeper than the corresponding water flows from the shelter, 200–8200 Bq/L;
- Waters with maximum tritium concentration in the northern direction, in which tritium originated from water flows from below or near the shelter.

Table 2 Activity of water samples collected in different reservoirs inside the shelter.

| Sample nr | Sampling site | $^3\text{H}$ (Bq/L) | $^{137}\text{Cs}$ (MBq/L) | $^{90}\text{Sr}$ (kBq/L) | $^{137}\text{Cs}/^3\text{H}$ | $^{137}\text{Cs}/^{90}\text{Sr}$ |
|-----------|---------------|---------------------|---------------------------|--------------------------|------------------------------|----------------------------------|
| 1281      | P.6           | $2.9 \times 10^3$   | 39.5                      | $12.6 \times 10^3$       | 13,600                       | 3.1                              |
| 1282      | P.8           | 47                  | 0.021                     | 2.2                      | 450                          | 10                               |
| 1283      | P.31(P.107)   | 20                  | 40.5                      | $8.4 \times 10^3$        | $2 \times 10^6$              | 4.8                              |
| 1284      | P.31(P.108)   | $3.7 \times 10^3$   | 45                        | $9.0 \times 10^3$        | 12,000                       | 5.0                              |
| 1285      | P.21          | $4.2 \times 10^3$   | 25.8                      | 390                      | 6190                         | 67                               |
| 1286      | P.111-2       | $3.1 \times 10^3$   | 8.2                       | 900                      | 2670                         | 9.1                              |
| 1287      | P.20          | $2.1 \times 10^3$   | 7.7                       | 180                      | 3750                         | 44                               |
| 1288      | P.30          | $2.1 \times 10^3$   | 13.8                      | $1.7 \times 10^3$        | 6700                         | 7.9                              |
| 1289      | P.32          | $2.8 \times 10^3$   | 47.3                      | $12.0 \times 10^3$       | 16,900                       | 3.9                              |
| 1290      | P.102         | $3.2 \times 10^3$   | 1.3                       | 0.59                     | 410                          | 2200                             |
| 1291      | P.110-2       | $4.0 \times 10^3$   | 11.0                      | $1.5 \times 10^3$        | 2750                         | 7.1                              |
| 1292      | P.110-3       | $3.2 \times 10^3$   | 7.6                       | 560                      | 2400                         | 13                               |
| 1293      | P.113         | $3.9 \times 10^3$   | 0.27                      | 18.0                     | 70                           | 15                               |
| 1294      | P.025         | $5.9 \times 10^3$   | 0.31                      | 0.34                     | 52                           | 920                              |

Figure 4 Logarithmic frequency distribution for tritium activity in water samples analyzed outside the shelter,  $n = 1950$ .

## CONCLUSIONS

Observed data show that highly contaminated soils could not cause high tritium concentration in water. Low-level activities of  $^{90}\text{Sr}$  and  $^{137}\text{Cs}$  in water corresponded to their high sorption, which allows tritium to be traced while the water migrates. Migration of shelter waters is seen inside and outside the Chernobyl shelter. Waters of 2 wells with anomalously high  $^3\text{H}$  concentrations of 3000–4000 Bq/L, and, surprisingly, about 8200 Bq/L are undisturbed by  $^{90}\text{Sr}$ .

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