

USE OF TRITIUM AND CARBON-14 IN ESTIMATING THE APPARENT AGE OF A GROUNDWATER IN DOBROGEA

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Abstract. This paper deals with two important issues that ultimately concern the monitoring of tritium and ^{14}C in the environment. First, it concerns the establishing of radioactive concentration levels and provenance of tritium and carbon-14. Second, the determination of the most likely scenario for estimating an apparent age for a groundwater source aiming to be used as a “Baseline or Reference Background” for tracer studies in Dobrogea, Romania.

Keywords: tritium, carbon-14, groundwater, liquid scintillation spectrometry, accelerator mass spectrometry.

1. INTRODUCTION

Dobrogea area, Romania, being associated with the effluents from the Cernavoda NPP is favorable for studies related to releases into the atmosphere and waters, especially of tritium and carbon-14, useful as radiotracers for investigating the distribution pathways in the environment. The radioactivity levels of tritium and carbon-14 originating from nuclear activities overlap to those originating from continuous nuclear reactions in the upper layers of the atmosphere. Spreading by the water and carbon dioxide cycles in nature, these cosmogenic and at the same time anthropogenic radionuclides require monitoring and, if possible, detection of their origin.

In 2024, during field campaign in Dobrogea area, a series of spring and groundwater samples were collected to obtain a distillate fractions with the lowest values for tritium and carbon-14. These fractions are usually used as a “Baseline or Reference Background” in liquid scintillation spectrometry for other environmental samples associated for same year.

In the last 30 years, for Dobrogea, there have been several sources of “Reference Background” used in the liquid scintillation spectrometry laboratory at IFIN-HH starting with the pre-operational phase of the Cernavoda NPP – Unit 1 commissioning, between the commissioning of U1 and U2, and then in the normal operation stage of these two units [1–3]. They varied depending on access, but also on alteration of water source over time. Previous sampling points were located in the perimeter of city of Mangalia (covered well having a depth of about 300 m and subsequently another location with catchment from the same deep-water source, having a constant flow, distributed by a pipe), then in the Cheile Dobrogei / Dobrogea Gorges natural reservation (medium-depth underground spring caught near the surface, with natural flow distribution through a pipe).

In recent years, the water from the underground spring located in the Dobrogea Gorges area was a good reference for the analysis of tritium in surface water, vegetation and soil samples [4–6]. However, a depreciation occurred over time, explained by the modification of the water source into underground and by a possible contamination with surface water and atmospheric air (moisture and meteoric waters).

Therefore, a re-evaluation of the locations that could provide a new water source with these particularities prevailed.

Water samples were collected from several locations across the Dobrogea region; the sampling sites and their characteristics are presented in Table 1. A water sample collected from the underground lake at the Unirea Salt Mine, Slănic-Prahova, is also included for comparison.

Table 1

Sampling characteristics of water samples potentially considered as “Baseline or Reference Background”

Location name	Geographic coordinates	Water source characterization
Dobrogea Gorges – spring, at the source	44°30'27.68"N; 8°25'50.82"E	Spring water, at the source; starting with 2023 the water no longer comes to the surface through the pipe, but by side areas of penetration, forming a small pool before turning into a stream.
Dobrogea Gorges – stream	44°30'4.64"N; 28°25'32.82"E	Stream water, approx. 1 km downstream from the source of Dobrogea Gorges spring.
Histria – the fountain	44°32'46.30"N; 8°46'13.10"E	Medium-deep water, brought to the surface with a pump; no contact with atmospheric air, collected and distributed through a pipe with a tap. The fountain emerged as part of the museum building renovation by 1982, and 2011.
Unirea Salt Mine – underground lake	45°14'7.59"N; 25°56'34.45"E	Deep water and surface water infiltration; the underground lake located in the Unirea Salt Mine, Slănic-Prahova is approx. 600 m beneath the current zero elevation of the land; in contact with air inside of the mine, partially isolated from surface air through the access tunnel.

After sampling, the water samples were distilled at atmospheric pressure to remove inorganic and organic contaminants. Measurement of the distillate in commercial scintillation cocktail was performed on the Quantulus 1220 ultra-low level liquid scintillation analyzer (LSC method). According to results, a new source for the coming years has been established, i.e. water from the Histria Museum Complex (see Table 1). Low tritium values were obtained for this sample. Concerning carbon-14 from the solid carbonaceous deposits issued after distillation in a vacuum rotary evaporator, unexpectedly high values were obtained. These measurements were performed using Accelerator Mass Spectrometry (AMS method). These results may have several explanations and require the investigation on the origin and estimation of the age of the underground water deposit.

This paper aims to review possible scenarios for cases such as the water from Histria, and to establish a method for cross-dating an underground water source, using tritium and carbon-14 as radiotracers.

2. MATERIALS AND METHODS

The water samples were collected in glass bottles, filled to the top, and stored in the dark under constant temperature and humidity conditions. Being collected from springs or underground water sources, they were not filtered through a Millipore filter, thus avoiding prolonged contact with the laboratory air. The samples were first distilled at atmospheric pressure, under the conditions recommended by the standard in force and after that under vacuum, using the Heildolph Hei-VAP Value rotary evaporator [7, 8]. The distillates were kept in safe conditions until measurements.

Each distillate was measured in 20 mL polyethylene vials (standard geometry for Quantulus 1220 measurements), in a volumetric ratio of 5:15 with the commercial Ultima Gold PerkinElmer scintillation cocktail, for a total time of 1,000 minutes, on energy channels 5 – 320 for tritium. The calculations were made according to the recommendations in the literature [9, 10].

For calculation and comparison, two reference samples were used: one with a very low tritium content (well below 10 TU; 1 TU = 0.118 Bq/dm³), originating from the Frățești 4 deep borehole (having a depth of about 300 m) which is used as a “Measurement Background” (the liquid scintillation analyzer technique, the LSC method, being relative), and another from the Unirea Salt Mine, Slănic-Prahova underground lake (see

Table 1). While the sample from the Unirea Salt Mine is always accessible, the drilling water has limited access. The underground water source represents the Frătești aquifer, Giurgiu, the second largest aquifer system in Romania, placed as a formation in the Lower Pleistocene [11].

For the Histria water sample (Table 1), the analyses were continued by evaporation to dryness using the same rotary evaporator. The carbonaceous deposits within the glass flask were finally dried for 4 hours at 60°C, in a VacuCell vacuum oven. After recovery from the glass flask, the solid phase was graphitized using the CHS – AGE 3 system (IonPlus, ETH Zürich, CH) at RoAMS laboratory, IFIN-HH. Carbon-14 determination was done using AMS method, performed at 1 MV HVEE Cockroft-Walton Tandetron linear accelerator [12, 13]. Primary data processing was performed using BATS Program v. 4.06, with calibration by the OxCal Online Program v. 4.4 [14, 15].

To evaluate the tritium content present as tritiated water in the atmospheric air humidity of the laboratory, during distillations, an original method developed at the URPMB laboratory, IFIN-HH was used. The condensate is collected into the TROTEK TTK 100 S dehumidifier. It is distilled at atmospheric pressure and measured under the same conditions as the water samples. The temperature, relative humidity and wet bulb temperature, for the considered interval, were recorded using VOLTcraft DL-140TH.

To evaluate the level of carbon-14 associated with carbon dioxide in the laboratory air, sodium hydroxide tablets, Lachner manufacturing, were used as trapping reagent [16]. The resulting sodium carbonate was evaluated on an Elementar vario Micro Cube elemental analyzer, establishing the chemical formula and the number of hydration water molecules. It was graphitized and measured under the same conditions as the Histria deposits, by the AMS method. The carbon dioxide concentration in the laboratory air during experiments was monitored by Air CO2ntrol 3000.

3. RESULTS AND DISCUSSION

3.1. Experimental results

The radioactive concentrations of tritium present as tritiated water in distillates, expressed in Bq/dmc, are given in Table 2. Table 3 presents the AMS results expressed in modern carbon fractions, F14C obtained for carbon-14 in Histria carbonaceous deposits, together with carbon-14 in sodium carbonate monohydrate control sample.

The average level of tritium present as tritiated water in the atmospheric humidity of the laboratory was characterized by: A (measured activity of the distilled sample) \leq MDA (Minimum Detectable Activity, calculated); $A' \leq 5.18$ BqT total (estimated as total tritium content inside the laboratory at the time of sampling); $A''_{fin} \leq 0.0389$ Bq/m³ aspirated air, corrected (activity per cubic meter of air, determined by calculations); $A''' \leq 0.0395$ Bq/m³ air in the room, estimated (estimated activity per room cubic meter); $\alpha'/V = 15.25$ g water/mc air in the room (closed windows); No. of cycles \cong 10 times (how many times the air in the room of known volume was passed through the dehumidifier during sampling interval); MDA = 1.12 Bq/dm³ of Measurement Background water (< 10 TU). The normal indoor values are between 0.0400 – 0.0800 Bq/dm³ of air [17].

The average carbon dioxide level monitored during experiments was 600 ppm CO₂ (at 23.5°C average temperature, 12.58% average relative humidity and 14.64°C wet bulb temperature average value). Normal ranges for the environment are 350 – 450 ppm CO₂ away from pollution sources, and 450 – 600 ppm CO₂ for the air inside buildings in urban centers [18, 19].

The mass percentage of carbon (%C) established at Elementar, prior to graphitization, for the carbonated sodium hydroxide tablet at equilibrium with atmospheric humidity, was 9.41%C. This value was obtained in the pre-screening phase for estimating of the sodium carbonate degree of hydration and implicitly of the sample mass required for CHS. Starting from the chemical formulas of the different forms of hydration of sodium carbonate, it was established that this is Na₂CO₃·H₂O (sodium carbonate monohydrate) for which the theoretical value is 9.67%C. Based on this formula, approximately 35 mg for graphitization at CHS is needed, corresponding to about 1.52 mg of natural carbon intimately deposited on the iron catalyst – the final material introduced into aluminum cathode for AMS measurements.

Table 2

Radioactive concentration of tritium, as tritiated water, expressed in Bq/dmc, determined by LSC method, measured on Quantulus 1220; MDA = 1.12 Bq/dmc

Sample type	Method of preparation	Tritium concentration value, $A \pm SD$, [Bq/dmc]
Dobrogea Gorges – spring 1	Distillation at atmospheric pressure	2.12 ± 0.08
Dobrogea Gorges – spring 2	Vacuum distillation	7.43 ± 0.27
Dobrogea Gorges – stream 1	Distillation at atmospheric pressure	4.83 ± 0.18
Dobrogea Gorges – stream 2	Vacuum distillation	8.30 ± 0.30
Histria – fountain 1	Distillation at atmospheric pressure	≤ 1.12
Histria – fountain 2	Vacuum distillation	1.14 ± 0.04
Unirea Salt Mine – underground lake 1	Distillation at atmospheric pressure	1.14 ± 0.05
Unirea Salt Mine– underground lake 2	Vacuum distillation	1.60 ± 0.07

Table 3

Radiocarbon dates obtained by AMS method for Histria carbonaceous deposits and for sodium carbonate monohydrate control sample, obtained at 1 MV HVEE Cockroft-Walton Tandetron

RoAMS code	$\delta^{13}\text{C}$ ‰	Modern carbon fraction, F14C	Measurement uncertainty, %	Isotopic ratio $^{14}\text{C}/^{12}\text{C} \times 10^{-12}$	Isotopic ratio $^{13}\text{C}/^{12}\text{C}$ (‰)
Histria test	39.7	1.5536	0.45	1.6364	1.1004
Na_2CO_3 test	14.2	1.0670	0.44	1.1211	1.0989

3.2. Discussion and interpretation

Considerations on tritium levels. The level of tritium in the laboratory, present as tritiated water in air humidity was within the limits of the natural environmental background.

Table 2 shows a difference for the same sample between the radioactive concentrations of tritium present as tritiated water in the distillates, depending on the process applied. Distillations at atmospheric pressure proceed without isotopic fractionation, as also results from the literature data [7, 8]. In contrast, distillation under vacuum leads to an enrichment in HTO of the condensed fraction, by isotopic fractionation (sequential releasing from the sample of H_2O , D_2O and HTO, in this order).

Fractionation occurs on the separation column. H_2O , D_2O and HTO are not collected in the condensate flask in the same proportions as in the sample within distillation still. A small part of the light fraction is discharged to the outside by the vacuum pump; another part of the light fraction together with the heavier fraction condense in the condensate flask. By varying the angle at which the column is inclined to the vertical, between 30° and 40° , part of the condensate returns to the distillation still, increasing the concentration in the heavier water fractions. For 100 ml of sample initially added to the distillation still, and extending the separation time by the occurrence of reflux depending on the inclination angle, after a prolonged contact at the liquid-vapor equilibrium, a value above MDA is obtained. It can be an easy-to-use method, a simple alternative to more rigorous electrolytic enrichment equipment [20].

For optimal conditions, the degree of enrichment in the distillate (value in vacuum / value at atmospheric pressure) can be established. This can be applied in the formula for calculating the radioactive concentration of the sample. It can be used when low values or within the MDA limit are obtained for distillation at atmospheric pressure.

In Table 2, the lowest tritium values are observed for the Histria sample – an initial indicator of the water source's origin.

Considerations on carbon-14 levels. The carbon-14 levels in Histria sample and sodium carbonate monohydrate are very different: 155.36 pMC (percentage of modern carbon; $\text{F14C} \times 100$ [%]), and 106.70 pMC for the control (Table 3).

Based on previous AMS determinations, the expected radiocarbon level for the Histria water sample should be much lower, with calibrated values associated with an age around 23,000 years, corresponding to the groundwater of various depths in Dobrogea [21]. The value is unexpectedly high.

A suspicion arises of a possible contamination with carbon dioxide from inside the laboratory, during the experiments. The CO₂ level was relatively high (600 ppm), and the value of the modern carbon-14 percent of 106.7 MC represents the environmental level at the time of the formation of sodium carbonate. The contamination of the sample from Histria could have occurred, as in the case of the control sample, through a 100% transfer of carbon-14 from the air, but in no case higher.

Distillation in a rotary evaporator and drying in a vacuum oven do not allow contact of solid carbonaceous fractions (bearing carbon-12, carbon-13 and carbon-14) with air during operation, as in the case of water vapors. The hypothesis of naturally contaminated water with carbon-14 and no with tritium appears.

Previous experiments in RoAMS laboratory have established that thermal treatments at atmospheric pressure or under vacuum could produce, through inherent contact with air during or after operation, apparent ages younger than the control value: the IAEA-C2 reference material (marble; measured value of 0.3 pMC) or the IAEA-C1 reference material (travertine; measured value of 41.81 pMC), close in chemical composition to the deposits from Histria. The corresponding radiocarbon ages for IAEA-C1 and IAEA-C2 were: $46,716 \pm 174$ years BP and $7,004 \pm 27$ years BP, respectively [22]. Applying the correction given by the radiocarbon calibration curve, equilibrated to 100% atmospheric CO₂, the Histria sample should lie between these values, very close to the groundwater from the deep well used in the previous experiments, i.e. $30,183 \pm 113$ years BP (2.3 pMC). This liquid sample, collected and stored under insulating conditions, was graphitized directly on the CHS – AGE 3 system. [22]. Carbonaceous deposits obtained by various processes at atmospheric pressure and under vacuum were graphitized under the same conditions. The highest contribution of atmospheric CO₂ to the deposits occurred during slow evaporation on an electric hotplate, where contact during the entire experiment, under thermal influence, produced a transition from 2.3 pMC to 16.5 pMC [22].

For Histria water sample, the thermal treatment under vacuum in the rotary evaporator is involved, the air coming into contact with the sample, until equilibration, only when the installation is switched to atmospheric pressure, by the admission of air when the distillation stops. The same observation is valid for the final drying in the vacuum oven. Most likely the effect will be cumulative.

These questions arise: is the unexpectedly high value due to the influence of the Cernavoda NPP releases or to the air in the laboratory? And what is the real value?

Considerations on the origin of the water source using tritium and carbon-14 results. Processes governing groundwater chemistry are detailed in the previous publication [22]. The literature provides details on the mechanisms by which radiocarbon age is interpreted in terms of residence time, expressing the time of groundwater source formation [23, 24]. Tritium and carbon-14 levels are expected to be very low. The discrepancy between the levels of tritium and carbon-14 in the Histria sample can be explained in three ways:

a) a shallow groundwater source in permanent contact with surface waters; may explain the tritium level in the water, but cannot explain the carbon-14 level in the carbonates. High carbon-14 values can be expected in the vicinity of the Cernavoda NPP, but not at a distance of ca. 40 km away from the nuclear facility [25]. Laboratory records and published data refute this hypothesis.

b) an isolated groundwater source, having tritium and carbon-14 levels corresponding to the calibrated radiocarbon date. In the absence of carbon-14 exchange on stratigraphic level, the concentration of this radioisotope would correspond with a 90.6% probability to the interval 1969-1970 and with a 4.8% probability to the year 1971. The histogram issued by OxCal program does not converge with recent observations on the dynamics of geology within the perimeter of the Histria Museum Complex nor with possible anthropogenic transformations caused by the reconstruction of the museum, in 1981 and 2011 [26]. The ancient fortress of Histria was located on the shores of the Black Sea. About 1,400 years ago, a marine field began to form in front of the fortress, subject to intense neotectonics movements that resulted in the submergence of the central part with the formation of the Sinoe lagoon. On the other hand, from the perspective of the radioactive decay equation, the tritium level in the isolated sample from the surface should be 23.52 Bq/dmc, a value completely different from the measured one. In the Cabernet Sauvignon wine from SCDVV Murfatlar, produced in 1966, a value of 50 Bq/dmc of distilled water was determined [27]. At that time, in the absence of the Cernavodă

NPP, the value came exclusively from anthropogenic tritium released into the atmosphere between 1950 and 1965. This hypothesis is also very unlikely.

c) a water table that has been present for 1,400 years ago [26]. If for the water from the deep well in [22], the actual level is 2.30 pMC, assuming a constant level of 106.7 pMC in the carbon dioxide in the laboratory air, to obtain an apparent level of 2.42 pMC by evaporation in the vacuum oven, the calculated contamination is 0.05% at a contamination factor given by the ratio $2.42 / 2.30$. A similar calculation for vacuum evaporation is of 0.34% modern carbon-14, corresponding to the ratio $3.50 / 2.30$. These percentages quantify the exchange during handling at the end of drying (by introducing air into the vacuum oven or rotary evaporator, respectively).

For Histria, starting from the final value of 155.36 pMC, the following system of equations appears:

$$\text{pMC-H}' / \text{pMC-H} = 3.50 / 2.30$$

$$155.36 / \text{pMC-H}' = 2.42 / 2.30$$

where: pMC-H, pMC-H' and pMC-H'' are different percentages of modern carbon-14 in the carbonaceous deposits, supposing that the exchanging rate is the same for equivalent processes, during experiments.

The initial modern carbon-14 percentage in carbonaceous deposits could be estimated at 93.07 pMC level. Keeping the same value of the measurement uncertainty, the calibrated intervals become those represented by Fig. 1.

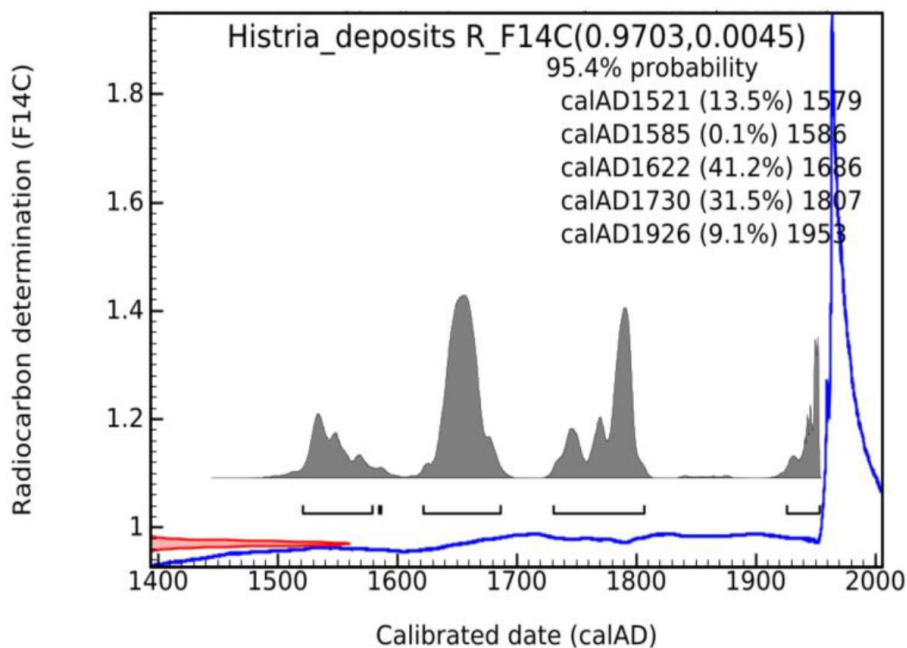


Fig. 1 – Histogram for carbonaceous deposits in water from Histria, after pMC corrections.

The dominant age interval in Fig. 1 is placed in the 17th century. This result supports previous conclusions regarding the formation of the marine field. The high rates of subsidence movements, the highest in Dobrogea [26], can explain a possible contamination with surface waters, a hypothesis supported by the tritium value. If the isolation had “closed” the groundwater, the tritium value would have been at the level of several centuries ago, estimated at $0.1 - 0.6 \text{ Bq/dm}^3$ before 1945 [28], much closer to that of the “Measurement Background” water, regardless of the distillation process applied. Considering the radioactive decay equation, and the values measured in the summer of 2016: $2.17 \pm 0.12 \text{ Bq/dm}^3$ in Lake Sinoe (sampling point 500 m from the fountain) and from Lake Golovăț, interconnected, of $2.86 \pm 0.11 \text{ Bq/dm}^3$ [29], we can say that the value around 1.14 Bq/dm^3 represents a time recharge with tritium at surface waters levels, of approximately 12 years (a half-life of tritium).

4. CONCLUSIONS

Recent search for a new water source that could be used as a “Reference Background” in tritium and carbon-14 determinations in environmental samples from Dobrogea, by liquid scintillation spectrometry, offered the opportunity to develop some original aspects in URPMB and RoAMS laboratories of IFIN-HH.

Distillation of several water samples from shallow and medium-depth underground sources led to the optimization of results that are usually placed around the Minimum Detectable Activity on the Quantulus 1220 liquid scintillation analyzer. Combining the information provided by: distillation at atmospheric pressure; distillation under vacuum on a rotary evaporator by choosing a volume of 100 ml per sample, an inclination angle between 30° – 40° of the distillation column, and calculating a correct fractionation coefficient depending on the type of sample, can provide a result of the radioactive concentration of tritium as HTO in the initial sample, without the need to use a special electrolytic enrichment installation.

The recovery of carbonaceous deposits from the Histria sample, by water removing under vacuum in a rotary evaporator and drying it in a vacuum oven, produced a radiocarbon fraction datable by accelerator mass spectrometry at the 1 MV HVEE Cockroft-Walton Tandetron accelerator. The result was well above the environmental background, which is why possible sources of groundwater contamination were explored. The measured value of 155.36 pMC includes the contribution of the background of 106.7 pMC to the real value of carbon-14 in the sample, enhanced by drying methods used. The real value is 97.03 pMC. The dominant calibrated interval corresponds to the 17th century AD.

Combining the tritium and carbon-14 data led to the most likely scenario: a water deposit formed starting 1,400 years ago, different from the geology of continental Dobrogea, and which is renewed with surface water with an exchange rate of approx. 10 – 12 years. Thus, the real radiocarbon age becomes an apparent age. However, there are other parameters that lead to a real value of the residence time, this research direction deserving to be explored in the future. For now, it remains the most probable hypothesis and Histria, the best choice for the “Reference Background” water.

FUNDING

Tritium analyses were carried out within the NUCLEU project, Project PN 23210202, financed by the Ministry of Research, Innovation and Digitization, Romania. The radiocarbon dating experiments were supported by the Romanian Government Program through the National Program for Infrastructure of National Interest (IOSIN funds).

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Received June 10, 2025