



## Measurement of tritium in the free water of milk : spotting and quantifying some biases and proposing ways of improvement



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### ABSTRACT

As one of the three natural isotopes of hydrogen, tritium is ubiquitous and may potentially be present in any water or organic molecule that constitutes a biological matrix. Milk is one of the most frequently monitored foodstuffs in the vicinity of chronic release of radionuclides, as it is a very common food product and also because it integrates deposition on large areas of grass or crops at a local scale. Different parameters have been studied to assess their impact on the reliability of tritium measurements in the free water of milk. The volume of the sample, the technique used to extract the water and the level of dehydration modulate the results but in different ways: dispersion of results and under- or over-estimation of the tritium activity. The influence of sample storage and preparation has also been investigated. Methodological improvements of tritium measurements in the free water of milk are proposed. An original fractionation effect during distillation of milk is also described.

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### 1. Introduction

Among the unstable isotopes released by the nuclear industry, the quantities of tritium reaching the environment are usually small and generally fit easily within regulatory limits. As tritium was massively released during the atmospheric nuclear tests between 1945 and 1980, it has become widely dispersed in the environment and in food chains. Its quantity in the atmosphere peaked in 1963 and has been decreasing ever since. It is now mainly localized in the water of oceans (about 99%) (Jacobs, 1968; UNSCEAR, 2008; Weaver et al., 1969). Nevertheless, tritium along with <sup>14</sup>C and noble gases remain the dominant radionuclides released into the atmosphere by the nuclear industry. The main anthropic sources of tritium are weapon facilities, nuclear power plants, reprocessing facilities, the production and use of labelled compounds for medical use, research or even self-powered lighting products and research facilities for nuclear fusion (Guétat et al., 2008; IRSN/DEI, 2010).

Being an isotope of hydrogen, tritium can be incorporated into almost all components of biological systems: water (HTO) or organic molecules (Diabaté and Strack, 1993) (so-called Organically Bound Tritium or OBT). When dealing with OBT, two categories of atomic bonds are generally distinguished:

- binding to a nitrogen, oxygen or sulphur atom, i.e. labile bonds. It can easily be exchanged with labile hydrogen of other functional groups or molecules in its near vicinity, especially water; this fraction is called exchangeable Organically Bound Tritium (eOBT).
- binding to a carbon atom. Such covalent bounds are stable and therefore hydrogen atoms (or isotopes) are incorporated in the metabolic cycle of each molecule with more or less complex and lengthy features. This latter type of bound tritium is known as non-exchangeable Organically Bound Tritium (neOBT).

Exposure of individuals depends on the type of the tritiated molecule(s) incorporated as well as on its/their metabolism. When tritium originates from tritiated water release and is further integrated in the food chain by, for example, going through photosynthesis (see further details in (Boyer et al., 2009)), some simplifications are considered to define a single

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“dose per unit intake factor” (Diabaté and Strack, 1993; ICRP, 1989, 1997):

- considering exchangeable and non-exchangeable proportions to be equal in OBT,
- considering an average biological half-life of 40 days for all non-exchangeable tritium of all organic molecules.

Some experiments are actually performed which demonstrate these general considerations are still under discussion: see for example Kim and Korolevych, 2013 and Taylor, 2003.

When using liquid scintillation counting, measurements of tritium specific activity in water allow the lowest limit of determination to be reached. Laboratories that measure tritium in environmental samples frequently use the same protocol:

- extraction of the free water of the sample to measure Free Water Tritium, then
- on the one hand: oxidation of the dry fraction resulting in the production of combustion water, then measurement of total organic tritium (i.e. the sum of eOBT and neOBT),
- on the other hand: isotopic exchange of hydrogen isotopes by washing the dry fraction with tritiated water, thus a second extraction of water to measure (if possible) eOBT and oxidation of the “washed” and dried fraction to measure the neOBT as combustion water.

Frequently, eOBT is not measured but deduced from the following simple relation:

$$\text{eOBT} = \text{OBT} - \text{neOBT} \quad (1)$$

Every isotope or inaccuracy effect in every step of the procedure may induce errors in the measurement of the specific activity of extracted free water and of OBT (Baumgärtner and Kim, 1990; Kim and Baumgärtner, 1991).

Usually, water is extracted from fresh samples or after isotopic rinsing by at least one of the following four techniques:

- filtration: this allows quick and easy recovery of the main part of the dry matter, except soluble molecules which are in the filtrate. The bias induced depends on the filtration technique (i.e. characteristics of the filter) and on the nature of the sample. Retentate and distillate both need further treatment prior to measurement.
- distillation: this is performed under atmospheric pressure or under reduced pressure, it allows the recovery of almost pure water. Under reduced pressure, it is possible to completely distil at lower temperature (which induces less degradation of organic samples), to prevent the risk of contamination of extracted water by pyrolytic products (Wood et al., 1993) and to limit the isotopic effect during evaporation.
- azeotropic distillation extracts water at lower temperatures than distillation. As it uses organic compounds, it is more difficult to perform and it can additionally induce contamination of the dry matter by hydrocarbons.
- Freeze drying: i.e. extraction of water via sublimation; it has the same advantages as distillation under reduced pressure. The size of the apparatus, the temperature of the cold trap (usually  $> -20$  °C) and the time required to completely extract the water may induce biases by condensing atmospheric vapour before starting or during the process.

Repetition of measurements performed in our laboratory on the free water of a given tritiated milk obtained by distillation under reduced pressure or by freeze-drying, have shown certain

systematic errors and dispersion of the values beyond the basic uncertainties of the measurements. The reasons underlying these differences have been sought and improvements of the reliability of tritium measurements are proposed.

Four possible hypothetical origins of the observed differences in measured specific activities were identified:

- the influence of sample storage: as ambient levels of tritium at the Valduc Centre of the French Atomic Agency can be higher than those of the environment where the samples were collected, they may become significantly more tritiated during their storage.
- the influence of the water extraction technique used: the usual techniques of dehydration differ from each other by their conditions of pressure, temperature and the apparatus used. These different factors may lead to biases in the measurement.
- the influence of the mass of sample: as each water removal technique has a specific dead volume and a specific geometry, the global yield of dehydration can be influenced and thus be the origin of a bias in the measurement of specific activity.
- the influence of the final degree of dehydration: if isotopic fractionation occurs during water removal, the final level of dehydration will influence the specific activity measured.

## 2. Materials and methods

Water was extracted from nineteen aliquots of the same milk sample (collected in the vicinity of the Valduc Centre of the French Atomic Agency) using three different dehydration techniques. The experiments were completed with twenty-one measurements performed on milks collected for our routine activity. Each time, weights of fresh milk, of dry matter and of collected water were noted.

Once collected, samples have been stored at  $-25$  °C in polyethylene bottles placed in a double-welded vinyl pocket. When samples were to be prepared before a week, they were stored in polyethylene bottle at  $3$  °C.

### 2.1. Analytical method

Specific tritium activities were measured by liquid scintillation counting (PerkinElmer Tri-Carb 2910 TR) with an overall precision ( $2\sigma$ ) of  $\pm 17\%$ . The scintillator used was Ultima Gold™ LLT (Packard). Quenching effects of the measuring system were carefully examined and the results corrected accordingly.

### 2.2. Storage of samples

The commercially available source water Volvic is considered to have very low levels of tritium. It is commonly used in laboratories as a blank. In order to check if storage of samples in Valduc induced biases in the measurement of the specific activity, samples of Volvic water were stored in different conditions and their specific activity was been measured after 6 h, 16 h, 24 h, 48 h, 96 h, 1 week, 2 weeks, 3 weeks or 30 days of storage.

Modifications in the conditions of storage were performed to test the influence of the temperature and the type of bottle in which the samples were stored.

Four sets of nine samples of 50 mL of Volvic water were stored in 150 mL polyethylene bottles at  $-25$  °C,  $3$  °C,  $20$  °C and  $40$  °C.

Five other sets of nine samples of Volvic were stored in different kind of bottles:

- 50 mL of Volvic water in 150 mL high density polyethylene (HDPE) bottles,
- 150 mL of Volvic water in the same kind of bottles,

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