Improving tritium determination from environmental water samples by the 3He ingrowth method by means of an ultrapure 4He spike

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Clarke et al. (1976) described a new method based on mass spectrometric measurement of 3He to deter-mine low level tritium concentrations of water samples [1]. The method consists of three major steps: 1) The water samples are put into glass bulbs. The dissolved gases including helium are removed from the water by vacuum pumping. 2) The sample are stored for several months or years so that 3He atoms are produced from tritium decay. 3) The amount of the tritiogenic 3He is measured mass spectrometrically. Since then numeru-ous laboratories adopted this method [2-5] as noble gas mass spectrometers became commercially available. The measurements are usually calibrated by means of well known air aliquots, which in size can be compared to the helium amount from the tritium sample. The 3He/4He ratio of samples can differ considerably from that of air used for standardization. For this reason it has to be kept in mind that a possible discrimination of 3He by 4He is not necessarily corrected by the air stan-dards [3]. Additionally, the mass spectrometric sensi-tivities of the different helium isotopes depend on the pressure at the ion source [6]. In case of tritium meas-urements, the overall pressure of the helium in the mass spectrometer is much lower than that of the helium from the air calibration.

We use air aliquots that contain $7 \cdot 10^{-9}$ to $2 \cdot 10^{-7}$ ccSTP of 4He and $5 \cdot 10^{-15}$ to $1.5 \cdot 10^{-13}$ ccSTP of 3He. The relative standard deviations of the calibration measurements vary between 1-2 %, and the non-linearity effect is always taken into account. The over-all helium amount in the mass spectrometer in case of a tritium sample is usually less than $3 \cdot 10^{-10}$ ccSTP that derives, of cource, from the 4He [5]. As the amount of the calibration sample converges to that of tritium samples, we loose the good statistical error of the 3He measurement being counted by an electro-multiplier. It seems that the large diiference of the helium pressure in the ion source between a sample and the calibration makes a different ionization efficiency for the tritio-genic 3He. In our case, even if the air calibration seems to be good, this pressure-dependent effect caused a changing systematic error of 10 to 40 % for the stan-dard water samples of known tritium concentration. Within a short period of a few weeks, the systematic difference between the expected and measured values of standard samples of known tritium concentration was quite stable allowing us to use a correction factor, that was usually used to correct the measured values of a sample. To solve this problem, we have decided to increase the helium pressure in the ion source for a tritium sam-ple by adding an ultrapure 4He spike to each tritium sample during the inlet. We built a reservoir of 6230 cm3 that was filled with 4He at about $1 \cdot 10^{-5}$ mbar, and CO_2 at 1030 mbar. Pipetting aliquots from this spike reservoir we can prepare 4He samples of $7.6 \cdot 10^{-8}$ ccSTP that is always added to the tritium samples. Hence the helium pressures are always within the same order of magnitude.

This ultrapure 4He was prepared by Yoshiki et al. [7] using a superleak made of compacted aluminium oxide nano powder of 200 to 500 Å. Liquid helium of 1.5 K was let through this superleak. The superfluid component, that composed of solely 4He bozons passed easily the superleak while the non-superfluid and gas components were retained. Our measurements con-firmed that this helium hardly contained any 3He: the measured 3He/4He isotope ratio is lower than $5 \cdot 10^{-10}$, that is extremely perfect for our purpose.

Since we use this isotope dilution technique, namely the 4He spiking, the standard measurement be-came very precise: the measured values are within 2 to 4 % around the expected values. The significance of this new method is beyond the tritium measurements. In all cases of helium measurements where precise he-lium isotope ratio measurements is needed, but the pressures are different, the 4He isotope dilution can be a way.

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