A procedure for the determination of
very low activity levels of tritium in water samples

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We describe the procedure developed for the electrolytic concentration of ^3H in water, together with systematically applied checks to guarantee the reproducibility of the process and to minimize the variability between water samples concentrated simultaneously in the different electrolytic cells. Starting from initial volume of 250 ml water, we obtained enrichment parameters normally greater than 70%, with a dispersion always less than 5%. Measuring the concentrated and the unelectrolyzed samples under the same conditions, we found that the lowest detectable activities had been improved from around 1.5 to 0.3 Bq/l. This allowed us to quantify the ^3H activity levels of 100% of the rainwater samples collected in Cáceres from 1994 to 1996. The resulting average value for this period was (0.79±0.38) Bq/l.

Introduction

A notable rise in the levels of ^3H in rainwater began in 1945 due to atmospheric nuclear blasts, reaching 400 Bq/l in 1963.[1] Since this date, the values have been steadily falling down. At present, with the exception of relatively small areas near facilities which contribute to the rise in the local tritiuminventory, such as nuclear power plants, large hospitals, or research centres,[2,3] it is frequent to find that the tritium content in waters are near[4] or below the detection limit of the iquid scintillation counters usually employed for ^3H determination, around 2 Bq/l.[5] The quantification of these low levels is the rincipal problem faced by investigators who use ^3H in numerous environmental applications, such as hydrogeological studies[6,7] or as a parameter to model the dispersion of other radionuclides within a mass of water.[8]

In a previous work,[9] we presented the methodology used for the measurement of the ^3H content of water samples. We achieved a chemical yield close to 100%, a figure of merit of 323, and a lowest detectable activity of 1.4 Bq/l.[9] This procedure, however, does not allow us to quantify the tritium concentration in waters where there has been no man-made contribution.[10] We have, therefore, put into practice a technique of concentrating ^3H in water samples by low temperature electrolysis at an alkine pH based on the isotopic fractionation of the hydrogen isotopes due to their mass differences. We present here a detailed study of the influence of the main working variables, temperature, total applied charge, conductivity and the algorithm used to calculate the specific activity of tritium. Applying this technique, we were able to quantify the temporal evolution of the tritium levels in rainwater of Cáceres (Spain) during the years of 1994 to 1996.

Experimental

Instrumentation

The measuring equipment consists of a Quantulus 1220 liquid scintillation spectrometer,[11] whose main characteristic is its relatively low background count rate (1.4 cpm in the ^3H region, channels of (1–230) thanks to the combination of active and passive (lead, copper, and cadmium) shielding. It also includes two multichannel analyzers which allow to collect spectral information for both the sample and background, facilitating the detection of any anomaly in the same. The spectrometer requires a detection efficiency calibration as a function of the quenching. This calibration was performed with ^3H standards of known activity subjected to different degrees of quenching with CCl_4, the standard efficiency of the unquenched standards being 22%.

The vials used for the measurements were of teflon-coated polythene with 20 ml capacity. This material is mechanically tough, has a low intrinsic radioactivity, and maintains the contents at a high degree of stability.[9] The scintillator cocktail used was Optiphase Hisafe 3, which we systematically mixed with the aqueous assay sample in the proportion 8/12. This allows the minimum detectable activity to be reduced by using a relatively large volume of water, without producing heterogeneity in the water-scintillator mixture.[9]

Electrolytic procedure

The procedure that we follow in electrolytically concentrating the tritium consists of the series of steps shown in Fig. 1.
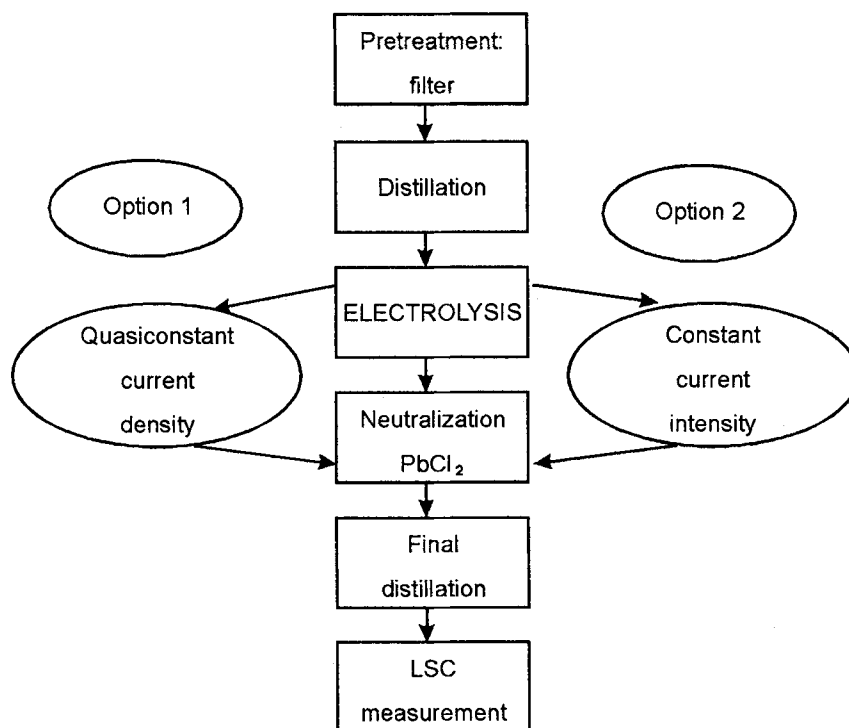
Fig. 1. Diagram of the complete procedure followed for ^3H assay by means of electrolytic concentration prior to measurement by liquid scintillation
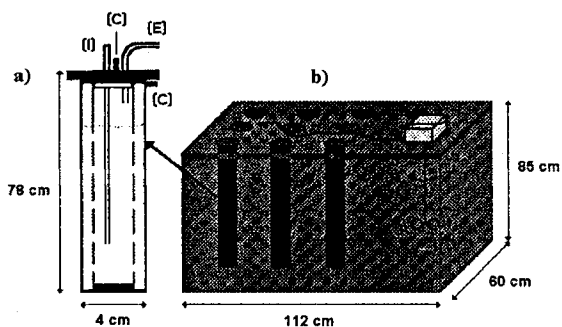

Fig. 2. Diagram of the experimental setup used for the electrolytic concentration of ^3H in water samples. (a) sectional view of an electrolytic cell, specifying its dimensions, the position of the anode (A), the cathode (C) and the gas outlet tube (E). (b) Arrangement of the cells and the stirrer in the refrigerating container

Sample pretreatment

After collecting 350 to 400 ml of water to be assayed it was filtered through 0.45 µm pore diameter membranes and then distilled at atmospheric pressure with no additives. All contact with the atmosphere was avoided by connecting a silicone trap to the condensation flask. We have verified that the tritium content of the sample was unaltered by this procedure,[9] allowing a nearly 100% recovery. Waters with a wide range of salinity[12] thereby have their specific conductivity reduced to values below 10 µS/cm. The mean value after distillation was $(3.5 \pm 3.2 \ \mu S/cm$ (mean±S.D.).

Electrolysis

The equipment used for the electrolytic concentration consists of a power supply unit providing currents of between 0 and 18 A to a series of 10 electrolytic cells placed in a refrigerating container. A diagram of the cells and their layout in the container is shown in Fig. 2. The cells were designed on the basis of those used by the DPSR.[13] They have a cylindrical geometry, with some 400 ml capacity, and close hermetically. The electrodes are of stainless steel to avoid corrosion. They are arranged concentrically, and electrically insulated by plastic on the top and bottom. The anode (A) is external and the cathode (C) is perforated to facilitate the homogeneity of the sample. Each cell presents an outlet tube for gases which is connected to a silicone trap through which the oxygen and hydrogen generated in the electrolytic reaction pass.

The cells are placed in a water-antifreeze filled refrigerating container, which is endowed with a strirrer to homogenize the temperature and a thermostat to select the temperature chosen to work at. In general, we work at sub-zero temperatures to counteract the heat generated by the electrolysis, and to have this take place at as close as possible to the freezing point of the solution to be electrolyzed. This allows one to achieve the greatest possible isotopic separation[14] and to avoid losses by evaporation, nebulization, or bubbling.

Initially, 250 ml of previously distilled water are electrolyzed in each cell. The quantity is determined by weighing for great precision. To each sample 1.0 g of Na_2O_2 is added, an electrolyte which forms NaOH in water and yields an alkaline medium favourable to electric conduction and hence to the reaction of water electrolysis. As all the cells have very similar ionic conditions, the electrolysis should occur in a reproducible manner.

Study of the electrical magnitudes

The amount of charge applied to each of the electrolytic cells is the main parameter in any electrolysis reaction. The charge can be applied in various forms, the most utilized being a constant current density $J(t)$ or constant current intensity $I(t)$.

For the cylindrical geometry of the electrolysis cells that we use, given that the anode has a radius r and that initially the volume of water V_0 to electrolyze would cover an area S_0 of the said electrode, the value of $J(t)$ will depend on the decrease of the active area $\Delta S(t)$ according to Eq.(1). The active area is in contact with the water at each instant of the reaction, and its decrease is a consequence of the development of the electrolysis during time t:

$$J(t) = \frac{I(t)}{S(t)} = \frac{I(t)}{S_0 - \Delta S(t)} \qquad (1)$$

From this equation, the amount of water electrolyzed, $\Delta m(t)$, can be obtained knowing its density ρ, the stoichiometry of the electrolytic reaction according to which 2.975 A·h are required for each gram of water decomposed, and the total charge $Q(t)$ applied:

$$\Delta m(t) = \frac{\rho \cdot r}{2} \cdot \left[S_0 - \frac{I(t)}{J(t)} \right] = \frac{Q(t)}{2.975} \qquad (2)$$

Taking into account that Eq. (2) establishes a linear relationship between the electrolyzed mass and the quantity of charge $Q(t)$ supplied during time t, it seems, in principle, that the best operative option available would before the electrolysis at $J(t) =$ const. It will then be possible to guarantee that a constant quantity that determines the degree of the electrolysis applied to the solution independently of the volume of the solution

which is left for electrolysis. This would imply, however, a linear continuous decrease of the intensity of the applied electric current, with which there may be a concomitant permanent instability in its supply. The most advisable solution may, therefore, be to carry out the electrolysis at a quasiconstant current density, i.e., varying $I(t)$ in a stepwise fashion, to emulate the aforementioned situation.

In order to select the procedure that is best suited to our experimental setup, i.e., to perform the electrolysis at constant current intensity or at quasiconstant current density, we carried out two series of experiments of electrolytic concentration, analyzing in each of them the mass loss, $\Delta m(t)$, that occurs in each electrolytic cell over the course of the reaction. In both procedures, however, we raised the current intensity gradually from 0 A to 6 A during 10 hours so that the start of the electrolysis should occur progressively and not violently. Once the said current intensity was reached, one of the two aforementioned procedures was followed. Figure 3 shows the results obtained for the each of the 10 cells on subjecting them simultaneously to a constant current intensity of 6 A, Fig. 3a, or to a quasiconstant current density of 0.022 A/cm^2, Fig. 3b. As can be seen, the mass loss achieved is similar on the two trials: after 97 h of electrolytic concentration, the mass losses in each trial are, as noted explicitly in fig. 3a and Fig. 3b, $[\Delta m(a)]/m = 62\%$, and $[\Delta m(b)]/m = 71\%$, respectively. On analyzing the mass loss in more detail, however, we found that there is a greater dispersion of the values for the 10 cells subjected to quasiconstant current density. For instance, when the total charge supplied in the two cases was $Q = 510$ A·h, the average mass loss was (170.0 ± 7.1) g for the electrolysis carried out at constant current intensity, and (174.9 ± 15.5) g for the electrolysis at quasiconstant current density.

Therefore, given that in the procedure we shall follow for the calculation of the yield of the electrolytic reaction, and consequently of the activity of the sample, it is absolutely necessary for the results to possess good homogeneity and reproducibility in each and every one of the ten cells used, we considered it most appropriate to perform the electrolysis at a constant current intensity, in particular in our case at 6 A.

Since the isotopic effect depends on the temperature, to achieve a similar enrichment in all cells requires the reaction to take place in each of them at as homogenous temperature as possible. Therefore, we monitored the spatial-temporal evolution of the temperature of the water-antifreeze solution filling the refrigerating container in which the electrolytic cells were immersed. With our experimental setup, we observed a maximum temporal variations of temperature of ±1 °C around 0 °C, and maximum spatial variations of ±0.2 °C. Within the intervals mentioned we observed no appreciable negative effects on the progress of the reaction.
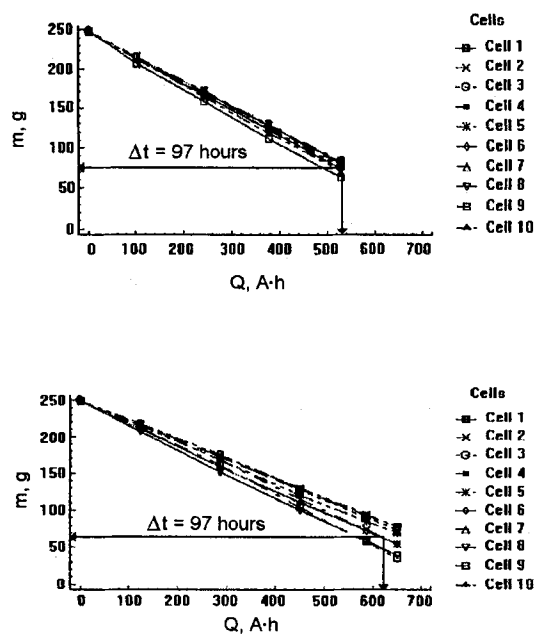
Fig. 3. Temporal evolution of the mass of the water in each of the ten cells during the electrolysis carried out at constant current intensity (a) and quasiconstant current density (b)

Neutralization with PbCl₂

After the electrolysis of the sample, the content of each cell was neutralized, since the medium in which the electrolysis took place is strongly alkaline. There exist a variety of methods for this purpose, such as bubbling CO_2 through the cell, or using $Pb(NO_3)_2$ [15] or $PbCl_2$. We used the latter salt, as this is less hygroscopic and dissociates less with heat than $Pb(NO_3)_2$.[16] The quantity of $PbCl_2$ added to reach an approximately neutral pH was some 4 g per 15 ml of sample electrolyzed, followed by measuring the value of the pH after each neutralization to verify the suitability of its value.

Final distillation

The sample is subsequently subjected to a single distillation in order to eliminate the salts formed in the previous neutralization, since a high degree of salinity may produce heterogeneity in the sample-scintillator mix.[12] The possible interchange of HTO with the atmosphere has to be avoided, using a silicone trap connected to the condensate collection flask. Following the indications of TAYLOR,[16] we chose a working temperature of around 150 °C. The mean values of the final specific conductivity that we obtained in the distilled samples were (299±159) μS/cm, this reduction in the conductivity after a single distillation being

sufficient to guarantee the homogeneity of the mixture of the distilled sample and the liquid scintillator.

Measurements

There are different methods for determining the enrichment due to the electrolysis, amongst others, assaying the deuterium content before and after the process.[17] In our laboratory, however, we use a method based on the ^3H determination by means of liquid scintillation spectrometry which is similar to that used by other groups,[13] and which we shall describe briefly.

The characteristics of our electrolytic container, see Fig.2, allow us to assay ^3H in 5 water samples in each electrolytic series. The remaining 5 cells of the series are needed to evaluate the enrichment that takes place during the electrolysis. Given the homogeneous and reproducible working conditions attained for the set of 10 cells, this allows us to extrapolate the calculated enrichment to the problem samples in a reliable way. Together with the water samples whose tritium content we wish to determine, in another three cells, we electrolyze water with as low a tritium content as possible to which we add known activities of this isotope. These labeled samples will allow us to determine the yield of the electrolysis. Another two cells, the so called background samples, contain these low tritium content waters to be concentrated without the addition of any radioactive tracer. These background samples have a twofold purpose: as blanks to be subtracted from the labeled samples so as to correct for the small, but not zero tritium concentration present in the water with which they were prepared; and as background to serve as a check for any possible contamination during the electrolytic concentration process.[18] With each of these components – labeled samples, background samples, and the problem samples – vials are prepared for the liquid scintillation specrometric determination of the ^3H content. In addition to the above 10 vials, we also have to measure an unelectrolyzed background water vial, to quantify the background noise of the scintillation spectrometer. It is also necessary to carry out a previous detection efficiency calibration of the spectrometer as a function of the quenching. This calibration must be renewed periodically.[19]

To obtain the specific ^3H activity, A_0 (Bq/l), of the water referred to the day of collection of the sample *si*, which was subsequently concentrated electrolytically prior to its assay, we use the expressions suggested by TAYLOR and FAÍSCA,[16,13] which when applied to our method of measurement yield the following final relationship:

$$A_0 = \frac{1000}{60 \cdot V} \cdot \left[\frac{R_{si}}{\varepsilon_{si}} - \frac{R_b}{\varepsilon_b} \right] \cdot e^{\frac{-0.693 \cdot t}{T_{1/2}}} \cdot \frac{1}{Fe_{si}} \qquad (3)$$

where, R_{si} and R_b are the count rates (cpm) of the electrolytically concentrated sample and of the unelectrolyzed spectrometer background sample, respectively; ε_{si} and ε_b are the liquid scintillation spectrometer efficiencies for the sample si and the background, b, respectively; V is the volume (ml) of the sample which is mixed with the liquid scintillator in each vial; $T_{1/2}$ is the half-life of ^3H, 12.43±0.05 years,[18] t is the time elapsed between the collection of the sample and its assay and Fe_{si} is the enrichment factor for sample si, calculated according to the expression:

$$Fe_{si} = e^{Pem \frac{\ln Wo_{si}}{\ln W_{si}}} \qquad (4)$$

where Wo_{si} and W_{si} are the initial and final masses of the sample si, respectively, and Pem is the mean enrichment parameter which we assume to be common to all samples, and is determined as the arithmetic mean of the enrichment parameter, Pe_{ti}, found for each of the aforementioned labeled water samples ti. Pe_{ti} are evaluated from the increases of the ^3H concentration due to isotopic fractionation in each of the labeled samples (quantified in the numerator of Eq.(5)), using the count rate of the labeled sample, R_{ti}, and the mean electrolyzed background rate, R_{bem}, as well as the activity of the label initially added to each cell, A_{ti}, duly corrected for the elapsed time, and the detection efficiency, ε_{ti}, for the labeled sample in question. The denominator of Eq.(5) takes into account the corresponding mass reductions that occur in the labeled samples, where the suffices indicate whether the mass W of each labeled sample ti is the initial or the final value:

$$Pe_{ti} = \frac{\ln \frac{R_{ti} - R_{bem}}{A_{ti} \cdot \varepsilon_{ti}}}{\ln \frac{Wo_{ti}}{W_{ti}}} \qquad (5)$$

We calculate the detection limits according to Currie.[20] The error associated with the specific activity was calculated by determining the latter at 98% confidence level, including the uncertainty due to the electrolytic enrichment process and the dispersion of the enrichment found for the three radioactively labeled samples that we used in each electrolytic series.

Discussion

Evaluation of the quality of the method

To assess the quality of the results obtained with the electrolytic concentration procedure prior to the determination of the specific activity of tritium in the water samples, Table 1 lists the experimental results corresponding to the measurement of 13 water samples with different activity levels. For each of the electrolytically concentrated samples, we give the value

of the mean enrichment parameter of the respective electrolytic concentration trial, Pem, together with the corresponding dispersion, ($\%D$), which in all cases was less than 5%. Thus with the concentration procedure followed here and the systematically applied checks, we can affirm that we achieve good repoducibility in the functioning of the different cells making up a given run of electrolytic concentration. The differences between the enrichment parameter values for the different samples listed in Table 1 reflect whether they belong to different runs of electrolytic concentration, and if so were thereby subjected to different values of the total charge Q.

Table 1 also gives the specific activity, A_o, and the corresponding associated errors, $e_a(A_o)$, or the values of the detection limits, and the minimum detectable activities, MDA, for each of the water samples analyzed. These values were all obtained for both of the treatments systematically applied to each sample, i.e., with and without electrolytic concentration prior to assay. In all cases, the initial volumes of the electrolyzed samples were 250 ml, and of the unelectrolyzed samples 8 ml, in all cases using measurement times of 8 cycles of 100 minutes each. To each activity level, we associate its quadratic error of measurement, taking into account the uncertainties of all the variables involved in the calculation of the activity. In the case of samples prepared in triplicate, such as numbers 7, 10, and 13 in the treatment with electrolytic concentration prior to measurement, the error that we associate to the same and that is listed in Table 1 is the greater of the values from comparing that of the dispersion and the quadratic error of measurement. Only, for sample number 10, dispersion was the dominant uncertainty.

From the values given in Table 1, the following results stand out:

(1) There is a notable decline in the minimum detectable activity, MDA, when the electrolytic concentration method is applied. While this value is always greater than 1.4 Bq/l for the water samples not subjected to prior electrolytic concentration, with this procedure the enrichment values of as low as 0.2 Bq/l are obtained (the typical value of the minimum detectable activity for our working conditions is 0.3 Bq/l).

(2) There is a good agreement between the levels of activity detected for each water sample on applying or not the electrolytic concentration procedure. For those samples whose activity levels are below the detection limit obtained without electorlytic concentration, when this procedure is applied the resulting levels of net activity are below the said limits. Also, for those other samples with levels of net activity which are quantifiable with or without prior electrolytic concentration, the difference between the two values is generally less than 5%. It is difficult to reduce further this relatively small

difference, as it is very close to the relative uncertainty of the quantification of tritium without prior electrolysis, and to the relative dispersion introduced into the enrichments because of electrolysis. The distillation process, to which some authors attribute an error of between 5 and 10%,[21] may have a certain relative importance in the total uncertainty. However, we have found experimentally[10] that in our setup the error mentioned is very small and perfectly delimitable.

^3H levels in rainwater collected in Cáceres

The technique of electrolytic concentration applied to the water samples allowed us to quantify the presence of

^3H radionuclide in rainwater samples collected monthly from 1994 to 1996 in the city of Cáceres (Spain). As there is no significant artificial ^3H source nearby, the rainwater would contain extremely low levels of the order of the natural cosmogenic origin.

The results obtained are listed in Table 2. The monthly levels for 1994, 1995, and 1996 are given for the ^3H specific acitivity measured in rainwater samples subjected or not subjected to the electrolytic concentration procedure prior to their assay.

Table 1. Values obtained in the analysis of the ^3H content of 13 water samples subjected or not subjected to prior electrolytic concentration

Sample No.	Pem(D, %)	With electrolytic concentration		Without electrolytic concentration	
		$A_o \pm e_a (Ao)$, Bq/l	MDA, Bq/l	$A_o \pm e_a (Ao)$, Bq/l	MDA, Bq/l
1	0.78(1.92)	206 ± 7	0.4	193 ± 10	1.5
2	0.78(1.92)	148 ± 4	0.4	153 ± 8	1.5
3	0.69(0.73)	1.17 ± 0.11	0.7	<1.6	1.6
4	0.69(0.73)	0.39 ± 0.05	0.3	<1.4	1.4
5	0.78(1.28)	0.44 ± 0.06	0.3	<1.5	1.5
6	0.74(3.16)	0.82 ± 0.04	0.3	<1.5	1.5
7.	0.74(3.34)	71.2 ± 3.0	0.4	65 ± 4	1.5
8	0.77(3.60)	0.56 ± 0.04	0.3	<1.5	1.5
9	0.77(3.60)	0.71 ± 0.03	0.2	<1.4	1.4
10	0.78(0.41)	0.87 ± 0.09	0.3	<1.6	1.6
11	0.74(3.16)	1.06 ± 0.05	0.3	<1.4	1.4
12	0.74(3.16)	0.81 ± 0.04	0.3	<1.5	1.5
13	0.77(3.16)	2.75 ± 0.11	0.4	1.8 ± 1.4	1.5

Pem mean enrichment parameter of the corresponding electrolytic concentration run.
D percentage dispersion.
A_o net activity level or its detection limit.
e_a associated absolute uncertainty.
MDA minimum detectable activity.

Table 2. Results for the specific acitivity of tritium, A_o in (Bq/l), with the corresponding associated absolute error, obtained with and without prior electrolytic concentration for rainwater from the city of Cáceres collected monthly from 1994 to 1996

| Month, No.	$A_o \pm e_a(A_o)$, Bq/l					
	1994		1995		1996	
	Without electrolysis	With electrolysis	Without electrolysis	With electrolysis	Without electrolysis	With electrolysis
1	<1.6	0.38±0.05	1.3±1.2	0.62±0.05	<1.5	0.65±0.04
2	<1.5	0.79±0.06	<1.4	0.70±0.04	<1.5	0.64±0.04
3	NR	NR	<1.4	0.44±0.06	<1.5	1.15±0.04
4	<1.2	0.76±0.05	<1.4	0.79±0.06	<1.5	0.88±0.04
5	1.9±1.1	1.98±0.06	NR	NR	<1.4	0.86±0.05
6	NR	NR	<1.6	0.57±0.08	NR	NR
7	NR	NR	1.4±1.1	1.59±0.06	NR	NR
8	NR	NR	NR	NR	NR	NR
9	NR	NR	<1.5	1.30±0.05	<1.5	0.42±0.08
10	1.6±1.2	0.79±0.05	<1.5	0.70±0.04	<1.5	0.36±0.02
11	1.4±1.1	0.87±0.04	<1.3	0.53±0.05	<1.4	0.70±0.03
12	1.3±1.1	1.01±0.04	<1.3	0.41±0.05	<1.5	0.56±0.03

NR: No rainfall.
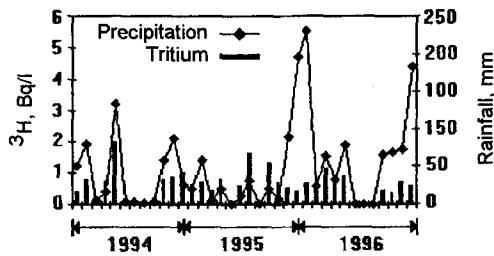
Fig. 4. Temporal evolution of the activity levels of tritium in the rainwater collected monthly in the city of Cáceres (Spain) from 1994 to 1996, and the total monthly precipitation amounts recorded during the cited sampling period

On determining the tritium levels in rainwater without prior electrolytic concentration, we obtained a net activity in 23% of the months in which there was significant rainfall, the mean value for the period of study was (1.5 ± 0.2) Bq/l (as always, at a 98% confidence level). The application of the concentration technique described here allowed us to quantify the tritium concentration for the same months in 100% of the cases, with a mean value for the activity of (0.79 ± 0.38) Bq/l. This reduction by some 50% in the mean value, as compared to the rainwater samples that we had already determined a net activity for without using prior electrolytic concentration, is due to the improved accuracy and precision, and to the contribution to the cited average of rainwater samples with net tritium activity levels that were relatively low.

The temporal evolution of the tritium levels in rainwater is shown in Fig. 4, together with the precipitation recorded for the aforementioned sampling period. We found no significant correlation $(r^2<0.25)$ between the two variables, and neither did we observe any autocorrelation in the data. However, we can conclude that the values found follow a stochastic Gaussian distribution around their mean, with the values of May 1994 (1.98 Bq/l) and July 1995 (1.95 Bq/l) being relatively anomalous with respect to this distribution.

We, therefore, believe that the HTO levels recorded in the rainwater of Cáceres can be attributed to the environmental background of natural origin, with the levels observed in other points of Spain[22] and in other parts of the world before the bomb tests[23] and lower than the activity levels measured around nuclear facilities.[24,3]

Conclusions

We have developed a technique to determine the tritium content of water at low activity levels, based on the electrolytic concentration. With this procedure and our experimental setup we are able to carry out the electrolytic concentration of five different water samples simultaneously. The procedure has a great degree of stability, the observed thermal variations being less than ±1 °C, as well as a great reproducibility, with a percentage dispersion less than 5%. It also considerably reduces the detection limit, since from an initial volume of 250 ml of water, one obtains enrichment parameters close to 80% and minimum detectable activities of the order of 0.3 Bq/l. The systematic application of the concentration procedure prior to measurement allowed us to study the temporal variation of the levels of tritium in rainwater from the city of Cáceres. When the electrolytic technique was not used, we only obtained net activity values in 23% of the samples, with a mean value of 1.5 Bq/l. The use of our technique led to estimate the ^3H concentration with greater precision: the mean value of the activity for the years 1994 to 1996 was (0.79 ± 0.38) Bq/l.

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References

1. R. M. BROWN, Proc. Workshop on Tritium and Advanced Fuels in Fusion Reactors, CEC Publ. EUR 12540, Varenna, Italy, 1989.
2. S. OKADA, N. MOMOSHIMA, Health Phys., 65 (1993) 595.
3. A. BAEZA, L. M. DEL RÍO, A. JIMÉNEZ, C. MIRÓ, J. M. PANIAGUA, M. RUFO, J. Radioanal. Nucl. Chem., 207 (1996) 331.
4. N. MOMOSHIMA, T. KAJI, I. T. POPPY, N. INOUE, Y. TAKASHIMA, J. Radioanal. Nucl. Chem., 150 (1991) 163.
5. M. J. WOOD, R. G. C. MCELROY, R. A. SURETTE, R. M. BROWN, Health Phys., 65 (1993) 610.
6. P. THEODORSSON, Isotopes in Hidrology, IAEA, Vienna, 1967.
7. J. SHIMADA, H. MOMOTA, Y. ONO, Subsurface Space, Pergamon Press, Stockholm, 1980.
8. IAEA, Tritium in Some Typical Ecosystems, Tech. Rept. No. 207, IAEA, Vienna, 1981.
9. A. BAEZA, L. M. DEL RÍO, E. GARCÍA, A. JIMÉNEZ, C. MIRÓ, J. PANIAGUA, M. RUFO, Anal. de Física, 93 (1997) 177.
10. A. BAEZA, E. GARCÍA, M. DÍAZ, C. MIRÓ, Proc. XXVI Reunión, Bienal de Física. Las Palmas de Gran Canaria, Spain, 1997.
11. WALLAC, Quantulus: Liquid Scintillation Counter. 1220, Instrument Manual, LKB Wallac, 1987.
12. E. GARCÍA, Puesta a punto de un espectrómetro de centelleo líquido y ultrabajo fondo para la medida de tritio en muestras de agua, Universidad de Extremadura, Spain, 1995.
13. M. C. FAÍSCA, Proc. 4ª Conf. Nac. de Física, Évora, Portugal, 1984.
14. O. SEPALL, S. G. MASON, Can. J. Chem., 23 (1960) 2024.
15. P. BENZI, F. NEBBIA, R. RIGHETTI, P. VOLPE, J. Radioanal. Nucl. Chem., 196 (1995) 15.
16. C. B. TAYLOR, Proc. Intern Symp. on Methods of 'ow-Level Counting and Spectrometry, IAEA, Berlin, 1981.
17. M. KAKIUCHI, K. TANAKA, K. KIGOSHI, J. Appl. Radiation Isotopes, 8 (1991) 741.

18. T. FLORKOWSKI, Low-Level Tritium Assay in Water Samples by Electrolytic Enrichment and Liquid-Scintillation Counting in the IAEA Laboratory, IAEA, No. 252, 1963.
19. A. BAEZA, L. M. DEL RÍO, E. GARCÍA, A. JIMÉNEZ, C. MIRÓ, J. PANIAGUA, M. RUFO, Proc. 10ª Conf. Nac. de Física, Faro, Portugal, 1996.
20. L. A. CURRIE, Anal. Chem., 40 (1968) 586.

21. R. MOORE, E. R. BUSKIRK, Nature, 189 (1961) 149.
22. A. PLATA, Proc. Curso sobre Hidrología Isotópica, Cedex, Madrid, 1996.
23. S. KAUFMAN, K. F. LIBBY, Phys. Rev., 93 (1954) 1337.
24. K. MATSUURA, Y. SASA, C. NAKAMURA, H. KATAGIRI, J. Radioanal. Nucl. Chem., 197 (1995) 295.