Minimizing new tritium line sensitivity by a quality process implemented at Madagascar-I.N.S.T.N

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A quality process rigorously implemented in the Isotope Hydrology Laboratory of Madagascar-I.N.S.T.N. has significantly contributed to minimize the sensitivity of a recently installed tritium line used for groundwater dating. The ISO/CEI 17025 standard has been applied to fifteen (15) groundwater samples collected from different boreholes in the semi-arid South of Madagascar. The results are in agreement with the spikes analyses results which show that the mean value of the enrichment factor is 23.78 and the enrichment parameter is 0.88 for a preliminary test. Such values are much higher than the usual ones (approximately of 18) for a first enrichment, indicating electrolytic cells optimised work. In addition, the standard deviations are respectively 1.6 and 0.02 for the enrichment factor and parameter, meaning therefore that the cells performances are relatively good. In addition, background measurement was carried out on a dead water sample and produced a relatively low value of 1.07 cpm, then simultaneous activities measurement of indoor and outdoor control water samples gave approximately the same values. The latter results prove that there is no indoor contamination of the samples. Finally, the groundwater samples analysis results show that the water activities vary from 0.27 TU to 2.97 TU confirming that the tritium line sensitivity is lower than 0.30 TU and that the system is able to determine groundwater ages up to one thousand years (1000 a), whereas usual tritium lines sensitivities are around 0.80 TU.

1. INTRODUCTION

Since 1998, Madagascar-I.N.S.T.N. has been involved in groundwater investigations in the semi-arid Southern part of the island, in collaboration with the Water Ministry. These investigations have been carried out within the frame of regional and national projects sponsored by the International Atomic Energy Agency (I.A.E.A.). The main contribution of the latter projects is to determine groundwater age, recharge, renewal rate, flow velocity, mineralization, pollution and vulnerability to contaminants, through specific use of isotope tracers. Environmental Tritium and Carbon-14 have been used as tracers to date younger and older groundwater respectively. Until January 2009, all isotope analysis was carried out abroad, whereas chemical analyses are carried out in Madagascar-I.N.S.T.N. laboratories. From then on, a new tritium analysis laboratory has been installed in the latter institute in order to allow local younger groundwater dating. In order to comply to ISO 17025 requirements, a Quality Assurance process has been implemented in the new laboratory.

Tritium ^3H originates from cosmic nuclear reactions and from nuclear plant fission products release. Since most countries have signed the Non-Proliferation treaty, the concentration of atmospheric tritium has significantly decreased. Thus, research for more sensitive analytical methods has been developed during these last years. Madagascar-I.N.S.T.N. is taking part in this project.

2. LABORATORY EQUIPMENT AND ANALYTICAL PROCEDURES

2.1. Analytical Procedure

There are four main stages:

-Distillation of samples;

-Electrolytic enrichment in tritium;

-Neutralization of electrolysis residue;

-Liquid Scintillation Counting (LSC): TRI-CARB 3172/SL Model, Softwares: Quanta Smart and Spectraworks

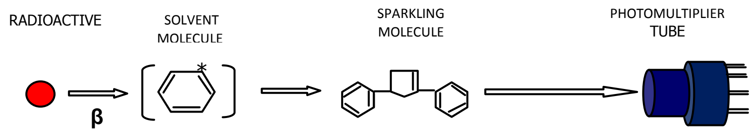


Figure 1. LSC counting scheme

2.2. Activity Measurement [1]

The following corrective parameters for tritium activity measurement have to be taken into account:

- Enrichment Parameter: it characterises the electrolysis capability to electrolyse a molecule of water

$$P=\frac{(Wi-Wf)}{Q/2.975}*\frac{\ln(ZIS)}{\ln\frac{[Wi]}{[Wf]}} \quad (1)$$

2.975 Ah: necessary electrical load to electrolyse 1g of water

Wi, Wf: initial and final masses of water

Q: total electrical load consumed

ZIS: enrichment factor relative to spikes electrolysis

- Enrichment Factor Z (sample): it refers to the degree of tritium enrichment of a water sample after electrolysis

$$Z=\exp\left[\frac{Pavg*Q}{2.975(Wi-Wf)}*\ln(\frac{Wi}{Wf})\right] \quad (2)$$

Pavg being the mean value of enrichment parameters for three spikes cells

Hence, the Sample Tritium Activity is

$$A_T=\frac{N_{SA}*A_{ST}}{N_{ST}*Z_T}*D \quad (3)$$

D: radioactive decay correction (exp(-λt))

Nsa: sample count rate

Nst: standard spike count rate

Ast: standard spike activity

2.3. Sensitivity calculation

For a minimum counting time greater than 50 mn, the system sensitivity is characterized by the following,

. LSC Lowest level of Detection (LLD) $LLD=\frac{2.71+4.65*\sqrt{BF*t}}{t}$ [2] (4)

BF: background noise

t: counting time

. Sample Minimum Detectable Activity $MDA = \frac{LLD}{\varepsilon * V * 60 * Z_i}$ (5)

ε : LSC efficiency

V: sample volume

Z: enrichment factor

(Unit: 1 TU = 3.193 pCi.L-1 = 0.118 Bq.L^{-1})

2.4. Quality approach

The Quality approach implemented in this work is summarized in the Deming Wheel stages [3]

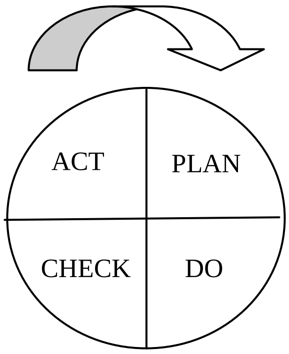


Figure 2. Deming Wheel

Plan: technical and administrative audit (physical parameters study)

Do: objectives and procedures implementation

Check: that all procedures have been rigorously applied and that the results obtained are in accordance with the quality objectives

Act: to take any necessary actions, which may improve the technical performance

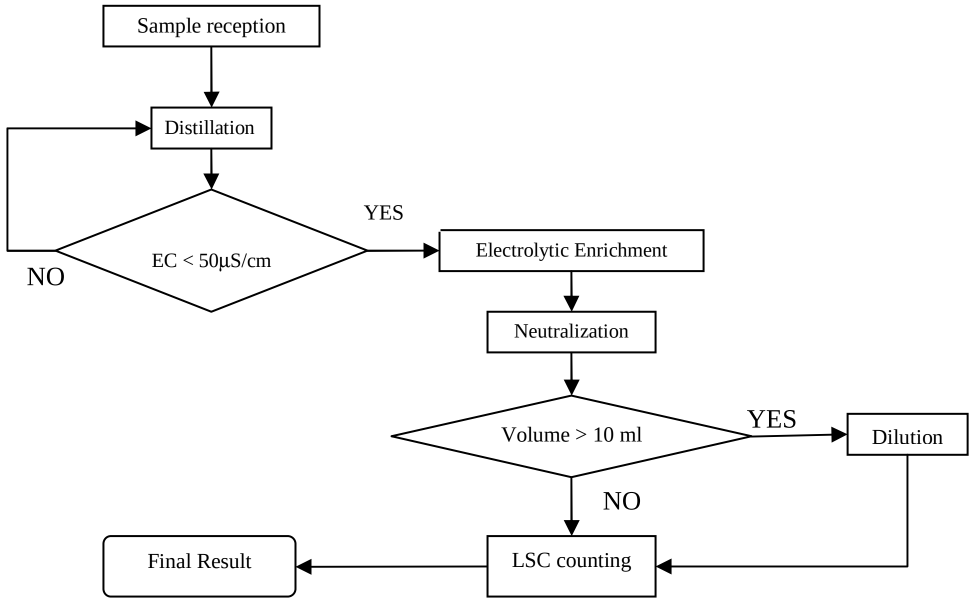


Figure 3. Operational procedure flow diagram [4]

2.5. Environmental quality procedure implemented

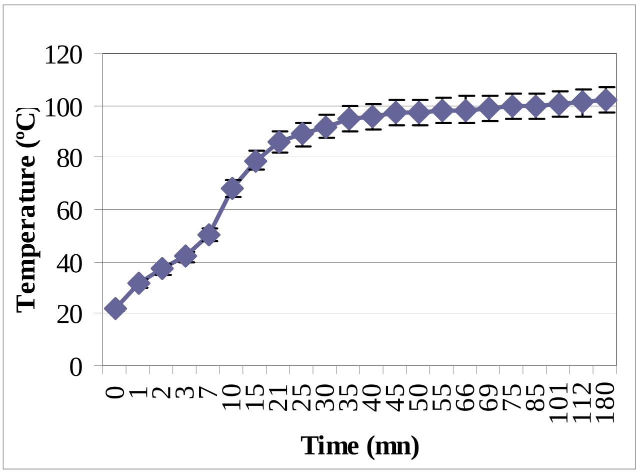
- Indoor and outdoor atmospheric monitoring
- Electrolysis cells reconditioning (post Zi monitoring treatment)
- LSC calibration
- Record (logbook)
- Ambient temperature around 15°C (lab indoor)
- Any laboratory work is away from any radioactive sources in order to obtain non contaminated equipment
- Quality of sample preparation: control with dead water (no significant concentration change before and after electrolysis), spikes must have relatively the same Pi
- Measurement quality: (i) depends on the equipment performance (ii) Sparkling cocktail properly mixed and not exposed to light (iii) Counting temperature requirement respected [5]

3. RESULTS AND INTERPRETATION

3.1. Physical parameter study

In order to optimize the method sensitivity, the following parameters correlation study is carried out.

- Distillation Heater Temperature Variation vs Time (figure 4),
- Cells voltages for I = 6A (figure 5),
- Reduction factor for each cell (figure 6).



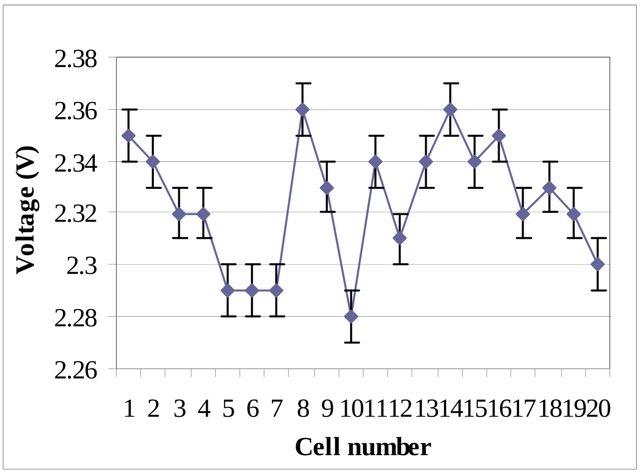


Figure 4. Distillation Heater Temperature Variation vs Time Figure 5. Cells voltages for I = 6A

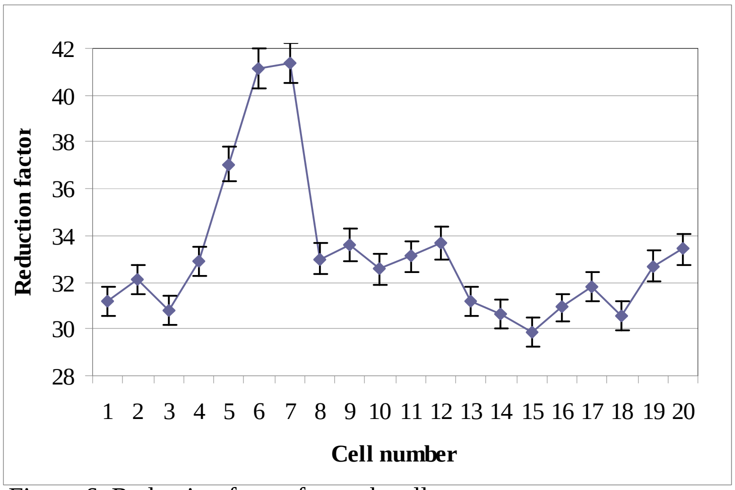


Figure 6. Reduction factor for each cell

3.2. Environmental tritium contamination check results

- Atmospheric tritium content: 1.25 TU, in accordance with Antananarivo precipitation tritium content [6]
- Dead water activity remains relatively constant: 0.24 TU, thus it is assumed that there is relatively low contamination (dead water standard activity: 0.05 TU)
- The mean values of LSC counting before and after electrolysis enrichment are respectively 1.1 cpm and 1.2 cpm, therefore there is no contamination during the electrolysis enrichment process.
- Background check: 4 tests are carried out and after 3 months the background is significantly improved (figure 7).

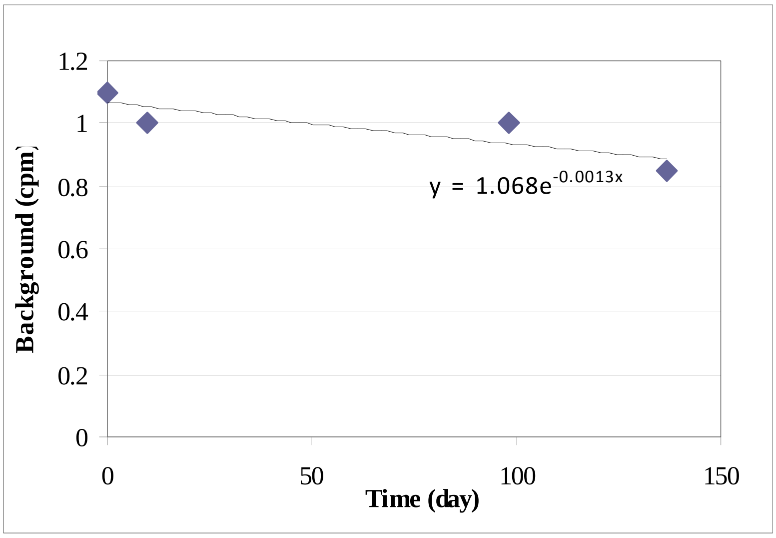


Figure 7. Background variation vs time

3.3. Electrolysis cells quality check

The enrichment factors Z comparison between spike and sample shows a similar trend (figure 8), which is an indicator of proper equipment work [7].

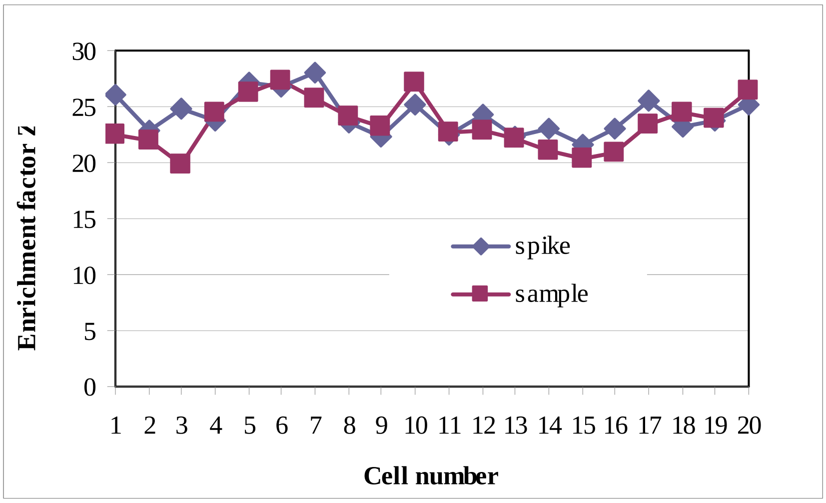


Figure 8. Enrichment factor comparison between spike and sample

3.4. LSC quality check results

The radioactive decay measurement of a diluted spike activity for 2 samples of the same spike is clearly shown by figure 9, despite a slight deviation between the two decay lines which is due to different enrichment factors. Thus a proper LSC work can be inferred.

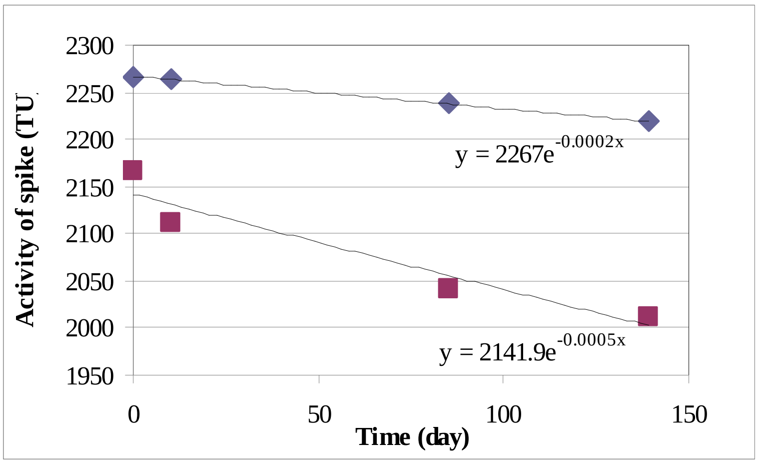


Figure 9. Radioactive decay of two samples fro the same spike

3.5. Analysis results validation

The mean mass of the samples before electrolysis is 498.91 ± 0.415g, therefore we can conclude to a proper sample preparation, since the relative uncertainty is lower than 0.1 %.

- B16bis/08012M sample distillation has to be resumed because of conductivity higher than 50 µS/cm.

-The enrichment factor P, around 0.88, is quite similar and close to 100 % for three spikes cells. In addition the mean mass of the samples after electrolysis is 12.84 g, which is not far from the calculated value of 9 g of remaining mass corresponding to a total consumed electrical current of 1420 Ah, and the mean value of the enrichment factor Z is 23.89. These results are indicators of a relatively good sample enrichment process.

- Neutralization of the enriched samples leads to an acceptable pH of 5 to 7.

- Most reduced samples volumes after enrichment are greater than 10 mL, and therefore do not need any necessary dilution which can be source of additional contamination risk.

- The LSC efficiency is 24.38 %, which is acceptable (manual recommended value: 28%). The standard deviation of the samples mean count value for the 10 tests is 0.41 cpm, and that of the spikes is 2.85 cpm,. The relatively low standard deviation values indicate counting stability.

By the way, the statistical uncertainties on counting Ux vary from 0 to 0.52 cpm.

Application of the rejection procedure (rejection of non acceptable results): All standard deviations relatively to the mean values from the 10 tests are lower than 2.8*Ux [8], therefore acceptable.

- Method Sensitivity: the above mentioned quality approach lead to the following values of Lowest Level Detection and Minimum detectable activity,

LLD = 0.818 cpm MDA = 0.229 TU

The lowest sample activity measured by this quality approach reaches 0.27 TU, which is in accordance with the MDA.

4. CONCLUSION

The implementation of the Quality approach to the tritium line laboratory has contributed to optimize the analytical approach, leading to the following results:

- Enrichment system is optimized;
- Proper samples preparation;
- Minimized indoor contamination;
- Lower sensitivity of less than 0.3 TU, whereas the world common sensitivity of tritium lines is around 0.7 TU. Thus it is possible to determine groundwater ages up to 1000 a when applying strict Quality approach to the tritium enrichment method.

Acknowledgements

Our sincere gratitude to the International Atomic Energy Agency for its support within the frame of training, expertise and equipment, and to the Governmental authorities for their administrative and financial contributions. Many thanks to HEP'MAD 09 organizing Committee.

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