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DETERMINATION OF TRITIUM IN WATER USING ISOTOPIC ENRICHMENT. METHODOLOGY IMPROVEMENTS

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LSC 2017

Advances in Liquid Scintillation Spectrometry

1-5 May, Copenhagen

LOCATION

TÉCNICO LISBOA

Instituto Superior Técnico, Campus Tecnológico e Nuclear

Lisbon, Portugal

Laboratory of Radiological Protection and Safety (LPSR)

INTRODUCTION

Tritium (^3H)

✓ present in the environment as a result of both natural and anthropogenic sources

^3H	Half-life	Pure beta emitter
	12.31 years	Emax = 18.6 KeV

✓ produced in the atmosphere through nuclear reactions between fast neutrons resulting from cosmic radiation and nitrogen atoms

Nuclear tests (1945-1963) → **Contamination by Fallout**

Nowadays → **Levels near the minimum detectable concentrations**

METHODOLOGY

Electrolytic enrichment

1. Purification by vacuum distillation
   - ✓ Addition of $Na_2S_2O_3$ and Na_2CO_3 to a volume of about 500 mL

2. Electrolysis in direct current
   - ✓ 14 cells: 3B; 3SPK; 8 Samples

≅ 1 week

3. Distillation with $PbCl_2$

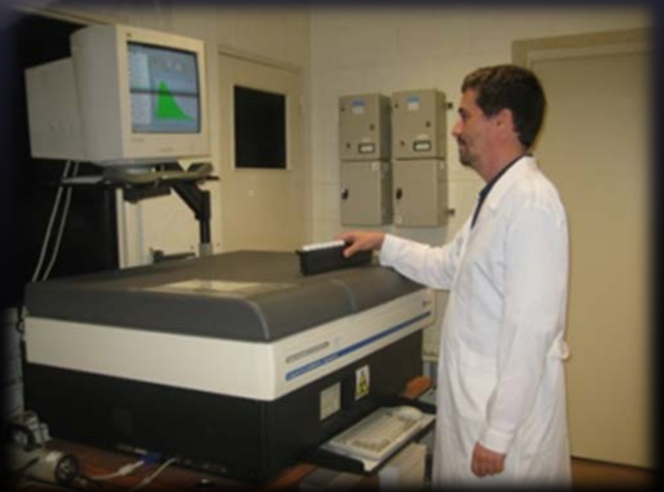
Electrolytic system

METHODOLOGY

Electrolytic enrichment

4. An aliquot of the distillate (about 8 g) is mixed with 12 g of Ultima Gold LLT® scintillation cocktail in borosilicate glass vials

5. Measurement
   - ✓ Samples are stabilized in the dark
   - ✓ Tri-Carb 3170 TR/SL (PerkinElmer), in low level mode
   - ✓ DL ≅ 0.4 $Bq.L^{-1}$, 300 min (routine analysis)



QUALITY CONTROL

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Improvements

✓ Uncertainty budget

- Gross sample count rate,
- Background count rate,
- Counting efficiency,
- ^{3}H half-life.

QUALITY CONTROL

Improvements

✓ **Uncertainty budget - More parameters**

- Gross sample count rate,
- Background count rate,
- Counting efficiency,
- ^{3}H half-life,
- Weighings,
- Direct current,
- Electrolytic enrichment factor (Z),
- Enrichment parameter (P).

Homemade software calculations

QUALITY CONTROL

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Improvements

✓ Activity Concentration

$$C_A = \frac{n}{\varepsilon . S . f_D}$$

$$\varepsilon = a_0 + a_1 \cdot tSIE \qquad S = \frac{m \cdot Z_{smp}}{1000 \cdot \rho}$$

$$f_D = e^{-\frac{\ln(2)}{T_{1/2}(\,^{3}H)}(t-t_0)}$$

$$Z_{smp} = e^{\left(\frac{E_p \cdot I \cdot log\left(\frac{m0}{mf}\right)}{(m0-mf) \cdot F}\right)}$$

C_A	**Activity Concentration, Bq.L^{-1}**
n	Net count rate, cps
ε	Efficiency
S	Sample quantity, Kg
f_D	Decay factor
tSIE	Special index of spectrum external standard transformed
m	Transferred sample to scintillation vial, g
Z_{smp}	Electrolytic enrichment factor of sample
ρ	Water density, g cm^{-3}
I	Current intensity, A
mo	Initial sample mass, g
mf	Final sample mass, g
$T_{1/2}$ (^{3}H)	Tritium half-life, s
F	Faraday constant

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Improvements

- ✓ **Activity Concentration**
- ✓ **Uncertainty budget**

$$u(C_A) = C_A \cdot \sqrt{\left(\frac{u(n)}{n}\right)^2 + \left(\frac{u(\varepsilon)}{\varepsilon}\right)^2 + \left(\frac{u(S)}{S}\right)^2 + \left(\frac{u(f_D)}{f_D}\right)^2}$$

$$u(n) = \sqrt{{u_r}^2(g) + {u_r}^2(b)}$$ *Net count rate*

$$u(\varepsilon) = \sqrt{u^2(a_0) + tSIE^2 \cdot u^2(a_1) + a_1^2 \cdot u^2(tSIE)}$$ *Efficiency*

$$u(S) = S \cdot \sqrt{{u_r}^2(m) + {u_r}^2(Z_{smp}) + {u_r}^2(\rho)}$$ *Sample quantity*

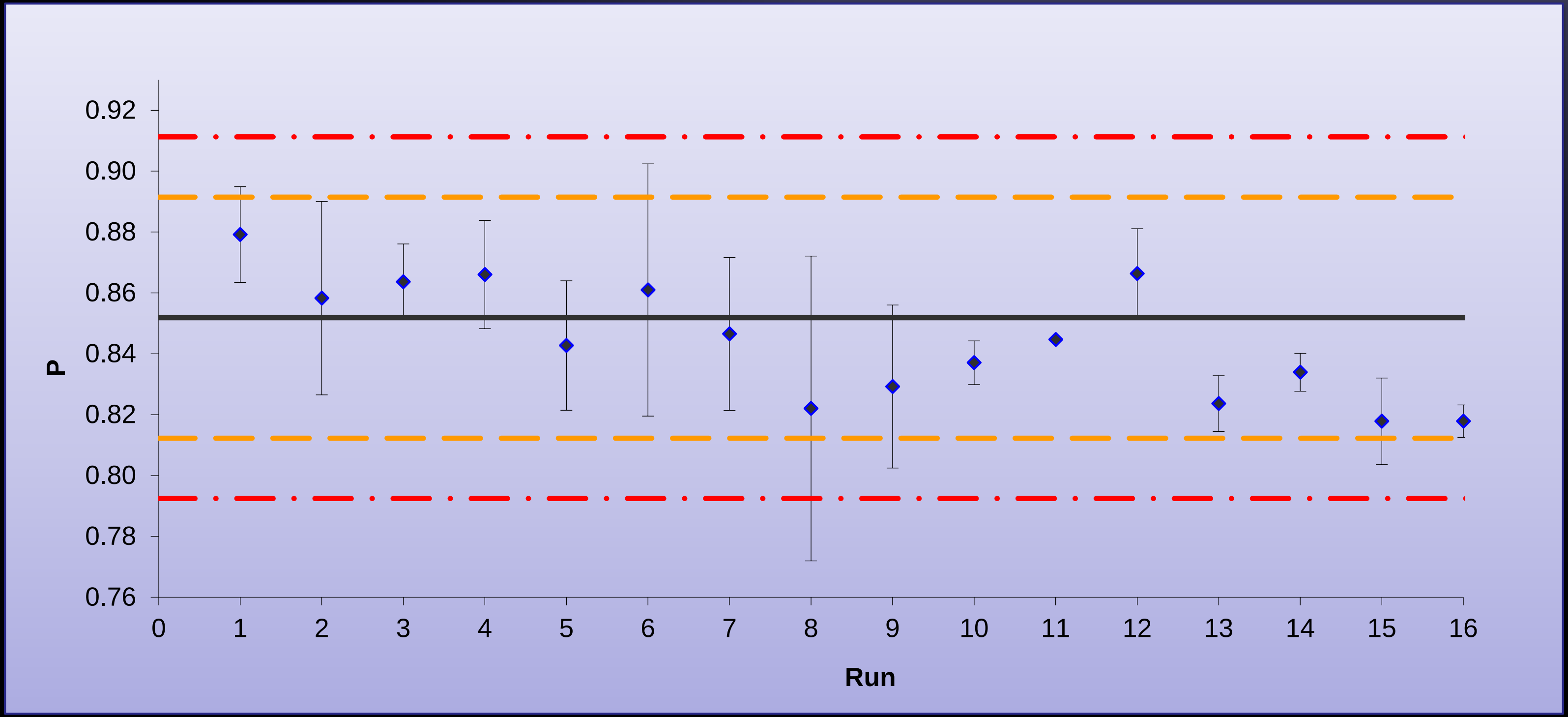
$$u(f_D) = \frac{\ln(2)}{T_{1/2}^2(^3H)} f_D(t - t_0) u\left(T_{1/2}(^3H)\right)$$ *Decay factor*

QUALITY CONTROL

Improvements

Control charts

✓ Enrichment parameter (P)

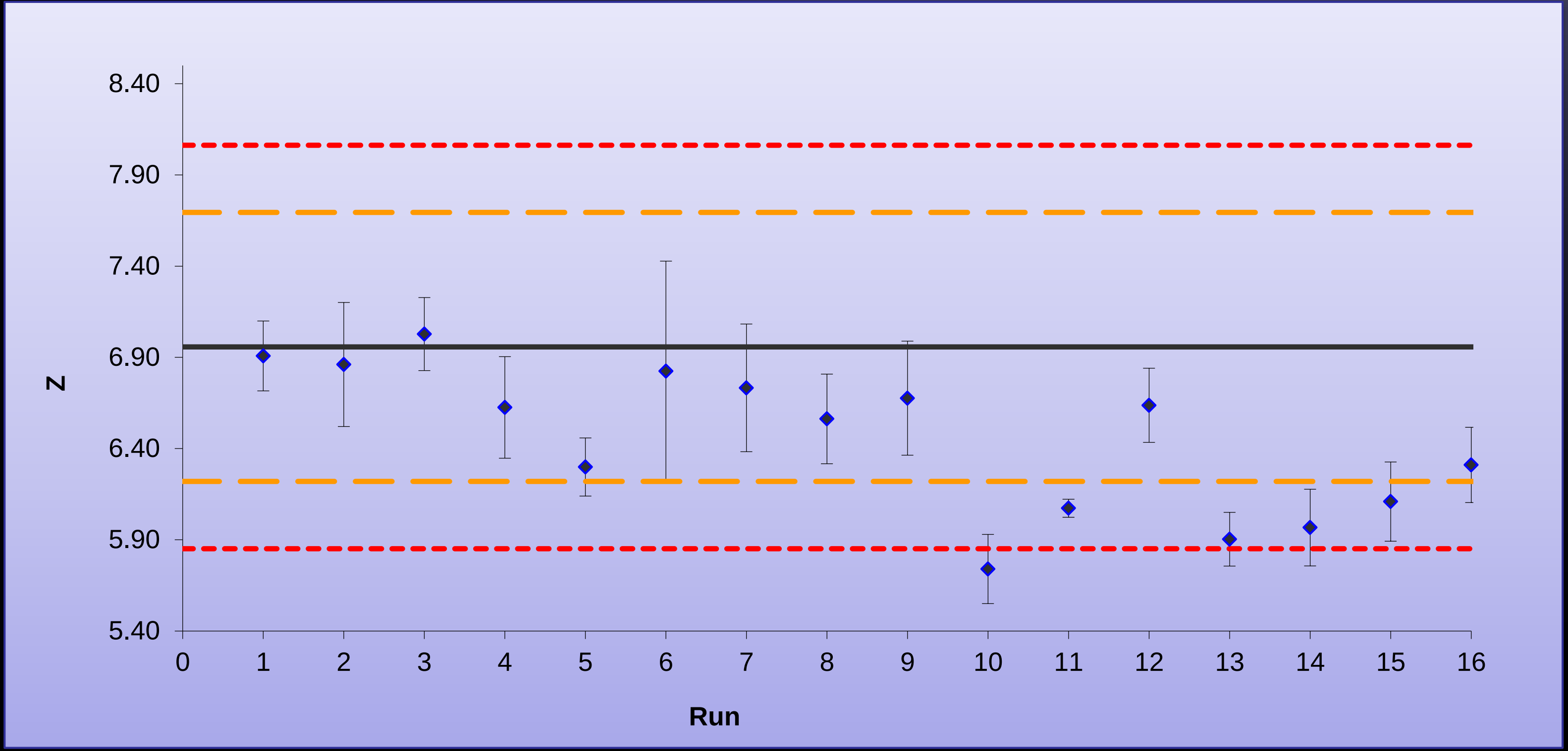


QUALITY CONTROL

Improvements

Control charts

- ✓ Enrichment parameter (P)
- ✓ Electrolytic enrichment factor (Z)



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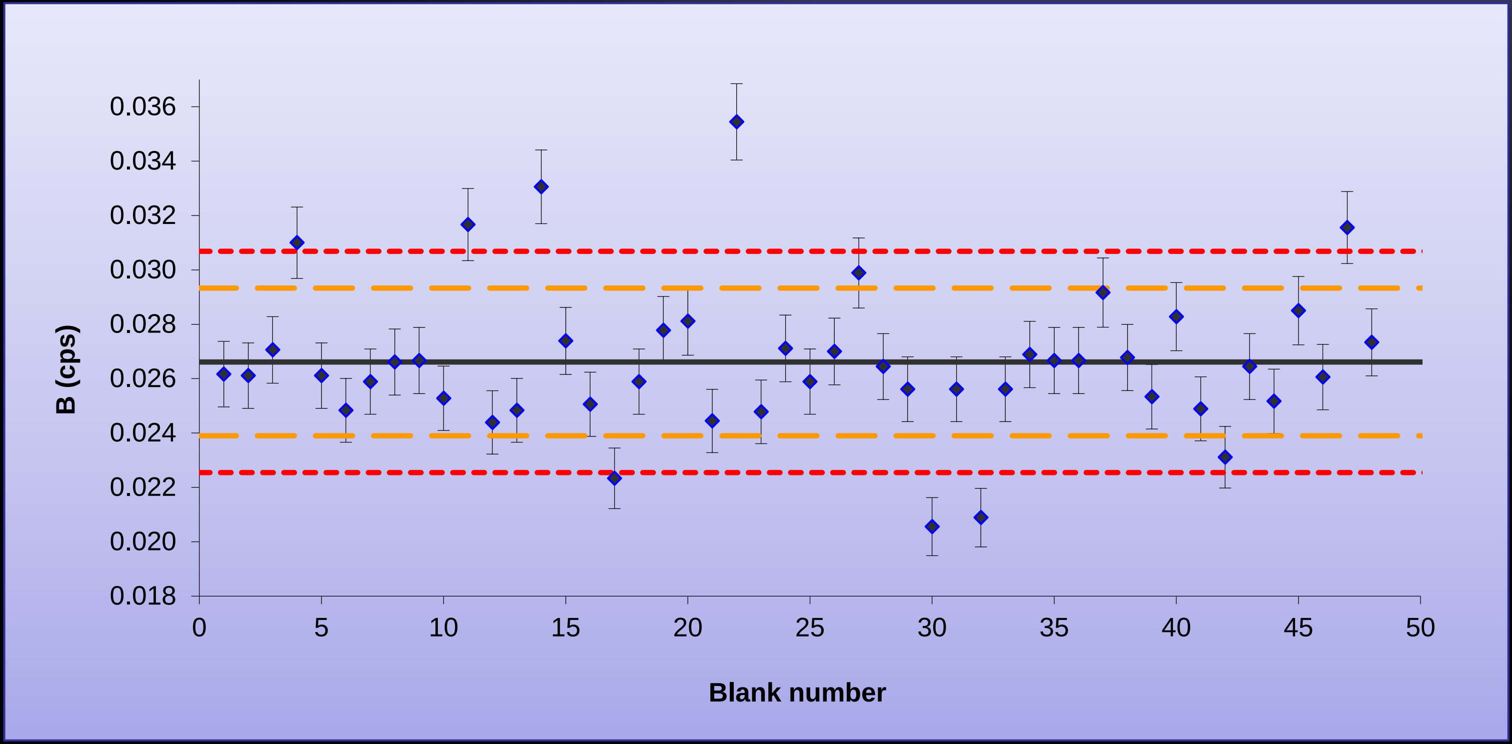
Improvements

Control charts

- ✓ Enrichment parameter (P)
- ✓ Electrolytic enrichment factor (Z)
- ✓ Blank samples (B)



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Intercomparison participations in 2014 and 2015

- ✓ **International Atomic Reference Material Agency (IARMA)** ETRIT-PT-2014 - IARMA Proficiency Test on the Determination of Tritium in Water at Environmental Levels

1 Bq/Kg ⇒ 8.390 ± 0.015 TU

Dead water with tritium (NIST)					
Sample	**Reference Values (TU)**	**Laboratory values (TU)**	**Reference Values ($Bq.L^{-1}$)**	**Laboratory values ($Bq.L^{-1}$)**	**Evaluation**
IARMA-005 Level A	<0.5	<3.7	<0.060	<0.44	A
IARMA-006 Level B	6.1 ± 0.2	5.7 ± 2.4	0.727 ± 0.024	0.68 ± 0.29	A
IARMA-007 Level C	21.9 ± 0.5	22.7 ± 3.4	2.610 ± 0.060	2.71 ± 0.41	A
IARMA-008 Level D	110.2 ± 3.0	108 ± 10	13.13 ± 0.36	12.9 ± 1.2	A
IARMA-009 Level E	21.9 ± 0.5	18.0 ± 3.2	2.610 ± 0.060	2.14 ± 0.38	A
IARMA-010 Level F	110.2 ± 3.0	96.5 ± 8.4	13.13 ± 0.36	11.5 ± 1.0	A

QUALITY CONTROL

Intercomparison participations in 2014 and 2015

- ✓ **International Atomic Reference Material Agency (IARMA)** ETRIT-PT-2014 - IARMA Proficiency Test on the Determination of Tritium in Water at Environmental Levels
- ✓ **Consejo de Seguridad Nuclear (CSN, Spain)** - Intercomparación analítica entre laboratorios de radiactividad ambiental - 2015

Seawater			
A ($Bq.L^{-1}$)	**U ($Bq.L^{-1}$)**	**Z**	**Z (ML)**
5.57	0.58	0.81	0.45

$$individual\ z-score\ (Z) = \frac{x - X}{\sigma_p}$$

$$median\ z-score\ (Z\ ML) = \frac{x - ML}{DER}$$

Satisfactory: |z-*score*| ≤2

CONCLUSIONS

Method ptimization

Improvements

- Uncertainty budget
- Control charts

Accuracy validation

- Different ranges of tritium in waters
- Seawater

Remaining Challenges

Improve

- P and Z parameters
- Cells washing process
- Establish levels in DC counter
- Automatic control charts

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Thank you for your time!
Questions?

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