



LNF-02/013 (P)
2 Luglio 2002

**EVIDENCE OF ANOMALOUS TRITIUM EXCESS IN D/PD OVERLOADING
EXPERIMENTS**

**Francesco CELANI⁽¹⁾, A. Spallone⁽¹⁾, P. Marini⁽²⁾, V. di Stefano⁽²⁾, M. Nakamura⁽²⁾,
E. Righi⁽¹⁾, G. Trenta⁽¹⁾, P. Quercia^(3,1), A. Mancini⁽⁴⁾, G. D'Agostaro^(5,1), C. Catena^(5,1),
S. Sandri⁽⁶⁾, C. Nobili⁽⁶⁾, V. Andreassi⁽¹⁾**

⁽¹⁾ *INFN-LNF, Via Enrico Fermi, 00044 Frascati (Roma), Italy*

⁽²⁾ *EURESYS, Via Lero 30, 00129 Roma, Italy*

⁽³⁾ *ASL-RmH, Via E.Fermi1, 00044 Frascati (Roma)—Italy*

⁽⁴⁾ *ORIM, SrL, Via Concordia 65, 62100 Piediripa (Mc)—Italy*

⁽⁵⁾ *ENEA-CRCasaccia, Via Anguillarese 301, 00060 Roma—Italy*

⁽⁶⁾ *ENEA Ion-Irp, Frascati, Via E.Fermi45, 00044 Frascati (Roma)—Italy*

Abstract

Measurements of Tritium have been performed, using a very low background and accurate instrumentation, on electrolytes before and after Deuterium absorption in Palladium wires.

Tritium was always present in the electrolytic cells, having long and thin Palladium wires (carefully degassed) as cathode and Platinum wire as anode, because “normal contamination” of deuterated liquids.

Two different kinds of electrolytes were used (unusual, for several aspects, to conventional ones adopted in Cold Fusion experiments): the first one was composed by heavy water in DCl acidic environment (pH=4.5) with the addition of Strontium (and Mercury) salts at micro-molar concentration, the second one was composed by heavy ethyl alcohol--heavy water solution (concentration ratio about 11:1), acidic environment (DCl+D₂SO₄), with the addition of Strontium and Mercury concentrated as before.

We have found ***anomalous Tritium production*** (at large statistical significance) **only** when the achieved loading ratio (**D/Pd**) was quite large (about **0.95**) and **several loading/deloading** cycles had been performed.

1. INTRODUCTION

In these last months we were testing, at Frascati National Laboratory of National Institute of Nuclear Physics (INFN-LNF), our electrochemical D-Pd loading procedures using two different kind of electrolytes:

- heavy water with small amounts of strontium carbonates and mercury chloride (both in the range of about 10^{-5} -- 10^{-4} M);
- heavy ethyl alcohol (C_2H_5OD) and heavy water (ratio about 11:1) with strontium chloride, sulphuric acid and mercury chloride (all in the same range of about 10^{-5} -- 10^{-4} M).

We were contemporaneously testing our new calorimetric device (flow calorimeter, about 0.1W resolution) in order to measure eventual excess heat occurred during the loading/overloading processes.

Type b) solution, i.e. alcohol+water, was specially adopted from our group because discovery of 2 new kinds of bacteria living in heavy water. One of these, *Ralstonia* genera (from us named species *detusculanense*, i.e. *de* because deuterium and *tusculanense* because the old, latin, name of Frascati city), was proved to “absorb” even the poisonous Hg ions (as $HgCl_2$) added to the solution in order **to reduce damage of Pd wire due to H, D absorption.**

We like to notify that both new species of bacteria, discovered in heavy water, were formally registered in June 2000 (accepted 19-JAN-2002) from the properly devoted International Biological Institutions (DDBJ in Japan and NCBI in USA, ref.1, 2).

The loading results achieved with both the electrolytes are, at the present, such to determinate a wire resistance variation in the range of $R/R_0 = 1.75$ -- 1.65 ($D/Pd = 0.91$ -- 0.95). We just note that similar loading procedures, performed using light alcohol-water, gave resistance ratio **as good as** 1.1—1.3 and this procedure was **fully reproducible**. Replication experiments has been performed at: Pirelli Labs, Milan-Italy (both electrolytes, ref. 3, 4, 5) and SRI International, Stanford-USA (only electrolyte type “a”).

Recently, we have been allowed to use a very sensitive instrument for Tritium measurement (Wallac 1414, WinSpectral v1.20, located at ENEA-Frascati, Ion-Irp radio-protection group) in order to measure the Tritium content in the electrolyte before and after the loading experiments. It is based on the, well known, Liquid Scintillation Counting procedure.

We have presently found quite clear evidences of Tritium in excess in the electrolytes, in particular when the D/Pd ratio was close to **0.95** and **many loading--deloading cycles** have been performed (deloading was accomplished by anodic stripping).

2. EXPERIMENTAL TESTS

--- Exp. 1

Loading test with D_2O solutions (**max D/Pd ratio 0.93**).

Instrumental background, 6 dpm/ml, subtracted.

* Electrolyte composition (all in D_2O):

$\text{SrCO}_3=17\text{mg}$; $\text{SrCl}_2[10^{-2}\text{M}]=3\text{cc}$; $\text{DCl}[10^{-2}\text{M}]=4\text{cc}$; $\text{HgCl}_2[10^{-2}\text{M}]=2\text{cc}$; $\text{D}_2\text{O}=400\text{cc}$.

- * Cathode: Pd wire (diameter $100\mu\text{m}$, length 15 cm) in central position.
- * Anode : 4 Pt wires (diameter 1mm) surrounding the central cathode (mean distance between cathode and anodes about 2.5 cm).
- * Electrolytic current: 10mA.

- * **Starting Tritium** content in the electrolyte:**244**($\pm 1\%$) dpm/ml.
- * Ten loading-deloding cycles have been performed with the same electrolyte and the same Pd wire.
- * Deloading was forced by anodic stripping.
- * Total time of experiment: 4 weeks.
- * **Final Tritium** content in the electrolyte:**251** ($\pm 1\%$) dpm/ml.

--- Exp. 2

Loading test #1 with $\text{C}_2\text{H}_5\text{OD}-\text{D}_2\text{O}$ solutions (*max D/Pd ratio 0.95*), salts and acids in D_2O .
Instrumental background, 6 dpm/ml, subtracted.

- * Electrolyte composition:
 $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}=90\text{mg}$; $\text{HgCl}_2[10^{-2}\text{M}]=5\text{cc}$; $\text{D}_2\text{SO}_4[10^{-2}\text{M}]=4\text{cc}$; $\text{DCl} [10^{-1}\text{M}]=2\text{cc}$; $\text{Ba}(\text{OH})_2 [10^{-2}\text{M}]=1\text{cc}$;
 $\text{C}_2\text{H}_5\text{OD}=662\text{cc}$ (T=20.3 dpm/ml); $\text{D}_2\text{O}=51\text{cc}$ (T=219.6 dpm/ml).
- * Cathode: Pd wire (diameter $50\mu\text{m}$, length: 60cm);
- * Anode: Pt wire (4 twisted, each one 0.1mm diameter). Electrodes geometry: side by side, distance 4 cm.
- * Electrolytic current: typical 10mA ($\rightarrow J=10\text{mA}/\text{cm}^2$).
- * **Starting tritium** content in the electrolyte: **36.45** ($\pm 2\%$) dpm/ml; *expected (by calculation of tritium content of each component): 34.6 dpm/ml.*
The starting solution ($\text{C}_2\text{H}_5\text{OD}+\text{D}_2\text{O}$), before use, was twice distilled and on-line 100nm PTFE filtered (home-made, modified “vacuum distillation” procedure based on “Rotavapor” machine).
- * Six loading-deloding cycles performed.
- * Properly added, according to our previous experience with light ethyl alcohol and water, the 12cc of acid and salts (detailed in the “electrolyte composition”) during electrolysis in order to maximise the loading.
- * Deloading was forced by long (typically 2 hours at 2mA, 10 minutes “final” at 10mA) anodic stripping.
- * Total time of experiment: 2 weeks.
- * **Final tritium** content in the electrolyte: **51.85**($\pm 2\%$)dpm/ml; **expected : 37.62**
=> clear evidence of anomalous Tritium increase. <=

--- Exp. 3

Loading test #2 with $\text{C}_2\text{H}_5\text{OD}-\text{D}_2\text{O}$ solutions (*max D/Pd ratio 0.91*), salts and acids in D_2O .
Instrumental background, 5dpm/ml, subtracted.

- * Electrolyte composition:
SrCl₂*6H₂O=90mg; HgCl₂[10⁻²M]=5cc; D₂SO₄ [10⁻²M]=4cc; C₂H₅OD=662cc; D₂O=51cc
- * Same experimental conditions as Exp.#2, but C₂H₅OD-D₂O *not twice distilled and filtered* (used as received).
- * *Several impurities (because corrosion problem) dissolved in the solution during electrolysis.*

- * **Starting Tritium** content in the electrolyte: **61.5** (+2%) dpm/ml.
The C₂H₅OD comes from different batch in respect to Exp. 2).
- * Added 9 cc of acid /salt as detailed.
- * One loading-deloding cycle.
- * No final anodic stripping (wire broken).
- * **Final Tritium** content in the electrolyte: **45**(+2%) dpm/ml.

3. FURTHER DETAILS and COMMENTS

****Degassing****

- * We recall that the thin Pd wire (50μm), just before electrolysis, was carefully degassed (in order to allow any gas trapped, T included, to escape), in air by Joule heating (from 20 to 700°C, red colour) cycles.

Current (mA) pattern was as following:

0→10→50→10→100→10→200→10→300→10→350→10→400→10→450→10→500→10
→525→10→550→10→580→10→0

- * The cooling from high to low current was made slowly (several minutes), specially at high values of current, in order to avoid quenching effects of Pd lattice and related stress.
- * The typical resistance decrease, after proper Joule heating, was 2--3%.

****Tritium measurement details****

- * Tritium measurement made using the Wallac 1400 (EG&G Company), protocol 34 PROCORAD 98.
T=20°C. Measuring time=1800sec.
- * Liquid Scintillation Cocktail: Ultima Gold from Packard. The liquid is specially used for wide range of aqueous and nonaqueous samples, alcohol included.
No chemiluminescence effect (anyway we waited 4 hours, after preparation, before start of measurements).
- * Vial: PE, 20ml total, 16ml of Ultima Gold and 4ml of solution to be analysed.
- * Measured overall efficiency, by calibration with T standards, about 35%.

****Pd wire (50μm) measurement details****

- * Wire resistance measurement by AC method:
J=1000A/cm²; v=10KHz; Square wave (t_r, t_f<10ns).
- * Every 200 seconds the “most” and “less” cathodic sides of long Pd wire are cyclically reversed and there is a short time (about 1 ms) during that the wire is not powered.

****Tritium balance****

* The total amounts of Tritium atoms produced (in 2 weeks of experiments), in the best experiment, was:

$$>10^{11}$$

* The ratio between the Tritium atoms produced and Pd atoms of the wire was:

$$>10^{-8}$$

* Typically, when there is no overloading, the total T content of solution decreases (from 5 to about 30%),

depending mainly on current density pattern adopted and number of cathodic-anodic cycles.

* We can detect increase of T, with enough good statistical significance, only because we used heavy ethyl alcohol: original T content about 10 times lower than even a “low tritium content “ heavy water.

* According to our recent results, that need obviously further confirmation from other Laboratories, it seems that “anomalous” Tritium production is related to large overloading of Deuterium into Palladium by proper electrolytic procedures.

ACKNOWLEDGEMENTS

We are indebted to Prof. Piergiorgio Sona at CESI (Milan, Italy) because very long and stimulating discussion about our, unusual, experimental set-up and electrolytes.

We would like to notify that Dr. Naoto Asami and Kazuaki Matsui, now at Institute of Applied Energy of Tokyo (Japan), were the first people that realised about NON-inorganic pollution of heavy water during Cold Fusion experiments (NHE Project, Sapporo, Japan). Their observations were for us starting points for further analysis.

We deeply thank Prof. Akito Takahashi, (Osaka University, Japan), because useful suggestion and criticism related with low-level Tritium measurements.

We can't forget the very fine work about replications, and several times their original (and wonderful) improvements, of our experimental procedure, made at Pirelli Labs (Milan, Italy) from Flavio Fontana, Daniele Garbelli, Donato Azzarone and Luca Gamberale.

We would like to thank Giannantonio Cibirin (LNF-INFN) because skilful assistance during preparation of the manuscript in addition to very useful suggestions and criticisms.

REFERENCES

- [1] D'Agostaro, G.A.F., Celani, F.J.V.A., (.....) and Nakamura, M.
National Centre Biology Information:
LOCUS AF280433; 1537 bp DNA linear BCT 19-JAN-2002
DEFINITION *Ralstonia detusculanense*
ORGANISM *Ralstonia detusculanense*
Bacteria; Proteobacteria; beta subdivision; Ralstonia group; Ralstonia.
Submitted (20-JUN-2000)
<http://www.ncbi.nlm.nih.gov>
- [2] D'Agostaro, G.A.F., Celani, F.J.V.A., (....) and Nakamura, M.
National Centre Biology Information:
LOCUS AF280434; 535 bp DNA linear BCT 19-JAN-2002
DEFINITION *Stenotrophomonas detusculanense*
ORGANISM *Stenotrophomonas detusculanense*
Bacteria; Proteobacteria; gamma subdivision; Xanthomonas group; Stenotrophomonas.
Submitted (20-JUN-2000)
<http://www.ncbi.nlm.nih.gov>
- [3] F.Celani, A.Spallone et al.
“HIGH HYDROGEN LOADING INTO THIN PALLADIUM WIRES THROUGH
PRECIPITATE OF ALKALINE-EARTH CARBONATE ON THE SURFACE OF CATHODE:
EVIDENCE OF NEW PHASES IN THE Pd-H SYSTEM AND UNEXPECTED PROBLEMS
DUE TO BACTERIA CONTAMINATION IN THE HEAVY WATER.”
Proceedings of the “8th International Conference on Cold Fusion”, SIF - Conf. Proc. Vol. 70 pg 181-
190, Lerici (La Spezia), Italy 21-26 May 2000; Edited by F. Scaramuzzi, Compositori–Bologna, Italy
(2000).
- [4] A. Spallone, F. Celani, P. Marini and V. di Stefano.
“NEW ELECTROLYTIC PROCEDURE FOR THE OBTAINMENT OF VERY HIGH H/Pd
LOADING RATIOS. PRELIMINARY ATTEMPTS FOR ITS APPLICATION TO THE D-Pd
SYSTEM.”
Proceedings of the “8th International Conference on Cold Fusion”, SIF - Conf. Proc. Vol. 70 pg 191-
198, Lerici (La Spezia), Italy 21-26 May 2000; Edited by F. Scaramuzzi, Compositori–Bologna, Italy
(2000).
- [5] F.Celani, A. Spallone et al.
“Electrochemical H-D loading of Palladium wires by hydro-alcoholic electrolytes related to the new
discovered *Ralstonia* bacteria into heavy water”.
JCF3-5 3rd Meeting of Japan CF_Research Society October 25-26, 2001; Yokohama National
University.
<http://fomcane.nucl.eng.osaka.u.ac.jp/jcf/>

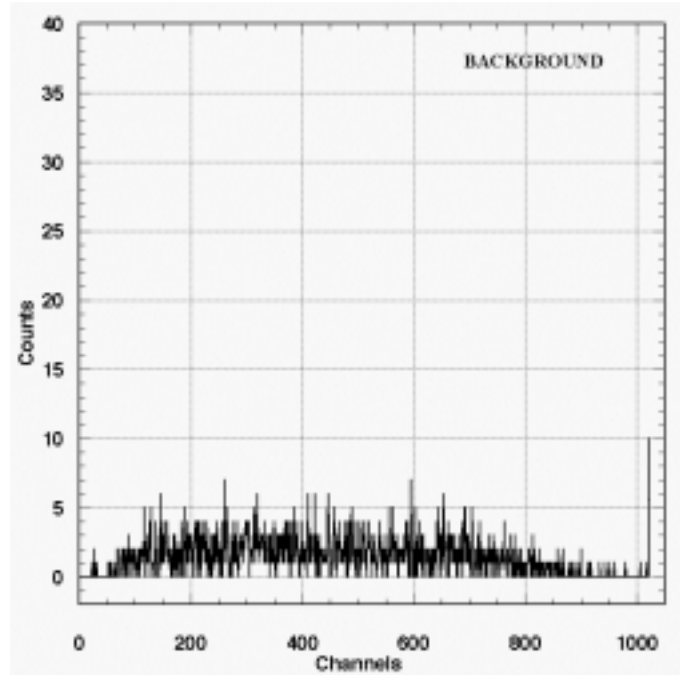


Fig. 1 – Raw data Wallac instrument background spectrum. Acquisition time: 1800 sec. Tritium spectrum between channels 20 and 220: equivalent to the end point at 18.58 KeV of β^- T decay (mean β energy at 5.68 KeV).

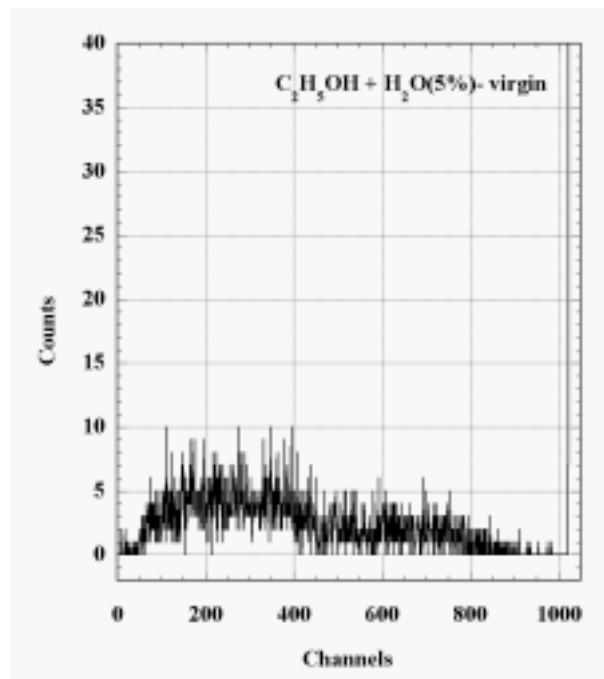


Fig. 2 – Raw data Spectrum of commercial, natural wine origin, ethyl alcohol, 95% v.v. (H₂O 5%) concentrated, virgin. Used as cross-reference for Tritium measurements.

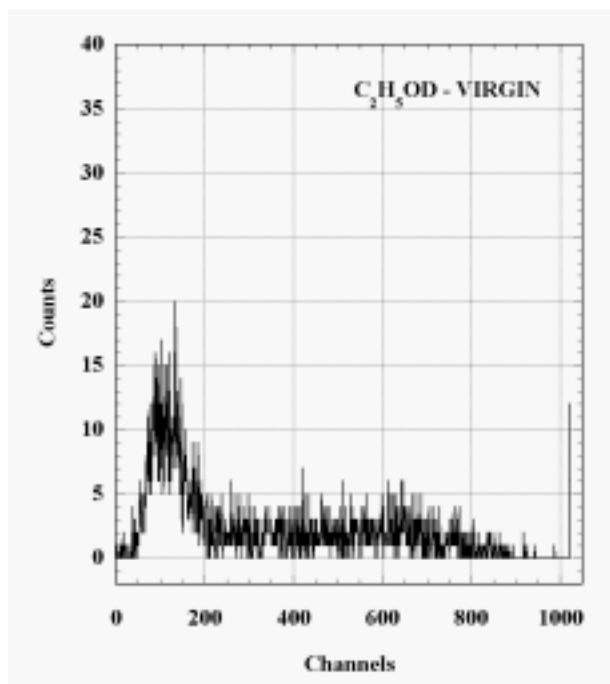


Fig. 3 – Raw data. Spectrum of ethyl alcohol-d from Aldrich, Purity 99.5+atom%D. Vacuum distilled and 100nm, on line, PTFE filtered before use.

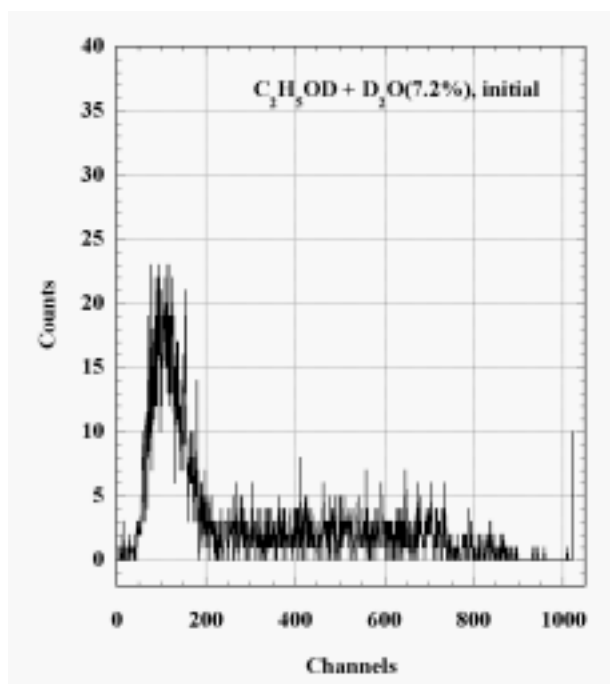


Fig. 4 – Raw data. Spectrum of solution obtained mixing 7.2% v.v. D₂O with heavy ethyl alcohol. Solution twice distilled and on line 100nm PTFE filtered. Total volume: 710cc. This is the initial solution before addition of 12 cc of salts and acids.

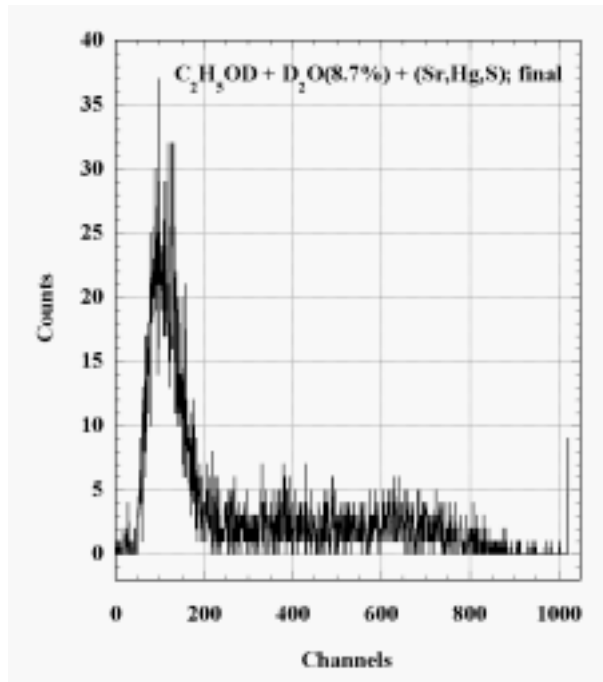


Fig. 5 – Raw data. Measurement of final solution at the end of experiment #2. Added other 12 cc of acid and salts in D₂O (Hg, Sr, S), i.e. D₂O concentration increased from 7.2% to 8.7%.

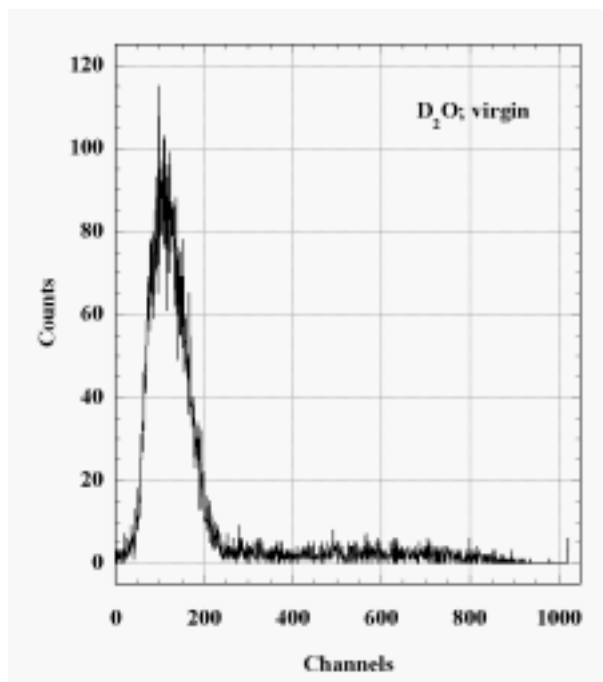


Fig. 6 – Raw data. Spectrum of virgin, “low tritium content”, heavy water. In our procedure, the electrolyte has been twice distilled under vacuum and on-line filtered.

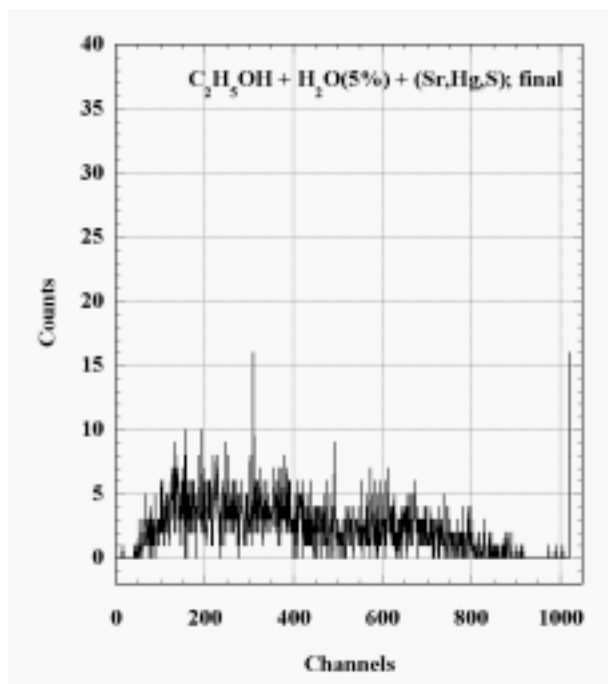


Fig. 7 – Raw data. Measurement of final solution at the end of one experiment using light ethyl alcohol and water. Added 12 cc of salts and acids in H_2O (Hg, Sr, S).

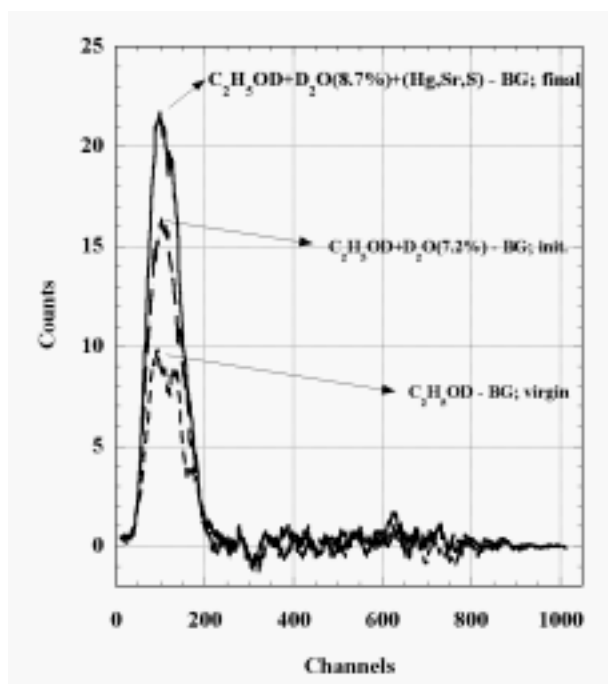


Fig. 8 – Final data with background subtraction (20 channels “binning”), showing an increase of Tritium peak after electrolysis. In fact, the lower curve corresponds to virgin heavy alcohol, the middle one represents the initial electrolyte solution, the higher curve has been obtained after the end of the electrolysis process.