Unexpected effects due to voltage waveform at anode, in gaseous LENR experiments based on sub-micrometric surface coated Constantan wires[1].

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[1] *[Some of the slides presented at "2019 MIT Colloquium…"; March 23-24, 2019; MIT (Cambridge, MA-USA). DOI: 10.13140/RG.2.2.16626.76480]*

OUTLINE

A) Motivations: steps to overcome conflicting requirements (a “mission impossible contest”).

B) Background Information & Some of the key observations were anticipated and discussed at the *2019 MIT Colloquium*:

- **the role of electrons (electron conduction, vacuum tube)**
- **use of low work function materials to stimulate the AHE effects**
- **the need for high temperature and low pressure, (as suggested by Richardson law).**

C) Analogy with Paschen Curves. Observation of the typical behavior of gas discharges despite the use of low frequency and tension between anode and cathode.

D) The recombination of atomic H (or D), produced by Constantan:

- **an advantage? (local temperature, in proper conditions, up to 36000 °C),**
- **or an issue?** [i]

E) Recent results using AC, 50Hz "excitation": observation of plasma discharge

F) Tentative Conclusions and next steps.

Motivations

A) In principle, obtaining some kind of thermal anomalous effect exposing certain elements (Pd, Ti, Ni, alloys,…) to Hydrogen and/or their isotopes, is rather simple:

- **You need to reach a significant absorption of hydrogen on the surface and bulk of the chosen material, (especially in its nanometric forms),**
- **"Enable" the Hydrogen to move (i.e. "to flow") in/out of the material,**
- **Avoid that the Hydrogen leaks/leaves the system[ii].**
- **Add a flow of electrons for its tendency to increase the effects.**

B) Recently, we have observed in gaseous High Temperature LENR systems, that the AHE decreases over time, *often completely disappearing after few days*:

- **In other words, the system reaches an equilibrium were AHE is absent.**

- **On the other hand, we have found that periodic external "excitations", are able to keep the AHE "alive".[2]**

C) Furthermore, in accordance with our experiments, AHE phenomena have conflicting requirements for their occurrence:

1. **High pressure (as high as possible) of H_2 (or D_2) is needed to enable the loading of the active material[iii]**
2. **Low pressure on the other hand is needed to allow an emission of electrons from the active material, H loaded, at sufficiently high temperature.**
3. **Unfortunately, a combination of low pressure and high temperature causes a "unloading" of the stored H.**

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2 **Details reported at the *2019 MIT Colloquium.***

D) The use of mild pressures and high *voltage* (Paschen curve) in the counter electrode is a compromise among such conflicting requirements. Obviously, the distance among the 2 electrodes must be kept as low as possible (few millimeters) to prevent the need of prohibitively high voltages.

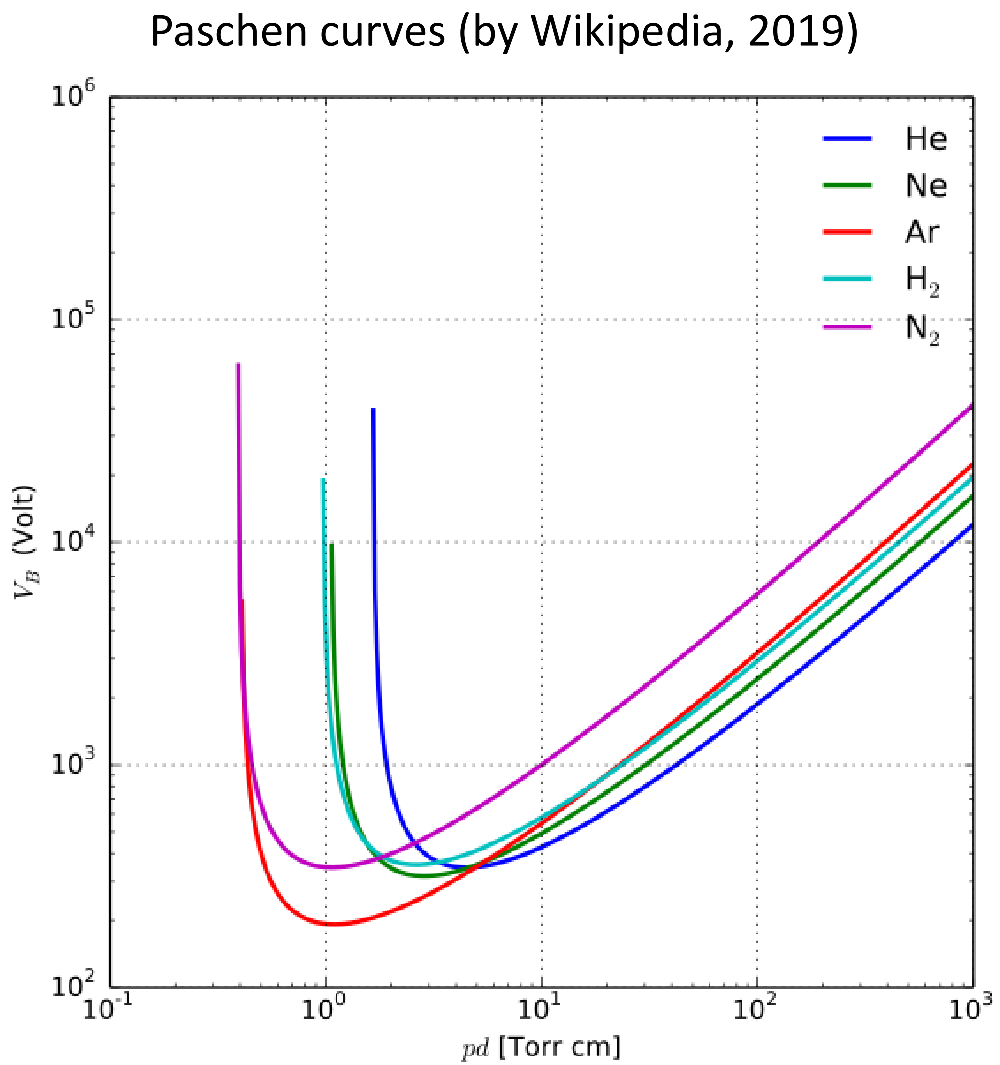

Fig.1_P. Paschen curves for helium, neon, argon, hydrogen and nitrogen, using the expression for the breakdown voltage (V_b) as a function of the parameters A, B (interpolate the first Townsend coefficient). For further details specific link to Wikipedia.

Vertical axis =Voltage; Horizontal=Pressure (Torr; 760 Torr=1.0133 bars)* Distance (cm). Both Log scale.

Short overview of the reactor and role of emitted electrons:

Observation of analogies with the Richardson's effect.

(most of these slides were previously presented at "*2019 MIT Colloquium…", figures are coded as _M.*)

Introduction and Motivations

(extracted from ICCF21 and IWAHLM13, with several updating)

- **Anomalous Heat Effects (AHE) have been observed by us in wires of $Cu_{55}Ni_{44}Mn_1$ (Constantan) exposed to H_2 and D_2 in multiple experiments along the last 9 years.**

- **The Constantan, a quite low-cost and old alloy[3], has the peculiarity to provide extremely large values of energy (1.56--3.16 eV) for the catalytic reactions toward Hydrogen (and /or Deuterium) *dissociation from molecular to atomic state*[iv] ($H_2 \rightarrow 2H$).**

- **Part of *H* is likely to be *stored inside the Constantan lattice*[4], after its absorption at high temperatures (> 180°C), few bar of pressure, several hours.**

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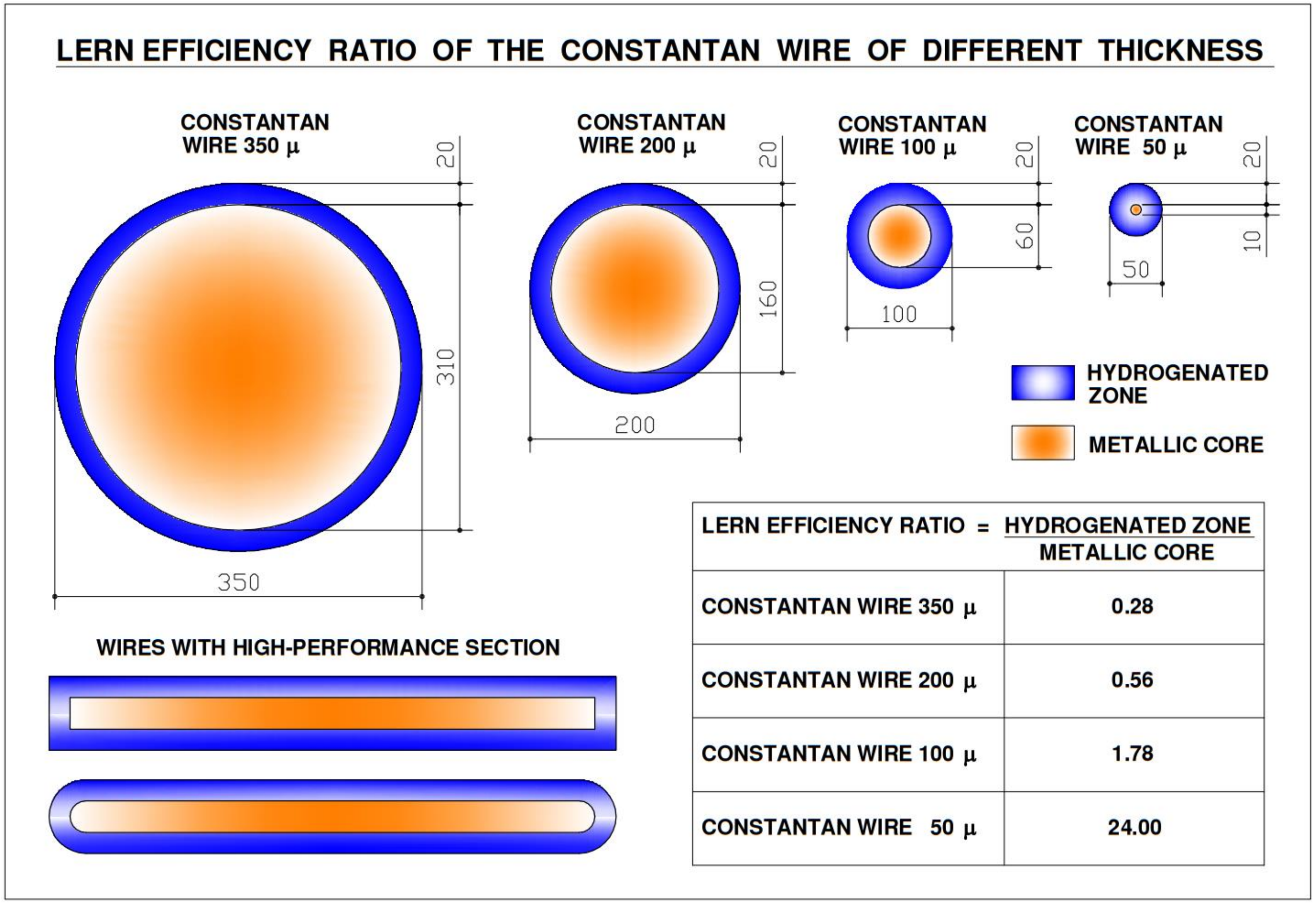
[3] Constantan was developed around 1890

[4] according to resistance reduction value up to 20-25 %; first measurements by German Scientists on 1989

- The ***ratio among the active volume*** (i.e. the thickness of sub-micrometric one) ***and the bulk*** (used mainly as support), **increases reducing the diameter of the wire** as shown ***in a schematic drawing in Fig. 1***. We observed (by SEM) that, at least in our experimental conditions of wires preparation, the thickness of active section is of the order of 10-30 μm. The main drawback in using wires with reduced thickness is the tendency of the wire to break, in particular when the diameter is below 100 microns[5] (Φ<100 μm).

[5] Moreover such deleterious effect is worsened at the highest (and most useful!!) temperatures (>700°C) operated in the test.



LERN EFFICIENCY RATIO =	HYDROGENATED ZONE / METALLIC CORE
CONSTANTAN WIRE 350 μ	0.28
CONSTANTAN WIRE 200 μ	0.56
CONSTANTAN WIRE 100 μ	1.78
CONSTANTAN WIRE 50 μ	24.00

Fig. 1_M. Qualitative sketch of the ratio among the “active region” (sub-micrometric sponge) for fast Hydrogen absorption/storage (blue color, thickness 20 μm), and the metallic bulk (brown color), changing the initial diameter of the wire.

- **Improvements in the magnitude and reproducibility of AHE were reported by the Authors of the present work in the past and related to wire preparation and reactor design.**

- **In facts, an oxidation of the wires by several hundred pulses of high intensity electrical current (up to 10-20 kA/cm^2, even neglecting skin effects present because fast rise time, <1 μs, of the pulses) in air (and related quenching) creates a rough surface *(like sponge)*. It is featured a *sub-micrometric texture* that proved particularly effective at inducing thermal anomalies (once the H, D is absorbed/adsorbed) when *both temperatures* exceeds 300-400 °C *and* proper kinds of *non-equilibrium conditions* are promoted. *The effects increase as temperatures are increased, until adverse self-sintering effects (almost out of control, at the moment) damage the sponge structures and most of the AHE vanish.***

- **The hunted effect appears also to be increased substantially by deposing segments of the wire with a series of elements: Fe, Sr (via thermal decomposition of their nitrates) properly mixed with a solution of $KMnO_4$ (all diluted in acidic heavy-water solution).**

- **The magnetic proprieties of constant wires change dramatically after the coating of Fe nitrate (further decomposed to FeOx) from “a-magnetic” to strong ferromagnetic. The special geometry of *Capuchin knot*, as speculation, could enhance such aspects. It is noteworthy that FeOx are recently reported to have magnetic properties enhanced up to 100-10000 times when at low dimensionality (10 micron down to 10 nm) as in our specific fabrication procedures (multilayer).**

- **Furthermore, an increase of AHE was observed after introducing the treated wires inside a sheath made of *borosilicate* glass (mainly Si-B-Ca; *BSC*), and even more after impregnating, the sheath with the same elements (Fe, Sr, K, Mn) used to coat the wires. Liquid nitrated compounds were first dried and later-on decomposed to oxides by high temperature (400-500 °C) treatments. The procedure was repeated several times.**

- **Finally, AHE was augmented after introducing equally spaced knots (the knots were locally coated with the mixture of Fe, Mn, Sr, K) to induce thermal gradients along the wire (knots become very hot spots when a current is passed along the wire).**

- **Interestingly, the coating appears to be nearly insulating and it is deemed being composed of mixed oxides of the corresponding elements (mostly FeO_x, SrO).**

- **Having observed a degradation of the *BSC* fibers at high temperature, an extra sheath made of quartz fibers was used to prevent the fall of degraded fibers from the first sheath, i.e. made a sort of *coaxial construction.* Main drawback was its large dimensionality.**

- **In 2014, the Authors introduced a second independent wire, "floating" in the reactor chamber, and observed, just by chance, a weak electrical current (hundreds of μA, with several mV at the end of the wire), flowing in it while power was supplied to the first.**

- **At that time the sheaths were NOT impregnated by nitrate/oxide mixtures, so, possible leakage currents were unlucky to happen. The effect was also confirmed/certified (at Frascati Laboratory by their own instrumentations and specific SW for data acquisition) and (later-on) independently reproduced, by the MFMP group (M. Valat, B. Greeiner).**

- **This current proved to be strongly related to the temperature of the first wire and clearly turned to be the consequence of his *Thermionic Emission* (where the treated wire represents a *Cathode* and the second wire an *Anode*), according to the Richardson law.**

- **The key parameter of thermionic emission is the Work Function (Φ), usually 1.5-5 eV, for electron emission, from the surface of the materials:**

- **$J = A_g T^2 \exp(-\Phi / K_B T)$**

- **where:**
- **J=emission current density [A/m^2];**
- **Ag= $\lambda_R A_0$; λ_R is a correction factor depending on the material (0.5—1);**
- **$A_0=(4\pi q_e m_e k_B^2)/(h^3)=1.2*10^6$ [A/m^2K^2], *Richardson constant***
- **$q_{e=}1.6*10^{-19}$ C, electron charge;**
- **$m_e=5.11*10^5$ eV, electron mass;**
- **$k_B=8.617*10^{-5}$ eV/K, Boltzmann constant.**

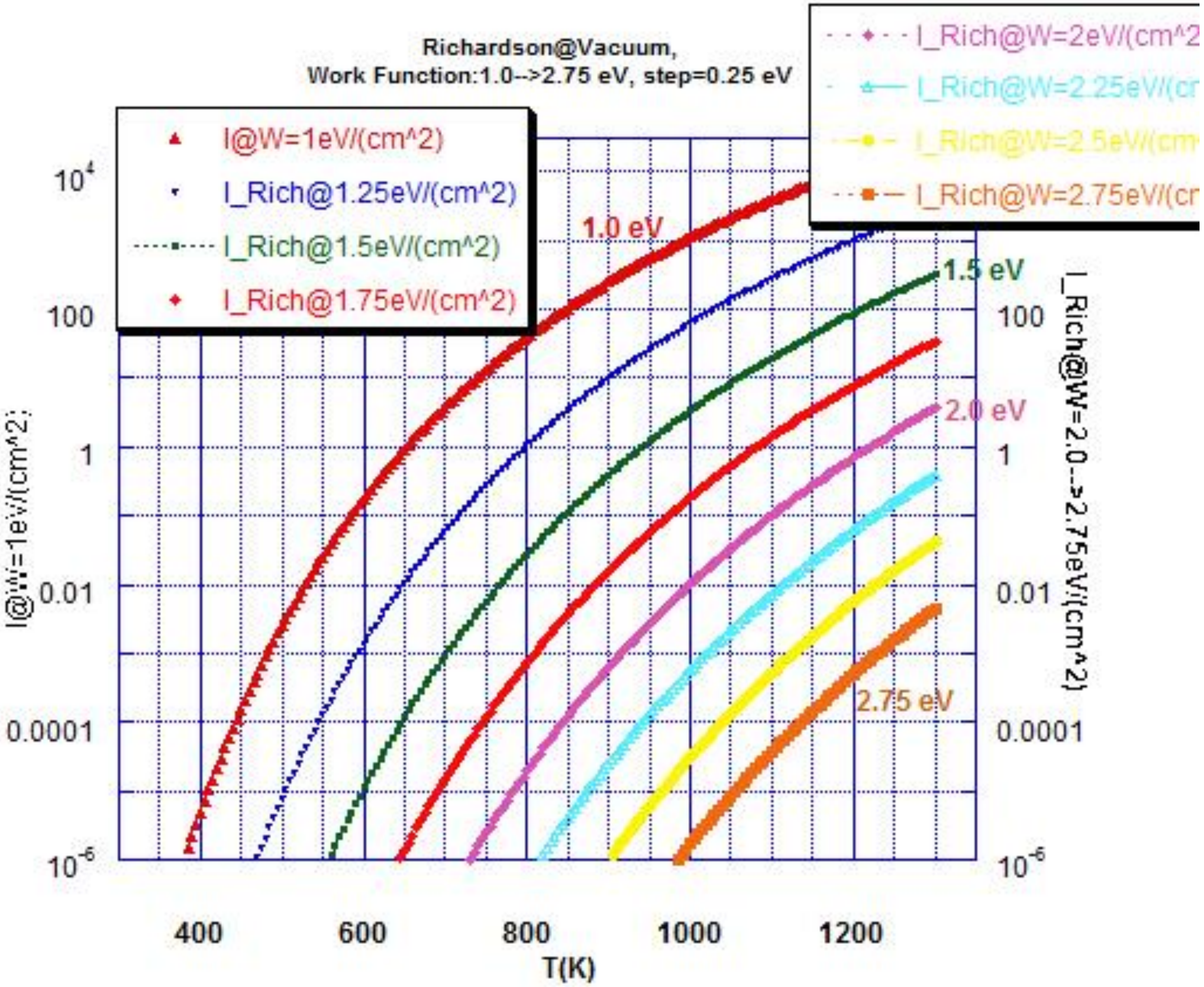


Fig.2_M. Dependence of electron emission on Temperature (300--1300K) and Work Function (1--2.75 eV)

- **The presence of the thermionic effect and a spontaneous tension between the two wires did strongly associate to AHE.**

- **The thermionic effect is enhanced, in our specific procedures, by deposition of Low Working Function materials (LWFm), like SrO, at the surface of the constant wire, several thin layers.**

- ***In the Cold Fusion-LENR-AHE studies the Researcher that first (1996) introduced, intentionally, LWFm was Yasuhiro Iwamura at Mitsubishi Heavy Industries (Yokohama-Japan). Since that time he used CaO and later-on also Y_2O_3, both in electrolytic and gas diffusion experiments at mild (<80 °C) temperatures.***

- **All these observations were reported at various Conferences, and tentative explanations were provided for the observed effects.**

- **The presence of thermal and chemical gradients has been stressed as being of relevance, especially when considering the noteworthy effect of knots on AHE.**

- **The ICCF21 Conference, held on June 2018, marked a turning point: the scientific community did show a notable interest on the effects of knots and wire treatments, further increasing the confidence on the described approach.**

- **From that moment, attempts to further increase AHE focused on the introduction of different types of knots, leading to the choice of the *"Capuchin"* type (see Fig. 3) and, very recently, to the *"advanced Capuchin knot".***

- ***The knot design, specially Capuchin one, leads indeed to very hot spots along the wire and features three areas characterized by a temperature delta up to several hundred degrees.***

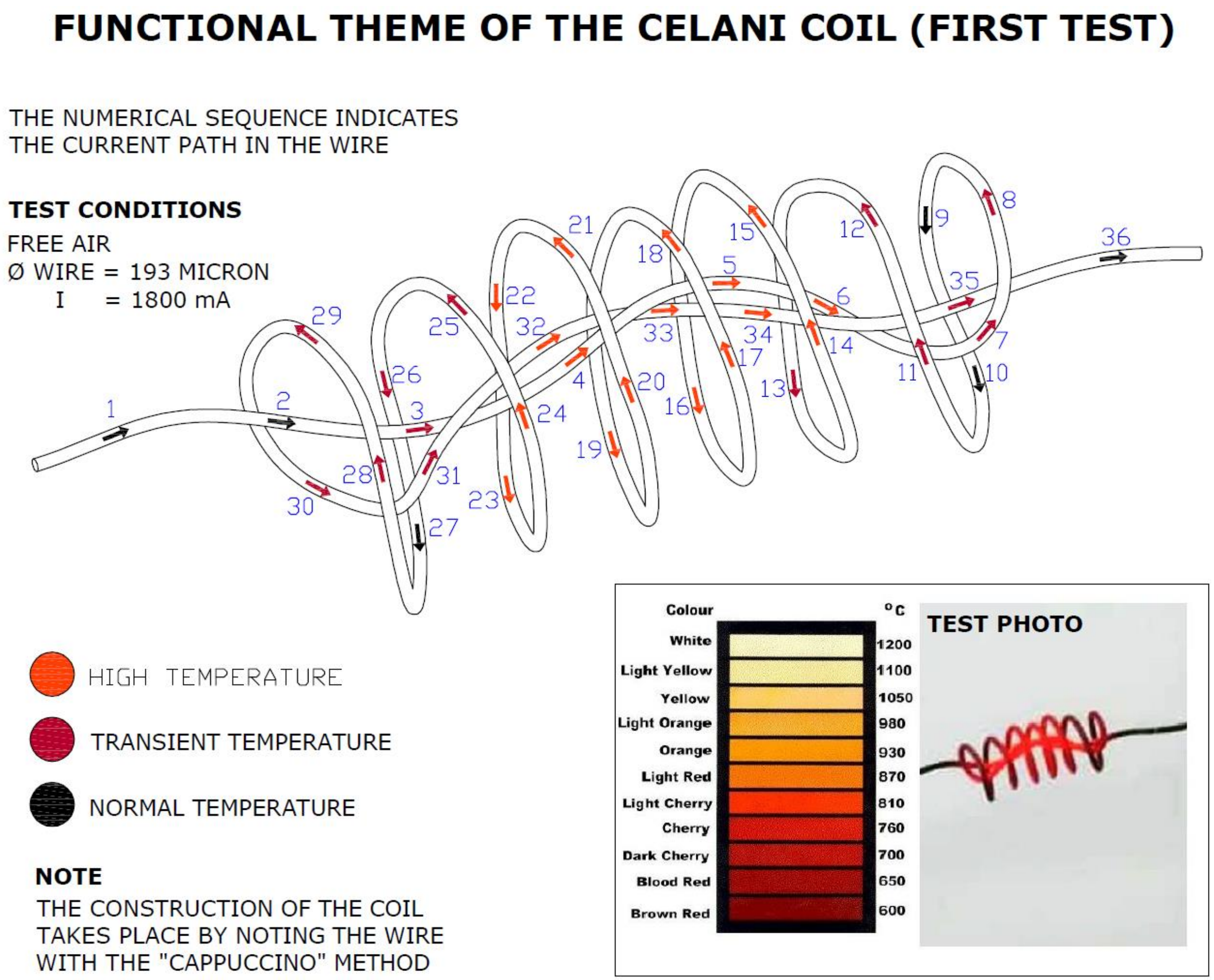


Fig. 3_M. Photo, in DC, I=1900 mA, of a piece of Constantan wire having a diameter of 193 µm. Capuchin knots with 8 turns. Temperatures estimated by color. The dark area is at temperature <600°C, the external helicoidal section is at about 800 °C, the inmost section, linear, up to 1000 °C in some areas.

Advanced Capuchin coil construction

The construction of new geometry was quite complex and several measures were provided to fulfill the specific requirements of the experiments, several times conflicting each-other.

Some of the main problems/solution are resumed, as following:

A) **The new system is (partially) based, about the main geometry of Constantan "turning", on the well-known methodologies adopted (since about 1930) for the construction of the filaments of *incandescent light bulbs.***

In other words, the wires have a geometry of coils with both distance among spirals and diameter of the coil as short as possible.

B) To avoid short circuitry among adjacent spires, the wires are put inside insulating sheaths able to withstand high temperatures, i.e. the hybrid one before quoted (up to 1200 °C).

C) As final effect, part of the energy emitted from the (incandescent) wire is self-concentrated at the center of the coil where are located: a) the initial and final parts of the wire, b) a thermometer (type K thermocouple, SS covered and electric insulated, for local temperature measurement purposes), c) another wire (at large surface and inert in respect to H adsorption) used as the anode or generally *counter-electrode* of the system.

D) The effect of (partial) reflection of IR emitted is reinforced by a SS316 tube that reflects efficiently the temperature.

E) The construction is modular and the thick wall (3mm) glass reactor is the main container of 3 independent type of wires, each into an independent SS tube. One wire is used as general purposes test (made by Pt, identified as V1 because 100 μm wire diameter).

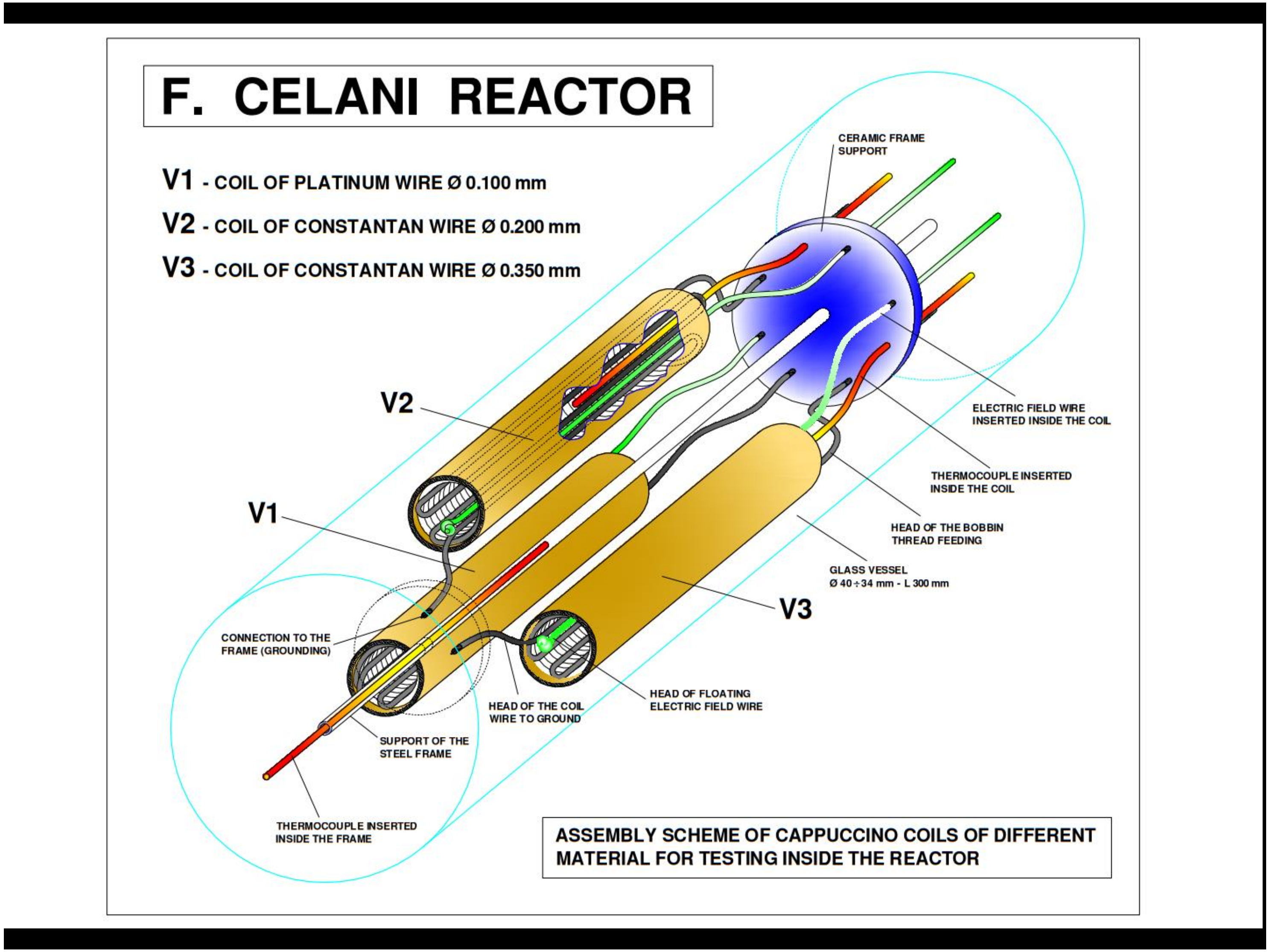


Fig.4_M. Overview of the assembling of the SS tube, each filled by coiled Constantan wire, except V1 (by Pt).

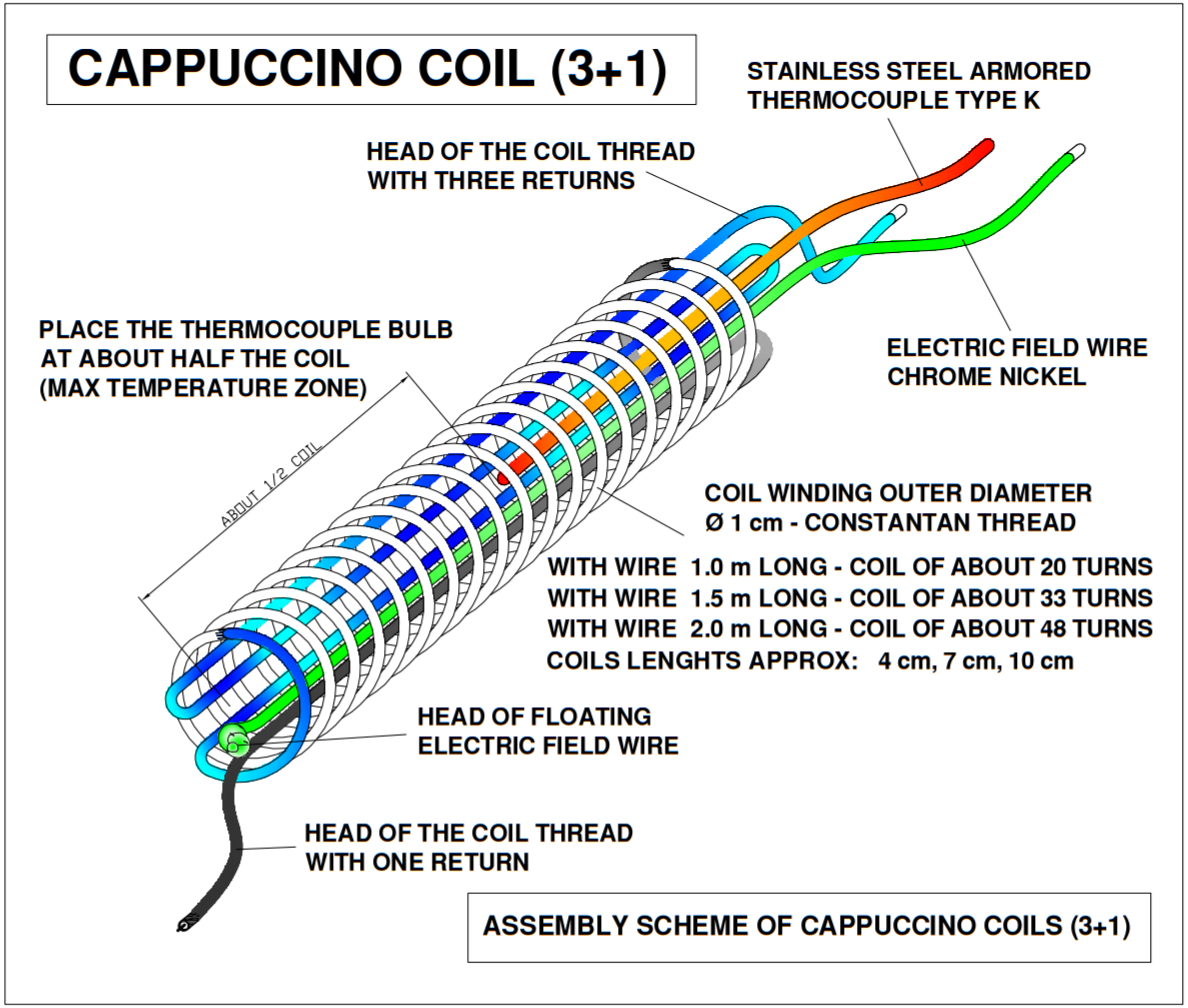


Fig. 5_M. Details of the assembling of typical "*Advanced Capuchin knot*": thermocouple and Anode wire.

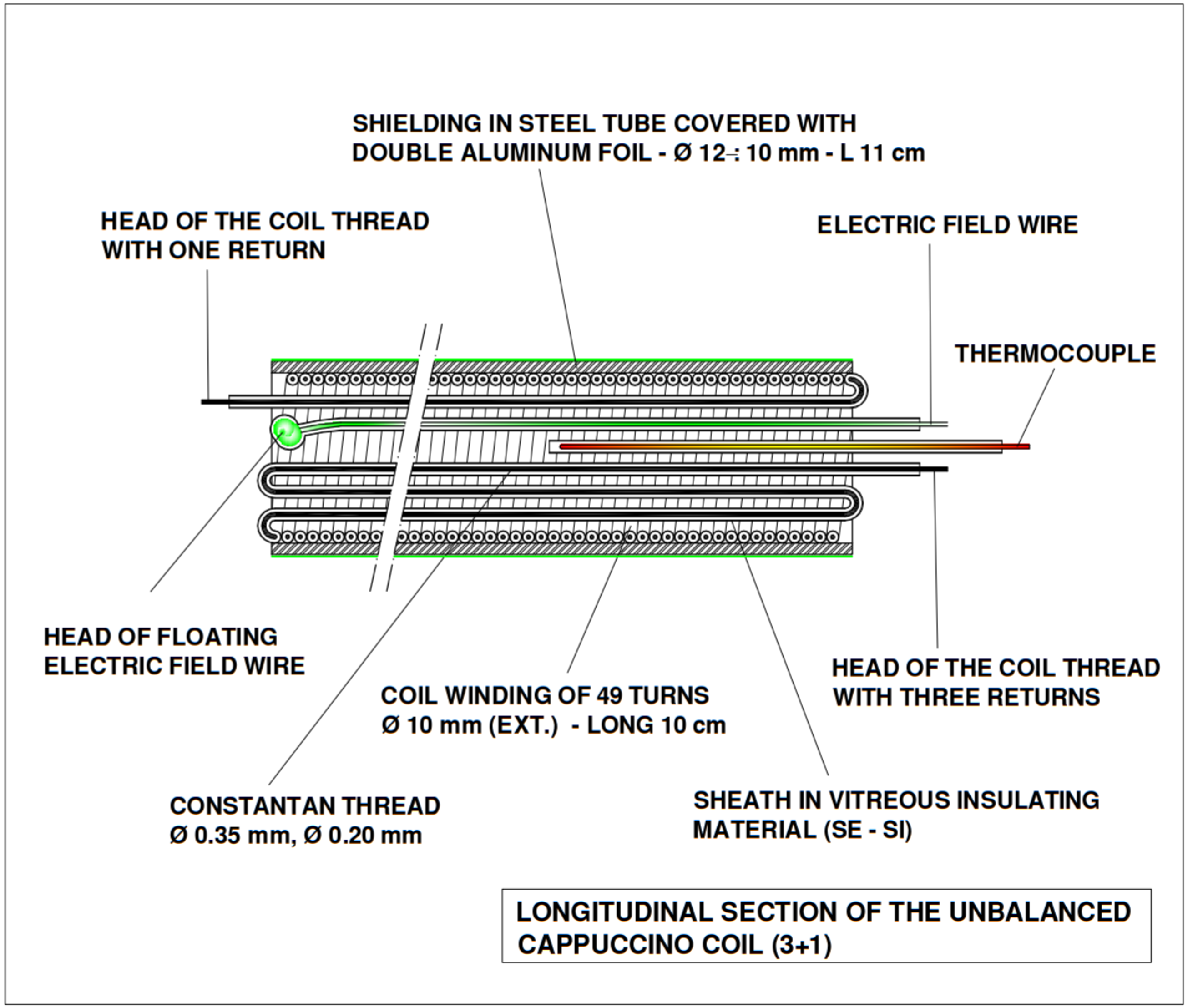


Fig. 6_M. Further details about *Advanced Coil* construction.

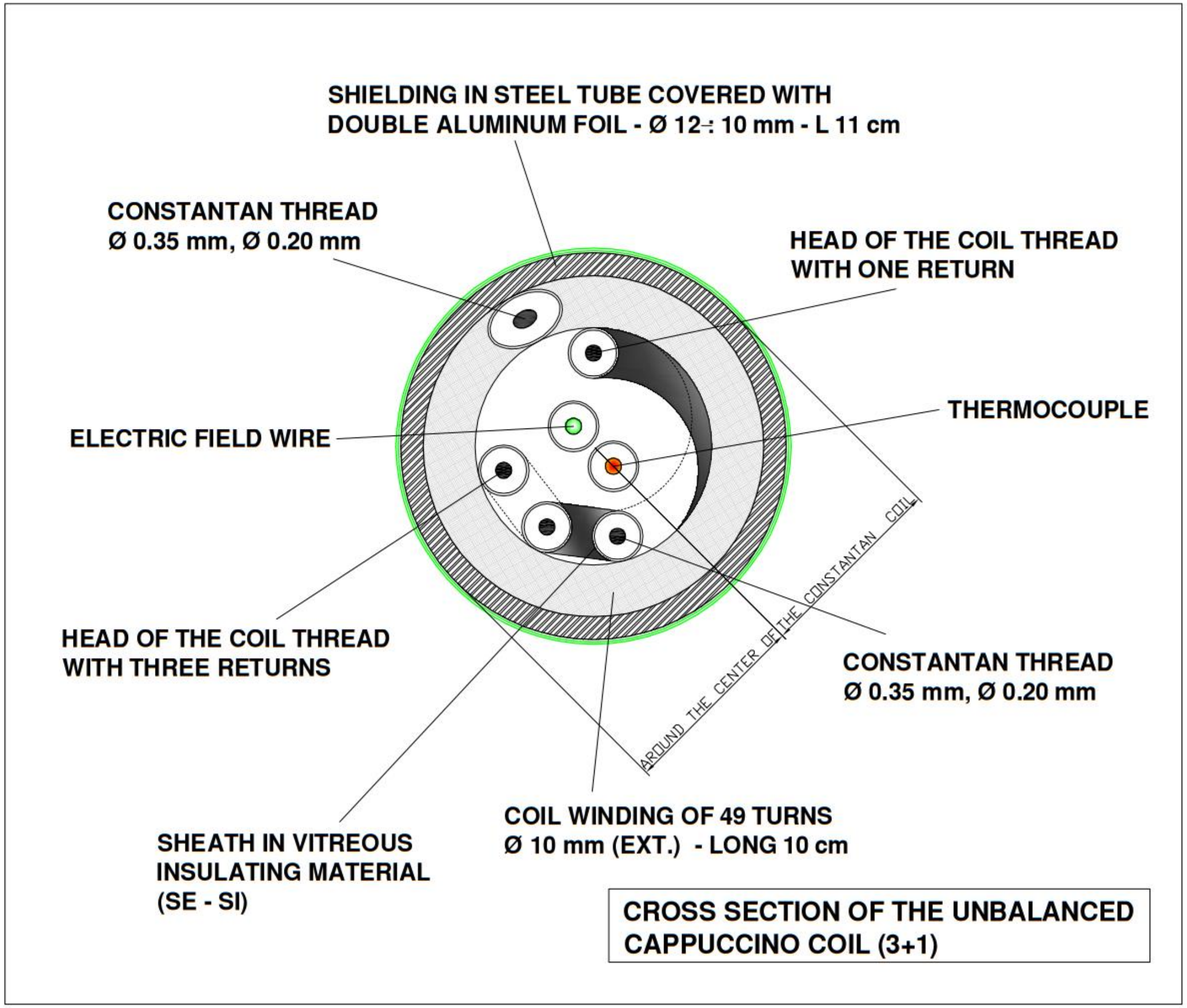


Fig. 7_M. Cross section of the *Advanced Capuchin coil*

Fig. 8_M. Photo of the reactor assembled, just before to be located into the air flow calorimeter.

Fig. 9_M. Picture of the reactor, and calibrator (Ni-Cr wire) inside the calorimeter (advanced version, comprising 2 insulating and reflecting walls)

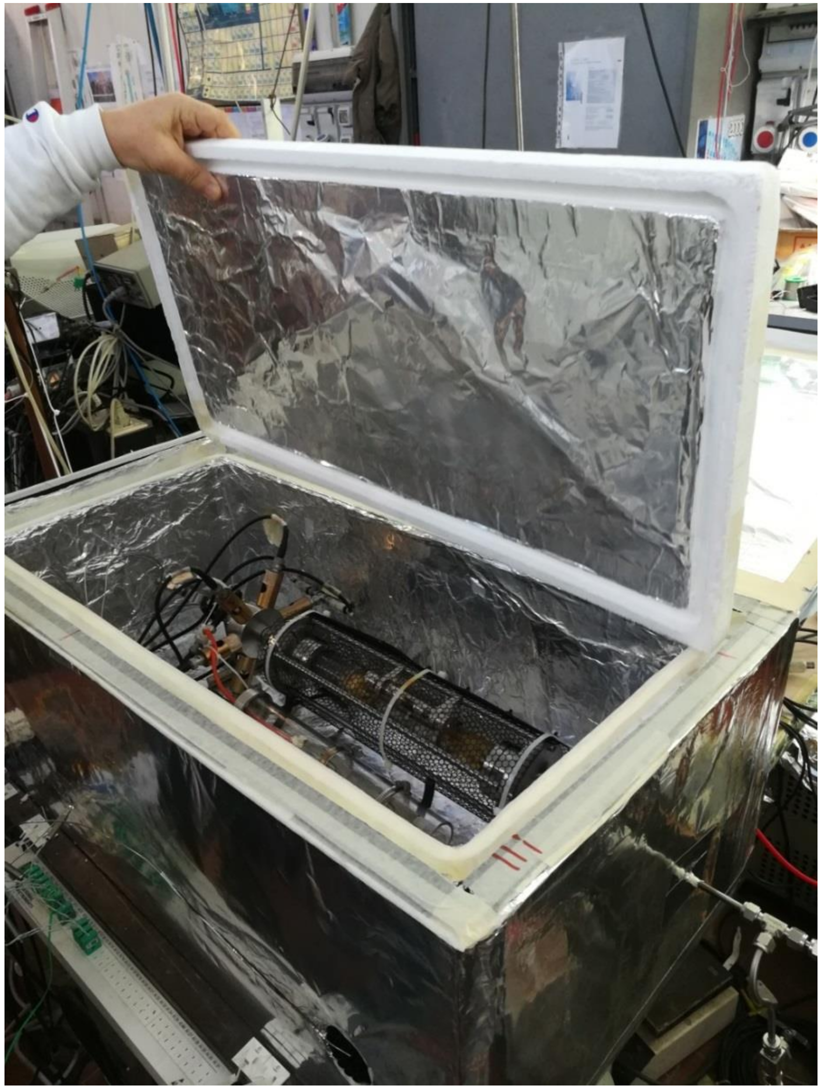


Fig.10_M. Photo of the Calorimeter, air flow, just before closing the cover. Glass reactor protected by SS net.

Our reactor: characteristic of observed Paschen regime, changing gas and pressure.

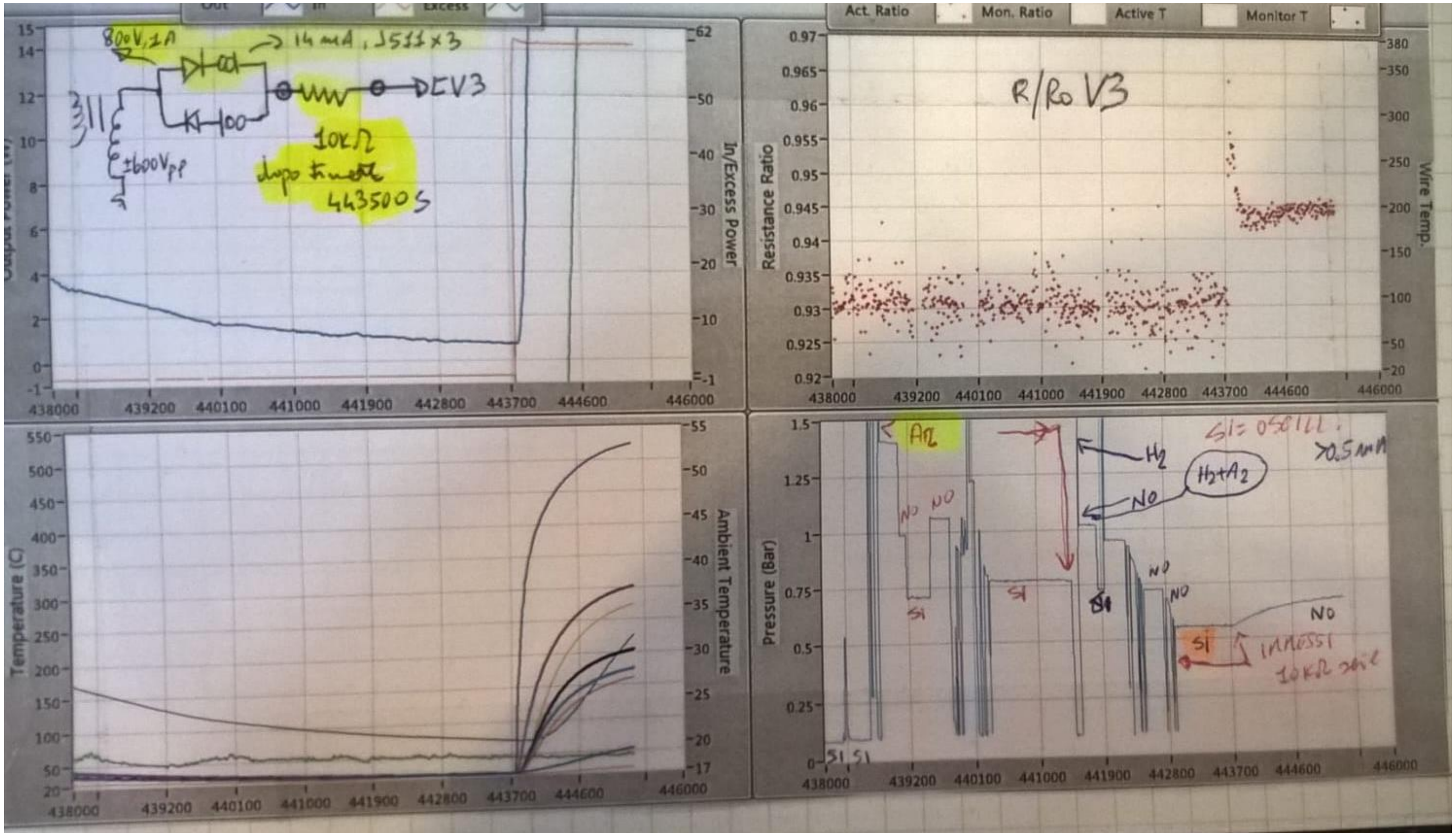


Fig1A_P. Voltage applied up to 600 Vpp. Test with Ar and Ar-H_2 mixtures, changing the total gas pressure. In the lower side- right, the term NO means no strong Paschen oscillations, i.e. plasma regime. The term SI means strong plasma oscillations. After addition of the 10 kOhm resistor, between the generator and the anode, the value of current injected went under control (<<1 mA rms) in the case of Paschen regime.

Explorative test, with pure Ar, at mild pressure.

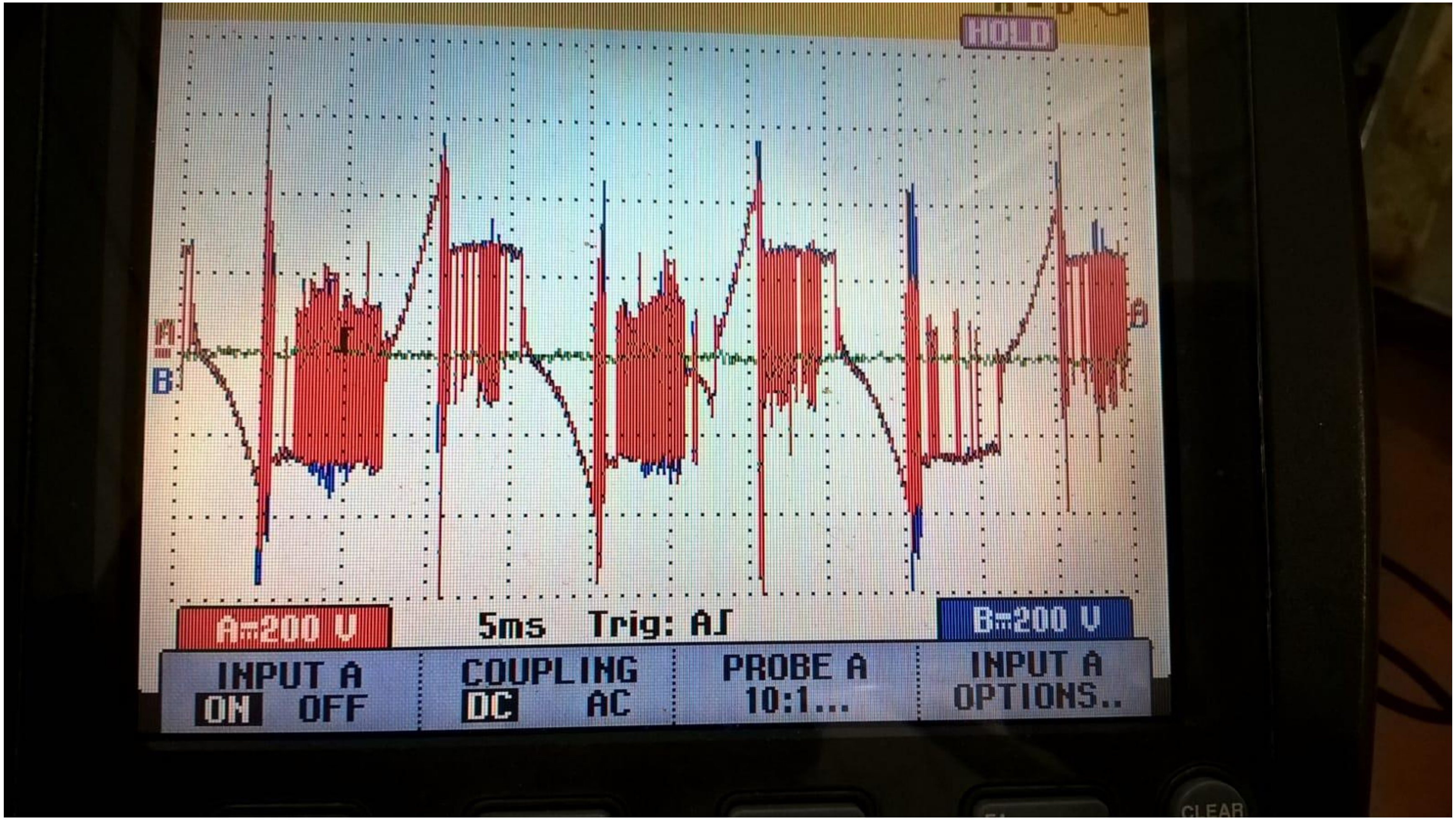


Fig.2_P. AC excitation up to 600 Vpp. Pure Argon at 0.5 bar, RT. *Uncontrolled current flowing*, according to Paschen curves. Pw, i.e. current, limited only by the CCD (3x J511 in parallel). No external resistor to limit and/or measure current: explorative test.

Test with pure H_2 and some (uncontrolled) air. Total pressure of only 20 mbar.

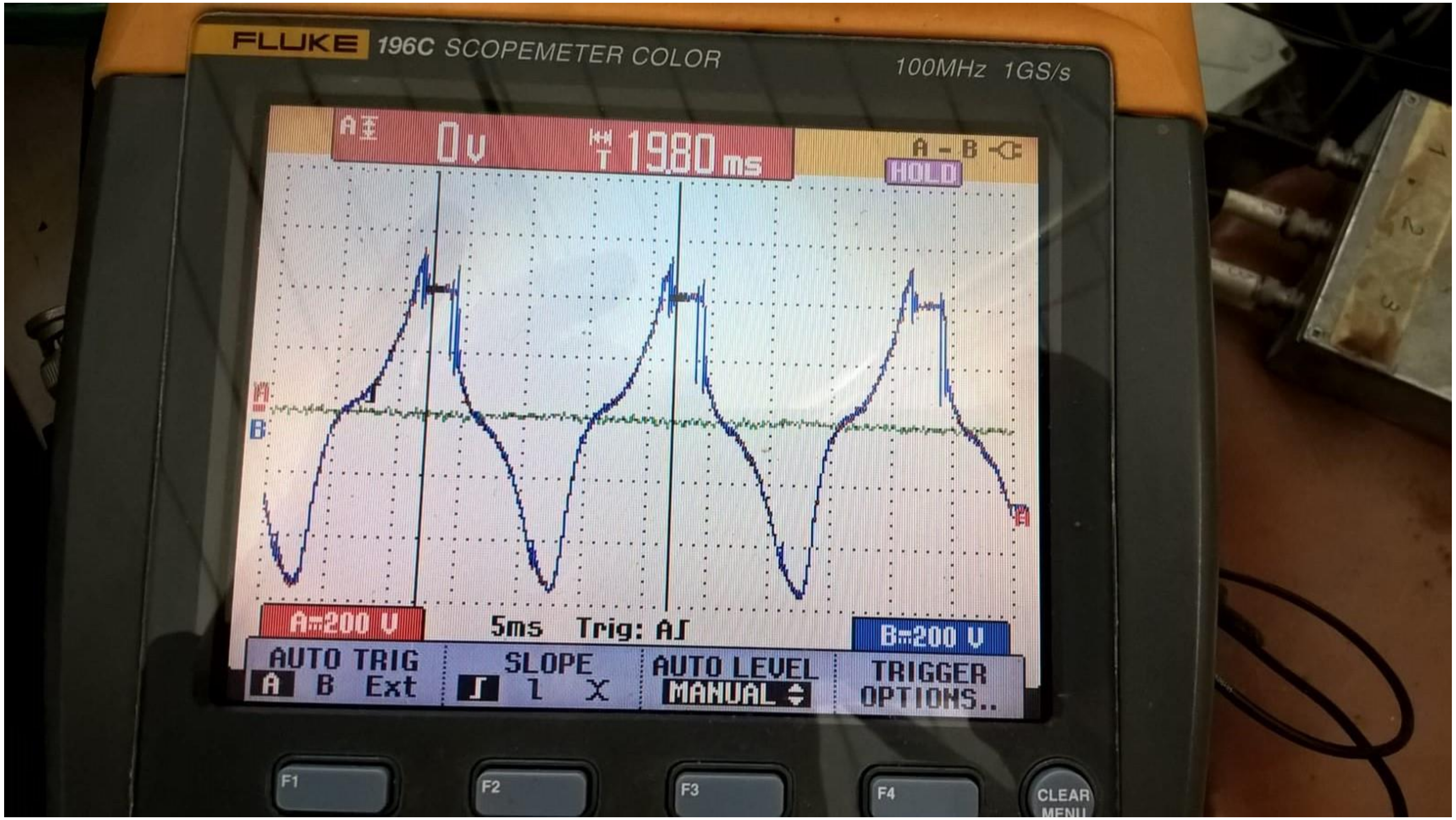


Fig.3_P. Pressure 20 mbar (H2+ uncontrolled air). T=100 *C. At low pressures the emission from the electrons seems dominant: only the positive branch of the curve is involved, the negative is almost unperturbed. No current measurements resistor installed (initial test).Green line is the voltage drop among the CCD diodes. Promising results, according to specific Paschen curve at very low pressures.

Paschen regime, measured by 10 kOhm resistor. Ar=H2, 0.5 bar total.

Fig.4_P. Intense Paschen regime. Gas mixing: Ar=H_2, 0.5 bar total; T=RT.

Current (green color), measured by 10 kOhm resistor; Imax=28mA (over current of CCD).

Voltage (200V/cm) at the ends of resistor: red color input; blue color output, toward field wire into reactor.

Oscillation due to the main line (50 Hz, 230 Vrms, 325 Vpp). Input voltage increased from 325 to 600 V by 2 transformer in cascade. Fast spikes due to the beginning of Paschen regime

Controlled Pashen regime. Pw injected quite low (>0.3W).

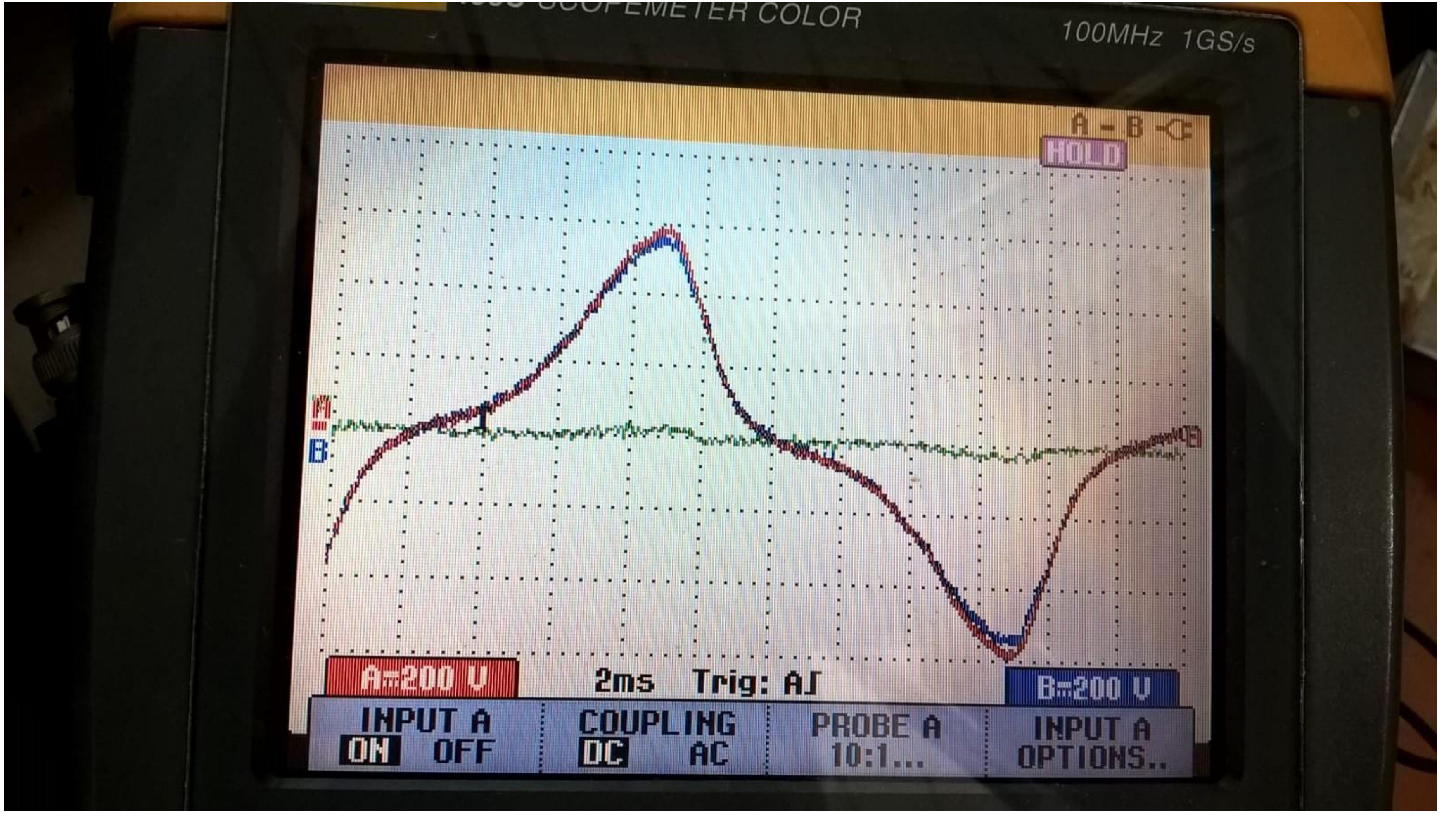


Fig.5_P. Typical operating regime with mild Paschen regime. Pw=100 W. Gas: Ar=H_2=0.42 bar tot and uncontrolled air intake. Pressure final measured=0.8 bar. Pw_rms<0.3 W, by Fluke 187 and Tektronix DMM916 true rms multimeter. Shown also by the green line plot (I measured by 10 kOhm resistor).

Auxiliary studies. Pressure effect versus local temperature of wire.

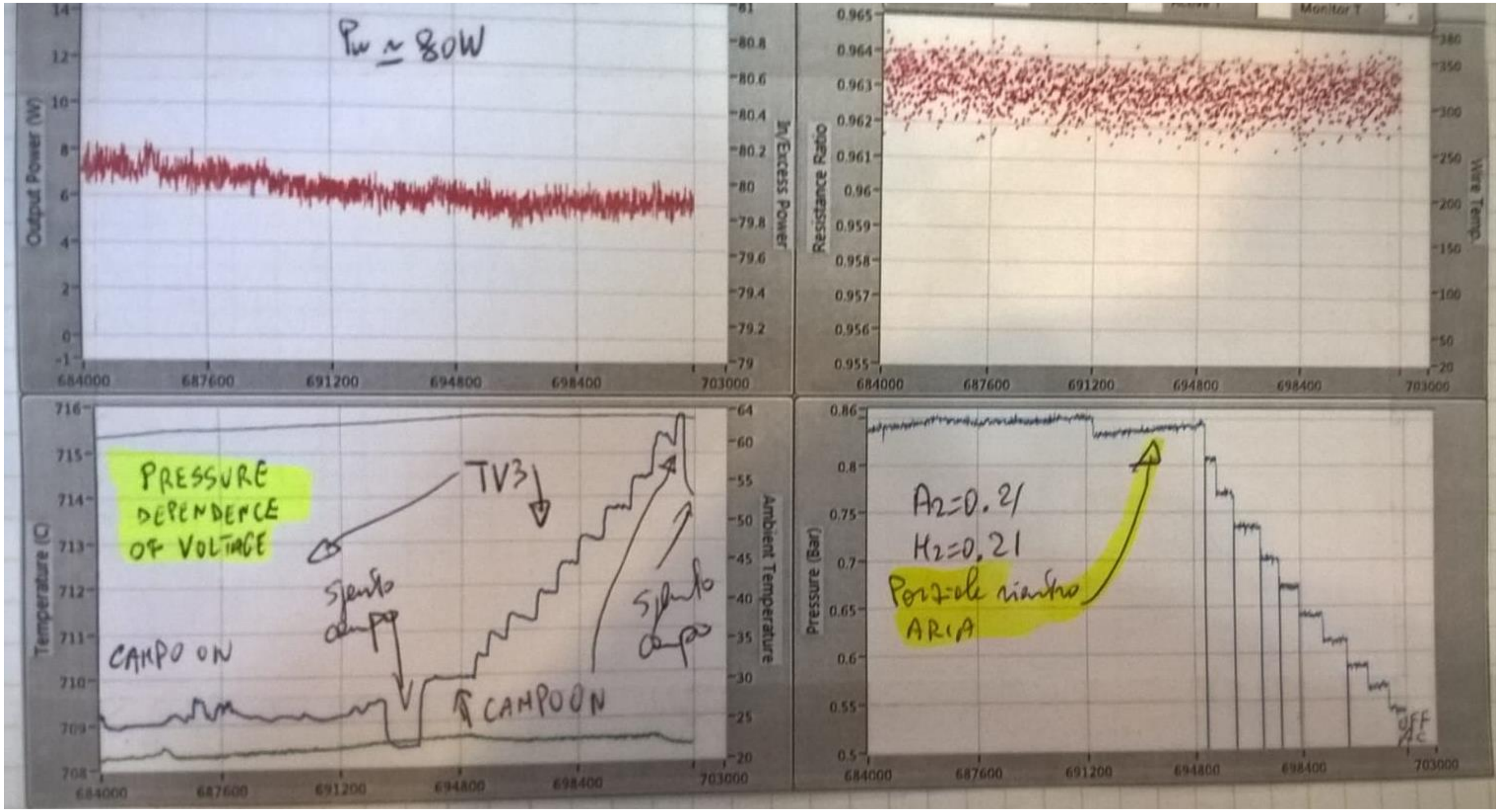


Fig.6_P. Measurements at 700*C. Pw=80 W. Ar=H_2 and some air inside. Effects of external field (ON→OFF→ON) at constant pressure and reducing it, from the point of view of local wire temperature. Effects of pressure reduction are of limited amount.

Main result: The reactor, with 80 W of input Pw, was operated for 1 day with the external excitation (mean extra Pw <0.3 W) active. AHE reached, *in comparison with calibrations (Joule heater)*, almost steadily, values of +7.8 W. Later, for subsequent 3 days, the excitation was OFF: AHE dropped to -0.2 W. Later the excitation was restored and the AHE , after 2h, went to +4.2 W. The effect was reconfirmed although the atmosphere of reactor was partially filled with air (uncontrolled leakage, pressure below ambient).

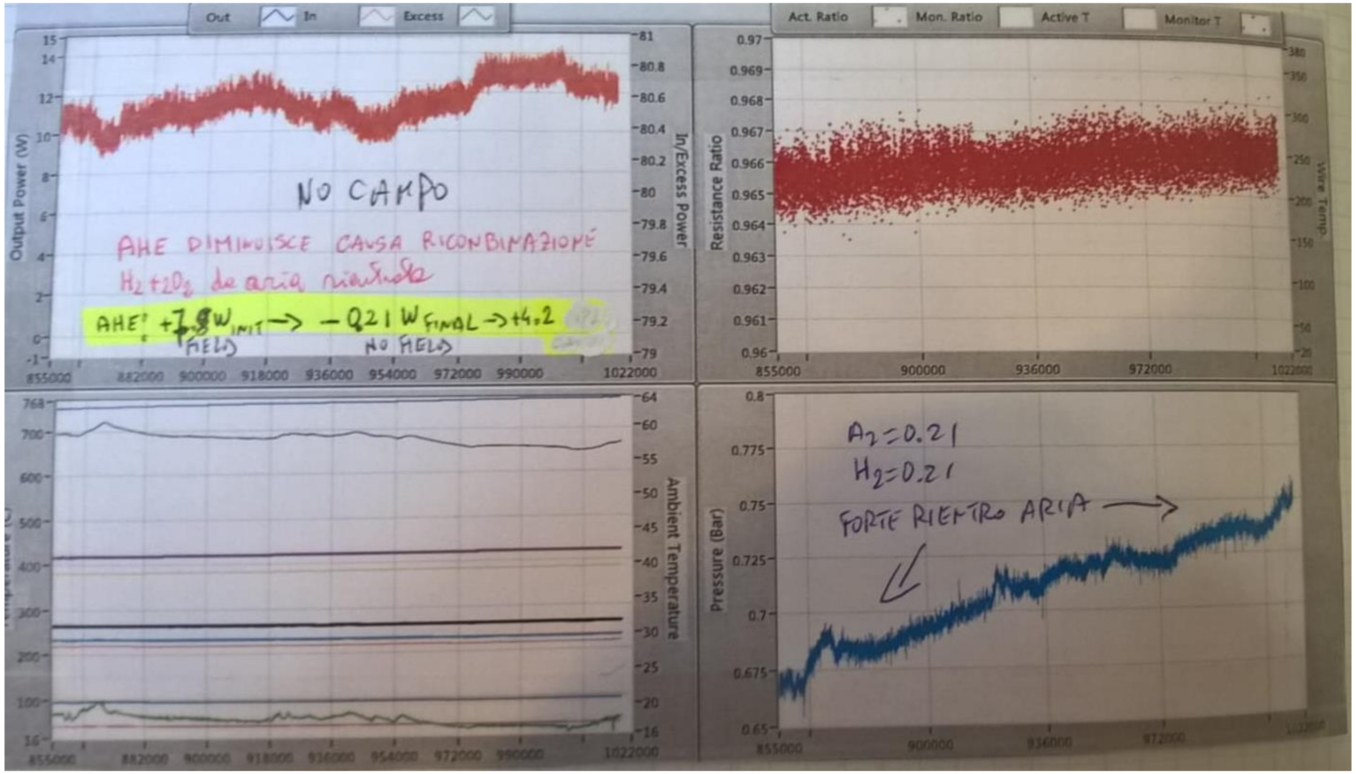


Fig.7_P. Effect of AC excitation on AHE behaviors.

Two giant events, about temperature increase at the core of the reactor, after cycling unipolar and bipolar pulses for excitation. Gas: Xe=0.65, D_2=0.38 bar at RT. Effect not possible to reproduce.

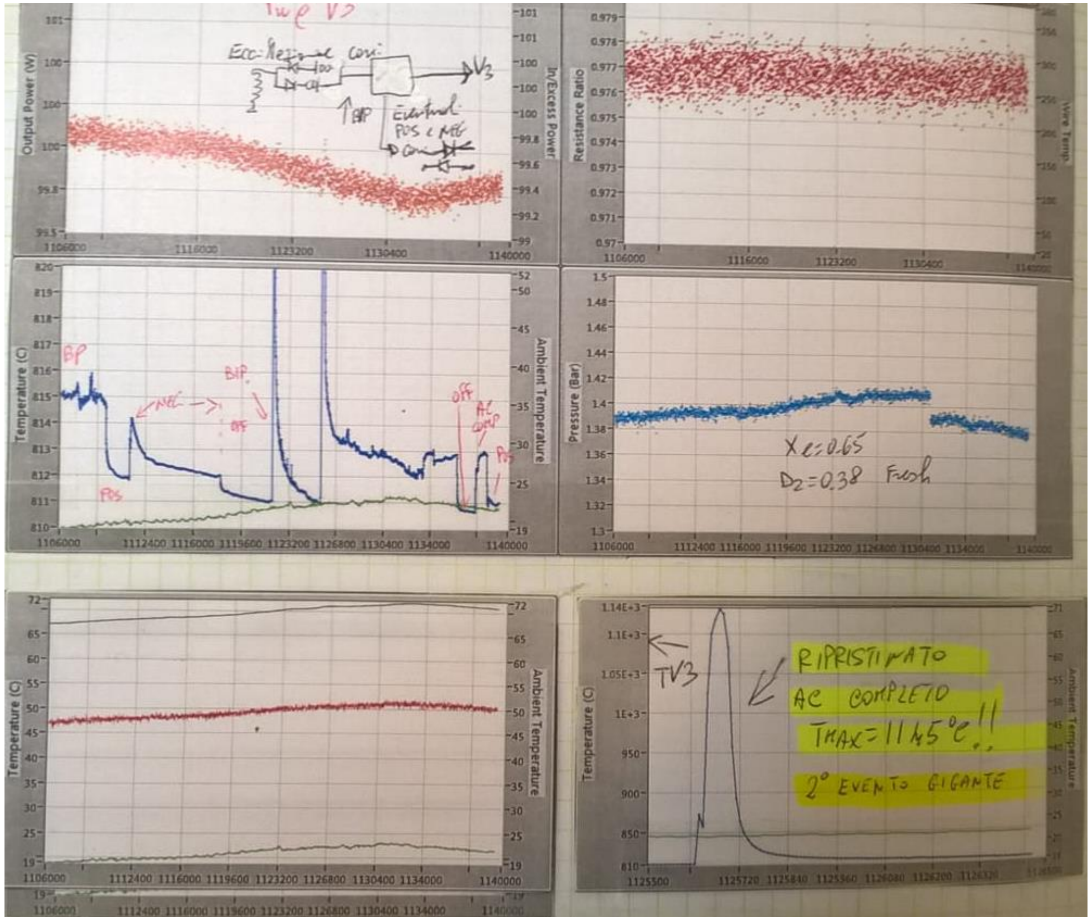


Fig.8_P. Plot of 2 giant events, after sequence of stimulation unipolar and bipolar. The event were accompanied also by remarkable gamma-like emission (Geiger counter, radiation monitor TENMARS mod. TM-91). With first event (Tmax= 912*C), Signal/Bk=3; with second event (Tmax=1145*C), Signal/Bk=26.

Correlated temperature increase of other thermometers inside the reactor.

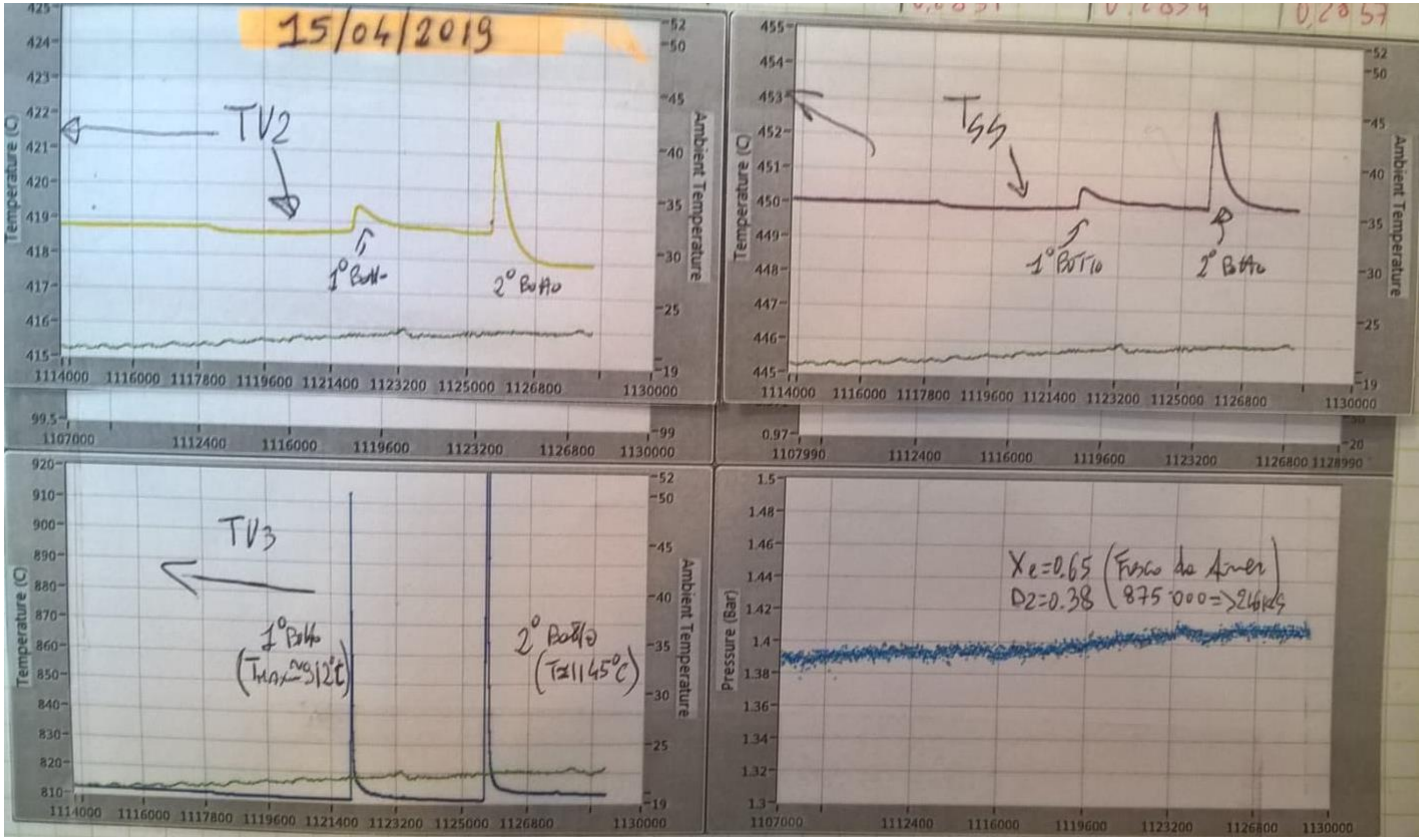


Fig.9_P. Other 2 thermometer inside the reactor, one central (identified as Tss) and the second inside the other coil (identified as TV2), give, in coincidence, measurable increase of temperatures and usual exponential decay.

Conclusions

(although work in progress)

A) The complex phenomenology of LENR-AHE seems to show that the AHE effect needed external stimulations: it is NOT spontaneous.

B) The objective is to keep the power used for stimulation as low as possible in respect to the total excess Pw generated.

C) The Paschen regime about the kind of gas, pressure, temperature, voltage, waveform seems to fulfill most of the constrain of so complex system.

D) Some dedicated computer and automatized devices to control, at least, pressure and voltage, seems necessary to allow properly stable operations for practical use.

E) Aging effects studies of the main components of reactor (active materials and specially sintering problems) are necessary.

[i] **Some specific borosilicate glasses, like that used by us (produced by SIGI-Favier) are a local tank of atomic Hydrogen (effect discovered on 1928 by Langmuir). Needed low pressures (Langmuir law) to minimize uncontrolled recombination (H+H→H2 and about -4.5eV, i.e. esothermic reaction)**

[ii] **e.g. experiments by Iwamura, Celani, Preparata, M.C.Kubre**

[iii] **historically pure Pd, Ti, Ni; more recently nanostructured alloys such as Ni-Cu; or Cu-Ni-Mn tertiary alloys (featuring sub-micrometric surfaces) coated with Fe, Sr, K, Mn, following a procedure developed by the Authors. Also, in accordance with the experiments of L. Holmlid we speculate on the presence of ultradense form of Hydrogen or Deuterium.**

[iv] **In comparison, the most known and very costly Pd (a precious metal) can provide only 0.424 eV of energy: computer simulation from S. Romanowsky et al., 1999. The energy given out during fast recombination process is quite high (about 4.5 eV): one of the largest among the chemical reactions. In deep space, at low Hydrogen pressures, the measured temperature is 36000 K: equilibrium among dissociation vs recombination.**