EXPERIMENTAL TECHNIQUES FOR DETECTING SMALL QUANTITIES OF ^{4}He GAS: PROBLEMS AND SOLUTIONS

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ABSTRACT

The problems arising from the techniques of measurement so far used to detect 4He in the gases coming out from Fleishmann-Pons cells are discussed. Innovative solutions are proposed. The results of extensive tests carried out with a facility built at ENEA Frascati are reported, which prove the ability of this equipment to overcome the problems discussed in this paper.

1. INTRODUCTION

The correlation between excess heat production and the achievement of a high deuterium loading ratio in a host metal M, has been assessed by many experiments [1,2]. This result is consistent with the theory proposed by G. Preparata [3], predicting the formation of coherence domains in the lattice of a hydrogen-metal system, provided that a sufficiently high (≥ 1) concentration D/M is reached. Both deuterons and the conduction electrons of the host metal behave as coherent systems, each described by a unique wave function. This theoretical analysis predicts a large increase in the cross section of D-D fusion reaction with respect to usual *"vacuum"* conditions; moreover, the resulting excited D-D compound nuclei may be cooled down by the coherent electrons system. Depending upon the fraction of electrons in the coherent state, the *"hot"* nuclei may thermalize in a time shorter than their lifetime, thus being prevented from splitting into the conventional reaction products. The 24 *MeV* energy of the excited state, which in vacuo is released as the kinetic energy of the emitted projectiles (nucleons or γ rays), is mostly absorbed by the coherent system as heat, accounting for both the observed excess energy production and the lack of neutrons and other "conventional" nuclear ashes. If such a theoretical approach is correct, we may expect that ^{4}He is the main reaction product of excess heat phenomena. The detection of ^{4}He in the gases evolving from *"cold fusion"* experiments is therefore a main issue, since it can provide evidence of this *"anomalous"* nuclear origin of the phenomena.

2. PROBLEMS AND SOLUTIONS

Many attempts have been so far carried out in several laboratories, using high resolution mass spectroscopy techniques, to analyze the gases collected throughout the whole loading process. However, the peculiar composition of the gas mixture to be analyzed in these experiments, and the risk of contamination, add up significant complexity to that already inherent to mass spectrometry itself (as extensively discussed in reference [4]), frequently leading to somewhat ambiguous results. This approach therefore requires both "blank" and "black" experiments to be carried out many times, in order to compare the results on a statistical basis and provide some evidence of excess ^{4}He production during "positive" experiments. However, the high loading required for excess heat occurrence was not so easy to achieve, as researchers in all over the world have experienced so many times during past years. Moreover, bulk cathodes usually require a very long time (weeks or even months) to be loaded, while thin film cathodes, which may be usually loaded in a few hours, were often unable to withstand the excess heat over a long period of time, frequently resulting in a premature conclusion of the experiments. This uneasy situation frustrated most of these efforts.

The introduction of reproducible loading procedures, as well as of suitable cathode geometries and construction methods, allowing to rapidly achieve and then to withstand the experimental conditions required for excess heat production, is of course a crucial issue. Carrying out periodical sampling of the gas evolving from the electrolysis during the loading experiment (provided that no perturbation is introduced), to compare the content of ^{4}He with the excess heat measurement, would also strongly simplify this

investigation. Such an "on line" analysis method would in addition provide a more convincing proof of the correlation between heat and ^{4}He production. These problems were all faced and finally solved in our laboratory. High loading of long-lasting Pd cathodes under heavy water electrolysis is systematically achieved using the "Preparata" effect (formerly "Cöhn-Aharonov" effect); details on this topic are discussed separately in a dedicated paper [5].

An innovative "pseudo-static" gas analysis method, based on the use of non evaporable getter (NEG) pumps, was proposed at the previous ICCF8 [4] and preliminary tested to demonstrate the feasibility of the concept. The test facility was upgraded during the last two years, allowing to get rid of any ambiguity in the results of gas analysis. For instance, cryosorption pumps have been eliminated in the present configuration, since they may give rise to some trapping of helium in the condensates, resulting in a random underestimation of the helium content. The equipment turns out to be of simple use, and provides reliable and precise measurements of the content of inert components in any gas mixture. A particular effort have been made, when designing the sampling circuit, to allow for on-line analysis during the loading experiment without introducing any perturbation of the electrolytic process.

3. CALIBRATIONS

The quadrupole mass analyzer (QMA) was calibrated according to recommended practice, using pure N_2, Ar, ^{4}He and D_2. In the case of both ^{4}He and Ar, calibrations were also carried out in the "pseudo-static" mode, introducing known amounts of gas into the analyzer. The gas pre-load was accomplished by filling a known volume (3.32 ± 0.01 cc) with pure helium or argon at a known pressure, as monitored by accurate capacitive baratron gauges. The pressure inside the analysis chamber was monitored by the same ion

gauge used for dynamic calibrations, in order to compare the results. Figure 1 shows the excellent agreement between these two calibration methods. The apparent deviation from linearity of static data at very low pressures is due to the residual pressure at the ultimate vacuum. In the high resolution mode, the QMA was calibrated using ^{4}He and D_2. Since, during analysis of gas samples, the getter pumps ensure that all the deuterium eventually present in the gaseous mixture is effectively removed, it

Figure 1 - Comparison between static and dynamic ^{4}He calibrations

isn't necessary to push the resolution at its maximum level. A suitable compromise was thus chosen in order to achieve enough resolution to clearly distinguish the two peaks, without loosing too much sensitivity. Cross contributions were carefully measured in order to evaluate the appropriate correction to be introduced in the dynamic analysis of ^{4}He-D_2 mixtures. Checks with such mixtures (about 67% - 32% and 50%) were carried out to test the method. The partial pressures of the two components were calculated dividing the intensities of the two peaks (after subtracting cross contributions) by the corresponding sensitivity of the pure gases, and accounting for the relative sensitivity of the hot cathode ion gauge (a conversion factor 6 for ^{4}He and 2.6 for D_2). The measured concentrations turned out to be in good agreement with the nominal composition.
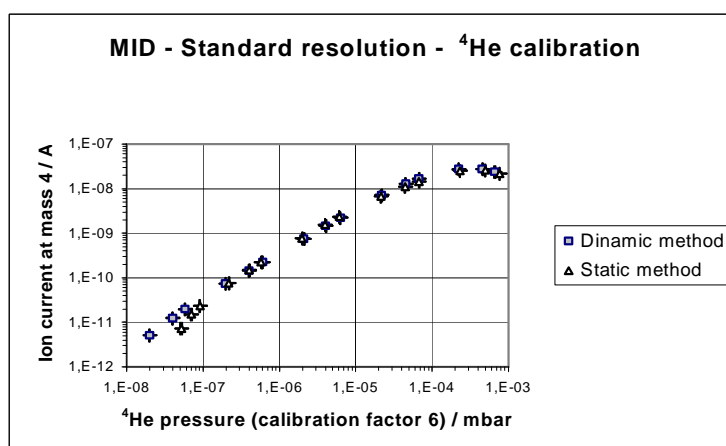
4. INTRODUCTORY TESTS.

Extensive introductory tests were carried out to check the performance of the system. As a first attempt, small samples from a 50 cc bottle, filled with air from the environment, were analyzed. Figure 2 is a typical residual spectrum of an air sample. All active components are effectively removed in a few tens of seconds, showing an excellent qualitative behavior. To properly test the performance of the analysis system from a quantitative point of view, we used a laser mixture with a known composition (82% ^{4}He - 13.5% N_2 -

4.5% CO_2). A reservoir was filled from the mixture bottle at about 0.5 bar. The gas was then admitted, by means of a metering valve, in a relatively small volume ($\approx$ 400 cc) equipped with an accurate capacitive baratron gauge (0.1 torr FS), at the desired pressure. A small sample volume (4.38 $\pm$ 0.04 cm^3) was finally fed with the mixture from this intermediate volume, through a capillary tube and a valve. Many samples, at different pressures, were analyzed to measure their ^{4}He content, as shown in figure 3. Black dots represent data recorded at increasing sample pressures, i.e. by adding mixture from the reservoir to the
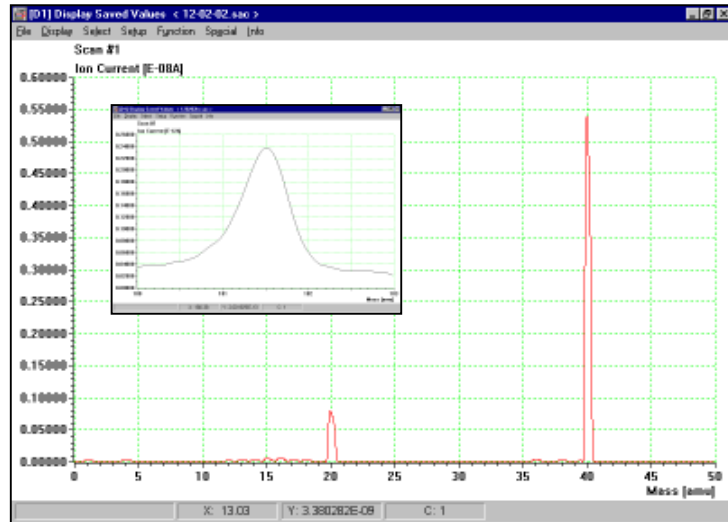

Figure 2 - Typical residual spectrum of an air sample.

intermediate volume. White squares are instead relative to samples taken at decreasing pressures, allowing the residual gas in the intermediate volume to expand in the sample volume, with no further addition from the reservoir. The small hysteresis observed can be easily understood as a consequence of the different ability of the various gases in the mixture to flow across a capillary tube, giving rise to a progressive reduction in the concentration of light components in the upstream region. The ^{4}He concentration in the laser mixture samples was measured to be 86.5 $\pm$ 0.6%, in reasonable agreement with the nominal value, if we consider that the procedure used to fill the sample volume, through a metering valve and a capillary tube, unavoidably gives rise to some enrichment of the mixture downstream. The linear fit of the experimental data shows the very high precision of the measurement (R^2 = 9.9995).
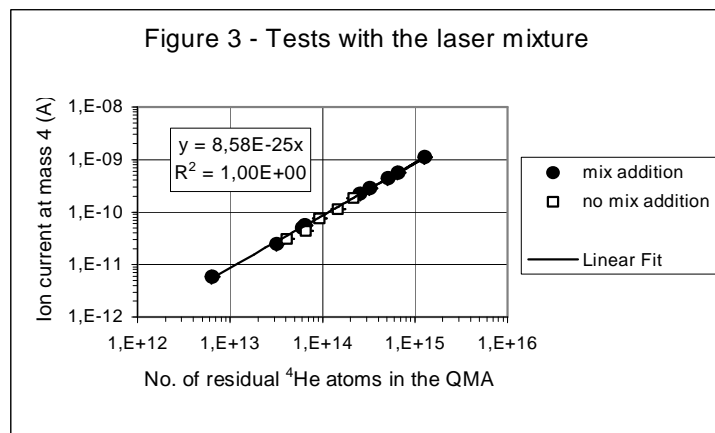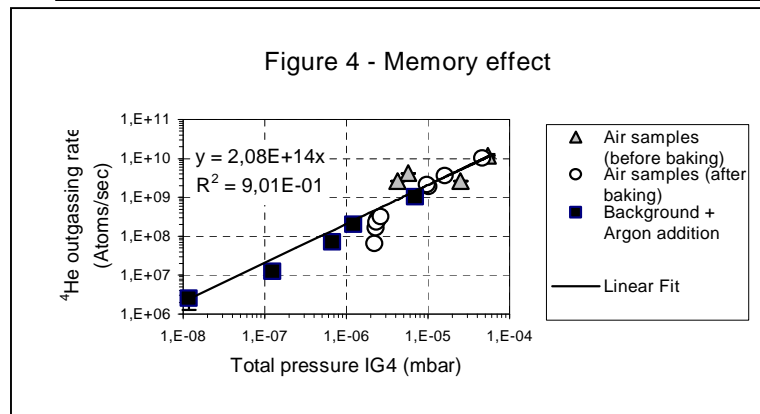

5. MEMORY EFFECT.

When pure helium or a laser mixture sample is admitted in the analyzer, the ion current at mass 4 suddenly rises up and sticks to a rigorously constant value, as expected. A different behavior is instead observed with air samples. After the initial step up, the ion current at mass 4 begins to slowly increases with time. No similar effect is exhibited by the Argon signal. This effect vanishes soon after a baking of the UHV chamber, then it appears again and becomes more and more evident (see figure 4) as the experiments go on. This would obviously suggest that ^{4}He is adsorbed in the wall of the analysis chamber and successively

released. However, this helium outgassing does not take place spontaneously; for instance, it isn't observed by merely excluding the turbo molecular pump leaving the chamber in the "pseudo static" mode.

We argued that the co-presence of a much larger amount of argon, during air tests, is responsible for this effect, due to the bombardment of the walls by the argon atoms. We checked this hypothesis, injecting increasing amounts of argon in the chamber, under "pseudo static" vacuum condition. The results are plotted again in figure 4. It is quite evident that the effect increases linearly with the Ar pressure. The occurrence of this phenomenon may be significantly reduced by regularly baking the UHV chamber, however the error introduced by this effect may be corrected, once its nature and its quantitative contribution has been assessed.

6. THE "ON LINE" ANALYSIS TECHNIQUE

The electrochemical cell is connected to the analyzer through a storage circuit purposely designed to allow for on line analysis of the evolving gases. Maximum care is taken in order to prevent any possible helium contamination. Before starting an experimental run, both the cell and the circuit must be preliminary evacuated and tested against leakages, then purged and finally buffered with high purity N70 nitrogen (99.99999%). The cell is then filled with the electrolyte. The whole circuit has been built up using ultra high vacuum (UHV) components. The cell is moreover enclosed inside an UHV containment vessel, which undergoes the same initial testing and purging procedure and is finally filled with N70 nitrogen to prevent helium permeation from the surroundings. Buffering of the cell and the sampling circuit is necessary to prevent boil off of the liquid electrolyte during the experiment. Due to the ≈ 10 ppbV content of ^{4}He in the high purity nitrogen, the background in the analyzer is set to about 10^{12} atoms. A sample of the N70 nitrogen buffer, however, must be always analyzed at the end of the preliminary purging procedure (before starting the electrolysis) to set the zero of each experimental run. All the operations, from initial purging to sample drawing and analysis, are carried out under automatic control, in order to ensure a quite perfect reproducibility of the whole process. Relevant parameters are logged on a PC.

The gases evolving during the experiment are collected in the storage volume, which is held at a constant pressure (1050 ± 2 mbar). A 6.29% aliquot of this gas is then periodically sent to the QMA to be analyzed. Since equal quantities of gas are drawn at each sampling, it is very easy to compare, time by time, the results of the analysis. Moreover, the particular procedure adopted in the present configuration, actually gets rid of any need to refill the system with pure N_2 after a sample has been drown off, allowing to not perturb the electrolytic experiment at all.

The analyzer was recently connected to an electrochemical cell, in order to preliminary test the performance of the "on line" sampling arrangement. Except for some minor adjustments of the control software, the system performed very satisfactorily and reliably since these very early tests. After a few days of work in these conditions, the getter pumps showed to somehow suffer from the excessive sample drawing rate. The introduction of the Pd alloy catalyst, which was removed during these tests, should however get rid of this problem.

7. CONCLUSIONS

The limits of conventional mass spectroscopic techniques, so far used to analyze the gases evolving from Fleishmann-Pons cells, have been pointed out. A new "pseudo-static" method has been proposed, based on the use of NEG pumps. A facility built at ENEA Frascati, which was upgraded to allow for "on line" analysis of gas samples during the loading experiments, underwent extensive tests exhibiting very good performance and an excellent reliability. Preliminary tests of the "on line" sampling arrangement showed very promising performance.

8. ACKNOWLEDGMENTS

9. REFERENCES

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