

Hydride Compressor Sorption Cooler and Surface Contamination Issues

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Abstract. A continuous-duty hydrogen sorption cryocooler is being developed for the Planck spacecraft, a mission to map the cosmic microwave background beginning in 2007. This cryocooler uses six individual compressor elements (CEs) filled with the hydriding alloy $\text{LaNi}_{4.78}\text{Sn}_{0.22}$ to provide high-pressure (50 bar) hydrogen to a Joule-Thomson (J-T) expander and to absorb low-pressure (~ 0.3 bar) gas from liquid hydrogen reservoirs cooled to $\sim 18\text{K}$. Quadrupole Mass Spectrometry (QMS) showed methane in these hydride beds after cycling during initial operation of laboratory tests of the Planck engineering breadboard (EBB) cooler. These contaminants have caused problems involving plugged J-T expanders. The contaminants probably come from reactions with residual hydrocarbon species on surfaces inside the hydride bed. The hydride bed in each CE is contained in an annular volume called a "gas-gap heat switch," which serves as a reversible, intermittent thermal path to the spacecraft radiator. The gas-gap is either "off" (i.e., its pressure < 1.3 Pa), or "on" (i.e., hydrogen gas at ~ 4 kPa). The hydrogen pressure is varied with an independent hydride actuator containing ZrNiH_x . Early EBB cooler tests showed increasing parasitic heat losses from the inner beds, suggesting residual pressures in the gas gap during its "off" state. The pressure was shown to be due to hydrogen from outgassing from metallic surfaces in the gas gap and hydrogen permeation through the inner sorbent bed wall. This gas accumulation has serious end-of-life implications, as the ZrNi actuator has limited storage capacity and any excess hydrogen would necessarily affect its operation. This paper summarizes experiments on the behavior of hydrogen in the gas gap switch and formation of methane in the CE sorbent beds.

INTRODUCTION

Planck is a space observatory that will image the temperature anisotropies of the Cosmic Microwave Background (CMB) radiation over the entire sky at extreme sensitivity and resolution [1]. Planck will provide much new information on several key cosmological and astrophysical issues that will be used to test theories of the early universe and the origin of cosmic structure. To achieve these objectives, state-of-the-art broadband detectors covering the frequency range ~ 30 to ~ 1000 GHz must be operated at cryogenic temperature [1-3]. The Jet Propulsion Laboratory (JPL) is developing hydrogen sorption

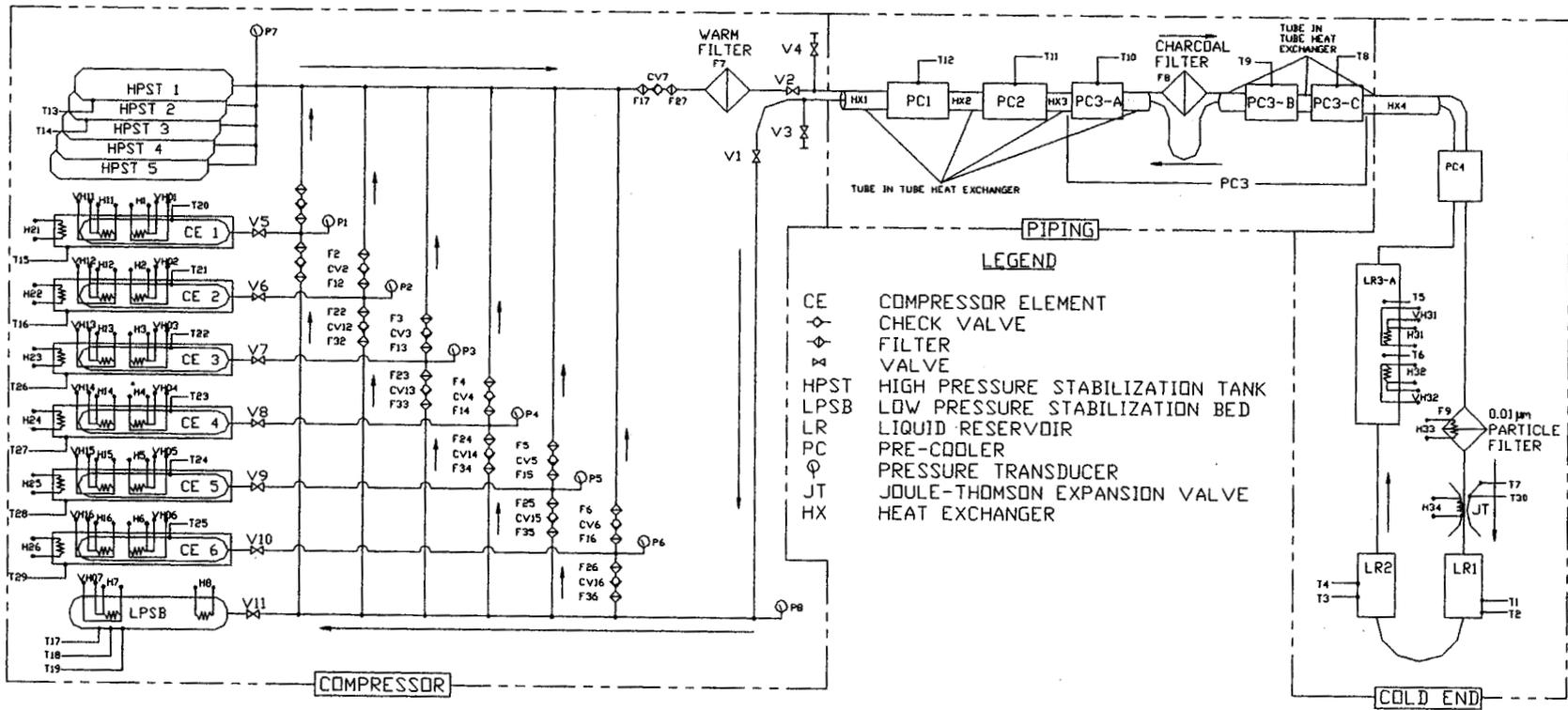


FIGURE 1. Schematic diagram of the Engineering Bread Board (EBB) 19 K sorption cryocooler for Planck that identifies major components. The arrows denote the flow direction for the hydrogen refrigerant.

cryocoolers [3] to provide cooling at ~ 18 K for the Planck instruments. Laboratory testing of a full-scale Engineering Bread Board (EBB) version of the Planck sorption cooler was started [4] in January 2002. The EBB cooler was built to be functionally equivalent to the flight design. A schematic of this cooler is shown in Fig. 1. The as-built EBB compressor is very similar to the flight design while the flight cryostat design is somewhat different. The EBB sorption compressor consists of six Compressor Elements (CE) filled with $\text{LaNi}_{4.78}\text{Sn}_{0.22}$ alloy that provide continuous circulation of hydrogen at the appropriate pressure and flow rate. A thorough description of the design and behavior of the hydride compressor elements that were utilized in the EBB cooler was recently presented [5]. Each CE uses a gas gap heat switch to isolate the sorbent during heating and desorption while permitting heat removal during cool down and absorption. The Gas Gap Actuator (GGA) uses $\text{ZrNiH}_{1.5}$ to reversibly vary hydrogen pressure between <1.3 Pa and >1.3 kPa by alternately heating and cooling this hydride [6]. Passive check valves that are protected by porous sintered disc filters to prevent leaks by entrapped particles direct hydrogen flow in the cooler. Fig. 1 shows the 5 one-liter high-pressure stabilization tanks (HPST) in the high-pressure manifold as well as the low-pressure stabilization hydride bed (LPSB). The LPSB, in addition to damping pressure oscillations in the low-pressure manifold, is used to store hydrogen gas so that the cooler can be shipped with hydrogen gas below atmospheric pressure. The EBB Cold End consists of a tube-in-tube heat exchanger, three pre-coolers, a porous plug J-T expander, and two liquid reservoirs. The EBB cryostat uses a discrete heat exchanger (DHX) that fixes the JT temperature and serves to keep the liquid dry-out point fixed [7]. The three pre-coolers are designed to operate at 160 K, 100 K, and 50-60 K. The two liquid reservoirs LR1 and LR2 for the EBB cooler simulate cooling interfaces to the Planck HFI and LFI instruments, respectively [2,3].

Performance testing of the Planck EBB cooler has been underway at JPL since January 2002 where nearly all of the design requirements have been successfully demonstrated [4,8]. However, two problems were discovered during initial operation [4] that can be associated with the compressor elements. First, intermittent plugging of the J-T valve occurred and was attributed [4,5] to freezing of methane in the hydrogen refrigerant gas. Secondly, excessive input power to the compressor element was required during extended operation that was traced to the build-up of hydrogen pressure in the "Off" insulating state of the gas gap heat switch. This paper describes the subsequent investigations into the causes and extent of these problems.

DESCRIPTION OF COMPRESSOR ELEMENTS

The compressor element, which contains the hydride sorbent bed, is the critical component of any hydrogen sorption cryocooler [9,10]. A schematic of the CE design for the Planck coolers is shown in Fig. 2. As described previously [5,10], the closed-cycle J-T refrigeration process results from sequential heating and cooling of the sorbent beds in several CEs (six in the case of the Planck cooler). During ground testing and space flight operation each Planck CE will undergo nearly 20,000 heating and cooling cycles.

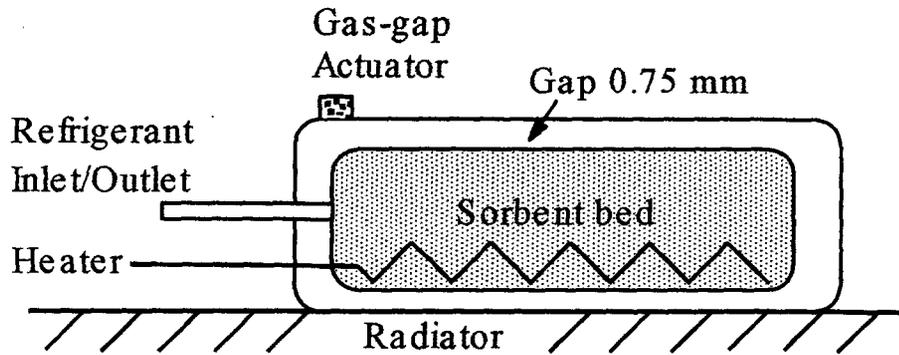


FIGURE 2. Schematic diagram of hydride compressor element developed for the Planck Sorption Cooler.

To minimize input power during the heating and desorption phases [3,5,10,11], a reversible gas gap heat switch is incorporated into each CE [3,6]. Two generations of CE have been built at JPL for the Planck cooler. The first version did not contain a hydride GGA for the heat switch, but it instead used hydrogen tank and valve combination with an oil-free vacuum pump during the temperature cycling [11,12]. These life-cycle compressor elements (LCE) were subjected to over 5000 absorption-desorption cycles to assess initial CE performance and to determine degradation in the hydride sorbent material during heating and cooling conditions that simulate cooler operation. One of the LCE units is shown in Fig. 3. The second version of CE units had integral GGA with a ZrNi hydride sorbent and was used in the EBB cooler shown in Fig. 1. An EBB-CE is shown in Fig. 4.

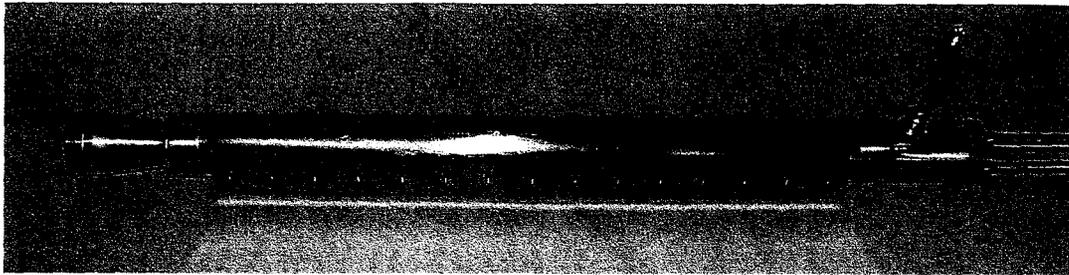


FIGURE 3. Photograph of an assembled life-cycle compressor element without a gas gap actuator.

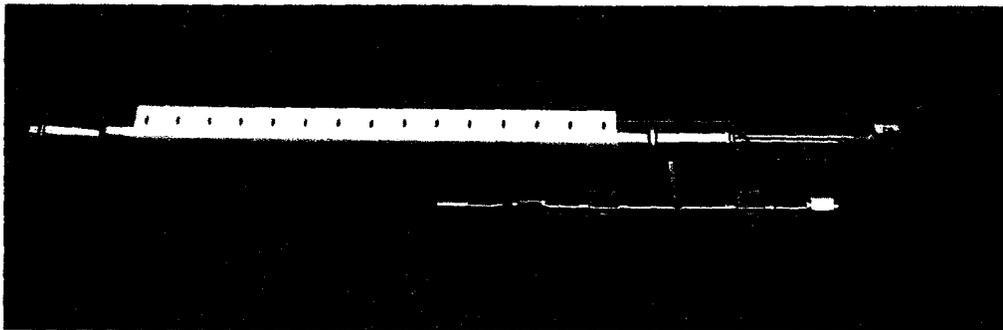


Figure 4. Photograph of an assembled EBB compressor element with a ZrNi hydride gas gap actuator.

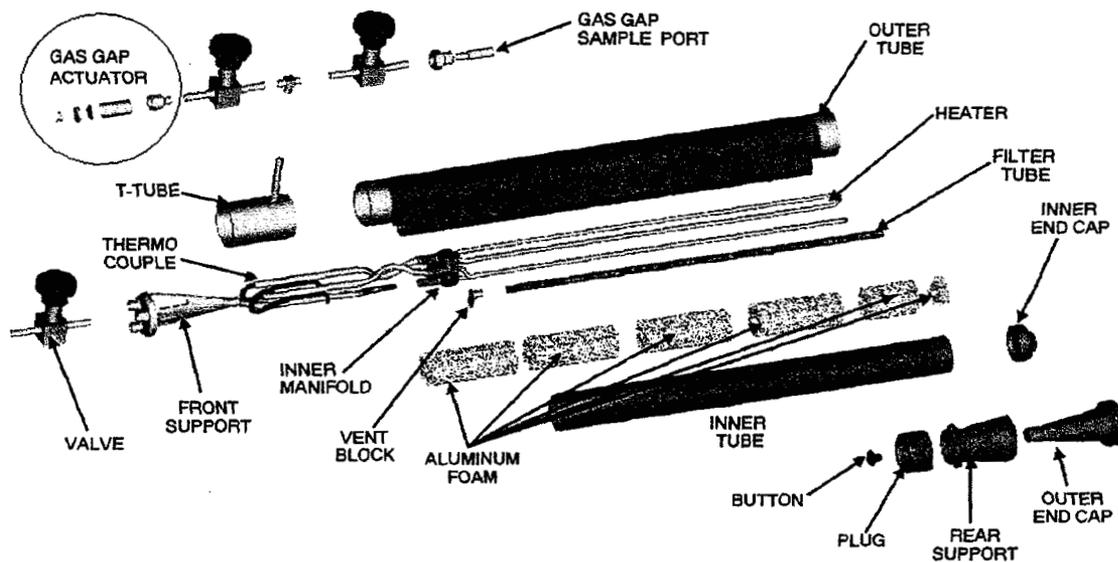


FIGURE 5. Exploded view of the components used in the compressor elements of the Planck EBB cooler. Powder of the hydrogen sorbent alloy $\text{LaNi}_{4.78}\text{Sn}_{0.22}$ fills the voids in the aluminum foam pieces.

Each compressor element contains 615 grams of the hydride alloy $\text{LaNi}_{4.78}\text{Sn}_{0.22}$ in its sorbent bed. The CEs are independently heated and cooled through a series of heat-up, desorption, cool-down, and absorption steps to provide compression and circulation of the hydrogen refrigerant gas during closed-cycle J-T process that generates liquid hydrogen at ~ 18 K in the cryostat. The CEs are directly mounted to a radiator that is sized to reject the heat from the input power and exothermic hydrogen absorption by the alloy at $270 \text{ K} + 10 \text{ K} / -20 \text{ K}$. An exploded view of components for the compressor elements used in the EBB cooler is given in Fig. 5. The central portion of the outer tube is aluminum metal type 6061-T6, the foam is also 6061 aluminum at $\sim 11\%$ of its bulk density, the button is A286 stainless steel (SS), and all other components in contact with hydrogen are made from 316L stainless steel. To minimize sources of contamination and enhance impurity removal, all surfaces of the 316L SS were electropolished giving bright surfaces. The outer surface of the inner tube assembly and both surfaces of the aluminum portion of the outer tube were electroplated with gold films to reduce thermal emissivity in the gas gap volume. There is a 0.75 mm gas gap separation between the inner and outer tubes. The thickness of the wall for the inner tube is 1.22 mm except at the weld zones on the ends where it is 1.52 mm. The porous filter tube ensures that hydride powder contained in the Al foam does not migrate from the sorbent bed during the temperature and pressure cycling. Tight physical contact of the Al foam with the inner surface of the tube wall provides heat transfer from the sorbent bed to the gas gap. The sorbent bed is attached to the outer housing only at the ends using the supports shown in Fig. 5. All assembly joints are made using automatic orbital-tube welding under argon/3% H_2 gas. Beyond the addition of the GGA to the first version of the Planck compressor element, several modifications were done in the EBB-CEs to make the unit more robust during launch vibrations, to reduce thermal gradients in the sorbent bed, etc. However, nearly identical processing was followed for the electropolishing, gold electroplating, and sorbent bed activation [5, 11, 12].

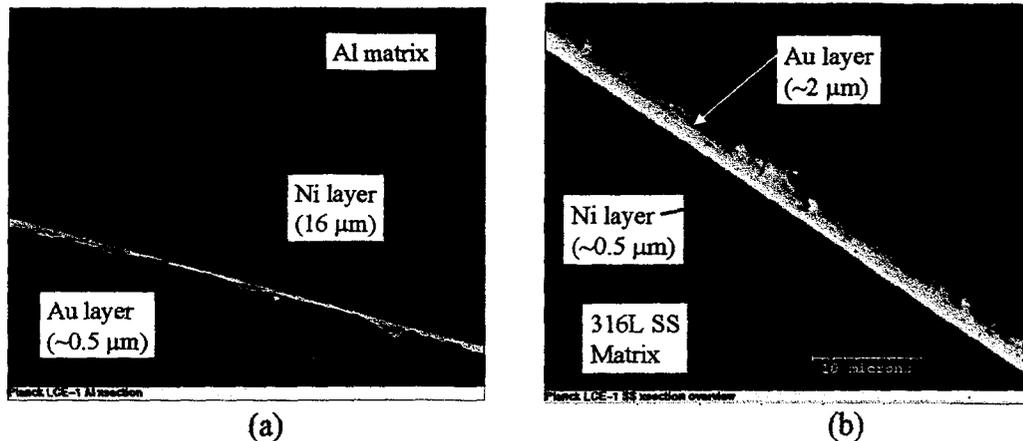


Figure 6. Cross-Section SEM images of the electroplated Au/Ni layers on (a) the inner surface of the Al outer manifold and (b) 316L Outer End Cap for the gas gap region of Planck Compressor Element LCE-1.

Electroplated gold films cover most of the surface area of the gas gap volume where a nickel layer was initially deposited to promote better bonding with the 316L SS and Al substrates. Fig. 6 presents cross-sectional scanning electron microscope (SEM) images of the Au/Ni layers on both host metals from the LCE-1 compressor element. In addition, x-ray fluorescence (XRF) was used to provide independent measurement of the thickness of these gold layers. XRF indicated the gold thickness varied from 0.7-1.0 μm on the 316L SS substrates and 0.2-0.5 μm on the Al substrate while the Ni sublayer was $\sim 0.5 \mu\text{m}$ thick on SS and 16-18 μm on Al. SEM and XRF measurements of the Au and Ni layers for the compressor element EBB-2 gave similar results of $\sim 0.2 \mu\text{m}$ Au and 16-19 μm Ni layers on the Al substrate and $\sim 0.9 \mu\text{m}$ Au and $\sim 0.3 \mu\text{m}$ Ni layers on the 316L SS substrate. The total surface area of the gas gap in the EBB units (exclusive of the GGA isolated by the valve shown in Figs. 4 and 5) is about 940 cm^2 and is comprised of 340 cm^2 of Au-plated SS, 380 cm^2 of Au-plated Al, and 220 cm^2 of bare electropolished 316L SS. The gas gap volume for EBB-7 was determined to be 120.6 cm^3 to give a surface-to-volume ratio of 7.8 cm^{-1} , which is 8.0 times larger than this ratio for a sphere of the same volume. Hence, effects from surface properties such as outgassing and permeation will be very significant for these CE gas gap volumes.

Following the sequential integration of a gold-plated inner bed assembly to the outer tube assembly and a GGA unit for EBB compressor elements, the gas gap volume was treated to an extended hydrogen gas fill and evacuation process. The inner bed was heated to $\sim 670 \text{ K}$ with its internal heater while distilled water that was heated to $\sim 360 \text{ K}$ was circulated through a chiller plate mounted on the outer shell, which was covered in an insulation blanket. The gas gap volume was alternatively filled with purified hydrogen at ~ 1 bar pressure and evacuated with a turbomolecular pumping station. These fill-evacuate cycles were repeated until the mass spectrum from a quadrupole mass spectrometer (QMS) indicated no hydrocarbon species above instrumental background levels (i.e., usually between 50 - 100 cycles were required to obtain sufficient cleaning) in the vacuum state.

Because the gas gap heat switches for LCE beds were operated with a vacuum pump to create its "off" state [11,12], no bake out or other cleaning treatments were applied to the gas gap surfaces. While the surfaces of the LCE inner bed walls exceeded 500 K during bed activation and cycling tests, the Au/Ni plated Al outer housing did not warm above ~330 K since it was mounted to a chiller plate that provided continuous cooling at ~270 K.

The GGA for each EBB unit contains 0.28 gms of ZrNi alloy that was reacted with sufficient hydrogen to give a hydride composition of $ZrNiH_{1.5}$ ($=31.3 \text{ scm}^3$ of hydrogen gas), which is near the middle of the two-phase β - γ region for this hydride [13,14]. This composition provides the appropriate pressures for an effective heat switch [6,15] when the GGA temperature is varied between 270 K and 500 K. If the $ZrNiH_x$ hydride composition exceeds $x \sim 2.5$ the equilibrium pressure will rise very rapidly [13,14] and permit enhanced heat transfer in its low pressure "off" state. This condition reduces the performance of the sorption cooler by requiring larger input power to maintain the supply pressure and flow rate to the J-T expander [4,6].

HYDROGEN OUTGASSING INTO GAS GAP VOLUMES

After completion of the characterization tests of the individual EBB compressor elements and before the start of the initial cooler operation, the two manual valves for the gas gap volume (see Figs. 4 and 5) remained closed isolating the ZrNi hydride from the rest of the gas gap volume. As reported previously [5], the pressures in the isolated gas gap volumes were found to range from 70 Pa to 700 Pa (i.e., 0.5 – 5.0 Torr) following ambient temperature storage between two and six months. Several tests identified hydrogen was responsible for this entire pressure rise. Because the $ZrNiH_x$ gas gap sorbent was configured to work in the middle of its plateau region during heat switch cycling, it can accommodate a limited amount (i.e., < 15-20 scc for the EBB GGAs) of additional hydrogen without significant performance impact. From analyses of the performance degradation (i.e., increasing input power requirements) of the compressor elements during initial EBB cooler operation [4], hydrogen pressures in the range of 2.7 – 8.0 Pa (20 - 60 mTorr) were estimated for the gas gap volume during the "off"-state (i.e., vacuum). Since the residual hydrogen pressure in the gas gap volume is controlled by the pumping effectiveness of the $ZrNiH_x$ bed, there are two prime candidates for this pressure rise. The first is the absorption of "outgassed" hydrogen by the hydride until compositions are reached such that the equilibrium pressure at 280 K for the hydride approaches and then exceeds the "off" values. Consequently, quantitative assessment of amount of hydrogen became imperative before the design of the compressor elements could be finalized and the flight units fabricated. The second process is the impediment of hydrogen absorption by the hydride sorbent due to surface contamination in the presence of other molecular species that react with the ZrNi. The formation of these surface barriers can significantly retard the absorption rates in the low-pressure regime and short transient requirements imposed on the heat switch. Thus, the pressure in the gas gap volume remains above the expected equilibrium values to produce undesirable parasitic heat losses.

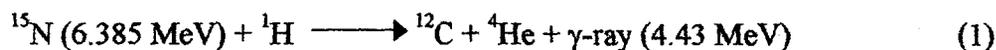
There are several possible sources for hydrogen in the gas gap that can cause the behavior described in the previous paragraph. These include:

- Outgassing from 316SS/Al walls enhanced by Au electroplating processing
- Hydrogen permeation through 0.12 cm inner bed walls during desorption step
- Hydrogen leaks through weld zones.
- Inadequate removal of contaminants during cleaning of gas gap volume.

The challenge is to identify and control those processes actually dominating this system.

Measurements of the rate of pressure increase in the gas gap volumes of two of the EBB compressor elements were recently initiated under various conditions [5]. The preliminary observed rates for the quantity of gas produced in units of standard cubic centimeters per second (scc/s) were nearly independent of the pressure and gas composition in the sorbent bed, but were strongly temperature dependent [5]. The rates ranged from about 4×10^{-8} scc/s at 293 K to $\sim 5 \times 10^{-5}$ scc/s at 525 K. These values are consistent with hydrogen outgassing and permeation rates reported for stainless steel and other metals [16-19]. These tests have since been completed and additional measurements were made to determine the total hydrogen contents in the electroplated gold films, the nickel under layers, and host 316L SS and Al metals. The information on hydrogen content in the structural materials and outgassing/permeation rates have been used to increase the size the gas gap actuators and make other modifications to provide efficient heat switch performance during the planned operational life of the Planck sorption cooler.

Although the solubility of hydrogen is expected to be very low in stainless steel and aluminum metal at 300 K, various processing steps can introduce large amounts of hydrogen into fabricated parts and components [20,21]. Especially high hydrogen contents (i.e., approaching 10 at. %) have been found in electroplated films on SS [22,23]. The best method for determining hydrogen contents in the near surface regions (i.e., to depths up to $\sim 0.5 \mu\text{m}$) for most materials is Nuclear Reaction Analysis (NRA) using MeV ion beams [24,25]. The ion accelerator facility of the SUNY-Albany, which is described elsewhere [25], was used for H-profiling samples taken from two compressor elements. The nuclear reaction between protons and ^{15}N as shown below:



was used in these measurements and the data were corrected for background contributions [25]. The hydrogen contents determined on the gas gap surfaces for samples from LCE-1 and EBB-CE#2 walls are presented in Fig. 7. The very high hydrogen contents at the surfaces are attributed to contaminant oils and/or water films from sample preparation and handling while the hydrogen levels detected at depths of $0.05 \mu\text{m}$ and deeper are believed to be the actual contents in the Au/Ni films and electropolished SS. Repeated NRA measurements at the same location and ion energy gave decreasing signal intensity that suggest labile hydrogen species, which migrate under the combination of high vacuum and ion flux. Hence, it was difficult to determine accurately the stable hydrogen concentrations in the surface regions for these samples. The ranges of hydrogen for the different regions are presented in Table 1 along with previously published data for stainless steel and various electroplated layers [20-23]. The present results for the Au and Ni layers are in reasonable agreement with past work while the rather high value for the 316L SS surface of LCE-1

compared to the previously found by Westerberg, et al. [20,21] may reflect hydrogen incorporation from its electropolishing treatment.

Although the new NRA results in Table 1 do not provide a precise determination of the total hydrogen retained within the electroplated Au/Ni layers and the electropolished 316LSS surfaces of the gas gap volumes, the amount of hydrogen within the total 20- μm surface layer is estimated to range from a minimum of 5+ scc to over 70 scc. This upper limit is at least twice the quantity necessary to saturate completely the ZrNiH_x sorbent in the GGA for the EBB compressor element. Even 10 scc would cause an observable change in the sorbent isotherms [13,14] and GGA performance. However, the actual behavior would be very dependent on both the accessibility and mobility of the retained hydrogen as its release will be influenced by temperature and cycling parameters. Since the inner sorbent

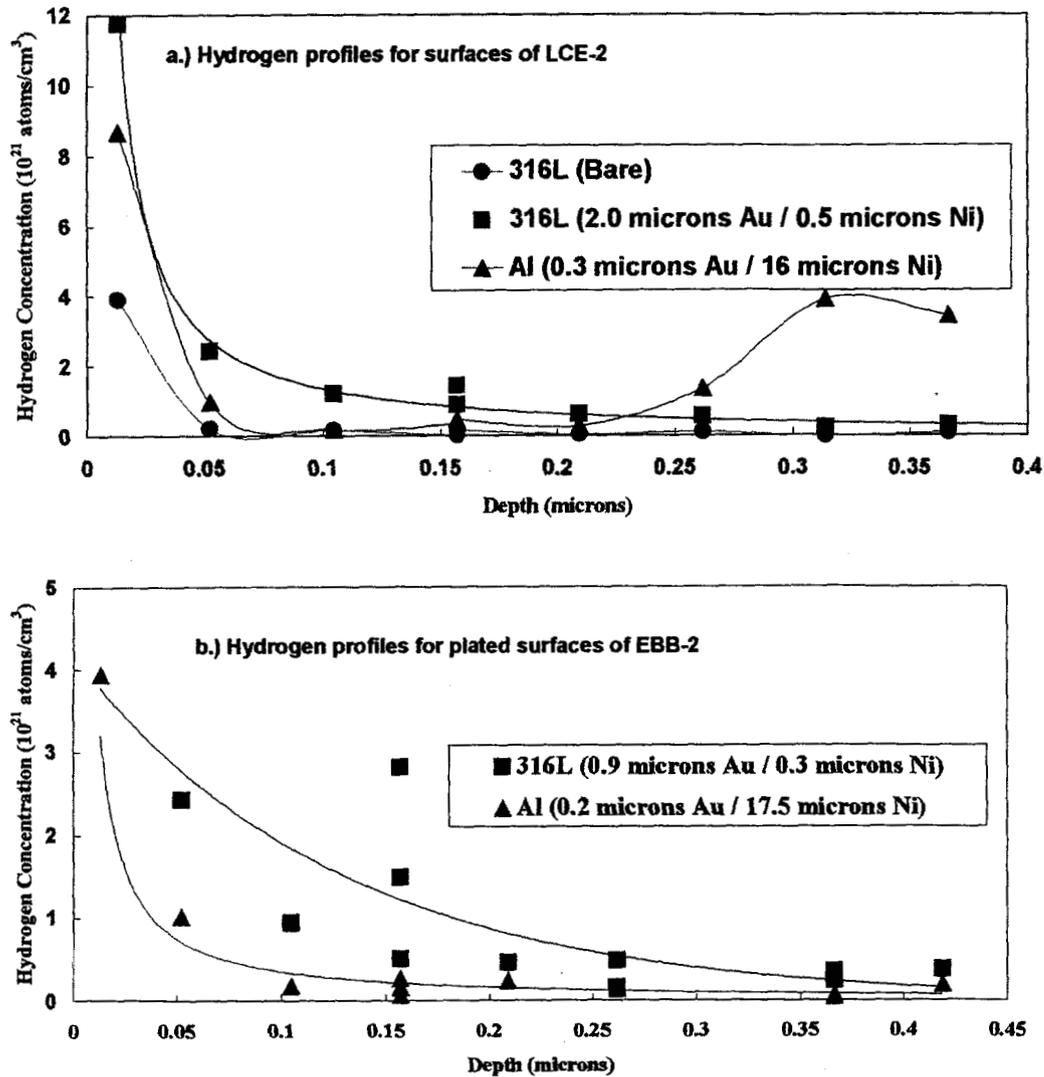


FIGURE 7. Hydrogen concentration profiles measured by nuclear reaction analysis (NRA) method.

Table 1. Hydrogen Contents Obtained with ^{15}N Resonant Nuclear Reactions

Layer	Sample (layers)	H-content (10^{21} atoms/cm ³)	Reference
Au	LCE-1 (Au/Ni/SS)	0.75	Present Work
Au	LCE-1 (Au/Ni/Al)	0.3 - 1.0	Present Work
Ni	LCE-1 (Au/Ni/Al)	3.7	Present Work
316L-SS	LCE-1 (bare)	0.1	Present Work
Au	EBB-2 (Au/Ni/SS)	0.2 - 2.8	Present Work
Au	EBB-2 (Au/Ni/Al)	0.1 - 0.2	Present Work
Au	Pure Hard	1.4	Clark, et al. (1978) ²²
Au	Cl-type	3.5 - 5.3	Clark, et al. (1978) ²²
Cu	Electrodeposit	0.2 - 0.6	Ruckman, et al. (1994) ²³
304L-SS	Untreated	0.02	Westerberg, et al. (1997) ²¹
316L-SS	Water Jet Cut	0.1	Westerberg, et al. (1996) ²⁰

bed is periodically heated to above 450 K during CE operation, the layers on these walls will clearly dominate hydrogen outgassing. Furthermore, the presence of a 50 bar hydrogen pressure within the sorbent bed during the desorption step will promote permeation through its hot walls – irrespective of the characteristics of the Au/Ni outer surface layer. In the absence of a quantitative prediction of the amount of hydrogen that can evolve into the gas gap volume, direct determinations of hydrogen outgassing and permeation were started [5].

The rates of hydrogen pressure increase in the gas gap volume have been measured in the two EBB compressor elements EBB-CE#2 and EBB-CE#7 as a function of temperature and internal pressure in the inner bed. Results were obtained with the inner bed volume under vacuum, with helium ($\sim 1 \text{ bar} < \text{pressure} < 50 \text{ bar}$), and hydrogen desorbed from the bed at pressures from $\sim 0.5 \text{ bar}$ to $\sim 50 \text{ bar}$ (where this upper pressure was used for all H_2 measurements with $T > 390 \text{ K}$). The test facility previously assembled [5] at JPL for characterization of the integrated CE-GGA units prior to their installation into the EBB compressor assembly was used after reconditioning and making two significant alterations. First, the Stanford Research Systems model RGA-200 was mounted on the Leybold TOPS turbomolecular vacuum station in a manner that eliminated extraneous impurity gas signals from the QMS spectra. Second, the 2 Torr maximum pressure MKS Baratron vacuum gauge was replaced with a calibrated 0.1 Torr MKS Type 627B capacitance manometer for enhanced accuracy in measuring low pressures of the gas gap volume. All volumes in the gas gap manifold were calibrated using volumetric expansion methods. Refrigerant liquid at 290 K – 294 K was constantly circulated through the chiller plate attached to the CE outer shell. The experiments were controlled and data collected using a modified version of the LabView software developed for the original characterization testing [5] of the EBB CE-GGA units. The usual test procedure was to heat the inner bed to the desired temperature while pumping on the gas gap with the turbomolecular vacuum station using the QMS to assess the composition of the evolved gases. After stable conditions are reached, the valves isolating the combined gas gap and pressure transducer volumes are closed and the increase in pressure is recorded. Data are collected until either the gas gap pressure exceeded the

0.1 Torr (13.3 Pa) maximum of the MKS 627B gauge or the bed temperature fell from parasitic heat leaks to the shell at the available power to the sorbent bed heater. The rate of hydrogen evolved into the gas gap volume was calculated from a simple average over the linear portion ($\Delta P/\Delta t$) of the pressure change and the measured volume.

Hydrogen outgassing measurements were first performed on the gas gap of EBB-CE#2 with about 1.3 bar of helium (He) and argon (Ar) gases in the sorbent bed. While hydrogen outgassing was observed, the QMS indicated He and Ar were also in the gas gap in addition to H₂. A helium leak detector found a leak rate of $\sim 8.5 \times 10^{-7}$ cc-atm/s from the inner bed into the gas gap volume. After evacuation of the sorbent bed, hydrogen-outgassing rates within the gas gap volume were measured at several temperatures. The CE unit was then removed from the test facility. Subsequent helium check after removal of the outer housing located the leak at one of the welds of the inner bed.

The EBB-CE#7 unit was next installed into the CE-GGA characterization test facility. No helium leaks, above leak detector background, were observed between the sorbent bed and gas gap volumes under conditions that included pressurizing the sorbent bed with 50 atm of He and heating the inner bed to 500 K. Hydrogen evolution/accumulation rates were measured on this unit under various conditions including heating to 540 K with ~ 50 atm of hydrogen pressure in the sorbent bed with the outer tube maintained near 293 K. Plots of these rates for EBB-CE#7 and some fits for data at $T > 390$ K are given in Fig. 8. Also plotted in this figure are the predicted hydrogen permeation rates at 50 atm (5.07 MPa) and 0.1 atm (10.1 kPa) pressure into the gas gap volume from the inner bed surface area using the “best-fit” permeation constant (P_m) relation:

$$P_m[\text{scc/s(H}_2\text{)/cm}^2\text{s atm}^{0.5}] = \{2.33 \times 10^{-2}\} \exp[-65.7(\text{kJ/mol})/RT] \quad (2)$$

from Le Claire’s [18] detailed assessments of numerous austenitic stainless steels (includes 316 L SS). This permeation constant is usually regarded as the upper limit as numerous factors involving steel composition, surface oxides, etc. all decrease the permeation and outgassing rates as widely reported in the vacuum technology literature [16-19, 26-28]. The product of the inner bed surface area and P_m was used to predict the temperature dependence of hydrogen permeation rate into the gas gap volume at the pressures representing the upper and lower bounds to be expected during sorption cooler operation.

The experimental hydrogen accumulations rates in Fig. 8 were obtained in four distinct test phases in the following temporal sequence:

- I. Helium gas only in the inner sorbent bed (Denoted in Fig. 8 as “H₂ - pre-desorb < 1 atm”), which is expected to reflect outgassing from the Au-plated surfaces of inner bed and outer tube walls.
- II. Hydrogen gas in the sorbent bed after reaction with the LaNi_{4.78}Sn_{0.22} alloy to first form the hydride and produce pressures between 40 – 55 atm as the sorbent bed is heated above 390 K (Denoted in Fig. 8 as “H₂ - pre-desorb > 1 atm”)
- III. After the hydrogen was removed from the sorbent bed by evacuation at ~ 540 K, the alloy was reacted with deuterium (D₂) gas. The accumulation of hydrogen isotopes in the gas gap volume was measured between 430 K and 510 K with ~ 50 atm of D₂ in

the sorbent bed and a measurement at 292 K with 0.4 atm D₂ pressure (Denoted in Fig. 8. as D₂ – post-desorb > 1 atm and < 1 atm, respectively).

IV. After all D₂ was removed from the sorbent bed by evacuation at ~670 K and the alloy reacted once again with hydrogen gas (Denoted as “H₂ – post-desorb > 1 atm”).

The hydrogen accumulation rates are nearly independent of temperature of the sorbent bed up to ~350 K (as well as the processing treatments) and are also more than an order of magnitude greater than rates predicted using the total gas gap surface area and typical hydrogen outgassing values [28] for clean stainless steel and aluminum. QMS indicated that the accumulated gas was nearly pure hydrogen (i.e., 98-99+%). It is concluded that the hydrogen contained in the electroplated Au and Ni films is responsible for all the gas released in this temperature range. In contrast, a rapid increase of hydrogen release rate is found as the sorbent bed temperature is raised above 400 K, which is attributed to both outgassing and permeation through the 316L SS walls of the heated bed.

The hydrogen accumulation rates for the Phase I and II measurements are nearly identical above 400 K and yielded an activation energy (E) of 75 kJ/mol, which is ~10 kJ/mol larger than Le Claire’s value in eqn. (2) for intrinsic permeation through stainless steel. Since there is also not the expected [17,18] increase with greater hydrogen pressure in the sorbent bed for these rates, surface oxide layers [16,27] appear to be controlling the hydrogen outgassing process. These oxide layers are consistent with obtaining the larger E value [27] during the current experiments. QMS measurements of the accumulated gases obtained during the Phase I and II tests were again found to be only molecular hydrogen.

In order to separate the relative contribution of permeation through the walls of a heated sorbent bed with its nominal 50 atm pressure of hydrogen from all other surface sources, the Phase III measurements were done after removing hydrogen by a 540 K evacuation of the sorbent hydride and reacting the bed with D₂ gas. Next, the gas

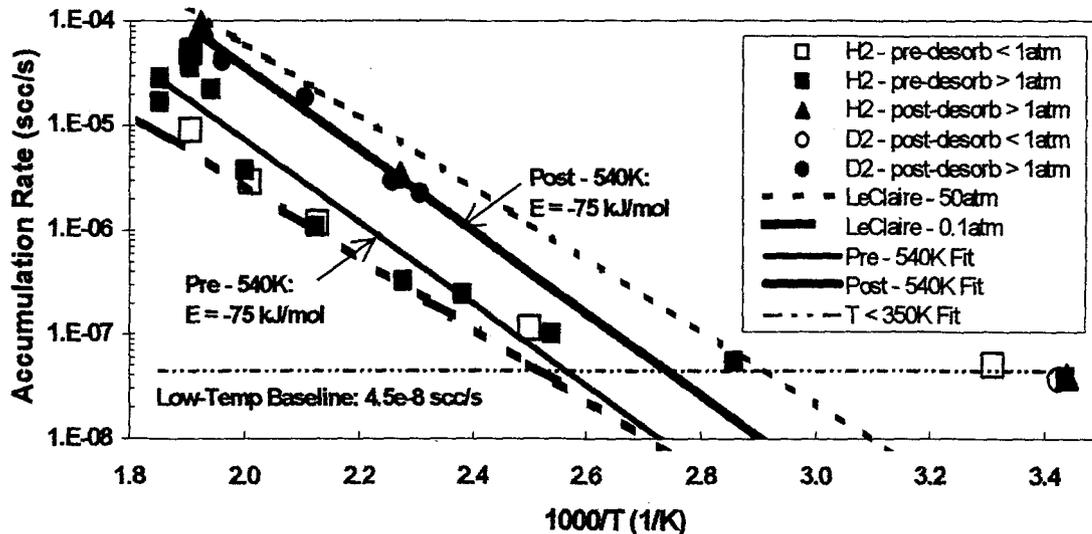


FIGURE 8. Temperature dependence of accumulation rates for hydrogen isotopes into the gas gap volume of the Planck compressor element EBB-CE#7

accumulation tests were performed with the bed of $\text{LaNi}_{4.78}\text{Sn}_{0.22}\text{D}_x$ heated between 430 K and 510 K and these data are included in Fig. 8. The released gas was found by QMS to be initially only protium (H_2); however, mass-3 (i.e., HD) and mass-4 (D_2) peaks were observed in the QMS spectra after several hours and their relative intensities increased as the tests were continued. This behavior is entirely consistent with a diffusion controlled "Breakthrough" as deuterium atoms migrated from within the bed through the walls and then reaching the outer surfaces for evolution into the gas gap volume. While the accumulation rates seen for Phase III are systematically faster relative to the Phase I and II rates, the temperature dependence is represented by the same $E = 75$ kJ/mol activation energy. This result implies that although the 540 K evacuation processing between phases II and III has reduced some of the surface barriers the permeation/outgassing mechanism probably has not changed. After these phase III measurements, the D_2 pressure in the sorbent was maintained at ~ 5 atm and it was sequentially heated to 570 K, 620 K, and 670 K while actively evacuating the gas gap volume with the turbomolecular pump and analyzing its composition with the QMS to monitor the relative abundance of the H_2 , HD, and D_2 species. The deuterium fraction continuously increased until it was over 90% of the residual gas. These results clearly establish that deuterium from within the sorbent bed permeates the 316L SS walls at these temperatures. In addition, much of the original protium within the wall has been displaced or replaced by deuterium species. The D_2 gas was vented from the sorbent bed while heated to ~ 670 K for about 120 hours with continuous vacuum pumping. After cooling the sorbent bed back to ~ 293 K, the alloy was reacted with H_2 gas to reform the hydride phase.

Phase IV measurements of gas accumulation in the gas gap volume were performed at a few temperatures. These data points are also shown in Fig. 8 and can be seen to lie on the line for the Phase III rates. Hence, little additional enhancement is indicated after the evacuations with the bed heated to 670 K. The surface states must be fairly stable at this point. The QMS spectra for the gas accumulated above 500 K show the clear presence of HD and D_2 while virtually no indications for these mass peaks were in the spectra for gas during 293K accumulations. This behavior is regarded as additional evidence for dominance by the electroplated films (Presumably on the Al outer tube, which was never heated during these experiments) on the outgassing properties near ambient temperature while permeation of gas from the heated sorbent controls the hydrogen isotope outgassing above ~ 400 K.

Predictions of quantity of hydrogen gas that could accumulate in the gas gap volume of a Planck sorption cooler CE have been made for a combination of six years of storage at ambient temperature and two years of continuous operation with the inner bed cycling between 280 K and ~ 470 K. The range is estimated to lie between 150 – 300 scc released into the gas gap volume, which depend upon variations in sorbent bed temperatures and the different rates indicated in Fig. 8. The upper bound correspond to using eqn. (2) for 50 atm and appears to be a worse case as none of the measured rates were that large. Nevertheless, the total excess hydrogen capacity for the GGA used in the Ebb cooler is clearly inadequate at only ~ 20 scc. Hence, the design for the flight GGA has been modified to provide a ZrNi hydride bed that is ten times bigger (i.e., 2.8 grams) than used with the EBB units. Since x-ray spectroscopy during SEM examination of discolored areas on the gold-plated SS surfaces of EBB-2 showed the presence of K, Na, S, Cl, P, Cr, Zn, Mn, and

O that imply deposited plating salts and cleansing agents, the $ZrNiH_x$ sorbent was also contaminated to some degree. All of the gold electroplating has been eliminated from the gas gap surfaces to avoid both sources of additional hydrogen and chemical contamination.

METHANE FORMATION IN SORBENT BEDS

Three LCE units were thermally cycled up to 5000 times, as reported previously [12]. The hydrogen gas from these sorbent beds has been analyzed by QMS and mass spectrometry. Representative QMS spectra obtained on two gas samples taken from the LCE-3 sorbent bed after 5004 cycles are shown in Fig. 9. Fig. 9a demonstrates that a substantial fraction (i.e., ~12%) of the gas in equilibrium with the hydride bed at ambient temperature is methane (CH_4) where the QMS peaks assigned to H_2O , CO/N_2 , and CO_2 are predominantly background species in the QMS pumping station. In contrast, Fig. 9b shows that no methane was detected in hydrogen gas desorbed from the hydride along with similarly low levels of the background species. Table 2 provides a summary of the methane content found in samples of the equilibrium hydrogen gas over the sorbent beds for three LCE units and EBB-CE#7. The concentrations of methane range from 40 to 370 ppm relative to the total hydrogen content. All the beds had been initially filled with research grade hydrogen gas (i.e., 99.999+% purity) that was further purified by flowing it through a Nanochem[®] chemical gas purifier and a carbon cold trap cooled in liquid nitrogen prior to admitting this gas into the hydrogen filling station. Hence, the impurities in the hydrogen gas seen after cycling were probably generated from residual hydrocarbons on surfaces of filters, foam, and other components even though vacuum and purge gas cleaning was performed during activation. While the formation of methane has rarely been reported in the metal hydride literature [29], Sandrock [30] has noted that its formation can be associated with the degradation in performance of many closed-cycle metal hydride devices such as heat pumps, etc. The hydrides may act as catalysts for the conversion of condensed organic impurities into methane, water, and CO. Since all these molecular species will form solids well above the temperature of liquid hydrogen, they can cause plugging at the J-T expansion valve. The Planck sorption coolers contain chemical purifiers/getters and a carbon trap cooled to 50 K to removed these condensable species from the hydrogen gas before entering the cold system and the J-T valve region. However, the cycling of the LCE beds and individual EBB CEs was done without any filtering or gettering to remove impurities from the hydrogen.

The remaining issue is how large to size these purification devices for the flight coolers to ensure the effective removal of the impurities during the nominal two years of flight operation? A methane level of 43 ppm was observed in the EBB CE after only 68 cycles. It is thus likely methane formation is most rapid at the beginning of cycling when the residual hydrocarbon content is expected to be the highest. A combination of initial cycling, evacuation and refilling with pure hydrogen should be a viable means of reducing, if not eliminating, long-term creation of methane and the other species. This supposition has been at least partially verified during further tests of the EBB cooler where minimal J-T plugging has occurred after a thorough evacuation and replacement with fresh purified hydrogen in the sorbent beds.

a.) Gas over hydride bed (~ 0.2% total H₂) is ~12 % methane b.) Gas desorbed from bed is 99+ % hydrogen

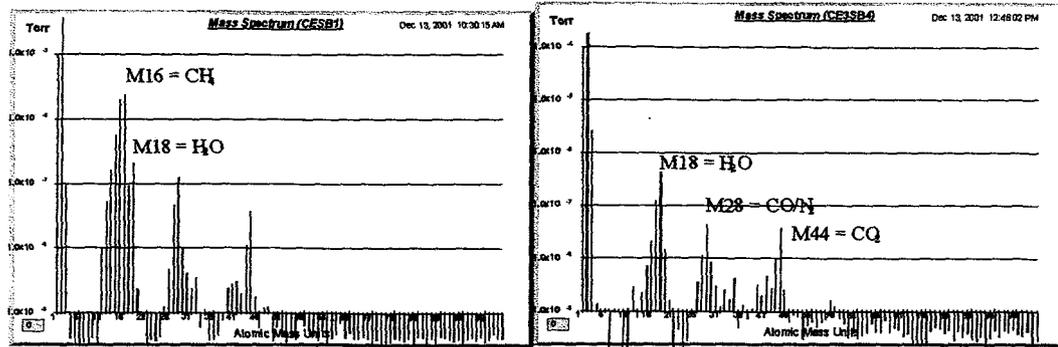


FIGURE 9. QMS spectra of hydrogen gas composition from LCE-3 sorbent bed after ~5000 cycles.

Table 2. Methane (CH₄) contents measured in the hydrogen (H₂) sorbent bed gas after temperature cycling.

Sorbent Bed Identity	Number of Cycles	Total Initial H ₂ Content (scc)	Volume of Gas Over Sorbent Bed (scc)	CH ₄ Fraction in Bed Over Gas (%)	Quantity of CH ₄ in Bed Over Gas (scc)	Ratio CH ₄ /Total Initial H ₂ (ppm)
LCE-1	5004	82,000	261	6.2	16.2	198
LCE-2	3075	82,200	204	8.3	16.8	204
LCE-3	5004	81,500	257	11.6	29.8	366
EBB-7	68	66,400	50.8	5.5	2.8	42

CONCLUSIONS

The Planck CE sorbent beds have been found to deliver and absorb hydrogen within the performance specifications required for sorption cooler operation [3,4,7,8]. Formation of methane has been observed during the temperature cycling of the CEs and this impurity must be removed from the hydrogen gas stream before entering the region of the J-T expansion valve. While the coolers have cold carbon traps for this purpose, improvements in cleaning processes will be used on the flight units. Accumulation of hydrogen gas in the gas gap volumes has been systematically investigated and shown to be a combination of outgassing from the surface layers that dominate below ~350 K and permeation through the sorbent bed walls when the bed is heated above 400 K. Consequently, more ZrNi alloy is required in a larger gas gap actuator to absorb this excessive hydrogen throughout the cooler operational lifetime.

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