

THE 2007 MARS PHOENIX THERMAL EVOLVED-GAS ANALYSIS: THE ROLE OF AN ORGANIC FREE BLANK IN THE SEARCH FOR ORGANICS. H. V. Lauer Jr.¹, D. W. Ming², B Sutter³, D. C. Golden⁴, R. V. Morris², and W. V. Boynton⁵, ¹ESCG/Barrios Technology, Houston, TX 77258 ²ARES NASA/JSC, Houston, TX 77058 (douglas.w.ming@nasa.gov); ³ ESCG/Jacobs, Houston, TX 77258 ⁴ ESCG/Hamilton Sundstrand., Houston, TX 77258, ⁵ University of Arizona, Tucson, AZ 85721

Introduction: The Thermal Evolved-Gas Analyzer (TEGA) instrument onboard the 2007 Phoenix Lander will perform differential scanning calorimetry (DSC) and evolved-gas analysis of soil samples collected from the surface. Data from the instrument will be compared with Mars analog mineral standards, collected under TEGA Mars-like conditions to identify the volatile-bearing mineral phases [1] (e.g., Fe-oxyhydroxides, phyllosilicates, carbonates, and sulfates) found in the Martian soil. Concurrently, the instrument will be looking for indications of organics that might also be present in the soil. Organic molecules are necessary building blocks for life, although their presence in the ice or soil does not indicate life itself.

The spacecraft will certainly bring organic contaminants to Mars even though numerous steps were taken to minimize contamination during the spacecraft assembly and testing. It will be essential to distinguish possible Mars organics from terrestrial contamination when TEGA instrument begins analyzing icy soils. To address the above, an Organic Free Blank (OFB) was designed, built, tested, and mounted on the Phoenix spacecraft providing a baseline for distinguishing Mars organics from terrestrial organic contamination.

Our objective in this report is to describe some of the considerations used in selecting the OFB material and then report on the processing and analysis of the final candidate material.

Materials and Methods: The OFB was included on the TEGA instrument to quantify possible terrestrial contamination. This will be done by drilling/rasping into the OFB material, discarding the powdered material from the outer portion of the blank and then using the material from deep inside the OFB to establish the instrument organic ground truth. This procedure establishes a baseline and defines some physical and chemical constraints on the blank material.

The OFB must be machinable to give the powder for analysis and must be able to withstand rigorous environmental testing, specifically thermal, shock, and vibration testing.

The organic content was the primary requirement for the chemical composition of the OFB material. Ideally, the OFB material should have less than 10 ppb total organic C, traceable to CO₂ released in the temperature range of 250 to 1000°C. Furthermore, the OFB should not evolve significant quantities of volatile gases during the heating process. Gases such as H₂O could complicate the detection of organic molecules in the OFB. Additionally a key requirement was that the OFB material was chemically inert and able to withstand the environmental conditions exposed to on Earth, during transit to Mars, and on the Martian surface.

The mission plan dictated that there would not be a cover or a hermetically sealed coating/foil around the OFB dur-

ing spacecraft assembly, flight to Mars, and Mars surface operation. This meant porous materials were not attractive because they would likely adsorb organic contamination into their matrices either during spacecraft assembly or from spacecraft material out gassing during the flight to Mars. In addition their structural strength makes them undesirable. Consequently, all of the porous materials were eliminated as candidates. Macor MGC, a fluorophlogopite mica and amorphous borosilicate glass was the only material found by the OFB science team that was non-porous and still machinable with the instrument rasp.

Macor is fabricated by Corning Glass in Corning, New York. The nominal total C content for commercial Macor is 290-300 mg/kg C. Although the production of Macor is a proprietary process, the high C content is either the result CO₃ inclusions in the Macor matrix from carbonates used as starting materials and/or atmospheric CO₂ gas entrapped in the Macor during cooling of the melt and subsequent ceramic process. By special request, Corning Glass produced a Macor using NO₃ starting materials and processed the material in a N₂/Ar atmosphere to minimize C contamination. Although NO₃ starting chemicals were used for the fabrication of the NO₃-Macor, the composition of the final product was essentially the same as the CO₃-Macor. We have adopted the names CO₃-Macor and NO₃-Macor to represent the Macor material that was produced from carbonate and nitrate starting materials, respectively.

The most important chemical property of the NO₃-Macor OFB is the reduced total C content. We have developed a procedure to measure the total C content in the blank material, which mimics the measurement procedure to be used the flight instrument. A set of C standards were prepared and measured in our TEGA test-bed 1 located at JSC. The key element to the process is that sample preparation and measurements must be performed in an organic-free environment. The test-bed and procedure are described next.

Several test-beds consisting of thermal analyzers (TA) integrated with evolved gas analyzers (EGA) have been designed and built at JSC to support the Phoenix TEGA. We modified our original TEGA test-bed [1,2] by removing the DSC and replacing it with a closed system quartz chamber inserted in a vertical tube furnace capable of reaching 1100°C. With this setup, we are able to more closely reproduce the flight TEGA geometry and operating conditions except for the heat flow measurement. Our TEGA test-bed 1 does not have the detection limits of flight TEGA due to the limitations of our quadrupole mass spectrometer (QMS), although we were successful in detecting total carbon down to ~1 ppm C.

Figure 1 shows a block diagram illustrating the components of the TEGA testbed-I used to analyze the Macor samples for carbon content. Research grade O₂ was used as the carrier gas in our experiments to insure that all C in the sample evolved as CO₂ by either evolution of CO₂

from residual carbonates or occluded CO₂ gas or by the combustion of any organics in the Macor. The O₂ carrier gas was purified (i.e., removal of organics, CO₂, and H₂O) by using a combination of a cold trap to remove H₂O and organics and a heat trap of CaO to remove CO₂. A series of metering valves, a mass flow meter, and a pressure transducer were used to regulate and monitor the carrier gas flow rate and pressure.

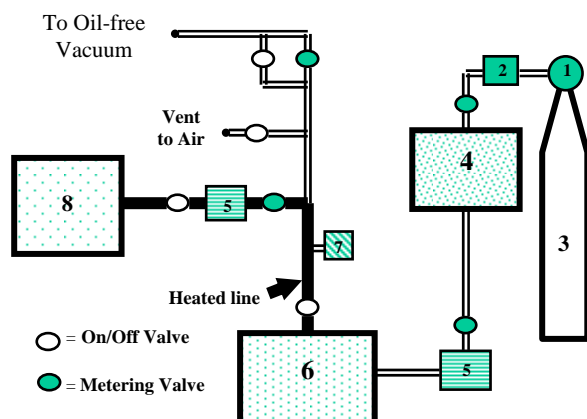


Fig.1 Block diagram of the TEGA testbed-I. Elements in the diagram are as follows: 1 Regulator, 2 LP Regulator, 3 Carrier Gas, 4 Gas Purifier, 5 Electronic Mass flow meter, 6 Sample Chamber & Furnace, 7 Digital Vacuum Gauge, and 8 Quadrupole Mass Spectrometer

The sample chamber consists of two different sized quartz tubes; one tube (smaller diameter) was open ended on both ends and the other one (larger) was closed on one end. The smaller tube was the carrier gas inlet and the larger tube defined the chamber. A small quartz “crucible” sat at the bottom of the chamber just below smaller diameter gas inlet tube. Two custom fabricated stainless steel fittings were used to make the chamber vacuum tight and direct the carrier gas into and out of the sample chamber assembly. The output from that fitting was connected to a heated stainless steel tube (150°C) that facilitated the transfer of the evolved gases into the mass spectrometer. The bottom ¾’s of the sample chamber assembly was suspended in the vertical 1100°C furnace; the quartz “crucible,” containing the sample, was positioned in the hot zone of the furnace. The thermocouple attached on the outside of the quartz tube recorded the sample temperature as the furnace was ramped up.

Analysis of the powdered Macor sample was always done in two steps. In the first step, a clean empty sample crucible was placed in the quartz reaction chamber and inserted in the testbed. The oil-free vacuum pump was then used to evacuate the sample chamber followed by back-filling with O₂ several times. With the O₂ carrier gas flowing, the furnace was ramped up to 1000 °C held there for five minutes and then ramped back down to room temperature. The QMS monitored the output carrier gas. If the CO₂ signal was at the normal background level throughout the entire heating process, that indicated that the sample chamber, sample crucible and test-bed were organic-free prior to the Macor sample being added for analysis. After

cooling and with the carrier gas flowing the sample chamber was quickly removed from the testbed and capped off with the appropriate clean stainless caps.

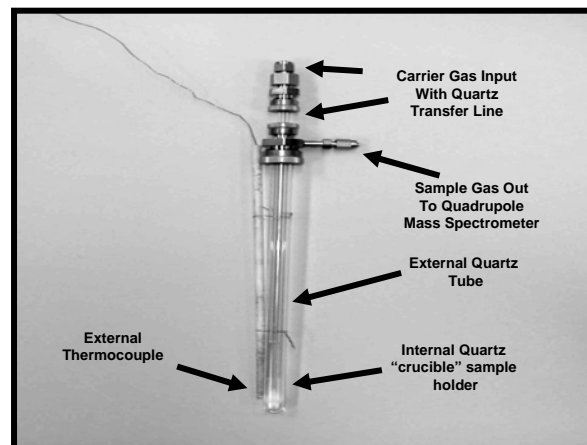


Fig. 2 Quartz sample chamber, gas inlet and external fittings for connecting to the carrier gas and the QMS.

The clean sample chamber was then transported to the clean room laboratory where it was transferred into a pristine grade glove box for sample loading. After loading Macor sample, the sealed quartz sample chamber was returned to the TEGA lab and quickly reloaded in the TEGA testbed. The sample chamber was evacuated and back filled with O₂ several times. The vacuum pump was then valved off from the system and flowing O₂ carrier gas was connected to the mass spectrometer. The system was then allowed to equilibrate for about an hour until the background levels for all analysis channels were stable at their normal background levels.

Using O₂ as the carrier gas to combust any organics contained in the Macor powder [3], the furnace was ramped up to 1000 °C, and held for several minutes; then ramped back down to room temperature. The QMS recorded the output carrier gas containing the evolved gas from the sample as a function of time (temperature). After the sample had cooled back to ambient it was reheated to 1000 °C again recording the output carrier gas from the sample chamber. The reheat run was always used to indicate the current background level of organics in the system post sample analysis. The area under the evolved CO₂ peaks from the initial heating was measured and compared with the data from the calibration runs to determine the C in the Macor sample being analyzed.

References: [1] Lauer Jr., H. V. et. al. (2000) LPSC31, Abs#1990 CD-ROM. [2] Golden, D. C. et. al. (1999) LPSC30, abs#2027 CD-ROM. [3] Lauer Jr., H. V. et. al. (2006) LPSC31, Abs#1780 CD-ROM.