

## INITIAL PERFORMANCES / OBSERVATIONS / RESULTS OF THE SAM GAS-CHROMATOGRAPH (SAM-GC) AT ROCKNEST SITE

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**Introduction:** among the SAM suite of instruments [1], SAM-GC (Gas Chromatograph) is designed to support analytical sequences devoted to identify and quantify volatiles evolved from the thermal/chemical treatment of any soil sample delivered to SAM. On November 6<sup>th</sup>, 2012, SAM-GC was commissioned in Curiosity at the Rocknest site. SAM-GC was the last instrument onboard Curiosity to be commissioned. Four SAM-GC runs have now been performed, identified as 25033 (no sample run), 25038 (scoop 5, sample 1), 25041 (scoop 5, sample 2), 25044 (scoop 5, sample 3). It is an appropriate time to report on the GC performance, observations and preliminary impact on Mars evolution/habitability.

**Performance of SAM-GC:** The first instrumental goal addressed by SAM-GC is the separation of the constituents of a complex gaseous mixture. To analyze the Rocknest samples, GC column n°5 was used. In

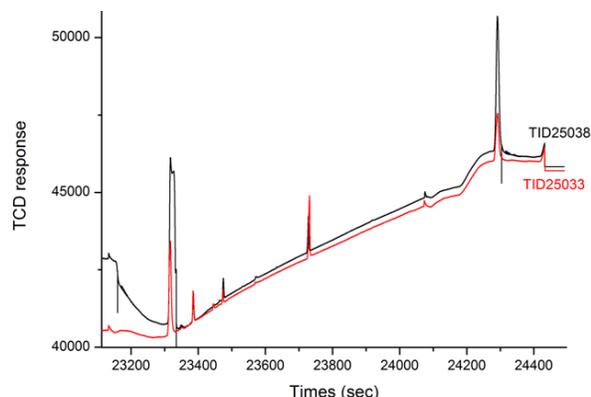


Figure 1: TCD (GC detector) signal overview for two different analyses of Rocknest campaign. Major signatures are common to the two chromatograms with same retention times, showing the accurate and repeatable separation of constituents of the gaseous mixture as a function of time.

column 5, compounds were separated on the MXT-CLP column (30 m x 0.25 mm I.D.). The column was set at an initial temperature of 50°C followed by heating to 220°C at 10°C/min. The separation performance

conforms well to ground qualification data and will be addressed more extensively in this paper. Figure 1 reveals these separation capabilities for two different analytical runs, where 25033 refers to an analytical sequence where no solid sample was delivered to SAM, and 25038 refers to an analytical run where scoop five, solid sample #1 was delivered. The overlap of the main signatures on the two runs emphasizes the reproducibility of the separation performance, in which the difference between the peak areas reveals the difference in the amount of compounds analyzed with GC.

From a quantitative point of view the GC is equipped with autonomous detectors known as nanoTCDs or TCDs (Thermal Conductivity Detectors). All GC columns, except column 1, incorporate a TCD that provides a signal independent of the mass spectrometer. The TCDs can detect chemical species down to the part per million level, with a  $10^5$  dynamic linear range. This detector, which generates a simple physical signal, provides an additional level of detection redundancy to the SAM QMS (Quadripole Mass Spectrometer). From a qualitative point of view, the chromatographic peak shapes derived from the TCDs can be utilized to better fit the GCMS chromatographic signatures to particular species. This is particularly useful as the QMS temporally under samples the GC signal,

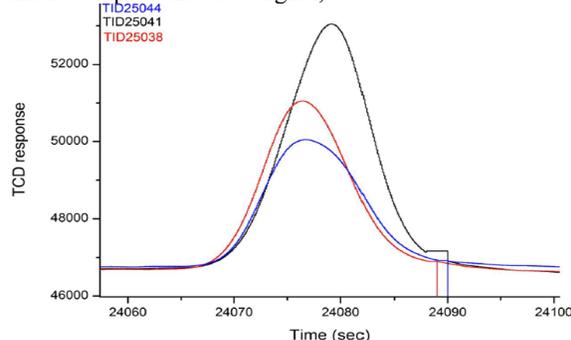


Figure 2: TCD (GC detector) signal overview of the same detected volatile for three different analyses of the sand of Rocknest. The time axis was rescaled for direct comparison.

especially when peaks are eluted [1]. An illustration of these acquired TCD signals are shown on Figure 2, where signals from three different runs of Rocknest samples are plotted together. Note the excellent Gaussian shape of the peak related to the eluted compound in all of the runs. This type of chromatographic peaks is known as a symmetrical normal error peak. This type of peak facilitates the treatment of equations governing chromatographic performance. In many cases, tailing or fronting peaks are observed. However, Figure 2, which is representative of the signal shape measured by the TCD, does not have these tailing characteristics.

**Observations partially supported by SAM-GC, and preliminary results:** Most of the analytical sequences used to address the content of Rocknest Soil samples were Solid Sample - Evolved Gases Analyses (SS-EGA, see [1]), with part of the released gases analyzed by Solid Sample - Gas Chromatograph Mass Spectrometer analysis (SS-GCMS, see [1]). The separation capacity of the GC plays an important role for tracking and identifying volatiles contained at the trace level in the gases evolved from Rocknest samples. As an illustration this separation strongly supports the identification of several methyl-chlorohydrocarbons [2], including specific ones as chloromethylpropene [3], and it confirms the identification of HCN in the gases evolved from the solid sample [4].

The separation performance of the GC allows the search for species in the chromatogram in a time range where the relevant signatures are expected. Figure 3

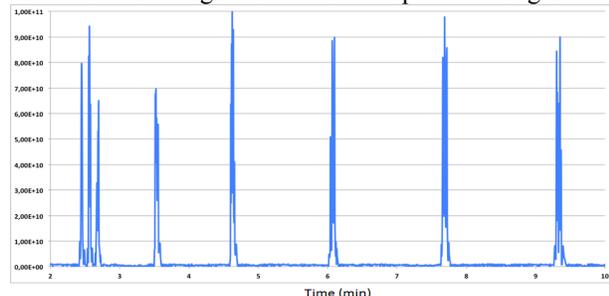


Figure 3: laboratory analysis of a pentane, hexane, benzene, octane, nonane, decane, undecane and dodecane (from the left to the right) mixture on a MXT-CLP wall coated open tubular chromatographic column, operating under He gas flow ( $\Delta P = 1$  bar), starting temperature of  $40^{\circ}\text{C}$  for 5 min then a heating rate of  $10^{\circ}\text{C}/\text{min}$  until  $250^{\circ}\text{C}$ .

illustrates from laboratory calibrations when to expect a given compound to elute. For example, the figure shows that dodecane elutes at around 9.5 minutes. If a sample contains dodecane, a peak should be found in this time range.

In such a framework we were searching for several organics from different chemical families in the gases evolved from the Rocknest soil samples, and especially

aromatics. This is addressed on figure 4 where signals indicating the release of organics should be seen if any compound of this chemical family is present.

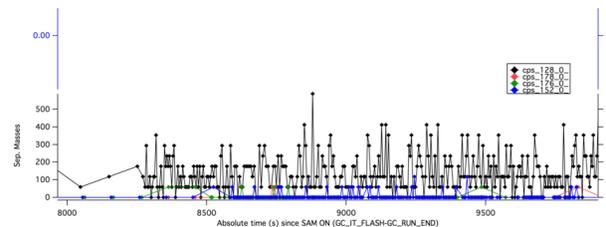


Figure 4: SS-GCMS analysis of the Rocknest soil focusing on single m/z ions related to simple 2 and 3 rings PAHs: naphthalene, anthracene and phenanthrene. No signal appears above the background level, assessing the non detection of these compounds in the gases evolved from the sample.

**Preliminary results:** one important result supported by SAM during the Rocknest campaign is clearly the presence of perchlorates in the soil. Since perchlorates have been detected with Phoenix lander [5] and then recently with Curiosity [6,2,3], the re-interpretation of the Viking data has to be looked at differently [7]. It is now more and more assumed that perchlorates, whatever their chemical nature is (this is still under investigation), are probably distributed throughout the entire Mars environment. This is a key parameter for future exploration of Mars, for Curiosity in the short term, and at much longer term for the development of future analytical instruments (payload of ExoMars mission for example).

The absence of PAH's release is also interesting, when it is known that micrometeorites containing PAHs still bring this organic material to the Mars surface today. This lack of detection defines an upper limit on the content of PAHs in the martian soil at the Curiosity site, but it could also be indicative of the presence of chemical mechanisms that process this type of material at the surface. In this last case, the investigation of the Gale crater environment with Curiosity instrumentation should help to determine which type of mechanisms are occurring on Mars.

**References:** [1] Mahaffy, P. et al. (2012) *Space Sci Rev*, 170, 401-478. [2] Glavin, D. et al. (2013), *this meeting*. [3] Eigenbrode, J. et al. (2013), *this meeting*. [4] Stern, J. et al. (2013), *this meeting*. [5] Hecht, M. H. et al. (2009), *Science*, 32, 64-67. [6] Sutter, B. et al., (2013) *this meeting*. [7] Navarro-Gonzalez, R. (2010), *J. Geophys. Res.* 115, E12010.

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