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## Performance of the SAM gas chromatographic columns under simulated flight operating conditions for the analysis of chlorohydrocarbons on Mars

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1 **Multi-column gas chromatography analysis of chlorohydrocarbons**  
2 **with the SAM experiment onboard NASA's Mars Curiosity rover**  
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47 **Abstract**

48

49         The Sample Analysis at Mars (SAM) instrument is a gas chromatograph-mass  
50 spectrometer onboard the NASA Curiosity rover, currently operating on the surface of Mars.  
51 Organic compounds are of major importance with regard to questions of habitability and the  
52 potential presence of life on Mars, and one of the mission's main objectives is to analyze the  
53 organic content of soil and rock samples. In SAM's first chromatographic measurements,  
54 however, unexpected chlorine-bearing organic molecules were detected. These molecules have  
55 different origins but the presence of perchlorates and chlorates detected at the surface of Mars  
56 suggests that reactivity between organic molecules and thermal decomposition products from  
57 oxychlorines is one of the major sources of the chlorinated organic molecules. Here we perform  
58 a comprehensive and systematic study of the separation of volatile chlorohydrocarbons with the  
59 chromatographic columns used in the SAM instrument. Despite the constrained operating  
60 conditions of the flight instrument, we demonstrate that SAM's capillary chromatographic  
61 columns allow for effective separation and identification of a wide range of chlorine-bearing  
62 species. We also show that instrumental limitations prevent the detection of certain molecules,  
63 obscuring our ability to make definitive conclusions about the origin of these organic materials.

64 **Highlights**

- 65         • *In situ* analysis of organic molecules on Mars with GCMS
- 66         • Chlorohydrocarbons unexpectedly produced during heating of solid samples on Mars
- 67         • Multi-columns chromatograph for separation and identification of chlorohydrocarbons

68 **Keywords**

69 Sample Analysis at Mars, chlorinated hydrocarbons, gas chromatography, mass spectrometry,  
70 efficiency, separation

## 71 **1. Introduction**

72

73 Since the successful landing of NASA's Curiosity rover in Gale Crater, Mars, on August 6<sup>th</sup>,  
74 2012 (1), the Sample Analysis at Mars (SAM) experiment (2) onboard the rover has analyzed the  
75 molecular composition of surface samples collected with the rover robotic arm. Organic  
76 molecules in rocks and soil are of particularly high interest because they may be related to an  
77 ancient biological activity and/or prebiotic chemistry. Along with the presence of liquid water  
78 and a source of energy, the presence of organic molecules is necessary to make an environment  
79 habitable according to our current knowledge of life (3). It is now well accepted that liquid water  
80 and energy were present in the past history of Mars, demonstrated in particular by the Mars  
81 Exploration Rovers (4, 5). But no organic molecules had been detected on the surface of Mars  
82 before the Mars Science Laboratory mission. Despite the fact that meteoritic infall at the surface  
83 of Mars is a likely continuous source of organic material (6), the conclusion of the *in situ*  
84 measurements performed with the Viking landing probes in the late 1970's was organic  
85 molecules were not present in the regolith. Chlorohydrocarbons were detected by Viking, but at  
86 the time, the science team believed the chlorinated molecules were sourced from terrestrial  
87 contamination (7). We have now discovered that the martian soil contains various oxychlorine  
88 species (8, 9). Because these molecules are strong oxidants, capable of chlorinating organic  
89 molecules under high temperature, this result has led to a reconsideration of the conclusions of  
90 the Viking GCMS measurements. It is now believed that the chlorohydrocarbons detected could  
91 have actually been produced in the pyrolytic process of extraction of the organic materials  
92 present in the presence of oxychlorine (10). Moreover, the SAM experiment has shown, for the  
93 first time, that organic matter is definitively present on Mars (11). This was accomplished  
94 through the detection of chlorohydrocarbons mostly produced in the pyrolytic oven of the SAM  
95 instrument as part of reactions occurring between indigenous organic molecules in the  
96 mudstones collected in Gale crater and thermal decomposition products from oxychlorines also

97 present in the sample. Chlorobenzene, the most emblematic molecule of this discovery, has now  
98 been retrieved in the chromatograms recorded by the Viking GCMS (12) whereas it was not  
99 reported in the original data analyses suggesting the presence of organic materials indigenous to  
100 the samples collected by Viking landers.

101 Even though the detection of chlorohydrocarbons from Mars sample analyzed with pyro-  
102 GC-MS is now understood, the SAM gas chromatograph was developed before oxychlorines  
103 were discovered on Mars. At that time, the whole family of chlorohydrocarbons was not  
104 considered as a major source of analytes. Thus, the instrument's ability to separate and analyze  
105 chlorohydrocarbons with the different chromatographic columns used for the SAM gas  
106 chromatograph, under constrained flight operating conditions, was never characterized. Finally,  
107 from our knowledge, only a limited number of studies dealing with the separation of a limited  
108 variety of volatile chlorohydrocarbons was reported in the literature. For all these reasons, we  
109 have undertaken a systematic study of the analysis of chlorohydrocarbons, including linear and  
110 aromatic ones, with five of the six columns used in the SAM gas chromatograph specifically  
111 dedicated to analyze organic compounds. This laboratory work is primarily dedicated to properly  
112 process and interpret the data collected with the SAM instrument on Mars, but it could also be  
113 used as a reference work for other applications.

## 114 **2. Material and methods**

### 115 **2.1 Samples: the chlorohydrocarbons**

116 26 chlorinated hydrocarbons, listed in Table 1, were selected for this study. Most of them  
117 were detected in the first fifteen samples of sand and rocks analyzed with the SAM GC-MS  
118 experiment (11, 13, 14). The others, belonging to similar chemical categories (aromatics, etc.),  
119 were thought to be potentially present as well, or relevant to the search for organics in the future  
120 Martian samples (13, 15). All the chlorohydrocarbons were supplied by Sigma Aldrich and were

121 of pure analytical grade (>99.9%). They were injected into the GC-MS both as separate  
122 concentrated standards as well as mixed together in equimolar ratios.

## 123 **2.2 GC columns and stationary phases**

124 There are six columns on the SAM chromatograph. The PLOT Carbobond column  
125 (Agilent), located in channel 3 (GC-3), was not included in this study because it is fully devoted  
126 to the analysis of atmospheric and inorganic light molecules ( $< C_2$ ). Thus, GC-3 is not relevant  
127 for the analysis of chlorohydrocarbons. Of the remaining five, three have been used on Mars: the  
128 MXT-20 (GC-1), the Chirasil- $\beta$  dex (GC-4) and the MXT-CLP (GC-5), located in channels 1, 4  
129 and 5 respectively and the other two: the MXT-5 (GC-2) and PLOT MXT-Q (GC-6) columns  
130 located in channels 2 and 6, have not been used so far. To perform the laboratory experiments,  
131 five replicates of each SAM flight capillary column were purchased in 2007. The columns were  
132 each tested and qualified in the laboratory under the same conditions and with the same analytes  
133 as the columns used to build the SAM GC instrument. The best columns were selected to be  
134 integrated into three different models of the SAM GC. The two columns remaining were kept at  
135 Laboratoire Atmosphères Milieux Observations Spatiales (France) under controlled storage  
136 conditions for running laboratory tests which could not be completed with the integrated models  
137 of SAM. All the tested columns were 30 m long, with a 0.25 mm internal diameter, and were  
138 supplied by Restek (Bellefonte, PA, USA). Their film thickness was 0.25  $\mu\text{m}$  except for the  
139 PLOT MXT-Q column, which has a 10  $\mu\text{m}$  thick stationary phase. Their specifications are listed  
140 in Table 2.

## 141 **2.3 Gas chromatograph-mass spectrometer**

142 Measurements were performed with two instruments: a GC Trace chromatograph coupled to  
143 an ITQ MS, and a GC trace chromatograph coupled to an ISQ MS (both instruments from the  
144 ThermoFisher company). A split/splitless injector was used in split mode with a 1:50 mean split  
145 ratio. Low volume liquid and gas syringes (Hamilton), with 0.5  $\mu\text{L}$  and 1 mL volumes

146 respectively, were used to inject the different samples in the injector. The temperature of the  
147 injector, the GC-MS transfer line, and the ionization source were set at 250°C in order to prevent  
148 condensation of tested molecules in the instrument, as all tested compounds except  
149 pentachlorobenzene and hexachlorobenzene have lower boiling points. The MS was set to scan  
150 all the ions produced from the electron impact ionization source (electron energy of 70 eV) in the  
151 m/z 10 to 300 range that covers all the ions produced from the tested compounds according to  
152 the NIST MS spectrum library.

153 The carrier gas was helium (purity  $\geq 99.999\%$ ) to match the SAM GC-MS experiment on  
154 Mars. The temperatures of the columns and carrier gas flow conditions used are given in the  
155 following section.

## 156 **2.4 Analytical approach**

### 157 **• Reproducing the SAM-flight pressure in laboratory**

159 The carrier gas pressure drop between the injector and the detector of the  
160 chromatographic column is a key parameter of the chromatographic analysis. During the  
161 development of the SAM flight instrument, a 1.3 bar inlet carrier gas pressure was originally  
162 chosen as a good tradeoff between chromatographic efficiency and instrumental design  
163 constraints, essentially driven by the requirement that the pressure of the MS chamber remain  
164 low. However, during the last test campaign of the instrument before its integration into the  
165 rover, the inlet pressure was decreased to 0.9 bar to limit the risk of failure of the MS instrument.  
166 The carrier gas tank pressure was predicted to decrease with time over the course of the mission,  
167 but this change had an immediate effect on retention times and column efficiency.

168 With our laboratory instruments, it was not possible to set the absolute inlet pressure to  
169 0.9 bar as it is below ambient laboratory pressure ( $\sim 1$  bar). For that reason, we altered the flight  
170 carrier gas flow by using a deactivated fused silica capillary tube, 30 cm long and with a 50  $\mu\text{m}$   
171 internal diameter connected between the split/splitless injector and the column, following the

172 method suggested by DeZeeuw et al. (16). The appropriate tube length ( $L_{tube}$ ) was estimated  
173 using the Poiseuille's law, described by the following equation:

$$174 \quad \Delta P = \frac{8\eta}{\rho} \left[ \frac{L_{col}}{r_{col}^4} + \frac{L_{tube}}{r_{tube}^4} \right] Q$$

175 with  $\eta$ , the helium viscosity, at  $1.96 \cdot 10^{-5}$  Pa.s at  $20^\circ\text{C}$ ,  $L_{col}$  and  $L_{tube}$  as the respective lengths of  
176 the column and the tube,  $r$  as their radius (0.125 mm for the column and  $50 \mu\text{m}$  for the restrictor  
177 tube), and  $Q$  as the helium flow rate calculated from the mean gas velocity of  $16.28 \text{ cm}\cdot\text{s}^{-1}$  and  
178  $16.66 \text{ cm}\cdot\text{s}^{-1}$  observed in flight for the column from the GC-4 and GC-5 channels respectively.  
179 These velocities were calculated from the deadtime measured in flight chromatograms (3.07 min  
180 and 3.00 min respectively). For the GC-1 channel, the deadtime was difficult to determine  
181 because of the absence of a precise injection system in the flight experiment. For this reason, we  
182 used a 3.00 min estimate corresponding to a  $16.66 \text{ cm}\cdot\text{s}^{-1}$  carrier gas mean velocity. The pressure  
183 drop  $\Delta P$  was set to 100 kPa for the calculation as this corresponds approximately to the pressure  
184 drop in the SAM flight model instrument.

185 The restrictor tube length was calculated for four different internal diameters values varying  
186 from 5 to  $50 \mu\text{m}$ . The  $50 \mu\text{m}$  diameter tube was chosen for its realistic and reasonable tube length  
187 to cut and add to the column inside the GC oven. The tube length calculated was 30 cm. For the  
188 following set of experiments to work under SAM-flight pressure, a 30 cm long and  $50 \mu\text{m}$   
189 internal diameter restriction tube was used with each column replicate already used on Mars  
190 (GC-1, GC-4 and GC-5) in addition to the columns that have not yet been used (GC-2 and GC-  
191 6). This method enabled us to mimic the inlet gas vector flow of the SAM instrument.

192 Once the flow restrictor was installed, we studied the efficiency of the columns as a function  
193 of the inlet pressure by varying the inlet pressure from 1.1 bar, *i.e.* the minimum pressure that  
194 can be set on the laboratory instrument, up to 5 bars. For the study of the analytical capabilities  
195 of the column under SAM like operating conditions, the inlet pressure of the laboratory GC was



196 set to the value allowing us to obtain the deadtime representative of the flight model (~1.3 bar, as  
197 described in the results section).

198 • **Reproducing the SAM-flight temperatures of the GC columns in the laboratory**

199 To study the efficiency of the columns as well as their thermodynamics, we chose  
200 isothermal columns temperatures between 30°C and 200°C, the minimum and maximum  
201 temperatures the columns can reach in flight. To study the separation efficiency of the  
202 chlorohydrocarbons, we performed the laboratory experiments under SAM-like operating  
203 conditions, as close as possible of the flight temperature profiles. We applied identical  
204 temperature programs for the GC-1, GC-4 and GC-5 columns used on Mars to the columns we  
205 tested in the laboratory. For the GC-2 and GC-6 columns, standard temperature programs were  
206 applied considering their thermal constraints on SAM, so as to mimic the flight conditions for  
207 future analyses on Mars. These conditions are detailed in Table 5. Depending on the nature of  
208 the molecules analyzed and the column, the final temperature was held between 5 and 40  
209 minutes. When the highest temperature possible is reached for the column considered in flight, it  
210 immediately stops heating, as it is generally not possible to maintain a long plateau at the final  
211 temperature because of thermal constraints.

212 While the temperature programs of the three columns already used on Mars were mostly  
213 reproduced, some slight differences exist because the flight and laboratory set ups are not strictly  
214 identical. A comparison between the flight and laboratory temperature programs applied to the  
215 columns are presented in Figure 1. The slight difference observed between the flight and the  
216 laboratory temperature profiles is primarily due to the fact that temperature regulation of the  
217 columns is less accurate in the flight model because of the heating method used. However, the  
218 profiles are sufficiently similar to consider that the laboratory method mimics the flight  
219 temperature programs of the SAM-GC columns.

220 **3. Analytical performances of the SAM-flight GC columns**  
221

222 The investigation proceeded in three steps: first, an efficiency study as a function of the  
223 operating conditions to estimate the relevance of the conditions finally used in the flight model;  
224 second, a thermodynamic study to estimate the possible evolution of the elution order of the  
225 chlorohydrocarbons targeted within the temperature conditions; and third, the measurement of  
226 the retention times and determination of the separation power of each column for the  
227 chlorohydrocarbons studied. This last step was of critical importance in developing a reference  
228 database for analyzing the flight data.

### 229 **3.1 Efficiencies of the SAM-GC columns on chlorohydrocarbons**

230 The column's efficiencies were studied as a function of the temperature and the inlet  
231 carrier gas pressure, as the outlet column pressure is constant in the SAM instrument (~0 bar).  
232 The main objective was to determine the optimal carrier gas flow rate conditions to analyze  
233 chlorohydrocarbons. To perform these measurements, the carrier gas inlet pressure was varied  
234 from 110 kPa, the minimum absolute pressure possible on a GC laboratory, to 500 kPa. These  
235 pressures correspond to 7 to 39 cm.s<sup>-1</sup> mean linear velocities. Two isothermal temperature  
236 conditions were used, 35°C and 185°C. These temperatures were representative of the extreme  
237 temperatures used in the SAM GC instrument, taking into account the environmental conditions  
238 of the Mars surface and the instrumental constraints. Three light chlorohydrocarbons detected in  
239 the martian samples were selected for the low column temperature: dichloromethane, 1,2-  
240 dichloropropane (chiral), and chlorobenzene. The Chirasil-β dex (GC-4) column was used for the  
241 separation of the following chiral molecules: the 3-chloro-2-methyl-1-propene, also detected on  
242 Mars and the 1-chlorobutane, that was selected to replace the chlorobenzene, this last not being  
243 eluted at such low temperature. At high temperature, the same compounds were selected in  
244 addition to 1,2,4-trichlorobenzene and 1-chlorooctane (these two compounds have not been  
245 detected in the martian samples so far).

246 A previous study of the MXT-CLP (GC-5) column efficiency was performed (17) but the  
247 organic molecules targeted (alcohols, alkanes and aromatic hydrocarbons) did not include  
248 chlorohydrocarbons. For this study, the GC-5 column efficiency was evaluated on a variety of  
249 organic compounds including the major molecules detected by SAM at that time. The  
250 chlorohydrocarbons studied have different physical and chemical properties (molecular weight,  
251 boiling point, etc., see Table 1) and thus different retention time properties. The columns  
252 efficiency, estimated with the number of theoretical plates value N, was evaluated using the  
253 retention times and peak widths derived from the Total Ion Current (TIC) given by the  
254 laboratory MS, using the formula  $N=5.54(t_R/w_h)^2$  with  $t_R$  being the retention time and  $w_h$  the  
255 peak width at half height. The Height Equivalent to a Theoretical Plate (HETP or H in mm) was  
256 calculated using the formula  $H=L/N$  with L the column length and N the efficiency. The  
257 deadtime, required to calculate the mean carrier gas velocity, was measured using the elution  
258 time of air (essentially composed of N<sub>2</sub>, O<sub>2</sub> et CO<sub>2</sub> which are not retained on the studied  
259 columns), injected separately from the other compounds under the same operating conditions.

260 Finally, from the experimental points, the experimental evolution of H as a function of  
261 the mean linear velocity  $\bar{u}$  (cm.s<sup>-1</sup>) was fitted with the Van-Deemter Golay theoretical equation  
262 given as follows:

$$H = \frac{B}{\bar{u}} + C \cdot \bar{u}$$

263 A polynomial function was used to fit the efficiency of the GC-6 columns because the conditions  
264 of the Van-Deemter Golay equation were not met. This can be explained by its stationary phase,  
265 mostly dedicated to separate light organic molecules (<C<sub>5</sub> or <100 g.mol<sup>-1</sup>). This is the case for  
266 dichloromethane (M = 84 g.mol<sup>-1</sup>) but not the two other molecules (M ~112 g.mol<sup>-1</sup>). These  
267 heavier molecules have higher retention times compared to the analytical capabilities of the GC-  
268 6 column inducing broader tailing peaks from a longer time spent into the column. For this  
269 reason, the best fit was obtained with a second-degree polynomial function for this column.

270 Generally, HETP were optimal to few millimeters depending on the compounds, but the  
271 range of optimal velocities were similar for all the compounds when looking at a given column.  
272 Laboratory efficiencies were compared, when possible, to the flight efficiencies currently  
273 measured on the SAM-flight instrument of the chlorohydrocarbons detected which was the case  
274 for the MXT-CLP (GC-5), MXT-20 (GC-1), and Chirasil- $\beta$  Dex (GC-4) columns.

275  
276 For dichloromethane, the HETP minimum value was 1.7 mm for  $\bar{u}=12.5 \text{ cm.s}^{-1}$ . In the 9-  
277  $15 \text{ cm.s}^{-1}$  velocity range, the HETP value did not increase more than 10%. For chlorobenzene  
278 and 1,2-dichloropropane, the HETP minimum values were 2.8 and 3.1 mm respectively at 9  
279  $\text{cm.s}^{-1}$  and  $10 \text{ cm.s}^{-1}$  carrier gas speeds. HETP values did not increase more than 10% of the  
280 minimum in the 7 to  $12 \text{ cm.s}^{-1}$  velocity range.

281 No analyses of a Mars sample have been performed on the SAM flight model with the  
282 GC-6 column so far. However, a calibration test was performed on Mars with the GC-6 channel  
283 and the deadtime measured was 3.5 min at  $40^\circ\text{C}$ . This corresponds to a  $14.3 \text{ cm.s}^{-1}$  mean carrier  
284 gas velocity. However, no measurement of the deadtime was available on flight at  $185^\circ\text{C}$   
285 temperature column to calculate the carrier gas velocity at this temperature. But, the inlet column  
286 pressure is known (0.9 bar), as well as the deadtime measured on the columns that have been  
287 used in flight, and equal to about 3.9 min at  $185^\circ\text{C}$ . Knowing these values, we calculated the  
288 supposed average velocity of the carrier gas that would be equal to  $12.82 \text{ cm.s}^{-1}$  at  $185^\circ\text{C}$  for the  
289 current inlet column pressure, called " $\bar{u}_{\text{SAM}}$  theoretical" (Figure 2), value compatible with the  
290 carrier gas velocity of He in flight measured at  $40^\circ\text{C}$  column temperature.

291 From these measurements, we concluded that the optimal efficiency of the GC-6 column  
292 decreased with the retention times of the analyzed compounds, likely because of the increase of  
293 the peaks tailing with their retention due to the nature of the stationary phase. Moreover, when  
294 comparing the optimal velocity range of the column with the actual mean linear velocity

295 measured in the flight model, we noticed that the flight operating carrier gas flow was near  
296 optimal for this column and the tested compounds. However, the decrease of carrier gas velocity  
297 during the mission should not significantly influence the efficiency down to  $9 \text{ cm.s}^{-1}$ .

298 Figure 3 shows the evolution of the HETP as a function of the mean carrier gas velocity  
299 for all the SAM GC columns bonded with liquid stationary phases, for the two extreme  
300 temperatures used in the SAM GC flight model. Most curves show the usual behavior of the  
301 evolution of HETP with  $\bar{u}$ , yet we observed one phenomenon that we are unsure how to explain:  
302 that those obtained with the MXT-CLP columns at  $185^\circ\text{C}$  were rather flat for higher mean  
303 carrier gas velocities. All the values used to discuss the efficiencies of the columns bonded with  
304 liquid stationary phases are summarize in Table 3.

305

306 The MXT-20 column (GC-1) plot was consistent with the theoretical evolution of the  
307 Van-Deemter-Golay equation at high temperature for each molecule. The minimum H values  
308 were between 0.5 mm for dichloromethane and 1 mm for the other compounds at low  
309 temperature. The optimal velocity range was  $15\text{-}20 \text{ cm.s}^{-1}$  for dichloromethane and stayed  
310 optimal for the other compounds even at high carried gas speeds. At high temperature, plots had  
311 a minimum of 0.8 mm for the more retained compounds, to 1.4 mm for the less retained. The  
312 optimal velocity range was the same for each molecule and between 15 and  $20 \text{ cm.s}^{-1}$ .

313 In conclusion, the optimal velocity range for the GC-1 column did not depend on the  
314 temperature. The efficiency did not improve when the temperature increases and was slightly  
315 degraded (of  $\sim 0.4 \text{ mm}$ ), meaning the exchange between the mobile and stationary phases was  
316 more difficult at high temperature. At both temperatures, GC-1 was convenient and efficient for  
317 the analysis of low and high molecular weights chlorinated compounds and on a wide range of  
318 velocities with a slight better efficiency at low temperature.

319 The GC-1 column has since been used on Mars on the Windjana sample and in parallel  
320 with the GC-4 column on the Ogunquit Beach (OG) sample. However, the lack of efficient inlet  
321 injection system did not allow an ideal chromatographic analysis with symmetric and Gaussian  
322 peaks. In addition, without the injection time given by the thermal desorption for other columns  
323 used in SAM, it is impossible to precisely determine its deadtime. If the carrier gas velocity is  
324 estimated using the estimated deadtime, it equals 3.0 and 3.9 minutes at 35 and 185°C  
325 respectively. This corresponds to flight linear velocities of 16.66 and 12.82 cm.s<sup>-1</sup>. Compared to  
326 laboratory efficiencies, the flight efficiency was slightly degraded of 15% at high temperature.  
327 At low temperature, the efficiency was not degraded at SAM-flight pressure. At high  
328 temperature, it will have to be considered that GC peaks shape can be degraded, possibly  
329 resulting in a limitation of the separation power. This confirms that the GC-1 column has better  
330 analysis capabilities at low temperature regarding its efficiency and use at the *in situ* flight-  
331 pressure.

332 The MXT-5 (GC-2) column had experimental data close to the theoretical fit of the Golay  
333 equation. At low temperature, efficiencies values were similar for all compounds and between 1  
334 and 1.3 mm, corresponding to optimal carrier gas velocities between 15 and 20 cm.s<sup>-1</sup>. At high  
335 temperature, efficiencies were degraded and H values increase from 1.8 to 3 mm depending on  
336 the compounds. The limitation of experimental data at high pressure made the fitting of the plots  
337 difficult. The optimal velocity ranges varied from one compound to another of a few centimeters  
338 per second. For light compounds (dichloromethane, dichloropropane, and chlorobenzene), the  
339 optimal velocities ranged between 13 and 17 cm.s<sup>-1</sup>. The optimal velocities of 1,2,4-  
340 trichlorobenzene and 1-chlorooctane were between 13 and 19 cm.s<sup>-1</sup> and 10 and 15 cm.s<sup>-1</sup>  
341 respectively. In conclusion, this column was shown to be more efficient for the analyses of high  
342 molecular weight aliphatic chlorohydrocarbons (no loss of efficiency). Its efficiency decreased to  
343 25% for aromatics.

344 The MXT-5 (GC-2) column has not yet been used in flight. However, we were able to  
345 theoretically estimate its efficiency degradation under SAM-flight conditions. As for GC-1, the  
346 efficiency of GC-2 was optimal at low temperature, even at SAM-flight pressure. At high  
347 temperature, the efficiency was degraded for most compounds, except for chlorooctane. The  
348 current carrier gas velocity is thus ideal for the analysis of aliphatic high molecular weight  
349 compounds at high temperature. For low molecular weight organo-chlorinated or aromatic  
350 compounds, the flight-pressure was 20% weaker than the optimal one. As GC-1, GC-2 had better  
351 analysis capabilities at low temperature but was globally less efficient for the analysis of the  
352 targeted compounds, thus using GC-1 under these circumstances will be preferable.

353 The Chirasil- $\beta$  Dex (GC-4) column is dedicated to the analysis and separation of chiral  
354 molecules. From all selected compounds, 1,2-dichloropropane is the only chiral one. Both  
355 isomers of dichloropropane are partially co-eluted at low temperature and totally at high  
356 temperature.

357 At low temperature, efficiencies follow the theoretical evolution of Golay, except for  
358 dichloromethane. For this last, except at low velocities, points are irregular and do not present a  
359 minimum. Those results are difficult to interpret since all the analyses were performed in the  
360 same conditions for all molecules. For 1,2 dichloropropane, despite it includes enantiomers, its  
361 efficiency evolves as the other compounds. However, a higher HETP of 2.8 mm (compared to  
362 1.2 mm for chlorobutane and 3-chloro-2-methyl-1-propene) is obtained. These observations  
363 result from the likely slight separation of the enantiomers achieved on the column, broadening  
364 the peak observed on the chromatogram and resulting from the coelution of the peaks of the  
365 enantiomers. The results obtained for this compound should therefore be taken as indicative of  
366 the efficiency trend. The optimal gas velocities are between 13 and 18  $\text{cm}\cdot\text{s}^{-1}$  compared to 15-20  
367  $\text{cm}\cdot\text{s}^{-1}$  for dichloropropane. At high temperature, plots are atypical since even with the Golay's  
368 fits, they tend to parabolic equations implying steep slopes at high velocities. Consequently, the

369 optimal carrier gas velocities range is reduced compared to the other columns at the same  
370 temperature. Efficiencies improve with the temperature increase with H values between 0.9 and  
371 3.5 mm. In conclusion, the GC-4 column is more efficient for the highest molecular weight  
372 chlorohydrocarbons. However, the optimal gas velocities range is the same for all compounds  
373 and between 10 and 13  $\text{cm}\cdot\text{s}^{-1}$ , which is significantly reduced compared to the optimal range of  
374 the other columns.

375 The GC-4 column is now the privileged column for flight-GC analyses and was recently  
376 used in parallel of GC-1 to analyze the OG samples. Using the chromatogram from the Green  
377 Horn (GH) sample, the column deadtime was evaluated at 3.07 minutes. At both temperatures,  
378 the velocity range is optimal for the chlorinated compounds analyzed in the laboratory. At high  
379 temperature, the flight-mean carrier velocity is below the limit to which the loss of efficiency  
380 would be significant. At low temperature, Figure 3 shows that, despite the current flight-  
381 operating conditions, the efficiency is not degraded and consistent with the flight one. To  
382 confirm this hypothesis, the efficiency observed for dichloromethane, detected in GH, was  
383 measured and equals 1.5 mm. This value is consistent with the H value of chlorobutane and 3-  
384 chloro-2-methyl-1-propene, indicating that the laboratory conditions are representative of the  
385 flight ones. Moreover, when we compare the flight H value (1.5 mm) to the laboratory one for  
386 the dichloromethane (2.1 mm), we see that GC-4 is even more efficient in flight compared to the  
387 laboratory. In conclusion, the flight operating conditions of GC-4 are optimal at low temperature  
388 and correspond to the maximal column efficiency. The efficiency loss is negligible at high  
389 temperature. Despite the instrumental constraints, GC-4 allows analyses in optimal conditions, at  
390 both temperatures considered in flight.

391 The MXT-CLP (GC-5) column allowed the analyses and detection of all the  
392 chlorohydrocarbons detected in the martian samples so far. The efficiency of this column was  
393 previously studied for non-chlorinated compounds (17), but it was not clear how the column



394 efficiency behaves in the presence of chlorinated molecules. At 35°C, we found that 1,2-  
395 dichloropropane and chlorobenzene had the same behavior, and that the theoretical Golay curves  
396 fit correctly with the experimental data. However, dichloromethane efficiency is almost linear  
397 with no increase at the highest carrier gas velocities. Thus, dichloromethane is not well retained  
398 by the column and has a retention time close to the deadtime. The H values measured were: 2.3  
399 mm for dichloromethane and 1.6 mm for the other molecules. The optimal range of velocity for  
400 all three compounds was between 13 and 19 cm.s<sup>-1</sup>. Efficiencies were much improved at 185°C.  
401 Minimal H values were between 0.5 mm for the more retained chlorohydrocarbons to 0.8 mm  
402 for the less retained. The best efficiency was obtained for a carrier gas velocity of 24 cm.s<sup>-1</sup> and  
403 stayed mostly constant at high velocities, is consistent with previous studies (17) and also  
404 indicating that GC-5 appears to have the same behavior regarding all types of molecules.

405 A comparison between the flight and optimal laboratory efficiencies showed that the  
406 analysis conditions were quite optimal at low temperature but degraded at high temperature. The  
407 efficiency loss was evaluated at 4% at low temperature and 46% at high temperature (Table 3).  
408 The consequence is a degradation of the flight chromatograms compared to the optimal, through  
409 broader peaks and a more limited separation power of the column. To confirm that efficiencies  
410 are representative of SAM-flight operating conditions, we calculated the column efficiency for  
411 the dichloromethane detected in the Cumberland (CB) sample. At the SAM carrier gas velocity  
412 of 16.66 cm.s<sup>-1</sup>, the H value for dichloromethane is 2.65 mm, corresponding exactly to the  
413 laboratory efficiency for this compound. For chlorinated compounds, laboratory operating  
414 conditions are perfectly consistent with the flight ones and analyses were performed in analytical  
415 conditions close to the optimal, especially at low temperature.

416 A previous study demonstrated that the lowest carrier gas speed on SAM does not have a  
417 great influence on the GC-5 flight column efficiency regarding alcohols and alkanes (17) at low  
418 temperature, even with an efficiency loss of ~33%. This study demonstrated that the efficiency

419 loss in the case of chlorohydrocarbons was even lower (4%) and that GC-5 was best adapted for  
420 their analysis at low temperature. At high temperature, efficiency losses did not depend on the  
421 nature of the compound and were about 47% for all the compounds considered in both studies.

422 In conclusion, all five columns tested had similar ranges of optimal carrier gas velocities  
423 at low temperature. The obtained H minimum values (1-3 mm) show that, within the optimal  
424 carrier gas speed, all columns had high efficiencies and representative to the flight ones  
425 (measured with the dichloromethane for GC-4 and GC-5). The most efficient columns are GC-1  
426 and GC-2 both bonded with polydimethylsiloxane (80 and 95% respectively) and phenyl (20 et  
427 5%), followed by GC-4 and GC-5 (Table 3). Even if the GC-5 column is dedicated to the  
428 analysis of compounds with the same molecular weights as GC-1 and GC-2, the presence of  
429 cyanopropyle seemed to slightly limit its efficiency compared to the others. At high temperature,  
430 the optimal carrier gas velocity range is reduced for all columns (except GC-2), especially for the  
431 GC-4 and GC-5 columns. But within their optimal velocity range, their efficiencies are  
432 improved, with a broader dispersion for GC-4 (Table 3). The efficiency and optimal carrier gas  
433 velocity range of the GC-2 column depend on the nature of the chlorinated compounds  
434 considered. GC-2 seems indeed less efficient for the analysis of aromatic chlorohydrocarbons  
435 (e.g. chlorobenzene and 1,2,4-trichlorobenzene) and if used on SAM, this constraint will have to  
436 be considered.

437 The study of the SAM-GC columns efficiencies demonstrated that flight operating  
438 conditions were within or close to the optimal velocities range for the analysis and separation of  
439 aromatic and aliphatic chlorinated organics, and has a minor influence on the SAM analyses  
440 (Table 3). However, we note that columns efficiency would have been improved by using a  
441 higher carrier gas flow rate as initially planned. Moreover, the slight decrease of pressure in the  
442 SAM helium gas tank throughout the mission should not significantly influence the columns'  
443 efficiencies.  $U_{opt}$  was equivalent to  $u_{SAM}$  at low temperature, lower at high temperature for the

444 GC-1 and GC-5 columns and slightly higher for GC-4. The current flight carrier gas velocity  
445 works within the optimal carrier gas velocities at low temperature since efficiency losses are  
446 below 10% for all the SAM-GC columns. This is not the case at the highest temperature and  
447 degradations are observed: ~15, 25, 14 and 46% for GC-1, GC-2, GC-4 and GC-5 respectively.  
448 Thus, it is globally preferable to use the columns from the GC-1, 2 or 4 channels for the analysis  
449 of the chlorohydrocarbons, with GC-1 being the most efficient of all for each  
450 chlorohydrocarbons and at both SAM extreme temperatures. With time and the general decrease  
451 of the SAM mean carrier gas speed, efficiencies might significantly decrease except for the GC-  
452 4 column which should even have a better efficiency (Figure 3) and that should be the favorable  
453 column to use in future SAM analyses.

### 454 **3.2 Thermodynamic study**

455 Retention time, as mass spectrum, is a key parameter used for identifying the compounds  
456 detected with the SAM instrument. As the temperature of the columns changes during an  
457 analysis, it is of interest to follow the evolution of the retention times with the column  
458 temperature. This allows an assessment of the extent of evolution of the retention times as well  
459 as the possible modification of the elution order of the analytes. With this aim, we analyzed a  
460 few of the studied chlorohydrocarbons and measured their retention times obtained at different  
461 isothermal temperature programs in the 30-200°C range. Measuring the dead time for each  
462 analysis allowed us to calculate the capacity factor  $k'$ , with  $\ln(k') \sim \Delta H/T$ , with  $\Delta H$  the enthalpy  
463 of exchange of the solute between the mobile and the stationary phase. We observe that the plots  
464 are linear as expected, allowing us to calculate the values of  $\Delta H$  for all the compounds. Figure 4  
465 demonstrates the linear fits, and Table 4 summarizes the values of  $k'$  and  $\Delta H$  obtained with this  
466 study.

467 In Figure 4, we observe that the  $k'$  values are similar for all the WCOT columns, whereas the  
468 PLOT column gives higher  $k'$  values, representative of a higher retention power. We also

469 observe that for WCOT columns, the curves do not cross except possibly at high temperature.  
470 However, the technical constraints of the SAM chromatograph do not allow to reach such high  
471 temperatures. Therefore, a change in the order of elution of chlorohydrocarbons for these four  
472 columns is unlikely, regardless of the temperature of the columns in the SAM-GC. This property  
473 is of interest, as it makes the identification of the chlorohydrocarbons easier. For the GC-6  
474 channel, some inversion of elution order can occur at the lowest temperatures. But for these  
475 temperatures, the retention of the tested species was too high for their analysis with SAM within  
476 the operating conditions of the instrument. Therefore, once again, the order of elution should  
477 remain constant within the SAM operating conditions.

### 478 **3.3. Analytical ability of the SAM-GC to detect chlorohydrocarbons evaluated in** 479 **laboratory under simulated flight operating conditions**

#### 480 **3.3.1. Goal and experimental strategy**

481 The SAM-GCMS instrument has enabled the separation, detection and identification of  
482 organo-chlorinated compounds in different samples collected by Curiosity on Mars (11, 13, 14,  
483 17). To support ongoing work, and to better anticipate flight data and their interpretation, an  
484 additional objective of this study was to build a database of retention times of the chlorinated  
485 compounds detected or potentially present in the chromatograms obtained with SAM on Mars, or  
486 those which could potentially outgas from samples in future analyses. Although SAM analyses  
487 are constrained by various parameters that influence the analytical conditions, we were able to  
488 reproduce the constraints related to the GC columns operation. The two major constraints in  
489 reproducing flight conditions in the laboratory were a limited time of analysis related to the  
490 thermal constraints of the SAM instrument components, and the carrier gas pressure  
491 mechanically and permanently set at 0.9 bar.

492 For this part of the study, spare SAM GC columns were used (Table 2) in SAM-like  
493 operating conditions. To mimic the best SAM-flight carrier gas flow conditions, the flow

494 restriction method described in Section 2.4 was used. The temperature programs used for each  
495 column and their maximum time of analysis allowed (measured in flight or induced by the  
496 constraints of the analytical channel considered) are presented Table 5.

497

### 498 **3.3.2 Range of chlorohydrocarbons detectable under SAM flight operating conditions**

499 To evaluate the elution properties of the SAM-GC columns and help the attribution  
500 of peaks observed in SAM chromatograms, the retention times of 26 organo-chlorinated  
501 compounds (Table 1) were measured in the laboratory using both GCMS described in  
502 Section 2.3. The retention times measured are presented in Table 6. Figure 5 shows  
503 chromatograms obtained after analyzing the same set of chlorohydrocarbons on all four  
504 WCOT columns studied. Figure 6 presents the analytical capabilities of the PLOT column  
505 used for the GC-6 channel of the SAM instrument.

506 The maximal times of analysis of each column (Table 5) are represented by a double line  
507 in Table 6 and by a dash-line of the color corresponding to each column in the chromatograms  
508 (Figure 5 and Figure 6). All the chlorohydrocarbons with retention times lower or equal to these  
509 maximum time of analyses are detectable by the SAM-GC if they are present in the gases  
510 released by the solid samples collected by Curiosity and submitted to thermal or chemical  
511 treatment in SAM. The compounds eluted beyond these limits are not detectable within the  
512 current flight operating conditions. These results show that the columns bonded with liquid  
513 stationary phases are able to elute most of the tested chlorohydrocarbons within the limited time  
514 of analysis of the instrument for the columns considered. Only Hexachlorobenzene cannot elute  
515 on time for any of the SAM-GC WCOT columns, and Pentachlorobenzene would only be eluted  
516 on time with the GC-1 and GC-2 columns, in the flight conditions simulated in laboratory. With  
517 the PLOT column used in the GC-6 channel, only a limited number of compounds, among those  
518 selected for this study, elutes within the given maximum time of analysis, chloroethane being the

519 heavier one. Despite we were able to elute the 1,3,5-trichlorobenzene with a retention time of  
520 251.10 minutes in the laboratory, such a high retention time combined to the thermal limitations  
521 of the GC-6 column makes this molecule non detectable with the SAM instrument on Mars.

522 By the end of the Curiosity mission on Mars, some margins could be used to push the  
523 instrument to its limit, or develop new strategies to analyze a sample could be imagined (*e.g.* two  
524 successive chromatograms of the same sample to elute the compounds remaining in the column  
525 after a first run) to increase the maximum time of analysis on critical chromatographic channels  
526 (GC-5 for instance). However, the operating constraints are so tight that it is not expected to  
527 significantly increase this time without damaging the chromatograph. The consequence of these  
528 limitations is that the columns MXT-20 (GC-1), MXT-5 (GC-2), and Chirasil- $\beta$  Dex (GC-4) can  
529 elute and detect all the chlorohydrocarbons from chloromethane to pentachlorobenzene within  
530 the SAM instrument analytical conditions, and the MXT-CLP (GC-5) column is limited to the  
531 trichlorobenzene isomers. The Q-PLOT column (GC-6) is limited to the lightest gaseous  
532 chlorinated compounds such as the chloromethane and the chloroethane. However, its high  
533 retention power could be useful in the future to attempt quantifying the lightest  
534 chlorohydrocarbons which can be coeluted on the other columns.

535 To conclude, even if the limitation of the maximal time of analysis of the SAM-GC could  
536 result in the non-detection of chlorohydrocarbons because of their too late elution (*e.g.*  
537 tetrachlorobenzene on the GC-5 channel (14) the instrument is capable to elute and detect a wide  
538 range of alkyl and monoaromatic chlorohydrocarbons that can be formed during the pyrolysis or  
539 the derivatization of a sample of Mars rocks. This capability is sufficient to give an overview of  
540 the main chlorohydrocarbons released by the sample preparation process from which  
541 information about the nature of the sample compounds and reactivity can be deduced.

542

### 3.3.3 Separation power of the SAM-GC columns under the flight operating conditions

Under the nominal SAM-flight operating conditions which are similar for all the columns, we observe that the order of elution of the chlorohydrocarbons selected for the study is quite comparable. For GC-1 and GC-2, this is true for almost all the compounds. This could be expected as the stationary phases of the corresponding columns are very similar (polydimethylsiloxane partly (PDMS) substituted by phenyl), with only a difference in the concentration in phenyl (20% and 5% respectively). This means that the modification in polarity of the stationary phase induced by the variation of phenyl concentration is not sufficient to significantly change the retention mechanisms of the chlorohydrocarbons analyzed. With both columns, the number of coelution observed is limited (<2) and the peaks shape is quite nominal. For GC-4, more co-elutions are observed (>3) compared to GC-1 and GC-2. This difference is mainly due to a peak broadening generally observed with this type of stationary phase, and a modification in the retention of the compounds that lead to longer retention times for all the analytes, as it was previously described. In term of selectivity, even if not systematically, it seems that the multi-chlorinated alkyl chlorohydrocarbons are rather more retained with GC-4, leading to significant elution order changes, such as for 1,4-dichlorobutane. The source for this change of selectivity is difficult to determine as it can be due to the absence of phenyl in the stationary phase of the column, to the presence of cyclodextrin diluted in the PDMS, or both effects. Regarding GC-5, we notice that the separation pattern is very similar to the GC-2 one. The only exceptions are the multi-chlorinated methanes which are much less retained with GC5. This means that the stationary phases used in these columns are quite similar in term of polarity, at least for chlorohydrocarbons. Even if we have no details about the composition of the GC-5 stationary phase, our result show that it should be made of PDMS contain phenyl substituents at concentrations equivalent to the GC-2 stationary phase, and an additional substituent (CNPP)

568 explaining the few differences in retention observed. It is possible that the difference in  
569 selectivity between those two columns would be more important for other chemical families and  
570 would be a key parameter to select either GC-2 or GC-5 for an analysis.

571         Depending on the objective given for the analysis of a sample, it is possible to select the  
572 more appropriate column among the five ones integrated in the SAM-GC for analysing organic  
573 molecules. This is obvious that for a broad screening of chlorohydrocarbons, the four WCOT  
574 columns are more appropriate to be used, but we showed that GC-1, GC-2 and GC-5 channels  
575 are preferable as they achieve a reasonable separation of all the tested compounds, regardless of  
576 their mass. The last WCOT column, GC-4, shows a better separation of the lightest  
577 chlorohydrocarbons but more heavier compounds are coeluted. For this reason, GC-4 should be  
578 preferred to enhance the separation of the lightest chlorohydrocarbons if necessary. Finally, the  
579 PLOT column should be used to specifically resolve chloromethane from chloroethane, for  
580 quantification requirements for instance. It is interesting to underline that SAM-GC can work  
581 with two columns working in parallel. Also, if the separation of both light and heavier  
582 chlorohydrocarbons is required in one unique run, an analytical strategy can consist in selecting  
583 the appropriate complementary columns to meet this objective, *e.g.* GC-5 and GC-6. Finally, we  
584 must keep in mind that the chlorohydrocarbons analysed with the SAM instrument on Mars are  
585 not the only chemical compounds released by the sample. Also, even if the detection benefits  
586 from the mass spectrometric measurement, additional coelution with non chlorohydrocarbons  
587 organic compounds should be limited to prevent any ambiguity in the compounds identification  
588 (2, 17).

589         To conclude, the study of the separation achieved with the SAM chromatograph under  
590 flight-like conditions shows that the combination of columns selected are able to separate all the  
591 alkylated and mono-aromatic compounds tested within the limit of time imposed by the flight



592 instrument technical constraints, even if the instrument design did not originally consider the  
593 presence of these compounds among the chemical species released by the soil and rock samples.

#### 594 **4. Conclusion**

595         Whereas the detection of chlorohydrocarbons was not originally planned in the  
596 development of the SAM instrument, we showed that the set of five columns selected for  
597 achieving the chromatographic analysis of organic compounds is suited for the separation and  
598 detection of a wide range of aliphatic and monoaromatic chlorinated organics within the  
599 constrained operating conditions used on Mars. These operating conditions should allow a high  
600 level of efficiency of all the columns to be maintained throughout the duration of the mission.  
601 While the qualitative study of the columns used in the GC-5 channel already allowed to identify  
602 and quantify several chlorine bearing organic molecules (11, 14, 17), the work presented in this  
603 paper demonstrates the complementarity of the chromatographic columns bonded with different  
604 stationary phases and selected for the SAM instrument to achieve the separation and  
605 identification of alkyl chlorohydrocarbons up to 1-Chlorooctane, and monoaromatic  
606 chlorohydrocarbons up to Pentachlorobenzene. The conservation of the order of elution of the  
607 chlorohydrocarbons for all the columns regardless of the operating temperature used will also  
608 simplify the identification of the detected molecules throughout the Curiosity mission. This  
609 analytical capability will be precious in order to extract the most interesting information about  
610 the composition and reactivity of the Mars samples collected by the rover and analyzed with  
611 SAM, thus allowing to make great progress in the characterization of the Gale crater  
612 environment and its potential for past habitability.

613

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- 658

659 **Figure captions:**

660 **Figure 1.** Comparison of the temperature programs applied to the three GC columns that have been used in flight so  
661 far. The measured flight temperature program is plotted in blue and the temperature programs applied in the  
662 laboratory are represented with a red dash-line. The times to which the injection traps of the GC-4 and GC-5  
663 channels are activated are represented on the abscissa axis by black stars and are called « IT flash ». As the GC-1  
664 channel is not equipped with an injection trap, no black star is present in the graph.  
665

666 **Figure 2.** Evolution of the HEPT (mm) as a function of the mean linear carrier gas velocity  $\bar{u}$  (cm.s<sup>-1</sup>) for the GC-6  
667 column doted of a solid stationary phase. Points correspond to the experimental data and the lines to the fits from the  
668 Van-Deemter-Golay equation. The black line, represented at 12.82 cm.s<sup>-1</sup>, corresponds to the mean linear carrier gas  
669 velocity with the inlet column theoretical pressure on the SAM-flight instrument.  
670

671 **Figure 3.** Evolution of the HEPT (mm) as a function of the mean linear carrier gas velocity  $\bar{u}$  (cm.s<sup>-1</sup>) for the SAM-  
672 GC columns doted of liquid stationary phases. H (mm) is plotted in function of  $\bar{u}$  in cm.s<sup>-1</sup>. Points correspond to the  
673 experimental data and the lines to the fits plotted from the Van-Deemter Golay equation. The carrier gas velocities,  
674 corresponding to pressures measured in flight, were represented, when possible, by a black line, or theoretically  
675 evaluated. Crosses correspond to the H calculated from the flight data of dichloromethane, a chlorohydrocarbon  
676 systematically detected and present in all flight chromatograms.  
677

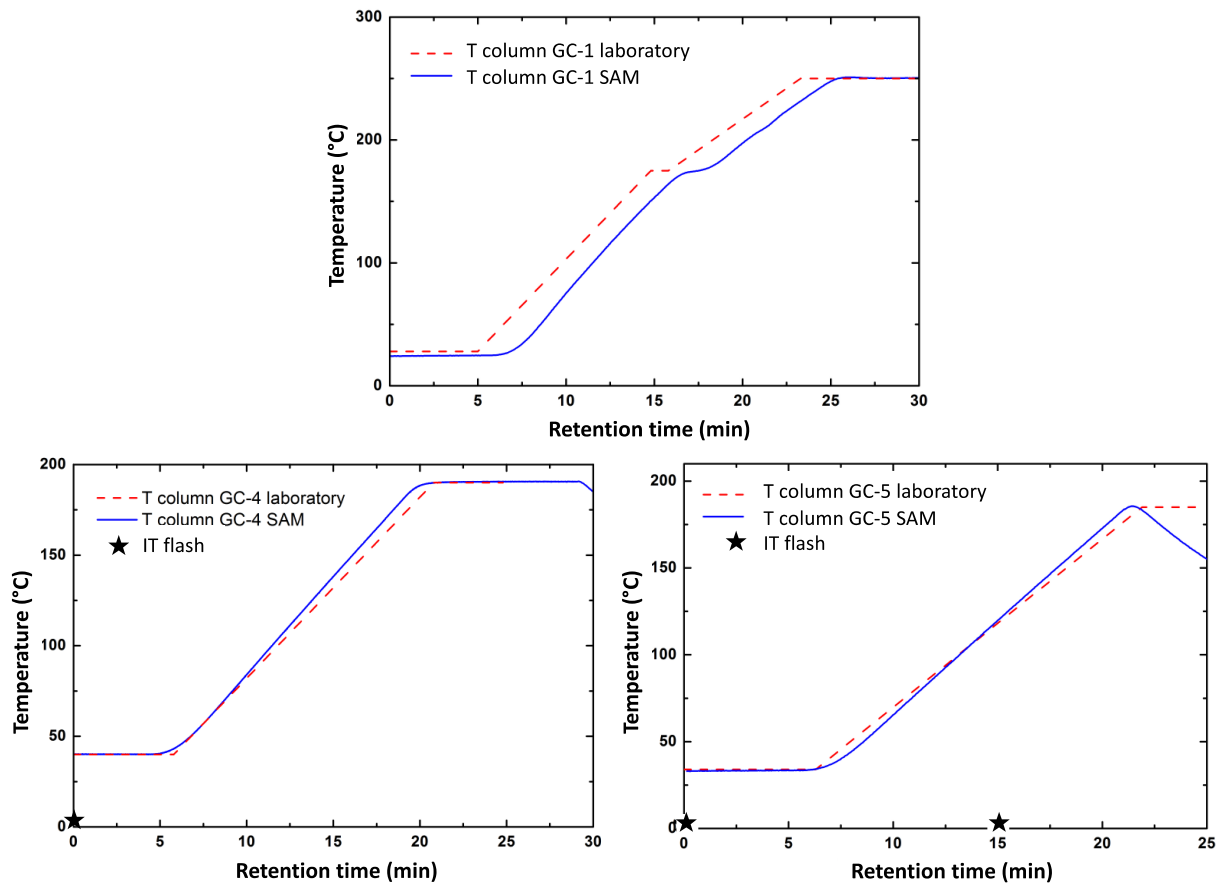
678 **Figure 4.** Evolution of  $\ln(k')$  in function of  $1000/T$  for the chlorinated compounds on the SAM-GC columns from  
679 channels GC-1, GC-2, GC-4, GC-5 and GC-6. Experimental data were obtained for a temperature range between 40  
680 and 200°C corresponding to the extreme temperatures used for SAM. A linear regression has been fitted to the  
681 experimental data points on the range of the figure.  
682

683 **Figure 5.** Chromatograms of the chlorohydrocarbons obtained for the channels GC-1 (MXT-20), GC-2 (MXT-5),  
684 GC-4 (Chirasil- $\beta$  Dex) and GC-5 (MXT-CLP) in SAM-flight operating conditions listed in Table 4. Compounds: 1:  
685 2-chloropropane, 2: dichloromethane, 3: 1-chloro-2-methyl-1-propene, 4: trichloromethane, 5: 3-chloro-2-methyl-1-  
686 propene, 6: 1-chlorobutane, 7: tetrachloromethane, 8: 1,2-dichloropropane, 9: 1,2-dichlorobutane, 10:  
687 chlorobenzene, 11: 1-chlorohexane, 12: 1,4-dichlorobutane, 13: 2-chlorotoluene, 14: 1,2-dichlorobenzene, 15: 1-  
688 chlorooctane, 16: 1,2,4-trichlorobenzene, 17: 1,3,5-trichlorobenzene, 18: 1,2,4,5-tétrachlorobenzene, 19:  
689 pentachlorobenzene, 20: 1-chloroheptane. Compounds marked with a star \* are co-eluted.  
690

691 **Figure 6.** Chromatogram of the chlorohydrocarbons obtained for the channel GC-6 (Q-Plot) in SAM-flight  
692 operating conditions listed in Table 4. Compounds: 1: Non-retained compound (Air), 2: chloromethane, 3:  
693 chloroethane, 4: dichloromethane, 5: 2-chloropropane, 6: trichloromethane, 7: 1-chloro-2-methyl-1-propene, 8: 3-  
694 chloro-2-methyl-1-propene, 9: 1-chlorobutane, 10: tetrachloromethane, 11: 1,2-dichloropropane, 12: 1,2-  
695 dichlorobutane, 13: Chlorobenzene, 14: 1-chlorohexane, 15: 1,4-dichlorobutane, 16: 2-chlorotoluene.

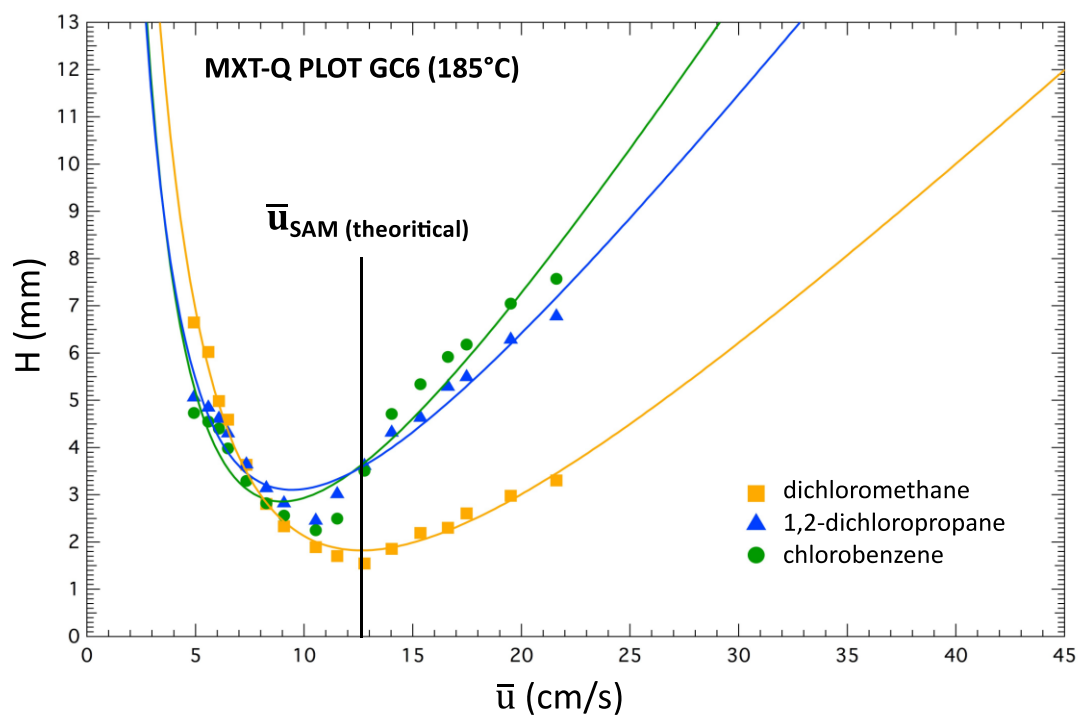
696

Figure 1

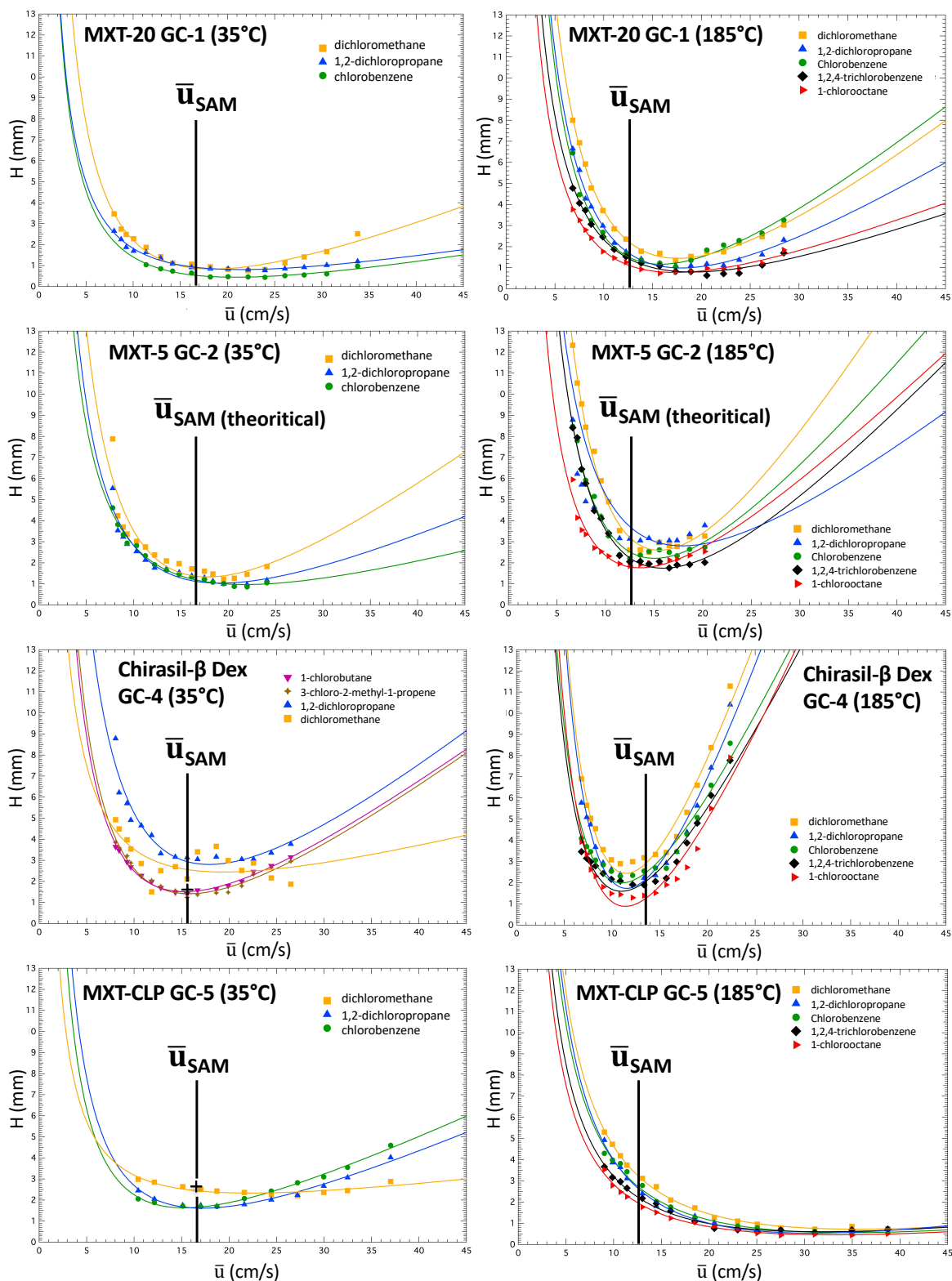


**Figure 1.** Comparison of the temperature programs applied to the three GC columns that have been used in flight so far. The measured flight temperature program is plotted in blue and the temperature programs applied in the laboratory are represented with a red dash-line. The times to which the injection traps of the GC-4 and GC-5 channels are activated are represented on the abscissa axis by black stars and are called « IT flash ». As the GC-1 channel is not equipped with an injection trap, no black star is present in the graph.

Figure 2

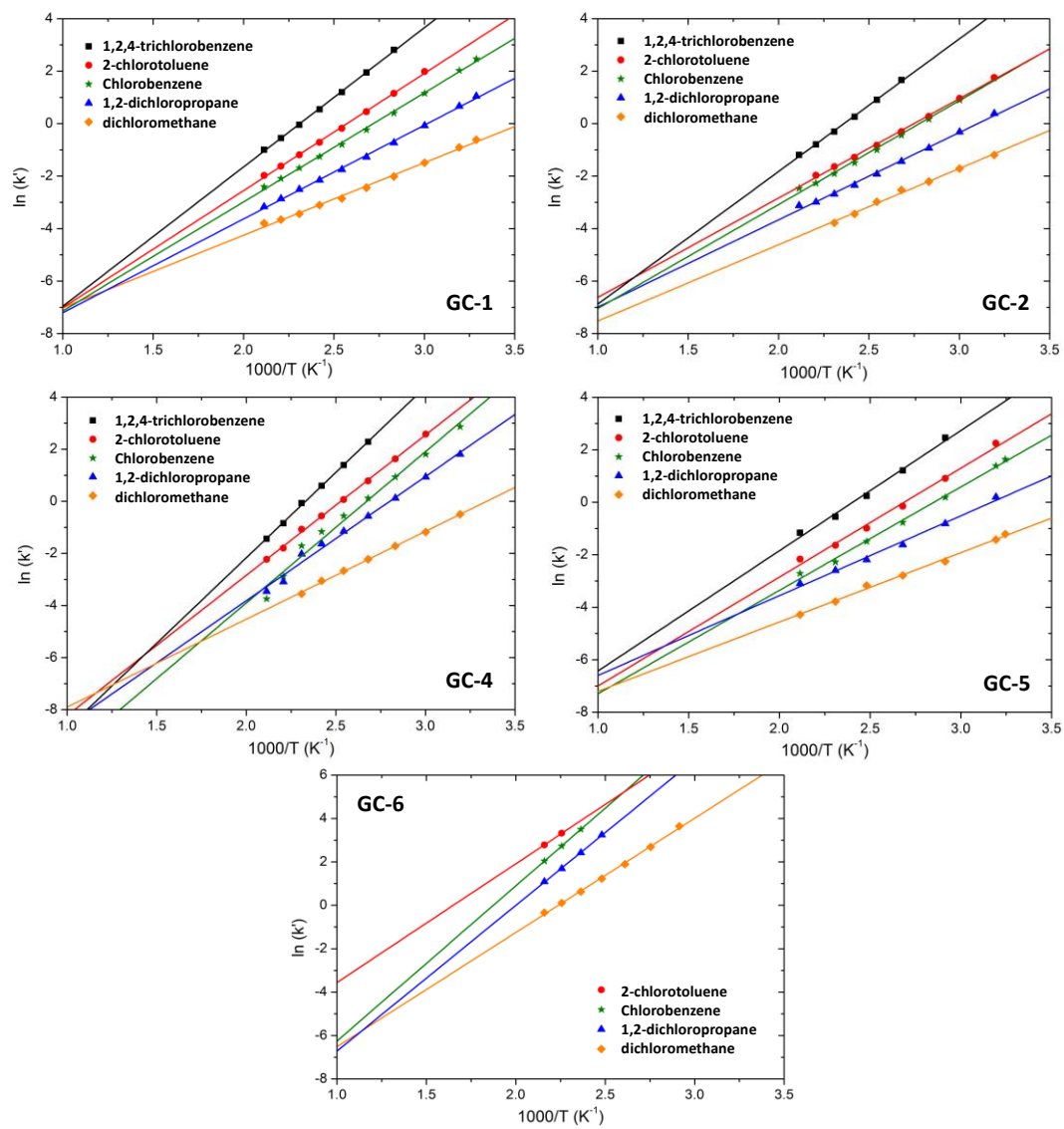


**Figure 2.** Evolution of the HEPT (mm) as a function of the mean linear carrier gas velocity  $\bar{u}$  ( $\text{cm}\cdot\text{s}^{-1}$ ) for the GC-6 column bonded with a solid stationary phase. Points correspond to the experimental data and the lines to the fits from the Van-Deemter-Golay equation. The black line, represented at  $12.82 \text{ cm}\cdot\text{s}^{-1}$ , corresponds to the mean linear carrier gas velocity with the inlet column theoretical pressure on the SAM-flight instrument.

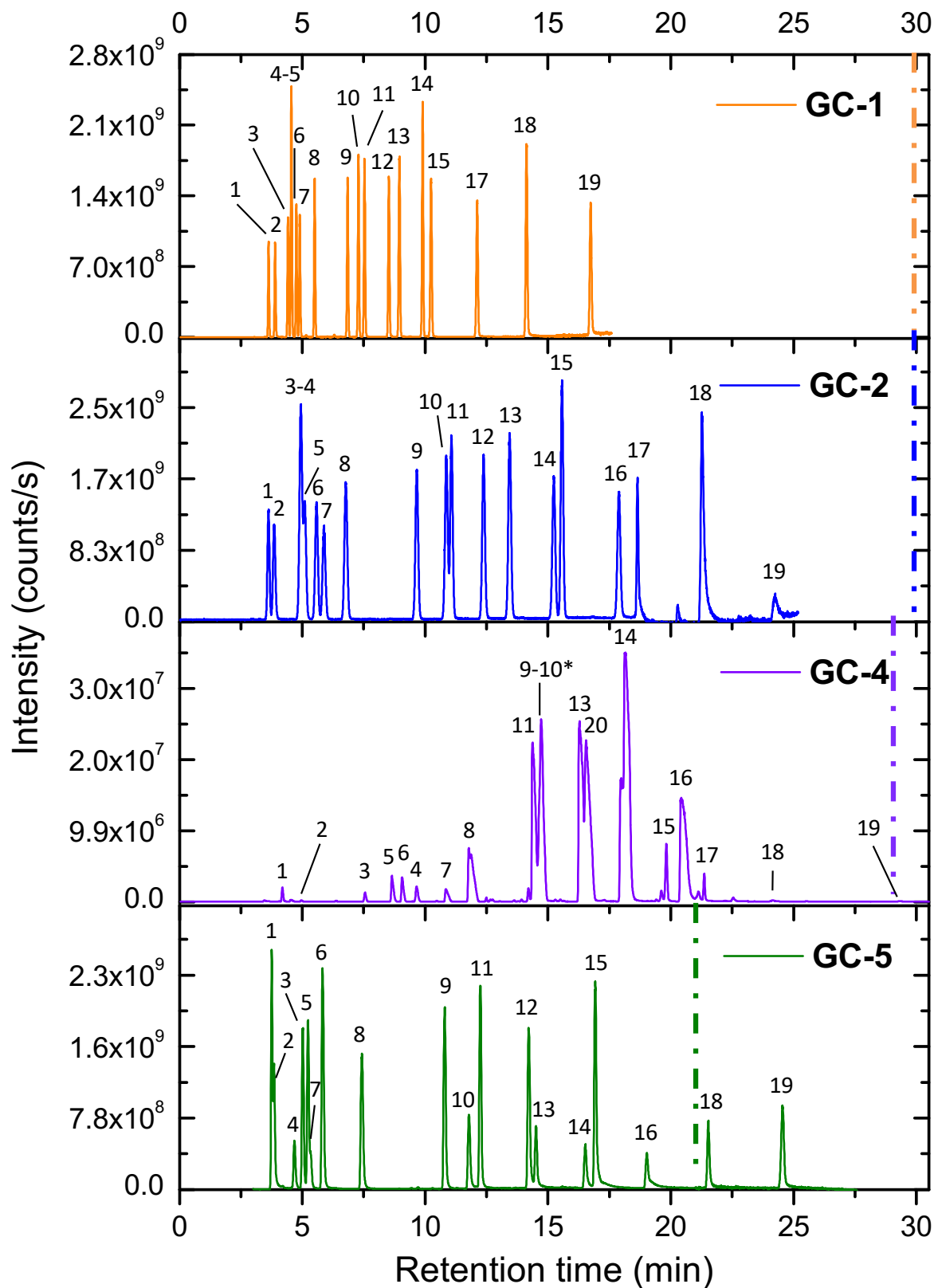


**Figure 3.** Evolution of the HEPT (mm) as a function of the mean linear carrier gas velocity  $\bar{u}$  ( $\text{cm}\cdot\text{s}^{-1}$ ) for the SAM-GC columns doted of liquid stationary phases.  $H$  (mm) is plotted in function of  $\bar{u}$  in  $\text{cm}\cdot\text{s}^{-1}$ . Points correspond to the experimental data and the lines to the fits plotted from the Van-Deemter Golay equation. The carrier gas velocities, corresponding to pressures measured in flight, were represented, when possible, by a black line, or theoretically evaluated. Crosses correspond to the  $H$  calculated from the flight data of dichloromethane, a chlorohydrocarbon systematically detected and present in all flight chromatograms.

Figure 4



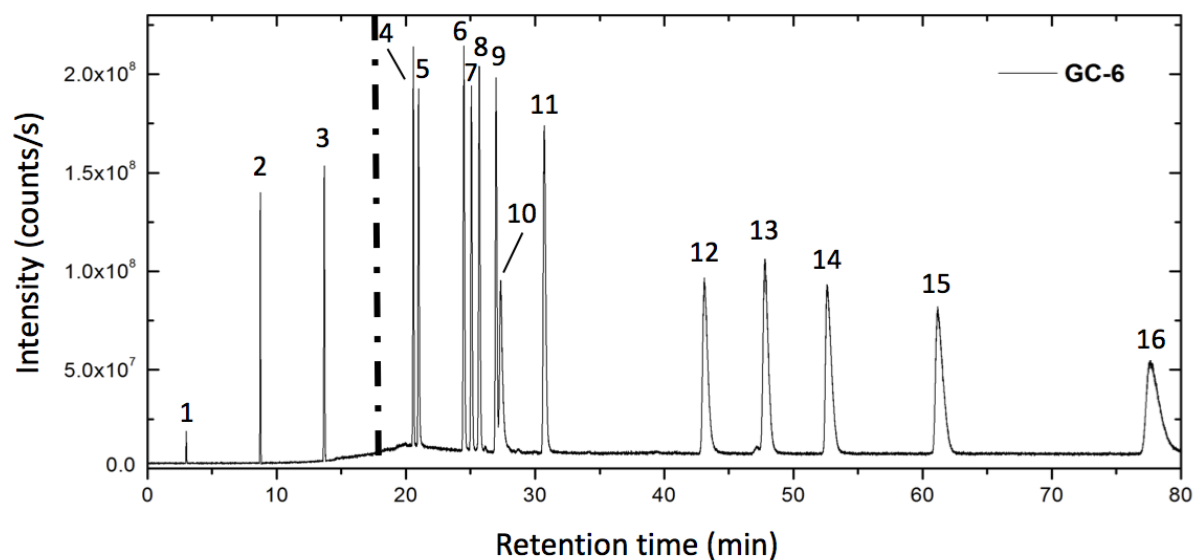
**Figure 4.** Evolution of  $\ln(k')$  in function of  $1000/T$  for the chlorinated compounds on the SAM-GC columns from channels GC-1, GC-2, GC-4, GC-5 and GC-6. Experimental data were obtained for a temperature range between 30 and 200°C corresponding to the extreme temperatures used for SAM. A linear regression has been fitted to the experimental data points on the range of the figure.

**Figure 5**

**Figure 5.** Chromatograms of the chlorohydrocarbons obtained for the channels GC-1 (MXT-20), GC-2 (MXT-5), GC-4 (Chirasil- $\beta$  Dex) and GC-5 (MXT-CLP) in SAM-flight operating conditions listed in Table 4. Compounds: 1: 2-chloropropane, 2: dichloromethane, 3: 1-chloro-2-methyl-1-propene, 4: trichloromethane, 5: 3-chloro-2-methyl-1-propene, 6: 1-chlorobutane, 7: tetrachloromethane, 8: 1,2-dichloropropane, 9: 1,2-dichlorobutane, 10: chlorobenzene, 11: 1-chlorohexane, 12: 1,4-dichlorobutane, 13: 2-chlorotoluene, 14: 1,2-dichlorobenzene, 15: 1-chlorooctane, 16: 1,2,4-trichlorobenzene, 17: 1,3,5-trichlorobenzene, 18: 1,2,4,5-tétrachlorobenzene, 19: pentachlorobenzene, 20: 1-chloroheptane. Compounds marked with a star \* are co-eluted.



Figure 6



**Figure 6.** Chromatogram of the chlorohydrocarbons obtained for the channel GC-6 (Q-Plot) in SAM-flight operating conditions listed in Table 4. Compounds: 1: Non-retained compound (Air), 2: chloromethane, 3: chloroethane, 4: dichloromethane, 5: 2-chloropropane, 6: trichloromethane, 7: 1-chloro-2-methyl-1-propene, 8: 3-chloro-2-methyl-1-propene, 9: 1-chlorobutane, 10: tetrachloromethane, 11: 1,2-dichloropropane, 12: 1,2-dichlorobutane, 13: Chlorobenzene, 14: 1-chlorohexane, 15: 1,4-dichlorobutane, 16: 2-chlorotoluene.

**Table 1**

Chemical and physical properties of the 26 chlorohydrocarbons selected for this study.

Chlorohydrocarbon name	Raw chemical Formula	Molar mass [g.mol <sup>-1</sup> ]	Boiling point [°C]	Vapor pressure (at 20°C) [kPa]	N° chlorine	Aromatic	Isomerism	
							Constitution	Chiral
Chloromethane	CH <sub>3</sub> Cl	50.5	-23.8	506.1	1	-	-	-
Dichloromethane	CH <sub>2</sub> Cl <sub>2</sub>	84.9	39.6	47.0	2	-	-	-
Trichloromethane	CHCl <sub>3</sub>	119.3	61.2	21.1	3	-	-	-
Tetrachloromethane	CCl <sub>4</sub>	153.8	76.7	11.9	4	-	-	-
Chloroethane	C <sub>2</sub> H <sub>5</sub> Cl	64.5	12.5	133.3	1	-	-	-
1-chloropropane	C <sub>3</sub> H <sub>7</sub> Cl	76.5	35.7	59.2	1	-	X	-
2-chloropropane	C <sub>3</sub> H <sub>7</sub> Cl	76.5	35.7	59.2	1	-	X	-
1-chlorobutane	C <sub>4</sub> H <sub>9</sub> Cl	92.5	78.0	10.6	1	-	X	-
2-chlorobutane	C <sub>4</sub> H <sub>9</sub> Cl	92.5	78.0	10.6	1	-	X	X
1-chloro-2-methylpropene	C <sub>4</sub> H <sub>7</sub> Cl	90.5	68.0	13.5	1	-	X	-
3-chloro-2-methylpropene	C <sub>4</sub> H <sub>7</sub> Cl	90.5	71.0-72.0	13.5	1	-	X	-
2-chlorotoluene	C <sub>7</sub> H <sub>7</sub> Cl	126.6	157.0-159.0	0.4	1	X	X	-
chlorobenzene	C <sub>6</sub> H <sub>5</sub> Cl	112.5	132.0	1.2	1	X	-	-
1,2-dichlorobenzene	C <sub>6</sub> H <sub>4</sub> Cl <sub>2</sub>	147.0	180.5	0.2	2	X	X	-
1,4-dichlorobenzene	C <sub>6</sub> H <sub>4</sub> Cl <sub>2</sub>	147.0	174.0	0.2	2	X	X	-
1,2,4-trichlorobenzene	C <sub>6</sub> H <sub>3</sub> Cl <sub>3</sub>	181.4	213.0	0.1	3	X	X	-
1,3,5-trichlorobenzene	C <sub>6</sub> H <sub>3</sub> Cl <sub>3</sub>	181.4	208.0	0.1	3	X	X	-
1,2,4,5-tetrachlorobenzene	C <sub>6</sub> H <sub>2</sub> Cl <sub>4</sub>	215.9	240.0-246.0	6.7.10 <sup>-3</sup> (25°C)	4	X	X	-
Pentachlorobenzene	C <sub>6</sub> HCl <sub>5</sub>	250.3	275.0-277.0	2.0.10 <sup>-3</sup> (25°C)	5	X	-	-
Hexachlorobenzene	C <sub>6</sub> Cl <sub>6</sub>	284.8	323.0-326.0	1.4.10 <sup>-6</sup>	6	X	-	-
1,2-dichloropropane	C <sub>3</sub> H <sub>6</sub> Cl <sub>2</sub>	112.9	96.0	5.3	2	-	X	X
1,2-dichlorobutane	C <sub>4</sub> H <sub>8</sub> Cl <sub>2</sub>	127.0	125.0	3.7 (32°C)	2	-	X	-
1,4-dichlorobutane	C <sub>4</sub> H <sub>8</sub> Cl <sub>2</sub>	127.0	161.0-163.0	0.5	2	-	X	-
1-chlorohexane	C <sub>6</sub> H <sub>13</sub> Cl	120.6	134.0	NA	1	-	X	-
1-chloroheptane	C <sub>7</sub> H <sub>15</sub> Cl	134.6	159.0-161.0	0.7 (34°C)	1	-	X	-
1-chlorooctane	C <sub>8</sub> H <sub>17</sub> Cl	148.6	183.0	13.6 (25°C)	1	-	X	-

**Table 2**

Spare column specifications used for laboratory experiments.

SAM Channel number Column name	Column type	Stationary phases	Target molecules
GC1 MXT-20	WCOT	80% polydimethylsiloxane with 20% phenyl	Medium weight (C <sub>5</sub> -C <sub>15</sub> )
GC2 MXT-5	WCOT	95% polydimethylsiloxane with 5% phenyl	High weight > C <sub>15</sub>
GC4 Chirasil-β dex	WCOT	Polydimethylsiloxane with β cyclodextrin	Medium weight and enantiomers (C <sub>5</sub> -C <sub>15</sub> )
GC5 MXT-CLP	WCOT	Polydimethylsiloxane with phenyl and cyanopropyle	Medium weight (C <sub>5</sub> -C <sub>15</sub> )
GC6 MXT-Q	PLOT	Divinylbenzene	Light weight (C <sub>1</sub> -C <sub>4</sub> )

**Table 3.** Summary of the values relative to the efficiency of the SAM-GC columns with liquid stationary phases: H range (minimum and maximum), the H<sub>SAM</sub> estimated when flight data were available, the optimal carrier gas velocity compared to the carrier gas velocities measured in SAM for each corresponding column or theoretically calculated and the estimated loss of efficiency in percentage compared to their laboratory capabilities for each column that has been used in flight so far.

Values relative to efficiency	GC-1		GC-2		GC-4		GC-5	
	35°C	185°C	35°C	185°C	35°C	185°C	35°C	185°C
H (mm)	0.5-1.0	0.8-1.4	1.0-1.3	1.8-3.0	1.2-2.8	0.9-3.5	1.6-2.3	0.5-0.8
H <sub>SAM</sub> (when applicable)	NA	NA	NA	NA	1.5	NA	2.65	NA
$\bar{u}_{opt}$ (cm.s <sup>-1</sup> )	15-25	15-20	15-20	11-19	13-20	10-13	13-19	24
$\bar{u}_{SAM}$ or $\bar{u}_{theoretical}$ (cm.s <sup>-1</sup> )	16.66	12.82	16.66	12.82	15.7 (40°C)	13.7	16.66	12.8
Estimated loss of efficiency (~%)	8	15	4-8	25	0-8	14	4	46

**Table 4.** Values of k' and -ΔH for the 5 SAM-GC columns studied. K' is given for each compound at 100°C. The -ΔH values were calculated from the slopes of the straight line ln(k') as a function of 1000/T from Figure 4.

Compound	GC-1		GC-2		GC-4		GC-5		GC-6	
	k' at 100°C	-ΔH (kcal. mol <sup>-1</sup> )	k' at 100°C	-ΔH (kcal. mol <sup>-1</sup> )	k' at 100°C	-ΔH (kcal. mol <sup>-1</sup> )	k' at 100°C	-ΔH (kcal. mol <sup>-1</sup> )	k' at 170°C	-ΔH (kcal. mol <sup>-1</sup> )
Dichloromethane	0.08	3.57	0.08	2.90	0.11	3.37	0.06	2.64	1.11	5.26
1,2-dichloropropane	0.27	4.22	0.24	3.32	0.56	4.77	0.20	3.04	5.43	6.71
Chlorobenzene	0.79	4.46	0.64	3.95	1.13	5.80	0.46	3.94	15.28	7.15
2-chlorotoluene	2.76	5.30	1.31	3.78	2.19	5.38	0.86	3.83	27.53	5.47
1,2,4-trichlorobenzene	7.00	4.15	5.25	5.05	9.78	6.56	3.36	4.58	-	-

**Table 5.** Temperature programs applied in laboratory to the SAM spare columns. The temperature programs used for the channels GC-4 and 5 are identical to those used on the SAM-flight instrument. The program temperature of the GC-1 channel is identical to the flight one except that no plateau at the initial temperature was used. Those used for the columns of the GC-2 and GC-6 channels are predictive since the related columns have not been used on Mars yet.

Chromatographic column	Temperature program	Maximum time of analysis
MXT-20 (GC-1)	Ti = 30°C - 15°C.min <sup>-1</sup> ramp up to 175°C then 10° C.min <sup>-1</sup> rate up to Tf = 250°C	30 min
MXT-5 (GC-2)	Ti = 40°C for 5 min – then 10° C.min <sup>-1</sup> rate up to Tf = 190°C	30 min
Chirasil-β Dex (GC-4)	Ti = 40°C for 5.8 min then 10° C.min <sup>-1</sup> rate up to Tf = 190°C	29 min
MXT-CLP (GC-5)	Ti = 35°C for 6.3 min then 10° C.min <sup>-1</sup> rate up to Tf = 185°C	21 min
MXT PLOT-Q (GC-6)	Ti = 40°C for 5 min then 10° C.min <sup>-1</sup> rate up to Tf = 190°C	18 min

**Table 6.** Retention times (RT) of the chlorohydrocarbons detected with the SAM instrument, or potentially present in the gases released by future martian solid samples analysed with the instrument. They are given in minutes in SAM-flight operating conditions for each SAM spare GC column. For each column, the double-line indicates the current maximal time of analysis for each SAM-GC column. ND: Non-detected.

Compound	RT (min) GC-1	RT GC-2	RT GC-4	RT GC-5	RT GC-6
Non retained compound (Air: $t_0$ )	3.00	2.98	3.07	2.98	3.00
Chloromethane	3.20	3.15	3.24	3.12	8.74
Chloroethane	3.42	3.25	3.61	3.37	13.70
2-Chloropropane	3.63	3.62	4.19	3.76	20.60
Dichloromethane	3.89	3.87	4.97	3.83	21.00
1-chloropropane	3.90	4.06	5.10	4.09	21.92
2-chlorobutane (chiral)	4.34	4.90	7.50- 7.58	4.66	25.30
1-Chloro-2-Methyl-1-Propene	4.44	5.01	7.55	5.00	25.09
Trichloromethane	4.55	4.99	9.65	4.68	24.50
3-Chloro-2-Methyl-1-Propene	4.56	5.22	8.65	5.21	25.70
1,2-dichloroethane	4.76	5.84	8.50	5.30	26.25
1-Chlorobutane	4.89	5.81	9.06	5.82	26.84
Tetrachloromethane	5.02	6.04	10.85	5.33	27.36
1,2-Dichloropropane (chiral)	5.52	6.95	11.77- 11.87	7.39	30.74
1,2-Dichlorobutane	6.85	9.90	14.72	10.85	43.13
Chlorobenzene	7.29	11.13	14.66	11.78	47.83
1-Chlorohexane	7.53	11.34	14.38	12.27	51.14
1,4-Dichlorobutane	8.53	12.68	17.99	14.27	60.05
2-Chlorotoluene	8.62	13.76	16.29	14.50	77.64
1-Chloroheptane	8.97	14.15	16.55	14.85	84.21
1,4-Dichlorobenzene	9.85	15.34	18.15	15.85	101.60
1,2-Dichlorobenzene	9.90	15.57	19.62	16.58	106.30
1-Chlorooctane	10.27	15.91	19.82	16.86	154.32
1,2,4-Trichlorobenzene	11.34	17.89	20.43	18.18	241.33
1,3,5-Trichlorobenzene	12.12	18.28	21.36	19.12	251.13
1,2,4,5-Tetrachlorobenzene	14.13	21.26	24.16	21.53	ND
Pentachlorobenzene	16.74	24.25	29.32	24.55	ND
Hexachlorobenzene	ND	ND	ND	ND	ND