Planetary and Space Science 122 (2016) 38–45

Contents lists available at ScienceDirect

Planetary and Space Science

journal homepage: www.elsevier.com/locate/pss

Evaluation of the robustness of chromatographic columns in a simulated highly radiative Jovian environment

C. Freissinet [a,b,*], S.A. Getty [a], M.G. Trainer [a], D.P. Glavin [a], P.R. Mahaffy [a], H.L. McLain [a], M. Benna [a,c]

[a] NASA Goddard Space Flight Center, Planetary Environments Laboratory, Greenbelt 20771, MD, USA
[b] NASA Postdoctoral Program, Oak Ridge Associated Universities, Oak Ridge 37830 TN, USA
[c] University of Maryland Baltimore County, Center for Space Science and Technology, Baltimore 21250, MD, USA

ARTICLE INFO

Article history:
Received 15 October 2015
Received in revised form
18 December 2015
Accepted 6 January 2016
Available online 15 January 2016

Keywords:
Capillary columns stationary phases
Radiations
Electrons
Icy moons
Gas chromatography mass spectrometry
Organics

ABSTRACT

Gas chromatography mass spectrometry (GCMS) is currently the most widely used analytical method for *in situ* investigation of organic molecules in space environments. Various types of GC column stationary phases have been, are currently, or will be used at the different solar system bodies including Mars, the Moon, Titan and comets. However, GCMS use in highly radiative environments such as Jupiter and its moons has never been explored and raises questions on the robustness of GC columns and stationary phases to extreme radiation. In this study, several types of GC columns were irradiated by high-energy electrons and protons in order to simulate the harsh conditions of a journey through Jupiter's radiation belts. Post-irradiation characterization shows that the three types of columns investigated, DB-5MS, CP-Chirasil-Dex CB and GS-GasPro, maintained their peak resolution and general separation performance after the radiation exposure. These results demonstrate that GCMS techniques can be applied to study the space environment of Jupiter's icy moons with no need for substantial radiation shielding of the columns.

1. Introduction

Europa and Mars are two prime targets in the search for extraterrestrial life in our solar system. NASA is currently targeting the Jovian environment to investigate if it could harbor conditions suitable for life. The Europa Multiple Flyby Mission (EMFM) is scheduled to conduct detailed reconnaissance of Jupiter's moon Europa. This increased interest in Europa raises the question of the instruments capabilities and limits in this highly radiative environment. An *in situ* investigation by a GCMS in a Jovian environment would help to elucidate the simple and complex organic composition of the exospheres and surfaces of key planetary targets, such as Jupiter's moons. For example, this technique might be applied on material collected on a flythrough of Europa's exosphere and possibly even through the plumes detected from Hubble Space Telescope observations (Roth et al., 2014). The GCMS technique has the capability to separate and identify volatile inorganic and organic molecules, either present in the atmosphere by direct analysis, or after volatilization of the compounds by pyrolysis of aerosols or solid samples (Sternberg et al., 2007). GC column retention and selectivity result from the partitioning of the molecules between the stationary phase (inner coating) and the mobile phase, a mechanism that may be sensitive to damage and degradation of column performance. In certain harsh space environments, modification of the chemical properties of the stationary phase could progressively degrade performance over the duration of a mission. Other possible degradation mechanisms could include extreme bleeding of the stationary phase that may lead to a loss of detection efficiency and potentially to obstruction of the column or damage to the detector. Thermal damage is the most common cause of degradation of capillary GC columns, especially in the presence of oxygen. Although no damage is observed to a column used below a recommended temperature limit, overheating of the column results in accelerated degradation of the stationary phase and tubing surface, causing permanent loss of efficiency.

Robustness of GC columns to vibration, long periods of reduced environment pressure, drastic temperature variations and low-levels of radiation (with a maximum of 14 krad) has previously been demonstrated in the framework of the Rosetta mission (Meierhenrich et al., 2013; Szopa et al., 2002, 2014). Some GC columns were qualified for operations over temperatures that range from −50 to 300 °C and can survive at much lower temperatures. *In situ* performance of the columns have been well demonstrated and documented over the previous Viking mission (Biemann et al., 1977). Also, GCMS is successfully

* Corresponding author at: NASA Goddard Space Flight Center, Planetary Environments Laboratory, Greenbelt 20771, MD, USA. Tel.: +1 301 614 6854.
E-mail address: caroline.freissinet@nasa.gov (C. Freissinet).

http://dx.doi.org/10.1016/j.pss.2016.01.004
0032-0633/

operating on Sample Analysis at Mars (SAM) onboard the Curiosity rover since November 2012 (Freissinet et al., 2015). The GCMS of the ExoMars 2018 Mars Organic Molecule Analyzer (MOMA) experiment is under development and it can be expected that the performances should be similar to those of the SAM experiment, considering the similar environmental conditions. However, even though the Jovian environment has been considered for GCMS *in situ* exploration (Gershman et al., 2003), the robustness of GC columns under such doses of radiation has never been explored.

This study explores the tolerance of GC columns to high-doses of energetic particles in anticipation of future exploration of Jupiter's icy moons (particularly Europa). The astrobiological potential of these moons could be directly assessed by a GCMS technique by sampling the exosphere, including sputtered surface species, or those brought into space by a plume of water released from a deep source. During such a mission in Jupiter's high-radiation environment, the GC columns would be exposed to a very high-dose of ionizing radiation with energies up to tens of MeV (Paranicas et al., 2007b). The Jovian radiation environment is dominated by energetic electrons from hundreds of keV to hundreds of MeV. However, the presence of a moon substantially reduces the electron fluence compared to a similar Jovian orbital distance far from a moon. The near-space environment has much lower ion and electron fluxes than the surrounding medium, even for the satellite Europa which has no permanent magnetic field of its own (Paranicas et al., 2007a). The electron and proton fluences have been estimated for a flight mission to Europa in the Environmental Requirements Document released by NASA Jet Propulsion Laboratory (JPL Europa Clipper Mission Environmental Requirements Document, 2014). To assess the potential damage that would affect the columns, we performed a proton and electron irradiation of a set of typical GC columns at the NASA Goddard Space Flight Center Radiation Effects Facility (REF), to reproduce the radiation environment in flight configuration, based on the estimated fluences expected for a EMFM-like mission. The GC columns were coated with three types of representative stationary phases: one Wall-Coated Open Tubular (WCOT) polysiloxane-based coating column (DB-5), one WCOT chiral phase column (Chirasil-β-Dex) and one Porous Layer Open Tubular (PLOT) column (GasPro). The chromatographic performance of each column was characterized prior to and after irradiation by injection of several key volatile compounds, representative of the different families of chemicals potentially present at Europa. The analysis of the compounds response includes their retention times, peak area, peak width at half-height and resolution.

2. Material and methods

2.1. GC columns

Evaluation of the column performance was performed on three capillary columns: an Agilent GS-GasPro fused silica column (PLOT-30 m in length × 0.32 mm in inner diameter), an Agilent DB-5MS fused silica column (WCOT-30 m in length × 0.25 mm in inner diameter × 0.25 μm in film thickness) and an Agilent CP-Chirasil-β-Dex CB fused silica column (WCOT-25 m × 0.25 mm × 0.25 μm). These three GC columns represent a diversity of stationary phases for separation of a wide range of molecules. Column 1 (GS-GasPro) is a PLOT-type column, which can be compared to the PLOT GC Carbobond on SAM instrument onboard the Curiosity Rover (Mahaffy et al., 2012), or to the PLOT Carbobond column on the COmetary and SAmpling and Composition (COSAC) experiment onboard Rosetta (Goesmann et al., 2007). Despite all being PLOT, these stationary phases differ, as it is a silica gel in the GS-GasPro and a carbon molecular sieve in Carbobond. The stationary phase of Column 1 is devoted to the analysis of noble and permanent gases and light hydrocarbons, allowing separation of CO from N_2 and detection of up to C_6 organics. Both Columns 2 (DB-5-MS) and 3 (Chirasil-β-Dex) are WCOT-type columns. Column 2 has a stationary phase similar to the SAM WCOT MXT-5 and to the general purpose RXT-5 column on the Mars Organic Molecule Analyzer (MOMA) instrument slated for the ExoMars 2018 mission. It is a general purpose non-polar stationary phase column used for separating medium to high molecular weight organics including aromatic hydrocarbons and other semi-volatiles compounds. Column 3 has the same phase than SAM-GC Chirsil-β-Dex for a chiral separation of enantiomeric compounds. This column is also present on the COSAC experiment and is planned to be one of the four GC columns on MOMA. All 3 columns investigated are bonded-type stationary phases to ensure the best robustness and least particle loss. All columns were conditioned a first time for the pre-irradiation analyzes, and conditioned a second time after irradiation before the post-irradiation analyzes Table 1.

2.2. Gases and reagents

The gas mixture used to characterize Column 1 (GS-GasPro) was an equivolume mixture of 5 cylinders: methane + ethane + propane + CO/H_2 1:1 + noble gas mix. The noble gas mix was composed of Ne (10%) + Ar (10%) + Kr (10%) + Xe (10%) in He balance (60%). The methane, ethane and noble gas mixture were acquired from MG Industries, the propane from Scott Specialty Gases and the CO/H_2 mixture was from Air Liquide. 100 μL of the gas mix was injected to the GCMS with a gas-tight syringe through the injector septum, with a split ratio of 1:10. The He carrier gas (purity 99.9995%) in the GC column was set at a constant flow of 2 mL min^{-1}. The oven program was set to start at −30 °C with a 2 min hold, then heated to 100 °C at a rate of 10 °C min^{-1} and to 260 °C at a rate of 20 °C min^{-1} with a 30 min hold at 260 °C. The gases were measured through Total Ion Chromatogram (TIC) mode for xenon, ethane and propane, and through Extracted Mass Chromatogram (EMC) mode for neon (*m/z* 20), methane (*m/z* 16) and krypton (*m/z* 84). Neon was used as the non-retained compound to determine the dead time.

Liquid standards, all with a 97% minimum purity, were purchased from Sigma-Aldrich. For the Column 2 (DB-5MS) investigation, an equivolume mixture of 17 compounds was prepared,

Table 1
Details of the GC columns tested.

Column	Wall	Type	Column specs	Stationary phase	Targets
Column 1 GS-GasPro	Fused silica	PLOT	30 m × 0.32 mm	Bonded silica	Inorganic gases, light hydrocarbons
Column 2 DB-5MS	Fused silica	WCOT	30 m × 0.25 mm × 0.25 μm	5% diphenyl 95% dimethyl polysiloxane	Wide range of hydrocarbons and semi-volatiles, aromatics
Column 3 CP-Chirasil-Dex CB	Fused silica	WCOT	25 m × 0.25 mm × 0.25 μm	β-cyclodextrin bonded to dimethylpolysiloxane backbone	Enantiomers of light and medium MW alcohols, aromatics, hydrocarbons and esters