



# Evaluating the robustness of the enantioselective stationary phases on the Rosetta mission against space vacuum vaporization

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## Abstract

The European Space Agency's Rosetta mission was launched in March 2004 in order to reach comet 67P/Churyumov–Gerasimenko by August 2014. The Cometary Sampling and Composition experiment (COSAC) onboard the Rosetta mission's lander "Philae" has been designed for the cometary *in situ* detection and quantification of organic molecules using gas chromatography coupled to mass spectrometry (GC–MS). The GC unit of COSAC is equipped with eight capillary columns that will each provide a specific stationary phase for molecular separation. Three of these stationary phases will be used to chromatographically resolve enantiomers, as they are composed of liquid polymers of polydimethylsiloxane (PDMS) to which chiral valine or cyclodextrin units are attached. Throughout the ten years of Rosetta's journey through space to reach comet 67P, these liquid stationary phases have been exposed to space vacuum, as the capillary columns within the COSAC unit were not sealed or filled with carrier gas. Long term exposures to space vacuum can cause damage to such liquid stationary phases as key monomers, volatiles, and chiral selectors can be vaporized and lost in transit. We have therefore exposed identical spare units of COSAC's chiral stationary phases over eight years to vacuum conditions mimicking those experienced in space and we have now investigated their resolution capabilities towards different enantiomers both before and after exposure to space vacuum environments. We have observed that enantiomeric resolution capabilities of these chiral liquid enantioselective stationary phases has not been affected by exposure to space vacuum conditions. Thus we conclude that the three chiral stationary phases of the COSAC experiment onboard the Rosetta mission lander "Philae" can be considered to have maintained their resolution capacities throughout their journey prior to cometary landing in November 2014.

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## 1. Introduction and motivation

The cornerstone mission "Rosetta" of the European Space Agency (ESA) was launched on March 2, 2004 in order to reach its target comet 67P/Churyumov–

Gerasimenko by August 2014 (Schulz et al., 2009). The landing unit "Philae" onboard this mission has been designed to separate from the Rosetta orbiter in November 2014 for soft-landing on the cometary surface (Biele and Ulamec, 2008). Philae has been equipped with ten different instruments, including the Cometary Sampling and Composition experiment (COSAC) (Goesmann et al., 2007, 2009). The main aim of the COSAC experiment is

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to provide the first *in situ* identification and quantification of organic molecules present in cometary ice. The COSAC instrument consists of a multi-column gas chromatograph coupled to a time-of-flight mass spectrometer (GC-TOF/MS). It is composed of eight parallel capillary columns and each of the columns is equipped with a different stationary phase. Three of these stationary phases were selected in order to search for and resolve any chiral compounds present on comet 67P as a means towards understanding the origins of the asymmetry present in all living organisms on Earth (Meinert et al., 2011; Evans et al., 2012). The enantioselective stationary phases of the COSAC GC include chiral moieties to allow for the separation of different types of molecular enantiomers present in the cometary ice. Frank developed the Chirasil-Val column (Frank et al., 1977) although it wasn't commercialized for several years afterwards. König did early cyclodextrin gas chromatography (König et al., 1988) and Armstrong invented the Chiraldex G-TA column (Li et al., 1990). Enantiomers of chiral amino acids (Thiemann and Meierhenrich, 2001), carboxylic acids (Meierhenrich et al., 2001a), hydrocarbons (Meierhenrich et al., 2001b, 2003), alcohols (Thiemann et al., 2001), diols and amines have all been demonstrated to be separable by the selected chiral stationary phases for the COSAC experiment. This experiment thus includes the first scientific instrumentation equipped with chiral stationary phases for the extraterrestrial determination and quantification of chiral molecules.

Prior to the launch of the Rosetta mission in 2004, all of the capillary columns of the COSAC experiment and their liquid stationary phases were subjected to irradiation tests and short-term thermo vacuum tests to simulate both launch and space conditions. After these tests were completed, no damage was observed to have occurred to any of the selected stationary phases (Szopa et al., 2002). However, it remained unknown whether long-term exposure to space vacuum of liquid stationary phases containing chiral moieties might provoke the evaporation of key monomers, volatiles and chiral units within the stationary phases. We have therefore exposed identical spare models of COSAC's chiral stationary phases to space vacuum conditions for eight years. We have now tested the resolution of a series of specific enantiomers both prior to and post-vacuum exposure and we can report that the integrity of the chiral resolution capacities of these columns remains intact.

## 2. Experimental part

Chirasil-Dex CB **1** (10 m length ( $L$ ), 0.25 mm inner diameter ( $ID$ ), 0.25  $\mu$ m film thickness ( $f$ ), Varian-Chrom-pack, Middelburg, the Netherlands), Chirasil-I-Val **2** ( $L = 12.5$  m,  $ID = 0.25$  mm,  $f = 0.12$   $\mu$ m, Varian-Chrom-pack) and Cyclodextrin G-TA **3** ( $L = 10$  m,  $ID = 0.25$  mm,  $f = 0.125$   $\mu$ m, Astec, Whippany, USA) stationary phases were chosen as the enantioselective chromatographic phases for the COSAC instrumentation (Goesmann et al., 2007; Giri et al., 2013). From 2005 to 2013 identical spare

models of these three capillary columns have been exposed to a vacuum of  $10^{-2}$  mbar in order to mimic the exposure of the COSAC experiment flight columns to space vacuum conditions. A dry pump was used to avoid oil contamination. The space vacuum in COSAC was much better but this is considered not to affect the results of the current study. The three tested capillary columns were – such as the COSAC flight columns – not sealed and open. The vacuum tests were performed at room temperature as the COSAC flight columns are located in the warm compartment of Rosetta's Philae lander with  $T \geq -20$  °C. The flight columns have never been exposed to space temperature. Prior being exposed to these long-term vacuum conditions, the capillary columns were tested with three chiral analytes in order to provide a baseline of separation capabilities. Due to the high stability of their *N*-trifluoroacetic acid (*N*-TFA) derivatives for more than 8 years, 2-aminoheptane, 1-aminoindane, and 2-methylpiperidine were selected as chiral analytes in form of their *N*-trifluoroacetic acid (*N*-TFA) derivatives. It is not anticipated that these *N*-TFA derivatives will be found in cometary ices (a list of Rosetta COSAC relevant molecules can be found at [www.unice.fr/meierhenrich/COSAC.html](http://www.unice.fr/meierhenrich/COSAC.html)); these molecules were chosen purely for their stability as chiral analytes.

Prior to evaluation, all columns were conditioned for 2 h at 190 °C in both 2005 and in 2013. The injector temperature was set to 230 °C and the transfer line was set at 200 °C. A split injection of 1:100 was applied as well as a solvent delay of 2 min. The columns were programmed with 2 °C/min from 40 °C to 180 °C, where the temperature was kept constant for 30 min. The carrier gas (He) flow was adjusted to 1.8 mL/min. In case of the Cyclodextrin G-TA phase the GC oven temperature was set to increase at 5 °C/min.

## 3. Results and discussion

Fig. 1 represents the gas chromatographic chiral resolution of the enantiomers of 2-aminoheptane (*N*-TFA), 1-aminoindane (*N*-TFA), and 2-methylpiperidine (*N*-TFA) analytes recorded on column **1**. The lower line illustrates the enantiomer resolution observed in July 2005 prior to vacuum exposure; the upper line depicts the resolution in June 2013 after 8 years of vacuum exposure. The gas chromatogram in Fig. 1 illustrates that the enantioselectivity of the Chirasil-Dex CB stationary phase **1** has not been degraded or damaged by exposure to high vacuum environments in space.

The increase in chromatographic noise observed in 2013 relative to 2005 is not attributable to the chiral stationary phase and is due to the quadrupole mass spectrometric detector. The resolution  $R_S$  of each pair of enantiomers was calculated by

$$R_S = \frac{2(t_{R2} - t_{R1})}{w_{h1} + w_{h2}}$$

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