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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 **Co**metary **Sa**mpling and **Co**mposition 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.

Keywords: Chiral stationary phases; Column robustness; COSAC; Enantiomer separation; Gas chromatography; Rosetta

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 **Co**metary **Sa**mpling and **Co**mposition 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 μm film thickness (f), Varian-Chrompack, Middelburg, the Netherlands), Chirasil-l-Val **2** ($L = 12.5$ m, $ID = 0.25$ mm, $f = 0.12$ μm, Varian-Chrompack) and Cyclodextrin G-TA **3** ($L = 10$ m, $ID = 0.25$ mm, $f = 0.125$ μm, 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 $T \geqslant -20$ °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); 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

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

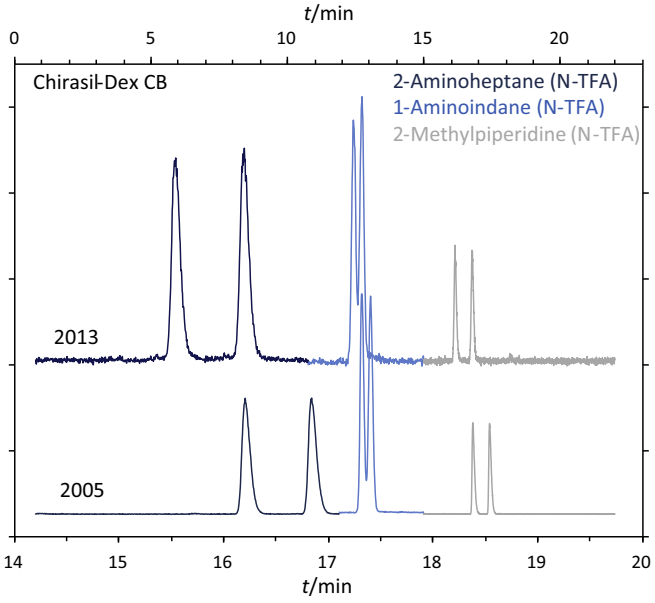

Fig. 1. Enantiomeric resolution of three chiral analytes as recorded on the Chirasil-Dex CB stationary phase **1** before (2005) and after (2013) exposure to high vacuum conditions. 2-Aminoheptane (dark blue), 1-aminoindane (light blue), and 2-methylpiperidine (grey) enantiomers were resolved as *N*-TFA derivatives. The retention times of 2-methylpiperidine follow the secondary *x*-axis. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

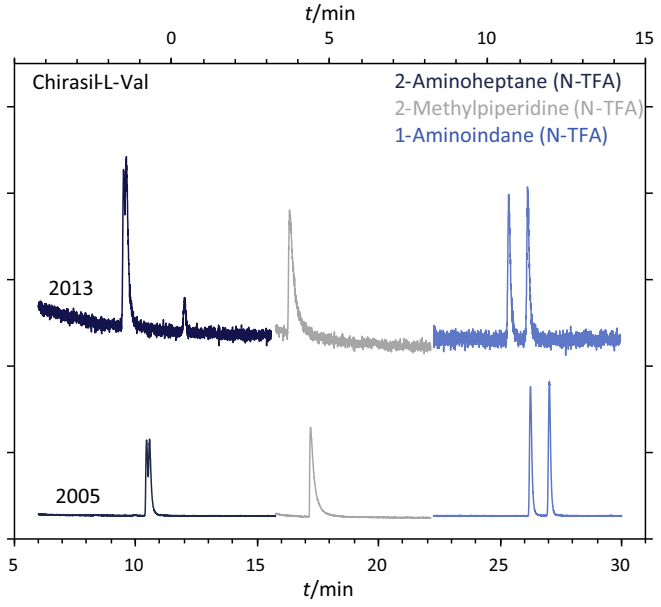

Fig. 2. Enantiomeric resolution of three chiral analytes by the Chirasil-L-Val stationary phase **2** before (2005) and after (2013) exposure to high vacuum. 2-Aminoheptane (dark blue), 2-methylpiperidine (grey), and 1-aminoindane (light blue) enantiomers were resolved as *N*-TFA derivatives. The retention times of 2-methylpiperidine follow the secondary *x*-axis. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

where t_{R1} and t_{R2} are the retention times of the first and second eluting enantiomer and w_h is their peak width at peak base (Table 1).

The chromatographic enantiomer resolution capabilities of the Chirasil-L-Val stationary phase **2** before and after vacuum exposure is shown in Fig. 2. It has been demonstrated that the enantiomers of 1-aminoindane (*N*-TFA) could be baseline-resolved into enantiomers both before and after vacuum exposure. It is known that 2-methylpiperidine (*N*-TFA) enantiomers cannot be resolved using the Chirasil-L-Val stationary phase, so this lack of resolution was not of great concern in this instance. The enantiomers of 2-aminoheptane (*N*-TFA) were not fully resolved either in 2005 or in 2013: the resolution achieved for these species is indicated in Table 1 and the degree of enantiomeric separation does not appear to have significantly changed over the eight year period of vacuum exposure. Thus we can conclude that the Chirasil-L-Val stationary phase has also not lost any resolution capacity after being exposed to the high vacuum conditions of space for long periods of time.

Table 1
Enantiomeric resolution R_S of the three enantioselective stationary phases **1**–**3** of COSAC for 3 *N*-TFA derivatized chiral analytes as recorded pre-(2005) and post-(2013) vacuum exposure.

Analyte	R_S (2005)	R_S (2013)
1-Aminoindane on **1**	1.16	1.08
2-Methylpiperidine on **1**	3.27	3.43
2-Aminoheptane on **1**	3.99	3.73
1-Aminoindane on **2**	4.21	3.33
2-Aminoheptane on **2**	0.60	0.56
1-Aminoindane on **3**	1.85	1.51
2-Aminoheptane on **3**	0.96	0.97

Error bars were determined with $\Delta R_S \cong \pm 0.2$.

The Chiraldex G-TA stationary phase is considered to be the most labile stationary phase and would be the phase most likely to experience thermal and irradiation damage. This is due to the fact that the pendant chiral cyclodextrin molecules are not actually covalently attached to the column's polymer (unlike the valine units used in Chirasil-L-Val and the cyclodextrin units used in the Chirasil-Dex CB stationary phase that are PDMS-linked). In the Chiraldex G-TA stationary phase the chiral selector is a neat amorphous liquid.

Fig. 3 depicts the chromatographic resolution capabilities of the Chiraldex G-TA stationary phase **3** for the three chosen chiral analytes before and after exposure to high vacuum conditions.

Again the enantiomeric resolution capabilities of the Chiraldex G-TA stationary phase have not significantly altered even after eight years of exposure to high vacuum. Table 1 depicts the enantiomer resolution R_S of the three chiral analytes as calculated for COSAC's three different chiral stationary phases. These data show, except for 1-aminoindane on **2**, that R_S is not significantly affected by the exposure of any of the chiral capillary columns to long-term vacuum conditions.

The retention time variation of 2-methylpiperidine on the G-TA stationary phase is due to variations in the GC

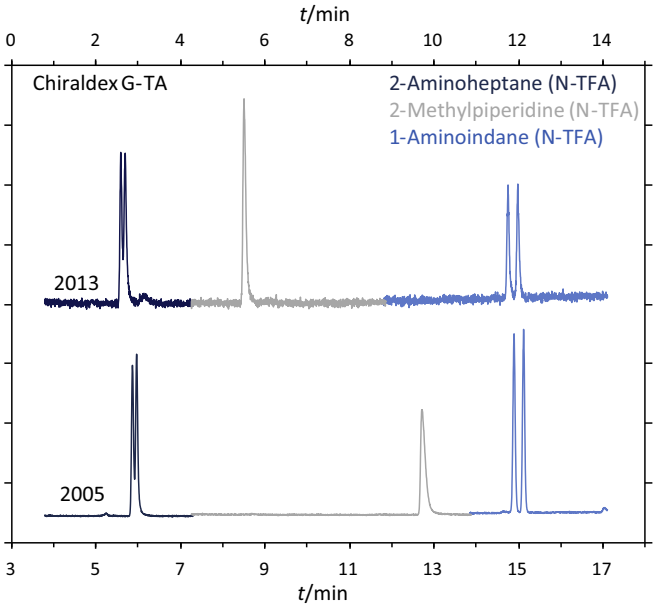

Fig. 3. Enantiomeric resolution of three chiral analytes as recorded on the Chiraldex G-TA stationary phase **3** before (2005) and after (2013) exposure to high vacuum conditions. 2-Aminoheptane (dark blue), 2-methylpiperidine (grey), and 1-aminoindane (light blue) enantiomers were resolved as their *N*-TFA derivatives. The retention times of 2-methylpiperidine follow the secondary *x*-axis. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

inlet pressure between 2005 and 2013. It is not due to effects in the stationary phase. We did not further investigate this effect because the enantiomers of 2-methylpiperidine have not been separated. This effect is probably due to inlet pressure variations because the inlet pressure of short 10 m capillary columns is difficult to stabilize, if a mass spectrometer working under high vacuum is used as detector on the outlet of the capillary column.

4. Conclusions and future work

In preparation for the chiral portion of the COSAC experiment, we have reported on the simulation of interstellar ices in the laboratory (Meierhenrich and Thiemann, 2001c) and we have identified and characterized the organic molecules present in these cometary ice simulations (Muñoz Caro et al., 2004; Meierhenrich et al., 2005) including chiral amino acids (Muñoz Caro et al., 2002; Meinert et al., 2012). The chirality of the amino acids observed during these experiments was further investigated: Due to the presence of circularly polarized (cp) electromagnetic radiation detected in interstellar star forming regions (Bailey et al., 1998) we hypothesize that cp light could induce small chiral asymmetries into amino acids under interstellar conditions (de Marcellus et al., 2011).

The chiral capillary columns of COSAC's GC onboard Rosetta's lander Philae will now allow the separation of the majority of chiral organic molecules present in the ices found on comet 67P/Churyumov–Gerasimenko. The research reported here fully confirms the capability of the chiral capillary columns to perform effective enantiomeric resolution even after lengthy exposure to the extensive high vacuum conditions present in space. Data on irradiation tests were reported previously (Szopa et al., 2002). The enantiomeric excesses that these columns will allow us to observe as part of the COSAC experiment represent a landmark attempt to evaluate interstellar chirality and will significantly enhance our understanding of the origin of the molecular asymmetry that characterizes all terrestrial life.

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References

Bailey, J., Chrysostomou, A., Hough, J.H., Gledhill, T.M., McCall, A., Clark, S., Ménard, F., Tamura, M., 1998. Circular polarization in star-formation region: implications for biomolecular homochirality. Science 281, 672–674.

Biele, J., Ulamec, S., 2008. Capabilities of Philae, the Rosetta lander. Space Sci. Rev. 138, 275–289.

De Marcellus, P., Meinert, C., Nuevo, M., Filippi, J.-J., Danger, G., Deboffle, D., Nahon, L., Le Sergeant d'Hendecourt, L., Meierhenrich, U.J., 2011. Non-racemic amino acid production by ultraviolet irradiation of achiral interstellar ice analogs with circularly polarized light. Astrophys. J. Lett. 727, L27.

Evans, A., Meinert, C., Giri, C., Goesmann, F., Meierhenrich, U.J., 2012. Chirality, photochemistry and the detection of amino acids in interstellar ice analogues and comets. Chem. Soc. Rev. 41, 5447–5458.

Frank, H., Nicholson, G.J., Bayer, E., 1977. Rapid gas chromatographic separation of amino acid enantiomers with a novel chiral stationary phase. J. Chromatogr. Sci. 15, 174–176.

Giri, C., Goesmann, F., Meinert, C., Evans, A.C., Meierhenrich, U.J., 2013. Synthesis and chirality of amino acids under interstellar conditions. Top. Curr. Chem. 333, 41–82.

Goesmann, F., Rosenbauer, H., Roll, R., Szopa, C., Raulin, F., Sternberg, R., Israel, G., Meierhenrich, U., Thiemann, W., Muñoz Caro, G.M., 2007. COSAC, the cometary sampling and composition experiment on Philae. Space Sci. Rev. 128, 257–280.

Goesmann, F., Rosenbauer, H., Roll, R., Szopa, C., Raulin, F., Sternberg, R., Israel, G., Meierhenrich, U.J., Thiemann, W., Munoz Caro, G.M., 2009. The cometary sampling and composition experiment on Philae. In: Schulz, R., Alexander, C., Boehnhardt, H., Glassmeier, K.H. (Eds.), ROSETTA – ESA's mission to the origin of the solar system. Springer, New York, pp. 633–650.

König, W., Lutz, S., Wenz, G., 1988. Modified cyclodextrins – novel, highly enantioselective stationary phases for gas chromatography. Angew. Chem. Int. Ed. 27, 979–980.

Li, W.-Y., Jin, H.L., Armstrong, D.W., 1990. 2,6-Di-O-pentyl-3-O-trifluoroacetyl cyclodextrin liquid stationary phases for capillary gas chromatographic separation of enantiomers. J. Chromatogr. 509, 303–324.

Meierhenrich, U.J., Thiemann, W.H.-P., Muñoz Caro, G.M., Schutte, W.A., Greenberg, J.M., 2001c. Simulated cometary matter as a test for enantiomer separating chromatography for use on comet 46P/wirtanen. Adv. Space Res. 27, 329–334.

Meierhenrich, U., Thiemann, W.H.-P., Rosenbauer, H., 2001a. Pyrolytic methylation assisted enantioseparation of chiral hydroxycarboxylic acids. J. Anal. Appl. Pyrolysis 60, 13–26.

Meierhenrich, U.J., Thiemann, W.H.-P., Goesmann, F., Roll, R., Rosenbauer, H., 2001b. Enantiomer separation of hydrocarbons in preparation of Rosetta's chirality-experiment. Chirality 13, 454–457.

Meierhenrich, U.J., Nguyen, M.-J., Barbier, B., Brack, A., Thiemann, W.H.-P., 2003. Gas chromatographic separation of saturated aliphatic hydrocarbon enantiomers on permethylated beta-cyclodextrin. Chirality 15, S13–S16.

Meierhenrich, U.J., Muñoz Caro, G.M., Schutte, W.A., Thiemann, W.H.-P., Barbier, B., Brack, A., 2005. Precursors of biological cofactors from ultraviolet irradiation of circumstellar/interstellar ice analogs. Chem. Eur. J. 11, 4895–4900.

Meinert, C., De Marcellus, P., Le Sergeant d'Hendecourt, L., Nahon, L., Jones, N.C., Hoffmann, S.V., Bredehöft, J.H., Meierhenrich, U.J., 2011. Photochirogenesis: photochemical models on the absolute asymmetric formation of amino acids in interstellar space. Phys. Life Rev. 8, 307–330.

Meinert, C., Filippi, J.-J., de Marcellus, P., le Sergeant d'Hendecourt, L., Meierhenrich, U.J., 2012. *N*-(2-Aminoethyl)glycine and Amino Acids in Interstellar Ice Analogues. ChemPlusChem 77, 186–191.

Muñoz Caro, G.M., Meierhenrich, U.J., Schutte, W.A., Barbier, B., Arcones Segovia, A., Rosenbauer, H., Thiemann, W.H.-P., Brack, A., Greenberg, 2002. Amino acids from ultraviolet irradiation of interstellar ice analogues. Nature 416, 403–406.

Muñoz Caro, G.M., Meierhenrich, U.J., Schutte, W.A., Greenberg, J.M., Thiemann, W., 2004. UV-photoprocessing of interstellar ice analogs: detection of hexamethylenetetramine-based species. Astron. Astrophys. 413, 209–216.

Schulz, R., Alexander, C., Boehnhardt, H., Glassmeier, K.H., Rosetta, 2009. ESA's Mission to the Origin of the Solar System. Springer, Heidelberg.

Szopa, C., Meierhenrich, U.J., Coscia, D., Janin, L., Goesmann, F., Sternberg, R., Brun, J.-F., Israel, G., Cabane, M., Roll, R., Raulin, F., Thiemann, W., Vidal-Madjar, C., Rosenbauer, H., 2002. Gas chromatography for in situ analysis of a cometary nucleus: IV. Study of capillary column robustness for space application. J. Chrom. A 982, 303–312.

Thiemann, W.H.-P., Meierhenrich, U., 2001. ESA mission ROSETTA will probe for chirality of cometary amino acids. Orig. Life Evol. Biosphere 31, 199–210.

Thiemann, W.H.-P., Rosenbauer, H., Meierhenrich, U.J., 2001. Conception of the chirality-experiment on ESA's mission ROSETTA to comet 46P/wirtanen. Adv. Space Res. 27, 323–328.