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Gas chromatography for in situ analysis of a cometary nucleus III. Multi-capillary column system for the cometary sampling and composition experiment of the Rosetta lander probe

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Abstract

The cometary sampling and composition (COSAC) experiment is one of the principal experiments of the surface lander probe of the European Space Agency Rosetta mission to be launched in January 2003. The instrument is designed for the in situ chemical analysis of a cometary nucleus as the details of the nucleus composition are of primary importance for understanding both the formation of the solar system, and the origin of life on Earth. The COSAC experiment consists of an evaporation/pyrolysis device and two analytical systems: a multi-column gas chromatograph and a high-resolution time-of-flight mass spectrometer which may either be operated alone or in a coupled mode. The gas chromatograph includes five general purpose chromatographic columns and three chiral ones, all mounted in parallel. Taking into account the chemical species potentially present in the cometary nucleus as well as the space constraints, a set of five complementary columns was selected to perform the separation and identification of the compounds present in the cometary nucleus. This set of columns includes a carbon molecular sieve porous-layer open tubular (PLOT) column used for the separation of both the noble and other permanent gases, and the C₁–C₂ hydrocarbons. A second PLOT column uses a divinylbenzene–ethylene glycol–dimethylacrylate porous polymer as stationary phase for the analysis of a wide range of C₁–C₂ organic molecules. Two complementary wall-coated open tubular (WCOT) columns with polydimethylsiloxane (PDMS) liquid stationary phases, one containing cyanopropyl–phenylsiloxane and the other diphenylsiloxane groups, are designed to target the same range of organic compounds (C₃–C₇) which could be representative of the widest range of cometary compounds. A third WCOT column with an apolar stationary phase made of non-substituted PDMS is used for the separation and identification of higher-molecular-mass compounds (up to C₁₀) and aromatic species (monoaromatic and polyaromatic). This paper describes these five general-purpose capillary PLOT and WCOT columns, selected to be used in the COSAC GC system. The analytical capabilities are examined with a special emphasis on the exobiological and planetological implications. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Stationary phases, GC; Instrumentation; Volatile organic compounds

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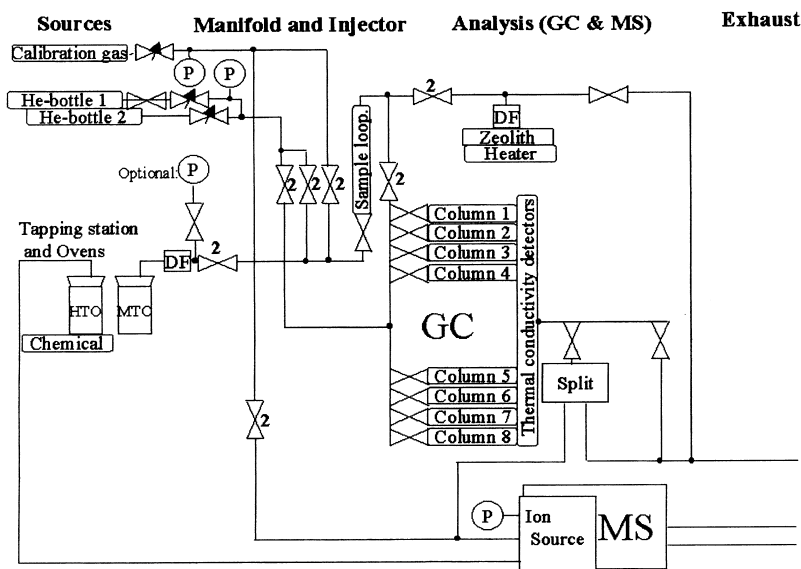


Fig. 1. Principle scheme of the COSAC experiment. Abbreviations: HTO=high-temperature oven, MTO=medium-temperature oven, DF=dust filter, P=pressure gauge, Chemical=derivatization agent.

1. Introduction

As reported in previous papers in this series [1,2], we are engaged in the development of an automatic gas chromatographic system dedicated to carry out in situ analyses of a cometary nucleus. This instrument is part of the cometary sampling and composition (COSAC) experiment (Fig. 1) [3] included in the lander of the European Space Agency (ESA) Rosetta mission [4].

The primary objective of the COSAC experiment is to analyze both the organic and inorganic species of the solid-phase nucleus. The organic fraction is expected to include a wide range of species, from highly volatile molecules such as CH_4 , HCN , HCOOH , CH_3OH and H_2CO to more complex organic molecules such as amino acids and high-molecular-mass refractory macromolecular organics; the inorganic fraction should include molecules such as H_2S , NH_3 , H_2O and permanent gases. The list of the compounds targeted by the GC subsystem developed at LISA is presented in Table 1. It includes the species detected in the gas phase and the dust of the coma of several comets, those detected in the

interstellar medium and also the species generated during experimental simulations aiming at reproducing the cometary composition [5,6]. This list is updated periodically by new ground-based measurements and simulation experimental data.

With the aim to separate and identify all the compounds listed in Table 1, several capillary columns with different solid and liquid stationary phases and with different characteristics were investigated. These studies were performed with laboratory chromatographs operating at atmospheric outlet pressure, using chemical standards mixtures representative of the target compounds. Part of these studies have already been published [1,2,7,8] and enabled one to define the best column configuration which is able to meet the measurement objectives. For that purpose the nature of the stationary phases and the geometry of the columns were optimized to fit the analytical performances of the multi-column system to both the scientific objectives and the measurement strategy accounting for the instrumentation and mission constraints. This paper describes the five capillary columns selected for the COSAC experiment and designed to give a detailed descrip-

Table 1
Cometary nucleus candidate compounds (from Ref. [1])

Detected compounds in comets (coma and tails)	Expected compounds from:		
	Experimental simulation		Interstellar comparison
Water	Formaldehyde	Methanol	Acetaldehyde
Ammonia	Paraformaldehyde	Ethanol	Acrylonitrile
Carbon monoxide	Ethanolamine	Pentanol	Methacrylonitrile
Carbon dioxide	Methylamine	2-Methyl-1-propanol	Propionitrile
Formaldehyde	Hexamethylene-tetramine	Butanediol	Isobutyronitrile
Formic acid	Ammoniac	Glycerol	Butyronitrile
Methanol	Formic acid	Ethylene glycol	Crotonitrile
Methane	Acetic acid	Methylbutanol	Aminoacetonitrile
Ethane	Lactic acid*	Acetone	2-Propanol
Acetonitrile	Glycolic acid*	Hydroxypropanone	1-Butanol
Methyl formate	Oxamic acid*	Hydroxybutanone	Ethylamine
Ethyne	Glyceric acid*	Methyl formate	Diethylene
Hydrocyanic acid	Hydroxypropionic acid	Methyl acetate	Ethyl acetate
Hydrogen isocyanide	Formamide	Methyl propionate	Heptane
Cyanoacetylene	Acetamide	Dimethyl ether	Aromatic compounds and PAHs
Sulfur dioxide	Urea*	Dimethoxymethane	
Hydrogen sulfide	Oxamide*	Methane	
Carbon sulfoxide	Bi-urea*	Ethane	
Nitrogen	Glyceramide*	Propane	
Disulfur	Glycolamide	Butane	
Argon	Aminobutyric acid*	Pentane	
	Acetonitrile	Methylpentane	
	Hydrocyanic acid	Hexane	
	Hydrogen isocyanide	Cyclopentane	
	Cyanamide*	Methylhexane	
	Cyanic acid	Glycine	
	Carbon suboxide	L-Alanine	

*: Compounds non eluted by the presented GC system without derivatization.

tion of the cometary nucleus composition (excluding chirality), by analyzing the target compounds of the Rosetta mission.

2. Experimental

2.1. Gas chromatographic instrumentation

Gas chromatographic (GC) measurements were carried out with a Varian CP-3800 gas chromatograph, equipped with two nano-thermal conductivity detection (nano-TCD) systems similar to the flight experiment ones and a linear temperature programmer. During measurements, the TCD systems were heated at 110 °C and their signals were con-

nected to a Varian Star data acquisition system. Gaseous samples were injected with two electro-pneumatic gas sampling valves (Valco, Schenkon, Switzerland), with 0.2 µl and 2 µl sampling loops heated at 120 °C, using the splitless mode. The liquid solutions were injected through a split/splitless syringe injector set in the split mode with a mean split ratio of 1:200. Experiments were also performed by simultaneously connecting two columns to the syringe injector thanks to a double hole ferrule system.

The carrier gas was helium (purity ≥ 99.995%), as helium will be used in the COSAC flight experiment. A series of three commercial filters were used for removing traces of water, hydrocarbons and oxygen in the carrier gas and improving its purity level. The

GC columns were operated isothermally at temperatures in the range of 30–90 °C, as required by the flight experiment constraints, with an absolute inlet pressure identical to the flight instrument one, i.e., 150 kPa. Outlet column pressure was atmospheric pressure.

2.2. Reagents

Liquid components were purchased from Aldrich (Strasbourg, France), Acros (Noisy-le-Grand, France) and Merck (Nogent-sur-Marne, France). The gaseous components were bought from Linde (Lyon, France) and Air Liquide (Moissy Cramayel, France). Except for formaldehyde which was diluted in water (65%), all compounds were of pure analytical grade.

When using the split/splitless syringe injector, direct injections of pure compounds and mixed samples (gas or liquid) were performed with a syringe injector septum by using Hamilton liquid (1 to 10 μ l) or gas (1 ml) syringes equipped with a tight stopcock. Gas mixtures were obtained as previously described [8].

2.3. Chromatographic columns

Considering the constraints imposed by the mission (short analysis time, low energy and carrier gas consumption) [9], a close collaboration was developed with manufacturers and the special requirements in the capillary column design were met by Varian-Chrompack (Middelburg, The Netherlands) and Restek (Bellefonte, PA, USA). It was necessary to obtain robust metallic columns of very low internal diameter (I.D.) withstanding the space instrumental constraints. Moreover, the stationary phases were selected not only on the basis of their separation characteristics, but also because of their long-term stability under the harsh conditions of the interplanetary medium, such as vacuum, radiation and strong temperature variations (flight qualification tests to be published).

The first column of the GC subsystem is a carbon molecular sieve Carbobond porous-layer open tubular (PLOT) column (15 m \times 0.25 mm I.D.) provided by Varian with a 10 μ m thick carbon porous layer bonded to the internal capillary wall. The second column is also a PLOT column with a porous

polymer made of divinylbenzene–ethylene glycol–dimethylacrylate as stationary phase (10 m \times 0.18 mm I.D.) having a 2 μ m film thickness. The third and fourth columns are wall-coated open tubular (WCOT) capillary columns (15 m \times 0.18 mm I.D.) which will analyze the same range of target organic compounds. With this aim, two complementary polysiloxane-based liquid stationary phases are used, one with 14% cyanopropylphenyl/86% dimethyl and the other with 20% diphenyl/80% dimethyl substituents with film thicknesses of 1 and 1.2 μ m, respectively. Finally the last selected column is a 100% polydimethylsiloxane (PDMS) stationary phase WCOT capillary column (10 m \times 0.18 mm I.D.) with a 0.1 μ m film thickness.

3. Results and discussion

3.1. Separation of permanent gases and hydrocarbons up to C₂

The observations of comets Hyakutake (1996) and Hale–Bopp (1995–1997) have considerably increased our knowledge about the parent molecules present in the coma, which are produced by the sublimation of the icy nucleus when the comets get close to the sun. The number of molecular species identified in the coma has practically doubled thanks to the observations of these two bright comets. Among the new molecules detected, methane (CH₄), acetylene (C₂H₂) and ethane (C₂H₆) were identified at abundance relative to water, respectively, around 1, 0.3 and 0.5% [10]. As these molecules have also been detected in interstellar molecular clouds, the collapse of which gives birth to planetary systems, the observation of similar relative abundance in the nucleus should be of prime importance for the understanding of comets' origin [11,12]. Moreover, for the first time, a noble gas (Ar) was possibly detected in the coma of the Hale–Bopp comet [13]. Detection of such gases is essential to determine the thermal history of comets, as their trapping in cometary ices depends on the temperature of formation of the ice [14]. Finally, the noble gas abundances and their isotopic ratios would enable one to evaluate the importance and the role of comets in

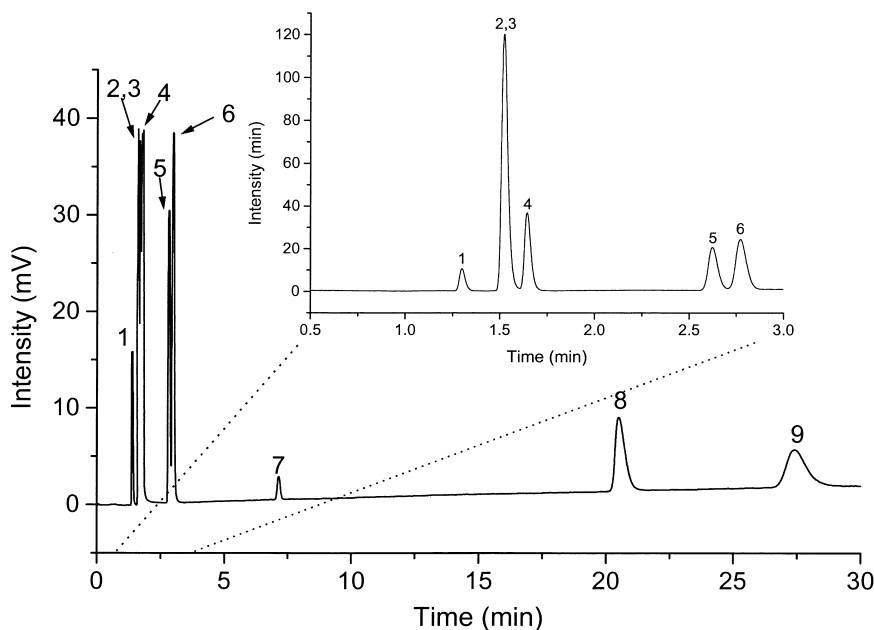


Fig. 2. Separation of the light hydrocarbons and the permanent gases (from Ref. [2]) on the Carbobond PLOT capillary column (15 m×0.25 mm I.D., $d_f=10\ \mu\text{m}$). Carrier gas: He. Detection: nano-TCD. Temperature: 30 °C. Pressure drop: 50 kPa. Peaks: (1) neon, (2) nitrogen, (3) argon, (4) carbon monoxide, (5) methane, (6) krypton, (7) carbon dioxide, (8) acetylene, (9) xenon.

bringing volatiles to form a part of their atmospheres [15].

To operate the separation of these compounds, a PLOT capillary column (Carbobond PLOT), with a carbon molecular sieve as stationary phase was selected. It is the first time that such a column has been used for this application, thus leading to a

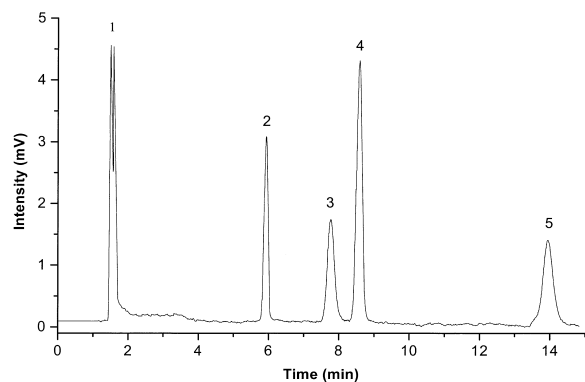


Fig. 3. Separation of the two-carbon hydrocarbons on the Carbobond PLOT column. Carrier gas: He. Detection: nano-TCD. Temperature: 60 °C. Pressure drop: 50 kPa. Peaks: (1) air, (2) acetylene, (3) xenon, (4) ethylene, (5) ethane.

significant improvement for the adaptation of GC to space requirements when compared to the packed columns previously used. The performances of the optimized Carbobond PLOT column are illustrated in the chromatogram of Fig. 2.

As observed with the other carbon molecular sieve columns, all the targeted compounds, except N_2 and Ar which are co-eluted, are well separated with symmetrical peaks. These two co-eluted solutes which have different molecular masses, should be easily resolved by MS detection when using the GC–MS operation mode for the analysis. Moreover, it was shown that C_2 hydrocarbons are well separated (Fig. 3) but their elution time is greater than 17 min when the experiments are carried out at atmospheric outlet pressure, using the experimental setup of Fig. 2. However, when vacuum outlet pressure (about 10 kPa) is used to simulate the in situ operating outlet pressure, retention time is decreased below 17 min [2] and is thus lying within the range of the analysis time fixed by the constraints of the COSAC instrument. It must be emphasized that the hydrophobic properties of this stationary phase enables to elute water without any loss of the column

analytical performances, on the opposite of the behavior of the other PLOT columns usually used for this task [16,17]. This property is interesting as water is the most abundant volatile component of the cometary nucleus, and will be sampled at the same time as the species targeted by this column.

3.2. Separation of low-molecular-mass molecules up to C_2

Ammonia, formaldehyde, and methanol are compounds of primary interest for exobiology because they are involved in the formation process of key prebiotic compounds such as amino acids and sugars which are part of the living cells [18]. Their identification and abundance characterization are therefore of first importance from an exobiological point of view.

Given their fast elution with liquid stationary phases, preventing satisfying separation, these species can only be analyzed by gas–solid chromatography within the space instrumental constraints. Moreover, because of the strong adsorption of these compounds on many supports, gas–solid chromatography on relatively inert porous materials of large specific surface area is the only elution mode for analyzing such volatile compounds. Among the several commercially available porous materials adapted for such a separation, the ethylene glycol–dimethyl acrylate–divinylbenzene (commonly named

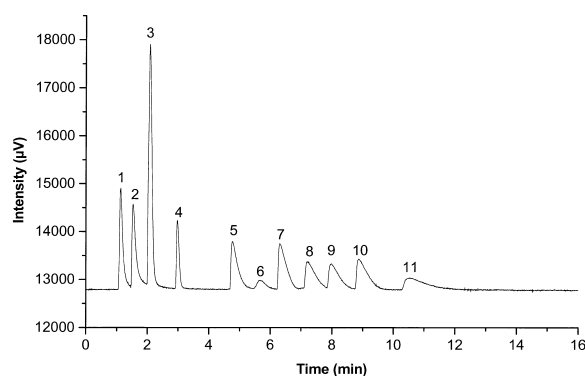


Fig. 4. Separation of the low-molecular-mass compounds on the MXT U PLOT capillary column (10 m×0.18 mm I.D., $d_i=1-2$ µm). Carrier gas: He. Detection: TCD. Temperature: 90 °C. Pressure drop: 50 kPa. Peaks: (1) formaldehyde, (2) water, (3) methanol, (4) acetaldehyde, (5) methyl formate, (6) ethanol, (7) pentane, (8) acetonitrile, (9) acetone, (10) propanol, (11) methyl acetate.

polymer U) was selected because of its polarity and its selectivity towards the targeted compounds [8]. Due to the time of analysis constraints imposed by the mission, a custom made capillary column with a small inner diameter and a thin stationary phase film was developed by Restek, and was selected for the space experiment. Fig. 4 shows the separation of the low-molecular-mass organic species, including both oxygen and nitrogen containing chemical functions. They are eluted within 12 min under outlet atmospheric pressure and isothermal conditions (90 °C). However, due to the energetic constraints of the space experiment, the operating temperature should not exceed 60 °C. Because of the large adsorption heats of all compounds on the polymer, the analysis time will be significantly increased if the operating temperature is maintained at 60 °C. The species eluted within 17 min are then limited to the compounds of each family having the lowest molecular mass, with the exception of hydrocarbons, as the retention time of butane lies in the time range defined by the space experiment [8]. As observed with the Carbobond PLOT column, the hydrophobic nature of the porous polymer of the MXT U PLOT column allows the injection of samples containing water without any change of the column behavior as there is no adsorption of water on the support. In addition, the advantage of the MXT U PLOT column is its ability to elute completely the C_2 hydrocarbons within a short time of analysis at the in situ operating conditions [8]. This column is thus complementary of the Carbobond PLOT column as it enables to analyze a range of compounds of higher boiling point than those separated by the Carbobond PLOT column. Moreover, the first species eluted on this column is the last one separated with the Carbobond PLOT column. Finally, this support has an excellent inertness for sulfur gases (such as hydrogen sulfide, a compound detected in several comae). Their analysis is important for the same reasons as for the noble gases ones as they are tracers of the thermal history of comets. It should be possible with this column to separate these compounds within the time and the temperature range imposed by the instrumental constraints.

However, it must be underlined that in spite of its suitability to achieve the separation of low molecular mass compounds targeted by the space experiment, the thickness of the porous layer selected is very

small. The PLOT column thus contains a very low amount of porous polymer and a rapid overloading of the stationary phase is observed, as shown by the non Gaussian profile of the peaks observed in Fig. 4, confirming the small sample capacity of the porous polymers. Nevertheless, this column was selected because the targeted compounds are of first importance and also because there is no column available with any other liquid or solid stationary phase, which is able to replace this one, considering the space instrumental requirements. This is one of the reasons why experimental and numerical programs allowing the interpretation of complex non-linear chromatograms are currently being developed in relation to the present studies [19].

3.3. Separation of medium-molecular-mass organic compounds, up to C_6

The data obtained from laboratory experimental simulations (irradiation of ices reproducing the assumed primordial ices of the interstellar medium or the solar system [20]), and from in situ measurements (impact mass spectrometry of the dust grains in the tail of comet P/Halley [21]) have pointed out the presence in comets of large amounts of organic compounds belonging to a wide range of chemical families [22]. Most of these organic species could have been involved in prebiotic chemistry processes that could have occurred on the Earth or in other places of the solar system [23] and have led to the emergence of life. Therefore their identification and their quantitative detection in the nucleus could give rise to essential information concerning the organic material which could have been used in terrestrial pre-biotic chemistry.

Due to the numerous species expected in this range of chemical species, two capillary columns were dedicated to the separation of these compounds in order to allow their unambiguous identification. The same targeted species are analyzed on two complementarity columns, but the order of elution is not the same because of the differences of polarity between the stationary phases.

An experimental study was carried out to study the effect of varying the content of the diphenyl substituent in the polysiloxane stationary phase [1]. In addition, a theoretical approach using modeling software (ez-GC, Analytical Innovation, Beaver-

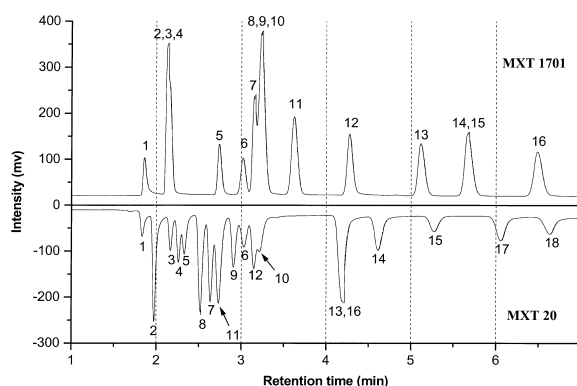


Fig. 5. Separation of a mixture of various organic compounds of cometary interest analyzed on the MXT 20 (15 m \times 0.18 mm I.D., d_f =1 μ m) and the MXT 1701 WCOT capillary columns (15 m \times 0.18 mm I.D., d_f =1.2 μ m). Carrier gas: He. Detection: nano-TCD. Temperature: 60 $^{\circ}$ C. Pressure drop: 50 kPa. Peaks: (1) acetaldehyde, (2) methanol, (3) methyl formate, (4) pentane, (5) ethanol, (6) methylpentane, (7) acetone, (8) propanol, (9) methyl acetate, (10) hexane, (11) methyl propanol, (12) acrylonitrile, (13) ethyl acetate, (14) methyl propionate, (15) heptane, (16) propanenitrile, (17) crotonitrile, (18) acetol.

creek, USA) [1], enabled to select the optimal PDMS stationary phase, a 1 μ m thick film which contains 20% of diphenyl substituent (MXT 20 column). The second column (MXT 1701) is more polar, because it contains 14% of cyanopropyl–phenyl substituent in the PDMS phase. The latter's film thickness (1.2 μ m) is close to the previous one. It should be emphasized that a similar column, the first capillary one to be used in space exploration, is currently mounted in the GC–MS instrument aboard the Cassini–Huygens mission [24] flying toward Saturn and Titan.

Fig. 5 illustrates the complementarity of these two columns. The same sample mixture has been injected simultaneously into both columns. One can observe that the separation achieved by each column differ significantly: with the MXT 1701 column, the peaks are rather well distributed in the elution time whereas with the MXT 20 column, peak clusters appear at the beginning of the chromatogram. Moreover, by comparing both columns and considering their very close geometry and film thickness, the stationary phase with cyanopropyl groups is more polar, as the elution time of polar compounds (alcohols, nitriles) is significantly larger on the MXT 1701 column, while that of alkanes is almost the same. This tandem

column system presents interesting properties, from the separation point of view.

(i) The doublet and triplets of the co-eluted compounds 2, 3, 4–8, 9, 10 and 14, 15 on column MXT 1701 are well separated on column MXT 20. Reciprocally, compounds 13 and 16, which are coeluted on column MXT 20 are well separated on column MXT 1701.

(ii) A cross-check of the data recorded with the two columns allows one to identify compounds which are coeluted on both columns (as compound 10) by generating a kind of two-dimensional chromatographic data set.

Thus the application of such a system should resolve most of the coelutions. Therefore one can get an unambiguous identification of all the compounds injected into these columns, even if the resulting chromatograms are complex. Finally due to the lack of data on the long term stability of these stationary phases, the use of two different ones increases the probabilities of success of this separation, even if one of the phases was damaged.

3.4. Separation of high-molecular-mass compounds

Many polycyclic aromatic hydrocarbons (PAHs) were detected in the interstellar medium and their

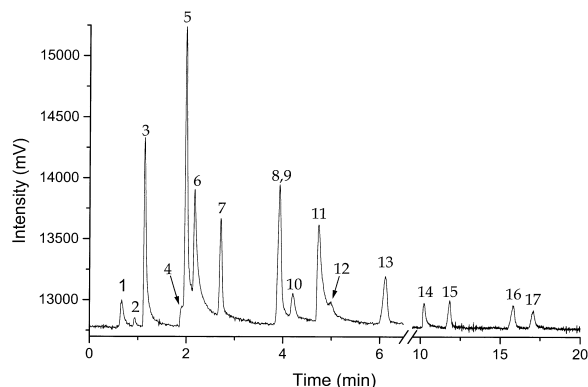


Fig. 6. Separation of a mixture of complex organic compounds with the MXT 1 WCOT capillary column (10 m×0.18 mm I.D., $d_f=0.1\ \mu\text{m}$). Carrier gas: He. Detection: TCD. Temperature: 30 °C. Pressure drop: 50 kPa. Peaks: (1) air, (2) water, (3) benzene, (4) pyridine, (5) toluene, (6) pentanol, (7) octane, (8) *m*-xylene, (9) ethylbenzene, (10) *p*-xylene, (11) cyclohexanone, (12) *o*-xylene, (13) nonane, (14) benzonitrile, (15) trimethylbenzene, (16) *p*-cymene, (17) indene.

presence in comets could confirm the interstellar origin of the cometary ices and specifically the role of comets as a link between the solar system and the interstellar medium. Moreover measurements of the dust composition of the comet P/Halley and models have shown the probable presence of heavy refractory compounds, including polymeric species [25,26] which have never been clearly identified. These latter compounds are of interest as they could play a role in the existence of extended sources, i.e., sources different from the nucleus, of small molecules in the comae, such as CO [27]. Moreover, they could be used as bases for prebiotic chemistry processes. Consequently, in order to elute as many "heavy" compounds as possible within the operating conditions (low temperature and short analysis time), a column having an apolar stationary phase (100% PDMS) with the thinnest possible film (i.e., 0.1 μm) was selected for the flight instrument, because of its weak retention properties. One can observe in Fig. 6 the elution of molecules having up to nine carbon atoms, such as trimethylbenzene, in less than 15 min at atmospheric outlet pressure. The separation of the monoaromatic species is all the more important as the identification of the refractory part composition should be operated by coupling the GC experiment to pyrolysis that could produce this family of compounds. Moreover, using vacuum as the outlet pressure, the elution of naphthalene, the PAH of lowest molecular mass, is possible ($t_R \approx 6$ min at 60 °C) within the COSAC time constraints (results to be published). Thus, the presence of PAHs in comets, already tentatively identified in the coma [28] of comet P/Halley, could effectively be confirmed by the COSAC GC subsystem. Finally, this column also enables to analyze the last compounds eluted by the other WCOT columns of the GC subsystem, such as pentanol (with $k'=2.1$ at 60 °C). Therefore, the continuity of the analysis with the other WCOT columns is ensured, and again, it allows useful cross-checking for a better component identification.

4. Conclusion

GC is a powerful technique for in situ analysis of planetary atmospheres and surfaces as shown by the successful missions Venera and Vega toward Venus,

and Viking toward Mars. However, for the first time with the GC experiments of COSAC, a large number of columns, all capillary ones, will be used in space in combination with two types of detection, TCD and time-of-flight MS. This work has demonstrated that with a configuration of five optimized and well-tuned capillary columns, an important part of the COSAC scientific objectives can be achieved in spite of the constraints related to the operating conditions required in space instrumentation. Nevertheless, the columns' measurement strategy is not yet completely defined, as it relies upon the nature of the molecules evolved from the sample during the stepwise heating in the micro-oven. These five columns should enable the separation and the unambiguous identification of most of the initially targeted compounds (Table 1). Only the non volatiles compounds (such as the amino acids) require the use of preparative methods such as chemical derivatization or pyrolysis which are also included in the COSAC experiment [29].

The expected results obtained by the COSAC GC instrument will be of tremendous importance for a better understanding of the origin and evolution of the solar system, the possible role of comets in the emergence of life on Earth and also, the relationship between the nucleus and the coma chemistry. It is obvious that comets and their composition are various, and that a more accurate knowledge of the constitution of one comet can give only very partial information. That is the reason why several spacecraft missions to comets are under progress or planned to be launched within the next decade. They would probably contribute to a better understanding of the nature and the origin of comets and reveal their role in the solar system formation and evolution.

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