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Gas chromatography for in situ analysis of a cometary nucleus: characterization and optimization of diphenyl/dimethylpolysiloxane stationary phases

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Abstract

The development of a gas chromatograph for the cometary sampling and composition (COSAC) experiment is described in the context of the preparation for the European Space Agency (ESA) Mission Rosetta for investigation of a cometary nucleus. COSAC is one out of ten experiments on the Rosetta Lander. Its scientific goal is to analyze in situ the chemical composition of the volatile constituents of the nucleus of the target comet P/Wirtanen. Constituted of several (up to eight) capillary wall-coated and porous-layer open tubular columns operating in parallel, the GC system is designed to separate and identify both organic and inorganic compounds which evolve from the comet naturally or are obtained from cometary samples through stepwise heating in a miniaturized pyrolyzer. In this first part of our study, dimethylpolysiloxane (DMPS) stationary phases with increasing percentages of diphenyl substituted group (DP) have been investigated. A coupled experimental and theoretical approach has been taken in order to predict chromatographic data. By the use of a four-point experimental calibration (0 to 65% diphenyl group) in conjunction with Pro ezGC modeling software, results in prediction of multicomponent chromatograms with a mean error less than 5% for each compound retention time were obtained, irrespective of the stationary phase's diphenyl content and column physical parameters. The possibility to associate such phases is illustrated by the evolution of coelutions obtained on a non-polar (100% DMPS) and a medium polar (65% DP-DMPS) stationary phase, respectively. This study showed that with a small number of well tuned DP-DMPS columns, the separation and identification of most of the targeted compounds can be achieved with a minimum amount of coelutions and within the experiment requirements. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Diphenyl/dimethylpolysiloxane stationary phases; Stationary phases, GC; Cometary nucleus analysis

1. Introduction

Comets are relevant for the understanding of the

solar system as well as the origin of life on Earth. The interest in these interplanetary bodies arises mainly for two reasons [1]. First, they formed at the same time as the planets and have since remained in the furthest and coldest regions of the solar system. As a consequence, their chemical composition might

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not have been modified since their formation and the elemental composition should be representative of the process of formation of the solar system. Secondly, comets could have brought to the Earth a part of its water as well as organic compounds which may have been employed in the prebiotic chemistry which led to the apparition of life on Earth. HCN, HC₃N, HCHO and CO have been detected on comets and may have contributed to the synthesis of key prebiotic compounds, as alcohols, sugars and amino acids.

However, only little direct information about the cometary nucleus' chemical composition is yet available. Today, all we know are results from experimental simulations, spectroscopic observations of the comae and in situ analysis of gas and grain during the Halley flyby [2–4]. Therefore, the ability to conduct in situ molecular analysis of cometary nuclei will be of great importance for our understanding of the origin of the solar system and life on Earth.

1.1. The Rosetta mission and the cometary sampling and composition (COSAC) experiment

In an attempt to perform such an exploration, the European Space Agency (ESA) will launch the Rosetta mission in 2003 [5] to investigate the nucleus of comet P/Wirtanen. The probe is composed of two main parts:

(1) An orbiter carrying scientific instruments intended to study the coma and the tails of the comet as well as study and map its nucleus by remote sensing.

(2) A lander (Surface Science Package, SSP), which will be ejected from the orbiter and descend to the surface of the comet's nucleus. Its objective is the characterization of the nucleus' chemical composition and physical properties, its morphology and internal structure. It will contain ten instrument packages, two of them being evolved gas analyzers dedicated to the chemical analysis of the nucleus. The first, named COSAC, will be mainly aimed at general and chiral analysis, in particular the detection and identification of large organic molecules, including their chirality, whereas the second will mainly determine isotopic composition.

The COSAC instrument is a pyrolysis–gas chro-

matography–mass spectrometry (Py–GC–MS) system [6] built, designed and constructed by the Max-Planck-Institut für Aeronomie at Lindau (Germany), with H.R. as the principal investigator. The GC subsystem can be used as a stand alone instrument or be coupled to a time-of-flight mass spectrometry (TOF-MS) system. It will be able to analyze gases either directly sampled from the nucleus' atmosphere, or provided by the heating of nucleus material collected by the lander's sampler which can drill to a depth of at least 20 cm.

If we except the sampling system, which is common to all instruments, COSAC is composed of three main parts (Fig. 1). Part I contains carrier and calibration gases as well as a pyrolyzer which comprises micro-ovens, mounted on a carousel and “tapping stations”. These allow vaporisation by stepwise heating of the solid sample collected at or below the comet surface. The second part is the transfer system of the gas between the pyrolyzer and the analyzing part. It mainly contains manifolds, valves and filters. The latter are required for protection of the analyzer from compounds which could degrade stationary phases and water which is contained in a cometary nucleus at a large amount. The third part is the analysis system composed by the GC and the MS subsystems.

The GC subsystem contains eight columns divided into two sets of four sharing a common injector. Up to four columns, which can be selected individually, can be operated in parallel in the temperature range 0–200°C. GC detection is performed by miniaturized thermal conductivity detection (TCD) systems mounted downstream of each column. Five of the GC columns are dedicated to general chemical composition analysis. The other columns are for chiral analysis. These columns are under study at Bremen University (Professor W. Thiemann, co-investigator). Clearly, all columns must offer a high resolution and a wide dynamic range of concentration. Special requirements result from the fact that the measurements have to be done in space under harsh conditions and the matter to be analyzed is unusual and vastly unknown.

Because of the restrictions in carrier gas and power, the GC subsystem must be able to analyze simultaneously most of the expected nucleus components within a short time (less than 15 min). For

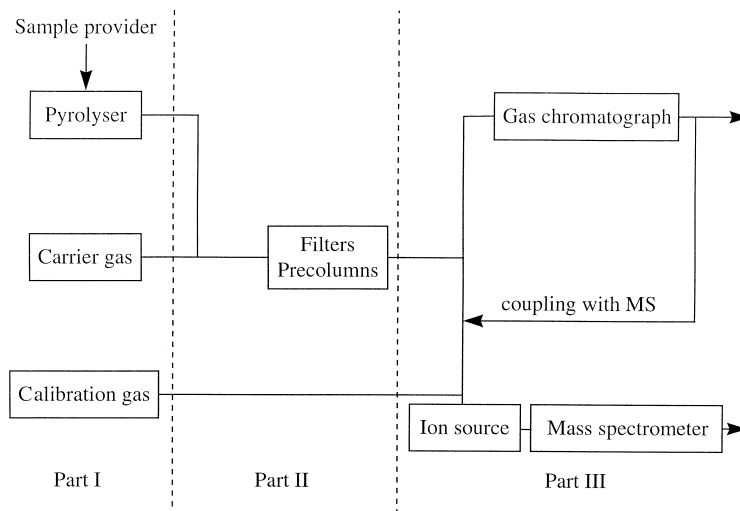


Fig. 1. Simplified scheme of the COSAC instrument.

decreasing the power consumption further, the average analyzing temperature must be kept as low as possible, and for minimizing the carrier gas consumption, capillaries with small inner diameter must be used. Lastly, measurements must be achieved in the presence of large amounts of water as well as sulphur compounds expected in the samples.

We must equally take into account the fact that during the nine-year flight to the comet, the experiment will be exposed to the space environment: vacuum, temperature cycles (between -55°C and $+70^{\circ}\text{C}$) and penetrating radiation. Therefore, its different components must be able to resist these extreme conditions which can cause damage, particularly to stationary phases. Besides, the GC section of the instrument must fulfil other constraints: it must not exceed a mass of approx. 1.5 kg and resist strong vibrations and shocks mainly imposed by the launch. Concerning the chromatographic columns and their stationary phases, studies are under progress at Service d'Aéronomie (Verrière le Buisson, France) in order to evaluate the effects of such constraints.

1.2. GC columns and stationary phases

Previous studies on GC columns for space application, performed for the development of the GC–MS experiment aboard the Huygens probe, showed that

narrow bore capillary columns had the best properties for such applications (high resolution, high efficiency and low carrier gas flow) [7–15].

More recent developments in column technology have provided a wider choice of stationary phases which can be either cross-linked or cross-bonded to the wall of the capillary tubes in order to improve their robustness. In addition, more and more stationary phases have become available with columns made of deactivated stainless steel tubes, which offer a better mechanical strength than fused-silica capillaries. At last, a new generation of PLOT (porous-layer open tubular) columns, more resistant than previous ones, should allow the separation of light hydrocarbons and permanent gases under the conditions dictated by the mission. As a consequence, they could replace packed columns, allowing a lower carrier gas flow-rate and consumption.

Due to the few data available about the chemical composition of cometary nuclei, the development of the GC systems, particularly the selection of the columns, is based on a list (see Table 1) of chemical compounds which are suspected to be present in the cometary nucleus from observations of the coma and laboratory simulations [3]. Therefore, by considering the diversity of these components, we selected, in a first step, “classical” WCOT (wall-coated open tubular) stationary phases covering a wide range of polarity. These phases are unsubstituted di-

Table 1
Components expected to be found in the cometary nucleus

Detected compounds in the comet environment (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	Hexamethylenetetramine	Butanediol	Isobutyronitrile
Formic acid	Ammoniac	Glycerol	Butyronitrile
Methanol	Formic acid	Ethylene glycol	Crotonitrile
Methane	Acetic acid	Methyl butanol	Aminoacetoneitrile
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 polycyclic aromatic hydrocarbons (PAHs)
Sulfur dioxide	Urea	Dimethoxymethane	
Hydrogen sulfide	Oxamide	Methane	
Carbon sulfoxide	Bi-urea	Ethane	
Nitrogen	Glyceramide	Propane	
Disulfur	Glycolamide	Butane	
	Aminobutyric acid	Pentane	
	Acetonitrile	Methylpentane	
	Hydrocyanic acid	Hexane	
	Hydrogen isocyanide	Cyclopentane	
	Cyanamide	Methylhexane	
	Cyanic acid	Glycine	
	Carbon suboxide	L-Alanine	

methylpolysiloxane (DMPS), DMPS substituted with diphenyl groups (DP-DMPS) or cyanopropylphenyl groups (CPP-DMPS), polyethylene glycol (PEG), and trifluoropropylphenyl polysiloxane (TFPP). Fig.

2 shows the classification of stationary phases according to their polarity.

The work reported here deals with DMPS and DP-DMPS stationary phases. These phases are the

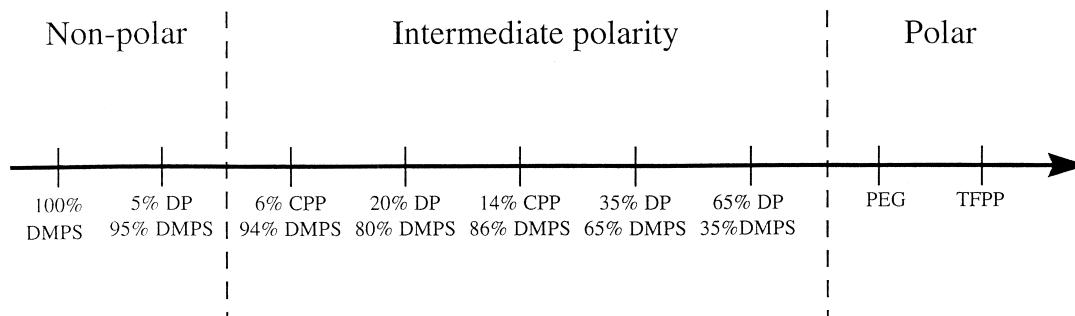


Fig. 2. Polarity scale for the different studied stationary phases.

most commonly used ones because of the wide range of components they allow to analyze and separate, as well as their resistance properties: long lifetime, low bleeding, thermal stability and good surface coating [16,17]. These performances and properties are obviously very suitable for space instrumentation. Moreover, we can fit their polarity by modifying the diphenyl percentage included in the stationary phase, as the introduction of diphenyl groups increases the polarity.

As a consequence, for column selection purpose, it was interesting to characterize the DP-DMPS stationary phases with the aim to: (1) evaluate and select the optimum percentages of diphenyl group for the chromatographic columns of the COSAC GC subsystem, (2) predict retention times for the listed compounds with the maximum accuracy (through experimental and numeric simulation) in order to determine the optimum column geometry (length and internal diameter), film polarity and thickness, and experimental conditions (inlet pressure and temperature), and (3) estimate the complementarity between DP-DMPS stationary phases of different polarities, or with other phases. An ideal set of two “complementary” columns should lead to a non ambiguous qualitative analysis of each detected compound by resolving all the coelutions and by obtaining correlated retention times.

2. Experimental

2.1. Columns

Six columns were selected for this study (Table 2), all provided by Restek (Bellefonte, PA, USA). RTX and MXT correspond, respectively, to polyim-

ide and deactivated stainless steel (Silcosteel) tubing. According to the manufacturer, the material used for the tube does not have any influence on stationary phases chromatographic performance.

2.2. Gas chromatograph

Columns were mounted in a split mode (splitter ratio \approx 250:1) on a Perkin-Elmer Autosystem chromatograph equipped with a flame ionisation detection (FID) system, a TCD system and a linear temperature programmer. The signal was connected to a PE-Nelson Turbochrom IV data acquisition system. The injector temperature was 150°C and the detector temperature was 200°C throughout. The carrier gas was helium as will be used for the COSAC experiment. Computer simulations based upon retention index calculation were performed using the Pro ezGC modeling software (Analytical Innovation, Beavercreek, USA).

2.3. Reagents

Liquid and solid components were provided by Aldrich (Strasbourg, France), Acros (Noisy-le-Grand, France) and Merck (Nogent-sur-Marne, France), whereas gaseous components were bought from Linde (Lyon, France) and Air Liquide (Moissy Cramayel, France). Purity of the components was between 90 and 98% for solid state ones, 97 and nearly 100% for the gaseous ones and at least 96% for liquids.

We performed direct injections of pure compounds (gas, liquid or solvated solid) through the injector septum using Hamilton gas (1 ml) or liquid (1 to 10 μ l) syringes equipped with a tight stopcock. Gas

Table 2
Experimentally studied columns

Column number	1	2	3	4	5	6
Column name	RTX 1	RTX 5	RTX 20	RTX 20	MXT 35	MXT 65
Film thickness (μ m)	0.4	0.4	0.4	1	0.4	0.4
Internal diameter (mm)	0.18	0.18	0.18	0.25	0.18	0.18
Column length (m)	10	10	10	15	10	10
Phase ratio (β)	112.5	112.5	112.5	62.5	112.5	112.5
Diphenyl percentage (%)	0	5	20	20	35	65

mixtures were obtained as previously described for Huygens GC studies [7].

3. Results and discussion

3.1. Efficiency

In order to evaluate the effect of the stationary phase polarity on the efficiency of the chromatographic separation, Golay curves were plotted for columns 1, 2, 5 and 6 at 60°C (the mean temperature of analysis) using a mixture of compounds selected to be representative of the different chemical families (Table 3). Comparison between these curves showed that the optimum efficiencies and the corresponding mean linear gas velocities were similar for all compounds whatever the column is. Their respective values are about 1.3–1.5 mm and 10–15 cm/s (corresponding to a head column carrier gas pressure of about 30 kPa).

Therefore, the modification of the stationary phase polarity, by increase of the diphenyl group content up to 65%, does not significantly influence the optimum efficiency of the columns. Moreover, whatever the component or the stationary phase are, the optimum analysis conditions are obtained for a column head pressure of 30 kPa. This parameter is of primary importance for the selection of the COSAC GC configuration, because columns will operate in parallel and use a single head pressure. The required optimum inlet pressure under low outlet pressure

conditions at the detector side (currently under study), in case of the COSAC experiment, should be close to the determined optimum inlet pressure under atmospheric conditions.

3.2. Stationary phase selection and columns optimization

Measurements were performed at the columns' optimal operating conditions described above. A total of 58 components, out of the 78 selected, (Table 1) were analyzed separately. Retention times versus stationary phase diphenyl group content were recorded (Table 4) and corresponding curves were plotted for representative compounds (Fig. 3). The retention times (t_R) of all compounds increase with the percentage of diphenyl group (% DP) in the stationary phase. This effect has been quantified by calculating the mean slope $\Delta t_R / \Delta(\% DP)$, for each representative component (Table 5), of the curves obtained by linear fitting of the experimental points. The validity of such linear fittings have been verified by the obtention of correlation factors in the range of 0.94 to 0.99. The slopes are less than 0.01 for the apolar and slightly polar compounds, and between 0.04 and 0.05 for the high polarity compounds. As a consequence, the increase of polarity of the stationary phase improves the separation of the mid-polar and highly polar compounds (85% of the listed compounds). Therefore, the stationary phase with 65% diphenyl group content seems to be the most

Table 3

List of the selected representative components with their dipolar momentum and molecular mass

Chemical family	Representative compound	Dipolar momentum (D)	Molecular mass (g/mol)
Aldehyde	Formaldehyde	2.33	30.03
Alcohol	Propanol	1.58	60.1
	Pentanol		88.15
Alkane	Butane	0	58.12
	Heptane	0	100.2
Ketone	Acetone	2.88	58.08
Nitrile	Propanenitrile	4.29	55.08
	Butanenitrile		69.11
Ester	Ethyl acetate	1.78	88.11
Carboxylic acid	Formic acid	1.41	46.03

Table 4
Retention times obtained for eluted components at 60°C and 30 kPa of carrier gas head pressure on columns 1, 5 and 6

Chemical family	Compounds	Retention time (min) on column:		
		1	5	6
Alkane	Methane	1.19	1.37	1.49
	Hexane	1.85	1.86	1.89
	Ethane	1.20	1.40	1.51
	Propane	1.23	1.42	1.53
	Butane	1.36	1.49	1.57
	Pentane	1.45	1.61	1.69
	Methylpentane	1.76	1.80	1.88
	Heptane	2.72	2.59	2.40
	Cyclopentane	1.69	1.93	1.94
Alcohol	Methanol	1.29	1.49	1.64
	Ethanol	1.36	1.63	1.80
	Pentanol	3.69	5.11	5.62
	Propanol	1.45	1.72	1.91
	Butanol	2.27	2.94	3.28
	Methylpropanol	1.47	1.80	1.96
	Ethylene glycol	2.62	4.40	
Aldehyde	Formaldehyde ^a	1.62	2.08	2.40
	Acetaldehyde ^a	1.28	(1.5)	1.70
Amine	Pyridine	3.41	5.94	7.87
	Pyrrole	n.t.	6.46	n.t.
	Ethanolamine	n.t.	4.39	n.t.
Carboxylic acid	Formic acid ^a	1.44	1.68	1.86
	Acetic acid ^a	1.79	2.35	2.65
Ketone	Acetone	1.44	1.82	2.04
	Acetol	2.12	3.88	4.85
Nitrile	Acetonitrile	1.43	1.95	2.27
	Acrylonitrile	1.53	2.07	2.34
	Methacrylonitrile	1.79	2.62	2.95
	Propanenitrile	1.65	2.59	3.13
	Isobutanenitrile	1.92	3.02	3.49
	Butanenitrile	2.26	4.07	4.85
	Crotonitrile	2.11/2.35	3.50/4.25	4.18/5.31
Ester	Methyl formate	1.29	1.57	1.74
	Ethyl acetate	1.90	2.47	2.73
	Methyl acetate	1.57	1.93	2.13
	Methyl propionate	1.97	2.67	2.95
Etheroxyde	Diethyl ether	1.50	1.7	1.79
	Dimethoxymethane	1.54	1.8	1.98
Alkene	Toluene	3.83	5.48	5.69
Alkyne	Ethyne	1.23	n.t.	1.52

^a Components for which peaks are not well resolved.

appropriate for the separation of the major part of the targeted compounds.

Each “retention time versus phase polarity” curve

has then been used to predict the retention times for different percentages of DP group content (between 0 and 65%) stationary phases. Table 6 and Fig. 4,

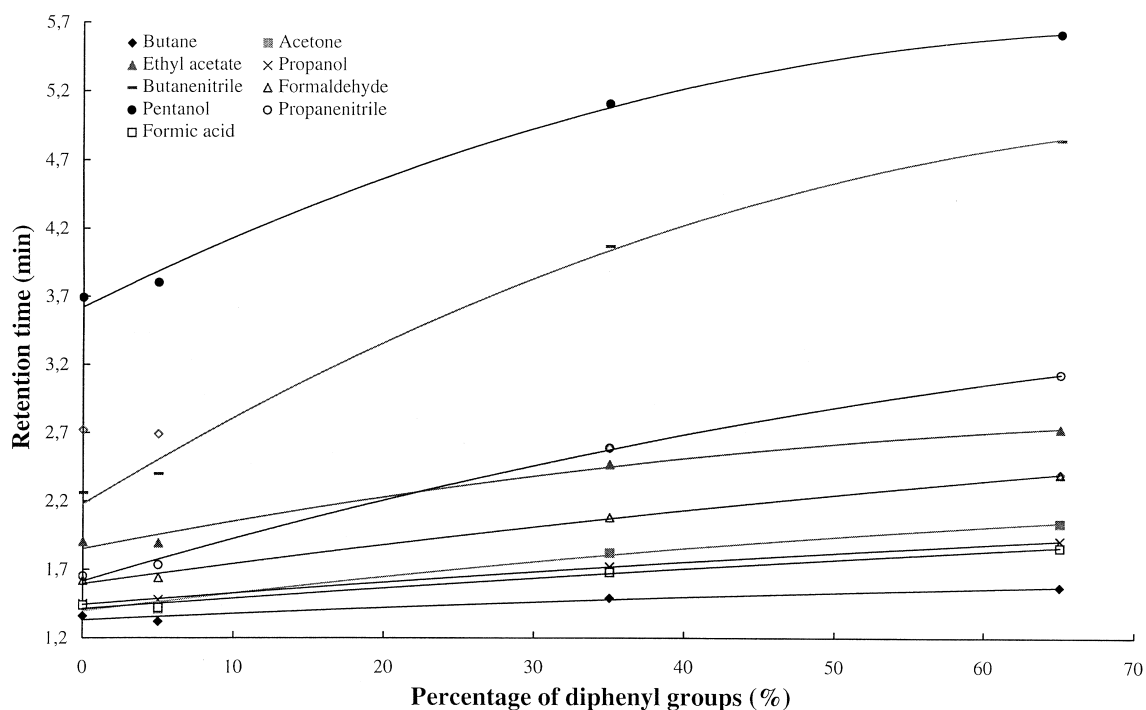


Fig. 3. Experimental variation of retention times with diphenyl groups content of the DP-DMPS stationary phases for 10 m×0.18 mm I.D., 0.4 μ m film thickness columns.

respectively, reference and compare the predicted and the measured retention times obtained on a column (No. 3) of identical physical characteristics and with a DP group content of 20%. A good agreement is observed between the experimental and the predicted retention times with the difference not

Table 5

Retention times obtained for the representative components at 60°C and 30 kPa of carrier gas head pressure on columns 1, 2, 5 and 6

	Retention time (min) obtained with column:				Mean slope
	1	2	5	6	
Butane	1.36	1.32	1.49	1.57	0.0037
Pentanol	3.69	3.8	5.11	5.62	0.0312
Propanol	1.45	1.48	1.72	1.91	0.0072
Butanenitrile	2.26	2.40	4.07	4.85	0.0416
Propanenitrile	1.65	1.73	2.59	3.13	0.0235
Formic acid	1.40	1.42	1.68	1.86	0.0069
Formaldehyde	1.62	1.64	2.08	2.40	0.0124
Acetone	1.44	1.41	1.82	2.04	0.0100
Ethyl acetate	1.90	1.89	2.47	2.73	0.0137

exceeding 5.5% and below 1.5% for the major part of them. This difference is not really significant if we take into account the instrumental uncertainties as well as the accuracy of the function describing the behavior of the retention time. This method shows the possibility to predict, with a high accuracy, the chromatographic behavior of a “non built” DP-DMPS column and allows to design the best DP-DMPS stationary phases tuning for separation and identification of the largest number of listed compounds.

In order to be able to optimize not only the stationary phase but also the column geometry, the previous set of experimental data has been combined with the Pro ezGC modeling software. Simulated chromatograms were plotted for four “non built” columns of 15 m×0.25 mm I.D., 1 μ m film thickness with the DP group content (0, 5, 35 and 65%) of the previous study.

As for the previous study, Table 7 reports the simulated and experimental retention times obtained for a column (No. 4) of 15 m×0.25 mm I.D., 1 μ m

Table 6

Comparison between experimental and predicted retention times obtained on a 20% DPCG stationary phase at 60°C and 30 kPa of carrier gas head pressure

Results obtained with column number	Component	Predicted retention time (min)	Measured retention time (min)	Error percentage (%)
3 ^a	Butane	1.42	1.37	3.64
	Heptane	2.65	2.65	0.15
	Propanol	1.61	1.60	0.54
	Pentanol	4.55	4.75	4.13
	Propanenitrile	2.22	2.25	1.27
	Butanenitrile	3.68	3.49	5.50
	Ethyl acetate	2.24	2.21	1.25
	Formic acid	1.57	1.58	0.89
	Formaldehyde	1.88	1.87	0.44
	Acetone	1.65	1.64	0.32
4 ^b	Butane	2.12	2.03	4.20
	Heptane	4.98	5.19	4.14
	Propanol	2.52	2.55	1.32
	Pentanol	9.53	10.35	7.95
	Propanenitrile	4.01	4.27	6.08
	Butanenitrile	6.58	7.21	8.79
	Ethyl acetate	4.03	4.26	5.45
	Formic acid	3.02	2.54	18.94
	Acetone	2.69	2.67	0.93

^a Prediction is based on experimental t_R vs. polarity curves.

^b Prediction is based on t_R vs. polarity curves obtained by numerical calculation.

film thickness with a DP group content of 20%. The difference between simulated and experimental retention times (except for formic acid) does not exceed 9%, the error percentage increasing with the retention time. If we consider that 80% of the separated compounds are eluted in less than 8 min, the accuracy of this predicting method, for all column geometries and stationary phase polarities, is better than 95%.

Due to weight and gas consumption concerns on the COSAC experiment, column lengths and inner diameters are strongly constrained and should be in the range of 10 m and 0.15–0.25 mm, respectively. Therefore, the modeling software has been used to optimize the film thickness parameter. Several simulated chromatograms were plotted as a function of the film thickness. This work has been performed on the stationary phases (0 to 65% DP group content) previously studied. Fig. 5 illustrates the results obtained on an MXT 65 column, which contains the DPGC stationary phase with the highest selectivity. The resolutions shown are derived from the simu-

lated chromatograms and are based on the retention gap between the named compounds and their adjacent peak.

A significant increase of the resolution as a function of the film thickness is observed for all the compounds. The upper limit is obtained for a 1.0 μm thickness. The optimal film thickness, providing good resolution and analysis time compatible with the in situ experimental constraints (less than 15 min), is about 0.7–0.8 μm . Specially designed columns with optimal simulated film thickness are under development by Restek and will be tested in order to validate the simulation.

Table 6 references the simulated retention times obtained for a 10 m \times 0.18 mm I.D., 1 μm film thickness MXT 65 column. By comparison with experimental retention times obtained for a 0.4 μm film thickness column, the separation is effectively improved within the imposed analyzing time (less than 15 min). Similar comparisons performed with the other phases show that this effect seems to be less pronounced for the non-polar stationary phase.

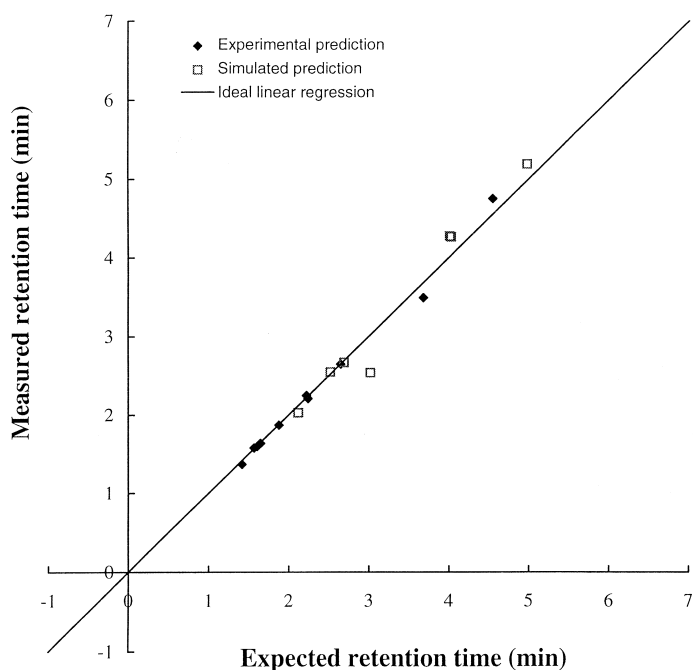


Fig. 4. Comparison between predicted and experimental retention times obtained on columns 3 (experimental) and 4 (simulated) for a sample of representative components.

3.3. Column configuration

In order to be able to analyze and separate as many compounds as possible, the COSAC experiment will use up to four columns simultaneously. Concerning the DP-DMPS stationary phases, the nature of the compounds expected to be evolved from a cometary sample through the different steps

of heating and pyrolysis (16 steps) will determine their optimal polarity and the measurement strategy (number of columns to be operated in parallel).

Since the COSAC experimental approach is to develop a “stand alone” GC subsystem (columns coupled to individual thermal conductivity detectors), the use of two DP-DMPS columns and the complementarity between their stationary phases (ob-

Table 7

Comparison of the experimental and simulated retention times obtained on MXT 65 column (10 m×0.18 mm), respectively for 0.4 and 1 μm film thickness

Component	Retention time (min) obtained with a 0.4 μm film thickness	Retention time (min) obtained with the optimized 1 μm film thickness
Butane	1.57	1.85
Formic acid	1.86	2.09
Propanol	1.91	2.49
Acetone	2.04	2.8
Heptane	2.4	3.76
Ethyl acetate	2.73	4.74
Propanenitrile	3.13	5.37
Butanenitrile	4.85	9.69
Pentanol	5.62	12.18

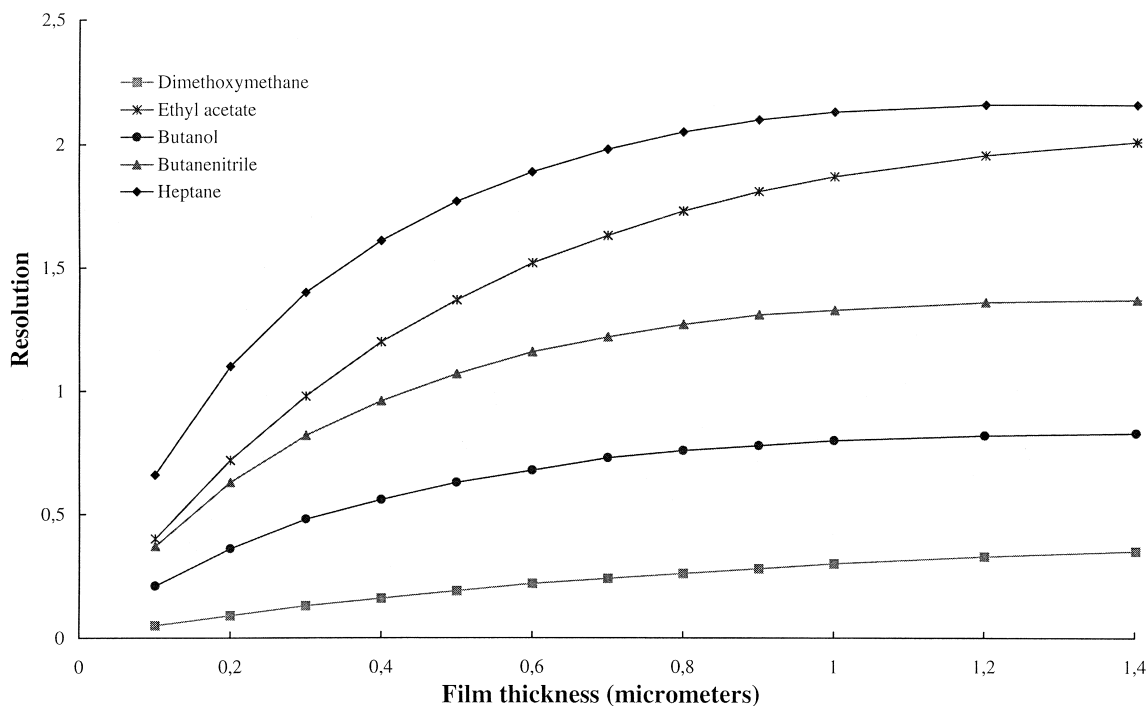


Fig. 5. Simulated variation of resolution with film thickness for a mixture of representative components on column 5 at 60°C, 30 kPa of head pressure.

tained by fine polarity) is important. It should permit not only enhanced compounds separation (larger number of peaks) but also unambiguous identification by appropriate cross-checks without the requirement of a systematic MS coupling.

In order to illustrate this complementarity, a test sample of 14 components has been studied on both RTX 1 (No. 1) and MXT 65 (No. 6) columns (Fig. 6). The difference of selectivity between these two phases provides different coelutions. For example, hexane, ethyl acetate and isobutanenitrile, which are coeluted on the non-polar phase, can be separated on the 65% DP-DMPS one. Inversely, methanol and pentane can be separated with RTX 1 column whereas they are coeluted with MXT 65.

4. Conclusions

The COSAC experiment GC subsystem requires several capillary columns. Each selected column, connected to its own detection system (nano TCD),

contains a stationary phase targeted for one (or a limited number of) specific group of compounds. Five DP-DMPS stationary phases, with, respectively, 0, 5, 20, 35 and 65% of substituted diphenyl group, have been studied. The combination of experimental and modeled data provided a method for predicting retention times of the components to be separated. A deviation smaller than 5% is observed between the predicted and measured retention times of 15 representative compounds on a 20% coated DP-DMPS column. This method allows to design the optimized DP-DMPS columns, the combination of which should permit the separation and identification of a maximum number of the targeted compounds. A comparative study of two different columns has illustrated the diphenyl group content effect on the compounds retention times and coelutions.

Complementary work is under progress on the selection of stationary phases for compounds not or poorly (like carboxylic acid) eluted on DP-DMPS columns: for organics, highly polar phases like polyethylene glycol or specially designed high con-

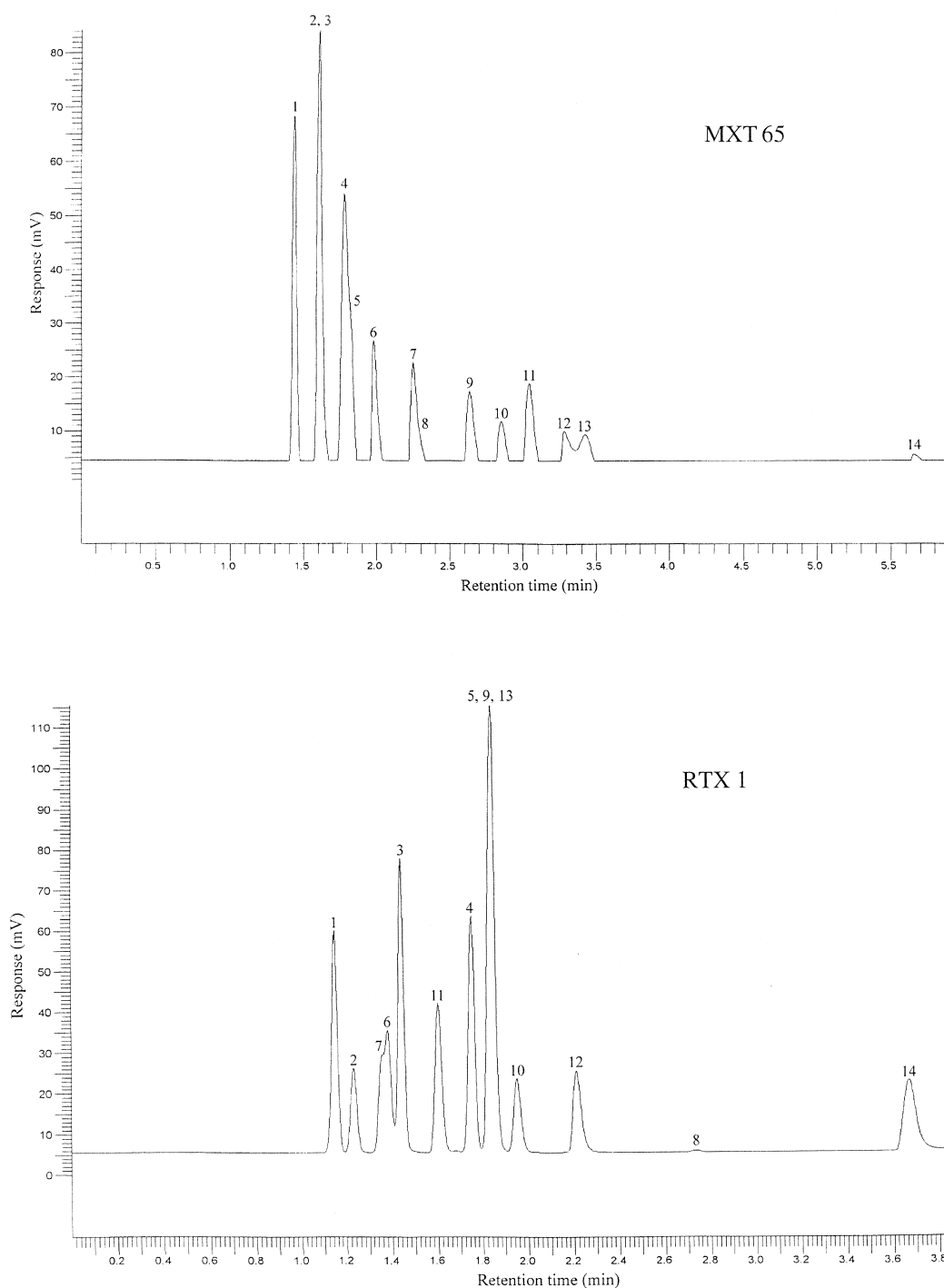


Fig. 6. Chromatograms obtained with the same mixture of components and the same experimental conditions (60°C and 30 kPa of head pressure) on RTX 1 (No. 1) and MXT 65 (No. 6) columns (10 m×0.18 mm, 0.4 μm). Peaks: 1=methane, 2=methanol, 3=pentane, 4=methyl pentane, 5=hexane, 6=acetone, 7=acetonitrile, 8=heptane, 9=ethyl acetate, 10=methyl propionate, 11=propanenitrile, 12=butanol, 13=isobutanenitrile, 14=pentanol.

tent DP-DMPS phases; for inorganics, PLOT columns with an adsorbent layer similar to carbon molecular sieve. The final goal is the calibration of the whole GC subsystem under flight conditions using artificially made cometary analogs.

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References

- [1] J. Oro, C.B. Cosmovici, in: C.B. Cosmovici, S. Bowyer, D. Werthimer (Eds.), *Astronomical and Biochemical Origins and the Search For Life in the Universe*, Compositori, Bologna, 1997, p. 97.
- [2] J. Crovisier, in: J.M. Greenberg (Ed.), *Solids and Volatiles in Comets, Proceedings of the Formation and Evolution of Solids in Space Conference*, Erice, Kluwer, Dordrecht, 10–20 March 1997.
- [3] H. Cottin, M.-C. Gazeau, F. Raulin, *Planet. Space Sci.* 47 (1999) 1141.
- [4] J.M. Greenberg, *Astron. Astrophys.* 330 (1998) 375.
- [5] M. Verdant, G.H. Schwehm, *ESA Bull.* 93 (1998) 38.
- [6] H. Rosenbauer, S.A. Fuselier, A. Ghielmetti, J.M. Greenberg, F. Goesmann, S. Ulamec, G. Israel, S. Livi, J.A. MacDermott, C.T. Pillinger, F. Raulin, R. Roll, W. Thiemann, *Adv. Space Res.* 23 (1999) 333.
- [7] L. Do, F. Raulin, *J. Chromatogr.* 481 (1989) 45.
- [8] L. Do, F. Raulin, *J. Chromatogr.* 514 (1990) 65.
- [9] L. Do, F. Raulin, *J. Chromatogr.* 591 (1992) 297.
- [10] E. de Vanssay, P. Capilla, D. Coscia, L. Do, R. Sternberg, F. Raulin, *J. Chromatogr.* 639 (1993) 255.
- [11] A. Aflalaye, R. Sternberg, F. Raulin, C. Vidal-Madjar, *J. Chromatogr. A* 708 (1995) 283.
- [12] A. Aflalaye, S. Anguel, R. Sternberg, F. Raulin, C. Vidal-Madjar, *J. Chromatogr. A* 746 (1996) 63.
- [13] A. Aflalaye, R. Sternberg, D. Coscia, F. Raulin, C. Vidal-Madjar, *J. Chromatogr. A* 761 (1997) 195.
- [14] V. Navale, D. Harpold, A. Vertes, *Anal. Chem.* 70 (1998) 689.
- [15] R. Sternberg, C. Szopa, D. Coscia, S. Zubrzycki, F. Raulin, C. Vidal-Madjar, H. Niemann, G. Israel, *J. Chromatogr. A* 846 (1999) 307.
- [16] L. Blomberg, J. High Resolut. Chromatogr. *Chromatogr. Commun.* 5 (1982) 520.
- [17] M.L. Lee, R.C. Kong, C.L. Woolley, J.S. Bradshaw, *J. Chromatogr. Sci.* 22 (1984) 136.