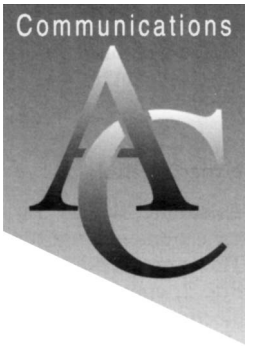

Retention Behaviour of C_1–C_4 Hydrocarbons on Copper(II) Complexes of Cyano- and Mercaptopropyl Bonded Phases

Samuel O. Akapo

SETI Institute, NASA-Ames Research Center, Mail Stop 239-12, Moffett Field, California 94035-1000, USA. E-mail: Samuel_Akapo@qmgate.arc.nasa.gov

The retention behaviour of light (C_1–C_4) hydrocarbons on micropacked cyano- and mercaptopropyl bonded silica columns and their copper(II) complexes was examined by GC under isothermal conditions (25 °C). All the phases gave excellent separation of a mixture of methane, ethane, propane and butane with high reproducibility of retention times. Presumably due to specific metal–olefin interactions, the metal-containing packings gave a better separation of a ten-component mixture of C_1–C_4 saturated and unsaturated hydrocarbons. However, this effect appears to be weaker than the dispersive interactions between the solutes and the hydrocarbon chains of the bonded ligands as their chromatograms are similar to those obtained on micropacked *n*-alkyl and bidentate alkylsilane silica columns. Among the phases examined, a 3 m column of cyanopropyl-copper(II) complex offered a better resolution of a ten-component mixture of C_1–C_4 hydrocarbons.

The chromatographic as well as kinetic properties of a number of micropacked alkyl-bonded silica columns have been reported during the course of the present investigations on the potential of these types of column for GC analysis of light hydrocarbons in planetary atmospheres.[1–5] As reported in these papers, some of the columns evaluated allowed rapid and efficient separation of the test solutes under isothermal conditions (25 °C). However, the complex nature of gas mixtures in planetary atmospheres may require the use of two or three parallel columns containing different stationary phases for maximal resolution of the sample components.[6–8] It is therefore necessary to conduct similar studies on polar bonded phases under identical chromatographic conditions.

Amongst the reported polar phases,[9,10] transition metal complexes of cyano-, thiol-, diphenylphosphino- and aminoalkyl phases have been shown to exhibit excellent selectivity for olefins (C_5 and above) and their geometric isomers.[11–15] While the high separation efficiency of these phases resulted from the ability of the transition metals to enter into pi-interaction with electron-donor compounds, the strength of the interaction during the chromatographic process varied with the pi-electron density of the adsorbate molecule and the number of the free d orbitals in the metal salt. Also, the formation of a coordinate bond between the metal and the terminal polar functional group of the bonded ligand increased the stability as well as the chromatographic performance of the columns when compared with pure or support-coated metal salt columns.[11]

In order to determine their suitability for GC experiments aboard a spacecraft and for the lack of information on their selectivity for light hydrocarbons, this paper describes the GC properties of cyano- and mercaptopropyl bonded phases and their copper(II) complexes for the separation of C_1–C_4 saturated and unsaturated hydrocarbons.

Experimental

Reagents

Bis(3-cyanopropyl)dichlorosilane, 3-mercaptopropyltrimethoxysilane, hexamethyldisilazane (HMDS) and trimethylchlorosilane (TMCS) were purchased from United Chemical Technologies (Bristol, PA, USA) and used as received. Analytical-reagent grade *p*-dioxane, tetrahydrofuran (THF), methylene chloride, and methanol were obtained from general sources. Prior to use, *p*-dioxane and THF were distilled and dried with sodium metal. Porasil C (particle size, 149–177 μm; surface area, 100 $m^2\ g^{-1}$; pore diameter, 300 Å) was obtained from Waters Associates (Millipore, Milford, MA, USA) and acid-washed as previously described[1] before use.

Bonded-phase Preparation

To a warm solution of 5.0 ml of bis(3-cyanopropyl)dichlorosilane or 3-mercapto-propyltrimethoxysilane in 50 ml of dry *p*-dioxane placed in a 100 ml two-neck round-bottom flask was added 5.0 g of Porasil C. The mixture was heated to reflux for 5 h at 110 °C under gentle helium (99.999% UHP He) flow. After cooling, the silylated silica was washed consecutively with three 50 ml portions of dry *p*-dioxane, methylene chloride, methanol, methanol–water (50:50 v/v) and methanol under suction. The cleaned particles were then endcapped as described elsewhere.[1–3] Next, 2.5 g of the endcapped product was suspended in a 15 ml saturated solution of copper(II) chloride (Matheson Coleman & Bell, Norwood, OH, USA) in THF for 5 d in a screw-cap brown bottle at room temperature. Subsequently, the particles were filtered, washed with THF and then extracted with the same solvent for 3 h in order to remove any residual salt. Finally, the cleaned particles were dried in a vacuum oven at 100 °C overnight and kept in dry bottles for evaluation. The remaining part of the endcapped products was evaluated as packings containing free cyano or thiol groups. The identity of the phases together with their elemental chemical composition is given in Table 1.

Chromatography

The bonded phases were dry packed in vertical position with vibration into stainless steel tubes (2.0 m × 1.07 mm id; No. 304) fitted with Swagelok low dead volume connectors. A complete description of the column pre-treatment, packing procedure, conditioning, the gas chromatographic system and the gas mixtures used for column evaluation can be found elsewhere.[1,4] All analyses were carried out at 25 °C using helium (99.999% ultrahigh purity He) as the carrier gas.

Results and Discussion

Fig. 1 shows the separation of a mixture of methane, ethane, propane and butane in helium under isothermal conditions (25 °C). All the columns gave baseline separations of the solutes at short analysis times ranging from 2.56 min in column 1 to 2.91 min in column 4. The excellent reproducibility of the separations is quantified by the data presented in Table 2 where the retention times of the solutes were virtually the same in four successive injections. Based on the butane peak, column efficiencies, calculated from the expression: $N = 5.54(t_R/w_{0.5})^2$, where t_R is the solute retention time and $w_{0.5}$ is the peak width at half-height in time units, are 1576, 1670, 1054, and 1289 plates per metre on columns 1, 2, 3, and 4, respectively. Thus, bonding of copper onto the modified support slightly increased the separation efficiency. While polar functional groups and/or metal atoms interact very weakly with saturated compounds,[13,14] the observed increase in efficiency may be due to effective dispersive interactions between the solutes and the hydrocarbon chains of bonded ligands. It is interesting to note that the present columns are more efficient for the separation of C_1–C_4 saturates compared to some similar columns containing *n*-alkyl or bidentate bonded phases.[1,2] They also gave shorter analysis times than nonporous glass beads impregnated with heteropoly compounds for the separation of the same solutes under isothermal conditions.[16,17]

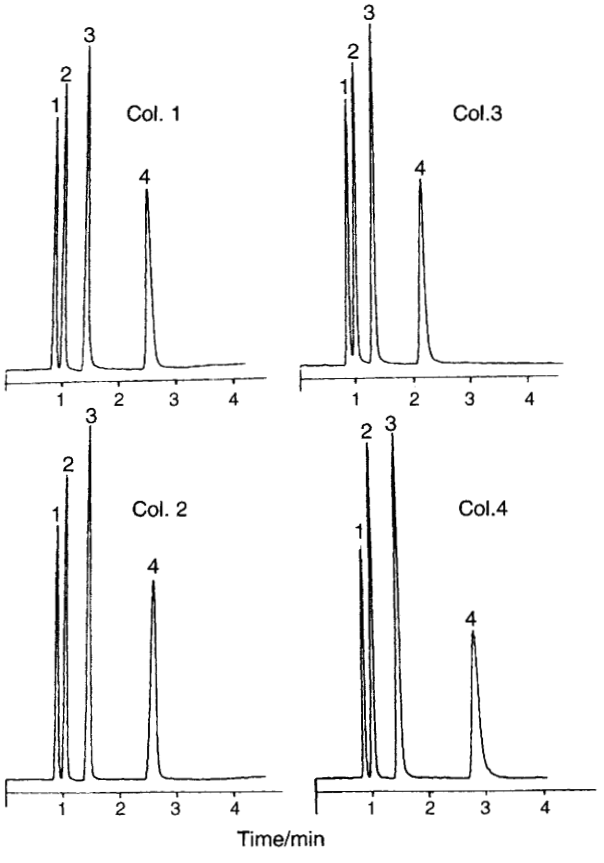

Fig. 1 Chromatograms of C_1–C_4 saturates. Column: 2 m × 1.07 mm id. Conditions: temperature 25 °C; TC detector; inlet pressure 1.49 kg cm^{-2}; He 5.12 ml min^{-1}; 100 µl injection loop. Peaks: 1, methane; 2, ethane; 3, propane; 4, butane.

Fig. 2 shows the analysis of a ten-component mixture of C_1–C_4 saturated and unsaturated hydrocarbons. As can be seen, none of the columns produced a complete resolution of the sample components. However, better separations were achieved on the copper-containing packings (columns 2 and 4) compared with their corresponding parent packings (columns 1 and 3). For instance, butane and propyne which co-eluted on column 1 were partially separated on column 2. Also, acetylene was separated from ethane and ethene and propene from propane on column 4 compared to column 3 where they co-eluted. Worthy of note is the elution of propyne before butane on column 2 which is a reversal of the elution order of the two compounds as generally observed on similar columns packed with *n*-alkyl, isocyanate or isothiocyanate bonded silicas.[1–5,18] While no reason could be given for the change in elution order, this result showed approximately 50–60% reduction in the retention time of propyne when compared to that obtained on alkyl bonded phases[1,5] at almost the same carrier gas flow rate (≈ 5 ml min^{-1}) and about 85% decrease in the elution time of the same solute compared to that achieved on isocyanate or isothiocyanate columns at a higher carrier gas flow rate (15 ml min^{-1}). In general, the introduction of copper into the bonded phases improved the resolution of the unsaturated compounds presumably owing to their effective pi-interactions with the metal. However, this effect, found to be the predominant factor for the high selectivity of higher hydrocarbons (C_5 and above) and their isomers on copper-containing packings,[13,14] appears to be weaker than the dispersive interactions between the type of solutes employed in the present study and the bonded ligands.

In order to improve the resolution of the same sample mixture, the length of column 2, which exhibits better selectivity for the solutes (see Fig. 2) was increased to 3 m. The

Table 2 Reproducibility of retention times (n = 4)

Col. No.	Statistical value	Retention times/min			
		Methane	Ethane	Propane	Butane
1	Mean	0.88	1.03	1.44	2.58
	± s (× 10^{-3})	1.01	1.16	1.20	1.09
	RSD (%)	0.10	0.03	0.09	0.11
2	Mean	0.90	1.06	1.48	2.66
	± s (× 10^{-3})	1.50	1.02	1.08	1.10
	RSD (%)	0.20	0.10	0.14	0.08
3	Mean	0.88	1.04	1.48	2.69
	± s (× 10^{-3})	1.06	1.13	1.11	1.02
	RSD (%)	0.06	0.17	0.10	0.09
4	Mean	0.87	1.04	1.50	2.91
	± s (× 10^{-3})	1.00	1.16	1.07	1.12
	RSD (%)	0.06	0.08	0.10	0.08

Table 1 Elemental chemical composition of the bonded phases

Col. No.	Bonded phase	Elements (m/m %)				
		C	H	N	S	Cu
1	≡Si–$CH_2CH_2CH_2CN$	3.51	0.60	0.75	—	—
2	≡Si–$CH_2CH_2CH_2CN.CuCl_2$	3.55	0.54	0.75	—	1.69
3	≡Si–$CH_2CH_2CH_2SH$	2.20	0.44	—	0.60	—
4	≡Si–$CH_2CH_2CH_2SH.CuCl_2$	2.23	0.42	—	0.61	1.01

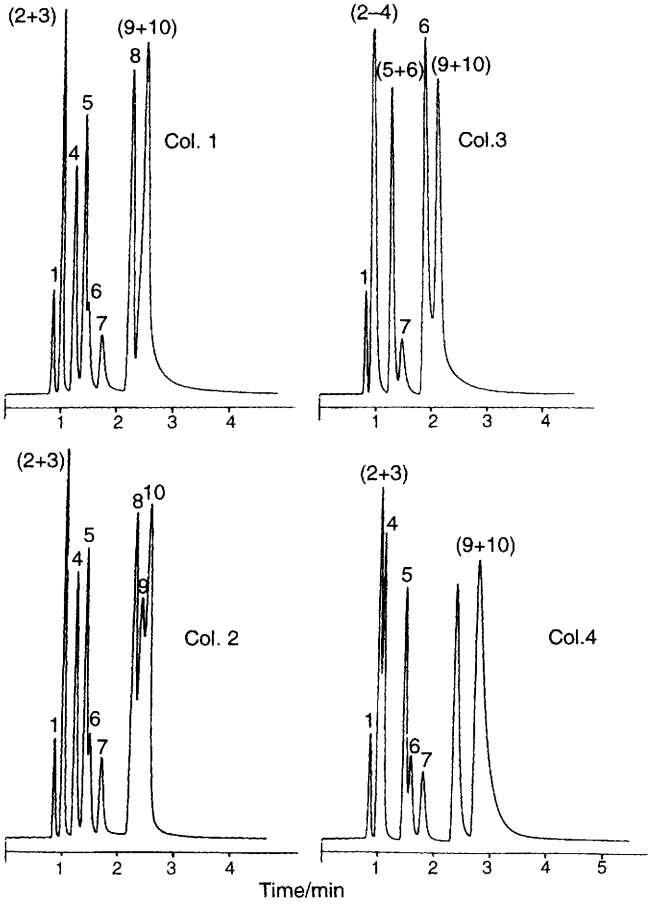

Fig. 2 Chromatograms of a C_1–C_4 saturated and unsaturated hydrocarbon mixture. Column: 2 m × 1.07 mm id. Conditions as in Fig. 1. Peaks: 1, methane; 2, ethane; 3, ethene; 4, acetylene; 5, propane; 6, propene; 7, propadiene; 8, isobutane; 9, propyne; 10, butane.

separation obtained on this column is shown in Fig 3. With the exception of propyne which appeared as a shoulder peak, all the sample components were almost baseline resolved. However, ethane and ethylene are still eluted as a single peak. While the resolution of some of the sample components are somewhat better on the conventional packed or micropacked columns for similar hydrocarbon mixtures,[19,20] this column provides fast separation of the test solutes at conditions suitable for GC experiments aboard a spacecraft. For example, butane was eluted within 4 min at 25 °C (He flow-rate 5.49 ml min^{-1}) on the present column (see Fig. 3) compared with ≈ 6 min at 125 °C on Porapak Q (He flow rate 58 ml min^{-1}).[19] With the exception of ethane and ethene, the resolution of C_1–C_3 hydrocarbons on this column compare favourably with those obtained on porous-layer open tubular (PLOT) capillary columns containing Carboxen carbon molecular sieves[21,22] at a much faster analysis time even though the solutes were separated on the PLOT columns under temperature programming conditions.

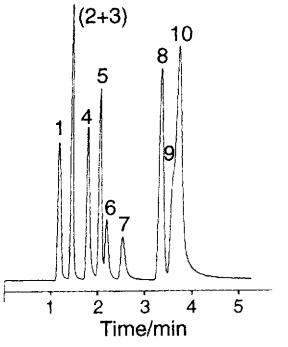

Fig. 3 Separation of a ten-component mixture of C_1–C_4 saturated and unsaturated hydrocarbons on 3 m × 1.07 mm id column packed with a copper(II) complex of cyanopropyl bonded phase. Conditions: temperature 25 °C; TC detector; inlet pressure 1.97 kg cm^{-2}; He 5.49 ml min^{-1}; 100 µl injection loop. Peaks as in Fig. 2.

This work was funded by NASA-Ames Research Center through the Exobiology Program (Contract NCC 2-650).

References

1 Akapo, S. O., *J. Chromatogr. A*, 1995, **709**, 291.
2 Akapo, S. O., *J. Chromatogr. Sci.*, 1996, **34**, 130.
3 Akapo, S. O., Dimandja, J.-M. D., Matyska, M. T., and Pesek, J. J., *Chromatographia*, 1996, **42**, 141.
4 Akapo, S. O., Dimandja, J.-M. D., Matyska, M. T., and Pesek, J. J., *J. Microcolumn Sep.*, 1996, **8**, 189.
5 Akapo, S. O., Dimandja, J.-M. D., Matyska, M. T., and Pesek, J. J., *Anal. Chem.*, 1996, **68**, 1954.
6 Raulin, F., de Vanssay, E., Do, L., and Paillous, P., *LC-GC Int.*, 1992, **5**, 117.
7 Wilhite, W. F., and Hollis, O. L., *J. Chromatogr. Sci.*, 1968, **6**, 84.
8 Wilhite, W. F., *J. Gas Chromatogr.*, 1966, **4**, 47.
9 Rotzsche, H., *Stationary Phases in Gas Chromatography*, Journal of Chromatography Library, vol. 48, Elsevier, Amsterdam, 1991.
10 *Packings and Stationary Phases in Chromatographic Techniques* Chromatographic Science Series, vol. 47, ed. Unger, K. K., Marcel Dekker, New York, 1990.
11 Wasiak, W., and Szczepaniak, W., *Chromatographia*, 1984, **18**, 205.
12 Wasiak, W., *Chromatographia*, 1986, **22**, 147.
13 Wasiak, W., *Chromatographia*, 1987, **23**, 423.
14 Wasiak, W., *Chromatographia*, 1987, **23**, 427.
15 Wasiak, W., *J. Chromatogr.*, 1991, **547**, 259.
16 Nayak, V. S., *J. Chromatogr.*, 1990, **498**, 349.
17 Nayak, V. S., *J. Chromatogr.*, 1991, **556**, 425.
18 Pollock, G. E., Kojiro, D. R., and Woeller F. H., *J. Chromatogr. Sci.*, 1982, **20**, 176.
19 Dave, S. B., *J. Chromatogr. Sci.*, 1969, **7**, 389.
20 Papic, M., *J. Gas Chromatogr.*, 1968, **6**, 493.
21 Betz, W. R., and Lambiase, S. J., *J. Chromatogr.*, 1991, **556**, 433.
22 Betz, W., and Keeler, M., *Supelco Rep.*, 1996, **15**, 1.

Paper 6/04221J
Received June 16, 1996
Accepted July 22, 1996