

CHROM. 11,262

## COORDINATION POLYMERS AS ADSORBENTS AND STATIONARY PHASES IN GAS CHROMATOGRAPHY

### III. POLY[COPPER(II) DI-*n*-HEXYLPHOSPHINATE]

WALENTY SZCZEPANIAK and JACEK NAWROCKI

*Institute of Chemistry, A. Mickiewicz University, 60-780 Poznań (Poland)*

(First received March 7th, 1978; revised manuscript received June 12th, 1978)

---

#### SUMMARY

As a continuation of a previous study on the application of polymers containing transition metals to gas chromatography<sup>1,2</sup>, the chromatographic properties and some applications of poly[copper(II) di-*n*-hexylphosphinate] are described.

---

#### INTRODUCTION

Transition metals which specifically interact with almost all organic molecules (except for *n*-alkanes) can play a role as a solid-phase selectivity-enhancing factor. The nature of these specific interactions depends mainly on the kind of organic molecules. In general,  $\pi$  and  $\sigma$  complexes between a transition metal and a sorbate can be formed. The elution order of sorbates forming such complexes depends, among other things, on the stability constant of the newly created adduct. Some interesting possibilities of selective action arise in organic polymers having "built-in" metals.

In a previous papers<sup>2</sup> some applications of poly[chromium(III) diphenylphosphinate] as a gas chromatographic adsorbent were described. In this work we present the results of a study on the application of poly[copper(II) di-*n*-hexylphosphinate], DHP-Cu, as a stationary phase and gas chromatographic adsorbent. The object of this work was to investigate the ability of DHP-Cu to undergo specific interactions. In order to evaluate the magnitude of these interactions, the results obtained with DHP-Cu-containing columns are compared with those on DHP-Mg.

#### EXPERIMENTAL

The experimental procedure and the apparatus were as described previously<sup>2</sup>.

##### *Preparation of phosphinates*

Di-*n*-hexylphosphinic acid was prepared as described by Williams and Hamilton<sup>3</sup>. Poly[copper(II) di-*n*-hexylphosphinate] was obtained as follows. Di-*n*-hexyl-

TABLE I  
RETENTION VOLUMES AND THE RETENTION INDEXES (*I*) FOR PACKINGS CONTAINING 5% DHP-Cu AND 5% DHP-Mg, RESPECTIVELY

Adsorbate	${}^{\circ}T V_A$ (ml/m <sup>2</sup> ) at $T_k = 80^{\circ}C$		<i>I</i> for DHP-Cu				<i>I</i> for DHP-Mg				$\Delta I/\Delta T$
	5% DHP-Cu	5% DHP-Mg	58° C	66,5° C	80° C	90° C	58° C	80° C	90° C	90° C	
Pentane	0.047	0.042	500	500	500	500	500	500	500	500	0
1-Pentene	0.054	0.041	556	531	529	513	502	500	498	500	-0.18
cis-2-Pentene	0.056	0.050	556	543	534	527	536	531	526	526	-0.45
Cyclopentane	0.065	0.066	550	550	555	557	565	562	568	568	+0.14
Cyclopentene	0.077	0.068	609	590	584	569	576	569	573	573	-0.14

phosphinic acid (4.69 g) was dissolved in 50 ml of methanol and 20 ml of 1 *N* potassium hydroxide, 0.5 g potassium carbonate and water were added to give a total volume of 100 ml. The solution of potassium di-*n*-hexylphosphinate prepared in this way was then added, while stirring slowly, to 1.6 g of copper(II) sulphate in 50 ml of water. The reaction mixture was then heated to boiling. The green precipitate which formed was extracted with *n*-hexane in a soxhlet apparatus to give the blue-green polymer of DHP-Cu. The compound was identified by its IR spectrum and elemental analysis [C, H on a Perkin-Elmer Model 240 Elemental Analyzer; P, spectrophotometrically<sup>4</sup> and Cu by titration with ethylenediaminetetraacetate (EDTA)<sup>5</sup>]. The results of the elemental analysis for the assumed formula  $\text{Cu}[\text{OOP}(\text{C}_6\text{H}_{13})_2]_2$  are: Calc. C 54.37%, H 9.89%, P 11.69%, Cu 11.99%; Found C 55.0%; H 9.9%; P 11.6%; Cu 11.5%.

Magnesium di-*n*-hexylphosphinate (DHP-Mg) was obtained as follows. Di-*n*-hexylphosphinic acid (10 g) was dissolved in 100 ml of ethanol and 100 ml of an ethanolic solution of magnesium acetate (3.04 g) were added. A white precipitate was formed. The mixture was evaporated to one third of its initial volume, 100 ml of water were added and the solution was again evaporated to one third of its volume. After cooling, solid magnesium di-*n*-hexylphosphinate was filtered off and then extracted with hexane in a Soxhlet apparatus. The product, m.p. 100–101°C, was identified by its IR spectrum and by the elemental analysis. The results of the elementary analysis for the formula  $\text{Mg}[\text{OOP}(\text{C}_6\text{H}_{13})_2]_2$  are: Calc. C 58.72%; H 10.68%; P 12.62%; Mg 4.96%; Found C 58.7%; H 10.6%; P 12.5%; Mg 4.6%.

### Columns

There are two methods of the application of DHP-Cu and DHP-Mg in gas chromatography: (a) as adsorbents on developed surface supports, *e.g.*, on Spherosil. Such columns were used below the melting point of the polymer. (b) As a stationary liquid phase deposited on some common supports. This technique can be applied above the melting points, *i.e.*, 110°C for DHP-Cu and 100°C for DHP-Mg.

In the case of gas-solid chromatography (GCS), weighed amounts of the phosphinates were dissolved in *n*-hexane and then supported on the developed surface carrier, Spherosil XOB-030 silanized with dimethyldichlorosilane DMCS in a vacuum evaporator. After evaporation of the solvent under reduced pressure, the packing material was placed in a stainless-steel column (1 m × 4 mm) which was then conditioned for 8 h at 180°C in a stream of dry argon. Packing materials containing 3%, 5% and 10% of DHP-Cu as well as 5% of DHP-Mg were prepared.

The columns for gas-liquid chromatography (GLC) were prepared in an analogous way, except that 10% of the stationary phase was deposited on Chromosorb W HMDS (60–80 mesh). The packings containing DHP-Cu and DHP-Mg were then placed in the columns (2 m × 4 mm I.D.).

## RESULTS AND DISCUSSION

### DHP-Cu as an adsorbent

The specific retention volumes and values of the retention indexes are presented in Table I for several hydrocarbons on packings containing 5% DHP-Cu and 5% DHP-Mg, respectively. The increase in the values of the specific retention volumes for alkenes indicates the occurrence of specific interactions between DHP-Cu and

unsaturated hydrocarbons. The same conclusion can be drawn from an analysis of the temperature dependences of the retention indexes. If DHP-Cu can form complexes with alkenes, then: (a) their retention indexes should rapidly decrease with the increase of temperature; (b) the indexes should be larger than those obtained on the DHP-Mg packings.

The value of the retention index indicates, in other words, between which two *n*-alkanes a compound is eluted. The temperature dependence of the retention index is negligible, and the retention indexes of *n*-alkanes are constant by definition. A sharp temperature dependence of the retention indexes of alkenes suggests that there is an interaction between the polymer and the unsaturated hydrocarbon, the strength of which is temperature dependent.

A comparison of the retention indexes and the values of  $\Delta I/\Delta T$  for DHP-Cu and DHP-Mg indicates significant differences in the interaction with alkenes for these two phases. Copper and magnesium have very similar ionic radii, thus the differences cannot be explained in terms of dipole-induced dipole interaction, which in the case would be expected to be similar. However, copper, in contrast to magnesium, forms  $\pi$ -complexes with alkenes and this is believed to cause the above differences.

The values of the thermodynamic functions of adsorption calculated for several hydrocarbons also indicate a strong interaction of olefins with DHP-Cu. Table II lists values of the adsorption heats and entropies of pentane and several pentenes

TABLE II  
ENTROPIES AND HEATS OF ADSORPTION

Adsorbate	$-\Delta S$ ( $\text{cal} \cdot \text{mole}^{-1} \cdot ^\circ\text{K}^{-1}$ )		$-\Delta H$ ( $\text{kcal/mole}$ )		$-\Delta(\Delta H)_s$ ( $\text{kcal/mole}$ )
	5% DHP-Cu	5% DHP-Mg	5% DHP-Cu	5% DHP-Mg	
Pentane	22.1	18.1	5.66	4.16	—
1-Pentene	29.1	19.0	8.24	4.48	2.26
<i>cis</i> -2-Pentene	27.7	19.2	7.77	4.67	1.60
Cyclopentane	23.9	16.0	6.51	3.74	—
Cyclopentene	30.0	16.9	8.83	4.09	1.97
Hexane	24.3	16.1	6.89	3.94	—
Heptane	26.1	18.8	8.00	5.35	—

on adsorbents containing 5% DHP-Cu and 5% DHP-Mg. The contribution of the specific interaction energy of olefins,  $-\Delta(\Delta H)_s$ , to the total adsorption heat on packings containing 5% DHP-Cu is also presented. These values were calculated by the method of Kiselev<sup>6</sup>, on the basis of a comparison of the adsorption heats on DHP-Cu and DHP-Mg:

$$-\Delta(\Delta H)_s = (\Delta H_A - \Delta H_B)_{\text{Cu}} - (\Delta H_A - \Delta H_B)_{\text{Mg}}$$

where  $\Delta H_A$  and  $\Delta H_B$  are the heats of adsorption of an alkene and an alkane, respectively, and the subscripts Cu and Mg denote packings containing 5% DHP-Cu on Spherosil XOB-030 DMCS and 5% DHP-Mg on Spherosil XOB-030 DMCS, respectively. Thus the values of  $-\Delta(\Delta H)_s$  indicate how much more heat is evolved

during the adsorption of 1 mole of an alkene on adsorbents containing DHP-Cu than on adsorbents containing DHP-Mg. In other words, it is the increase in the adsorption heat of an alkene resulting from a specific interaction with copper atoms. If this interaction were to originate in the di-*n*-hexylphosphinate groups, it would also occur for DHP-Mg packings.

### Gas-liquid chromatography

The use of copper and magnesium phosphinates deposited on some common supports in GLC at temperatures above the melting points of the phosphinates was

TABLE III  
RETENTION VOLUMES AND RETENTION INDEXES FOR DHP-Cu AND DHP-Mg PACKINGS  
SRI = Standard retention index; *r* = relative retention volume.

Adsorbate	$^{PT}V_a$ (ml/g)		<i>r</i>		$I_R$		SRI
	DHP-Cu	DHP-Mg	DHP-Cu	DHP-Mg	DHP-Cu	DHP-Mg	
Pentane*	7.59	8.53	1.000	1.000	500	500	500
1-Pentene	7.37	8.69	0.972	1.019	495.0	503.4	495
<i>cis</i> -2-Pentene	8.82	10.44	1.163	1.224	526.2	536.2	503
<i>trans</i> -2-Pentene	8.25	9.97	1.088	1.168	514.5	527.8	499
Cyclopentane*	14.34	16.04	1.000	1.000	610.1	613.0	548
Cyclopentene	14.03	16.06	0.979	1.001	606.4	613.2	532
Hexane*	13.51	14.90	1.000	1.000	600	600	600
1-Hexene	13.87	15.27	1.026	1.025	604.4	604.4	587
<i>trans</i> -3-Hexene	14.36	16.12	1.062	1.082	610.3	613.9	594
<i>cis</i> -3-Hexene	14.87	16.56	1.100	1.111	616.6	618.6	
2,4-Hexadiene	25.93	29.96	1.918	2.010	711.2	724.2	648
Cyclohexane*	27.62	28.71	1.000	1.000	722.1	716.6	644
Cyclohexene	32.83	34.96	1.188	1.218	751.6	751.9	652
1,3-Cyclohexadiene	33.33	36.42	1.206	1.269	754.2	759.3	647
1,4-Cyclohexadiene	42.27	47.00	1.530	1.636	795.0	805.0	660
Benzene	35.97	40.15	1.302	1.398	767.3	776.7	642
Toluene	66.47	73.40	2.406	2.570	872.8	884.7	747
Ethylbenzene	112.46	117.92	4.070	4.130	963.1	970.0	844
Styrene	163.29	175.08	5.910	6.132	1027.2	1041.2	879
Cumene	153.69	156.05	5.563	5.465	1016.8	1020.4	908
<i>o</i> -Xylene	145.85	156.99	5.279	5.498	1007.8	1021.5	875
<i>m</i> -Xylene	119.39	133.57	4.321	4.678	973.4	992.4	854
<i>p</i> -Xylene	118.25	130.94	4.280	4.586	971.7	988.8	853
Fluorobenzene	37.96	—	1.374	—	776.5	—	—
Chlorobenzene	137.97	145.65	4.994	5.101	998.2	1008.0	827
Bromobenzene	257.57	265.75	9.323	9.307	1105.5	1116.3	924
Heptane*	24.28	26.18	1.000	1.000	700	700	700
1-Heptene	24.85	26.48	1.023	1.011	703.9	702.0	684
<i>trans</i> -3-Heptene	26.01	27.20	1.071	1.039	711.7	706.9	
<i>cis</i> -3-Heptene	26.64	28.44	1.097	1.087	715.8	714.9	
Octane*	43.52	45.70	1.000	1.000	800	800	800
1-Octene	44.16	45.91	1.015	1.004	802.5	800.8	
2,2,4-Trimethyl- pentane*	22.92	23.11	1.000	1.000	690.1	677.8	703
2,4,4-Trimethyl-2- pentene	29.78	31.07	1.299	1.345	734.9	730.8	726

\* Reference.

expected to demonstrate the stronger interactions of DHP-Cu with molecules having multiple bonds relative to DHP-Mg. However, in both phases appeared to behave in a similar manner. The specific and the relative retention volumes as well as the retention indexes have similar values for both phases at 115° C (Table III).

The similarity of the chromatographic properties of the melted phosphinates is due to the dominance of dispersive interactions of the hydrocarbon radicals with the sorbates. Such non-specific interactions do not exclude the existence of specific interactions between the unsaturated hydrocarbons and DHP-Cu. Indeed, the existence of specific interactions is demonstrated by the dissolution heats calculated from the temperature dependence of the retention volumes.

The heats of dissolution  $-\Delta H_r$ , and heats of specific interaction,  $-\Delta(\Delta H_r)_s$ , were calculated for DHP-Cu and DHP-Mg by the method of Kiselev<sup>6</sup> and are presented in the Table IV. Aliphatic hydrocarbons have higher heats of dissolution on DHP-Mg than on DHP-Cu, but for aromatic hydrocarbons this situation is reversed. For adsorbents which are able to form complexes, one can calculate values of  $-\Delta(\Delta H_r)_s$  from the above equation. Thus  $-\Delta(\Delta H_r)_s = 0.5-1$  kcal/mole for alkenes and a second double bond causes an increase in this value (e.g., 2,4-hexadiene and 1,3-cyclohexadiene). Aromatic compounds exhibit higher values of the heats of specific interactions, and it is interesting that they follow a sequence which is analogous to

TABLE IV  
HEATS OF SOLUTION,  $-\Delta H_r$ , AND HEATS OF SPECIFIC INTERACTION,  $-\Delta(\Delta H_r)_s$ , (kcal/mole)

Adsorbate	$-\Delta H_r$		$-\Delta(\Delta H_r)_s$
	DHP-Cu	DHP-Mg	
Cyclopentane*	6.38	7.34	—
Cyclopentene	6.74	7.16	0.54
Hexane*	5.72	7.54	—
1-Hexene	6.34	7.73	0.43
<i>trans</i> -3-Hexene	6.79	7.99	0.62
<i>cis</i> -3-Hexene	6.70	8.13	0.39
2,4-Hexadiene	8.50	8.74	1.58
Heptane*	6.35	8.69	—
1-Heptene	7.06	8.77	0.63
<i>cis</i> -3-Heptene	7.32	8.75	0.91
<i>trans</i> -3-Heptene	7.76	8.80	1.30
Octane*	6.94	9.72	—
1-Octene	7.55	9.63	0.70
2,2,4-Trimethylpentane*	5.76	8.26	—
2,4,4-Trimethyl-2-pentene	6.75	8.98	0.27
Cyclohexane*	7.66	8.08	—
Cyclohexene	8.73	8.15	1.00
1,3-Cyclohexadiene	9.19	8.12	1.49
Benzene	9.82	8.23	2.01
Toluene	10.51	9.25	1.68
Ethylbenzene	10.96	10.07	1.31
Styrene	12.17	10.69	1.90
Cumene	10.99	10.72	0.69

\* Reference.

that of the formation heats of some  $\pi$ -complexes with poly[chromium(III) diphenylphosphinate]<sup>7</sup>. The strongest interaction with DHP-Cu is shown by tetrahydrofuran. The ability of this compound to form  $\sigma$ -complexes with the transition metals results from the very strongly basic character of the oxygen electron pair, and had been demonstrated previously by gas chromatography method<sup>8,9</sup>.

In conclusion, the specific interactions of DHP-Cu with unsaturated hydrocarbons are strongly temperature dependent. Below its melting point, DHP-Cu shows much stronger interactions with sorbates than DHP-Mg. However, above their melting points, both compounds exhibit similar chromatographic behaviour.

#### *Examples of the application of DHP-Cu and DHP-Mg to gas chromatography*

The efficiency of adsorption columns containing DHP-Cu depends strongly on the quantity of phosphinate used. A column containing 10% DHP-Cu on Spherosil XOB-030 DMCS has about 660 theoretical plates per metre (t.p./m), and one containing 5% DHP-Cu has about 1250 t.p./m. The adsorbent containing 3% DHP-Cu appeared to be the most efficient. The efficiency of this packing was 2000 t.p./m in the range of optimal flow-rates of the carrier gas. It was used for the separations of saturated and unsaturated hydrocarbons as shown in Fig. 1.

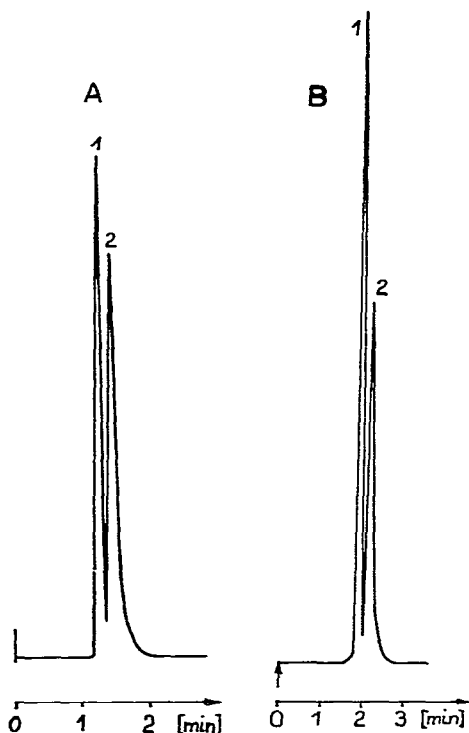


Fig. 1. Separation of cyclopentane (1) and cyclopentene (2) (A), and hexane (1) and 1-hexene (2) (B), on 3% DHP-Cu on Spherosil XOB-030 DMCS. Column (1 m  $\times$  0.4 cm I.D.) temperature, 58° C; carrier gas (argon) flow-rate, 24 ml/min; detector, FID.

The 3% DHP-Cu packing was also applied at temperatures higher than its melting point. It still has a high efficiency and can be used for the fast separation of mixtures of compounds belonging to different classes (Fig. 2).

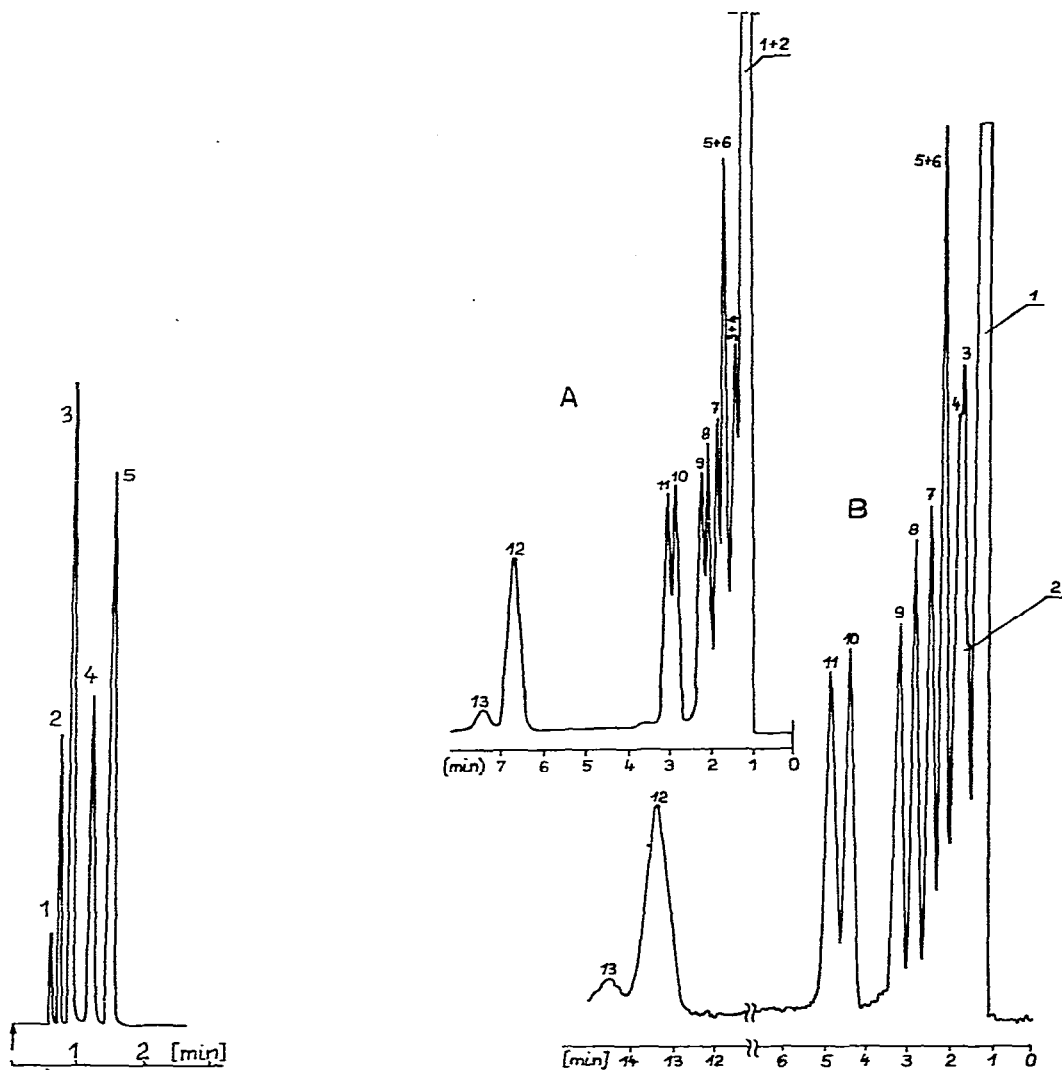


Fig. 2. Separation of methylene dichloride (1), thiophene (2), toluene (3), chlorobenzene (4) and di-*n*-butyl ether (5). Column temperature, 130.7 °C; carrier gas (argon) flow-rate, 23 ml/min. Column as in Fig. 1.

Fig. 3. Separation of a mixture of ketones on 10% DHP-Cu-Chromosorb W HNDS above (A) and below (B) the polymer melting point. Column, 2 m × 0.4 cm I.D. Column temperature: 116° C (A), 99° C (B); carrier gas (argon) flow-rate, 22 ml/min. Peaks: 1 = diethyl ether; 2 = acetone; 3 = 2-butanone; 4 = methyl vinyl ketone; 5 = 3-pentanone; 6 = 2-pentanone; 7 = methyl isobutyl ketone; 8 = diisopropyl ketone; 9 = 2-hexanone; 10 = 4-heptanone; 11 = 3-heptanone; 12 = 5-nonanone; 13 = unidentified.



Above the melting point of phosphinate, the efficiency of the column containing DHP-Cu on Chromosorb W appeared to be about 1000 t.p./m. The use of this column below the melting point of the DHP-Cu decreases the efficiency, but the column can still be used to separate mixtures demanding lower temperatures as shown in Fig. 3.

The phosphinate packing can be used for the separations of isomers, e.g., C<sub>9</sub> aromatic hydrocarbons (Fig. 4) or 1,3- and 1,4-cyclohexadienes (Fig. 5).

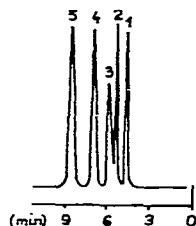


Fig. 4. Separation of cumene (1), *n*-propylbenzene (2), 1,3,5- (3), 1,2,4- (4) and 1,2,3-trimethylbenzenes (5). Column temperature, 116.6° C; carrier gas (argon) flow-rate 22.4 ml/min. Column as in Fig. 3.

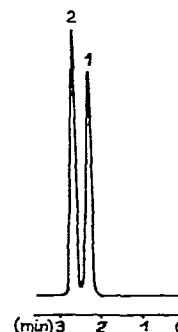


Fig. 5. Separation of 1,3- (1) and 1,4-cyclohexadienes (2). Column temperature, 99° C; carrier gas (argon) flow-rate, 21.9 ml/min. Column as in Fig. 3.

These examples of the application of DHP-Cu as a stationary phase in gas chromatography indicate the high selectivity of the polymer. The rapidity of separation should allow the analysis of mixtures of compounds exhibiting a very wide range of boiling points without using a temperature program.

#### REFERENCES

- 1 W. Szczepaniak, and J. Nawrocki, *Chem. Anal. (Warsaw)*, 19 (1974) 375.
- 2 W. Szczepaniak and J. Nawrocki, *J. Chromatogr.*, 138 (1977) 337.
- 3 R. A. Williams and R. A. Hamilton, *J. Amer. Chem. Soc.*, 74 (1952) 5418.
- 4 E. A. Peregud, *Khimicheskii analiz vozdukha*, Khimia, Leningrad, 1976.
- 5 F. Welcher, *Analityczne Zastosowanie Kwasu Wersenowego*, WNT, Warszawa, 1963.
- 6 A. V. Kiselev, *Uspekhy khromatographii*, Nauka, Moscow, 1972, p. 33.
- 7 W. Szczepaniak and J. Nawrocki, *J. Chromatogr.*, 168 (1979) 89.
- 8 B. Feibush, M. F. Richardson, R. E. Sievers and C. S. Springer, *J. Amer. Chem. Soc.*, 94 (1972) 6717.
- 9 V. Schurig, R. C. Chang, A. Zlatkis and B. Feibush, *J. Chromatogr.*, 99 (1974) 147.