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COORDINATION POLYMERS AS ADSORBENTS AND STATIONARY PHASES FOR GAS CHROMATOGRAPHY

V. APPLICATION POSSIBILITIES OF POLY[COPPER(II) DI-*n*-HEXYLPHOSPHINATE]

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SUMMARY

The separation properties of poly[copper(II) di-*n*-hexylphosphinate] as a column packing were studied and homologous series, isomers and compounds with close boiling points were separated. The separation of impurities in α-methylstyrene is demonstrated as an example of contamination analysis.

INTRODUCTION

The analytical usefulness of a packing depends on its application possibilities. McReynolds and Rohrschneider constants, thermal stability and the height equivalent to a theoretical plate provide only an approximate description of packing properties, and the most important information needed by an analyst is the substances that can be separated using a given packing. Literature reports of new chromatographic packings are often accompanied by descriptions of the separations of a few artificially prepared mixtures. However, it is usually possible to select some artificial mixture that can be separated on a new packing and such results may not be a good guide to applications to real samples. Therefore, we propose to determine the properties of new adsorbents and stationary phases in relation to several kinds of mixtures:

(a) *Homologous series*. The separation of compounds belonging to the same homologous series is usually the easiest test to perform because of the considerable differences in the physical properties of members of the series. Therefore the separation properties of a packing should be tested by using several homologous series, *e.g.*, alkanes, halogenides, ethers, esters, ketones, aldehydes and alcohols.

(b) Mixtures of compounds having the same number of carbon atoms but containing different functional groups. The separation of such a mixture provides information about which classes or organic compounds interact strongly with a packing and which interact more weakly. This test also indicates which classes of compounds will be difficult to separate.

(c) Mixtures of compounds with close boiling points. The separation of this type of mixture is a good measure of the selectivity of a packing. On the other hand, if strong interactions of a stationary phase with some sorbates occurs, wrong conclusions could be drawn about the real selectivity of the packing. Therefore, support from another test is important.

(d) Mixtures of isomers. A good separation of isomers is evidence of a high selectivity of a packing. Mixtures of isomers can be divided into "easy" and "difficult" ones. Mixtures of isomers that differ considerably in their physical properties (boiling points, polarity, vapour pressure, etc.) belong to the former group, whereas such isomers as *cis-* and *trans-* and *ortho-*, *meta-* and *para-*enantiomers to the latter.

The last stage in the assessment of the separating capability of a packing is its application to real instead of artificial mixtures. At least five different mixtures should be examined in order to obtain a fairly objective picture of the properties of a packing.

We should emphasize that the tests proposed above should (or could) be applied in addition to existing tests for the characterization of new stationary phases, and not instead of them.

EXPERIMENTAL

Packings consisting of 8.8% (w/w) poly[copper(II) di-*n*-hexylphosphinate] (DHP-Cu) on Chromosorb W DMCS (100–120 mesh) and 5% (w/w) DHP-Cu on Porasil C DMCS were examined. The columns were made of stainless steel, of dimensions 2 m × 4 mm I.D. for the first packing and 1 m × 4 mm I.D. for the second. The procedure for the synthesis of DHP-Cu and the preparation of the packings and columns have been described previously[1,2].

DHP-Cu melts at 110° and is thermally stable up to 280°. It is soluble in non-polar organic solvents and insoluble in water. The physical properties and IR spectra of DHP-Cu are very similar to those of poly [copper(II) di-*n*-octylphosphinate], which has the structure of a trimer[3]. The maximal recommended temperature for gas chromatographic (GC) columns containing DHP-Cu is 200°.

TABLE I

CHARACTERISTICS OF COLUMNS USED

T_c = column temperature; F_0 = flow-rate of carrier gas; b_0 = width of starting peak; b_{10} = width of peak at k = 10; a = slope of function $b_{0.5}$ = f(k); r = correlation coefficient; n_{real} = real plate number; h_{real} = real plate height; TZ_{10} = number of peaks between k = 0 and k = 10; TZt = separation power number; Q_s = dosage and connection quality[4].

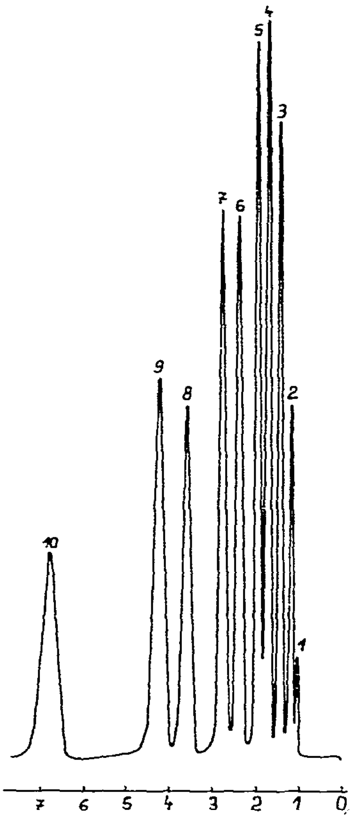
Parameter	*5% DHP-Cu on Porasil C DMCS*	*8.8% DHP-Cu on Chromosorb W DMCS*
T_c (°C)	120	120
F_0 (ml Ar/min)	18.5	21.6
b_0 (sec)	2.76	3.38
b_{10} (sec)	19.24	34.20
a	1.648	3.083
r	0.998	0.9984
n_{real}	2364	2315
h_{real}	0.42	0.86
TZ_{10}	14.5	15.8
TZt (sec^{-1})	0.04	0.023
Q_s	0.75	0.82

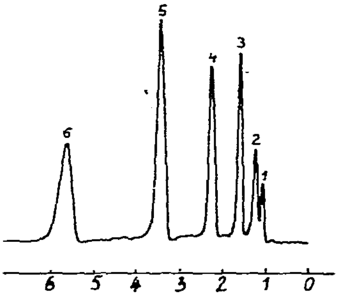
A column consisting of 8.8% DHP-Cu–Chromosorb W DMCS can be used in principle[1,2] above the melting point of the polymer, *i.e.*, in the range 110–200°. A column consisting of 5% DHP-Cu–Porasil C DMCS can operate below the melting point of DHP-Cu as an adsorbent.

RESULTS AND DISCUSSION

Table I shows the results obtained when the columns packed with DHP-Cu were tested by the Kaiser method[4]. Argon was used as the carrier gas and the flow-rates were close to the optimal values.

The HETP values were also calculated by the classical method under the same





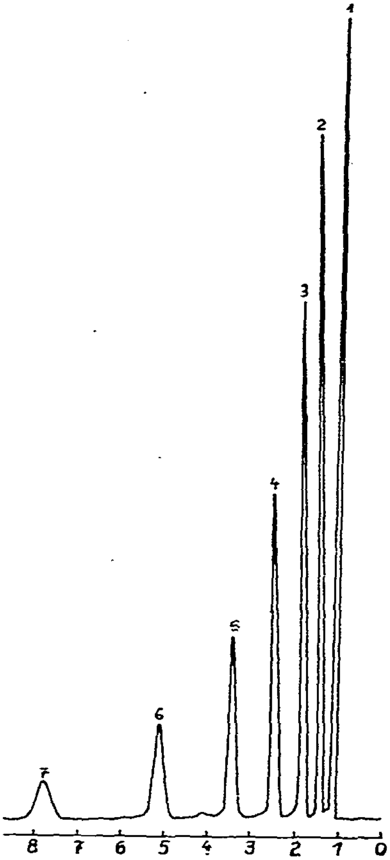
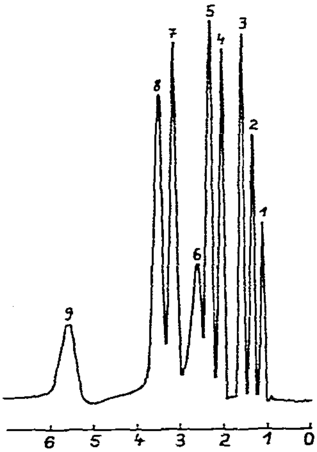


Fig. 1. Separation of esters: methyl acetate (1), methyl propionate (2), methyl butanoate (3), ethyl butanoate (4), methyl pentanoate (5), propyl butanoate (6), methyl hexanoate (7), ethyl hexanoate (8), methyl heptanoate (9), methyl octanoate (10). Column, 8.8% DHP-Cu-Chromosorb W DMCS at T_c = 122°; argon flow-rate, F_0 = 30.7 ml/min.

Fig. 2. Analysis of aldehydes: propanal (1), butanal (2), pentanal (3), hexanal (4), heptanal (5), octanal (6). Column as in Fig. 1 at T_c = 118° and F_0 = 25 ml/min.

Fig. 3. Separation of alkyl chloride: *n*-butyl chloride (1), *n*-pentyl chloride (2), *n*-hexyl chloride (3), *n*-heptyl chloride (4), *n*-octyl chloride (5), *n*-nonyl chloride (6), *n*-decyl chloride (7). Column as in Fig. 1 at T_c = 144° and F_0 = 24.2 ml/min.



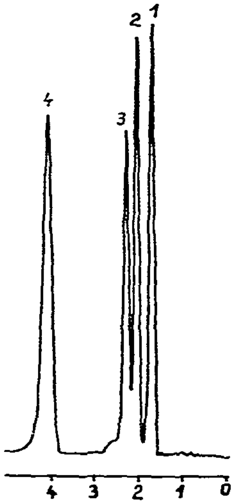
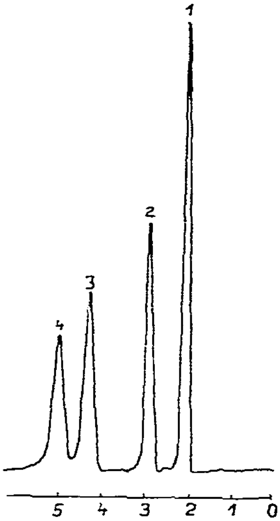


Fig. 4. Separation of C_8 compounds: isooctane (1), octane (2), di-*n*-butyl ether (3), ethylbenzene (4), octanone-2 (5), *n*-octanal (6), *n*-octyl chloride (7), methyl octanoate (8), *n*-octanol (9). Column as in Fig. 1 at T_c = 147° and F_0 = 27.7 ml/min.

Fig. 5. Separation of C_6 ketones; 4-methylpentanone-2 (1), hexanone-2 (2), 4-methyl-3-pentenon-2 (3), cyclohexanone (4). Column as in Fig. 1 at T_c = 118° and F_0 = 25 ml/min.



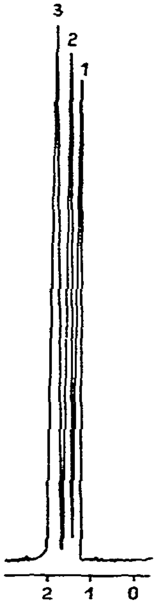


Fig. 6. Separation of C_5 alcohols: *tert.*-pentanol (1), 2-pentanol (2), 4-methylbutanol-1 (3), pentanol-1 (4). Column as in Fig. 1 at T_c = 110° and F_0 = 24.8 ml/min.

Fig. 7. Separation of C_6H_{10} hydrocarbons; hexadiene-1,5 (1), hexyne-1 (2); hexadiene-2,4 (3). Column as in Fig. 1 at T_c = 101° and F_0 = 26 ml/min.

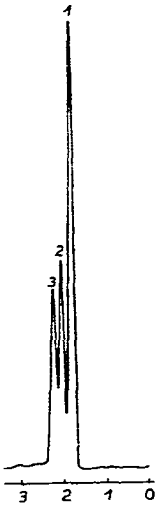


Fig. 8. Separation of compounds with similar boiling points: *tert.*-pentanol (T_b = 102°) (1), methylcyclohexane (T_b = 101°) (2), *n*-butyl bromide (T_b = 101.6°) (3). Column as in Fig. 1 at T_c = 110° and F_0 = 20.1 ml/min.

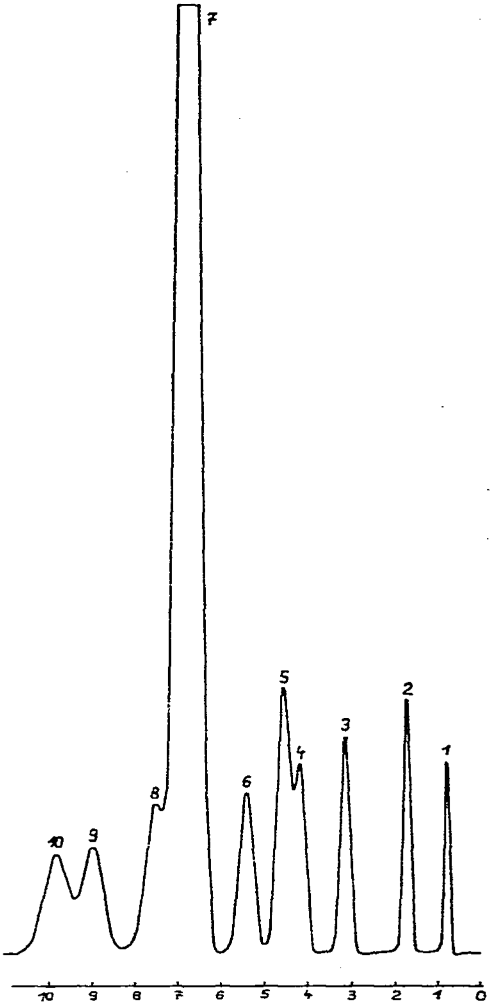


Fig. 9. Analysis of α-methylstyrene contaminants: benzene (1), toluene (2), ethylbenzene (3), styrene (4), cumene (5), *n*-propylbenzene (6), α-methylstyrene (7), *sec.*-butylbenzene (8), β-methylstyrene (9), *n*-butylbenzene (10). Column: 5% DHP-Cu–Porasil C DMCS at T_c = 110° and F_0 = 23.8 ml/min.

conditions. They ranged between 0.91 and 0.56 mm for the 5% DHP-Cu–Porasil C DMCS column and between 0.98 and 0.91 mm for the 8.8% DHP-Cu–Chromosorb W DMCS column.

DHP-Cu allows the separation of compounds belonging to different homologous series. The separations of esters, aldehydes and halogen derivatives are shown in Figs. 1, 2, and 3, respectively.

It is important that a wide variety of compounds can be separated in a short time. The analysis of nine C_8 compunds with different functional groups is shown in

Fig. 4, and the separation of a mixture of compounds having the same number of carbon atoms and the same functional group (C_6 ketones) is presented in Fig. 5.

Separations of isomeric mixtures are shown in Figs. 6 and 7.

In an earlier paper[2] we described the application of DHP-Cu to the separation of a mixture of compounds with close boiling points. Another example of that application is presented in Fig. 8, where an incomplete separation of three compounds with close boiling points, *viz.*, *tert.*-pentanol (102°), methylcyclohexane (101°) and 1-bromobutane (101.6°) is shown.

From the chromatograms shown above, the following conclusions can be drawn: alcohols have the strongest interaction with DHP-Cu; steric hindrance appears to play a role in the interaction between the adsorbate and the packing; among the pentanols, the interaction with DHP-Cu is weakest with *tert.*-pentanol (however, it should be taken into account that differences in the retention volumes of the pentanols are also due to differences in their boiling points); and with a mixture of compounds with similar boiling points (see Fig. 8), the interaction of *tert.*-pentanol is weaker than that of a hydrocarbon, methylcyclohexane, which interacts with DHP-Cu only via the so-called "cyclic effect"[2,5]. The interaction of a halogen atom is stronger than the "cyclic effect".

DHP-Cu can be used to separate the products of many catalytic reactions, in the analysis of sewage and to determine contaminants in chemical compounds. As an example of the last application, the analysis of impurities in α-methylstyrene is shown in Fig. 9. The use of DHP-Cu led to a significant reduction in the analysis time. According to available literature data, the above analysis normally requires about 70 min[6], whereas with DHP-Cu it requires only about 10 min.

DHP-Cu can be applied to the analysis of almost all classes of organic compounds with the exception of amines and acids. According to the procedure given earlier[1,2], DHP-Cu is always applied as a covering on a support. On the basis of our results, we believe that it is worth synthesizing organic adsorbents (such as Porapak, Chromosorb Century Series) containing transition metal phosphinates.

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