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Gas-chromatographic separation of phenols on nickel, copper and zinc diethyldithiocarbamates

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The title complexes were prepared and used as stationary phases in complexation GC for the separation of phenols; the best separation for chlorophenols was achieved with copper diethyldithiocarbamate.

The determination of phenols is necessary because of their toxicity and widespread use in industry. To avoid GC peak tailing, phenols are derivatised to give less polar compounds.[1]

The sorbents containing metal diethyldithiocarbamate (DEDTC) complexes on silica allow the separation of compounds with electron-donor properties. Such sorbents usually show high selectivity, thermal stability and resistance to external factors.[2] The use of complexation properties of metals in gas chromatography is well known.[4] A number of metals complexes including beryllium, aluminium, nickel and zinc complexes of β-diketones,[5] nickel, palladium and platinum complexes of glyoximes,[6] metal phthalocyanine complexes[7] have been used as stationary phases for gas chromatography. Investigations of the influence of salts and metal complexes on chromatographic parameters have been done.[8]

The chromatographic properties of sorbents with Hg^{II}, Cu^{II}, Cd^{II} and Zn^{II} dithiocarbamate complexes were used as stationary phases for separation of dialkyl sulfides.[9] DEDTC complexes of metals are capable of separating polar substances without peak tailing. Such a form of peaks of phenols is observed in separation on various sorbents including metal-containing complexes.[1(c),10] This work was aimed at the use of the sorbents containing Zn^{II}, Cu^{II} and Ni^{II} DEDTC complexes for the separation of phenols.†

The retention and selectivity of the separation of the following phenols were studied on these stationary phases: phenol, *o*-cresol, *p*-cresol, *m*-cresol, 2,4-dimethylphenol, 2,4,6-trimethylphenol, 2-chlorophenol, 2,4-dichlorophenol and 2,4,6-trichlorophenol.

p-Cresol, *m*-cresol and 2,4-dimethylphenol were coeluted at a column temperature of above 150 °C. The retention of samples increased with decreasing column temperature, and the peak shape was improved. The best resolution was found for 120 °C.

For phenol, more substituent methyl groups lead to more electron-rich benzene rings and hence to larger ΔH values. The infinite-delution solute partial molar enthalpy was obtained by the equation[11] $\ln V_g^0 = -\Delta H/RT + \text{const}$. The ΔH values increase in the order: phenol, *o*-cresol, 2,4-dimethylphenol and 2,4,6-trimethylphenol. Meanwhile the solute–solvent interaction is stronger for the zinc complex than that for the nickel complex.

† Silica (Silipor 075) was obtained from Lachema (Czech Republic). The stock solutions of phenols (0.2 g) were prepared in butyl acetate and stored at 6 °C.

Chromatographic measurements were performed on a Chrom 5 gas chromatograph (Czech Republic) with a flame-ionization detector. Glass columns (1.2 m × 3 mm i.d.) were used. The procedure for the preparation of metal DEDTC complexes was reported.[9]

The metal DEDTC complexes dissolved in toluene were mixed with silica (5 wt%) and stirred for 1 h at 60 °C. Excess solvent was removed under reduced pressure. The packed column was then conditioned for 8 h at 150 °C. The column efficiency was 748, 812 or 733 plate $m^{-1/2}$ for DEDTC-Ni, DEDTC-Cu and DEDTC-Zn, respectively.

Elemental analysis was performed on a MAES-10 Elemental Analyser (Russia). Specific surface areas were determined by BET using an AUS-5 instrument (Russia). The specific surface area of initial Silipor 075 was 96 $m^2\ g^{-1}$ and that of DEDTC-Ni, DEDTC-Cu or DEDTC-Zn containing sorbent was 92, 87 or 89 $m^2\ g^{-1}$, respectively.

Table 1 Retention factors [$k = (t_x - t_0)/t_0$] and heats of adsorption (ΔH^0) (n = 3–4, P = 0.95, RSD_k = 0.04, $RSD_{\Delta H}$ = 0.09).

Substance	bp/°C	DEDTC-Cu		DEDTC-Ni		DEDTC-Zn	
		k	ΔH^0	k	ΔH^0	k	ΔH^0
Phenol	180	9.43	4.45	10.06	2.49	9.96	2.57
o-Cresol	191	9.94	4.81	10.94	2.52	11.27	2.63
p-Cresol	202	12.99	4.98	13.59	2.55	15.07	2.65
m-Cresol	203	13.24	5.14	14.47	2.58	15.76	2.76
2,4-Dimethylphenol	210	17.94	5.43	17.63	2.61	20.49	2.82
2,4,6-Trimethylphenol	220	18.24	5.95	18.73	2.78	23.94	3.17
2-Chlorophenol	174	9.55	4.52	10.52	2.50	10.27	2.69
2,4-Dichlorophenol	210	22.17	6.60	23.37	3.01	27.12	3.42
2,4,6-Trichlorophenol	246	23.87	8.12	28.75	3.75	35.75	4.25

The elution mainly follows the order of boiling points of tested substances. Deviations from the elution order were observed only for the pair 2-chlorophenol/phenol. Phenols are expected to form complexes with a metal ion of DEDTC complexes supported on silica. Any change in the substituent of phenols had pronounced effects on the retention time. Chlorine is an electron-donating atom and 2-chlorophenol forms a stronger complex than phenol; thus, phenol is eluted first. Methyl is an electron donating group, the effect of the substituent is much greater in the case of *p*-isomers. Hence, the elution order of the positional isomers was $m < p$.

Chlorine atoms, because of their high electron affinity, cause a decrease in the electron density of the aromatic system. On the other hand, it increases metal–sorbate interactions, because it makes this part of sorbate molecule which is capable of interacting specifically due to a chlorine electron pair. This can be seen for the retention parameters of methyl-substituted substances are lower in comparison with phenols.

The Ni-, Cu- and Zn-DEDTC complexes can be used for the separation of phenols in gas chromatography. The optimum conditions for the separation of phenols are as follows: stationary phase, 5% DEDTC-Ni on Silipor 075; programmed temperature, 80 °C (4 min) to 170 °C at 2.5 K min^{-1}; injection temperature, 230 °C. The detection limit of phenols is 120 ng.

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