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## THERMODYNAMIC DISTINCTION IN DONOR-ACCEPTOR INTERACTIONS OF ORGANIC BASES WITH KF AND $\text{Na}_3\text{PO}_4$ ON HYDROGENATED APIEZON COLUMNS

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### SUMMARY

The retention indices,  $I$ , and the partial molar free energies of sorption,  $\Delta G$ , have been determined for  $n$ -alkanes, aromatic hydrocarbons, aliphatic and aromatic amines and pyridine on three columns with hydrogenated Apiezon L containing equimolar quantities of KOH, KF and  $\text{Na}_3\text{PO}_4$ . It is shown that neither  $I$  nor  $\Delta G$  of  $n$ -alkanes and aromatic hydrocarbons depends on the support treatment. The differences in the abilities of organic bases to undergo donor-acceptor interactions with KOH, KF and  $\text{Na}_3\text{PO}_4$  under the conditions prevalent in gas chromatography have been estimated thermodynamically. It is shown that the contribution of the donor-acceptor interaction energy to the total partial molar free energy of sorption is the same for KOH and KF, but is higher for  $\text{Na}_3\text{PO}_4$  and dependent on the type of organic base.

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### INTRODUCTION

The chromatographic separation of polar compounds such as organic bases is carried out on supports specially treated to suppress adsorption on the acid centres. It has been shown that treatment of a support with an alkali reduces the contribution of adsorption to the retention volume by only 1%, compared with the 10% observed on alkali-free sorbents<sup>1</sup>. There are two methods of preparing such columns. In the first, the adsorbent is neutralized, prior to application of the stationary phase, by washing with 1-5% alkali solution in water or alcohol<sup>2-4</sup>. In the second method, the stationary phase and inorganic compounds capable of donor-acceptor interaction with the solute are applied on the adsorbent surface<sup>5-7</sup>.

Thermodynamic data for amine sorption on these two kinds of columns are scarce. The effect of alkali-metal halides (lithium, sodium and potassium chlorides, bromides and iodides) on the retention parameters of acid amides has been investigated on polar packed columns and the excess free energies of mixing have been determined<sup>8</sup>. The formation of hydrogen bonds between primary and secondary amines and solid NaOH under gas chromatographic (GC) conditions has been demonstrated<sup>9</sup>. It has also been found that  $\text{Na}_3\text{PO}_4$  is capable of interacting with

organic bases via the donor-acceptor mechanism<sup>10</sup>. On the basis of the concept of NaOH and Na<sub>3</sub>PO<sub>4</sub> as weak complexing agents in amine analysis, a method has been developed for the preparation of highly effective and selective glass capillary columns containing KF which can form hydrogen bonds with the proton donor amines<sup>11</sup>.

The energy contributions of the functional groups of amines and alcohols to the total partial molar free energy of sorption on capillary columns with KOH, KF and Na<sub>3</sub>PO<sub>4</sub> have been determined<sup>12</sup>. However, the methods of preparation of capillary columns present difficulties in the interpretation of the differences in complexing activities of KF and Na<sub>3</sub>PO<sub>4</sub>. In order to study such complexing activities we compared the sorption characteristics of three GC columns containing equimolar amounts of KOH, Na<sub>3</sub>PO<sub>4</sub> and KF and the non-polar stationary phase, hydrogenated Apiezon L, on Chromosorb G. The differences in the donor-acceptor interactions of KOH, KF and Na<sub>3</sub>PO<sub>4</sub> with organic bases have been estimated thermodynamically.

## EXPERIMENTAL

For the preparation of GC columns Chromosorb G AW (100-120 mesh) (Johns-Manville) was used. The parameters of the columns are given in Table I. Apiezon L (Apiezon Products, U.K.) was hydrogenated as described<sup>13</sup>. The degree of hydrogenation was monitored spectrophotometrically in cyclohexane solution at wavelengths of 238 and 260 nm. The molecular weight of the hydrogenated Apiezon L determined ebullioscopically was 2400.

Potassium fluoride (p.a.), trisodium phosphate (p.a.) and potassium hydroxide (p.a.) were used. Because of its extreme hygroscopicity, potassium fluoride was heated to melting to yield the hydrate KF · 2H<sub>2</sub>O. The column packings were prepared as follows. To 33 g of Chromosorb G AW were added 50 ml of distilled water and 0.59 g of KF · 2H<sub>2</sub>O (or 2.29 g Na<sub>3</sub>PO<sub>4</sub> · 12H<sub>2</sub>O, or 0.33 g KOH). Water was removed

TABLE I  
CHARACTERISTICS OF HYDROGENATED APIEZON L COLUMNS CONTAINING KOH, KF AND Na<sub>3</sub>PO<sub>4</sub>

<i>Parameter</i>	<i>KOH</i>	<i>KF</i>	<i>Na<sub>3</sub>PO<sub>4</sub></i>
Content of additives			
% of the weight of Chromosorb G	1.00	1.04	3.04
moles	0.004	0.004	0.004
Content of Apiezon			
% of the weight of Chromosorb G	4.0	4.0	4.0
moles	0.00037	0.00037	0.00037
Efficiency with respect to tripropylamine	1800	2250	1900
Selectivity for			
xylene-toluene pair	0.69	0.70	0.70
dibutylamine-triethylamine pair	0.23	0.21	0.35
Thermodynamic selectivity, $-\delta(\Delta G)_{1,2}$ in cal/mol for			
xylene-toluene pair	1180	1180	1190
dibutylamine-triethylamine pair	260	250	380

on a bath of boiling water by means of a rotary evaporator and then all three supports were dried over  $P_2O_5$  at  $260^\circ C$  and 4 mmHg for 5 h. The stationary phase, hydrogenated Apiezon L (3.96 g) was dissolved in 150 ml of abs. petroleum ether; 50 ml of this solution were added to each of the three support samples. To improve the support wettability, a detergent (Perkin-Elmer) was added to the solution (2% of the mass of hydrogenated Apiezon L). The solvent was evaporated by means of the rotary evaporator on the bath of boiling water. The resulting sorbents were dried at  $200^\circ C$  and 4 mmHg for 1 h.

Before packing, the glass columns ( $270 \times 0.4$  cm I.D.) were washed with 50 ml of 2.5% KOH solution in methanol and dried in a stream of nitrogen. The columns were packed with sorbent with the help of a manually operated vibrator, and then conditioned in a flow of high purity nitrogen at  $180^\circ C$  for 24 h. The following compounds were used for testing the sorption characteristics of the three columns:  $C_6$ - $C_{11}$  *n*-alkanes; benzene; toluene; *o*-, *m*-, *p*-xylenes; *n*-hexylamine; dipropylamine; dibutylamine; *N*-methylaniline; *N,N*-dimethylaniline; aniline; triethylamine; pyridine; tripropylamine; *N,N*-dimethylhexylamine; *N*-methylhexylamine. The last three amines were prepared by known procedures<sup>14</sup>. The boiling points of all the compounds were consistent with the literature data.

The above compounds were analyzed with a Pye-Unicam 104 chromatograph and a flame ionization detector. The temperature was  $100^\circ C$ , the carrier gas was helium and the flow-rate 20 ml/min. The compounds were analyzed as solutions in pentane. The samples (1  $\mu$ l) contained 5-10  $\mu$ g of each compound.

To obtain the partial molar free energies of sorption,  $\Delta G$ , the specific retention volumes for the compounds analyzed were determined using the formula<sup>15</sup>

$$V_g = \frac{273}{T} \frac{t' v}{w} \cdot \left( 1 - \frac{P_{H_2O}}{P_0} \right) \cdot j \quad (1)$$

where  $t'$  is the corrected retention time in min,  $v$  is the bulk flow-rate (ml/min) of the carrier gas measured at room temperature with a foam flow-rate meter,  $w$  is the mass (g) of the stationary phase in the column,  $T$  is the room temperature ( $^\circ K$ ),  $1 - P_{H_2O}/P_0$  is a correction for the water vapour pressure at room temperature and  $j$  is a factor taking account of the pressure drop in the column

$$j = \frac{3}{2} \cdot \frac{(P_i/P_0)^2 - 1}{(P_i/P_0)^3 - 1}$$

where  $P_i$  is the inlet pressure and  $P_0$  is the outlet pressure.

The partial molar free energies of sorption were determined by the equation<sup>15</sup>

$$\Delta G = -2.3 RT \log \frac{V_g M}{273 R'} \quad (2)$$

where  $M$  is the molecular weight of the hydrogenated Apiezon L,  $T$  is temperature ( $^\circ K$ ) of analysis,  $R$  is the gas constant equal to 1.987 cal/mol  $\cdot$   $^\circ K$  and  $R'$  is the gas constant equal to 82.057  $cm^3 \cdot atm/mol \cdot ^\circ K$ .



The thermodynamic selectivity,  $\delta(\Delta G^E)$ , of the columns was calculated by the formula<sup>16</sup>

$$\delta(\Delta G^E)_{1,2} = -2.3 RT \left( \frac{b\delta I_{1,2}}{100} + \log \frac{P_1^s}{P_2^s} \right) \quad (3)$$

where  $b$  is the logarithm of the ratio of the corrected retention times of two successive  $n$ -alkane homologue,  $\delta I_{1,2}$  is the difference in retention indices of compounds 1 and 2 on a given column and  $P_1^s$ ,  $P_2^s$  are the saturated vapour pressures of compounds 1 and 2 over a pure liquid at the analysis temperature.

## RESULTS AND DISCUSSION

Thermodynamic data on the donor-acceptor interactions of organic bases with inorganic compounds under GC conditions were reported previously<sup>8,9</sup>. The enthalpy and entropy of the hydrogen-bond formation between primary and secondary amines and NaOH have been determined and it has been shown that in the case of primary amines the enthalpy is about twice as large as in the case of secondary amines<sup>9</sup>. It should be noted that the presence of alkali-metal halides and potassium hydroxide could affect the properties of polyethylene glycol (PEG) as the stationary phase<sup>8,17</sup>, but no experiments were undertaken to study the sorption capacity of PEG in the presence of additives. According to the previous work<sup>8</sup>, there is additional retention of acid amides on the column due to the ion-dipole interaction with salts which results in bonds between the salt anion and the  $\text{NH}_2$  group and between the cation and  $\text{C}=\text{O}$  group. The ability of the salts KF and  $\text{Na}_3\text{PO}_4$  to form complexes with amines in GC capillary columns has been demonstrated<sup>12</sup>. However, the difficulty of determining the amount of salt on the glass capillary surfaces renders impracticable their use for thermodynamic measurements. Besides, experimental data on the effect of salts on thermodynamic sorption parameters are available mainly for columns containing polar stationary phases, *viz.*, polyethylene glycols, which further hampers the interpretation of the available data. We tried to solve this problem by using a column packed with a non-polar stationary phase on a sorbent comprising equimolar amounts of inorganic compounds, since this allows one to compare the donor-acceptor interactions and determine their individual features. Interactions between organic bases and the inorganic compounds KOH,  $\text{Na}_3\text{PO}_4$  and KF selected for this study may yield complexes of two types in which the amine group may act either as an electron donor,  $\text{>N:}\cdots\text{P}^{\ominus}$  (ref. 10), or as a proton donor,  $\text{>N-H}\cdots\text{O}^{\ominus}$  (ref. 9),  $\text{>N-H}\cdots\text{F-K}$  (ref. 11),  $\text{>N-H}\cdots\text{O}=\text{P}^{\ominus}$  (ref. 10). A further problem in the investigation of the complexes between amines and  $\text{Na}_3\text{PO}_4$  is that primary and secondary amines can react in both these ways.

Theoretical considerations show that the partial molar free energy of the interaction of substances with the stationary phase in GC is the sum of the energies of the intermolecular interactions, non-specific ones due to the Van der Waals forces, *viz.*, dispersive, inductive and orientational interactions, and specific donor-acceptor interactions. In the case of non-polar stationary phases used for the analysis of polar compounds, the inductive interactions are small and the partial molar free energy of

TABLE III  
 SPECIFIC RETENTION VOLUMES,  $V_g$ , RETENTION INDICES,  $I$ , AND PARTIAL MOLAR FREE ENERGIES OF SORPTION OF AROMATIC HYDROCARBONS,  $\Delta G$   
 Columns with hydrogenated Apiezon L in the presence of KOH, KF and  $\text{Na}_3\text{PO}_4$  at 100°C.

Compound	KOH		KF		$\text{Na}_3\text{PO}_4$		
	$V_g$ (ml/g)	$I$	$\Delta G$ (cal/mol)	$V_g$ (ml/g)	$I$	$\Delta G$ (cal/mol)	
Benzene	25.8	698	750	26.1	699	760	
Toluene	53.3	798	1290	53.8	800	1300	
<i>p</i> -Xylene	111.2	900	1840	110.8	899	1840	
<i>m</i> -Xylene	113.3	902	1850	112.8	902	1850	
<i>o</i> -Xylene	134.6	926	1980	132.9	924	1970	
				$V_g$ (ml/g)	$I$	$\Delta G$ (cal/mol)	$\Delta G$ (cal/mol)
				25.9	698	750	750
				53.9	800	1300	1300
				111.7	901	1840	1840
				113.0	902	1850	1850
				133.8	925	1980	1980

solution is determined mainly by the dispersive interaction. The contribution of adsorption on the support may be ignored<sup>1</sup>. It is therefore advantageous to use non-polar phases that are inert to inorganic salts for the investigation of the specific interactions between the analyzed compounds and the inorganic materials.

We employed hydrogenated Apiezon L<sup>13</sup> possessing a reduced number of double bonds and aromatic systems. Three columns containing 4% of hydrogenated Apiezon L and 0.004 mol of KOH, KF or Na<sub>3</sub>PO<sub>4</sub> were prepared. The inorganic additives are probably distributed by diffusion within a micro-layer of the stationary phase, covering the support surface. To verify that the salts do not affect the properties of Apiezon L, its dispersive interactions with the analyzed compounds were investigated by measuring the partial molar free energy of solution of the methylene group in *n*-alkanes,  $\Delta G^{\text{CH}_2}$  (ref. 16). Table II shows that the specific retention volumes, partial molar free energies of sorption of *n*-alkanes and the  $\Delta G^{\text{CH}_2}$  values were practically the same for all three columns. The  $\Delta G^{\text{CH}_2}$  values, measured with an accuracy of  $\pm 10$  cal/mol, were 530–550 cal/mol. Thus, the dispersive interaction energy is the same throughout the C<sub>6</sub>–C<sub>11</sub> *n*-alkane series. It follows that the dispersive interactions of the stationary phase are not affected by the presence of the inorganic additives KOH, KF and Na<sub>3</sub>PO<sub>4</sub>. This result was confirmed by analysis of aromatic hydrocarbons.

In gas chromatography, benzene serves as a test compound for ability of the stationary phase to undergo dispersive interactions and  $\pi$ -complex formation. The aromatic hydrocarbons studied (Table III) permitted us to estimate the dispersive interaction energy and compare the  $\Delta G^{\text{CH}_2}$  values with those obtained for *n*-alkanes. Attachment of a CH<sub>2</sub> group to the benzene ring increases  $\Delta G$  by 540 cal/mol, as seen from a comparison of the free energies of sorption of toluene and benzene, *i.e.*, the same value as for addition of a methylene group to a *n*-alkane. Comparison of the partial molar free energies of sorption in the series benzene, toluene, *p*-xylene, *m*-xylene indicates that the ability of hydrogenated Apiezon L to undergo inductive interactions is small. The retention parameters of *p*- and *m*-xylene are very similar, despite the fact that the latter has a dipole moment. Comparison of the partial molar free energies of sorption of aromatic hydrocarbons on the three columns shows that the values for each compound are practically the same on all columns. It follows that the columns with KOH, KF and Na<sub>3</sub>PO<sub>4</sub> do not differ on their ability to undergo dispersive, inductive and  $\pi$ -complex formation interactions with aromatic compounds.

The differences in column properties are manifested in the analysis of organic bases capable of specific interactions. It is known that the retention of compounds is determined by partition coefficients. In our case, on each of the columns containing Na<sub>3</sub>PO<sub>4</sub> and KF, the partial molar free energy of sorption of amines is the sum of the contributions

$$\Delta G_1 = \Delta G_{\text{sol.}} + \Delta G_{\text{d-acc.Na}_3\text{PO}_4} + \Delta G_{\text{ads.}}$$

$$\Delta G_2 = \Delta G_{\text{sol.}} + \Delta G_{\text{d-acc.KF}} + \Delta G_{\text{ads.}}$$

where  $\Delta G_{\text{sol.}}$  is the free energy of amine solution in the stationary phase,  $\Delta G_{\text{d-acc.Na}_3\text{PO}_4}$ ,  $\Delta G_{\text{d-acc.KF}}$  are the energies of the donor-acceptor interactions of the

TABLE IV  
SPECIFIC RETENTION VOLUMES,  $V_g$ , RETENTION INDICES,  $I$ , AND PARTIAL MOLAR FREE ENERGIES OF SORPTION,  $\Delta G$ , OF ORGANIC BASES

Columns with hydrogenated Apiezon L in the presence of KOH, KF and  $\text{Na}_3\text{PO}_4$  at 100°C.

Compound	KOH			KF			$\text{Na}_3\text{PO}_4$		
	$V_g$ (ml/g)	$I$	$-\Delta G$ (cal/mol)	$V_g$ (ml/g)	$I$	$-\Delta G$ (cal/mol)	$V_g$ (ml/g)	$I$	$-\Delta G$ (cal/mol)
Pyridine	37.6	750	1030	36.9	748	1020	48.0	784	1220
Triethylamine	32.1	683	670	23.7	686	690	29.1	714	840
N,N-Dimethylhexylamine	108.2	895	1820	108.6	896	1820	123.3	915	1920
Dipropylethylamine	71.3	838	1510	71.2	838	1510	73.4	842	1530
Tripopylamine	127.5	918	1940	126.3	917	1930	132.3	923	1970
N,N-Dimethylamine	472.5	1095	2910	475.8	1096	2920	475.8	1096	2920
Hexylamine	72.5	841	1520	72.3	840	1520	99.6	884	1760
N-Methylhexylamine	99.8	884	1760	98.3	882	1750	131.9	924	1970
Dipropylamine	37.7	750	1040	37.4	749	1030	49.9	789	1240
Dibutylamine	159.7	949	2110	159.3	948	2110	198.7	978	2270
Aniline	186.5	970	2220	184.5	968	2210	291.8	1030	2550
N-Methylamine	371.0	1063	2730	367.9	1061	2730	439.8	1086	2860



amine with the salts  $\text{Na}_3\text{PO}_4$  and  $\text{KF}$  respectively and  $\Delta G_{\text{ads}}$  is the energy of adsorption on the surface of the stationary phase film. Since the specific retention volumes for *n*-alkanes, benzene and its methyl derivatives on the three columns containing  $\text{KOH}$ ,  $\text{KF}$  and  $\text{Na}_3\text{PO}_4$  are similar within the experimental error (Tables II and III) and the hydrogenated Apiezon L is inert with respect to the additives, it may be assumed that the contributions  $\Delta G_{\text{sol}}$  and  $\Delta G_{\text{ads}}$  are the same on these columns for the same compounds. The different retention volumes observed on columns with  $\text{KF}$  and  $\text{Na}_3\text{PO}_4$  in analyses of organic bases are due to the additional contribution from donor-acceptor interactions. In each case this energy is proportional to the number of moles of the complexing salt applied to the support. Since the number of moles of  $\text{KF}$  and  $\text{Na}_3\text{PO}_4$  is the same in our two columns, the difference  $\Delta G_1 - \Delta G_2 = \delta(\Delta G)_{1,2}$  will represent the difference in the ability of salts to undergo complex formation.

The data given in Table IV indicate that the donor-acceptor properties of  $\text{KOH}$  and  $\text{KF}$  are similar. The retention indices and differential molar free energies of sorption of amines coincide to within 3 index units and 20 cal/mol, respectively. For most organic compounds the  $V_g$  and  $I$  values are much higher on the column with  $\text{Na}_3\text{PO}_4$ . As the reference column for the study of trisodium phosphate interactions with amines we used the one with  $\text{KF}$  in which the salt acts mainly as a proton acceptor<sup>12</sup>.

It was expected that the ability of amines to undergo specific interactions with salt would be dependent on their basicities. The lower the basicity in the gas phase, the more readily the primary and secondary amine groups act as hydrogen donors. Published data show that the basicity of amines in non-polar solvents (benzene, hexane)<sup>18</sup> varies with the proton affinity (PA) in the gas phase<sup>19,20</sup>. The basicity of the amines might be expected to be similar in the case of dissolution in the pure Apiezon L stationary phase. When there complexing agents are present, the ability of the amino group to form complexes will depend on the basicity of the amine.

A comparison of the free energies of sorption of nitrogen-containing compounds capable of acting as proton donors (Table V) shows that the highest energy for the donor-acceptor interaction with trisodium phosphate is observed for aniline which has the lowest PA value. Among aliphatic amines, hexylamine has the lowest PA and the highest  $\delta(\Delta G)_{1,2}$  values.

In the case of tertiary amines (strong bases<sup>21</sup>) which do not contain amino hydrogen atoms it was expected that the higher the  $\delta(\Delta G)_{1,2}$  value the higher would be the PA value if the other component were also a strong complexing agent. The salt  $\text{Na}_3\text{PO}_4$  is a weak complexing agent and therefore it is difficult to observe a clear correlation between the  $\delta(\Delta G)_{1,2}$  values and the basicities of the amines. Apart from the basicity, the ability to undergo specific interactions is affected by the presence of alkyl groups (for tertiary amines) that provide steric hindrance to the complexing process. It is seen in Table V that dipropylethylamine and tripropylamine have the highest PA values but the differences in the free energies of sorption on the columns with  $\text{KF}$  and  $\text{Na}_3\text{PO}_4$  are small, 20 and 40 cal/mol, respectively. These amines have propyl groups that hinder access to nitrogen. Probably, in this case the "propyl anomaly" effect is also manifested in decreased retention volumes<sup>22</sup> and lower abilities to undergo specific interactions. Pyridine, which has the lowest PA value and no steric hindrance, is the most susceptible to complexing and one observes the max-

TABLE V  
DIFFERENCE IN THE PARTIAL MOLAR FREE ENERGIES OF SORPTION  $\delta(\Delta G)_{1,2}$  OF ORGANIC BASES ON COLUMNS WITH HYDROGENATED APIEZON L IN THE PRESENCE OF  $\text{Na}_3\text{PO}_4$  AND KF

PA represents the negative enthalpy of interaction between a proton and the organic base in the gas phase<sup>19,20</sup>.

Base (proton donor)	$-\delta(\Delta G)_{1,2}$ (cal/mol)	Proton affinity, PA (kcal/mol)	Base (electron donor)	$-\delta(\Delta G)_{1,2}$ (cal/mol)	Proton affinity, PA (kcal/mol)
Aniline	340	215.9	Pyridine	200	225.6
N-Methylaniline	130	222.0	N,N-Dimethylaniline	0	228.7
Hexylamine	240	225.6	N,N-Dimethylhexylamine	100	—
N-Methylhexylamine	220	—	Triethylamine	150	235.5
Dipropylamine	210	231.4	Dipropylethylamine	20	—
Dibutylamine	160	232.5	Tripropylamine	40	237.7

imum difference in sorption energies (200 cal/mol) for it on columns with  $\text{Na}_3\text{PO}_4$  and KF (see Table V). The  $\delta(\Delta G)_{1,2}$  values for tertiary amines are, apparently, wholly due to complexing with trisodium phosphate, since it had been shown earlier that KF does not form complexes with tertiary amines<sup>12</sup>.

Thus, both KF and  $\text{Na}_3\text{PO}_4$  interact with amines that are capable of being hydrogen donors via the donor-acceptor mechanism, the energy contribution to re-formation of the complex formation with  $\text{Na}_3\text{PO}_4$  being higher than those with KF and KOH. Only  $\text{Na}_3\text{PO}_4$  forms complexes with tertiary amines via an electron-acceptor mechanism. It is probable also that amines are capable of interacting electrostatically with salt cations, but the contribution of this interaction is insignificant. Inorganic additives (KOH, KF and  $\text{Na}_3\text{PO}_4$ ) affect column selectivity (*cf.*, Table I). The individual selectivities with respect to the *p*-xylene-toluene pair are practically the same, whereas the selectivity of the column with  $\text{Na}_3\text{PO}_4$  with respect to the dibutylamine-triisopropylamine pair is substantially higher. The selectivities of the columns with KOH and KF with respect to this pair of amines are very similar.

In the analysis of primary and secondary amines, the peaks are more symmetrical and the efficiency higher on the columns with KF compared with those containing  $\text{Na}_3\text{PO}_4$  and KOH. Using the technique proposed in this work it is possible to prepare KF-containing packed columns that are suitable for analysis of not only organic bases but also other polar compounds, including those that decompose in the presence of solid alkali.

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