Thermodynamic Studies on a Hydrogen Bonded Acidic (HBA) 3,5-bis(trifluoromethyl)phenol-Functionalized Polymer as a Gas Chromatography Stationary Phase for Selectively Speciating Chemical Warfare Agents

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Abstract

We describe for the first time hydrogen bonded acid (HBA) polymer, poly{methyl[3-(2-hydroxy, 4,6-bistrifluoromethyl)phenyl]propylsiloxane}, (DKAP), as stationary phase for gas chromatography (GC) of organophosphate (OP), chemical warfare agent (CWA) surrogates, dimethylmethylphosphonate (DMMP), diisopropylmethylphosphonate (DIMP), diethylmethylphosphonate (DEMP), and trimethylphosphate (TMP), with high selectivity. Absorption of OPs to DKAP was one-to-several orders of magnitude higher relative to commercial polar, mid-polar, and nonpolar stationary phases. We also present for the first-time thermodynamic studies on the absorption of OP vapors and quantitative binding energy data for interactions with various stationary phases. These data help to identify the best pair of hetero-polar columns for a two-dimensional GC system, employing a nonpolar stationary phase as GC1 and DKAP as the GC2 stationary phase, for selective and rapid field detection of CWAs.

Keywords: DKAP, thermodynamics, chemical warfare agents, hydrogen bonded acid, GC stationary phase, Organophosphates
Introduction

Certain organophosphates (OPs) have been used as chemical warfare agents (CWA). Sarin was used in the 1995 terrorist attack on Tokyo subway, a deadly reminder of CWAs continued threat. On-site detection of CWAs benefits from miniaturized systems combining portability, analytical speed, sensitivity, and selectivity. A micro gas chromatography (µGC) system with CWA-selective stationary phase columns would meet such requirements. We describe for the first time a hydrogen-bonded acid (HBA), 3,5-bis(trifluoromethyl)phenol functionalized polymer, poly{methyl[3-(2-hydroxyl, 4,6-bistrifluoromethyl)phenyl]propylsiloxane}, (named, “DKAP”), as a GC stationary phase for the selective absorption and rapid separation of CWA surrogates, dimethyl methylphosphonate (DMMP), diethylmethylphosphonate (DEMP) diisopropylmethylphosphonate (DIMP), and trimethylphosphate (TMP). Sorption properties of DKAP for CWA surrogates were compared to several polar, mid-polar, and nonpolar stationary phases. We also describe for the first time, rejection of interferents using DKAP, and quantitative thermodynamic data on the binding energies of these interactions. This work helps to identify the best pair of hetero-polar columns for two-dimensional systems employing nonpolar stationary phase as GC1 to reject interfering molecules and DKAP as GC2 stationary phase for the selective, sensitive, rapid, and field detection of CWAs.

Experimental

Reagents, chemicals and DKAP polymer
All chemicals including the OPs, DEMP (152.13 g/mol, b.p. ~192 °C; CAS Number 683-08-9), TMP (140.08 g/mol, b.p. 197 °C; CAS Number: 512-56-1), and DMMP (124.08 g/mol, b.p. 181 °C; CAS Number: 756-79-6), along with the “control” n-hexadecane (226.41 g/mol; CAS Number: 544-76-3), were from Sigma-Aldrich, St. Louis, MO and used as received. The OP DIMP (180.18 g/mol, b.p. 215 °C; CAS Number 1445-75-6) was purchased from Alfa Aesar, Haverhill, MA. Methane gas (16.04 g/mol; CAS Number 74-82-8) was obtained from Matheson Tri-Gas Inc., Albuquerque, NM. All chemicals were of analytical reagent quality. The DKAP polymer (Fig. 1) was synthesized as described previously. Briefly, 3,5-bistrifluoromethylphenol (CAS Number 444-30-4; Sigma-Aldrich) was reacted with allyl bromide (CAS Number: 106-95-6; Sigma-Aldrich) under basic conditions to provide 1-(allyloxy)-3,5-bis(trifluoromethyl)benzene, which was heated to 250 °C to facilitate a Claisen rearrangement to generate 2-allyl-3,5-bis(trifluoromethyl)phenol. This intermediate underwent hydrosilylation with polymethylhydrosiloxane in toluene with Karstedt's catalyst. Heating at 100 °C for several hours yielded the DKAP polymer, and its identity was confirmed by ¹H-NMR and ¹³C-NMR.

**DKAP GC column fabrication**

A 10 m long commercial intermediate polarity guard capillary column from Restek (Bellefonte, PA) with an internal diameter (i.d.) of 530 µm was coated with DKAP under static conditions as described below. The column was rinsed with isopropanol and dried completely under vacuum. This was followed by filling the column with 10% (v/v) dimethylvinylsilane in CH₂Cl₂ solution, sealing the end, and heating the sealed column for one hour at 60 °C. The liquid was then expelled using 30 psi N₂. A coating solution of ~0.1% (w/v) DKAP and a thermally-activated
free radical initiator (~0.3% of polymer mass) were prepared in CH₂Cl₂. The solution was transferred to a column-rinsing apparatus (Supelco, Sigma/Millipore, Bellefonte, PA). A 30 psi head pressure of N₂ was used to fill the column with the polymer solution. The column exit was sealed taking care to avoid bubbles, and a vacuum was pulled on the open end at a constant temperature of 40 °C, to evaporate the solvent, leaving a thin uniform film of DKAP on the surface. The column was then purged with H₂ at 60 °C to promote crosslinking. The final DKAP-coated GC column had a nominal stationary phase film thickness ($d_f$) of 0.113 µm. The phase volume ratio, $V_r$ (polymer volume/gas phase volume), was estimated by the reciprocal of the phase ratio, $\beta$, which in turn equaled the internal capillary GC column radius divided by 2$d_f$. The calculated $\beta$ and $V_r$ values for DKAP polymer-coated GC column were ~1176 and 8.5 x 10⁻⁴, respectively. Approximately 1 meter of column was cut from each end to avoid end effects of the coating process, yielding a final column length of 8 meters.

**Commercial GC columns**

Commercial columns are listed in Table 1. Abbreviations are indicated as follows: PDMS, polydimethyl siloxane; TFPMPS, trifluoropropylmethyl polysiloxane; 50% PPSPS, 50% phenyl polysilphenylene siloxane; 50% CPPMPS, 50% cyanopropyl-50% phenylmethyl polysiloxane; PEG, polyethylene glycol; 90% CPPPS, 90% cyanopropyl polysilphenyl siloxane; and 1,12-TPPDDBTFMSI, 1,12-di(tripropylphosphonium) dodecane bis(trifluoromethanesulfonyl)amide.

**GC operation**

All column testing was done with an Agilent (Santa Clara, CA) 7890A system. The
split/splitless inlet temperature was 250 °C and detection was by a flame ionization detector (FID), with signal output recorded as picoamps (pA). Column operation was in split mode with a 25 : 1 split ratio. Ultra-High-Purity (UHP) N₂ was used as the makeup gas at a flow of 30 mL/min and the detector temperature was 300 °C. The carrier gas was UHP-H₂ at a flow rate of 1.75 mL/min. Septum purge was 3 mL/min. A 5 µL injection of methane was used to measure the system’s transport time (tₚ). Analytes were prepared at a concentration of 1 µL/mL in CS₂, and 0.2 µL was injected using 7693 Agilent autosampler. Columns were operated at 80 °C (353.15 K); 90 °C (363.15 K); 100 °C (373.15 K); 110 °C (383.15 K); 120 °C (393.15 K); 130 °C (403.15 K); 140 °C (413.15 K); 150 °C (423.15 K); and, 170 °C (443.15 K), for calculating thermodynamic parameters.

**Thermodynamics**

The free energy of solvation for an analyte in a polymer, coating the walls of capillary GC columns, can be determined from van ‘t Hoff plots.³ GC elution is given by equation 1, where tᵢᵢ is the retention time of an analyte i, tᵥ is the column void time.

\[ tᵢᵢ = tᵥ(k + 1) \]  

(1)

Time (tᵢᵢ) required for an unretained species to traverse the column length, and the retention factor (k) for analyte i, can be calculated using methane as an unretained species to measure void time and isothermal retention time of a compound by rearranging equation 1:

\[ k = \frac{tᵢᵢ}{tᵥ} - 1 \]  

(2)

Partition coefficient, K, for an analyte in the polymer is given by equation 3.

\[ K = k/Vᵢ \]  

(3)

The value of Vᵢ for a column is calculated from dᵢ and inner radius, r, using equation 4.

\[ Vᵢ = 2πrᵢdᵢ - dᵢ² / (r - dᵢ)² \]  

(4)
Phase volume is calculated from coating volume, polymer mass, and polymer density. For known \( V_r \), \( d_f \) can be calculated by rearranging equation 4 into quadratic equation 5.

\[
V_r^2 - (V_r + 1)2rd_f + (V_r + 1)d_f^2 = 0 \quad (5)
\]

Gibbs free energy of solvation for ideal solutions, \( \Delta G_{solv} \), is related to \( K \) by equation 6, where \( T \) is the temperature (K), \( \ln \) is the natural logarithm, and \( R \) is the gas constant.

\[
\Delta G_{solv} = -RT\ln K \quad (6)
\]

The \( \Delta G_{solv} \) is related to enthalpy (\( \Delta H_{solv} \)) and entropy (\( \Delta S_{solv} \)) of solvation by equation 7.

\[
\Delta G_{solv} = \Delta H_{solv} - T\Delta S_{solv} \quad (7)
\]

Equations 6 and 7 can be combined into the van ‘t Hoff equation 8,

\[
\ln K = -\Delta H_{solv}/R + \Delta S_{solv}/R \quad (8)
\]

Isothermal GC data can then be used to calculate \( K \), and plots of \( \ln K \) versus \( 1/T \), yields a slope and intercept equal to \(-\Delta H_{solv}/R\) and \(\Delta S_{solv}/R\), respectively\(^3\).

**Data analysis**

Each analyte was run at least thrice for 5 minutes at each temperature for statistical rigor. The initial isothermal temperature (30 °C) was increased in 10 °C increments. Samples were analyzed at each temperature until a calculated \( k \) value was derived and data from a minimum of three temperatures had been collected. Standard errors of slope and \( y \)-intercept were calculated from residuals (difference between measured and calculated \( y \) values) of the equation \( y = bx + a \), where \( b \) is the regression line slope and \( a \) is the \( y \)-intercept, based on least squares method. Average and standard deviation values were also calculated. Linearity correlation coefficient, \( r^2 \) were generated using Kaleidagraph (Synergy Software, Reading, PA).
Results and Discussion

GC materials

We are developing µGC systems for sensitive, selective, and rapid analysis of chem/bio threat agents. Here, we used non-lethal OPs (Fig. 1) as surrogate for nerve agents. Using non-lethal surrogates for system optimization is acceptable, since OPs are CWA model compounds. Indeed, DMMP is used as a simulant during sarin training exercises. DMMP is similar to sarin in polarity, volatility, and chemistry (Fig. 1). With a vapor pressure of 2.31-112 Pa at 25 °C, surrogate OPs like DMMP, enabled low vapor concentration testing. The double-bonded oxygen atom on DMMP or sarin has higher electronegativity than phosphorus, which provides a dense electron cloud around the oxygen. The electron-rich oxygen acts as a base and hydrogen bonding occurs between DKAP’s pendant phenol and the oxygen of OPs (Fig. 1).

Solute-solvent interactions of HBA polymers involve van der Waals forces and hydrogen bonding. Organophosphates being strongly hydrogen-bonded bases (HBB), bond formation occurs between CWA/surrogate and phenol. Terminal hydroxyl groups offer moderate acidity for interactions with target HBB. The phenolic-functionalized DKAP is a strong HBA due to electron withdrawing trifluoromethyl groups (Fig. 1). Electron withdrawal increases the acidity of hydroxyl group, thus activating it as electron acceptors, leading to hydrogen bonding, as confirmed by IR data. Bonding is enhanced, whilst minimizing basicity of hydroxyl oxygen, thereby eliminating self-association. Thus, the phenolic pendant has hydrogen bonding capability on the polydimethylsiloxane (PDMS) backbone.

Phenolic-polymers such as DKAP, require low glass-to-rubber transition temperature (T<sub>g</sub>) for
GC applications. Solute absorption is rapid above $T_g$ due to segmental chain motion for rapid equilibrium between solute and solvent (vapors diffuse slowly in glassy polymers). PDMS has a low $T_g$, high porosity, and freely rotating Si-O-Si bonds, for rapid vapor diffusion. Sandia’s DKAP, employs HBA functionality that is limited as a 3,5-bis(trifluoromethyl)phenolic pendant to the PDMS backbone (Fig. 1); the most acidic of such phenols, with a solvation parameter ($\Sigma\alpha^2$) of 0.82, low $T_g$ of ~20 °C, conferring high analyte diffusivity and thermal stability.

**DKAP-GC**

Prior to GC of OPs, the effect of carrier gas velocity on height equivalent theoretical plate (HETP) was established using phosphonates, hydrocarbons, and various stationary phases (Table 1). To illustrate, for DKAP-DMMP pair, HETP was 0.267 cm and for RTX-1-DMMP pair, it was 0.107 cm. Phosphonate concentration on retention time and FID amplitude were also standardized. The data in Fig. 2 is the first demonstration of DKAP GC capillary stationary phase clearly separating CWA surrogates. It is possible to substitute FID with miniaturized pulsed discharge helium ionization detector for field analysis.

Chromatographic separation depends on the differences in retention strengths of analytes at the interface of stationary and mobile phases. Film diffusion is a rate limiting step and the optimum $d_f$ of DKAP provided clean separations (Fig. 2). Inadequate $d_f$ results in insufficient capillary wall coating, with interfacial absorption of analytes. While larger $d_f$ enables greater retention and better separation, a $d_f$ that is too thick, leads to poor efficiency. Generally, a doubling of $d_f$ increases the elution temperature by 15–20 °C under isothermal conditions. The $d_f$ affects $\beta$ (Table 1), which is important when deciding column i.d.. When i.d. increases, $d_f$
must also increase to provide similar retention and resolution. The 530 µm column i.d. provided a lower surface contact angle increasing the probability of surface wetting with the polar DKAP stationary phase, thereby providing a good balance of efficiency, resolution, and analysis time (Fig. 2). The DKAP column length (8 m) was well-suited for resolution (resolution is proportional to square root of column efficiency). Doubling column length would have only increased resolving power by ~40% which was unnecessary based on observed performance (Fig. 2). Shorter columns lead to reduced peak capacity. Sample concentration exceeding column capacity, leads to resolution loss, decreased reproducibility, and peak distortion. The higher resolving power of longer columns is offset by a doubling of analysis time under isothermal ramp conditions. Column downsizing offers other benefits such as temperature programmed elution (due to smaller heat capacity), reducing chemical concentrations, and testing a limited-availability material such as DKAP, as a GC stationary phase. The minor peak asymmetry (Fig. 2) is a known challenge with OPs for commercial columns as well as the DKAP column tested here, due to OPs strong affinity for active silanol sites. The peak asymmetry on DKAP column was as good or better than commercial columns tested.

**Selectivity**

DKAP polymer showed exceptional selectivity toward CWA surrogates (Fig. 3). Relative to commercial stationary phases, DKAP showed high retention of G-agent surrogate DIMP and correspondingly low retention for the hexadecane interferent. The ratio of 183 for DIMP/hexadecane (Fig. 3, inset), demonstrated the high selectivity of DKAP for CWA surrogates by excluding hydrocarbon vapors. Differences in the affinity of analytes relative to interferents contributes to better rejection properties of DKAP. We and others have shown no effect of a broad range of interferents including acetone, ethanol, dichloroethane, n-hexane, and
toluene on DKAP-DMMP interactions. It is seen that RTX-1 (Fig. 3) has poor retention for DIMP, but high retention for hexadecane. This retention reversal suggested that DKAP/RTX-1 will make a good \( \mu \text{GC}\times \mu \text{GC} \) pair for CWAs, by excluding interferents. Amongst columns tested, only SLB-IL59 showed some discrimination between OPs and hydrocarbons (Fig. 3), and SLB-IL-59 was selected for comparative thermodynamic analysis vis-à-vis DKAP.

**Thermodynamics**

Investigating phase equilibrium and thermodynamics helps to understand analyte absorption/retention behavior on stationary phases and to study changes in enthalpy (\( \Delta H^\circ \)) and entropy (\( \Delta S^\circ \)) accompanying analyte transfer from mobile to stationary phase.\(^{14}\) Gibbs free energy change, \( \Delta G^\circ \), describes the partition of a solute between mobile and stationary phases. Using \( \Delta G^\circ \), solvation thermodynamics can be determined. We analyzed the temperature dependence on the retention factor (\( k \)), retention equilibrium/partition coefficient (\( K \)), and selectivity (\( \alpha \)). We used van ‘t Hoff equation for deriving changes in enthalpy, entropy, and free energy, to understand the influence of stationary phase chemistry on retention behavior from a thermodynamic standpoint.\(^{14}\)

Retention factor is the ratio of the amount of time an analyte spends in the stationary phase relative to its time in mobile phase and defines the rate of analyte migration through a column. The retention profiles of OPs in DKAP and SLB-IL59 stationary phases are shown in Fig. 4. Data was also obtained with the remaining stationary phases (Table 1). Retention profiles were more linear with DKAP compared to SLB-IL59. Temperature clearly influenced retention behavior; however, when analyzing compounds with different polarities, determining elution order based on boiling point of analytes might not be straightforward due to chemical
interactions between the analytes and the stationary phase (Fig. 1). The DKAP retentivity based on Fig. 4 was: DIMP > DEMP > DMMP > TMP (longer the elution time, greater the retention), with TMP being the least absorbed to DKAP and DIMP most strongly retained. The same behavior was seen in Fig. 2. Retention data (Fig. 4) showed a closer relationship between DIMP/DEMP pair and DMMP/TMP pair. Each pair of analytes is closer to each other but separated from the other pair. This trend is also reflected in the elution order, based on separation distance for these pairs (Fig. 2). At higher temperatures, retention behavior of analytes on SLB-IL59 was closer to DKAP (Fig. 4). There was a noticeable bending of the SLB-IL59 retention factor profiles (Fig. 4) as well as the van ’t Hoff profiles (Fig. 5) at higher temperatures (140 °C to 150 °C). This behavior might indicate a phase transition taking place with SLB-IL59 at elevated temperatures. Investigating this phenomenon further was beyond the scope of the present work, which is focused on the novel GC stationary phase DKAP, and its interactions with CWA surrogates. The retention profiles of OPs on other stationary phases overlapped with DKAP as follows: SLB-IL59 > RTX-Wax > RTX-200 = RTX-225 = BPX-90 > Rxi-Sil-MS > RTX-1 (SLB-IL59 demonstrating most overlap with DKAP and RTX-1, the least).

A van ‘t Hoff analysis yields thermodynamic data of analytes and their retention on a particular stationary phase to describe absorption and desorption. The positive profiles with no deviations from simple linear van ‘t Hoff relationship, and negative ΔH° values (Table 2), confirmed the exothermic nature of the absorption process, consistent with hydrogen bond formation and van der Waals interactions. Retention time usually decreases with increasing temperature, and enthalpy values (ΔH°) will be negative (Table 2). Linear van ‘t Hoff plots with DKAP (Fig. 5, Table 2) suggested a constant retention mechanism and constant thermodynamic behavior over the temperature range studied. The higher negative ΔH° values with DKAP
relative to SLB-IL59 (Table 2) indicated stronger interactions of OPs with DKAP. Increased spacing between van ‘t Hoff lines for DIMP and DEMP on DKAP relative to SLB-IL59 demonstrated greater retentivity and selectivity, (Fig. 5), matching the elution profile (Fig. 2). At lower temperatures, slight separation of DMMP and TMP profiles was observed on DKAP compared to SLB-IL59. However, at no temperature did the profiles intersect (Fig. 5), confirming no coelution (Fig. 2). In contrast, the close spacing between the profiles with SLB-IL59 (Fig. 5), suggested coelution and poorer resolution of OPs with this stationary phase. The $\Delta H^o$ ranking was: DIMP > DEMP > DMMP > TMP (Table 2). Based on the degree of overlap between CWA simulants with DKAP relative to other stationary phases, the interactions could be rank-ordered as: SLB-IL59 > RTX-Wax = RTX-1 = RTX-200 = Rxi-Sil-MS = BPX-90 = RTX-225 (most to least overlap with DKAP).

Decrease in free energy ($\Delta G^o$) (Table 3) demonstrated that absorption was less favorable at elevated temperatures, leading to the transfer of analytes from the stationary phase back into the mobile phase, and eventually to the detector. Due to enthalpy change being negative, solubility of gases decreases with increasing temperature. At very high temperatures, vapor pressures and diffusion coefficients of analytes increase, resulting in poor focusing and broad peaks, and at the limit, there will be no separation of analytes due to very high temperatures. Slopes from the van ‘t Hoff plots depend on the type of polymer coating. The negative entropy change ($\Delta S^o$) (Table 2) corresponds to a decrease in the degrees of freedom of adsorbed molecules. Thus, the concentration of OPs in the stationary-mobile interface decreases and their concentrations in DKAP phase increases (tighter sorption) due to intermolecular forces.

Another technique to compare DKAP and SLB-IL59 is to plot selectivity, $\alpha$, as a function of $1/T$. This method is immune to $d_\ell$ differences amongst stationary phases. Selectivity relates to
a stationary phase preferentially adsorbing an analyte over other(s), based on solute-stationary phase interactions due to van der Waals and dispersion forces, and hydrogen bonding. Selectivity was calculated by the retention factor ($k$) ratio for two different compounds, an OP and hexadecane: $\alpha = k_i/k_2$, where, $k_i$ is the OP retention factor and $k_2$, the retention factor for hexadecane, at each temperature (Fig. 6). It is important to note the logarithmic ordinate of the selectivity chart. All commercial stationary phases (Table 1) were less selective for CWA surrogates relative to DKAP (Fig. 6).

Between 80-100 °C, there was one to three orders of magnitude offset between DKAP selectivity for OPs compared to SLB-IL59. This offset of selectivity profiles, especially for DIMP and DEMP with DKAP compared to SLB-IL59, was remarkable (Fig. 6). It demonstrated that DKAP had higher selectivity compared to SLB-IL59. Other polar, mid-polar, and nonpolar stationary phases (Table 1) displayed even greater offset compared to DKAP than SLB-IL59 (data not shown). RTX-1 and Rxi-Sil-MS were the least selective, while the rest had lower selectivity compared to SLB-IL59. Thus, DKAP offered better resolution between CWA simulants and hydrocarbon interferents at all temperatures, and relative to all other stationary phases (Table 1).

Selectivity of a capillary GC column is directly related to the interaction of analytes with the stationary phase, with strong interactions arising from strong intermolecular forces. Selectivity is determined by the stationary phase chemical functionalities. With an increase in temperature the differences between retention factors for various analytes decrease, and $\alpha$ approaches unity, with ($\alpha - 1/\alpha$) nearing zero. When temperature becomes too high, no separation may occur. Thus, knowledge of the structures of the analytes and of the stationary phase is crucial for optimizing GC performance.
Stability and shelf life

Traditional polar polymer stationary phases are appropriate for CWA separation. However, typical polar polymers necessary for hetero-polar μGCxμGC stationary phases often suffer degradation due to oxidation, moisture, and heat. DKAP is a stable polymer and its interactions with OPs are reversible, simply by purging with N₂ to restore its former pristine state and the regenerated DKAP polymer is reusable multiple times.⁶ DKAP is resistant to humidity, since phenolic oxygen (Fig. 1) lone pairs are not basic. Water molecules, with acidic hydrogen atoms, do not bind well to DKAP, mitigating background humidity effects.⁶

Thermal resistance was confirmed by an absence of change in $R_3$ (or $k$) after using DKAP at elevated temperatures over several months. Linear thermodynamic charts (Figs. 4-6) between 30 °C-170 °C was consistent with excellent heat-resistance of DKAP.³ Constant thermodynamic behavior and thermal stability (Figs. 4-6) permit temperature-programmed elution.³ Furthermore, van ‘t Hoff approximation suggests reaction rate increases by 2-4-fold as temperature increases by 10 K; therefore, separation times can be shortened by increasing the oven temperature, owing to DKAP’s thermal stability. DKAP-coated columns were stored at ~25 °C for ~2 years without performance degradation. Shelf life was attributed to C-F bond stability relative to C-H bonded polymers. Reproducible DKAP-GC analyses were conducted more than two months apart, and the same analysis by two different investigators, conducted on two separate days, all yielding similar results. Thermodynamic analyses done two months apart also yielded nearly identical values with small standard deviations (≤ 1.4%). Considered collectively, DKAP polymer GC coating demonstrated stability, sensitivity, selectivity, repeatability, and reproducibility, as defined previously.¹⁷
Conclusions

Rapid, sensitive, and selective detection of CWAs are critical during a terrorist event or to the warfighter. We describe for the first time DKAP polymer as a stationary phase in capillary GC of CWA surrogates. Thermodynamics of surrogates’ interactions with DKAP are also described for the first time along with quantitative data on binding energies. These data help to select hetero-pair columns for 2D systems for rejecting interferents and identifying CWAs using $\mu$GCx$\mu$GC, with nonpolar GC1 stationary phase and DKAP as GC2 stationary phase. Since analytes undergo orthogonal separation, $\mu$GCx$\mu$GC offers better sensitivity and selectivity, and our miniaturized components$^{5,7,8}$ will enable field analyses.

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Fig. 1  Chemical structures of DKAP and OPs
Fig. 2. DKAP-GC of OPs. 1 = TMP; 2 = DMMP; 3 = TEP (triethylphosphate); 4 = DEMP; 5 = DIMP. Column operating temperature in this experiment was 90 °C.
Fig. 3. Selectivity of DKAP and commercial stationary phases. Stationary phases listed on the abscissa are: A, DKAP; B, RTX-1; C, RTX-Wax; D, SLB-IL59; E, Rxi-17Sil-MS; and F, RTX-200. **Panel A symbols:** dotted, DMMP; black, DIMP; striped, DEMP; grid, hexadecane. **Panel B symbols:** black, DIMP; clear, hexadecane. Column operating temperature in both these experiments was 90 °C.
Fig. 4. Retention factors of OPs with DKAP and SLB-IL59.
Fig. 5. van ‘t Hoff plots of OPs with DKAP and SLB-IL59.
Fig. 6. Selectivity of OPs with DKAP and SLB-IL59.
Table 1. Properties of commercial GC columns

| Name        | Length (m) | i.d. (µm) | $d_f$ (µm) | $\beta$ ($r/2d_f$) (µm) | $V_r$ (1/β) | Film type | Polarity | Vendor     |
|-------------|------------|-----------|------------|--------------------------|-------------|-----------|----------|------------|
| RTX-1       | 10         | 530       | 0.25       | 530                      | 0.001887    | PDMS      | Nonpolar | Restek     |
| RTX-200     | 30         | 250       | 0.25       | 250                      | 0.004000    | TFPMPS    | Mid-polar | Restek     |
| Rxi-17sil   | 30         | 250       | 0.25       | 250                      | 0.004000    | 50%PPSPS  | Mid-polar | Restek     |
|             | MS         |           |            |                          |             |           |          |            |
| RTX-225     | 15         | 530       | 0.10       | 1325                     | 0.000755    | 50%CPPMPS | Polar    | Restek     |
| RTX-Wax     | 30         | 250       | 0.25       | 250                      | 0.004000    | PEG       | Polar    | Restek     |
| BPX-90      | 15         | 250       | 0.25       | 250                      | 0.004000    | 90%CPPSPS | Highly-polar | SGE*     |
| SLB-IL59    | 30         | 250       | 0.25       | 250                      | 0.004000    | 1,12-TPPDBTFMSI | Highly-polar | Supelco |

*SGE Analytical, Trajan Scientific Americas, Austin, TX

Table 2. Thermodynamics of OPs absorption to DKAP and SLB-IL59

| Analyte | DKAP | SLB-IL59 |
|---------|------|----------|
|         | $\Delta H^o$ (kJ/mol) | $\Delta S^o$ (kJ/mol.K) | $r^2$ | $\Delta H^o$ (kJ/mol) | $\Delta S^o$ (kJ/mol.K) | $r^2$ |
| DIMP    | −94.6 | −0.16 | 0.99962 | −56.0 | −0.078 | 0.99352 |
| DEMP    | −91.1 | −0.16 | 0.99945 | −55.0 | −0.075 | 0.99374 |
| DMMP    | −80.6 | −0.14 | 0.99920 | −50.6 | −0.067 | 0.99386 |
| TMP     | −79.3 | −0.14 | 0.99887 | −51.5 | −0.068 | 0.99393 |
Table 3. $\Delta G^\circ$ change with increasing temperature for OPs (DKAP versus SLB-IL59)

| Temp. ($^\circ$C) | DKAP, $\Delta G^\circ$ | SLB-IL59, $\Delta G^\circ$ |
|------------------|------------------------|----------------------------|
|                  | DMMP | DIMP | DEMP | TMP | DMMP | DIMP | DEMP | TMP |
| 80               | -31.2 | -38.1 | -34.6 | -29.9 | -26.9 | -28.5 | -28.5 | -27.5 |
| 90               | -29.8 | -36.5 | -33.0 | -28.5 | -26.3 | -27.7 | -27.8 | -26.8 |
| 100              | -28.4 | -34.9 | -31.4 | -27.1 | -25.6 | -26.9 | -27.0 | -26.1 |
| 110              | -27.0 | -33.3 | -29.8 | -25.7 | -24.9 | -26.1 | -26.3 | -25.4 |
| 120              | -25.6 | -31.7 | -28.2 | -24.3 | -24.3 | -25.3 | -25.5 | -24.8 |
| 130              | -24.2 | -30.1 | -26.6 | -22.9 | -23.6 | -24.6 | -24.8 | -24.1 |
| 140              | -22.8 | -28.5 | -25.0 | -21.5 | -22.9 | -23.8 | -24.0 | -23.4 |
| 150              | -21.4 | -26.9 | -23.4 | -20.1 | -22.2 | -23.0 | -23.3 | -22.7 |
| 170              | -18.6 | -23.7 | -20.2 | -17.3 | -20.9 | -21.4 | -21.8 | -21.4 |
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