# Supplementary Information for;

# Multivariate Optimization of Tenax TA-Thermal Extraction for Determining Gaseous Phase Organophosphate Esters in Air Samples

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**Text S1**

**Instrumental analysis**

Thermal desorption was performed using a commercial desorption unit, TDS-3 (Gerstel) connected to a programmed-temperature vapouriser (PTV) injector/cooled injection system (CIS – 3) (Gerstel) by a heated transfer line. The CIS was equipped with a baffled glass liner and was cooled by liquid nitrogen for analyte trapping prior to injection into a chromatographic column for analytical separation and detection. Moreover, a baffled glass liner has been shown to provide good responses in a number of studies involving SVOCs.[1,2,3] The temperature program for desorption was 30 ℃ (delay time of 0.2 minutes), then ramped at 130°C/minute to 290°C, held for 10 minutes. The desorption unit, TDS-3 was operated in a splitless mode. The temperature of the transfer line was set at 290°C. The CIS was cooled with liquid nitrogen to 20°C. After desorption and cryotrapping, cryo-desorption was carried out at 10°C per second from 20°C to 295°C ,held for 6 minutes, for quantitative sample transfer into the chromatographic column for analyte separation. Meanwhile, the desorbed analytes were being carried in helium gas at 95mL$min^{-1}$. The CIS was also operated in a splitless mode. The TDS-3 device was connected to a Shimadizu GC coupled to a MS (GCMS-QP2010 Ultra). Gas chromatography/mass spectrometry parameters have been reported in our previous study.[1]

| Experimental Factors and their letter codes | Experimental Factor Levels and their codes | | |
|---|---|---|---|
| | Low (-1) | Center (0) | High (+1) |
| Desorption Flow (A) | 20 | 60 | 100 |
| Desorption Temperature (B) | 260 | 290 | 320 |
| TDS Transfer Temperature (C) | 260 | 290 | 320 |
| Desorption Time (D) | 5 | 10 | 15 |
| Cryofocusing Temperature (E) | -100 | -20 | 60 |
| Cryodesorption Temperature (F) | 260 | 290 | 320 |
| Cryodesorption Time (G) | 2 | 6 | 10 |

| | Experimental factor settings at each run | | | | | | | Response Factors (Compound Specific Chromatographic Areas) | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Run | A | B | C | D | E | F | G | TEP | TPP | TNBP | TCEP | TCIPP | TDCIPP | TBOEP | TPHP | EHDPP | TEHP |
| 1 | 100 | 320 | 320 | 5 | 60 | 260 | 2 | 451704.5 | 1056466.0 | 675385.5 | 133531.5 | 88479.5 | 45542.0 | 28719.5 | 253084.5 | 453589.0 | 1211914.5 |
| 2 | 100 | 260 | 260 | 15 | 60 | 320 | 2 | 526735.5 | 1286762.0 | 830984.0 | 178161.0 | 109761.0 | 63169.0 | 61049.0 | 352863.5 | 621392.5 | 1719607.0 |
| 3 | 20 | 260 | 320 | 15 | 60 | 260 | 2 | 408225.0 | 1384418.0 | 1135416.0 | 244902.0 | 145930.0 | 93538.0 | 61170.0 | 499499.0 | 930945.0 | 2315544.0 |
| 4 | 20 | 260 | 320 | 5 | 60 | 320 | 10 | 640922.5 | 1687884.0 | 1129207.5 | 220883.5 | 144792.5 | 79661.5 | 55578.5 | 425920.0 | 696135.5 | 2046014.0 |
| 5 | 100 | 260 | 320 | 15 | -100 | 260 | 10 | 723155.5 | 1881437.5 | 1251537.0 | 242739.5 | 158709.5 | 90071.0 | 69104.5 | 439617.5 | 927317.5 | 2632893.0 |
| 6[a] | 60 | 290 | 290 | 10 | -20 | 290 | 6. | 308746.5 | 1324942.5 | 926822.5 | 266503.5 | 124268.5 | 122458.0 | 139601.0 | 626554.5 | 1313301.0 | 3161711.0 |
| 7 | 60 | 290 | 290 | 5 | -100 | 260 | 10 | 226337,0 | 1307480.5 | 1028516.0 | 288552.5 | 148598.0 | 98278.5 | 69579.0 | 526802.5 | 962212.5 | 2492056.5 |
| 8[a] | 60 | 290 | 290 | 10 | -20 | 290 | 6 | 289871,0 | 1455719.0 | 802766.0 | 282503.5 | 112137.0 | 106589.0 | 140179.0 | 560532.0 | 1001512.5 | 2744051.5 |
| 9 | 100 | 260 | 320 | 5 | -100 | 320 | 2 | 384496,0 | 1025152.0 | 650979.5 | 56484.0 | 75923.5 | 11046.5 | 4290.5 | 57860.5 | 103947.0 | 378548.5 |
| 10 | 20 | 320 | 260 | 5 | 60 | 320 | 2 | 385844.5 | 1115201.0 | 774053.0 | 79814.5 | 89805.5 | 13996.5 | 4086.5 | 70800.5 | 136561.0 | 846249.5 |
| 11[a] | 60 | 290 | 290 | 10 | -20 | 290 | 6 | 263023,0 | 1144365.0 | 694889.0 | 287697.0 | 112258.0 | 111610.0 | 123315.0 | 490482.0 | 991590.0 | 2412535.0 |
| 12 | 20 | 260 | 260 | 5.0 | -100 | 260 | 2 | 539502.5 | 1462634.0 | 910382.0 | 128325.5 | 103434.0 | 26100.5 | 9539.0 | 142639.5 | 314977.5 | 1315715.5 |
| 13 | 100 | 320 | 260 | 15 | -100 | 260 | 2 | 316586.5 | 1407336.5 | 1058002.0 | 289870.0 | 146214.5 | 111634.0 | 84859.5 | 563080.5 | 1125788.0 | 2908618.5 |
| 14 | 20 | 260 | 260 | 15 | -100 | 320 | 10 | 255369.5 | 1198366.5 | 705135.5 | 12251.0 | 47336.0 | 3121.0 | 1669.0 | 17755.0 | 24012.5 | 98961.0 |
| 15 | 20 | 320 | 260 | 15 | 60 | 260 | 10 | 309795,0 | 851746.0 | 524690.0 | 28150.0 | 62033.0 | 6275.0 | 779.0 | 20107.0 | 39216.0 | 437800.0 |
| 16 | 20 | 320 | 320 | 15 | -100 | 320 | 2 | 300141.5 | 1365388.5 | 942845.0 | 300560.0 | 134072.5 | 121387.5 | 93982.5 | 597146.5 | 1141368.0 | 2759217.5 |
| 17 | 100 | 320 | 260 | 5 | -100 | 320 | 10 | 793397,0 | 2077767.5 | 1455719.5 | 328124.0 | 187987.5 | 134800.5 | 114968.0 | 754426.5 | 1463732.0 | 3619735.0 |
| 18 | 100 | 260 | 260 | 5 | 60 | 260 | 10 | 408328.5 | 1401793.0 | 990983.0 | 209843.0 | 123675.0 | 82130.0 | 61808.5 | 448626.0 | 802767.5 | 2182119.5 |
| 19 | 100 | 320 | 320 | 15 | 60 | 320 | 10 | 272184,0 | 1121369.5 | 928838.0 | 236523.5 | 131648.0 | 86856.5 | 53871.5 | 441180.0 | 856743.0 | 2071634.0 |

[a] refers to the center points of the screening design.

**Table S1.** Experimental factors, codes, and levels in the $2^{7-3}$ eighth fractional factorial design and the corresponding average compound peak areas.

| Experimental Factors and Letter Codes | Experimental Factor Levels and their codes | | |
|---|---|---|---|
| | Low (-1) | Center (0) | High (+1) |
| Desorption Flow (A) | 20 | 60 | 100 |
| Cryofocusing Temperature (B) | -100 | -20 | 60 |
| Cryodesorption Temperature (C) | 260 | 290 | 320 |

Experimental factor settings at each run

| | | | | Response Factors (Compound Specific Chromatographic Areas) | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Run | A | B | C | TEP | | TPP | | TNBP | | TCEP | | TCIPP | |
| | | | | Actual | Predicted | Actual | Predicted | Actual | Predicted | Actual | Predicted | Actual | Predicted |
| 1 | 20.0 | -20.0 | 320.0 | 922208.0 | 1170880.0 | 2341327.0 | 3001260.0 | 1516043.5 | 1917380.0 | 312759.5 | 374208.0 | 159056.5 | 197382.0 |
| 2 | 60.0 | -100.0 | 260.0 | 857785.0 | 877999.0 | 2238820.0 | 2621740.0 | 1414727.5 | 1722920.0 | 237028.5 | 258081.0 | 160049.0 | 190166.0 |
| 3 | 20.0 | -100.0 | 290.0 | 710402.0 | 615658.0 | 2474229.5 | 2230460.0 | 1761650.5 | 1607190.0 | 294577.0 | 251074.0 | 193083.5 | 184836.0 |
| 4 | 100.0 | -20.0 | 320.0 | 1695451.5 | 1620920.0 | 4424775.5 | 4563920.0 | 2803856.5 | 2957600.0 | 590934.0 | 568484.0 | 290491.0 | 312360.0 |
| 5[a] | 60.0 | -20.0 | 290.0 | 1507348.0 | 1606140.0 | 4047543.5 | 4484590.0 | 2580844.5 | 2936570.0 | 498191.0 | 548977.0 | 272580.0 | 314910.0 |
| 6[a] | 60.0 | -20.0 | 290.0 | 1588502.5 | 1606140.0 | 4340267.5 | 4484590.0 | 2805147.0 | 2936570.0 | 519892.5 | 548977.0 | 291682.0 | 314910.0 |
| 7 | 100.0 | -20.0 | 260.0 | 1629748.5 | 1381080.0 | 4598243.0 | 3938310.0 | 2980115.0 | 2578780.0 | 613775.5 | 552327.0 | 328037.5 | 289713.0 |
| 8 | 20.0 | 60.0 | 290.0 | 617384.0 | 388925.0 | 3503504.5 | 3226480.0 | 2353480.5 | 2260340.0 | 478381.0 | 437985.0 | 252880.0 | 244672.0 |
| 9 | 60.0 | 60.0 | 320.0 | 481635.5 | 461421.0 | 4113335.5 | 3730420.0 | 2992992.5 | 2684800.0 | 671822.5 | 650770.0 | 321764.5 | 291648.0 |
| 10 | 60.0 | 60.0 | 260.0 | 236390.5 | 390320.0 | 3567739.0 | 3983910.0 | 2731648.5 | 2978530.0 | 684918.5 | 702864.0 | 328521.5 | 358599.0 |
| 11 | 100.0 | -100.0 | 290.0 | 941389.0 | 1169850.0 | 2952669.0 | 3229690.0 | 1955490.5 | 2048630.0 | 207962.0 | 248358.0 | 209483.5 | 217692.0 |
| 12 | 60.0 | -100.0 | 320.0 | 1114979.5 | 961050.0 | 3466242.5 | 3050070.0 | 2352306.0 | 2105430.0 | 353064.0 | 335118.0 | 269365.5 | 239288.0 |
| 13 | 100.0 | 60.0 | 290.0 | 314529.5 | 409273.0 | 4032421.5 | 4276190.0 | 3075998.5 | 3230460.0 | 778378.5 | 821881.0 | 370401.5 | 378649.0 |
| 14 | 20.0 | -20.0 | 260.0 | 1182047.0 | 1256580.0 | 3591177.0 | 3452030.0 | 2361172.0 | 2207430.0 | 342973.0 | 365423.0 | 259728.0 | 237859.0 |
| 15[a] | 60.0 | -20.0 | 290.0 | 1722575.0 | 1606140.0 | 5065956.0 | 4484590.0 | 3423728.0 | 2936570.0 | 628848.0 | 548977.0 | 380469.0 | 314910.0 |

| Run | A | B | C | TDCIPP | | TBOEP | | TPHP | | EHDPP | | TEHP | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | Actual | Predicted | Actual | Predicted | Actual | Predicted | Actual | Predicted | Actual | Predicted |
| 1 | 20.0 | -20.0 | 320.0 | 112062.5 | 136903.0 | 116688.0 | 109911.0 | 470025.0 | 564627.0 | 1057562.5 | 1195010.0 | 3310298.0 | 3938950.0 |
| 2 | 60.0 | -100.0 | 260.0 | 38897.0 | 42543.6 | 18023.0 | 6039.5 | 153062.0 | 144445.0 | 463195.0 | 488782.0 | 2217466.0 | 2727000.0 |
| 3 | 20.0 | -100.0 | 290.0 | 69213.5 | 58102.9 | 40123.5 | 31391.8 | 308220.0 | 297996.0 | 714784.0 | 626298.0 | 3327482.5 | 3121420.0 |
| 4 | 100.0 | -20.0 | 320.0 | 235183.5 | 227719.0 | 221664.5 | 200949.0 | 999300.0 | 980459.0 | 2158696.0 | 2095800.0 | 6533647.0 | 6837110.0 |
| 5[a] | 60.0 | -20.0 | 290.0 | 198883.0 | 219836.0 | 157377.0 | 174225.0 | 812895.0 | 922826.0 | 1881157.5 | 2122790.0 | 6119793.0 | 6921490.0 |
| 6[a] | 60.0 | -20.0 | 290.0 | 205903.5 | 219836.0 | 159285,0 | 174225.0 | 823900.5 | 922826.0 | 1992677.0 | 2122790.0 | 6740108.0 | 6921490.0 |
| 7 | 100.0 | -20.0 | 260.0 | 219622.5 | 194782.0 | 163279.5 | 170057.0 | 870684.5 | 776083.0 | 2086644.0 | 1949190.0 | 6206228.5 | 5577570.0 |
| 8 | 20.0 | 60.0 | 290.0 | 196239.5 | 175045.0 | 121144.0 | 115938.0 | 796777.5 | 693559.0 | 1581362.0 | 1469500.0 | 5166159.0 | 5047030.0 |
| 9 | 60.0 | 60.0 | 320.0 | 262223.5 | 258577.0 | 234485.5 | 246469.0 | 1029696.0 | 1038310.0 | 2527982.5 | 2502400.0 | 7560157.0 | 7050630.0 |
| 10 | 60.0 | 60.0 | 260.0 | 259307.0 | 273037.0 | 247585.5 | 232077.0 | 1009825.5 | 1094200.0 | 2618338.0 | 2667300.0 | 7450197.0 | 7872790.0 |
| 11 | 100.0 | -100.0 | 290.0 | 50428.0 | 71622.3 | 15071.0 | 20277.3 | 254986.5 | 358205.0 | 451951.0 | 563815.0 | 3112110.0 | 3231230.0 |
| 12 | 60.0 | -100.0 | 320.0 | 125466.0 | 111736.0 | 60761.5 | 76270.4 | 631771.5 | 547394.0 | 1056406.5 | 1007440.0 | 4840960.0 | 4418370.0 |
| 13 | 100.0 | 60.0 | 290.0 | 320904.0 | 332015.0 | 323235.5 | 331967.0 | 1393097.0 | 1403320.0 | 3305604.5 | 3394090.0 | 8877605.5 | 9083670.0 |
| 14 | 20.0 | -20.0 | 260.0 | 107645.0 | 115109.0 | 35465.0 | 56180.2 | 403102.0 | 421943.0 | 924965.0 | 987865.0 | 4632754,0 | 4329290.0 |
| 15[a] | 60.0 | -20.0 | 290.0 | 254722.5 | 219836.0 | 206013.0 | 174225.0 | 1131682.0 | 922826.0 | 2494531.5 | 2122790.0 | 7904560,0 | 6921490.0 |

**[a]** refers to the center points of the screening design.

**Table S2.** Box-Behnken response surface design matrix and the corresponding average (actual and model predicted) compound peak areas

**Table S3**
Analysis of variance (ANOVA) of the response surface regression model for EHDPP.

| Source | Sum of squares | Degrees of freedom | Mean square | F-ratio | p-value |
|---|---|---|---|---|---|
| A:Desorption flow | 1.73373E12 | 1 | 1.73373E12 | 28.33 | 0.0031 |
| B:Cryofocusing Temperature | 6.74721E12 | 1 | 6.74721E12 | 110.25 | 0.0001 |
| C:Cryodesorption Temperature | 6.25705E10 | 1 | 6.25705E10 | 1.02 | 0.3584 |
| AA | 4.77031E11 | 1 | 4.77031E11 | 7.79 | 0.0384 |
| AB | 9.87117E11 | 1 | 9.87117E11 | 16.13 | 0.0102 |
| AC | 9.16439E8 | 1 | 9.16439E8 | 0.01 | 0.9074 |
| BB | 2.3063E11 | 1 | 2.3063E11 | 3.77 | 0.1099 |
| BC | 1.16816E11 | 1 | 1.16816E11 | 1.91 | 0.2256 |
| CC | 1.5727E11 | 1 | 1.5727E11 | 2.57 | 0.1698 |
| Lack of fit | 1.197E12 | 6 | 1.996E11 | 1.869 | 0.389 |
| Pure error | 2,135E11 | 2 | 1.068E11 | | |
| Total error | 3.05997E11 | 5 | 6.11994E10 | | |
| Total (corr.) | 1.07139E13 | 14 | | | |

R-squared = 97.1439 percent
R-squared (adjusted for d.f.) = 92.003 percent
Standard Error of Est. = 247385.
Mean absolute error = 112933.
Durbin-Watson statistic = 1.48657 (P=0.2925)
Lag 1 residual autocorrelation = 0.0000359516

**Table S3.** Analysis of variance (ANOVA) of the response surface regression model for EHDPP.

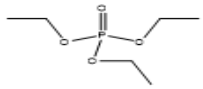
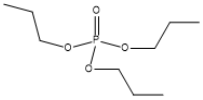
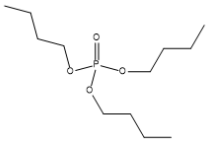
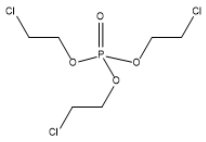
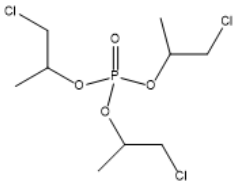
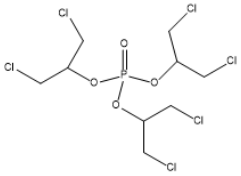
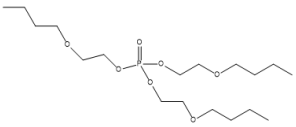
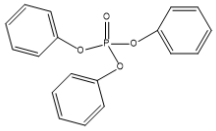
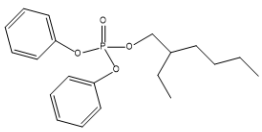
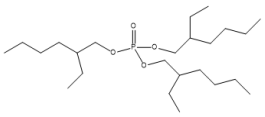
| No. | Compound | Practical Abbreviation (PRAB) | B.p (℃) | Structure | CAS Number | MW | Log $K_{ow}$ | Koc | Vapour Pressure (Pa) | $Log\ K_{OA}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | Triethyl phosphate | TEP | 216 |  | 78-40-0 | 182.16 | 0.80 | 36 | 5.25E+01 | 6.1 |
| 2 | Tri-n-propyl phosphate | TPP | 254 |  | 513-08-6 | 224.24 | 1.87 | 676 | 5.77E-01 | 6.4 |
| 3 | Tri-n-butyl phosphate | TNBP | 289 |  | 126-73-8 | 266.32 | 3.60 | 977 | 1.71E00 | 8.2 |
| 4 | Tris(2-chloroethyl) phosphate | TCEP | 351 |  | 115-96-8 | 285.49 | 1.47 | 150 | 1.44E-02 | 7.4 |
| 5 | Tris(2-chloroisopropyl)phosphate | TCIPP | 342 |  | 13674-84-5 | 327.56 | 2.59 | 275 | 2.69E-03 | 8.2 |
| 6 | Tris(1,3-dichloro-2-propyl) phosphate | TDCIPP | 457 |  | 13674-87-8 | 430.90 | 3.27 | 1440 | 5.43E-06 | 10.6 |
| 7 | Tris(2-butoxyethyl) phosphate | TBOEP | 414 |  | 78-51-3 | 398.48 | 3.75 | 1020 | 3.33E-06 | 13.1 |
| 8 | Triphenyl phosphate | TPHP | 370 |  | 115-86-6 | 326.29 | 4.59 | 2630 | 8.37E-03 | 8.5 |
| 9 | 2-Ethylhexyl diphenyl phosphate | EHDPP | 375 |  | 1241-94-7 | 362.40 | 5.73 | 9499 | 6.20E-04 | 11.3 |
| 10 | Tris(2-ethylhexyl) phosphate | TEHP | 220 |  | 78-42-2 | 434.64 | 9.49 | 617000 | 1.10E-05 | 15.0 |

**Table S4**. Names, abbreviations, structures and other properties of the target compounds

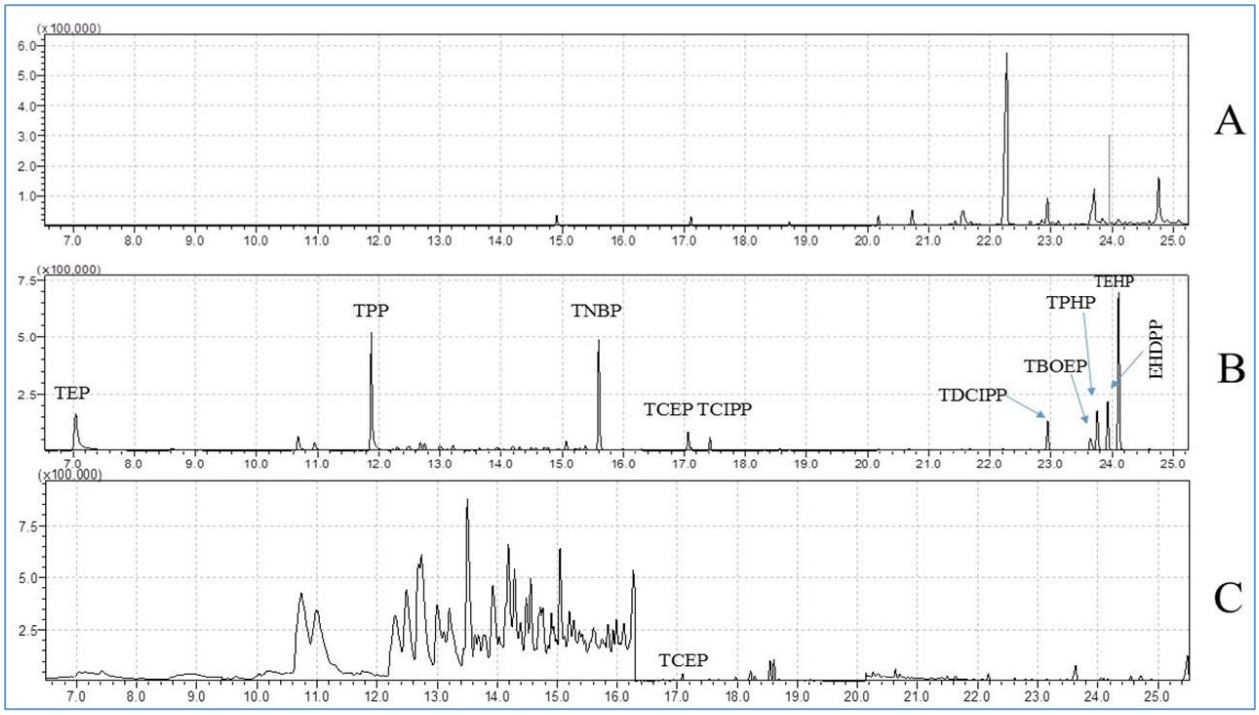
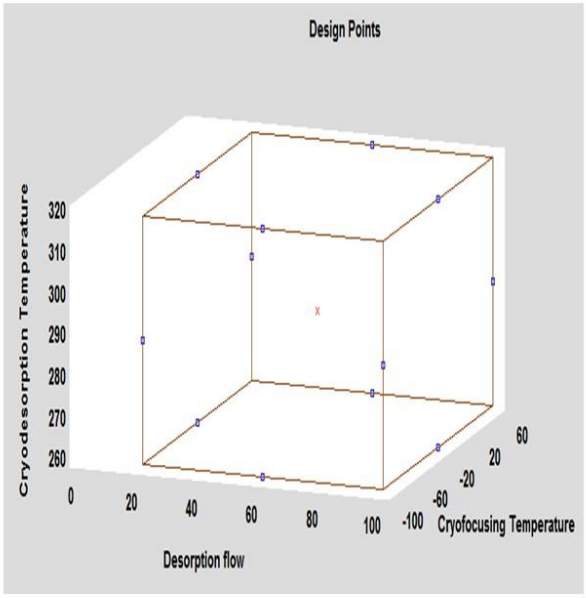



**Figure S1.**Total Ion Chromatograms (TIC) laboratory blank tube (A), intermediate calibration concentration level (B) and real air sample collected from the car (C)

A




B

| Run | A | B | C |
|---|---|---|---|
| 1 | -1 | 0 | +1 |
| 2 | 0 | -1 | -1 |
| 3 | -1 | -1 | 0 |
| 4 | +1 | 0 | +1 |
| 5 | 0 | 0 | 0 |
| 6 | 0 | 0 | 0 |
| 7 | +1 | 0 | -1 |
| 8 | -1 | 0 | 0 |
| 9 | 0 | +1 | +1 |
| 10 | 0 | +1 | -1 |
| 11 | +1 | -1 | 0 |
| 12 | 0 | -1 | +1 |
| 13 | +1 | +1 | 0 |
| 14 | -1 | 0 | -1 |
| 15 | 0 | 0 | 0 |

**Figure S2.** Box-Benken Design plot (A) and Matrix codes (B).

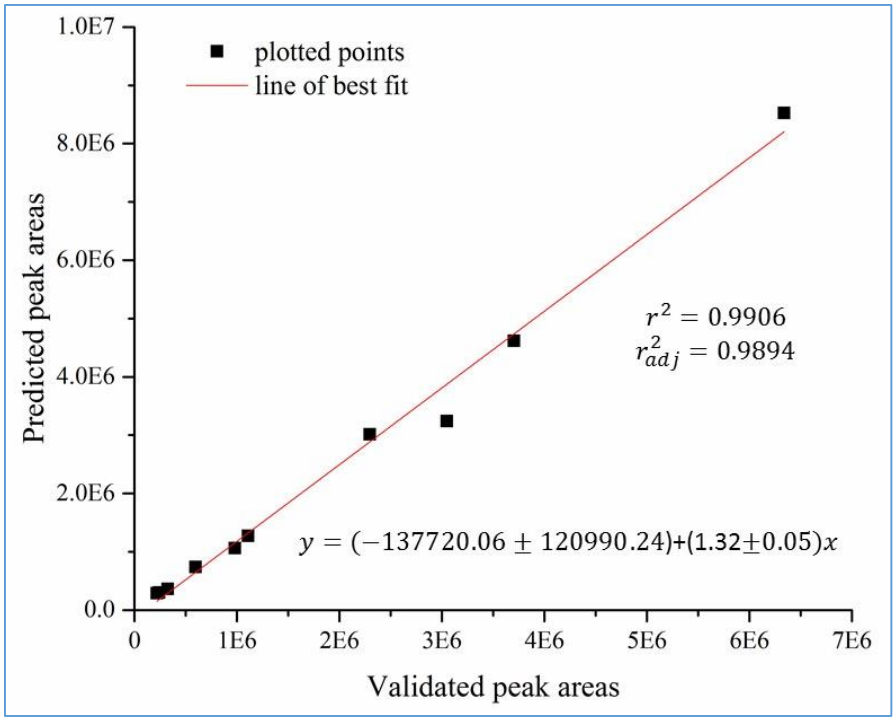
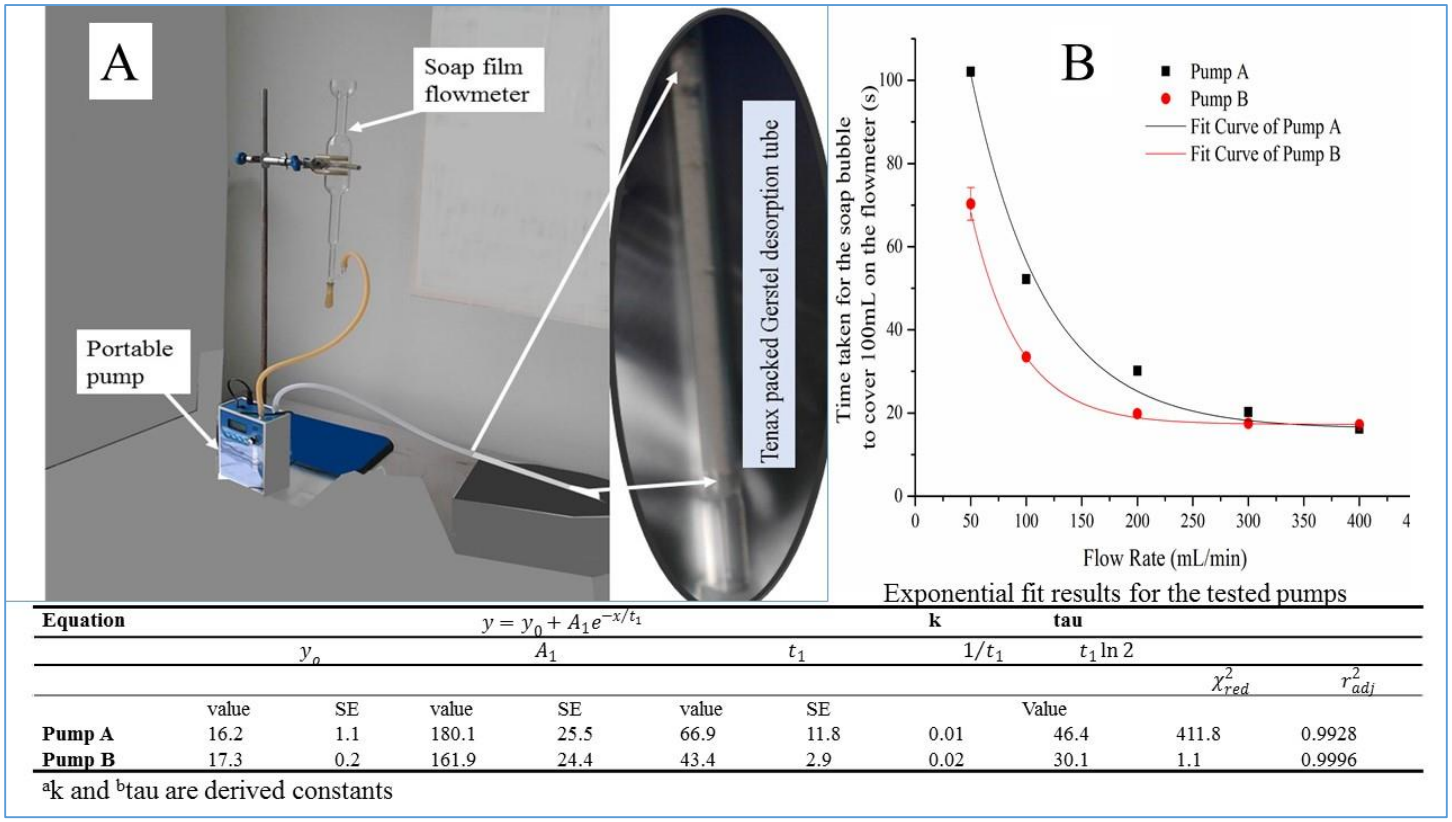



**Figure S3.** Scatter plot illustrating the relationship the modelled and experimental/validated peak areas.




Exponential fit results for the tested pumps

| **Equation** | $y = y_0 + A_1 e^{-x/t_1}$ | | | | | | **k** | **tau** | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | $y_o$ | | $A_1$ | | $t_1$ | | $1/t_1$ | $t_1 \ln 2$ | $\chi^2_{red}$ | $r^2_{adj}$ |
| | value | SE | value | SE | value | SE | | Value | | |
| **Pump A** | 16.2 | 1.1 | 180.1 | 25.5 | 66.9 | 11.8 | 0.01 | 46.4 | 411.8 | 0.9928 |
| **Pump B** | 17.3 | 0.2 | 161.9 | 24.4 | 43.4 | 2.9 | 0.02 | 30.1 | 1.1 | 0.9996 |

[a]k and [b]tau are derived constants

**Figure S4.** Calibration set up (A) and calibration curves (B, n=3) for the two tested QC-IC pumps.

**References**

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