HANSEN SOLUBILITY PARAMETERS IN CHROMATOGRAPHIC SCIENCES

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SOLUBILITY PARAMETER THEORY

- Energy of vaporization

$$-E = \Delta_l^g U + \int_{V=Vpar}^{V=\infty} \left(\frac{\partial U}{\partial V} \right)_T dV$$

- Cohesive energy density

$$c = \frac{-E}{V}$$

$$\delta = \sqrt{c} = \sqrt{\frac{E_{coh}}{V}} = \sqrt{\left(\frac{\Delta H_w - RT}{V} \right)}$$

Solubility parameter units : cal/cm^3)$^{1/2}$, (J/m^3)$^{1/2}$, (MPa)$^{1/2}$

HANSEN SOLUBILITY PARAMETERS (HSP)

$$E = E_d + E_p + E_h$$

$$\frac{E}{V} = \frac{E_d}{V} + \frac{E_p}{V} + \frac{E_h}{V}$$

$$\delta_T^2 = \delta_d^2 + \delta_p^2 + \delta_h^2$$

$$\delta_T^2 = \delta_d^2 + \delta_o^2 + \delta_a \delta_b$$

$$ln\, \gamma_i^h = \frac{V^i}{RT}\left[\left(\delta_d^i - \delta_d^j\right)^2 + \left(\delta_o^i - \delta_o^j\right)^2 + 2\left(\delta_a^i - \delta_a^j\right)\left(\delta_b^i - \delta_b^j\right)\right]$$

$$\ln K^i = \frac{V^i}{RT}\left[\left(\delta_T^{m2} - \delta_T^{S2}\right) + 2\delta_d^i\left(\delta_d^S - \delta_d^m\right) + 2\delta_o^i\left(\delta_o^S - \delta_o^m\right) + 2\delta_a^i\left(\delta_b^S - \delta_b^m\right) + 2\delta_b^i\left(\delta_a^S - \delta_a^m\right)\right]$$

R.Tijssen H.A.H.Billet, P.J.Schoenmakers, Use of solubility parameters for predicting selectivity and retention in Chromatography, J.Chromatogr., 122 (1976) 185-203

Liquid solid chromatography

$$\Delta E_{lsc} = -n(\Delta E^A)_{j/ad} - (\Delta E^s)_{i/j} + (\Delta E^A)_{i/j} + (\Delta E^A)_{i/ad}$$

j = solvent; *ad* – adsorbent; *i* = solute

$$(\Delta E^s)_{i/j} = V^i\left[\left(\delta^j\right)^2 - 2\delta_d^i\delta_d^j - 2\delta_o^i\delta_o^j - 2\delta_{in}^i\delta_{in}^j - 2\delta_a^i\delta_b^j - 2\delta_a^j\delta_b^i\right]$$

$$(\Delta E^A)_{i/ad} = V^i\left[\delta_d^i\delta_d^{ad} + \delta_o^i\delta_o^{ad} + \delta_{in}^{ad}\delta_d^i + \delta_{in}^i\delta_d^{ad} + \delta_a^i\delta_b^{ad} + \delta_a^{ad}\delta_b^i\right]$$

$$\Delta E_{lsc} = (\Delta E^A)_{i/ad} - \frac{A_i}{A_j}(\Delta E^A)_{j/ad}$$

A_i, A_j – molecular area of "*i*" and "*j*"; δ – total solubility parameter; δ_d - dispersion solubility parameter; δ_o - orientation solubility parameter; δ_{in} - induction solubility parameter; δ_a - proton donor solubility parameter; δ_b - proton akceptor solubility parameter

B.L.Karger, L.Snyder, C. Eon, Expanded Solubility Parameter Treatment for Classification and Use of Chromatographic Solvents and Adsorbents, Analytical Chemistry, 50 (1978) 2126-2136

Liquid liquid chromatography

$$i_{(j)} \leftrightarrow i_{(k)}$$

j = solvent; k – liquid stationary phase; i = solute

$$\Delta E^M = V^i\left[(\delta^i)^2 + (\delta^j)^2 - 2\delta_d^i\delta_d^j - 2\delta_{in}^i\delta_d^j - 2\delta_{in}^j\delta_d^i - 2\delta_a^i\delta_b^j - 2\delta_a^j\delta_b^i\right]$$

$$\Delta E^S = V^i\left[(\delta^j)^2 - 2\delta_d^i\delta_d^j - 2\delta_o^i\delta_o^j - 2\delta_{in}^i\delta_d^j - 2\delta_{in}^j\delta_d^i - 2\delta_a^i\delta_b^j - 2\delta_a^j\delta_b^i\right]$$

$$\Delta E_{llc} = \left(\Delta E^M\right)^k - \left(\Delta E^M\right)^j \qquad \Delta E_{llc} = \left(\Delta E^S\right)^k - \left(\Delta E^S\right)^j$$

$$\Delta E_{llc} = V^i\left[(\delta^k)^2 - (\delta^j)^2 - 2\delta_d^i(\delta_d^k - \delta_d^j) - 2\delta_{in}^i(\delta_d^k - \delta_d^j) - 2\delta_d^i(\delta_{in}^k - \delta_{in}^j) - 2\delta_o^i(\delta_o^k - \delta_o^j)\right.$$

B.L.Karger, L.Snyder, C. Eon, Expanded Solubility Parameter Treatment for Classification and Use of Chromatographic Solvents and Adsorbents, Analytical Chemistry, 50 (1978) 2126-2136

Retention in gas-liquid chromatography

$$\delta I^{i/j} = RI^{i/j} - RI^{al/j}$$

$\delta I^{i/j}$ retention index difference between a solute „*i*" and hypothetical n-alkane „*al*" of the same molar volume as „*i*" on stationary phase „*j*"

$$\delta I^{i/j} = \frac{200\, V^i}{(\Delta E^S)^{CH_2/j}} \left[(\delta^{al} - \delta_d^i)(\delta_d^j + \delta_{in}^j) - \delta_o^i \delta_o^j - \delta_{in}^i \delta_d^j - \delta_a^i \delta_b^j - \delta_b^i \delta_a^j \right]$$

B.L.Karger, L.Snyder, C. Eon, Expanded Solubility Parameter Treatment for Classification and Use of Chromatographic Solvents and Adsorbents, Analytical Chemistry, 50 (1978) 2126-2136

SOLUBILITY PARAMETER – IGC

- Flory–Huggins interaction parameter

$$\chi_{12}^{\infty} = \ln\left(\frac{273.15 \cdot R}{p_1^o \cdot V_g \cdot M_1}\right) - \frac{p_1^o}{R \cdot T} \cdot \left(B_{11} - V_1^o\right) + \ln\left(\frac{\rho_1}{\rho_2}\right) - \left(1 - \frac{V_1^o}{V_2^o}\right)$$

1 and *2* denotes the solute and examined material, M_1-the molecular weight of the solute, p_1^0-the saturated vapor pressure of the solute, B_{11}-the second virial coefficient of the solute, V_1^0 -the molar volume, ρ_i-the density, *R* -the gas constant.

$$\chi_{12}^{\infty} = \ln\left(\frac{273.15 \cdot R \cdot \nu_2}{p_1^o \cdot V_g \cdot V_1^o}\right) - \frac{p_1^o}{R \cdot T} \cdot \left(B_{11} - V_1^o\right) - 1$$

GUILLET - DI PAOLA BARANYI APPROACH

$$\chi^{\infty} = \left(\frac{V_1}{RT}\right)(\delta_1 - \delta_2)^2 + \chi_s^{\infty}$$

$$\frac{\delta_{1i}^2}{RT} - \frac{\chi_{(12)i}^{\infty}}{V_{1i}} = \frac{2\delta_2}{RT}\delta_{1i} - \left(\frac{\delta_2^2}{RT} + \frac{\chi_s^{\infty}}{V_{1i}}\right)$$

HSP THROUGH IGC PROCEDURES

- Combination of the experimental data of Flory-Huggins interaction parameter with components of solubility parameter for test solute and examined material

$$\chi_{12}^{\infty} = \alpha \frac{V_1^o}{RT}\left(\left(\delta_{1,d} - \delta_{2,d}\right)^2 + 0{,}25\left(\delta_{1,p} - \delta_{2,p}\right)^2 + 0{,}25\left(\delta_{1,h} - \delta_{2,h}\right)^2\right)$$

where α, V , R, T are a corrective coefficient, molar volume of the test solute, gas constant and temperature of measurement, respectively.

K. Adamska, R. Bellinghausen, A. Voelkel, New procedure of the determination of Hansen Solubility Parameters by means of inverse gas chromatography, J. Chromatogr. A, 1195 (2008) 146-149.

BASIC RELATIONS

$$V_N = V_L K_L + K_{GL} A_{GL} + K_{LS} A_{LS}$$

$$V_g = \frac{3}{2} \cdot \frac{t_R^{'} \cdot j \cdot F \cdot 273.15}{m_w \cdot T}$$

SOLUBILITY PARAMETER FOR SOLIDS

- Model of adsorption described by Snyder and Karger

$$\ln V_g = -\left(E^A / RT\right) + const$$

$$-\Delta E^A = V_i\left(\delta_d^i \delta_d^j + \delta_p^i \delta_p^j + \delta_h^i \delta_h^j\right)$$

HSP FOR SOLIDS

$$\begin{pmatrix} -\Delta E_1 \\ \dots \\ -\Delta E_n \\ \dots \\ -\Delta E_N \end{pmatrix} = \begin{pmatrix} V_1\delta_{1d} & V_1\delta_{1p} & V_1\delta_{1h} \\ \dots & \dots & \dots \\ V_n\delta_{nd} & V_n\delta_{np} & V_n\delta_{nh} \\ \dots & \dots & \dots \\ V_N\delta_{Nd} & V_N\delta_{Np} & V_N\delta_{Nh} \end{pmatrix} * \begin{pmatrix} \beta_1 \\ \dots \\ \beta_n \\ \dots \\ \beta_N \end{pmatrix} + \begin{pmatrix} \varepsilon_1 \\ \dots \\ \varepsilon_n \\ \dots \\ \varepsilon_N \end{pmatrix}$$

$$Y = X\beta + \varepsilon$$

- *Y* - the column vector containing the *N* values of experimental measurements of the energy of adsorption ($-E_N$) of *N* solutes,
- X - the experimental matrix, formed of elements (X_{nk}) , where , V_n is the molar volume of the nth solute and δ_{nk} is one of the Hansen Solubility Parameters of type *k* (*k* = *d*, *p*, or *h*) of the respective test solute,
- *B* - the vector which contains the real values of HSPs of the adsorbent,
- ε – the vector which corresponds to the experimental errors, ε_n.

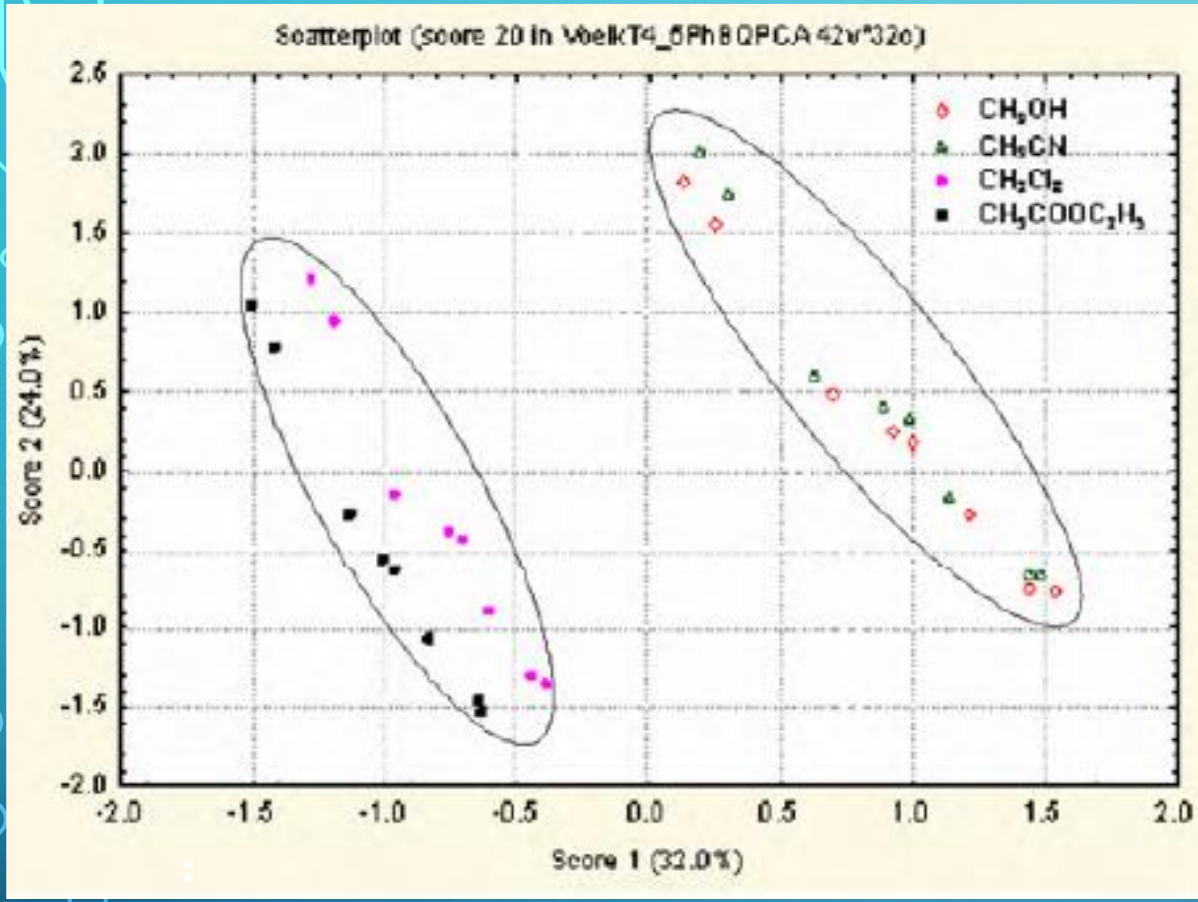
Role of Hansen solubility parameters in solid phase extraction

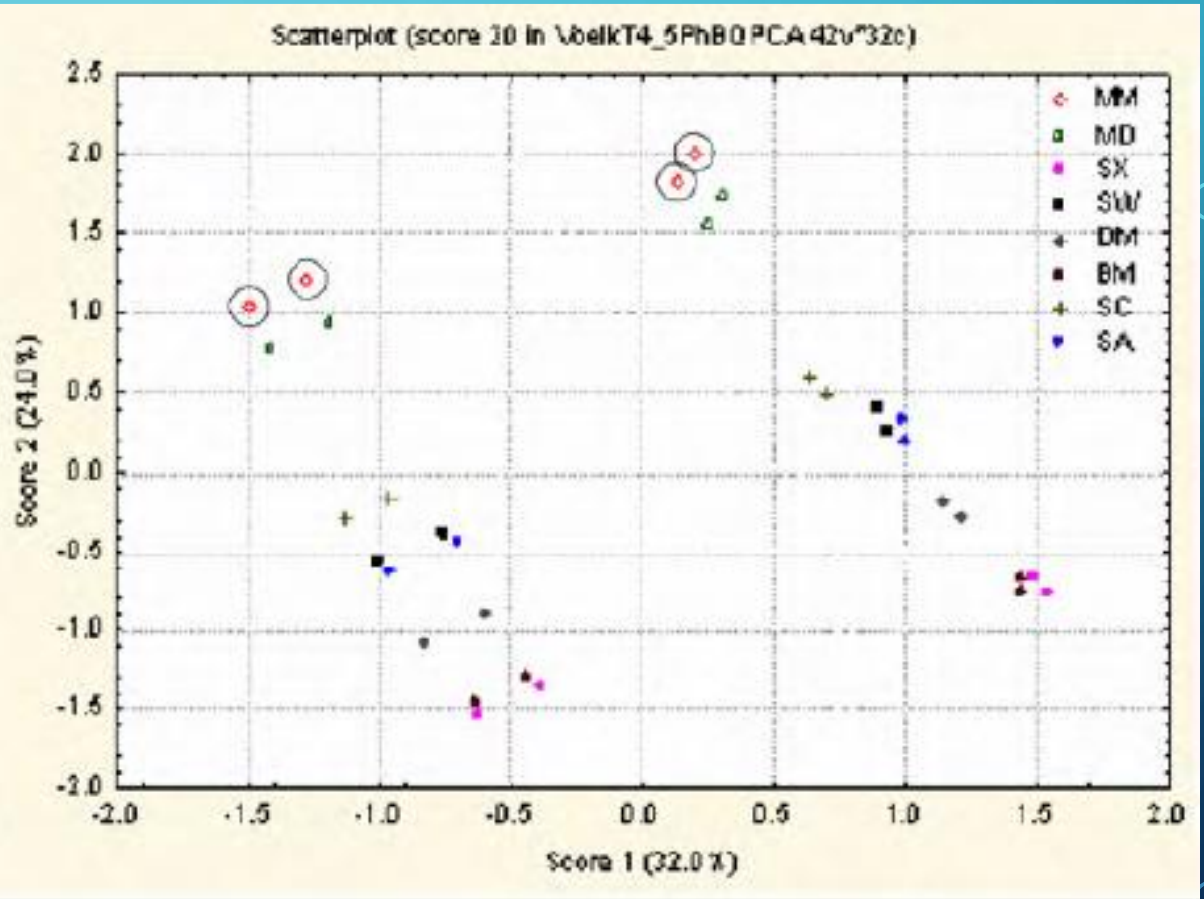
HSPs and total solubility parameter for sorbents, eluents and analytes

	δ_T [(J/cm^3)$^{1/2}$]	δ_D [(J/cm^3)$^{1/2}$]	δ_p [(J/cm^3)$^{1/2}$]	δ_H [(J/cm^3)$^{1/2}$]
Analytes				
Phenol	27.4	21.2	6.6	16.1
p-Benzoquinone	19.6	14.4	10.1	8.71
Solvents				
Metanol	36.5	20.5	16.2	25.5
Acetonitrile	35.3	21.0	27.2	7.9
Dichloromethane	29.0	18.2	22.3	4.0
Ethyl acetate	23.1	18.5	10.7	8.9
Sorbents				
MEDDE–DVB	23.1	19.2	4.1	12.3
MEMDE–DVB	23.6	19.4	4.4	12.7
BM–DVB	20.3	16.1	8.5	9.1
DMN–DVB	19.6	17.8	5.3	6.3
StrataX	18.7	16.7	5.2	6.8
StrataX-C	22.4	18.5	9.5	8.4
StrataX-CW	20.5	18.5	3.0	8.3
StrataX-AW	20.1	18.2	1.5	8.5

K. Bielicka-Daszkiewicza, A. Voelkel, M. Pietrzyńska, K. Heberger, J. Chromatogr. A, 1217 (2010) 5564–5570

Score plots for sorbent-analyte, solvent-analyte, sorbent-solvent systems





left – indicated position of solvents

right - indicated position of sorbents

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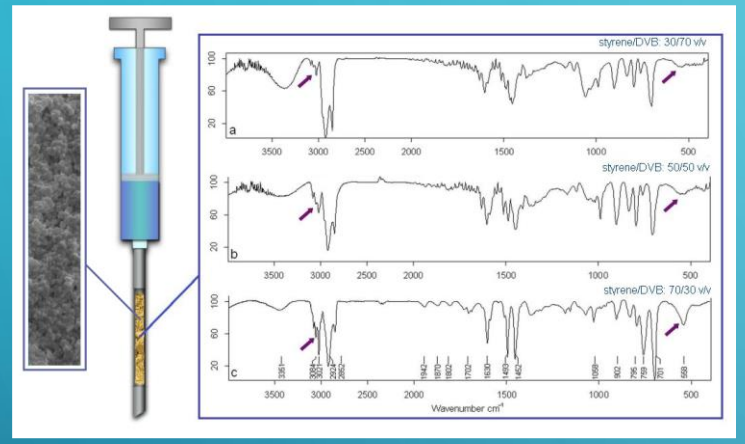
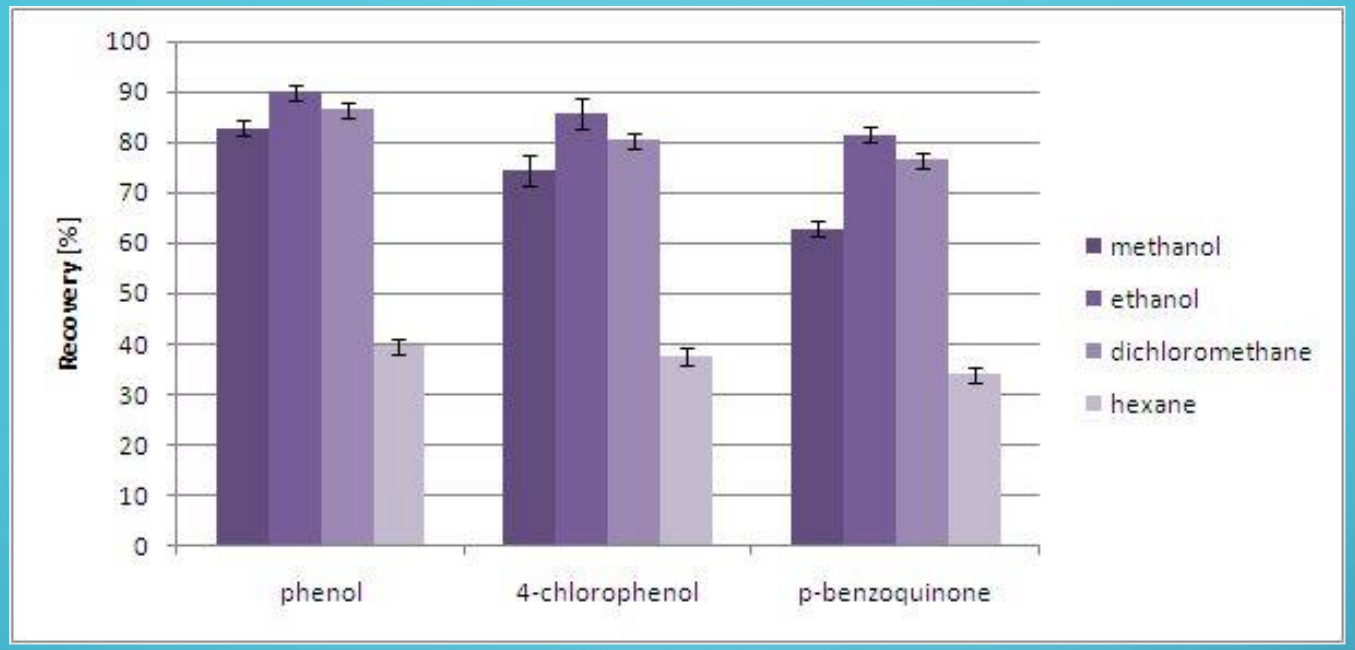
$(\delta_P-\delta_A)^2$ $[J/cm^3)^{1/2}]$			
polymer (Sorbent - Styrene/DVB)	Analytes		
	phenol	4-chlorophenol	p-benzoquinone
30/70% v/v	0.89	4.23	9.58
50/50% v/v	2.51	7.26	13.95
70/30% v/v	4.67	10.69	18.58



Squares of differences fo sorbent-analyte pairs

Squares of differences fo sorbent-solvent (eluent) pairs

$(\delta_P-\delta_S)^2$ $[(J/cm^3)^{1/2}]$				
polymer (Sorbent - Styrene/DVB)	solvents (eluents)			
	methanol	ethanol	dichloromethane	hexane
30/70% v/v	41.64	11.34	8.71	68.14
50/50% v/v	50.30	16.06	5.35	57.99
70/30% v/v	58.79	21.00	3.02	49.56



Taking into account that the use of ethanol allowed to achieve better recovery, it can be concluded that:

i) the sorbent for which the lowest $(\delta_P - \delta_A)^2$ value is found should be selected as a material of filling the needle device;

ii) the value of $(\delta_P - \delta_S)^2$ does not have to be as small as possible,

iii) the interactions between the analyte and the solvent are more important for the extraction process than the interactions between the polymer and solvent.

Therefore, for the selection of a suitable extraction system should start from finding lowest value for $(\delta_P - \delta_A)^2$.

THANK YOU FOR YOUR ATTENTION

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