Mechanisms and facts in accumulative sampling of condensable and volatile organics: substance/interceptor/mass transfer ←→ equilibrium

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thermal gasification

General

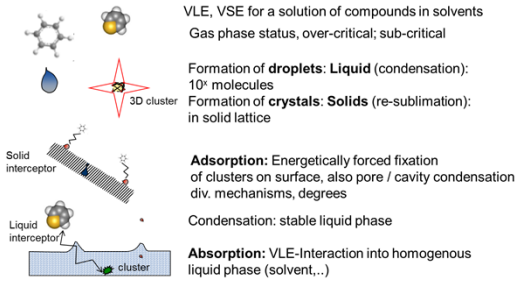
Accumulative sampling procedures of volatile organics underlie combined mechanisms of **mass transfer, phase transition** and **equilibrium**.

The extraction of the sampling gas is often already accompanied from beginning phase transition like resublimation and condensation, or the deposition of solid and liquid aerosols. Afterwards the expected accumulation from the 'gas phasis' on solid substrates (SPA/SPE) or in cooled solvents is carried out. Extraction of the sampling gas is very often combined with the solid precipitation of particulate and aerosol matter from the sampling gas. A certain share of this collection is desired, but side effects like adsorption, aerosol interception not (Figure 2).

In accumulation itself a **complete capture** should be reached, but is interfered from water content. Finally the type of sample produced should be best compatible with the planned analysis, by means of identification and quantification.

Effects during sampling

If sampling gases are extracted from a process flow the following effects are occurring:



Substance classes, pure substances

The following organic substances of Table 1 are representative for sampling. (Fullerenes, asphaltenes not included)

Table 1: Data of common substances (pyrolysis only reference substances)

	formular	molar mass	boiling point	melting point
		[g/mol]	[°C]	[°C]
benzene	C_6H_6	78,11	80,1	5,5
toluene	C_7H_8	92,14	111	-95
xylene(-s)	C_8H_{10}	106,17	138-144	-25,2-13,8
styrene	C_8H_8	104,15	145	-30,6
ethylbenzene	C_8H_{10}	106,17	136	-95
guaiacol	$C_7H_8O_2$	124,13	205	27-29
eugenol	$C_{10}H_{12}O_2$	164,2	253	-9
furfural	$C_5H_4O_2$	96,08	167	-37
thiophene	C_4H_4S	84,14	84	-38
benzothiophene	C_8H_6S	134,2	222	28-32
dibenzothiophene	$C_{12}H_8S$	184,26	332	97-100

	formular	molar mass	boiling point	melting point
		[g/mol]	[°C]	[°C]
napthalene	$C_{10}H_8$	128,16	218	80
ace-napthalene	$C_{12}H_8$	152,2	275	93
acetyl-napthalene	$C_{12}H_{10}$	154,21	279	96
fluorene	$C_{13}H_{10}$	166,22	295	117
phenanthrene	$C_{14}H_{10}$	178,22	340	100
anthracene	$C_{14}H_{10}$	178,22	342	218
fluoranthrene	$C_{16}H_{10}$	202,26	393	110
pyrene	$C_{16}H_{10}$	202,26	404	156
a-phenylene anthracene	$C_{18}H_{12}$	228,29	435	159
chrysene	$C_{18}H_{12}$	228,29	448	256
b-phenylene-flouorene	$C_{20}H_{12}$	252,32	393	168
bk-f	$C_{20}H_{12}$	252,32	480	217
ba-p	$C_{20}H_{12}$	252,32	496	177
indeno(1,2,3,c,d)-pyrene	$C_{22}H_{12}$	276,34	534	162
di-benzo (a,h) anthracene	$C_{22}H_{14}$	278,35	535	262
benzo(g,h,i)perylene	$C_{22}H_{12}$	276,34	542	273

Saturation pressure of single substance

The most descriptor of present substances is the saturation pressure (Figure 1): For **high melting** substances **sublimation** (solid-gas; table 1) must be considered.

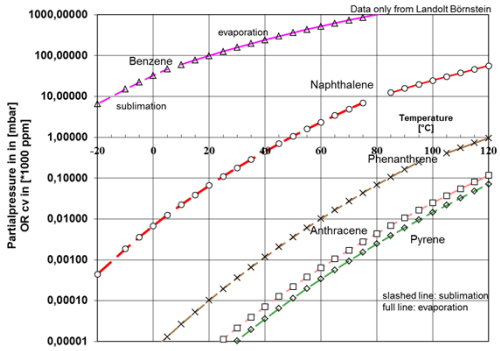


Figure 1: Saturation pressure of single compounds, no interaction

Visualisation of common known effects

A typical setting of a sampling line is shown in the Figure 2 and good an bad effects are indicated, right side concentration is shown.

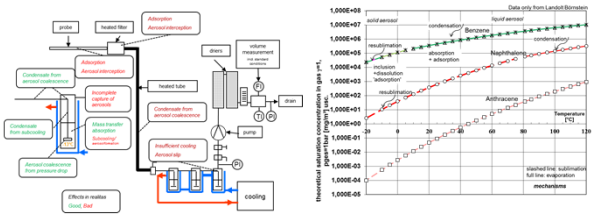


Figure 2: Equipment of sampling line with real-effects

Section	Mechanism	Reversibility	others
Sampling probe	Aerosol interception, adsorption	De/Dedsorption	Polymerisation can occur
Particulate filter			
Transfer line	Condensation Aerosol growing	Aerosol evaporation	Gas/liquid interaction
SPE/SPA-cartridge	Condensation Adsorption	Desorption Dissolution	'overheating' Polymerisation can occur
Impinge tube	Condensation Aerosol growing	Dissolution	Cooling
Gas distributor	clouding Aerosol growing	Deposition residues	Gas/liquid interaction
Buble swarm	Traditional mass transfer subcooling	Equilibrium	Cooling

Interaction of substances: VLE-limits

Phase change thermodynamic of **pure** substances:

Vapour← → Liquid: condensation and evaporation

‚activity gas= activity liquid'

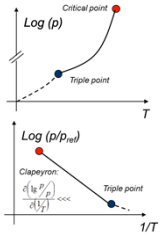
$$p_i = p_{total} \cdot y_i \cdot \varphi_i\big|_{gas} = p_i^* \cdot x_i \cdot \gamma_i\big|_{liquid}$$

Vapour ← → Solid: re-sublimation and sublimation

‚activity gas = activity solid'

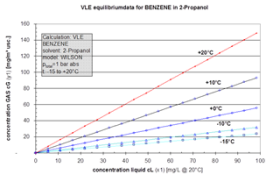
$$p_i = p_{total} \cdot y_i \cdot \varphi_i\big|_{gas} = p_i^* \cdot x_i \cdot \gamma_i\big|_{\text{solid condensed}}$$

The clear and correct description of real substances is not as easy as it looks.
(serveral data ref.; missing data,..)



Equilibrium effects VLE

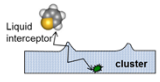
In Figure 3 the VLE of benzene in different solvents is selected:



In term of pressure:

A partial pressure below saturation can be reached, because of homogeneous dissolution in liquid phase: **Law of Raoult.**

e.g. when x_i <<<<!



$$p_i = p_{total} \cdot y_i \cdot \varphi_i\big|_{gas} = p_i^* \cdot x_i \cdot \gamma_{i,in\,\text{solvent}}\big|_{liquid}$$

Absorption: VLE-Interaction into homogenous liquid phase (solvent,..)

Capture Efficiency: e.g. accumulation in liquid

In Figure 4 the situation of 'in stationary' capture is shown:

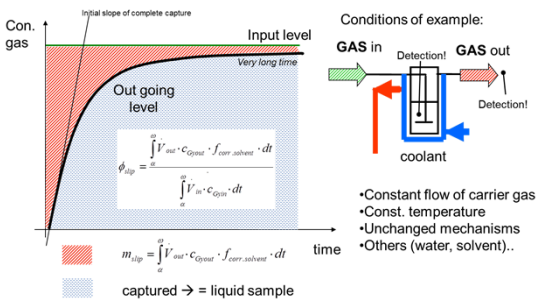


Figure 4: Phases of complete capture, transition & saturation

Comparative descriptors of capture potential is: *[k.A]* of a bubble-swarm: This can include all effects (Figure 2) after the transfer-line. In a Figure ***'capture efficiency'*** the situation of 'in stationary' capture is shown (other poster).

Present poster was prepared for the *3rd. International Gas Analysis Workshop*, about detail 'tar & sulphur' sampling and analysis. *21st. European Conference about Biomass in Kopenhagen June 2013.*

In detail the poster is presenting specific knowledge, which is relevant within the working area of sampling and analysis.

Specific experience in this item is useful for comprehension.

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