

GC of VOCs

Volatile organic compounds (VOCs):

- Organic chemicals with a high vapour pressure at room temperature.
- High vapour pressure results from a low boiling point.
- The World Health Organization (WHO) defined a VOC as any organic compound whose boiling point is in the range from 50-260 °C, corresponding to saturation vapour pressures greater than 100 kPa at 25°C.

Products used at home or work can release VOCs into the air when used and stored.

Examples of Household Products	Possible VOC Ingredients
Fuel containers or devices using gasoline, kerosene, fuel oil and products with petroleum distillates: paint thinner, oil-based stains and paint, aerosol or liquid insect pest products, mineral spirits, furniture polishes	BTEX (benzene, toluene, ethylbenzene, xylene), hexane, cyclohexane, 1,2,4-trimethylbenzene
Personal care products: nail polish, nail polish remover, colognes, perfumes, rubbing alcohol, hair spray	Acetone, ethyl alcohol, isopropyl alcohol, methacrylates (methyl or ethyl), ethyl acetate
Dry cleaned clothes, spot removers, fabric/ leather cleaners	Tetrachloroethene (perchloroethene (PERC), trichloroethene (TCE))
Citrus (orange) oil or pine oil cleaners, solvents and some odor masking products	d-limonene (citrus odor), a-pinene (pine odor), isoprene
PVC cement and primer, various adhesives, contact cement, model cement	Tetrahydrofuran, cyclohexane, methyl ethyl ketone (MEK), toluene, acetone, hexane, 1,1,1-trichloroethane, methyl-iso-butyl ketone (MIBK)
Paint stripper, adhesive (glue) removers	Methylene chloride, toluene, older products may contain carbon tetrachloride
Degreasers, aerosol penetrating oils, brake cleaner, carburetor cleaner, commercial solvents, electronics cleaners, spray lubricants	Methylene chloride, PERC, TCE, toluene, xylenes, methyl ethyl ketone, 1,1,1-trichloroethane
Moth balls, moth flakes, deodorizers, air fresheners	1,4-dichlorobenzene, naphthalene
Refrigerant from air conditioners, freezers, refrigerators, dehumidifiers	Freons (trichlorofluoromethane, dichlorodifluoromethane)
Aerosol spray products for some paints, cosmetics, automotive products, leather treatments, pesticides	Heptane, butane, pentane
Upholstered furniture, carpets, plywood, pressed wood products	Formaldehyde

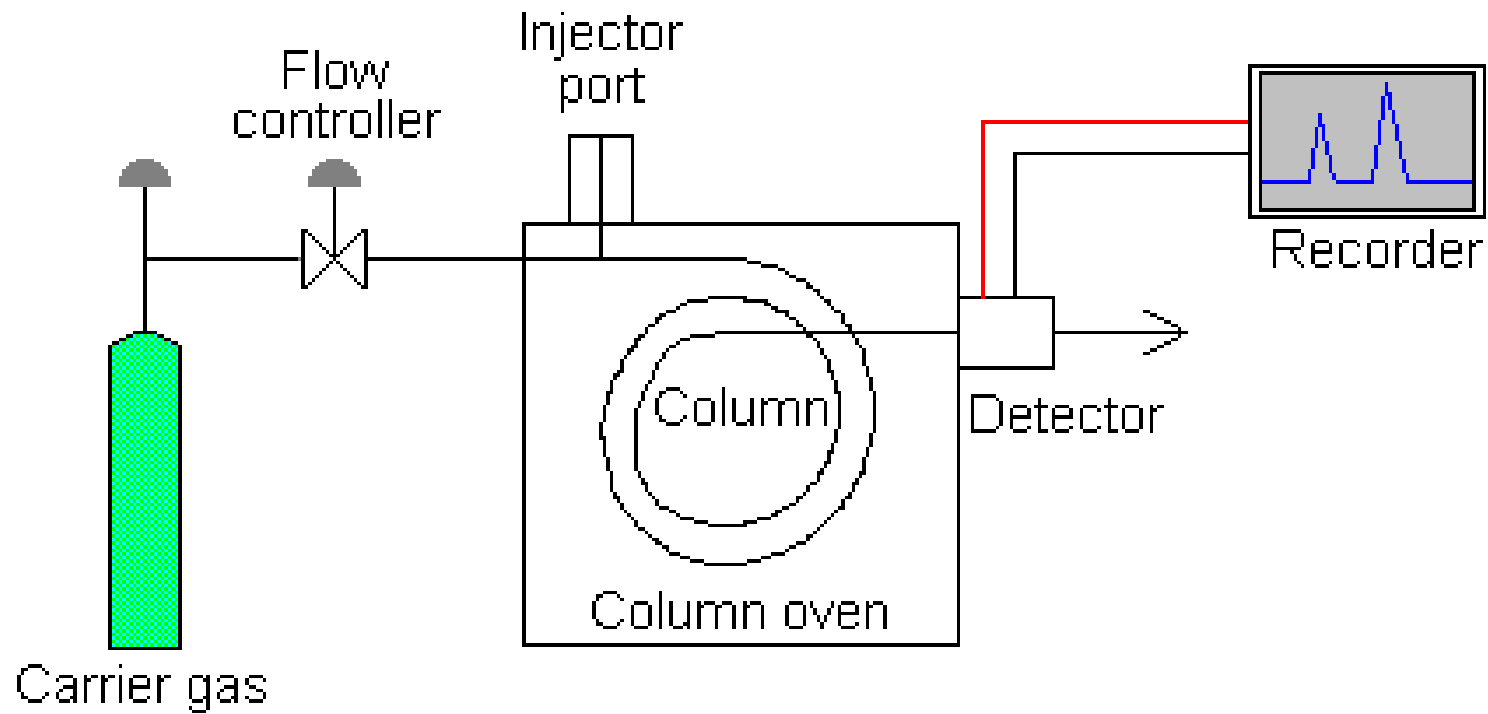
Gas Chromatography

GC : most widely used analytical technique in the world

- Over 50 years in development
- 2000 instruments sold/yr
- 25000+ in use in industry, universities, government labs, hospitals

Most popular technique for the separation and analysis of volatile compounds

- Gases, liquids, dissolved solids
- Mostly organic, but also inorganic materials



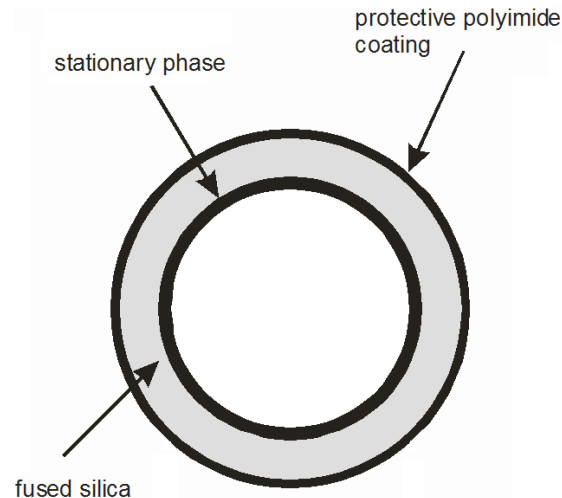
Two types of GC

GSC: based on a solid stationary phase. Analytes are retained by physical adsorption (not used anymore).

GLC: the analyte partitions between the gaseous mobile phase and a liquid immobilized on the walls of capillary tubing.



- Column Length (15-60 m)
- Diameter (0.05-0.5 mm)
- Film composition (e.g. DB1, DB5)
- Film thickness (0.1-5 μm)



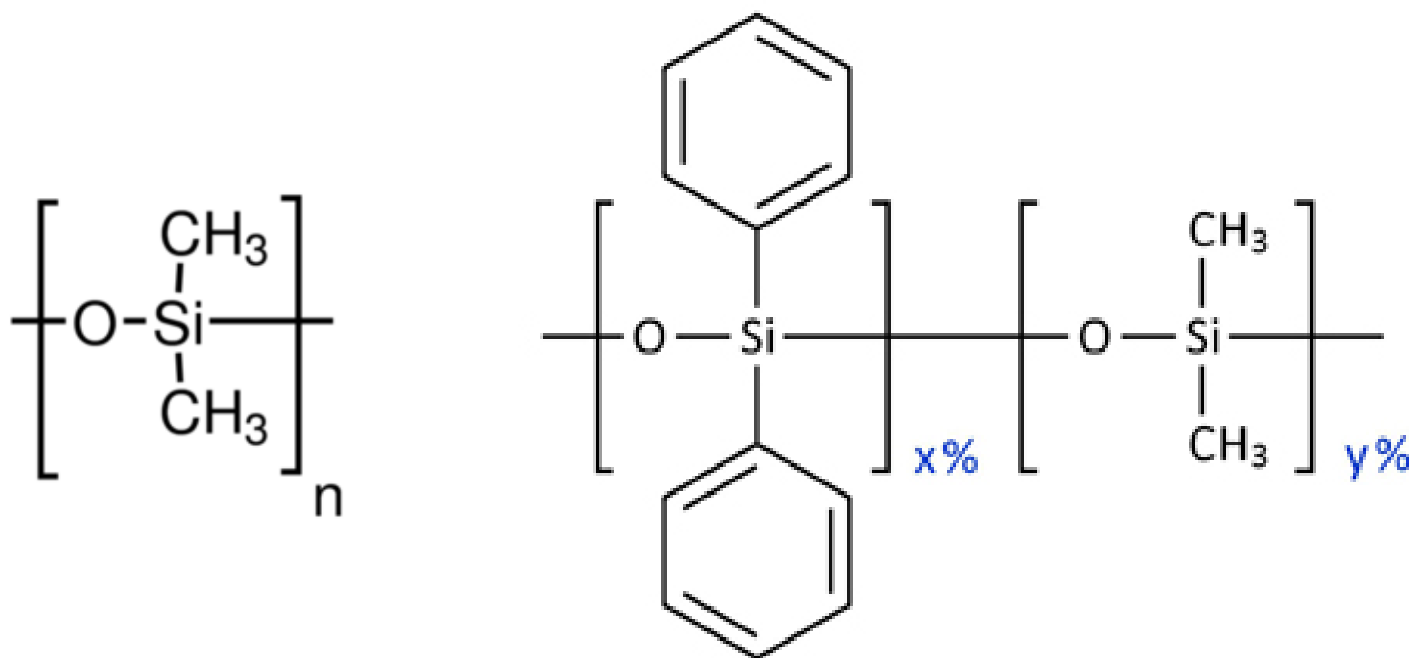
GSC



GC Column Cross-Reference: Columns by Phase

Fused Silica Columns

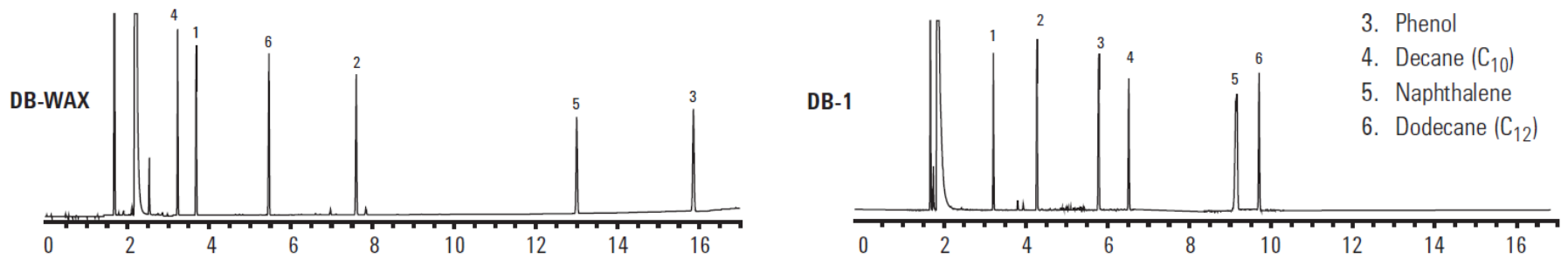
Restek	Phase Description	USP Nomenclature	Agilent	SGE	Phenomenex	Machery-Nagel	Supelco
Rtx-1	dimethyl polysiloxane	G1, G2, G38	HP-1, DB-1, CP-Sil 5 CB	BP1	ZB-1	OPTIMA 1	SPB-1
Rtx-5	diphenyl dimethyl polysiloxane	G27, G36	HP-5, DB-5 CP-Sil 8 CB	BP5	ZB-5	OPTIMA 5	SPB-5



Effects of stationary phase

Figure 4: Hydrogen Bonding Interactions

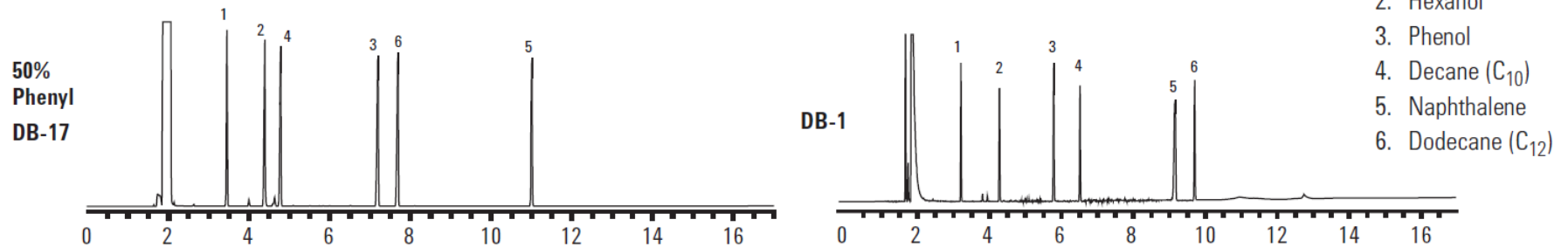
Column: 15 m x 0.25 mm id, 0.25 μ m



DB-1 does not undergo hydrogen bonding interactions. The change in the elution order of hexanol and phenol with DB-WAX is a combination of the dipole and hydrogen bonding interaction.

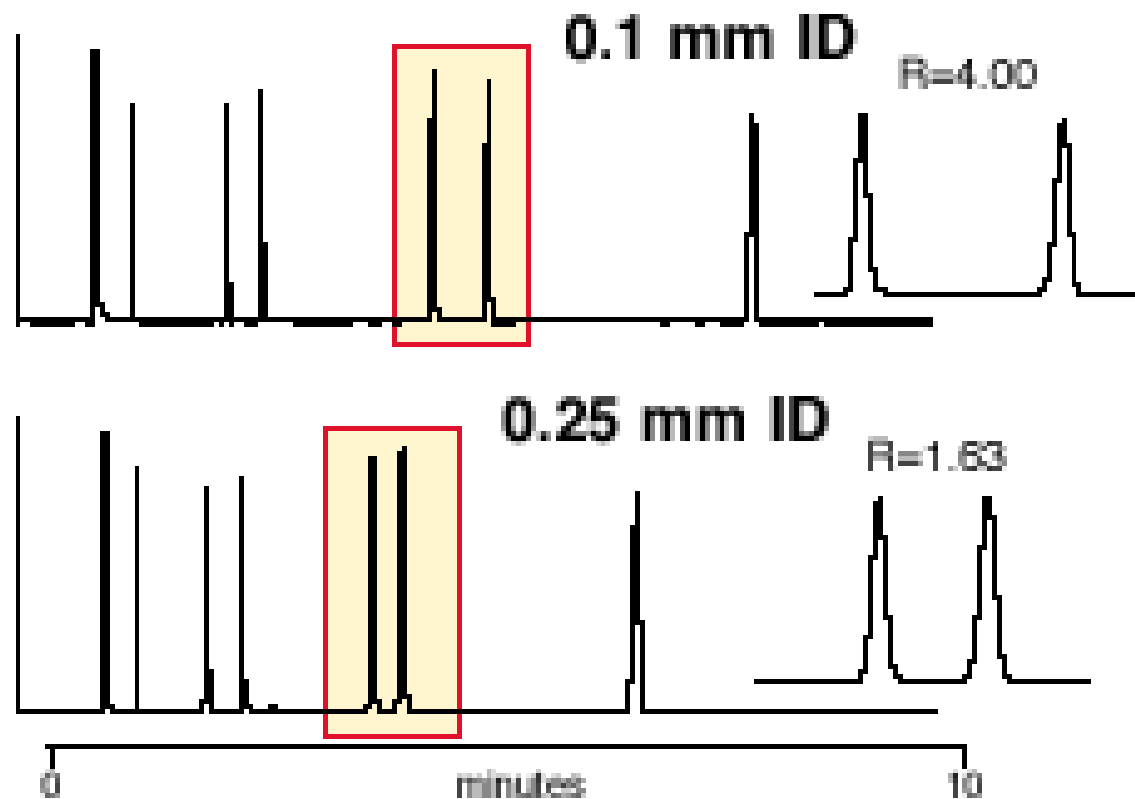
Figure 5: Phenyl Content Retention

Column: 15 m x 0.25 mm id, 0.25 μ m

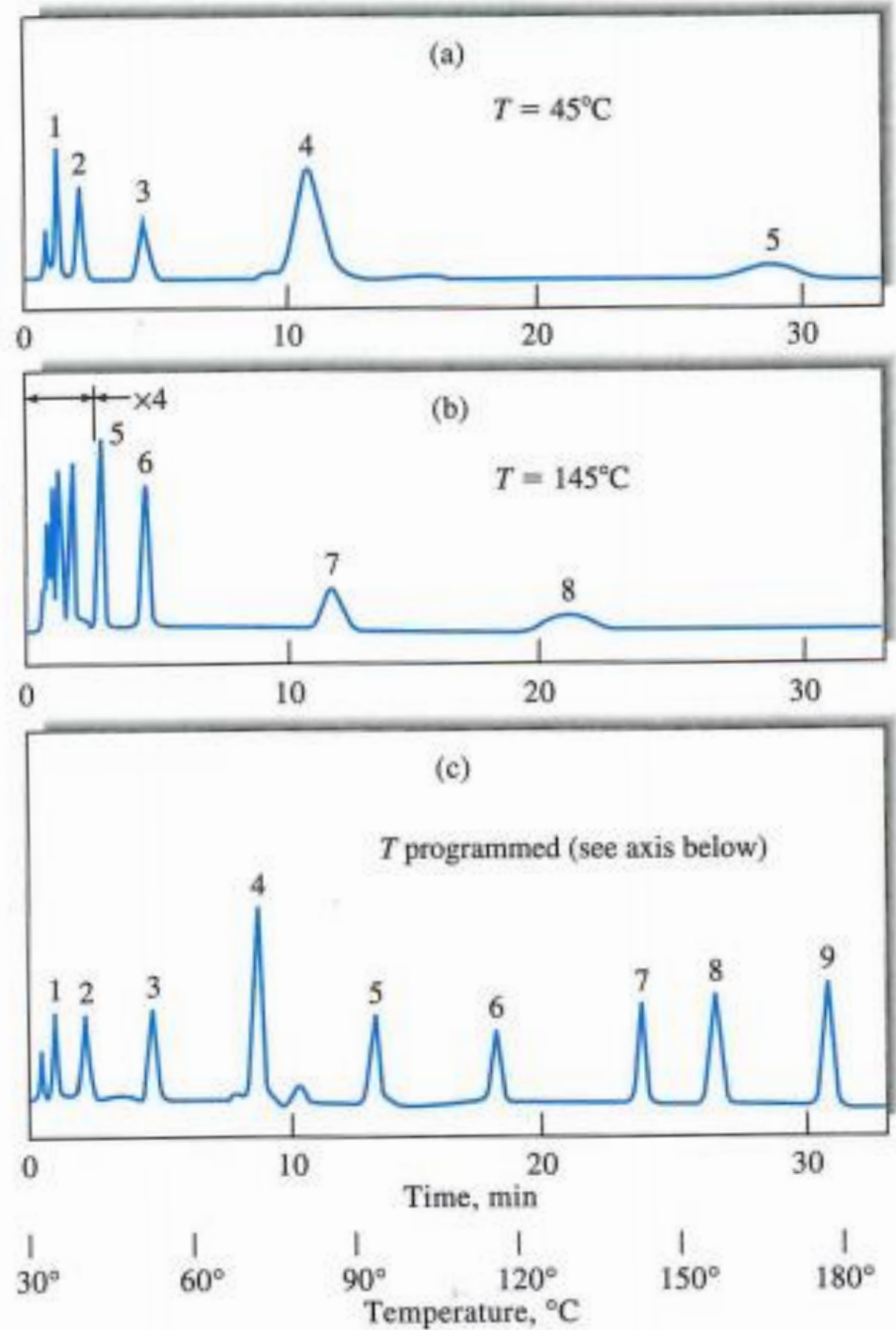


The aromatics increase in retention relative to the hydrocarbons for the DB-17 columns. DB-17 contains 50% phenyl substitution. DB-1 contains no phenyl substitution.

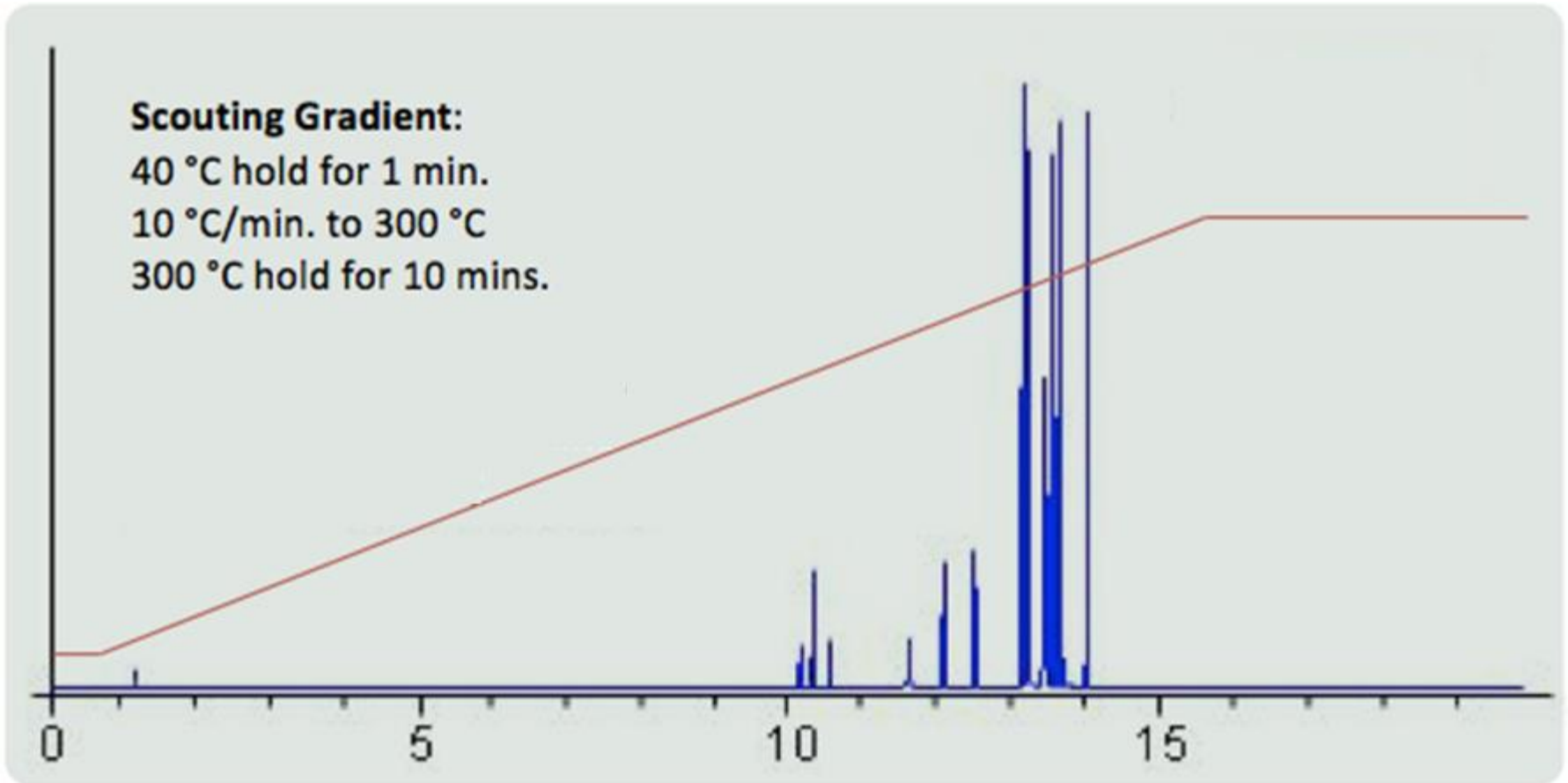
Effect of Column Diameter



Effect of temperature: Figure 27-7

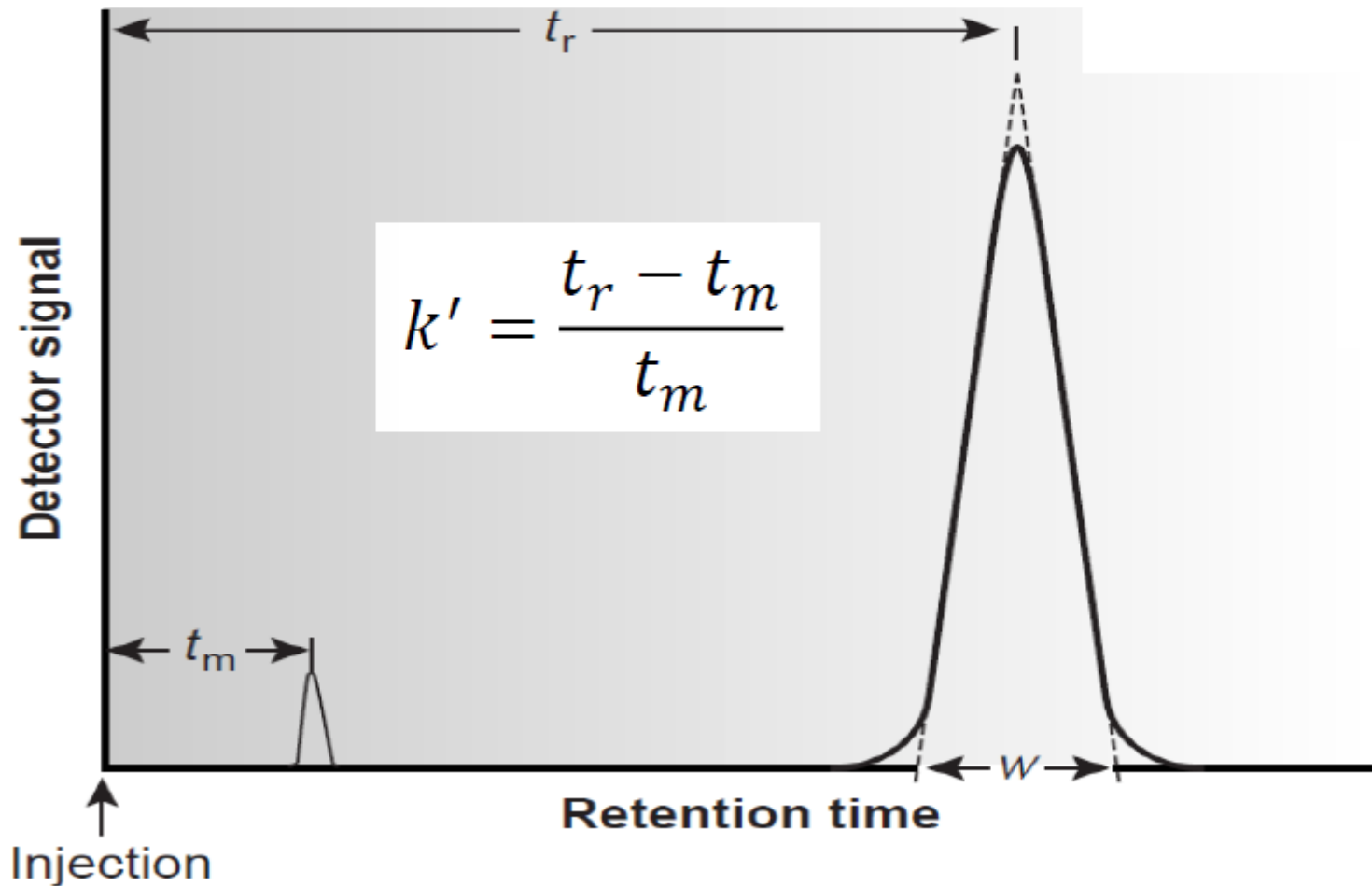


Example of oven temperature programming



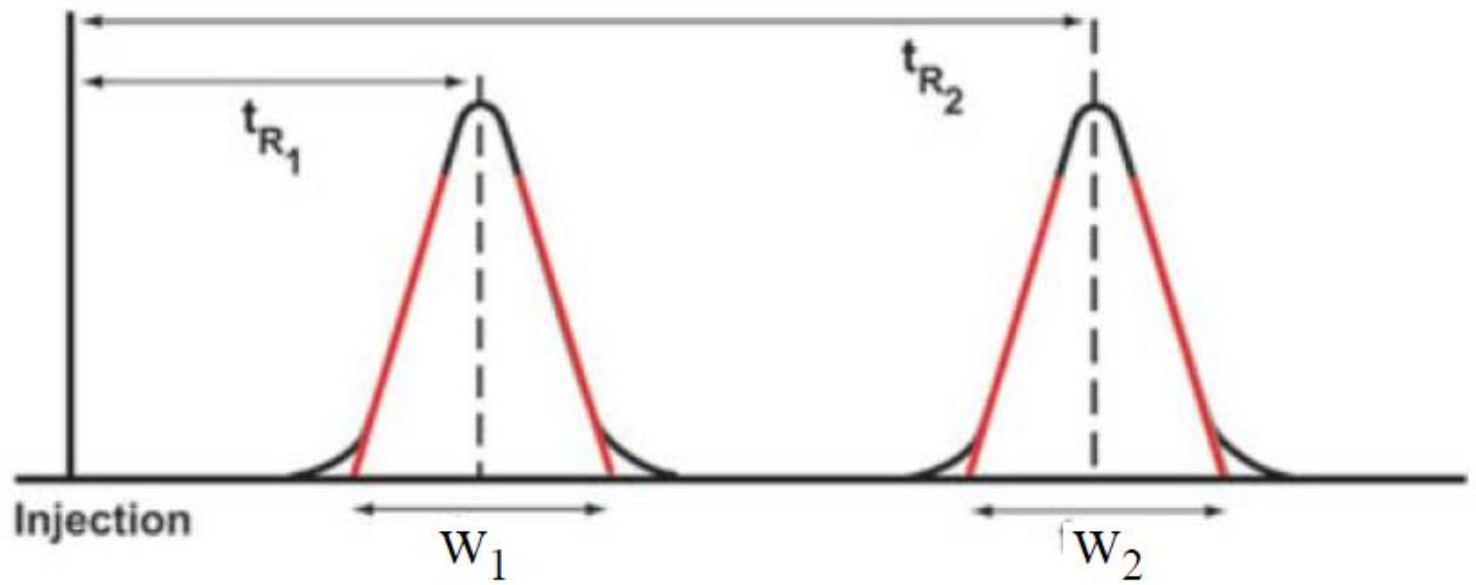
Chromatographic parameters

Capacity factor



Chromatographic Resolution (R)

$$R = \frac{t_{r,2} - t_{r,1}}{0.5(w_2 + w_1)} = \frac{2\Delta t_r}{w_2 + w_1}$$



Selectivity

$$\alpha = k'_2/k'_1$$

Number (N) and height (H) of theoretical plates

$$N = \frac{L}{H}$$

L = column length

$$N = 16 \left(\frac{t_r}{W} \right)^2$$

Expression of the resolution as a function of global parameters:

$$R = \frac{1}{4} \sqrt{N} \times \frac{\alpha - 1}{\alpha} \times \frac{k}{1 + k}$$

↑ ↑ ↑
efficiency selectivity retention

The van Deemter plot and equation

$$HETP = A + \frac{B}{u} + (C_s + C_m) \cdot u$$

- HETP = height equivalent to a theoretical plate, a measure of the resolving power of the column [m]
- A = Eddy-diffusion parameter, related to channeling through a non-ideal packing [m]
- B = diffusion coefficient of the eluting particles in the longitudinal direction, resulting in dispersion [$\text{m}^2 \text{s}^{-1}$]
- C = Resistance to mass transfer coefficient of the analyte between mobile and stationary phase [s]
- u = Linear velocity [m s^{-1}]

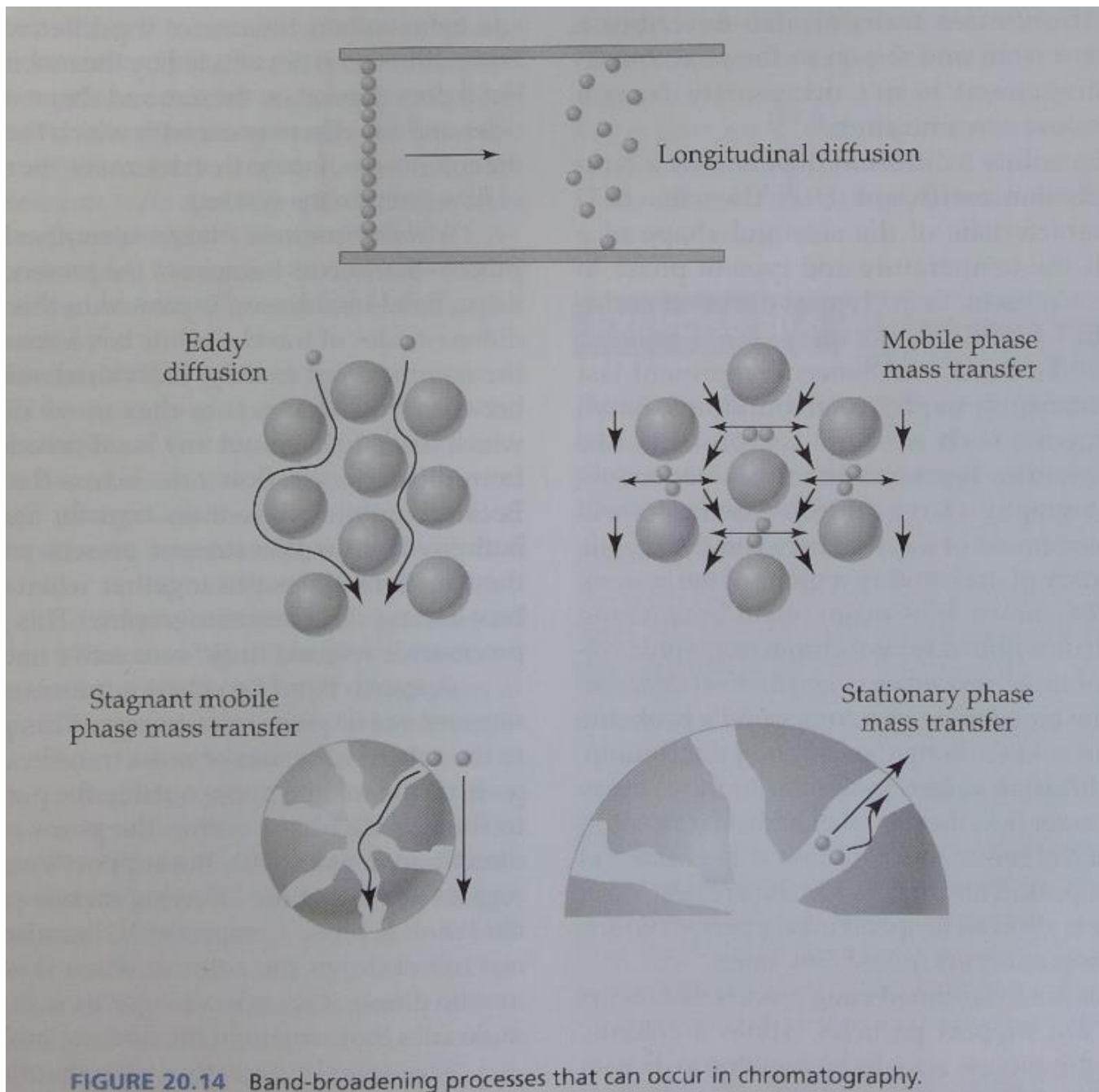
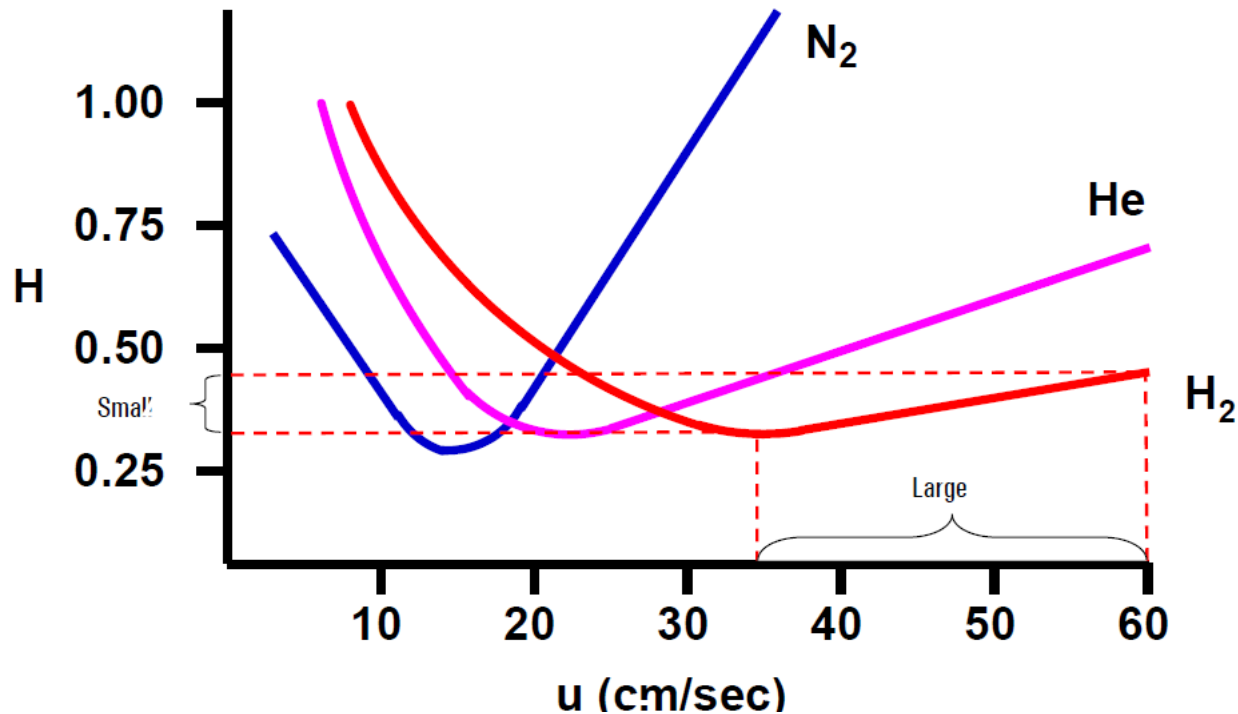


FIGURE 20.14 Band-broadening processes that can occur in chromatography.

In open tubular capillaries, $A = 0$. A is related to the multiple routes an analyte could take in a packed column.

HETP reaches a minimum value at a particular flow velocity. At this flow rate, the resolving power of the column is maximized.

VAN DEEMTER CURVES



CARRIER GAS

Gas	Advantages	Disadvantages
Nitrogen	Cheap, Readily available	Long run times
Helium	Good compromise, Safe	Expensive
Hydrogen	Shorter run times, Cheap	Explosive*

* difficult to explode under GC conditions

Identification of compounds: retention indices

- Retention index system first proposed by Kovats in 1958
- Requires standards with predetermined retention indices
- Standards bracket the unknown compounds
- Scale based on normal alkanes

Isothermal mode

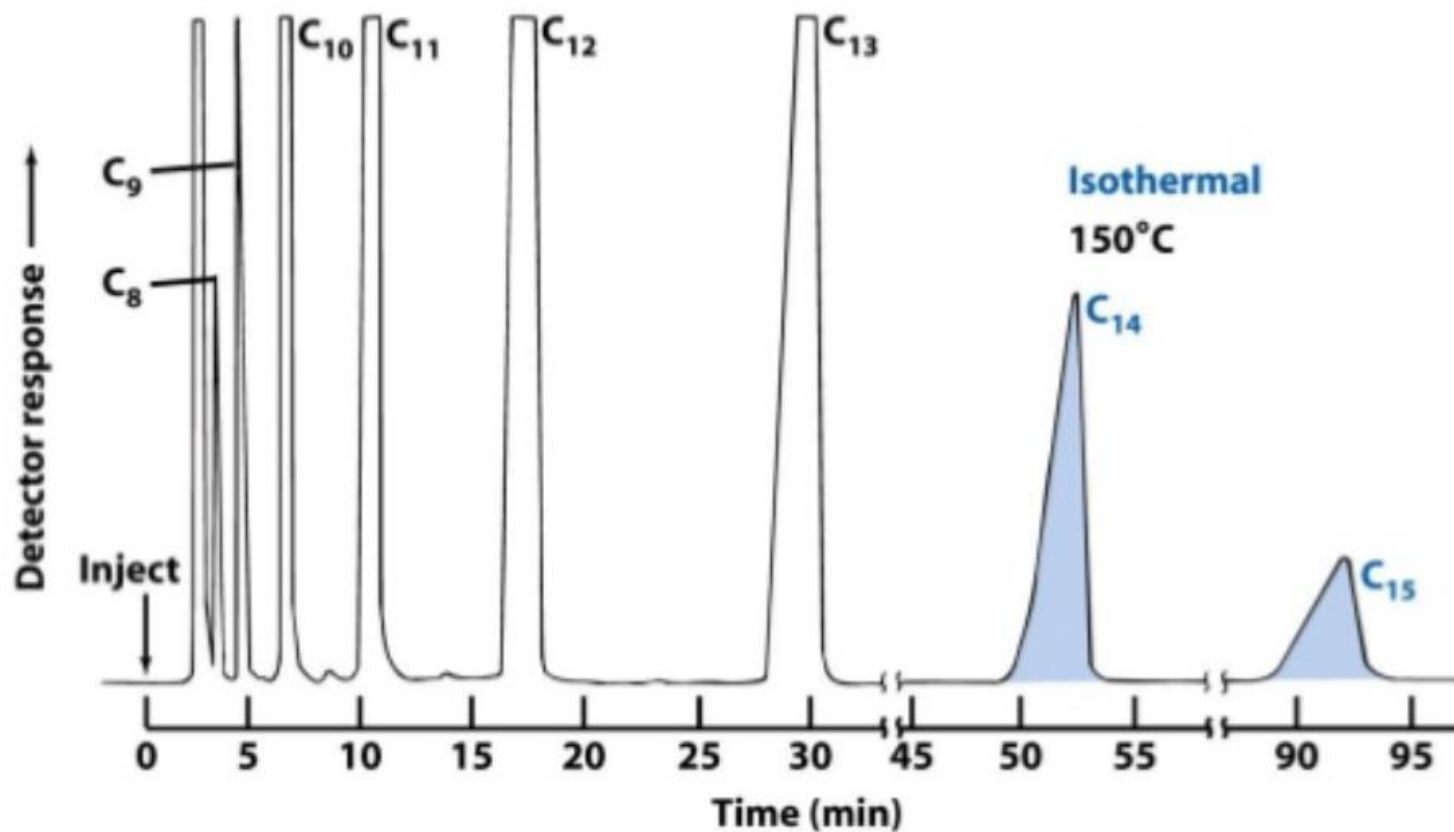


Figure 24-10a
Quantitative Chemical Analysis, Seventh Edition
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$$I = 100 \times \left[n + \frac{\log(t'_{r(\text{unknown})}) - \log(t'_{r(n)})}{\log(t'_{r(N)}) - \log(t'_{r(n)})} \right]$$

Temperature programming mode

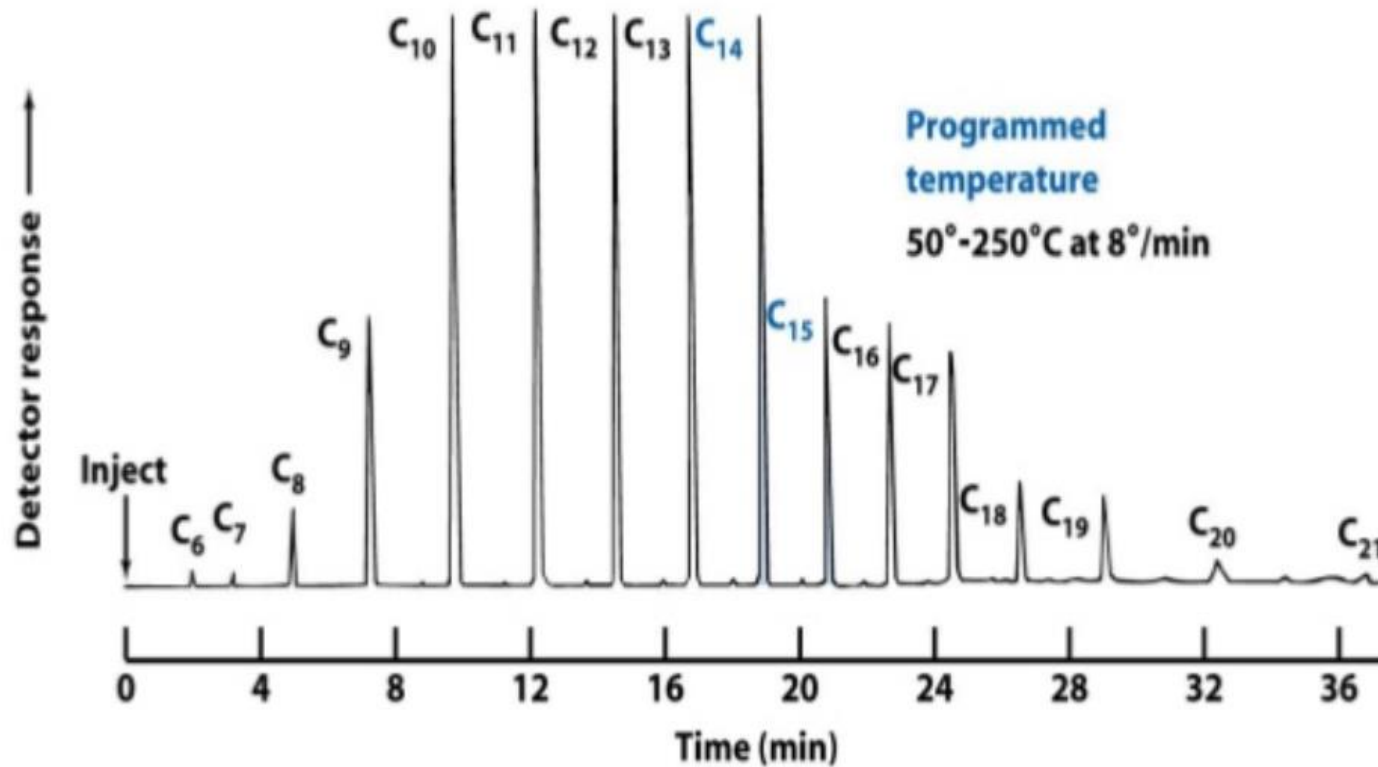


Figure 24-10b
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$$I = 100 \times \left[n + \frac{t_{r(\text{unknown})} - t_{r(n)}}{t_{r(N)} - t_{r(n)}} \right]$$

Where:

I = Kovats retention index,

n = the number of carbon atoms in the smaller n-alkane,

N = the number of carbon atoms in the larger n-alkane,

t_r = the retention time.

GC application



Contents lists available at SciVerse ScienceDirect

Journal of Chromatography A

journal homepage: www.elsevier.com/locate/chroma

Determination of polycyclic aromatic hydrocarbons in soil samples using flotation-assisted homogeneous liquid–liquid microextraction

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ARTICLE INFO

Article history:

Received 1 July 2012

Received in revised form

26 September 2012

Accepted 27 September 2012

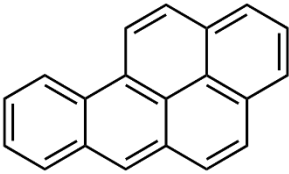
Available online 3 October 2012

Keywords:

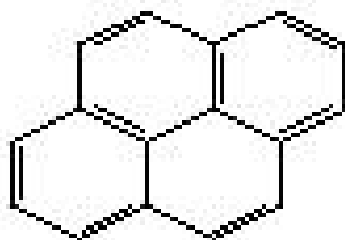
Flotation-assisted homogeneous
liquid–liquid microextraction
Polycyclic aromatic hydrocarbons
Gas chromatography
Soil samples

ABSTRACT

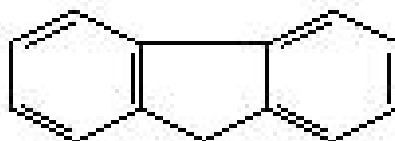
In this study, flotation-assisted homogeneous liquid–liquid microextraction (FA-HLLME) was developed as a fast, simple, and efficient method for extraction of four polycyclic aromatic hydrocarbons (PAHs) in soil samples followed by gas chromatography–flame ionization detector (GC-FID) analysis. A special home-made extraction cell was designed to facilitate collection of the low-density extraction solvent without a need for centrifugation. In this method, PAHs were extracted from soil samples into methanol and water (1:1, v/v) using ultrasound in two steps followed by filtration as a clean-up step. The filtrate was added into the home-made extraction cell contained mixture of 1.0 mL methanol (homogenous solvent) and 150.0 μ L toluene (extraction solvent). Using N_2 flotation, the dispersed extraction solvent was transferred to the surface of the mixture and was collected by means of a micro-syringe. Then, 2 μ L of the collected organic solvent was injected into the GC-FID for subsequent analysis. Under optimal conditions, linearity of the method was in the range of 40–1000 μ g kg⁻¹ soil (dry weight). The relative standard deviations in real samples varied from 5.9 to 15.2% ($n = 4$). The proposed method was successfully applied to analyze the target PAHs in soil samples, and satisfactory results were obtained.

Agency	PAH Compound(s)	Carcinogenic Classification
U.S. Department of Health and Human Services (HHS)	<ul style="list-style-type: none"> • benz(a)anthracene, • benzo(b)fluoranthene, • benzo(a)pyrene, • dibenz(a,h)anthracene, and • indeno(1,2,3-c,d)pyrene. 	<p>Known animal carcinogens</p> 
International Agency for Research on Cancer (IARC)	<ul style="list-style-type: none"> • benz(a)anthracene and • benzo(a)pyrene. 	Probably carcinogenic to humans
	<ul style="list-style-type: none"> • benzo(a)fluoranthene, • benzo(k)fluoranthene, and • ideno(1,2,3-c,d)pyrene. 	Possibly carcinogenic to humans
	<ul style="list-style-type: none"> • anthracene, • benzo(g,h,i)perylene, • benzo(e)pyrene, • chrysene, • fluoranthene, • fluorene, • phenanthrene, and • pyrene. 	Not classifiable as to their carcinogenicity to humans

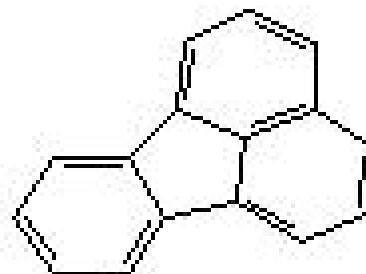
Each PAH (anthracene, fluorene, pyrene, and fluoranthene, 0.01 g) was dissolved in a 10 mL mixture of acetonitrile and dichloromethane (4:1) to obtain a standard stock solution of 1000 mg/L.



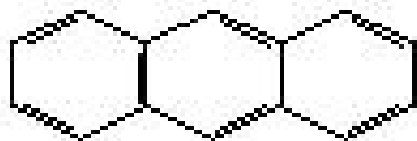
Pyrene



Fluorene



Fluoranthene



Anthracene

Sample prep

Soil samples were collected from Tehran (Iran).

All large stones and extraneous material were removed by hand.

Then the soil samples were pulverized and passed through a 500-um sieve.

After washing with water and acetone, they were dried at 105°C (24 h).

Then, the soil samples were air dried on trays at a temperature not exceeding 30°C.

Of each soil sample, 50.0 g was accurately weighed and an appropriate amount of the standard stock solution was added until methanol solution completely covered the soil sample.

Methanol was evaporated from soil samples and samples were dried at room temperature.

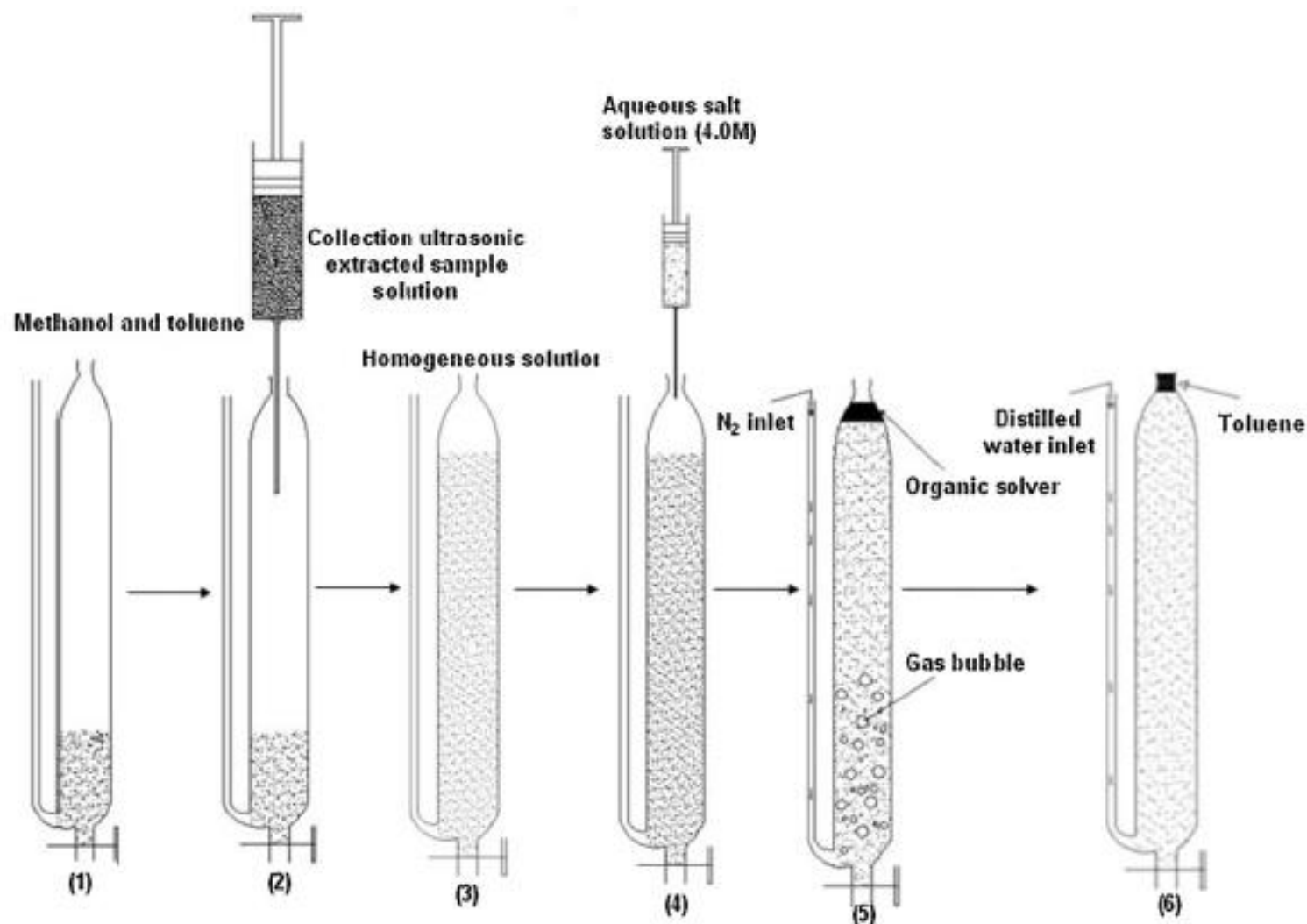


Fig. 1. Schematic FA-HLLME procedure (1) a mixture of 1.0 mL methanol containing 150.0 μL toluene was added to the home-designed microextraction cell, (2) 20.0 mL of the collected ultrasonic extract was added into the microextraction cell, (3) a homogeneous solution was formed in the cell, (4) 3.0 mL of aqueous salt solution (NaCl 4.0 M) was added into the cell, (5) using N₂ flotation, organic solvent was moved to the top of the solution, (6) a small volume of distilled water was added into the glass tube on the side of the cell.

Instrumentation

A gas chromatograph (Buck Scientific model 910, USA) with a split/splitless injector system and a flame ionization detector was used.

Pure helium (99.999%) was used as the carrier gas.

The injection port was held at 250°C and used in the splitless mode.

A DB-5 (5% phenyl + 95% polydimethylsiloxane) fused-silica capillary column (30 m × 0.25 mm i.d. and 0.25 μm film thickness) was used.

The column oven was initially held at 100°C for 5 min, ramped to 265°C at a rate of 20°C/min, and remained at this temperature for 15 min.

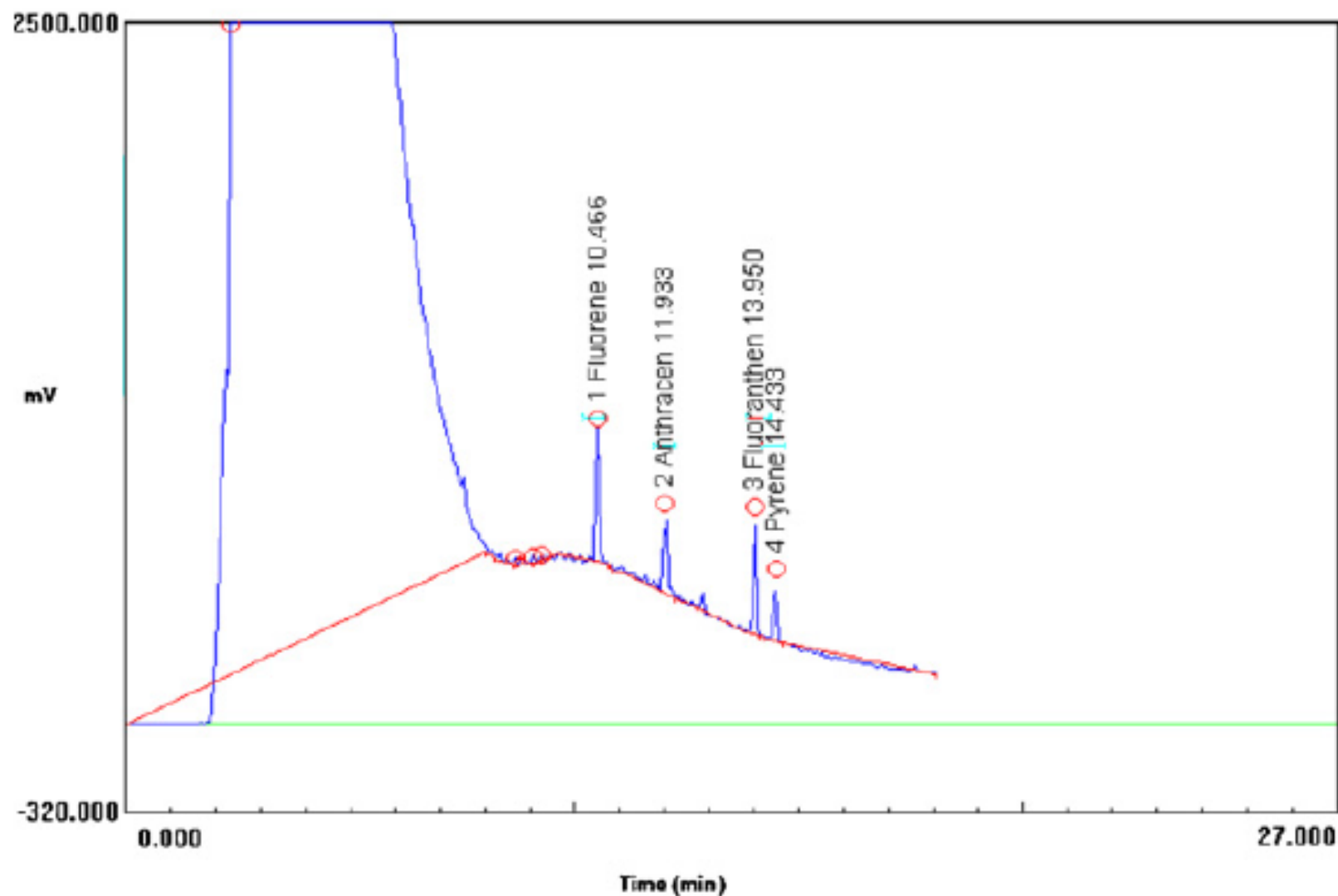


Fig. 5. Chromatogram of the PAHs extracted from soil sample. Extraction conditions: homogeneous solvent (methanol) volume, 1.0 mL; extraction solvent (toluene) volume, 150.0 μ L; NaCl concentration, 4.0 M.

Table 2

Determination of PAHs in soil samples.

Sample	Fluorene	Anthracene	Fluoranthene	Pyrene
Tehran land				
Initial concentration ^a	<LOD	<LOD	<LOD	<LOD
Add	0.40	0.30	0.30	0.30
Found ^b	0.41	0.27	0.29	0.34
Error %	2.5	-10.0	-3.3	13.3
RSD %	12.2	7.4	6.9	5.9
Esfahan 1 (Zayanderud land)				
Initial concentration ^a	<LOD	<LOD	<LOD	<LOD
Add	0.060	0.060	0.060	0.060
Found ^b	0.070	0.065	0.053	0.073
Error %	16.7	8.3	-11.7	21.7
RSD %	10.6	15.2	7.8	10.9
Esfahan 2 (Zayanderud land)				
Initial concentration ^a	<LOD	<LOD	<LOD	<LOD
Add	0.100	0.070	0.500	0.040
Found ^b	0.110	0.077	0.487	0.045
Error %	10.0	9.1	-2.6	12.5
RSD %	7.7	14.8	8.2	11.7

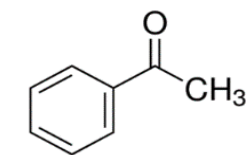
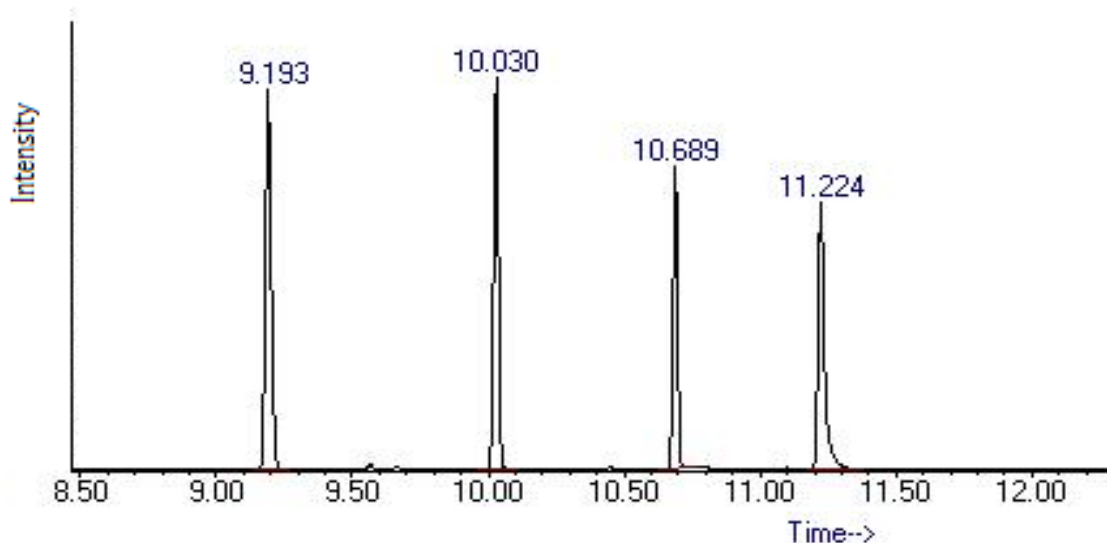
^a All concentrations are in $\mu\text{g kg}^{-1}$.^b Concentration of PAHs in spiked samples that found by proposed HLLME-FA method.

Summary on GC of VOCs

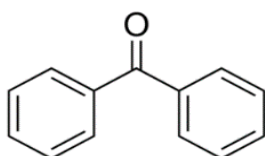
- Analytes can be injected directly without derivatization
- Nowadays only GLC
- Different detectors possible (FID, NPD, ECD, MS: next classes)
- Quantitative and qualitative analysis possible
- Not overly expensive, most chem labs have a GC

Questions

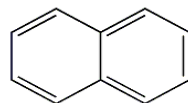
1. A mixture of the four compounds analyzed by gas chromatography (GC) produced the following result:



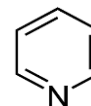
acetophenone



benzophenone



naphthalene



pyridine

- Assign each compound to its appropriate peak. Justify.
- Give three parameters that could be changed to make all compounds elute faster.

2. Given the four following compounds: Acetone, acetaldehyde, ethane, ethanol.

a) What would be their elution order in gas chromatography (GC)? Justify.

3. Give the two gas chromatograms below, obtained without temperature programming, determine the retention indices for isooctane, 2,4-dimethylhexane and 3-methylheptane.

