Metrological traceability for benzo[a]pyrene quantification in airborne particulate matter

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Scope of the work

Metrologically traceable procedure for the quantification of benzo[a]pyrene (BaP) in airborne particulate matter (PM)

REASONS

- PM is one of the most important sources of **urban pollution**
- PM is a vehicle of exposure to Polycyclic Aromatic Hydrocarbons (PAHs): relevant under a **toxicological** point of view
- Need for **accurate** and **comparable** analytical results, hence **traceable**

↓ Representative epidemiological studies

↓ Planning of preventive actions

Airborne particulate matter

Liquid droplets and **solid** particles having different origins dispersed in air

PRIMARY → Directly from natural or anthropogenic emissions

SECONDARY → From chemical reactions occurring in atmosphere

NATURAL SOURCES

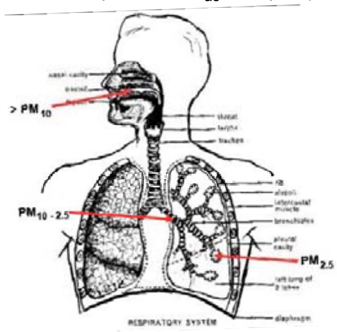
bushfires, volcanic eruptions, biogenic emissions…

ANTHROPOGENIC SOURCES

heating plants, vehicle engines, industrial processes…

DIMENSIONAL DISTRIBUTION

- Sand and coarse dust: d_{ae}>10 µm
- Coarse inhalable particulate matter: 2,5 µm <d_{ae}<10 µm (PM_{10})
- Fine particles: d_{ae}<2,5 µm ($PM_{2,5}$)
- Ultrafine particles: d_{ae}<0,1 µm (UFP)

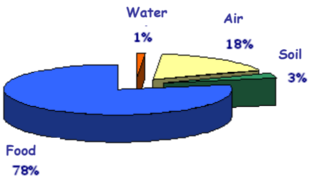


Polycyclic Aromatic Hydrocarbons

Class of organic compounds having similar chemical structure, with two or more condensed benzene rings

Deriving from the incomplete combustion of organic matter and fossil fuels in vehicle engines, heating plants, power stations

THEY ARE UBIQUITOUS CONTAMINANTS



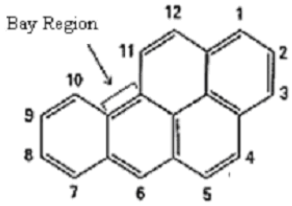
Shibamoto T., *Chromatographic Science Series*, 77, (1998)

16 priority PAHs for US EPA

PAH	Formula	Molecular weight (g/mol)	CAS N.	Chemical structure
Naphtalene	$C_{10}H_8$	128.18	91-20-3	
Acenaphthylene	$C_{12}H_8$	152.20	208-96-8	
Acenaphthene	$C_{12}H_{10}$	154.20	83-32-9	
Fluorene	$C_{13}H_{10}$	166.23	86-73-7	
Phenanthrene	$C_{14}H_{10}$	178.2	85-01-8	
Anthracene	$C_{14}H_{10}$	178.2	120-12-7	
Fluoranthene	$C_{16}H_{10}$	202.3	206-44-0	
Pyrene	$C_{16}H_{10}$	202.3	129-00-0	
Benz[a]anthracene	$C_{18}H_{12}$	228.3	56-55-3	
Chrysene	$C_{18}H_{12}$	228.3	218-01-9	
Benzo[b]fluoranthene	$C_{20}H_{12}$	252.32	205-99-2	
Benzo[k]fluoranthene	$C_{20}H_{12}$	252.32	207-08-9	
Benzo[a]pyrene	$C_{20}H_{12}$	252.3	50-32-8	
Indeno[1,2,3-cd]pyrene	$C_{22}H_{12}$	276.34	193-39-5	
Benzo[ghi]perylene	$C_{22}H_{12}$	276.34	191-24-2	
Dibenz[a,h]anthracene	$C_{22}H_{14}$	278.35	53-70-3	

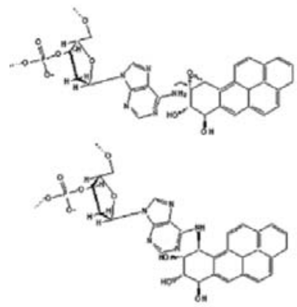
Polycyclic Aromatic Hydrocarbons (II)

- IARC classification: benzo[a]pyrene is in Group 1 (carcinogenic agent for humans). **Marker of the carcinogenic risk for the whole class!**
- 1 ng/m^3: target value for European legislation



benzo[a]pyrene structure

- They are pro-mutagenic molecules
- They can originate metabolites that bond to DNA (*Bay Region Theory*)
- PAHs having more than **5 benzene rings** are almost completely adsorbed onto the **particulate matter** (>90%) → means of exposure



European Legislation

- Directive 2008/50/EC of the European Parliament and of the Council of 21 May 2008 on ambient air quality and cleaner air for Europe
- Directive 2004/107/EC of the European Parliament and of the Council of 15 December 2004 relating to arsenic, cadmium, mercury, nickel and polycyclic aromatic hydrocarbons in ambient air

Standard method for BaP in air

EN 15594 – "Air Quality – Standard method for the measurement of concentration of benzo[a]pyrene in ambient air" (2008)

- Use of an isotopically labelled compound, like BaP-d_{12} as internal standard (**IS**)
- A response factor ***f*** is calculated using calibration solutions according to:

$$f = \frac{A_{\mathrm{IS}} \cdot m_{\mathrm{c}}}{A_{\mathrm{c}} \cdot m_{\mathrm{IS}}}$$

- The **mass of BaP** (m_E) in the sample extracts is calculated according to

$$m_{\mathrm{E}} = \frac{f \cdot A_{\mathrm{E}} \cdot m_{\mathrm{ISE}}}{A_{\mathrm{ISE}}}$$

- m_E is corrected for the recovery efficiency in order to obtain the mass of BaP sampled on the filter (m_F), then divided by the volume of sampled air (in m^3) to give the **concentration of BaP in ambient air** (ng/m^3)

$$C = \frac{m_{\mathrm{F}}}{V_{\mathrm{air}}}$$

INRIM method

Determination of the mass of the filter by weighing

Sampling

Determination of the mass of the particulate by weighing

Soxhlet extraction (C_6H_{12})

Concentration of the extract

Determination of the volume of the extract by weighing

Analysis by GC-MS

In order to establish a correct metrological traceability chain to SI, all the steps have to be considered

Preparation of calibration solutions (gravimetric dilution of a CRM)

GC-MS calibration

RESULTS (m_E)

Method validation

- **Recovery** (%): spiking of blank filters with a suitable CRM (PAHs of interest)
- **Limit of detection** (LOD): repeated analyses of blank filters: 0,02 ng/m^3 < 0,04 ng/m^3 (for BaP)
- **Limit of quantification** (LOQ): 10 times the standard deviation of the repeated analyses of blanks (0,09 ng/m^3 for BaP)

Quantification procedure

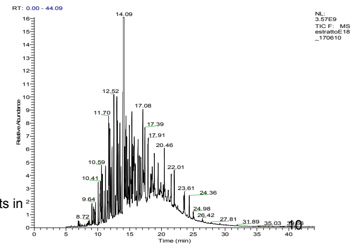
a) Choice of a suitable CRM → SRM NIST 2260a, which contains 36 aromatic hydrocarbons in toluene (the CRM assures metrological traceability to the masses of PAHs)

b) Preparation of calibration solutions by gravimetric dilution of the CRM in three steps (1: tare, 2: tare + solution to be diluted, 3: tare + solution to be diluted + diluting solvent)

c) Determination of the mass fractions of the BaP (ng/g) according to the equation:

$$w_{\text{fin}} = w_{\text{in}} \cdot \frac{m_2 - m_1}{m_3 - m_1}$$

d) Calibration of the GC-MS



Uncertainty evaluation

Model equation:

$$C = \frac{m_E \cdot V_E \cdot C_i \cdot V_i}{V_f \cdot X_a \cdot V_{air}} \cdot 10^3$$

The uncertainty propagation law can be simplified to the subsequent expression, for equations that comprise only ratios or products of quantities:

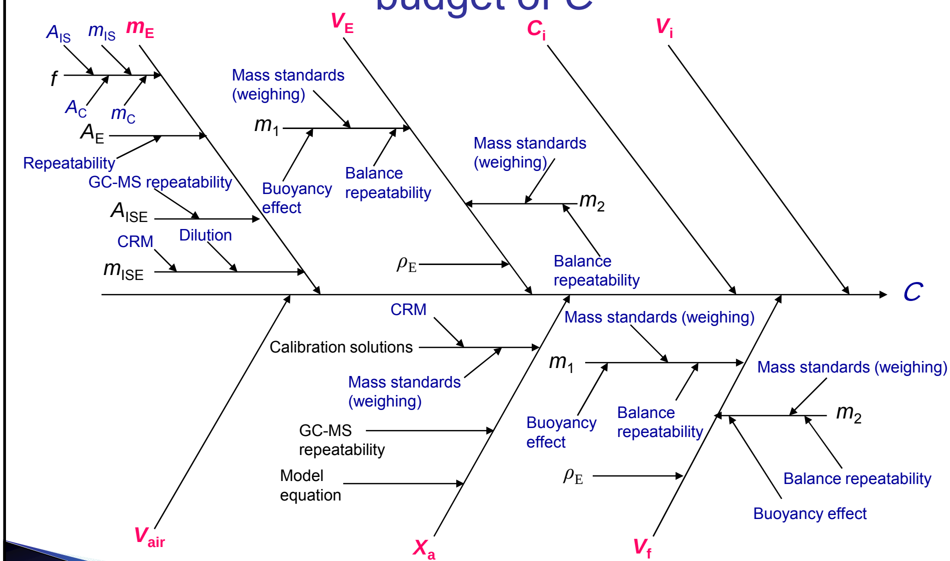
$$u_c(y) = y\sqrt{\left(\frac{u(p)}{p}\right)^2 + \left(\frac{u(q)}{q}\right)^2 + ...}$$

$u(p)/p$ e $u(q)/q$ are the uncertainties of the single parameters, expressed as **relative standard deviations**.

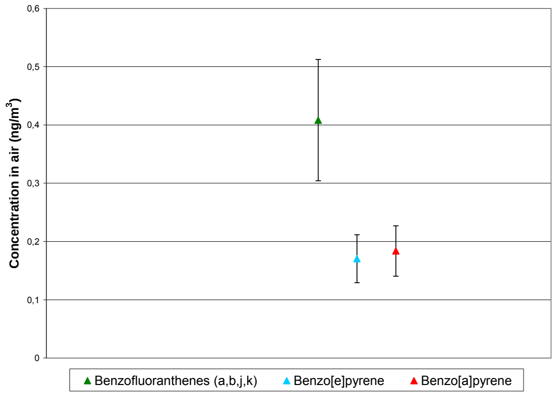
Input quantity x_i	Uncertainty component $u(x_i)$	Uncertainty source	Input quantity value x_i	Standard uncertainty value $u(x_i)$	Contribution to $u(C_{fin})/C_{fin}$ $u(x_i)/x_i$
m_E	$u(m_E)$	BaP mass in the sample extract	0,373 ng	0,015 ng	0,041
V_E	$u(V_E)$	Final volume of the sample extract	331,276 µl	0,098 µl	0,00030
C_i	$u(C_i)$	Concentration of BaP in the CRM used for spiking	4,710 µg/g	0,085 µg/g	0,018
V_i	$u(V_i)$	CRM volume spiked onto the blank filter	30,0 µl	2,9 µl	0,096
V_f	$u(V_f)$	Final volume of the spiking extract	175,879 µl	0,098 µl	0,00056
X_a	$u(X_a)$	Mass fraction of BaP measured in the spiking extract	526 ng/g	21 ng/g	0,040
V_a	$u(V_a)$	Sampled air volume	121,80 m³	0,85 m³	0,0070
	$cov(V_E, V_f)$	Covariance between V_E and V_f			$2,6 \cdot 10^{-7}$
C_{fin} = 1,55 ng/m³					
$u_c(C_{fin})$ = 0,18 ng/m³					

Example of uncertainty budget for BaP concentration

Cause-effect diagram for the uncertainty budget of *C*

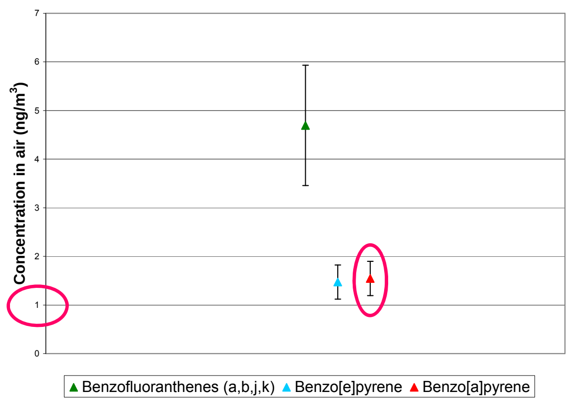


Results (I)



Concentration in ng/m^3 of BaP, BeP and benzofluoranthenes, found in the airborne particulate matter sampled on 25th-29th **May** 2009

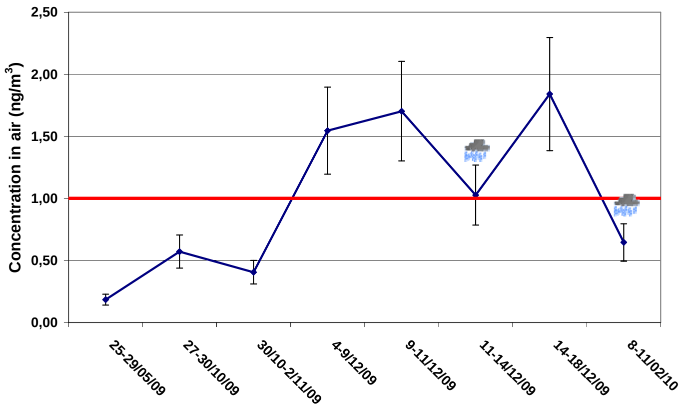
Results (II)



Concentration in ng/m^3 of BaP, BeP and some benzofluoranthenes, found in the airborne particulate matter sampled on 4th-9th **December** 2009

Benzo[a]pyrene

Target value: 1 ng/m^3 total content in the PM_{10} fraction, averaged over a calendar year



Concentration in ng/m^3 of BaP in airborne particulate matter, compared to the target value (Directive 2004/107/EC)

Conclusions

- Establishment of a **metrological traceability chain** for all the steps involved in the analytical procedure →except for the sampling step
- BaP **seasonal trends** were confirmed
- The ratios of BaP, BeP and benzofluoranthenes are **not affected** by seasonal changes

Further developments

- Establishment of traceability for the sampling step
- Extension to other matrices (**food**, **sediments**)

THANK YOU FOR YOUR ATTENTION!

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