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

**DIMENSIONAL DISTRIBUTION**
- Sand and coarse dust: \( d_{ae} > 10 \mu m \)
- Coarse inhalable particulate matter: \( 2.5 \mu m < d_{ae} < 10 \mu m \) (PM\(_{10}\))
- Fine particles: \( d_{ae} < 2.5 \mu m \) (PM\(_{2.5}\))
- Ultrafine particles: \( d_{ae} < 0.1 \mu m \) (UFP)

**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...

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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**

- Food
- Water
- Air
- Soil

16 priority PAHs for US EPA

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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/m³: target value for European legislation
- 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

Standard method for BaP in air


- 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:

\[
f = \frac{A_{IS} \cdot m_{IS}}{A \cdot m_{m}}
\]

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

\[
m_E = \frac{f \cdot A_E \cdot m_{ISE}}{A_{ISE}}
\]

- \( m_E \) 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\(^3\))

\[
C = \frac{m_F}{V_{se}}
\]

INRIM method

- Determination of the mass of the filter by weighing
- Sampling
- Determination of the mass of the particulate by weighing
- Soxhlet extraction (C\(_6\)H\(_{12}\))
- 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

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/m³ < 0.04 ng/m³ (for BaP)

- **Limit of quantification** (LOQ): 10 times the standard deviation of the repeated analyses of blanks (0.09 ng/m³ 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:

\[
W_{\text{lin}} = W_{\text{in}} \cdot \frac{m_2 - m_1}{m_3 - m_1}
\]

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:

\[ u_i(y) = \sqrt{\left( \frac{u(p)}{p} \right)^2 + \left( \frac{u(q)}{q} \right)^2 + \ldots} \]

\( u(p)/p \) and \( u(q)/q \) are the uncertainties of the single parameters, expressed as relative standard deviations.

Example of uncertainty budget for BaP concentration

Cause-effect diagram for the uncertainty budget of \( C \)
Results (I)

Concentration in ng/m³ of BaP, BeP and benzofluoranthenes, found in the airborne particulate matter sampled on 25th-29th May 2009.

Results (II)

Concentration in ng/m³ 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/m³
total content in the PM10 fraction, averaged over a calendar year

Concentration in ng/m³ 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!