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Thermal desorption GC–MS as a tool to provide PAH certified standard reference material on particulate matter quartz filters

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ABSTRACT

Reference materials for particulate matter (PM) on filter media are not available for the quantification of polycyclic aromatic hydrocarbons (PAHs) in ambient air. This is due to the difficulty of obtaining reference material that has a homogeneous distribution on a filter surface that is large enough for characterization and distribution.

High volume sample filters from different locations and seasons were considered to validate the feasibility of the use of quartz filters as reference material for PAH concentrations. A rapid thermal desorption (TD) technique coupled with gas chromatography/mass spectroscopy was applied to characterise the material for the content of fifteen different PAHs. TD technique allowed for rapid and accurate analysis of small sections of filter (5 mm diameter), leaving enough material for the production of twenty sub-filter cuts (42 mm diameter) that could be used for distribution and control.

Stability and homogeneity tests required for material certification were performed as indicated by the ISO guide 34:2009 and ISO 35:2006. The contribution of the heterogeneous distribution of PAHs on the filter surface resulted generally lower than 10% and higher for more volatile PAHs. One year of storage at −18 °C indicated no significant variation in PAH concentrations. Nevertheless, a methodology for shipping and storing of the filter material at ambient temperature in especially designed plastic envelopes, was also shown to allow for stabile concentrations within twenty days.

The method accuracy was confirmed by the analysis of NIST SRM 1649a (urban dust) and PAH concentrations were validated against the reference values obtained from an inter-laboratory exercise. In the case of benzo[a]pyrene for masses quantified between 100 pg and 10 ng the TD method provided expanded uncertainties of circa 10%, while the inter-laboratory reference value uncertainties ranged between 15 and 20%.

The evaluation of these results supports the use of the presented methodology as a valid approach for the certification of PAH concentrations in PM10 quartz filters. The methodology allows for the production of a certificate of analysis for a single high volume filter, the concentration of which can easily be adjusted by selecting an appropriate sampling location.

1. Introduction

The use of an appropriate reference material for PAHs analysis in air is a very relevant issue in the quality assurance and control of any analytical laboratory. Certified standard solutions are available in the market for calibration purpose (such as NIST 1647 and NIST 2260). However, these solutions do not cover the possible matrix effect derived from real samples. Solution extracts, such as standard reference material (SRM) 1975-diesel PM extract, may partially cover such an effect, but no information on extraction efficiencies can be derived from their use. SRM in powder could represent a better approach for estimating extraction efficiencies, but these efficiencies may also differ from those obtained with filter samples. Typical powder reference materials are: SRM 1649 (urban dust) [1], SRM 1650 (diesel particular matter, PM), SRM 2975 (diesel PM from industrial forklift), SRM 2787 (PM10), SRM 2786 (PM4).

PM collected on a filter would be most desirable as a reference material for PAHs. Such materials have been produced by sampling re-suspended SRMs on quartz filters [2], i.e., SRM 1649a or RM 8785 for certified carbon composition [3] and could be produced similarly for certified PAHs. An important aspect to consider is that the use of filters eliminates the problem of weighing low quantities of powder (milligrams or micrograms), required to test analytical techniques at low concentration level, increasing the uncertainty of the weighing and the heterogeneity of the PAH distribution in the sample. In fact, SRM 1950b has been shown to be heterogeneous for PAHs at mass sizes

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around 100–110 mg and SRM 1649a was found to be heterogeneous even at relatively larger sample sizes (330–380 mg) [4]. Nevertheless, the former filters loaded with re-suspended PM may possibly suffer from limitations with regard to reproducibility and representativeness of extraction efficiencies due to differences in the genesis of the collected material.

An alternative to surrogated re-suspended SRM would be the use of real air particulate sample filters. These filters could be representative of the typical composition and concentration of air samples, especially if collected in the same place. The reference material would also share the same type of matrix with real samples and consequently similar behaviour during the different analytical steps. Unfortunately, such a SRM is currently not available.

Homogeneous PM filters by sampling under appropriated flow control conditions upon verification by means of non destructive analytical methods such as EDXRF or micro-XRF have been produced in the past [2,5,6]. In fact, a study aimed to evaluate the sources of uncertainty in the determination of PAH concentrations in high volume air sampler filters showed that the contribution due to the surface distribution was estimated around 3% [7]. However, the production of a high number of filters per batch or the collection of particle matter on large surfaces could result in poor homogeneous distribution. Such a problem during preparation of reference ambient aerosol filter material for inorganic elements have already been described in bibliography [8]. Therefore, in spite of the possible operational limitations, the individual control of the filter homogeneity and its stability after sampling is essential in order to produce an ad-hoc certified reference material.

The objective of this work is to demonstrate the feasibility of producing certified reference concentrations of PAHs on real PM ambient air filters by using a methodology that allows: (i) a rapid and accurate analyses of PAHs on small pieces of filter; (ii) the selection of sample filters under similar conditions as environmental samples; (iii) homogeneity and stability testing of the filter composition.

In order to achieve these objectives a high volume sampled filter from Andersen HVS was used to provide twenty sub-filter cuts (equivalent to low volume (LV) sampling) linked to one certificate of analysis and homogeneity. Thermal desorption (TD) technique coupled with gas chromatography/mass spectroscopy (GC/MS) is presented as the more appropriate technique to reduce sample handling, by eliminating extraction and concentration steps, and to increase sensitivity [9–14]. This technique allows analysis of small pieces of filter taken from the inter-spaces between the LV cuts of the HVS filter.

PAH determined concentrations were validated against reference values from an inter-laboratory comparison exercise involving several laboratories and analytical techniques. The evaluation of these results, together with the expanded uncertainties obtained by our measurements, were used to support the proposed methodology and technique for use in the production of certified PAH concentrations in PM10 quartz filters.

2. Experimental section

2.1. Sampling

PM10 sampling was performed in background areas of two European cities both during summer and winter time: “Sinesio Delgado” in Madrid (Spain) and “Libus” in Prague (Czech Republic). The samples were collected on heat treated (at 300 °C for a minimum of 3 h) quartz filters (QM-A, 20.3 × 25.4 mm, Whatman International Ltd., England) using a Anderson HVS. Four samples, one for each location and season, and two travelling blanks, one for each location, were selected for the intercomparison. An additional filter (F31) was used by our laboratory to study the stability of PAH concentrations with time. Table 1 reports the list of the filters with their relative identification code, sampling parameters and meteorological data.

2.2. Filter handling (cutting)

Each of the selected QM-A rectangular filters (mother filters) was cut into 20 circles of 39 mm diameter, corresponding to low volume filter samples. The circles were systematically cut by means of a mould (Fig. S1) specifically designed for this purpose. Low volume dimension filters were carefully prepared for distribution to the participating laboratories: the filters were folded in two, wrapped in aluminium foil, placed into a plastic rectangular envelope (43 mm by 25 mm), labelled and stored at −18 °C. The remaining part of the rectangular filter was also stored at −18 °C and used for the storage effect study.

2.3. Target compounds

Fifteen different PAHs were selected for the scope of this study, seven of which were marked as priority since they are considered for ambient air sampling in the Directive 2004/107/EC [15] (see Table 2). For evaluation purpose, the sum of isomers were taken in the case of difficult separation (i.e., Chry+Tph and B[b+j+k]F).

2.4. Analytical methodologies

TD and conventional liquid extraction (LE) followed by gas chromatograph separation and mass spectrometer detection were both used for analysis and quantification of PAHs. TD was performed using a thermal desorption unit (TDU) coupled with a cryogenic trap (CIS4) and an autosampler (MPS 2XL, Gerstel GmbH & Co. KG, Germany). This system allows for the direct introduction in the TDU of a glass liner previously prepared with a plug of a few mm of glass wool overlaid by a 5 mm diameter quartz filter placed on the bottom. The liners were pre-cleaned at 400 °C for 4 h in an oven and for 1 h under a nitrogen stream of 20 mL/min at the same temperature. The sample filters (5.3 or 2.15 mm diameter for sample filters and 12 mm for blank filters) were deposited over the liner filter and spiked with 1 μL of

Table 1
Filter codes and sampling variables.

Code	B3	B2	F10	F3	F30	F31	F21
Location/season	Prague	Madrid	Madrid/winter	Madrid/summer	Prague/winter	Prague/winter	Prague/summer
Sampling period	–	–	25–27/11//2009	6–8/7/2009	21–22/11/2009	20–21/11/09	27–28/7/2009
Sampling volume (m^3)	–	–	3190	3090	1708	1716	1590
Temperature (°C)	–	–	9.2	24.9	7.29	6.59	22.8
Relative humidity (%)	–	–	90	32	87	84	63
PM10 (μg/m^3)	–	–	21	30	89	26	24.3
PM2.5 (μg/m^3)	–	–	n.a.	11	64	17	16.7
Ozone (ppb)	–	–	n.a.	37	5	6	70

Table 2
List of compounds quantified on the filters and their corresponding acronyms.

Single compound	Compounds	Acronym
	Phenanthrene	Phe
	Anthracene	Anth
	Fluoranthene	Flu
	Pyrene	Pyr
	Benzo[a]anthracene	B[a]A
	Chrysene	Chry
	Benzo[b]fluoranthene	B[b]F
	Benzo[k]fluoranthene	B[k]F
	Benzo[j]fluoranthene	B[j]F
	Benzo[e]pyrene	B[e]P
	Benzo[a]pyrene	B[a]P
	Perylene	Per
	Indeno[1,2,3,-c,d]pyrene	IP
	Dibenzo[a,h]anthracene	DB[a,h]A
	Benzo[g,h,i]perylene	B[g,h,i]P
Combination of isomers	**Compounds**	**Acronym**
	⁎Chrysene + triphenylene	Chry + Tph
	⁎Benzo[b + j + k]fluoranthene	B[b + j + k]F

appropriate concentration of internal standard mixture (IS, 9D mixture Dr. Ehrenstorfer GmbH). This solution contained the respective deuterated PAHs for each target, exception for the deuterated B[j]F, B[e]P and Per, for which the deuterated compounds of closest RT were used as internal standard for quantification. The liners were placed on the autosampler tray of the TD injection system for injection into a gas chromatograph–mass spectrometer (GC 6890, MS 5975C Agilent Technologies) with a Rxi®-17Sil MS column (30 m, 0.25 mm, 0.25 μm, Restek). The oven start temperature was set at 60 °C and held for 1 min. The oven was heated with a first ramp of 15 °C/min to 200 °C followed by a second ramp of 6 °C/min to 310 °C and held for 15 min. The analytes were detected by a low resolution mass spectrometer (MS 5973 inert series, Agilent Technologies) in scan mode and single ion monitoring mode simultaneously. Details of the parameters used for thermal desorption and for detection can be found elsewhere [10].

In parallel, the 42 mm diameter filters were liquid extracted using a microwave apparatus. Before extraction the filters were spiked with an appropriate aliquot of IS. Extraction conditions and the following clean up procedure are described elsewhere [10]. The extract was then analyzed in GC–MS (GC 6890 and MS 5973 network series, Agilent Technologies) using a column DB-17 (30 m, 0.25 mm, 0.25 μm, Agilent Technologies) with same oven program reported for TD analysis. Analytical blanks were performed for both methods, in particular clean up and extraction blanks for LE and system blanks for TD.

3. Results and discussion

3.1. Analysis of NIST SRM 1649a (urban dust)

The TD efficiency was checked against a SRM in powder (1649a—Urban Dust, National Institute of Standards and Technology) as described in a previous work [10]. The SRM was analyzed in the range of masses from 70 to 450 μg ($n=10$) compatible with the expected concentrations of PAHs on the filter samples. The average values resulting from these analyses showed good agreement with the certified concentrations (Fig. S2 supporting info). However, the scattering of the biases between analyzed and certified material was increasing with the reduction of the overall amount of SRM analyses. This suggests difficulties in obtaining reproducible fractions of the SRM, probably due to the uncertainty in the weighting step and to a poor homogeneity in the sub-samples as described in literature [4].

3.2. Blank levels

The average PAH concentrations from the two blank filters (B2 and B3) analyzed by TD and liquid extraction together with the levels found in the sample filters and the limits of detection (LOD) for both methods are reported in Fig. 1. For comparative purposes these data are reported as total mass of the compound contained in the filter section (LVS size filter).

Blanks levels in liquid extraction were always higher than those attributed to thermal desorption, being particularly high for Phe, Anth and Flu, which exceeded the concentrations determined in filter F3 and F21. In fact, all these compounds, with the exception of the F30, were under the LOD for the liquid extraction in all filters. This was also the case of Pyr for filters F3 and F21.

Thermal desorption was, however, characterised by lower blanks levels and detection limits. This was a consequence of the reduction of the sample preparation (i.e., extraction, concentration and clean-up) and the direct injection of the whole sample into the GC column with minimum splits conditions. For example, the relative amount of Phe (the compound resulting in the highest contamination levels) in the blank filters with respect to the lower quantified amount in the sample filter (F21) was circa a 5%.

3.3. Homogeneity

The selection of a mother filter for SRM should be done under criteria of homogeneity by analyzing random cuts of filter [16–18]. Filters cuts, between 2 and 5 mm diameter, randomly distributed on the mother filter were analyzed by TD to calculate a relative standard deviation (RSD_{hg}) that could be used as indicator of the filter homogeneity.

Since TD analyses are destructive, the contribution from the analytical repeatability ($RSD_{\mathrm{L\text{-}r}}$) was evaluated through the injection of liquid standards. To calculate the RSD_{hg}, considering the matrix effect negligible, the analytical repeatability $RSD_{\mathrm{L\text{-}r}}$ was subtracted from the reproducibility analysis of the cut filters ($RSD_{\mathrm{F\text{-}R}}$), as described in Eq. (1). In case $RSD_{\mathrm{L\text{-}r}}$ was higher than $RSD_{\mathrm{F\text{-}R}}$, RSD_{hg} was considered being represented by $RSD_{\mathrm{F\text{-}R}}$. (Eq. (2)). Under these circumstances, it is understood that the quartz filter matrix provided a certain stability during the desorption and injection steps, in particular, at lower concentrations.

$$RSD_{hg} = \sqrt{RSD_{F-R}^2 - RSD_{L-r}^2} \tag{1}$$

$$RSD_{hg} = RSD_{F-R}, \quad \text{if } RSD_{L-r}^2 \geq RSD_{F-R}^2 \tag{2}$$

The RSD_{hg} is calculated assuming no covariance exists between $RSD_{\mathrm{F\text{-}R}}$ and $RSD_{\mathrm{L\text{-}r}}$. This may lead to an underestimation of the RSD_{hg} when $RSD_{\mathrm{L\text{-}r}}$ gets close to $RSD_{\mathrm{F\text{-}R}}$, with the afore-mentioned extreme case where $RSD_{\mathrm{L\text{-}r}} \geq RSD_{\mathrm{F\text{-}R}}$. To compensate such an effect the geometrical mean (G_{mean}) between RSD_{hg} and $RSD_{\mathrm{L\text{-}r}}$ was used as value to discriminate a filter for its use as a mother filter for inter-laboratory comparison. In this geometrical mean the homogeneity of the filter and the specific analytical difficulties are both considered as discriminatory criteria.

According to these definitions, Fig. 2 shows the results obtained from five different PM10 quartz filters. The *RSD*% values correspond to those calculated from Eq. (1), whilst highlighted in black those values derived from Eq.(2). Although the G_{mean} was for all cases lower than 10%, an increase of the $RSD_{\mathrm{L\text{-}r}}$ for filters with low PAH concentration (F3 and F21) is observed. On the

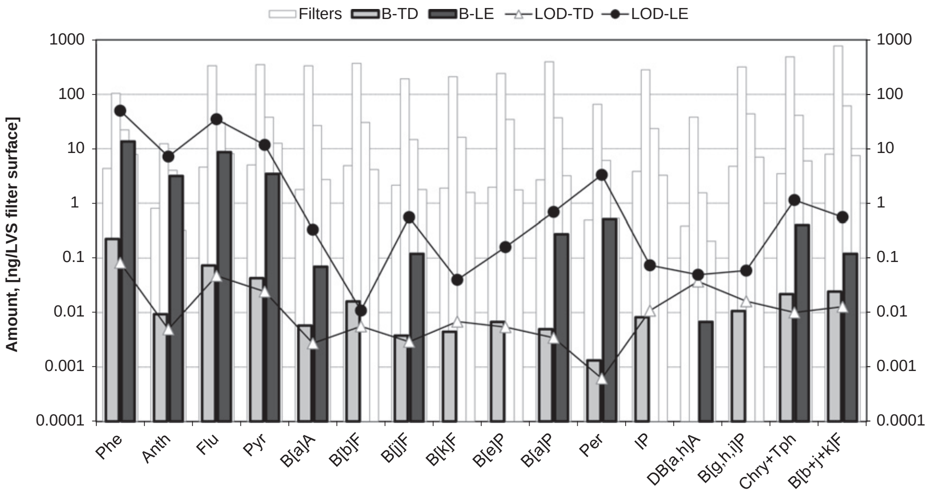

Fig. 1. Filters, blank levels and limit of detection for liquid (LE) and thermal desorption (TD) determinations.

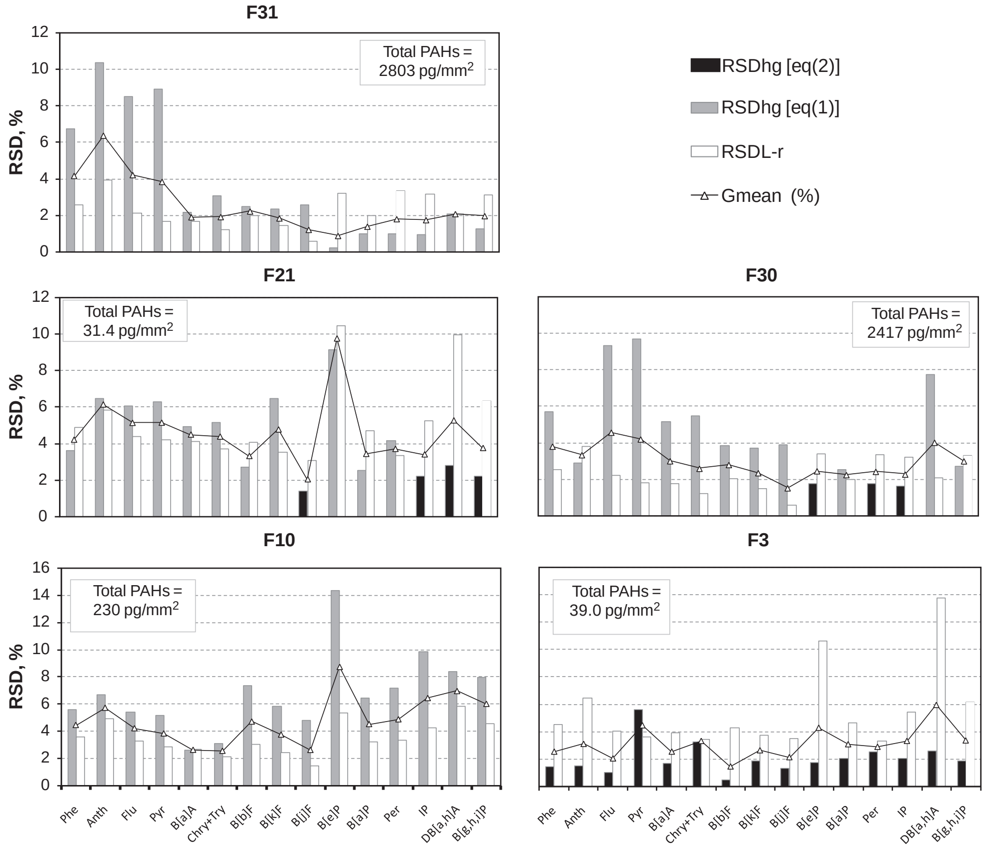

Fig. 2. Results of the homogeneity tests for the PM10 filters. $RSD_{L\text{-}r}$: repeatability standard deviation, RSD_{hg}: homogeneity standard deviation, G_{mean}: geometric mean between RSD_{hg} and $RSD_{L\text{-}r}$.

other hand, the more volatile PAHs (Phe, Anth, and Flu) tend to show higher RSD_{hg}.

3.4. Storage

Filters F31, F10 and F30 were used to evaluate eventual changes of concentrations during storage at different conditions. Filter F31 was cut in 39 mm circles similar to the samples mailed for the intercomparison exercise. Half of these sub-filters were stored in freezer and half at ambient laboratory temperature (20 ± 1 °C). Smaller sections from filters F10 and F30 (5.54 and 2.15 mm diameter, respectively) were stored in 1.5 ml amber vials at ambient temperature. The rest of the filter was kept in freezer (−18 °C).

After more than 1 year of storage in the freezer, PAH determination shows little variation in respect to the initial values for all the three filters (Fig. 3A). In filter F31, biases with respect to the initial determined value ranged from −17% to 19% (except for Anth that was greatly overestimated in the samples after storage at very low concentrations because of its partial overlapping with Phe). The average temporal biases with respect to the initial value was −3%. Filter F30 showed a maximum bias

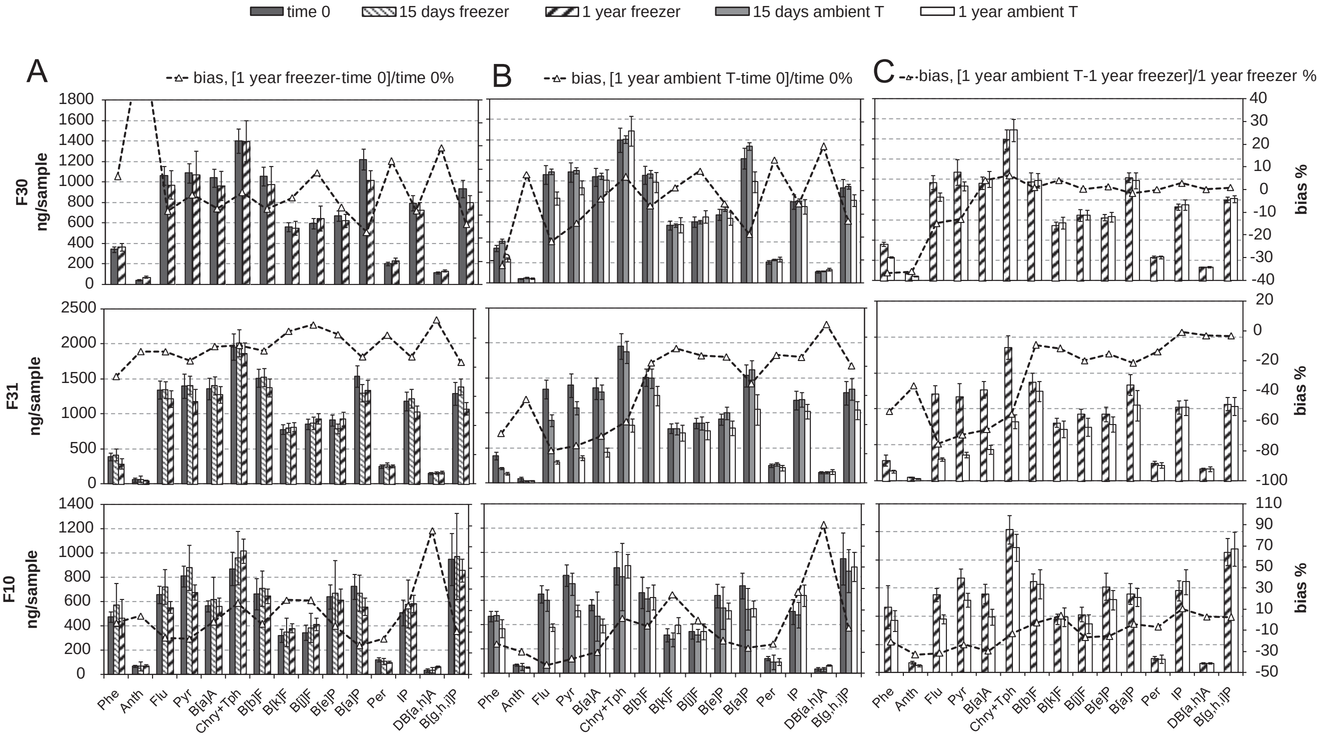

Fig. 3. A–C—PAH concentrations in filter after storage at −18 °C (freezer) and 20 °C (ambient temperature). (A) time effect at −18 °C, (B) time effect at 20 °C, (C) temperature effect after one year of storage.

of −28% for Phe; whilst for the other compounds, biases ranged from −15% to 13%, being the inter-compound average value of −2.4%. Finally, for filter F10 the biases ranged from −23 to 20%, with an inter-compound average value of −0.55%, excluding DB[a,h]A that showed a positive bias of circa 85%. With the exception of Anth and DB[a,h]A, no correlation between biases and PAH concentration level or volatility was observed. Therefore, the scattering of the temporal variability of the analysis was attributed to the reproducibility of the analytical method, in which different calibration curves and columns were used.

The storage of the filters at ambient temperature (20 °C, Fig. 3B) was carried out in two different ways: (1) by wrapping the filter in a plastic envelop as described under filter handling of the experimental sections (F31) and (2) by keeping the filter in a closed amber vial (F30, F10). In the former case, slight decrease in concentrations for the more volatile PAH was observed. After more than a year of storage, only Phe (−32%) and Flu (−22%) showed significant biases according to the analytical reproducibility, whilst for the other compounds biases were progressively decreasing with the volatility until B[a]A (−3%). For filters stored in vials a positive correlation between volatility and losses was observed, i.e., for the filter F30 biases with respect to the initial value were −70% for Phe decreasing progressively until reaching a −15% for B[b]F. The filter F10 only showed significant losses for Flu, Pyr and B[a]A.

Filters that were stored for 20 days at ambient temperature did not show any significant losses, except for more volatile PAHs from filter stored in vials (filter F30).

The effect of the storage temperature and type of container is shown in Fig. 3C, where PAH concentrations from filter storage for more than a year in freezer and ambient temperature are also represented. Filters storage at ambient air temperature in vials showed significant losses for most of the compounds, being positively correlated with the concentration level too. However, no effect was observed in the case of the filter storage by the described envelop technique for those compounds less volatile than Pyr (F31). In general, this last method of storage allows PAH concentrations in PM10 filters stable enough to carry out consistent inter-laboratory comparison and is compatible with ambient temperature expedition of the filter to the participating laboratories. For times longer than 20 days PAH concentrations in PM10 filters are kept constant at storage temperature of −18 °C.

3.5. Reference and uncertainty values

The described thermal desorption technique allows a high number of repetitions with a minimum consumption of filter material, leaving most of the filter surface intact for the preparation of certified material and reducing the associated uncertainty of the analysis according to Eq. (3):

$$EU = k\cdot\sqrt{\left[\frac{stdev(c_i)}{\sqrt{n}}\right]^2 + u_{Cl}^2 + u_{Blk}^2 + u_{FiltCut}^2} \tag{3}$$

where

- k is the coverage factor for the 95% confidence level; c_i is the determined concentration of analyte for the filter i;
- n is the number of filters/injections;
- u_{Cl} is the uncertainty associated with the calibration curve. It was estimated by the following expression: $u_{\mathrm{Cl}}=0.0250+0.0113\times(C_{\mathrm{a}}/C_{\mathrm{IS}})^{-0.3477}$, being C_{a} and C_{IS} the concentrations of the analyte and of the internal standard, respectively. This expression is including the uncertainty related to the reference standard used for instrument calibration as well as the corresponding gravimetric dilutions and spiking of the internal standard.
- u_{Blk} is the uncertainty related to the blank levels of the instrument, calculated from the expression: $u_{Blk} = \sqrt{\left[\frac{stdev(blank_i)}{\sqrt{m}}\right]^2 + \overline{blank_i^2}}$, where $\overline{blank_i}$ is the average analyte concentration of m system

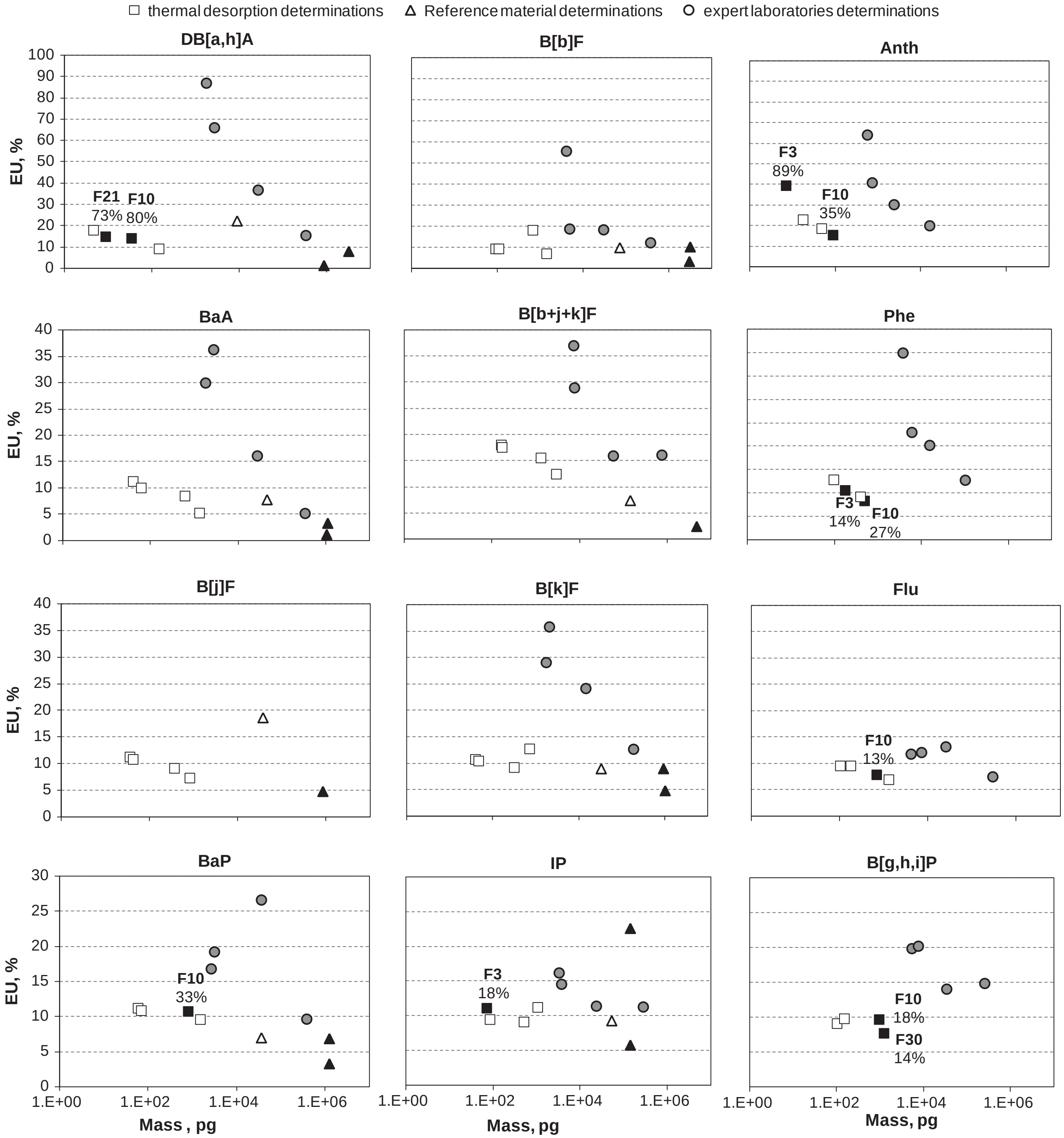

Fig. 4. Expanded uncertainties versus PAH reference mass: for thermal desorption determinations (square symbols); for reference materials SRM 1649a, SRM 1649b (black triangles) and ERM CZ-100 (white triangles); for intercomparison reference values (round circles).

blank injections and blank$_i$ is the analyte concentration detected in a blank injection i.

- u_{Filtcut} is the uncertainty related to the filter cut, estimated from the following expression:

$$u_{Filtcut} = 0.0076 \times Ci.$$

Fig. 4 shows the relative expanded uncertainties of filters quantified by thermal desorption (square symbols) and the expanded uncertainties corresponding to certificate of similar amounts of reference materials in powder (when available): SRM 1649a, SRM 1649b and ERM CZ-100 [19] (triangular symbols). The relative expanded uncertainties are referred to the compounds concentrations for the considered amount of analyzed material during certification (for 50 mg for ERM reference material and 500 mg for NIST reference materials).

Filters with lower amounts resulted in uncertainty values generally higher than those reported from SRM in powder. This is a consequence of the lower concentration ranges. PAHs amounts determined in these filters are comparable to typical concentrations of ambient air low volume samples, and therefore, the given expanded uncertainties are representative of real monitoring samples.

The expert laboratory values to which the thermal desorption analysis results are compared and their corresponding uncertainties, where derived from an inter-laboratory comparison exercise (EUR 25170EN, [20]). These values were obtained through a robust average of the reported expert values in accordance with the ISO-13528 [21], as described in the afore-mentioned report.

Due to the limited number of reported data from the expert laboratories, no reference values were derived for B[j]F, B[e]P and Per. Therefore, these compounds are not taken into consideration for the following discussion.

As criteria of equivalence it is accepted that the bias between the analytical result and the reference value should be lower than the combined expanded uncertainty of the reference and the analytical value, as it is described by Eq. (4), which is in agreement with a En value of 1 according to ISO/EC guide 43-1:1997 [22]

$$bias = (C - C_{REF}) \leq \sqrt{U^2 + U_{ref}^2} \tag{4}$$

When the bias is greater than the combined expanded uncertainties, i.e., $En > 1$, the equivalence can be respected upon the increase of the corresponding analytical uncertainty. Therefore, the corrected relative analytical expanded uncertainty can be calculated as follows:

$$EU(\%) = \frac{\sqrt{bias^2 - U_{ref}^2}}{C} \times 100. \tag{5}$$

In TD determinations, Eq. (5) was only applied in a few cases in which En resulted higher than 1. Such cases are represented in Fig. 4, with a black square symbol and the value obtained by Eq. (5) is highlighted in the graph.

The need for a higher expanded uncertainty, according to Eq. (5), was evident in the case of DB[a,h]A and Anth. Their low concentrations in the PM filter made difficult their resolution and quantification, resulting in an over- and under-estimation for Anth and DB[a,h]A, respectively. These difficulties were also noticed in the analysis of the SRM in powder. Apart from TD determinations, most of the participating laboratories reported higher uncertainty values for these compounds in particular at low concentration (filters F21, F3 and F10).

In filter F10, disagreements between reported and calculated uncertainties were found for Phe, Anth, B[a]P and DB[a,h]A with $EU_{\mathrm{cal}} > 20\%$, although the uncertainties associated to Anth and DB[a,h]A could be reduced by improving chromatographic separation conditions. In the case of B[a]P, the expanded uncertainty derived from the inter-laboratory comparison is equal to 27% (round symbol in Fig. 4) and represents almost twice the expected expanded uncertainty for that level of concentration. This value agrees with the reported uncertainty from TD by Eq. (5) (33%).

Filter F10, as well as F3, was sampled with a higher air volume ($> 3000\ \mathrm{m}^3$), twice the volume normally sampled in this kind of HVS filters. This could have affected the distribution and the stability of the more volatile and reactive compounds, such as Phe and B[a]P.

4. Conclusions

This study demonstrates the feasibility of using directly PM10 HVS standard filter samples as certified material for PAH content. The methodology implies the use of TD technique that can perform a high number of determinations with a minimum utilization of filter surface. This characteristic permits to reduce the uncertainty of the final certified value to the level of other reference materials in powder with similar analyte content (i.e., ~10% for BaP). The homogeneity tests revealed for the heaviest PAHs, mean *RSD* values between 2 to 4% depending on the loading of the filter. Furthermore, the proposed storage method based on the use of individual envelops for each filter was found suitable to maintain constant PAH concentrations for at least 20 days at 20 °C or 1 year at −18 °C, with no significant variations among filters and compounds. By mean of this methodology, it was possible to prepare in a quick and reproducible way, 20 certified LVS equivalent filters for eleven PAHs: Phe, Flu, Pyr, B[a]A, Chry+Tph, B[b]F, B[j]F, B[k]F, B[a]P, IP, B[g,h,i]P and the sum of B[b+j+k]F. In addition, this matrix is in line with the typical PM10 and PM2.5 collecting method from the ambient air monitoring stations in Europe [23,24].

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Appendix A. Supporting information

Supplementary information associated with this article can be found in the on line version at http://dx.doi.org/10.1016/j.talanta.2012.11.047, including a picture of the mould used for the subdivision of the high volume filters and results of analyses of SRM 1649a.

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