



Evaluation of Uncertainty Associated with Determination of Particle-bound PAHs in Ambient Area by TD-GC/MS and Soxhlet-GC/MS

Iñaki Elorduy^{*}, Nieves Durana, José Antonio García, María Carmen Gómez, Lucio Alonso

Chemical and Environmental Engineering Department, School of Engineering, University of the Basque Country, Alameda de Urquijo s/n, E-48013, Bilbao, Spain

ABSTRACT

Knowing the uncertainty associated with an analytical method is necessary to evaluating the quality of the results. In this work, the uncertainty associated with the analytical measurement of polycyclic aromatic compounds (PAHs) in ambient air using thermal desorption coupled with gas chromatography-mass spectrometry (TD-GC/MS) was evaluated. The study focused on analyses of the particulate phase (PM₁₀), and the results were compared to those obtained with a conventional solvent extraction (Soxhlet-GC/MS). The main sources of the combined uncertainty were the calibration curve, recovery of the extraction stage, area or volume of the sample and volume of air. TD-GC/MS reported a lower combined uncertainty (< 10%) than Soxhlet-GC/MS (values between 11% and 18%) for the measurement of particle-bound PAHs in the air, which was primarily contributed by the recovery of the analyzed PAHs and the calibration curves.

Keywords: Uncertainty; PAHs; Thermal desorption; Soxhlet extraction; GC-MS; PM₁₀ samples.

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are a group of organic compounds containing only carbon and hydrogen atoms, constituted by two or more condensed aromatic rings. These substances are generated by all incomplete combustion processes of organic material, being the anthropogenic activities their major sources (Ravindra *et al.*, 2008).

PAHs have aroused global concern due to their high persistence within the environment and their adverse health effects. As result of this, several international agencies have listed PAHs as priority pollutants (US EPA, 1982; ATSDR, 1995; WHO, 1998). Although the analysis of PAHs in air is of considerable importance for air quality assessment, PAH data in air is still scarce, and most of the studies show large spatial and temporal uncertainties due to the complex sampling and analytical procedures required.

The environmental samples of PAHs can be difficult to analyze due to their complexity (multi-phase and multi-component samples in very low concentrations). For this reason, a solvent extraction and pre-concentration technique in combination with a chromatographic method (liquid and/or gas chromatography) is the most frequently used methodology for the determination of PAHs (US EPA, 1999;

ISO 12884:2000; ISO 16362:2005; Poster *et al.*, 2006). Conventional sample preparation methods involve several steps leading to the possibility of loss or contamination. Since PAH concentrations in ambient air are low, it is essential to reduce the number of pretreatment steps and the solvent volume in order to reduce the level of blank contamination and the risk of losing analytes by evaporation in the concentration steps (Delgado-Saborit, 2010). Among the solvent extraction and pre-concentration techniques, thermal desorption (TD) provides advantages that overcomes the main drawbacks of the conventional solvent extractions (Van Drooge *et al.*, 2009). The features of this technique (the absence of sample manipulation, high desorption efficiency, good sensitivity and reproducibility, elimination of interferences, and lower extraction times and costs) provide a faster, simpler, and more sensitive and accurate method to determine trace level PAHs in ambient air (Kim and Kim, 2015). TD technique coupled with gas chromatography/mass spectrometry (GC/MS) has been mainly applied for the analysis of particle-bound PAHs (Bates *et al.*, 2008; Gil-Molto *et al.*, 2009; Van Drooge *et al.*, 2009).

According to the international standard (ISO 20988:2007) the uncertainty of a measurement is defined as “a parameter associated with the result of a measurement that characterizes the dispersion of the values that could reasonably be attributed to the measurand”. Estimation of uncertainty leads to better measurement reliability, renders data from inter-laboratory studies comparable, and helps to assess the statistical significance of the difference between

^{*} Corresponding author.

Tel.: +34 946017297

E-mail address: inaki.elorduy@ehu.eus

the measurement and a relevant reference value. In case of regulated pollutants such as PAHs, the measurement uncertainty is necessary to evaluate the quality of the results and for their proper interpretation.

The aim of this study was to evaluate the major uncertainty contributions associated with the determination of particle-bound PAHs in air samples by an analytical method based on TD-GC/MS. This technique has been previously optimized and applied to determine these compounds in real 8-h samples (PM₁₀) (Elorduy *et al.*, 2016). Furthermore, the uncertainties associated with the conventional analytical method (Soxhlet-GC/MS) were also determined in order to compare the reliability of measurements obtained from each method. One important contribution of this work is that there are few studies in the literature that provide a comprehensive evaluation of the uncertainty derived from the determination of PAHs by TD technique.

EXPERIMENTAL

Reagents and Materials

The PAH standards used were SV Calibration Mix 5 from Restek Corporation (Bellefonte, PA, USA) containing 2000 µg mL⁻¹ of naphthalene (Naph), acenaphthylene (Acy), acenaphthene (Ace), fluorene (FL), phenanthrene (Phe), anthracene (Ant), fluoranthene (Ft), pyrene (Pyr), benzo[a]anthracene (BaA), chrysene (Chry), benzo[b]fluoranthene (BbFt), benzo[k]fluoranthene (BkFt), benzo[a]pyrene (BaP), indeno[1,2,3-cd]pyrene (IP), dibenzo[a,h]anthracene (DBaA), and benzo[ghi]perylene (BghiP) in methylene chloride.

The pre-deuterated PAHs used were naphthalene-d₈ (Naph-d₈), biphenyl-d₁₀ (Biph-d₁₀), phenanthrene-d₁₀ (Phe-d₁₀), pyrene-d₁₀ (Pyr-d₁₀), benzo[a]anthracene-d₁₂ (BaA-d₁₂), benzo[a]pyrene-d₁₀ (BaP-d₁₀) and benzo[ghi]perylene-d₁₂ (BghiP-d₁₂), from Chiron (PAH Mixture 6, Trondheim, Norway), 200 µg mL⁻¹ in toluene.

Decafluorobiphenyl, 4,4'-dibromooctafluorobiphenyl, 4,4'-dibromobiphenyl (Restek, 2000 µg mL⁻¹ in methylene chloride) and indeno[1,2,3-cd]pyrene-d₁₂ (Chiron, 100 µg mL⁻¹ in toluene) were used as recovery standard for the assessment of Soxhlet extraction efficiency.

Solutions were prepared by appropriate dilution in methanol HPLC grade (99.9%, Lab-Scan Analytical Sciences, Poland).

Standard Reference Material (SRM) 1649b urban dust, obtained from the National Institute of Standards and Technology (NIST, Gaithersburg, Md., USA) was used in the validation of the analytical methods.

Sample Collection

Airborne particulate matter (PM₁₀) samples were collected on pre-heated (at 500°C for 24 h) quartz fiber filters (150 mm diameter, Whatman International Ltd., United Kingdom) using a high volume sampler (Digitel DHA-80, Digitel Elektronik AG, Switzerland) with a flow rate of 30 m³ h⁻¹. After sampling, the filters were put into individual Petri dishes, wrapped in aluminum foil, and kept in a 4°C freezer

until analysis (< 15 days) according to ISO 12884:2000.

Analytical Procedure

TD-GC/MS

Each loaded filter were randomly cut into 8 portions of 1 cm² and introduced into stainless-steel tubes (90 mm length × 6 mm o.d. × 5 mm i.d., Perkin Elmer S.L., Spain). This was performed in the same way as other studies (Ringuelet *et al.*, 2012; Grandesso *et al.*, 2013), which demonstrated good homogeneity results when using small sections of the filters. Before the analysis, the loaded filters were spiked with 1 µL of deuterated PAH solution (20 ng µL⁻¹). Pre-heated (500°C, 24 h) silanized glass wool (Supelco Inc., Bellefonte, USA) was introduced at the end, and at the head of the desorption tubes in order to prevent system contamination.

The analysis of the samples was performed using an automatic thermal desorption unit (PerkinElmer Turbomatrix 150 ATD) coupled by a fused-silica capillary transfer line (0.32 mm i.d.) to GC/MS (PerkinElmer Clarus 500). TD-GC/MS method was developed and applied for the measurement of particle-bound PAHs in ambient air (Elorduy *et al.*, 2016). The thermal desorption was carried out in two stages. In the “primary desorption” stage, the sampling tubes were placed into the desorption oven at ambient temperature. After a leak test and ambient temperature purge by carrier gas (helium) to remove oxygen, the samples were thermally desorbed at 350°C for 10 min using a flow of inert gas (in this work, helium at 173 mL min⁻¹) to extract analytes from the sample. These analytes were refocused on a Peltier-cooled trap at -10°C. Once the primary desorption was complete, the trap was quickly heated until 325°C for 6 min (the “secondary desorption” stage). The trapped analytes were released and swept (by a helium flow of 12 mL min⁻¹) through the heated transfer line (at 280°C) to the GC column.

The chromatographic separation of PAHs was conducted on a Meta.X5 (silphenylene phase) capillary column: 30 m length × 0.25 mm i.d. × 0.25 mm film thickness (Teknokroma, Spain). The helium gas carrier pressure employed in the GC/MS system was 21 psi and the column temperature was programmed as follows: initial temperature 100°C for 3 min, ramp of 10 °C min⁻¹ until 250°C, ramp of 5 °C min⁻¹ until 320°C, and finally temperature held at 320°C for 10 min. The total analysis time was 42 min per sample. The MS operated simultaneously in full scan (SCAN) and selective ion monitoring (SIM) modes with the transfer line (from GC to MS) and the source at 280°C and 250°C, respectively. Analytes were afterwards identified by comparing their retention times and mass-to-charge ratios (m/z) with standards and literature data.

Soxhlet-GC/MS

The Soxhlet extraction was performed by Büchi extraction system B-811, an automated system that can be used to perform an extraction according to the original Soxhlet principle. The loaded filters (150 mm diameter) were extracted with hexane using the Soxhlet Warm mode. This mode demonstrated advantages for reducing extraction time against conventional Soxhlet extraction in previous

works in our laboratory (Elcoroaristizabal *et al.*, 2014), allowing an optimal extraction in 3 hours.

Before the extraction, the loaded filter was spiked with 1 μL of a solution ($0.5 \text{ ng } \mu\text{L}^{-1}$) of the recovery standards.

After Soxhlet extraction process, the extracts of 5 mL were concentrated by a stream of dry nitrogen to a volume less than 0.5 mL. Finally, these extracts were diluted to 1.5 mL with methanol and 25 μL of a deuterated PAHs solution ($20 \text{ ng } \mu\text{L}^{-1}$) were spiked.

2 μL aliquots from each extract were injected into the GC/MS with split mode. Table 1 collects the timed events and the oven program used in the Soxhlet-GC/MS method.

Also, in this method, PAHs were identified based on their retention times and m/z value.

RESULTS AND DISCUSSION

Validation

The performance of both methods when applied to atmospheric PM samples was determined using Standard Reference Material (SRM) 1649b, urban dust. The repeatability and recovery of the method were calculated by adding known amounts of the SRM 1649b to blank quartz fiber filters (Whatman International Ltd, United Kingdom)

In TD-GC/MS method, $10.3 \pm 0.3 \text{ mg}$ were weighted and deposited on one-eighth of a 47 mm diameter filters ($n = 10$), which were rolled and put into the desorption tubes.

Silanized glass wool (Supelco Inc., Bellefonte, USA) was introduced at the end, and at the head of the desorption tubes in order to prevent system contamination.

In the case of Soxhlet-GC/MS method, $412.5 \pm 76.8 \text{ mg}$ were deposited on one-eighth of a 150 mm diameter filters ($n = 7$). Before the extraction, the loaded filter was spiked with 1 μL of a solution ($0.5 \text{ ng } \mu\text{L}^{-1}$) of the recovery standards.

Prior to use, glass wool plugs and filters were heated at 350°C for 24 h to remove trace organic compounds. Before the analysis, filters were spiked with a deuterated PAH internal standard solution (1 μL and 25 μL of $20 \text{ ng } \mu\text{L}^{-1}$ for TD and Soxhlet method, respectively).

Table 2 and 3 lists the results of the comparison between the calculated concentrations and the certificate values obtained for each PAH and method.

Although the chromatographic column used in this study demonstrated a good resolution for the 16 EPA PAHs, the presence of other PAHs in the standard reference material can generate co-elution problems (Bordajandi *et al.*, 2008). Thus, in the results obtained from the analysis of SRM 1649b, the BbFt and DBaA presented co-elution with the benzo[*j*]fluoranthene (BjFt) and dibenzo[*a,c*]anthracene (DBaA), respectively.

The most compounds for both methods accomplished the quality objectives for ambient air PAHs stated by ISO 12884:2000, which establishes recovery efficiency between 75 and 125%, and a precision of $\pm 25\%$. However, the

Table 1. Timed events and oven program used in direct injector mode.

Event	Timed event		Oven program			
	Flow (mL min^{-1})	Time (min)	Ramp	Rate ($^\circ\text{C min}^{-1}$)	Temperature ($^\circ\text{C}$)	Hold (min)
Split	0	-0.51	Initial	0	45	1
Split	50	1	1	20	200	0
Split	20	5	2	4	320	5

Table 2. TD-GC/MS method validation parameters for the 16 EPA PAHs in NIST SRM 1649b urban dust ($n = 10$).

PAH	Experimental mean (ng) ^a	NIST certified value (ng) ^a	RSD (%)	Recovery (%)
Naph	3694.41 ± 1082.45	26.75 ± 2.98	46.33	13808.82
Acy	6.97 ± 0.61	1.99 ± 0.24	13.86	351.11
Ace	1.57 ± 0.19	2.03 ± 0.41	19.53	77.25
FL	2.06 ± 0.21	2.29 ± 0.67	16.40	89.88
Phe	42.70 ± 3.25	45.28 ± 0.21	12.02	94.30
Ant	12.59 ± 0.78	10.06 ± 0.22	9.82	125.12
Ft	59.57 ± 3.22	67.91 ± 0.41	8.56	87.71
Pyr	51.76 ± 2.80	51.24 ± 1.44	8.56	101.01
BaA	19.26 ± 1.06	21.71 ± 0.51	8.70	88.70
Chry	26.17 ± 1.32	31.33 ± 0.29	7.95	83.52
BbFt + BjFt	75.00 ± 6.17	81.34 ± 2.29	13.01	92.21
BkFt	16.09 ± 1.37	17.51 ± 0.50	13.43	91.85
BaP	20.38 ± 1.48	25.42 ± 2.47	11.52	80.18
IP	35.49 ± 1.94	29.74 ± 1.65	8.63	119.34
DBaA + DBaC	6.35 ± 0.93	6.02 ± 0.11	23.11	105.42
BghiP	37.21 ± 2.19	40.85 ± 0.41	9.31	91.10
Average ^b	-	-	12.18	96.67

^a expanded uncertainty about the mean, with coverage factor, $k = 2$.

^b except Naph and Acy.

Table 3. Soxhlet extraction-GC/MS method validation parameters for the 16 EPA PAHs in SRM 1649b (n = 7).

PAH	Experimental mean (ng) ^a	NIST certified value (ng) ^a	RSD (%)	Recovery (%)
Naph	67.32 ± 18.60	391.64 ± 35.43	33.84	17.19
Acy	20.17 ± 5.91	79.90 ± 9.48	35.86	25.24
Ace	24.99 ± 5.41	81.56 ± 16.48	26.53	30.65
FL	32.60 ± 9.18	92.32 ± 14.42	34.49	35.31
Phe	1215.35 ± 331.78	1668.42 ± 24.72	33.43	72.84
Ant	104.55 ± 25.71	169.12 ± 1.65	32.53	61.82
Ft	2392.52 ± 559.83	2573.91 ± 32.96	30.95	92.95
Pyr	1914.67 ± 398.71	2054.18 ± 57.68	27.55	93.21
BaA	808.28 ± 148.46	870.34 ± 20.60	24.30	92.87
Chry	1632.01 ± 464.16	1256.02 ± 11.54	37.62	129.94
BbFt + BjFt	3144.07 ± 800.72	3260.70 ± 91.88	33.69	96.42
BkFt	921.46 ± 319.73	702.05 ± 20.19	45.90	131.25
BaP	1019.58 ± 271.00	1018.84 ± 98.88	35.16	100.07
IP	1109.96 ± 296.97	1192.08 ± 65.92	35.39	93.11
DBahA + DBacA	507.81 ± 176.18	241.30 ± 4.53	45.90	363.16
BghiP	2143.65 ± 580.24	1777.81 ± 32.96	35.81	120.58
Average ^b	-	-	34.85	120.69

^a expanded uncertainty about the mean, with coverage factor, $k = 2$.

^b except Naph, Acy, Ace and FL.

lowest molecular weight PAHs (Naph and Acy) were overestimated (recoveries > 125%) when they were analyzed by the TD-GC/MS method. These compounds could suffer losses during the sample preparation due their high volatility.

In the case of Soxhlet extraction, the lightest PAHs (Naph, Acy, Ace and FL) showed low recoveries (< 75%). The loss of these analytes during the extraction process in the Soxhlet Warm mode could be the main reason for these low recoveries. On the other hand, the DBahA concentration (pair DBahA-DBacA) was overestimated (recovery of 210%).

Hence, the PAHs that did not accomplish the quality objective stated by ISO 12884:2000 were excluded from the study.

Uncertainty Estimation

The particle-bound PAH concentrations in the air samples, expressed in ng m^{-3} , are obtained from the following equations, Eq. (1) for TD-GC/MS and Eq. (2) for Soxhlet-GC/MS:

$$\text{Concentration} (\text{ng} \cdot \text{m}^{-3}) = \frac{C (\text{ng} \cdot \text{mL}^{-1}) \cdot A_s (\text{m}^2)}{V_{\text{air}} (\text{m}^3)} \quad (1)$$

$$\text{Concentration} (\text{ng} \cdot \text{m}^{-3}) = \frac{C (\text{ng} \cdot \text{mL}^{-1}) \cdot V_s (\text{mL})}{V_{\text{air}} (\text{m}^3)} \quad (2)$$

where C is the concentration of the target compound obtained from the calibration (ng m^{-2} or ng mL^{-1}); A_{sample} is the final area of the analyzed filter (m^2); V_{sample} is the final volume of the sample (mL); V_{air} is the volume of the air sampled (m^3).

According to Eqs. (1) and (2), the main uncertainty sources that contributed to the determination of particle PAHs in air are:

- Analytical determination (calibration).
- Extraction stage (recovery).
- Applicability in ambient air samples (A_s or V_s and V_{air}).

The uncertainty associated with the method (u_{comb}) was calculated by combining the uncertainty derived from each source (Eq. (3)).

$$\left(\frac{u_{\text{comb}}}{C}\right)^2 = \left(\frac{u(\text{Cal})}{C}\right)^2 + \left(\frac{u(R)}{R}\right)^2 + \left(\frac{u(A_s \text{ or } V_s)}{A_s \text{ or } V_s}\right)^2 + \left(\frac{u(V_{\text{air}})}{V_{\text{air}}}\right)^2 \quad (3)$$

where $u(\text{Cal})$ is the calibration uncertainty (ng); $u(R)$ is the uncertainty derived from recovery; $u(A_s \text{ or } V_s)$ is the uncertainty derived from area (m^2) or volume (μL) of sample; $u(V_{\text{air}})$ is the uncertainty derived from air volume; C is the amount of analyte (ng); R is the recovery; A_s is the area of the filter (m^2); V_s is the volume of sample injected (μL) and V_{air} is the volume of air sampled (m^3).

Uncertainty Derived from the Analytical Determination

The uncertainty associated with calibration, $u(\text{Cal})$, was determined by taking the square root of the sum of the squares of the uncertainty derived from calibration curve adjustment and solutions preparation (standard and internal standard solutions) (Eq. (4)):

$$\left(\frac{u(\text{Cal})}{C}\right)^2 = \left(\frac{u(C_x)}{C_x}\right)^2 + \sum_{i=1}^n \left(\frac{u(\text{std})}{C_{\text{std}}}\right)^2 + \sum_{j=1}^m \left(\frac{u(\text{is})}{C_{\text{is}}}\right)^2 \quad (4)$$

where $u(C_x)$ is the uncertainty derived from linear least squares adjustment; $u(\text{std})$ is the uncertainty derived from standard solution preparation; $u(\text{is})$ is the uncertainty

derived from internal standard solution preparation; C_x is the predicted analyte concentration; C_{std} is the standard solution concentration; C_{is} is the internal standard solution concentration; n is the level of target compounds in the calibration curve; and m is the level of deuterated compounds in the calibration curve.

Uncertainty Derived from Linear Least Squares Adjustment, $u(C_x)$

The uncertainty derived from the linear least squares adjustment is mainly due to the variability in the responses shown by the instrument, and it is evaluated from standard deviations of slope and intercept in calibration line. The relative uncertainty of the predicted analyte concentration ($u(C_x)/C_x$) from linear least squares adjustment was calculated applying the following equation (Barrado-Olmedo *et al.*, 2012):

$$\left(\frac{u(C_x)}{C_x}\right)^2 = \frac{u_y^2}{(y-b)^2} + \frac{u_b^2}{(y-b)^2} + \frac{u_m^2}{(m)^2} \quad (5)$$

where y is the mean value of the analytical response of the calibration curve; u_y is the uncertainty of the response deduced from its standard deviation (s_y) for n calibration points (s_y/\sqrt{n}); b is the y -intercept of the calibration curve; u_b is the uncertainty of y -intercept deduced from its standard deviation (s_b) for n calibration points (s_b/\sqrt{n}); m is the slope; and u_m is the uncertainty of slope deduced from its standard deviation (s_m) for n calibration points (s_m/\sqrt{n}).

In both methods (TD-GC/MS and Soxhlet-GC/MS), internal calibration curves of five concentration levels were used to calibrate. Internal calibration curves were plotted as the ratio of peak area (analyte/deuterated) versus the ratio of amount in ng (analyte/deuterated). In TD-GC/MS, different amounts of PAHs (from 2.5 ng to 45 ng) and the same amount of deuterated compounds (25 ng) were spiked in a portion of filter introduced into sampling tube. In the case of Soxhlet-GC/MS, PAH levels between 0.2 and 5 ng and deuterated PAHs of 1 ng were used to calibrate.

For example, an internal calibration curve of BaP by TD-GC/MS was performed (Fig. 1), showing a slope value

of 1.170 and a correlation coefficient of 0.998. The mean value of the area ratio (the analytical response of curve) was 0.841.

Finally, the relative ($u(C_x)/C_x$) for BaP was determined by Eq. (6):

$$\frac{u(C_x)}{C_x} = \sqrt{\frac{(0.040/\sqrt{5})^2}{(0.841)^2} + \frac{(0.019/\sqrt{5})^2}{(1.170)^2}} = 0.02 \quad (6)$$

Table 4 shows the relative uncertainty associated with the calibration curve for each PAH in both methods (TD-GC/MS and Soxhlet-GC/MS). The results ranged between 0.02 and 0.06 for TD-GC/MS, and between 0.01 and 0.04 for Soxhlet-GC/MS.

Uncertainty Derived from Standard Solution Preparation, $u(std)$

Uncertainty associated with the preparation of calibration standards includes the uncertainty of the stock solution according to certificates and dilution chain. This uncertainty is a combination of the uncertainty of the glassware used and stock solutions. In this study, the standards were prepared using syringes (*syr*) and volumetric flask (*flask*). Eqs. (7) and (8) were used to determine $u(std)$ (Aslan-Sungur *et al.*, 2014).

$$\left(\frac{u(std)}{C_{std}}\right)^2 = \left(\frac{u(stock)}{C_{stock}}\right)^2 + \left(\frac{u(f)}{f}\right)^2 \quad (7)$$

$$u(f) = \sqrt{\left(\frac{u(syr)}{V_{syr}}\right)^2 + \left(\frac{u(flask)}{V_{flask}}\right)^2} \quad (8)$$

where $u(f)$ is the uncertainty of the dilution factor; $u(syr)$ is the uncertainty of the syringe; $u(stock)$ is the uncertainty of the stock solution; $u(flask)$ is the uncertainty of the volumetric flask; f is the dilution factor; C_{stock} is the amount of analyte in the stock solution; V_{syr} is the volume of the syringe and V_{flask} is the volume of the flask.

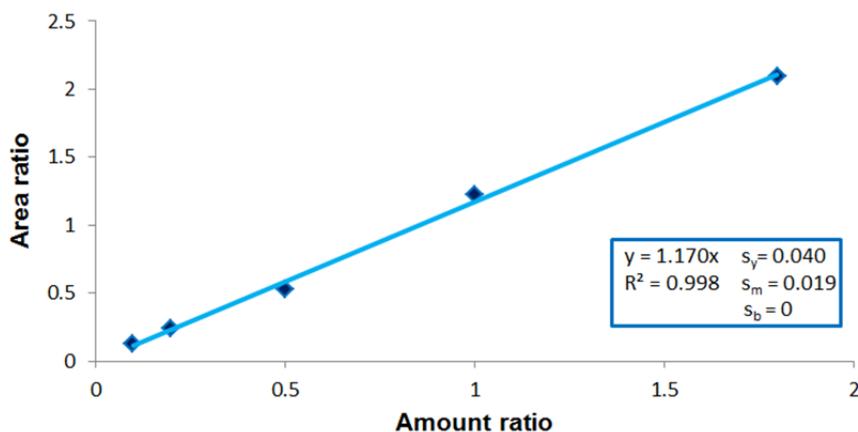


Fig. 1. Calibration curve of BaP in TD-GC/MS.

Table 4. Relative uncertainty from linear least squares adjustment for each PAH in TD-GC/MS and Soxhlet-GC/MS method.

PAH	$(u(C_x)/C_x)$	
	TD-GC/MS	Soxhlet-GC/MS
Ace	0.04	-
FL	0.06	-
Phe	0.02	0.03
Ant	0.03	0.01
Ft	0.03	0.02
Pyr	0.03	0.03
BaA	0.02	0.03
Chry	0.04	0.02
BbFt	0.03	0.01
BkFt	0.04	0.02
BaP	0.02	0.04
IP	0.05	0.02
DBahA	0.05	0.03
BghiP	0.03	0.02

The $u(syr)$ and $u(flask)$ were calculated as the combination of the uncertainty coming from the calibration of the tool, $u(syr_{cal})$ or $u(flask_{cal})$, and the uncertainty source from the temperature, $u(T)$ (Eqs. (9) and (10)).

$$u(syr) = \sqrt{(u(syr_{cal}))^2 + (u(T))^2} \quad (9)$$

$$u(flask) = \sqrt{(u(flask_{cal}))^2 + (u(T))^2} \quad (10)$$

The uncertainties from the calibration of the item, $u(syr_{cal})$ and $u(flask_{cal})$, were calculated by using manufacturer's data (Table 5), assuming a rectangular distribution.

According to the Eurachem/CITAC (2012) guide, the temperature effect is the result of the variation in temperature in the laboratory which is generally accepted as $\pm 3^\circ\text{C}$ and can be calculated by the next equation (Yenisoy-Karakaş, 2012):

$$u(T) = \frac{3 \cdot V \cdot Q}{1.73} \quad (11)$$

where $u(T)$ is the standard uncertainty of the temperature; V measured volume and Q is the coefficient of volume expansion of the solvent used in the preparation.

Table 5 introduces the manufacturer's specification data of items used to prepare the standard solution.

In this study, the stock solution for the TD-GC/MS method was the standard certificated mixture of 16 EPA PAHs (SV Calibration Mix 5, Restek, 2000 $\mu\text{g mL}^{-1}$). To prepare the calibration standards (solutions of 2.5, 5, 12.5, 25, and 45 $\text{ng } \mu\text{L}^{-1}$), two dilution stages were necessary. In the first, 50 μL were removed from the stock solution and diluted in 1 mL of methanol, obtaining a 100 $\text{ng } \mu\text{L}^{-1}$ solution. Subsequently, and depending on the target concentration of calibration solution, different volumes were removed from it and diluted with 1 mL of methanol (e.g., to obtain a concentration of 2.5 $\text{ng } \mu\text{L}^{-1}$; 25 μL of a 100 $\text{ng } \mu\text{L}^{-1}$ solution were necessary). These two dilution stages should be considered in the expression of uncertainty in the dilution, where the suffixes 1 and 2 mark the dilution stage (Eq. (12)).

$$u(f) = \sqrt{\left(\frac{u(syr)_1}{V_{syr_1}}\right)^2 + \left(\frac{u(flask)_1}{V_{flask_1}}\right)^2 + \left(\frac{u(syr)_2}{V_{syr_2}}\right)^2 + \left(\frac{u(flask)_2}{V_{flask_2}}\right)^2} \quad (12)$$

Tables 6 and 7 summarize the uncertainties obtained for each dilution stage and the calibration solution in the preparation of standard solutions.

The relative uncertainty associated with standard solution preparation ($u(std)/C_{std}$) presented very similar values for the different calibration solutions (ranging between 2.91×10^{-3} and 2.95×10^{-3}). The contribution of temperature in the uncertainty of syringe and volumetric flask was negligible, being the uncertainty of the stock solution the major uncertainty contributor to the uncertainty in the preparation of the standard solution.

The same calculations were performed for the Soxhlet-GC/MS. In this method, the calibration standards (solutions of 0.1, 0.25, 0.5, 1 and 2.5 $\text{ng } \mu\text{L}^{-1}$) were prepared in three dilution stages:

- 50 μL were removed from the stock solution (SV Calibration Mix 5, Restek, 2000 $\mu\text{g mL}^{-1}$) and diluted in 1 mL of methanol, obtaining a 100 $\text{ng } \mu\text{L}^{-1}$ solution.

Table 5. The manufacturer's specification data of lab tools, PAH standard and solvents

Item	Amount	Manufacturer's specification
Volumetric flask	1 mL	$\pm 2.50 \times 10^{-2}$ mL ^a
Syringe	2; 25; 50; 125; 250; 500 μL	$\pm 1\%$ nominal volume ^a
Standard 16 EPA-PAHs	2000 $\text{ng } \mu\text{L}^{-1}$	± 11.63 $\text{ng } \mu\text{L}^{-1}$ ^b
Internal deuterated PAHs	200 $\text{ng } \mu\text{L}^{-1}$	± 4 $\text{ng } \mu\text{L}^{-1}$ ^a
Methanol thermal expansion (at 25°C)	-	1.15×10^{-3} $^\circ\text{C}^{-1}$
Methylene chloride thermal expansion (at 25°C)	-	1.44×10^{-3} $^\circ\text{C}^{-1}$
Toluene thermal expansion (at 25°C)	-	1.11×10^{-3} $^\circ\text{C}^{-1}$
n-Hexane thermal expansion (at 25°C)	-	1.14×10^{-3} $^\circ\text{C}^{-1}$

^a accuracy.

^b expanded uncertainty (95%).

Table 6. Uncertainty associated with syringe and volumetric flask during the standard solution preparation for each dilution stage (TD-GC/MS method).

Dilution stage	Solution concentration (ng μL^{-1})	V_{syr} (μL)	$u(\text{syr}_{\text{cal}})$ (μL)	$u(T)$ (μL)	$u(\text{syr})$ (μL)
1 st	100	50	0.29	0.13	0.31
2 nd	2.5	25	0.14	0.05	0.15
2 nd	5	50	0.29	0.10	0.31
2 nd	12.5	125	0.72	0.25	0.76
2 nd	25	250	1.44	0.50	1.53
2 nd	45	450	2.60	0.90	2.75
Dilution stage	Solution concentration (ng μL^{-1})	V_{flask} (μL)	$u(\text{flask}_{\text{cal}})$ (μL)	$u(T)$ (μL)	$u(\text{flask})$ (μL)
1 st , 2 nd	100; 2.5; 5; 12.5; 25; 45	1000	14.43	2	14.57

Table 7. Relative uncertainties associated with dilution and standard solution preparation for each calibration solution (TD-GC/MS method).

Solution concentration (ng μL^{-1})	f	$u(f)$	C_{stock} (ng μL^{-1})	$u(\text{stock})$ (ng μL^{-1})	$u(\text{std})/C_{\text{std}}$
2.5	800	0.02	2000	5.82	2.91×10^{-3}
5	400	0.02	2000	5.82	2.91×10^{-3}
12.5	160	0.02	2000	5.82	2.91×10^{-3}
25	80	0.02	2000	5.82	2.92×10^{-3}
45	44	0.02	2000	5.82	2.95×10^{-3}

- 100 μL of 100 ng μL^{-1} solution were diluted in 1 mL of methanol (10 ng μL^{-1} solution).
- Finally, from 10 ng μL^{-1} solution, different volumes were removed and diluted to obtain the calibration solutions.

Table 8 shows the results obtained in the determination of the uncertainties associated with lab tools for the Soxhlet-GC/MS method.

The results of Table 8 were used in Eqs. (12) and (7), obtaining the same relative uncertainty in the preparation of the different calibration solutions, 2.91×10^{-3} . This value was the same as that obtained for the preparation of solutions of 2.5, 5 and 12.5 ng μL^{-1} in the TD-GC/MS method. Again, the uncertainty of the stock solution was the main contributor to the uncertainty in the preparation of the standard solution, whereas the effect of the temperature was negligible in the uncertainty associated with lab tools.

Uncertainty Derived from Internal Standard Solution Preparation, $u(is)$

To determine the uncertainty associated with internal standard solution preparation the same methodology was used in the assessment of $u(\text{std})$.

In the TD-GC/MS, a solution of 25 ng μL^{-1} was prepared from stock solution (Predeuterated internal standard PAH Mixture 6 Chiron, 200 $\mu\text{g mL}^{-1}$), removing 125 μL and diluting them in 1 mL of methanol. For the Soxhlet-GC/MS, the internal solution added to samples was the result of two dilution stages: 100 μL of stock solution (the same as in the TD-GC/MS method) was removed and diluted in 1 mL of methanol, obtaining a 20 ng μL^{-1} ; subsequently, 25 μL from this solution were diluted in 1 mL of methanol to get a final concentration of 0.5 ng μL^{-1} .

The relative uncertainty $u(is)/C_{is}$ obtained for the TD-GC/MS and Soxhlet-GC/MS methods were 0.02 and 0.01 respectively. In the case of the TD-GC/MS, due to the

dilution factor was low ($f = 8$), both terms of Eq. (7) (stock solution and dilution factor) had a similar contribution to the uncertainty in the preparation of the internal standard solution. In contrast, for the Soxhlet-GC/MS method, the effect of the dilution factor was negligible, being the uncertainty of the stock solution the main contributor.

Uncertainty Derived from Calibration, $u(\text{Cal})$

Once $(u(C_x)/C_x)^2$, $(u(\text{std})/C_{\text{std}})^2$ and $(u(is)/C_{is})^2$ had been calculated, the relative uncertainty derived from the calibration was estimated according to Eq. (4). For BaP (determined by the TD-GC/MS method) the calculation was as follows:

$$\left(\frac{u(\text{Cal})}{C}\right)^2 = (0.02)^2 + (2.91 \cdot 10^{-3})^2 + (2.91 \cdot 10^{-3})^2 + (2.91 \cdot 10^{-3})^2 + (2.92 \cdot 10^{-3})^2 + (2.95 \cdot 10^{-3})^2 + (0.02)^2 = 8.43 \cdot 10^{-4} \quad (13)$$

$$\frac{u(\text{Cal})}{C} = \left(\sqrt{8.43 \cdot 10^{-4}}\right) = 0.03 \quad (14)$$

The relative uncertainty $u(\text{Cal})/C$ associated with the calibration for each PAH in the TD-GC/MS and Soxhlet-GC/MS methods are summarized in Table 9.

The relative uncertainty associated with calibration in both methods showed slightly lower values for Soxhlet-GC/MS (between 0.01 and 0.04 for most PAHs) since the calibration in this method was carried out by direct injection into the GC/MS. In both methods, the uncertainty derived from standard solution preparation was negligible, being the linear least squares adjustment and the internal standard solution preparation the main contributors to the uncertainty of the calibration.

Table 8. Uncertainties associated with syringe and volumetric flask during the standard solution preparation for each dilution stage (Soxhlet-GC/MS method).

Dilution stage	Solution concentration (ng μL^{-1})	V_{syr} (μL)	$u(\text{syr}_{\text{cal}})$ (μL)	$u(T)$ (μL)	$u(\text{syr})$ (μL)
1 st	100	50	0.29	0.13	0.31
2 nd	10	100	0.58	0.20	0.61
3 rd	0.1	10	0.06	0.02	0.06
3 rd	0.25	25	0.14	0.05	0.15
3 rd	0.5	50	0.29	0.10	0.31
3 rd	1	100	0.58	0.20	0.61
3 rd	2.5	250	1.44	0.50	1.53
Dilution stage	Solution concentration (ng μL^{-1})	V_{flask} (μL)	$u(\text{flask}_{\text{cal}})$ (μL)	$u(T)$ (μL)	$u(\text{flask})$ (μL)
1 st , 2 nd , 3 rd	100; 10; 2.5; 5; 12.5; 25; 45	1000	14.43	2	14.57

Table 9. Relative uncertainty for each PAH in the TD-GC/MS and Soxhlet-GC/MS methods.

PAH	$u(\text{Cal})/C$	
	TD-GC/MS	Soxhlet-GC/MS
Ace	0.04	-
FL	0.06	-
Phe	0.03	0.04
Ant	0.04	0.02
Ft	0.04	0.02
Pyr	0.04	0.03
BaA	0.03	0.03
Chry	0.05	0.02
BbFt	0.04	0.01
BkFt	0.05	0.02
BaP	0.03	0.04
IP	0.05	0.02
DBahA	0.06	0.04
BghiP	0.03	0.02

Uncertainty Derived from Recovery, $u(R)$

The recovery of PAHs (R) and its uncertainty ($u(R)$) were determined from replicate measurements of standard reference material (SRM 1649b, urban dust). R was considered as the ratio ($C_{\text{obs}}/C_{\text{SRM}}$) of the observed amount of analyte C_{obs} (mean of replicate analysis) to a reference value C_{SRM} . The relative uncertainty for recovery was calculated by using the following equations (Barwick and Ellison, 1999):

$$\left(\frac{u(R)}{R}\right)^2 = \left(\frac{u(C_{\text{obs}})}{C_{\text{obs}}}\right)^2 + \left(\frac{u(C_{\text{SRM}})}{C_{\text{SRM}}}\right)^2 \quad (15)$$

$$\frac{u(C_{\text{obs}})}{C_{\text{obs}}} = \frac{SD}{C_{\text{obs}} \cdot \sqrt{n}} \quad (16)$$

where $u(C_{\text{obs}})/C_{\text{obs}}$ is the relative uncertainty derived from the observed amount of analyte after the extraction; $u(C_{\text{SRM}})/C_{\text{SRM}}$ is the relative uncertainty derived from the amount of analyte in the SRM; SD is the standard deviation of the results from the replicate analyses of the SRM and n is the number of replicates.

For BaP, determined by the TD-GC/MS method:

$$\frac{u(R)}{R} = \sqrt{\left(\frac{0.74 \text{ ng}}{20.38 \text{ ng}}\right)^2 + \left(\frac{1.24 \text{ ng}}{25.42 \text{ ng}}\right)^2} = 0.06 \quad (17)$$

The R and $(u(R)/R)$ values for each PAH were determined for both methods (Table 10) from results obtained during the method validations (Tables 2 and 3).

Regarding relative recovery uncertainty, for TD-GC/MS method, it ranged from 0.03 to 0.15 for target PAHs. Among the compounds, only Ace and FL showed the highest values (> 0.07). Their low concentrations in particulate phase and their high volatility could explain this increase in the relative recovery uncertainty.

In contrast, Soxhlet-GC/MS method showed higher relative recovery uncertainty (values between 0.09 and 0.17).

Uncertainty Derived from the Applicability in Ambient Air Samples, $u(A_s)$ or $u(V_s)$ and $u(V_{\text{air}})$

In the TD-GC/MS the possible size variations in the cutting of the filter could be a source of uncertainty. Grandesso *et al.* (2013), analyzing particle PAHs by TD-GC/MS method, estimated a relative uncertainty derived from cutting (u_{cut}/C) of 7.60×10^{-3} . Thus, this value was considered in this study for the TD-GC/MS method. The term of $u(A_s)/A_s$ in

Table 10. Relative recovery uncertainties of PAH obtained from the analysis of NIST SRM 1649b ($n = 10$) by TD-GC/MS and Soxhlet-GC/MS ($n = 7$).

PAH	$u(R)/C$	
	TD-GC/MS	Soxhlet-GC/MS
Ace	0.12	-
FL	0.15	-
Phe	0.03	0.14
Ant	0.03	0.12
Ft	0.03	0.12
Pyr	0.03	0.11
BaA	0.03	0.09
Chry	0.03	0.14
BbFt	0.04	0.13
BkFt	0.04	0.17
BaP	0.06	0.14
IP	0.04	0.14
DBahA	0.07	-
BghiP	0.03	0.14

the combined uncertainty expression (Eq. (3)) was replaced by u_{cut}/C for the TD- GC/MS method.

In the Soxhlet-GC/MS method the sample is injected directly into the CG/MS system, thus, the uncertainty associated with the sample in this case was the uncertainty of the syringe. The injected volume was 2 μL and relative ($u(V_s)/V_s$) was calculated by the Eq. (12), obtaining a value of 0.01 for each PAH.

($u(V_{\text{air}})/V_{\text{air}}$) is related to the uncertainty of the air sampler. In both methods (TD-GC/MS and Soxhlet-GC/MS), the air sampler (Digitel DHA-80) worked at 30 $\text{m}^3 \text{h}^{-1}$ during 8 h (total volume of air collected per sample of 240 m^3). The relative uncertainty of this sampler in the flow (u_{sampler}) was estimated by the manufacturer in $\pm 1.03\%$; thus, the relative uncertainty derived from the air volume for both methods is as follows:

$$\frac{u(V_{\text{air}})}{V_{\text{air}}} = \frac{2.47\text{m}^3}{240\text{m}^3} = 0.01 \quad (18)$$

Combined Uncertainty, u_{comb}

Finally, the relative combined uncertainty for 16 EPA PAHs in each method was calculated by Eq. (3). BaP (determined by the TD-GC/MS method) is given as an example calculation in Eq. (19).

$$\frac{u_{\text{comb}}}{C} = \sqrt{(0.03)^2 + (0.06)^2 + (7.60 \cdot 10^{-3})^2 + (0.01)^2} = 0.07 \quad (19)$$

Table 11 shows the relative combined uncertainty in % for each PAH in both methods.

According to the results, the TD-GC/MS method was more reliable than Soxhlet-GC/MS for the determination of particulate PAHs, with lower combined uncertainties ($< 8\%$ for most PAHs), since the Soxhlet extraction requires a slower and laborious sample preparation stage, which increases the measurement uncertainty.

In terms of the contribution, for TD-GC/MS the recovery uncertainty had similar values than calibration uncertainty. Therefore, the highest impacts on measurement uncertainty for this method arise from calibration and recovery, except in the determination of the lowest molecular weight PAHs (Ace and FL), where the recovery was the main uncertainty contributor. In the case of Soxhlet-GC/MS, the highest uncertainty source came from recovery of extraction stage.

CONCLUSIONS

Two analytical methods based on different extraction techniques (TD-GC/MS and Soxhlet-GC/MS) were applied to analyze particle-bound PAHs in air samples. Both methods were validated by standard reference material (urban dust), and the results indicate that TD-GC/MS is a more reliable method of determining these compounds in aerosol samples, with an average recovery efficiency of 96.67 and a mean RSD value of 12.18.

The uncertainties associated with the determination of

Table 11. u_{comb}/C and for 16 EPA PAHs in both methods.

PAH	u_{comb}/C (%)	
	TD-GC/MS	Soxhlet-GC/MS
Ace	13	-
FL	17	-
Phe	5	14
Ant	5	13
Ft	5	12
Pyr	5	11
BaA	4	10
Chry	6	15
BbFt	6	13
BkFt	7	18
BaP	7	15
IP	7	14
DBahA	9	-
BghiP	5	14

particle-bound polycyclic aromatic hydrocarbons (PAHs) in air samples using TD-GC/MS and Soxhlet-GC/MS were estimated. The calibration curve, recovery, area or volume of the sample and volume of air were identified as the primary sources of uncertainty for both methods. The combined uncertainty associated with the TD-GC/MS method was about 5–9% for most of the PAHs, with the calibration curve and the recovery being the main contributors.

The extraction of PAHs by a solvent extraction-based method (Soxhlet extraction) showed higher uncertainty (percentages between 11% and 18% for most compounds), mainly due to the recovery. The high manipulation of the sample during Soxhlet extraction may explain these values.

ACKNOWLEDGMENTS

The authors gratefully thank the University of the Basque Country UPV/EHU (Ref.: GIU 13/25, GIU 16/03, UFI 11/47) and the Spanish Ministry of Science and Innovation (MICINN) for financing the project PROMESHAP (Ref.: CTM 2010-20607). Iñaki Elorduy wants to thank MICINN for his doctoral grant.

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Received for review, December 15, 2017

Revised, March 23, 2018

Accepted, March 23, 2018