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1 **Impact of recovery correction or subjecting calibrators to sample preparation on**
2 **measurement uncertainty: PAH determinations in waters**
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4 Rocío Mateos^a, Cristina M. Oliveira^b, Ana María Díez-Pascual^{a,c}, Soledad Vera-
5 López^{a,c}, María Paz San Andrés^{a,c},** Ricardo J. N. Bettencourt da Silva^{b,*}
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9
10 ^aDepartment of Analytical Chemistry, Physical Chemistry and Chemical Engineering,
11 Faculty of Sciences, University of Alcalá, Ctra. Madrid-Barcelona, Km. 33.6, 28871
12 Alcalá de Henares, Madrid, Spain
13
14

15
16 ^bCentro de Química Estrutural - Faculdade de Ciências da Universidade de Lisboa,
17 Edifício C8, Campo Grande, 1749-016 Lisboa, Portugal
18
19

20
21 ^cInstitute of Chemistry Research, “Andrés M. del Río” (IQAR), University of Alcalá,
22 Ctra. Madrid Barcelona, Km. 33.6, 28805 Alcalá de Henares, Madrid, Spain.
23
24

25
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27 * Corresponding Author. e-mail address: rjsilva@fc.ul.pt
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30 ** Corresponding Author. e-mail address: mpaz.sanandres@uah.es
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ABSTRACT

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2 The decision on the fitness of a measurement for its intended use and the interpretation
3 of an analytical result requires the assessment of the measurement uncertainty.
4 Frequently, the determination of analytes in complex matrices involves demanding
5 sample preparations in which analyte losses are observed. These losses should be
6 considered when reporting the results, which can be corrected for low recovery by
7 taking the mean recovery observed in the analysis of reference items (e.g. spiked
8 samples) or, alternatively, by subjecting calibrators to the same pre-treatment performed
9 on the samples. In these cases, neat (NC) or adjusted (AC) calibrators are used,
10 respectively. The way analyte losses are handled impacts on the measurement
11 uncertainty. The top-down evaluation of the measurement uncertainty involves
12 combining precision, trueness and additional uncertainty components. The trueness
13 component is quantified by pooling various analyte recovery determinations. This work
14 assesses and compares the uncertainty of polycyclic aromatic hydrocarbons (PAHs)
15 measurements in water based on HPLC-FD calibrations with NC or AC. The trueness
16 component is estimated by pooling mean recoveries observed from the analysis of
17 different spiked samples to which mean recovery uncertainty and degrees of freedom
18 are used to estimate a weighted mean recovery and respective uncertainty. The
19 performance of measurements based on NC and AC are associated with equivalent
20 uncertainty except when large analyte losses are observed, namely in the determination
21 of Naphtalene. In this case, the processing of AC reduces the expanded relative
22 uncertainty from 9.9 % to 3.5 %. The evaluated expanded uncertainty ranged from
23 3.5 % to 12 % of the measured value.
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KEYWORDS

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46 Uncertainty, Recovery correction, Solid Phase Extraction, PAH
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1. INTRODUCTION

The analysis of trace levels of organic compounds in complex matrixes by chromatographic methods involves demanding sample preparations to transfer analyte to a solvent suitable for the chromatographic determination, and/or to remove chromatographic or matrix interferences. Chromatographic interferences overestimate the analyte level (concentration or mass fraction), while matrix effects can underestimate or overestimate it. Matrix effects can be handled by the standard addition method although this involves a time-consuming preparation of calibrators on each sample matrix. When these analyses are not significantly affected by interferences, analyte losses are expected due to multiple mass transfer steps during the sample preparation. If these losses are not considered, the analyte level is underestimated.

Any relevant systematic effect on the analyte measurement in the sample must be considered in the result reported [1,2]. The compensation of these effects can be performed by a mathematical correction of the results based on a prior knowledge of the systematic effect or by subjecting analytical instrument calibrators to the same preparation performed on the samples.

When systematic effects are proportional to the analyte level, the mathematical correction factor of the initial result is the mean analyte recovery, \bar{R} . This parameter is estimated by analysing n samples with known reference value, Q_i , and by determining the mean of several ratios between the estimated, q_i , and reference values (i.e. $\bar{R} = \sum R_i/n = \sum (q_i/Q_i)/n$). The initial sample result, q_{In} , is corrected by multiplying by the inverse of the mean analyte recovery, leading to a result corrected for recovery, q_R ($q_R = q_{In}/\bar{R}$) (“R” stands for “corrected recovery”) [3–6].

When systematic effects are constant, additive correction factors have to be considered [7,8].

The reference samples should have a matrix analytically equivalent to the analysed samples. The reference samples can be prepared either in the laboratory or externally producing internal or external reference materials, respectively. The addition of known amounts of an analyte to a sample, named as spiking, leads to internal reference materials, whereas when the reference value is obtained externally, such as in a Certified Reference Material, external reference materials are obtained.

1 An alternative way of compensating for proportional systematic effects is to subject
2 instrument calibrators to a preparation equivalent to that performed on samples. In such
3 case, analyte losses occurring in the sample are reproduced in the calibrators. This
4 procedure mitigates the need for a mathematical correction of the results, hence the
5 reported results, q_C , take into account the analyte losses (“C” stands for “recovery
6 compensated”). However, this approach is more time-consuming due to the preparation
7 of the calibrators. If analyte recoveries in the samples and calibrators are different due
8 to relevant matrix effects, these differences must be considered in the results, q_{CR} , that
9 should be compensated and subsequently corrected for recovery (“CR” stands for
10 “recovery compensated and corrected”). The standard addition method can be used as
11 an alternative to this recovery correction or even to both recovery compensation and
12 correction by subjecting the sample aliquot and respective standard additions to the
13 sample preparation. However, both options are too time-consuming since must be
14 performed on each sample.
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26 Since the developed evaluation procedure can be applied to the determination of a
27 concentration c in mol L^{-1} , a mass concentration γ in mg L^{-1} , a mass fraction w in mg kg^{-1}
28 or any other magnitude, the general description of the methodology uses q for
29 quantity, while γ is used for the determination of the mass concentrations of the studied
30 analytes.
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36 The way systematic effects are managed (i.e. by recovery correction or calibrators
37 processing) impacts on the measurement uncertainty. When calibrators are subjected to
38 a complex processing, their values are more uncertain than when calibrators only
39 involve the dilution of a stock solution (neat calibrators). However, if results are
40 corrected for recovery, the uncertainty of the sample preparation impacts on the
41 correction factor (i.e. $1/\bar{R}$).
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48 This work discusses and compares the uncertainty of measurements corrected for
49 recovery or compensated for this recovery by taking processed calibrators. Top-down
50 evaluations are described since are more easily applied to complex measurements
51 [3,5,6,9]. This study also presents an equation for weighing the calculated mean
52 recovery with the degrees of freedom of the pooled recoveries. The equation for the
53 determination of the weighted mean recovery proposed by Palma et al. [6] is only
54 applicable when pooled recoveries are associated with the same degrees of freedom.
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1 The developed methodology was applied to the analysis of four Polycyclic
2 Aromatic Hydrocarbons, PAHs, in water samples by High-Performance Liquid
3 Chromatography with Fluorescence Detection, HPLC-FD, after analyte solid phase
4 extraction using Graphene/sepiolite, G/Sep, mixtures as sorbent in the extraction
5 process.
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10 Among the most problematic contaminants in the environment are PAHs, formed
11 by the incomplete combustion of organic matter by natural or anthropogenic processes
12 [10]. Several analytical procedures have been developed for PAHs analysis in different
13 types of water based on quantifications by LC-MS, GC-MS or HPLC-FD [11]. The
14 determination of PAHs by these chromatographic methods involves a demanding
15 sample preparation aiming at reducing instrumental quantification interferences,
16 concentrating the analyte in the sample solution and/or transferring the analyte to a
17 solvent that can be analysed by the chromatographic method [12]. The mass transfer
18 steps during the sample preparation are responsible for analyte losses that, if not
19 considered, can underestimate the analyte level in the sample.
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31 **2. THEORY**

32 **2.1 Top-down evaluation of the measurement uncertainty**

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37 The top-down evaluation of the measurement uncertainty involves quantifying and
38 combining the uncertainty associated with the intermediate precision, trueness and
39 additional uncertainty components. The additional uncertainty components are
40 responsible for systematic and/or random effects on the results that were not considered
41 in the first two components. These components are adequately combined using the law
42 of propagation of the uncertainty [3–6].
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49 The trueness uncertainty evaluation includes assessing if relevant systematic effects
50 are observed that can be overcome by correcting the result or by subjecting calibrators
51 to the same systematic effects that affect the sample. The assessment of the relevance of
52 systematic effects involves determining whether the mean recovery confidence interval
53 includes the ideal 100 % recovery [3–6]. This can be performed by checking whether
54 the following condition is valid: $|1 - \bar{R}|/u_T \leq t$ where u_T is the trueness standard
55 uncertainty, that is, the standard uncertainty associated with the mean recovery, and t is
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1 the value of the Student's t distribution for the degrees of freedom associated with u_T at
2 a 95 % confidence level. Frequently, the degrees of freedom associated with u_T are
3 those related with the estimated intermediate precision of the analyte recovery [5,6].
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6 Since the uncertainty varies with the measured level in a predictable way, the
7 analytical interval can be divided in two intervals where absolute or relative
8 uncertainties are approximately constant. In Interval I, below twice the Limit of
9 Quantification, $2q_{LOQ}$, the absolute standard uncertainty of the measurement is
10 estimated by: $u_q\langle I \rangle = (u_1^2\langle I \rangle + u_T^2\langle I \rangle + u_A^2\langle I \rangle)^{1/2}$, where $u_1\langle I \rangle$, $u_T\langle I \rangle$ and $u_A\langle I \rangle$ are the
11 standard uncertainties associated with precision, trueness and additional uncertainty
12 components, respectively, expressed in the measurement results units. Usually,
13 quantifications are performed above the Limit of Quantification, q_{LOQ} , making Interval
14 I extremely narrow [q_{LOQ} , $2q_{LOQ}$]. Below q_{LOQ} , the confidence interval for the
15 measurement results can predict negative measurand values, that is, the quantities
16 intended to be measured [2], which are impossible for concentrations, mass
17 concentrations or mass fractions. In such case, a Bayesian assessment of the
18 measurement results should be performed by taking into account prior knowledge [13–
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33 Above $2q_{LOQ}$, in Interval II, the relative measurement results become
34 approximately constant being estimated $u'_q\langle II \rangle$ (where $u'_q\langle II \rangle = u_q\langle II \rangle/q$; q is the
35 measured quantity and the apostrophe identifies relative parameters). In that case,
36 $u'_q\langle II \rangle$ is estimated by:
37 $u'_q\langle II \rangle = (u_1'^2\langle II \rangle + u_T'^2\langle II \rangle + u_A'^2\langle II \rangle)^{1/2}$, where $u_1'\langle II \rangle$, $u_T'\langle II \rangle$ and $u_A'\langle II \rangle$ are the
38 relative standard uncertainties associated with precision, trueness and additional
39 uncertainty components, respectively. In this case $u_q\langle II \rangle = qu'_q\langle II \rangle$.
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48 In addition, $u_1\langle I \rangle$ and $u_1'\langle II \rangle$ are estimated from the standard deviation or relative
49 standard deviation of the measurements performed at Interval I or II, respectively, under
50 intermediate precision conditions.
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54 Cordeiro et al. [5] and Palma et al. [6] described the quantification of trueness
55 uncertainty from different types of reference materials and for quantifying the impact of
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matrix effects on the measurement uncertainty. These researches did not consider the degrees of freedom of pooled recoveries in the mean recovery determination.

If the uncertainty components are not estimated from few experimental results, the combined uncertainty can be expanded to approximately 95 % or 99 % confidence level by using a coverage factor of 2 or 3, respectively.

2.2 Weighted mean recovery

This work proposes the determination of a weighted mean recovery, \bar{R}_w , by combining N mean recoveries, \bar{R}_i , ($i = 1$ to N) estimated from the analysis of different reference items in which mean recovery uncertainties, $u(\bar{R}_i)$, and respective degrees of freedom, ν_i , are considered in the weighing factors. ν_i is equivalent to the degrees of freedom of the standard deviation of the recoveries: $\nu_i = n_i - 1$; where n_i is the number of recovery tests used to estimate \bar{R}_i . Eq. (1) and Eq. (2) present the formulas used to estimate \bar{R}_w and the corresponding standard uncertainty, $u(\bar{R}_w)$.

$$\bar{R}_w = \frac{\sum_{i=1}^N \left(\frac{\bar{R}_i \nu_i}{u^2(\bar{R}_i)} \right)}{\sum_{i=1}^N \left(\frac{\nu_i}{u^2(\bar{R}_i)} \right)} \quad (1)$$

$$u_{\Gamma} = \sqrt{\frac{\sum_{i=1}^N \{ \bar{R}_i^2 u'^2(\bar{R}_i) \nu_i \}}{\sum_{i=1}^N \nu_i}} = \sqrt{\frac{\sum_{i=1}^N \left\{ \bar{R}_i^2 \left[\left(\frac{u_1(\bar{q}_i)}{\bar{q}_i} \right)^2 + \left(\frac{u(Q_i)}{Q_i} \right)^2 \right] \nu_i \right\}}{\sum_{i=1}^N \nu_i}} \quad (2)$$

where $u_1(\bar{q}_i)$ is the intermediate precision standard deviation associated with the estimated mean value, \bar{q}_i , of the i -th reference material and $u(Q_i)$ the standard uncertainty associated with the reference value Q_i . $u_1(\bar{q}_i)$ is the intermediate precision standard deviation of the mean, \bar{q}_i , equal to the standard deviation of the single measurements divided by $\sqrt{n_i}$.

3. EXPERIMENTAL

3.1 Chemicals and water samples

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AvanGRAPHENE, graphene powder with lamellar structural morphology comprising less than 6 layers with a thickness ≤ 2 nm and a specific surface of $480 \text{ m}^2 \text{ g}^{-1}$, was provided by Avanzare Innovación Tecnológica, SL (Logroño, Spain). High purity sepiolite (> 95 %), with composition of (wt %): 60.2 % SiO_2 , 1.7 % Al_2O_3 , 0.7 % Fe_2O_3 , 0.4 % CaO , 26.1 % MgO , 0.1 % Na_2O and 0.3 % K_2O , particle size smaller than $75 \mu\text{m}$ and a specific surface area of $290 \text{ m}^2 \text{ g}^{-1}$ was supplied by Sepiol SA (Azuqueca de Henares, Spain). Naphtalene (Nap, 99 %) was supplied by Sigma (Madrid, Spain), phenanthrene (Phe, 97 %) and pyrene (Pyr, 96 %) were supplied by Merck (Madrid, Spain) and benzo(a)pyrene (BaP, 96 %) was obtained from Sigma (Madrid, Spain). The surfactant polyoxyethylene-23-lauryl ether (Brij L23, $\text{C}_{12}\text{H}_{25}(\text{OCH}_2\text{CH}_2)_{23}\text{OH}$, $\text{Mw} = 1198.56 \text{ g mol}^{-1}$, $\text{CMC} = 91 \mu\text{M}$) was purchased from Sigma (Madrid, Spain). All the reagents were of analytical grade and were used without further purification. The aqueous solutions were prepared using ultrapure water obtained from a Milli-Q system (Millipore, Milford, USA).

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A stock solution of PAHs (1000 mg L^{-1}) was prepared by weighing the appropriate amount and filling up to 25 mL with methanol. Then, another stock solution ($1000 \mu\text{g L}^{-1}$) was prepared by diluting with methanol, which was subsequently diluted to prepare the calibrators (i.e. standard solutions). The PAHs solutions were stored at $4 \text{ }^\circ\text{C}$ in dark.

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Water samples were taken at the entrance and exit of sewage treatment plants in Móstoles, from the exit of sewage treatment plants in Sevilla and Cádiz (Spain), and from a river that flows along an industrial area in Alcalá de Henares (Spain). No PAHs were detected in the water samples.

3.2 Instruments

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HPLC measurements were carried out on a chromatographic system equipped with a binary LC pump 250 (Perkin-Elmer, Massachusetts, USA), a manual six-port Rheodyne injection valve with a $20 \mu\text{L}$ loop, a Jet-Stream Plus column thermostat (Knauer, Berlin, Germany), and a 200 series programmable fluorescence detector (Perkin-Elmer, Massachusetts, USA). The fluorescence detector was programmed at the maximum excitation and emission wavelengths of each PAH by changing the parameters before each analyte elution. These values were 280 nm/335 nm from 0 min to 4 min (for Nap), 250 nm/365 nm from 4 min to 6 min (for Phe), 335nm/ 374 from

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6 min to 8 min (for Pyr) and 295 nm/ 405 nm from 8 min to the end of the chromatogram (for BaP). The acquisition and processing of the chromatographic data was carried out using TotalChrom v6.3.2 software (Perkin-Elmer, Massachusetts, USA). The analytical column was a KhromaPhase RP-18 (5 μm , 150 \times 4.6 mm), from Scharlab (Barcelona, Spain). The degasification of the mobile phases was carried out in an Ultrasounds-3000683 ultrasonic bath (Selecta, Barcelona, Spain).

A mechanical stirrer Vibromatic (Selecta, Barcelona, Spain) was used for shaking the mixtures that were centrifuged using a Digicen refrigerated centrifuge (Ortoalresa, Madrid, Spain).

3.3 Sample preparation and HPLC-FD quantification

The five samples were filtered with a 0.45 μm pore size nylon syringe filter, spiked between two to five times the Limit of Quantification (Nap: 1.00 $\mu\text{g L}^{-1}$, Phe: 0.80 $\mu\text{g L}^{-1}$, Pyr: 1.50 $\mu\text{g L}^{-1}$ and BaP: 0.70 $\mu\text{g L}^{-1}$), subjected to a Dispersive Solid-Phase Extraction, dSPE, [17] where 10 mg of the sorbent (G/Sep: 2/98 w/w) was added to 50 mL of sample, shaken for 5 min, centrifuged for 5 min and separated. The PAH were desorbed from the sorbent with 10 mL of Brij L23 100 mM aqueous solution and the extracts quantified by HPLC-FD after calibration. These calibrators were used directly to calibrate the chromatograph (Neat Calibrators, NC) or subjected to the same preparation performed on samples (Adjusted Calibrators, AC). The instrumental signal has a homoscedastic variance and varies linearly with the analyte concentration. The homoscedasticity and linearity were tested by the Levene's test and ANOVA lack-of-fit test, respectively, for a 99 % confidence level.

Four samples were used for the top-down measurement uncertainty evaluation (MUE) and one of the samples was used for an independent control (IC) of the uncertainty evaluation. **Table 1** presents the spiked samples used for the analysis.

3.4 Validation procedure

Two measurement procedures were validated: involving the calibration of the HPLC-FD with NC or AC to the solid phase extraction used for the analysis of the samples.

1 The alternative measurement procedures, based on NC or AC, were validated
2 through the analysis of samples spiked slightly above twice the LOQ, $2\gamma_{\text{LOQ}}$ (mass
3 concentration symbol γ). The γ_{LOQ} was estimated as 10 times a maximum repeatability
4 standard deviation observed close to this limit (i.e. less than five times different than the
5 limit) [18].
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10 The performance was assessed between $2\gamma_{\text{LOQ}}$ and $5\gamma_{\text{LOQ}}$ since it can be used to
11 overestimate the absolute or relative uncertainty below or above that level, respectively.
12 This approach allows a cost-effective assessment of the measurement procedure.
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17 The results from the analysis of the spiked samples were used to evaluate precision
18 and trueness uncertainty components. After combining the uncertainty components and
19 expanding the combined uncertainty, the relative expanded uncertainties were compared
20 with a relative target expanded uncertainty of 50 % [19, 20]. This target value was
21 defined by taking the target expanded uncertainty defined for the demanding control of
22 drinking waters by European Union legislation. The Commission Directive 2015/1787
23 [21], to be enforced at the beginning of 2020, defines a target expanded uncertainty of
24 50 % for the maximum permissible value. Although most wastewater and river waters
25 have more complex matrices than drinking waters, there is no need to define a larger
26 target uncertainty.
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36 **3.5 Independent assessment of the uncertainty evaluation**

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38 The developed uncertainty models were tested through the analysis of five spiked
39 samples. The metrological compatibility, i.e. metrological equivalence [2], between the
40 reference ($\gamma_{\text{Ref}} \pm 2u_{\text{Ref}}$) and estimated analyte concentrations ($\gamma \pm 2u_{\gamma}$) proves
41 uncertainty evaluation was adequate. These two results are compatible if the following
42 conditions is valid:
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$$48 |\gamma - \gamma_{\text{Ref}}| \leq 3 \sqrt{u_{\gamma}^2 + u_{\text{Ref}}^2} \quad (3)$$

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53 this assessment being performed at approximately 99 % confidence level. Eq. (3)
54 assesses if the absolute measurement error ($|\gamma - \gamma_{\text{Ref}}|$) is smaller than its expanded
55 uncertainty (right term of the equation) for approximately 99 % confidence level.
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2 **4. RESULTS AND DISCUSSION**
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5 **Tables 2 and 3** summarise the performance of PAHs measurements in water based
6 on HPLC with neat, NC, or adjusted, AC, calibrators, respectively.
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10 It can be observed that the LOQ is slightly larger or, for BaP, two times larger than
11 for AC. LOQ differences are not in agreement with intermediate precision differences
12 since the LOQ was estimated under repeatability conditions.
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16 The intermediate precision standard deviation from quantifications based on NC
17 and AC are equivalent for a 99 % confidence level with the exception for Nap
18 determination where AC improved precision significantly. The trueness standard
19 uncertainties are equivalent for both calibration types.
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24 The analyte recovery is lower when NC are used, being the difference larger for
25 Nap. However, the processing of calibrators does not avoid the need for correcting the
26 measurement results for low recovery, which is attributed to matrix effects observed in
27 the analysis of complex solutions. If adjusted calibrators were spiked wastewaters,
28 probability the recovery would become metrologically equivalent to 100 %.
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35 In these examples, the estimated mean and weighted mean recoveries are only
36 different at the fourth or fifth significant figure.
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40 The uncertainty of measurements based on NC or AC are equivalent with the
41 exception for Nap quantification where the processing of calibrators reduces the relative
42 expanded uncertainty significantly from 9.9 % to 3.5 %. All the evaluated measurement
43 uncertainties are smaller than the target relative expanded uncertainty of 50 %.
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48 Therefore, the processing of calibrators improved significantly measurements
49 affected by relevant systematic effects.
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53 The performed uncertainty evaluation was 100 % successful when applied to the
54 analysis of five spiked samples independent of the ones considered in the top-down
55 uncertainty evaluation. The estimated measurement results are metrologically
56 compatible with the reference values, for a 99 % confidence level, given the respective
57 uncertainties.
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2 **5. CONCLUSIONS**
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5 The developed methodology for the top-down evaluation of the measurement
6 uncertainty was successfully used to assess and compare the uncertainty of PAHs
7 measurements in water based on HPLC calibrations with neat calibrators or calibrators
8 subjected to a process equivalent to that of the sample. The trueness uncertainty was
9 estimated by calculating a weighted mean recovery in which weighing factors decrease
10 with recovery uncertainty and increase with the respective degrees of freedom. It can be
11 concluded that the expanded measurement uncertainty can be significantly reduced
12 when calibrators are subjected to the sample pre-treatment if large analyte losses are
13 observed. Regarding Nap, 51.3 % of the analyte is lost during the sample preparation
14 and processing calibrators reduce the relative expanded uncertainty from 9.9 % to
15 3.5 %. In this work, the processing of calibrators did not avoid the need for analyte
16 recovery correction observed in the analysis of wastewaters and river waters due to
17 differences in the matrix effects between calibrators and samples. The developed
18 uncertainty evaluation was successfully applied to the analysis of spiked samples
19 independent of those used for uncertainty calculations. All the estimated results for the
20 five spiked samples are metrologically compatible with the reference value for a 99 %
21 confidence level (20 comparisons for the four analytes). The estimated measurement
22 uncertainty is smaller than the defined target (i.e. maximum admissible) uncertainty
23 (50 % of the measured value).
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Table 1. Spiked samples analysis used for measurement uncertainty evaluation (MUE) and for an independent control (IC) of this evaluation.

Reference	Type of water	Use	Number of replicates
Ref. 1	Móstoles sewage water plant – Influent	MUE	5
Ref. 2	Móstoles sewage water plant – Effluent	MUE	10
Ref. 3	Cádiz sewage water plant – Effluent	MUE	5
Ref. 4	Alcalá de Henares – River	MUE	5
Ref. A to E	Sevilla sewage water plant – Effluent	IC	5

Note: Samples were spiked close to two times the Limit of Quantification and analysed under intermediate precision conditions.

Table 2. Performance of PAH measurements in waters based on calibrations with neat calibrators (NC).

Analyte:	Naphthalene	Phenanthrene	Pyrene	Benzo(a)Pyrene
γ_{LOQ} ($\mu\text{g/L}$):	0.21	0.24	0.47	0.16
γ_{SL} ($\mu\text{g/L}$):	1.00	0.80	1.50	0.70
$u_{\text{I}}\langle\text{I}\rangle$ ($\mu\text{g/L}$) ^a :	0.046	0.041	0.018	0.015
$u'_{\text{I}}\langle\text{II}\rangle$ (%):	4.6	5.1	1.2	2.2
u_{T} (absolute):	0.010	0.030	0.010	0.010
Mean recovery, R (%):	48.7	91.5	78.6	70.1
Weighted mean rec., R_{w} (%):	48.7	91.5	78.6	70.1
Is R_{w} equivalent to 100 %:	No	No	No	No
$u_{\gamma}\langle\text{I}\rangle$ ($\mu\text{g/L}$):	0.050	0.048	0.026	0.018
$u_{\gamma}'\langle\text{II}\rangle$:	5.0	5.9	1.9	2.8
$U_{\gamma}\langle\text{I}\rangle$ ($k = 2$) ($\mu\text{g/L}$):	0.10	0.097	0.052	0.037
$U_{\gamma}'\langle\text{II}\rangle$ ($k = 2$) (%):	9.9	12	3.7	5.7
Compatibility of estimated and reference values:	5 in 5	5 in 5	5 in 5	5 in 5
$U_{\gamma}^{\text{tg}}\langle\text{I}\rangle$ ($\mu\text{g/L}$) ^b :	0.50	0.40	0.75	0.35
$U_{\gamma}^{\text{tg}}\langle\text{II}\rangle$ (%):	50	50	50	50

γ_{LOQ} - Limit of quantification; γ_{SL} - Samples' spiking level; Interval I: Between γ_{LOQ} and γ_{SL} ; Interval II: Above γ_{SL} ; ^a - $u_{\text{I}}\langle\text{I}\rangle = u'_{\text{I}}\langle\text{II}\rangle \cdot \gamma_{\text{SL}}$; ^b - $U_{\gamma}^{\text{tg}}\langle\text{I}\rangle = U_{\gamma}^{\text{tg}}\langle\text{II}\rangle \cdot \gamma_{\text{SL}}$.

Table 3. Performance of PAH measurements in waters based on calibrations with adjusted calibrators (AC).

	Analyte: Naphthalene	Phenanthrene	Pyrene	Benzo(a)Pyrene
γ_{LOQ} ($\mu\text{g/L}$):	0.28	0.32	0.69	0.31
γ_{SL} ($\mu\text{g/L}$):	1.00	0.80	1.50	0.70
$u_{\text{I}<\text{I}>}$ ($\mu\text{g/L}$) ^a :	0.010	0.038	0.030	0.016
$u'_{\text{I}<\text{II}>}$ (%):	1.0	4.7	2.0	2.3
u_{T} (absolute):	0.013	0.017	0.014	0.018
Mean recovery, R (%):	94.0	92.5	97.0	94.9
Weighted mean rec., R_{w} (%):	94.0	92.5	97.0	94.9
Is R_{w} equivalent to 100 %:	No	No	No	No
$u_{\gamma}<\text{I}>$ ($\mu\text{g/L}$):	0.017	0.040	0.037	0.021
$u_{\gamma}'<\text{II}>$:	1.7	5.1	2.4	3.0
$U_{\gamma}<\text{I}>$ ($k = 2$) ($\mu\text{g/L}$):	0.034	0.081	0.074	0.042
$U_{\gamma}'<\text{II}>$ ($k = 2$) (%):	3.5	10	4.9	5.9
Compatibility of estimated and reference values:	5 in 5	5 in 5	5 in 5	5 in 5
$U_{\gamma}^{\text{tg}<\text{I}>}$ ($\mu\text{g/L}$) ^b :	0.50	0.40	0.75	0.35
$U_{\gamma}^{\text{tg}<\text{II}>}$ (%):	50	50	50	50

γ_{LOQ} - Limit of quantification; γ_{SL} - Samples' spiking level; Interval I: Between γ_{LOQ} and γ_{SL} ; Interval II: Above γ_{SL} ; ^a - $u_{\text{I}<\text{I}>} = u'_{\text{I}<\text{II}>} \cdot \gamma_{\text{SL}}$; ^b - $U_{\gamma}^{\text{tg}<\text{I}>} = U_{\gamma}^{\text{tg}<\text{II}>} \cdot \gamma_{\text{SL}}$.