



IMEP-23: the eight WFD PAHs in water in presence of humic acid

Interlaboratory Comparison Report

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Ofelia Bercaru, Marina Ricci, Berit Sejerøe-Olsen, Penka Shegunova and Andrea Bau'**



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Contents

1	Summary	5
2	IMEP support to EU policy	5
3	Introduction	6
4	Scope and aim	7
5	Time frame	8
6	Test material	8
	6.1 General remarks	8
	6.2 Preparation	8
	6.3 Blanks	9
	6.4 Homogeneity	10
	6.5 Stability	10
	6.6 Distribution	11
7	Participant invitation, registration and information	11
	7.1 Confidentiality and participation fees	13
	7.2 Sample reconstitution, measurement and reporting	13
8	Reference values and their uncertainties	14
	8.1 Target values	14
	8.2 Reference laboratory measurements	14
	8.3 Establishing reference values and uncertainties	15
9	Reported results	18
	9.1 General observations	18
	9.2 Measurement results	19
10	Scoring of results	21
	10.1 The scores and their settings	21
	10.2 Scoring the reported measurement results	22
11	Further information extracted from the results	23
	11.1 Methods of analysis	23
	11.2 A representative study	23
	11.3 Use of standards	24
	11.4 Determination of uncertainty	24
	11.5 Comments	25
12	Conclusion	25
	Acknowledgements	26
	Abbreviations	27
	References	28
	Annexes	29

1 Summary

The Water Framework Directive (WFD) 2000/60/EC provides a legislative framework for the protection of inland and coastal waters in the EU. Decision 2455/2001/EC defines the major (priority) water pollutants and Proposal 2006/0397/EC their maximum levels. These include seven polycyclic aromatic hydrocarbons (PAHs): naphthalene, anthracene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*a*]pyrene, indeno[1,2,3-*cd*]pyrene and benzo[*ghi*]perylene, plus fluoranthene as an indicator substance.

These eight PAHs are the subject of this study. The matrix is ground water with humic acid which was added to simulate colloidal organic matter in surface water. The PAH concentrations were set close to the levels of the Proposal when practically feasible. The concentrations of six congeners were certified (i.e. given a reference value plus the associated uncertainty) whereas only indicative values could be attributed to benzo[*a*]pyrene and benzo[*ghi*]perylene.

The presence of humic acid made the certification campaign very complicated. PAHs adsorb onto humic acid and this can lead to material losses that may remain undetected if no internal standard is used or the internal standard is given insufficient time to reach the adsorption equilibrium before further sample treatment. There are indications that a number of participating routine laboratories have overlooked this effect.

The 59 participants were invited via different channels: the IMEP Regional Coordinators, the IRMM website, the European Co-operation for Accreditation, the International Committee for Protection of the Danube River and the International Committee for Protection of the Rhine.

z scores were calculated with a target standard deviation of 20% of the reference value. Reported results for the two uncertified congeners were not assessed. The scores were satisfactory for approximately 80% of the participants. In addition, zeta scores were calculated for those participants who had reported an uncertainty estimate. These were however less satisfactory on average.

In summary, the measurement capabilities of those laboratories involved in routine PAH measurements in the frame of the WFD appear quite positive, despite some clear points for improvement.

2 IMEP support to EU policy

The International Measurement Evaluation Programme IMEP is organised by the Joint Research Centre - Institute for Reference Materials and Measurements. IMEP provides support to the European measurement infrastructure in the following ways:

- IMEP **distributes metrology** from the highest level down to the field laboratories. These laboratories can benchmark their measurement result against the IMEP certified reference value. This value is established according to metrologically best practice.
- IMEP helps laboratories to assess their estimate of **measurement uncertainty**. The participants are invited to report the uncertainty on their measurement result. IMEP integrates the estimate into the scoring, and provides assistance for the interpretation.

IMEP supports EU policies by organising intercomparisons in the frame of specific EU Directives, or on request of a specific Directorate-General. IMEP-23 provided specific support to the following stakeholders:

- the **European Co-operation for Accreditation (EA)** in the frame of a formal collaboration on a number of metrological issues, including the organisation of intercomparisons. National accreditation bodies were invited to nominate a limited number of laboratories for free participation in IMEP-23. Mr. André Barel from RvA, the Dutch Accreditation Council liaised between EA and IMEP for this intercomparison. This report does not discern the EA nominees from the other participants. Their results are however summarised in a separate report to EA.
- the **International Committee for Protection of the Danube River (ICPDR)** and the **International Committee for Protection of the Rhine (ICPR)** in the frame of the IRMM support to the WFD. These committees coordinate the water quality monitoring activities of these two largest river basins in Europe. Laboratories involved in these activities were invited via these committees to participate in IMEP-23.

3 Introduction

The Water Framework Directive (WFD) 2000/60/EC [1] is the most substantial piece of EU water legislation to date. It requires all inland and coastal waters to reach "good status" by 2015. The WFD requires establishment of a river basin district structure within which demanding environmental objectives are set. The WFD is complemented by Decision 2455/2001/EC [2] defining priority chemical substances, and Proposal 2006/0397/EC [3] defining their maximum levels. Priority substances include pesticides, herbicides, bulk industrial chemicals, trace metals, solvents and other chemicals, among them PAHs.

Polycyclic Aromatic Hydrocarbons (PAHs) arise from the incomplete combustion of recent and fossil organic matter in flames, engines and industrial processes, from emissions of non-combustion derived matter and from the post-depositional transformation of biogenic precursors. Many PAHs are environmental pollutants that can have a detrimental effect on the flora and fauna of affected habitats. Their uptake in food chains may lead to serious health problems and genetic defects in humans.

Consequently, some of them are listed as priority pollutants for remediation. These are naphthalene, anthracene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*a*]pyrene, indeno[1,2,3-*cd*]pyrene and benzo[*ghi*]perylene. Fluoranthene is listed as an indicator substance for other, more dangerous PAH congeners.

PAHs enter **surface waters** via atmospheric fallout, urban runoff, municipal effluents and oil spillage or leakage. The concentrations of dissolved PAHs in water are very low due to their hydrophobic nature. PAHs associate easily with particulate organic matter and are finally deposited onto the sediment. Natural organic matter has a complex structure containing different organic compounds, primarily stemming from the decay of plants. This material is present in all water sources and the majority exists as water soluble, colloidal aquatic humic substances or *humic acid*. Recent studies show that a considerable degree of PAHs in surface water can be adsorbed onto humic acid [4].

4 Scope and aim

This ILC aims at laboratories with PAH monitoring activities in the frame of the WFD. Parameters are the PAH congeners listed in Decision 2455/2001/EC at levels approximating those laid down in Proposal 2006/0397/EC [2,3] where practically feasible.

Measurands and matrix

Measurands are the total concentrations of naphthalene, anthracene, fluoranthene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*a*]pyrene, indeno[1,2,3-*cd*]pyrene and benzo[*ghi*]perylene. The matrix is ground water with humic acid which was added to simulate colloidal organic matter in surface water.

Envisaged participants

This ILC aims in particular at laboratories from the Rhine and Danube river basin monitoring networks and other laboratories involved in similar activities, nominated by EA. A comparison of laboratory results within these sub groups is subject to separate analyses.

Subsidiary aims

This ILC also aims at generating input into the WFD Chemical Monitoring Activity (CMA) expert group in which (amongst others) quality assurance and quality control issues for WFD monitoring are discussed. A further aim of this ILC is to study whether the sample kit configuration is fit for its purpose. The sample constituents (water, humic acid and PAHs) are stored in separate containments to enhance their stability. The participants were asked whether this setup meets their requirements. IRMM will use this knowledge for the development of certified reference materials.

Part of IMEP

The organisation of the ILC follows the standard procedures of IMEP, the International Measurement Evaluation Programme of the Institute for Reference Materials and Meas-

urements (IRMM) of the Joint Research Centre, a Directorate-General of the European Commission. This programme is accredited according to ISO Guide 43-1. The designation of this interlaboratory comparison is IMEP-23.

5 Time frame

From May to July 2007, ICPR and ICPDR were invited to approach laboratories within their networks for participation. In the same time, EA was invited to nominate laboratories in the frame of the EA-IRMM collaboration agreement. Further laboratories were contacted via the IMEP regional coordinators and publicly invited via the IMEP website in September 2007. Registration opened on 4 July 2007 and closed on 30 September 2007. A confirmation of registration was sent to the participants in the first week of September, and the samples were dispatched in the second week. Reporting deadline was 9 November 2007. This deadline was extended by one week for four participants who received the samples late. The participants received a set of preliminary graphs showing the results of all participants in November 2007. The homogeneity and stability studies were carried out between May and October 2007. Certification of the sample material was done between November 2007 and January 2008.

6 Test material

6.1 General remarks

The sample kit consisted of two bottles with 500 ml groundwater each, a crimp-cap amber glass bottle with 15 ml of a humic acid solution in water and an ampoule with 5 ml of a PAH solution in acetonitrile. The three materials were kept separately until use to enhance stability. Details of the sample preparation, stability and homogeneity are given below. Further details on these issues are included in a separate report that is available from the ILC organiser on request [5].

6.2 Preparation

Preparation of the groundwater samples

The sampling of the groundwater took place in April 2007 in Bree, Belgium with the support of the Flemish Environmental Agency (see Figure 1). The well from which the water was taken is part of the groundwater monitoring network of the Flanders region. The water was pumped up, filtered over a 0.45 µm membrane filter and filled into a 200 l polyethylene drum. To allow sedimentation, the drum was stored at 4 °C at IRMM for about one month. Then the water was filtered through a 0.2 µm membrane filter and filled into 500 ml polypropylene bottles. These bottles were stored at 4 °C until dispatch.

Figure 1: Pumping up water from a well in Flanders



Preparation of the humic acid solution

Three aliquots of 7.5 g humic acid each (Fluka, technical grade) were weighed into three beakers. The beakers were filled with 500 ml MilliQ water each and placed in a sonication bath for 1 h at 40 °C to enhance dissolution. Then the content of the beakers was centrifuged and filtered through a 0.45 µm membrane filter. The filtrates were pooled. The humic acid concentration of the resulting solution was approx. 2 g·l⁻¹. Crimp-cap amber glass bottles of 30 ml volume were filled with 15 ml solution each. These bottles were stored at 4 °C until dispatch.

Preparation of the PAH spiking solution

For the preparation of the spiking solution, high purity crystalline substances provided by IRMM and Dr. Ehrenstorfer (Augsburg, Germany) were used. For each PAH an individual stock solution was prepared as follows. From each individual congener, an aliquot of 10 to 30 mg was weighed on a semi-microbalance and dissolved in approx. 25 ml of a mix of acetonitrile and toluene (in case of benzo[ghi]perylene) or acetonitril only (all other congeners). The IMEP PAH spiking solution was obtained by mixing and diluting aliquots from these stock solutions. Amber glass ampoules of 10 ml volume were filled with 5 ml PAH solution each. The ampoules were filled with argon and sealed in April 2007. They were stored at 4 °C until dispatch.

6.3 Blanks

The humic acid powder was free of measurable PAH amounts as previously demonstrated in [4]. The water sample contained naphthalene at a level below the LOQ (8 ng·l⁻¹).

6.4 Homogeneity

Homogeneity studies were carried out by VITO and IRMM on the humic acid and PAH solutions, respectively.

The relative between bottle standard deviation s_{bb} of the humic acid samples is 3.3%. This is considered negligible considering the excess humic acid present in the final sample solution. The relative between bottle standard deviation s_{bb} of the PAH spike solution samples is $\leq 4.7\%$ for each of the congeners (see Table 1). Par. 8.3 describes how heterogeneity data were included in the measurement uncertainties associated with the PAH reference values. These uncertainties play a role in the calculation of the zeta scores.

Both ISO 13528 [6] and the IUPAC Harmonised Protocol [7] describe tests to determine whether an ILC material is sufficiently homogeneous for its purpose. Essentially, these tests compare the between bottle heterogeneity with the standard deviation for proficiency assessment $\hat{\sigma}$. Both tests indicate that the PAH solution is sufficiently homogeneous for all congeners in the frame of this ILC. Calculations are included in annex 1.

Table 1: Homogeneity and stability data for the eight PAHs

	Heterogeneity s_{bb} [%]	Instability due to storage during two months @ 18°C, s_{its} [%]
Naphthalene	1.0	0.4
Anthracene	4.7	0.6
Fluoranthene	1.6	0.6
Benzo[<i>b</i>]fluoranthene	1.5	1.1
Benzo[<i>k</i>]fluoranthene	2.9	1.1
Benzo[<i>a</i>]pyrene	1.8 *	1.0
Indeno[1,2,3- <i>cd</i>]pyrene	3.6	0.6
Benzo[<i>ghi</i>]perylene	1.2 *	0.9

* This is the relative maximum heterogeneity that could be hidden by method repeatability (u_{bb}^*). It is larger than (and therefore replaces) the relative between bottle standard deviation s_{bb} .

6.5 Stability

A stability study with isochronous setup at two temperatures (18 °C and 60 °C) was carried out by IRMM with the aim to:

- find suitable temperature conditions for sample dispatch to the participants. Linear regression of the stability data indicated sufficient stability of both the humic acid and the PAH solutions for a one week dispatch at 60 °C. It was thus decided to dispatch under uncooled conditions.
- quantify the potential degradation during the entire interlaboratory comparison study (approximately two months). The certifiers and participants were instructed to store the material ≤ 18 °C after receipt. Under these conditions, the humic acid solutions showed only marginal (0.9%) degradation. This was considered negligible in view of the excess humic acid present in the solutions of the final samples. The degradation of the PAH solution was demonstrated to be $\leq 1.1\%$ for each of the congeners.

Par. 8.3 describes how stability data were included in the measurement uncertainties associated with the PAH reference values. These uncertainties play a role in the calculation of the zeta scores. Details of the long term stability study are included in annex 2. Table 1 summarises the results.

6.6 Distribution

The ILC samples were dispatched to the participants by IRMM on 10 and 11 October 2007. Each participant received two packages. Package 1 contained one ampoule with a 5 ml solution of the PAHs in acetonitrile. It was labelled as "dangerous goods in excepted quantities". Package 2 contained two bottles with 500 ml water each, one bottle with a 10 ml humic acid solution in water, a letter with instructions on sample handling, reconstitution and reporting and a form to confirm receipt of the packages.

The stability tests on the PAH and humic acid solutions (see par. 6.5) show that there was no significant degradation of the samples to be expected during the period of dispatch. The dispatch was followed by the messenger's parcel tracking system on internet. In a few cases, the dispatch took longer than the one-week period. It was however assumed that the parcel was not submitted continuously during this period to the high temperatures that were used to assess the short term stability, and that potential degradation was still negligible.

7 Participant invitation, registration and information

Invitations for participation were sent via the IMEP Regional Coordinators for distribution to potentially interested laboratories in their countries (cf. annex 3) as well as to the EA (cf. annex 4), and the ICPR and ICPDR (cf. annex 5) contact persons for distribution to nominated, resp. interested laboratories. The instructions also informed on the confidentiality of results and the fee for participation. A call for participation was also released on the IRMM website.

A confirmation of registration was sent to those participants who had registered (cf. annex 6). This confirmation contained further details on the envisaged time frame. Instructions on measurands, sample storage, reconstitution and measurement were sent to the participants together with the samples. The instructions also contained the individual code for access to the result reporting website (cf. annex 7).

The participants who had submitted a result received a set of preliminary graphs showing the results of all participants two weeks after the reporting deadline. The reference values were not available at that time, and not included in the graphs. Table 2 lists the participating countries, the regional coordinators involved in IMEP-23, the number of registrations and the number of reported results.

Table 2: Participating countries, number of reported results and regional coordinators

Country	Coordinating body	Number of registrations and results	
		reg.	res.
Australia		2	2
Belgium		2	2
Bosnia and Herzegovina	University of Sarajevo	2	2
Cyprus	State General Laboratory	1	1
Czech Republic	Czech Metrology Institute	3	3
Denmark	Danish Fundamental Metrology	3	3
Finland		2	2
France	Bureau National de Metrologie	7	7
Germany	Federal Institute for Materials Research and Testing	2	2
Greece	Aristotle University of Thessaloniki	2	2
Hungary	National Office of Measures	2	2
Ireland		1	0
Israel		4	3
Latvia	Latvian National Accreditation Bureau	1	1
The Netherlands	NMI Van Swinden Laboratorium	3	3
Norway	National Veterinary Institute	3	3
Poland	Warsaw University	2	2
Portugal	Associação dos Laboratórios Acreditados de Portugal	3	3
Romania	National Institute of Metrology	2	2
Serbia	Bureau of Measures and Precious Metals	2	2
Slovakia	Slovak Institute of Metrology	3	3
Slovenia	Metrology Institute of the Republic of Slovenia	1	1
Spain		2	2
Sweden	Swedish National Testing and Research Institute	2	2
Taiwan		1	1
Ukraine		1	0
United Kingdom	LGC Ltd.	3	3

7.1 Confidentiality and participation fees

EA was invited to nominate laboratories for participation. The following confidentiality statement was made to EA: "Confidentiality of the participants and their results towards third parties is guaranteed. However, IMEP will disclose details of the participants that have been nominated by EA to the EA working group for ILCs in Testing. The EA accreditation bodies may wish to inform the nominees of this disclosure."

Laboratories involved in WFD related monitoring activities in the Danube and Rhine basins were approached via the respective Committees. These Committees received an invitation letter for the dissemination to the laboratories stating that the "measurement results will be disclosed to the European Co-operation for Accreditation (EA) in an anonymous way, i.e. without disclosing your identity".

Laboratories nominated by EA were exempt of charge, as were those laboratories that are involved in Danube and Rhine basin water quality monitoring activities in the frame of the WFD, and who had been approached via the respective Committees. The participation fee for other laboratories was € 200.

7.2 Sample reconstitution, measurement and reporting

The letter accompanying the samples provided the following instructions for sample reconstitution: "Take one bottle of IMEP-23 ground water and transfer approximately 450 ml into a 500 ml glass volumetric flask. Take the bottle IMEP-23 humic acid and shake it for 1 min. Then take 1 ml from the bottle by means of a pipette and add it to the volumetric flask. Shake thoroughly the volumetric flask for 1 minute. Take 1 ml of the IMEP-23 PAH spiking solution by means of a 1 ml glass pipette and add it into the water sample by immersing the tip of the pipette into water (just below the water surface) and let the solution flow out of the pipette by gravity (don't blow out). Shake the volumetric flask manually for 1 minute and fill up to the mark with IMEP-23 ground water. Shake the volumetric flask manually again for another minute to achieve good homogeneity. Please pay attention not to lose any drops of sample while shaking. Now leave the solution for 24 h in a cold and dark place (e.g. refrigerator). Shake the flask again for one minute after this period. The sample is now ready to be treated according to your laboratory procedure. Proceed immediately with the analysis."

Laboratories were instructed to perform two independent analyses, one per water bottle. They were asked to report both measurement values and the mean, together with its associated uncertainty with the expansion factor. Participants were invited to follow their routine procedures. The results were to be reported in the same manner (e.g., number of significant figures) as those normally reported to the customer.

Participants used an online form to report their measurement results and complete the related questionnaire (cf. annex 8). They received an individual code to access this online form. Optional reporting units were $\text{mg}\cdot\text{l}^{-1}$ and $\text{ng}\cdot\text{l}^{-1}$.

8 Reference values and their uncertainties

8.1 Target values

Table 3 lists the maximum tolerable concentrations of the eight PAHs according to Proposal 2006/0397/EC [3]. The concentrations in IMEP-23 are based on both these requirements and the current measurement capability of routine laboratories.

Table 3: Maximum concentrations for the PAHs cf. Proposal 2006/0397/EC

	Proposed maximum concentrations [$\text{ng}\cdot\text{l}^{-1}$]
Naphthalene	1200
Anthracene	100-400
Fluoranthene	100-1000
Benzo[<i>b</i>]fluoranthene	30 in total
Benzo[<i>k</i>]fluoranthene	
Benzo[<i>a</i>]pyrene	50-100
Indeno[1,2,3- <i>cd</i>]pyrene	2 in total
Benzo[<i>ghi</i>]perylene	

8.2 Reference laboratory measurements

Two reference laboratories were selected as certifiers of the sample material: the Federal Institute for Materials Research and Testing BAM (Berlin, Germany) and the Vlaamse Instelling voor Technologisch Onderzoek VITO (Mol, Belgium). Both have a proven record for this type of measurements. The results of their certification measurements are included in Table 4.

Procedure

BAM and VITO followed the same sample preparation protocol as the ILC participants. Both prepared six samples: three for measurement on one day, three for measurement on the next day as to reach intermediate precision conditions. Both laboratories submitted their measurement results between December 2007 and January 2008.

BAM measurements

The measurements by BAM were performed on a GC/MS under routine conditions. The results were in good agreement with the IRMM weighing values for most of the congeners. However, large deviations from the weighing values (20%) were observed for naphthalene and anthracene. Moreover, the reported uncertainties seemed unduly small for all congeners.

To clarify these issues renewed measurements were done on three samples using a column with improved resolution. The results of these measurement were close to the values measured earlier for six of the eight congeners, whereas the values for naphthalene and anthracene now appeared much closer to the weighing values.

The six original measurement results for naphthalene and anthracene were thus rejected and replaced by the three improved results. The results for the other congeners were established as follows. The three *original* results from the day 1 sample were combined with the three *new* results from the day 2 sample. In this way, the BAM approach reached nearly reproducibility conditions. This also caused the small uncertainties reported earlier to increase.

VITO measurements

VITO performed GC/MS measurements under routine conditions. Their results were in good agreement with the results from BAM and the IRMM weighing values for five congeners. For benzo[*a*]pyrene, indeno[1,2,3-*cd*]pyrene and benzo[*ghi*]perylene however, the values were considerably lower than those from BAM and the weighing values.

Understanding the differences

The key to understanding these unexpected differences is the moment when the internal standard was added to the sample. Both BAM and VITO used a mixture of deuterated PAHs including the eight congeners as internal standard. BAM reconstituted the sample from its components and waited one day before adding the internal standard and another day before further analysis. VITO however reconstituted the sample and waited one day, after which it added the internal standard and proceeded to sample analysis.

The one-day period had been added to the sample reconstitution protocol by the ILC organiser to facilitate adsorption of the PAH congeners onto the humic acid, a well-known process that can take several hours to complete.

Similarly, if an internal standard is added just before analysis and given insufficient time to reach the adsorption equilibrium, its recovery is higher than the recovery of the sample and this leads to an underestimation of the measurand.

This effect is known to increase with increasing hydrophobicity and ring number. The underestimation is relatively small for the 2, 3 and 4 ring congeners and can be very large for the 5 and 6 ring congeners, e.g. 60% for benzo[*ghi*]perylene [4]. This effect can explain the different concentrations for the larger congeners as reported by BAM and VITO.

8.3 Establishing reference values and uncertainties

Establishing reference values

The explicit aim of the ILC was to determine *total* concentrations, and thus the BAM values were given priority over the VITO values for establishing the reference values. IRMM weighing values were only used as supportive information since they originate from the

preparation of the stock solutions with no correction for any potential losses due to e.g. adsorption and evaporation up to the stage of sample reconstitution. Accordingly, the following policy was used to establish the reference values X_{ref} :

- Scenario a:** BAM and VITO values in agreement and confirmed by the weighing value.
Then: X_{ref} established from BAM and VITO values.
- Scenario b:** BAM and VITO values in agreement but not confirmed by the weighing value. Then: X_{ref} established from BAM and VITO values.
- Scenario c:** BAM value not in agreement with VITO value but confirmed by the weighing value. Then: X_{ref} established from BAM value.
- Scenario d:** BAM, VITO and weighing values not in agreement.
Then: X_{ref} established from BAM value but only indicative.

In scenarios a and b the reference values were calculated by averaging the two values. A correction for the naphthalene concentration measured in the water blank sample (see par. 6.3) was not made because it was below LOQ and already included in the reported certification measurement values.

Table 4 lists the measurement results obtained by BAM and VITO as well as the weighing values, the scenarios followed and the resulting IMEP-23 reference values X_{ref} . Colours were used in the table for clarity. Green indicates agreement, orange disagreement between measurement results. Agreement was assumed if the zeta score equation $|X_1 - X_2| \leq 2\sqrt{(u_1^2 + u_2^2)}$, which is a pragmatic simplification of the calculations described in [8]. Uncertainties listed in the table are standard uncertainties.

Table 4: Values from weighing and characterisation measurements by BAM and VITO. All uncertainties are standard uncertainties if not stated otherwise. All values in [ng.l⁻¹]

Compound	Characterisation										Homogeneity	Stability	IMEP Reference Values			Comments
	Weigh.	BAM Results		VITO Results		Combination		U _{char}	U _{bb} (*)	U _{lis} (*)			X _{ref}	U _{ref}	U _{ref} (§)	
		X _{weigh}	X _{BAM}	U _{BAM}	X _{VITO}	U _{VITO}	Scenario									
Naphthalene	127	127.3	9.1	125	17	a (BAM, VITO)	10	2.4	0.6	126	11	22				
Anthracene	106	110.6	4.9	113	7.9	a (BAM, VITO)	5	5.4	0.8	112	8	16				
Fluoranthene	92.4	94.4	6.6	85.5	6.0	a (BAM, VITO)	4	1.9	0.7	90	5	10				
Benzo[b]fluoranthene	83.0	77.3	1.6	76.3	4.6	b (BAM, VITO)	3	1.5	1.2	77	4	8				
Benzo[k]fluoranthene	85.0	84.1	3.8	79.7	10	a (BAM, VITO)	5	2.8	1.2	82	6	12				
Benzo[a]pyrene	78.4	68.8	2.5	57.2	4.0	d (BAM)	-	-	-	69	-	-	indicative			
Indeno[1,2,3-cd]pyrene	71.0	69.9	1.9	47.5	7.1	c (BAM)	2	3.2	0.5	70	4	8				
Benzo[ghi]perylene	88.6	80.1	2.4	57.1	11	d (BAM)	-	-	-	80	-	-	indicative			

(*) Calculated from the measurements on the undiluted PAH ampoules, and then divided by a factor of 500 which is the dilution factor of the solution.
 (§) This is an expanded uncertainty with a coverage factor k=2 which corresponds to a level of confidence of about 95%, as defined in the GUM [12]

Establishing associated uncertainties

The uncertainties associated with the reference values were calculated by propagating contributions for characterisation (u_{char}), homogeneity (u_{bb}) and stability between the moment of measurement by the routine laboratories and certification (u_{ITS}) as follows [9]:

$$u_{\text{ref}} = \sqrt{(u_{\text{char}}^2 + u_{\text{bb}}^2 + u_{\text{ITS}}^2)} \quad (\text{all standard uncertainties})$$

The uncertainties of characterisation u_{char} were calculated from the uncertainties reported by BAM and VITO following the same scenarios that were discussed in par 8.3. Where both BAM and VITO values were taken into account, they were combined as follows [8]:

$$u_{\text{char}} = [\sqrt{(u_{\text{bam}}^2 + u_{\text{vito}}^2)}] / 2 \quad (\text{all standard uncertainties})$$

Table 4 lists the uncertainty contributions u_{char} , u_{bb} and u_{ITS} for each of the congeners. No u_{ref} was determined where X_{ref} is only indicative.

Summary: reference values and their uncertainties

Table 4 lists the IMEP-23 reference values X_{ref} and their associated standard uncertainties u_{ref} and expanded uncertainties U_{ref} ($k=2$).

9 Reported results

9.1 General observations

From the 62 laboratories that registered for participation, 59 submitted their results and completed the associated questionnaire and 3 cancelled their participation. One laboratory reported for each congener only a "<" sign which was treated as not reporting. Some laboratories did not report values for all of the congeners, or reported that one or more values were below their limit of quantification (LOQ). Such values were not assessed. Most of participants however reported measurement values for all of the eight congeners.

A few reported results showed anomalies that could be interpreted as mistakes. One participant reported results that were a factor 1000 higher than expected. They would have led to insensible z scores and the erroneous results were thus considered as being not reported. Another participant reported a mean with an uncertainty that was significantly larger than the reported value itself and completely out of line with the other uncertainties reported by that participant. One laboratory reported for the uncertainty of each of the congeners a coverage factor of approx. 100. All mistakes in the uncertainty statements remained uncorrected and were included in the zeta score calculations as such.

It was noted that some of the laboratories reported values that were uncorrected regarding their analytical recoveries despite the definition of the measurands as "total concentra-

tions". This phenomenon was not systematically investigated but it could well be that some of the reported results are lower than expected because they were not corrected.

One laboratory reported one value for benzo[*b*]fluoranthene and benzo[*k*]fluoranthene together because of coelution. This value was not useable in the frame of this ILC and thus neglected. One of the laboratories who reported a "<" value indicated that its methods were used to determine PAHs in soil, i.e. when much larger quantities were available. A similar remark was made several times, i.e. the amount of water provided was not always sufficient.

The laboratories were asked to perform two replicates, and to report them together with the mean, its associated uncertainty and the expansion factor. Some laboratories also reported the uncertainty associated with the single replicate results. These laboratories typically derived the uncertainties of the means by averaging the uncertainties of the single measurements, which is fundamentally incorrect. One laboratory reported only one replicate per congener. One laboratory asked, *how do you calculate the "uncertainty value", and what is the "coverage factor"*.

9.2 Measurement results

Annexes 9-16 list the individual measurement results and display overview graphs. The graphs show a roughly normal distribution with no irregularities. There are however a few peculiarities.

Tendency towards lower concentrations

It appears that the distribution of the results is not symmetric around the reference value: the lower concentrations outweigh the higher for all congeners. This tendency may be due to participants underestimating the effect of adsorption onto the humic acid. This can easily happen when no internal standard is used, or when the internal standard is added too late in the analytical process, see the discussion in par. 8.2.

The kernel density plots displayed in annex 17 seem to confirm this assumption. The plots of the five and six ring congeners show an increased tailing towards lower concentrations. That is, a number of laboratories underestimates the influence of adsorption which is known to be an issue especially for the larger congeners.

Method dependence

A detailed analysis of the kernel density plots reveals a further tendency. The plots can be considered as the sum of two different distributions stemming from the two methods of analysis. Approximately half of the participants used HPLC with fluorescence detector, the other half GC/MS as the method of analysis. There were only a few exceptions in the type of detection. Measurement results obtained with HPLC are frequently characterised by a larger median than those obtained with GC, whilst the robust standard deviation remains comparable. These data are listed in Table 5 and exemplarily visualised for indeno[1,2,3-*cd*]pyrene in Figure 2.

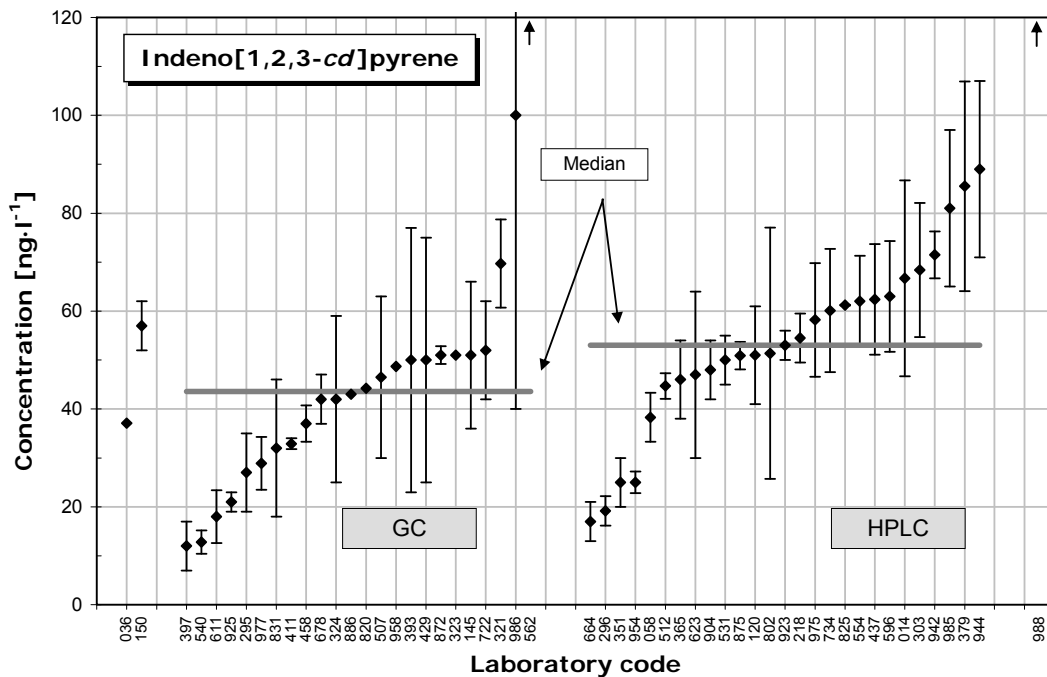
A two-tailed *t* test however shows that the means of both populations are not significantly different at the level of 95% confidence for most congeners (see the p values in Table 5). Nevertheless, the same trend can be observed for seven of the eight congeners and this may add an additional dimension which is subject of further study outside the frame of this interlaboratory comparison.

Table 5: Robust estimates of the mean and standard deviation for different sets of results

	X_{rob} [ng·l ⁻¹] (*)			sd_{rob} [ng·l ⁻¹] (*)			Two-tailed <i>t</i> test
	All data	GC	HPLC	All data	GC	HPLC	p ($\alpha=0.05$)
Naphthalene	120	120	112	33	33	38	0.77
Anthracene	89	83	99	16	11	15	0.01
Fluoranthene	83	77	90	18	16	15	0.13
Benzo[<i>b</i>]fluoranthene	69	70	69	22	24	18	0.91
Benzo[<i>k</i>]fluoranthene	73	73	73	20	21	18	0.57
Benzo[<i>a</i>]pyrene	63	57	64	20	18	19	0.59
Indeno[1,2,3- <i>cd</i>]pyrene	50	44	53	17	12	13	0.23
Benzo[<i>ghi</i>]perylene	65	50	69	25	26	14	0.09

(*) X_{rob} is the median, sd_{rob} the robust standard deviation calculated as 1.5·MAD, the median absolute deviation

Figure 2: A comparison of analytical methods



The software used to calculate robust statistics and kernel densities was provided by the Statistical Subcommittee of the Analytical Methods Committee (AMC) of the Royal Society of Chemistry [10,11].

10 Scoring of results

10.1 The scores and their settings

Individual laboratory performance is expressed in terms of z and zeta scores in accordance with ISO 13528 [6] and the IUPAC International Harmonised Protocol [7]:

$$z = \frac{X_{\text{lab}} - X_{\text{ref}}}{\hat{\sigma}} \quad \text{and} \quad \text{zeta} = \frac{X_{\text{lab}} - X_{\text{ref}}}{\sqrt{u_{\text{ref}}^2 + u_{\text{lab}}^2}}$$

Where

X_{lab} is the measurement result reported by a participant

X_{ref} is the certified reference value (assigned value)

u_{ref} is the standard uncertainty of the reference value

u_{lab} is the standard uncertainty reported by a participant

$\hat{\sigma}$ is the standard deviation for proficiency assessment

Both scores can be interpreted as: satisfactory result for $|\text{score}| \leq 2$, questionable result for $2 < |\text{score}| \leq 3$ and unsatisfactory result for $|\text{score}| > 3$.

z score

The IMEP-23 z score indicates whether a laboratory is able to perform the measurement in accordance with what can be considered as good practice within the EU. The standard deviation for proficiency assessment $\hat{\sigma}$ is accordingly based on experience with ILCs organised earlier by IRMM, performance criteria set by other ILC providers, and the measurement results reported by the ILC participants.

The IUPAC International Harmonised Protocol [7] suggests that participants can apply their own scoring settings and recalculate the scores if the purpose of their measurements is different.

In this ILC, $\hat{\sigma} = 0.2 \cdot X_{\text{ref}}$ for those congeners where a reference value was established: naphthalene, anthracene, fluoranthene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene and indeno[1,2,3-*cd*]pyrene. No reference value was established for benzo[*a*]pyrene and benzo[*ghi*]perylene, and the participants' measurement results were not scored for these congeners. ILC participants are however advised to compare their measurement results with the results obtained by other laboratories for these two compounds.

zeta score

The zeta score provides an indication of whether the estimate of uncertainty is consistent with the laboratory's deviation from the reference value [7]. It is calculated only for those results that were accompanied by an uncertainty statement. The interpretation is similar to the interpretation of the z score. An unsatisfactory zeta score may be caused by an underestimated uncertainty or by a large deviation from the reference value.

The standard uncertainty of the laboratory (u_{lab}) was calculated as follows. If an uncertainty was reported, it was divided by the coverage factor k . If no coverage factor was provided, the reported uncertainty was considered as the half-width of a rectangular distribution. The reported uncertainty was then divided by $\sqrt{3}$, in accordance with recommendations issued by Eurachem and CITAC [12].

10.2 Scoring the reported measurement results

A z score was calculated for all participants except for those who reported no value, a "<" value or an obviously erroneous value (see also par. 9.1). These results were not used in any statistical calculation. A zeta score was calculated for results that were accompanied by an uncertainty statement. Annexes 9-16 list the scores per congener and laboratory in detail, and annex 18 summarises the scores per participant.

Table 6 summarises the scores per congener. A large share of participants reported satisfactory measurement results, a small share unsatisfactory results. This observation shows that the participants performed quite well. Other ILCs with similar results are frequently operated with higher concentrations or broader assessment criteria, see e.g. [13].

Table 6: Overview of scores: S(atisfactory), Q(uestionable), U(nsatisfactory)

	z score				zeta score				both z and zeta scores
	S	Q	U	n (*)	S	Q	U	n (*)	
Naphthalene	81%	6%	13%	47	68%	10%	22%	41	28
Anthracene	86%	12%	2%	49	51%	19%	30%	43	22
Fluoranthene	87%	11%	2%	53	64%	17%	19%	48	30
Benzo[b]fluoranthene	78%	12%	10%	50	61%	9%	30%	46	28
Benzo[k]fluoranthene	80%	14%	6%	51	66%	2%	32%	47	30
Benzo[a]pyrene	no scoring				no scoring				
Indeno[1,2,3-cd]pyrene	68%	13%	19%	53	35%	13%	52%	48	16
Benzo[ghi]perylene	no scoring				no scoring				

(*) n is the number of results for which a score was given.

The total number of participants (with and without a score) is 59.

Most of the participants provided an uncertainty estimate, and most of these estimates were accompanied by a coverage factor. These encouraging figures contrast with the modest share of results with a satisfactory zeta score. It shows that many laboratories still encounter difficulties to provide a reasonable uncertainty estimate. This may also be due to a lack of experience in uncertainty estimation: more than half of the participants stated that they do not usually report the uncertainty to their customers. These laboratories are well advised to become familiar with the principles of uncertainty estimation as described by the GUM [12] and in related guidance for the field of analytical chemistry, e.g. the EURACHEM / CITAC Guide [14].

11 Further information extracted from the results

In addition to submission of the results, the participants were asked to answer a number of questions relating to the measurements. All participants completed the questionnaire. Issues that may be relevant to the outcome of the intercomparison are discussed below.

11.1 Methods of analysis

There is not much variation in the sample preparation. Only three laboratories applied a filtration step. Approximately two-third of the laboratories used liquid-liquid extraction with n-hexane, cyclohexane, petroleum ether, dichloromethane or methanol. One-third of the laboratories used solid phase extraction, usually with acetonitrile and/or dichloromethane. One laboratory used polydimethylsiloxane stir bar sorption. There is no obvious correlation between the type of extraction and the measurement results.

The only two methods of analysis that were applied are GC and HPLC. Approximately half of the participants used HPLC with fluorescence detector, the other half GC/MS as the method of analysis. There were only very few exceptions in the type of detection. The differences between the measurement results obtained with GC and HPLC are discussed in par. 9.2.

11.2 A representative study

All but two laboratories indicated that the measurements were done by their routine analyst and with their routine methods. Most participants appeared to be experienced or very experienced: 83% indicated to analyse at least 50 samples, 46% at least 250 samples per year, only 17% less than 50 samples per year. On average, the laboratories had a number of years experience in the field (robust mean: 9 years, robust standard deviation: 7 years). Most of the participants (89%) stem from various countries in Europe with a good distribution among these countries, 11% stems from other countries. These figures suggest that IMEP-23 has representatively studied the current capability of European laboratories for routine control measurements of the eight WFD PAHs in water.

11.3 Use of standards

Internal or external standards were used by virtually all participants. They used:

- no standard (2 laboratories);
- an internal standard only (21 laboratories), usually deuterated compounds;
- an external standard only (26 laboratories), usually certified PAH mixtures;
- both an internal and an external standard (10 laboratories).

The laboratories were asked to specify their internal standards (if any). These appeared to differ from the eight PAHs in almost all cases. Frequently, a mix of several deuterated isotopes was used that matched only part of the eight PAH congeners. Some laboratories used a single surrogate standard only. The question arises whether these relatively simple mixtures are suitable to mimic the different behaviour of all eight congeners.

Recoveries were determined by 35 laboratories and were for all congeners typically around 80-90% (robust mean) with a robust standard deviation of 12-18%. Some of the laboratories may have reported measurement results without correction for recovery, despite definition of the measurands as "total concentrations" of the eight PAH congeners. This approach was explicitly confirmed by two laboratories in the course of the result reporting process but not studied in further detail.

Many of the reported recoveries may appear too high for the larger congeners. The degree of PAH adsorption by the humic acid may be correctly accounted for if an internal standard is added well before sample treatment (see par. 8.2). It is assumed that many participants overlooked the importance of equilibration and thus reported too optimistic recoveries.

11.4 Determination of uncertainty

A very high share of 90-95% (depending on the measurand) of the participants reported a measurement uncertainty. About 85% of this group also provided a coverage factor. These figures are very high when compared with earlier IMEP studies. Many participants (50%) however do not usually report the uncertainty to their customers.

The basis of the reported uncertainty estimates is (more than one reply possible) ... :

- in-house method validation (mentioned 24x)
- measurement of replicates (i.e. precision) (mentioned 13x)
- use of interlaboratory comparison data (mentioned 11x)
- ISO Guide to the Expression of Measurement Uncertainty (mentioned 10x)
- known uncertainty of the standard method (mentioned 6x)
- expert judgement (mentioned 1x)

Most of the laboratories who based their uncertainty on replicate measurements used this as the only source of their estimate. They are likely to underestimate their uncertainty by excluding other sources of uncertainty.

11.5 Comments

The questionnaire invited laboratories to provide comments. It was suggested (10 times) to provide one liter of water sample and (7 times) to make the online reporting process shorter and smoother.

12 Conclusion

IMEP-23 studied the capability of analytical laboratories to measure total concentrations of the eight WFD PAHs in the presence of humic acid in a water matrix. Humic acid was added as a simulation of natural colloidal organic matter and is known to adsorb PAHs. As explained in recent literature this requires timely addition of a standard. If an internal standard is added just before analysis and given insufficient time to reach the adsorption equilibrium, its recovery is higher than the recovery of the sample and this leads to an underestimation of the measurand.

This effect was exemplarily demonstrated by one of the two laboratories involved in the test material certification. It had added the internal standard just before analysis and reported very low concentrations for three of the largest congeners. Though not studied in detail, there are clear indications that a number of the participating routine laboratories followed the same approach. These laboratories are strongly recommended to update their methods of analysis.

The concentrations of six congeners were certified and the reported results scored against these values. On average 80% of the z scores was satisfactory. No scores were calculated for benzo[*a*]pyrene and benzo[*ghi*]perylene as their concentrations could not be certified. Zeta scores were calculated when an uncertainty estimate was reported. On average these were less satisfactory than the z scores and this shows that many laboratories encounter difficulties to provide a reasonable uncertainty estimate.

In summary, the measurement capabilities of laboratories involved in routine PAH measurements in the frame of the WFD appear positive, despite points for improvement.

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Abbreviations

AMC	Analytical Methods Committee of the Royal Society of Chemistry
BAM	Bundesanstalt für Materialforschung und –prüfung
CITAC	Co-operation for International Traceability in Analytical Chemistry
CMA	Chemical Monitoring Activity
CRM	Certified Reference Material
EA	European Co-operation for Accreditation
EC	European Commission
ERM	European Reference Materials
EU	European Union
EURACHEM	A focus for Analytical Chemistry in Europe
GC	Gas Chromatography
GUM	Guide to the Expression of Uncertainty in Measurement
HPLC	High pressure liquid chromatography
ICPDR	International Committee for Protection of the Danube River
ICPR	International Committee for Protection of the Rhine
ILC	Interlaboratory Comparison
IMEP	International Measurement Evaluation Programme
IRMM	Institute for Reference Materials and Measurements
ISO	International Organisation for Standardisation
IUPAC	International Union for Pure and Applied Chemistry
JRC	Joint Research Centre
LOQ	Limit of Quantification
MS	Mass Spectrometry
PAH	Polycyclic Aromatic Hydrocarbon
SI	International System of Units
VITO	Vlaamse Instelling voor Technologisch Onderzoek
WFD	Water Framework Directive

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Annexes

Annex 1: Homogeneity tests	31
Annex 2: Stability tests	32
Annex 3: Invitation sent via regional coordinators	33
Annex 4: Invitation to EA to nominate laboratories	34
Annex 5: Invitation to ICPR and ICPDR to nominate laboratories	35
Annex 6: Confirmation of registration	36
Annex 7: Instructions for measurement and reporting.....	38
Annex 8: Questionnaire	40
Annex 9: Results for Naphtalene	42
Annex 10: Results for Anthracene	44
Annex 11: Results for Fluoranthene.....	46
Annex 12: Results for Benzo[<i>b</i>]fluoranthene.....	48
Annex 13: Results for Benzo[<i>k</i>]fluoranthene	50
Annex 14: Results for Benzo[<i>a</i>]pyrene.....	52
Annex 15: Results for Indeno[1,2,3- <i>cd</i>]pyrene.....	54
Annex 16: Results for Benzo[<i>ghi</i>]perylene	56
Annex 17: Kernel densities.....	58
Annex 18: Summary of lab scores.....	59

Annex 1: Homogeneity tests

	Naphthalene		Anthracene		Fluoranthene		Benzo[b]fluoranthene		Benzo[k]fluoranthene		Benzo[a]pyrene		Indeno[1,2,3-cd]pyrene		Benzo[ghi]perylene	
Measurement results [$\mu\text{g}\cdot\text{l}^{-1}$]																
Bottle Nr.	R1	R2	R1	R2	R1	R2	R1	R2	R1	R2	R1	R2	R1	R2	R1	R2
102	80,9	81,6	63,6	62,0	57,8	57,9	49,2	51,3	51,0	49,0	41,1	42,8	41,7	41,3	55,4	55,3
31	79,6	80,5	61,2	62,7	57,2	57,9	51,5	49,0	48,4	47,5	43,7	41,5	43,5	42,8	57,4	56,9
52	80,2	79,4	60,6	61,2	57,7	57,6	50,2	49,2	45,6	47,9	44,1	44,2	44,7	43,5	52,0	54,8
120	81,0	81,0	59,4	60,3	58,6	58,5	50,1	48,0	45,9	46,9	43,4	44,9	44,3	42,8	57,4	53,0
160	82,9	82,9	59,0	59,0	58,0	59,6	50,9	51,0	46,8	47,5	44,5	44,4	45,0	44,2	53,5	54,9
89	80,3	80,2	57,4	58,0	57,9	59,0	51,7	49,9	48,9	49,5	39,6	46,8	45,0	46,1	55,0	53,1
145	80,9	80,4	59,7	57,9	57,7	56,5	47,2	49,6	44,7	46,9	45,2	43,6	45,8	42,7	56,0	53,4
71	79,9	80,4	57,5	56,5	57,7	57,5	50,6	50,0	47,1	46,4	43,7	46,3	45,1	45,2	53,3	55,3
45	81,6	81,9	55,6	55,7	58,4	58,1	51,3	49,6	51,4	49,0	45,9	45,6	47,7	44,5	54,9	55,5
111	80,2	83,1	55,7	55,8	58,4	57,2	52,6	50,9	46,2	51,2	44,0	43,0	45,1	45,8	55,8	53,8
116	82,7	82,8	55,9	55,5	57,0	56,6	52,7	52,4	47,8	51,8	43,1	41,0	45,5	44,0	55,0	55,6
50	78,7	80,7	53,5	52,8	59,9	57,9	49,0	53,4	48,7	49,9	44,2	43,6	42,4	45,4	56,1	54,6
Mean	81.0		58.2		57.9		50.5		50.5		43.8		44.3		54.9	
$\hat{\sigma}$ (20%)	16.2		11.6		11.6		10.1		10.1		8.78		8.86		11.0	
Homogeneity test according to the IUPAC International Harmonised Protocol [7] (values in [$\mu\text{g}^2\cdot\text{l}^{-2}$])																
s_{an}^2	0.623		0.469		0.478		10.1		2.73		3.21		1.57		2.12	
s_{sam}^2	0.884		8.15		0.195		0.204		1.06		0		0.763		0.178	
σ_{all}^2	23.6		12.2		12.1		9.17		8.35		1.72		1.77		2.71	
critical (value)	42.8		22.2		22.0		18.2		17.3		5.84		4.52		6.68	
$s_{sam}^2 \leq \text{critical} ?$	Yes		Yes		Yes		Yes		Yes		Yes		Yes		Yes	
Test result	passed		passed		passed		passed		passed		passed		passed		passed	
Homogeneity test according to ISO 13528 [6] (values in [$\mu\text{g}\cdot\text{l}$])																
$0.3 \hat{\sigma}$	4.86		3.54		3.48		3.01		2.87		2.63		2.66		3.29	
s_x	0.873		2.24		0.481		0.864		1.41		1.02		1.23		0.918	
s_w	0.675		0.665		0.552		1.14		1.42		1.74		1.05		1.42	
s_s	0.730		2.19		0.282		0.310		0.995		0		0.982		0	
$s_s \leq 0.3 \hat{\sigma} ?$	Yes		Yes		Yes		Yes		Yes		Yes		Yes		Yes	
Test result	passed		passed		passed		passed		passed		passed		passed		passed	

Notes

R1 denotes Replicate 1, R2 denotes Replicate 2. For all other abbreviations, see the respective references. The standard deviation for proficiency assessment $\hat{\sigma}$ that is used in this table was calculated as a fraction of the mean calculated from the homogeneity data, not as a fraction of the certified reference value.


Annex 2: Stability tests


	Naphthalene		Anthracene		Fluoranthene		Benzo[b]fluoranthene		Benzo[k]fluoranthene		Benzo[a]pyrene		Indeno[1,2,3-cd]pyrene		Benzo[ghi]perylene	
Measurement results (0, 1, 2 and 3 months @ 18°C) [$\mu\text{g}\cdot\text{l}^{-1}$]																
Months	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1
Bottle 1	79.34	80.28	66.78	66.77	56.4	57.7	54.8	52.0	50.4	50.0	42.7	43.1	46.3	45.1	51.6	52.3
Bottle 2	78.90	79.09	67.91	65.96	57.9	58.1	57.6	53.3	55.6	53.0	41.8	45.4	46.2	46.5	49.0	52.6
Bottle 3	81.29	80.79	66.62	66.57	57.3	55.9	54.3	56.3	53.8	54.9	42.9	42.1	46.4	47.3	53.7	50.5
Bottle 4	81.80	80.41	66.52	63.40	55.8	57.5	54	52.8	52.7	51.8	42.1	43.3	46.4	46.0	51.6	52.8
Months	2	3	2	3	2	3	2	3	2	3	2	3	2	3	2	3
Bottle 1	81.10	81.69	68.80	66.25	56.2	56.4	54.3	56.9	52.2	50.5	43.2	40.9	45.1	45.2	51.6	54.2
Bottle 2	80.04	79.69	67.43	66.46	59.3	57.1	55.9	58.2	54.9	54.6	43.7	44.5	44.8	47.3	51.9	52.8
Bottle 3	79.19	81.69	64.96	65.55	56.6	57.9	54.3	54.7	52.5	54.7	45.0	43.0	45.8	45.5	51.2	49.7
Bottle 4	81.15	80.61	67.02	67.32	58.7	58.1	55.2	52.2	51.8	51.3	44.5	44.1	47.1	46.8	53.1	50.8
Linear regression of the data (2 months @ 18°C)																
Slope	0.168		-0.032		0.121		0.211		-0.038		0.148		-0.014		0.067	
SE Slope	0.166		0.214		0.176		0.313		0.313		0.211		0.140		0.244	
Intercept	80.15		66.58		57.10		54.43		52.86		43.01		46.19		51.72	
SE Intercept	0.380		0.490		0.404		0.718		0.718		0.483		0.322		0.559	
Correlation coeff.	0.068		0.002		0.032		0.031		0.001		0.034		0.006		0.005	
Slope significant (99%) ?	no		no		no		no		no		no		no		no	
Test result	stable		stable		stable		stable		stable		stable		stable		stable	
Calculation of u_{ITS} (2 months @ 18°C)																
u_{ITS} [$\mu\text{g}\cdot\text{l}^{-1}$]	0.332		0.414		0.346		0.615		0.606		0.414		0.272		0.473	
u_{ITS} [%]	0.4		0.6		0.6		1.1		1.1		1.0		0.6		0.9	

Notes

u_{ITS} denotes the standard uncertainty associated with long term material stability

Annex 3: Invitation sent via regional coordinators

 **EUROPEAN COMMISSION**
DIRECTORATE-GENERAL
Joint Research Centre



Geel, 7 September 2007
IM/L/66/07
D04-IM(2007)D/20682 annex

To Laboratories involved in water quality monitoring activities
Re Launch of IMEP-23: The eight WFD PAHs

Dear Colleague,

The Institute for Reference Materials and Measurements (IRMM) launches IMEP-23, an intercomparison for the determination of the eight polycyclic aromatic hydrocarbons that are considered priority substances by the EU Water Framework Directive (WFD).

These substances are naphthalene, anthracene, fluoranthene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, indeno(1,2,3-cd)pyrene and benzo(ghi)perylene. The sample matrix is water with added humic acids.

A major characteristic of the study is its high metrological standard. This may be of particular interest to you if you are involved in water quality monitoring activities. The measurement results are evaluated against traceable reference values where possible, and if you provide an uncertainty statement it is included in the evaluation. Besides, the study helps you to benchmark yourself with your peers throughout Europe. The participation fee is 200 €, including dispatch. How do you register for participation:


1. **Enter** your laboratory details online at www.irmm.jrc.be/imepapp/registerForComparison.action?comparison=89
2. **Print** the completed form when the system asks you to do so
3. **Write** "RC" on the printout (which means you received this invitation via a regional IMEP coordinator, and not via another channel)
4. **Send** the printout to me preferably by fax or email (details see below)

Deadline for registration is **30 September 2007**. Your registration is only valid if you receive our written confirmation early October (the number of participants is restricted). Sample dispatch is scheduled for October. We are looking forward to receiving your registration!

With kind regards


Johanne| van de Kleeke

Johannes van de Kreeke
IMEP-23 Coordinator


Institute for Reference
Materials and Measurements

Reifesweg 111, 2440 Geel, Belgium
Tel.: +32 (0)14-571 882 • Fax: +32 (0)14-571 865
jrc-irmm-imep@ec.europa.eu • <http://www.irmm.jrc.be>

 **EUROPEAN COMMISSION**
DIRECTORATE-GENERAL
Joint Research Centre



Geel, 7 September 2007
IM/L/65/07
D04-IM(2007)D/20682

To the IMEP Regional Coordinators

Launching of IMEP-23: The 8 WFD priority PAHs

Dear Colleague,

In recent years you have kindly helped us to bring IMEP intercomparisons to the laboratories in your country. Now we are planning a smaller size intercomparison for which we ask your support: IMEP-23 - Determination of the 8 PAHs that are considered priority substances by the EU Water Framework Directive. The matrix is artificial river water: ground water with added humic acids.

Many laboratories who are active in this field have already been invited to participate via the European Co-operation for Accreditation and the respective management boards of the Danube and Rhine rivers.

However, other laboratories involved in water quality monitoring activities may also have an interest to participate since IMEP-23 sets particularly high metrological standards and enables laboratories to benchmark themselves with their peers in Europe.

We need your assistance to reach this group of laboratories. If you have such laboratories in your network, we kindly ask you to send them the attached invitation. The participation fee is 200 €. Deadline for registration is 30 September 2007.

This is all, there is no further action for you. We hope we can count on your support. Please inform us if you do not wish to, or cannot assume this task or if you have any questions or comments. Thank you very much for your assistance!

With kind regards from Belgium

Johanne| van de Kleeke

Johannes van de Kreeke
IMEP-23 coordinator

Attachment: Invitation for laboratories


Institute for Reference
Materials and Measurements

Reifesweg 111, 2440 Geel, Belgium
Tel.: +32 (0)14-571 882 • Fax: +32 (0)14-571 865
jrc-irmm-imep@ec.europa.eu • <http://www.irmm.jrc.be>

Annex 4: Invitation to EA to nominate laboratories

Registration of participants is open until **15 September 2007**. Distribution of the samples is foreseen for October 2007. In order to register, laboratories must:

1. **Enter** their details online:
www.irmm.jrc.be/imepapp/registerForComparison.action?comparison=89
2. **Print** the completed form when the system asks to do so
3. **Send** the printout to both the IMEP-23 and the EA-IMEP-23 coordinators:

IMEP-23 coordinator Mr. Johannes van de Kreeke Fax +32-14-571865 E-mail jrc-irmm-imep@ec.europa.eu	EA-IMEP-23 coordinator Mr. André Barel Fax + 31-30-2394539 E-mail andre.barel@va.nl
--	--


Please contact me if you have any questions or comments. We are looking forward to our cooperation!


With kind regards

Johanne | van de Kreeke

Johannes van de Kreeke
IMEP-23 Coordinator

Reflesweg, 2440 Geel, Belgium
Tel: +32-(0)14-571 862 • Fax: +32-(0)14-571 865
jrc-irmm-imep@ec.eu.int • <http://www.irmm.jrc.be>



 **EUROPEAN COMMISSION**
DIRECTORATE-GENERAL
Joint Research Centre

Geel, 4 July 2007
IM/L/56/07
D04-IM(2007)D/16069

Raad voor Accreditatie
T.a.v. Mr. André Barel
Postbus 2768
3500 GT Utrecht
Nederland

Dear André,

Intercomparison for PAHs in the frame of the WFD


The Institute for Reference Materials and Measurements (IRMM) organises an interlaboratory comparison for the determination of the eight polycyclic aromatic hydrocarbons (PAHs) that are considered as priority substances by the EU Water Framework Directive (WFD). The sample matrix is river water.

In the frame of the EA-IRMM collaboration agreement, IRMM kindly invites EA to nominate laboratories for free participation. These laboratories must be involved in river water quality monitoring activities and hold (or be in the process of obtaining) an accreditation for this type of measurement.


I suggest that you forward this invitation to the national EA accreditation bodies for their consideration. There is a maximum number of 50 samples at your disposal, i.e. ca. 2 nominees per country. Please notice that some of the laboratories may have already registered via parallel channels.

Confidentiality of the participants and their results towards third parties is guaranteed. However, IMEP will disclose details of the participants that have been nominated by EA to the EA working group for ILCs in Testing. The EA accreditation bodies may wish to inform the nominees of this disclosure.


Reflesweg, 2440 Geel, Belgium
Tel: +32-(0)14-571 862 • Fax: +32-(0)14-571 865
jrc-irmm-imep@ec.eu.int • <http://www.irmm.jrc.be>



Annex 5: Invitation to ICPR and ICPDR to nominate laboratories



EUROPEAN COMMISSION
DIRECTORATE-GENERAL
Joint Research Centre



Geel, 5 July 2007
IM/L/57/07
D04-IM(2007)0/16204

To Laboratories involved in Danube and Rhine water quality monitoring activities

Dear Colleague,

Intercomparison for PAHs in the frame of the WFD

The Institute for Reference Materials and Measurements (IRMM) organises an interlaboratory comparison for the determination of the eight polycyclic aromatic hydrocarbons (PAHs) that are considered as priority substances by the EU Water Framework Directive (WFD). The sample matrix is artificial river water.

IRMM supports the WFD and invites a restricted number of laboratories that are involved in Danube and Rhine water quality monitoring activities to participate free of charge. Registration of participants is open until **15 September 2007**. Distribution of the samples is foreseen for October 2007. In order to register, you should:

1. **Enter** your laboratory details online: www.irmm.jrc.be/imepapp/registerForComparison.action?comparison=89
2. **Print** the completed form when the system asks to do so
3. **Write** "DANUBE" or "RHINE" (or both) on the printout
4. **Send** the printout to the intercomparison coordinator:


IMEP-23 coordinator
Mr. Johannes van de Kreeke
Fax: +32-14-571865
E-mail: jrc-irmm-imep@ec.europa.eu

Please note that your measurement results will be disclosed to the European Cooperation for Accreditation (EA) in an anonymous way, i.e. without disclosing your identity. Please contact me if you have any questions or comments.

With kind regards

Johannes van de Kreeke

Johannes van de Kreeke
IMEP-23 Coordinator



Institute for Reference
Materials and Measurements

Rettlesweg, 2440 Geel, Belgium
Tel.: +32-(0)14-571 882 • Fax: +32-(0)14-571 865
jrc-irmm-imep@ec.eu.int • <http://www.irmm.jrc.be>

Annex 6: Confirmation of registration

From: VAN DE KREEKE, Johannes (JRC) on behalf of JRC IRMM IMEP
Sent: Wednesday 3 October 2007 14:10
To: JRC IRMM IMEP
Cc: 'siobodnik@ei.sk'; marc.braun@lkr.de
Subject: Confirmation: registration for IMEP-23
Dear colleague,

I confirm your registration for IMEP-23. You have been invited for participation via either the International Committee for the Protection of the Rhine (ICPR) or the International Committee for the Protection of the Danube River (ICPDR). For you this implies that there is no fee for participation.

The sample dispatch is scheduled for the second week of this month. Deadline for reporting your results is four weeks later. You will receive detailed instructions on sample handling and result reporting together with the samples.

Part of the material is so-called "Dangerous goods in excepted quantities". Please let me know in advance if you expect any customs issues. You can always contact me if you have any questions or need any help.

Met vriendelijke groeten / Mit freundlichen Grüßen / With kind regards
Johannes van de Kreeke

Dr. Johannes van de Kreeke
European Commission - Joint Research Centre
Institute for Reference Materials and Measurements
Retseweg 111, 2440 Geel, Belgium
Voice +32 14 571 682
Fax +32 14 571 865
Email jrc-irmm-imep@ec.europa.eu
<http://www.irmm.jrc.be>

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From: VAN DE KREEKE, Johannes (JRC) on behalf of JRC IRMM IMEP
Sent: Wednesday 3 October 2007 12:41
To: JRC IRMM IMEP
Cc: 'André Bare'
Subject: Confirmation: registration for IMEP-23
Dear colleague,

I confirm your registration for IMEP-23. You have been nominated for participation by your accreditation body in the frame of a collaboration agreement between the European Co-operation for Accreditation (EA) and IRMM. For you this implies that your measurement result may be disclosed to EA on their request, and that there is no fee for participation.

The sample dispatch is scheduled for the second week of this month. Deadline for reporting your results is four weeks later. You will receive detailed instructions on sample handling and result reporting together with the samples.

Part of the material is so-called "Dangerous goods in excepted quantities". Please let me know in advance if you expect any customs issues (probably not in Europe). You can always contact me if you have any questions or need any help.

Met vriendelijke groeten / Mit freundlichen Grüßen / With kind regards
Johannes van de Kreeke

Dr. Johannes van de Kreeke
European Commission - Joint Research Centre
Institute for Reference Materials and Measurements
Retseweg 111, 2440 Geel, Belgium
Voice +32 14 571 682
Fax +32 14 571 865
Email jrc-irmm-imep@ec.europa.eu
<http://www.irmm.jrc.be>

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From: VAN DE KREEKE Johannes (JRC) on behalf of JRC IRMM IMEP
Sent: Wednesday 3 October 2007 14:13
To: JRC IRMM IMEP
Subject: Confirmation: registration for IMEP-23

Dear colleague,

I confirm your registration for IMEP-23. The fee for participation is € 200 including dispatch. The sample dispatch is scheduled for the second week of this month. Deadline for reporting your results is four weeks later. You will receive detailed instructions on sample handling and result reporting together with the samples. Part of the material is so-called "dangerous goods in excepted quantities". Please let me know in advance if you expect any customs issues (probably not in Europe). You can always contact me if you have any questions or need any help.

Met vriendelijke groeten / Mit freundlichen Grüßen / With kind regards
Johannes van de Kreeke

Dr. Johannes van de Kreeke
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Email jrc-irmm-imep@ec.europa.eu
<http://www.irmm.jrc.be>

Disclaimer required under the terms and conditions of use of the internet and electronic mail from Commission equipment: The views expressed are purely those of the writer and may not in any circumstances be regarded as stating an official position of the European Commission.

Annex 7: Instructions for measurement and reporting

Preparing the samples for analysis
Please prepare the IMEP-23 samples following the protocol below. This protocol will yield two independent samples ready for one analysis each.

Perform the following operation for each bottle of IMEP-23 ground water. Take one bottle of IMEP-23 ground water and transfer approximately 450 ml into a 500 ml glass volumetric flask. Take the bottle IMEP-23 humic acid and shake it for 1 min. Then take 1 ml from the bottle by means of a pipette and add it to the volumetric flask. Shake thoroughly the volumetric flask for 1 minute. Take 1 ml of the IMEP-23 PAH spiking solution by means of a 1 ml glass pipette and add it into the water sample by immersing the tip of the pipette into water (just below the water surface) and let the solution flow out of the pipette by gravity (don't blow out). Shake the volumetric flask manually for 1 minute and fill up to the mark with IMEP-23 ground water. Shake the volumetric flask manually again for another minute to achieve good homogeneity. Please pay attention not to lose any drops of sample while shaking. Now leave the solution for 24 h in a cold and dark place (e.g. refrigerator). Shake the flask again for one minute after this period. The sample is now ready to be treated according to your laboratory procedure. Proceed immediately with the analysis.


The procedures you follow for this exercise should resemble as close as possible those that you use in routine sample analysis. Please keep in mind that collusion is contrary to professional scientific conduct and serves only to nullify the benefits of proficiency tests to customers, accreditation bodies, and analysts alike.

Result reporting
Please report your results online at www.immm.itc.be/imesapp/isp/loginResult.jsp. Your personal code for access is: **Code**. The website will guide you through the reporting procedure. Please enter for each parameter:

- In the space allocated for "measurement 1" and "measurement 2": the two measurement results and the technique you used, but not the uncertainty for each individual measurement
- In the space allocated for "measurement 3": the mean of these two results, the technique you used, and the uncertainty of the mean, including the expansion factor.

The results should be reported in the same form (e.g. number of significant figures) as those normally reported to the customer. After reporting your results, please complete the subsequent questionnaire. Do not forget to submit and confirm when required. Directly after completing the measurement results and questionnaire parts, you will be prompted to print the completed report form. Please do so, sign this paper version and return it to IRMM by fax or e-mail. Check your results carefully for any errors before submission, since this is your definitive confirmation.

Deadline for reporting the results is 9 November 2007.



EUROPEAN COMMISSION
JOINT RESEARCH CENTRE
Institute for Reference Materials and Measurements
Isotope measurements

Geel, 10 October 2007
IM/L/76/07
D04-IM(2007)D/23.543

Name
Company
Street
Address
Country

Subject: IMEP-23 - Determination of the 8 WFD priority PAHs in water

Dear Name,

Thank you very much for participating in IMEP-23, an interlaboratory comparison for the determination of the eight EU Water Framework Directive [1] priority PAHs in a matrix of simulated river water. Please find further relevant information regarding your participation below.

Packages and content
There are 2 sample packages mailed to you. They may arrive at the same time, or one after the other. You can start your analysis as soon as you have both packages.

- Package 1 contains two bottles with 500 ml water each, one bottle with a 10 ml humic acids solution in water, this letter, and a confirmation of receipt form
- Package 2 contains one ampoule with a 5 ml solution of the PAHs in acetonitrile

Please check whether the contents of the packages have remained undamaged during transport, and confirm undamaged receipt with the FAXBACK form. Please store the samples in a dark and cold (≤ 18 °C) place until analysis.

Measurands and matrix
Measurands are total concentrations of naphthalene, anthracene, fluoranthene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, indeno[1,2,3-*cd*]pyrene and benzo[*ghi*]perylene. The sample matrix is ground water with added humic acids.

Result assessment

Your results will be assessed against certified reference values and their uncertainties where available. The scores applied by IMEP are z and $zeta$ scores cf. ISO 13528 [2]. For each of the eight PAHs, the z score criterion for assessment (i.e. the denominator of the z score equation) will be approx. 15-20% of the respective reference value.

Your participation in this project is greatly appreciated. If you have any remaining questions, please contact me by e-mail: irc-irmm-imep@ec.europa.eu.

With kind regards

Johanne| van de Kreeke

Dr. Johannes van de Kreeke
IMEP-23 Coordinator

[1] Directive 2000/60/EC of the European Parliament and of the Council of 23 October 2000, establishing a framework for Community action in the field of water policy

[2] ISO 13528:2005; Statistical Methods for Use in Proficiency Testing by Interlaboratory Comparisons

Annex 8: Questionnaire

1. What is the level of confidence reflected by the coverage (k) factors?

I did not estimate the uncertainty

68%

95%

Other

If other, please specify:

2. What is the basis of your uncertainty estimate?

I did not estimate the uncertainty

uncertainty budget calculated according to ISO-GUM

known uncertainty of the standard method

uncertainty of the method as determined during in-house validation

measurement of replicates (i.e. precision)

expert judgement

use of interlaboratory comparison data

Other

If other, please specify:

3. Do you usually provide an uncertainty to your customers?
 Yes No

4. Did you use a filtration step in your sample preparation?:
 Yes No
 If yes, please provide further details (e.g. pore size):

5. Did you use an extraction step in your sample preparation?:
 Yes No
 If yes, please provide further details (e.g. method and solvent):

6. Did you use a chromatography step in your sample preparation?:
 Yes No
 If yes, please provide further details (e.g. LLE, SPE):

7. Further details on the sample preparation:

8. Did you use an external standard for quantification?
 Yes No
 If yes, which?:

9. Did you use an internal standard (similar material) for quantification?
 Yes No
 If yes, which?:

10. Did you use a standard addition (same material) for quantification?
 Yes No

11. In case you used a spike, at which moment did you add it to the sample?

I did not spike the sample material

before the 1-day equilibration of the materials

after the 1-day equilibration of the materials

after the sample preparation

Other

If other, please specify:

12. **Did you calibrate your instrument directly before the measurements?**
 Yes No

13. **Did you determine the recovery?**
 Yes No
 If yes, what was the recovery (R, %) for:
 naphthalene

 anthracene

 fluoranthene

 benzo[b]fluoranthene

 benzo[k]fluoranthene

 benzo[a]pyrene

 indeno[1,2,3-cd]pyrene

 benzo[ghi]perylene

14. **How many PAH in water samples does your laboratory analyse per year?**
 <50
 50-250
 >250

15. **Since when (approximately) does your laboratory analyse PAHs in water?**

16. **Is your laboratory accredited for the analysis of PAHs in water?**
 Yes No Partially
 If partially, please specify

17. **Were these samples analysed under routine conditions?**

	Yes	No
The samples were processed by the routine analyst if no, please specify	<input type="radio"/>	<input type="radio"/>
<input type="text"/>		
The samples were processed using your routine analytical methods if no, please specify	<input type="radio"/>	<input type="radio"/>
<input type="text"/>		

18. **Do you have any comments regarding the questions above (max. 150 characters)?**

19. **Protocol for reconstitution of the samples**

	Yes	No
Was the text easy to understand?	<input type="radio"/>	<input type="radio"/>
Was the procedure easy to put into practice?	<input type="radio"/>	<input type="radio"/>
Comments and suggestions for improvement:		
<input type="text"/>		

20. **Sample set**

	Yes	No
Were the sample containments (bottles, ampoules) easy to handle?	<input type="radio"/>	<input type="radio"/>
Was the water volume adequate to mimic your daily practice?	<input type="radio"/>	<input type="radio"/>
Does the matrix simulate your routine samples well enough?	<input type="radio"/>	<input type="radio"/>
Comments and suggestions for improvement:		
<input type="text"/>		

21. **Overall opinion of the set**

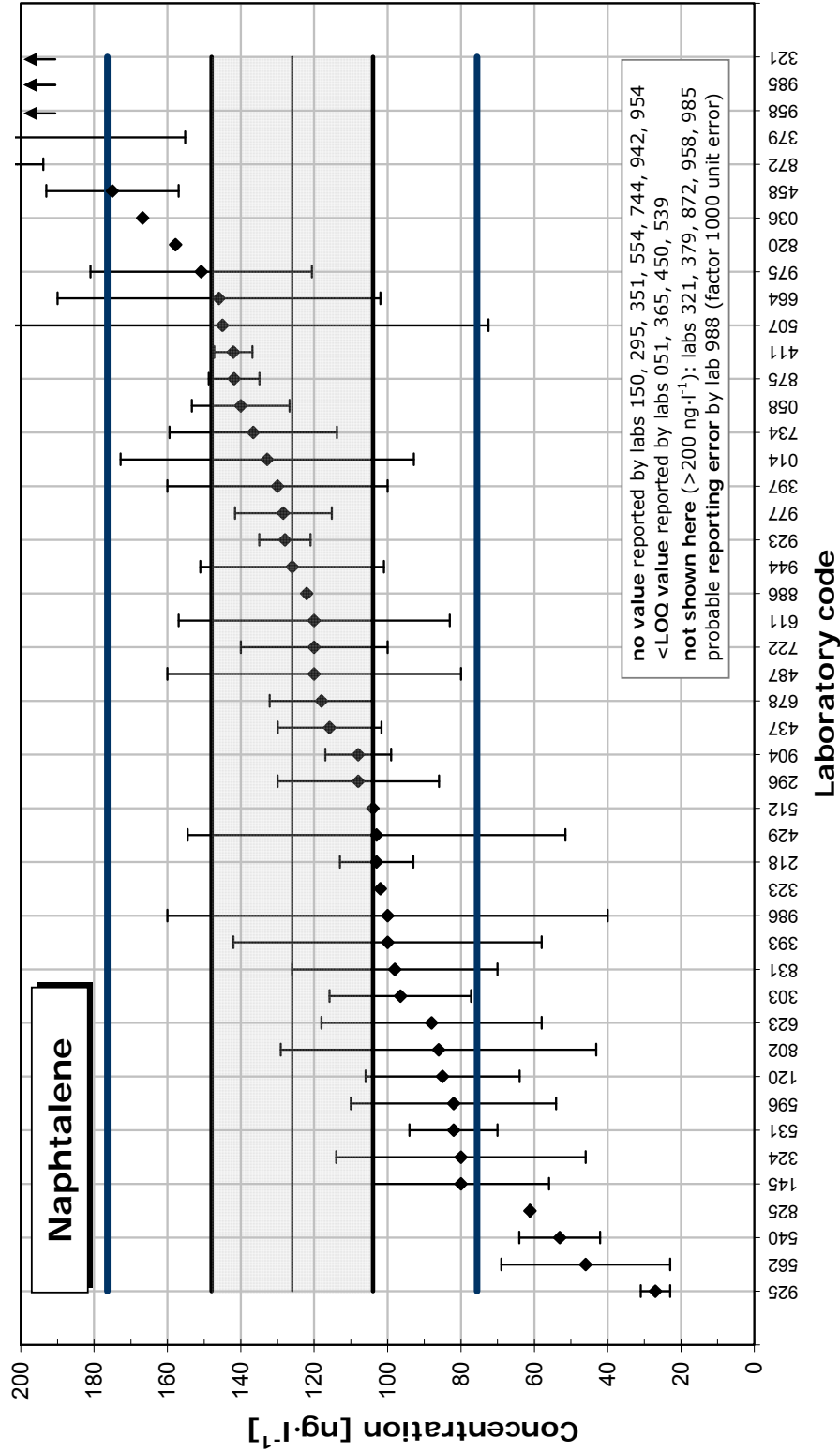
	Yes	No	
Do you use any similar in-house quality control materials for PAHs in water?	<input type="radio"/>	<input type="radio"/>	
	better	equally	less
If YES, Are these better / equally / less suitable compared with the IMEP-23 sample set?	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>
It has been suggested to make this a Certified Reference Material. Would you use it in your laboratory?	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>
Do you think that a similar (multi-component) set could also be useful for other classes of organic compounds?	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>
If YES, Which one(s)?			
<input type="text"/>			
Comments and suggestions for improvement:			
<input type="text"/>			

Annex 9: Results for Naphtalene

Laboratory	Analytical method	Reported concentration [ng·l ⁻¹]	Reported uncertainty [ng·l ⁻¹]	Calculated standard uncertainty [ng·l ⁻¹]	Coverage factor <i>k</i>	z score	zeta score
014	HPLC-FLU	132,8	40	20,0	2	0,3	0,3
036	Capillary GC-MS	166,8				1,6	
051	Capillary GC-MS	< 1000					
058	HPLC-FLU	140	13,3	6,7	2	0,6	1,1
120	LC	85	21	10,5	2	-1,6	-2,7
145	GC-MS	80	24	13,9		-1,8	-2,6
150							
218	HPLC-FLU	103	10	5,8		-0,9	-1,9
295	GC/MS/SBSE						
296	HPLC	108	22	11,0	2	-0,7	-1,2
303	HPLC-FLD (EN ISO 17993)	96,5	19,3	9,7	2	-1,2	-2,0
321	GC-IRMS	478	43,2	21,6	2	14,0	14,5
323	GC-MS	102				-1,0	
324	GC-MS	80	34	19,6		-1,8	-2,0
351							
365	GC-MS	< 500					
379	HPLC, FD	207	51,8	25,9	2	3,2	2,9
393	Capillary GC-MS	100	42	21,0	2	-1,0	-1,1
397	GC-MS	130	30	15,0	2	0,2	0,2
411	Capillary GC-MS	142	5,2	2,6	2	0,6	1,4
429	GC-MS-MS	103	51,5	25,8	2	-0,9	-0,8
437	HPLC-FLU	115,8	14,1	7,1	2	-0,4	-0,8
450	Capillary GC-MS	< 1000					
458	GC-MS	175	18	10,4		1,9	3,2
487	Capillary GC-MS	120	40	23,1		-0,2	-0,2
507	GC-MS/MS	145	72,5	36,3	2	0,8	0,5
512	Capillary GCMS, unvalidated	104				-0,9	
531	HPLC-FLU	82	12	6,0	2	-1,7	-3,5
539	Capillary GC-MS	< 25000					
540	GC-MS	53,1	11	5,5	2	-2,9	-5,9
554							
562	GC-FID	46	23	13,3		-3,2	-4,6
596	HPLC-FLU	82	28	14,0	2	-1,7	-2,5
611	GC-MS	120	37	18,5	2	-0,2	-0,3
623	HPLC-UV	88	30	15,0	2	-1,5	-2,0
664	HPLC-FLU	146	44	22,0	2	0,8	0,8
678	GC-MS	118	14,16	14,2	1	-0,3	-0,4
722	Capillary GC-MS	120	20	10,0	2	-0,2	-0,4
734	HPLC-FLU	136,6	22,8	11,4	2	0,4	0,7
744	Capillary GC-MS						
802	HPLC-FLU	86,08	43	21,5	2	-1,6	-1,7
820	Capillary GC-MS	157,8				1,3	
825	HPLC	61,2	0,1	0,1	2	-2,6	-5,9
831	GC/MSD	98	28	14,3	1,96	-1,1	-1,6
872	Capillary GC-MS	200,9	7,1	3,6	2	3,0	6,5
875	Capillary GC-MS	141,8	6,9	3,5	2	0,6	1,4
886	Capillary GC-MS	122				-0,2	
904	HPLC-FLU	108	9	4,5	2	-0,7	-1,5
923	HPLC-FLU	128	7	3,5	2	0,1	0,2
925	Capillary GC-MS	27	4	2,0	2	-3,9	-8,9
942	HPLC-FLU						
944	HPLC-FLU	126	25	14,4		0,0	0,0
954							
958	GC-MS	209,06				3,3	
975	HPLC	150,8	30,2	15,1	2	1,0	1,3
977	Capillary GC-MS	128,4	13,2	6,6	2	0,1	0,2
985	HPLC-UV	339	102	51,0	2	8,5	4,1
986	Capillary GC-MS	100	60	34,6		-1,0	-0,7
988	Capillary GC-MS	17800	1000	577,4			

IMEP-23 (PAHs in water): results for naphthalene

Certified value: $X_{ref} = (126 \pm 22) \text{ ng}\cdot\text{l}^{-1}$ ($k=2$)



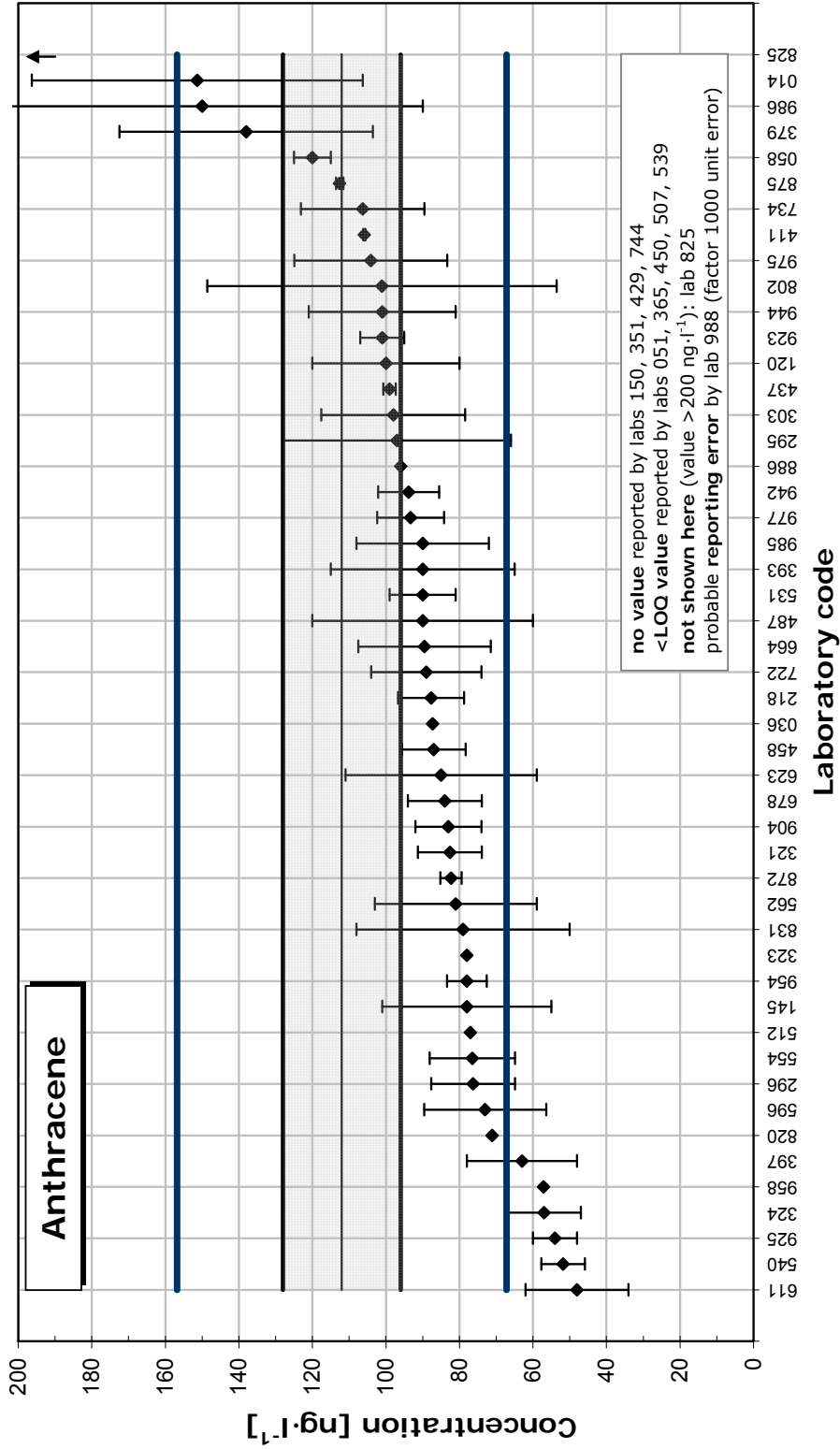
This graph displays all measurement results and their associated uncertainties. These uncertainties are shown as reported, with various expansion factors and levels of confidence. The grey band represents the reference interval ($X_{ref} \pm 2u_{ref}$), the thick blue lines delimit the target interval ($X_{ref} \pm 2\sigma$).

Annex 10: Results for Anthracene

Laboratory	Analytical method	Reported concentration	Reported uncertainty	Calculated standard uncertainty	Coverage factor <i>k</i>	z score	zeta score
		[ng·l ⁻¹]	[ng·l ⁻¹]	[ng·l ⁻¹]			
014	HPLC-FLU	151,3	45	22,5	2	1,8	1,6
036	Capillary GC-MS	87,3				-1,1	
051	Capillary GC-MS	< 1000					
058	HPLC-FLU	120	5	2,5	2	0,4	1,0
120	LC	100	20	10,0	2	-0,5	-0,9
145	GC-MS	78	23	13,3		-1,5	-2,2
150							
218	HPLC-FLU	87,7	9	5,2		-1,1	-2,5
295	GC/MS/SBSE	97	31	15,5	2	-0,7	-0,9
296	HPLC	76,3	11,4	5,7	2	-1,6	-3,6
303	HPLC-FLD (EN ISO 17993)	98	19,6	9,8	2	-0,6	-1,1
321	GC-IRMS	82,6	8,7	4,4	2	-1,3	-3,2
323	GC-MS	78				-1,5	
324	GC-MS	57	10	0,1	104	-2,5	-6,9
351							
365	GC-MS	< 500					
379	HPLC, FD	138	34,5	17,3	2	1,2	1,4
393	Capillary GC-MS	90	25	12,5	2	-1,0	-1,5
397	GC-MS	63	15	7,5	2	-2,2	-4,5
411	Capillary GC-MS	105,9	0,3	0,2	2	-0,3	-0,8
429	GC-MS-MS						
437	HPLC-FLU	99	1,7	0,9	2	-0,6	-1,6
450	Capillary GC-MS	< 1000					
458	GC-MS	87	8,7	5,0		-1,1	-2,6
487	Capillary GC-MS	90	30	17,3		-1,0	-1,2
507	GC-MS/MS	< 22					
512	Capillary GCMS, unvalidated	77				-1,6	
531	HPLC-FLU	90	9	4,5	2	-1,0	-2,4
539	Capillary GC-MS	< 25000					
540	GC-MS	51,8	5,9	3,0	2	-2,7	-7,1
554		76,5	11,6	5,8	2	-1,6	-3,6
562	GC-FID	81	22	12,7		-1,4	-2,1
596	HPLC-FLU	73	16,6	8,3	2	-1,7	-3,4
611	GC-MS	48	14	7,0	2	-2,9	-6,0
623	HPLC-UV	85	26	13,0	2	-1,2	-1,8
664	HPLC-FLU	89,5	18	9,0	2	-1,0	-1,9
678	GC-MS	84	10,08	10,1	1	-1,3	-2,2
722	Capillary GC-MS	89	15	7,5	2	-1,0	-2,1
734	HPLC-FLU	106,3	16,8	8,4	2	-0,3	-0,5
744	Capillary GC-MS						
802	HPLC-FLU	101,06	47,5	23,8	2	-0,5	-0,4
820	Capillary GC-MS	71,08				-1,8	
825	HPLC	250,4	0,1	0,1	2	6,2	17,3
831	GC/MSD	79	29	14,8	1,96	-1,5	-2,0
872	Capillary GC-MS	82,3	2,9	1,5	2	-1,3	-3,7
875	Capillary GC-MS	112,6	1	0,5	2	0,0	0,1
886	Capillary GC-MS	96				-0,7	
904	HPLC-FLU	83	9	4,5	2	-1,3	-3,2
923	HPLC-FLU	101	6	3,0	2	-0,5	-1,3
925	Capillary GC-MS	54	6	3,0	2	-2,6	-6,8
942	HPLC-FLU	93,8	8,3	2,8	3	-0,8	-2,2
944	HPLC-FLU	101	20	11,5		-0,5	-0,8
954		78	5,4	2,7	2	-1,5	-4,0
958	GC-MS	57,09				-2,5	
975	HPLC	104,1	20,8	10,4	2	-0,4	-0,6
977	Capillary GC-MS	93,3	9,1	4,6	2	-0,8	-2,0
985	HPLC-UV	90	18	9,0	2	-1,0	-1,8
986	Capillary GC-MS	150	60	34,6		1,7	1,1
988	Capillary GC-MS	63400	3400	1963,0			

IMEP-23 (PAHs in water): results for anthracene

Certified value: $X_{ref} = (112 \pm 16) \text{ ng}\cdot\text{l}^{-1}$ ($k=2$)

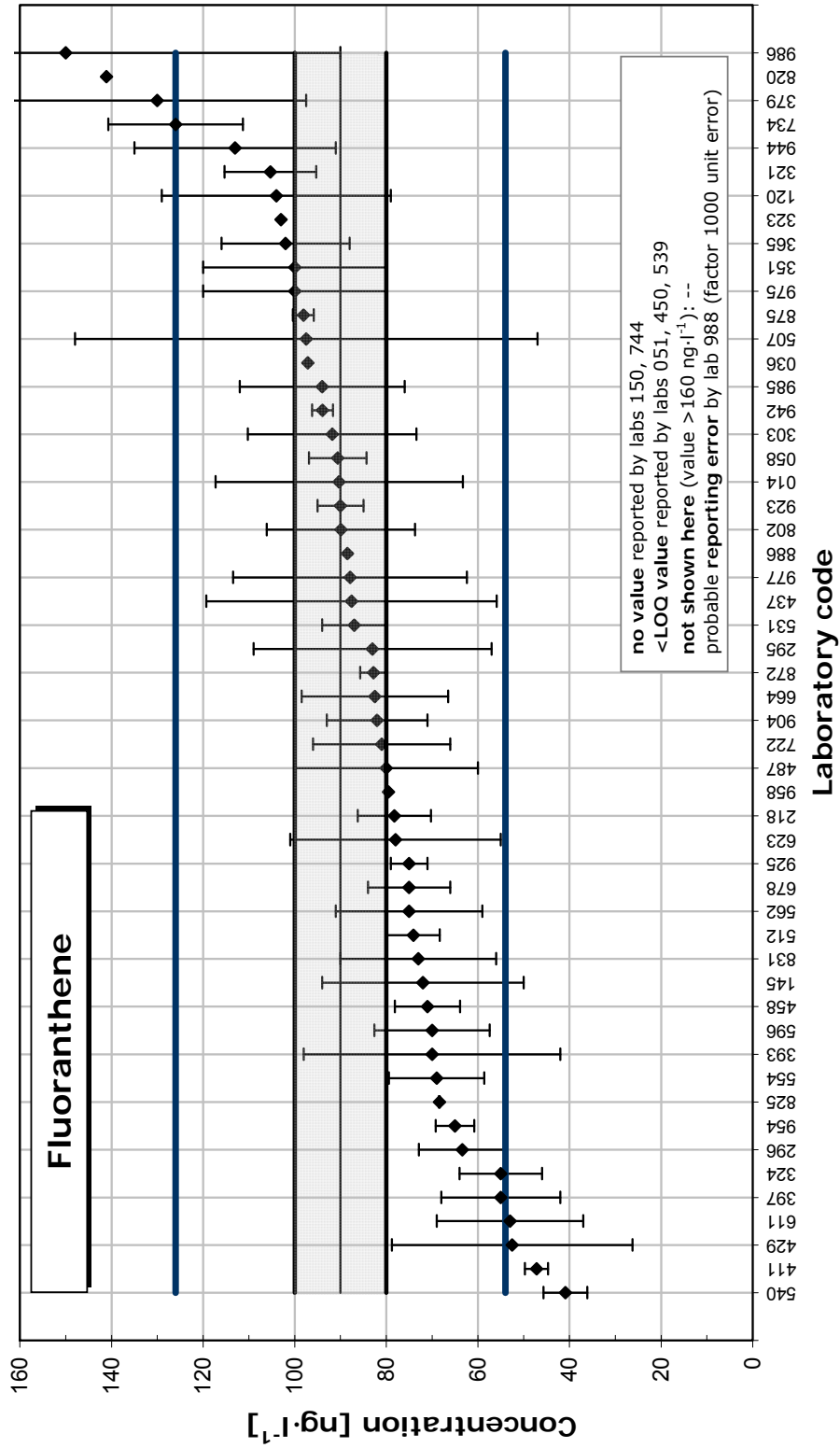


This graph displays all measurement results and their associated uncertainties. These uncertainties are shown as reported, with various expansion factors and levels of confidence. The grey band represents the reference interval ($X_{ref} \pm 2u_{ref}$), the thick blue lines delimit the target interval ($X_{ref} \pm 2\sigma$).

Annex 11: Results for Fluoranthene

Laboratory	Analytical method	Reported concentration [ng·l ⁻¹]	Reported uncertainty [ng·l ⁻¹]	Calculated standard uncertainty [ng·l ⁻¹]	Coverage factor <i>k</i>	z score	zeta score
014	HPLC-FLU	90,3	27	13,5	2	0,0	0,0
036	Capillary GC-MS	97,1				0,4	
051	Capillary GC-MS	< 1000					
058	HPLC-FLU	90,6	6,3	3,2	2	0,0	0,1
120	LC	104	25	12,5	2	0,8	1,0
145	GC-MS	72	22	12,7		-1,0	-1,3
150							
218	HPLC-FLU	78,2	8	4,6		-0,7	-1,7
295	GC/MS/SBSE	83	26	13,0	2	-0,4	-0,5
296	HPLC	63,4	9,5	4,8	2	-1,5	-3,9
303	HPLC-FLD (EN ISO 17993)	91,8	18,4	9,2	2	0,1	0,2
321	GC-IRMS	105,3	10	5,0	2	0,9	2,2
323	GC-MS	103				0,7	
324	GC-MS	55	9	0,1	101	-1,9	-7,0
351		100	20	10,0	2	0,6	0,9
365	GC-MS	102	14	7,0	2	0,7	1,4
379	HPLC, FD	130	32,5	16,3	2	2,2	2,4
393	Capillary GC-MS	70	28	14,0	2	-1,1	-1,3
397	GC-MS	55	13	6,5	2	-1,9	-4,3
411	Capillary GC-MS	47,2	2,5	1,3	2	-2,4	-8,3
429	GC-MS-MS	52,5	26,25	13,1	2	-2,1	-2,7
437	HPLC-FLU	87,6	31,7	15,9	2	-0,1	-0,1
450	Capillary GC-MS	< 1000					
458	GC-MS	71	7,1	4,1		-1,1	-2,9
487	Capillary GC-MS	80	20	11,5		-0,6	-0,8
507	GC-MS/MS	97,5	50,5	25,3	2	0,4	0,3
512	Capillary GCMS, unvalidated	74,1	5,8	2,9	2	-0,9	-2,8
531	HPLC-FLU	87	7	3,5	2	-0,2	-0,5
539	Capillary GC-MS	< 43000					
540	GC-MS	40,9	4,8	2,4	2	-2,7	-8,9
554	0	69	10,4	5,2	2	-1,2	-2,9
562	GC-FID	75	16	9,2		-0,8	-1,4
596	HPLC-FLU	70	12,6	6,3	2	-1,1	-2,5
611	GC-MS	53	16	8,0	2	-2,1	-3,9
623	HPLC-UV	78	23	11,5	2	-0,7	-1,0
664	HPLC-FLU	82,5	16	8,0	2	-0,4	-0,8
678	GC-MS	75	9	9,0	1	-0,8	-1,5
722	Capillary GC-MS	81	15	7,5	2	-0,5	-1,0
734	HPLC-FLU	126	14,7	7,4	2	2,0	4,0
744	Capillary GC-MS						
802	HPLC-FLU	89,89	16,18	8,1	2	0,0	0,0
820	Capillary GC-MS	141,1				2,8	
825	HPLC	68,41	0,1	0,1	2	-1,2	-4,3
831	GC/MSD	73	17	8,7	1,96	-0,9	-1,7
872	Capillary GC-MS	82,8	2,9	1,5	2	-0,4	-1,4
875	Capillary GC-MS	98,1	2,3	1,2	2	0,5	1,6
886	Capillary GC-MS	88,5				-0,1	
904	HPLC-FLU	82	11	5,5	2	-0,4	-1,1
923	HPLC-FLU	90	5	2,9		0,0	0,0
925	Capillary GC-MS	75	4	2,0	2	-0,8	-2,8
942	HPLC-FLU	93,9	2,3	0,8	3	0,2	0,8
944	HPLC-FLU	113	22	12,7		1,3	1,7
954		65	4,2	2,1	2	-1,4	-4,6
958	GC-MS	79,53				-0,6	
975	HPLC	100	20	10,0	2	0,6	0,9
977	Capillary GC-MS	87,9	25,5	12,8	2	-0,1	-0,2
985	HPLC-UV	94	18	9,0	2	0,2	0,4
986	Capillary GC-MS	150	60	34,6		3,3	1,7
988	Capillary GC-MS	101800	1800	1039,3			

IMEP-23 (PAHs in water): results for fluoranthene
 Certified value: $X_{ref} = (90 \pm 10) \text{ ng}\cdot\text{l}^{-1}$ ($k=2$)



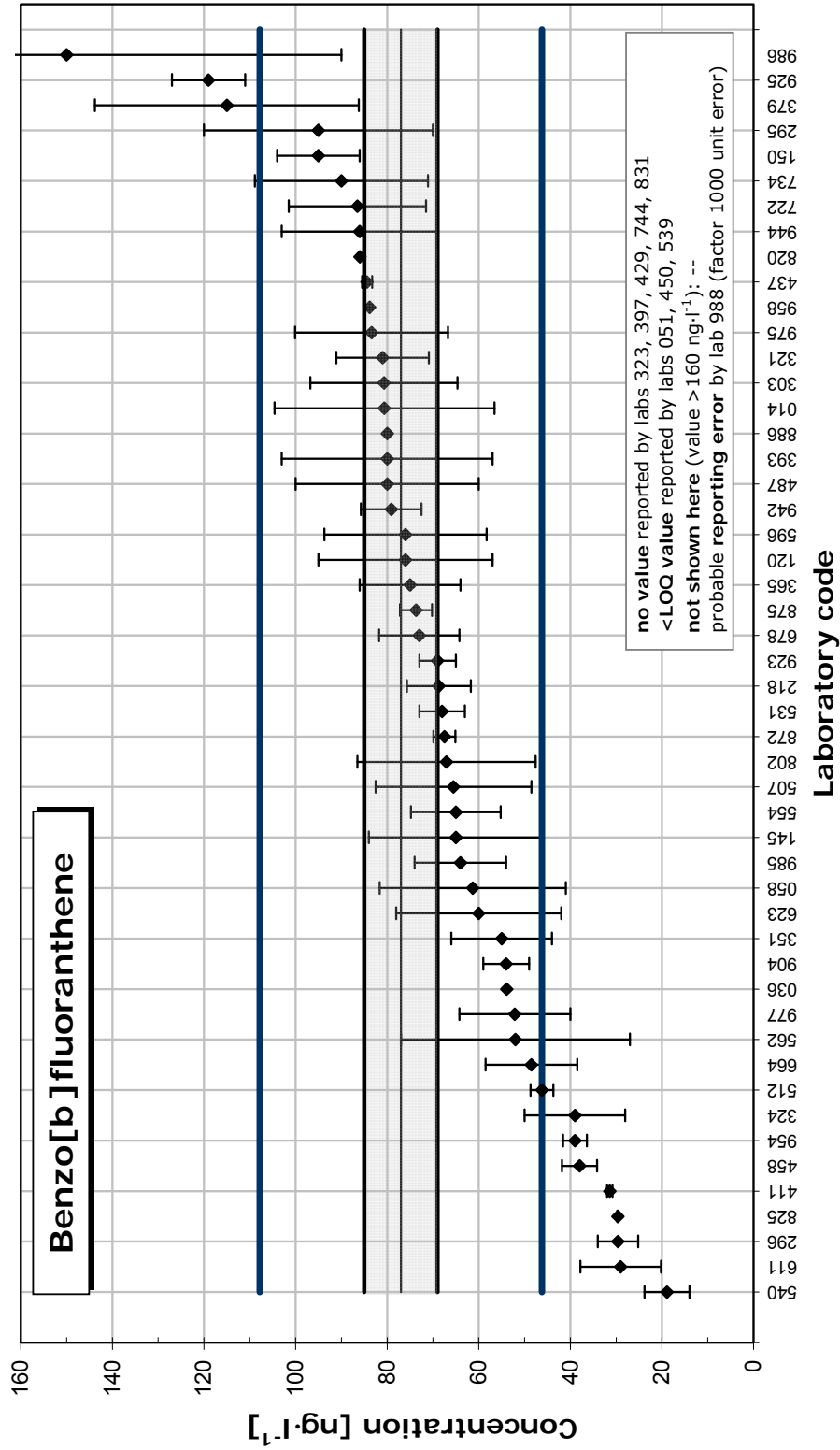
This graph displays all measurement results and their associated uncertainties. These uncertainties are shown as reported, with various expansion factors and levels of confidence. The grey band represents the reference interval ($X_{ref} \pm 2u_{ref}$), the thick blue lines delimit the target interval ($X_{ref} \pm 2\sigma$).

Annex 12: Results for Benzo[b]fluoranthene

Laboratory	Analytical method	Reported concentration	Reported uncertainty	Calculated standard uncertainty	Coverage factor <i>k</i>	z score	zeta score
		[ng·l ⁻¹]	[ng·l ⁻¹]	[ng·l ⁻¹]			
014	HPLC-FLU	80,6	24	12,0	2	0,2	0,3
036	Capillary GC-MS	53,9				-1,5	
051	Capillary GC-MS	< 1000					
058	HPLC-FLU	61,3	20,3	10,2	2	-1,0	-1,4
120	LC	76	19	9,5	2	-0,1	-0,1
145	GC-MS	65	19	11,0		-0,8	-1,0
150		95	9	5,2		1,2	2,7
218	HPLC-FLU	68,7	7	4,0		-0,5	-1,5
295	GC/MS/SBSE	95	25	12,5	2	1,2	1,4
296	HPLC	29,6	4,4	2,2	2	-3,1	-10,4
303	HPLC-FLD (EN ISO 17993)	80,7	16,1	8,1	2	0,2	0,4
321	GC-IRMS	81	10,1	5,1	2	0,3	0,6
323	GC-MS						
324	GC-MS	39	11	0,1	110	-2,5	-9,5
351		55	11	5,5	2	-1,4	-3,2
365	GC-MS	75	11	5,5	2	-0,1	-0,3
379	HPLC, FD	115	28,8	14,4	2	2,5	2,5
393	Capillary GC-MS	80	23	11,5	2	0,2	0,2
397	GC-MS						
411	Capillary GC-MS	31,4	0,6	0,3	2	-3,0	-11,4
429	GC-MS-MS						
437	HPLC-FLU	84,4	1,1	0,6	2	0,5	1,8
450	Capillary GC-MS	< 1000					
458	GC-MS	38	3,8	2,2		-2,5	-8,5
487	Capillary GC-MS	80	20	11,5		0,2	0,2
507	GC-MS/MS	65,5	17	8,5	2	-0,7	-1,2
512	Capillary GCMS, unvalidated	46,2	2,5	1,3	2	-2,0	-7,3
531	HPLC-FLU	68	5	2,5	2	-0,6	-1,9
539	Capillary GC-MS	< 67000					
540	GC-MS	18,9	4,9	2,5	2	-3,8	-12,4
554		65	9,8	4,9	2	-0,8	-1,9
562	GC-FID	52	25	14,4		-1,6	-1,7
596	HPLC-FLU	76	17,7	8,9	2	-0,1	-0,1
611	GC-MS	29	8,8	4,4	2	-3,1	-8,1
623	HPLC-UV	60	18	9,0	2	-1,1	-1,7
664	HPLC-FLU	48,5	10	5,0	2	-1,9	-4,5
678	GC-MS	73	8,76	8,8	1	-0,3	-0,4
722	Capillary GC-MS	86,5	15	7,5	2	0,6	1,1
734	HPLC-FLU	90	18,9	9,5	2	0,8	1,3
744	Capillary GC-MS						
802	HPLC-FLU	67,03	19,44	9,7	2	-0,6	-0,9
820	Capillary GC-MS	85,93				0,6	
825	HPLC	29,61	0,1	0,1	2	-3,1	-11,8
831	GC/MSD						
872	Capillary GC-MS	67,5	2,4	1,2	2	-0,6	-2,3
875	Capillary GC-MS	73,7	3,5	1,8	2	-0,2	-0,8
886	Capillary GC-MS	80				0,2	
904	HPLC-FLU	54	5	2,5	2	-1,5	-4,9
923	HPLC-FLU	69	4	2,0	2	-0,5	-1,8
925	Capillary GC-MS	119	8	4,0	2	2,7	7,4
942	HPLC-FLU	79,1	6,6	2,2	3	0,1	0,5
944	HPLC-FLU	86	17	9,8		0,6	0,8
954		39	2,6	1,3	2	-2,5	-9,0
958	GC-MS	83,83				0,4	
975	HPLC	83,4	16,7	8,4	2	0,4	0,7
977	Capillary GC-MS	52,1	12,1	6,1	2	-1,6	-3,4
985	HPLC-UV	64	10	5,0	2	-0,8	-2,0
986	Capillary GC-MS	150	60	34,6		4,7	2,1
988	Capillary GC-MS	94800	9200	5311,8			

IMEP-23 (PAHs in water): results for benzo[b]fluoranthene

Certified value: $X_{ref} = (77 \pm 8) \text{ ng}\cdot\text{l}^{-1}$ ($k=2$)

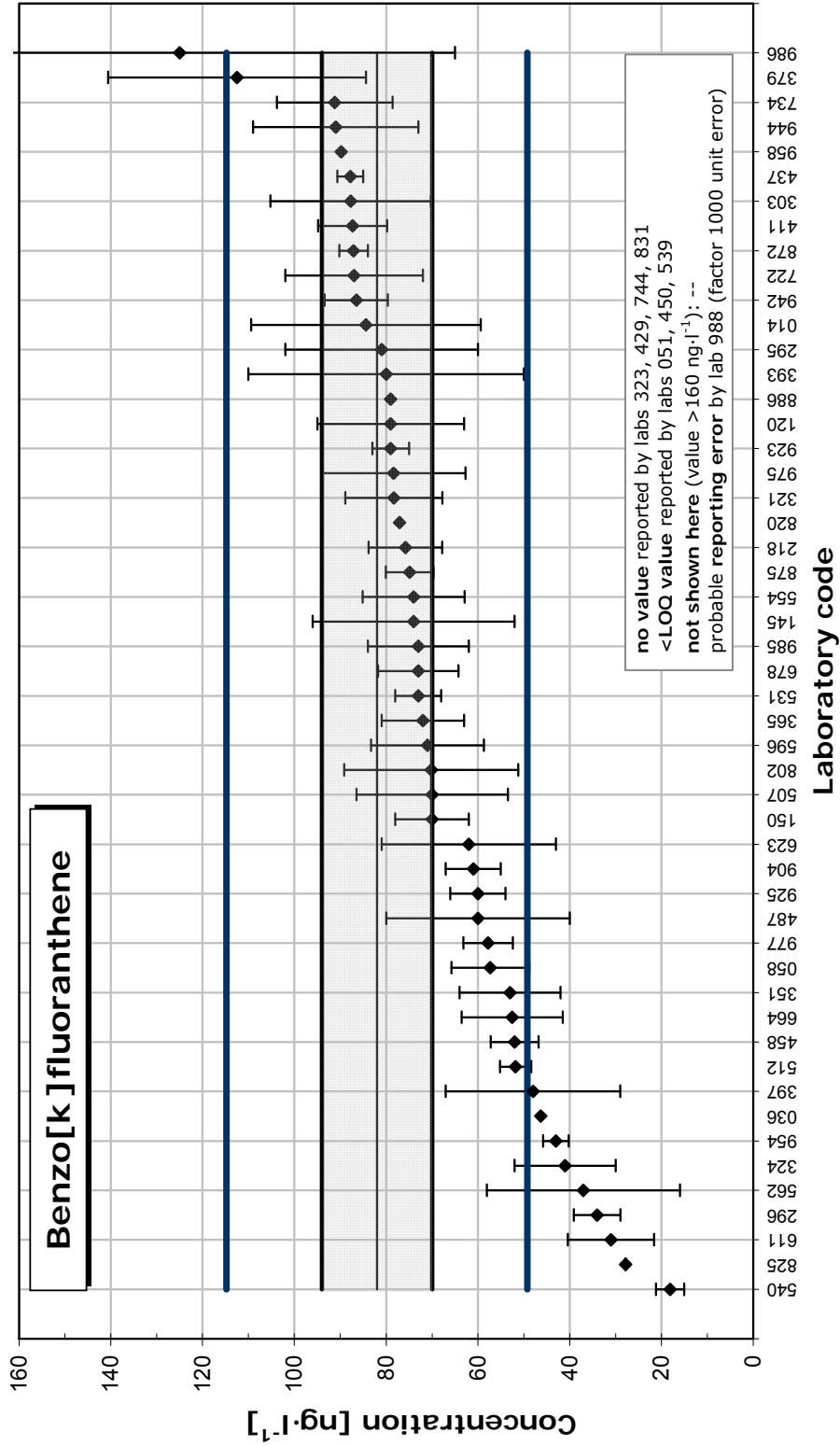


This graph displays all measurement results and their associated uncertainties. These uncertainties are shown as reported, with various expansion factors and levels of confidence. The grey band represents the reference interval ($X_{ref} \pm 2u_{ref}$), the thick blue lines delimit the target interval ($X_{ref} \pm 2\sigma$).

Annex 13: Results for Benzo[k]fluoranthene

Laboratory	Analytical method	Reported concentration	Reported uncertainty	Calculated standard uncertainty	Coverage factor <i>k</i>	z score	zeta score
		[ng·l ⁻¹]	[ng·l ⁻¹]	[ng·l ⁻¹]			
014	HPLC-FLU	84,4	25	12,5	2	0,1	0,2
036	Capillary GC-MS	46,3				-2,2	
051	Capillary GC-MS	< 1000					
058	HPLC-FLU	57,3	8,5	4,3	2	-1,5	-3,4
120	LC	79	16	8,0	2	-0,2	-0,3
145	GC-MS	74	22	12,7		-0,5	-0,6
150		70	8	4,6		-0,7	-1,6
218	HPLC-FLU	75,8	8	4,6		-0,4	-0,8
295	GC/MS/SBSE	81	21	10,5	2	-0,1	-0,1
296	HPLC	34	5,1	2,6	2	-2,9	-7,4
303	HPLC-FLD (EN ISO 17993)	87,7	17,5	8,8	2	0,3	0,5
321	GC-IRMS	78,3	10,6	5,3	2	-0,2	-0,5
323	GC-MS						
324	GC-MS	41	11	0,1	97	-2,5	-6,8
351		53	11	5,5	2	-1,8	-3,6
365	GC-MS	72	9	4,5	2	-0,6	-1,3
379	HPLC, FD	112,5	28,1	14,1	2	1,9	2,0
393	Capillary GC-MS	80	30	15,0	2	-0,1	-0,1
397	GC-MS	48	19	9,5	2	-2,1	-3,0
411	Capillary GC-MS	87,3	7,5	3,8	2	0,3	0,7
429	GC-MS-MS						
437	HPLC-FLU	87,8	2,8	1,4	2	0,4	0,9
450	Capillary GC-MS	< 1000					
458	GC-MS	52	5,2	3,0		-1,8	-4,5
487	Capillary GC-MS	60	20	11,5		-1,3	-1,7
507	GC-MS/MS	70	16,5	8,3	2	-0,7	-1,2
512	Capillary GCMS, unvalidated	51,8	3,4	1,7	2	-1,8	-4,8
531	HPLC-FLU	73	5	2,5	2	-0,5	-1,4
539	Capillary GC-MS	< 67000					
540	GC-MS	18,1	3,1	1,6	2	-3,9	-10,3
554		74	11,1	5,6	2	-0,5	-1,0
562	GC-FID	37	21	12,1		-2,7	-3,3
596	HPLC-FLU	71	12,3	6,2	2	-0,7	-1,3
611	GC-MS	31	9,4	4,7	2	-3,1	-6,7
623	HPLC-UV	62	19	9,5	2	-1,2	-1,8
664	HPLC-FLU	52,5	11	5,5	2	-1,8	-3,6
678	GC-MS	73	8,76	8,8	1	-0,5	-0,8
722	Capillary GC-MS	87	15	7,5	2	0,3	0,5
734	HPLC-FLU	91,2	12,6	6,3	2	0,6	1,1
744	Capillary GC-MS						
802	HPLC-FLU	70,18	18,95	9,5	2	-0,7	-1,1
820	Capillary GC-MS	77,09				-0,3	
825	HPLC	27,82	0,1	0,1	2	-3,3	-9,0
831	GC/MSD						
872	Capillary GC-MS	87,1	3,1	1,6	2	0,3	0,8
875	Capillary GC-MS	74,9	5,2	2,6	2	-0,4	-1,1
886	Capillary GC-MS	79				-0,2	
904	HPLC-FLU	61	6	3,0	2	-1,3	-3,1
923	HPLC-FLU	79	4	2,0	2	-0,2	-0,5
925	Capillary GC-MS	60	6	3,0	2	-1,3	-3,3
942	HPLC-FLU	86,5	6,9	2,3	3	0,3	0,7
944	HPLC-FLU	91	18	10,4		0,5	0,7
954		43	2,8	1,4	2	-2,4	-6,3
958	GC-MS	89,78				0,5	
975	HPLC	78,4	15,7	7,9	2	-0,2	-0,4
977	Capillary GC-MS	57,8	5,4	2,7	2	-1,5	-3,7
985	HPLC-UV	73	11	5,5	2	-0,5	-1,1
986	Capillary GC-MS	125	60	34,6		2,6	1,2
988	Capillary GC-MS	76400	2800	1616,6			

IMEP-23 (PAHs in water): results for benzo[k]fluoranthene
 Certified value: $X_{ref} = (82 \pm 12) \text{ ng}\cdot\text{l}^{-1}$ ($k=2$)



This graph displays all measurement results and their associated uncertainties. These uncertainties are shown as reported, with various expansion factors and levels of confidence. The grey band represents the reference interval ($X_{ref} \pm 2u_{ref}$), the thick blue lines delimit the target interval ($X_{ref} \pm 2\sigma$).

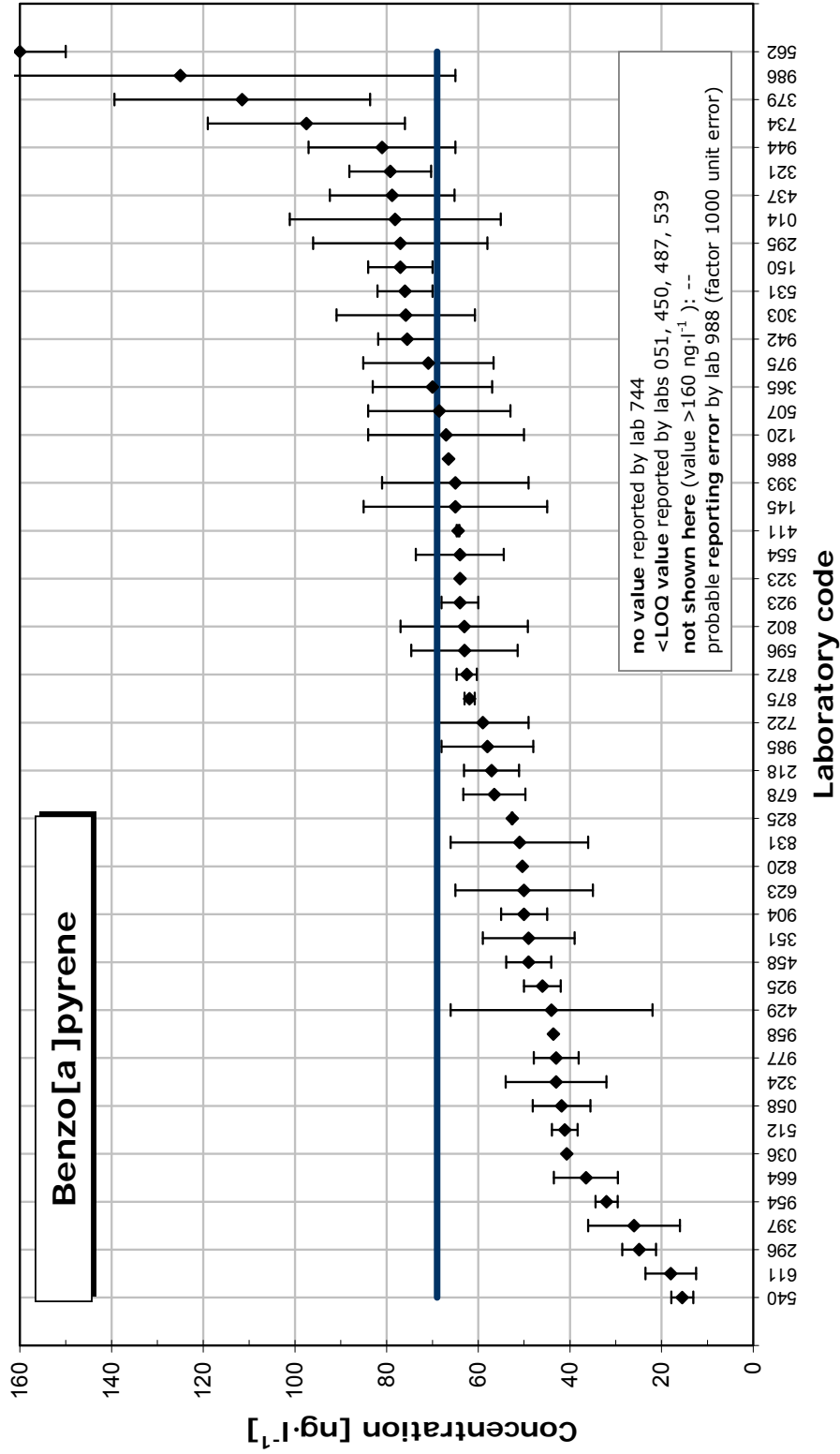
Annex 14: Results for Benzo[a]pyrene

Laboratory	Analytical method	Reported concentration	Reported uncertainty	Calculated standard uncertainty	Coverage factor <i>k</i>	z score	zeta score
		[ng·l ⁻¹]	[ng·l ⁻¹]	[ng·l ⁻¹]			
014	HPLC-FLU	78,1	23	11,5	2		
036	Capillary GC-MS	40,7					
051	Capillary GC-MS	< 1000					
058	HPLC-FLU	41,8	6,3	3,2	2		
120	LC	67	17	8,5	2		
145	GC-MS	65	20	11,5			
150		77	7	4,0			
218	HPLC-FLU	57,1	6	3,5			
295	GC/MS/SBSE	77	19	9,5	2		
296	HPLC	24,9	3,7	1,9	2		
303	HPLC-FLD (EN ISO 17993)	75,8	15,1	7,6	2		
321	GC-IRMS	79,2	8,9	4,5	2		
323	GC-MS	64					
324	GC-MS	43	11	0,1	100		
351		49	10	5,0	2		
365	GC-MS	70	13	6,5	2		
379	HPLC, FD	111,5	27,9	14,0	2		
393	Capillary GC-MS	65	16	8,0	2		
397	GC-MS	26	10	5,0	2		
411	Capillary GC-MS	64,4	0,3	0,2	2		
429	GC-MS-MS	44	22	11,0	2		
437	HPLC-FLU	78,8	13,6	6,8	2		
450	Capillary GC-MS	< 1000					
458	GC-MS	49	4,9	2,8			
487	Capillary GC-MS	< 50					
507	GC-MS/MS	68,5	15,5	7,8	2		
512	Capillary GCMS, unvalidated	41,1	2,8	1,4	2		
531	HPLC-FLU	76	6	3,0	2		
539	Capillary GC-MS	< 38000					
540	GC-MS	15,5	2,4	1,2	2		
554		64	9,6	4,8	2		
562	GC-FID	160	10	5,8			
596	HPLC-FLU	63	11,6	5,8	2		
611	GC-MS	18	5,5	2,8	2		
623	HPLC-UV	50	15	7,5	2		
664	HPLC-FLU	36,5	7	3,5	2		
678	GC-MS	56,5	6,78	6,8	1		
722	Capillary GC-MS	59	10	5,0	2		
734	HPLC-FLU	97,5	21,5	10,8	2		
744	Capillary GC-MS						
802	HPLC-FLU	63,05	13,87	6,9	2		
820	Capillary GC-MS	50,36					
825	HPLC	52,61	0,1	0,1	2		
831	GC/MSD	51	15	7,7	1,96		
872	Capillary GC-MS	62,5	2,2	1,1	2		
875	Capillary GC-MS	61,9	1,1	0,6	2		
886	Capillary GC-MS	66,5					
904	HPLC-FLU	50	5	2,5	2		
923	HPLC-FLU	64	4	2,0	2		
925	Capillary GC-MS	46	4	2,0	2		
942	HPLC-FLU	75,5	6,3	2,1	3		
944	HPLC-FLU	81	16	9,2			
954		32	2,4	1,2	2		
958	GC-MS	43,6					
975	HPLC	70,9	14,2	7,1	2		
977	Capillary GC-MS	43	4,9	2,5	2		
985	HPLC-UV	58	10	5,0	2		
986	Capillary GC-MS	125	60	34,6			
988	Capillary GC-MS	70000	2000	1154,7			

no scoring

IMEP-23 (PAHs in water): results for benzo[a]pyrene

Assigned value (indicative only): $X_{ref} = 69 \text{ ng}\cdot\text{l}^{-1}$

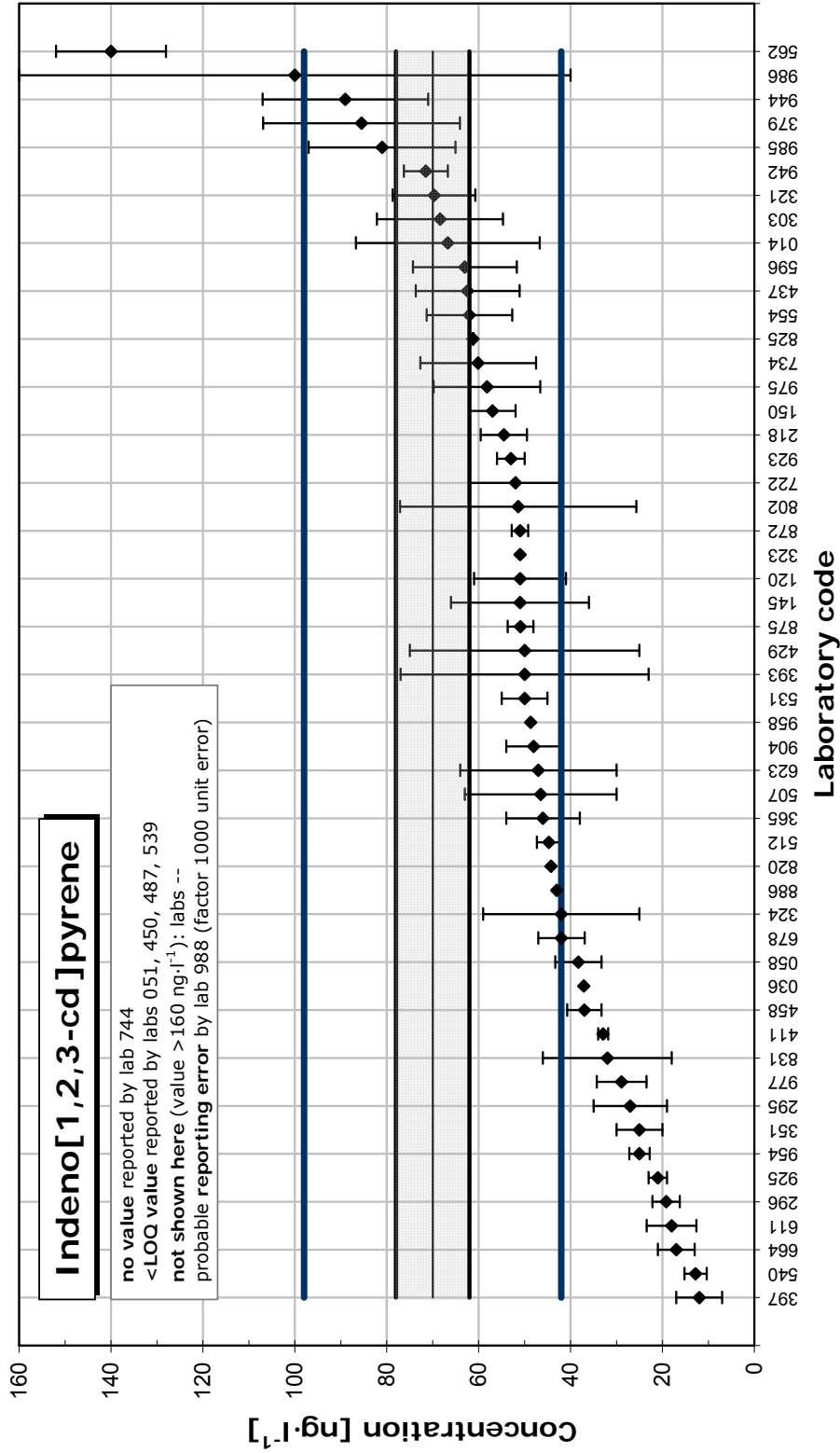


This graph displays all measurement results and their associated uncertainties. These uncertainties are shown as reported, with various expansion factors and levels of confidence. The thick blue line marks the indicative assigned value (X_{ref}).

Annex 15: Results for Indeno[1,2,3-cd]pyrene

Laboratory	Analytical method	Reported concentration	Reported uncertainty	Calculated standard uncertainty	Cover- age fac- tor <i>k</i>	z score	zeta score
		[ng·l ⁻¹]	[ng·l ⁻¹]	[ng·l ⁻¹]			
014	HPLC-FLU	66,7	20	10,0	2	-0,2	-0,3
036	Capillary GC-MS	37,1				-2,4	
051	Capillary GC-MS	< 1000					
058	HPLC-FLU	38,3	5	2,5	2	-2,3	-6,7
120	LC	51	10	5,0	2	-1,4	-3,0
145	GC-MS	51	15	8,7		-1,4	-2,0
150		57	5	2,9		-0,9	-2,6
218	HPLC-FLU	54,5	5	2,9		-1,1	-3,1
295	GC/MS/SBSE	27	8	4,0	2	-3,1	-7,6
296	HPLC	19,2	3	1,5	2	-3,6	-11,9
303	HPLC-FLD (EN ISO 17993)	68,4	13,7	6,9	2	-0,1	-0,2
321	GC-IRMS	69,7	9	4,5	2	0,0	0,0
323	GC-MS	51				-1,4	
324	GC-MS	42	17	0,2	112	-2,0	-7,0
351		25	5	2,5	2	-3,2	-9,5
365	GC-MS	46	8	4,0	2	-1,7	-4,2
379	HPLC, FD	85,5	21,4	10,7	2	1,1	1,4
393	Capillary GC-MS	50	27	13,5	2	-1,4	-1,4
397	GC-MS	12	5	2,5	2	-4,1	-12,3
411	Capillary GC-MS	32,9	1,1	0,6	2	-2,7	-9,2
429	GC-MS-MS	50	25	12,5	2	-1,4	-1,5
437	HPLC-FLU	62,4	11,3	5,7	2	-0,5	-1,1
450	Capillary GC-MS	< 1000					
458	GC-MS	37	3,7	2,1		-2,4	-7,3
487	Capillary GC-MS	< 50					
507	GC-MS/MS	46,5	16,5	8,3	2	-1,7	-2,6
512	Capillary GCMS, unvalidated	44,7	2,6	1,3	2	-1,8	-6,0
531	HPLC-FLU	50	5	2,5	2	-1,4	-4,2
539	Capillary GC-MS	< 31000					
540	GC-MS	12,8	2,4	1,2	2	-4,1	-13,7
554		62	9,3	4,7	2	-0,6	-1,3
562	GC-FID	140	12	6,9		5,0	8,7
596	HPLC-FLU	63	11,3	5,7	2	-0,5	-1,0
611	GC-MS	18	5,4	2,7	2	-3,7	-10,8
623	HPLC-UV	47	17	8,5	2	-1,6	-2,4
664	HPLC-FLU	17	4	2,0	2	-3,8	-11,9
678	GC-MS	42	5,04	5,0	1	-2,0	-4,4
722	Capillary GC-MS	52	10	5,0	2	-1,3	-2,8
734	HPLC-FLU	60,1	12,6	6,3	2	-0,7	-1,3
744	Capillary GC-MS						
802	HPLC-FLU	51,39	25,7	12,9	2	-1,3	-1,4
820	Capillary GC-MS	44,23				-1,8	
825	HPLC	61,21	0,1	0,1	2	-0,6	-2,2
831	GC/MSD	32	14	7,1	1,96	-2,7	-4,6
872	Capillary GC-MS	51	1,8	0,9	2	-1,4	-4,6
875	Capillary GC-MS	50,9	2,8	1,4	2	-1,4	-4,5
886	Capillary GC-MS	43				-1,9	
904	HPLC-FLU	48	6	3,0	2	-1,6	-4,4
923	HPLC-FLU	53	3	1,5	2	-1,2	-4,0
925	Capillary GC-MS	21	2	1,0	2	-3,5	-11,9
942	HPLC-FLU	71,5	4,8	1,6	3	0,1	0,3
944	HPLC-FLU	89	18	10,4		1,4	1,7
954		25	2,2	1,1	2	-3,2	-10,8
958	GC-MS	48,68				-1,5	
975	HPLC	58,2	11,6	5,8	2	-0,8	-1,7
977	Capillary GC-MS	28,9	5,4	2,7	2	-2,9	-8,5
985	HPLC-UV	81	16	8,0	2	0,8	1,2
986	Capillary GC-MS	100	60	34,6		2,1	0,9
988	Capillary GC-MS	68400	3600	2078,5			

IMEP-23 (PAHs in water): results for indeno[1,2,3-cd]pyrene
 Certified value: $X_{ref} = (70 \pm 8) \text{ ng}\cdot\text{l}^{-1}$ ($k=2$)



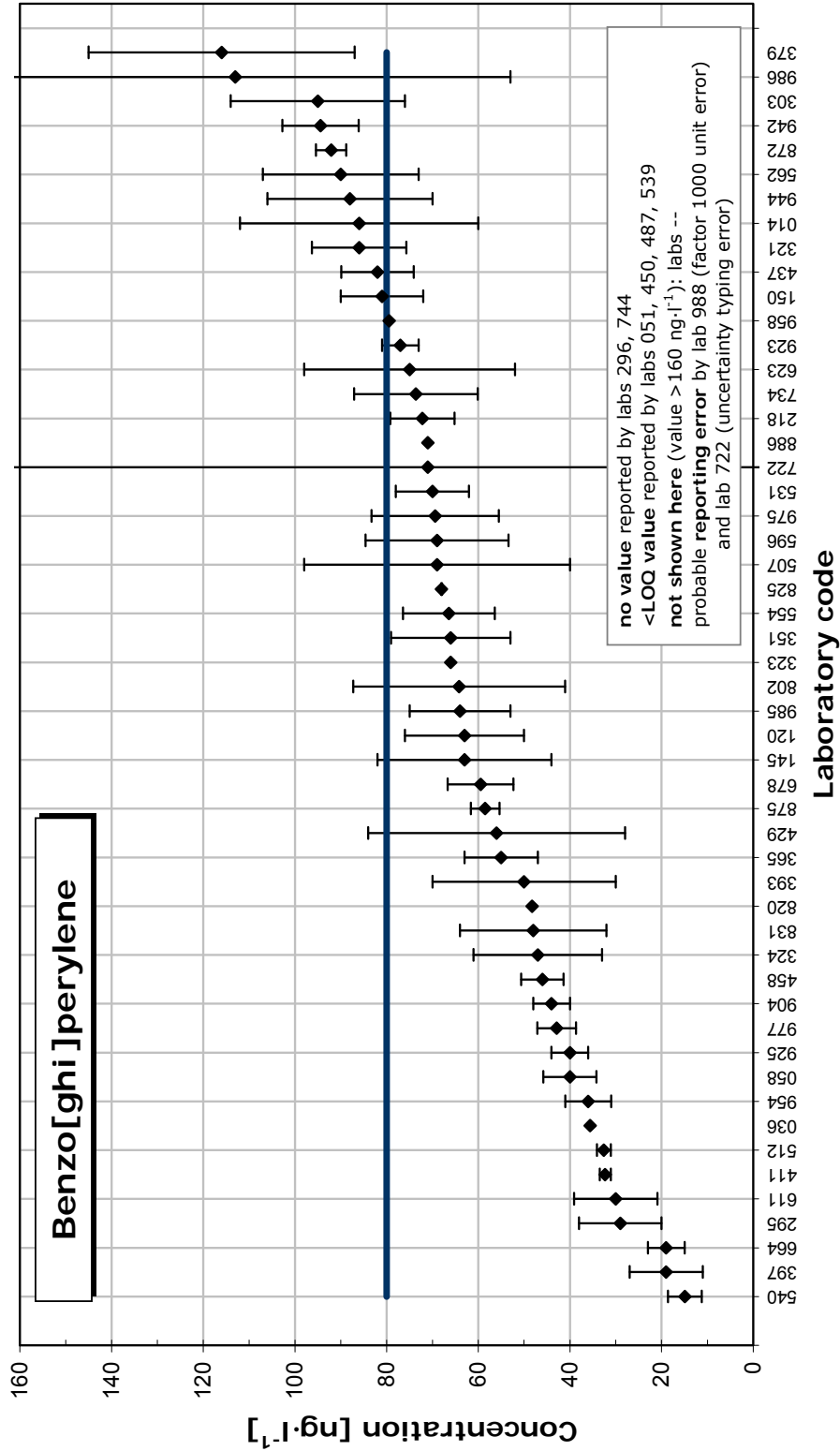
This graph displays all measurement results and their associated uncertainties. These uncertainties are shown as reported, with various expansion factors and levels of confidence. The grey band represents the reference interval ($X_{ref} \pm 2u_{ref}$), the thick blue lines delimit the target interval ($X_{ref} \pm 2\sigma$).

Annex 16: Results for Benzo[ghi]perylene

Laboratory	Analytical method	Reported concentration	Reported uncertainty	Calculated standard uncertainty	Coverage factor <i>k</i>	z score	zeta score
		[ng·l ⁻¹]	[ng·l ⁻¹]	[ng·l ⁻¹]			
014	HPLC-FLU	86	26	13,0	2	no scoring	
036	Capillary GC-MS	35,6					
051	Capillary GC-MS	< 1000					
058	HPLC-FLU	40	5,8	2,9	2		
120	LC	63	13	6,5	2		
145	GC-MS	63	19	11,0			
150		81	9	5,2			
218	HPLC-FLU	72,2	7	4,0			
295	GC/MS/SBSE	29	9	4,5	2		
296	HPLC						
303	HPLC-FLD (EN ISO 17993)	95	19	9,5	2		
321	GC-IRMS	86	10,3	5,2	2		
323	GC-MS	66					
324	GC-MS	47	14	0,1	103		
351		66	13	6,5	2		
365	GC-MS	55	8	4,0	2		
379	HPLC, FD	116	29	14,5	2		
393	Capillary GC-MS	50	20	10,0	2		
397	GC-MS	19	8	4,0	2		
411	Capillary GC-MS	32,3	1,2	0,6	2		
429	GC-MS-MS	56	28	14,0	2		
437	HPLC-FLU	82	7,9	4,0	2		
450	Capillary GC-MS	< 1000					
458	GC-MS	46	4,6	2,7			
487	Capillary GC-MS	< 50					
507	GC-MS/MS	69	29	14,5	2		
512	Capillary GCMS, unvalidated	32,6	1,5	0,8	2		
531	HPLC-FLU	70	8	4,0	2		
539	Capillary GC-MS	< 41000					
540	GC-MS	14,9	3,7	1,9	2		
554		66,4	10	5,0	2		
562	GC-FID	90	17	9,8			
596	HPLC-FLU	69	15,6	7,8	2		
611	GC-MS	30	9,1	4,6	2		
623	HPLC-UV	75	23	11,5	2		
664	HPLC-FLU	19	4	2,0	2		
678	GC-MS	59,5	7,14	7,1	1		
722	Capillary GC-MS	71	156	78,0	2		
734	HPLC-FLU	73,6	13,5	6,8	2		
744	Capillary GC-MS						
802	HPLC-FLU	64,19	23,11	11,6	2		
820	Capillary GC-MS	48,26					
825	HPLC	68	0,1	0,1	2		
831	GC/MSD	48	16	8,2	1,96		
872	Capillary GC-MS	92,1	3,3	1,7	2		
875	Capillary GC-MS	58,5	3,1	1,6	2		
886	Capillary GC-MS	71					
904	HPLC-FLU	44	4	2,0	2		
923	HPLC-FLU	77	4	2,0	2		
925	Capillary GC-MS	40	4	2,0	2		
942	HPLC-FLU	94,4	8,3	2,8	3		
944	HPLC-FLU	88	18	10,4			
954		36	5	2,5	2		
958	GC-MS	79,41					
975	HPLC	69,4	13,9	7,0	2		
977	Capillary GC-MS	42,9	4,2	2,1	2		
985	HPLC-UV	64	11	5,5	2		
986	Capillary GC-MS	113	60	34,6			
988	Capillary GC-MS	44200	4200	2424,9			

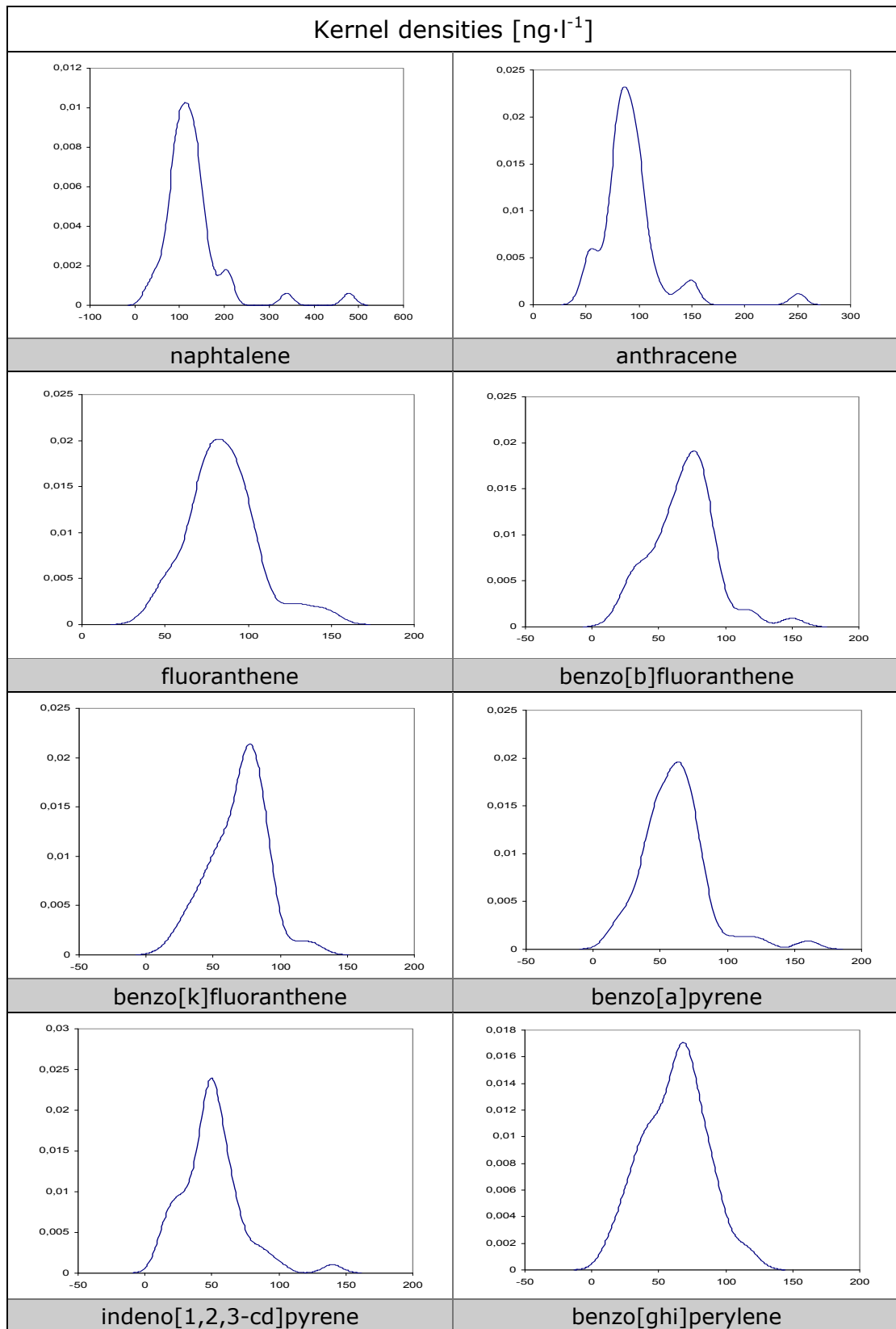
IMEP-23 (PAHs in water): results for benzo[ghi]perylene

Assigned value (indicative only): $X_{ref} = 80 \text{ ng}\cdot\text{l}^{-1}$



This graph displays all measurement results and their associated uncertainties. These uncertainties are shown as reported, with various expansion factors and levels of confidence. The thick blue line marks the indicative assigned value (X_{ref}).

Annex 17: Kernel densities



Annex 18: Summary of lab scores

Lab	Naphtalene		Anthracene		Fluoranthene		Benzo[b]-fluoranthene		Benzo[k]-fluoranthene		Benzo[a]-pyrene	Indeno-[1,2,3-cd]pyrene		Benzo[ghi]-perylene
	z	zeta	z	zeta	z	zeta	z	zeta	z	zeta		z	zeta	
014	0,3	0,3	1,8	1,6	0,0	0,0	0,2	0,3	0,1	0,2		-0,2	-0,3	
036	1,6		-1,1		0,4		-1,5		-2,2			-2,4		
051														
058	0,6	1,1	0,4	1,0	0,0	0,1	-1,0	-1,4	-1,5	-3,4		-2,3	-6,7	
120	-1,6	-2,7	-0,5	-0,9	0,8	1,0	-0,1	-0,1	-0,2	-0,3		-1,4	-3,0	
145	-1,8	-2,6	-1,5	-2,2	-1,0	-1,3	-0,8	-1,0	-0,5	-0,6		-1,4	-2,0	
150							1,2	2,7	-0,7	-1,6		-0,9	-2,6	
218	-0,9	-1,9	-1,1	-2,5	-0,7	-1,7	-0,5	-1,5	-0,4	-0,8		-1,1	-3,1	
295			-0,7	-0,9	-0,4	-0,5	1,2	1,4	-0,1	-0,1		-3,1	-7,6	
296	-0,7	-1,2	-1,6	-3,6	-1,5	-3,9	-3,1	-10,4	-2,9	-7,4		-3,6	-11,9	
303	-1,2	-2,0	-0,6	-1,1	0,1	0,2	0,2	0,4	0,3	0,5		-0,1	-0,2	
321	14,0	14,5	-1,3	-3,2	0,9	2,2	0,3	0,6	-0,2	-0,5		0,0	0,0	
323	-1,0		-1,5		0,7							-1,4		
324	-1,8	-2,0	-2,5	-6,9	-1,9	-7,0	-2,5	-9,5	-2,5	-6,8		-2,0	-7,0	
351					0,6	0,9	-1,4	-3,2	-1,8	-3,6		-3,2	-9,5	
365					0,7	1,4	-0,1	-0,3	-0,6	-1,3		-1,7	-4,2	
379	3,2	2,9	1,2	1,4	2,2	2,4	2,5	2,5	1,9	2,0		1,1	1,4	
393	-1,0	-1,1	-1,0	-1,5	-1,1	-1,3	0,2	0,2	-0,1	-0,1		-1,4	-1,4	
397	0,2	0,2	-2,2	-4,5	-1,9	-4,3			-2,1	-3,0		-4,1	-12,3	
411	0,6	1,4	-0,3	-0,8	-2,4	-8,3	-3,0	-11,4	0,3	0,7		-2,7	-9,2	
429	-0,9	-0,8			-2,1	-2,7						-1,4	-1,5	
437	-0,4	-0,8	-0,6	-1,6	-0,1	-0,1	0,5	1,8	0,4	0,9		-0,5	-1,1	
450														
458	1,9	3,2	-1,1	-2,6	-1,1	-2,9	-2,5	-8,5	-1,8	-4,5		-2,4	-7,3	
487	-0,2	-0,2	-1,0	-1,2	-0,6	-0,8	0,2	0,2	-1,3	-1,7				
507	0,8	0,5			0,4	0,3	-0,7	-1,2	-0,7	-1,2		-1,7	-2,6	
512	-0,9		-1,6		-0,9	-2,8	-2,0	-7,3	-1,8	-4,8		-1,8	-6,0	
531	-1,7	-3,5	-1,0	-2,4	-0,2	-0,5	-0,6	-1,9	-0,5	-1,4		-1,4	-4,2	
539														
540	-2,9	-5,9	-2,7	-7,1	-2,7	-8,9	-3,8	-12,4	-3,9	-10,3		-4,1	-13,7	
554			-1,6	-3,6	-1,2	-2,9	-0,8	-1,9	-0,5	-1,0		-0,6	-1,3	
562	-3,2	-4,6	-1,4	-2,1	-0,8	-1,4	-1,6	-1,7	-2,7	-3,3		5,0	8,7	
596	-1,7	-2,5	-1,7	-3,4	-1,1	-2,5	-0,1	-0,1	-0,7	-1,3		-0,5	-1,0	
611	-0,2	-0,3	-2,9	-6,0	-2,1	-3,9	-3,1	-8,1	-3,1	-6,7		-3,7	-10,8	
623	-1,5	-2,0	-1,2	-1,8	-0,7	-1,0	-1,1	-1,7	-1,2	-1,8		-1,6	-2,4	
664	0,8	0,8	-1,0	-1,9	-0,4	-0,8	-1,9	-4,5	-1,8	-3,6		-3,8	-11,9	
678	-0,3	-0,4	-1,3	-2,2	-0,8	-1,5	-0,3	-0,4	-0,5	-0,8		-2,0	-4,4	
722	-0,2	-0,4	-1,0	-2,1	-0,5	-1,0	0,6	1,1	0,3	0,5		-1,3	-2,8	
734	0,4	0,7	-0,3	-0,5	2,0	4,0	0,8	1,3	0,6	1,1		-0,7	-1,3	
744														
802	-1,6	-1,7	-0,5	-0,4	0,0	0,0	-0,6	-0,9	-0,7	-1,1		-1,3	-1,4	
820	1,3		-1,8		2,8		0,6		-0,3			-1,8		
825	-2,6	-5,9	6,2	17,3	-1,2	-4,3	-3,1	-11,8	-3,3	-9,0		-0,6	-2,2	
831	-1,1	-1,6	-1,5	-2,0	-0,9	-1,7						-2,7	-4,6	
872	3,0	6,5	-1,3	-3,7	-0,4	-1,4	-0,6	-2,3	0,3	0,8		-1,4	-4,6	
875	0,6	1,4	0,0	0,1	0,5	1,6	-0,2	-0,8	-0,4	-1,1		-1,4	-4,5	
886	-0,2		-0,7		-0,1		0,2		-0,2			-1,9		
904	-0,7	-1,5	-1,3	-3,2	-0,4	-1,1	-1,5	-4,9	-1,3	-3,1		-1,6	-4,4	
923	0,1	0,2	-0,5	-1,3	0,0	0,0	-0,5	-1,8	-0,2	-0,5		-1,2	-4,0	
925	-3,9	-8,9	-2,6	-6,8	-0,8	-2,8	2,7	7,4	-1,3	-3,3		-3,5	-11,9	
942			-0,8	-2,2	0,2	0,8	0,1	0,5	0,3	0,7		0,1	0,3	
944	0,0	0,0	-0,5	-0,8	1,3	1,7	0,6	0,8	0,5	0,7		1,4	1,7	
954			-1,5	-4,0	-1,4	-4,6	-2,5	-9,0	-2,4	-6,3		-3,2	-10,8	
958	3,3		-2,5		-0,6		0,4		0,5			-1,5		
975	1,0	1,3	-0,4	-0,6	0,6	0,9	0,4	0,7	-0,2	-0,4		-0,8	-1,7	
977	0,1	0,2	-0,8	-2,0	-0,1	-0,2	-1,6	-3,4	-1,5	-3,7		-2,9	-8,5	
985	8,5	4,1	-1,0	-1,8	0,2	0,4	-0,8	-2,0	-0,5	-1,1		0,8	1,2	
986	-1,0	-0,7	1,7	1,1	3,3	1,7	4,7	2,1	2,6	1,2		2,1	0,9	
988														

no scoring

no scoring

European Commission

EUR 23287 EN – Joint Research Centre – Institute for Reference Materials and Measurements

Title: The eight WFD PAHs in water in presence of humic acid

Authors: Johannes van de Kreeke, Beatriz de la Calle, Saskia Bynens, Inge Verbist, Philip Taylor, Ofelia Bercaru, Marina Ricci, Berit Sejerøe-Olsen, Penka Shegunova and Andrea Bau'

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Abstract

The Water Framework Directive (WFD) 2000/60/EC provides a legislative framework for the protection of inland and coastal waters in the EU. Decision 2455/2001/EC defines the major (priority) water pollutants and Proposal 2006/0397/EC their maximum levels. These include seven polycyclic aromatic hydrocarbons (PAHs): naphthalene, anthracene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*a*]pyrene, indeno[1,2,3-*cd*]pyrene and benzo[*ghi*]perylene, plus fluoranthene as an indicator substance.

These eight PAHs are the subject of this study. The matrix is ground water with humic acid which was added to simulate colloidal organic matter in surface water. The PAH concentrations were set close to the levels of the Proposal when practically feasible. The concentrations of six congeners were certified (i.e. given a reference value plus the associated uncertainty) whereas only indicative values could be attributed to benzo[*a*]pyrene and benzo[*ghi*]perylene.

The presence of humic acid made the certification campaign very complicated. PAHs adsorb onto humic acid and this can lead to material losses that may remain undetected if no internal standard is used or the internal standard is given insufficient time to reach the adsorption equilibrium before further sample treatment. There are indications that a number of participating routine laboratories have overlooked this effect.

The 59 participants were invited via different channels: the IMEP Regional Coordinators, the IRMM website, the European Co-operation for Accreditation, the International Committee for Protection of the Danube River and the International Committee for Protection of the Rhine.

z scores were calculated with a target standard deviation of 20% of the reference value. Reported results for the two uncertified congeners were not assessed. The scores were satisfactory for approximately 80% of the participants. In addition, zeta scores were calculated for those participants who had reported an uncertainty estimate. These were however less satisfactory on average.

In summary, the measurement capabilities of those laboratories involved in routine PAH measurements in the frame of the WFD appear quite positive, despite some clear points for improvement.

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