Research Article

A Study of the Critical Uncertainty Contributions in the Analysis of PCBs in Ambient Air

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The measurement of polychlorinated biphenyls (PCBs) in ambient air requires a complex, multistep sample preparation procedure prior to analysis by gas chromatography—mass spectrometry (GC-MS). Although routine analytical laboratories regularly carry out these measurements, they are often undertaken with little regard to the accurate calculation of measurement uncertainty, or appreciation of the sensitivity of the accuracy of the measurement to each step of the analysis. A measurement equation is developed for this analysis, and the contributory sources to the overall uncertainty when preparing calibration standards and other solutions by gravimetric and volumetric approaches are discussed and compared. For the example analysis presented, it is found that the uncertainty of the measurement is dominated by the repeatability of the GC-MS analysis and suggested that volumetric (as opposed to gravimetric) preparation of solutions does not adversely affect the overall uncertainty. The methodology presented in this work can also be applied to analogous methods for similar analytes, for example, those used to measure polycyclic aromatic hydrocarbons (PAHs), pesticides, dioxins, or furans in ambient air.

1. INTRODUCTION

Polychlorinated biphenyls (PCBs) (Figure 1) are a group of highly toxic persistent organic pollutants (POPs) which exist in 209 congener forms defined by the number and location of chlorine atoms substituted onto the phenyl rings. In UK, PCBs were first produced commercially in the 1930s and by the middle of the twentieth century their production was widespread (66500 tonnes per annum in UK alone) [1]. Industrial applications included the manufacture of electronic devices (as transformers and capacitors), heat-exchange fluids, and as additives in paints, sealants, and plastics. Their use was phased out voluntarily throughout the 1970s and a total ban on their use in new plants and equipment was introduced in 1986 [2]. Despite this ban, concerns over the exposure of humans to PCBs remain due to their long-term stability in the environment—the dangers to health have been identified in a number of reports [3, 4].

In UK in 2004, the annual release of PCBs into the air was estimated to be 1330 kg, 68% of which originated from electronic devices [5]. Other sources were identified as waste burning and energy production. Humans are additionally exposed to PCBs through contaminated soil [6], water [7], and food [8–10]. The presence of PCBs in breast milk [9, 11, 12] is detrimental to the health of newborn babies, for example, affecting their immune system [13].

To limit the release of PCBs (and other POPs) into the environment, the European Union's Waste Electrical and Electronic Equipment (WEEE) Directive [14, 15] sets limits on the levels on electronic waste that may be sent to landfill. One consequence of this is that an increasing quantity of unwanted electronic devices is being disassembled at specialist plants, a number of which are located in East Asia. Recent measurements undertaken at these sites show that workers are exposed to levels of POPs orders of magnitude greater than the general population [16].

The concern over the long-term accumulation of these species in the environment leads to PCBs being covered by the Stockholm Convention on persistent organic pollutants [17]—a treaty signed by 151 states with the aim of protecting human health and the environment by reducing and eliminating the release of these toxic species. The UK Government
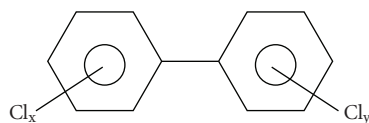
FIGURE 1: Structure of PCBs.

has recently developed a plan on how to implement the findings of the treaty [1].

Accurate measurement of PCBs in ambient air (and other environmental matrices) is therefore of great importance to legislators, industry, and the general public, and a number of documentary standard methods are available for their analysis [18–20]. The most widely used analytical method involves solvent extraction followed by sample clean up and analysis by gas chromatography—mass spectrometry (GC-MS) or high-resolution GC-MS.

Although the measurement of PCBs is now treated as routine by many laboratories (a number of who are accredited to carry out the analysis by national accreditation organisations), the complex, multistage nature of the analysis means that it is likely that most measurements of PCBs are carried out without a rigorous assessment of the uncertainty inherent in the final result. With the increasing legislative importance of the accurate measurement of PCBs (and similar species), there is a pressing need to determine these uncertainties correctly in order to provide all interested parties with the confidence in the measurements that they require. This is exacerbated by the automation of many of the preparative and analytical processes involved in the measurement. The absence of intervention by skilled operators can also result in large analytical errors, especially when the sensitivities of the result to aspects of the method are not properly understood.

This paper first presents a measurement equation for the analysis of PCBs, using the analysis of an urban dust certified reference material as an example. This measurement equation is then used to develop a full uncertainty budget for the analysis, highlighting the main contributory factors to the overall uncertainty of the final result. The advantages and disadvantages of using gravimetric or volumetric techniques for the preparation of calibration standards and other solutions are quantified, and it is discussed whether calculations should be carried out in the mass fraction or mass concentration domain in order to minimise uncertainty. Although the measurement equation and uncertainty budget presented here are specific to this method, it is hoped that the reader will find it easy to adapt for use in other laboratories. It may also be used as a basis to determine the uncertainty in the measurement of similar analytes in ambient dust, for example, polycyclic aromatic hydrocarbons (PAHs), dioxins, furans, and chlorinated pesticides.

2. EXPERIMENTAL

2.1. Materials and reagents

Calibration solutions were prepared from a certified multicomponent PCB stock solution of nominal mass concen-tration $2\,\mu g\cdot mL^{-1}$ (LGC Promochem, Teddington, UK), diluted as required with hexane (PAH analysis grade, Acros, Geel, Belgium, UK). Solutions of the internal standard (d_{14}-p-terphenyl) and one injection standard (d_{10}-acenapthene) were prepared from stock solutions of nominal mass concentrations $500\,\mu g\cdot mL^{-1}$ and $200\,\mu g\cdot mL^{-1}$, respectively (LGC Promochem); solutions of the second internal standard (d_{12}-perylene) were prepared from the pure material (LGC Promochem). The internal standard was used to define the efficiency of the extraction and workup process, the injection standard to correct for the temporal drift in sensitivity of the GC-MS.

The certified reference material (CRM) analysed was NIST SRM 1649a "urban dust" (National Institute of Standards and Technology, Gaithersburg, MD, USA). Hexane and diethyl ether (analytical reagent grade, Fisher, Loughborough, UK) were used as extraction solvents, and nonane ($\geq 99\%$ grade, Sigma-Aldrich, Gillingham, UK) was added as a "keeper" solvent (to prevent the solution being reduced to dryness). Extracts were cleaned up using silica (60 to $200\,\mu m$, Acros), potassium hydroxide (AnalaR grade, VWR, Lutterworth, UK), sulphuric acid (AnalaR grade, BDH), silver nitrate (reagent grade, Fisher), sodium sulphate (reagent grade, Acros), activated aluminium oxide (50 to $200\,\mu m$, Acros), hexane, toluene (GLC analysis grade, Fisher, UK), and dichloromethane (Baker analysed grade, J. T. Baker, Phillipsburg, NJ, USA). Helium was used as the GC-MS carrier gas (BIP grade, Air Products, Crewe, UK).

2.2. Overview of analysis method

The extraction, clean-up, and GC-MS procedures used were based on methods in the literature [21] and in documentary standards covering the measurement of PCBs in ambient air and other matrices [18–20]. An overview of the analytical procedure, showing the solvent(s) used at each stage is given in the flowchart in Figure 2. Note that the details of the method, particularly the types and volume of solvents used, may be unique to this analysis, but the same principles can be easily applied to cover the methods used in other laboratories.

2.3. Extraction

An appropriate portion (typically 0.3 g–0.5 g) of the predried CRM was Soxhlet extracted for 24 hours at 4 cycles per hour. Prior to extraction, all samples were spiked with a predetermined quantity of the internal standard (d_{14}-p-terphenyl) solution added such that the target mass fraction of the internal standard in the final solution would be approximately $50\,ng\cdot g^{-1}$, if complete recovery was to be achieved. The resulting extract had $100\,\mu L$ of nonane added as a "keeper" solvent and was condensed using a rotary evaporator (Büchi, Flawil, Switzerland) to a volume of less than 1 mL.
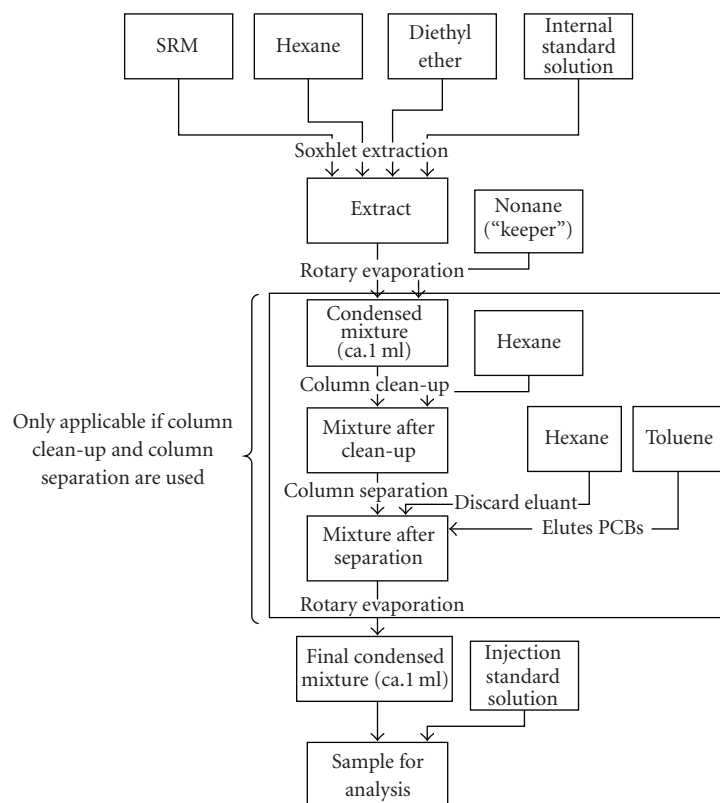
FIGURE 2: Flowchart outlining the analytical method employed.

TABLE 1: GC-MS method and optimisation parameters.

Gas chromatograph parameters	
Injection mode	Splitless
Injection port temperature	275°C
Injection volume	$2\,\mu L$
GC to MS transfer line temperature	290°C
Carrier gas and flow rate	Helium; $1.8\,mL \cdot min^{-1}$
Column	HP-5MS [(5% phenyl-) methyl-polysiloxane], $30\,m \times 0.25\,mm \times 0.25\,\mu m$ (film thickness)
Temperature program	(1) 70°C-hold for 2 minutes (2) ramp to 150°C at $15°C \cdot min^{-1}$-no hold (3) ramp to 300°C at $10°C \cdot min^{-1}$-hold for 5 minutes [Total time of program = 27.3 minutes]
Mass spectrometer parameters	
Ion source temperature	250°C
Quadrupole temperature	150°C
Electron multiplier voltage	2800 V
Other tuning parameters	Optimised automatically

2.4. Clean-up

Two successive column clean-up procedures were used—the first as a general clean-up of the sample and the second to separate PCBs from other similar species, for example, polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs).

Column one (300 mm long × 35 mm internal diameter) consisted of successive layers of silica, potassium hydroxide-coated silica, silica, sulphuric acid coated silica, silica, silver nitrate-coated silica, and sodium sulphate. The column was prewashed with 120 mL of hexane and the sample then added, followed by 250 mL of hexane. The resulting eluant contained the PCBs (and other similar species, e.g., PCDDs

TABLE 2: Ions monitored in GC-MS single ion monitoring mode.

Group	PCB congener(s) measured	m/z (1)	m/z (2)
Mono (Cl_1) PCBs	1, 3	188.1	152.1
Di (Cl_2) PCBs	4, 15	222.0	152.1
Tri (Cl_3) PCBs	19, 37	255.9	186.0
Tetra (Cl_4) PCBs	54, 77, 81	291.9	220.0
Penta (Cl_5) PCBs	104, 105, 114, 118, 123, 126	325.9	254.0
Hexa (Cl_6) PCBs	155, 156, 157, 167, 169	359.8	289.9
Hepta (Cl_7) PCBs	188, 189	393.9	323.9
Octa (Cl_8) PCBs	202, 205	429.8	359.9
Nona (Cl_9) PCBs	206, 208	463.8	393.8
Deca (Cl_{10}) PCB	209	499.6	429.8
Analyte	Use	m/z (1)	m/z (2)
d_{14}-p-terphenyl	Internal standard	164.1	162.1
d_{10}-acenapthene	Injection standard 1	224.2	—
d_{12}-perylene	Injection standard 2	264.1	—

and PCDFs were retained for separation by the second column).

Column two (250 mm long × 22 mm internal diameter) consisted of a bottom layer of 25 g of aluminium oxide under a layer of 5 g of sodium sulphate. The column was pre-washed with 60 mL of hexane and the sample added. Successive elutions were then carried out using 60 mL hexane (discarded), 90 mL toluene (eluant contained PCBs—retained for GC-MS analysis), and finally 200 mL hexane and dichloromethane (1 : 1 v/v) (eluant contained PCDDs and PCDFs—retained for separate analysis if required). The retained eluant was condensed to a volume of approximately 1 mL.

Finally, a quantity of the injection standard solution (containing d_{10}-acenapthene and d_{12}-perylene) was added volumetrically so that the mass fraction of injection standards in the final solution would be approximately 15 ng·g^{-1}. (The mass of the solution was recorded before and after each of the above additions.) The samples were then transferred to the GC-MS for analysis. If this analysis was not to take place immediately, the samples were stored in sealed amber-coloured vessels in a refrigerator in order to prevent thermal or photodegradation.

2.5. Preparation of calibration solutions

All calibration solutions were prepared gravimetrically in hexane using a model LA230S balance (Sartorius, Goettingen, Germany). (This is discussed fully in a subsequent section, where the approaches of preparing solutions volumetrically or gravimetrically are compared). A range of standards was prepared to cover the expected mass fraction range of the extracted samples, each of which also contained a known mass fraction of approximately 50 ng·g^{-1} of the internal standard and approximately 15 ng·g^{-1} of the injection standard. All solutions were stored in amber flasks in a refrigerator.

2.6. GC-MS analysis

GC-MS analysis was performed using a model 5890 gas chromatograph with a model 6973 electron ionisation mass spectrometer detection system (Agilent, Wokingham, UK). An autosampler was used to allow automated injection of a large number of samples and calibration standards. Full GC-MS method and optimisation parameters are given in Table 1. The mass spectrometer was operated in selected ion monitoring (SIM) mode with the m/z ratio(s) monitored for each analyte shown in Table 2. Each sample and calibration solution was analysed at least three times. To correct for the drift of the instrument, the ratio of analyte peak area to the injection standard peak area was calculated for each run—the mean and standard deviation of these ratios were then determined. The generalised least squares calculations were carried out using XLGENLINE (National Physical Laboratory, UK) [22].

3. RESULTS AND DISCUSSION

As discussed in the introduction, there is a pressing need to determine the uncertainty in the measurement of PCBs rigorously and in a robust manner in order to provide legislators, government, industry, and the general public with sufficient confidence in the measurement. This paper determines the uncertainty of the measurement by developing an uncertainty budget for three different approaches in turn:

(1) gravimetric preparation of solutions: calculations carried out in the mass fraction domain;

(2) volumetric preparation of solutions: calculations carried out in the mass concentration domain;

(3) an intermediate approach where the solutions are prepared gravimetrically, but calculations and the labelling of solutions are carried out in the mass fraction domain.

3.1. Gravimetric preparation of solutions (mass fraction domain)

When following the procedure outlined in the Guide to Uncertainty in Measurement (GUM) [23], the first step to the development of an uncertainty budget is to produce a measurement equation. Assuming that all calibration standards and other solutions are prepared gravimetrically, the measurement equation for the analysis method described above is shown below. The equation presented here is of course specific to this experimental method, but it is intended that it is presented in such a manner that it should be able to be easily adapted by the reader for use with other similar analyses.

The measurement equation is

$$x_{\text{PCB, SRM}} = \frac{x_{\text{PCB, ext}} \cdot m_{\text{ext}} \cdot \delta}{\eta_e \cdot m_{\text{SRM}}}, \tag{1}$$

$$x_{\text{PCB, ext}} = \frac{\overline{A}_{\text{PCB, ext}}}{\overset{\bullet}{V}_{\text{PCB}}}, \tag{2}$$

$$\eta_e = \frac{\overline{A}_{\text{int, ext}} \cdot x_{\text{int, cal}} \cdot \delta}{\overline{A}_{\text{int, cal}} \cdot x'_{\text{int, ext}}}, \tag{3}$$

$$\delta = \frac{\rho_{\text{cal}}}{\rho_{\text{ext}}}. \tag{4}$$

In (1), $x_{\text{PCB, SRM}}$ is the calculated mass fraction of the PCB analyte in the SRM, $x_{\text{PCB, ext}}$ is the measured mass fraction of the PCB analyte in the extract, m_{ext} is the mass of the extract, δ is a bias correction to account for differences between the densities of the analysed extract and calibration solutions, η_e is the extraction efficiency, and m_{SRM} is the mass of SRM extracted.

In (2), $\overline{A}_{\text{PCB, ext}}$ is the average, injection standard-corrected, peak area of the PCB analyte in the extract, and $\overset{\bullet}{V}_{\text{PCB}}$ is the gradient of the calibration curve for the PCB analyte.

In (3), $\overline{A}_{\text{int, ext}}$ and $\overline{A}_{\text{int, cal}}$ are the average, injection standard-corrected, peak areas of the internal standard in the extract, and a calibration solution, respectively, $x_{\text{int, cal}}$ is the mass fraction of the internal standard in this calibration solution, $x'_{\text{int, ext}}$ is the theoretical mass fraction of the internal standard in the extract (assuming complete recovery), and δ is the bias correction which also appears in (1).

In (4), ρ_{ext} is the density of extract and ρ_{cal} is the density of calibration solution.

Equation (1) is the top-level measurement equation and is input into directly by each of (2), (3), and (4). Equation (4) also inputs into (3). It is important to note that when (3) is substituted into (1), the δ terms cancel—this is the subject of later discussion. Each of these equations is now discussed in turn and the uncertainty of each component in each equation estimated.

Equation (4) describes a correction required because the density of the calibration solutions is very likely to be different than the density of the extract [24]. When, as in the case described here, calculations are carried out in terms of mass fraction, this correction is required to account for differences in the mass injected into the GC-MS using a fixed-volume injection. This difference arises because the density of the calibration solutions and the extract is likely to vary for one of two reasons. Firstly, following the multistage sample workup process (outlined in Figure 2), the resulting extract solution is likely to comprise a mixture of solvents and will inevitably have a different density to that of the calibration solutions, which are prepared in hexane. Secondly, the extract contains a complex mixture of species extracted from the CRM. It is obvious from simple observation of the condensed extract that its properties differ significantly from the calibration solutions—the extracts are often yellow-brown in colour and viscous in nature. In this example, it is assumed that the density of the calibration solution is the same as hexane, that is, $\rho_{\text{cal}} = (0.65936 \pm 0.00137)\,\text{g·mL}^{-1}$ (from above), and the density of the extract, that is, ρ_{ext} is $(0.85 \pm 0.07)\,\text{g·mL}^{-1}$. This gives a value for δ of 0.775. (In this example, this value for ρ_{ext} has been approximated and a large standard uncertainty (8% relative) with a rectangular uncertainty function has therefore been applied. ρ_{ext} could also be determined experimentally by drawing the extract into a suitable syringe, recording its volume and using this value along with the mass of the extract. This mass may be measured by weighing the syringe with and without extract or by transferral to an alternative vessel.)

As described above, the two δ terms in the measurement equation cancel. This is because each injection into the GC-MS is used for two purposes: determination of the amount of PCB present in the sample (by (1)), and calculation of the extraction efficiency (by (3)). As both of these determinations suffer from the same bias, δ, associated with the difference in density, this means that the uncertainty in δ can be assigned to be zero. Despite the δ terms cancelling, the presence of (3) increases the overall uncertainty through the introduction of two further instrument repeatability terms and two further standard preparation terms. This would not be required if a method was used, where η_e is not part of the measurement equation but is simply calculated as part of a quality assurance procedure, that is, (3) is not part of the measurement equation. In these cases, which are discussed further below, the uncertainty contribution from δ in (1) must be considered fully.

Equation (3) calculates the extraction efficiency of the analysis by comparing the measured mass fraction of the internal standard in the analysed extract to its theoretical mass fraction calculated from the quantity spiked prior to extraction. This theoretical mass fraction, $x'_{\text{int, ext}}$ in (3), can be determined from the mass fraction and volume of the internal standard solution used to carry out the spiking. In this study, an internal standard (d_{14}-p-terphenyl) solution of mass fraction $(1284.6 \pm 4.5)\,\text{ng·g}^{-1}$ was used. (The calculations of the uncertainty in the mass fraction of this and all other solutions used have been carried out assuming that the uncertainty in a balance reading is 0.5 mg). A volume of $50\,\mu\text{L}$ of this solution was used to spike the sample prior to extract. If it is assumed that the standard

uncertainty in the volume spiked was 0.25 μL and the density of the solution was the same as that of hexane (i.e., (0.65936 ± 0.00137) g·mL^{-1}), this gives the total mass of solution spiked as (32.97 ± 0.18) mg and therefore a d$_{14}$-p-terphenyl mass of (42.35 ± 0.27) ng. (The value used for the density of hexane is the figure at 20°C given by [25] and the uncertainty in this figure covers the given densities for temperatures between 18.5°C and 21.5°C—a reasonable assumption in a controlled laboratory environment.) Using data from a typical analysis as example, the mass of the total extract after condensation to just over 1 mL in volume was (1032.2 ± 0.6) mg, giving $x'_{\text{int, ext}}$ in this instance to be (41.03 ± 0.27) ng·g^{-1}. (The uncertainty in each of the above quantities has been calculated by combination of the constituent uncertainties in quadrature.)

The above calculation demonstrates the degree that knowledge of the density of the organic solvent(s) used to prepare the solutions has on the overall measurement. As stock solutions purchased from suppliers are in the vast majority of cases certified in mass concentrations units (e.g., ng·mL^{-1}), the use of a gravimetric preparation approach, such as that described here, necessitates that the density is first used to convert these into mass fractions before being used again in the above calculation.

The other mass fraction term in (3), $x_{\text{int, cal}}$, is the mass fraction of the internal standard in one of calibration solutions used. As described in the above experimental section, the target mass fraction of internal standard in each calibration solution was 50 ng·g^{-1}, but the actual value and uncertainty can be determined accurately from the gravimetric data, ensuring that the uncertainties are propagated correctly. Taking one of the midrange calibration solutions as an example, the mass fraction and standard uncertainty of the internal standard in this solution were determined to be (58.90 ± 0.45) ng·g^{-1}, with the uncertainty here being calculated by propagation of the uncertainties of each individual weighing (0.5 mg), and the uncertainties in the density and mass concentration of the stock solution.

The bias correction term, δ, is discussed above. The two remaining terms in the equation, $\overline{A}_{\text{int, ext}}$ and $\overline{A}_{\text{int, cal}}$, are the mean, injection standard-corrected responses for the internal standard in the extract and a calibration solution, respectively. An injection standard correction is used to improve the repeatability of a measurement by reducing effects caused by instrumental drift and differences in the volume of sample injected into the GC-MS. In the method used here, all solutions analysed contained two injection standards—it was the injection standard with the retention time nearest to the analyte of interest that was used to provide the correction. The uncertainties in $\overline{A}_{\text{int, ext}}$ and $\overline{A}_{\text{int, cal}}$ can be estimated by simply calculating the standard deviation of the ratios $A_{\text{int, ext}, i}/A_{\text{inj, ext}, i}$ and $A_{\text{int, cal}, i}/A_{\text{inj, cal}, i}$, respectively, where $A_{\text{inj, ext}, i}$ is the peak area recorded for the injection standards from i repeat analyses of the extract and $A_{\text{inj, cal}, i}$ the analogous term for the calibration solution. Exemplar standard deviations for both of the above ratios are 2.5%, however this standard deviation is likely to vary with mass fraction [26, 27]. It should also be noted that the peak areas discussed throughout this paper are blank subtracted peak areas, that is, peak areas after subtraction of a solvent blank (which for these analytes are often found to be zero).

Returning to the discussion of extraction efficiency, η_e, if all of the internal standard spiked prior to extraction is recovered in the final GC-MS analysis, then η_e is equal to unity. It is more than likely that $\eta_e < 1$, and in this case two different strategies can be applied. The first is to use the calculated value of η_e, no matter how large or small. The alternative approach is to set minimum and/or maximum allowable values for η_e, such as $0.50 < \eta_e < 1.2$. In this approach, if the value of η_e falls within this range, then the extraction is said to be valid and a value of $\eta_e = 1$ is used in (1). On the other hand, if the value of η_e is below this minimum, the extraction is said to be not fit for purpose and the results discarded. Although both of these approaches have their advantages and disadvantages, here the former is chosen, that is, the calculated values of η_e are input into (1). (Some documentary standards for similar analyses (e.g., [28]) use the latter approach, however, this is not strictly valid without the use of an uncertainty contribution for the term $(1 - \eta_e)$, a fact ignored by most analysts.)

Equation (2) calculates the mass fraction of PCB congener in the extract by the use of generalised least-squares (GLSs) [29, 30]. GLS is a fitting procedure that takes account of the uncertainties inherent in both the x-axis and y-axis data and performs a fit weighted to these uncertainties. The term on the denominator of (2), $\overset{\bullet}{V}_{\text{PCB}}$, is the gradient of the GLS fitted curve of the mass fraction of PCB congener in each calibration solution, $x_{\text{PCB, cal}}$ (x-axis), against the average injection standard corrected peak area from the PCB congener in the calibration solution, $\overline{A}_{\text{PCB, cal}}$ (y-axis). $\overset{\bullet}{V}_{\text{PCB}}$ and its uncertainty are determined automatically in a GUM-compliant manner by the software program used [22] and the uncertainty includes contributions from the uncertainties in the data on the x-axis and y-axis, $u(x_{\text{PCB, cal}})$ and $u(\overline{A}_{\text{PCB, cal}})$, respectively. Note that (2) assumes that the intercept of the calibration curve is zero—this is a valid assumption that can be tested by analysing solvent blank samples for the PCB congeners of interest—their levels are typically found to be below the instrumental of detection. The GLS fit can be constrained to give a zero intercept by including a point at $(0, 0)$ with uncertainties on both axes which are very small compared to those of the other data points into the calibration curve. A typical value for $\overset{\bullet}{V}_{\text{PCB}}$ and its uncertainty obtained here is $(2.58 \times 10^{-3} \pm 0.08 \times 10^{-3})$ g·ng^{-1}.

The remaining term in (2) is analogous to $\overline{A}_{\text{int, cal}}$ in (3), but in this instance $\overline{A}_{\text{PCB, ext}}$ relates to the corrected intensity of the PCB congener in the extract. $u(\overline{A}_{\text{PCB, ext}})$ can be estimated by calculating the standard deviation of the ratios $A_{\text{PCB, ext}, i}/A_{\text{inj, ext}, i}$ obtained from each repeat injection. Due to the complex nature of the sample and the large number of potentially interfering species in the sample (even following clean-up), separation of the species by GC retention time and/or MS target ion(s) is more difficult than for the calibration standards. Typical values of $u(\overline{A}_{\text{PCB, ext}})$ are between approximately 5% and 20% relative depending on

the quantity of PCB present in the sample: in this example, a value of $u(\overline{A}_{PCB,ext})$ of 10% relative is used.

Finally, (1) calculates the mass fraction of the PCB in the SRM and contains the terms δ, η_e, and $x_{PCB,ext}$ described in (4), (3), and (2), respectively. The values and uncertainties of the remaining two terms, the mass of the extract analysed by GC-MS (m_{ext}), and the mass of the SRM used (m_{SRM}) can be determined straightforwardly by gravimetry. Typical values from this work are $m_{ext} = (1032 \pm 1)$ mg and $m_{SRM} = (397.1 \pm 0.5)$ mg.

Tables 3(a) to 3(d) show the full uncertainty budget for the analysis determined from (1) to (4) using the values and uncertainties discussed above. Each table represents one of these equations and contains the following columns (from left to right):

(i) the quantity contained within the equation;

(ii) the symbol used to represent the quantity;

(iii) the estimated value of the quantity;

(iv) the sensitivity coefficient (the partial derivative of the output quantity with respect to the quantity in question);

(v) the estimated uncertainty of the quantity;

(vi) the shape of the probability distribution of the uncertainty;

(vii) the divisor which this distribution confers on this uncertainty;

(viii) the contribution to the standard uncertainty.

Note that some values in the table contain a large number of significant figures—these are used to avoid introducing rounding errors into the calculations. Fewer significant figures (appropriate to the overall relative uncertainty) are used when reporting the final results and, even then, the nonlinearity of the GUM for large relative uncertainties [31] such as those here means that the final significant figure should be used with caution.

The calculated output quantity for each table is given at the bottom of the third column. The uncertainty in this value, which is calculated by combining the individual contributions in quadrature, is given in the bottom right-hand cell of each table. In the example shown here, the measured mass fraction of the PCB analyte in the SRM, $x_{PCB,SRM}$, is therefore calculated from Table 3(a) to be 24.5 ng·g^{-1} with a standard uncertainty of 2.7 ng·g^{-1}.

The relative contribution to the overall uncertainty of each of the quantities in (1) taken from Table 3(a) is shown in Figure 3. This shows that by far the largest contributor is $x_{PCB,ext}$ (as calculated by (2)) and then η_e (as calculated by (3)). The contribution from the two gravimetric quantities, m_{ext} and m_{SRM}, are relatively very small and, as discussed above, the uncertainty in δ has been assigned to be zero.

Finally, the expanded uncertainty $U(x_{PCB,SRM})$ can be calculated by multiplying the standard uncertainty by a coverage factor:
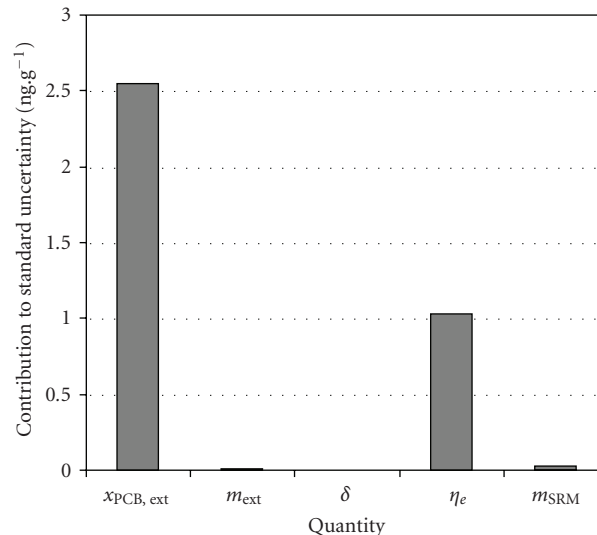
$$U(x_{PCB,SRM}) = k \cdot u(x_{PCB,SRM}), \qquad (5)$$

FIGURE 3: Graph showing the contribution of each of the five quantities in (1) to the uncertainty in $x_{PCB,SRM}$ for the gravimetric approach (mass fraction domain).

where k is the coverage factor and $u(x_{PCB,SRM})$ is the standard uncertainty in $x_{PCB,SRM}$. For this application, it is assumed that the effective degrees of freedom of the measurement are sufficient to assign a value of $k = 2$ in order to calculate the expanded uncertainty with a level of confidence of approximately 95%.

From Table 3(a), it can be determined that the overall expanded uncertainty for this exemplar analysis is 22.4% relative. Although this initially seems large in comparison to some analytical chemical measurements, it is likely to be more than fit for purpose for these challenging analyses at low levels and is of the order of magnitude generally expected for measurements of the composition of ambient material. As a comparison, the target uncertainties for similar trace analytes in ambient air are significantly larger than this. For example, for benzo(a)pyrene and other PAHs in ambient air, the legislative requirement is an expanded uncertainty of 50% for the particulate phase and 70% for total deposition at the target mass concentration of 1 ng·m^{-3} [32].

3.2. Volumetric preparation of solutions (volume fraction domain)

The implications on the uncertainty of the measurement if the solutions used in the procedure are prepared volumetrically rather than gravimetrically are now considered. Volumetric production of solutions as used by the majority of analytical laboratories generally results in a higher uncertainty than gravimetry but has the advantage of being a more rapid process, thus saving time and costs. For the analysis of PCBs and similar species, the issue likely to work in the favour of volumetric preparation is that the density of the extract solution, which is required for the solely gravimetric approach, is difficult to determine accurately.

TABLE 3

(a) Table calculating the uncertainty in the mass fraction of PCB in the SRM using (1) and the gravimetric approach (mass fraction domain).

Quantity	Symbol	Value	Sensitivity coefficient	Uncertainty	Probability distribution	Divisor	Contribution to standard uncert
Mass fraction of PCB in the extract (ng·g^{-1})	$x_{\text{PCB, ext}}$	8.244	2.97	0.857	Normal	1	2.545
Total mass of extract (g)	m_{ext}	1.0322	23.7	0.0005	Normal	1	0.010
Bias correction (no units)	δ	0.775	31.6	0	Normal	1	0.000
Extraction efficiency (no units)	η_e	0.679	−36.1	0.029	Normal	1	−1.030
Mass of SRM extracted (g)	m_{SRM}	0.397	−61.6	0.001	Normal	1	−0.031
Mass fraction of PCB in the SRM (ng·g^{-1})	**$x_{\text{PCB, SRM}}$**	**24.475**	**—**	**—**	**Normal**	**1**	**2.746**

(b) Table calculating the uncertainty in the measured mass fraction of PCB in the extract using (2) and the gravimetric approach (mass fraction domain).

Quantity	Symbol	Value	Sensitivity coefficient	Uncertainty	Probability distribution	Divisor	Contribution to standard uncert
Average injection standard corrected peak area of PCB in the extract (no units)	$\overline{A}_{\text{PCB, ext}}$	0.0213	387	0.0021	Normal	1	0.824
Gradient of the calibration curve for the PCB (g·ng^{-1})	$\dot{V}_{\text{PCB}}$	0.00258	−3191	0.00007	Normal	1	−0.236
Measured mass fraction of PCB in the extract (ng·g^{-1})	**$x_{\text{PCB, ext}}$**	**8.244**	**—**	**—**	**Normal**	**1**	**0.857**

(c) Table calculating the uncertainty in extraction efficiency using (3) and the gravimetric approach (mass fraction domain).

Quantity	Symbol	Value	Sensitivity coefficient	Uncertainty	Probability distribution	Divisor	Contribution to standard uncert
Average, injection standard-corrected, peak area of the internal standard in the extract (no units)	$\overline{A}_{\text{int, ext}}$	0.298	2.28	0.007	Normal	1	0.017
Mass fraction of the internal standard in a calibration solution (ng·g^{-1})	$x_{\text{int, cal}}$	58.90	0.012	0.45	Normal	1	0.005
Bias correction (no units)	δ	0.775	0.876	0	Normal	1	0.000
Average, injection standard-corrected, peak area of the internal standard in a calibration solution (no units)	$\overline{A}_{\text{int, cal}}$	0.489	−1.79	0.012	Normal	1	−0.022
Theoretical mass fraction of the internal standard in the extract (assuming complete recovery) (ng·g^{-1})	$x'_{\text{int, ext}}$	41.03	−0.021	0.27	Normal	1	−0.006
Extraction efficiency (no units)	**η_e**	**0.679**	**—**	**—**	**Normal**	**1**	**0.029**

(d) Table calculating the uncertainty in the bias correction to account for differences between the densities of the analysed extracts and calibration solutions using (4) and the gravimetric approach (mass fraction domain).

Quantity	Symbol	Value	Sensitivity coefficient	Uncertainty	Probability distribution	Divisor	Contribution to standard uncert
Density of calibration solution (g·mL^{-1})	ρ_{cal}	0.659	1.18	0.001	Normal	1	0.002
Density of extract (g·mL^{-1})	ρ_{ext}	0.850	−0.912	0.070	Rectangular	$\sqrt{3}$	−0.064
Bias correction (no units)	**δ**	**0.775**	**—**	**—**	**—**	**—**	**0***

*As discussed in the main text, the standard uncertainty in δ has been assigned to be zero.

The measurement equation for the volumetric preparation approach is very similar to that for the gravimetric case, but as no correction is necessary to account for the volumetric injection into the GC-MS, the bias correction term δ is not required. The measurement equation is outlined below:

$$x_{\text{PCB, SRM}} = \frac{c_{\text{PCB, ext}} \cdot v_{\text{ext}}}{\eta_e \cdot m_{\text{SRM}}}, \qquad (6)$$

$$c_{\text{PCB, ext}} = \frac{\overline{A}_{\text{PCB}}}{\overset{\bullet}{V}_{\text{PCB}}}, \qquad (7)$$

$$\eta_e = \frac{\overline{A}_{\text{int, ext}} \cdot c_{\text{int, cal}}}{\overline{A}_{\text{int, cal}} \cdot c'_{\text{int, ext}}}. \qquad (8)$$

In the above equations, c represents mass concentration and these symbols replace the corresponding symbols x (mass fraction) in (1), (2), and (3), for example, $c_{\text{PCB, ext}}$ is the measured mass concentration of the PCB analyte in the extract. The only "new" term in the above expression is the total volume of extract v_{ext}. Note that (7) and (8) both input directly into (6), and, importantly, the above expressions do not require the determination of the density of any solution because injection into the GC-MS is also carried out in a volumetric manner.

As before, each equation is now studied in turn, but this time the discussion is limited to the parameters that are different to those in the gravimetric approach. Note that this assumes that similar solutions to those used in the gravimetric case had been prepared volumetrically by usual laboratory methods. The calculations of the uncertainty in the mass concentrations of the solutions used here have been carried out assuming that the standard uncertainty in a single volumetric addition is as stated on a pipette (e.g., 0.05 mL for a 10 mL pipette and 0.1 mL for a 25 mL pipette) or equal to half the graduation of a syringe (e.g., 2.5 μL for a 250 μL syringe with 5 μL graduations).

In (8), $c'_{\text{int, ext}}$ is the theoretical mass concentration of internal standard in the extract, which is calculated to be (33.21 ± 0.54) ng·mL^{-1} for the example presented here. This value is determined from the mass concentration of the spiking solution $((826.3 \pm 12.7)$ ng·mL$^{-1})$, the volume spiked $((50.0 \pm 0.25) \mu$L), and the measured volume of the extract $((1.244 \pm 0.006)$ mL) assuming that the temperature of the laboratory was $(20 \pm 2)°$C. The mass concentration of the internal standard, $c_{\text{int, cal}}$, in one of calibration solutions is calculated to be (33.21 ± 0.54) ng·mL^{-1}, and the remaining two terms in the expression, $\overline{A}_{\text{int, ext}}$ and $\overline{A}_{\text{int, cal}}$ are assumed to be the same as for the gravimetric approach. This is an approximation as due to small differences in the preparation methods, the mass concentrations of the solutions used in the approach are not exactly equivalent to those in the gravimetric approach (if the latter were calculated by converting from mass fraction). However, this approximation is valid for this example considering the relatively large uncertainty of the overall method.

Note that the value of η_e calculated by this approach is slightly different than from the gravimetric approach
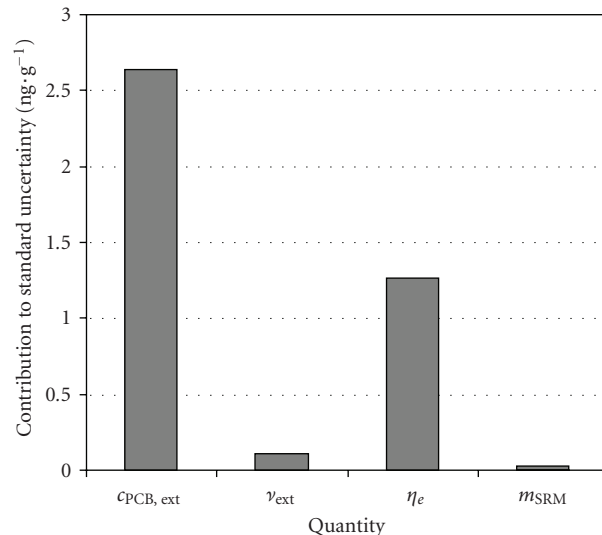

FIGURE 4: Graph showing the contribution of each of the four quantities in (6) to the uncertainty in $x_{\text{PCB, SRM}}$ for the volumetric approach (mass concentration domain).

(although the two values do actually agree within their expanded uncertainties). This is a result of two factors: the assumption regarding the use of the same values for $\overline{A}_{\text{int, ext}}$ and $\overline{A}_{\text{int, cal}}$ (discussed above) and the fact that, due to the complex preparation route of the calibration standards which involves a number of stock solutions in different solvents, the ratio of mass fraction to mass concentration is similar to, but not exactly equal to, the density of hexane—the solvent in which the calibration solutions are prepared.

Equation (7) calculates the mass concentration of PCB congener in the extract, again by the use of GLS. If a similar solution was analysed as in the gravimetric approach, the value of $\overline{A}_{\text{PCB, cal}}$ would not change, but the gradient $\overset{\bullet}{V}_{\text{PCB}}$ would report a different value and uncertainty, in this case $(3.78 \times 10^{-3} \pm 0.12 \times 10^{-3})$ mL·ng^{-1}.

Finally, (6) calculates the mass concentration of the PCB in the SRM. v_{SRM} can be determined by measuring the volume of the extract in a suitable syringe and in this example was (1.244 ± 0.006) mL. All the other parameters in the equation either come directly from previous equations or remain unchanged from the gravimetric example.

Tables 4(a) to 4(c) show the full uncertainty budget for the analysis for the volumetric preparation approach. The format of the table is identical to that of Table 3. In the example shown here, the measured mass fraction of the PCB analyte in the SRM, $c_{\text{PCB, SRM}}$, is calculated to be 25.1 ng·g^{-1} with a standard uncertainty of 2.9 ng·g^{-1}. This result differs slightly from that from the gravimetric approach due to the differences in extraction efficiency discussed above, but it should be noted that this difference is more than covered by the uncertainty. The expanded uncertainty, $U(c_{\text{PCB, SRM}})$, calculated by the use of (5) is 23.3% relative, slightly larger than that for the gravimetric approach.

The relative contribution to the overall uncertainty of each of the quantities in (6) as taken from Table 4(a) is shown

in Figure 4. As for the gravimetric approach, the largest contributors are $c_{PCB, ext}$ (as calculated by (7)) followed by η_e (as calculated by (8)). The contributions from v_{ext} and m_{SRM} are much smaller.

3.3. Gravimetric preparation of solutions: conversion to mass concentration domain

A third approach may also be taken—preparation of the solutions gravimetrically but then converting to the mass concentration domain for analysis. This approach benefits from the small uncertainties produced by the gravimetric process, although this is to some extent compromised by the need to convert each weighing into a volume by use of the density of the solvent, which also has an inherent uncertainty. An example of the respective uncertainties from each approach can be obtained by comparing the standard uncertainty of the PCB content in nominally the same calibration standard prepared by each approach (before the addition of the injection standards)—0.60% relative for the gravimetric approach (mass fraction domain), 1.58% relative for the volumetric approach (mass concentration domain), and an intermediate 0.76% relative for this third approach— gravimetry followed by conversion to the mass concentration domain.

Tables 5(a)-5(c) show the full uncertainty budget for the analysis for this third approach; the format of the table is identical to that of Tables 3 and 4. Because the solutions used are identical to those in the discussion of the gravimetric approach, the values and uncertainties of the three average, internal standard corrected peak areas, $\overline{A}_{PCB, ext}$, $\overline{A}_{int,ext}$, and $\overline{A}_{int, cal}$ are the same as in Table 3.

In the example shown here, the measured mass fraction of the PCB analyte in the SRM, $x_{PCB, SRM}$ is calculated to be 26.9 ng·g^{-1} with a standard uncertainty of 3.0 ng·g^{-1}— the expanded uncertainty $U(c_{PCB, SRM})$ is therefore 22.7% relative. Again, this value differs from that calculated by the gravimetric (mass fraction domain) approach, but the two values are clearly within the uncertainty of the measurement. The relative contribution to the overall uncertainty of this third approach (taken from Table 5)(a) is shown in Figure 5, which shows a very similar pattern to Figure 4.

3.4. Comparison of approaches

The values of $x_{PCB, SRM}$ calculated by each of the three approaches are compared in Table 6. The three relative uncertainties are very similar (between 22.4% and 23.3%) and, as discussed earlier in this paper, are all fit for purpose for the analysis as they exceed the confidence levels provided by legislators. The similarity between these values indicates that the vast majority of uncertainty in the example presented here comes from the GC-MS analysis—the contributions from the gravimetric and volumetric preparation methods are relatively small. This can be seen in Figures 3–5 and is demonstrated further by Figure 6, which shows the relative contributions to the overall uncertainty of η_e as calculated by (3) for the gravimetric approach (mass fraction domain). The dominant factors are $\overline{A}_{int, ext}$ and $\overline{A}_{int, cal}$, the
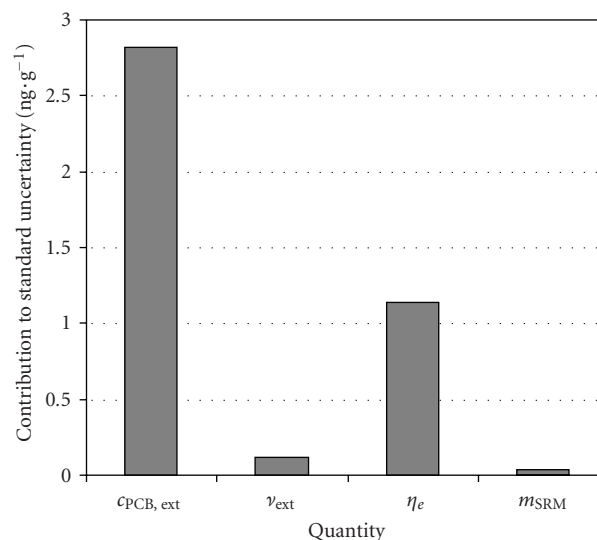

FIGURE 5: Graph showing the relative contribution of each of the four quantities in (3) to the uncertainty in $x_{PCB, SRM}$ for the third approach (gravimetric preparation: calculations in the mass concentration domain).

uncertainties of which are determined by the repeatability of the GC-MS analysis. The contributions of these factors to the overall uncertainty in η_e are approximately three to five times those from $x_{int, cal}$ and $x'_{int, ext}$. The bias correction δ has been assigned an uncertainty of zero. A further indication of the dominance of the uncertainty contributions from the GC-MS analysis is obtained if the overall uncertainty of the process is calculated assuming the uncertainty in the GC-MS analysis is zero, that is, if $u(\overline{A}_{int, ext})$, $u(\overline{A}_{int, cal})$, and $u(\overline{A}_{PCB, ext})$ are all set to zero. In this case, the expanded relative uncertainties of each approach are 2.5% for the gravimetric approach (mass fraction domain), 8.2% for the volumetric approach (mass concentration domain) and 7.6% for the third approach—gravimetry followed by conversion to the mass concentration domain.

The dominance of the uncertainty of the GC-MS analysis over that from the preparation of the solutions used in the analysis means that in addition to being more efficient, the volumetric approach does not compromise the uncertainty of the overall measurement. We therefore propose that, for the example presented here, the preferred approach for the analysis of PCBs in ambient air is to remain in the mass concentration domain at all times, that is, to prepare solutions volumetrically.

4. CONCLUSIONS

This paper has presented a detailed measurement equation and developed a full uncertainty budget for the analysis of PCBs in an urban dust reference material. Three approaches for preparing calibration standards and other solutions have been compared, namely,

(1) gravimetric preparation of solutions: calculations carried out in the mass fraction domain;

TABLE 4

(a) Table calculating the uncertainty in the mass concentration of PCB in the SRM using (6) and the volumetric approach (mass concentration domain).

Quantity	Symbol	Value	Sensitivity coefficient	Uncertainty	Probability distribution	Divisor	Contribution to standard uncert
Mass fraction of PCB in the extract (ng·mL^{-1})	$c_{\text{PCB, ext}}$	5.640	4.45	0.593	Normal	1	2.638
Total volume of extract (mL)	v_{ext}	1.244	20.2	0.006	Normal	1	0.113
Extraction efficiency (no units)	η_e	0.704	−35.7	0.035	Normal	1	−1.266
Mass of SRM extracted (g)	m_{SRM}	0.397	−63.2	0.001	Normal	1	−0.032
Mass fraction of PCB in the SRM (ng·g^{-1})	$\mathbf{x_{\text{PCB, SRM}}}$	**25.108**	—	—	**Normal**	**1**	**2.929**

(b) Table calculating the uncertainty in the measured mass concentration of PCB in the extract using (7) and the volumetric approach (mass concentration domain).

Quantity	Symbol	Value	Sensitivity coefficient	Uncertainty	Probability distribution	Divisor	Contribution to standard uncert
Average injection standard corrected peak area of PCB in the extract (no units)	$\overline{A}_{\text{PCB, ext}}$	0.0213	264	0.0021	Normal	1	0.564
Gradient of the calibration curve for the PCB (mL·ng^{-1})	$\dot{V}_{\text{PCB}}$	0.00378	−1494	0.00012	Normal	1	−0.182
Measured mass concentration of PCB in the extract (ng·mL^{-1})	$\mathbf{c_{\text{PCB, ext}}}$	**5.640**	—	—	**Normal**	**1**	**0.593**

(c) Table calculating the uncertainty in extraction efficiency using (8) and the volumetric approach (mass concentration domain).

Quantity	Symbol	Value	Sensitivity coefficient	Uncertainty	Probability distribution	Divisor	Contribution to standard uncert
Average, injection standard-corrected, peak area of the internal standard in the extract (no units)	$\overline{A}_{\text{int, ext}}$	0.298	2.36	0.007	Normal	1	0.017
Mass concentration of the internal standard in a calibration solution (ng·mL^{-1})	$c_{\text{int, cal}}$	38.32	0.018	1.24	Normal	1	0.023
Average, injection standard-corrected, peak area of the internal standard in a calibration solution (no units)	$\overline{A}_{\text{int, cal}}$	0.489	−1.44	0.012	Normal	1	−0.018
Theoretical mass concentration of the internal standard in the extract (assuming complete recovery) (ng·mL^{-1})	$c'_{\text{int, ext}}$	33.21	−0.021	0.54	Normal	1	−0.012
Extraction efficiency (no units)	η_e	**0.704**	—	—	**Normal**	**1**	**0.035**

(2) volumetric preparation of solutions: calculations carried out in the mass concentration domain;

(3) an intermediate approach where the solutions are prepared gravimetrically, but calculations and the labelling of solutions are carried out in the mass fraction domain.

Calculation of the overall expanded uncertainty of the measurement resulting from these three approaches has shown that they are very similar for the example presented here, ranging from 22.4% to 23.3%. These values are all fit for purpose for the analysis. Examination of the uncertainty budget has revealed that the dominant contributory factor to the calculated uncertainty is the repeatability of the GC-MS analysis, and that the method chosen to prepare the calibration standards and other solution contributes relatively little. For this reason, it is suggested that the solutions should be prepared in the most convenient manner possible—this is likely to be the volumetric approach (mass concentration domain). Of course, different laboratories

TABLE 5

(a) Table calculating the uncertainty in the mass concentration of PCB in the SRM using (6) and the third approach (gravimetric preparation: calculations in the mass concentration domain).

Quantity	Symbol	Value	Sensitivity coefficient	Uncertainty	Probability distribution	Divisor	Contribution to standard uncert
Mass fraction of PCB in the extract (ng·mL^{-1})	$c_{PCB, ext}$	5.640	4.76	0.593	Normal	1	2.821
Total volume of extract (mL)	v_{ext}	1.244	21.6	0.006	Normal	1	0.121
Extraction efficiency (no units)	η_e	0.658	−40.8	0.028	Normal	1	−1.139
Mass of SRM extracted (g)	m_{SRM}	0.397	−67.6	0.001	Normal	1	−0.034
Mass fraction of PCB in the SRM (ng·g^{-1})	**$x_{PCB, SRM}$**	**26.853**	**—**	**—**	**Normal**	**1**	**3.045**

(b) Table calculating the uncertainty in the measured mass concentration of PCB in the extract using (7) and the third approach (gravimetric preparation: calculations in the mass concentration domain).

Quantity	Symbol	Value	Sensitivity coefficient	Uncertainty	Probability distribution	Divisor	Contribution to standard uncert
Average injection standard corrected peak area of PCB in the extract (no units)	$\overline{A}_{PCB, ext}$	0.0213	265	0.0021	Normal	1	0.564
Gradient of the calibration curve for the PCB (mL·ng^{-1})	$\dot{V}_{PCB}$	0.00378	−1494	0.00012	Normal	1	−0.182
Measured mass concentration of PCB in the extract (ng·mL^{-1})	**$c_{PCB, ext}$**	**5.640**	**—**	**—**	**Normal**	**1**	**0.593**

(c) Table calculating the uncertainty in extraction efficiency using (8) and the third approach (gravimetric preparation: calculations in the mass concentration domain).

Quantity	Symbol	Value	Sensitivity coefficient	Uncertainty	Probability distribution	Divisor	Contribution to standard uncert
Average, injection standard-corrected, peak area of the internal standard in the extract (no units)	$\overline{A}_{int, ext}$	0.298	2.21	0.007	Normal	1	0.016
Mass concentration of the internal standard in a calibration solution (ng·mL^{-1})	$c_{int, cal}$	36.79	0.018	0.83	Normal	1	0.015
Average, injection standard-corrected, peak area of the internal standard in a calibration solution (no units)	$\overline{A}_{int, cal}$	0.489	−1.35	0.012	Normal	1	−0.016
Theoretical mass concentration of the internal standard in the extract (assuming complete recovery) (ng·mL^{-1})	$c'_{int, ext}$	34.10	−0.019	0.28	Normal	1	−0.005
Extraction efficiency (no units)	**η_e**	**0.658**	**—**	**—**	**Normal**	**1**	**0.028**

TABLE 6: Comparison of the values of $x_{PCB, SRM}$ and its expanded uncertainty calculated by each of the three approaches discussed in the main text.

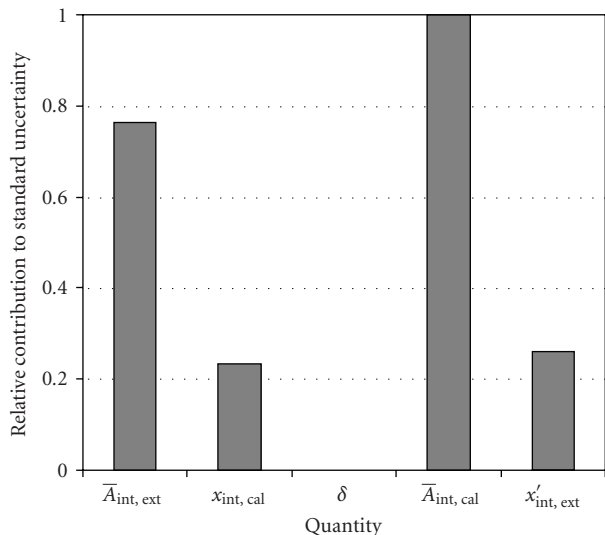| Approach	$x_{PCB, SRM}$	$U(x_{PCB, SRM})$	$U(x_{PCB, SRM})/x_{PCB, SRM}$
(1) Gravimetric (mass fraction domain)	24.5	5.5	22.4%
(2) Volumetric (mass concentration domain)	25.1	5.9	23.3%
(3) Gravimetric: calculations in the mass concentration domain	26.9	6.1	22.7%

Figure 6: Graph showing the contribution of each of the five quantities in (3) to the uncertainty η_e (normalised to the largest contribution) for the gravimetric approach (mass fraction domain).

using different methods may obtain different conclusions, for example, if the accuracy of the GC-MS analyses was much improved, the volumetric approach may have a significant contribution to the overall uncertainty and a gravimetric approach may be preferred. This can easily be investigated by use of the measurement equation presented here.

The use of a bias correction term, δ, introduced to account for differences in the densities of the calibration solution and analysed extract has also been discussed. This term is only required for the gravimetric approach (mass fraction domain) to correct for the response of the GC-MS to a fixed volume injection. However, as δ is used to calculate both the amount of PCB in the sample and the extraction efficiency of the method, the two δ terms cancel in the top-level measurement equation. Although δ can therefore be assigned an uncertainty of zero, knowledge of the density of both the calibration solutions and analysed extract is still required at other stages in the measurement equation. If η_e is not included in the measurement equation, then accurate knowledge of δ and its uncertainty are required.

Although this work has focussed on the analysis of PCBs, the authors hope that it can be applied easily to analogous methods for similar analytes, for example, those used by routine analytical laboratories to measure polycyclic aromatic hydrocarbons (PAHs), pesticides, dioxins, or furans.

ACKNOWLEDGMENTS

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