BAM-U030

Pentachlorophenol in Wood

Certification Report

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List of abbreviations

ECD	electron capture detection
FID	flame ionisation detection
GC	gas chromatography
MS	mass spectrometry
PCP	pentachlorophenol
PTFE	polytetrafluoroethylene
SD	standard deviation
u	uncertainty
U	expanded uncertainty
u_{char}	uncertainty contribution from characterisation
u_{com}	combined uncertainty
u_{pur}	uncertainty contribution from purity
r	relative

1 Introduction

In view of an efficient and sustainable use of natural resources, the recycling of waste materials is a matter of growing economic and public concern. In this context increasing attention is paid to the utilisation of recovered waste wood originating in large amounts from construction and demolition activities. As industrially treated waste wood often contains meanwhile restricted hazardous substances, in several European countries the utilisation of waste wood (recycling or combustion) is regulated by legislation defining permissible limits for the content of several elements and organic compounds which are classified as priority environmental pollutants. The corresponding values laid down in the German Ordinance on the Management of Waste Wood [1] are given in Table 1.

Tab. 1: Limit values for wood chips used in the manufacture of derived timber products [1]

Analyte	Permissible content in mg/kg
Arsenic	2
Cadmium	2
Chlorine	600
Chromium	30
Copper	20
Fluorine	100
Lead	30
Mercury	0.4
Pentachlorophenol	3
Polychlorinated biphenyls	5

Thus, for decision-making with respect to waste wood management reliable analytical data are needed and – due to their great economic and environmental impact – must be assured by appropriate quality control. One aspect of quality assurance of analytical measurement results is the application of suitable certified reference materials (CRM). In 2009 BAM produced ERM-CD100 for the determination of the heavy metals and pentachlorophenol (PCP) which were (and partly are) in use as wood preservatives. This CRM has been sold out and it was decided to close this gap with separate CRMs for PCP and the heavy metals. As the respective analytical procedures require different extraction or digestion procedures a subsample of a wood material can only be used for either one of the analytes. In order to enable the use of the material efficiently BAM-U030 was certified for Pentachlorophenol only. The certification was carried out on the basis of ISO 17034 [2] and the relevant ISO-Guides [3-4].

2. Production of the candidate material

The material was prepared at BAM using PCP contaminated wood (North American pine) obtained from a 1970s US Army ammunition chest. The wood had been treated industrially with PCP as preservative. Boards from a dismantled chest were cut to cm-size chips and then milled with a cutting mill after embrittlement with liquid nitrogen using a bottom sieve of 2 mm mesh size. Untreated beech wood was chopped with a commercial shredder and then milled as described for the PCP contaminated wood. Contaminated and untreated wood were separately classified using an automatic sieving station and the fractions between 0.25 and 1 mm were blended and homogenised using a drum hoop mixer. A total of 16.25 kg of homogenised wood material was submitted to bottling by means of a spinning riffler with 10 downpipes. 400 units of (40.4 ± 0.2) g were bottled using the "cross-riffling" procedure in 100 mL amber glass containers with screw caps equipped with PTFE insert and sealed with shrinking foil. The bottles were stored at (-20 ± 2) °C in the dark.

3 Homogeneity study

15 units were selected equidistantly from the batch of 400 bottles in order of bottling. They were analysed three times each according to standard operating procedure BAM-1.7-PV034 using a sample intake of 6 g. The procedure involved pressurised fluid extraction with methanol, followed by derivatisation with acetic anhydride and GC-MS determination using [$^{13}C_6$]-pentachlorophenol as internal standard. The whole set of 15 bottles was extracted once on each of three consecutive days. Processed extracts were analysed by GC-MS under repeatability conditions such that all 45 extracts were quantified against one calibration. Means and standard deviations are summarised in Figure 1. For the measurement data and the analysis of variance see ANNEX 1. No evidence suggesting a rejection of the hypothesis that the material is sufficiently homogeneous was observed. The mean of the homogeneity study was 7.186 mg/kg and the uncertainty of the PCP content between the bottles u_{bb} was estimated as 0.2674 mg/kg or expressed in relative terms as $u_{bb,r}$ as 0.0372.

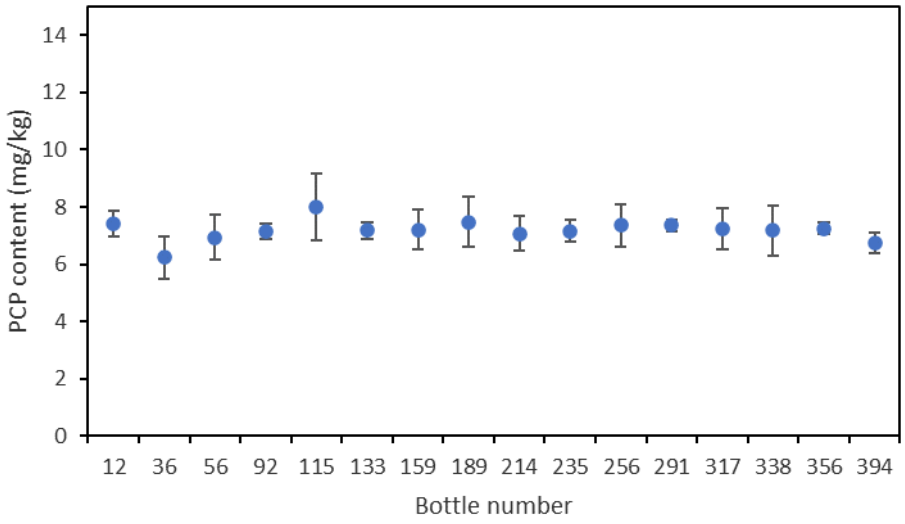

Fig. 1: Homogeneity study on selected bottles using GC-MS after extraction with methanol and derivatisation with acetic anhydride [5] (means and standard deviations n = 3).

4 Stability study

Though many organics in various matrices display a temperature-driven deterioration [6] the PCP content has been shown repeatedly to remain stable even at elevated temperatures in reference materials prepared from the very same source material [7, 8]. Nevertheless, selected units of the candidate material were submitted to a so-called isochronous accelerated ageing [9] at temperatures between +4 and +60 °C over periods of 1 - 12 months as shown in Table 2. After the respective periods of time the individual units were stored at -20 °C. All units were analysed for PCP in triplicate under repeatability conditions together with reference samples which had been kept at –20 °C and -80 °C since bottling and using the analytical procedure described for the homogeneity study. For the individual measurement data see ANNEX 1. No significant deterioration of the PCP content was detected. Selected units of BAM-U030 will be kept at +4 °C and +20 °C for two more years to enable a stability monitoring of units not stored under freezing as recommended.

Table 2: Accelerated ageing of selected units of BAM-U030: exposition temperatures, periods and numbers of exposed units.

Ageing time [Months]	+4 °C	+20 °C	+40 °C	+60 °C	Remark
1	2	2	2	2	*initial study*
3	2	2	2	2	*initial study*
6	2	2	2	2	*initial study*
12	2	2	2		*initial study*
24	2	2			*post certification monitoring*
36	2	2			*post certification monitoring*
48					*post certification monitoring*
60					*post certification monitoring*

5 Certification study

5.1 Selection of participating laboratories

A total of eight laboratories were invited to participate in the certification exercise on grounds of their satisfactory performance in three proficiency testing rounds on PCP analysis in wood operated by BAM in 2016, 2018 and 2020. At least two successful participations including the most recent round (2020) were required (relative laboratory performance < 1) and no unsatisfactory results in any round were accepted. Further selection criteria were the confirmations to use certified native PCP-Standards for calibration and to follow the analytical procedure laid down in the German Waste Wood Ordinance [1, 5] or a procedure with documented comparability. Additionally, the BAM laboratory responsible for candidate material production as well as homogeneity and stability measurements took part in this certification intercomparison. The participants are listed in alphabetical order of locations in Table 3 (not identical with the numbering in the results Table 4).

Table 3: Participants in the certification exercise in alphabetical order of location

Pfleiderer Deutschland GmbH	Arnsberg, Germany
M&S Umweltprojekt GmbH	Bad Muskau, Germany
Bundesanstalt für Materialforschung und -prüfung (BAM)	Berlin, Germany
Lobbe Entsorgung West GmbH	Iserlohn, Germany
Wood Technology Institute	Poznan, Poland
Dr. Marx GmbH	Spiesen-Elversberg, Germany
SGS-Analytik GmbH	Spremberg, Germany
Wessling GmbH	Weiterstadt, Germany
Nano GmbH	Weitnau, Germany

Six replicate PCP determinations using an intake of 6 g of the candidate material were to be performed by each laboratory. A questionnaire on the laboratory procedures had to be filled in. Results returned to BAM were scrutinised for consistency. No enquiries due to unclear or inconsistent data were regarded necessary. All invited participants performed extraction with methanol and derivatisation with acetic anhydride according to [5]. All but one laboratory reported to hold a respective accreditation according to ISO/IEC 17025.

5.2 Evaluation of results and certified values

5.2.1 Treatment of laboratory results

The results of the certification study are collected in Table 4 and were evaluated in accordance with ISO Guide 35 [2]. A scrutiny of the laboratory protocols revealed in case of C03 the failure to use an internal standard as technical reason to exclude the data from the evaluation of the certified value.

Although all participants in the intercomparison followed largely the standardised procedure [1, 5], significant differences caused by different implementations in different laboratories were to be expected. Thus, there was no good reason for assuming that the single values measured by the different laboratories would belong to a common mother distribution. This was confirmed by the statistical analysis within which the following statistical parameters were obtained using the software SoftCRM [10] before elimination of outliers:

- the mean of all laboratory means w_{char}: 6.88 mg/kg
- the standard deviation of the distribution of laboratory means s: 0.713 mg/kg
- the standard deviation of the mean of laboratory means (standard uncertainty u_{char}): 0.24 mg/kg

The following statistical tests were carried out (at significance levels α of 0.05 and 0.01):

- Cochran test for the identification of outliers with respect to laboratory variance
- Grubbs test for the identification of outliers with respect to the mean
- Dixon and Nalimov tests for the verification of possible outlier indications
- Kolmogorov-Smirnov test (Lilliefors version) for the normality test
- Tests for variance homogeneity, skewness and kurtosis

The main features are as follows:

- Scheffé test: Many laboratory data sets differ significantly if compared directly.
- Snedecor F test: Differences between laboratories are statistically significant (α=0.01).
- Bartlett test: Variances are not homogeneous ((α=0.01).
- Cochran test: C03 is outlier (α=0.01).
- Dixon test: No outliers detected.
- Nalimov test: C08 is a straggler (α=0.05).
- Grubbs test: No outliers detected.
- Kolmogorov-Smirnov-Lilliefors test: Laboratory means normally distributed.
- Skewness & kurtosis test: Laboratory means are not normally distributed.

As C03 did not use an internal standard and the respective data set was additionally identified as Cochran outlier the whole data set of C03 was removed from further evaluation of results. As a consequence, the data set of C08 displaying an obvious bias to the rest of laboratories was also eliminated. C09 used solid PCP for calibration with a purity of 98.01% (see Clause 5.2.3). The following results were obtained:
Mean of laboratory means w_{char}: 7.163 mg/kg
Standard deviation SD of the laboratory means: 0.391 mg/kg
Standard uncertainty u_{char} of the laboratory means (=SD/$n^{½}$ with n = number of laboratories): 0.1478 mg/kg
Relative standard uncertainty $u_{char,r} = u_{char}/w_{cert}$: 0.03295.

It should be noted that this consensus value is very close to that of BAM (C09) the only participant that used $^{13}C_6$-PCP as internal standard (see also 5.2.2).

Table 4: Data sets received from the participants in the certification study of BAM-U030

Laboratory	Replicate							
	# 1	# 2	# 3	# 4	# 5	# 6	mean	SD[a]
	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
C01	7.79	6.17	7.18	9.18	7.15	7.1	7.43	1.00
C02	8.78	6.75	6.38	8.00	8.16	6.84	7.49	0.96
C03	5.59	7.83	4.58	6.58	7.47	5.29	6.22	1.28
C04	7.67	7.59	7.51	7.49	7.58	7.54	7.56	0.07
C05	6.8	7.05	6.78	7.18	7.21	6.55	6.93	0.26
C06	6.984	5.94	7.182	5.76	6.246	6.552	6.44	0.57
C07	7.514	7.66	6.781	6.885	7.662	7.177	7.28	0.39
C08	5.341	5.685	5.667	5.57	5.348	5.021	5.44	0.25
C09	7.43	7.15	7.21	7.15	7.23	6.75	7.15[b]	0.22

[a] standard deviation

[b] after correction for calibrant purity: 7.01 mg/kg

5.2.2 Traceability

The certified value for PCP refers to the extractable amount according to [1, 5] and is conventional to this extent. However, different extraction methods and solvents (including methanol and toluene/H_2SO_4) have been investigated in an earlier study [11] and were shown to be equivalent regarding the completeness of PCP extraction. It was demonstrated that extraction, e.g. with methanol yields a PCP recovery close to 100% from the contaminated pine wood material also used for BAM-U030 [8, 12]. In order to ensure traceability of the extractable content as defined above, BAM employed certified solid PCP calibration standards (LGC Ehrenstorfer DRE-C15970000) and $^{13}C_6$-labelled PCP (LGC Ehrenstorfer DRE-C15970100) as internal standard. DAkkS accreditation number for both standards: D-RM-19883-01 & D-PL-19883-01. The other participating laboratories used one of two calibrants containing PCP in solution available from Neochema or Sigma-Aldrich, respectively. both providers are accredited as RM producers according to ISO 17034.

5.2.3 Certified value and combined uncertainty

The estimate for the certified value w_{cert} is derived from w_{char} (mean of the certification study). Since CO9 (BAM) used a solid PCP calibrant an additional purity investigation was performed (see ANNEX 2). The laboratory mean of C09 was multiplicated with f_{pur} (0.9801) prior to calculation of w_{cert}. The corresponding combined uncertainty is composed of the uncertainty of characterisation u_{char}, the contribution due the inhomogeneity between bottles u_{bb}, and the uncertainty u_{pur} due to the PCP content of the native calibrant according to Eq. 1 [13]:

$$u_{com,r}^2 = u_{char,r}^2 + u_{bb,r}^2 + u_{pur,r}^2 \qquad (1) \qquad\qquad u_{com} = w_{cert} \cdot u_{com,r} \qquad (2)$$

where the index *r* refers to the relative uncertainties. $u_{char,r}$ is taken from Clause 5.2.1 as 0.0329, and $u_{bb,r}$ from Clause 3 as 0.0372. For $u_{pur,r}$ the largest uncertainty of the employed PCP calibrants is taken as 0.0175 (see ANNEX 2). With Eq. 1 $u_{com,r}$ is evaluated as 0.0527 and with Eq. 2 u_{com} is then 0.3774.
The certified value w_{cert} and its combined uncertainty $u_{com} = w_{cert} \times u_{com,r}$ are given in Table 6. The expanded uncertainty $U = k\, u_{com}$ is obtained using a coverage factor k of 2 [2]. The certified value and the expanded uncertainty are rounded according to the recommendations of [14] and are given with respect to total sample mass. The water content of (6.95 ± 0.05) % remains stable if the material is handled according to the instructions in the certificate (see also Clause 6).

Table 5: Certified PCP content of BAM-U030 in mg/kg

	Certified value w_{cert}	Combined uncertainty u_{com} of the certified value	Expanded uncertainty U of the certified value
According to Eq. (1), (2)	7.163	0.377	0.754
After rounding	**7.17**	**0.40**	**0.80**

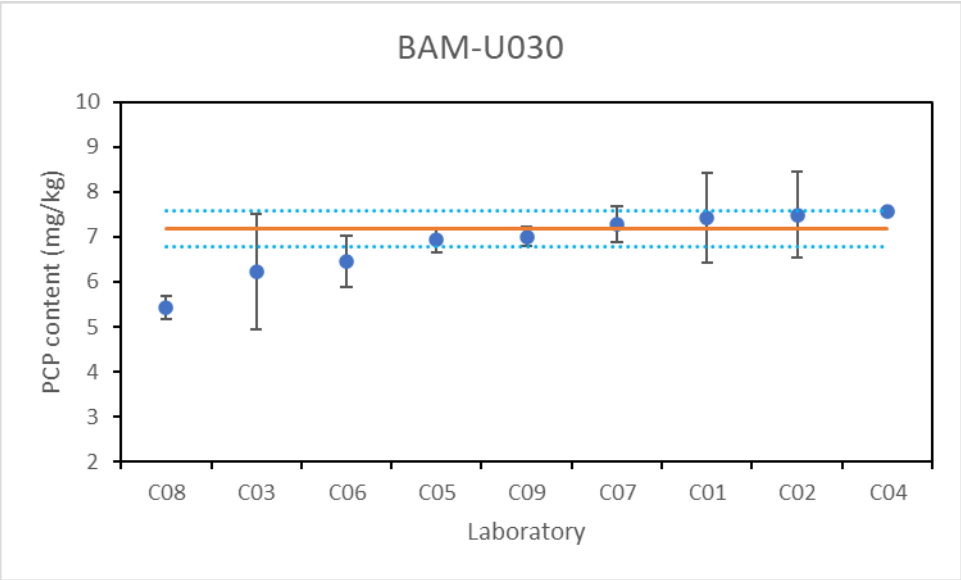

Fig. 2: Results of the interlaboratory comparison (means and standard deviations) with certified value w_{cert} and the confidence interval $w_{cert} \pm U$

6 Information on the proper use of BAM-U030

6.1 Shelf life

From the stability study no reasonable shelf life at -20 °C could be estimated as no decrease of the PCP content could be detected at temperatures up to 40 °C. There is no reason to assume any deterioration of PCP at – 20 °C. This in accordance with the observations made with earlier CRMs made of the same PCP-containing wood. A very conservative estimate for the stability at room temperature is six years from the date of certification. The validity of this estimate will be maintained by post-certification stability monitoring for five years after certification. The certificate will be valid for 24 months beginning with the dispatch of the material from BAM.

6.2 Transport, storage and use

The stability of the PCP content allows dispatching the material at ambient temperature. On receiving, it is to be stored at -20 °C. Before withdrawing a subsample the bottle must have reached ambient temperature. Thereafter, the bottle must be closed tightly and stored at -20 °C again. The water content remains stable when the material is treated as described.

6.3 Safety instructions

No hazardous effect is to be expected when the material is used under conditions usually adopted for the analysis of environmental matrices moderately contaminated with mineral oil hydrocarbons. Any unintended contact to this material should be treated as the contact to a dry wood without specifically hazardous properties. It is strongly recommended to handle and dispose of the reference material in accordance with the guidelines for hazardous materials legally in force at the site of end use and disposal.

6.4 Legal notice

Neither the Bundesanstalt für Materialforschung und -prüfung (BAM) nor any person acting on their behalf make any warranty or representation, express or implied, that the use of any information, material, apparatus, method or process disclosed in this document may not infringe privately owned rights or assume any liability with respect to the use of, or damages

resulting from the use of any information, material, apparatus, method or process disclosed in this document.

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ANNEX 1: Homogeneity and stability study

Results of the homogeneity study on BAM-U030 in mg/kg. SD – Standard deviation.

Bottle	**Replicate**				
No.	**1**	**2**	**3**	Mean	**SD**
12	6.91	7.63	7.73	7.43	0.45
36	5.42	6.84	6.44	6.23	0.73
56	7.70	7.02	6.11	6.94	0.80
92	7.42	6.85	7.18	7.15	0.28
115	7.99	6.85	9.17	8.01	1.16
133	7.16	7.47	6.88	7.17	0.30
159	7.40	7.78	6.47	7.21	0.67
189	6.88	7.05	8.49	7.48	0.88
214	6.70	6.74	7.77	7.07	0.61
235	7.52	7.18	6.75	7.15	0.38
256	8.12	7.32	6.65	7.36	0.73
291	7.16	7.30	7.59	7.35	0.22
317	6.43	7.51	7.75	7.23	0.70
338	7.78	6.18	7.61	7.19	0.87
356	7.35	7.03	7.38	7.26	0.19
394	6.34	7.01	6.90	6.75	0.36

ANOVA

Source of variability	*Sum of Squares (SS)*	*Degrees of freedom (df)*	*Mean sum of Squares (MS)*	*F-value*	*P-value*	*critical F-value*
between bottles	6.156710	15	0.410447347	0.9881	0.489	1.992
within bottles	13.29273	32	0.415398067			
total						

The grand mean of the homogeneity study is 7.1860 mg/kg. According to ISO Guide 35 the uncertainty between bottles $u_{bb} = s_{bb}$ is estimated as the result of Eq. (1) if F-value < 1. Eg. (1) yields u_{bb} = 0.2674 mg/kg.

$$s_{bb} = \sqrt{\frac{MS_{within}}{n}} \sqrt[4]{\frac{2}{N(n-1)}} \quad (1)$$

where: n = Number of replicate determinations per sample
N = Number of bottles analysed

The relative value $u_{bb,r}$ is 0.2674/7.1860= 0.0373.

Results of the stability study on BAM-U030 in mg/kg.

	Bottle	Replicate			Mean	SD
Exposure		1	2	3		
ref. -80 °C	93	6.91	7.16	8.23	7.43	0.70
ref. -20 °C	97	6.56	6.80	7.56	6.97	0.52
ref. -20 °C	98	6.82	7.55	8.91	7.76	1.06
+ 4°C, 1 month	99	6.62	7.26	7.39	7.09	0.42
+ 4°C, 1 month	100	6.91	7.55	6.20	6.89	0.68
+ 4°C, 3 months	101	6.45	7.48	7.19	7.04	0.53
+ 4°C, 3 months	102	6.46	7.28	7.44	7.06	0.53
+ 4°C, 6 months	103	7.22	7.31	8.43	7.65	0.67
+ 4°C, 6 months	104	7.67	8.65	7.69	8.01	0.56
+ 4°C, 12 months	105	6.33	8.25	7.15	7.24	0.96
+ 4°C, 12 months	106	6.70	7.26	6.69	6.88	0.33
+ 20°C, 1 month	109	6.40	7.16	7.19	6.92	0.45
+ 20°C, 1 month	110	6.01	6.71	7.28	6.67	0.63
+ 20°C, 3 months	111	6.45	8.56	6.93	7.31	1.11
+ 20°C, 3 months	112	7.19	6.94	7.69	7.27	0.38
+ 20°C, 6 months	113	6.07	7.21	5.93	6.40	0.70
+ 20°C, 6 months	114	6.40	6.63	7.19	6.74	0.40
+ 20°C, 12 months	116	6.53	7.91	6.76	7.07	0.74
+ 20°C, 12 months	117	7.28	8.21	8.48	7.99	0.63
+ 40°C, 1 month	120	7.05	7.30	7.66	7.33	0.31
+ 40°C, 1 month	121	6.49	6.99	7.19	6.89	0.36
+ 40°C, 3 months	122	5.87	6.92	7.07	6.62	0.66
+ 40°C, 3 months	123	6.24	7.83	7.48	7.19	0.83
+ 40°C, 6 months	124	6.85	6.80	7.81	7.15	0.57
+ 40°C, 6 months	125	6.18	6.76	9.34	7.43	1.69
+ 40°C, 12 months	126	7.27	7.28	7.13	7.23	0.09
+ 40°C, 12 months	127	8.46	6.61	6.82	7.30	1.01
+ 60°C, 1 month	128	7.47	7.63	8.25	7.78	0.42
+ 60°C, 1 month	129	7.11	7.31	8.32	7.58	0.65
+ 60°C, 3 months	130	8.70	7.05	8.35	8.03	0.87
+ 60°C, 3 months	131	7.45	6.85	7.82	7.37	0.49
+ 60°C, 6 months	132	8.50	8.38	8.97	8.62	0.31
+ 60°C, 6 months	134	7.87	7.45	8.82	8.05	0.71

SD: standard deviation

RSD: relative standard deviation

ANNEX 2: Purity of pentachlorophenol calibrants

Purity determination of solid PCP calibrant

Laboratory no. 9 (BAM) used sold native PCP as calibrant from LGC Ehrenstorfer (DRE-C15970000). Additional purity investigation using the 100% method was performed using GC-FID and two different columns. The purity was determined as 98.01% with an expanded uncertainty U of 0.104% (k = 2). Therefore, the mean of laboratory C09 was multiplicated with 0.9801 prior to calculation of w_{cert}.

GC-FID / Column 1 (HP-5)

	Replicate determination				
	-1	-2	-3	Mean	SD
PCP area	97.80%	98.07%	97.97%	97.95%	0.14%

GC-FID / Column 2 (DB-8270D+DG)

	Replicate determination				
	-1	-2	-3	Mean	STABW
PCP area	97.98%	98.06%	98.18%	98.08%	0.10%

Purity:	98.01%	(Mean from 6 replicate determinations)
$SD_{pur,r}$:	0.001279%	(relative Standard deviation SD_{pur} from 6 replicates)
$u_{pur,r}$:	0.0005222	(relative Standard uncertainty u_{pur} = SD_{pur}/n½)
$U_{pur,r}$:	0.001044	(relative expanded uncertainty U = 2 u_{pur})

The other participating laboratories used one of two calibrants containing PCP in solution available from Neochema or Sigma-Aldrich, respectively. Both providers are accredited as RM producers according to ISO 17034. The expanded uncertainty of the PCP concentrations U is 3.5% (k = 2). Therefore, an uncertainty contribution from calibrant purity of U/2 = 1.75% or $u_{pur,r}$ of 0.0175 was used as contribution from calibrant purity to the combined uncertainty u_{com} of w_{cert}.