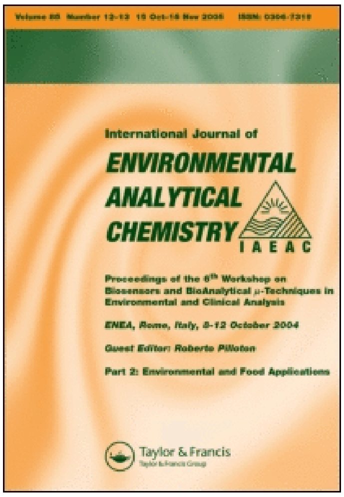

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

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To cite this Article Sutherland, Ross A.(2007) 'A re-examination of platinum-group element concentrations in the environmental certified reference material BCR-723', International Journal of Environmental Analytical Chemistry, 87: 7, 501 — 520

To link to this Article: DOI: 10.1080/03067310701336338

URL: http://dx.doi.org/10.1080/03067310701336338

Intern. J. Environ. Anal. Chem.
Vol. 87, No. 7, 15 June 2007, 501–520

A re-examination of platinum-group element concentrations in the environmental certified reference material BCR-723

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(*Received 2 August 2006; in final form 9 March 2007*)

A detailed statistical examination of replicated data used to certify platinum-group elements (PGEs) in environmental reference material BCR-723 is presented. Certification of Pt, Pd, and Rh concentrations in BCR-723 was based on 16, eight, and nine accepted data sets, respectively. Each accepted data set contained six replicated measurements for each PGE, and the statistical properties of these concentration data were examined, i.e. 96 for Pt, 48 for Pd, and 54 for Rh. This level of investigation has received limited attention but is critical in furthering our understanding of PGE variability and representativeness. Concentrations of Pt, Pd, and Rh were shown to differ significantly between accepted data sets. Palladium and Pt differed in their quantification between detection techniques. Additionally, Pd and Pt concentrations varied significantly between laboratories using a similar definitive method (inductively coupled plasma-isotope dilution mass spectrometry). The distribution of Pd concentrations was found to be bimodal, with a secondary population exhibiting a contamination signal of about 15%. The secondary population, not previously reported in BCR-723, is likely a measurement artifact and not due to a nugget effect. Comparisons of BCR-723 with other environmental media from Europe, i.e. airborne particulate matter, tunnel dust, and road-deposited sediment, indicated that Pd is uncommonly low in BCR-723 ($6.0\,\mathrm{ng\,g^{-1}}$) and is generally not representative in terms of its distribution relative to Pt and Rh. Serious consideration should be given to developing a new PGE certified environmental reference material.

Keywords: Interlaboratory comparison; Statistical methods; Palladium; Platinum; Rhodium; Certified reference material; Tunnel dust; Airborne particulate matter; Road-deposited sediment

1. Introduction

Recently, significant attention has been focused on platinum-group elements (PGEs) in a variety of solid environmental matrices [1–12]. Increasing interest in PGEs, specifically Pd, Pt, and Rh, relates to their significant environmental enrichment due to emissions from vehicle-based catalytic converters. However, their analysis has been problematic, even with new developments in technology, e.g. high

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International Journal of Environmental and Analytical Chemistry
ISSN 0306-7319 print/ISSN 1029-0397 online
DOI: 10.1080/03067310701336338

resolution-inductively coupled plasma-mass spectrometry (HR-ICP-MS). Difficulties in their quantification have resulted from their ultra-trace concentration levels (ng g^{-1}), and the most commonly used detection method (ICP-MS) suffers from a variety of spectral interferences. To alleviate, correct, or eliminate interferences, a number of strategies have been adopted, including sample dilution, chemical separation, matrix modification, alternative sample introduction systems, mathematical correction, or isotope dilution [13]. Of the three autocatalyst PGEs emitted to the environment, Pd has been the most problematic to measure. As Helmers *et al.* [14] succinctly noted 'Pd analysis is a difficult matter.'

To facilitate laboratory quality control/quality assurance (QC/QA) in PGE determination in solid matrices, a number of certified reference materials (CRMs) have been developed. Prior to 2000, the only CRMs available for PGEs were geological in origin, e.g. SARM-7, mineralized ore [15, 16]; TDB-1, diabase [17, 18]; WPR-1, altered peridotite diabase [17, 18], etc. These CRMs were unsatisfactory for environmental measurements, as concentrations were much higher, commonly in the mg kg^{-1} range, than those found in sediment, dusts, soil, or airborne particulate matter and there was little similitude between the geologic and environmental matrices. To fill this gap, the Standards, Measurements and Testing Programme (formerly BCR) of the European Commission funded the PACEPAC project in 1998 to produce a CRM (road/tunnel dust) for PGEs used in automotive catalytic converters [19]. The initial interlaboratory study analysed material collected in 1994 from the ceiling of the Tanzenberg Tunnel, Styria, Austria. The prepared sample, known as CW-7 (S. Hann personal communication, 2002), had the following indicative mean PGE values (±standard deviation, SD): Pt, 55 ± 8 ng g^{-1}; Pd, 4.0 ± 1.3 ng g^{-1}; and Rh 10.3 ± 1.4 ng g^{-1} [19]. The difficulty in Pd measurement was apparent from information given in Schramel *et al.* [19], with only 50% (seven of 14) of the submitted interlaboratory data sets accepted for final indicative value quantification. The Pd concentrations for excluded data ranged from 45 to 997 ng g^{-1}. The acceptance rates for Pt and Rh data submitted for CW-7 quantification were significantly higher, with 74% for Pt (14 of 19) and 70% for Rh (seven of 10). The results from the interlaboratory study of CW-7 were encouraging and resulted in the development of a CRM from road/tunnel dust collected in 1998 from the same location as CW-7.

The new PGE reference material was initially known as CW-8, until completion of the final certification process in 2002. It is officially known as BCR-723 and is available from the Institute for Reference Materials and Measurements (IRMM), Geel, Beligum [20, 21]. The certified means (±SD) are: Pt, 81.3 ± 4.6 ng g^{-1}; Pd, 6.0 ± 2.2 ng g^{-1}; and Rh 12.8 ± 1.6 ng g^{-1} [21].

Since the introduction of BCR-723 (CW-8), the only statistical exploration of the concentration data submitted for PGE certification was provided by the original studies of Zischka *et al.* [20, 21]. The objectives of this study are to present a new quantitative exploration of the original PGE data with robust procedures, examine particular claims made in the original certification documents, and compare PGEs in BCR-723 with those representative of various European environmental media.

2. Re-examination of certified PGE concentrations in BCR-723

2.1 *General background*

During the original certification process, participating laboratories performed a minimum of six independent replicate measurements of each element on at least two different bottles of BCR-723 on at least two different days [21]. The six averaged replicates from each accepted data set were tabulated in Zischka *et al.* [20], and an overall mean was computed for each. The focus of the certification process was not at the scale of replicate analyses (i.e. $n = 6$) but on the overall means of the accepted interlaboratory data sets. A traditional, non-robust approach was used to examine the interlaboratory mean data. The means of accepted data sets, i.e. a sampling distribution of means, were grouped, and a grand mean was computed. This is the traditional approach that invokes the central limit theorem, despite a relatively small number of accepted data sets (Pt, 16; Rh, 9; and Pd, 8).

We believe that an examination of the original replicate data for accepted data sets is a useful scale to explore (i.e. Pt, 96 values from 16 accepted data sets with six replicate values for each data set; Pd, 48 values; and Rh, 54 values), and not just the overall mean from a given accepted data set. Statistical explorations in this study will generally rely on robust approaches. Blind reliance on traditional parametric approaches, e.g. normal-distribution-based arithmetic means and confidence intervals, have been questioned, and robust methods provide a useful alternative with small sample sizes and non-normally distributed data. Another advantage of robust procedures is that they are designed to downplay outliers, and assume that contamination is a likely outcome of analytical measurement. Robust central tendency and location estimation, graphical exploratory data analysis (EDA), robust outlier examination, and bootstrapping are now widely accepted in environmental studies [22], in proficiency testing in analytical chemistry laboratories, and in interlaboratory data evaluations [23–30].

2.2 *An examination of Pt concentrations in BCR-723*

Graphical displays were used initially to visually examine 96 replicate values of Pt from the 16 accepted data sets (figure 1a and b). The histogram (figure 1a) appears normally distributed, and this was confirmed with the Kolmogorov–Smirnov test with Lilliefors significance correction [32] and the Shapiro–Wilk W-test at $\alpha = 0.05$ [33]. A Tukey-type box-and-whiskers diagram (box plot; figure 1b), provides a robust assessment of the data [22, 31]. The central box contains 50% of the data, between the 25th and 75th percentiles, with the central line being the median. Two low, empirically defined, outliers were flagged in figure 1b, and these values were 59.5 and 64.8 $\mathrm{ng\,g^{-1}}$, both from the same laboratory ('16 NAA,' codes as per Zischka *et al.* [20]) using radiochemical neutron activation analysis. Three additional outlier tests were also applied to the data. The robust MAD (median absolute deviation from the median)-based test of Davies [24] and Linsinger *et al.* [26], at 95% confidence, identified one outlier (59.5 $\mathrm{ng\,g^{-1}}$). The robust Z-modified approach using the normalized interquartile range (IQR), with $|Z| > 3$ [34] flagged the same outliers as the box plot. The traditional

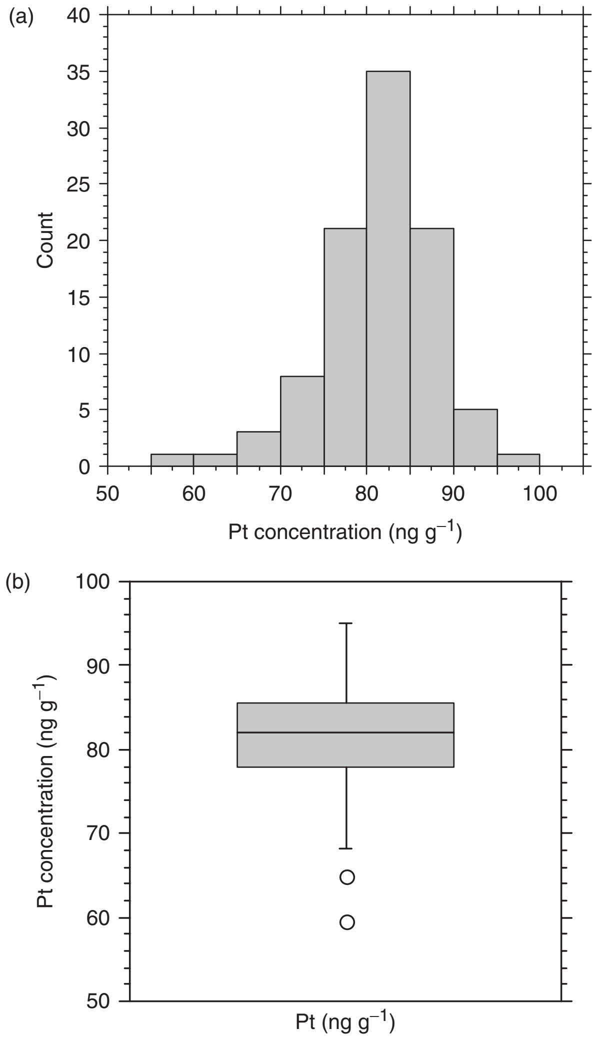

Figure 1. (a) Histogram of 96 replicated measurements of Pt in BCR-723. (b) Box plot of Pt concentrations in BCR-723. The box represents the central 50% of the data distribution, with the lower line the 25th percentile, the middle line being the median (50th percentile), and the upper line the 75th percentile. The 'whiskers' are empirically defined according to Tukey [31], and the circles reflect empirically defined outliers.

(non-robust) Grubb's approach at $\alpha = 0.05$ identified $59.5\,\mathrm{ng\,g^{-1}}$ as an outlier. Automatic exclusion of an outlier is not wise, unless it can be substantiated that a gross error or similar error has occurred. What outlier inclusion argues for is an examination of alternative (robust) approaches to characterizing central tendency, location, dispersion, and confidence intervals.

Summary statistics for Pt in BCR-723, normal distribution-based and robust approaches, are shown in table 1. Inclusion of outliers had only a negligible influence on Pt central tendency values, with the arithmetic mean (AM) being $81.3\,\mathrm{ng\,g^{-1}}$, compared with values of 81.8–$82.1\,\mathrm{ng\,g^{-1}}$ for the median, and three robust maximum-likelihood estimators (i.e. Huber's *M*, Tukey's Biweight, and Hampel's *M* [32]). Additionally, 95%

Table 1. Statistical summary of platinum-group element concentrations (ng g^{-1}) for BCR-723, based on all accepted replicated data published in Zischka *et al.* [20].

Statistics[a]	Pt	Pd	Rh
n	96	48	54
Outliers	1–2	0–2	0–1
Arithmetic mean ± SD	81.3 ± 6.23	6.05 ± 2.38	12.8 ± 1.97
95% CI of mean	80.1–82.6	5.36–6.75	12.3–13.4
Minimum	59.5	3.18	9.0
Maximum	95.0	12.7	18.1
Skewness	−0.62	1.20	0.49
Median ± IQR	82.1 ± 7.68	5.45 ± 2.58	12.8 ± 2.63
95% CI of median	80.9–83.3	4.87–6.03	12.2–13.4
Robust CV (%)	6.9	35.0	15.2
Huber's M-estimator	81.8	5.52	12.7
Tukey's Biweight	82.0	5.19	12.6
Hampel's M-estimator	81.8	5.49	12.7

[a] n, number of independent measurements; SD, standard deviation; CI, confidence interval; IQR, interquartile range; Huber's M (weighting constant of 1.339), Tukey's Biweight (weighting constant of 4.685), and Hampel's M (weighting constants of 1.7, 3.4, and 8.5) are robust estimators of central tendency [32].

confidence intervals (CIs) for the AM and the robust median only differed minimally, ≈1%.

2.3 *Pt accepted data set comparisons*

Robust methods identified one outlier in two of the 16 accepted data sets ('07 ICPMS,' and '12 ICPMS'). However, given that each data set contained only six replicated measurements, the power of the robust outlier tests must be viewed with some caution. A statistical summary is shown in table 2, and AM and corresponding 95% CIs for each accepted data set are plotted in relation to the certified Pt value and 95% CIs (figure 2).

For the 16 accepted data sets, arithmetic mean Pt concentrations (±95% CI) ranged from 71.7 ± 8.46 ng g^{-1} ('16 NAA') to 87.8 ± 5.19 ng g^{-1} ('05 DPCSV'; differential pulse cathodic stripping voltammetry). From figure 2, it is clear that not all accepted data sets overlap at the 95% level with the certified Pt confidence bands; and that not all accepted data sets have confidence intervals that overlap. The latter visual assessment was confirmed by using one-way analysis of variance (ANOVA). A test of homogeneity of variances (Levene statistic) indicated a significant inequality of accepted data set variances ($p = 0.0001$). Thus, the Brown–Forysthe and Welch statistics were used to test for equality of group means when the assumption of equal variance was violated. Results for both tests indicated significant differences in accepted data set group means at $p < 0.0001$, and this was also supported by the non-parametric Kruskal–Wallis test, ANOVA by ranks. *Post-hoc* testing indicated that accepted data set '08 ICP-IDMS' (inductively coupled plasma-isotope dilution mass spectrometry) and '06 NAA' were consistently different from other group means. These confirmatory results and the visual information in figure 2 call into question the statement by Zischka *et al.* [20] that their one-way ANOVA results demonstrate that the between-laboratory variation was not significant. Thus, application of a traditional (parametric) ANOVA to data that violate one of the fundamental assumptions of the procedure (i.e. equal variance between groups) is questionable.

Table 2. Summary statistics for individually accepted data sets for Pt concentrations (ng g^{-1}) in BCR-723 (each data set consists of six replicated independent measurements; data sets are ranked by arithmetic mean from lowest to highest concentrations).

Data set[a]	Mean ± SD	95% CIs mean[b]	Median ± IQR[c]	95% CIs median[b]
16 NAA	71.7 ± 8.46	62.8–80.6	73.0 ± 16.5	62.4–83.6
08 ICP-IDMS	74.4 ± 1.05	73.3–75.5	74.6 ± 1.53	73.6–75.6
03 NAA	76.2 ± 6.58	69.3–83.1	76.8 ± 14.1	67.8–85.8
06 NAA	76.7 ± 2.74	73.9–79.6	76.8 ± 5.33	73.4–80.2
13 ICPMS	79.7 ± 3.39	76.1–83.2	79.0 ± 6.00	75.2–82.8
07 ICPMS	79.7 ± 1.57	78.0–81.3	79.2 ± 2.03	77.9–80.5
02 ICPMS	81.5 ± 6.66	74.5–88.4	83.5 ± 12.7	75.3–91.7
12 ICPMS	82.4 ± 5.25	76.9–87.9	83.1 ± 6.60	78.9–87.3
14 ICPMS	83.3 ± 5.42	77.6–89.0	83.1 ± 10.1	76.6–89.6
09 DPCSV	83.5 ± 3.62	79.7–87.3	84.2 ± 5.58	80.6–87.8
01 ICPMS	83.8 ± 2.53	81.2–86.5	83.8 ± 4.53	80.9–86.7
11 DPCSV	83.9 ± 5.76	77.8–89.9	83.1 ± 10.1	76.6–89.6
01 DPCSV	83.9 ± 2.06	81.7–86.1	83.8 ± 3.83	81.3–86.3
14 ICPMS	86.1 ± 4.67	81.2–91.0	86.1 ± 9.33	80.1–92.1
04 ICP-IDMS	86.9 ± 3.35	83.3–90.4	88.3 ± 5.25	84.9–91.7
05 DPCSV	87.8 ± 5.19	82.4–93.3	87.5 ± 9.50	81.4–93.6

[a] Data set coding is that used by Zischka *et al.* [20]. DPCSV, differential pulse cathodic stripping voltammetry; ICPMS, inductively coupled plasma-mass spectrometry; ICP-IDMS, inductively coupled plasma-isotope dilution mass spectrometry; NAA, neutron activation analysis.

[b] CIs, represent confidence intervals.

[c] IQR, interquartile range.

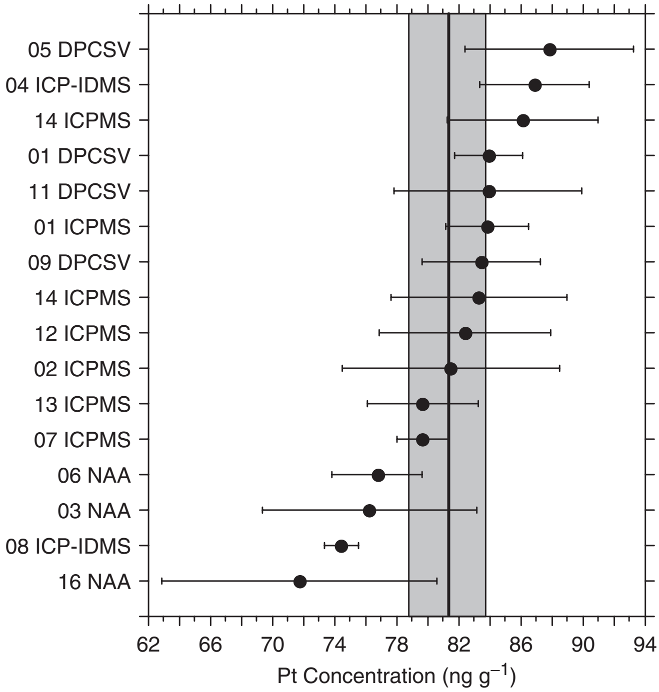

Figure 2. Ranked dot plot of arithmetic mean concentrations and 95% confidence intervals of 16 accepted Pt data sets. Codes on the *y*-axis are those used by Zischka *et al.* [20]. The shaded area represents the certified 95% confidence band about the mean.

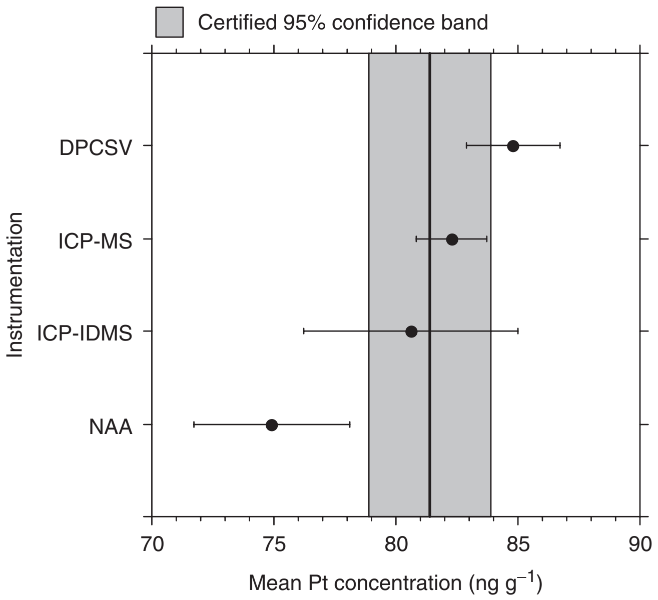

Figure 3. Ranked dot plot of arithmetic mean concentrations and 95% confidence intervals for four different detection methods used for quantifying Pt in BCR-723. The shaded area represents the certified 95% confidence band about the mean.

2.4 *Detection method comparisons of Pt in BCR-723*

In the original certification document for BCR-723 [20], the following claim is made: 'No substantial difference has been noted between the used methods' for individual PGE determinations. This statement was examined using the original Pt data from the 16 accepted data sets. Four detection-method groups were identified, regardless of differences in: sample mass, digestion procedures, or separation/pre-concentration procedures. The groups were DPCSV, ICP-IDMS, ICP-MS, and NAA.

No outliers were noted using robust approaches for the four detection methods measuring Pt in BCR-723. Normality testing indicated that the distribution of Pt measurements determined using ICP-IDMS ($n = 12$) was not normal ($p < 0.025$). Mean Pt values (±95% CIs of the AM) for each technique are plotted relative to the certified mean and 95% CIs in figure 3. A detailed statistical summary of the data is given in table 3. From figure 3, it is evident that no overlap exists between Pt measurements made using NAA ($n = 18$) and the certified values. Additionally, there is also no overlap between NAA measurements of Pt and those made using either DPCSV or ICP-MS. These instrument data associations were quantitatively explored, and robust tests indicated that group means were significantly different ($p < 0.0001$). *Post-hoc* testing indicated that Pt data from NAA were significantly different from ICP-MS and DPCSV, but not from ICP-IDMS. These robust statistical results do not support the earlier contention that there were no 'substantial' differences in methods used to determine Pt. Two questions arise from these new analyses: (1) were the three accepted NAA data sets statistically similar for Pt; and (2) should the BCR-723 certificate include a qualification for NAA analyses of Pt? The first question was answered using the robust equality of means tests—there were no significant differences in means between

Table 3. Statistical summary of platinum concentrations (ng g^{-1}) in BCR-723 determined using four separate detection methods.

Statistics[a]	NAA[b]	ICP-IDMS[b]	ICP-MS[b]	DPCSV[b]
Data sets	3	2	7	4
n	18	12	42	24
Mean ± SD	74.9 ± 6.44	80.6 ± 6.92	82.3 ± 4.72	84.8 ± 4.49
95% CIs of mean	71.7–78.1	76.2–85.0	80.9–83.8	82.9–86.7
Minimum	59.5	72.6	71.3	75.4
Maximum	83.5	89.6	92.5	95.0
Median ± IQR	75.9 ± 10.3	78.3 ± 14.1	82.3 ± 6.75	84.3 ± 6.48
95% CIs of median	72.1–79.7	71.9–84.7	80.7–83.9	82.2–86.4
Robust CV (%)	10.1	13.3	6.1	5.7
Huber's *M*	75.8	79.8	82.4	84.4
Tukey's Biweight	76.1	80.2	82.4	84.3
Hampel's *M*	75.7	80.6	82.4	84.5

[a] Data sets were those accepted for certification; *n*, number of independent measurements; SD, standard deviation; CI, confidence interval; IQR, interquartile range; Huber's *M*, Tukey's Biweight, and Hampel's *M* are robust estimators of central tendency [32].

[b] NAA, neutron activation analysis; ICP-IDMS, inductively coupled plasma-isotope dilution mass spectrometry; ICP-MS, inductively coupled plasma-mass spectrometry; DPCSV, differential pulse cathodic stripping voltammetry.

the six individual measurements for each of the three accepted NAA data sets ($p > 0.35$). Thus, when NAA measurements of Pt as a group differ from those of two common approaches, DPCSV and ICP-MS, there needs to be some qualification associated with the BCR-723 certificate.

2.5 *An examination of Pd concentrations in BCR-723*

A histogram of all Pd data from the accepted eight data sets ($n = 48$) clearly indicates a bimodal distribution of concentrations in the values used to certify BCR-723 (figure 4a). Seven Pd values occur in the secondary population, with values ≥ 10.1 ng g^{-1}. Five of these values come from one data set ('12 ICPMS') and two from another ('04 ICP-IDMS'). The box plot (figure 4b) is unable to display bimodality but does indicate two high 'outliers' from the same accepted data set, i.e. '12 ICPMS' (11.9 and 12.7 ng g^{-1}). Two other robust outlier procedures identified the two high outliers, but masking affected the traditional parametric based Grubb's test, and no outliers were identified at $\alpha = 0.05$. Tests indicated that Pd concentrations were not normally distributed.

Fifteen per cent of the accepted individual Pd measurements were ≥ 10.1 ng g^{-1}, and this may reflect either a potential 'nugget' effect or possibly a measurement bias problem. The two data sets that account for the secondary population all sampled at least the minimum recommended sample mass of 100 mg. Additionally, Sutherland [35] reviewed a number of studies employing BCR-723 in QC/QA protocols and found that the maximum Pd concentration reported was < 10 ng g^{-1}. Thus, the nugget effect seems unlikely, and some form of measurement bias has caused the problem. The statistical summary of Pd concentration data reported in table 1 must now be viewed with caution given the bimodality in the data distribution.

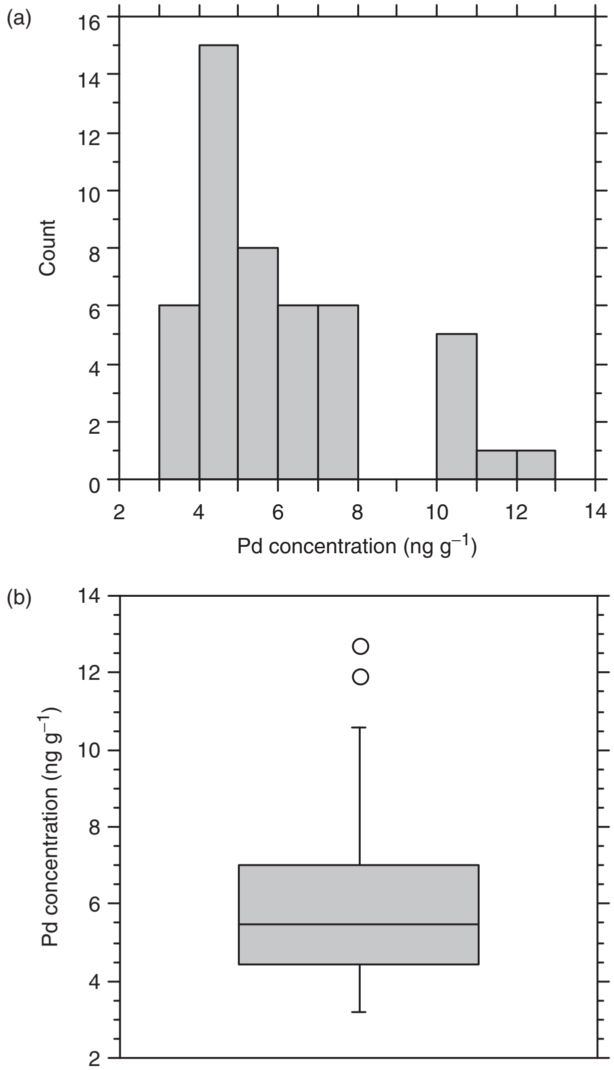

Figure 4. (a) Histogram of 48 replicated measurements of Pd in BCR-723. (b) Box plot of Pd concentrations in BCR-723. The circles reflect empirically defined outliers.

2.6 *Pd accepted data set comparisons*

The previous discovery of a potential secondary population of Pd values in BCR-72 was further explored using individual accepted data sets ($n=8$). A statistical summary for individual data sets is shown in table 4. Figure 5 displays the AMs and 95% CIs for the eight Pd data sets, and these can be visually related to the certified AM and 95% CIs for BCR-723. The average Pd concentrations from accepted data set '12 ICPMS' (10.5 ng g^{-1}) does not have 95% CIs that overlap with the certified values and only overlaps with accepted data set '04 ICP-IDMS.' At the other end of the spectrum, the average Pd concentration for data set '08 ICP-IDMS' (3.52 ng g^{-1}) did not have 95% CIs that overlap with the certified CIs of BCR-723 (4.22–7.88 ng g^{-1}) and only

Table 4. Summary statistics for individually accepted data sets for Pd concentrations (ng g^{-1}) in BCR-723 (each data set consists of six replicated measurements; data sets are ranked by arithmetic mean from lowest to highest concentrations).

Data set[a]	Mean ± SD	95% CIs mean[b]	Median ± IQR[c]	95% CIs median[b]
08 ICP-IDMS	3.52 ± 0.38	3.12–3.92	3.45 ± 1.34	3.08–3.82
09 AAS	4.47 ± 0.74	3.69–5.24	4.25 ± 1.03	3.59–4.91
05 TXRF	4.90 ± 0.51	4.37–5.43	4.80 ± 1.05	4.13–5.47
01 ICPMS	5.43 ± 1.16	4.22–6.65	5.05 ± 2.28	3.59–6.51
02 ICPMS	5.52 ± 1.15	4.31–6.72	5.10 ± 1.73	3.99–6.21
14 ICPMS	6.33 ± 1.08	5.20–7.46	6.40 ± 1.80	5.25–7.55
04 ICP-IDMS	7.80 ± 2.14	5.56–10.0	7.05 ± 4.33	4.28–9.82
12 ICPMS	10.5 ± 1.96	8.41–12.5	10.6 ± 2.78	8.77–12.3

[a] Data set coding is that used by Zischka *et al.* [20]. ICPMS, inductively coupled plasma-mass spectrometry; ICP-IDMS, inductively coupled plasma-isotope dilution mass spectrometry; TXRF, total reflection energy dispersive X-ray fluorescence spectrometry; AAS, atomic absorption spectrometry (as noted in the text, we retain the lab i.d. from [20] though final detection was by UV-VIS spectrophotometry at 274 nm).

[b] CIs, represent confidence intervals.

[c] IQR, interquartile range.

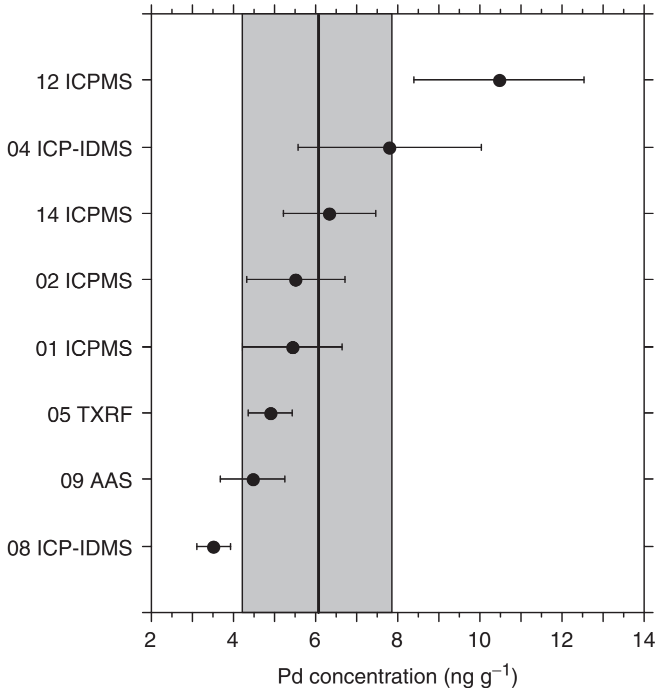

Figure 5. Ranked dot plot of arithmetic mean concentrations and 95% confidence intervals of eight accepted Pd data sets. The shaded area represents the certified 95% confidence band about the mean. Note lab code '09 AAS' has been retained for consistency with [20], though the detection method has been stated in the same publication as UV spectrophotometry at 274 nm.

overlapped with data set '09 AAS' (Note: in table 7.1 of [20], following high-performance liquid chromatography the final detection method for this data set is identified as UV detection at 274 nm and not AAS as it is in Annex table 2. For consistency, we keep the original designation used in [20]). Formal testing supported the visual observations. Variance differed significantly between Pd data sets ($p = 0.016$), and Welch and Brown–Forsythe tests indicated that means between accepted data sets were not equal ($p < 0.0001$). *Post-hoc* testing indicated that data set '08 ICP-IDMS' (minimum value in figure 5) and data set '12 ICPMS' (maximum value in figure 5) were the most statistically distinct. The threefold difference in Pd AMs (3.5 *vs.* 10.5 ng g^{-1}) is worrying, given that ICP-MS was used for both sets of determinations. Even more worrying would be a primary (reference) method, like ICP-IDMS, producing statistically different Pd results between accepted data sets. To explore this possibility, a comparison was made between the accepted lab results for '04 ICP-IDMS' and '08 ICP-IDMS'. Laboratory procedures differed minimally, with both using microwave-assisted high-pressure digestion. Lab '04' used HCl/HNO_3 followed by $HCl/HNO_3/H_2O_2 + HF$, while lab '08' used HCl/HNO_3 followed by HF. Both used anion-exchange chromatography (Dowex 1X-8), with lab '04' finishing with sector-field ICP-IDMS, and lab '08' with ultrasonic nebulization ICP-IDMS. In both labs, isotope dilution was conducted with enriched ^{108}Pd. An exact permutation test (two-tailed) indicated significant differences in Pd concentrations between labs (see table 4 for a data summary) at $p = 0.0022$. This p-value indicates that if there was no difference in mean Pd concentrations between labs, the difference observed (4.28 ng g^{-1}) would occur only 22 times in 10,000. This is strong evidence in support of procedural problems in implementing the reference method, or a statistical artifact of a bimodal distribution of Pd in BCR-723. Given that a similar statistical difference was noted for Pt between the same two laboratories ($p = 0.0020$, exact permutation test) using enriched ^{194}Pt, it is likely that a procedural problem is the cause of the concentration discrepancy between laboratories for the definitive ICP-IDMS method.

In summary, these findings call into question the statistical rigor in the original certification of Pd in BCR-723 and laboratory quantitation problems. Further, work needs to focus on Pd concentration measurements in BCR-723.

2.7 *Detection method comparisons of Pd in BCR-723*

Palladium concentrations differed between accepted data sets. Additionally, it was also shown that data from different labs using the same method produced statistically different Pd data, i.e. ICP-IDMS (and ICP-MS, data not shown). Nevertheless, it is still valuable to explore whether differences occurred between Pd concentrations in BCR-723 measured using different detection methods. Four detection methods were identified: ICP-MS, ICP-IDMS, TXRF (total reflection energy dispersive X-ray fluorescence spectrometry), and UV detection at 274 nm (identified incorrectly as AAS in [20]). Only one accepted data set, with six replicated measurements, is available for each of the techniques, TXRF and UV-274 detection. These single laboratory contributions produced well-constrained Pd measurements and low robust coefficients of variation (RCV = 16–18%), compared with the other two techniques that have several laboratories contributing data (RCV 34–58%) (table 5). A visual plot of AMs and 95% CIs for each detection technique, with superimposed certified Pd concentrations for BCR-723, are shown in figure 6. All 95% CIs of the detection techniques overlap with the certified 95% CI for BCR-723. However, 95% CIs for TXRF and UV detection methods do not 'catch' the certified mean and are biased low.

Table 5. Statistical summary of palladium concentrations (ng g^{-1}) in BCR-723 determined using four separate detection methods.

Statistics[a]	UV-274[b]	TXRF[b]	ICP-IDMS[b]	ICP-MS[b]
Data sets	1	1	2	4
n	6	6	12	24
Mean ± SD	4.47 ± 0.74	4.90 ± 0.51	5.66 ± 2.67	6.94 ± 2.48
95% CIs of mean	3.69–5.24	4.37–5.43	3.96–7.36	5.89–7.98
Minimum	3.80	4.30	3.18	4.40
Maximum	5.80	5.50	10.6	12.7
Median ± IQR	4.25 ± 1.03	4.80 ± 1.05	4.90 ± 3.82	6.25 ± 2.90
95% CIs of median	3.59–4.91	4.13–5.47	2.45–7.35	4.39–8.11
Robust CV (%)	17.9	16.2	57.8	34.4
Huber's *M*	4.30	4.86	5.12	6.32
Tukey's Biweight	4.19	4.88	4.93	6.09
Hampel's *M*	4.30	4.90	5.25	6.41

[a] Data sets were those accepted for certification; *n*, number of independent measurements; SD, standard deviation; CIs, confidence intervals; IQR, interquartile range; Huber's *M*, Tukey's Biweight, and Hampel's *M* are robust estimators of central tendency [32].

[b] TXRF, total reflection energy dispersive X-ray fluorescence spectrometry; UV-274, UV detection at 274 nm (as noted in the text the original publication [20] designates this incorrectly as AAS, i.e., '09 AAS'); ICP-IDMS, inductively coupled plasma-isotope dilution mass spectrometry; ICP-MS, inductively coupled plasma-mass spectrometry.

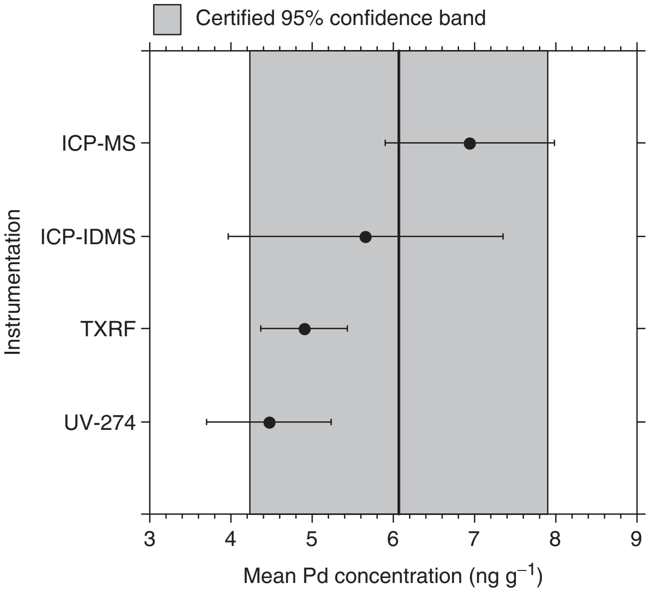

Figure 6. Ranked dot plot of arithmetic mean concentrations and 95% confidence intervals for four different detection methods used for quantifying Pd in BCR-723. The shaded area represents the certified 95% confidence band about the mean.

This of course assumes that the certified value is unbiased, and this is questionable given that the data distribution may contain up to 15% in 'contaminated' values.

Palladium concentrations measured using ICP-MS and ICP-IDMS were non-normally distributed ($p < 0.035$). Variances of the detection groups were not homogeneous ($p = 0.012$), and robust tests of equality of means indicated significant differences between methods ($p < 0.009$). Thus, as with Pt concentrations in BCR-723,

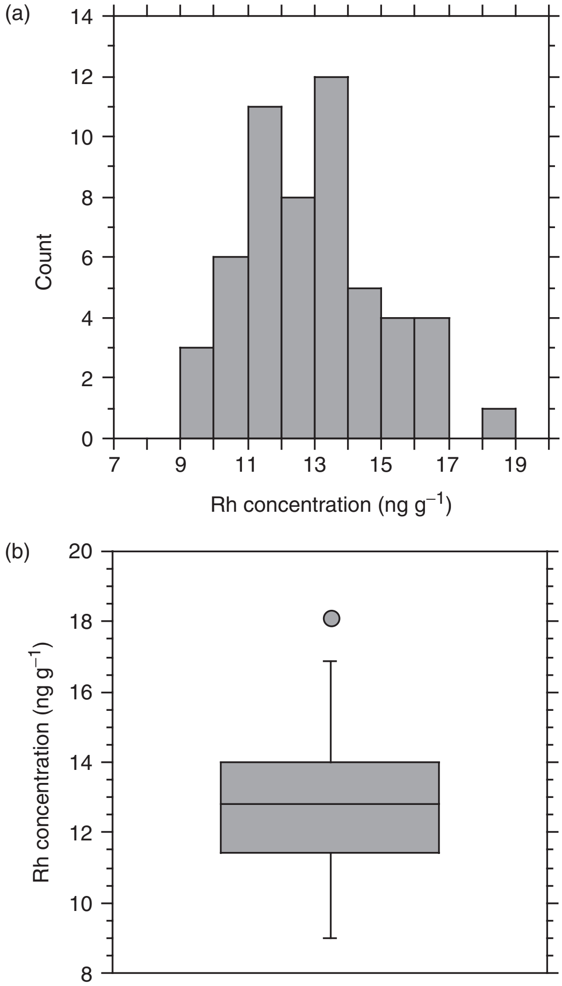

Figure 7. (a) Histogram of 54 replicated measurements of Rh in BCR-723. (b) Box plot of Rh concentrations in BCR-723. The circle reflects an empirically defined outlier.

statistically significant differences were observed in Pd values between different instrumental detection methods. This is worrying given that BCR-723 is a stringently prepared, homogeneous sediment sample ($<90\,\mu$m).

2.8 *An examination of Rh data in BCR-723*

A histogram of all Rh data (figure 7a) from the nine accepted data sets ($n = 54$) indicates a slight positive skew, but the distribution does not deviate significantly from normal ($p = 0.20$). One outlier was identified in the box plot (figure 7b), with an Rh concentration of 18.1 ng g^{-1} ('04 ICP-MS'). Summary statistics are shown for all data in table 1, with an RCV (15%) intermediate between Pt (7%) and Pd (35%). All robust and non-robust measures of central tendency agree within 0.2 ng g^{-1}, and range from

12.6 to 12.8 ng g^{-1}. The maximum to minimum Rh concentration measured for BCR-723 was 2.0, compared with Pt of 1.6, and Pd of 4.0.

2.9 *Rh accepted data set comparisons for BCR-723*

Statistical data for the nine accepted data sets are shown in table 6. All data sets tested normal ($p \geq 0.10$) using the Shapiro–Wilk W-test. The AM and 95% CIs for each data set are plotted in figure 8, with the certified Rh concentrations shown as the shaded area. One of the data sets does not overlap at the 95% confidence level ('04 ICP-MS'). A one-way ANOVA was used, as variances between data sets were homogeneous ($p = 0.82$). The F-ratio (8.1) was significant at $p < 0.0001$, indicating at least one pairwise difference between Rh concentration data sets used to certify BCR-723. This was explored further using the Bonferroni/Dunn *post-hoc* test, and results of multiple comparison tests are appended to figure 8 (i.e. data sets with the same letter are not significantly different at $\alpha = 0.05$). Results from '04 ICP-MS' and '12 ICPMS' were significantly different from three other accepted data sets ('14 ICPMS,' '01 DPCSV,' and '01 ICPMS'), two of which also used ICP-MS.

2.10 *Detection method comparisons for Rh in BCR-723*

Only two detection methods were used to certify Rh concentrations in BCR-723, DPCSV and ICP-MS. Data for the two methods are summarized in table 7. Both data sets were normally distributed and had homogeneous variances. An unpaired t-test indicated that there was no statistically significant difference between approaches ($p = 0.092$). But from figure 8, it was established that there were statistically significant differences within ICP-MS data sets; this was not the case for the two DPCSV data sets used to certify Rh in BCR-723.

The relative variability, RCV, of all detection methods in measuring the three autocatalyst PGEs in BCR-723 (TXRF and UV-274 detection were excluded, as each

Table 6. Summary statistics for individually accepted data sets for Rh concentrations (ng g^{-1}) in BCR-723 (each data set consists of six replicated measurements; data sets are ranked by arithmetic mean from lowest to highest concentrations).

Data set[a]	Mean ± SD	95% CIs mean[b]	Median ± IQR[c]	95% CIs median[b]
01 ICPMS	11.2 ± 1.46	9.71–12.8	11.6 ± 2.50	10.0–13.2
01 DPCSV	11.4 ± 1.09	10.3–12.6	11.1 ± 2.10	9.75–12.5
14 ICPMS	11.7 ± 1.41	10.2–13.2	11.7 ± 2.30	10.2–13.1
10 ICPMS	12.3 ± 1.79	10.4–14.1	12.5 ± 3.60	10.2–14.8
07 ICPMS	12.5 ± 0.95	11.5–13.5	12.8 ± 1.68	11.7–13.9
05 DPCSV	12.5 ± 1.23	11.2–13.8	13.0 ± 2.25	11.6–14.4
02 ICPMS	13.0 ± 1.52	11.4–14.6	12.6 ± 2.78	10.8–14.3
12 ICPMS	14.6 ± 1.57	13.0–16.3	14.1 ± 3.03	12.1–16.0
04 ICPMS	16.1 ± 1.12	14.9–17.3	16.0 ± 1.60	14.9–17.0

[a] Data set coding is that used by Zischka *et al.* [20]. ICPMS, inductively coupled plasma-mass spectrometry; DPCSV, differential pulse cathodic stripping voltammetry.
[b] CIs, represent confidence intervals.
[c] IQR, interquartile range.

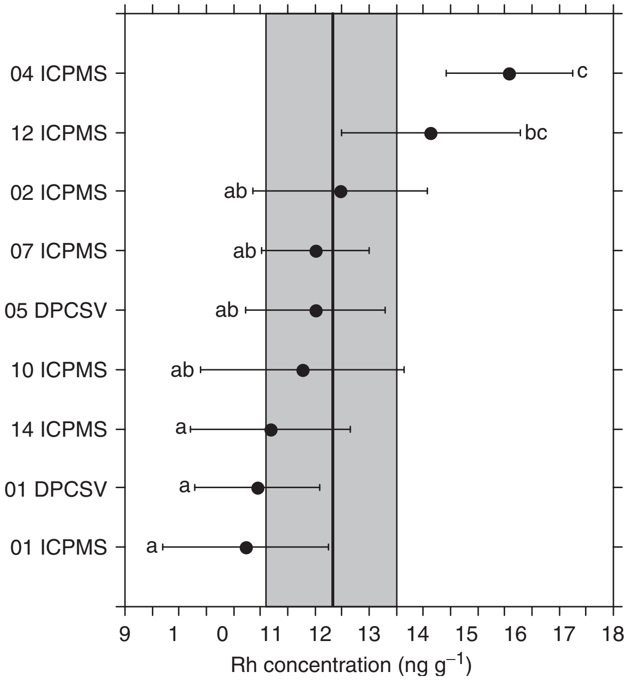

Figure 8. Ranked dot plot of arithmetic mean concentrations and 95% confidence intervals of nine accepted Rh data sets. The shaded area represents the certified 95% confidence band about the mean.

Table 7. Statistical summary of rhodium concentrations (ng g^{-1}) in BCR-723 determined using two separate detection methods.

Statistics[a]	DPCSV[b]	ICP-MS[b]
Data sets	2	7
n	12	42
Mean ± SD	12.0 ± 1.24	13.1 ± 2.08
95% CIs of mean	11.2–12.8	12.4–13.7
Minimum	10.3	9.00
Maximum	14.0	18.1
Median ± IQR	12.0 ± 2.15	13.0 ± 2.60
95% CIs of median	11.0–12.9	12.3–13.6
Robust CV (%)	13.3	14.9
Huber's *M*	11.9	12.9
Tukey's Biweight	11.9	12.9
Hampel's *M*	11.9	12.9

[a] Data sets were those accepted for certification; *n*, number of independent measurements; SD, standard deviation; CIs, confidence intervals; IQR, interquartile range; Huber's *M*, Tukey's Biweight, and Hampel's *M* are robust estimators of central tendency [32].

[b] DPCSV, differential pulse cathodic stripping voltammetry; ICP-MS, inductively coupled plasma-mass spectrometry.

reflects data from only one laboratory) follows the ranking, from least variable to most variable:

$$\mathrm{Pt}_{\mathrm{DPCSV}} \approx \mathrm{Pt}_{\mathrm{ICP\text{-}MS}} < \mathrm{Pt}_{\mathrm{NAA}} < \mathrm{Pt}_{\mathrm{ICP\text{-}IDMS}} \approx \mathrm{Rh}_{\mathrm{DPCSV}}$$
$$\approx \mathrm{Rh}_{\mathrm{ICP\text{-}MS}} < \mathrm{Pd}_{\mathrm{ICP\text{-}MS}} < \mathrm{Pd}_{\mathrm{ICP\text{-}IDMS}}.$$

Palladium has the poorest measurement precision. This reflects the greatest degree of spectral interference of the three PGEs, and the concentration levels of Pd are 2.1 and 13.6 times lower than Rh and Pt, respectively. A question that must be posed is whether such a low Pd concentration in BCR-723 (i.e. $6.0\,\mathrm{ng\,g^{-1}}$) is valuable in QC/QA programs when few recent studies have encountered such low values in environmental media.

3. PGE comparisons between BCR-723 and other solid sample matrices

Given that the material used to formulate BCR-723 was collected in 1998 from the ceiling of a tunnel in Austria, its PGE composition should be most similar to other tunnel 'dust' samples, airborne particulate matter, and road-deposited sediment from European countries. Here, we focus primarily on Pd concentrations, computing bivariate PGE ratios (Pt/Pd, Pt/Rh, and Pd/Rh), and determining relative proportions of each PGE, e.g. [Pd/(Pd + Pt + Rh)]. Data for BCR-723 are shown in table 8.

Ely *et al*. [36] defined three PGE ratio 'fields' for typical autocatalyst converters in Europe. These authors found the following 'fields': Pt/Pd, 1–2.5; Pt/Rh, 5–16; and Pd/Rh, 4–9. It is clear from the BCR-723 data (table 8) that the two ratios containing Pd produce atypical ratios. With a Pt/Rh ratio of 13.4 over five times the upper (typical) 'field' bound that was identified by Ely *et al* [36]. The lower 'field' bound typical of catalytic converters is 8.5 times higher than the Pd/Rh ratio of 0.47 defined for BCR-723. Thus, the representativeness of PGE concentrations in BCR-723 is questionable given these results.

3.1 *PGE comparisons between BCR-723 and airborne particulate matter*

Platinum-group element data from several studies of European airborne particulate matter sampled between 1997 and 2002 are shown in table 9. The distribution of PGEs in BCR-723 are most closely associated with the particulate matter from Karlsruhe, Germany, collected in 1997 by Schafer *et al*. [37]. The Pd concentration at Karlsruhe

Table 8. Summary of certified PGE concentrations, bivariate PGE ratios, and PGE partitioning for BCR-723.

Data[a]	Units	BCR-723
Pt, mean ± 95% CI	$\mathrm{ng\,g^{-1}}$	81.3 ± 2.45
Pd, mean ± 95% CI	$\mathrm{ng\,g^{-1}}$	6.0 ± 1.83
Rh, mean ± 95% CI	$\mathrm{ng\,g^{-1}}$	12.8 ± 1.22
Pt/Pd	–	13.4
Pt/Rh	–	6.35
Pd/Rh	–	0.47
Pt	%	81.17
Pd	%	6.04
Rh	%	12.79
Pd : Rh : Pt	–	1.00 : 2.12 : 13.4

[a] Concentrations and the 95% confidence intervals about the mean were from Zischka *et al*. [21]; all other data in the table were computed from the certified data.

was twice that recorded in BCR-723, but the Pt/Pd, Pt/Rh, and Pd/Rh ratios and the relative percentages were similar. It is also clear from table 9 that the BCR-723 distribution of PGEs is very different from the remaining European studies. Additionally, it is evident from table 9 that the bivariate ratios containing Pd are extremely variable (Pt/Pd ratios differ by a factor up to 77; and Pd/Rh ratios differ by up to 98 times), and few ratios of European airborne particulate matter fall within the 'fields' defined by Ely *et al.*

3.2 *PGE comparisons between BCR-723 and tunnel dust*

Helmers *et al.* [14] collected tunnel dust from the top of emergency telephones in a traffic tunnel in Munich in 1994 and found that the mean Pd concentration was $20 \pm 1.9\,\mathrm{ng\,g^{-1}}$ (±SD), and the Pt/Pd ratio was 8.6. Boch *et al.* [42], using the same dust sampling protocol as Helmers *et al.* [14], found significant temporal increases in Pd concentrations in Munich tunnels. In 1994, Pd concentrations ranged from 13.5 to $21.8\,\mathrm{ng\,g^{-1}}$, in 1997–1998 they ranged from 33 to $101\,\mathrm{ng\,g^{-1}}$, and in 2001 values ranged from 138 to $282\,\mathrm{ng\,g^{-1}}$. Data from Lesniewska *et al.* [12, 43] also indicated a significant Pd concentration increase with time in tunnel dust from Poland. In 2000, the Pd concentration was $23.9\,\mathrm{ng\,g^{-1}}$, and by 2003 it had increased 2.8-fold to $67.7\,\mathrm{ng\,g^{-1}}$. The Tanzenberg Tunnel dust in Austria, the site of BCR-723, showed only minimal increases in Pd concentration between 1994 and 1998. In 1994, the indicative value of Pd in this tunnel dust was $4.0\,\mathrm{ng\,g^{-1}}$ [19], and this had only increased marginally to $6.0\,\mathrm{ng\,g^{-1}}$ in 1998 [20]. These data indicate that the Tanzenberg Tunnel dust, i.e. BCR-723, is unusual in its very low Pd concentration, and limited increase over time compared with other European tunnel dust samples. Additionally, a comparison of Pd in the CRM NIES-8, a tunnel dust sample from Japan collected in 1987, $180 \pm 28\,\mathrm{ng\,g^{-1}}$ [44], also illustrates the exceedingly low value of Pd in BCR-723.

Only a limited number of studies are available that measure all three autocatalyst-associated PGEs in tunnel dust samples (table 10). Besides the Tanzenberg Tunnel dust measured in 1994, Study 2 (table 10) by Schramel *et al.* [19], the dust collected in Wattkoft Tunnel, Karlsruhe in 1997 by Schafer *et al.* [37] was most similar in

Table 9. Summary of European airborne particulate matter palladium concentrations, PGE ratios, and PGE partitioning.

Data	Study 1[a]	Study 2[a]	Study 3[a]	Study 4[a]	Study 5[a]	Study 6[a]	Study 7[a]
Pd ($\mathrm{pg\,m^{-3}}$)	12.7[b]	67.4	4.9	1.5	33.9	14.4	15.0
Pt/Pd	13.1	0.17	2.88	3.60	0.18	7.1	1.50
Pt/Rh	3.83	4.40	4.86	3.38	5.00	2.7	5.80
Pd/Rh	0.29	22.9	1.69	0.94	28.3	2.6	3.80
Pt (%)	74.78	23.07	64.38	63.53	14.60	64.47	54.76
Pd (%)	5.72	72.28	22.38	17.65	82.48	24.37	35.71
Rh (%)	19.50	4.65	13.24	18.82	2.92	11.16	9.53

[a] Study 1, Schafer *et al.* [37], Karlsruhe, Germany, July–September 1997, size range sampled not stated; Study 2, Petrucci *et al.* [38], Rome, Italy, 1998, particulate matter (PM) <10 µm; Study 3, Rauch *et al.* [39], Goteborg, Sweden, 1999, PM <10 µm; Study 4, Rauch *et al.* [39], Goteborg, Sweden, 1999, PM <2.5 µm; Study 5, Wichmann and Bahadir [40], Braunschweig, Germany, date sampled not stated, and particles sampled >0.5 µm; Study 6, Kanitsar *et al.* [41], Vienna, Austria, 2002, size 7.1 µm; and Study 7, Zereini *et al.* [11], Frankfurt, Germany, 2001–02, particles sampled had aerodynamic equivalent diameters <22 µm.

[b] Units are $\mathrm{ng\,g^{-1}}$, not $\mathrm{pg\,m^{-3}}$.

Table 10. Summary of European tunnel dust palladium concentrations, PGE ratios, and PGE partitioning.

Data	Study 1[a]	Study 2[a]	Study 3[a]	Study 4[a]
Pd (ng g^{-1})	3.0	17.4	4.0	23.9
Pt/Pd	5.00	3.61	13.8	0.98
Pt/Rh	5.00	6.69	5.3	3.50
Pd/Rh	1.00	1.85	0.39	3.50
Pt (%)	72.72	70.12	79.37	43.18
Pd (%)	13.64	19.40	5.77	44.29
Rh (%)	13.64	10.48	14.86	12.53

[a] Study 1, Schafer *et al.* [37], Wattkoft Tunnel, Karlsruhe, Germany, 1997, size range of particles sampled was not stated; Study 2, Kollensperger *et al.* [45] Tanzenberg Tunnel, Styria, Austria, 1994, particles sampled <90 μm; Study 3, Schramel *et al.* [19], Tanzenberg Tunnel, 1994, particle sampled <90 μm; and Study 4, Lesniewska *et al.* [43], Bialystok, Poland, 2000, particles sampled <75 μm.

Pd concentration. Kollensperger *et al.* [45] also present data from Tanzenberg Tunnel collected in 1994, and found a Pd concentration of 17.4 ng g^{-1}, and very different Pt/Pd and Pd/Rh ratios. The data from a tunnel in Bialystok, Poland sampled by Lesniewska *et al.* [43] in 2000 had a Pd concentration four times higher than BCR-723, and a very different distribution of PGEs.

3.3 *Pd concentrations in BCR-723 compared with road-deposited sediment*

Expectations are that road-deposited sediment, collected outside tunnels, should have Pd concentrations somewhat lower than tunnel dust samples, as there should be greater contributions from surrounding roadside soils, and thus greater dilution of the Pd signal. A summary of Pd concentrations in European road sediments is shown in table 11. Palladium in road-deposited sediment from seven countries indicates that the Pd concentration in BCR-723 is not representative of other solid media, with values 4–84 times lower than those in the literature.

4. Conclusions

The certification of Pd, Pt, and Rh concentrations in BCR-723 has resulted in the integration of this reference material into the QC/QA procedures for laboratories measuring ultra-trace autocatalyst-associated PGEs in environmental media. This study presents a detailed look at the individual replicated data that form the accepted data sets used to certify PGEs in BCR-723. This level of examination has not been attempted before, and it received almost no attention in the original certification document produced by IRMM [20], or in the published journal description by Zischka *et al.* [21]. Statistically significant differences were observed between accepted data sets for Pd, Pt, and Rh. These were ignored in the original certification process. Statistically significant differences were also observed between different detection methods for Pd and Pt; and between laboratories using the same detection method, for Pt (ICP-IDMS), Pd (ICP-MS and ICP-IDMS), and Rh (ICP-MS). Of the three autocatalyst PGEs certified in BCR-723, Pd is the most problematic. The original data show a clear

Table 11. Summary of palladium concentrations in European road-deposited sediment.

Reference	Location	Year[a]	Size (μm)	Pd ($\mathrm{ng\,g^{-1}}$)
[5]	Various German Highways	1999	<2000	60–95
[38]	Various urban sites, Rome, Italy	NS	<63	102–504
[46]	Göteborg, Sweden	NS	<63	83
[47]	B10, Karlsruhe, Germany	NS	<2000	21.3
[48]	Messina, Italy	2001	Various	120
[49]	M-30 A.I., Madrid, Spain	2000	<63	75
[49]	M-30 M.M., Madrid, Spain	2000	<63	26
[50]	Kayseri, Turkey	NS	Bulk	230
[51]	Bialystok, Poland	2001	<75	114–188
[51]	Bialystok, Poland	2003	<75	144–216

[a] NS, not stated in study.

bimodal distribution of Pd concentrations, with a 'contamination' rate of about 15%. Two of the eight accepted data sets contributed to this secondary population of Pd values. The use of the central limit theorem to compute the grand mean (certified value) from the eight accepted data sets will be biased, given the level of contamination in the original data. With these complications, it seems prudent to view the Pd concentration in BCR-723 reported in Zischka *et al.* [20, 21] as indicative rather than the more rigorous designation of 'certified'.

This is the first study to present a detailed comparison of BCR-723 PGE concentrations, bivariate ratios, and relative percentages to those for airborne particulate matter, tunnel dust, and road-deposited sediments from Europe. The conclusion from almost all comparisons is that the Pd concentration in BCR-723 is uncommonly low, and it is not currently representative of the typical concentrations found in environmental media throughout Europe. Though it could be argued that a low level of Pd in a CRM is valuable from an analytical standpoint, we feel that its concentration in BCR-723 is not well constrained in the first place as there is the problem with the secondary population which likely reflects measurement error, and not a nugget effect. Given these findings, it is suggested that there is value in developing a new environmental CRM with a more representative mix of PGEs, and one with significantly higher Pd concentrations.

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