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A two-step separation procedure for the IDMS-analysis of Pd and Pt was developed enabling the effective separation from interfering elements.
A new two-stage separation procedure for the IDMS based quantification of low Pd and Pt amounts in automotive exhaust emissions

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Received (in XXX, XXX) Xth XXXXXXXXXX 20XX, Accepted Xth XXXXXXXXXX 20XX
DOI: 10.1039/b000000x

A two step separation procedure for the quantification of Pd and Pt in automotive exhaust emissions using isotope dilution mass spectrometry was established using a combination of cation and anion exchange chemistry. AG 50 W-X12 was used as cation exchange resin and DGA as weakly basic anion exchange resin. This procedure enabled the effective separation of Pd and Pt from the matrix and from interfering elements. Additionally Pd and Pt were collected in separate chromatographic fractions, which increased the precision of the isotope ratio determination by separate measurements using a single collector sector field ICPMS. The analytical procedure was validated by analysing synthetically prepared samples and the certified reference materials BCR-723 (road dust) and IAEA-450 (algae). For the SI-traceable results complete uncertainty budgets were calculated yielding relative expanded uncertainties ($k = 2$) of $\approx 1\%$ for analyte masses in the ng range. Procedure blanks of 55 pg Pd and 3 pg Pt were obtained. Detection limits were calculated as 12 pg for Pd and 7 pg for Pt. Additionally, Pd and Pt blank levels of different filter materials are presented as well as first results for automotive exhaust particles collected on cellulose filters.

Introduction

Isotope dilution mass spectrometry (IDMS) is considered as one of the most powerful and most accurate method for determining amounts of substance. Contrary to other calibration approaches, IDMS does not directly suffer from long-time changes or drifts in instrument sensitivity. Moreover, provided isotopic exchange between sample and spike is ensured, losses of analyte do not affect the analytical result. Both advantages are based on the fact that IDMS only requires isotope ratio measurements and isotope ratios are largely unaffected by instrumental drift, setup or by matrix, unless an isobaric interference is present. Due to these advantages IDMS often is applied for quantification of platinum group elements (PGE), either for characterization of reference materials or for geochemical research. Besides the spike availability one crucial point is the separation of isobaric and molecular interferences, when using inductively coupled plasma mass spectrometry (ICPMS). This is more important the lower the PGE mass fractions are in the sample. PGE analysis is in the focus since decades and therefore several analyte separation and preconcentration procedures have been applied in the past. The most classical approach is the NiS fire assay, where a relatively large amount of sample (several g) is fused with a mixture of Na$_2$B$_4$O$_7$·10H$_2$O, Ni and S. After cooling down a NiS bead is formed, which contains the PGEs. The complete procedure, however, is complex and laborious. As a consequence of the added reagents the blanks for Pd (60 pg - 230 pg) and Pt (60 pg - 490 pg) are relatively high and variable. Additionally, a high concentration of salts is still present in the analyte solution after dissolution of the NiS bead. This additional matrix disturbs the isotope ratio determination and makes the procedure unsuitable for IDMS based reference measurements unless another separation is being carried out. Furthermore, some isobaric interferences such as Cd and Hg are still present.

The most commonly used separation procedures in IDMS are column chromatography based techniques, as they can be easily scaled to the analytical needs. Blanks and recoveries can be optimized and most important the analyte fraction is obtained in an aqueous, often acidified solution, which in most cases can be used directly for measurements. For PGE analysis cation as well as anion exchange resins have been used. When using cation exchange resins such as AG 50W-X8 in combination with hydrochloric acid Pd and Pt run through in form of chloro-complexes, while many cations are retained. Recoveries for Pd and Pt are close to 100 % and blank levels are comparatively low (40 pg Pt), allowing detection limits (LOD) of 86 pg/g for Pd and 26 pg/g for Pt. A major disadvantage is the coelution of some elements (e.g. Cd, Hg, Zr, Hf, W) generating isobaric and molecular interferences, which requires a continuous monitoring of these elements and consequently a mathematical interference correction, both increasing the measurement uncertainty and detection limits (LOD). Anion exchange resins such as AG 1-X8 offer a strong retention of Pd and Pt chloro complexes formed in hydrochloric acid. However, the retention is too strong for a quantitative elution under normal conditions and therefore the
recovered are rather low (Pd 19% - 35%; Pt 11% - 22%) while blanks are relatively high (85 pg Pd, 140 pg Pt). This observation leads to a modification in the authors’ lab such that the anion exchange resin was digested after sample loading and washing. This technique has been applied for the determination of the Pt mass fraction in CCQM-K75 and earlier by Brzezińska et al. who ashed the anion exchange resin in a muffle furnace. The advantage is a complete recovery combined with a removal of nearly all interferences to the expenses of comparatively high blanks (for Pt comparable to Nis fire assay). Hann et al. and Kanitsar et al. optimized the AG 1-X8 separation procedure such that total recoveries around 85% and low LODs for urban aerosol samples (Pd: 25 - 36 pg/filter; Pt: 20 - 44 pg/filter) were obtained. The main drawback here is the coelution of interfering elements such as Cu, Zn and Sr (recoveries ~ 40%, 87%, 35%) with the Pd containing fraction (14 mol/L HNO₃). Alternative separation techniques for Pt such as solid phase extraction using activated carbon, imprinted polymers or separation using immobilized microorganisms were published. The solid phase extraction techniques offer LODs of ~ 0.3 ng/mL for Pt being unsuitable for pg amounts. The separation by immobilized microorganisms yield a sufficiently low LOD (~ 20 pg/mL) for Pt, but the eluant is an aqueous 5 mol/L NaCl solution, which is unsuitable for ICPMS analysis. None of the described separation procedures fulfill the requirements for IDMS based quantification of Pd and Pt in automotive exhaust emissions collected on filter samples with total Pd and Pt masses in the low ng to the pg range. These requirements are low procedure blanks (< 100 pg), moderate to good recovery (> 50%) and removal of all elements generating isobaric and molecular interferences in ICPMS. Additionally, Pd and Pt should be obtained in the same separation procedure, but in separate elution fractions to enable smaller measurement uncertainties. Therefore, we developed a two-stage separation procedure fulfilling these requirements and enabling SI-traceable results for pg amounts of Pd and Pt in automotive exhaust emissions.

Experimental

IDMS strategy

Samples and procedure blanks were spiked with 0.3 g - 0.5 g of Pd and Pt single spike solutions with 106Pd and 194Pt mass fractions of 10 ng/g. Spike and back-spike were measured in each IDMS sequence. Using this approach the calculation of the K-factor for correcting mass discrimination effects is not necessary as the K-factor cancels down in the IDMS equation. A full uncertainty budget was calculated for each individual analysis as described earlier. The uncertainty for the mean value of independent blends was calculated by combining the uncertainties of the single results as described in eqn. 1 and adding the standard deviation of the mean as described in eqn. 2. This approach compensates for not completely known and considered uncertainty contributions deriving from sample preparation or analyte and/or matrix inhomogeneity.

$$\bar{u} = \sqrt{\frac{\Sigma u^2}{n}}$$

$$u_{total} = \sqrt{\bar{u}^2 + s_{mean}^2}$$

Chemicals, reagents, standards and reference materials

High purity water, double distilled acids and precleaned labwear was used for all preparation, as described earlier. H₂O₂ solution was purchased from Merck in suprapure quality. All listed reagents showed blank levels ≤ 0.4 pg/g for Pd and ≤ 0.2 pg/g for Pt. Elemental solutions used for interference checks and for simulating the matrix were prepared from ICP standard solutions (Merck, Germany). The CI resin, the Ni resin and the DGA resin were purchased from Triskem Int., France. The AG 1-X8 resin and the AG 30W-X12 resin were both purchased from BioRad, Germany.

IAEA-450, a reference material certified for Pt in algae, was purchased directly from the International Atomic Energy Agency (IAEA, Austria). BCR-723, a reference material certified for PGEs in road dust, was purchased from the Institute for Reference Materials and Measurements (IRMM, Belgium).

The Pd and Pt single spikes used in this work (Table 1) were diluted solutions of the candidate reference materials ERM-AE140 and -AE141, which have been characterized by MC-ICPMS at PTB using two back-spikes each for Pd and Pt.

Table 1 Mass fraction and amount-of-substance fraction of the Pd and Pt single spikes used in this work

<table>
<thead>
<tr>
<th>Spike solution</th>
<th>Mass fraction in ng/g</th>
<th>Amount-of-substance fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>w(106Pd)</td>
<td>w(194Pt)</td>
<td>m(106Pd)/m(Pd) m(194Pt)/m(Pt)</td>
</tr>
<tr>
<td>106Pd</td>
<td>9.8624 (22)</td>
<td>n/a</td>
</tr>
<tr>
<td>194Pt</td>
<td>n/a</td>
<td>10.5625 (32)</td>
</tr>
</tbody>
</table>

Sample preparation

Digestion of the samples and reference materials was performed in an Ethos 1600 microwave system (MLS, Germany) in 100 mL teflon vessels containing a 10 mL acid mixture of H₂O₂, H₂O, HCl and HNO₃ in a volumetric ratio of 2:2:2:3:3. Samples and spike were added under full gravimetric control. Using a heating rate of 7.5 °C/min the vessels were heated up to 200 °C, which was kept constant for 30 min followed by a cooling step (45 min). Alternatively a high pressure asher (HPA, Anton Paar, Austria) digestion procedure was applied, which showed no differences in Pd and Pt results. Here, quartz vessels with a volume of 90 mL were filled with 6 mL of the above described acid mixture with a volumetric ratio of 1:1:2:2. The vessels were heated up to 1 h to 300 °C, which was kept constant for 1 h and followed by a cooling step.

Subsequently the digested samples were dried down in 15 mL Savillex beakers and redissolved in 0.1 mol/L HCl for chromatographic separation. The different resin materials, which were suspended in high purity water prior to use, were filled in 2 mL Eichrom columns (Triskem Int., France) and washed several times followed by a conditioning step. Then the samples were evaporated to dryness again, were finally redissolved in 2% HCl and handed over to the isotope ratio determination.

All sample preparation was carried out under clean air conditions (< class 1000, MK Versuchsanlagen, Germany).

Mass spectrometric measurements

All, quantitative as well as isotope ratio, measurements were performed on an Element 2 sector field ICPMS (Thermo Fisher Scientific, Germany) in low resolution. Sample introduction was realized in self-aspirating mode using a MicroMist nebulizer, a
cyclonic glass spray chamber (both GlasExpansion, Australia) and an ASX-520 autosampler (Cetac, US). All measurements were performed in 2% HCl using polyethylene sample tubes.

The optimum settings for isotope ratio determinations are listed in Table 2. For Pt isotope ratio determinations m/z 194 (spike isotope) and 195 (natural reference isotope) were measured and in the case of Pd m/z 105 (natural reference isotope), 106 (spike isotope) and 111 were measured. The latter mass was used for monitoring any possible isobaric Cd interference.

In the case of the cation resin AG 50W-X12 the sample was loaded and eluted in 0.1 mol/L HCl. Pd, Pt and all elements, which form negatively charged chloro-complexes or which were weakly bound under these conditions such as Ge, Ru, W and Ir and partially Rb and Hg coeluted in the first fraction. The recoveries for Pd and Pt were between 95% to 100% and the obtained blanks were below 10 pg for Pd and Pt. Due to the incomplete matrix/interference separation the AG 50W-X12 resin did not fulfill the requirements.

Table 3 Composition of the synthetic test solution expressed as analyte mass in a test portion of 5 mL compared to the total analyte mass in the Pd and Pt fraction after separation obtained by ICP-MS (Fig. 1)

| Element | Analyte mass in ng a | Element | Analyte mass in ng
|---------|----------------------|---------|----------------------
| Pd | 5 | 4 | (1) | Sr | 10 | < 0.1 b |
| Pt | 5 | 5 | (1) | Ga | 20 | < 0.3 |
| Ge | 1 | < 0.1 | Mo | 20 | < 0.65 |
| Rb | 1 | < 0.05 | Pb | 20 | < 0.5 |
| Y | 1 | < 0.03 | Ni | 200 | < 3 |
| Zr | 1 | < 0.5 | Cu | 200 | < 10 |
| Ru | 1 | < 0.2 | K | 600 | < 50 |
| Cd | 1 | 0.06 (2) | Ca | 600 | < 100 |
| Hf | 1 | < 0.06 | Mg | 2000 | < 100 |
| W | 1 | < 0.05 | Zn | 2000 | < 100 |
| Ir | 1 | < 1 | Na | 16800 | < 1000 |
| Hg | 1 | < 0.05 |

a: Relative expanded uncertainties of the gravimetrically prepared test solutions are < 1 %; expanded uncertainties for the analyte masses in Pd/Pt fraction are given in brackets.

b: Determined after 1st separation step (cation separation)

DGA (exactly TODGA), which is a weak anion resin with N,N,N’,N”-tetra-0-cytdiglycolamid functional groups, is designed for actinide and lanthanide separation. This resin also retains Pd and Pt when loaded in 3 mol/L HCl. In the first tests...
order to reduce the blank. Then the resin was conditioned followed by the sample loading and cleaning, all with 3 mol/L HCl. Pd was eluted with 3 x 2 mL of 0.5 mol/L HCl and Pt was subsequently eluted with 3 x 2 mL of 0.04 mol/L HCl. Thereafter, the sample was evaporated to dryness and redissolved in 5 mL of 2 % HCl. The so prepared samples were used for isotope ratio determinations by ICPMS. The total recovery of the whole separation procedure was tested several times during the method development and was also continuously monitored via the spike isotope. The overall recovery was > 50 % for Pd and > 70 % for Pt. A substantial loss took place, because a part of Pt coelutes with Pd from the DGA resin and vice versa. Increasing the recoveries might be possible, potentially at the expenses of a Pd/Pt coelution and an incomplete interference separation. However, recoveries above 50 % are completely sufficient for IDMS analyses, as no severe fractionation effects can be expected, especially for medium and high mass elements.

Beyond analyte recovery, the coelution of interfering elements is of major concern. This was tested by using the test solution displayed in Table 3. The analyte masses for a test portion of 5 mL are given in the first column, while in the second column the remaining analyte masses in the Pd/Pt fraction after the two stage separation are given. These are mainly "less than" values, displaying either the detection limit or the highest value of 7 individual experiments, demonstrating that most elements can be removed or even reduced by a factor of at least 20.

In order to verify that even very low amounts of interfering elements do not cause biased results, their formation rates have been checked. The main interferences for $^{106}$Pd and $^{108}$Pd, as listed by Meisel et al. and others, are molecular ions (Cu-, Ga-, Zn-argides; Sr-, Rb-, Y-, Zr-oxides) excepting $^{106}$Cd. Although $^{106}$Cd is separated and has an isotope abundance of only 0.0125, it was continuously monitored showing values at or below the acid blank. The argide interferences were tested with 100 ng/g Cu and Dy standard solutions and showed formation rates of < 0.005 % for $^{64}$Cu$^{40}$Ar and $^{156}$Dy$^{40}$Ar. The oxide formation rate was < 0.07 % for $^{88}$Sr$^{16}$O and < 0.01 % for $^{88}$Sr$^{18}$O/H, tested with a Sr standard solution (100 ng/g). The oxide formation rate tested with Y (100 ng/g) resulted in a value of 9 %, which is far too high. As the isotope ratio of $^{16}$O/$^{18}$O and as significant impurities of Zn, Ga and Sr were present in the standard, a significantly lower formation rate is probable. Nevertheless, Y was completely separated and even a high oxide formation rate would not bias the result.

In the case of $^{195}$Pt and $^{197}$Pt only molecular interferences such as Cd-, Sm- and Tb-argides and chlorides as well as Hf- and Yb-oxides can occur. These formation rates were tested as well using Sr, Tb, Dy and Gd standard solutions, each containing 100 ng/g. The resulting formation rates were < 0.004 % for $^{156}$Dy$^{40}$Ar, < 0.009 % for $^{159}$Tb$^{18}$Cl and < 0.07 % for $^{88}$Sr$^{18}$O. Combining the information of the molecular ion formation rates and the maximum element masses after separation it can be stated that all interferences were reduced such that the resulting bias on the isotope ratio of $^{106}$Pd/$^{108}$Pd and $^{195}$Pt/$^{197}$Pt is well below 3 %, which is the precision of the isotope ratio determination for both.

**Procedure blanks**

The quantification of procedure blanks is of utmost importance for accurate Pd and Pt analysis in the pg range. As preliminary test blank digestions were carried out in the digestion vessels. The resulting blank solutions were analysed by ICPMS resulting
in blanks of (9 ± 3) pg Pd and (2 ± 1) pg Pt for the HPA quartz vessels (n = 9) and (11 ± 6) pg Pd and (2 ± 2) pg Pt for the microwave TFM vessels (n = 38), given with the corresponding standard deviation.

Then procedure blanks on the complete analytical procedure were performed. As the largest part of the analyte blank derives from the column separation, the procedure blanks were spiked after column separation to avoid any overestimation of the procedure blank due to incomplete spike recovery. The first procedure blanks with ± 160 pg for Pd and ± 22 pg for Pt nearly fulfilled the requirements (< 100 pg). Further improvement lead to procedure blanks of (55 ± 13) pg Pd and (3 ± 4) pg Pt, with the corresponding standard deviation (n = 18). The procedure blanks are nearly constant within each sample preparation series (n = 3; s ≤ 4 pg Pd; s ≤ 2 pg Pt), while they vary slightly more between the six series. Therefore, the LODs are calculated for each sample preparation series separately and the maximum value of these individual LODs, which are LOD_{Pd} = 12 pg and LOD_{Pt} = 7 pg, were taken as LOD for the analytical procedure. These procedure blanks and the resulting LODs are sufficient for determining Pd and Pt masses in the ng to pg range.

**Tested filter materials**

Several filter materials were tested regarding net blank levels (procedure blank corrected) and ease of digestion.

Texture filters made from borosilicate microfibers reinforced with woven glass cloth and bonded with PTFE showed very high Pd blank values of 17 ng, whereas quartz fibre filters showed very high Pd blank values of 2 ng. The highest blank values of all tested filter materials made these filters unsuitable for Pd and Pt analysis in the pg range.

Polycarbonate filters have a very smooth surface, from which soot particles easily fall off. Blank measurements reveal a dramatical drop in the Pd and Pt spike recovery down to < 10 % presumably caused by the dissolved filter matrix, which made the quantification by IDMS impossible. A semiquantitative estimation showed blank values in the range of the Pd and Pt procedure blanks. The specific characteristics made polycarbonate filters unsuitable for these analyses.

Teflon filters also offer a smooth surface similar to the polycarbonate filters. Teflon filters could not be digested. Leaching at temperatures above 150 °C lead to a shrinkage of the filtrate material, which may enclose particles. Due to this and Pt blanks of ≈ 57 pg, teflon filters also were assessed as unsuitable.

Cellulose and cellulose-ester filters hold the collected particles stronger than teflon and polycarbonate filters due to the textile type structure. Both filter types could be completely digested and offer the lowest Pd and Pt blank values of the tested filter materials: (21 ± 3) pg Pd and (39 ± 8) pg Pt for cellulose filter, (35 ± 2) pg Pd and (10 ± 4) pg Pt for cellulose-ester filter, given with expanded uncertainties (k = 2). Thus, cellulose and cellulose-ester filter are suitable for the intended task.

**Method validation**

The method validation is based on the use of reference samples and on the calculation of complete uncertainty budgets according to the Guide to the Expression of Uncertainty in Measurement.\(^8\) As for Pd and Pt in automotive exhaust emissions no suitable reference material were available, synthetic samples were prepared by doping the test solution (Table 3) on cellulose filters. Additionally, the reference materials BCR-723 and IAEA-450 were used. All samples were prepared such that a total amount of Pd and Pt from 1 ng to 10 ng was used, resulting in sample masses of 75 mg to 160 mg for BCR-723 and IAEA-450. The determined Pd and Pt mass fractions (Table 4), which were dry mass corrected, represent the mean of 3 independent analysis of the synthetic samples and 6 independent analysis of BCR-723 and IAEA-450, respectively.

The relative expanded measurement uncertainties (k = 2) for total Pd masses from 1 ng to 10 ng determined in one sample aliquot are typically ≤ 1 %. The significantly larger uncertainty for the mean value of BCR-723 is due to the spread between the 6 independently processed samples. It can be noted that the determined Pd mass fractions agree very well with the reference values within the associated uncertainties (Table 4). Standard deviations from 1.4 ng/g to 2.5 ng/g for 10 independent measurements of BCR-723 have been reported before by Alszen et al.,\(^1\) while Sutherland reported a spread in published Pd mass fractions from 3.7 ng/g to 8 ng/g.\(^2\) The GeoReM database showed a spread of Pd mass fractions from 4 ng/g to 9 ng/g and a twofold standard deviation of 2.4 ng/g for the listed IDMS results (Table 4).\(^2\) These data clearly point to a significant inhomogeneity of BCR-723 for sample masses ≤ 0.1 g.

Similar to Pd the relative expanded measurement uncertainties (k = 2) for total Pt masses from 1 ng to 10 ng determined in one sample aliquot are typically ≤ 1 %. The significantly larger uncertainty for the mean value of the synthetic sample is due to a relatively large variation in the filter blanks. In the case of BCR-723 it is due to the spread between independently processed samples. For IAEA-450, which homogeneity was demonstrated in CCQM-K75,\(^3\) the relative expanded measurement uncertainty (k = 2) for the mean value is 1.5 % and thus only slightly larger than those of the single values. The determined Pt mass fractions of the synthetic sample and of the certified reference material IAEA-450 agree very well with the reference values within the associated uncertainties (Table 4).

> Table 4 Determined Pd mass fractions compared with reference values for selected samples and reference materials used for method validation, given with expanded uncertainties (k = 2) or 2 s (GeoReM) in brackets.

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Sample</th>
<th>Matrix</th>
<th>Mass fraction in ng/g</th>
<th>Determined Reference a</th>
<th>GeoReM b</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd</td>
<td>Synthetic Filter + Interf.</td>
<td>9.57 (10)</td>
<td>9.486 (6)</td>
<td>n/a</td>
<td></td>
</tr>
<tr>
<td>Pd</td>
<td>BCR-723</td>
<td>Road dust</td>
<td>6.5 (2.2)</td>
<td>6.1 (1.9)</td>
<td>5.3 (2.4)</td>
</tr>
<tr>
<td>Pt</td>
<td>Synthetic Filter + Interf.</td>
<td>10.45 (34)</td>
<td>10.504 (6)</td>
<td>n/a</td>
<td></td>
</tr>
<tr>
<td>Pt</td>
<td>BCR-723</td>
<td>Road dust</td>
<td>88.5 (4.3)</td>
<td>81.3 (2.5)</td>
<td>89 (14)</td>
</tr>
<tr>
<td>Pt</td>
<td>IAEA-450</td>
<td>Algae</td>
<td>74.2 (1.1)</td>
<td>74 (2)</td>
<td>n/a</td>
</tr>
</tbody>
</table>

a Reference: gravimetric value for synthetic sample; certified value for BCR-723 and IAEA-450.

b Mean of the 3 IDMS results listed in GeoReM for BCR-723.\(^2\)

In the case of BCR-723 a value slightly higher than the certified value has been obtained, which, however, agrees very well with the IDMS mean value obtained from the GeoReM database (Table 4).\(^2\) Regarding the inhomogeneity of BCR-723 the situtation is similar to those for Pd: the spread of the analytical results in Sutherland’s review on BCR-723 (74 ng/g to 97 ng/g) and in the GeoReM database (64 ng/g to 101 ng/g) clearly point to an inhomogeneity of the material with respect to Pt.\(^2\) Based on the results for the reference materials and the establishment of complete uncertainty budgets, the newly developed IDMS procedure for Pd and Pt is fully validated.
Table 5 Pd and Pt masses and Pd and Pt emission in automotive exhaust particles collected on cellulose filters with the associated expanded uncertainty (k = 2) in brackets

<table>
<thead>
<tr>
<th>Filter No.</th>
<th>Engine</th>
<th>Test cycle °C</th>
<th>Analyte mass per filter in pg</th>
<th>Emission rate</th>
<th>Emission rate</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Pd</td>
<td>Pt</td>
<td>unit</td>
</tr>
<tr>
<td>1</td>
<td>Gasoline</td>
<td>CADC 7°C</td>
<td>6126 (61)</td>
<td>338 (5)</td>
<td>ng/km</td>
</tr>
<tr>
<td>2</td>
<td>Gasoline</td>
<td>NEDC</td>
<td>911 (10)</td>
<td>4295 (25)</td>
<td>ng/km</td>
</tr>
<tr>
<td>3</td>
<td>Gasoline</td>
<td>CADC</td>
<td>5732 (57)</td>
<td>372 (9)</td>
<td>ng/km</td>
</tr>
<tr>
<td>4</td>
<td>Diesel</td>
<td>WHTC cold</td>
<td>28 (5)</td>
<td>336 (18)</td>
<td>ng/kWh</td>
</tr>
<tr>
<td>5</td>
<td>Diesel</td>
<td>WHTC hot</td>
<td>17 (5)</td>
<td>13 (15)</td>
<td>ng/kWh</td>
</tr>
<tr>
<td>6</td>
<td>Diesel</td>
<td>WHTC hot</td>
<td>100 (4)</td>
<td>54 (13)</td>
<td>ng/kWh</td>
</tr>
</tbody>
</table>

CADC: Common Artemis Driving Cycle; NEDC: New European Driving Cycle; WHTC: World Harmonized Transient Cycle for heavy duty engines.

Notes and references