# Quantification of Ultra-Trace Levels of Pt, Ir and Rh in Polar Snow and Ice Using ICP-SFMS Coupled with a Pre-Concentration and Desolvation Nebulization System

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A revised analytical method is presented for the quantification of ultra trace level (fg mL$^{-1}$) PGEs (Pt, Ir and Rh) in polar snow and ice samples by focusing on the following issues: (i) evaluation of the efficiency of a non-boiling pre-concentration procedure for analyses at the fg mL$^{-1}$ level of PGEs in our laboratory; (ii) establishment of the appropriate instrumental conditions to obtain low detection limits, high accuracy and precision; and (iii) verification of the contributions of possible contamination during the ice core decontamination process using an artificial ice core as a sample.

**Laboratory Clean Conditions.** To avoid possible artificial contamination of extremely low concentration (fg mL$^{-1}$) PGEs in polar samples, all analytical procedures including sample handling and analyses were carried out in a class-10 clean booth or on a class-10 clean bench inside specially designed clean laboratories (class 1000) located at the Korea Polar Research Institute (KOPRI). The cleaning procedures for the experimental tools, including low- and high-density polyethylene bottles (LDPE and HDPE), Teflon beakers and stainless steel tools used for mechanical chiseling during the decontamination procedure of the ice core sample, were also performed in the class-10 clean booth according to the previously established cleaning protocol[1] (see supplementary material).

Ultrapure (UP) water was used for the final cleaning step and the preparation of reference standard solutions, was accomplished using a three-stage distillation process: Millipore RO water purification (Model Elix-3), Milli-Q purification (Millipore Corp., Model Milli-Q Academic) and the use of a sub-boiling double distillation still (Berghof BSB-939-IR, Germany).[1] The purest "Optima"-grade nitric acid (HNO$_3$), which was used in the final cleaning step, sample acidification and in the preparation of the reference solutions, was obtained from Fisher Scientific.

**Sample Treatment.** Pre-concentration of the samples was performed *via* a non-boiling evaporation method to increase the sample concentration by a factor of ~60.[1,2] An aluminum hot plate and pre-cleaned Teflon beakers were used for the sample evaporation procedure. Before using the beakers, they were pre-conditioned for 1 h on a hot plate with UP water. Melted 60 mL samples were pre-concentrated by sub-boiling to 0.5 mL at ~80 °C. A blank experiment was performed by using ultrapure water as a sample for each pre-concentration experiment. One pre-concentration experiment consisted of five samples and one blank. The evaporation of the samples for each pre-concentration set required approximately 6 h. To adjust the HNO$_3$ concentration to 1% in the final sample volume, 0.5 mL of 2% (m/m) UP HNO$_3$, which was prepared from UP water and "Optima"-grade HNO$_3$, was added to pre-concentrated samples (~0.5 mL). The pre-concentrated samples were then transferred to 4 mL HDPE bottles and kept frozen until analyses were performed.

**Instrumental Analyses.** Analysis was performed using a sector-field inductively coupled plasma mass spectrometer (ICP-SFMS) (Element2, Thermo Finnigan MAT, Germany) at KOPRI. An Apex high-sensitivity desolvation nebulizer system (Apex HF, ESA, USA) was incorporated to transport sample to the ICP-SFMS. The desolvation nebulizer reduced the oxide production rate (BaO/Ba < 0.02%) and increased the instrumental sensitivity by approximately 10 times relative to the standard instrument (~0.9 × 10$^6$ cps for 100 pg mL$^{-1}$ indium solution). To obtain the lowest blank level, ultrapure grade (99.999%) argon and nitrogen gases were used, and the entire analytical system, including the ICP-SFMS and the sample introduction system, was installed in a class-10 clean booth located in a class-1000 clean laboratory. The analysis for Pt and Ir and the analysis for Rh were performed separately using ICP-SFMS for each pre-concentrated sample. Details of the instrumental operating conditions and data acquisition parameters are illustrated in Table S1.

**Calibration and Detection Limits.** An external calibration method was applied for the quantification of Pt, Ir and Rh in the pre-concentrated samples. Reference standard solutions were prepared by sequential dilution from a 10 ppm PGE multi-element standard solution by weight base (CMS-2, Inorganic Ventures, Lakewood, New Jersey, USA) using UP 1% (m/m) HNO$_3$. The concentrations of the standard solutions used for the calibration curves were 0, 2, 5, 10, 15, 20 and 25 fg mL$^{-1}$ for Ir quantification and 0, 50,

100, 200, 500, 1000 and 2000 fg mL$^{-1}$ for Rh and Pt quantification. For these concentration ranges, the correlation coefficients (r$^2$) of the calibration curves were higher than 0.999 (Figure S1).

$^{195}$Pt, $^{193}$Ir and $^{103}$Rh isotopes were measured because $^{195}$Pt and $^{193}$Ir have the highest natural abundance and lowest interference, whereas $^{103}$Rh is the only naturally-occurring isotope of Rh (Table S2). Detection limits were calculated as three times the standard deviations (1σ) of 10 measurements of the blank (1% UP HNO$_3$ solutions). The instrumental detection limits obtained for Pt, Ir and Rh are 26 fg mL$^{-1}$, 3 fg mL$^{-1}$ and 9 fg mL$^{-1}$, respectively. The procedural detection limits are as low as 0.43 fg mL$^{-1}$, 0.05 fg mL$^{-1}$, and 0.15 fg mL$^{-1}$ for Pt, Ir and Rh, respectively, after correction with a pre-concentration factor of 60.

**Quality Control of Analyses.**

**Interferences:** To avoid contributions by interferents, the instrumental parameters were optimized daily for the lowest oxide production rate and the highest sensitivity, and the effects of potential interferences (Table S2) were checked daily before the analysis was performed. The interference check was performed by measuring the analytes ($^{195}$Pt, $^{193}$Ir and $^{103}$Rh) in 0-100 pg mL$^{-1}$ (pg = 10$^{-12}$ g) single-element standard solutions of interferents (Rb, Sr and Cu for $^{103}$Rh; Hf for $^{195}$Pt and $^{193}$Ir). The desolvation nebulization system and a good quality design of the instrumental conditions rendered the interference by interferent concentrations of up to 100 pg mL$^{-1}$ negligible. Thus, mathematical corrections were not required in this concentration range. The Hf concentrations, which is the potential interferent for Pt and Ir, were estimated to be lower than 100 pg mL$^{-1}$ in pre-concentrated snow samples, whereas the concentrations for the Rh interferents (Rb, Sr and Cu) were found to exceed 100 pg mL$^{-1}$ in some pre-concentrated snow samples based on the results of direct (without pre-concentration) measurements of 80 Antarctic snow samples and a pre-concentration factor of 60. Therefore, an analytical error range for Rh determination was estimated in a river water matrix, which is a matrix with much higher concentrations of potential interferents, such as Rb and Sr, than the polar samples. This protocol is described in the next section.

**Sensitivity Drift:** Internal standards are not preferred for high-purity polar ice and snow samples because their use can cause contamination at extremely low concentrations of analytes. We corrected the sensitivity drift over time by performing repeated analyses of the standard solutions between samples. After every five sample analyses (or every ~20 minutes), the instrumental sensitivity drift and blank levels were checked by measuring the standard (500 fg mL$^{-1}$) and blank (1% UP HNO$_3$) solutions. Correction was performed on the sample signals.

**Reliability:** Because no certified reference materials for polar ice and snow are available, riverine water certified reference materials (CRM) (SLRS4 and SLRS5, National Research Council of Canada, Ottawa, Canada) were used for accuracy control. First, the concentrations of Pt, Ir and Rh in the riverine water materials were determined because there

**Table 1.** Analytical results for river water CRMs (fg mL$^{-1}$) with standard deviations (1σ)

| PGE | CRM | This study | Literature | |
|-----|-----|-----------|------------|---|
| Pt | SLRS 4 | 1210 ± 96$^a$ | 1250 ± 146$^{(4)}$ | 1300 ± 100$^{(3)}$ |
| Ir | SLRS 4 | 6.9 ± 1.1$^a$ | 8 ± 4$^{(4)}$ | 300 ± 200$^{(3)}$ |
| | SLRS 4 | 8.7 ± 0.8$^b$ | 8 ± 4$^{(4)}$ | 300 ± 200$^{(3)}$ |
| | SLRS 5 | 4.8 ± 1.4$^b$ | - | - |
| Rh | SLRS 5 | 1690 ± 80$^a$ | - | - |
| | SLRS 5 | 1390 ± 90$^b$ | - | - |

$^a$Direct measurement. $^b$Standard addition method.

are only one or two comparable studies for Pt and Ir in SLRS4 and no comparable studies for Rh. The analytical results for Pt, Ir and Rh from direct measurements (by an external calibration method) and from a standard addition method (spiked by PGE standard solutions of 0, 5, 10, 15, 20 and 25 fg mL$^{-1}$ for Ir analyses and 0, 500, 1000, 1500, 2000 and 2500 fg mL$^{-1}$ for Rh analyses, Figure S2) for SLRS4 and SLRS5 are presented in Table 1. The Pt concentration in SLRS4 obtained by direct measurements was in good agreement with those available in the literature.$^{3,4}$ Thus, it was not necessary to check the results *via* the standard addition method because the concentration was relatively high, and the results were accurately obtained by direct measurement. Despite the very low concentration of Ir in SLRS4, the Ir results obtained by the direct and standard addition measurements were in good agreement with each other within the range of analytical error. These findings were also consistent with those reported in a previous study by the authors$^4$ but were two orders of magnitude lower than the findings obtained in another study.$^3$ In SLRS5, the Ir concentration was only determined by the standard addition method, and the Ir concentration was determined to be 4.8 ± 1.4 fg mL$^{-1}$. There is no published data pertaining to Rh concentrations in either SLRS4 or SLRS5 because of the hindrance of strong interferences and the ultra-low levels of Rh in riverine water. The analytical results for Rh in SLRS5 as obtained by direct measurement and the standard addition method were in agreement with each other within approximately 20%. The result for Rh using the standard addition method (1380 ± 90 fg mL$^{-1}$) is preferred; interference and matrix effects were eliminated because the samples and standards were both in the same matrix. In summary, the Pt and Ir results are consistent with the results from the literature and/or the results of the standard addition method, whereas an analytical error of approximately 20% for the measurement of Rh must be considered.

An accuracy check using riverine water CRM, however, cannot fully verify the reliability of snow and ice analyses because of considerable differences in the matrix and the concentration levels of the analytes between river water and polar snow and ice. For this reason, two reference solutions were prepared using the riverine water CRMs, which were more suitable for reliability checks of the PGE analyses of polar snow and ice samples. These references were (a) the SLRS4 riverine water CRM diluted 10 times and spiked

with 50 fg mL$^{-1}$ Ir (as Ir was expected to be too low (~0.8 fg mL$^{-1}$) in diluted SLRS4) for Pt and Ir analyses; and (b) the SLRS5 riverine water CRM diluted 5 times for Rh analysis. The final PGE concentrations in the reference materials were calculated to be 115 ± 9 fg mL$^{-1}$ Pt and 55 ± 5 fg mL$^{-1}$ Ir (A-solution) and 276 ± 18 fg mL$^{-1}$ Rh (B-solution). Despite the quite low concentrations of Pt, Ir and Rh in the prepared reference materials, all of the analytical results obtained by repeated measurements between samples agreed well with the expected concentrations within 10% for Pt and Ir and within 25% for Rh after blank and signal-drift corrections.

**Recovery and Precision of the Sample Pre-concentration Procedure.** To ensure accuracy, a recovery and precision test was performed using unacidified PGE multi-element standard solutions of 0.1, 0.5, 1, 5, 10 and 20 fg mL$^{-1}$ concentrations (prepared by weight base sequential dilution from a 10 ppm PGE standard solution) as samples with similar concentrations to those in polar snow and ice. For each concentration level, one (for Rh) or three (for Pt and Ir) standard solutions were pre-concentrated and analyzed. In order to avoid possible changes in extremely low concentrations in unacidified solutions, the solutions were prepared just before the experiment was conducted, and they were immediately transferred to acid-soaked PFA beakers (within 10 minutes after final dilution) for pre-concentration. Experimental blanks were evaluated with UP water as a sample and used as a correction for each pre-concentration set. The determined PGE concentrations are illustrated in Figure 1 as a function of the prepared (calculated) concentration. The slopes of the fitted lines indicate the recovery ratios of the pre-concentration procedures, which are 93% ± 1%, 101% ± 1% and 111% ± 2% for Pt, Ir and Rh, respectively. The intercepts of the fitted lines represent the average experimental blank levels from ultrapure water, nitric acid (used for sample acidification) and from the laboratory materials used throughout the experimental procedures. The intercepts were 0.11 ± 0.11 fg mL$^{-1}$, 0.10 ± 0.06 fg mL$^{-1}$ and 0.26 ± 0.11 fg mL$^{-1}$ for Pt, Ir and Rh, respectively. The average relative standard deviations of single measurements in pre-concentrated samples were 14% (0.4-52% for a concentration range of 1-20 fg mL$^{-1}$), 14% (0.2-67% for 0.1-20 fg mL$^{-1}$) and 10% (1.3-34% for 0.1-10 fg mL$^{-1}$) for Pt, Ir and Rh, respectively. The pre-concentration reproducibility was estimated based on the relative standard deviations of simultaneous determinations for the same concentration. On average, these deviations were as follows: 7% (3.5-10%) for a 1-20 fg mL$^{-1}$ concentration range (n = 6 for each concentration (3 samples × 2 measurements)) for Pt, 4% (0.9-15%) for a 0.1-20 fg mL$^{-1}$ concentration range (n = 6 (3 × 2)) for Ir and 15% (3.3-27%) for a 0.1-10 fg mL$^{-1}$ concentration range (n = 2 (1×2)) for Rh.

The collected results (i.e., recoveries, precisions and blank levels) for Pt, Ir and Rh in this study are superior to those obtained from previous studies performed using similar methods for the determination of PGEs[5] and other trace metals.[2]
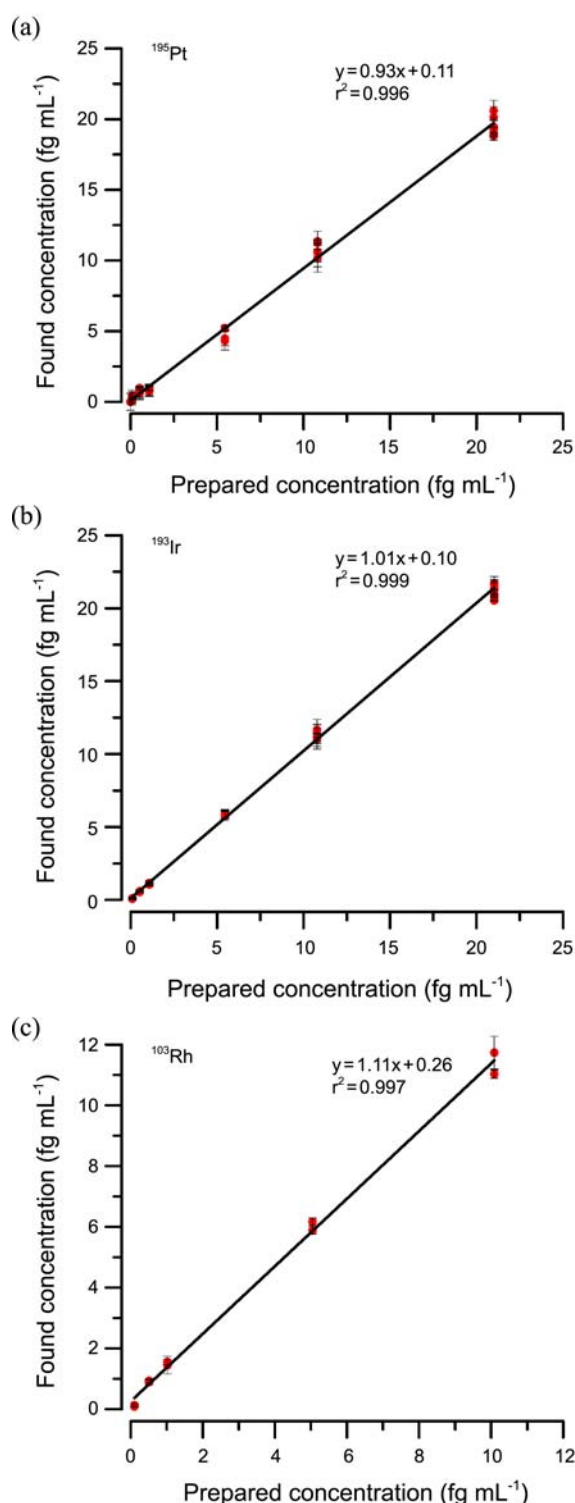


**Figure 1.** Calibration of the non-boiling evaporation procedure for (a) Pt, (b) Ir and (c) Rh using 60 mL of 0.1-20 fg mL$^{-1}$ standard solutions. Slopes of regression lines indicate recovery ratio, and intercepts indicate experimental blanks.

**Checking PGE Contributions from Decontamination.** When snow and ice cores are used for reconstructing past changes in atmospheric composition, decontamination of the outside of the sample is mandatory because the outer layers of the core samples are subject to contamination during the
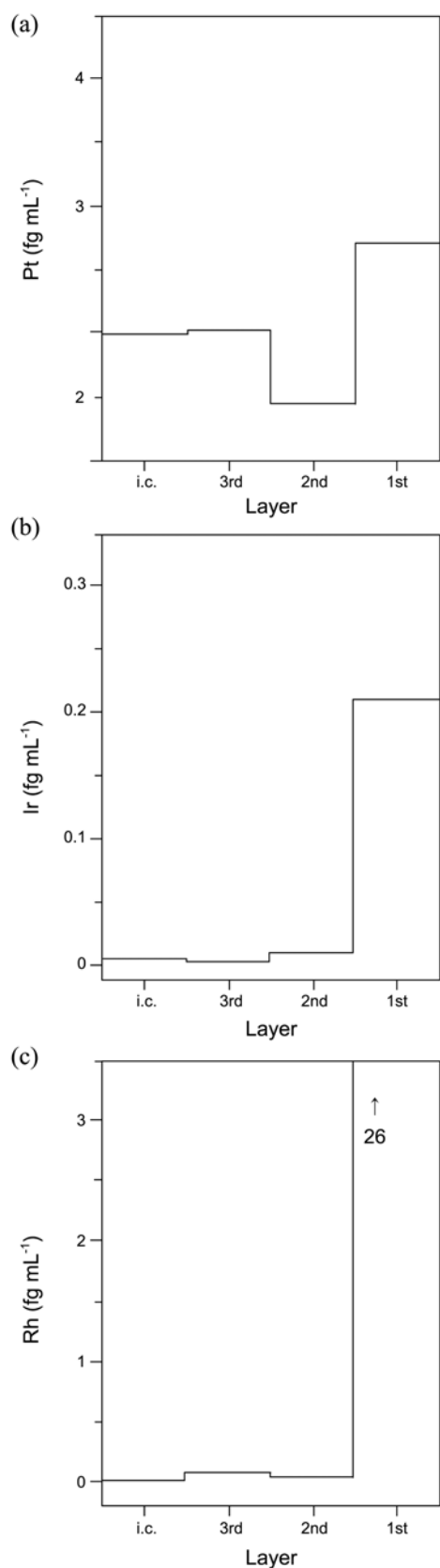
**Figure 2.** Changes in the concentrations of (a) Pt, (b) Ir and (c) Rh in the sample layers (from outside) and inner core (i.c.) of the artificial ice core.

drilling operation. Thus, evaluation of the efficiency and of the blank contributions of the decontamination procedure is absolutely necessary. For this purpose, we carried out a complete analytical procedure, i.e., decontamination, pre-concentration and instrumental analysis, on artificial ice core prepared using Milli-Q water. Approximately 2 L of Milli-Q water was frozen in a previously cleaned 2000 mL Teflon vessel (Savillex, Minnetonka, USA) for ~48 h. Careful elimination of the outside layer was then performed by mechanically chiseling consecutive layers of ice in progression from the outside toward the center of the artificial core under ultra-clean conditions. Detailed decontamination procedures by mechanical chiseling have been reported previously.[6] Through this procedure, the clean inner core of the artificial core section was obtained after three successive layers were removed from the outside toward the center. To confirm that the inner core was free from outside contamination, all of the layers were analyzed for PGEs. A non-boiling pre-concentration procedure was performed with a concentration factor of 60 (for the first outer layer) and a concentration factor of 120 (for the second and third layers and the inner core). The Pt, Ir and Rh concentrations as a function of the sample layer from the outside to the inside of the core are shown in Figure 2. The PGE concentrations in the outside layer (the first layer) were 2.7, 0.2 and 26 fg mL$^{-1}$ for Pt, Ir and Rh, respectively. Interestingly, the outside of the artificial core was found to be slightly contaminated with the most pronounced contamination for Rh. This result indicates that contamination of the samples could occur during handling of the core sections. We then observed well-established plateau values in the inner layers of the core for the three PGEs, indicating that no outside PGE contamination was present in the inner core as a result of the decontamination procedure. The inner core concentrations were close to or lower than the procedural detection limits of 0.43, 0.05 and 0.15 fg mL$^{-1}$ for Pt, Ir and Rh, respectively.

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# Supplementary Material

# Quantification of Ultra-Trace Levels of Pt, Ir and Rh in Polar Snow and Ice Using ICP-SFMS Coupled with a Pre-Concentration and Desolvation Nebulization System

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## Cleaning Procedures

The cleaning procedures for the experimental tools, including low- and high-density polyethylene bottles (LDPE and HDPE), Teflon beakers and stainless steel tools used for mechanical chiseling during the decontamination procedure of the ice core sample, were performed in the class-10 clean booth according to the previously established cleaning protocol.[1] Grease and other production materials on the bottles are first removed with chloroform, and the bottles are then rinsed well with Millipore RO water. The bottles are then immersed for a week in each of a series of three, covered acid cleaning baths, which include one 20 L carboy (Nalgene) filled with 25% Merck "Suprapur" $HNO_3$ and two 20 L carboys filled with 0.1% (v/v) Merck "Optima" grade $HNO_3$, before a final rinse with Milli-Q water. The bottles are then filled with 0.1% "Optima" grade $HNO_3$ in Milli-Q water, capped and packed in acid-washed polyethylene bags before use. Acid-cleaned polypropylene (PP) tongs were used to rinse and transfer all of the items immersed in the successive acid baths.[1] Further improvement in the described cleaning procedures of the protocol[1] was made by an additional step that involved soaking all labware in an initial acid bath filled with ~25% of guaranteed reagent (GR) grade $HNO_3$ before cleaning the items in the successive acid baths. The cleaning procedure for the PFA Teflon beakers and other small items is similar to that for the bottles except that they are immersed in concentrated Merck "Suprapur" $HNO_3$ at room temperature for at least a week before immersion in the second bath. PFA beakers used for the non-boiling pre-concentration of the samples are left immersed in the last acid bath until use. Polypropylene (PP) pipette tips are cleaned by immersion inside a 1000 mL PFA jar containing concentrated Merck "Suprapur" $HNO_3$ for a week. PP tips are cleaned by pipetting concentrated "Optima" grade $HNO_3$ into the tip, ejecting the acid and then washing with Milli-Q water many times just before use.

**Table S1.** Instrumental conditions and measurement parameters for the ICP-SFMS and the desolvation system

| Parameters | Values |
|---|---|
| Gas flow rates | |
|    Cool (L min$^{-1}$) | 16.00 |
|    Auxiliary (L min$^{-1}$) | 0.40-0.90* |
|    Sample (L min$^{-1}$) | 0.85-1.00* |
| Nitrogen flow rate (mL min$^{-1}$) | ~8* |
| Spray chamber (°C) | 100 |
| Chiller temperature (°C) | 2 |
| Washing time (min) | 1 (by 5% $HNO_3$) |
| | 1 (by 1% $HNO_3$) |
| Take up time (s) | 50 |
| Resolution | Low (m·$\Delta$m$^{-1}$) = 300 |
| Selected isotopes | $^{179}$Hf, $^{193}$Ir, $^{195}$Pt, $^{103}$Rh |
| Dwell time per acquisition points (ms) | 10 |
| Sample per peak | 200 |
| Total acquisition time (per mass segment, s) | 0.2 |
| Acquisition window (%) | 10 |
| Search window (%) | 0 |
| Integration window (%) | 10 |
| Run number | 9 |
| Pass number | 20 |

*Optimized daily to obtain maximal intensity.

**Table S2.** Potential interferences that could affect the determination of ultra trace levels of Pt, Ir and Rh in polar snow and ice samples

| Analyte | | Potential interference | |
|---|---|---|---|
| Isotope | Abundance (%) | Species | Abundance* (%) |
| $^{103}$Rh | 100 | $^{63}$Cu$^{40}$Ar | 68.89 |
| | | $^{87}$Sr$^{16}$O | 6.98 |
| | | $^{87}$Rb$^{16}$O | 71.99 |
| $^{193}$Ir | 62.7 | $^{177}$Hf$^{16}$O | 18.56 |
| $^{195}$Pt | 33.8 | $^{179}$Hf$^{16}$O | 13.60 |

*Calculated by multiplying the natural abundances of each isotope and dividing by 100.
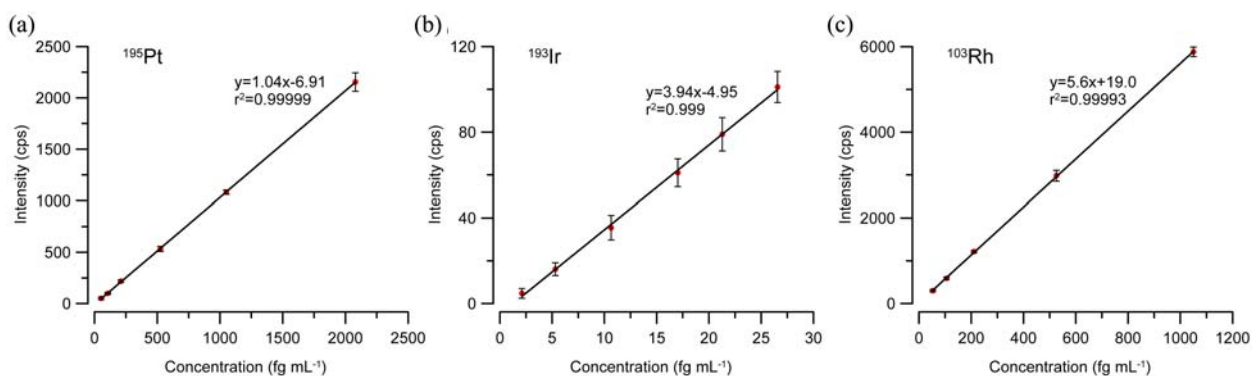
**Figure S1.** External calibration curves for (a) [195]Pt, (b) [193]Ir and (c) [103]Rh.
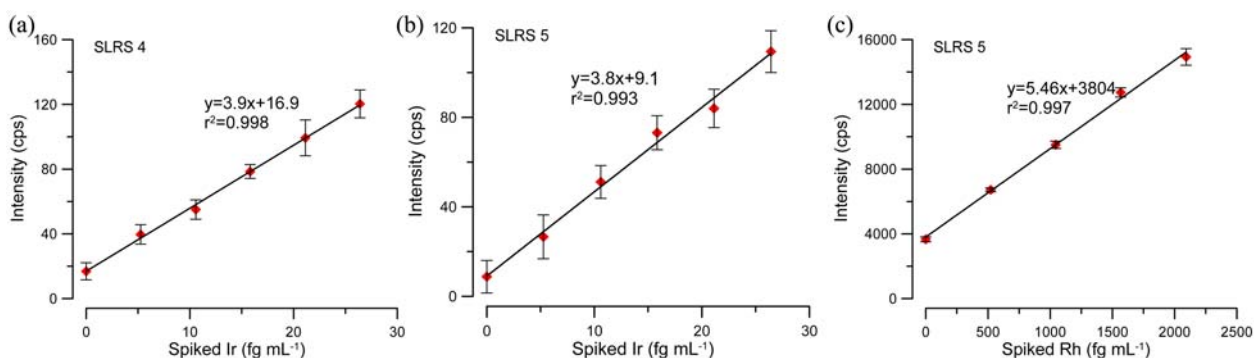


**Figure S2.** Calibration of the standard addition experiment using PGE standard solutions with a river water matrix. The concentrations of Ir and Rh in river water reference materials were calculated by $C = 2 \times (y/a)$, where $C$ is the concentration, 2 is the correction (dilution) coefficient, $y$ is the intercept and $a$ is the slope.