Supporting Information

For "Enhanced release of palladium and platinum from catalytic converter materials exposed to ammonia and chloride bearing solutions**"**

Authors and affiliations:

Deborah M. Aruguete[1*], Mitsuhiro Murayama[2,3], Terry Blakney[4] and Christopher Winkler[3]

[1]Department of Environmental Science, Penn State Behrend, 4205 College Drive, Erie, PA 16563, U.S.A.

[2]Department of Materials Science and Engineering, Virginia Tech, Blacksburg, VA, 24061, U.S.A.

[3]Institute for Critical Technology and Applied Science, Nanoscale Characterization and Fabrication Laboratory, Virginia Tech, Blacksburg, VA, 24061, U.S.A

[4]Department of Mathematics, Penn State Behrend, 4205 College Drive, Erie, PA 16563

*Corresponding author: aruguete@psu.edu

Number of pages (including cover): 15

Number of figures: 2

Number of tables: 17

I. Materials characterization.

Figure S1. X-ray diffractogram from whole powdered ACC material

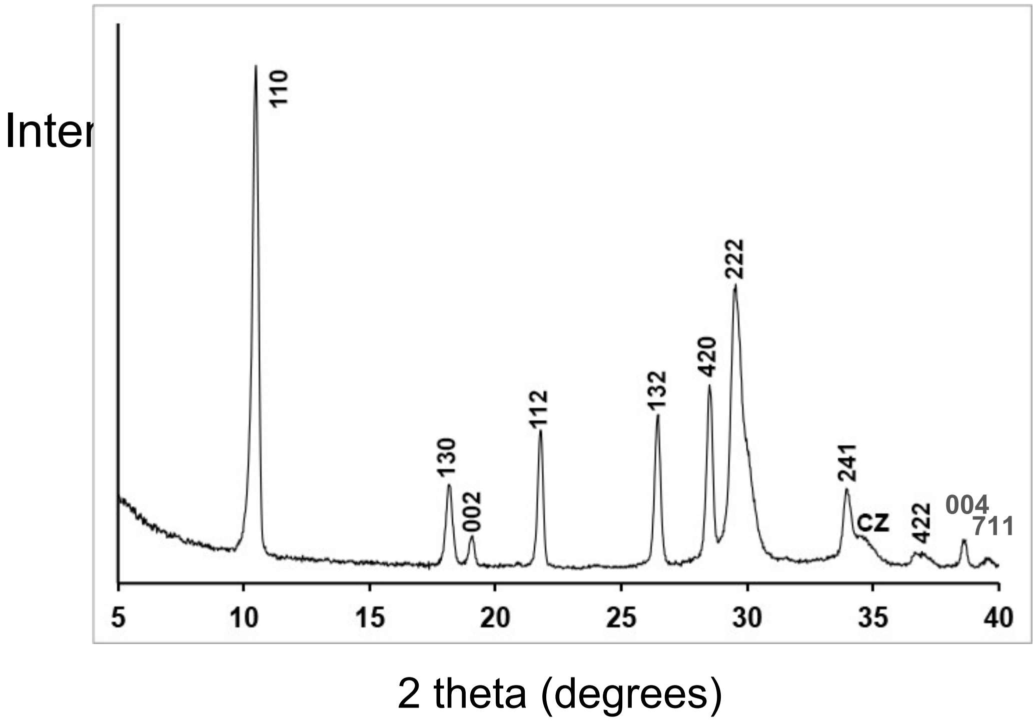

Figure S1. Powder X-ray diffraction from powdered ACC material. Peaks in this X-ray diffractogram are labeled with the corresponding reflections for cordierite (based on Gibbs, G.V. (1966) “The polymorphism of cordierite I: The crystal structure of low cordierite.” *American Mineralogist*, 15, pp. 1068-1087). The peak labeled “CZ” is consistent with the 200 reflection of ceria-zirconia.

Note. Fast Fourier Transform (FFT) analysis of figures 3D1 and 3D2.

Calculated FFT patterns were compared to simulations for Pd, Pt, Rh, γ-Al_2O_3, PdS, PdO, and NaCl. A pattern of PdO ([111] zone axis) matched the most closely to the FFT patterns, but the calculated d-spacings were smaller than the measured d-spacings.

Table S1. Figure 1E SAED Data and AMCSD Diffraction Data for CeO_2*

Experimental data			AMCSD data - CeO_2		
Ring	**d-spacing (Å)**	**AMCSD d-spacing (Å)**	**AMCSD Intensity**	**hkl**	**Multiplicity**
1	3.05	3.124	100	111	8

2	2.64	2.7055	27.73	200	6
3	1.86	1.9131	48.63	220	12
4	1.58	1.6315	35.71	311	24
5 (faint ring)	1.528	1.56	6.31	222	8
6 (faint ring)	1.322	1.3527	5.98	400	6
7	1.21	1.2414	11.84	331	24
8	1.189	1.2099	7.15	420	24
9	1.054	1.1045	10.51	422	24

Table S2. Figure 1F SAED Data and AMCSD Diffraction Data for γ-Al_2O_3[*]

Experimental data			AMCSD data - γ-Al_2O_3		
Ring	d-spacing (Å)	AMCSD d-spacing (Å)	AMCSD Intensity	hkl	Multiplicity
No ring observed		2.2805	4.18	111	8
1	1.976	1.9750	92.16	200	6
2	1.410	1.3965	100	220	12
no ring observed		1.1403	11.07	222	8

*For tables S1 and S2, indexing was performed by using the Digital Micrograph Ellipse Fitting Analysis program and the American Mineralogist Crystal Structure Database. (http://rruff.geo.arizona.edu/AMS/amcsd.php).

II. Mass spectrometry

Table S3. Operating conditions for Thermo Fisher Scientific X Series 2 ICP-MS (Penn State Energy and Environmental Sustainability Laboratory)

Plasma gas flow	13 L / min
Auxiliary gas flow	0.7 L / min
Nebulizer gas flow[*]	0.75 – 0.90 L / min
ICP RF power	1400 W
Mode of operation	He-H Collision Cell on
He-H gas flow	4.25 mL/min
Spray chamber temperature (Peltier cooler)	2° C
Sample uptake	~0.5 mL/min
Ion optic voltage[*]	Varies
Integration time	10 ms
Replicates / sample	3

Nebulizer type	C-Type Quartz from Precision Glassblowing
Spray chamber type	Quartz Conical from Precision Glassblowing
Sample cone	Ni with Cu core from Spectron US
Skimmer cone	Ni from Spectron US

*Tuned daily using standard ICP-MS-TS-8 (High Purity Standards) and Plasmalab autotune function.

Parameters for this instrument are adjusted to maximize ^{7}Li, ^{115}In and ^{238}U signals. Parameters were also adjusted to reduce the formation of doubly-charged species and oxides by minimizing the ratios of ^{137}Ba^{++}/^{137}Ba and ^{156}CeO/Ce (≤ 0.03). To reduce the amount of polyatomic species formed, a collision cell was utilized. He-H flow was tuned to keep ^{40}Ar^{38}Ar at a minimum (from ~3000 integrated counts per second (icps)) to <10 icps).

Table S5 below shows common expected interferences from polyatomic species formed with the metals Cu, Zn, Sr, Rb, Y, Zr, Mo, Gd, Hf, Ta, Pb as well as isotopes of Cd isobaric with isotopes of Pd. To be considered significant, signal counts of the interfering elemental isotope(s) in question had to be >5% of the putative Pd, Pt or Rh signal and have isotopic ratios consistent with natural abundances. In standard environmental samples, the majority, if not all of these interfering elements will be present. However, it was found that most interfering elements had signal << 5% of the putative Pd, Pt or Rh signal aside from Sr. This finding is not surprising as this is a simplified, laboratory-controlled system. The ACC material is from a catalytic converter that has not yet been used, hence no metal contaminants from exhaust are present. The remainder of the solutions are made with reagents of high purity (see main text).

The only potentially significant contaminant was Sr. Sr was correlated with Ba levels (Ba is used in catalytic converters to bind NO_x species), hence it was very likely an impurity from the Ba. Sr polyatomics have mass interferences with ^{105}Pd signal. To determine whether the Sr polyatomics significantly skewed signal at a mass of 105, isotopic ratios of the ^{105}Pd signal with signal from ^{106}Pd, ^{108}Pd and ^{110}Pd. Normally this would not have been possible because cadmium has isobaric isotopes at mass numbers of 106, 108, and 110. In this case, it was determined that Cd was not present in any detectable quantity because there was no significant signal at the mass numbers of 112 and 114, corresponding to the most abundant isotopes of (24.11% for ^{112}Cd and 28.75% for ^{114}Cd).

Table S4. Common mass interferences for platinum group elements*

Isotope	Common interferences
^{105}Pd	^{89}Y^{16}O, ^{40}Ar^{65}Cu, ^{93}Nb^{12}C, ^{88}Sr^{16}OH
^{106}Pd	^{106}Cd ^{40}Ar^{66}Zn, ^{90}Zr^{16}O, ^{89}Y^{16}OH
^{108}Pd	^{108}Cd, ^{40}Ar^{68}Zn, ^{92}Zr^{16}O, ^{92}Mo^{16}O
^{194}Pt	^{178}Hf^{16}O
^{195}Pt	^{179}Hf^{16}O, ^{178}Hf^{17}O, ^{177}Hf^{18}O, ^{14}N^{181}Ta, ^{40}Ar^{155}Gd
^{103}Rh	^{206}Pb^{2+}, ^{40}Ar^{63}Cu, ^{87}Sr^{16}O, ^{87}Rb^{16}O

*References:

Djingova, R., Heidenreich, H., Kovacheva, P. and Markert, B. “On the determination of platinum group elements in environmental materials by inductively coupled pass mass spectrometry and microwave digestion” *Analytica Chimica Acta* 489 (2003) 245-251.

Godlewska-Żyłkiewicz B., Leśniewska B. (2006) Sources of Error and their Elimination for Spectrometric Determination of Palladium in Environmental Samples. In: Zereini F., Alt F. (eds) Palladium Emissions in the Environment. Springer, Berlin, Heidelberg.

May, T.W. and Wiedmeyer, R.H. “A Table of Polyatomic Interferences in ICP-MS” *Atomic Spectroscopy* Vol 19(5) 1998 150-155.

Machado, R.C., Amaral, C.D.B., Schiavo, D., Nóbrega, J.A. and Nogueira, A.R.A. “Complex samples and spectral interferences in ICP-MS: Evaluation of tandem mass spectrometry for interference-free determination of cadmium, tin and platinum group elements.” *Microchemical Journal*, vol 130, 2017 271-275.

III. Statistical analysis

As per the main text, the term “control” refers to a 1.13 x 10^5 μM solution of $NaNO_3$. The term “Cl-only” refers to a 1.13 x 10^5 μM solution of NaCl (4000 ppm Cl^-). “TAN-Cl^-” solutions contain both AN and chloride (as NaCl) at a concentration of 1.13 x 10^5 μM.

A note regarding the units in this section: statistical analyses were performed upon concentrations in units of μg kg^{-1} (ppb), and, as such, these units are retained in this ESI. For consistency in the main manuscript, concentrations are reported in units of micromolarity (or micromolality for the analysis of solid catalytic converter material).

A. Palladium

Table S5. p-values from Andersen-Darling Testing of Palladium Datasets for Normality ($\alpha = 0.05$)

$NaNO_3$ only	**NaCl only**	**No NaCl added, 0.1 ppm TAN**	**With NaCl, 0.1 ppm TAN**	**No NaCl added, 1 ppm TAN**	**With NaCl, 1 ppm TAN**	**No NaCl added, 2147 ppm TAN**	**With NaCl, 2147 ppm TAN**
p-value =.033	p-value =.394	p-value =.506	p-value =.459	p-value =.233	p-value =.820	p-value = 0.068	p-value = 0.496
Non-normal	Normal	Normal	Normal	Normal	Normal	Normal	Normal

In order to determine how to analyze palladium concentration data for extracts, the Andersen-Darling test was used to determine (95% confidence level) whether the data had a normal distribution. If $p > 0.05$, the data was accepted as having a normal distribution. For datasets that were not normally distributed, alternative non-parametric analyses were employed.

Table S6. Pairwise Comparisons of Palladium Concentrations in Extracts With and Without Chloride for Varying TAN levels (95% confidence level)

TAN (ppm)	Test statistic	p value	Decision
0	Mann Whitney= 22	.0137	Difference
0.1	T= -3.72	.021	Difference
1	T=-5.63	.002	Difference
2147	T= -2.68	.037	Difference

Student's t-tests were employed to compare TAN-only versus TAN + Cl^- extracts. The Mann-Whitney test was used to compare the $NaNO_3$ extracts (TAN = 0 ppm) with chloride-only extracts, as the Pd data from $NaNO_3$ extracts were not normally distributed. From this analysis, it can be concluded that extracts with chloride have different palladium contents than those without.

Analysis of differences between control and TAN-only solutions (TAN = 0.1 ppm and 1 ppm). The data was analyzed with Mood's Median test (ANOVA was not employed due to non-normality of $NaNO_3$ data). For the control and TAN-only solutions with TAN = 0 ppm, 0.1 ppm, and 1 ppm, the Mood's Median test resulted in a p-value = 0.016. Within 95% confidence, this indicates that there is a significant difference between datasets. When datasets for only TAN = 0 ppm and TAN = 0.1 ppm were compared using Mann-Whitney testing, the resulting p-value was 0.5752, indicating no significant difference. Thus, relative to the control (TAN = 0 ppm), the Pd content of 1 ppm TAN-only solutions is different.

Simply stated, 1 ppm TAN increases the amount of Pd present, but a concentration of 0.1 ppm TAN has no discernible effect.

Analysis of differences between chloride-only and chloride + TAN extracts (TAN = 0.1 ppm and 1 ppm) The data was analyzed with Mood's Median test due to the variances being unequal between the levels of the normally distributed variables which violates the use of ANOVA. For the chloride-only and both TAN + Cl- solutions, the Mood's Median test resulted in a p-value = 0.02. Within 95% confidence, this indicates that there is a significant difference between datasets. When datasets for only chloride-only and 0.1 ppm TAN + Cl- solutions were compared with Mann-Whitney, the resulting p-value was 0.9273, indicating no significant difference. Thus, the Pd content of 1 ppm TAN showed the only statistical difference of the groups.

Simply stated, in the presence of chloride, 1 ppm TAN increases the amount of Pd present relative to a chloride-only solution, but a concentration of 0.1 ppm TAN has no discernible effect.

Analysis of differences from blanks. Reagent blanks were prepared by conducting batch dissolution experiments in the absence of ACC material (solution only) and subsequently conducting elemental analysis. Statistical analyses (pairwise comparisons conducted as above) were run for samples with low Pd concentrations. As per table S8 extracts were found to have higher concentrations of Pd than the blanks.

Table S7. Palladium content in extracts and corresponding blanks, with p-values for pairwise comparisons* and limits of detection (LODs)

	0 M TAN		low TAN		mid TAN		high TAN		0 M TAN + Cl^-		High TAN + Cl^-	
	Filt (ppb)	Bkgd (ppb)	Filt (ppb)	Bkgd (ppb)	Filt (ppb)	Bkgd (ppb)	Filt (ppb)	Bkgd (ppb)	Filt (ppb)	Bkgd (ppb)	Filt (ppb)	Bkgd (ppb)
avg	1.078	0.166	1.394	0.437	6.293	0.544	5929	0.014	25.53	0.013	7729	0.008
stdev	0.552	0.086	1.012	0.175	4.323	0.396	892	0.005	4.45	0.011	1583	0.004
LOD		0.424		0.962		1.732		0.029		0.046		0.020
p-value	0.011		0.0142**		0.042							
Decision	Difference		Difference		Difference							

* The Andersen-Darling test was used to determine (95% confidence level) whether the datasets were normally distributed. If so, the Student’s t-test was used for pairwise comparison. Otherwise the Mann-Whitney (alternative non-parametric analysis) was used.

**Mann-Whitney test conducted.

B. Platinum

As per the main text, the term “control” refers to a 0 ppm TAN and 0 ppm Cl^- solution (0.113 M $NaNO_3$). The term “Cl-only” refers to a 4000 ppm Cl^- solution (0.113 M NaCl). “x ppm TAN-Cl^-“ refers to 0.1 ppm or 1 ppm TAN solutions with a chloride concentration of 4000 ppm.

Table S8. Andersen-Darling Testing of Platinum Datasets for Normality ($\alpha = 0.05$)

$NaNO_3$ only	**NaCl only**	**No NaCl added, 0.1 ppm TAN**	**With NaCl, 0.1 ppm TAN**	**No NaCl added, 1 ppm TAN**	**With NaCl, 1 ppm TAN**	**No NaCl added, 2147 ppm TAN**	**With NaCl, 2147 ppm TAN**
Pval= 0.144	Pval= 0.066	Pval= 0.015	Pval= 0.494	Pval = 0.454	Pval = 0.161	Pval = 0.007	Pval = 0.034
Normal	Normal	Non-normal	Normal	Normal	Normal	Non-normal	Non-normal

In order to determine how to analyze the platinum content data from extracts, the Andersen-Darling test was used to determine (95% confidence level) whether the data had a normal distribution. If $p > 0.05$, the data was accepted as having a normal distribution. For datasets that were not normally distributed, alternative non-parametric analyses were employed.

Table S9. Pairwise Comparisons of Platinum Content in Extracts With and Without Chloride for Varying TAN levels (95% confidence level)

Tan (ppm)	Test statistic	p-value	Decision
0	Mann Whitney= 22	.0137	Difference
0.1	T= -3.72	.021	Difference
1	T=-5.63	.002	Difference
2147	Mann Whitney = 37	0.9273	No difference

Analysis of differences between control and TAN-only extracts (TAN = 0.1 ppm and 1 ppm). These data series were analyzed with Mood's Median test (ANOVA was not employed due to non-normality of 0.1 ppm TAN-only data). For the control and TAN-only solutions with TAN = 0 ppm, 0.1 ppm, and 1 ppm, the Mood's Median test resulted in a p-value = 0.214. Within 95% confidence, this indicates that the varying the TAN level alone (no chloride) has no effect upon platinum release.

Analysis of differences between chloride-only and chloride + TAN solutions (TAN = 0.1 ppm and 1 ppm) The data was analyzed with ANOVA with all data levels being normally distributed and with constant variance at each level. For the chloride-only and both TAN + Cl- solutions, the ANOVA resulted in a p-value = 0.016. Within 95% confidence, this indicates that there is a significant difference between datasets. Running Tukey's pairwise comparison test, chloride-only and 1 ppm TAN solutions were significantly different, however neither were considered statistically different to the 0.1 ppm TAN level. Simply stated, in the presence of chloride, 1 ppm TAN increases the amount of Pt present relative to a chloride-only solution, but a concentration of 0.1 ppm TAN has no discernible effect.

Analysis of difference between chloride-only and chloride + TAN solutions (TAN = 2147 ppm). A Mann-Whitney test revealed no statistically significant difference between these two treatments.

Analysis of differences from blanks. Detection of contamination was performed by conducting batch dissolution experiments in the absence of ACC material (solution only) and subsequently conducting elemental analysis. Statistical pairwise comparisons were conducted as for palladium.

Table S10. Platinum content in extracts and corresponding blanks, with p-values for pairwise comparisons* and limits of detection (LODs)

	0 M TAN		Low TAN only		Mid TAN		High TAN		0 M TAN + Cl^-		High TAN + Cl^-	
	Filt (ppb)	Bkgd (ppb)	Filt (ppb)	Bkgd (ppb)	Filt (ppb)	Bkgd (ppb)	Filt (ppb)	Bkgd (ppb)	Filt (ppb)	Bkgd (ppb)	Filt (ppb)	Bkgd (ppb)
avg	0.037	0.009	0.033	0.029	0.046	0.039	1.533	0.012	0.135	0.015	2.294	0.005
stdev	0.024	0.0001	0.010	0.014	0.013	0.025	0.714	0.001	0.105	0.005	1.731	0.004
LOD		0.0093		0.071		0.114		0.015		0.030		0.017
p-value	0.0142**		0.613		0.631		0.0282**		0.0051		0.0051	

decision	Difference	No difference	No difference	Difference	Difference	Difference

* The Andersen-Darling test was used to determine (95% confidence level) whether the datasets were normally distributed. If so, the Student's t-test was used for pairwise comparison. Otherwise the Mann-Whitney (alternative non-parametric analysis) was used.

**Mann-Whitney test conducted.

C. Rhodium

Figure S2. Box-and-whisker plots of rhodium concentrations in extracts

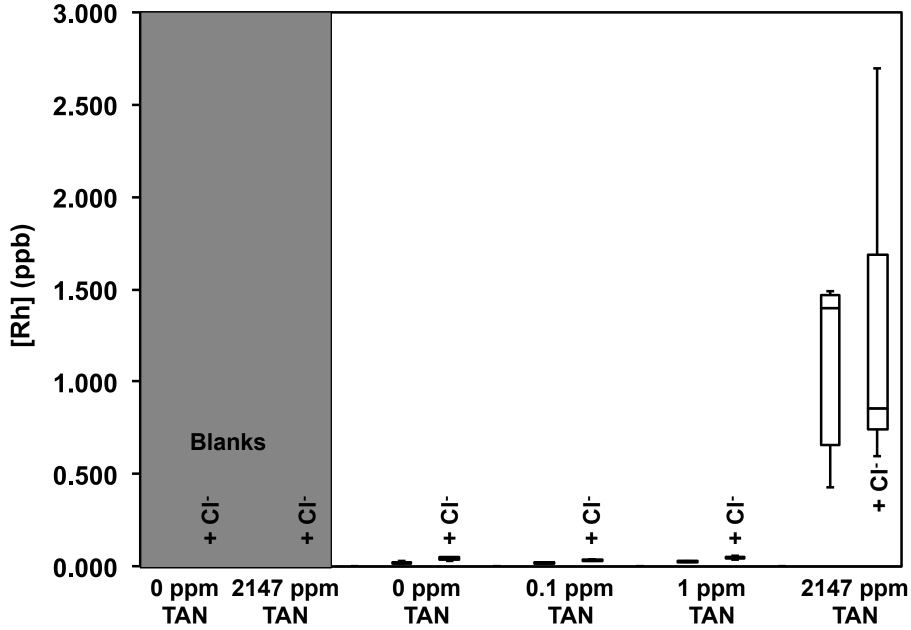

Figure S2. Box-and-whisker plots of Rh concentrations in extracts and reagent blanks. Data from TAN-only extracts are paired with the corresponding TAN + Cl^- extract. For convenience, not every single blank is included in this plot

Table S11. Rhodium content in extracts and corresponding blanks, with p-values for pairwise comparisons* and limits of detection (LODs)

	0 M TAN		Low TAN		Mid TAN		High TAN		0 M TAN + Cl^-		High TAN + Cl^-	
	Filt (ppb)	Bkgd (ppb)	Filt (ppb)	Bkgd (ppb)	Filt (ppb)	Bkgd (ppb)	Filt (ppb)	Bkgd (ppb)	Filt (ppb)	Bkgd (ppb)	Filt (ppb)	Bkgd (ppb)
avg	0.057	0.024	0.033	0.051	0.027	0.054	1.103	0.100	0.050	0.026	1.211	0.035
stdev	0.086	0.013	0.005	0.020	0.004	0.013	0.523	0.014	0.079	0.012	0.828	0.027
LOD		0.063		0.111		0.093		0.142		0.062		0.116
p-value	0.2703*		0.277		0.0350		0.0282		0.5940		0.0051	
decision	No difference		No difference		Difference†		Difference		No difference		Difference	

* The Andersen-Darling test was used to determine (95% confidence level) whether the datasets were normally distributed. If so, the Student's t-test was used for pairwise comparison. Otherwise the Mann-Whitney (alternative non-parametric analysis) was used.

**Mann-Whitney test conducted.

†The average concentration of Rh in the blanks is greater than that of the extract.

Analysis of differences from blanks for TAN = 0 ppm, 0.1 ppm and 1 ppm, with and without Cl^-. Detection of contamination was performed by conducting batch dissolution experiments in the absence of ACC material (solution only) and subsequently conducting elemental analysis. Statistical pairwise comparisons were conducted as for palladium. Rhodium levels were indistinguishable or less than levels in blanks, except for high TAN-only and high TAN-Cl solutions.

Analysis of differences between high TAN-only and high TAN-Cl extracts. The Student's t-test resulted in a p-value of 0.8102. Within 95% confidence, this indicates that there is no significant difference between datasets.

Analysis of differences between TAN-only and TAN-Cl extracts for TAN = 0 ppm, 0.1 ppm and 1 ppm. Mood's Median test was used and $p < 0.05$, indicating a systematic difference. Regardless, as stated above, these extracts were not significantly different (within 95% confidence) from the corresponding blanks. As such, we do not consider the observed difference meaningful, but rather indicative of a background source of rhodium.

Analysis of differences between control and TAN-only extracts (TAN = 0 ppm, 0.1 ppm and 1 ppm). The data was analyzed with Mood's Median test (ANOVA was not employed due to non-normality of data). For solutions with TAN = 0 ppm, 0.1 ppm, and 1 ppm, the Mood's Median test resulted in a p-value = 0.165. Within 95% confidence, this indicates that there is no significant difference between datasets.

Analysis of differences between Cl-only and TAN-Cl extracts (TAN = 0 ppm, 0.1 ppm and 1 ppm). The data was analyzed with Mood's Median test (ANOVA was not employed due to non-normality of data), resulting in a p-value of 0.097. Within 95% confidence, this indicates that there is no significant difference between datasets.

IV. Examination of solutions for particles < 200 nm.

After the batch dissolution experiments, resultant solutions were filtered through 0.2 µm PVDF syringe filters, acidified, then subjected to elemental analysis. To determine whether nanoparticles were contributing to the PGE signal, as opposed to ionic species, solutions were ultracentrifuged or ultrafiltered.

Ultracentrifugation

Extracts were acidified and then centrifuged in a Beckman Optima TL ultracentrifuge at Gannon University (Erie, PA). After ultracentrifugation, the top portion and bottom portion were separated and analyzed separately. It was expected that if PGE nanoparticles were present in significant quantity, the bottom portion of the centrifuged solution would have higher PGE concentrations than the upper portion. Data is provided in Table S13 below.

Paired testing (Student's t-test) resulted in p-values of 0.7337, 0.8055, and 0.9131 for [Pd], [Pt] and [Rh]. Within 95% confidence, this indicates that there is no significant difference in content of these metals between the top and bottom fractions.

Table S12. PGE concentrations of top and bottom fractions of ultracentrifuged solutions.

Sample type	[Pd] ppb	[Pt] ppb	[Rh] ppb
Top fraction	7604 (±839)	1.742 (±0.514)	0.708 (±0.231)
Bottom fraction	7461 (±341)	1.674 (±0.305)	0.694 (±0.154)

Solutions were centrifuged at the highest available speed for this particular instrument (75000 rpm, corresponding to an rcf (relative centrifugal force) value of 239000 × *g*, where *g* is the acceleration from gravity) for 1 hour. Using Stokes' Law, the smallest particle size that could be moved to the bottom of the centrifuge tube was estimated to be 2.4 nm. Details of this calculation are provided in the next section.

Estimation of minimum particle size to be separated by ultracentrifugation.

To estimate what size of particle could be moved to the bottom of the centrifuge tube under these conditions, first the minimum terminal velocity (v) needed to move a particle 3 cm (distance to bottom of tube) within one hour was estimated:

$$v = \frac{d}{t}$$

Where v = terminal velocity of particle
t = centrifugation time
d = distance

Setting $t = 3600$ s (1 hour) and $d = 3$ cm, $v = 8.3 \times 10^{-4}$ cm/s.

Subsequently, this value for v was used in Stokes' equation (rearranged) to estimate the minimum particle size that could be spun down under these conditions, assuming the particle was palladium,

$$r = \sqrt{\frac{9\mu v R}{2(\rho_P - \rho_f)}}$$

where
r = radius of particle
R = acceleration from centrifugal force
ρ_P = density of particle
ρ_f = density of fluid
μ = dynamic viscosity of fluid, and
v = terminal velocity of particle

Using values of $v = 8.3 \times 10^{-4}$ cm/s, $\rho_P = 12.02$ g/cm^3 (palladium), $\rho_f = 1$ g/cm^3 (water), μ = 1.0016 mPa • s (water), and $R = 239000 \times g$, a particle diameter of 2.4 nm was calculated.

Ultrafiltration

Per the experimental methods, a series of batch dissolution experiments were run with 0.113 M NH_4Cl (4000 ppm Cl^-, 2147 ppm TAN) and powdered ACC, then filtered through 0.2 µm PVDF syringe filters. The extracts were passed through Pall Macrosep centrifugal ultrafiltration devices with a molecular weight cutoff (MWCO) of 1 kDa, then centrifuged at 4000 rpm until approximately half of the filtrate passed through the ultrafilter and subsequently acidified. The ultrafiltration devices were pre-conditioned with 0.113 M NH_4Cl. The retentate (solution that did not pass through the ultrafilter) and ultrafiltrate were separately analyzed. Data is provided in Table S14 below.

Paired testing (Student's t-test) resulted in p-values of 0.9434, 0.9584, and 0.6521 for [Pd], [Pt] and [Rh]. Within 95% confidence, this indicates that there is no significant difference in content of these metals between retentates and ultrafiltrates.

Table S13. PGE concentrations in retentate and ultrafiltrate obtained from ultrafiltration (1 kDa MWCO)

Sample type	[Pd] ppb	[Pt] ppb	[Rh] ppb
Retentate	3974.5 (± 339.4)	0.80 (± 0.37)	0.53 (±0.11)
Ultrafiltrate	3957.7 (±310.1)	0.79 (±0.22)	0.49 (±0.14)

V. Thermodynamic and kinetic data from the literature.

Table S14. Selected thermodynamic data for palladium (complexation, ligand exchange, dissolution)

Chemical reaction	Equilibrium constant[a]	Log EC	Ionic strength[e] (mol/kg)	Solution content[f]	Reference
$Pd^{2+} + Cl^- \leftrightarrow PdCl^+$	β_1	5.00	0	---	(1)
$PdCl^+ + Cl^- \leftrightarrow PdCl_2^0$	β_2	8.42	0	---	(1)
$PdCl_2^0 + Cl^- \leftrightarrow PdCl_3^-$	β_3	10.93	0	---	(1)
$PdCl_3^- + Cl^- \leftrightarrow PdCl_4^{2-}$	β_4	13.05[d]	0	---	(1)

$Pd^{2+} + 3Cl^{-} + H_2O \leftarrow\rightarrow PdCl_3OH^{2-} + H^{+}$	β_{31}*[b]	20.21	0.1	KCl	(2)
$Pd^{2+} + NH_3(aq) \leftarrow\rightarrow Pd(NH_3)^{2+}$	β_1	9.6	0	---	(3)
$Pd(NH_3)^{2+} + NH_3(aq) \leftarrow\rightarrow Pd(NH_3)_2^{2+}$	β_2	18.5	0	---	(3)
$Pd(NH_3)_2^{2+} + NH_3(aq) \leftarrow\rightarrow Pd(NH_3)_3^{2+}$	β_3	26.0	0	---	(3)
$Pd(NH_3)_3^{2+} + NH_3(aq) \leftarrow\rightarrow Pd(NH_3)_4^{2+}$	β_4	32.8	0	---	(3)
$PdCl_4^{2-} + NH_3 \leftarrow\rightarrow PdCl_3(NH_3)^{-} + Cl^{-}$	K_1	7.3	1	NH_4NO_3, NH_4Cl	(4)
$PdCl_3(NH_3)^{-} + NH_3 \leftarrow\rightarrow PdCl_2(NH_3)_2^{0} + Cl^{-}$	K_2	5.7	1	NH_4NO_3, NH_4Cl	(4)
$PdCl_2(NH_3)_2^{-} + NH_3 \leftarrow\rightarrow PdCl(NH_3)_3^{+} + Cl^{-}$	K_3	4.8	1	NH_4NO_3, NH_4Cl	(4)
$PdCl(NH_3)_3^{+} + NH_3 \leftarrow\rightarrow Pd(NH_3)_4^{2+} + Cl^{-}$	K_4	4.2	1	NH_4NO_3, NH_4Cl	(4)
$Pd(OH)_2(\mathit{am}) + 2H^{+} \leftarrow\rightarrow Pd^{2+} + 2H_2O(\mathit{l})$	K_{sp}*[c]	-30.81	0.1	KCl, $NaClO_4$	(2)

(a) β_i is the cumulative stability constant, where i refers to the number of complexed ligands. Constants denoted with an asterisk are conditional, namely, they are only valid for the given ionic strength.
(b) β_{31}* [ref (7)] refers to the conditional cumulative stability constant for $PdCl_3OH^{2-}$
(c) K_{sp} refers to the conditional solubility product at I = 0.1. For standard conditions (ref 4), $K_{sp}° = -3.580$.
(d) Reference (5) provides a value of 11.7; the reported value, however, is from a far more current source.
(e) At 25°C.
(f) Equilibrium constant values at I = 0 from extrapolations.

Table S15. Thermodynamic data for platinum (complexation, ligand exchange, dissolution)

Chemical reaction	Equilibrium constant	Log EC	Ref
$Pt^{2+} + Cl^{-} \leftarrow\rightarrow PtCl^{+}$	β_1	4.97	(8)
$PtCl^{+} + Cl^{-} \leftarrow\rightarrow PtCl_2^{0}$	β_2	8.97	(8)
$PtCl_2^{0} + Cl^{-} \leftarrow\rightarrow PtCl_3^{-1}$	β_3	11.89	(8)
$Pt^{2+} + 4Cl^{-} \leftarrow\rightarrow PtCl_4^{2-}$	β_3	13.99	(8)
$Pt^{2+} + 4NH_3(aq) \leftarrow\rightarrow Pt(NH_3)_4^{2+}$	β_4	35.5	(5)

Table S16. Kinetic data for palladium (complexation, ligand exchange) at 25° C and 1 M ionic strength

Chemical reaction	Rate constant (forward)	Rate constant (reverse)	Ref
$Pd^{2+} + Cl^{-} \leftarrow\rightarrow PdCl^{+}$	$k_1 = 1.8 \times 10^4$ s^{-1} M^{-1}	$k_{-1} = 0.83$ s^{-1}	(6, 7)
$PdCl^{+} + Cl^{-} \leftarrow\rightarrow PdCl_2^{0}$	$k_2(cis) = 510$ M^{-1} s^{-1} $k_2(trans) = 3.5 \times 10^4$ M^{-1} s^{-1}	$k_{-2}(cis) = 0.37$ s^{-1} $k_{-2}(trans) = 5.6$ s^{-1}	(7)
$PdCl_2^{0} + Cl^{-} \leftarrow\rightarrow PdCl_3^{-}$	$k_3(cis) = 5400$ M^{-1} s^{-1}	$k_{-3}(cis) = 0.027$ s^{-1}	(7)

	$k_3(trans) = 22\ M^{-1}\ s^{-1}$		
$PdCl_3^- + Cl^- \leftrightarrow PdCl_4^{2-}$	$k_4 = 180\ s^{-1}\ M^{-1}$	$k_{-4} = 8.9\ s^{-1}$	(7)
$Pd^{2+} + NH_3(aq) \leftrightarrow Pd(NH_3)^{2+}$	$k_1 = 8 \times 10^4\ M^{-1}s^{-1}$	$k_{-1} \sim 2 \times 10^{-5}\ s^{-1}$	(6)
$Pd(NH_3)^{2+} + NH_3(aq) \leftrightarrow Pd(NH_3)_2^{2+}$	$k_2 = 1.46 \times 10^4\ M^{-1}s^{-1}$	$k_{-2} = 4.0 \times 10^{-4}\ s^{-1}$	(6)
$Pd(NH_3)_2^{2+} + NH_3(aq) \leftrightarrow Pd(NH_3)_3^{2+}$	$k_3 = 1.46 \times 10^4\ M^{-1}s^{-1}$	$k_{-3} = 4.0 \times 10^{-4}\ s^{-1}$	(3,6)
$Pd(NH_3)_3^{2+} + NH_3(aq) \leftrightarrow Pd(NH_3)_4^{2+}$	$k_4 = 1.8 \times 10^4\ M^{-1}s^{-1}$	$k_{-4} = 7.8 \times 10^{-4}\ s^{-1}$	(3,6)
$PdCl_4^{2-} + NH_3 \leftrightarrow PdCl_3(NH_3)^- + Cl^-$	$k_{f1} = 30\ s^{-1}$ $k_{f2} = 33\ M^{-1}s^{-1}$	$k_{r1} = 2.1 \times 10^{-6}\ s^{-1}$ $k_{r2} = 2.3 \times 10^{-6}\ M^{-1}s^{-1}$	(6)
$PdCl_3(NH_3)^- + NH_3 \leftrightarrow PdCl_2(NH_3)_2^0 + Cl^-$	Trans $k_{f1} = 1.0\ s^{-1}$ $k_{f2} = 1.8\ M^{-1}s^{-1}$ Cis $k_{r1} = 120\ s^{-1}$ $k_{f2} = 370\ M^{-1}s^{-1}$	Trans $k_{r1} = 3.7 \times 10^{-6}\ s^{-1}$ $k_{r2} = 1.8\ M^{-1}s^{-1}$ Cis $k_{r1} = 120\ s^{-1}$ $k_{r2} = 370\ M^{-1}s^{-1}$	(6)
$PdCl_2(NH_3)_2^- + NH_3 \leftrightarrow PdCl(NH_3)_3^+ + Cl^-$	Trans $k_{f1} = 112\ s^{-1}$ $k_{f2} = 3750\ M^{-1}s^{-1}$ Cis $k_{f1} = 15\ s^{-1}$ $k_{f2} = M^{-1}15\ s^{-1}$	Trans $k_{r1} = 0.0009\ s^{-1}$ $k_{r2} = 0.030\ s^{-1}$ Cis $k_{r1} = 0.0001\ s^{-1}$ $k_{r2} = 0.0001\ s^{-1}$	(6)
$PdCl(NH_3)_3^+ + NH_3 \leftrightarrow Pd(NH_3)_4^{2+} + Cl^-$	$k_{f1} = 11\ s^{-1}$ $k_{f2} = 70\ s^{-1}$	$k_{r1} = 0.0011\ s^{-1}$ $k_{r2} = 0.0071\ s^{-1}$	(6)

Table S17. Kinetic data for platinum (complexation, ligand exchange) at 25° C and 1 M ionic strength

Chemical reaction	Rate constant (forward)	Rate constant (reverse)	Ionic strength	Ref
$Pt^{2+} + Cl^- \leftrightarrow PtCl^+$	$k_1 = 2.66\ (\pm\ 0.04) \times 10^{-2}\ s^{-1}\ M^{-1}$	$k_{-1} = 2.7\ (\pm\ 0.8) \times 10^{-7}\ s^{-1}$	1, 25°C	(8)
$PtCl^+ + Cl^- \leftrightarrow PtCl_2^0$	$k_2(trans) = 0.46\ (\pm\ 0.03)\ M^{-1}\ s^{-1}$	$k_{-2}(trans) = 1.0\ (\pm\ 0.3) \times 10^{-4}\ s^{-1}$	1, 25°C	(8)
$PtCl_2^0 + Cl^- \leftrightarrow PtCl_3^-$	$k_3(trans) = 5.83\ (\pm\ 0.03) \times 10^{-5}\ M^{-1}\ s^{-1}$	$k_{-3}(trans) = 3.2\ (\pm\ 1.0) \times 10^{-8}\ s^{-1}$	1, 25°C	(8)

References for Tables S13 – S15

(1) Kitamura, Akira, Doi, Reisuke, & Yoshida, Yasushi (2014). Update of JAEA-TDB Update of thermodynamic data for palladium and tin, refinement of thermodynamic data for protactinium, and preparation of PHREEQC database for use of the Brønsted-Guggenheim-Scatchard model (JAEA-Data/Code--2014-009). Japan.

(2) Julie Van Middlesworth and Scott Wood "The Stability of palladium (II) hydroxide and hydroxy-chloride complexes: An experimental solubility study at 25-85 deg C and 1 bar" Geochimica et Cosmochimica Acta 63, 11/12 p. 1751-1765 1999

(3) Rasmussen, Lene; Jørgensen, Chr. Klixbüll Palladium(II) Complexes. I. Spectra and Formation Constants of Ammonia and Ethylenediamine Complexes. 2313-2323.

(4) The Kinetics of the Successive Ammonation Reactions of Tetrachloropalladate(I1) Ion' BY RICHARD A. REINHARDT AnD WILLIAM W. MONK

(5) Smith, R.M. and Martell, A.E. Critical stability constants volume 4: Inorganic Complexes. 1976, Springer US, New York.

(6) Equilibrium and Kinetics of some Simple Complexes of Palladium (II). NPS-61RI76071 1976-07-15

(7) Elding, L.I. "Palladium(II) halide complexes. II. Acid hydrolysis and halide anations of palladium(II) chloro and bromo aqua complexes" Inorganica Chimica Acta 6:4 1972

(8) Elding, L.I. "Stabilities of Platinum(II) Chloro and Bromo Complexes and Kinetics for Anation of the Tetraaquaplatinum(I1) Ion by Halides and Thiocyanate" Inorganica Chimica Acta 28 1978 255-262.