PRECIOUS METALS AND RHENIUM CONSORTIUM
PGM Project
Substance Sameness Meeting

Chairman: *D. Boyd (Johnson Matthey, United Kingdom)*
Secretariat: *K. Rothenbacher & C. Braibant (EPMF, Belgium)*

11 December 2012, 17.00 CET onwards
Metals Conference Centre – Gold Room
Rue du Duc 100 – 1150 Brussels (BELGIUM)

List of participants

1.	**Katrien Arijs**	ARCHE	*Belgium*
2.	**Dave Boyd**	Johnson Matthey	*United Kingdom*
3.	**Heike Kinz**	Umicore	*Germany*
4.	**Mark Raffray**	Johnson Matthey	*United Kingdom (By conf. call)*
5.	**Klaus Rothenbacher**	EPMF	*Belgium*
6.	**Rüdiger Thiele**	Heraeus	*Germany*
7.	**Klaus Zimmermann**	Umicore	*Germany*

DRAFT MINUTES

1 Welcome & Introduction *(D. Boyd)*

1.1. Confidentiality and Competition Law

1.2. Special reminder on modus operandi of this meeting (PMC)
Meeting participants were reminded that strict confidentiality has to be adhered to. PMC will distribute anonymised spectra for the purpose of the meeting; all written material used in the meeting will have to be returned to PMC at the end of the meeting and cannot leave the room. PMC will safely destroy the documents.

2 Materials and Methods

2.1. Scope of the meeting; general outline of discussions; methods

It was agreed, in line with previous sameness discussions, to base the sameness discussion on the following information:

- Raman spectra for solutions
- IR spectra for solids
- In order to establish sameness between solutions and solids, also Raman spectra for solids are required
- Other potentially supporting information, such as capillary electrophoresis or X-ray diffraction, was also requested

2.2. Materials

In preparation of the meeting, registrants were asked to provide typical spectra as outlined above. PMC then anonymised the received spectra and assigned a company code.

Not all registrants did provide spectra. PMC send several reminders and even followed up with phone calls. The data discussed at this meeting represented the information received by PMC by 10 December 2012. Spectra were received from 3 companies (companies A, B and E). The following spectra were provided:

Company Code	E	B	A
Pd - Palladium Dinitrate - solid	IR & Raman		IR & Raman
Pd - Palladium Dinitrate - solution	Raman	Raman	Raman (solution 1-3)
Pt - Platinum Dinitrate - solid	IR & Raman		
Pt - Platinum Dinitrate - solution	Raman	Raman	Raman (solution 1-2)
Rh - Rhodium Trinitrate - solid	IR & Raman		IR (no Raman)
Rh - Rhodium Trinitrate - solution	Raman	Raman	Raman
Company Code	E	B	A

No additional supporting data was provided.

Further, substance ID cards were prepared by PMC, based on the feedback received. For solutions this included the excess acid content and the concentration range of the substance in solution.

2.3. Solids vs. solutions

In order to better assess the relative importance of solutions vs. solid forms, it was suggested to collect information on the respective tonnages marketed.

Action: PMC to request information from registrants on the respective tonnages of

solids and solutions marketed of Palladium-, Platinum- and Rhodium nitrate.

2.4. References
Two publications were used as basis for the discussions:

- Structure of Rhodium (III) Nitrate Aqueous Solutions. An Investigation by X-ray Diffraction and Raman Spectroscopy; R Caminiti, D Atzei, P Cucca, A Anedda and G Bongiovanni, J Phys Chem 1986, 90, 238

  This paper provided, as the title suggests, reference spectra for aqueous Rhodium nitrate solutions. Characteristic Raman wave numbers were
  - ca. 370 and 530 for oct. Rhodium
  - ca. 727, 1052 and 1423 for free nitrates
  - ca. 781, 1300 and 1525 for bound nitrates

- Structure and chemical properties of Pt nitrate and application in three-way automotive emission catalysts; Danan Dou et al; Applied Catalysis B Environmental 30 (2001) 11-24 http://dx.doi.org/10.1016/S0926-3373(00)00223-X

  This paper confirms the presence of the Pt (IV) oxo/hydroxyl bridged polymers in an analogous way to the Rh-nitrate solutions identified by Caminiti et al. For the sake of the discussions it was assumed that the M (e.g., Rh or Pt) – 'nitrato' peaks will be in 'similar' positions for similar co-ordinated nitrato/aquo species for both metals, allowing to assign the Pt peaks on the same basis as the Rh species assigned by Caminiti et al. Similar considerations apply for the Palladium nitrate.

Action: PMC to distribute above references to participants.

3 Platinum nitrate

3.1. Platinum nitrate solution
Raman spectra were provided by companies A, B and E. Company A provided spectra of 2 different solutions. The assessment was based on the key peaks indicated by the Caminiti et al paper, which were assumed to exhibit a similar pattern as the Rh-spectra but with a possible shift in wave numbers.

Good matches were seen for 4 out of 6 key peaks of the Raman spectra of companies A, B and E. Some variability in the spectra was observed, e.g., the spectra by company E and the spectra of company A (solution 2) were similar.
It was concluded that the solutions contain the same species.

It was further concluded that the species present in the solutions was indeed platinum nitrate in all cases.

3.2. Solid Platinum nitrate
IR and Raman spectra were only provided by company E, so no sameness discussion could take place.

3.3. Sameness of solids and solutions

The key peak for free nitrate (at ca 1050) was absent in the solid, indicating that the substance is possibly not a nitrate. Therefore, no sameness between the 'platinum nitrate' solid and the platinum nitrate solution could be confirmed.
Action: PMC to ask company E for elemental analysis data of solid Platinum nitrate to evaluate the ratio Pt/N

4 Rhodium trinitrate

4.1. Rhodium trinitrate solution
Raman spectra were provided by companies A, B and E.
Some variability in the spectra was observed, and the resolution of the spectrum provided by company E was not ideal.
Action: PMC to ask Company E for a better spectrum of Rh-nitrate solution

Based on the key peaks indicated by the Caminiti et al paper, it was concluded that the species present was indeed rhodium nitrate for Company A and B. Clarification is needed for Company E, as the key peak for oct. Rhodium (at ca. 530) was absent.

It was further concluded that the spectra by companies A and B were from the same species.

4.2. Solid Rhodium trinitrate
4.2.1. Hydrated vs. anhydrous form
This point will be revisited once the below sameness discussion is concluded.
(Some companies reported the substance name as Rhodium (3+) nitrate hydrate (x $1H_20$ and $x2H_2O$). The actual material might be a mixture of the anhydrous, hydrate and dihydrate forms, with equilibrium depending on the process used. The PMC inventory name is 'Rhodium trinitrate')

4.2.2. Sameness
IR and Raman spectra were provided by company E and IR spectra by company A (no Raman spectra could be provided by company A due to fluorescence effects seen in the spectrum).
The spectra could not demonstrate that the (solid) compounds contained the same species.
Action: Dave Boyd to recommend way to overcome the fluorescence issue after discussion with Raman expert
Action: PMC to ask companies A and E for elemental analysis data of solid Rh-nitrate to evaluate the ratio Rh/N
Action: PMC to ask company E if they can provide better spectra of their solid Rh-nitrate
Action: PMC to ask company A if they can provide better IR and possibly also a Raman spectrum of their solid Rh-nitrate

4.3. Sameness of solids and solutions
The available spectra could not demonstrate that the solids contain the same species as the solutions.

5 Palladium nitrate

5.1. Palladium nitrate solution

Raman spectra were provided by companies A, B and E. Company A provided spectra of 3 different solutions. The assessment was based on the key peaks indicated by the Caminiti et al paper, which were assumed to exhibit a similar pattern but with a possible shift in wave numbers.

Good matches were seen for the Raman spectra. Solution 3 of Company A is missing the peak at 840, but overall it was concluded that the solutions contain the same species.

It was further concluded that the species present was indeed palladium nitrate in all cases.

5.2. Solid Palladium nitrate

IR and Raman spectra were provided by company A and E. Although there was some variability and clarification on the wide peak in the Raman spectrum of Company A is needed, overall the spectra demonstrated that the compounds contained the same species.

Action: PMC to ask company A for better spectra of solid Palladium nitrate (explanation for hump, could be artifact)

5.3. Sameness of solids and solutions

The available spectra did demonstrate that the solids contain the same species as the solutions for Company E. Clarification is needed for Company A.

6 Conclusions/Next Steps

Some spectra need to be confirmed (see above actions) and a follow-up meeting might be necessary to definitively confirm sameness. For the time being PMC will work based on the tentative conclusions above.

7 AOB, next meetings/calls and closing remarks

PdCl2 was reported both as a solid and as solution in HCl (the substance is insoluble in water). The expert group recommended to consider $PdCl_2$ in aq. HCl as H_2PdCl_4.