



Minutes

1. Welcome & Introduction (D. Boyd)

1.1. Confidentiality and Competition Law

1.2. Tour de table and apologies

1.3. Approval of the agenda

No remarks; the agenda was approved.

1.4. Approval of the minutes of the last meeting (11 December 2012)

No remarks; the minutes were approved.

1.5. Special reminder on modus operandi of this meeting (PMC)

Meeting participants were reminded that strict confidentiality has to be adhered to. PMC distributed 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.

It is noted that the modus operandi might have to be revisited in future for practicality reasons and we might have to consider virtual meetings.

1.6. Materials and 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;
- Raman spectra for solids (to establish sameness of solutions and solids);
- Other potentially supporting information, such as elemental analysis.

Following the last PGM sameness meeting, some registrants provided new/updated spectra, which were anonymised by the PMC and assigned a company code. Not all registrants provided spectra despite several reminders. The data discussed at this meeting represented the information received by PMC by 20 August 2013. Spectra were received from 3 companies (companies A, B and E). The following spectra were provided and used for sameness discussions (spectra received after the previous PGM sameness meeting are indicated in red):

Company code	E	B	A
Pd dinitrate - solid	IR & Raman	N/A	IR & Raman
Pd dinitrate - solution	Raman	Raman	Raman (solution 1-3)
Pt dinitrate - solid	IR & Raman	N/A	N/A
Pt dinitrate - solution	Raman	Raman	Raman (solution 1-2)
Rh trinitrate - solid	IR & Raman	N/A	IR & Raman
Rh trinitrate - solution	Raman	Raman	Raman
Company code	E	B	A

2. ID cards of PGM substances

Substance ID cards were prepared by PMC, based on the feedback received from all registrants. These ID cards will be further updated following the outcome of this meeting.

3. Sameness of PGM nitrates

Most PGM nitrates are reported as 'Substance x 0, 1, 2, or 3 H₂O'. However, the chemistry of these substances is more complex and typically involves 6 different ligands, which vary depending on the ionic environment. For this reason, the substances will be registered as UVCBs. We will need to document our rationale for this, and what exactly the registered substances cover. This should be

Contact Info of the Consortium

Avenue de Broqueville, 12 - BE-1150 Brussels

Tel.: +32 2 775 63 23 Fax: +32 2 779 05 23 Mobile: +32 473 52 52 73

E-mail: braibant@epmf.be Website: www.epmf.be



based on public domain information as well as expert judgment.

Action: Dave Boyd to put together a summary paper on the chemistry / substance identification of the 3 PGM nitrates. (Done - cf. Annex 1)

Action: PMC to check guidance on UVCBs regarding the registration of hydrated / anhydrous forms.

3.1. Palladium dinitrate

- **Sameness of solutions**
 - Was already confirmed at the last sameness meeting
- **Sameness of solids**
 - Company A was asked to provide better IR and Raman spectra
 - Some differences were observed between the IR spectra of company A and E in the 1200-1300 cm^{-1} region. However, the resolution of the spectrum of Company E was not optimal, and the peak at 1377 in the IR spectrum of company A was attributed to Nujol (used for sample preparation). The Raman spectra were very similar.
 - Sameness was concluded on the basis of the Raman spectra and the fact that the IR spectra were very similar; the slight differences between the IR spectra reflect the UVCB nature of Pd dinitrate.
- **Sameness of solids and solutions:**
 - At the last meeting, sameness of Pd dinitrate solids and solutions was concluded for company E.
 - Based on the new spectra provided by company A, sameness of solids and solutions for company A is now also confirmed.
- Different CAS numbers were reported by companies for Pd dinitrate (hydrate). It is noted that in the EINECS registry, only the anhydrous form of a substance can be registered (hydrated forms are considered registered together with the anhydrous form) hence only the CAS number of the anhydrous form is linked to the EINECS number.
Action: PMC to check if there is any fundamental difference between the different CAS numbers for Pd dinitrate. If not, companies are recommended to use the CAS number from the PMC inventory (10102-05-3).

3.2. Platinum dinitrate

- **Sameness of solutions**
 - Was already confirmed at the last sameness meeting.
- **Sameness of solids**
 - Not applicable, as only one company (comp. E) provided spectra for the solid form. Company E was asked for an elemental analysis to confirm the identity of Pt dinitrate.
- **Sameness of solids and solutions:**
 - At the previous meeting, no sameness of Pt dinitrate solids and solutions was concluded. The reason was that the characteristic peak for free nitrate at ca 1050 cm^{-1} in the Raman spectrum of the solution, was missing from the Raman spectrum of the solid.
 - From the Raman spectra, for the solutions it is not clear whether the nitrate associated with the peak at 1050 cm^{-1} represents coordinated nitrate or nitric acid from the solution. Danan Dou et al. (2001)¹ concluded that the species in Pt nitrate solutions are Pt (IV) oxo/hydroxyl bridged polymers. This is consistent with the chemistry of platinum, which prefers to coordinate to 'soft' ligands, such as halogens or sulphur, rather than 'hard' ligands, such as oxo species (nitrate, sulphate, phosphate etc). The stability of the oxo/hydroxyl species detected by Danan Dou is only due to the polymer framework.

¹ 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](http://dx.doi.org/10.1016/S0926-3373(00)00223-X)



- The difference observed between the Raman spectra of the Pt nitrate solid and solution may therefore be attributed to free nitrate from the nitric acid in the solution.
- Since apart from the peak at 1050 cm⁻¹ the spectra were directly comparable, it was concluded that Pt dinitrate solids and solutions are considered to be the same.
- **Action:** Dave Boyd to check availability of IR/Raman spectra of PGM nitrates in literature. (Done - only 2 literature references were found: a Raman spectrum of Rh nitrate from Caminiti et al. (1986)² and an IR spectrum of Pd nitrate from the AIST-Japan database.)

3.3. Rhodium trinitrate

- **Sameness of solutions:**
 - Was already confirmed at the last sameness meeting for company A and B.
 - Company E provided a better Raman spectrum for its Rh trinitrate solution and after comparison with the spectra of companies A and B and the reference spectrum from Caminiti et al. (1986)³, identity and sameness with other solutions was confirmed.
 - Overall, therefore sameness for the rhodium nitrate solutions of companies A, B and E was concluded (all available spectra)
- **Sameness of solids:**
 - Company A and E were asked to provide new spectra and elemental analysis.
 - The Raman spectra show some differences between company A and E, but the Raman spectrum of company A is considered an anomaly as it had been very difficult to record a spectrum and decomposition of the material seems to have again been observed.
 - The IR spectra of the solids were considered comparable (apart from the 1377 peak, which is attributed to Nujol). Therefore, sameness of Rh nitrate solids of company A and E was concluded on the basis of the IR spectra.
- **Sameness of solids and solutions:**
 - Sameness of Rh nitrate solids and solutions of company E is concluded on the basis of the Raman spectra.
 - The Raman spectrum of solid Rh nitrate of company A cannot be used to conclude on the sameness of solids and solutions of company A due to composition of the sample. Notwithstanding this unusable Raman spectrum:
 1. sameness of Rh nitrate solutions of company A and E has been shown,
 2. sameness of Rh nitrate solids of company A and E has been shown, and
 3. sameness of Rh nitrate solids and solutions of company E has been shown.Therefore, it was concluded that read-across from company E to company A can be applied and sameness of Rh nitrate solids and solutions can therefore be concluded for company A as well.Overall, sameness between solids and solutions of Rhodium nitrate was concluded.

4. DDP isomers

- ID card composition: it was discussed whether the compositions reported by each registrant should be listed in the ID card or if it would be better if the composition of the reference sample is reported in the ID card. In that case, companies can check if the test results apply to their situation (e.g. classification). For practicality reasons, PMC's preference would be to limit the reported compositions to the reference samples. As this is relevant for many

² 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

³ 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



substances, it was suggested to discuss this at the next PGM meeting.

Note: in case of low LODs for impurities in the representative sample, some companies may need to re-analyze to confirm that their substance composition is within the defined boundaries.

Action: PMC to add ID card composition issue to the agenda of the next PGM WG meeting.

- DDP Isomers:
 - PMC has not received any measured data on the DDP isomer ratio. However, based on the production process (“trans effect”), it is assumed that mainly trans-DDP will be present.
 - If trans-isomer is present > 80%, it should be registered as a mono-constituent substance with cis-DDP as an impurity.
 - As discussed at the previous PGM WG meeting, the biological difference between cis- and trans-DDP are likely to be small, as the reactivity of both DDP isomers is much higher than for the corresponding Pt analogues (e.g., Cisplatin). Both DDP isomers are therefore likely to react quickly with biological matrices. It was suggested to provide rationale for this when we register DDP.
 - IR spectra can be used to estimate the presence of cis- and trans isomers of DDP: in the IR spectrum of trans-DDP, a single peak is seen at 496 cm⁻¹ whereas for cis-DDP a double peak is seen⁴.
 - 3 companies (company A, E and H) provided IR spectra for DDP, 1 company provided a Raman spectrum. The 3 IR spectra indicate that mainly trans-DDP is present.

Action: Company B to provide IR spectrum of DDP

5. Sameness and skin corrosion testing solids/liquids

- It was agreed at the June PGM WG meeting to revisit the test results once sameness is established.
- The results are summarized in the table below. As can be seen in the table:
 - Both solids and solutions of PGM nitrates were tested.
 - The same test results were obtained for solids/solutions of PGM nitrates in all cases. This confirms the above conclusions that solids and solutions of PGM nitrates contain the same species.

Substance	Result	Comment
2. Platinum dinitrate (EC No. 242-383-9) - company 1 - solid	1B	
3. Platinum dinitrate (EC No. 242-383-9) - company 2 - solution	1B	
4. Platinum dinitrate (EC No. 242-383-9) - company 3		Substance not supplied
5. Dihydrogen tetrachloropalladate (EC No. 241-047-9) - solution PMRC	1A	
6. Palladium sulphate (EC No. 236-957-8) - solid		Substance N/A in solid form
7. Palladium sulphate (EC No. 236-957-8) - solution PMRC	1B	
8. Palladium dinitrate (EC No. 233-265-8) - company 1 - solid	1B	
9. Palladium dinitrate (EC No. 233-265-8) - company 2 - solution	1B	
10. Palladium dinitrate (EC No. 233-265-8) - company 3		Substance not supplied
11. Dirhodium trisulphate (EC No. 234-014-5) - solid PMRC	1B	
12. Dirhodium trisulphate (EC No. 234-014-5) - solution PMRC	1B	
13. Rhodium trinitrate (EC No. 233-397-6) - company 1 - solid	1B	
14. Rhodium trinitrate (EC No. 233-397-6) - company 2 - solution	1B	
15. Rhodium trinitrate (EC No. 233-397-6) - company 3		Substance not supplied
16. Ruthenium trichloride (EC No. 233-167-5) - solid PMRC	1B	
17. Ruthenium trichloride (EC No. 233-167-5) - solution PMRC	1B	

⁴ Nakamoto, K. (2008) Applications in Coordination Chemistry, in Infrared and Raman Spectra of Inorganic and Coordination Compounds: Part B: Applications in Coordination, Organometallic, and Bioinorganic Chemistry, Sixth Edition, John Wiley & Sons, Inc., Hoboken, NJ, USA. doi: 10.1002/9780470405888.ch1



Chairman: *D. Boyd (Johnson Matthey, UK)*
Secretariat: *K. Rothenbacher (EPMF, B) & K. Arijs (ARCHE, B)*

20 August 2013, 12:30 - 16:30 CET
Metals Conference Centre - Gold Room
Rue du Duc 100 - 1150 Brussels (BELGIUM)

18. Tris(nitrato-O)nitrosylruthenium (EC No. 252-068-8) - solid PMRC	1B	
20. Tris(nitrato-O)nitrosylruthenium (EC No. 252-068-8) - aq. solution PMRC	1B	

6. AOB, conclusions, next meeting

The conclusions on the sameness of the PGM nitrates are summarized in below table:

	Sameness solutions	Sameness solids	Sameness solids and solutions
Pd - Palladium Dinitrate	+	+	+
Pt - Platinum Dinitrate	+	N/A	+
Rh - Rhodium Trinitrate	+	+	+