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Impact of gamma-irradiation on the palladiumbehaviour in the PUREX process

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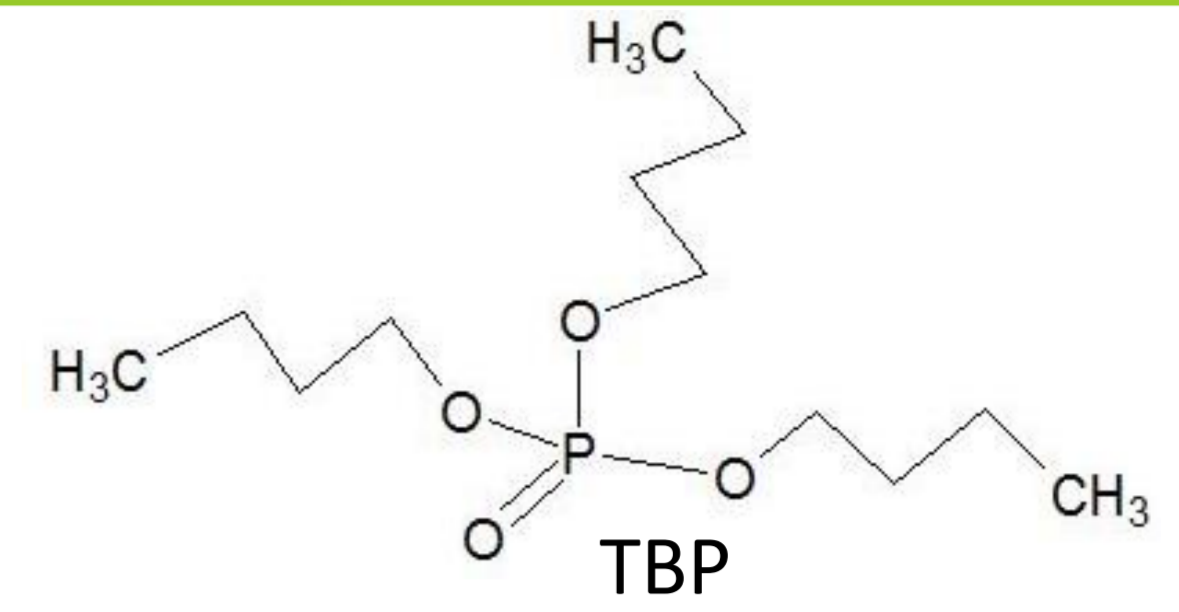
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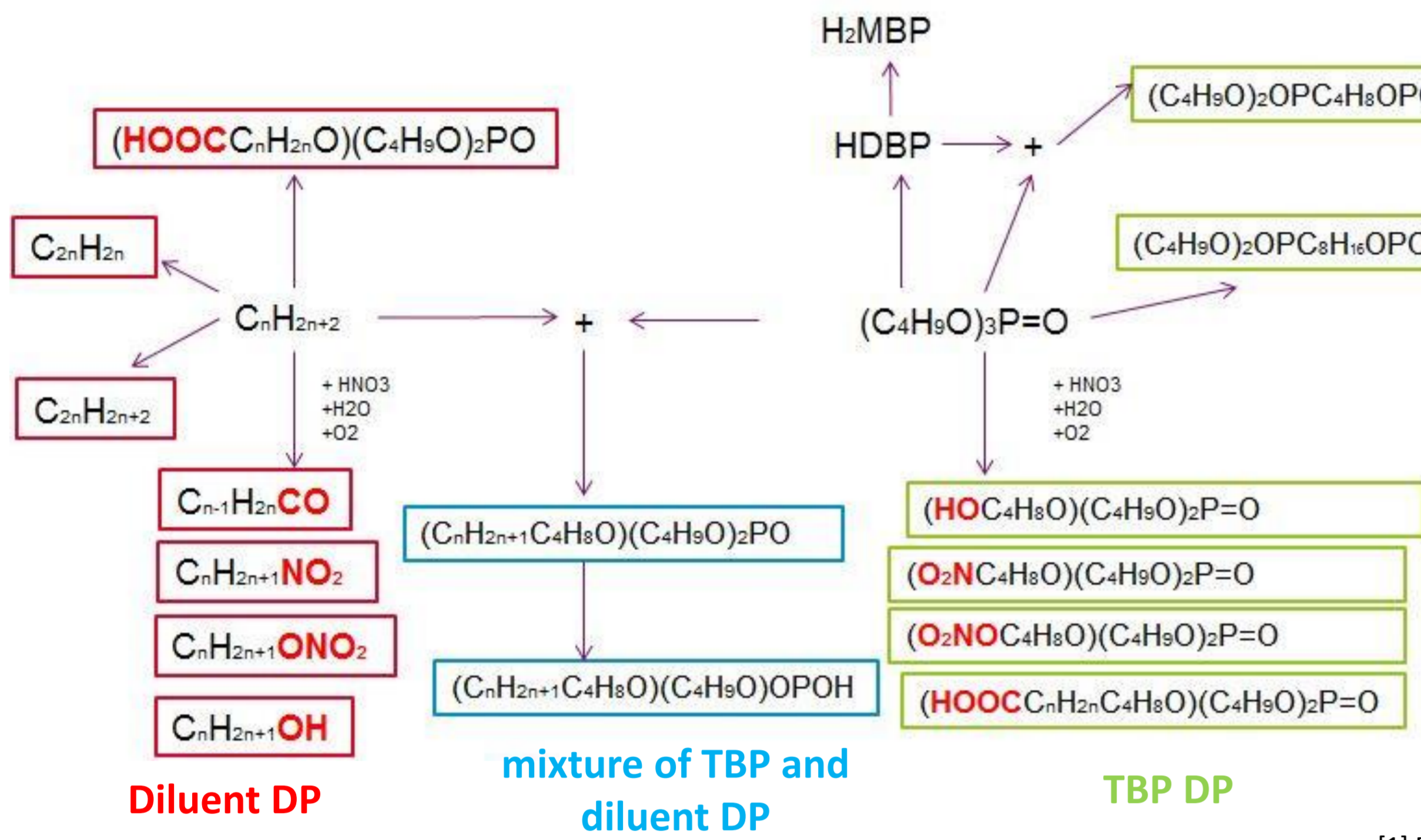
Context:

The PUREX process uses 30%_{Vol} tri-n-butylphosphate (TBP) diluted in TetraPropylen Hydrogen (TPH, an hydrocarbon diluent) to selectively extract uranium(VI) and plutonium(IV) towards fission products. During the different extraction cycles, solvent degradation products of the solvent are formed due to radiolysis. Very few studies report the impact of the radiolysis on the palladium behaviour. The aim of this work is to investigate the effect of the radiolysis on the Pd behaviour.

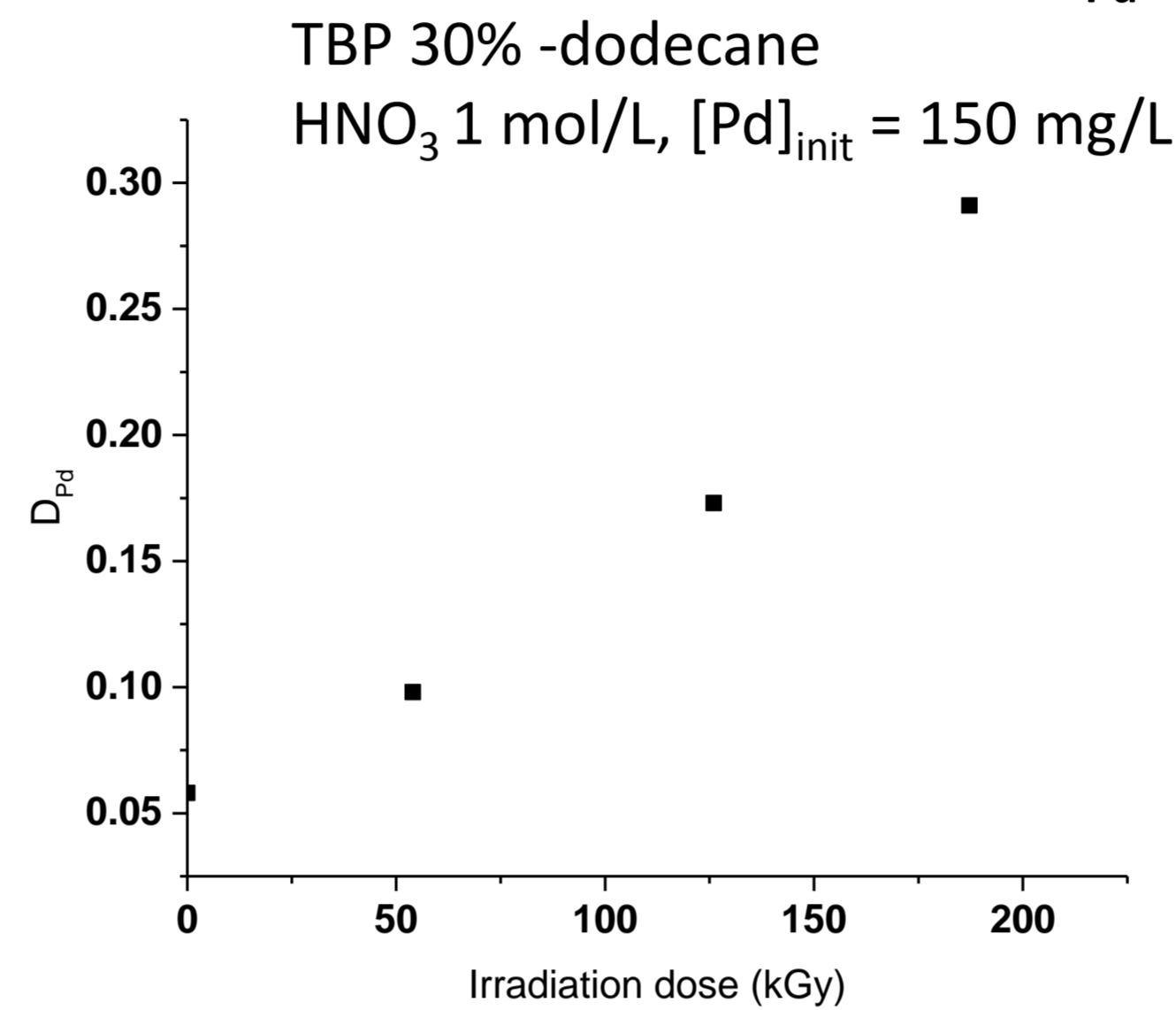


Bibliographic results on the impact of γ -irradiation of the TBP-alkane solvent:

Identification of degradation products (DP) [1]



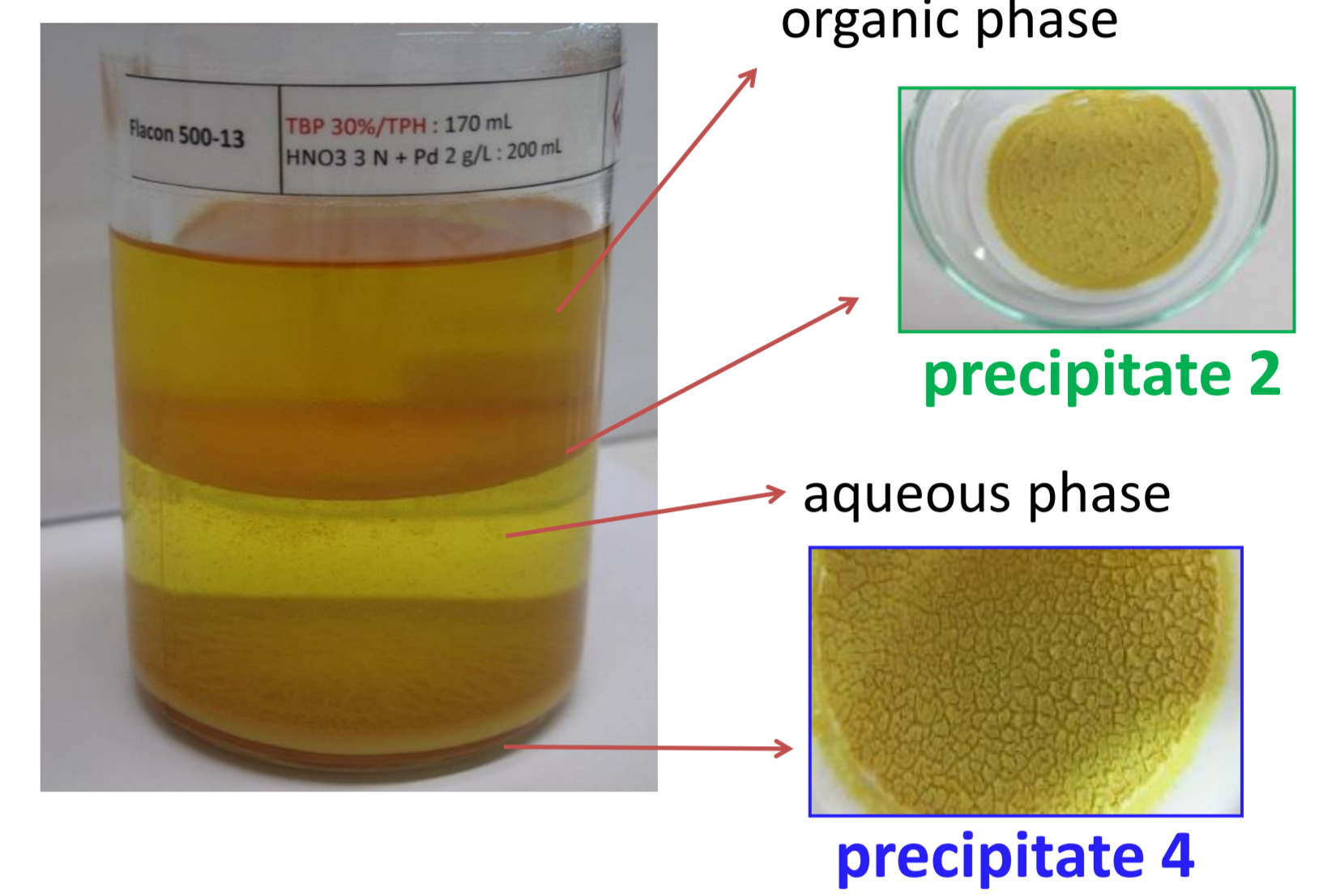
Palladium distribution ratio D_{Pd} [2]



Increase of palladium extraction in the organic phase with the irradiation dose

Experiments: γ -irradiation of the solvent in presence of palladium:

TBP 30% - TPH / HNO₃ 1 and 3 mol/L + Pd(NO₃)₂ ~ 2 - 10 g/L
Irradiated Mixture at 500 kGy



Degradation products formed in the organic phase for a TBP-alkane / nitric acid aqueous solution system

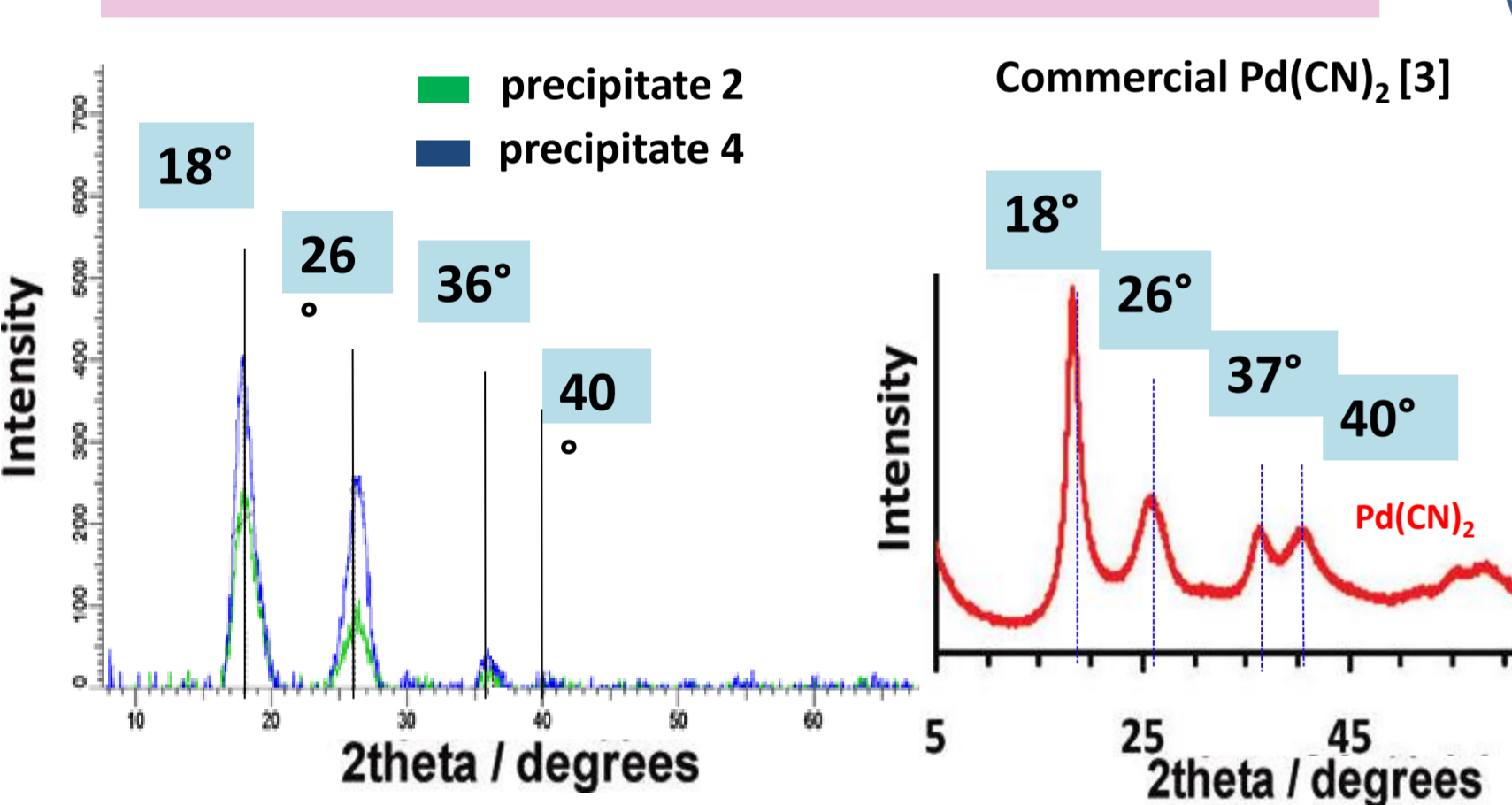
[1] D. Lesage, "Contribution à l'étude des produits de dégradation du solvant de retraitement des combustibles nucléaires par spectrométrie de masse, ses différents couplages ainsi que par l'emploi d'isotopes stables", *thesis*, 1995

[2] P.A. Zagorets, "Effect of irradiation on extraction palladium with tributyl phosphate from nitric acid solutions", *J. Radioana. Nucl. Chem.*, vol 24, n°1, p. 43-48, 1982

Characterizations of the precipitates:

Characterization of the solid

XRD analysis: powder pattern

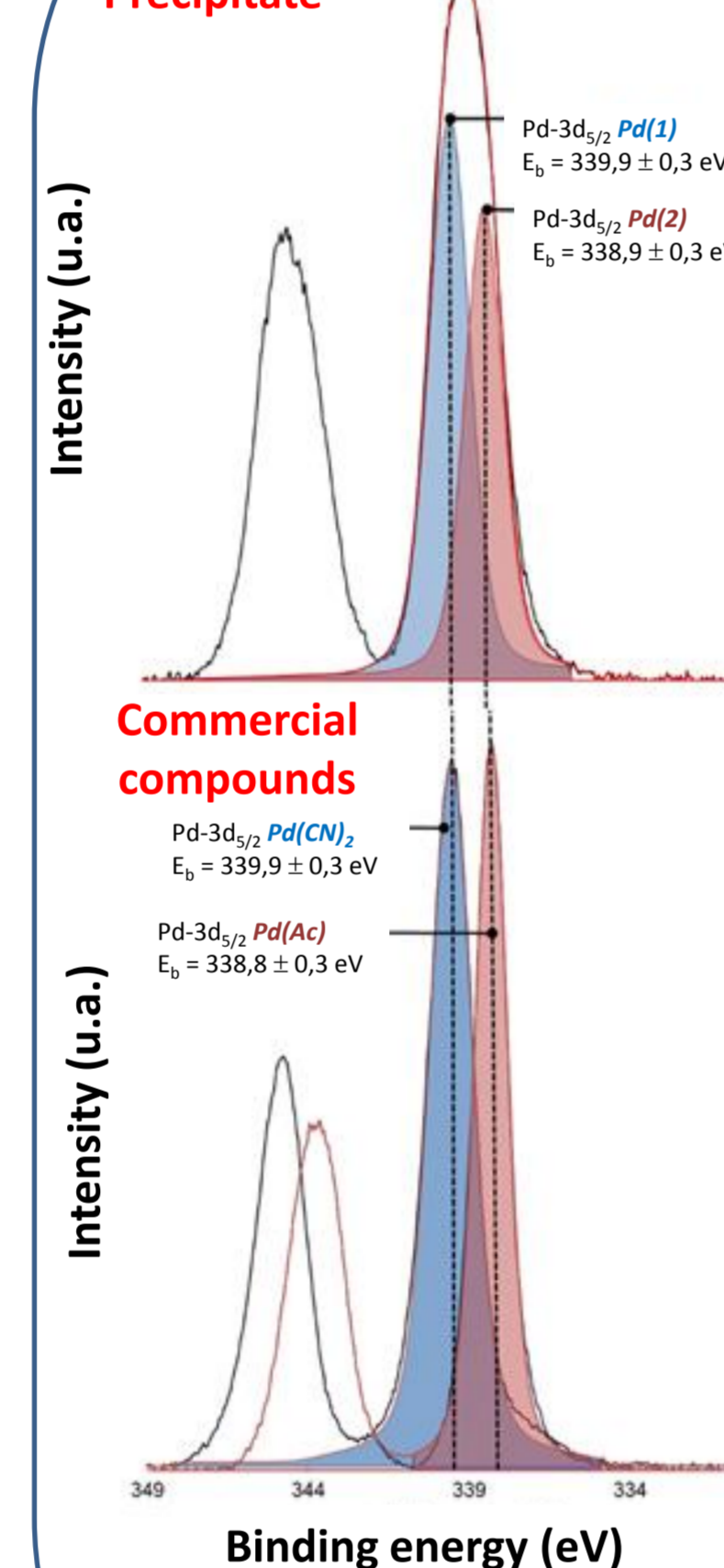


Powder pattern of the synthetic precipitates are close to that of commercial compound Pd(CN)₂

[3] Simon J. Hibble, « Structures of Pd(CN)₂ and Pt(CN)₂: Intrinsically Nanocrystalline Materials? », *Inorg. Chem.*, 2011, 50, 104-113

XPS analysis

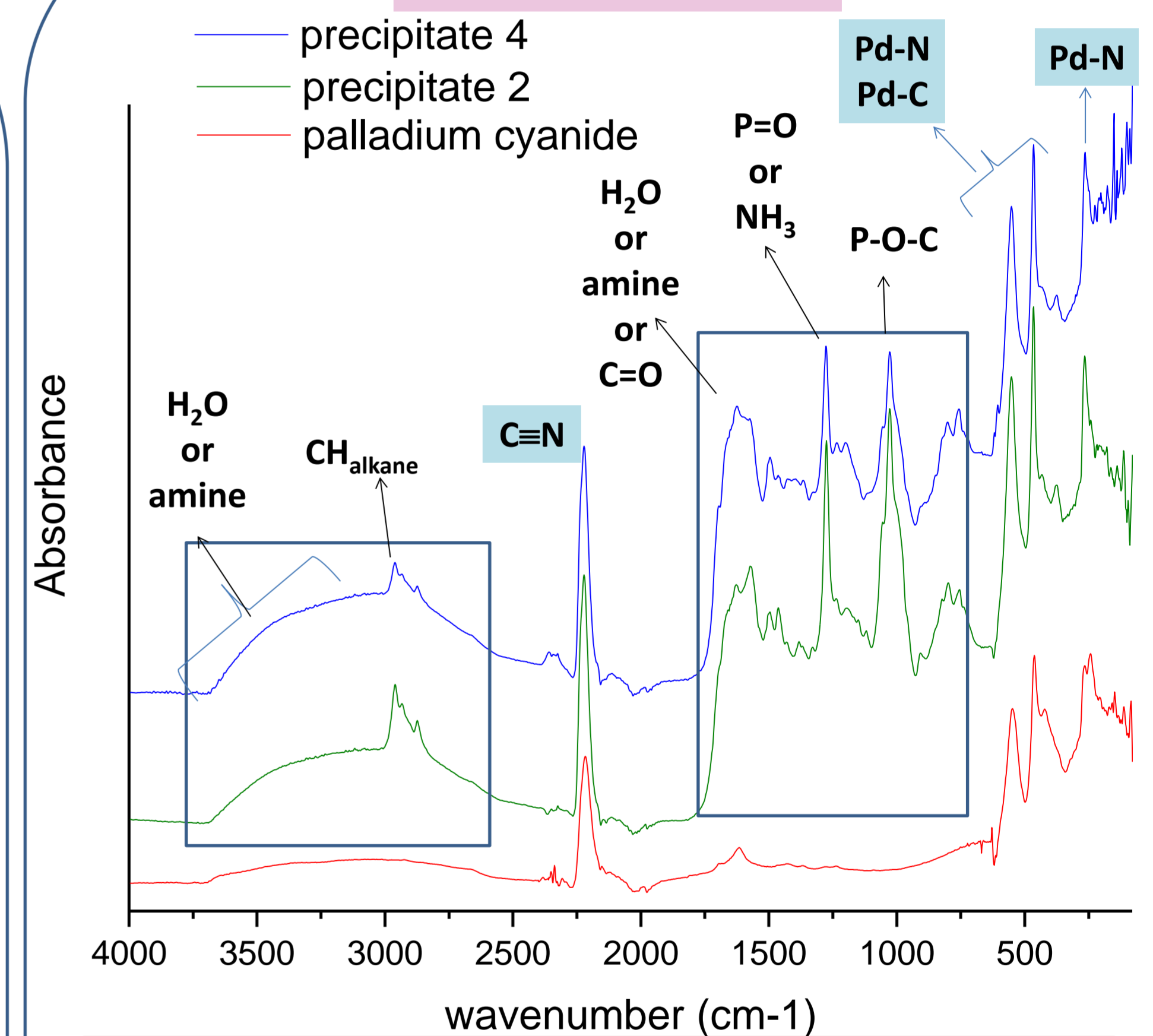
XPS Pd-3d_{5/2} Precipitate



Chemical formula	Binding energy (eV)	
	E _b (Pd) - 3d _{5/2}	E _b (N)
Precipitate 2	338,7 ± 0,3 (Pd(OCO-R))	399,8 ± 0,3 (C≡N)
	339,9 ± 0,3 (Pd(CN))	401,8 ± 0,3 (Hyp: Pd-NR ₄ ⁺)
Precipitate 4	338,7 ± 0,3 (Pd(OCO-R))	399,8 ± 0,3 (C≡N)
	339,8 ± 0,3 (Pd(CN))	401,9 ± 0,3 (Hyp: Pd-NR ₄ ⁺)
Palladium acetate	338,8 ± 0,3 (Pd(OCOCH ₃))	-
Palladium cyanide	339,8 ± 0,3 (Pd(CN) ₂)	400,7 ± 0,3 (CN)

Presence of Pd bonds: Pd-C≡N and Pd-OCO-R
Presence of N bonds: C≡N and hyp : NR₄⁺

IR-FT analysis



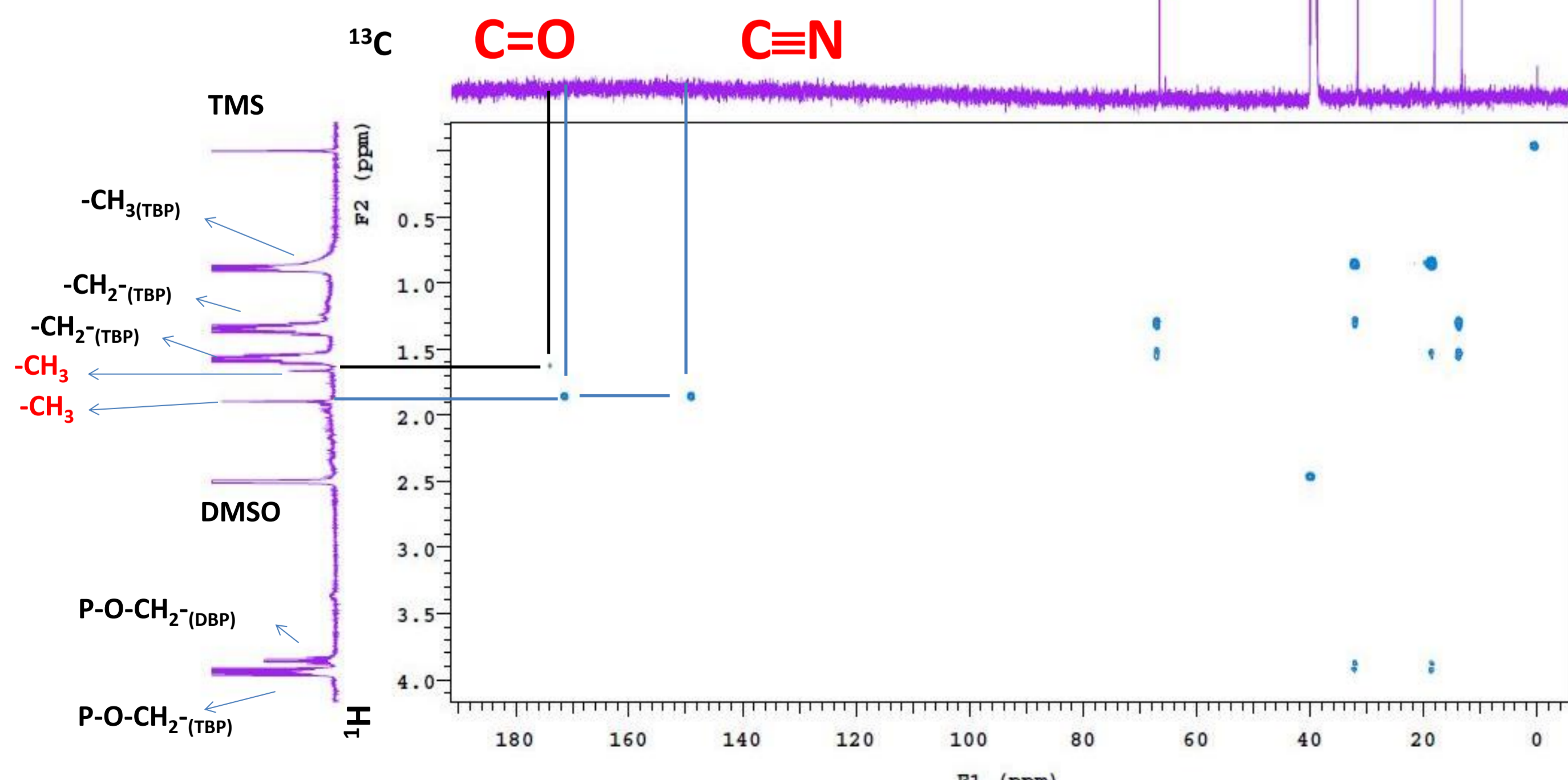
Same peaks of C≡N, Pd-C and Pd-N between Pd(CN)₂ and precipitates
Other peaks: H₂O, amine, C=O, P=O and P-O-C

Characterization of the solid after solubilisation

RMN analysis

precipitate 4 partially dissolved in deuterated DMSO - Spectra ¹³C - ¹H

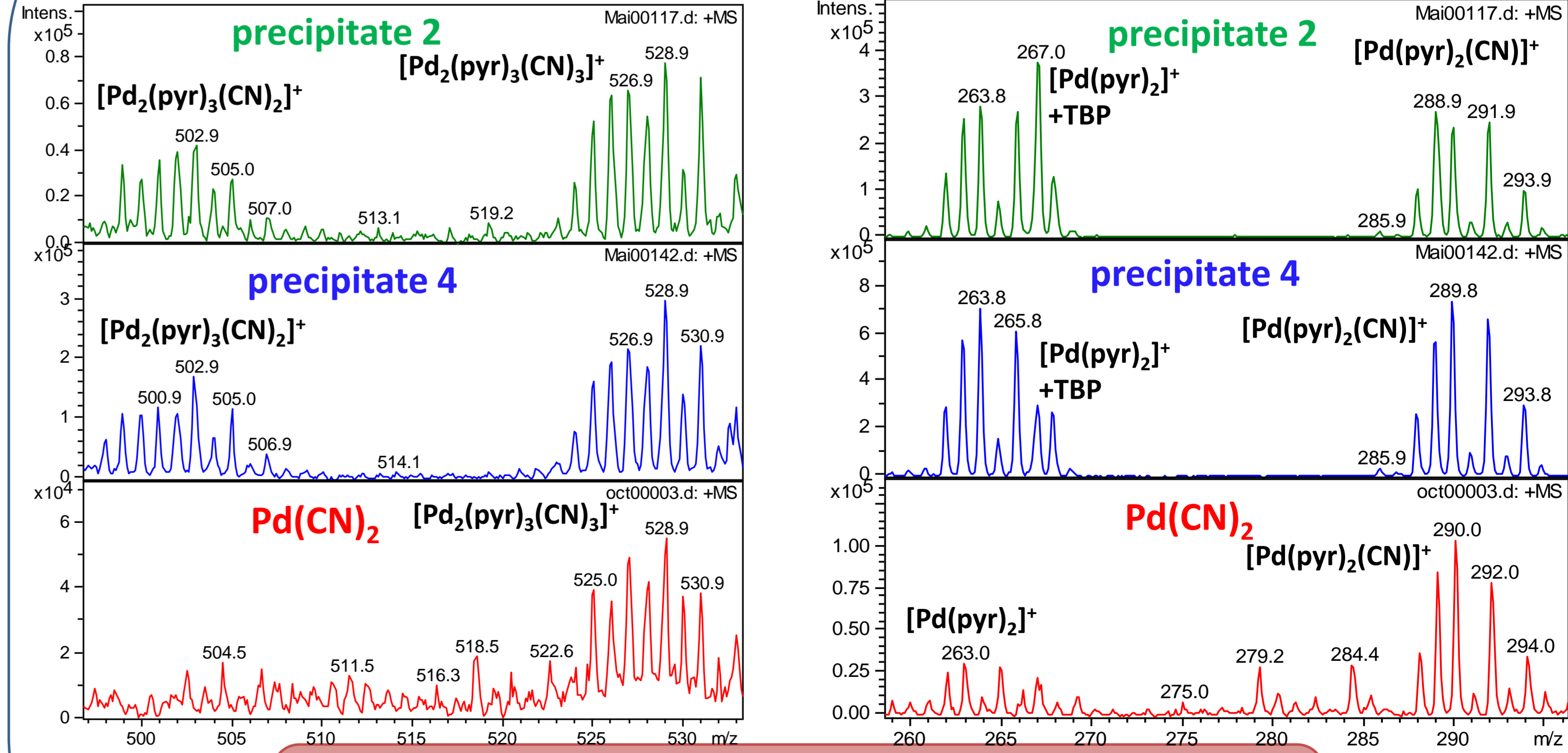
-172 ppm -150 ppm



Presence of C=O at -172 ppm
Presence of C≡N at -150 ppm

ESI-MS analysis

Compounds partially dissolved in solution in pyridine



Same ions observed for precipitate 2 and 4
Presence of dimers of Pd → Consistent with a Pd-CN network
Presence of C≡N in the precipitates (similarity with Pd(CN)₂)

Conclusions and Outlook:

- Presence of functions in the solids: cyanide (similarity with Pd(CN)₂), carboxylate and ammonium
- Isolation of different compounds present in the precipitate: selective dissolution
- Mechanism of formation of these precipitates

