Euro-GANEX SYSTEM BEHAVIOR UNDER GAMMA RADIATION

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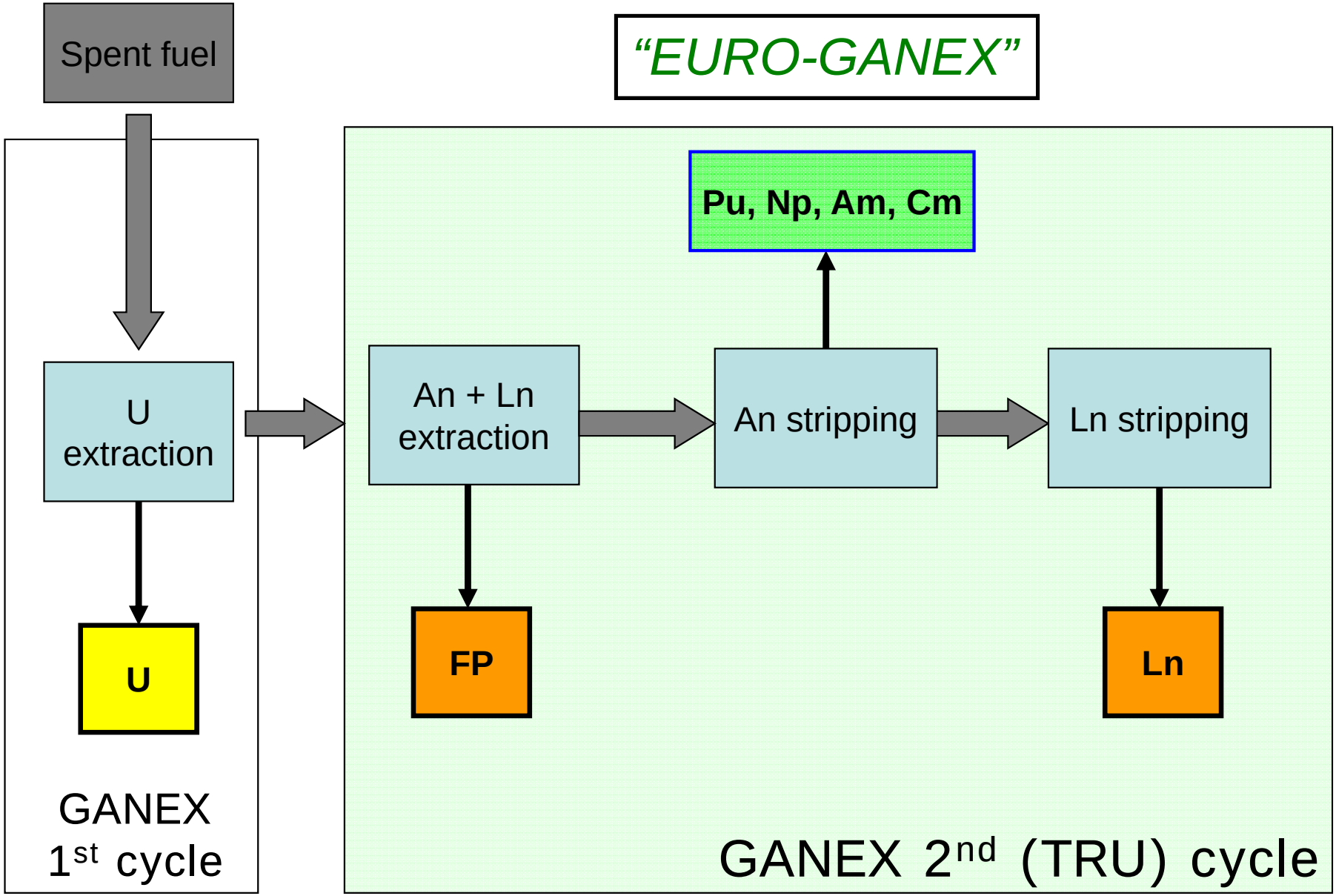
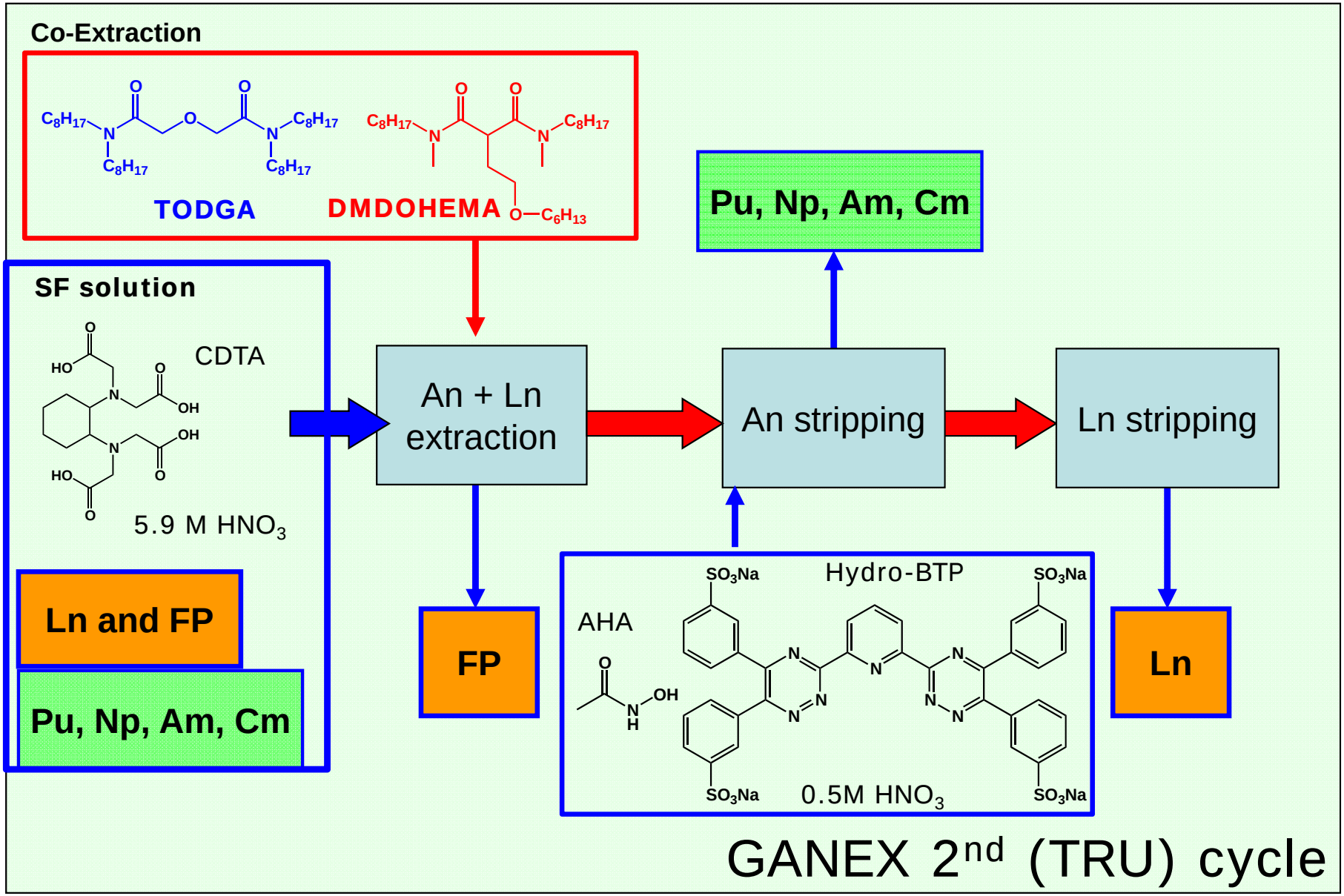
Introduction: GANEX Concept



M. Miguirditchian et al., GLOBAL, Paris, France, **2009**, pp. 1036-1040.

Introduction: Euro-GANEX flowsheet



Carrott, M. et al., *Solvent Extr. Ion Exch*. **2014,** *32(5),* 447.

Carrott, M. et al., *Hydrometallurgy* **2015**, *152, 139.*

Geist, A. et al., *Solvent Extr. Ion Exch*. **2012,** *30,* 433.

Sypula, M. et al., *Solvent Extr. Ion Exch*. **2012,** *30,* 748.

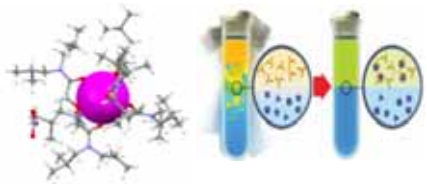
Introduction: Process development

Extraction process development

Euro-GANEX process

✓ **System selection**

Design and synthesis of ligands
Extracting and complexing properties



Industrial diluents
High affinity and selectivity
Good kinetics, viscosity, reversibility, etc
Low synthesis cost of simple molecules
Stability: recyclability

✓ **Process development and optimization**

✓ **Hot test**

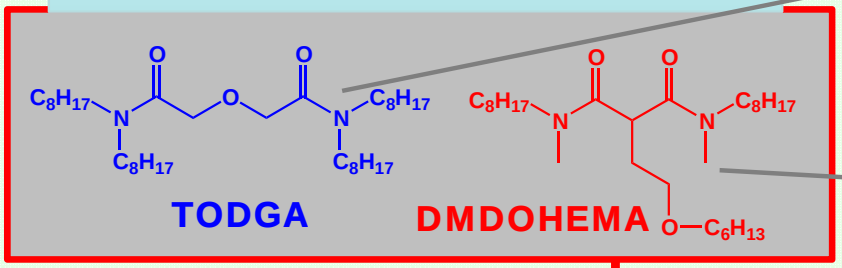
Scale-up

Industrial application

Safe long-term performance

Objetives: Euro-GANEX stability studies

Stability studies

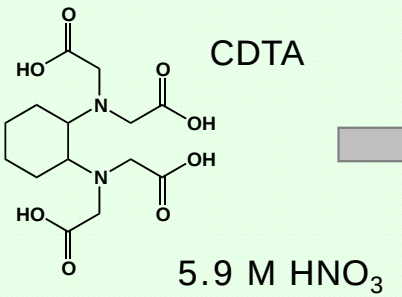


- Sugo, Y. et al. *Radiochimia Acta* **2002**, 90, 161.
- G. Modolo et al, Solv. Extr. Ion Exch., **2007**, 25, 703.
- Galán H., *et al. Procedia Chemistry*, **2012**, 195.
- Christopher, A. *et al*, Solv. Extr. Ion Exch.,**2015**, 1.

Pu

- Berthon, L *et al. Separation Science and Technology* **2001**, 365&6, 709.
- Berthon, L. *et al. Solvent Extr. Ion Exch: A series of Advances* **2010**, 19, PT Chapter 8, 429.

SF solution

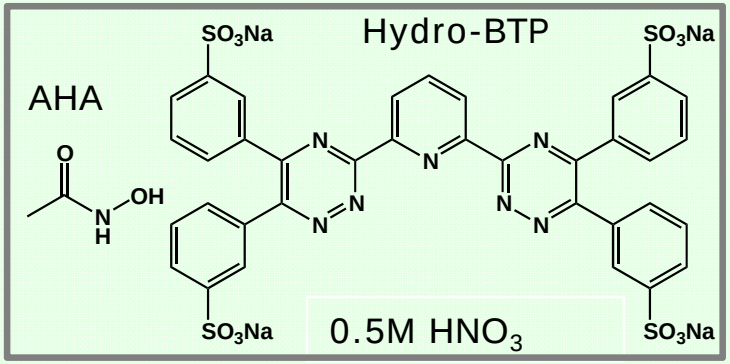


An + Ln extraction

An stripping

Ln stripping

FP



Ln

GANEX 2nd (TRU) cycle

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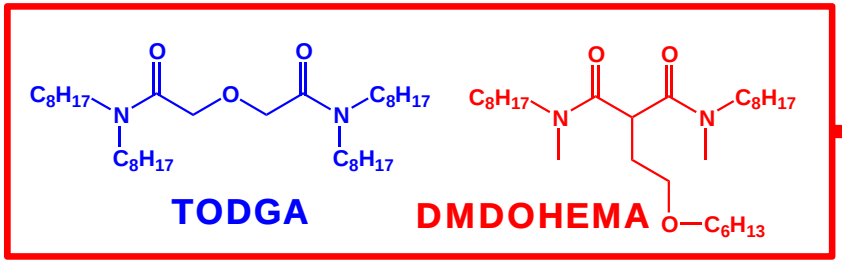
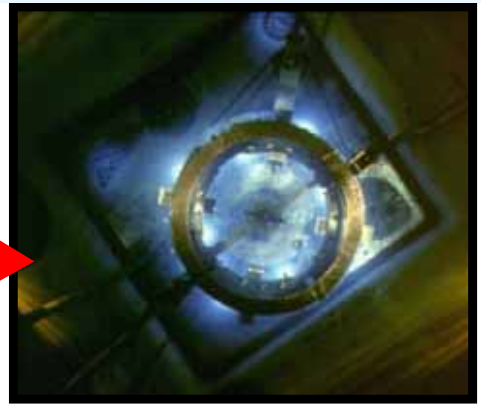
Stability studies performed after gamma radiation



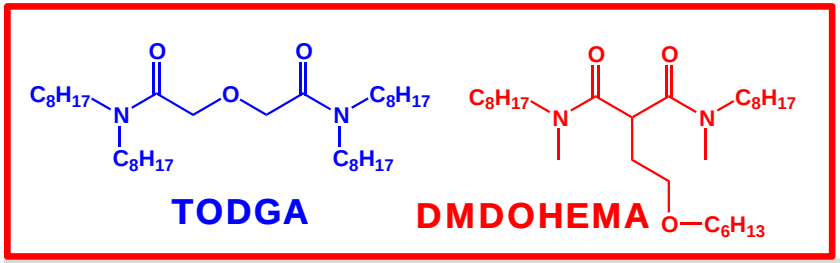
NÁYADE Irradiation Facility
External ^{60}Co Sources



Characterization of solvent after gamma radiation:

- *Behavior the degraded solvents:*
  - *Extraction and back-extraction of Ln/An/FP.*
- *Composition of the degraded solvents:*
  - *Extracting agents concentration.*
  - *Degradation compounds (DCs).*
- *The phisico-chemical changes and mass transferences.*

GAMMA irradiation experiments



- ✓ Euro-GANEX
- ✓ 0.2 M TODGA
- ✓ 0.5 M DMDOHEMA

In (100)% Kerosene (OK)

In (95:5)% OK/octanol

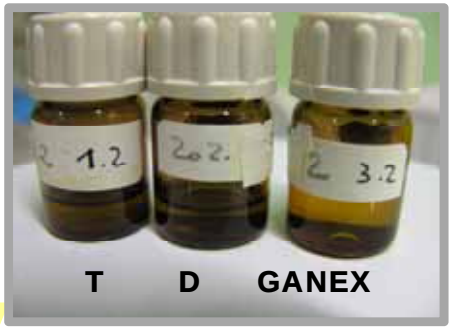
Parallel studies with TODGA and DMDOHEMA separately

- Fresh samples.
- Hydrolytic/chemical degradation.
  Aging control samples kept in the lab at 20ºC.
- Radiolytic degradation.
  Gamma irradiation at (^{60}Co, Náyade).
  - 100-1000 kGy, at 1.5-1.8 kGy/h.

Fresh GANEX pre-equilibrated with 5 M HNO_3

^{60}Co

1000 kGy



Aging, 0 kGy

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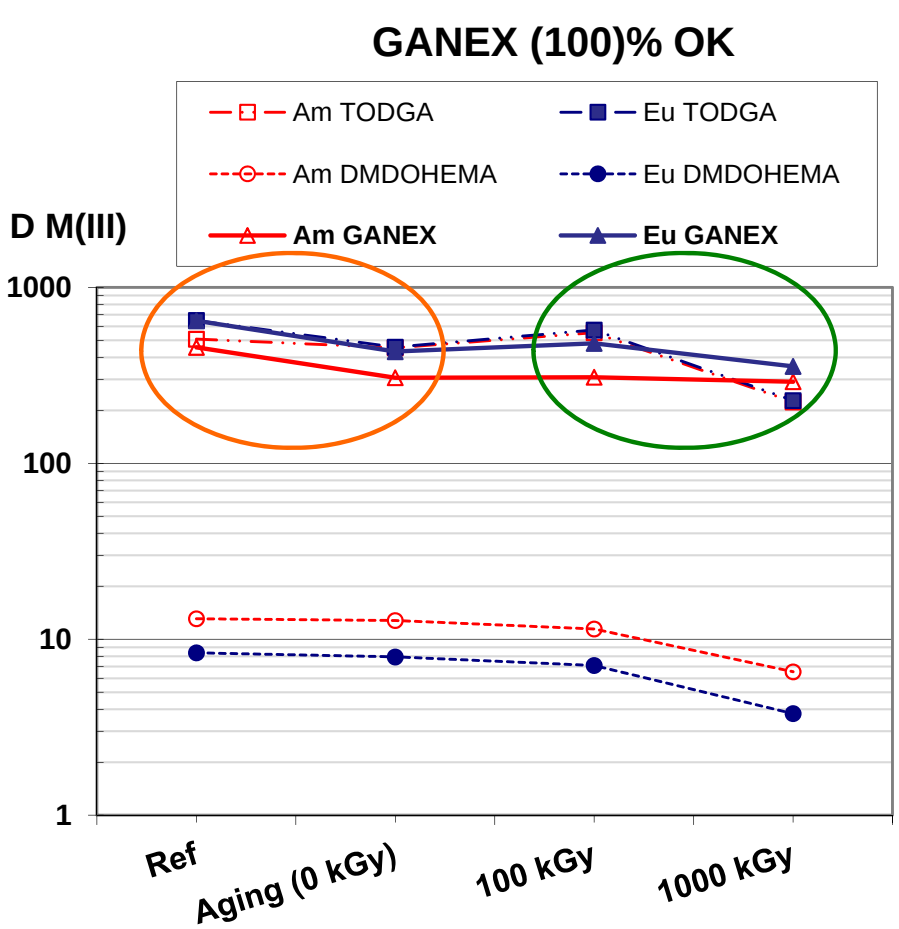
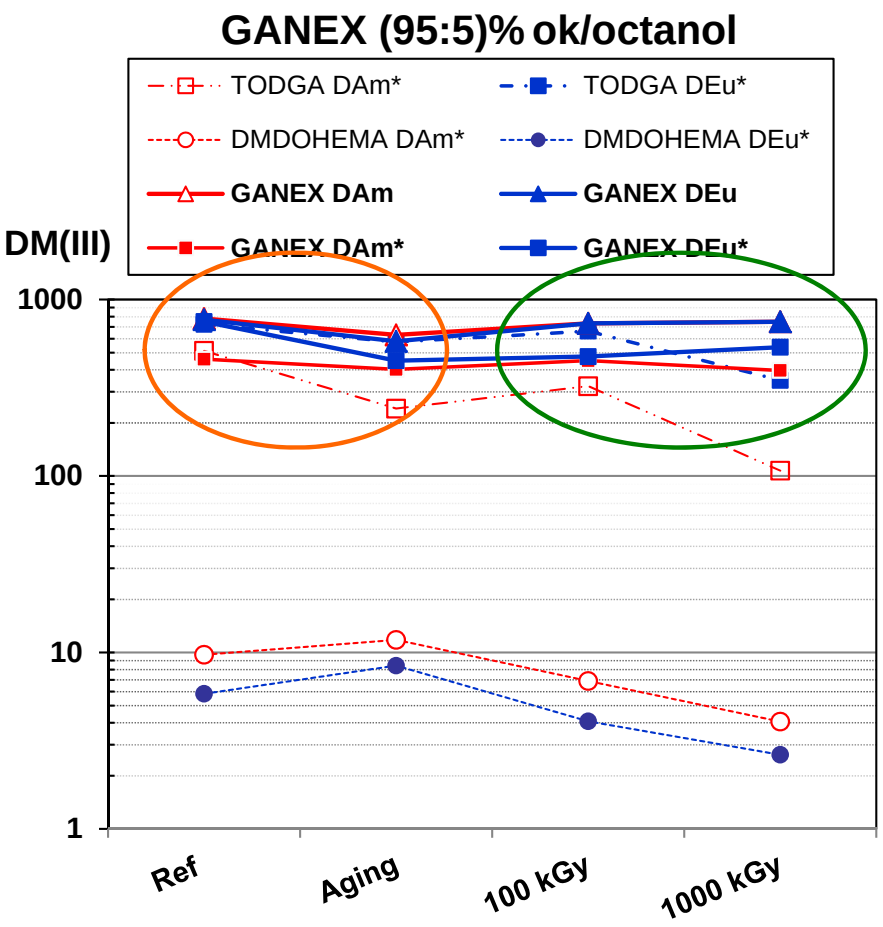
Extraction properties after gamma radiation

- *Am(III)/Eu(III) extraction by reference, aged and irradiated GANEX samples (at 1.78 kGy/h).*



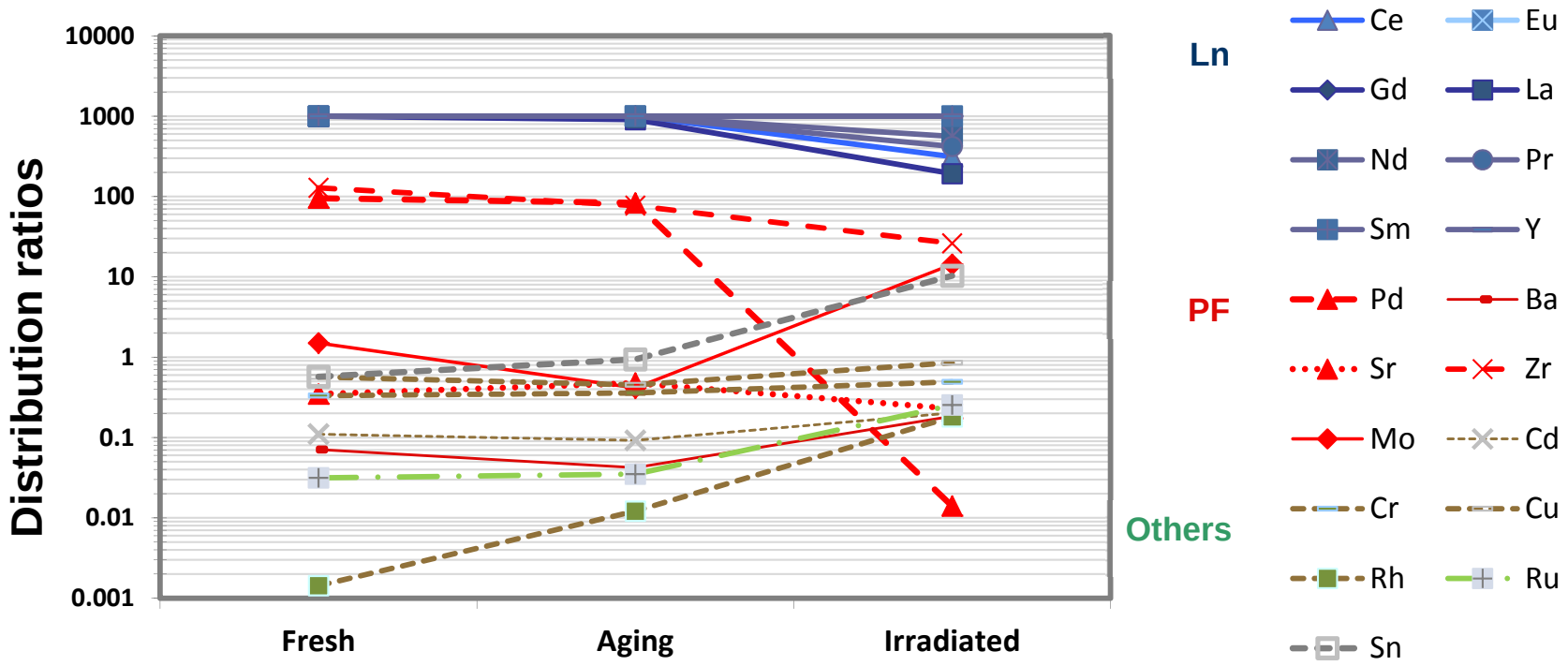


After high doses organic GANEX solvent keeps the Ln(III)/An(III) co-extraction

Extraction properties after gamma radiation

- *Extraction of elements presents in a HAR solution by fresh, aged and irradiated GANEX solvent (1000 kGy, 1.78 kGy/h)*

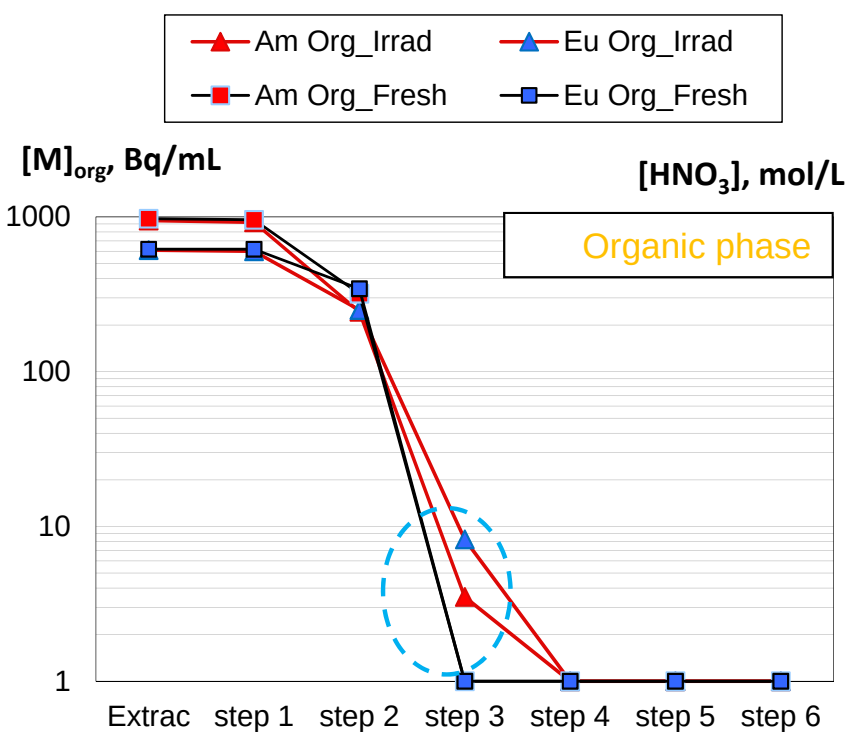
  - Weak decrease of Ln(III) extraction.
  - Increase of extraction of other metal, such as Rh and Sn.
  - Decrease some FP extraction (Zr and Pd), but an increase of others (Mo)



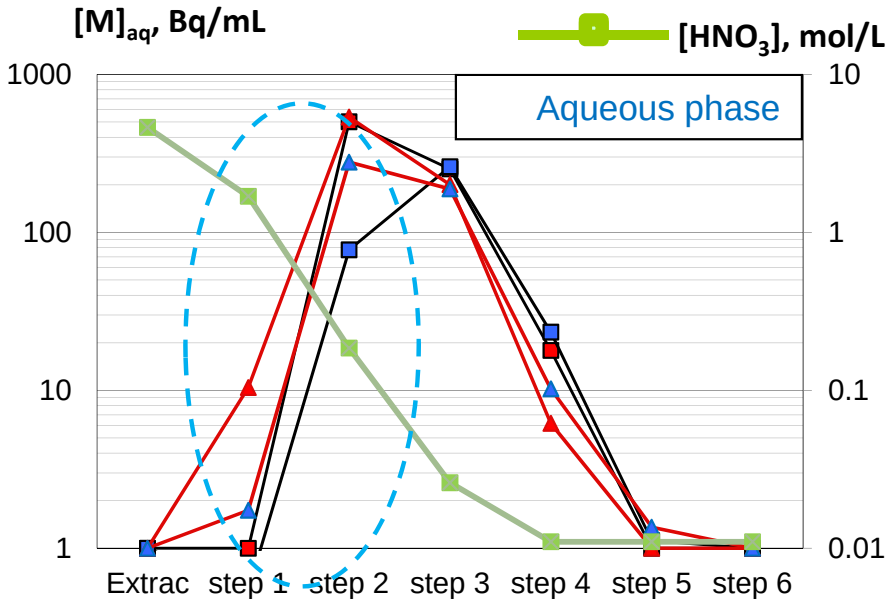
Organic phase: 0.2 mol/L TODGA and 0.5 mol/L DMDOHEMA in OK pre-equilibrated with 5 mol/L HNO_3.
Aqueous phase: 10% of simulated HAR solution (HNO_3 5 mol/L) in HNO_3 5 mol/L.

Back-extraction properties after gamma radiation

- *Ln(III)/An(III) back-extraction from a loaded irradiated GANEX solvent (1000 kGy, 1.78 kGy/h).*
  - Ln back-extraction at higher nitric acid concentration. SF Ln/An could be affected.
  - More difficult quantitative back-extraction of Ln/An.



It should be cheeked by using the corresponding aqueous phase (hydro-BTP)



Organic phase: 0.2 mol/L TODGA and 0.5 mol/L DMDOHEMA in 100% OK pre-equilibrated with 5 mol/L HNO_3.
Aqueous phase: Extrac, 10% of HAR solution in HNO_3 5 mol/L; back-extraction steps, 1.0 and, 0.01 mol/L HNO_3.

Back-extraction properties after gamma radiation

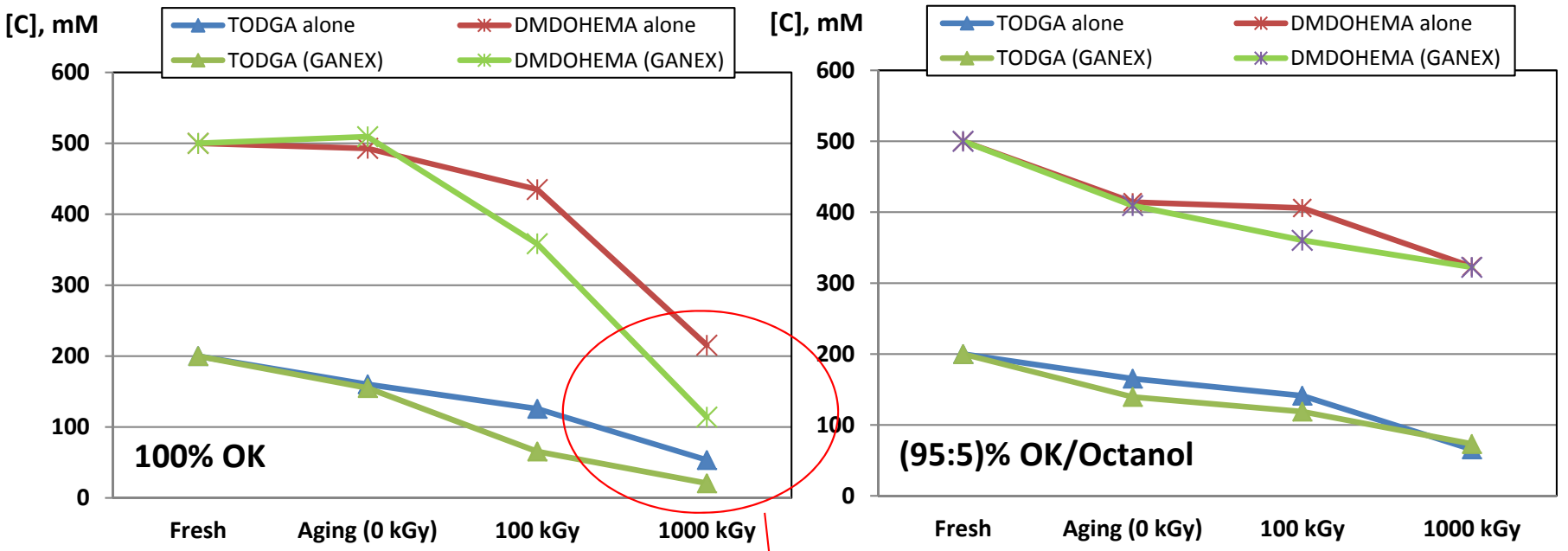
- *Ln(III)/An(III) back-extraction from a loaded irradiated GANEX solvent (1000 kGy, 1.78 kGy/h)*
  - Ln back-extraction at higher nitric acid concentration. SF Ln/An could be affected.
  - More difficult quantitative back-extraction of Ln/An.

- *Ln/An/FP back-extraction from a loaded irradiated GANEX solvent (1000 kGy, 1.78 kGy/h)*
  - Ln back-extraction at higher nitric acid concentration. SF Ln/An could be affected.
  - More difficult quantitative back-extraction of Ln/An.

The composition of the system should explain the difference observed

Remaining extracting agents concentration

- *Quantitative analysis by HPLC-DAD of TODGA and DMDOHEMA.*
  - ✓ *More than 50% degradation for both extracting agents.*
  - ✓ *Presence of octanol reduces partially the extractant degradation.*



Loading capacity study for Ln(III) and Pu(IV)!!!

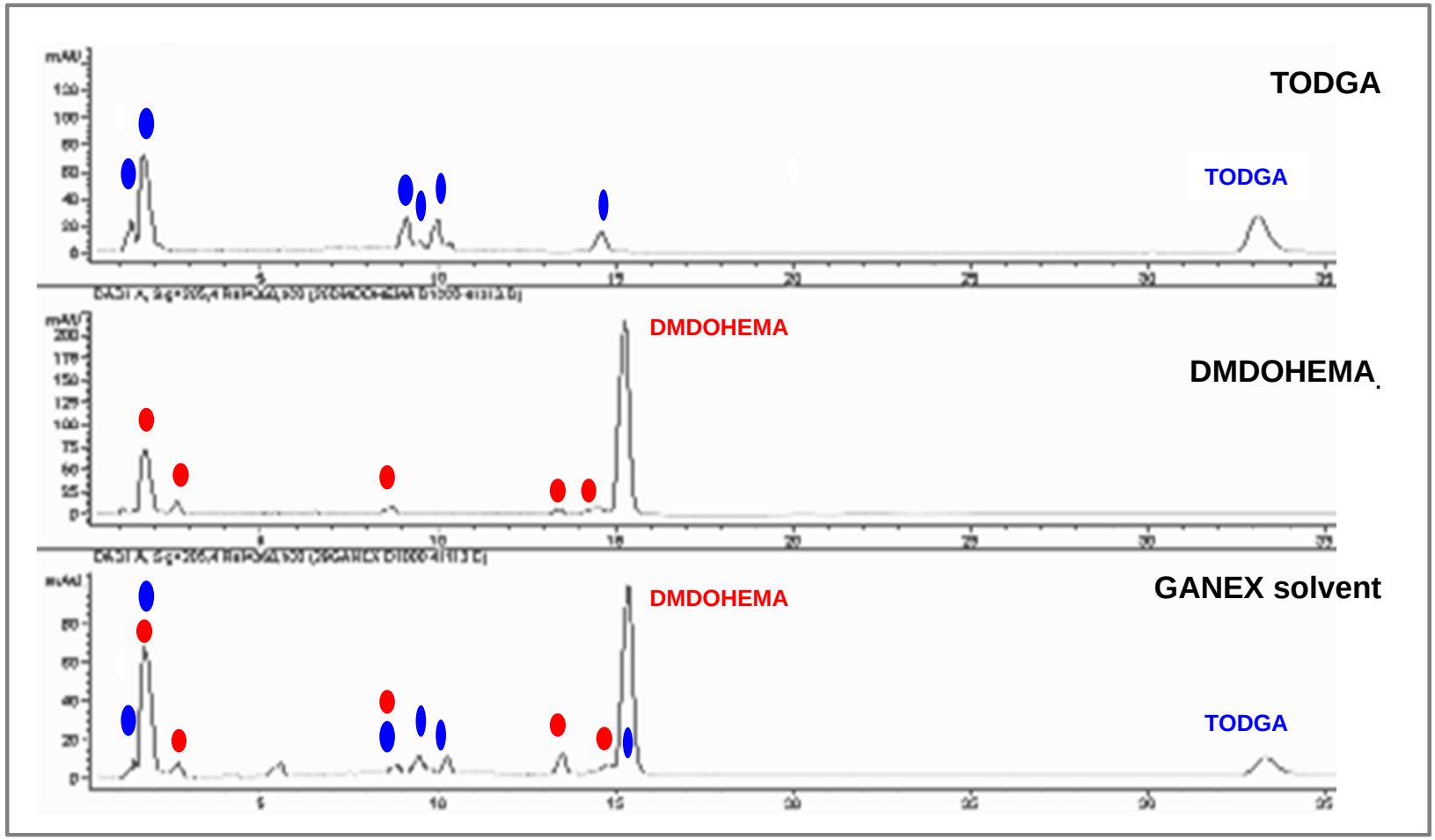
Composition of degraded organic GANEX solvents

- *HPLC-DAD qualitative studies after irradiation (1000 kGy, 1.78 kGy/h).*

✓ *Same qualitative degradation of ligands alone and as part of GANEX solvent.*

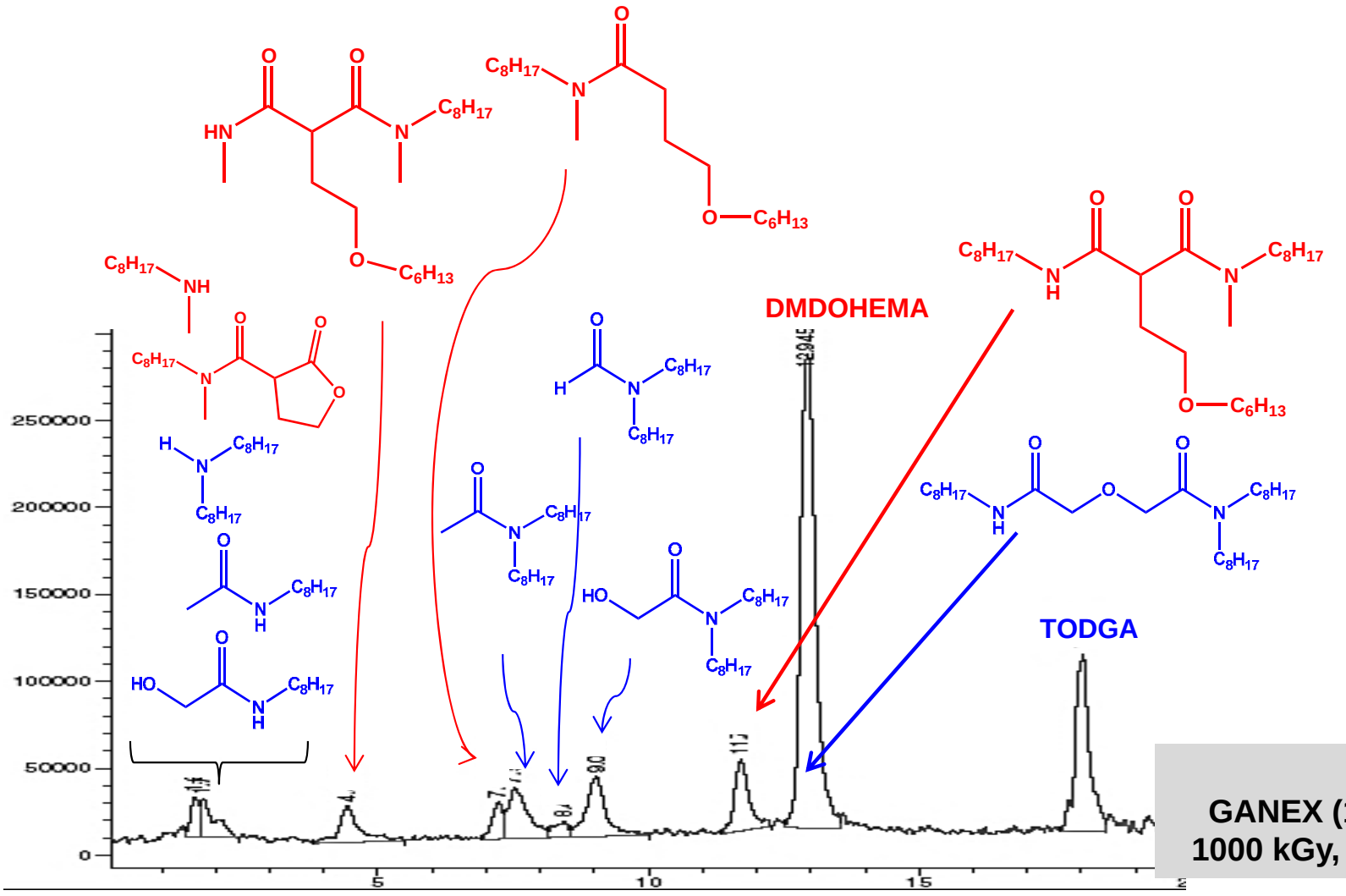
✓ *Higher number of signals in presence of octanol: ↑ hydrolytic degradation.*

(100)% OK, 1000 kGy



Identification of degradation compounds (DCs)

- *HPLC-MS (APCI⁺) qualitative studies after gamma irradiation*

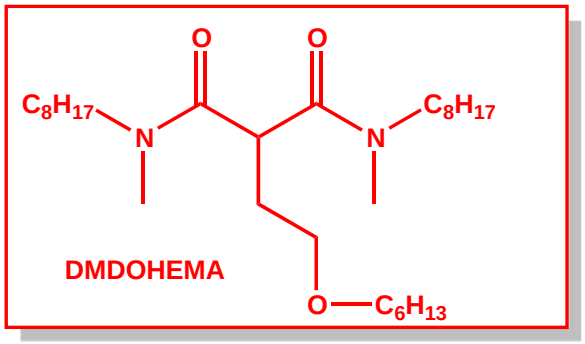


GANEX (100)% OK
1000 kGy, 1.78 kGy/h

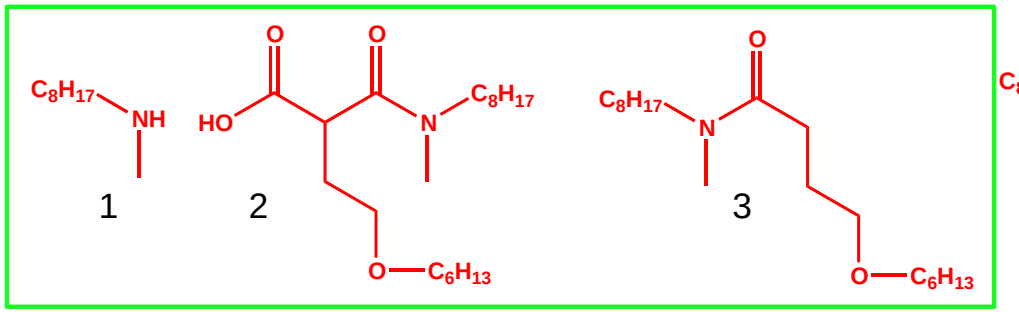
Galán H., et al. Procedia Chemistry, 2012, 195.
Berthon, L *et al. Separation Science and Technology* 2001, 365&6, pp. 709.

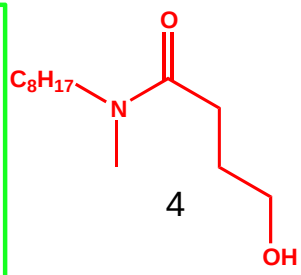
DMDOHEMA degradation compounds

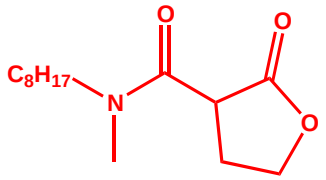
- *Identification of DCs by HPLC-MS*



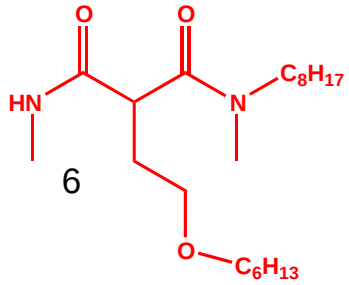
- *3 of them (1-3), reduce partially the efficiency of solvents based on DMDOHEMA.*

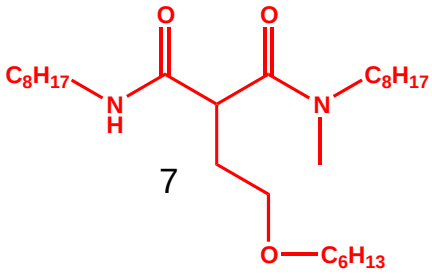


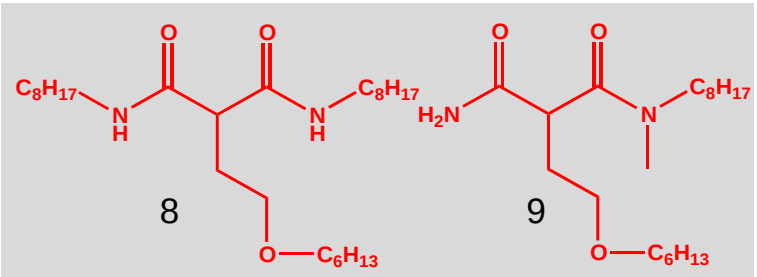




New possible structures

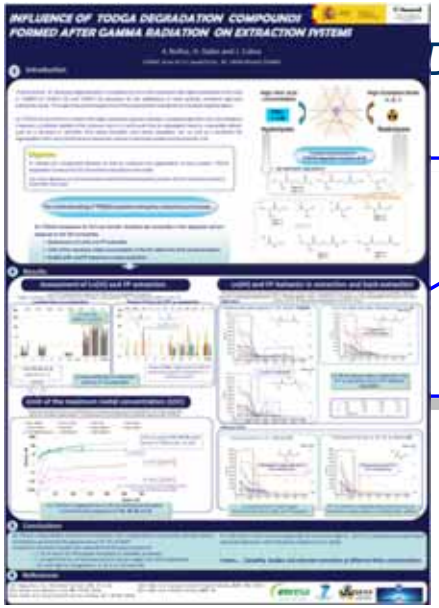




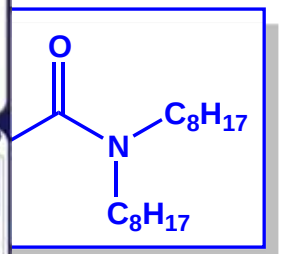


Berthon, L. *et al. Solvent Extr. Ion Exch: A series of Advances* 2010, **19**, PT Chapter 8, 429.
Berthon, L *et al. Separation Science and Technology* 2001, 365&6, pp. 709.

TODGA degradation compounds

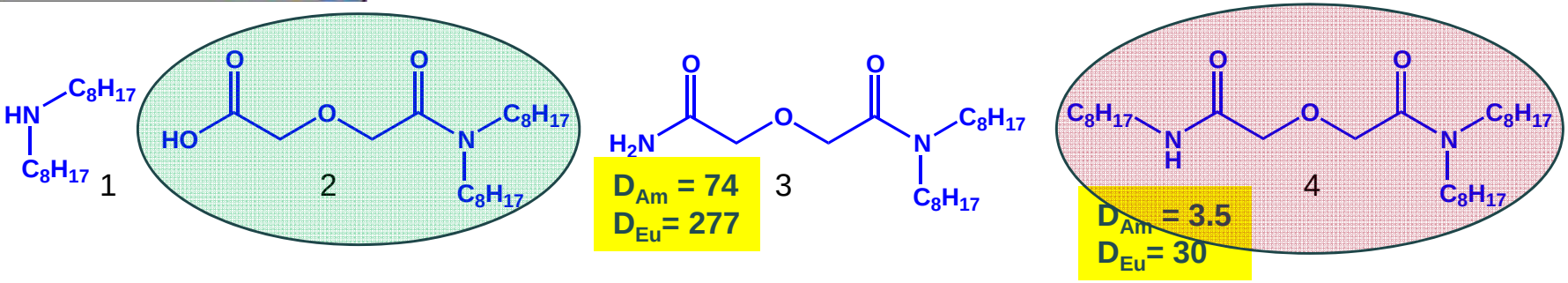


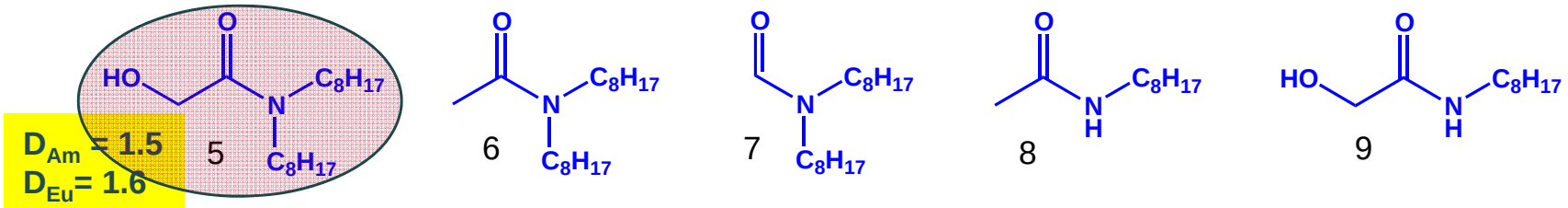
DCs by HPLC-MS



Effects on solvent formulation

- 3 of them (3-5), $D_{Ln/An(III)} > 1$ at 3 mol/L HNO_3.
- At least 1 of them (2), troubles in Ln back-extraction.
- 2 of them (4 and 5), possible troubles in SF Ln/An.





*A. Núñez et. al. Global **2015**,*
*H. Galán et.al. Procedia Chemistry **2012**, 195.*

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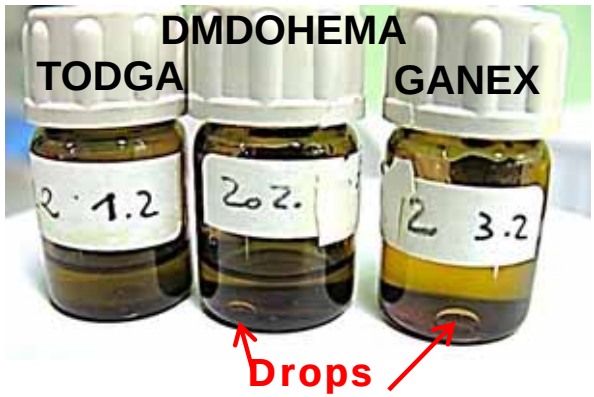
Phisico-chemical stability of organic GANEX solvent

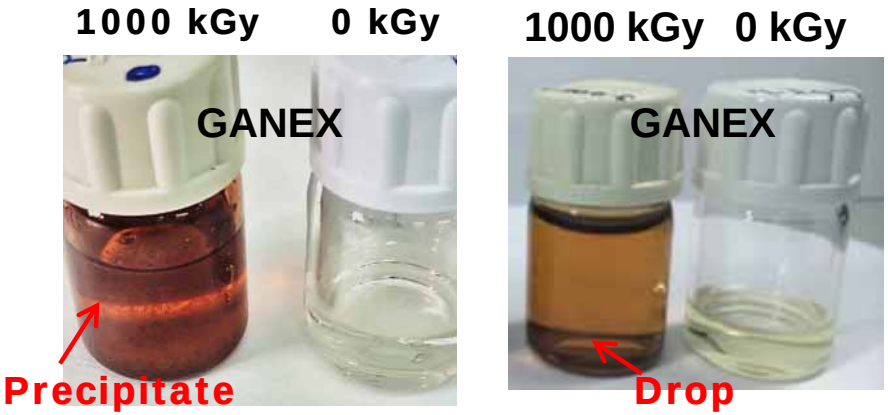
- *Insoluble drops and precipitates after irradiation up to 1000 kGy*

(95:5)% OK/Octanol



- ✓ *Mass transference studies*
- ✓ *Analysis of insolubilities*

100% OK



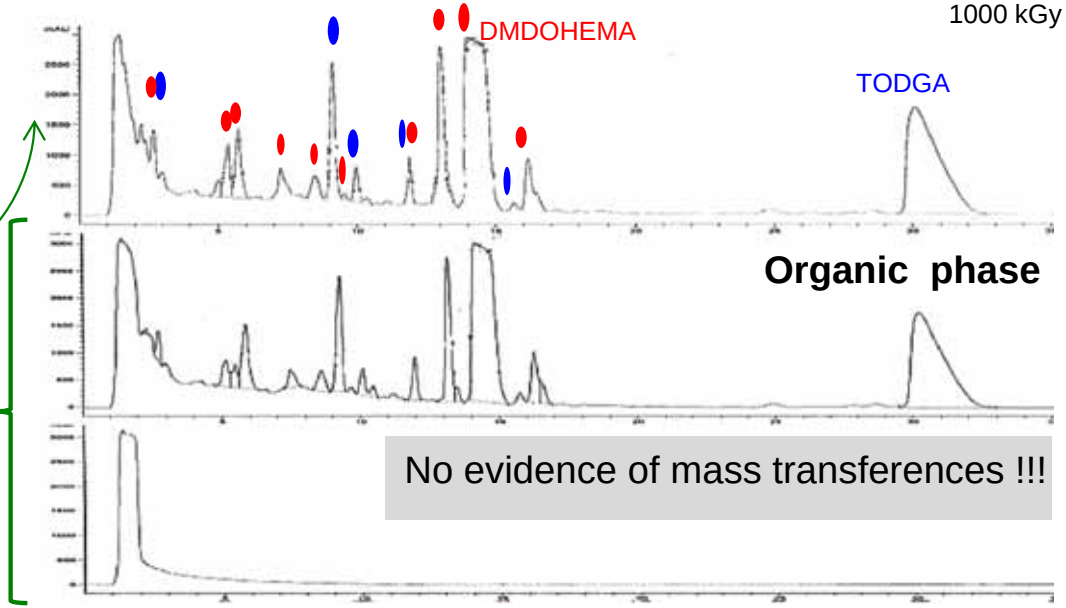
Phisico-chemical stability of org. GANEX solvent

- *Mass transferences between phases after irradiation*

HPLC-DAD chromatograms

(95:5)% OK/Octanol

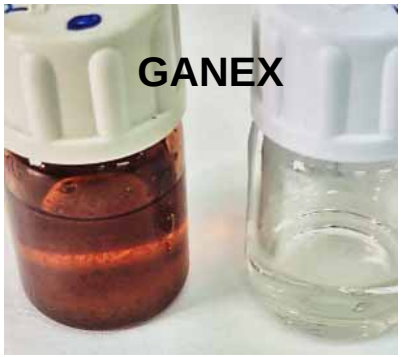
contact with 5 mol/L HNO_3.



No evidence of mass transferences !!!

100% OK

1000 kGy **0 kGy**

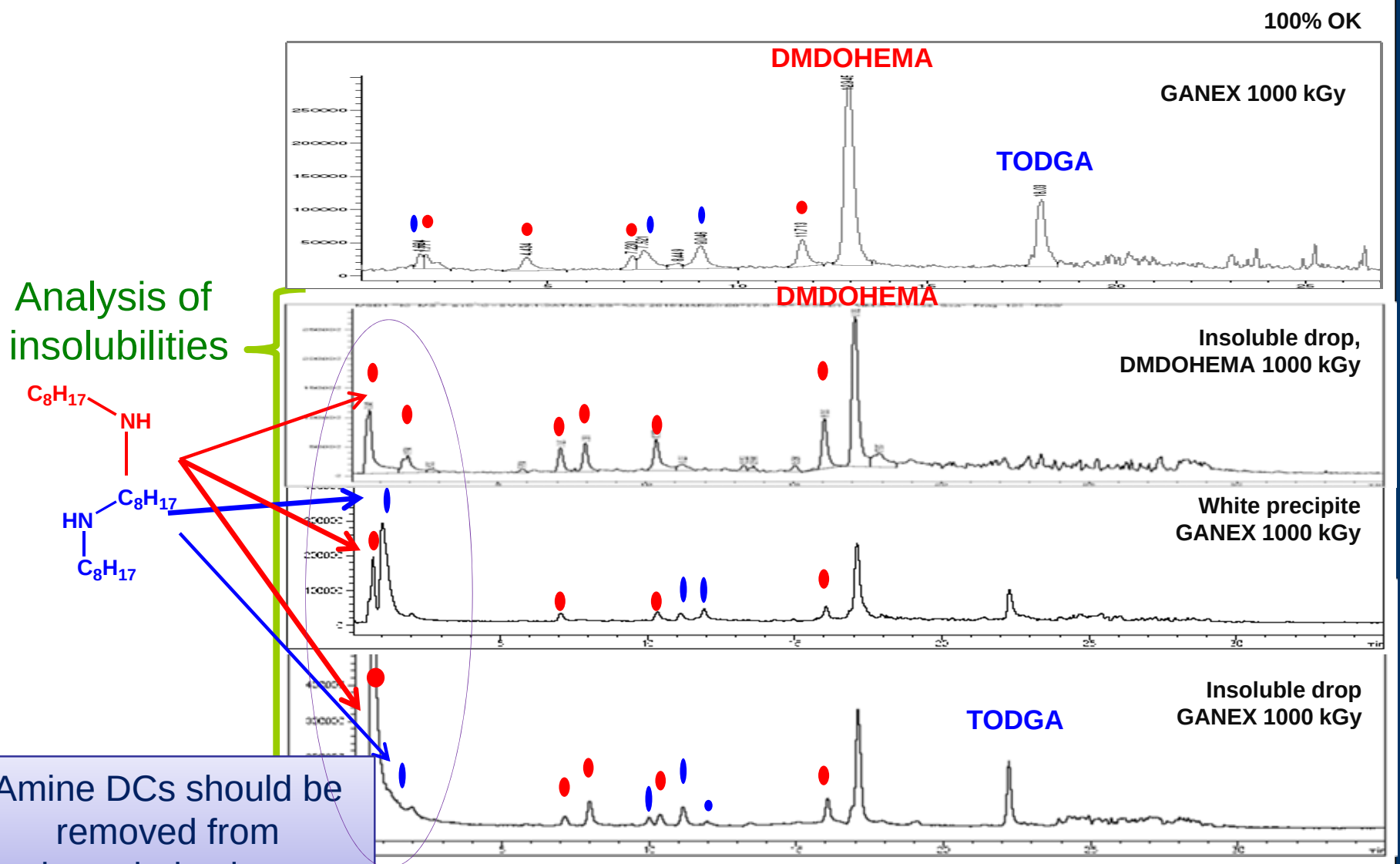


contact with 5 mol/L HNO_3.

No evidence of mass transference !!!

Responsible of insolubilities

- *Analysis by HPLC-MS(APCI)$^+$ of insolubilities of GANEX solvent*



Amine DCs should be removed from degraded solvent

What can we conclude about Euro-GANEX stability?

- *It keeps the co-extraction of Ln/An after gamma radiation.*
  - *High $D_{Ln/An}$ after 1000 kGy.*
- *Important reduction in TODGA and DMDOHEMA concentration:*
  - *Octanol: higher remaining concentration but lower $D_{Am/Eu}$.*
  - *At least 7 DCs of TODGA and 5 of DMDOHEMA are formed.*
- *It can be affected:*
  - *SF An/Ln.*
  - *Stripping Ln.*

Properties of of DCS

- *Responsible of insolubilities:*
  - *Aggregates of protonated **MeOctylNH** and $(Octyl)_2NH$.*

Future work

- *Ongoing studies about:*
  - *Extraction properties: $LOC_{Pu(IV)}$, $SF_{An/Ln}$ and Ln back-extraction with the corresponding aqueous phase.*
  - *Effects of DCs on degraded solvent.*
  - *Cleaning up experiments: MeOctylNH and $(Octyl)_2NH$.*

- ***Interaction between all solvents related along the Euro-GANEX process.***
  - ***Simulating an operative cycle:***
    - *Interaction between all phases/solvents involved in.*
    - *Looking for the limits of the systems.*

Acknowledgment

Ana Núñez, HLW Unit at Ciemat.

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Thank you for your attention

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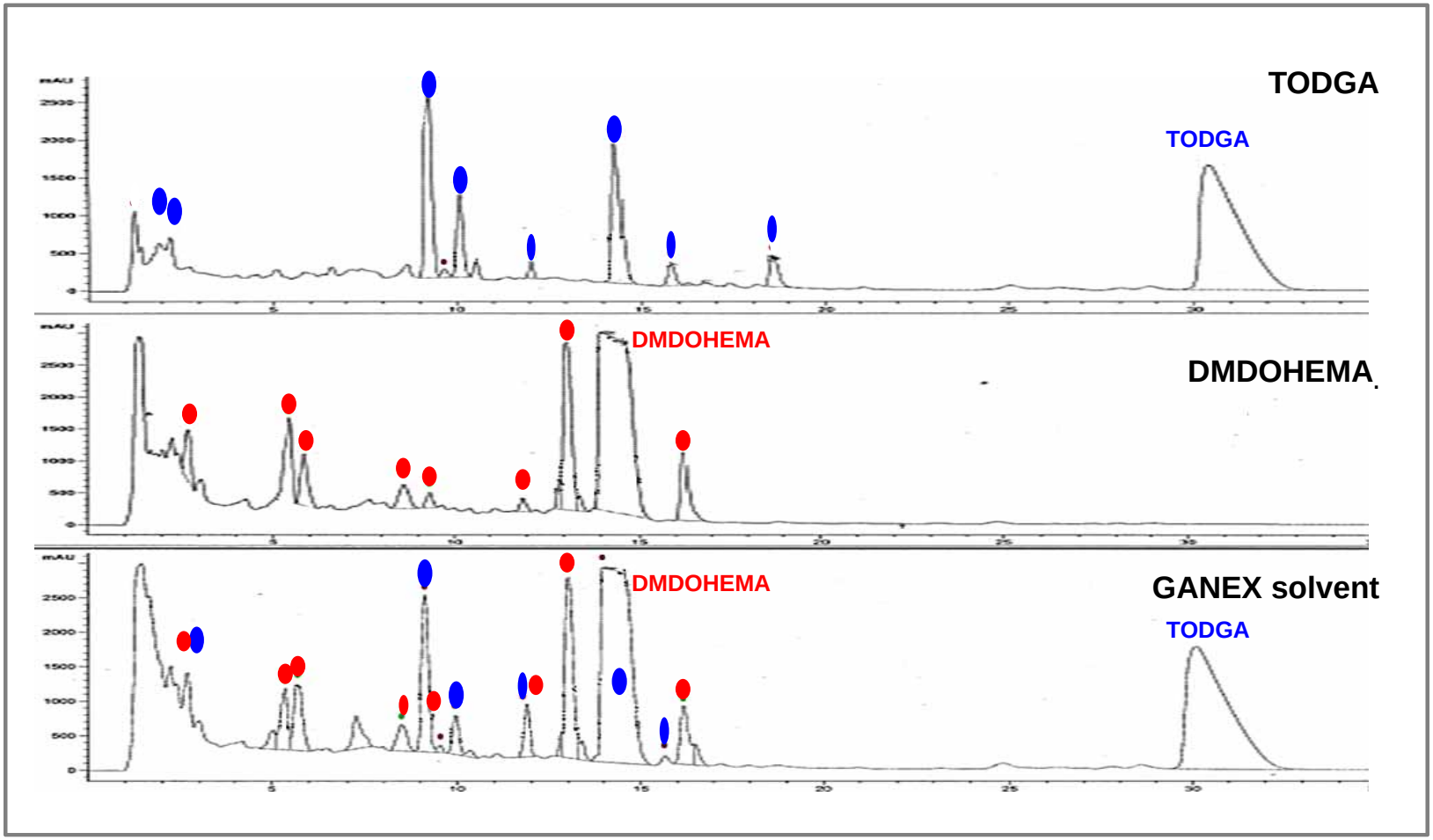
Composition of degraded org. GANEX solvents

- *HPLC-DAD qualitative studies after irradiation (1000 kGy, 1.78 kGy/h).*

✓ *Same qualitative degradation for TODGA and DMDOHEMA alone and in the GANEX.*

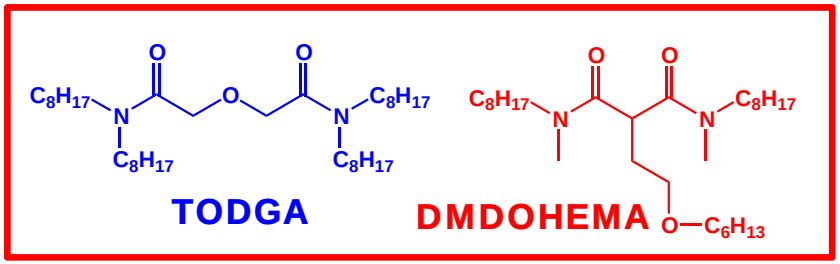
✓ *Higher number of signals for GANEX solvent in presence of octanol: hydrolytic degradation.*

(95:5)% OK/Octanol, 1000 kGy

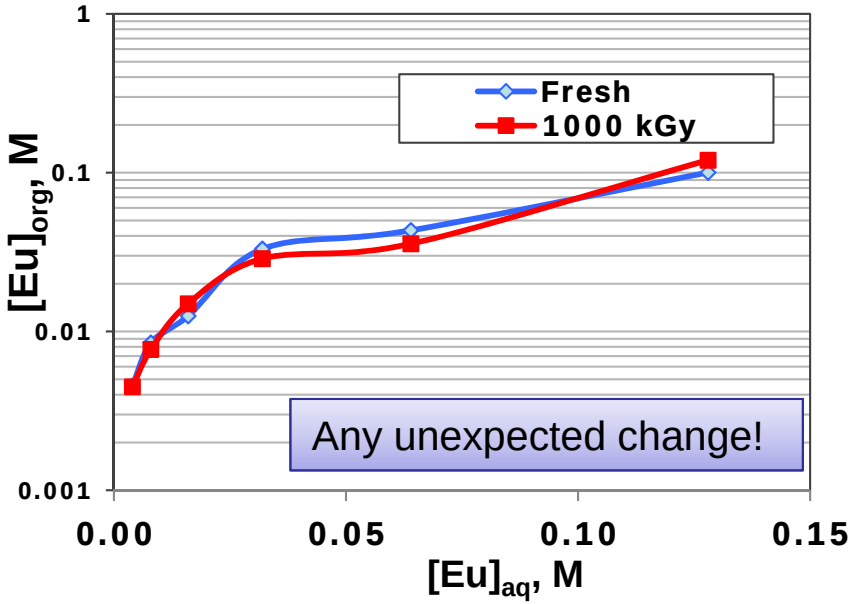


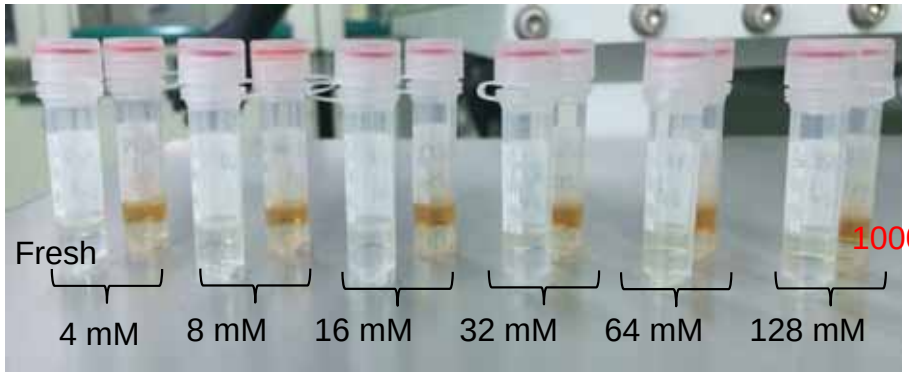
Remaining extracting agent concentration

- *Ln(III) loading capacity of after irradiation (1000 KGy, 1.50 kGy/h).*



- ✓ 0.2 mol/L TODGA
- ✓ 0.5 mol/L DMDOHEMA
- ✓ In kerosene (OK)





Organic Solution: 0.2 M TODGA + 0.5M DMDOHEMA in 100%OK.
Aqueous solution [HNO_3] = 4 M and Eu(III) concentrations from 0.004 M to 0.256 M, spiked with ^{152}Eu (1000 Bq/mL).

Responsible of Insolubilities

- *Analysis by HPLC-MS(APCI)$^+$ of insolubilities of GANEX solvent*