Safety of actinide separation processes

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Physico chemical modifications of irradiated i-SANEX diluents

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SUMMARY

1. ***INTRODUCTION***
   - *An/Ln separation*
   - *Radiolysis state-of-the-art*
2. ***AIM of the WORK***
3. ***RESULTS***
   - *0.25M and 0.5M HNO_3 system*
   - *0.44M HNO_3 + kerosene/1-octanol system*
4. ***FINAL REMARKS AND FUTURE WORKS***

1. INTRODUCTION - An/Ln separation

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Hydrometallurgical approach for Spent Nuclear Fuel partitioning

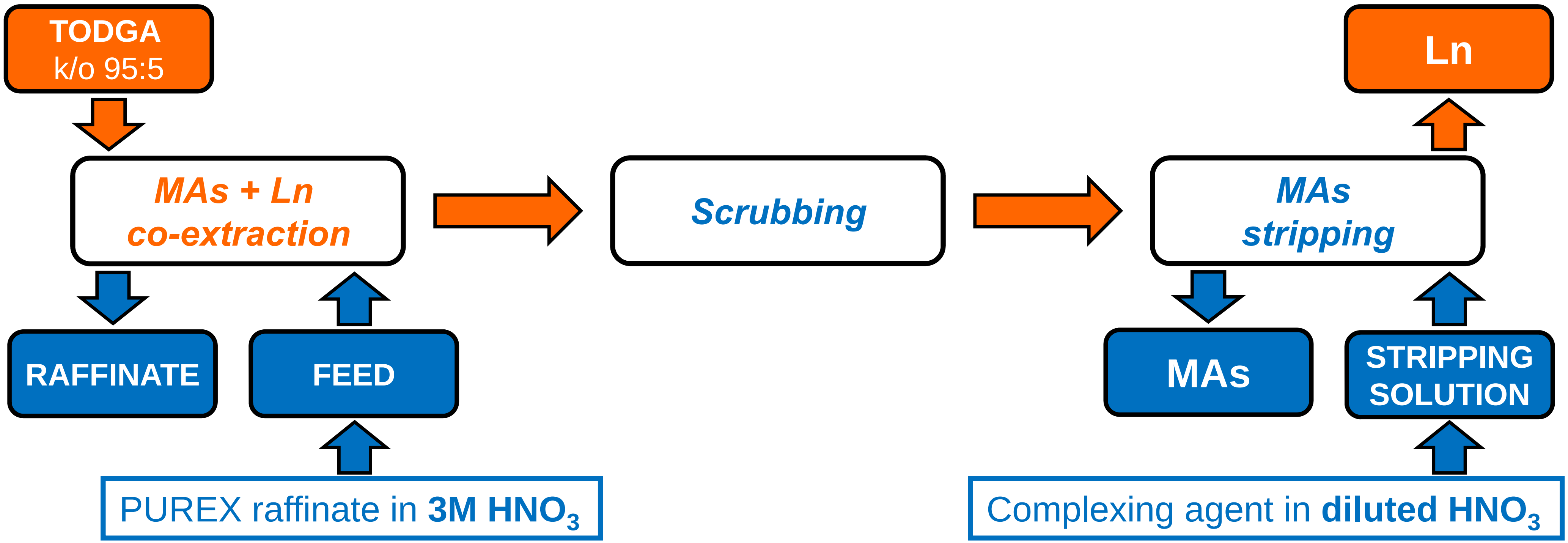
PUREX / UREX / COEX ⇨ **U and/or Pu, Np**

⇩

_i_-SANEX (_innovative_ - Selective ActiNide Extraction)

1st step: MAs and Ln co-extraction

2nd step: MAs / Ln separation



Harsh conditions of working environment

feed acidity

moderated temperature (up to 50°C) → **HYDROLYSIS**

high radiation field (MAs, FPs)

↓

RADIOLYSIS

DIRECT
diluent by-products

INDIRECT
ligand by-products

↓

Radiation-induced modifications may compromise
- Selectivity
- Fluid dynamics
- Safety

General reviews

Pikaev AK et al. (1988) Some radiation chemical aspects of nuclear engineering

Woods JW, Pikaev AK (1993) Applied radiation chemistry: radiation processing

Concentrated HNO_3

Radiolysis mechanism

LET effect

Savel'ev YI et al. (1967) ***α-Radiolysis*** *of aqueous solutions of nitric acid*

Kazanjian AR et al. (1970) *Radiolysis of nitric acid solutions:* ***L.E.T. effects***

Katsumura Y et al. (1994) ***γ-Radiolysis*** *study of concentrated nitric acid solutions*

Katsumura Y et al. (1991) ***Pulse radiolysis*** *study of aqueous nitric acid solutions. Formation mechanism, yield, and reactivity of* NO_3 *radical*

Actinide chemistry

Vladimirova MV (1990) *Radiation chemistry of actinides*

Pikaev AK et al. (1997) *Radiation chemistry of aqueous solutions of actinides*

Bhattacharyya PK et al. (1991) *Radiation chemistry of* ***actinide solutions***

PUREX solvent: concentrated HNO_3 - TBP - dodecane

Mincher BJ et al. (2009) The effects of radiation chemistry on solvent extraction 1: Conditions in acidic solutions and a review of TBP radiolysis

Radiolysis mechanism

- Nowak Z (1977) *Radiolytic **degradation of extractant-diluent** systems used in the PUREX process*
- Neace JC (1983) ***Diluent degradation products** in the PUREX solvent*
- …
- Mincher BJ et al. (2008) ***A pulse radiolysis** investigation of the reactions of TBP with the radical products of aqueous nitric acid irradiation*

Safety

Fluid dynamics

- Tripathi SC et al. (2001) *Studies on the identification of **harmful radiolytic products** of 30% TBP-n-dodecane- HNO_3 by gas liquid chromatography. I. Formation of diluent degradation products and their role in Pu retention behavior*
- Krishnamurthy MV et al. (1992) *Radiation-induced decomposition of the TBP-nitric acid system: Role of nitric acid*
- Tripathi SC et al. (2003) *Effect of radiation induced **physicochemical transformation** on density and viscosity of 30% TBP-n-dodecane-HNO_3 systems*

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MAs - Ln co-extraction solvent: concentrated HNO_3 - TPH/1-octanol
MAs/Ln separation solvent: diluted HNO_3 - TPH/1-octanol

Mincher BJ et al. (2009) *The effects of radiation chemistry on solvent extraction 3: A review of Actinide and Lanthanide extraction*

Mincher BJ et al. (2010) *The effects of radiation chemistry on solvent extraction 4: Separation of the trivalent Actinides and considerations for radiation-resistant solvent system*

Extractant radiolysis

- Sugo Y et al. (2002) *Studies on hydrolysis and radiolysis of N,N,N,N-tetraoctyl-3-oxapentane-1,5-diamide*
- Sugo Y et al. (2008) *Influence of diluent on radiolysis of amides in organic solution*
- Ansari SA et al. (2012) *Chemistry of **Diglycolamides**: Promising Extractants for Actinide Partitioning*
- Magnusson D et al. (2009) *Investigation of the radiolytic stability of a* ***$CyMe_4$-BTBP based SANEX solvent***
- Fermvik A et al. (2009) *Influence of dose rate on the radiolytic stability of a **BTBP solvent** for actinide(III)/lanthanide(III) separation*

Hydrophilic Complexing agent radiolysis?

Safety? Fluid dynamics?

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Scope

Evaluation of radiation-induced modifications of physico chemical properties resulting in possible alterations of the fluid-dynamics of the i-SANEX diluents

Experimental conditions

Systems:

- 0.25M and 0.5M HNO_3
- 0.44M HNO_3 + k/o 95:5 v/v

Irradiation in air with ^{60}Co sources:

- Low dose rate 0.2kGy/h: up to 50kGy
- High dose rate 2.5kGy/h: up to 100kGy

Physico-chemical parameters

- Density
- Viscosity
- phase transfers
- pH
- $[NO_3^-]$

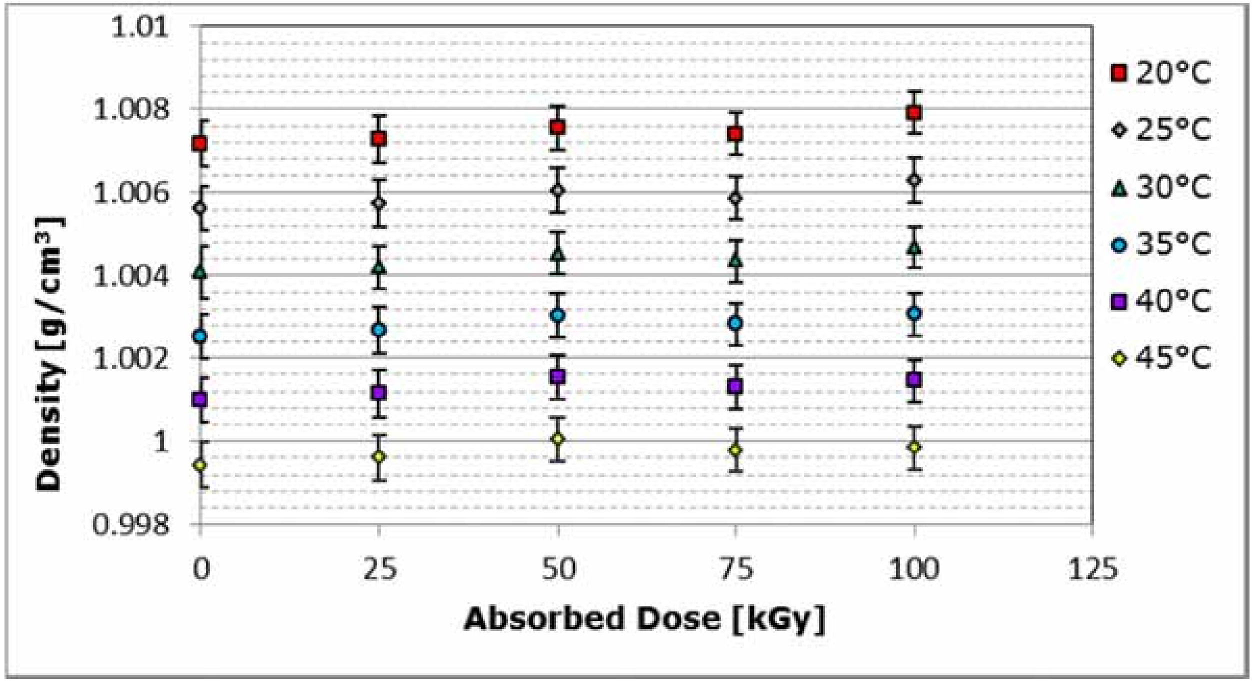
E. Mossini et. al., J Radioanal Nucl Chem (2015) Volume 304:395-400

DENSITY - 0.25M HNO_3

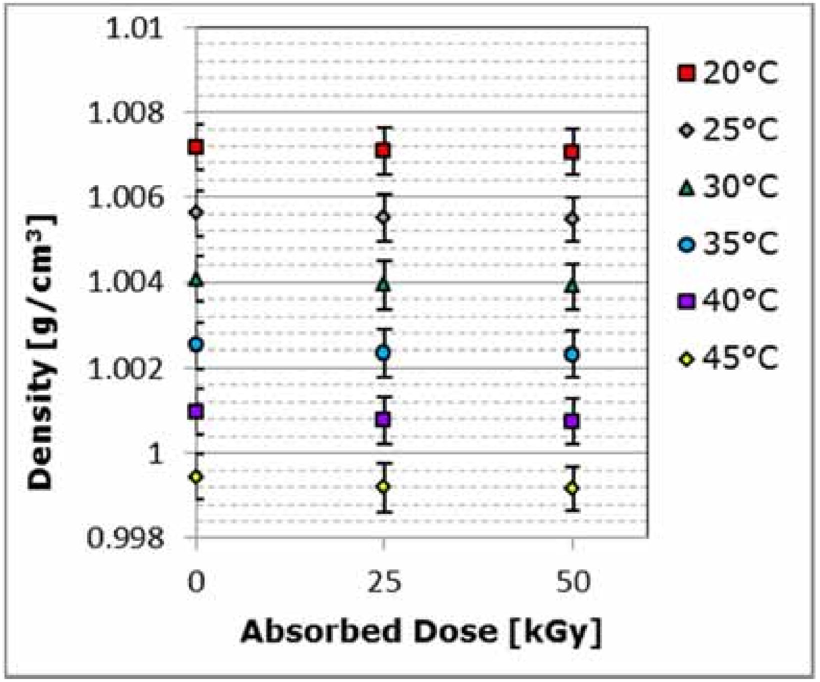
Temperature between 20°C and 45°C (±0.1°C) in thermostatic bath

DMA 35N Anton Paar portable density meter

High dose rate



Low dose rate



No modifications with the absorbed dose at both dose rates

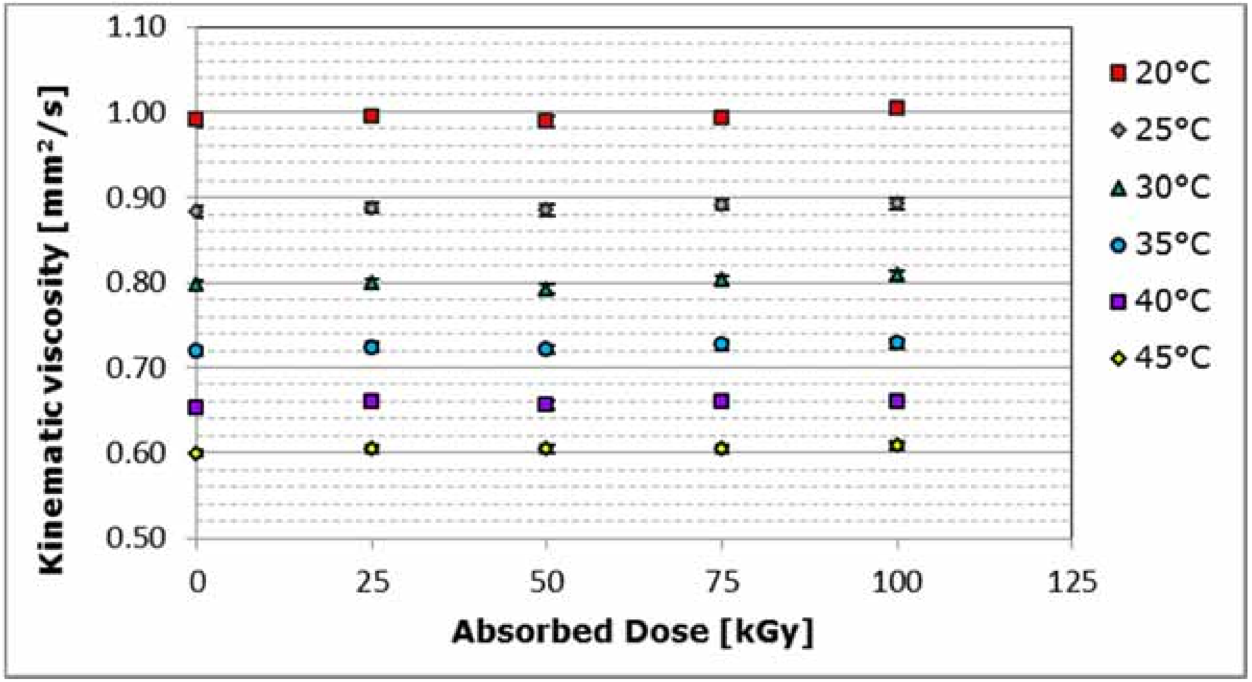
Similar trend for 0.5M HNO_3

3. RESULTS - 0.25M and 0.5M HNO_3 system

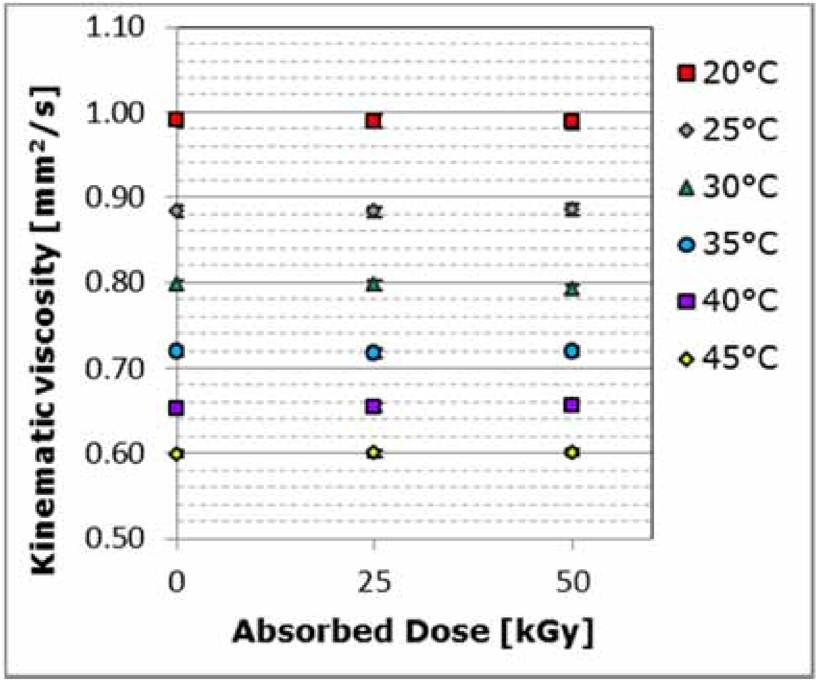
VISCOSITY - 0.25M HNO_3

Temperature between 20°C and 45°C (±0.1°C) in thermostatic bath
KPG-UBBELOHDE micro-viscometer

High dose rate



Low dose rate



No modifications with the absorbed dose at both dose rates

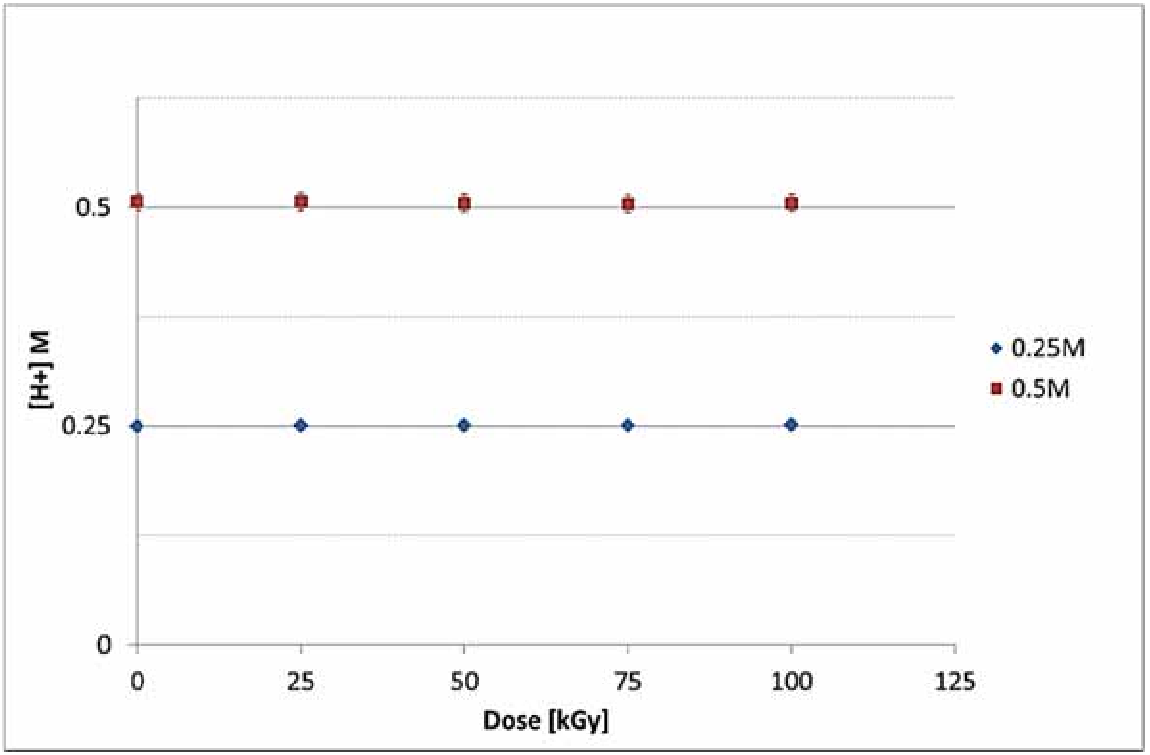
Similar trend for 0.5M HNO_3

3. RESULTS - 0.25M and 0.5M HNO_3 system

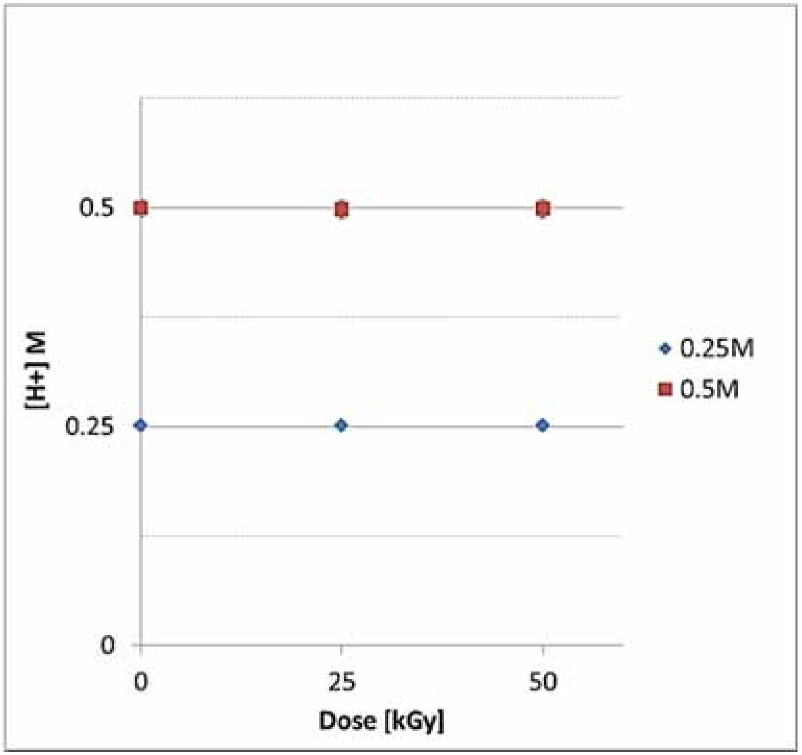
pH

Titration with 0.1M NaOH and with methyl orange 0.1% Fluka solution

High dose rate



Low dose rate



No modifications with the absorbed dose at both dose rates

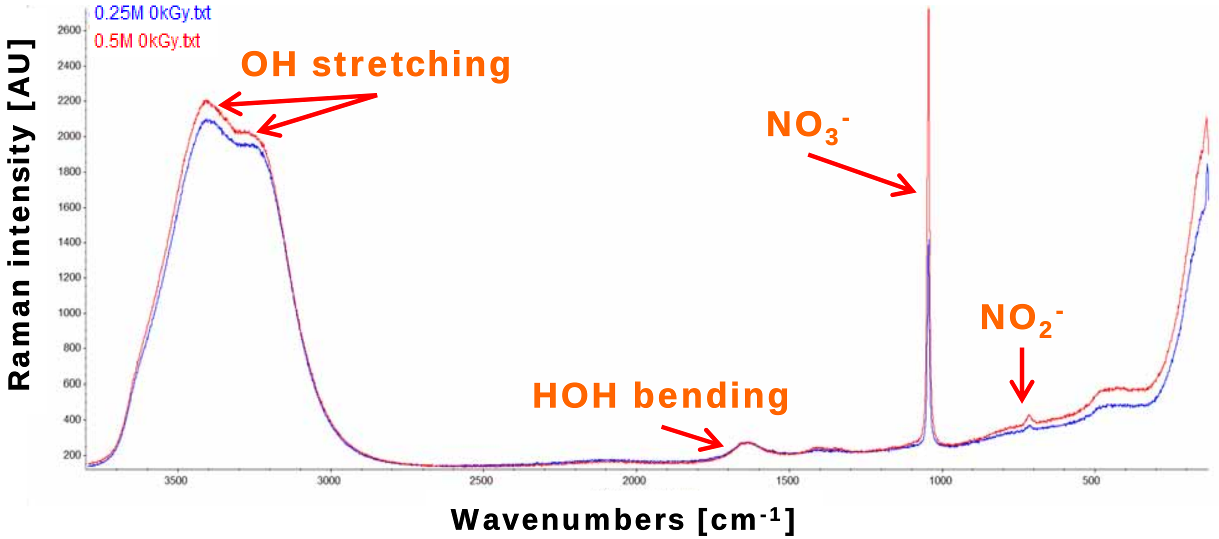
3. RESULTS - 0.25M and 0.5M HNO_3 system

$[NO_3^-]$ by Raman

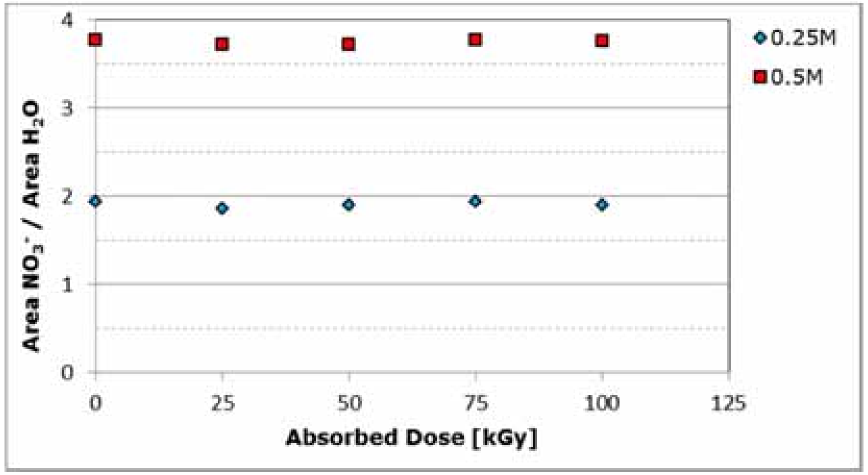
HR800 Raman spectrometer

514.5nm Ar^+ Laser, 75mWatt power on sample (in quartz NMR tubes)

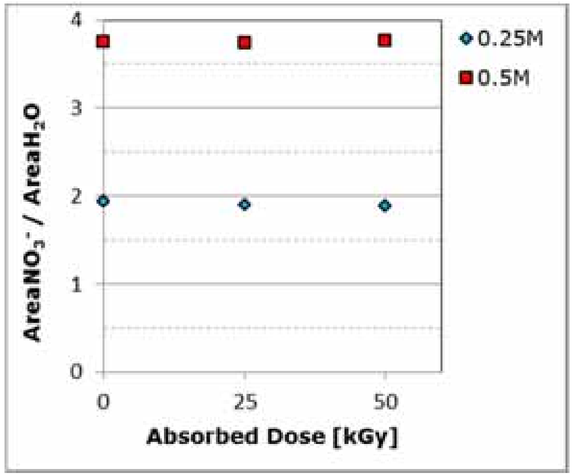
HOH bending as internal reference



High dose rate



Low dose rate

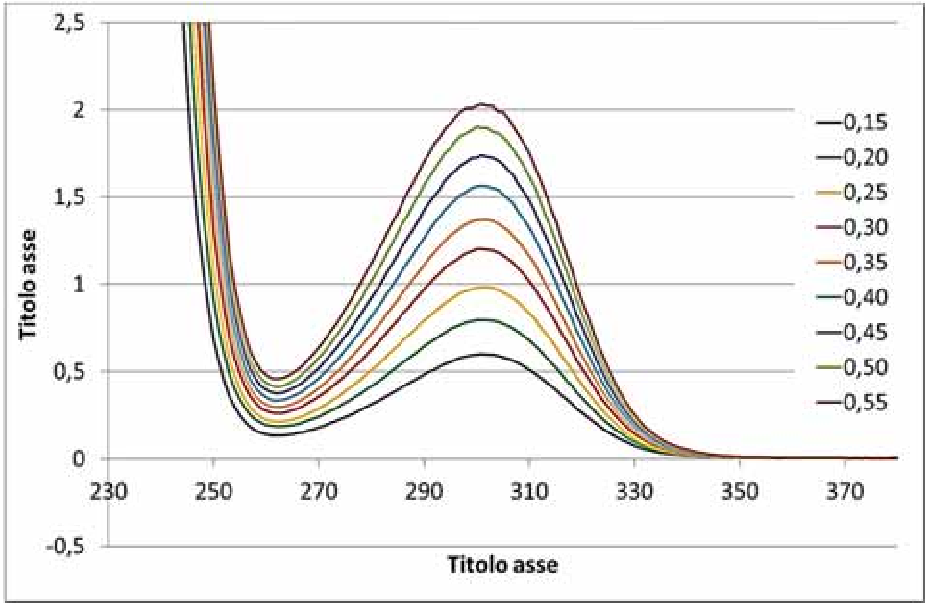


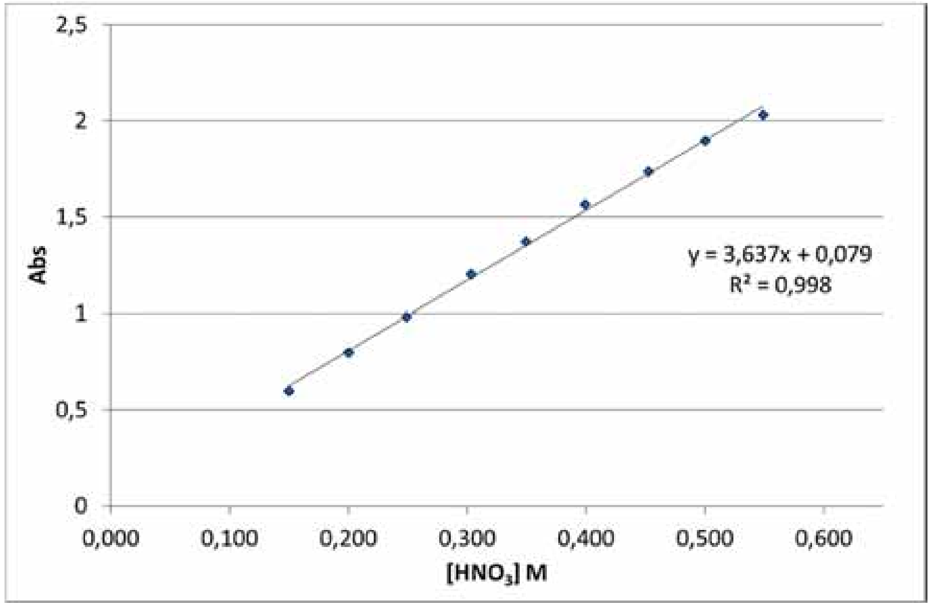
No modifications with the absorbed dose at both dose rates.

3. RESULTS - 0.25M and 0.5M HNO_3 system

$[NO_3^-]$ by UV/Vis

Calibration with 0.15M - 0.55M HNO_3 diluted 1:2 in water





High dose rate

	0 kGy	25 kGy	50 kGy	75 kGy	100 kGy
0.25 M	0.242±0.001	0.243±0.001	0.244±0.001	0.244±0.001	0.241±0.001
0.5 M	0.526±0.005	0.516±0.005	0.513±0.005	0.502±0.005	0.503±0.005
			- 2.4%		- 4.5%

Low dose rate

	0 kGy	25 kGy	50 kGy
0.25 M	0.250±0.001	0.250±0.001	0.249±0.001
0.5 M	0.523±0.005	0.505±0.005	0.502±0.005
			- 4%

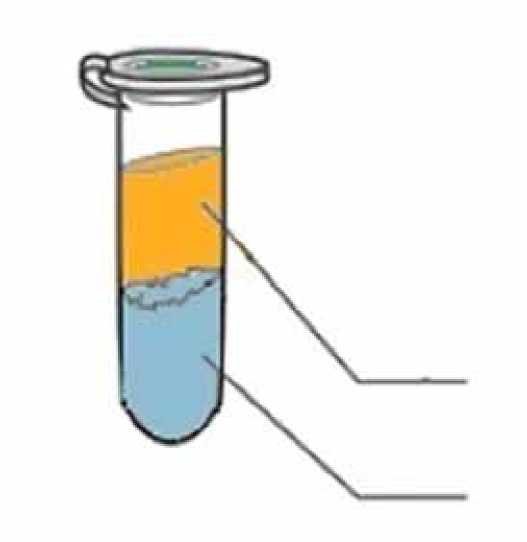
Slight decrease with absorbed dose at both dose rates only for 0.5M HNO_3 solutions

3. RESULTS - 0.44M HNO_3 + k/o 95:5 v/v system

PROCEDURE

IRRADIATION (2.5kGy/h)

in air, phases in contact



Sealed glass vials

10mL of solution

in 20mL vial

STORAGE

in the dark, at 4°C

for the same period

(same ageing)

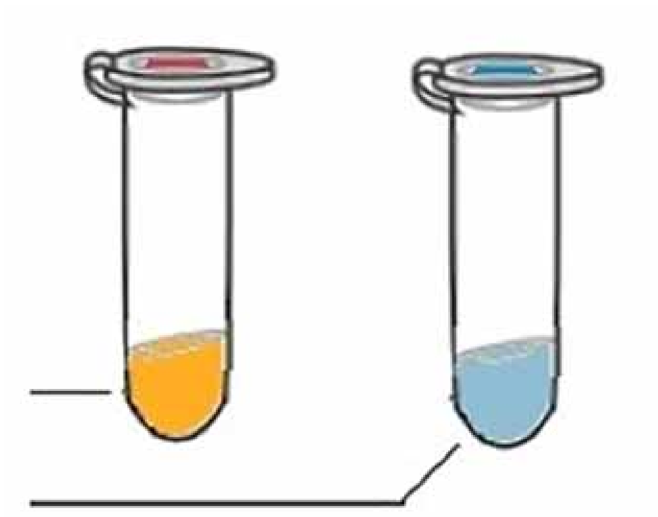
Organic phase

k/o 95:5 v/v

Aqueous phase

0.44M HNO_3

PHYSICAL SEPARATION

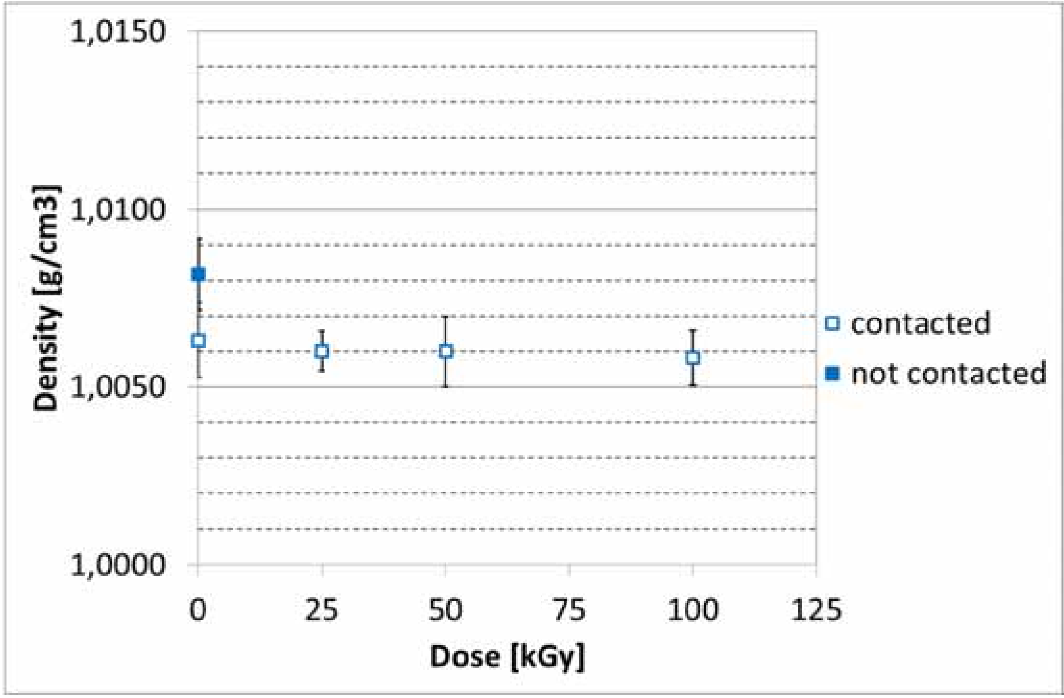


ANALYSES…

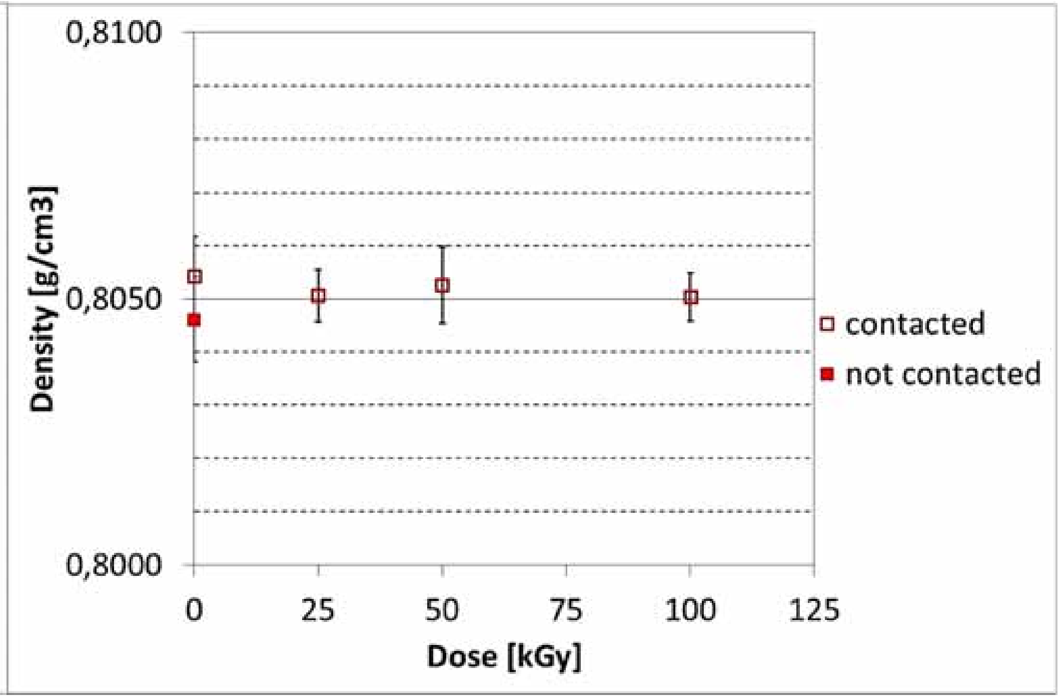
DENSITY (25°C)

Average over 3 measurements in 5mL flasks

Aqueous phase



Organic phase



Modification of density after phase contacting

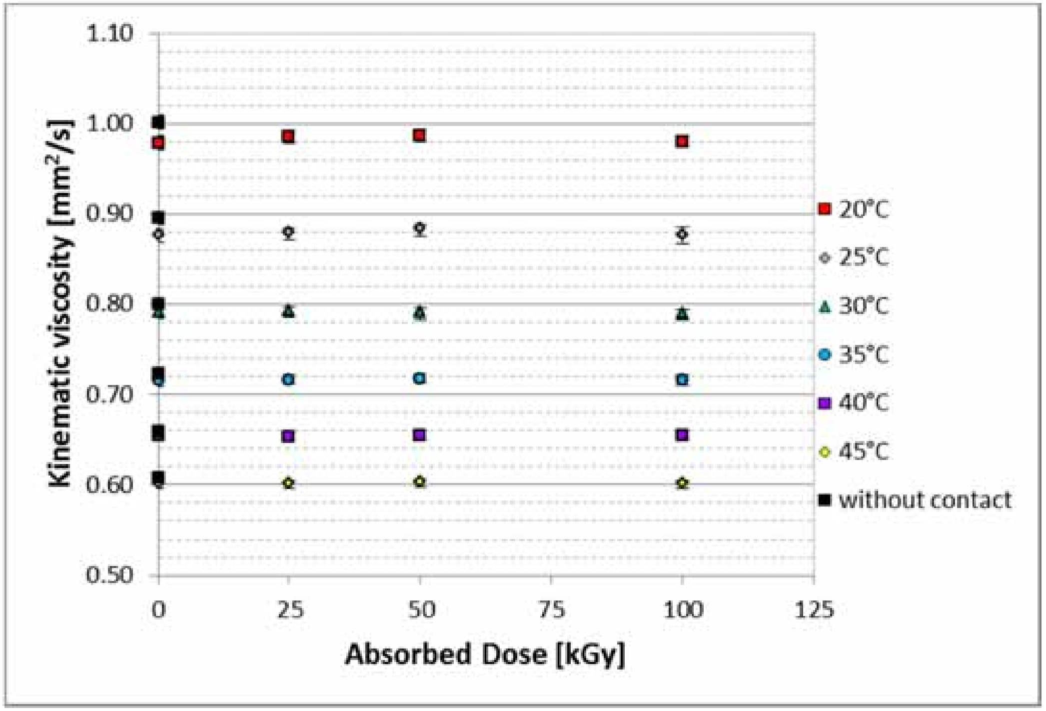
HNO_3 extraction in the organic phase due to contact

No modifications with the absorbed dose in the absorbed dose range considered

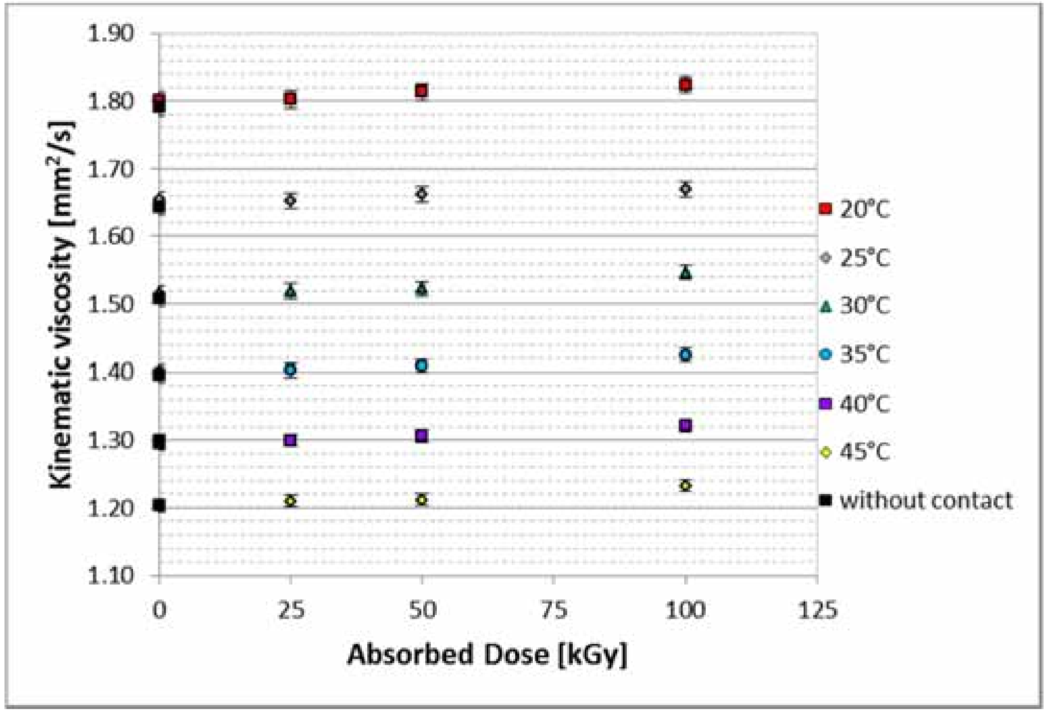
VISCOSITY

Temperature between 20°C and 45°C (±0.1°C) in thermostatic bath
KPG-UBBELOHDE micro-viscometer

Aqueous phase



Organic phase



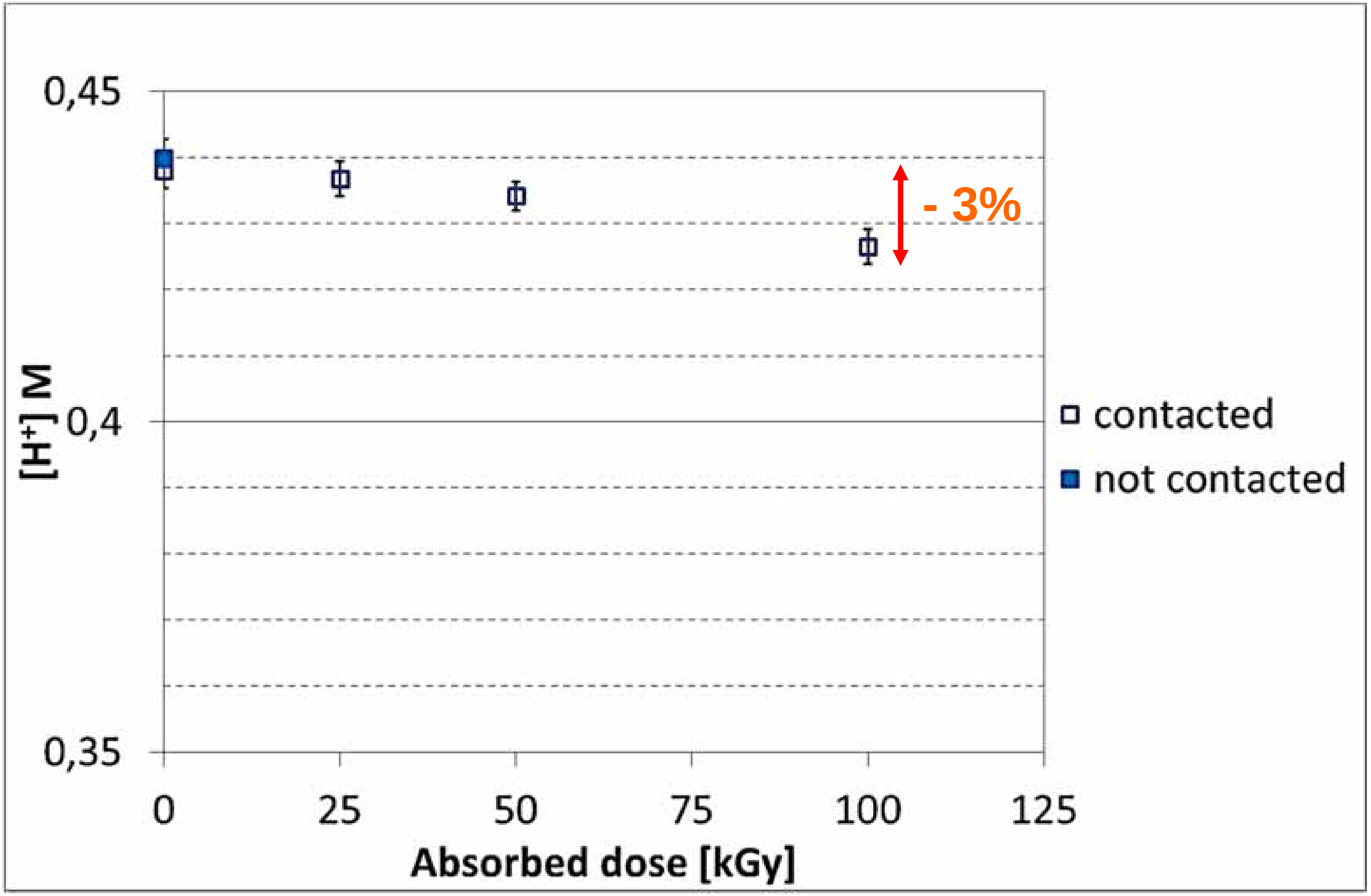
Modification of viscosity due to phase contacting, in agreement with density results

For the organic phase **slight increase of viscosity** with the absorbed dose

3. RESULTS - 0.44M HNO_3 + k/o 95:5 v/v system

pH (aqueous phase)

Titration with 0.1M NaOH and with methyl orange 0.1% Fluka solution

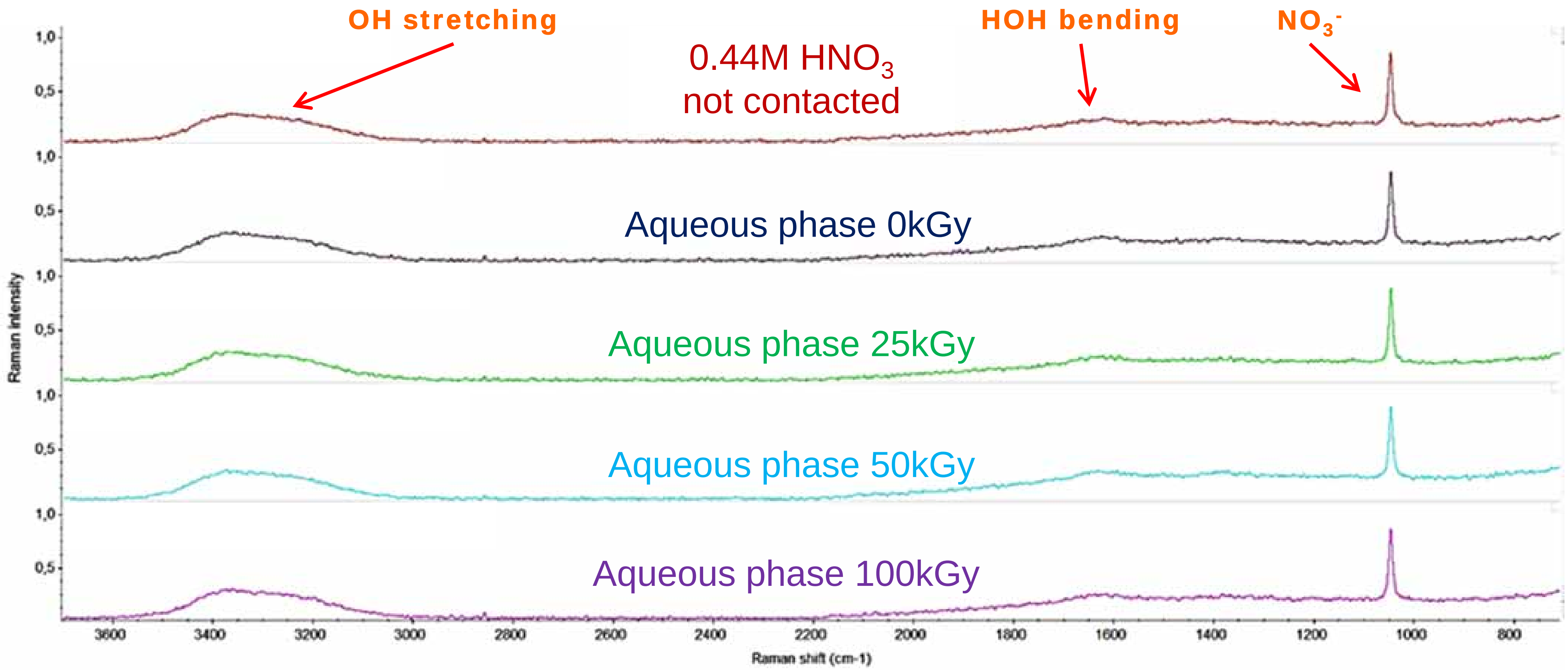


Slight acidity decrease with the absorbed dose

Investigations by FT-Raman (aqueous phase)

Thermo Electron NXR9650 FT-Raman spectrometer

1064nm Nd-YVO4 Laser, 500mWatt power on sample (in quartz NMR tubes)



No differences due to phases contact and irradiation

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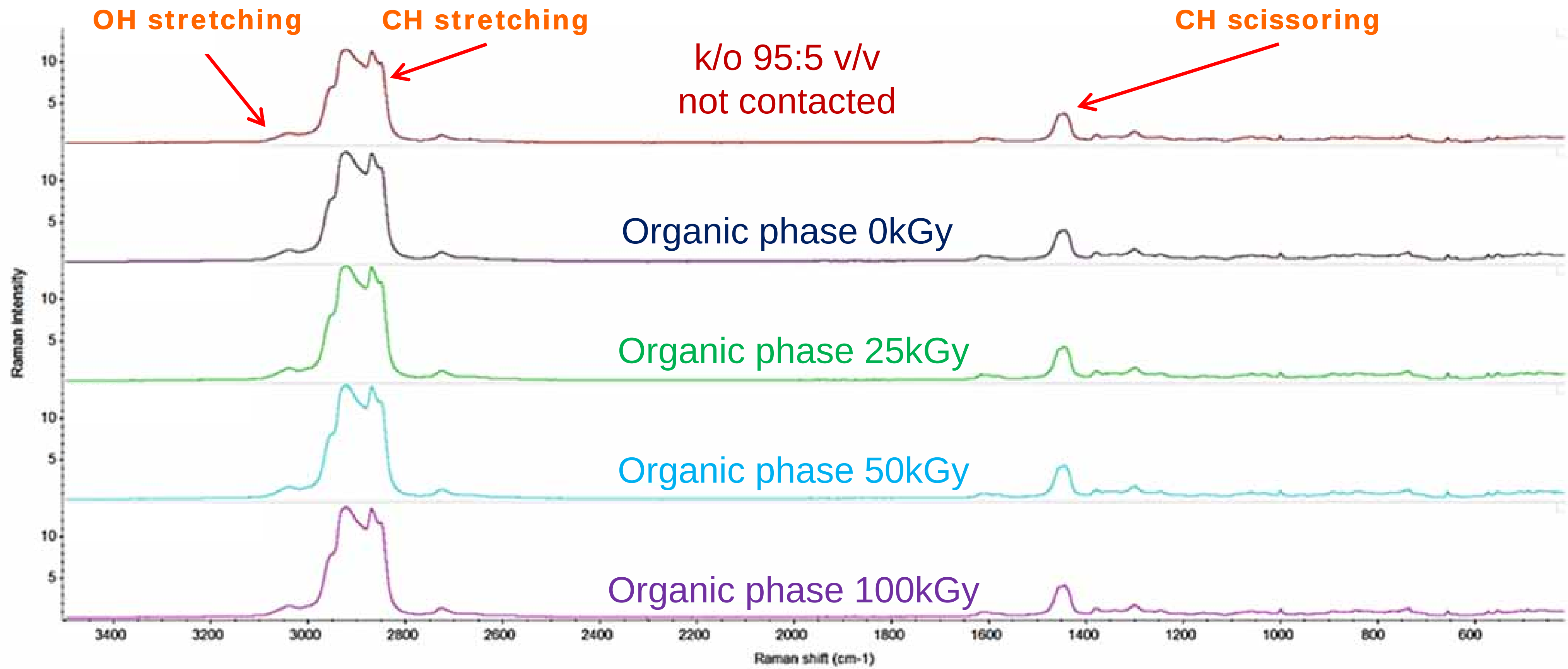
Investigations by FT-Raman (organic phase)

Thermo Electron NXR9650 FT-Raman spectrometer

1064nm Nd-YVO4 Laser, 500mWatt power on sample (in quartz NMR tubes)

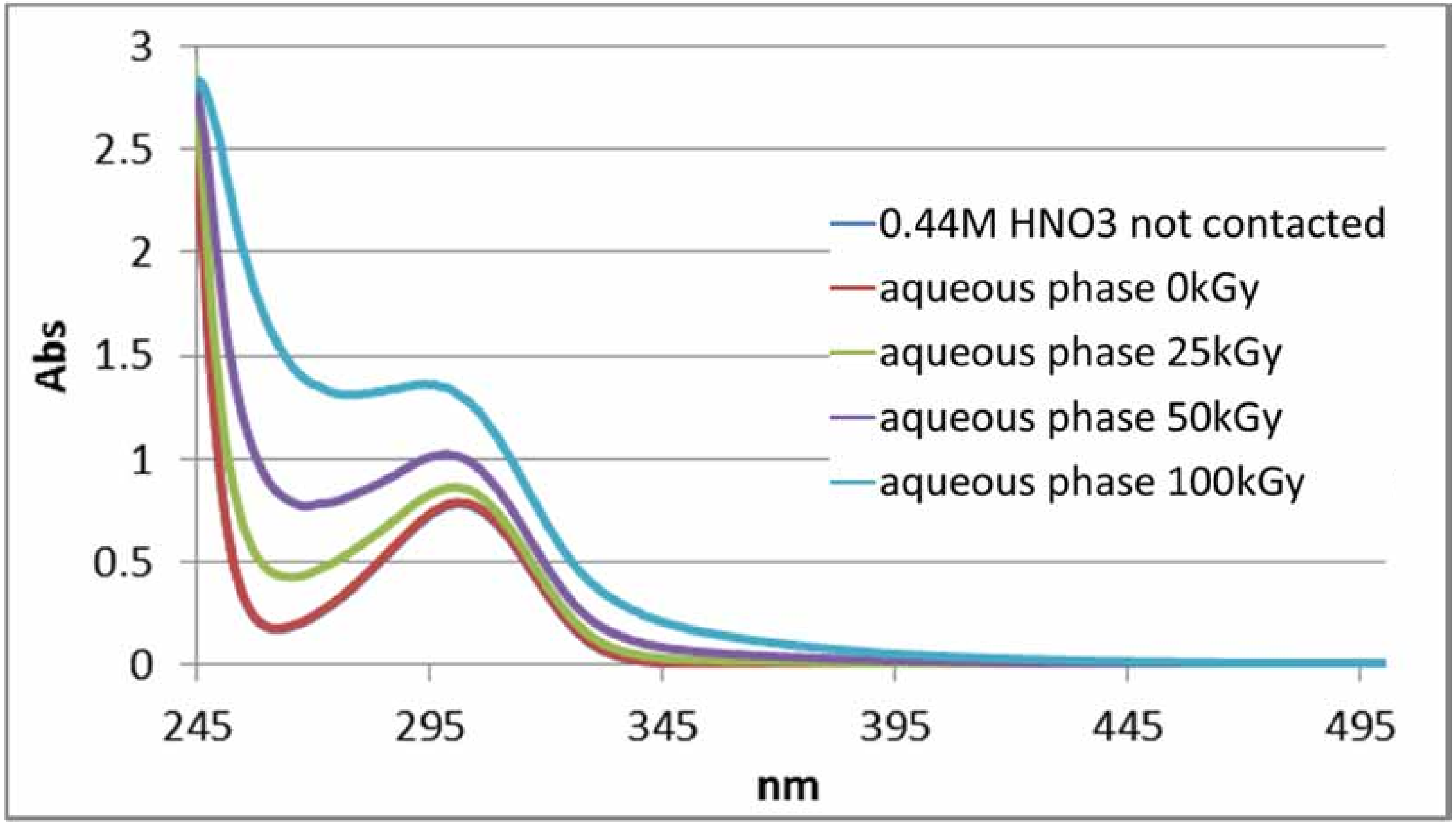


No differences due to phases contact and irradiation

3. RESULTS - 0.44M HNO_3 + k/o 95:5 v/v system

Aqueous phase [NO_3^-] by UV/Vis

Aqueous samples diluted 1:4 in water



No differences due to phases contact

[NO_3^-] evaluation not possible due to new signal at 250-280nm

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Final remarks

❑ **HNO_3 irradiated alone**

- No density, viscosity and pH modification due to irradiation
- $[NO_3^-]$ slightly decreases with irradiation

❑ **HNO_3 irradited in contact with kerosene/1-octanol**

- Density, viscosity and pH alteration due to 1-octanol/HNO_3 transfer
- Organic phase viscosity increases with absorbed dose
- Aqueous phase pH decreases with absorbed dose

Future work

➢ Investigations on by-products by GC-MS

➢ Phase transfer evaluation

- Assessment of FT-Raman sensibility
- FT-IR analyses on organic samples (higher sensibility)

➢ Study of complete i-SANEX solvent


232.038
+2
+3
+4
Th
ank
90
2-8-18-32-18-10-2
238.029
+2
+3
+4
+5
+6
Yo
U
92
2-8-18-32-21-9-2