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ICP-MS ANALYSES IN HYDRO-ORGANIC MATRICES: INTRODUCTION DEVICE SELECTION AND OPERATING PARAMETERS OPTIMIZATION

DE LA RECHERCHE À L'INDUSTRIE
cea den



European Winter Conference on Plasma Spectrochemistry

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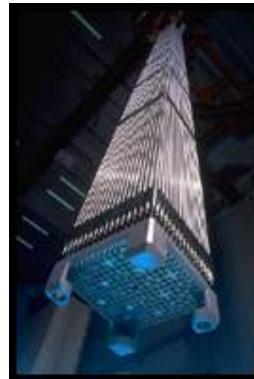
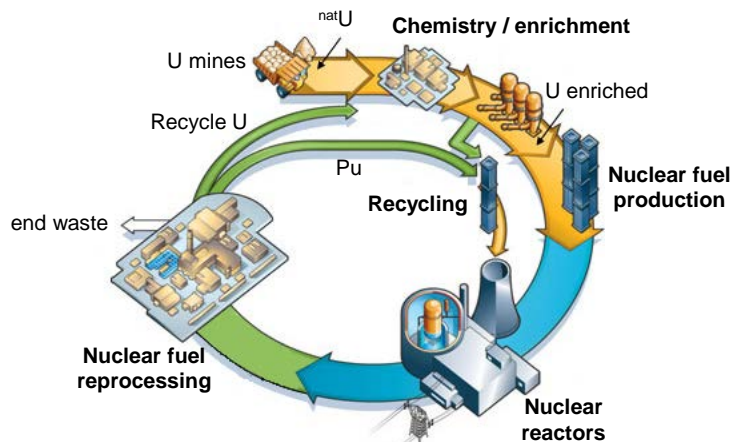
FEBRUARY 26, 2015

BACKGROUND & OBJECTIVES

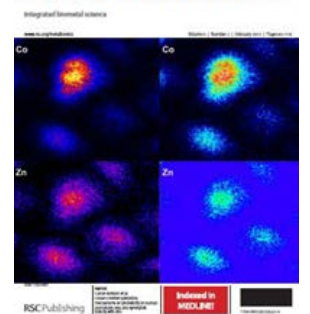
Nuclear applications

- High precision elemental & isotopic analyses of Actinides (An) & Fission Products (FP) by ICP-MS are required for fuel cycle characterizations & associated thematics:
 - Liquid-liquid extraction processes → process monitoring & nuclear waste management
 - Hyphenated separative techniques → spent nuclear fuel assay
 - Speciation studies → nuclear toxicology, etc.
 - Etc.

Analysis of samples in organic matrices



Metallomics

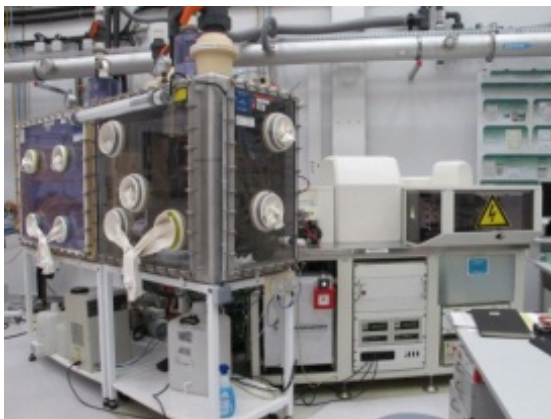


Objectives

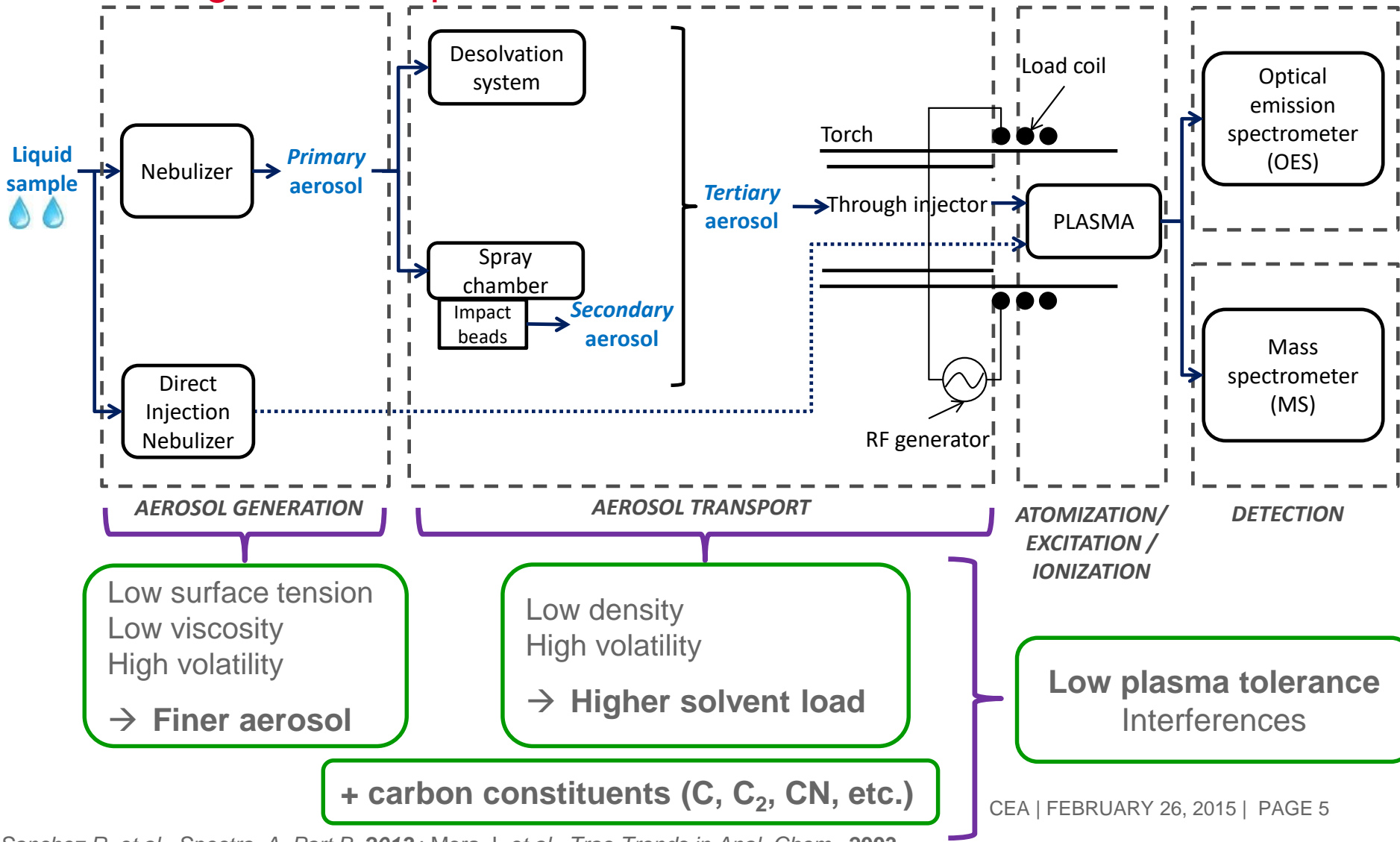
- CHOICE OF AN APPROPRIATE ICP INTRODUCTION DEVICE & OPTIMUM OPERATING CONDITIONS FOR VARIOUS NUCLEAR ORGANIC APPLICATIONS
 - Understanding organic solvents effects on ICP analytical performances
 - Comparative studies of various introduction devices
 - Optimization of relevant instrumental and operating parameters

- Additional constraints: radioactive samples
 - Nuclearized instruments
 - Glove box

} Adapted experimental setup



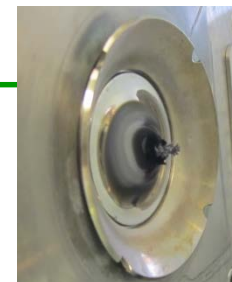
Organic vs. aqueous matrices



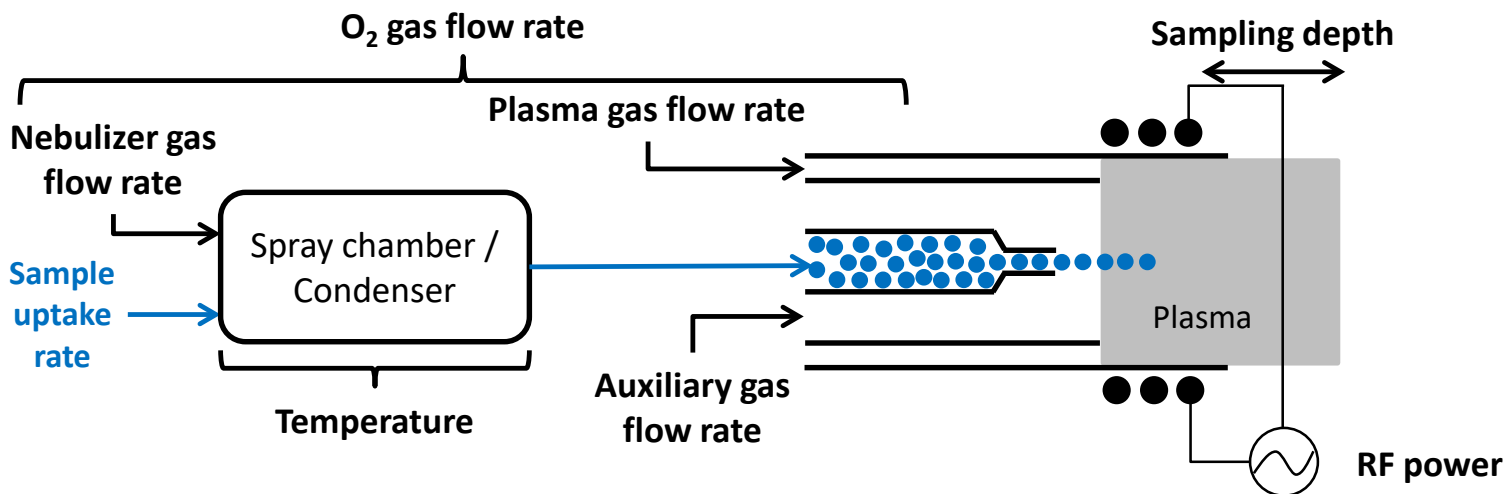
Organic matrices / ICP drawbacks

Modifications of analytical performances

- Plasma instabilities
- Spectral / non-spectral interferences
- Carbon deposition cone orifices clogging...
- Sensitivity losses
- Plasma switching off



ICP OPERATING PARAMETERS (sample introduction / plasma)



Organic matrices / ICP drawbacks

Degradation of analytical performances

- Plasma instabilities
- Spectral / non-spectral interferences
- Carbon deposition cone orifices clogging...
- Sensitivity losses
- Plasma switching off



ICP OPERATING PARAMETERS
(sample introduction / plasma)

INSTRUMENTATION



INJECTOR
- Inner diameter

INTRODUCTION DEVICES

FIRST FEASIBILITY TESTS WITH APEX

- **AcN**
 - Lack of literature data
 - Low plasma tolerance

- Constraints due to the glove boxes:
 - Small-sized introduction device
 - Easy-to-use & easy maintenance

INTRODUCTION DEVICES

- Classical spray chamber



- Basic configuration
 - Room temperature
 - No O₂ port

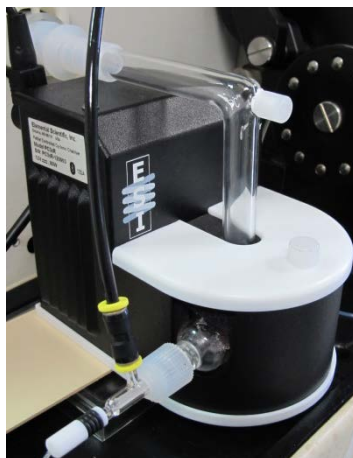
Low organic solvent tolerance

- Constraints due to the glove boxes:
 - Small-sized introduction device
 - Easy-to-use & easy maintenance

INTRODUCTION DEVICES

- Classical spray chamber
- Cooled (Peltier) cyclonic spray chamber with O₂ port (PC^{3X}, ESI)

PC^{3X}, ESI



- Widely studied in the state-of-art literature
- Tolerance for AcN to be confirmed
- O₂ port to avoid carbon deposition
- Cooling : ↘ solvent load

Intermediate organic solvent tolerance

Künnemeyer et al., EST, 2003
Gabel-Jensen et al., JAAS, 2008, 2009
Meermann et al., JAAS, 2010
Balcaen et al., Anal. Bioanal. Chem., 2007
 Etc.

- Constraints due to the glove boxes:
 - Small-sized introduction device
 - Easy-to-use & easy maintenance

INTRODUCTION DEVICES

- Classical spray chamber
- Cooled (Peltier) cyclonic spray chamber with O₂ port (PC^{3X}, ESI)
- Desolvation system (APEX, ESI)

APEX, ESI



- Less used in the state-of-art literature for high organic solvent contents
 - Desolvation: ↘ solvent load
 - ↗ sensitivity
 - No O₂ port
 - ACM & Spiro TMD membranes available

High organic solvent tolerance
Trace analyses

Analysis of 100 % AcN

INTRODUCTION DEVICE

- Desolvation device
(APEX, ESI)

- Less studied system
- Desolvation: \searrow solvent load
- \nearrow sensitivity: trace analysis
- No O₂ port
- Will be nuclearized with Neptune Plus

FIRST TESTS IN “STANDARDS” CONDITIONS (Q-ICP-MS):

- Different kinds of drawbacks: plasma extinction / carbon deposition



ANALYTICAL CONDITIONS

INSTRUMENTATION

Q-ICP-MS Xseries II Nebulizer PFA-ST, 100 $\mu\text{L min}^{-1}$
 APEX (ESI), -5 °C (multi-pass condenser) without
 spray chamber heating or additional N₂
 1 mm i.d. quartz injector (small orifice)

OPERATING CONDITIONS

P = 1.6 kW Nebulizer gas flow rate: 0.57 L min⁻¹
 O₂ gas flow rate: 60 mL min⁻¹

- Proven feasibility with good sensitivity up to 1 hour
- Design of experiment to be considered

OPERATING PARAMETERS

**MULTIPARAMETRIC & SYSTEMATIC
STUDIES FROM AQUEOUS TO HYDRO-
ORGANIC MATRICES**

**DESIGN OF EXPERIMENTS WITH
COOLED CYCLONIC SPRAY CHAMBER**

Optimization of operating parameters with AcN

Operating parameters

- Literature discrepancy (ex. RF power)
- Few statistical studies (parameters interactions)

INTRODUCTION DEVICE

- Cooled (Peltier) cyclonic spray chamber with O₂ port (PC^{3X}, ESI)

- Widely studied in the state-of-art literature
- Tolerance for AcN to be confirmed
- O₂ port to avoid carbon deposition
- Cooling : ↘ solvent load



PC^{3X}, ESI

DESIGN OF EXPERIMENTS (DOE)

1. Instrumental parameters hierarchy (Plackett & Burman design)
 - most relevant parameters for max. sensitivity / stability
2. Optimization of the main parameters (Doehlert optimization design)
 - parameter relationships

Reference test in aqueous medium

Hydro-organic medium

Künnemeyer et al., EST, 2003

Gabel-Jensen et al., JAAS, 2008, 2009

Meermann et al., JAAS, 2010

Balcaen et al., Anal. Bioanal. Chem., 2007

Etc.

Plackett & Burman design in aqueous medium (1/3)

— Reference test

ANALYTICAL CONDITIONS

SAMPLE

HNO₃ 2 %

Gd 6,1 ppb, Sm + Nd 8,5 ppb, Eu 2,5 ppb

INSTRUMENTATION

Q-ICP-MS Xseries II

Nebulizer PFA-ST

PC^{3X} (ESI)

2 mm i.d. quartz injector (standard)

SELECTED PARAMETERS

- Sample uptake rate ($\mu\text{L min}^{-1}$)
- Spray chamber temperature ($^{\circ}\text{C}$)
- Nebulizer gas flow rate (L min^{-1})
- Auxiliary gas flow rate (L min^{-1})
- Plasma gas flow rate (L min^{-1})
- Sampling depth (arbitrary unit)
- RF power (W)
- Extraction lens voltage (V)

Plackett & Burman design in aqueous medium (2/3)

— Reference test

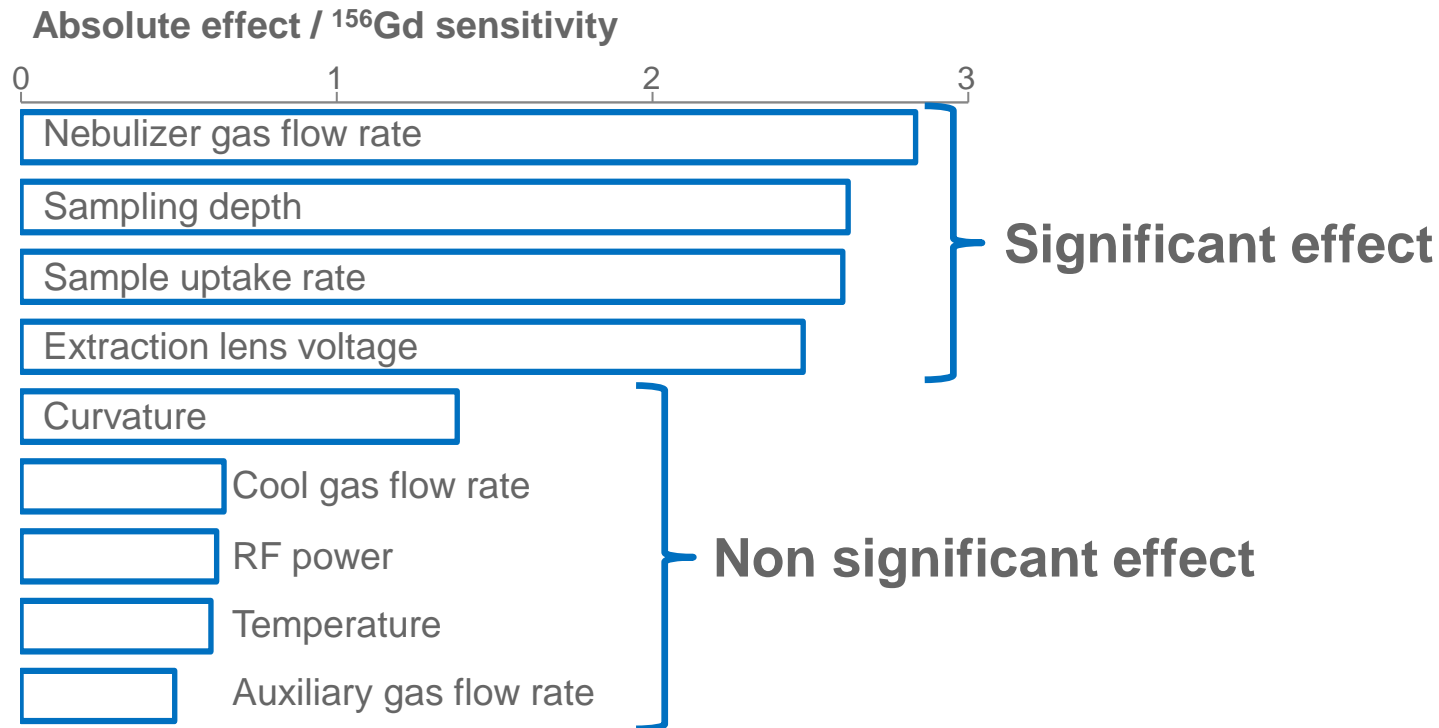
Variable Expe.	X1	X2	X3	X4	X5	X6	X7	X8
N°1	1	-1	1	-1	-1	-1	1	1
N° 2	1	1	-1	1	-1	-1	-1	1
N° 3	-1	1	1	-1	1	-1	-1	-1
N° 4	1	-1	1	1	-1	1	-1	-1
N° 5	1	1	-1	1	1	-1	1	-1
N° 6	1	1	1	-1	1	1	-1	1
N° 7	-1	1	1	1	-1	1	1	-1
N° 8	-1	-1	1	1	1	-1	1	1
N° 9	-1	-1	-1	1	1	1	-1	1
N° 10	1	-1	-1	-1	1	1	1	-1
N° 11	-1	1	-1	-1	-1	1	1	1
N° 12	-1	-1	-1	-1	-1	-1	-1	-1
N° 13 (n times)	0	0	0	0	0	0	0	0

Variable Expe.	-1	+1	0
Uptake	20	400	200
Temperature	+2	+6	+4
Neb. gas	0.6	1.0	0.8
Aux. gas	0.7	1.1	0.9
Cool gas	15.0	16.0	15.5
Sampling depth	70	300	185
RF power	1,400	1,500	1,450
Ext. lens voltage	-990	-690	-840

**Relevant instrumental parameters
limits experimentally determined
→ not an easy task**

Plackett & Burman design in aqueous medium (3/3)

— Reference test



→ 4 main parameters to be optimized in aqueous medium

Plackett & Burman design in hydro-organic medium (1/4)

ANALYTICAL CONDITIONS

SAMPLE

25 % AcN / 75 % HNO₃ 2 %

Gd 17 ppb, Sm + Nd 23 ppb, Eu 7 ppb

INSTRUMENTATION

Q-ICP-MS Xseries II

Nebulizer PFA-ST

PC^{3X} (ESI)

2 mm i.d. quartz injector (standard)

SELECTED PARAMETERS

- Sample uptake rate ($\mu\text{L min}^{-1}$)
- Spray chamber temperature ($^{\circ}\text{C}$)
- Nebulizer gas flow rate (L min^{-1})
- Auxiliary gas flow rate (L min^{-1})
- Plasma gas flow rate (L min^{-1})
- Sampling depth (arbitrary unit)
- RF power (W)
- ~~Extraction lens voltage (V)~~
- O₂ gas flow rate → fixed (10 mL min^{-1})

Variable \ Expe.	-1	+1	0
Uptake	20	100	50
Temperature	-3	+3	0
Neb. gas	0.6	0.9	0.8
Aux. gas	0.8	1.0	0,9
Cool gas	15.0	17.0	16.0
Sampling depth	70	300	185
RF power	1,300	1,500	1,400

↘ solvent load

wider range

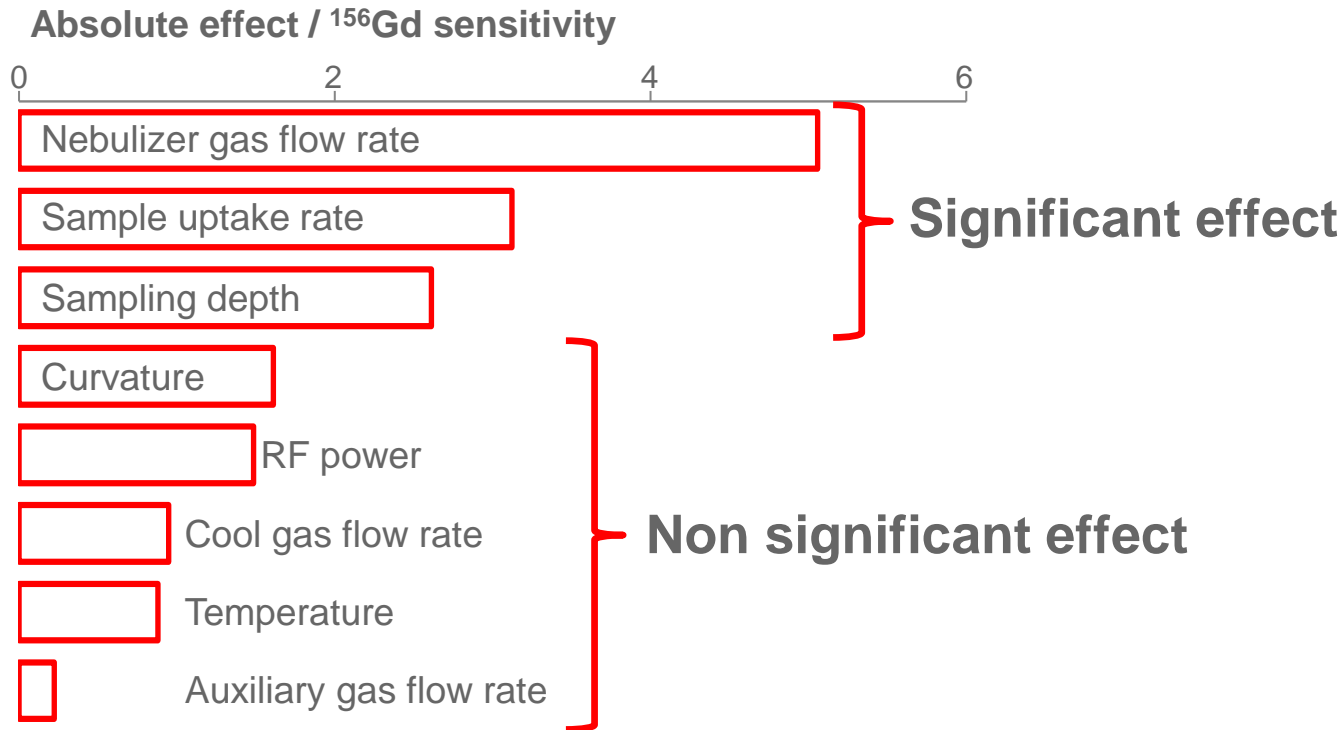
Relevant instrumental parameters limits experimentally determined

→ not an easy task

→ more difficult for organic vs. aqueous samples

→ O₂ introduction fixed (plasma extinction)

Plackett & Burman design in hydro-organic medium (2/4)



→ 3 main parameters to be optimized in hydro-organic medium

Plackett & Burman design in hydro-organic medium (3/4)

ANALYTICAL CONDITIONS

SAMPLE

25 % AcN / 75 % HNO₃ 2 %

Gd 17 ppb, Sm + Nd 23 ppb, Eu 7 ppb

INSTRUMENTATION

Q-ICP-MS Xseries II

Nebulizer PFA-ST

PC^{3X} (ESI)

1 mm i.d. quartz injector (reduced)

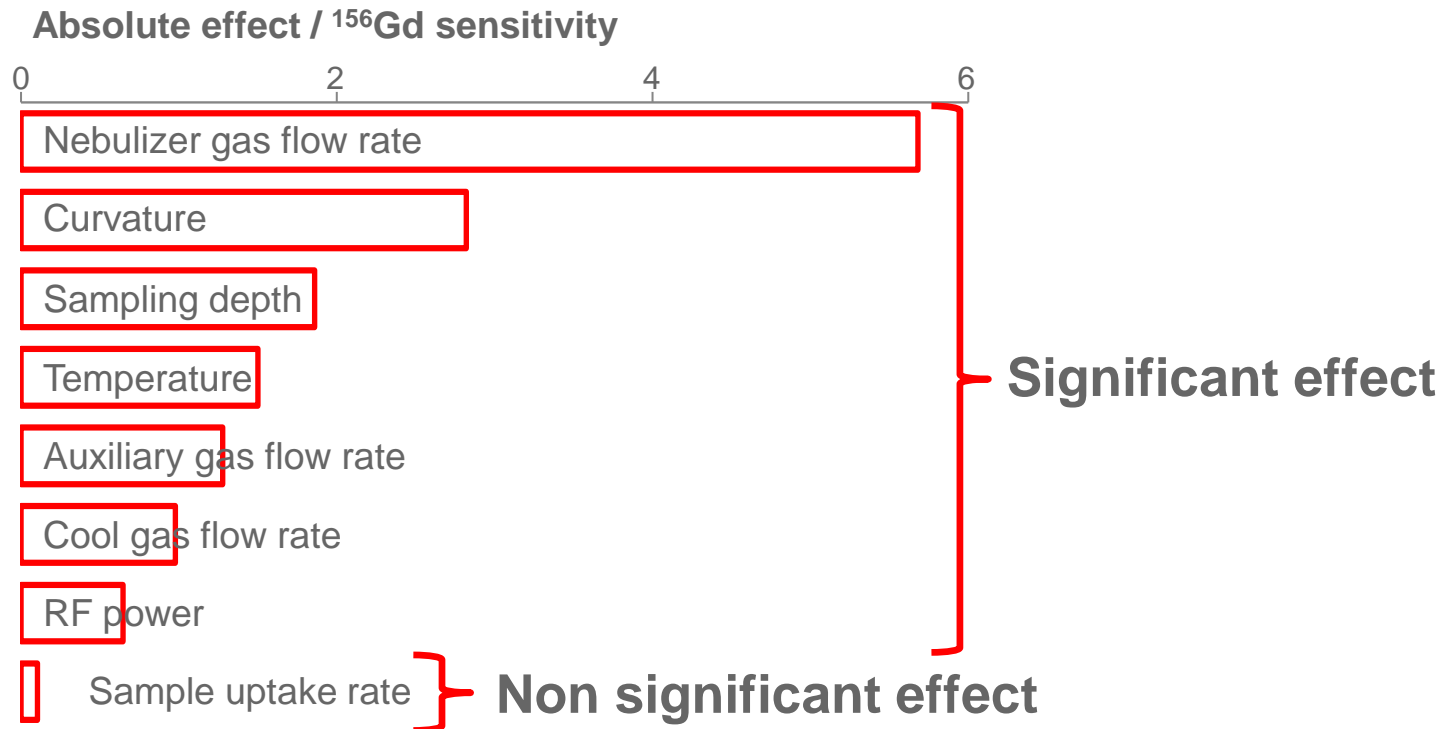
SELECTED PARAMETERS

- Sample uptake rate ($\mu\text{L min}^{-1}$)
- Spray chamber temperature ($^{\circ}\text{C}$)
- Nebulizer gas flow rate (L min^{-1})
- Auxiliary gas flow rate (L min^{-1})
- Plasma gas flow rate (L min^{-1})
- Sampling depth (arbitrary unit)
- Induced power (W)
- ~~Extraction lens voltage (V)~~
- O₂ gas flow rate → fixed (10 mL min^{-1})

Variable \ Expe.	-1	+1	0
Uptake	20	100	50
T. chamber	-3	+3	0
Neb. gas	0.4	0.7	0.8
Aux. gas	0.8	1.0	0,9
Cool gas	15.0	17.0	16.0
Sampling depth	70	300	185
Power	1,300	1,500	1,400

↗ residence time

Plackett & Burman design in hydro-organic medium (4/4)



- 6 main parameters to be optimized in hydro-organic medium
- Significant effect of the curvature

CONCLUSIONS AND OUTLOOK

Objectives

- CHOICE OF AN APPROPRIATE ICP INTRODUCTION DEVICE & OPTIMUM OPERATING CONDITIONS FOR VARIOUS NUCLEAR ORGANIC APPLICATIONS
 - Understanding organic solvents effects on ICP analytical performances
 - Comparative studies of various introduction devices
 - Optimization of relevant instrumental and operating parameters

FIRST FEASIBILITY TESTS WITH APEX

Proven feasibility at 100 %
AcN with good sensitivity in
1 hour

Outlook in organic medium

Use of desolvation membranes:

- ACM (Activated Cooled Membrane, ESI)
- Spiro TMD (Teflon® Membrane Desolvation, ESI)

APEX: DOE ?

Other introduction devices (miniaturized systems, etc.)

PLACKETT & BURMAN DOE WITH PC^{3X}

Aqueous medium
- 4 main parameters to be optimized

Hydro-organic medium

- 2 mm i.d. injector diameter: 3 parameters to be optimized
- 1 mm i.d. injector diameter: 6 parameters to be optimized

Outlook in hydro-organic medium

Doehlert optimization design
→ Parameter relationships

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THANK YOU FOR YOUR ATTENTION

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