Icp-ms analyses in hydro-organic matrices: introduction device selection and operating parameters optimization

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

European Winter Conference on Plasma Spectrochemistry

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EWCPS 2015

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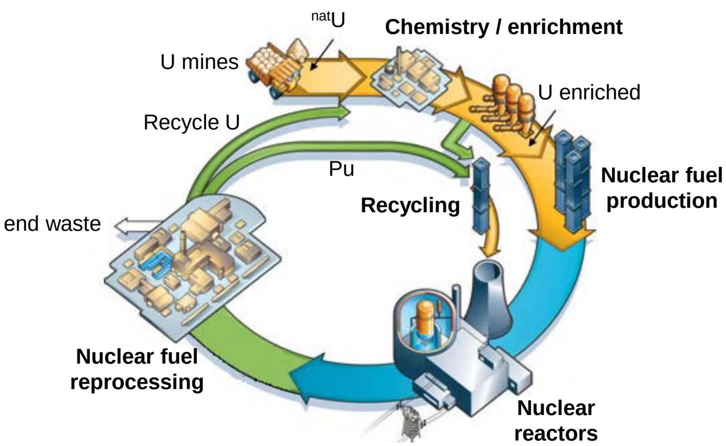
BACKGROUND & OBJECTIVES

BACKGROUND & OBJECTIVES (1/5)

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



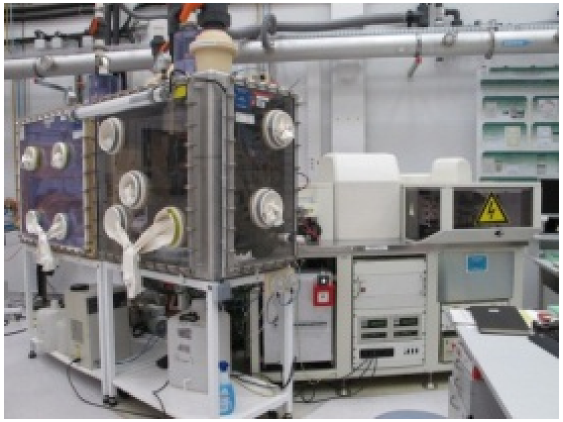
BACKGROUND & OBJECTIVES (2/5)

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

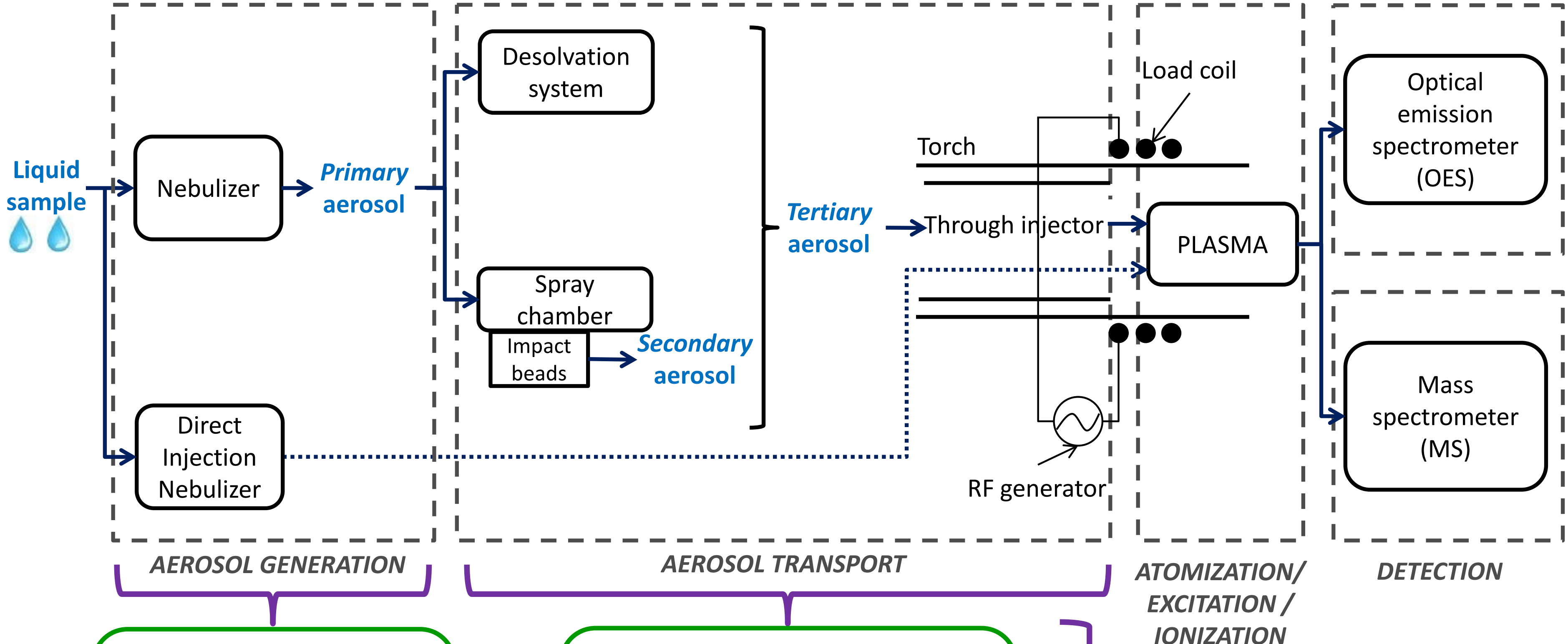
- Additional constraints: radioactive samples
  - Nuclearized instruments
  - Glove box

} **Adapted experimental setup**



BACKGROUND & OBJECTIVES (3/5)

Organic *vs.* aqueous matrices



Low surface tension
Low viscosity
High volatility

→ **Finer aerosol**

Low density
High volatility

→ **Higher solvent load**

Low plasma tolerance
Interferences

+ carbon constituents (C, C_2, CN, etc.)

Sanchez R. et al., Spectro. A. Part B, ***2013*** ; Mora J. *et al., Trac-Trends in Anal. Chem.*, **2003**

BACKGROUND & OBJECTIVES (4/5)

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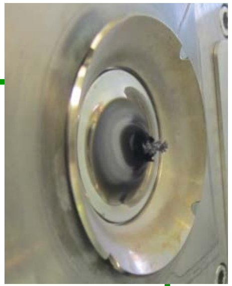
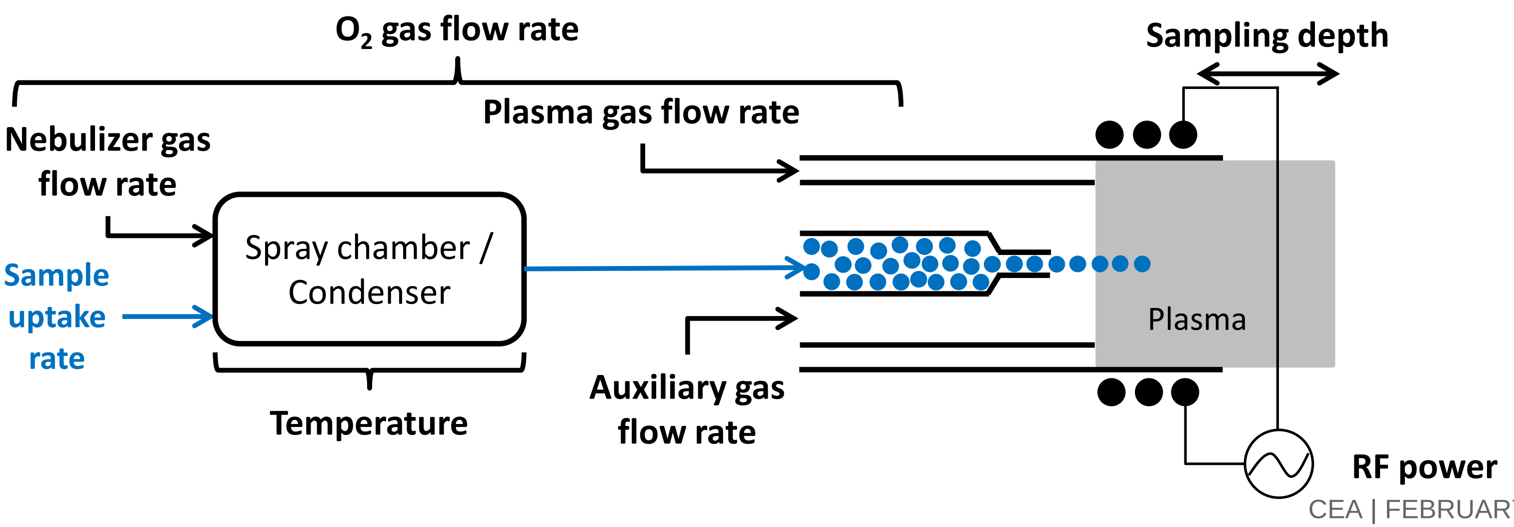
Organic matrices / ICP drawbacks

Modifications of analytical performances

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



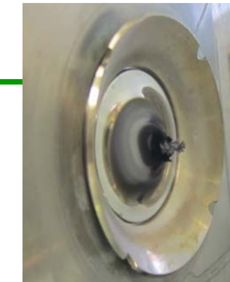
ICP OPERATING PARAMETERS
(sample introduction / plasma)



Albarede F. et al., Mine. Soc. Amer., ***2004*** ; Houk R.S., *Anal. Chem.*, **1986**

BACKGROUND & OBJECTIVES (5/5)

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

INTRODUCTION DEVICES (1/3)

- **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 O_2 port

Low organic solvent tolerance

INTRODUCTION DEVICES (2/3)

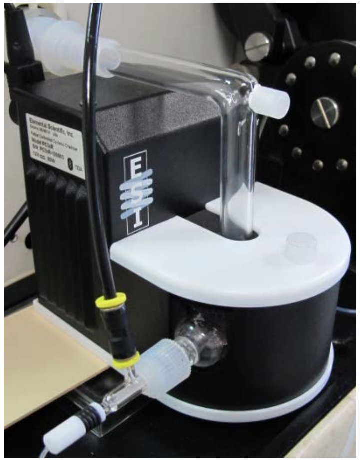
- Constraints due to the glove boxes:
  - Small-sized introduction device
  - Easy-to-use & easy maintenance

INTRODUCTION DEVICES

- Classical spray chamber

- Cooled (Peltier) cyclonic spray chamber with O_2 port (PC^{3X}, ESI)

PC^{3X}, ESI



- Widely studied in the state-of-art literature
- Tolerance for AcN to be confirmed
- O_2 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.

INTRODUCTION DEVICES (3/3)

- 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 O_2 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 O_2 port
  - ACM & Spiro TMD membranes available

High organic solvent tolerance
Trace analyses

Sacks et al., Anal. Chem., ***2006***

FIRST FEASIBILITY TESTS WITH APEX

Analysis of 100 % AcN

INTRODUCTION DEVICE

- Desolvation device (APEX, ESI)

→

- Less studied system
- Desolvation: ↘ solvent load
- ↗ sensitivity: trace analysis
- No O_2 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 µL min^{-1}**

APEX (ESI), **-5 °C (multi-pass condenser) without spray chamber heating or additional N_2**

1 mm i.d. quartz injector (small orifice)

OPERATING CONDITIONS

P = 1.6 kW Nebulizer gas flow rate: 0.57 L min^{-1}

O_2 gas flow rate: 60 mL min^{-1}

→ **Proven feasibility with good sensitivity up to 1 hour**

→ **Design of experiment to be considered**

OPERATING PARAMETERS

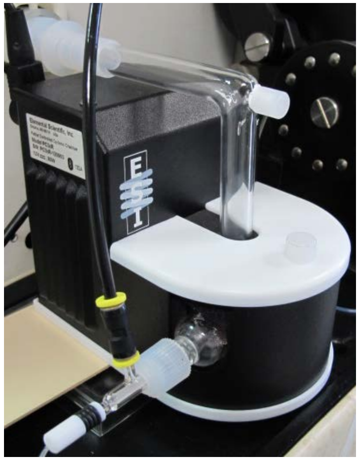
MULTIPARAMETRIC & SYSTEMATIC STUDIES FROM AQUEOUS TO HYDRO-ORGANIC MATRICES

DESIGN OF EXPERIMENTS WITH COOLED CYCLONIC SPRAY CHAMBER

DESIGN OF EXPERIMENTS (1/8)

Optimization of operating parameters with AcN

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



PC^{3X}, ESI

INTRODUCTION DEVICE

- Cooled (Peltier) cyclonic spray chamber with O_2 port (PC^{3X}, ESI)

→

- Widely studied in the state-of-art literature
- Tolerance for AcN to be confirmed
- O_2 port to avoid carbon deposition
- Cooling : ↘ solvent load

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.

DESIGN OF EXPERIMENTS (2/8)

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

- Reference test

ANALYTICAL CONDITIONS

SAMPLE
HNO_3 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 (µL min^{-1})
- Spray chamber temperature (°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)

DESIGN OF EXPERIMENTS (3/8)

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

- Reference test

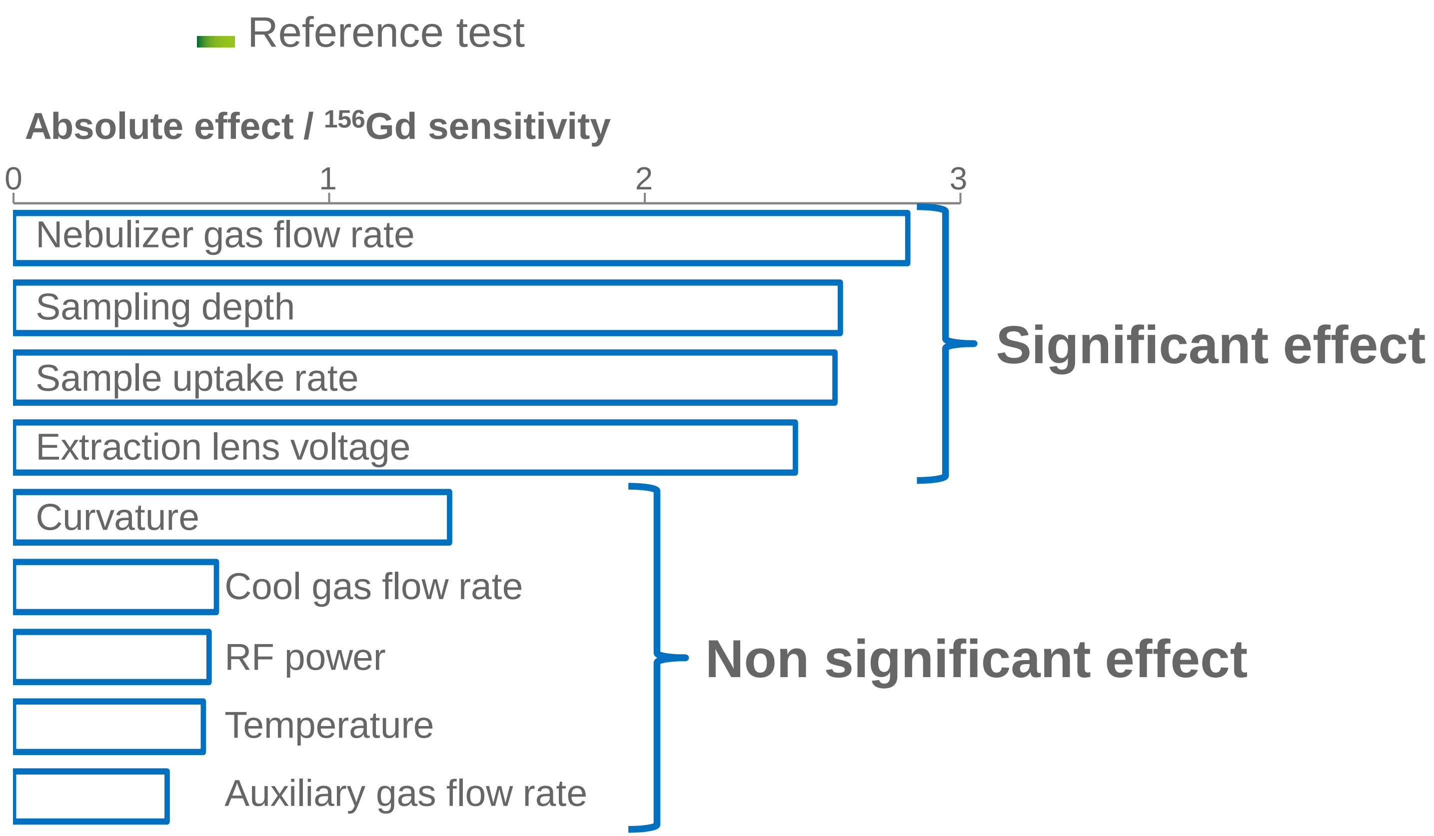
Expe. \ Variable	X1	X2	X3	X4	X5	X6	X7	X8
N°1	1	-1	1	-1	-1	-1	1	1
N° 2	1	1	-1	1	-1	-1	-1	1
N° 3	-1	1	1	-1	1	-1	-1	-1
N° 4	1	-1	1	1	-1	1	-1	-1
N° 5	1	1	-1	1	1	-1	1	-1
N° 6	1	1	1	-1	1	1	-1	1
N° 7	-1	1	1	1	-1	1	1	-1
N° 8	-1	-1	1	1	1	-1	1	1
N° 9	-1	-1	-1	1	1	1	-1	1
N° 10	1	-1	-1	-1	1	1	1	-1
N° 11	-1	1	-1	-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

DESIGN OF EXPERIMENTS (4/8)

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



→ **4 main parameters to be optimized in aqueous medium**

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DESIGN OF EXPERIMENTS (5/8)

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

ANALYTICAL CONDITIONS

SAMPLE

25 % AcN / 75 % HNO_3 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 (µL min^{-1})
- Spray chamber temperature (°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)~~
- O_2 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

Uptake to Aux. gas: **↘ solvent load**

Cool gas to RF power: **wider range**

Relevant instrumental parameters limits experimentally determined

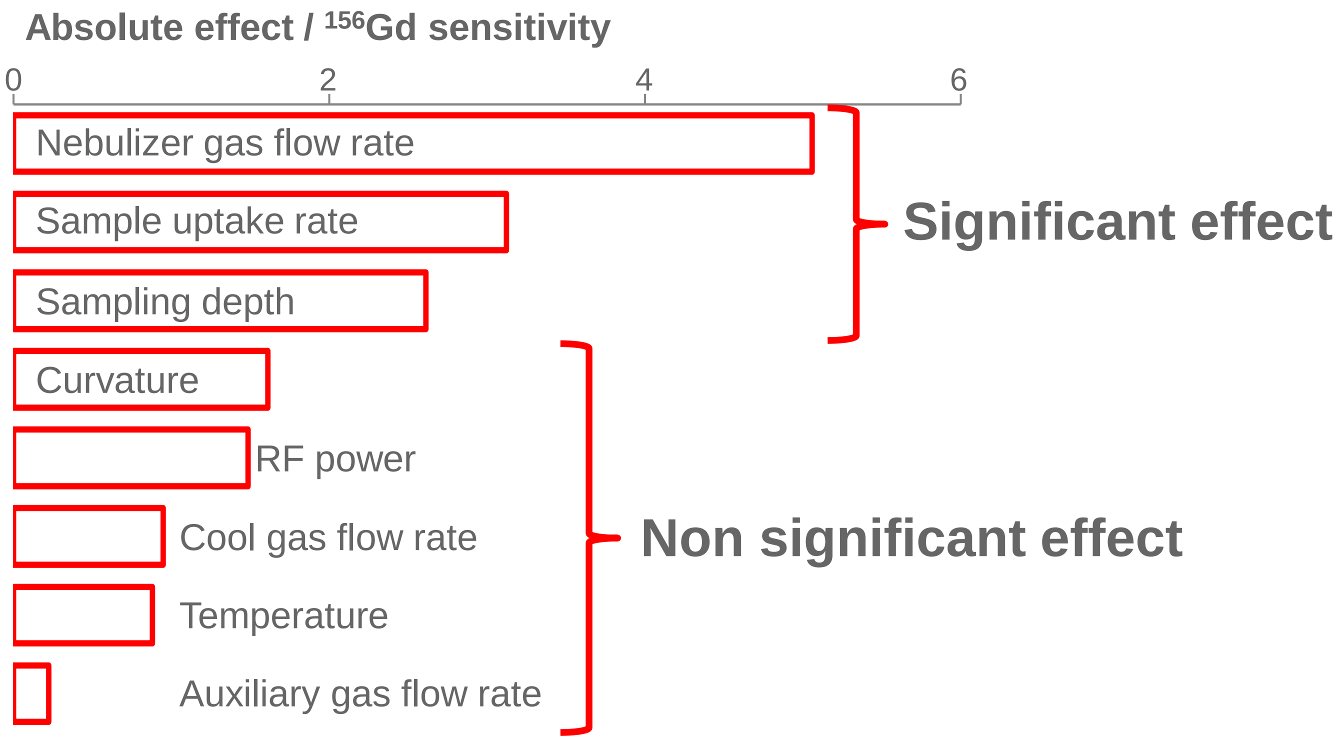
→ **not an easy task**

→ more difficult for organic vs. aqueous samples

→ O_2 introduction fixed (plasma extinction)

DESIGN OF EXPERIMENTS (6/8)

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



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

DESIGN OF EXPERIMENTS (7/8)

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

ANALYTICAL CONDITIONS

SAMPLE
25 % AcN / 75 % HNO_3 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

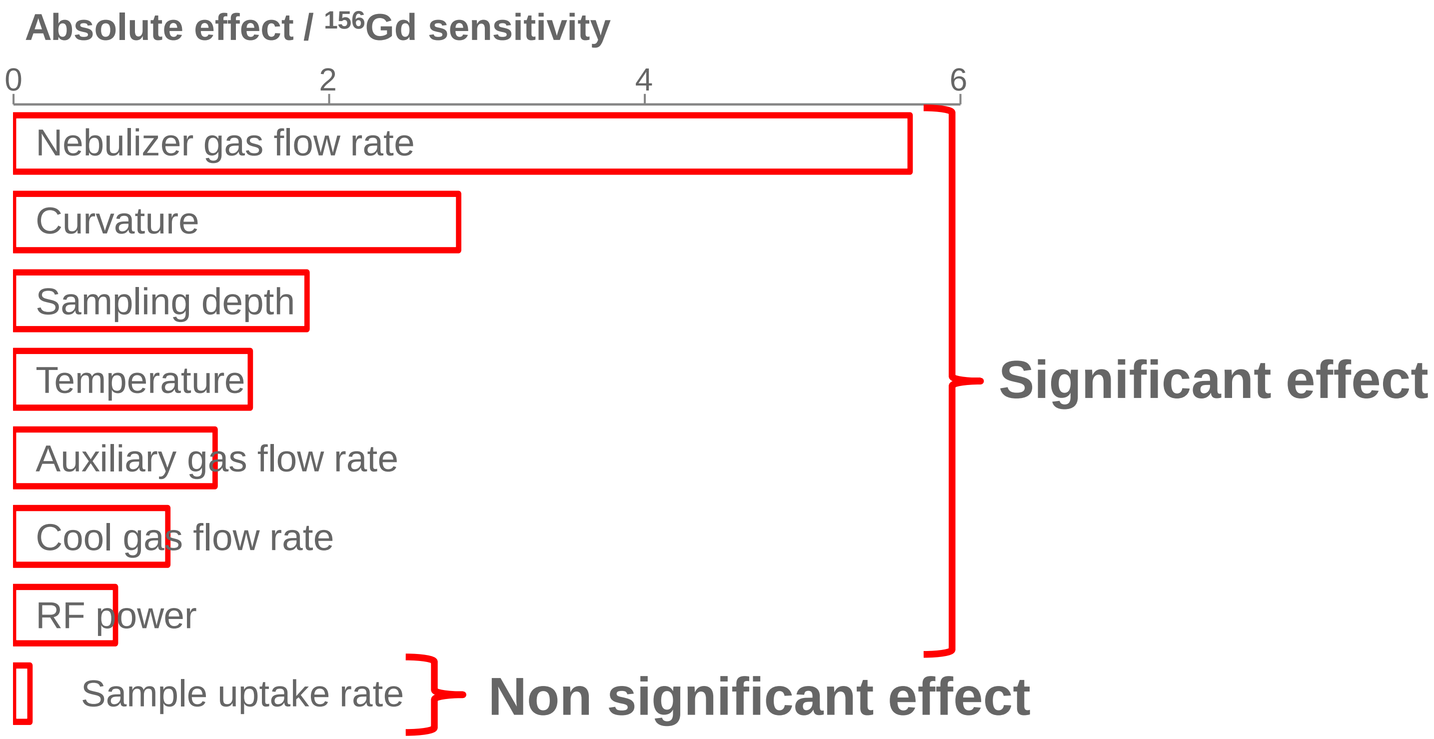
- Sample uptake rate (µL min^{-1})
- Spray chamber temperature (°C)
- Nebulizer gas flow rate (L min^{-1})
- Auxiliary gas flow rate (L min^{-1})
- Plasma gas flow rate (L min^{-1})
- Sampling depth (arbitrary unit)
- Induced power (W)
- ~~Extraction lens voltage (V)~~
- O_2 gas flow rate → fixed (10 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**

DESIGN OF EXPERIMENTS (8/8)

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

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 (Actived 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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