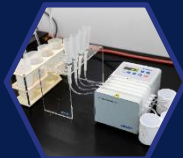


DEVELOPMENT OF NEW LOW-LEVEL METHOD FOR THE ANALYSIS OF IODINE 129 AND THE ISOTOPIC RATIO $^{129}\text{I}/^{127}\text{I}$ DETERMINATION

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RAN'0

3RD INTERNATIONAL CONFERENCE
ON RADIOANALYTICAL AND NUCLEAR
CHEMISTRY

7-12 May 2023
Budapest, Hungary

IODINE : ORIGIN AND INTEREST

Volatil halogen

Exist under many organic and inorganic forms

- I, 0, +I, +III, +IV and +VII
- IO_3^- , I^- , I_2 , CH_3I , HOI , HIO_4 , HIO_3 , I_3^- , IO_5H^{2-} , IO_5^{3-}



The only natural radioisotope of iodine

$T_{1/2} = 16.1 \times 10^6$ years

Natural origin:

- Reactions of cosmic rays with ^{129}Xe in the upper atmosphere
- Spontaneous fission of ^{238}U

Anthropogenic origin: produced by neutron-induced fission of ^{235}U and ^{239}Pu

Released simultaneously with ^{131}I ($t_{1/2} = 8.02$ days) in case of nuclear power plant accident

→ ^{129}I excellent tracer

Often measured by:

- Gamma and X-ray spectrometry
- Liquid Scintillation Counting

Don't allow the isotopic ratio $^{129}\text{I}/^{127}\text{I}$ determination

- $\beta^- \rightarrow E_{\text{max}} = 154$ keV (100%)
- $\gamma \rightarrow 39.6$ keV (7.42%)
- X $\rightarrow 29.8$ keV (37.8%)

- Accelerator mass spectrometry →

Not accessible to every laboratory

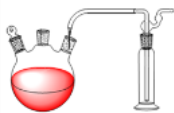


Objectives : 3 steps

Extraction

Large sample size
No loss of iodine

Acid digestion



Purification

Environmental friendly
Optimized purification
Adapted to measurement

Liquid chromatography



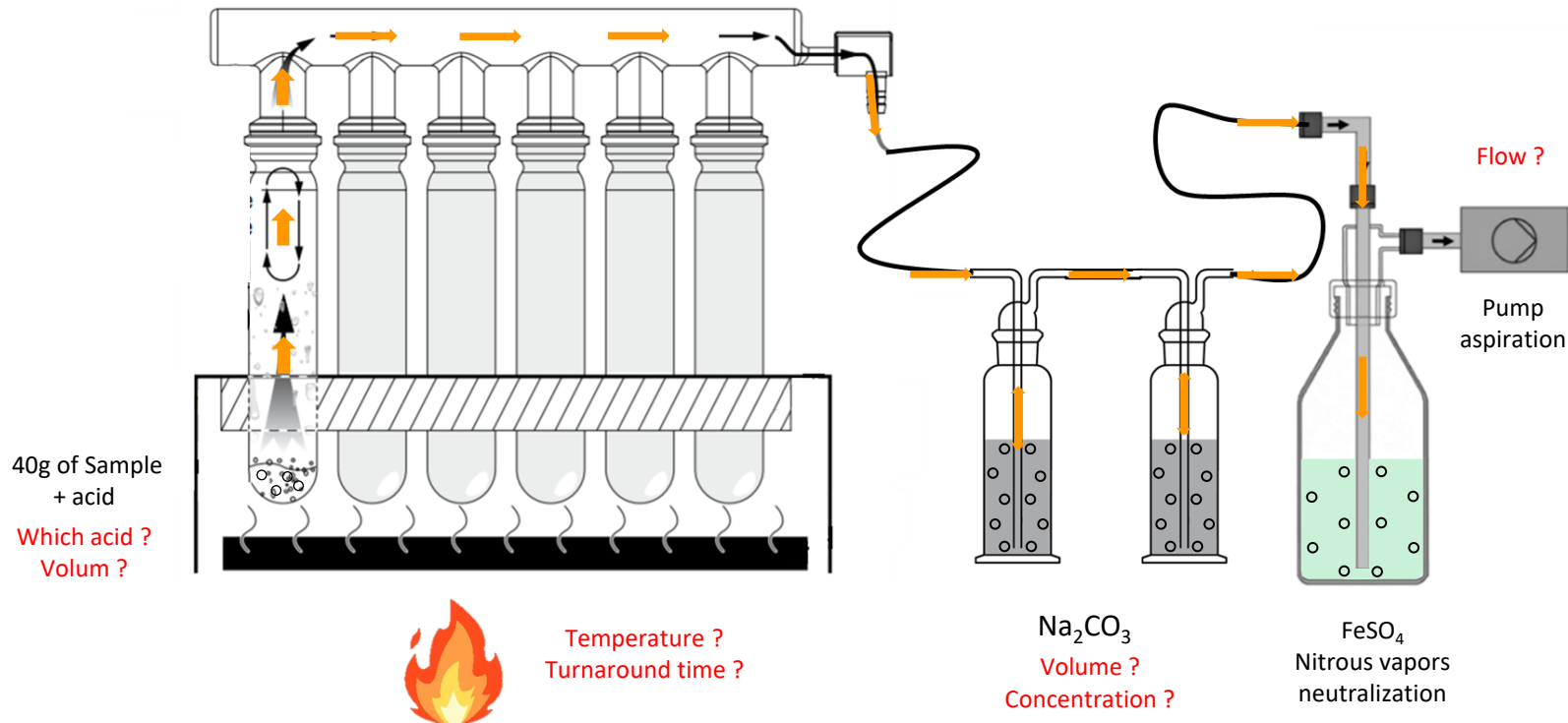
Mesure

Low detection limit
Isotopic ratio $^{129}\text{I}/^{127}\text{I}$
Optimized turnaround time

ICP-MS/MS



ACID DIGESTION : DESIGN OF EXPERIMENTS (DOE)



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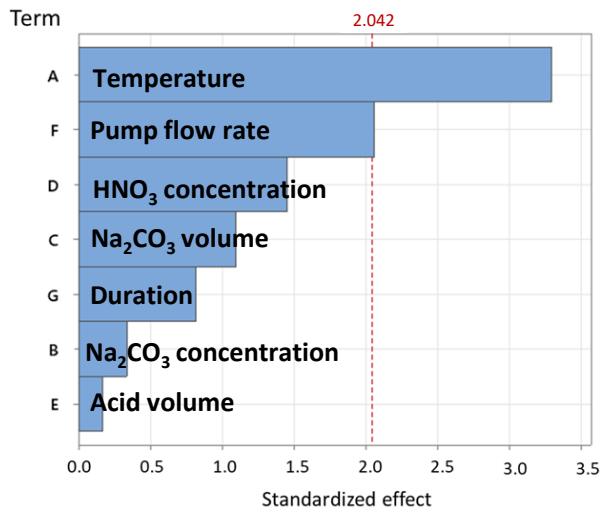
Resolution IV

2 double points

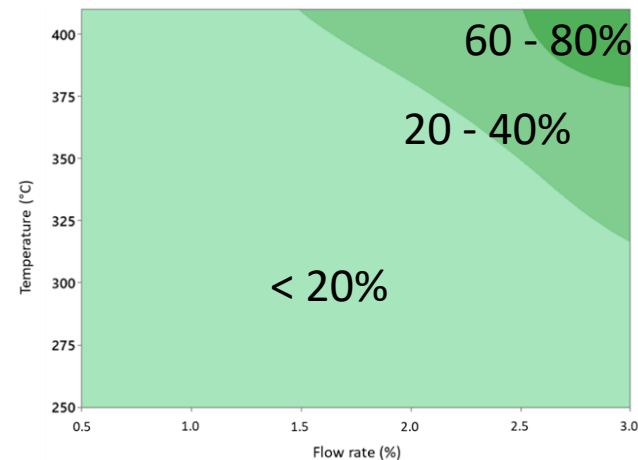
3 central points

→ 78 experiments

Parameter	Value
Pump flow rate	15 L/min
Acid volume	100 mL
HNO ₃ concentration	8 M
Na ₂ CO ₃ concentration	50 mL
Na ₂ CO ₃ volume	6 mM
Temperature	410 °C
Duration	30 min



Flow rate + temperature

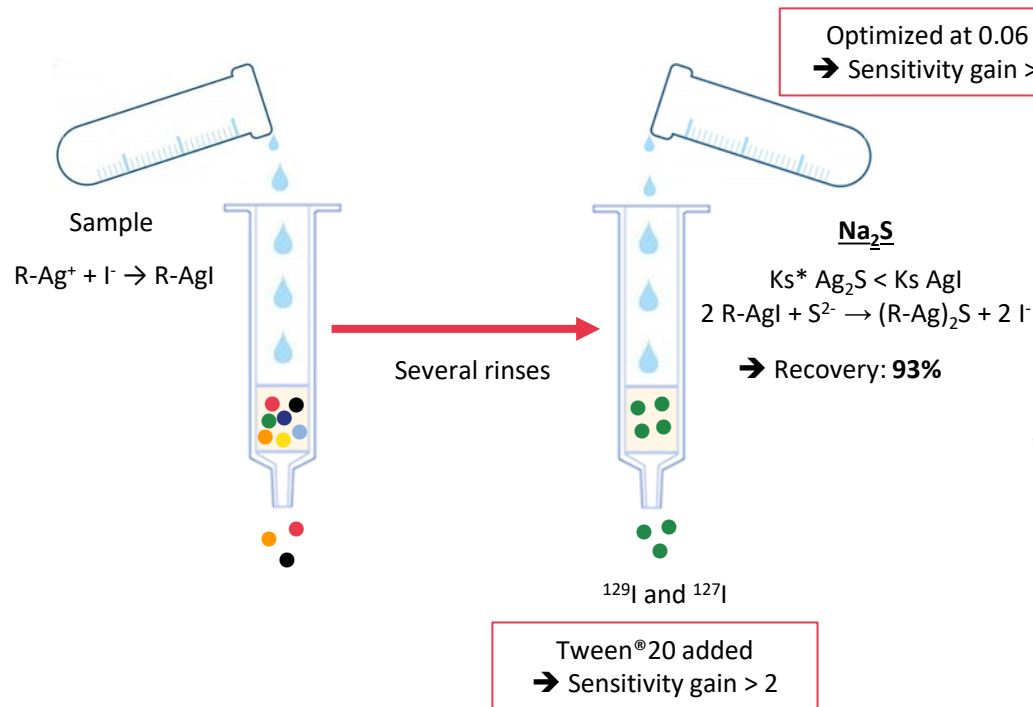


Variation of extraction yield with temperature and pump flow rate

Purification ?

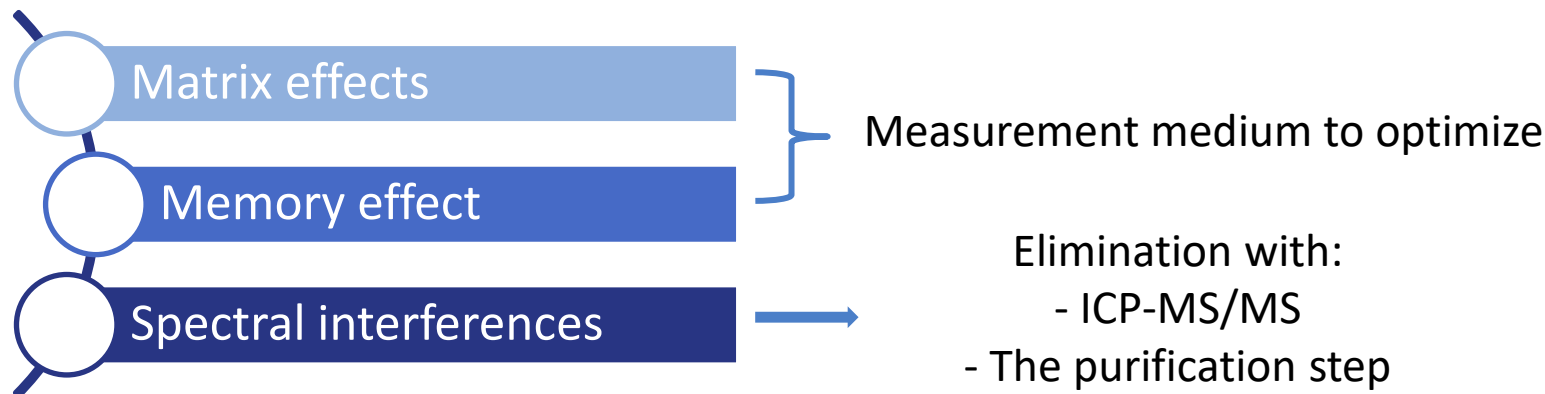
Sample purification

SOLID PHASE EXTRACTION (SPE): CL RESIN INITIALLY DESTINATED TO LSC* MEASUREMENT



- ✓ Purification duration < 40 min with optimized flow rates
- ✓ Optimization of the sample quantity
→ pre-concentration > 200
- ✓ Elimination of all the polyatomic interferences during ICP-MS measurement

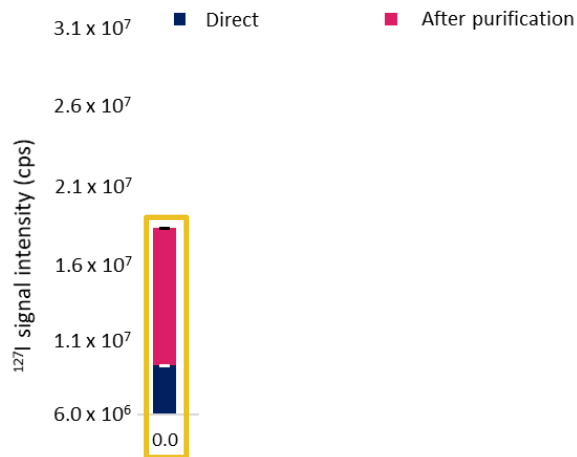
Iodine measurement by ICP-MS/MS (Agilent 8900) → Isotope separation by m/z ratio



	Element	Interferent	Interference type	Origin
¹²⁹I (m/z 129)	Xe	¹²⁹ Xe ⁺	Isobaric	Argon's impurity
	I	¹²⁷ IH ₂ ⁺ , ¹²⁷ ID ⁺ ,	Polyatomic	Sample
	Mo	⁹⁷ MoO ₂ ⁺		
	Cd	¹¹³ CdO ⁺		
	In	¹¹³ InO ⁺ , ¹¹⁵ In ¹⁴ N ⁺		
	Y	⁸⁹ Y ⁴⁰ Ar ⁺		



Non spectral interferences



Na_2S medium after purification
→ Tween®20 added (surfactant)

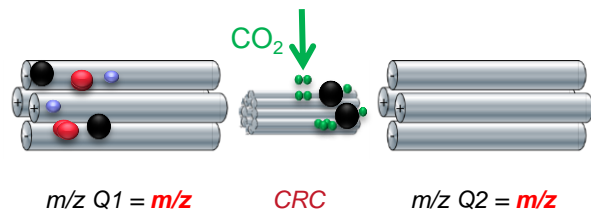
Measurement medium [1] :
0.06 M Na_2S
4.7% Tween®20

Sensitivity gain ~ 2

Medium used for the rest of this study

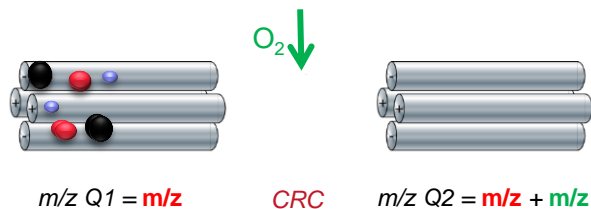
ELIMINATION OF $^{129}\text{Xe}^+$ INTERFERENCE WITH ICP-MS/MS

1/ On-mass



$$\begin{aligned} m/z \text{ (red)} &\neq m/z \text{ (blue)} \\ m/z \text{ (red)} &= m/z \text{ (black)} \\ m/z \text{ (red)} &\neq m/z \text{ (black)} + m/z \text{ (green)} \end{aligned}$$

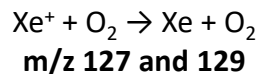
2/ Mass-shift



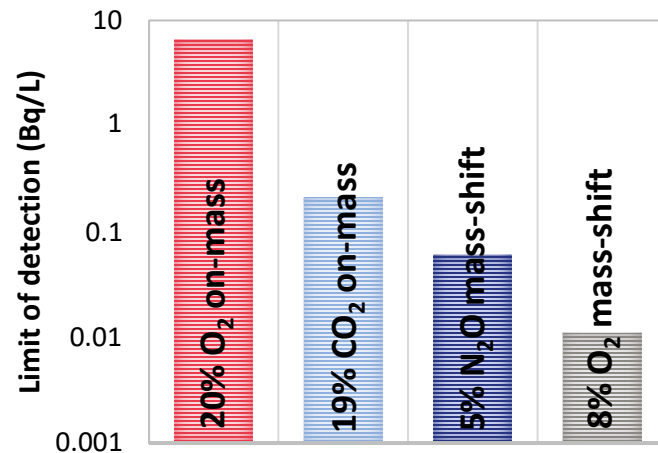
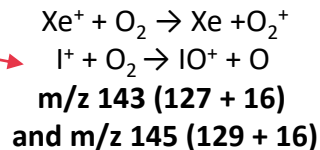
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^{129}I measurement in literature
 → O_2 en on-mass [1]
 2 possibilities:

on-mass →



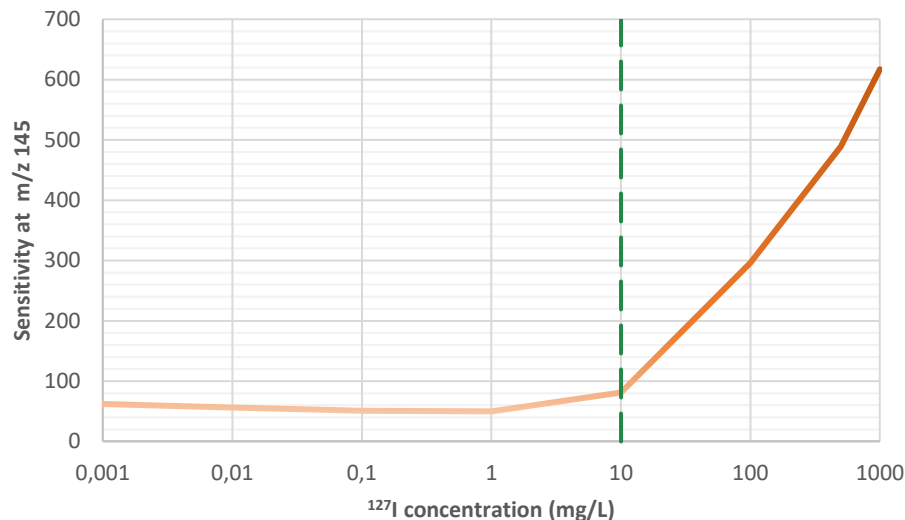
mass-shift →



✓ O_2 selected in mass-shift mode
 → theoretical LOD ~ 11 mBq/L

[1] Ohno et al., 2013; Yang et al., 2018

Polyatomic interference of IOH_2^+ and IOD^+ and abundance sensitivity

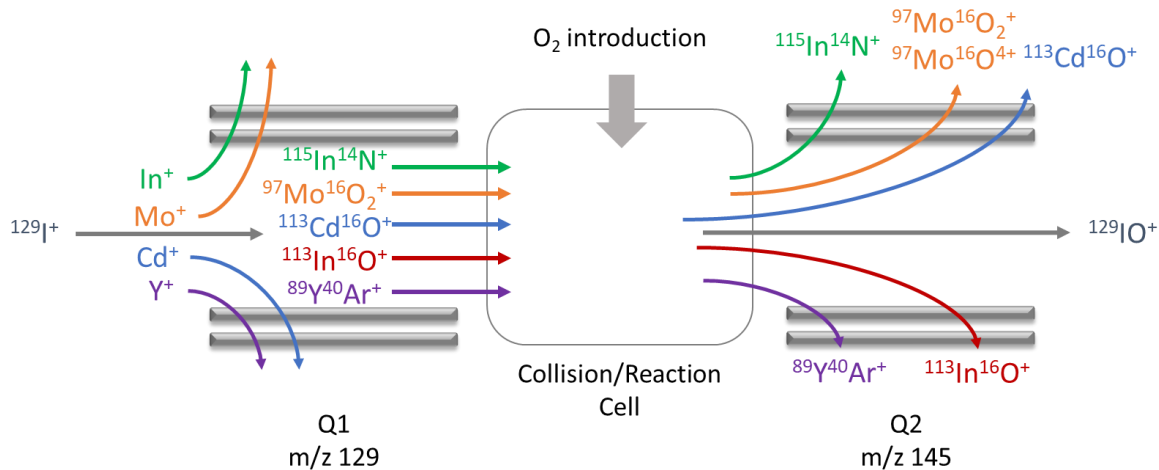


Significant contribution at m/z 145 start at 10 mg/L [1]

➔ Suppression with a $^{127}\text{IOH}_2^+ / ^{127}\text{IO}^+$ correction with to a reference material

And the other polyatomic interferences?

Other polyatomic interferences



Polyatomic interferences studied

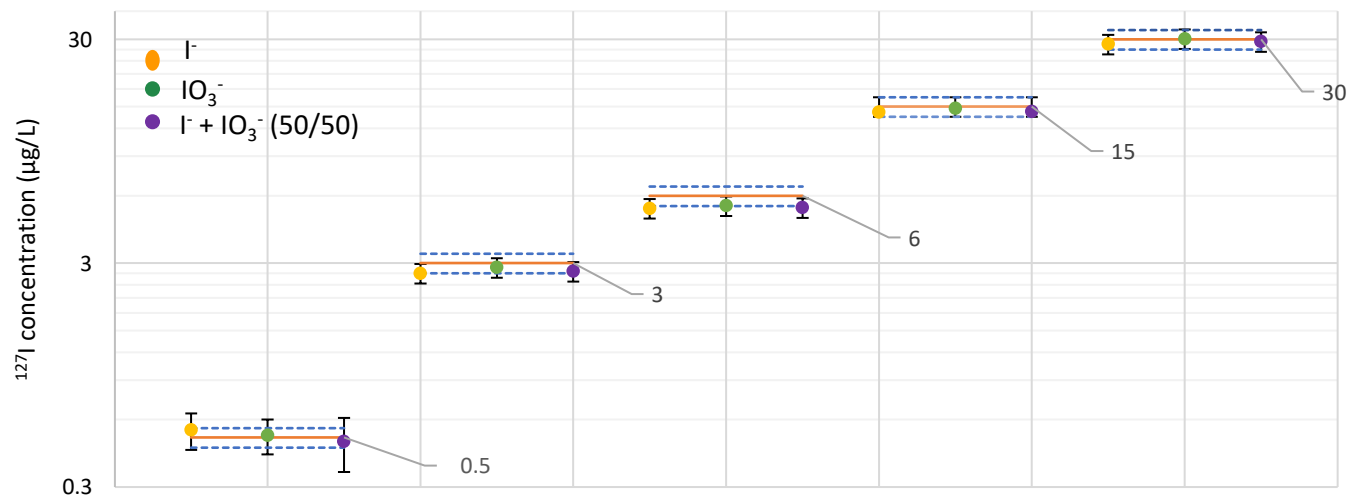
➔ The use of mass-shift mode allows to suppress all of them [1]

All interferences were suppressed

^{127}I determination with ^{126}Te as internal standard – Direct measurement by external calibration

Element	First ionization energy
Tellure-126	9.01 eV
Iode-127	10.45 eV

Quantification of ^{127}I by ICP-MS/MS



0.2 to 50 $\mu\text{g/L}$

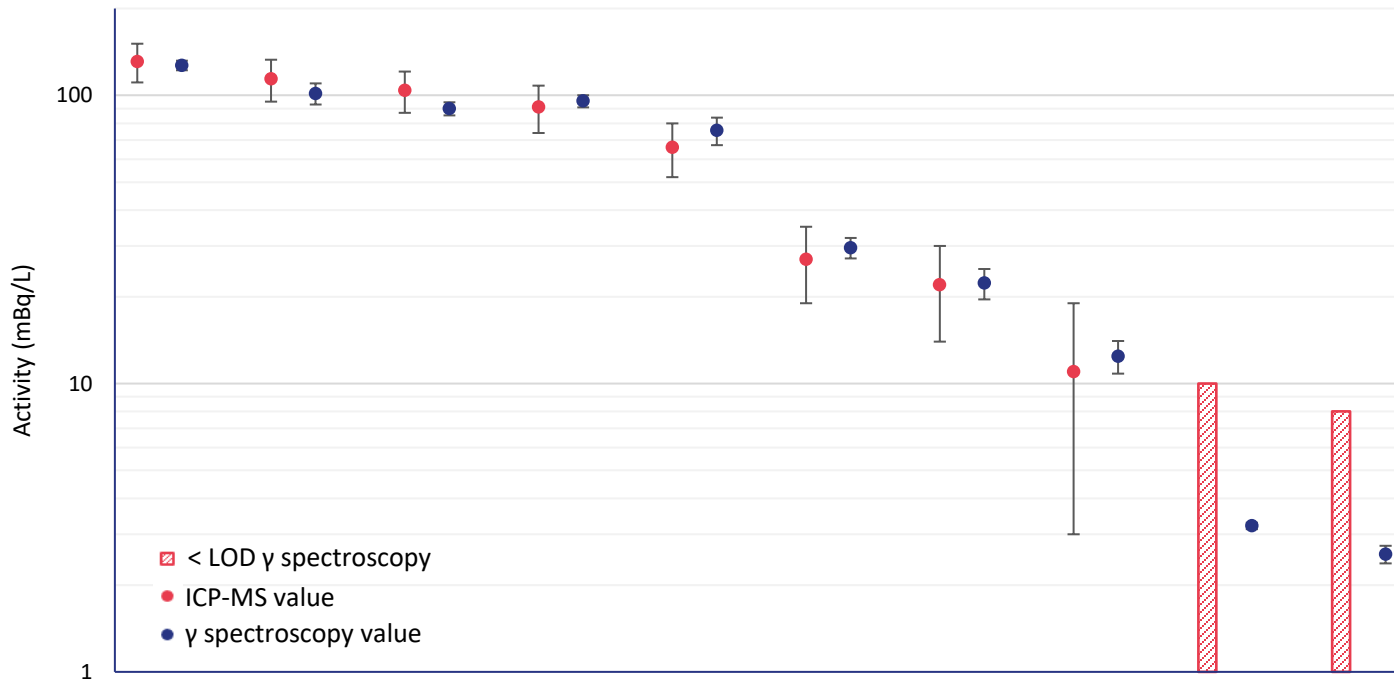


Good results

^{129}I measurement?

^{129}I Quantification – Isotopic dilution

SAMPLES: GASEOUS ^{129}I IN CHARCOAL TRAPPED NEAR REPROCESSING PLANT [1]

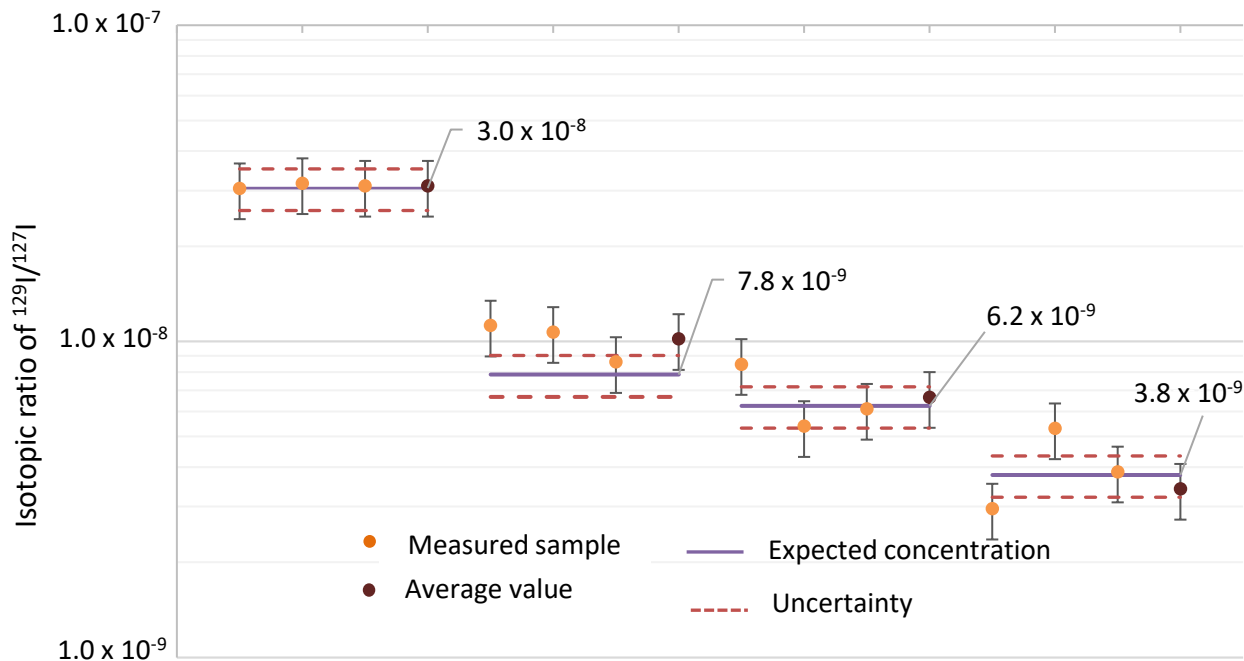


Charcoal trapped near reprocessing plant

- Sampling during discharges from ORANO La Hague
- Sampling when there are no discharge

- ✓ Excellent results
- ✓ Allow to reach lower ^{129}I activities in charcoal

Isotopic ratio $^{129}\text{I}/^{127}\text{I}$



LOD in litterature by ICP-MS/MS in on-mass mode [1], [2] :
 $^{129}\text{I}/^{127}\text{I} = 1.5 \times 10^{-8}$

Certificated ^{129}I material

Obtained isotopic ratio by ICP-MS/MS [3] :
 $^{129}\text{I}/^{127}\text{I} = 3.8 \times 10^{-9}$

[1] Diez-Fernández et al. 2020 [2] Fujiwara et al. 2011 [3] Carrier et al., 2022

Conclusion

- ✓ Sample extraction compatible with iodine's physicochemical properties
- ✓ Sample purification adapted to ICP-MS measurement
- ✓ Excellent purification recovery (> 90%)
- ✓ Mass-shift mode used with O₂ to suppress interferences
- ✓ LOD of this work : ~ 11 mBq/L and 2 mBq after chemical treatment
- ✓ Reached isotopic ratio $^{129}\text{I}/^{127}\text{I} = 3.8 \times 10^{-9}$

What's next?

- Validation of the method by AMS and certified materials
- Application to other samples (soil, grass, etc...)
- Other gas in the collision-reaction cell to improve the sensitivity



Thank you for your attention



- ➔ Carrier *et al.*, Mass-shift mode to quantify low level ^{129}I in environmental samples by ICP-MS/MS, JAAS
- ➔ Carrier *et al.*, Determination of environmental gaseous ^{129}I trapped in charcoal cartridges by ICP-MS/MS, JRNC

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