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Coralie Carrier, Azza Habibi, Celine Augeray, Didier Hebert, Denis Maro, et al.. Development of new low-level iodine 129 analysis methods applied to the understanding of iodine's transfer mechanisms in the environment. 60 ans de la CETAMA, Oct 2021, Nîmes (France), France. . irsn-04186994

HAL Id: irsn-04186994

<https://irsn.hal.science/irsn-04186994>

Submitted on 24 Aug 2023

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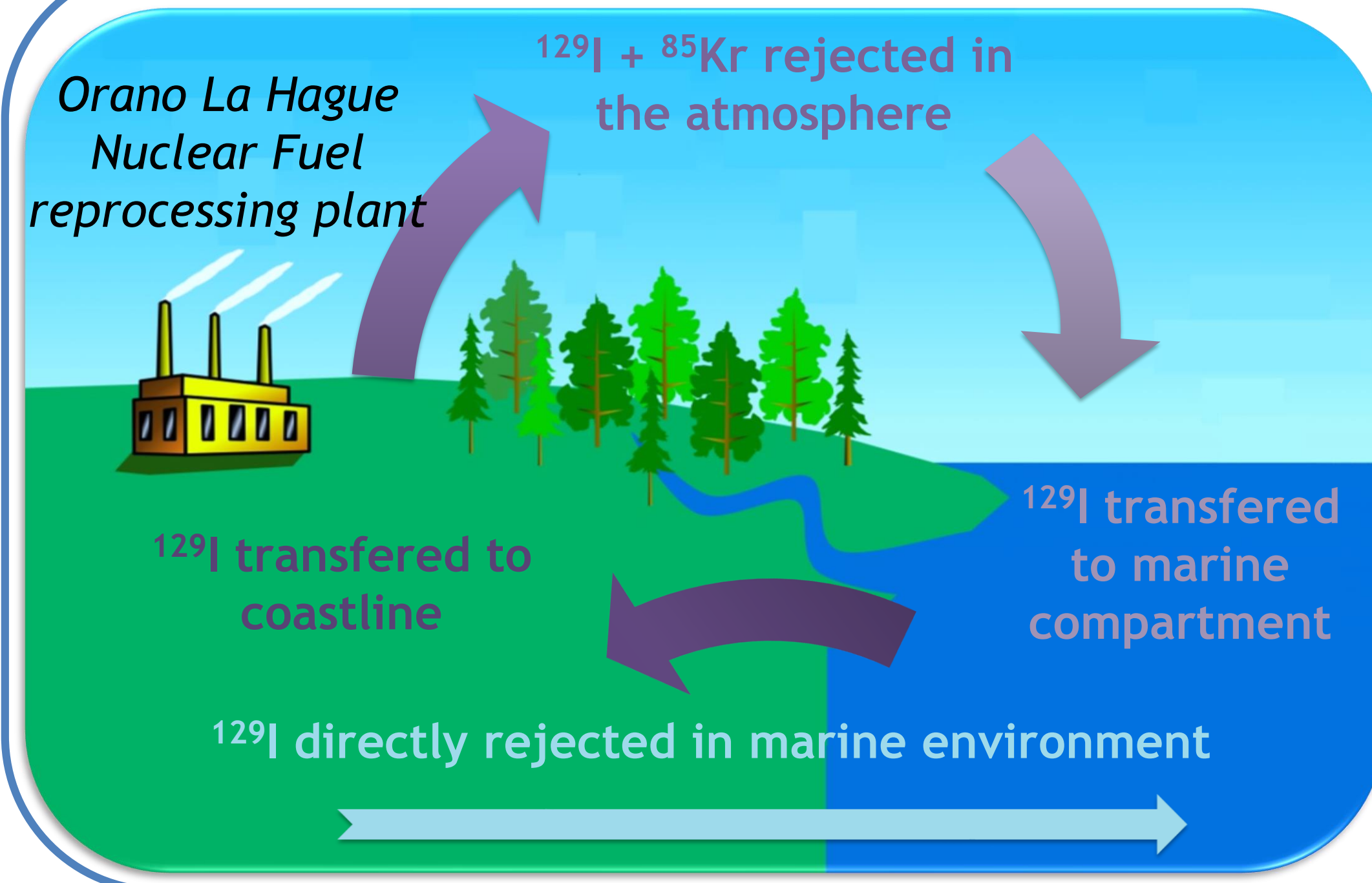
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INTRODUCTION
Iodine is a chemical element that could exist under many organic and inorganic forms and has 37 isotopes. ¹²⁷I is the only stable isotope and ¹²⁹I is the only natural radio-isotope with the natural isotopic ratio (¹²⁹I/¹²⁷I) ≤ 10⁻¹¹ [1]. Iodine ¹²⁹I is chronically released in the environment by nuclear fuel reprocessing plants [2]. This radionuclide is highly volatile and could easily be absorbed by the thyroid [3], it is then important to quantify ¹²⁹I and ¹²⁹I/¹²⁷I in order to study the complex transfer mechanisms and measure the health and environmental impact.

¹²⁹I and ¹²⁹I/¹²⁷I

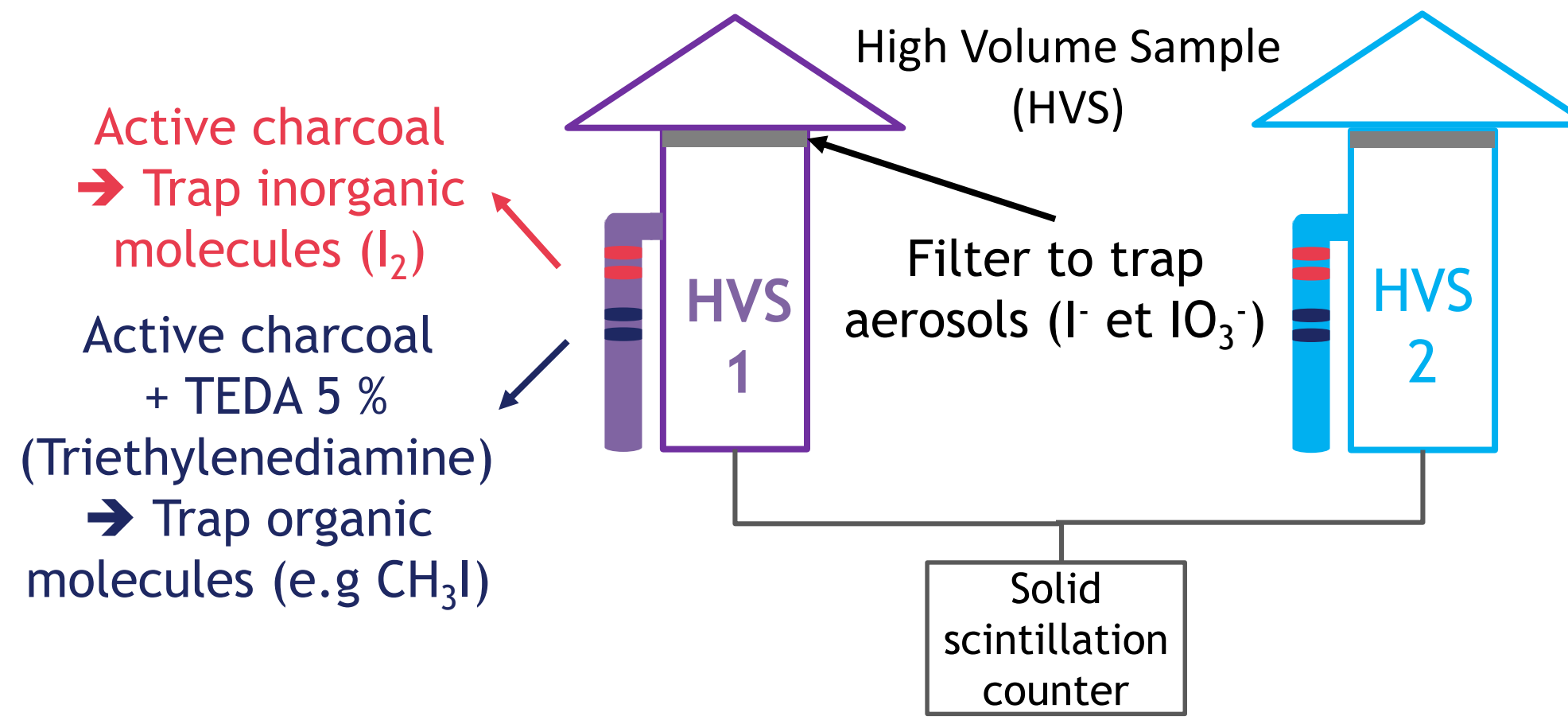
- Often measured by gamma spectroscopy: Low intensity emission at low energies
- High detection limits with this technic
- No access to the isotope ratio
- Chemical treatment could decrease the detection limit
- ICP-MS* [4] and AMS** [5] provide isotopic ratio information
- Reemission of iodine from the marine compartment to the coast under the form of aerosols or gases emission
- Never quantified versus direct atmospheric releases

OBJECTIVES

1/ Development of a new method to quantify low level ¹²⁹I and ¹²⁹I/¹²⁷I

2/ Study of the reemission of iodine from the marine compartment to the coastline

Sampling procedure



HVS 1 Started when ⁸⁵Kr is detected → iodine is directly rejected from Orano la Hague.

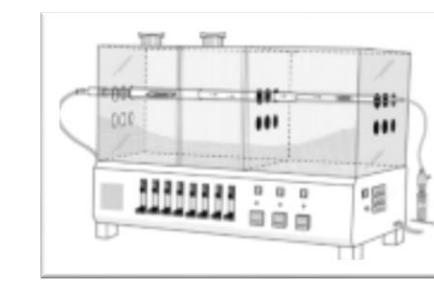
HVS 2 Started when ⁸⁵Kr is not detected → iodine is mainly due to reemission from marine environment.

METHOD

Comparison of pre-selected extraction and purification techniques to determine the most suitable protocol for the studied samples (seawater, filter and charcoal) while taking into account the physicochemical properties of iodine (its volatility and its multiple chemical forms).

Extraction

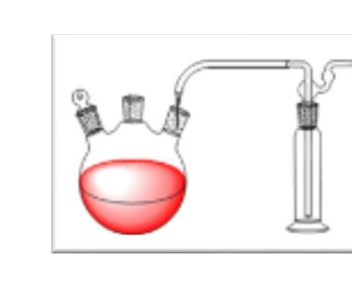
- Important sample size
- No loss of iodine



Combustion furnace [6]

Purification

- Environmental friendly
- Optimized purification time



Acid digestion [7]

Measure

- Low detection limit
- Isotopic ratio ¹²⁹I/¹²⁷I
- Optimized turnaround time



Liquid chromatography - (SPE***) [8]



ICP-MS

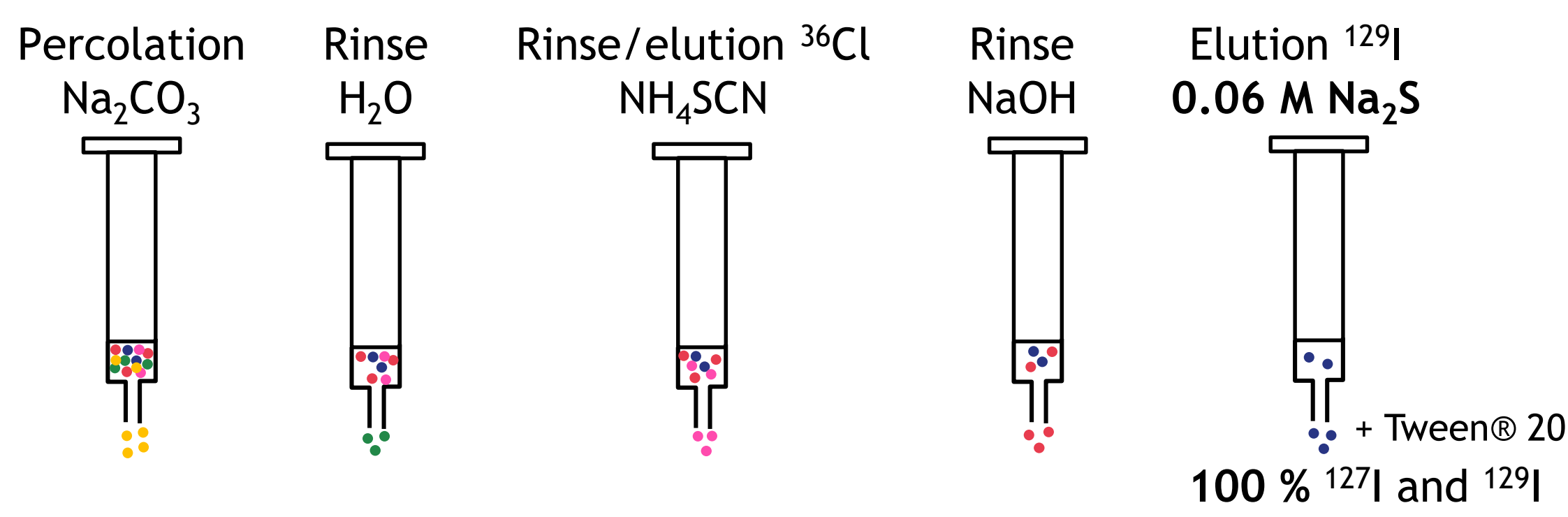
RESULTS

Newly developed ICP-MS measurement medium

0.1 % NH₄OH
3 % Tween® 20
1 % Acide ascorbique

Memories and matrix effect minimized

Sample purification adapted to ICP-MS



- ✓ Study of the elution and ICP-MS measurement media compatibility
- ✓ Optimization of Na₂S (elution solution) concentration → decrease the matrix effect
- ✓ Surfactant (Tween® 20) → increase sensitivity
- ✓ Purification time < 40 min with optimized flow rate
- ✓ Optimization of the sample quantity → pre-concentration > 200
- ✓ Elimination of polyatomic interferences: ⁹⁷MoO₂⁺, ¹¹³CdO⁺, ¹¹³InO⁺, ¹¹⁵In¹⁴N⁺, and ⁸⁹Y⁴⁰Ar⁺

¹²⁹I measurement by ICP-MS/MS

¹²⁹Xe⁺ isobaric interference elimination

The most used gas used to decrease ¹²⁹Xe⁺ interference
→ O₂ in on-mass mode

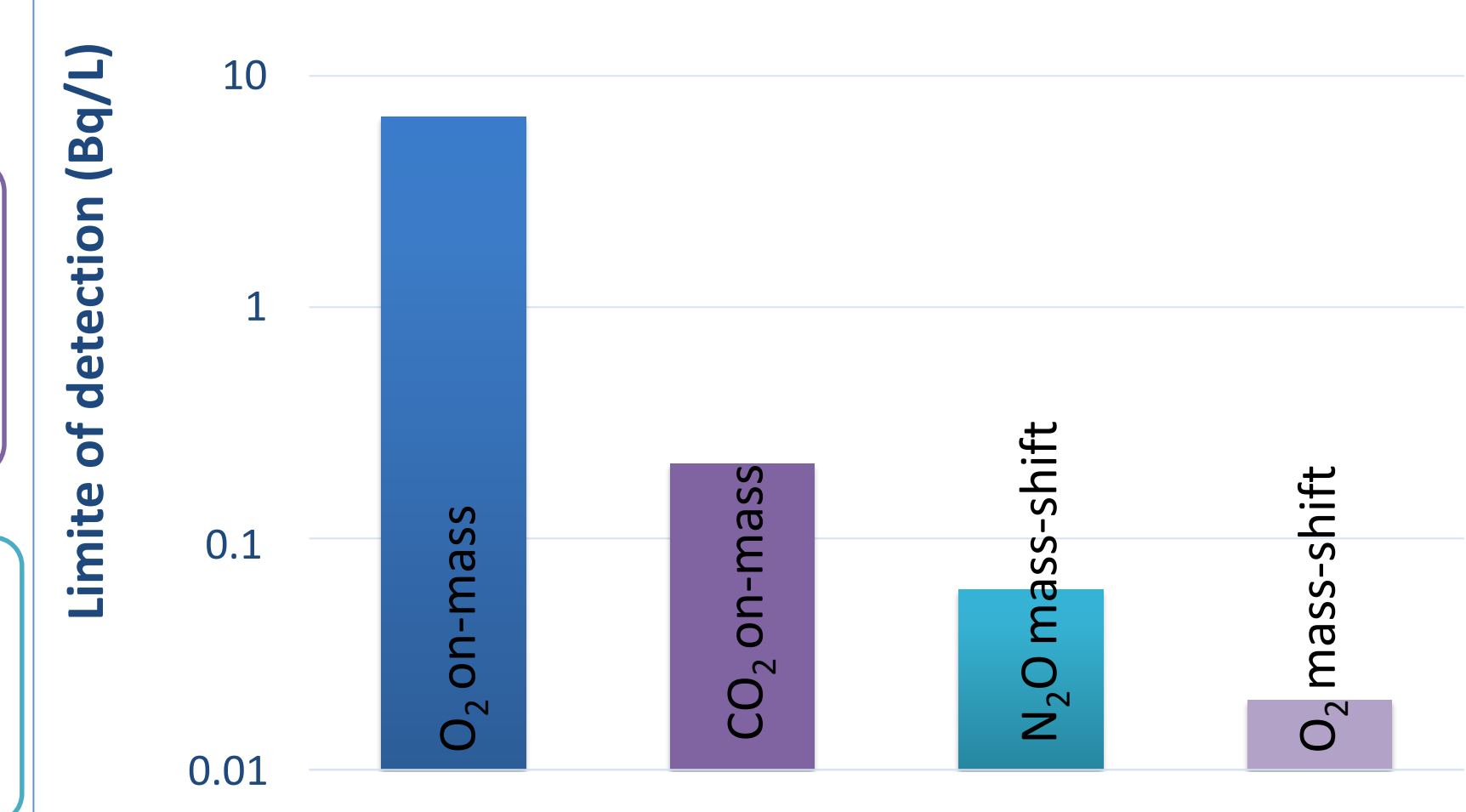
O₂ on-mass mode
Xe⁺ + O₂ → Xe + O₂⁺
m/z 127 and 129

CO₂ ?
Less oxidizing gas (stronger O-atom affinity than O₂)
→ On mass measurement

O₂ mass-shift mode
Xe⁺ + O₂ → Xe + O₂⁺
I⁺ + O₂ → IO⁺ + O
m/z 143 (127 + 16) and m/z 145 (129+16)

N₂O ?
More oxidizing gas (less O-atom affinity than O₂)
→ Mass-shift measurement

¹²⁹I limit of detection when O₂, N₂O and CO₂ are used in on-mass or mass shift mode



Polyatomic interferences

- ⁹⁷MoO₂⁺, ¹¹³CdO⁺, ¹¹³InO⁺, ¹¹⁵In¹⁴N⁺, and ⁸⁹Y⁴⁰Ar⁺ don't interfere when O₂ is used in mass shift mode
- ¹²⁷IH₂⁺ is also not disturbing up to 1 g/L of stable iodine in the sample

All interferences are suppressed with O₂ in mass-shift mode

Direct quantification's strategy



- ✓ Quantification's strategy determined
- ✓ Method validation with spiked water samples
- ✓ Bias < 15%
- ✓ Standardized deviation (SD) < 1

Efficient method

Standard Deviation (SD)

$$\frac{|^{127}\text{I}|_{\text{mes}} - |^{127}\text{I}|_{\text{th}}}{\sqrt{U^2 \cdot (|^{127}\text{I}|_{\text{mes}} + U^2 |^{127}\text{I}|_{\text{th}})^2}}$$

Sample	Theoretical activity (Bq. L ⁻¹), k=2	Measured activity (Bq. L ⁻¹), k=2	Bias (%)	SD
River water (Oraison, France)	0.020 ± 0.002	0.022 ± 0.002	8.6	0.002
	0.070 ± 0.007	0.070 ± 0.014	0.2	0.000
	0.200 ± 0.020	0.220 ± 0.020	10.1	0.021
	0.500 ± 0.050	0.476 ± 0.014	4.7	0.025
River water (Mirabeau, France)	0.020 ± 0.002	0.020 ± 0.002	0.3	0.000
	0.080 ± 0.008	0.072 ± 0.008	9.6	0.005

CONCLUSION

Direct measurement

- Measurement medium: Sensitivity gain ~ 3
- Gamma spectrometry detection limit [9]: 100 - 200 mBq/L
- Obtained ICP-MS limit of detection: ~ 11 mBq/L

Measurement after chemical treatment

- Measurement medium: Sensitivity gain > 20
Chemical yield > 90 %
Duration < 40 min
- Gamma spectrometry detection limit [9]: ~ 20 mBq/L
- Obtained ICP-MS limit of detection: ~ 0,06 mBq/L

Sampling system

Developed and successfully tested



WHAT'S NEXT ?

Adaptation of the method to the studied samples

Cross-analysis with Accelerator Mass Spectrometry and gamma spectroscopy

Iodine's reemission from sea to land study

Development of a protocol for the iodine's extraction from the matrix

Extraction and purification media compatibility study

Start of the sampling using HVS with a bimonthly frequency

