Development of an analytical strategy for the field dissolution of targeted species in country foods

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Introduction

Country foods play an important role in northern communities diet. These foods include caribou, beluga, birds and fish such as Arctic char. They are a rich source of essential nutrients, but may also contain levels of contaminants that can pose a health risk. Lead (Pb), mercury (Hg) and methylmercury (MeHg)[1] can be found in large concentration in animal flesh depending on the habitat, age, sex, sixe and others characteristics. Thus, the possibility to measure on site the level of contaminants in food could be attractive for population consuming country food. This project will address some scientific aspects associated with the on site monitoring of targeted species.
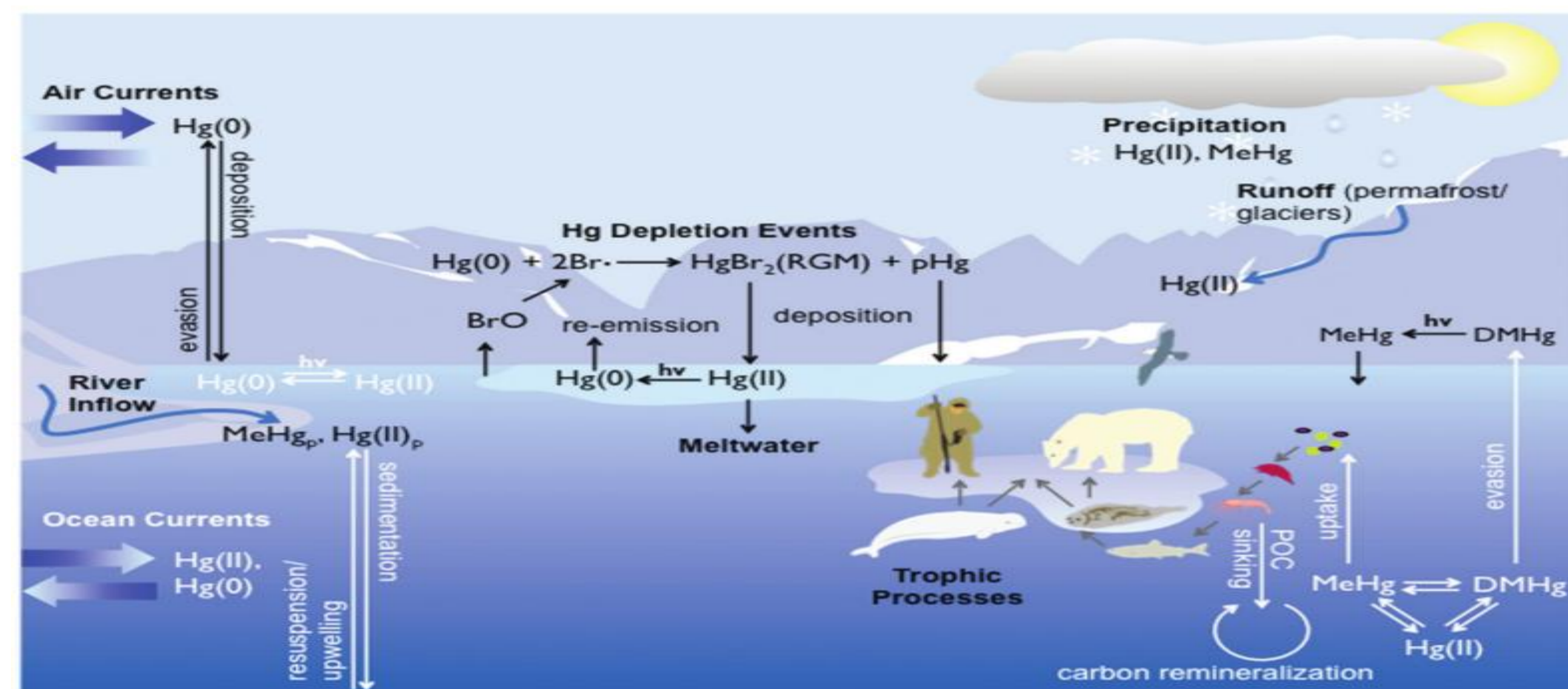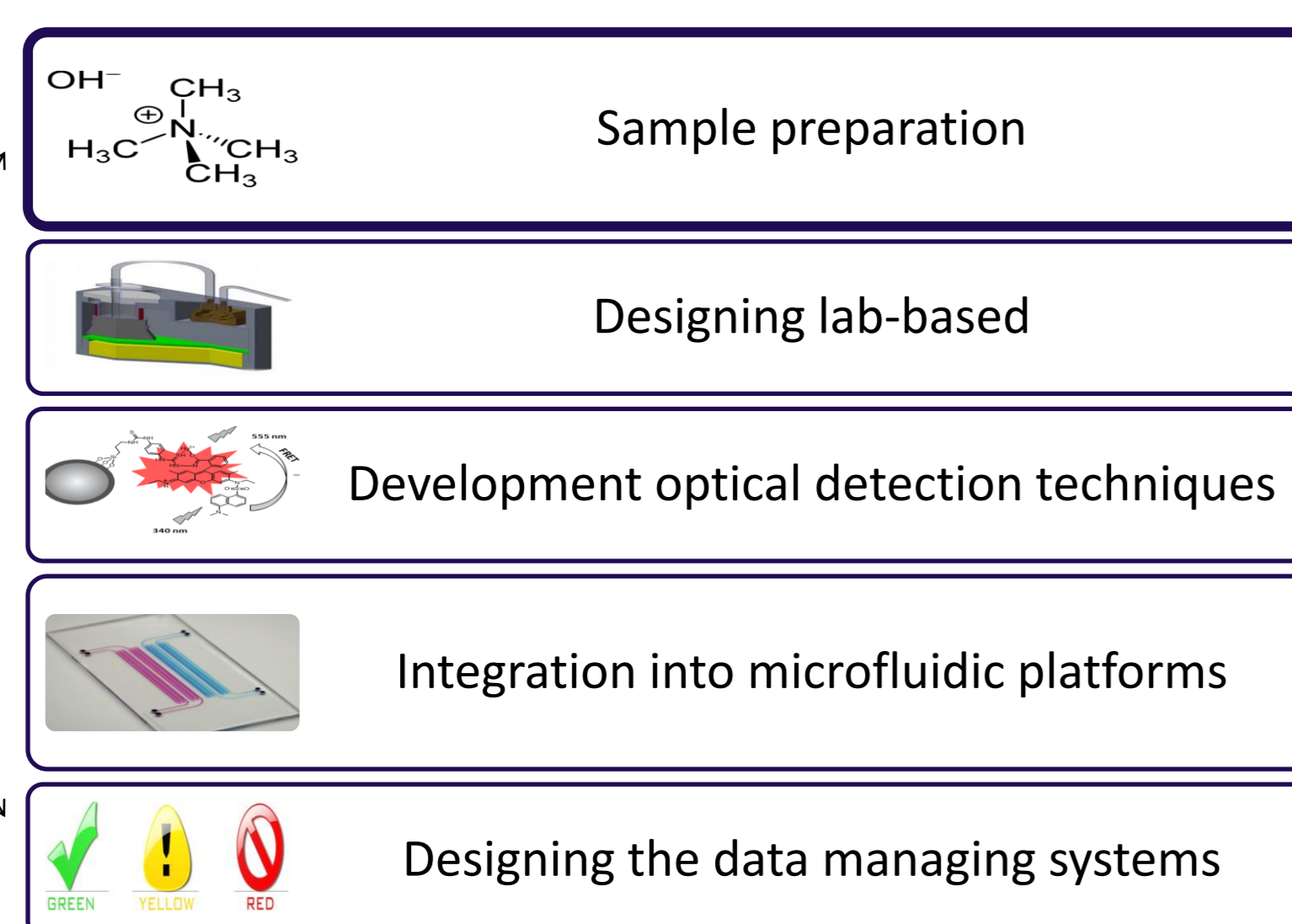

Figure 1: Biogeochemical cycle of mercury (Hg) in the northern environment [2]

Goals

To enabling tools for the monitoring of food quality in the Northern environment

- Sample preparation
- Designing lab-based
- Development optical detection techniques
- Integration into microfluidic platforms
- Designing the data managing systems

Fish tissues dissolution

	Microwave	Acidic	Ultrasound
🌡️	200 °C	160 °C	65 °C
⏱️	120 min	120 min	15 min
⏲️	55 bar	1 bar	1bar
⚗️	HNO_3 HCl	HNO_3 HCl	TMAH 10%

Alkaline dissolution using tetramethylammonium hydroxide (TMAH) and ultrasonic frequencies is a fast, simple technique that requires little energy and consumable, characteristics sought for field studies[3]. In order to achieve an effective dissolution in the shortest time possible, optimization of the dissolution process was performed using full factorial design.
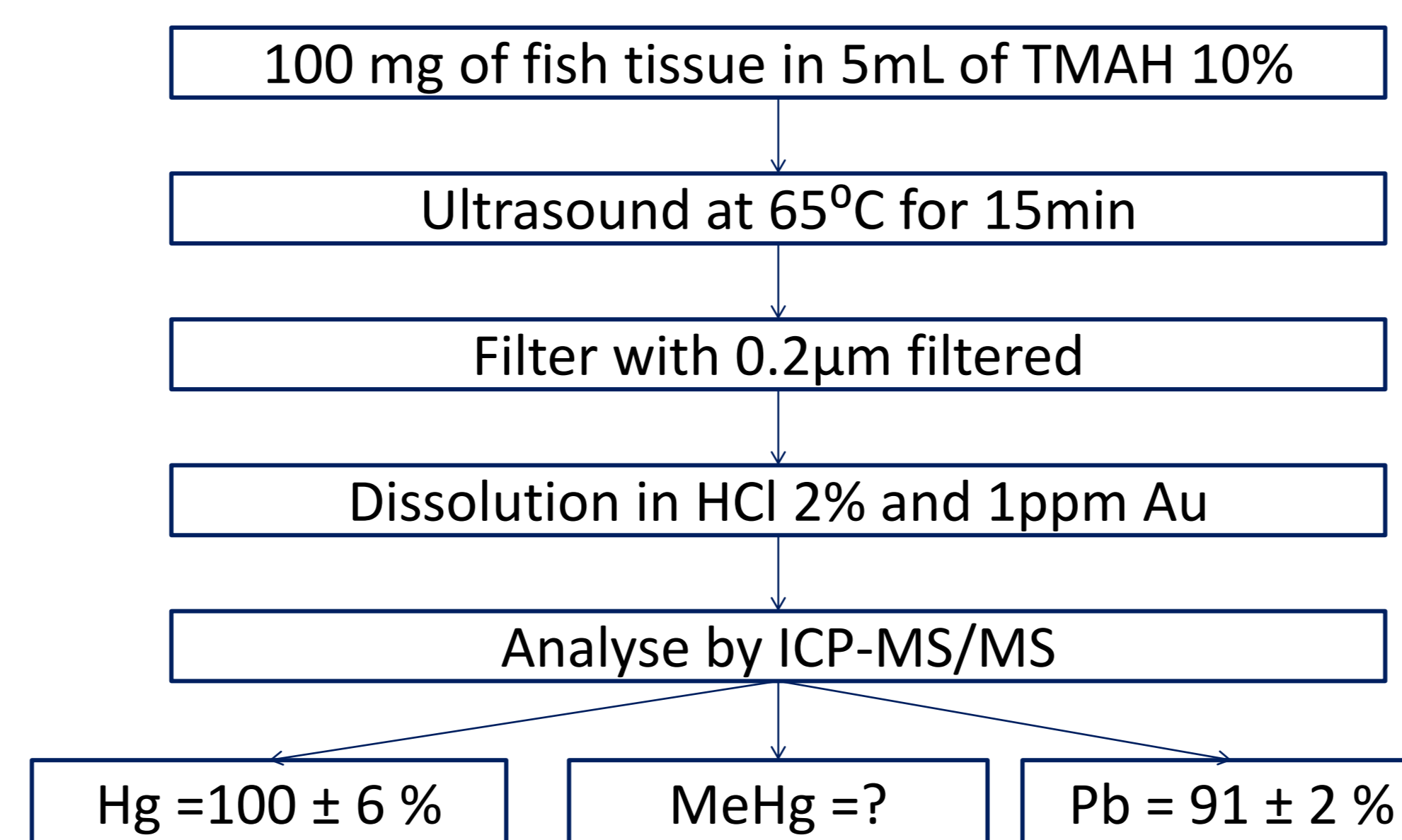
Optimization

- concentration [TMAH]
- time
- Temperature
- Masse on volume ratio

Full factorial design(FFD) allow the variation of several parameters simultaneously and allow the determination of the impact of each parameter on the recovery as well as the interactions between the parameters. Commercial Arctic Char tissues enriched in inorganic Hg and Pb were use to optimised the process.
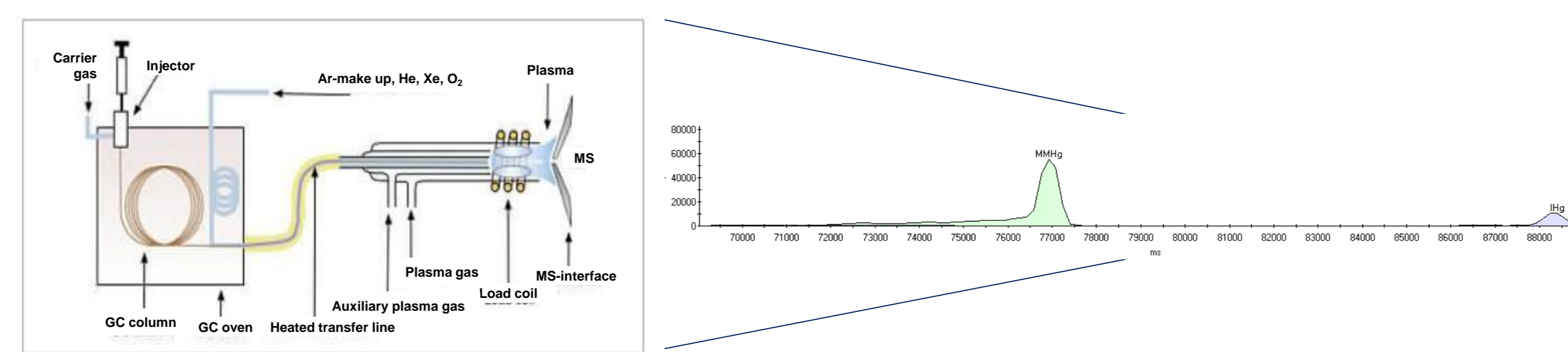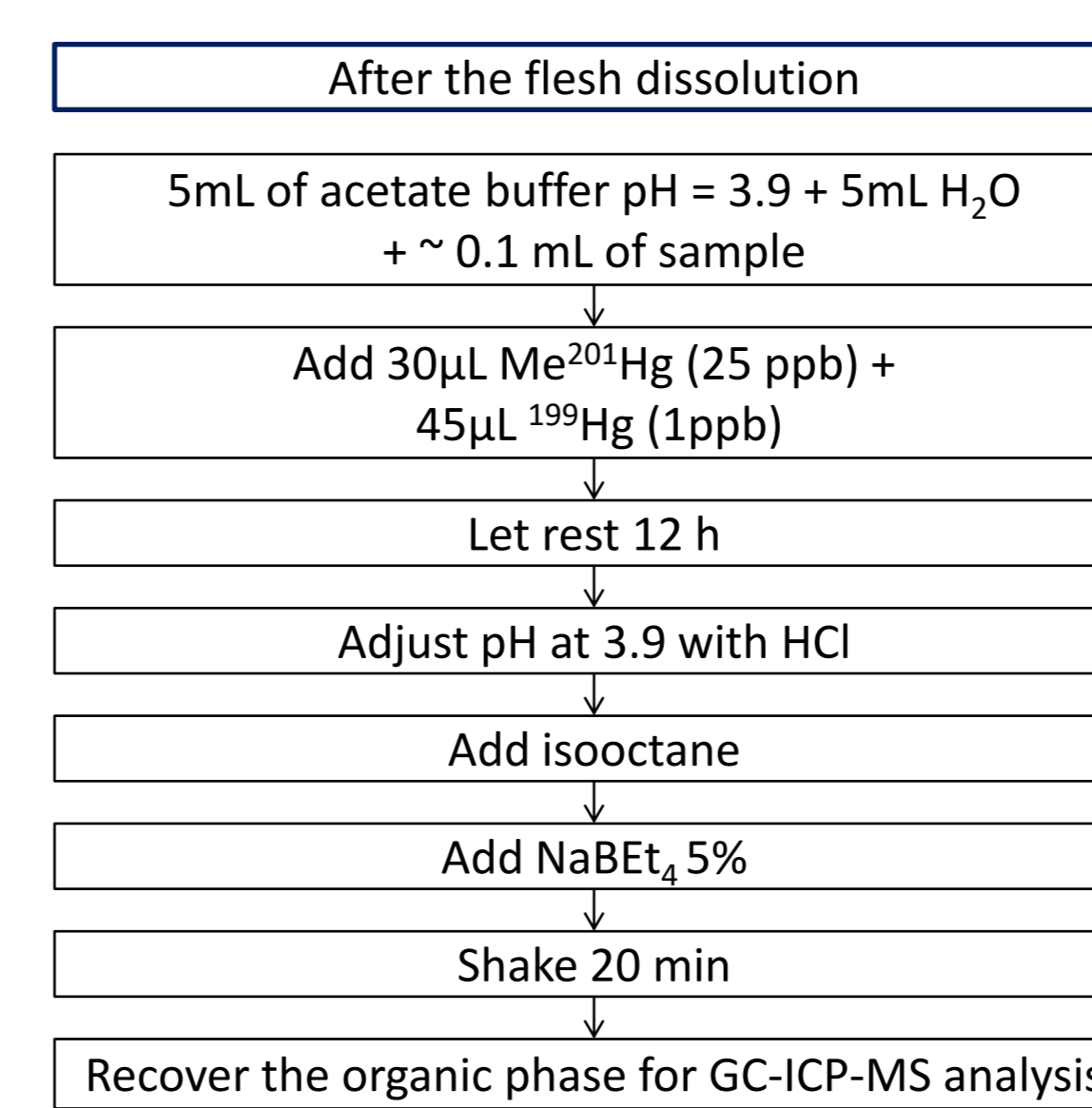

Ultrasound dissolution

The ultrasound dissolution in TMAH with a ultrasonic bath allow the dissolution of more then 90% of the inorganic targeted species. Ultrasound are known to poorly break the mercury carbon bound of the MeHg[4]. The ICP-MS/MS allow the quantification of different isotope after there ionisation in a plasma, the concentration of MeHg is therefore not determined. The Hg contain in fish tissue is in means 90% MeHg, to assure the food quality it is important to determine concentration of the total mercury (MeHg+Hg). To do so, fish tissue with certified concentration in Hg and MeHg, NIST-1947 is use. This certified reference material is made from fresh lake trout.

100 mg of fish tissue in 5mL of TMAH 10%

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Ultrasound at 65°C for 15min

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Filter with 0.2μm filtered

↓

Dissolution in HCl 2% and 1ppm Au

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Analyse by ICP-MS/MS

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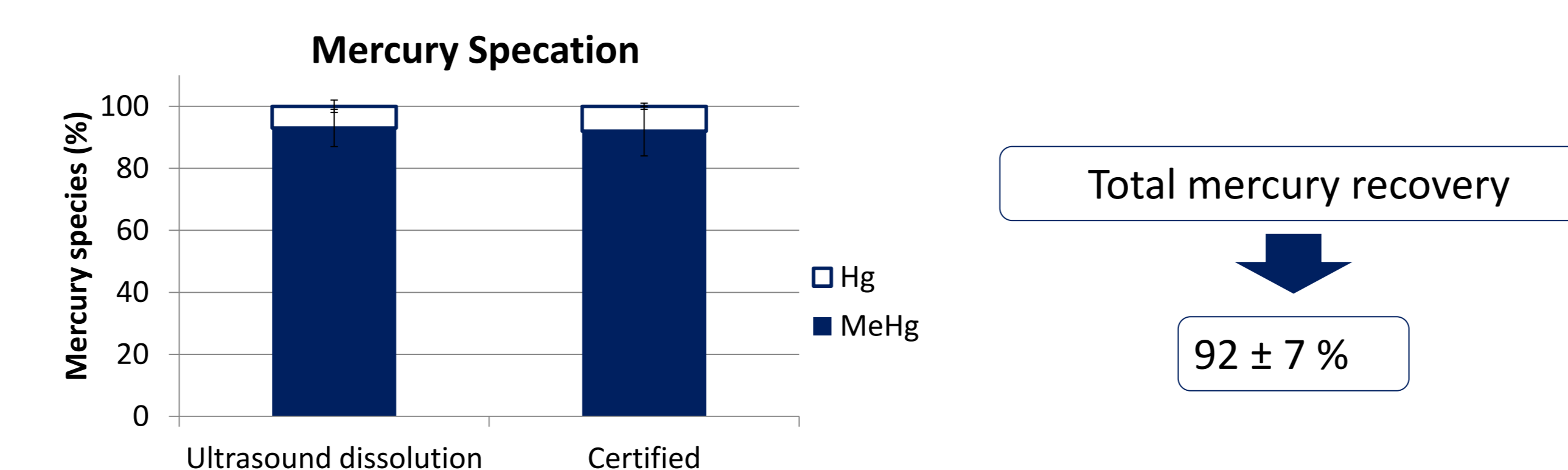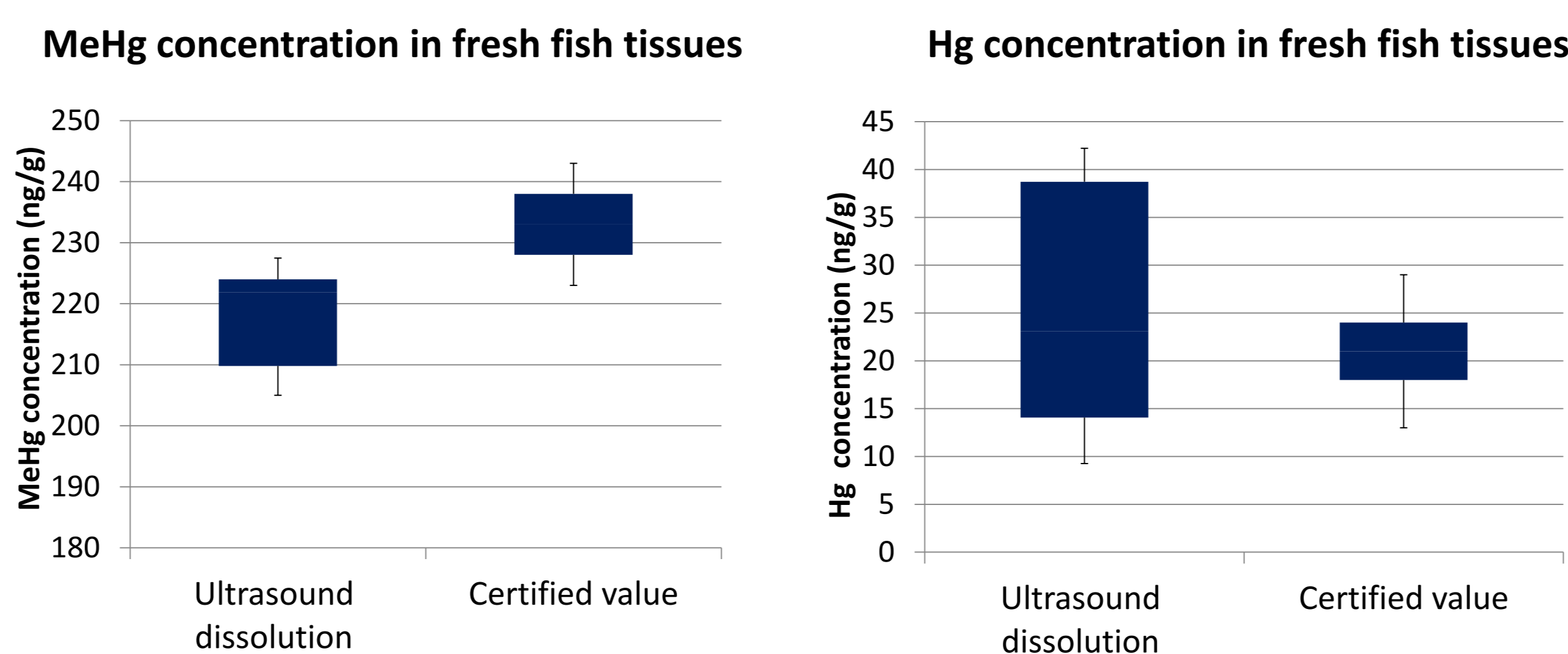| Hg =100 ± 6 % | MeHg =? | Pb = 91 ± 2 % |

GC-ICP-MS

The GC-ICP-MS allow the detection of different mercury species in the sample. Those analysis require the derivation of those species from the aqueous phase to an organic phase. To do so, NaBEt$_4$ complex the mercury species so than after agitation they can be recover in the isooctane. The use of isotopic marker (Me^{201}Hg and ^{199}Hg) allow the correction of the mercury lost during this process. The gas chromatography (GC) split the different species by their weight and the ICP-MS quantify them for the different isotopes.
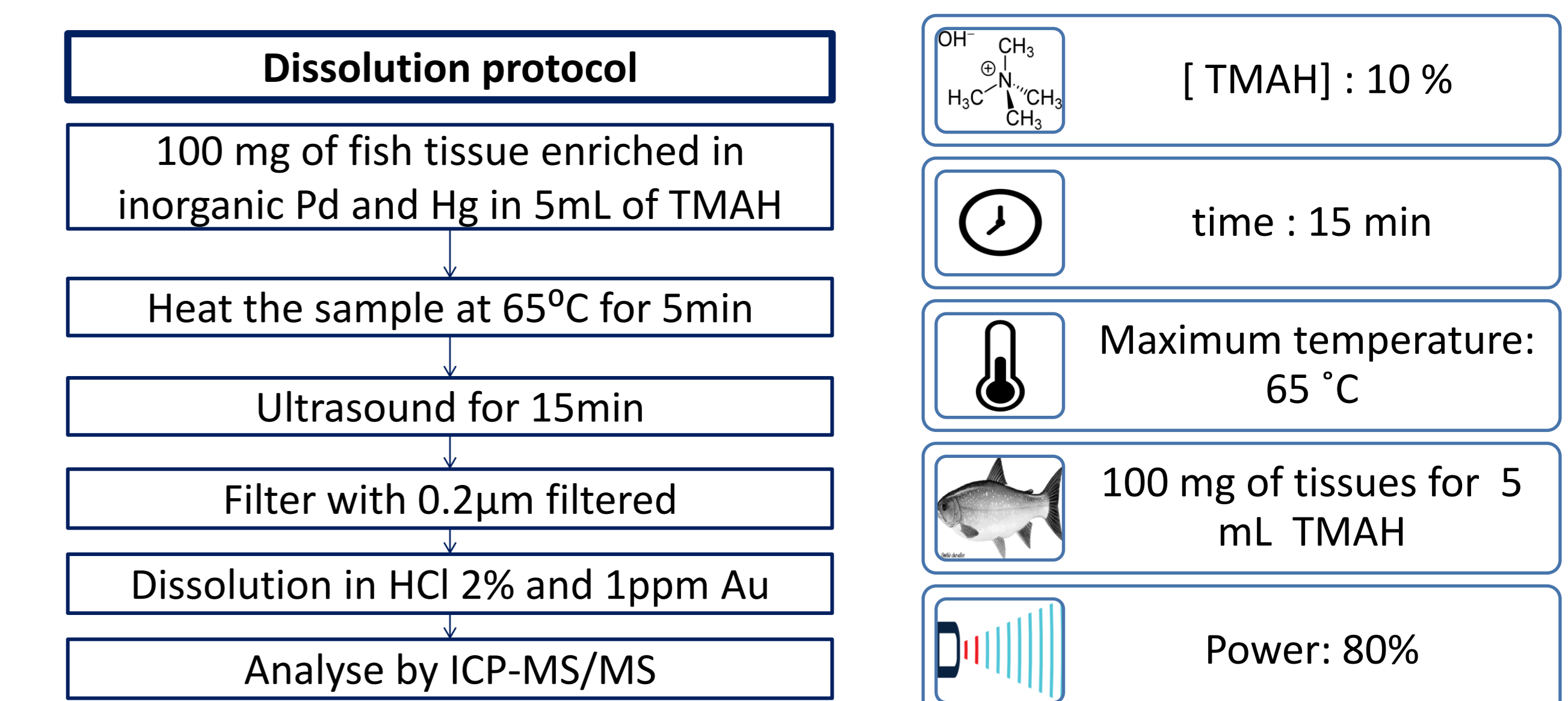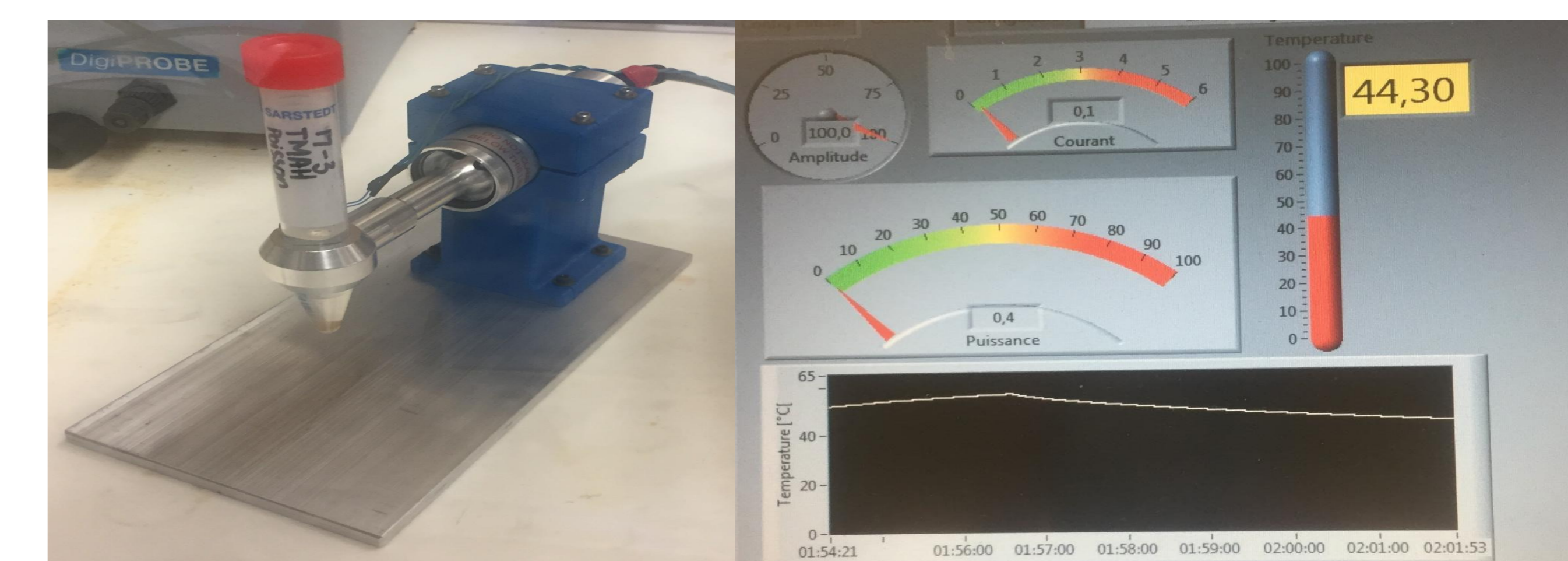
After the flesh dissolution

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5mL of acetate buffer pH = 3.9 + 5mL H$_2$O + ~ 0.1 mL of sample

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Add 30μL Me^{201}Hg (25 ppb) + 45μL ^{199}Hg (1ppb)

↓

Let rest 12 h

↓

Adjust pH at 3.9 with HCl

↓

Add isooctane

↓

Add NaBEt$_4$ 5%

↓

Shake 20 min

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Recover the organic phase for GC-ICP-MS analysis

GC-ICP-MS results

MeHg concentration in fresh fish tissues

Hg concentration in fresh fish tissues

Mercury Specation
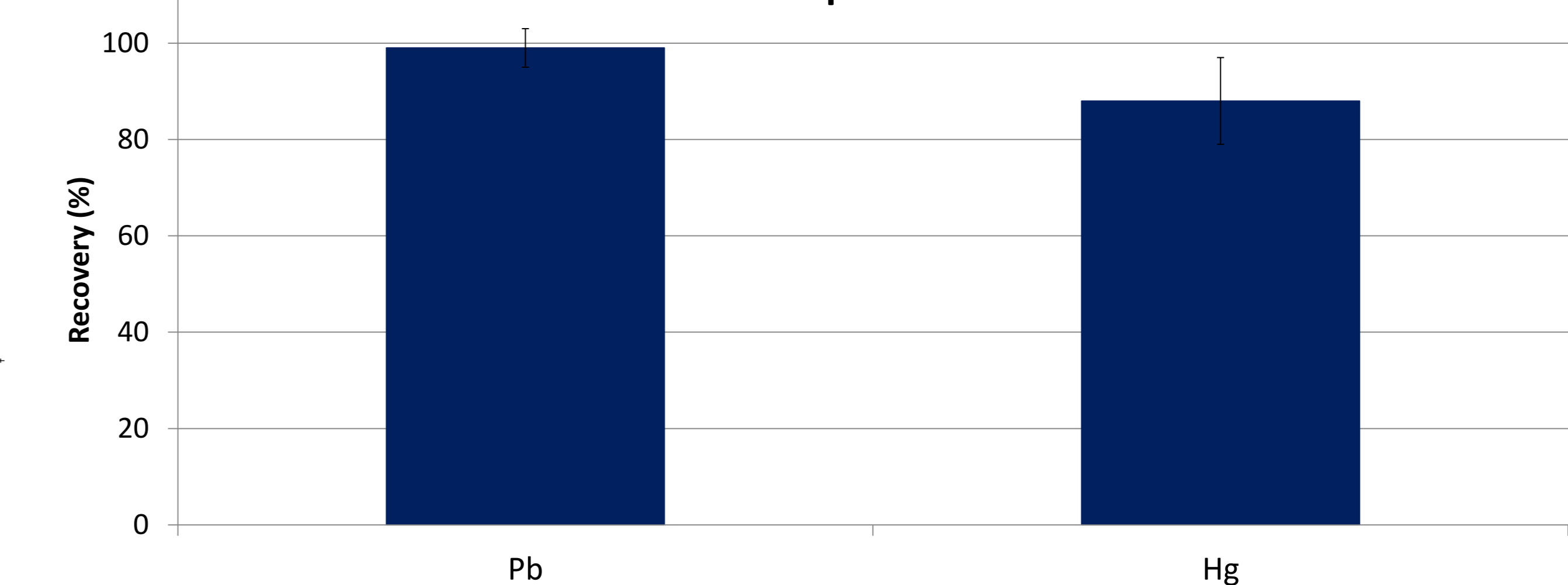
Total mercury recovery

92 ± 7 %

New ultrasound probe

The ultrasonic bath are not easy to carry out of the laboratory. To have a tool for on field analysis, we made a ultrasound probe. This new probe allow the control of the ultrasound power and temperature monitoring of the dissolution with a computer program. The probe carry out good recovery for inorganic Pb and Hg in fish tissues, but it does not heat up the sample. This new system is promising, the control of the ultrasound power will probably help reduce the dissolution time

Dissolution protocol

100 mg of fish tissue enriched in inorganic Pd and Hg in 5mL of TMAH

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Heat the sample at 65°C for 5min

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Ultrasound for 15min

↓

Filter with 0.2μm filtered

↓

Dissolution in HCl 2% and 1ppm Au

↓

Analyse by ICP-MS/MS

[TMAH] : 10 %	
time : 15 min	
Maximum temperature: 65 °C	
100 mg of tissues for 5 mL TMAH	
Power: 80%	

Recovery of targeted species after ultrasound dissolution with the new probe

Future works

- Optimise the dissolution with the new ultrasound probe system
- Assess the MeHg dissolution with the new ultrasound probe
- Develop a process to transform the MeHg in Hg after the dissolution
- Perform the separation and preconcentration of the different species

Thanks

References

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