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► To cite this version:

Elodie Mattio, Fabien Robert-Peillard, Bruno Coulomb, Jean-Luc Boudenne, Catherine Branger, et al.. 3D-printed system for the spectrophotometric determination of lead in water. 20th International Conference on Flow Injection Analysis and Related Techniques, Oct 2016, Palma de Majorque, Spain. , 2016. hal-01437858

HAL Id: hal-01437858

<https://hal.science/hal-01437858>

Submitted on 17 Jan 2017

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3D printed system for the spectrophotometric determination of lead in water



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CONTEXT

Over the last few years, the development of **3D printing** has enabled numerous advances in research. This type of printing technology opens a vast array of possibilities in **analytical chemistry**, and more particularly in the field of **flow analysis**. Ease of fabrication and flexibility of this technology has led to the development of a new type of system for the determination of lead in natural waters. This device is composed of three units: a column for selective retention of **lead**, a mixing coil and a microfluidic cell for **UV-Vis spectroscopy**. The final goal is to get a fast system which can be used on site, which a low limit of detection and quantification.

DESIGN AND PRINTING OF THE SYSTEM

The first step for the fabrication of the device is to draw each unit with the desired criterion on a 3D software :

- ① A reservoir for a resin column for lead retention, which is tightly closed by a screw piece with 3 entry channels for injection of sample and reagents/eluents.
- ② A mixing coil for mixing eluted lead with a chromogenic reagent.
- ③ A classical cell for UV-spectroscopy with a 5 cm optical path length.

The three units are printed separately with **screws** or corresponding screw threads to assemble the whole system. In this way, all the parts can be changed with others units: the type of detection and the sample treatment will be **easily selected** according to the analytical needs.

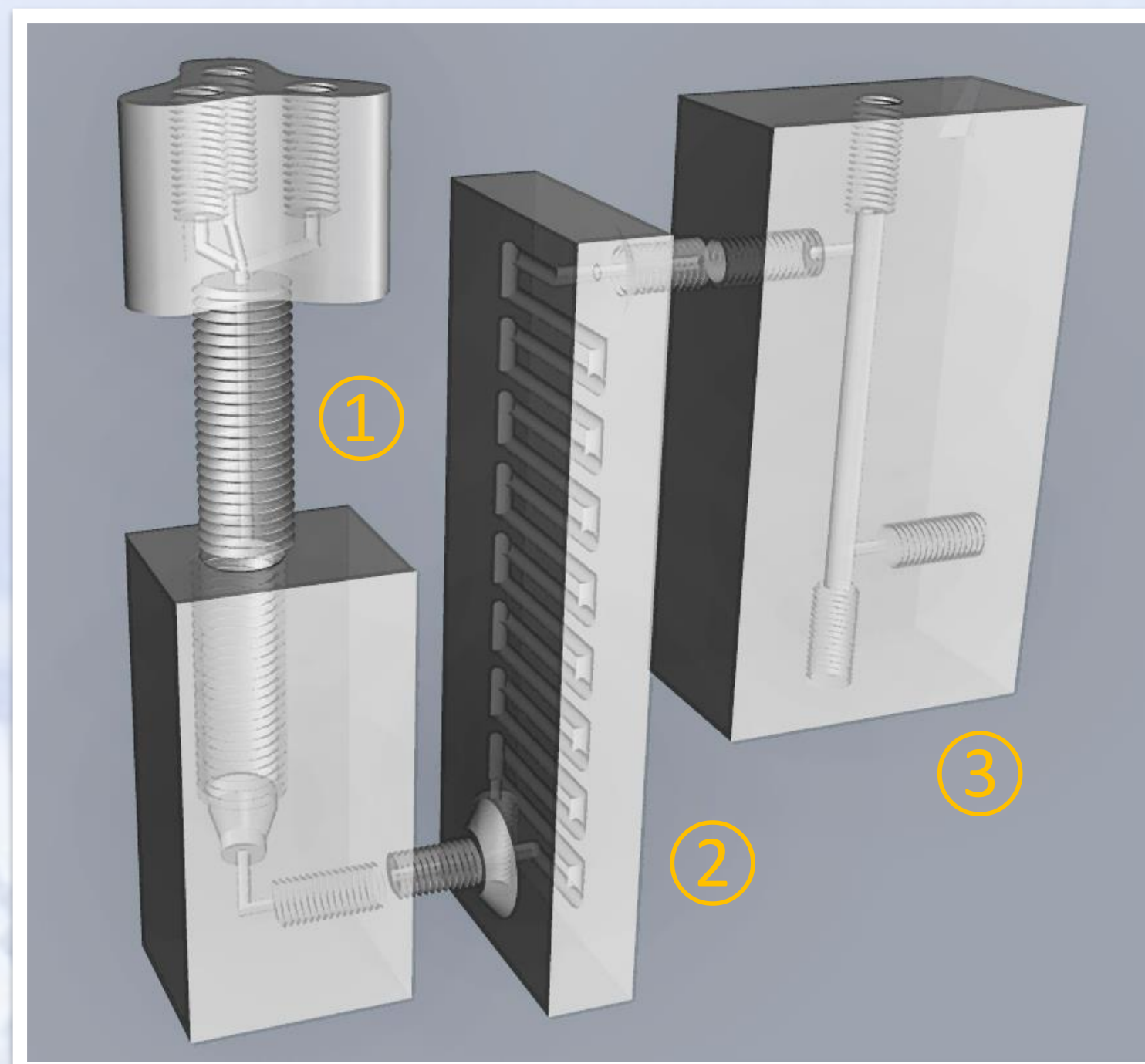


Fig. 1: Schema of system on the 3D software

Designed pieces were printed using the Form 1+ by formlabs. This printer uses the **stereolithographic technology**: a mobile platform dives in a resin tray and a 405nm laser polymerizes this resin layer by layer according to the 3D model on the platform.

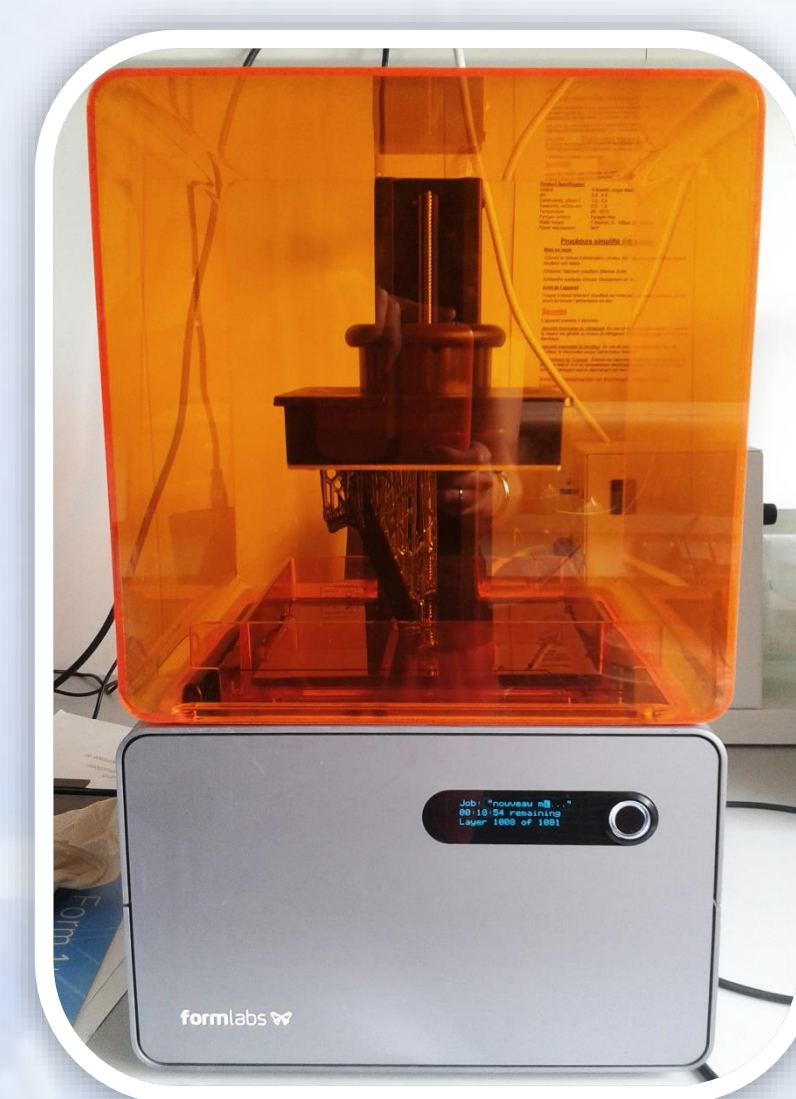


Fig. 2: Form 1+ by formlabs used at laboratory

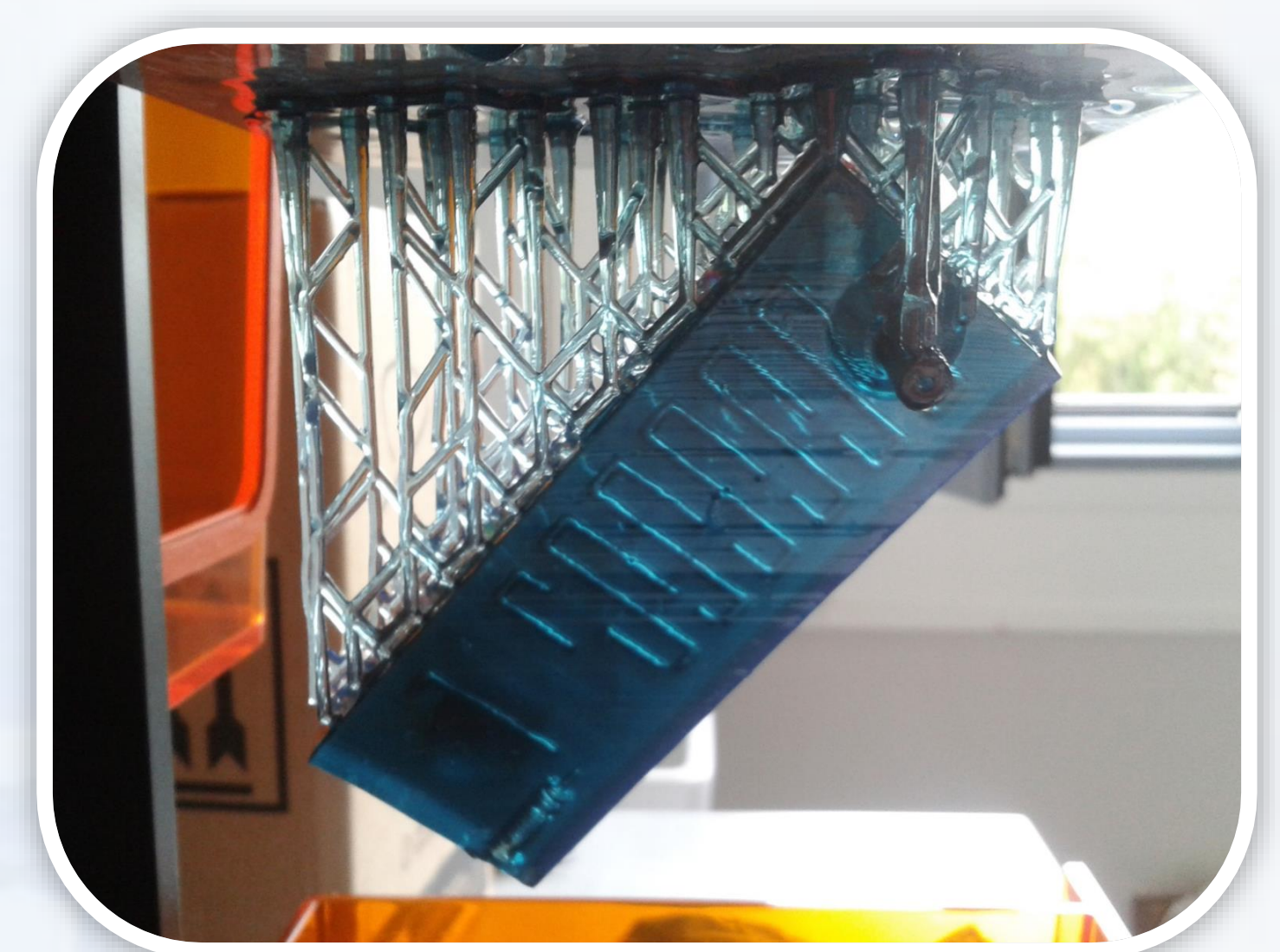


Fig. 3: Mixing coil at the end of printing

Advantages of 3D printing :

- Replace quickly and at a lower cost used parts: for example, the printing price has been calculated for the 3 pieces, including supports, **250mL of resin** is necessary, corresponding to a price of **44 euros**. Printing time for the whole system is about 16 hours.

- Many possibilities of fabrication; **different types of pieces** can be created depending on the 3D software possibilities and printing parameters.

- Creation of entirely modular systems, with different types of detection and sample treatments units that can be easily created to **adapt the system** according to samples or analytes.

DEVELOPMENT AND OPTIMISATION

For the lead retention, the **resin PB TRISKEM**, constituted by crown ethers, was used. This extraction step was paired with an UV detection by adding 4-(2-Pyridylazo)resorcinol after elution with ammonium oxalate. The analytical protocol was as follows:

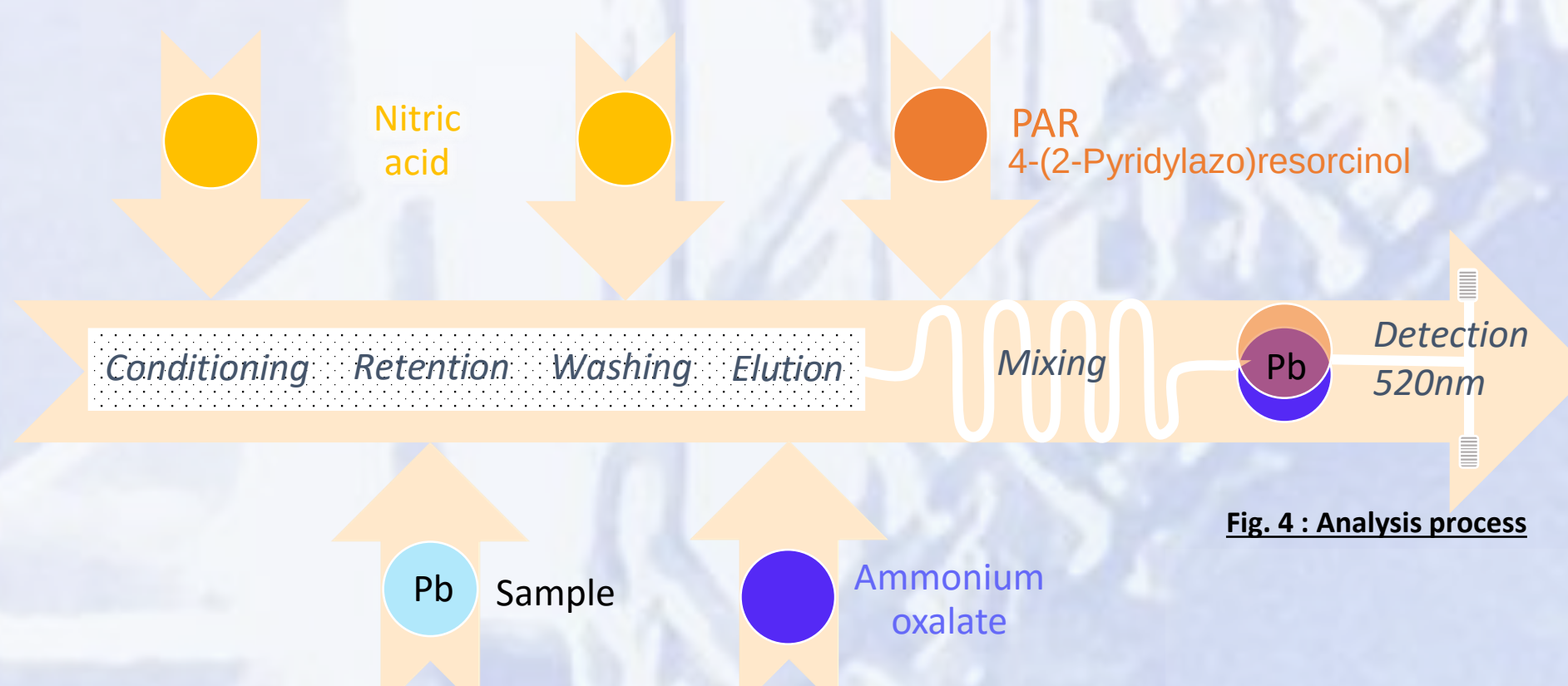


Fig. 4: Analysis process

Several parameters in this protocol needed to be optimised. First, the selectivity of the resin has been tested at different concentrations of nitric acid with 9 metal cations, the multi-elements solutions being analysed by ICP-AES.

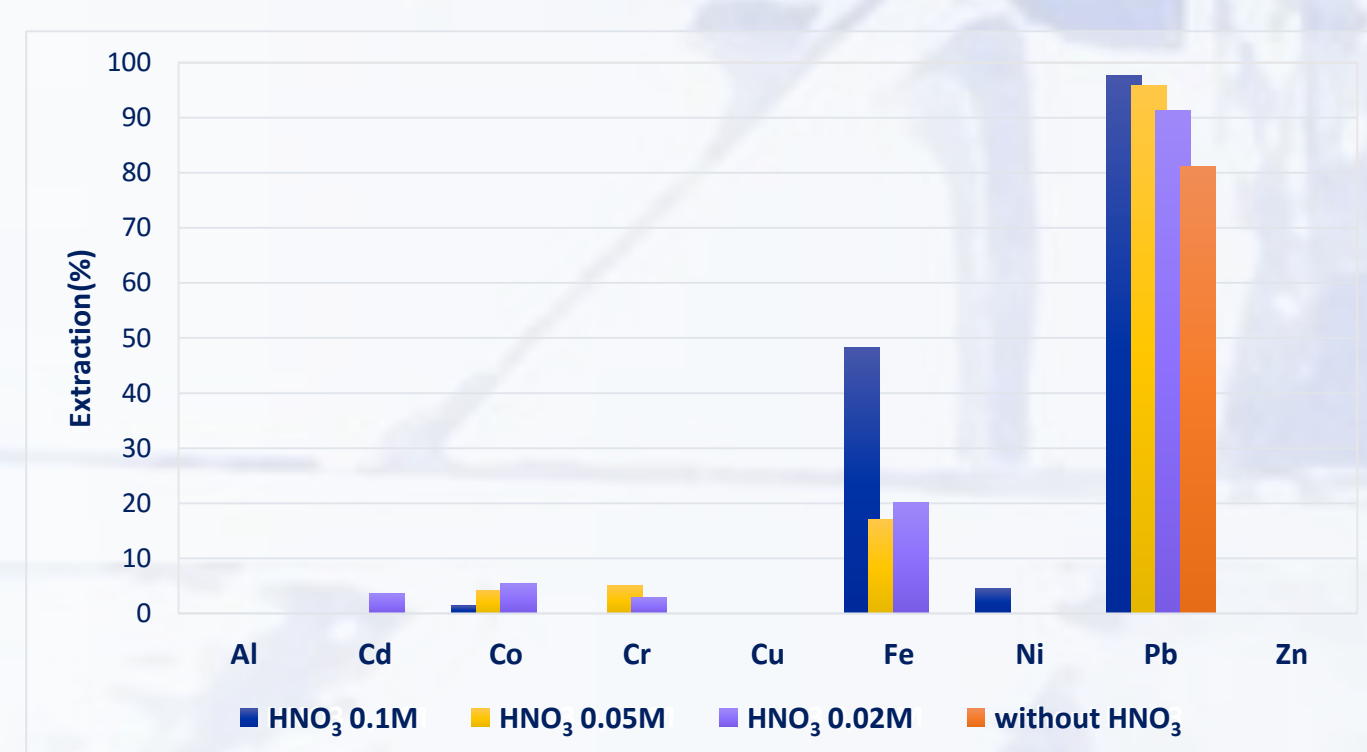


Fig. 5: Extraction of several metals for different concentrations of nitric acid

The results showed a **good extraction of lead** in presence of nitric acid; however, iron was also partially extracted (20-50%, depending on the acid concentration). The best lead extraction (97%) was obtained with HNO₃ 0.1M. Apart from the iron which could be masked by NTA, the resin had an excellent selectivity toward others metals.

After retention of metals, the **washing step of the resin with different concentrations of nitric acid** had also been studied. As can be seen in Fig.6 the amount of both iron and lead washed out decreased with increasing HNO₃ concentration. 0.1M HNO₃ implied that only 5% of lead and 40% of iron were respectively washed out. Consequently, a **concentration of 0.1M in nitric acid** was chosen.

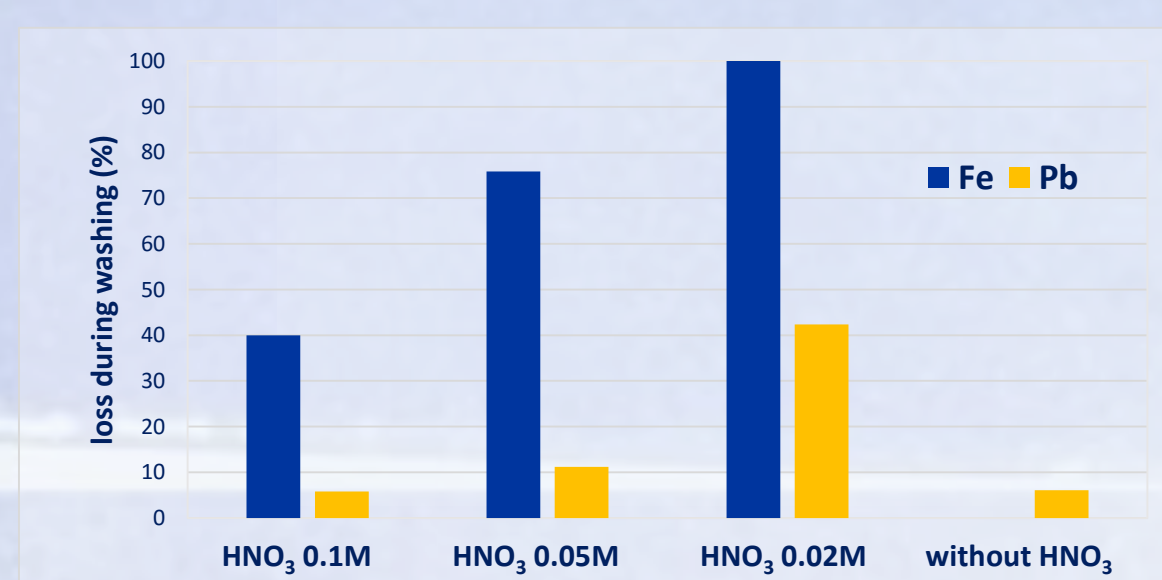


Fig. 6: Iron and lead washed out during washing step

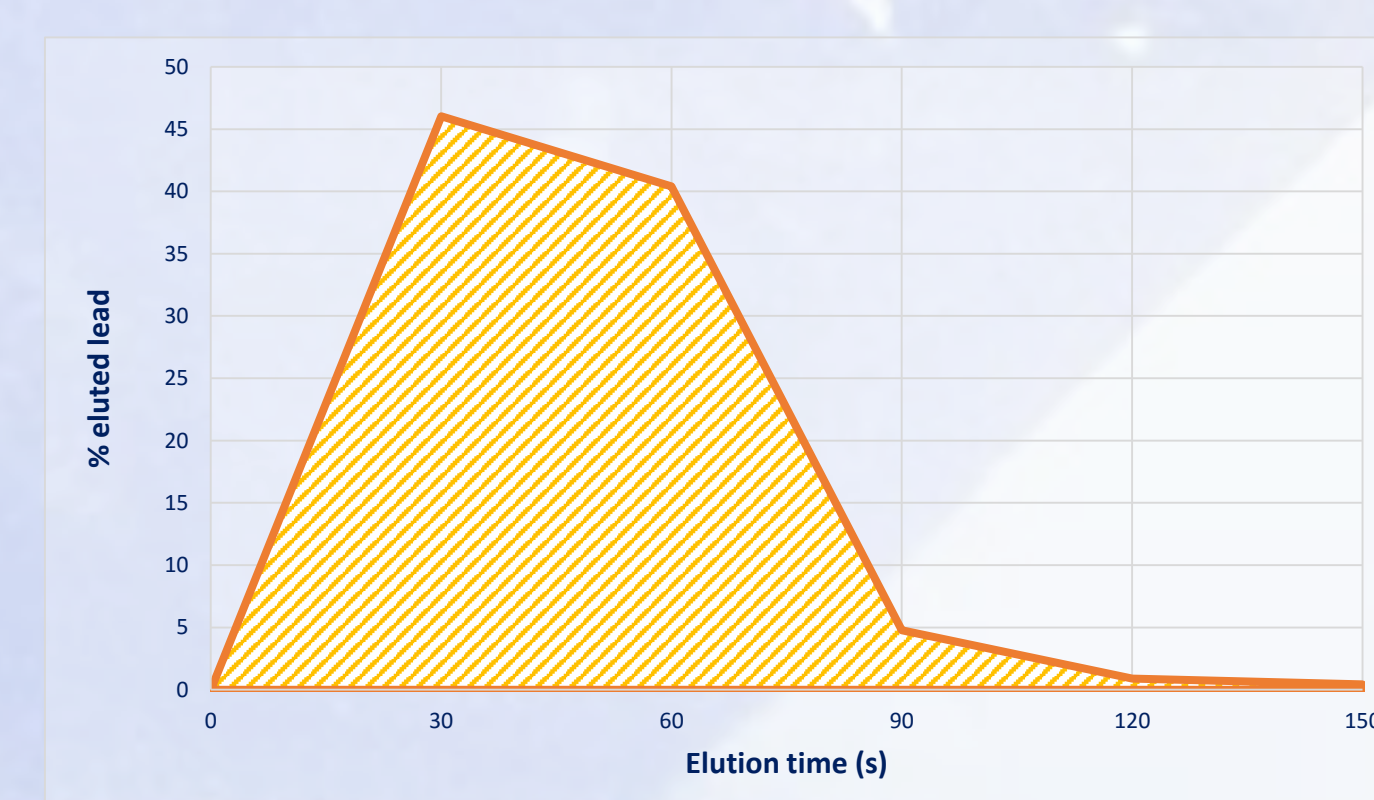


Fig. 7: Elution of lead with ammonium oxalate (0.1M) at 2mL/min

The lead elution has also been studied at different concentrations of ammonium oxalate. Its flow rate has been adjusted at 4mL/min according to the resin manufacturer instructions.

The results obtained between 0.025M and 0.1M were not significantly different. Below 0.005M, the elution rates were much lower.

Consequently, to have a **higher elution**, the concentration of ammonium oxalate was adjusted to **0.025M**.

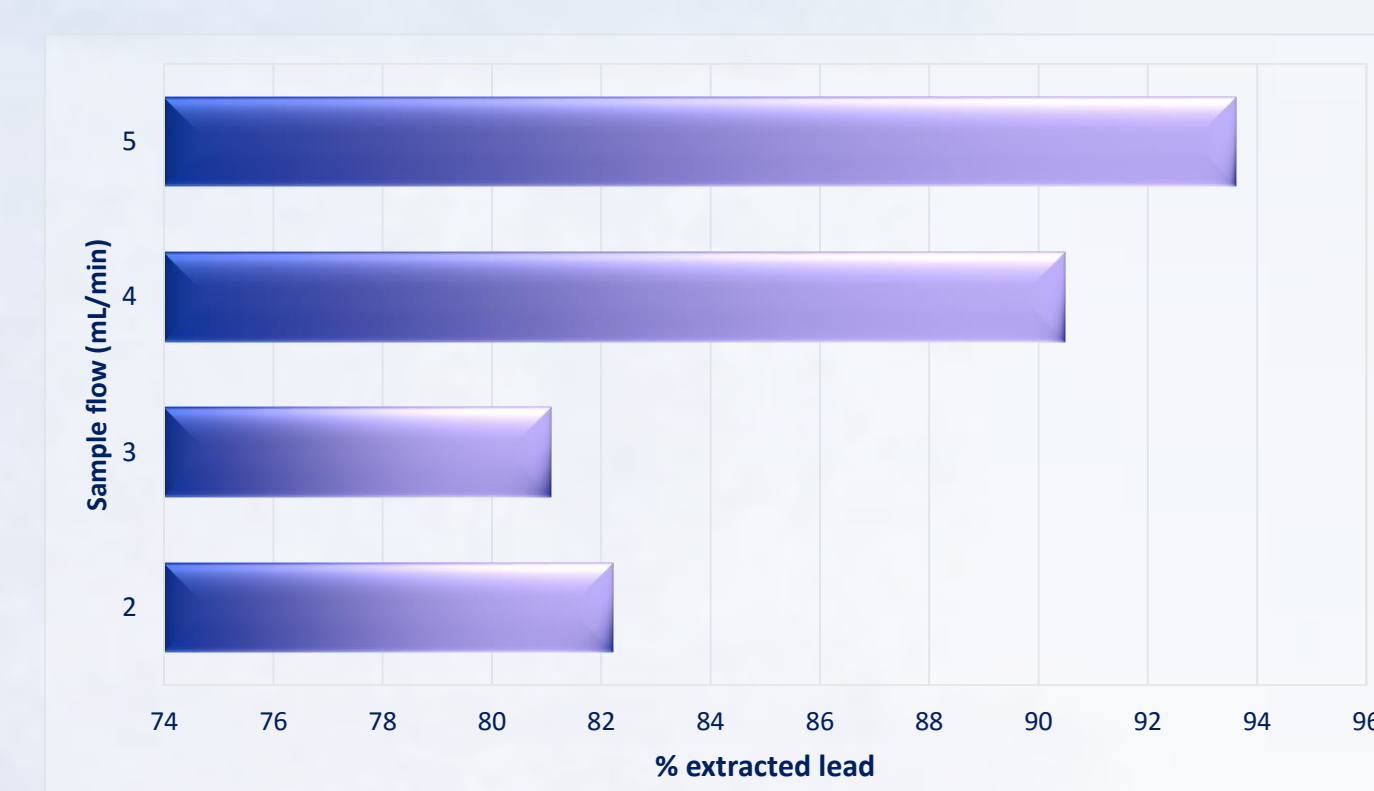


Fig. 9: Extraction of lead at different sample flows

Afterwards, the lead elution profile has been studied to optimise the volume of ammonium oxalate (0.1M). Fractions were collected every 30s (≈1mL) and analysed in AAS. **91% of lead** was eluted during the first **3 minutes**. The derivative reagent (PAR) will thus be pumped through the mixing coil (at the same flow rate) during this time.

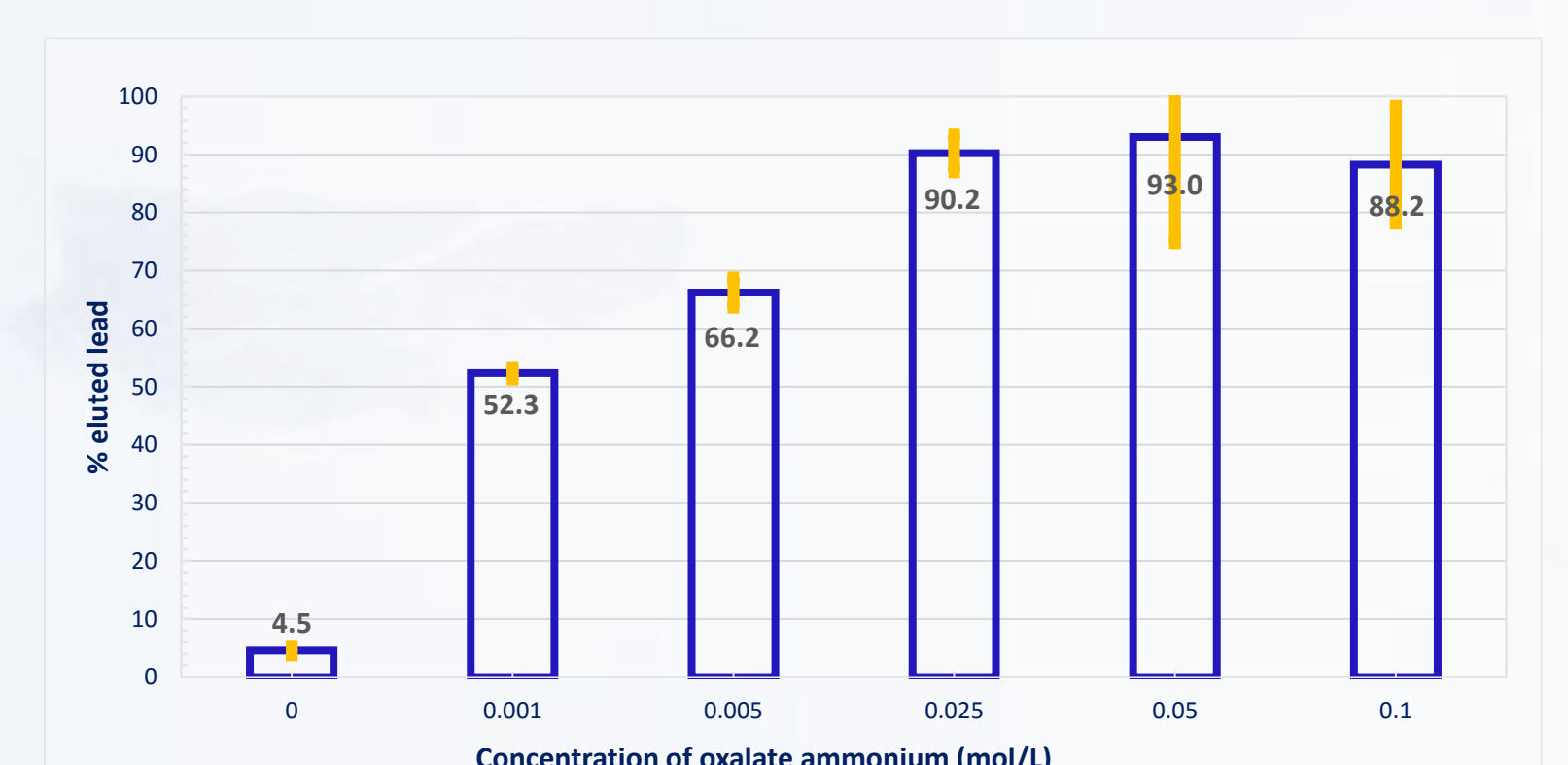


Fig. 8: Elution of lead at different concentrations of ammonium oxalate

A number of experiments have been made to optimise the sample flow rate. The results showed an **increase of extracted lead** at 4 and 5mL/min. These flow rates were higher than those usually fixed in traditional systems containing a resin column. Although solenoids pumps are not usually suitable for resin extraction, it seems that high sample flow rates allow to fluidize the resin bed and thus to obtain a good lead extraction.

Furthermore no overpressure problem of solenoid pumps or clogging was detected during this study. A 5mL/min flow rate was thus chosen for the system.

VALIDATION AND REAL SAMPLES

From the optimised parameters, calibration curves have been constructed for various sample volumes (10, 25 and 42mL). After study of LOQ, LOD and CV, the **curve with 42mL is the most adapted** for typical lead concentrations in natural waters:

Sample volume: 42mL LOD: 2.7µg/L CV: 5.4%

Real samples:

River name -Sample location	Lead concentration (µg/L)	
	ICP-AES	3D system
The Arc – Industrial zone (electronic manufacturing) (upstream)	17.4 ± 1.6	15.8 ± 2.5
The Arc – Industrial zone (electronic manufacturing) (downstream)	15.1 ± 0.8	13.5 ± 1.5
The Arc – WWTP (upstream)	16.5 ± 1.8	18.7 ± 2.1
The Arc – WWTP (direct downstream)	17.4 ± 2.2	16.6 ± 0.8
The Arc – (12km downstream)	12.9 ± 0.4	10.3 ± 1.4

Domain range was linear between 3 and 120µg/L, which seems appropriate for natural waters analysis. Coefficient of variation obtained with optimised conditions was good (CV=5%) and LOD was acceptable, but sample volume can potentially be increased if lower LOD needs to be reached.

To validate the system, five samples of **freshwater** have been collected at purposely chosen points in a coastal river "The Arc" in south of France. The samples were UV-photo-oxidized before analysis. These samples have been analysed in duplicate by **ICP-AES** and developed 3D printed system.

The values obtained by the two methods were consistent. A difference on average of 13% was observed, which could be explained by an increase of measurement variation because these values were closed to LOQ.

CONCLUSIONS AND PERSPECTIVES

The 3D system developed in this study can analyse **lead in natural waters** for concentrations between 3 and 120µg/L. The sample volume can be decreased to allow analysis of industrial waters or increased in order to reach higher preconcentration factor and thus lower LOD.

Reagents and sample concentrations and flow rates have been optimised. Values obtained from real samples with ICP-AES and 3D printed system showed that both methods were consistent. Thereafter, other matrices such as seawater will be tested to check system compatibility and interference absence.

The next step will be to study **the iron extraction** and its masking in more detail: many possibilities are considered, the main being the addition of a complexing reagent (NTA for example), which doesn't interfere with lead measurement.

Later, **the system will be extended to enable cadmium detection**: this step will probably require the replacement of UV spectroscopy flow cell by a fluorescence flow cell, in order to enable the use of a fluorescent reagent complexing cadmium and lead selectively towards other metals. Since the TRISKEM Pb Resin does not extract cadmium and since the complexing reagent shows similar fluorescence emission spectra for both lead and cadmium, the quantification of these two metals could be possible by a two steps procedure.

Acknowledgements: This work was included in the project Lab-on-ship, funded by The French National Research Agency (ANR-14-CE-0004).